2003

Annual Progress Report

HYDROGEN, FUEL CELLS AND INFRASTRUCTURE TECHNOLOGIES PROGRAM

U.S. Department of Energy
Energy Efficiency and Renewable Energy

President Bush Launches the Hydrogen Fuel Initiative

"Tonight I am proposing $1.2 billion in research funding so that America can lead the world in developing clean, hydrogen-powered automobiles."

"A simple chemical reaction between hydrogen and oxygen generates energy, which can be used to power a car producing only water, not exhaust fumes. With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom so that the first car driven by a child born today could be powered by hydrogen, and pollution-free."

"Join me in this important innovation to make our air significantly cleaner, and our country much less dependent on foreign sources of energy."

President George W. Bush
2003 State of the Union Address
January 28, 2003

Benefits of a Hydrogen Economy

The President's FreedomCAR and Hydrogen Fuel Initiative is designed to reverse America's growing dependence on foreign oil by developing the technology to enable production of hydrogen-powered fuel cell vehicles and fueling infrastructure to support them. This initiative was chosen not only because of the energy security benefits associated with a domestic fuel that can be produced from a wide range of feedstocks, but also because of the potential environmental benefits in both transportation and stationary markets.

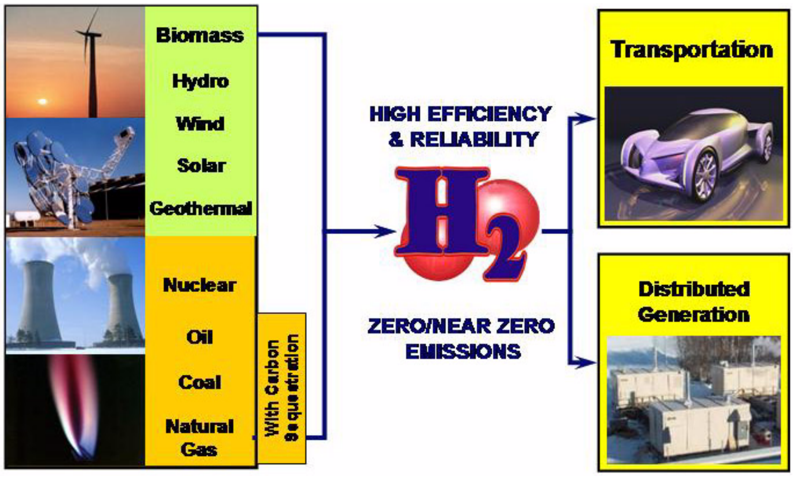
Energy Security

America's transportation sector relies almost exclusively on refined petroleum products. More than one-half of the petroleum consumed in the United States is imported, and that percentage is expected to rise steadily for the foreseeable future. Even with the significant energy efficiency benefits that gasoline-electric hybrid vehicles and diesels can provide, we must ultimately find an alternative fuel that can be domestically produced. Hydrogen (along with biofuels) is a versatile energy carrier that is environmentally clean and could be produced in large quantities entirely from domestic sources. Traditional sources of energy - fossil fuels like natural gas and coal; renewable energy sources such as solar radiation, wind and biomass; and nuclear energy can all be used to produce hydrogen. Its use as a major energy carrier would provide the United States with a more diversified energy infrastructure.

> ***"Hydrogen fuel cells represent one of the most encouraging, innovative technologies of our era.... One of the greatest results of using hydrogen power, of course, will be energy independence for this nation... think about a legacy here at home, about making investments today that will make future citizens of our country less dependent on foreign sources of energy. And so that's why I'm going to work with the Congress to move this nation forward on hydrogen fuel cell technologies. It is in our national interest that we do so."***
>
> President George W. Bush
> The National Building Museum
> February 6, 2003

Environmental

While addressing the energy security issue, we must also address our environmental viability. Air quality is a major national concern. It has been estimated that 60% of Americans live in areas where levels of one or more air pollutants are high enough to affect public health and/or the environment. Personal vehicles and electric power plants are significant contributors to the nation's air quality problems. Most states are now developing strategies for bringing their major metropolitan areas into compliance with the requirements of the Clean Air Act. Widespread use of fuel cell vehicles, because they are zero-emission vehicles and have no on-road emission deterioration, could have a measurable effect on reducing nitrogen oxides, volatile organic compounds, and particulate matter produced by light-duty vehicles.



Emission of greenhouse gases, such as carbon dioxide and methane, has been cited as a major global concern. Build-up of these gases in the atmosphere is thought to have detrimental effects on the global climate. Although there is not yet agreement on what the exact impact will be, when it will be realized, or how best to address the issue, there is agreement that emissions of these gases needs to be reduced. Hydrogen offers a unique opportunity to address this problem, since carbon emissions can be decoupled from energy use and power generation. When used in a fuel cell, the only emission is water vapor. Efficient hydrogen production technologies and the possibility of carbon sequestration make natural gas and coal viable feedstock options, even in a carbon-constrained environment. In the case of renewable and nuclear options, greenhouse gases can virtually be eliminated.

Economic Competitiveness

Abundant, reliable, and affordable energy is an essential component in a healthy economy. When energy prices spike, as has occurred several times recently due to supply interruptions and/or high demand, Americans suffer, particularly those in lower-income brackets. Hydrogen offers unique opportunities to drastically increase the efficiency with which we generate and use energy. And because it can be produced from a wide variety of domestically-available resources, we can reduce the impact of externalities on energy prices.

The technical and economic success of hydrogen-based distributed energy systems will stimulate new business ventures. Hydrogen power parks will provide an economic development path for the integrated production of energy services such as electricity, transportation fuels, and heating and cooling. This may lead to the creation of high-tech jobs to build and maintain these systems. Hydrogen also offers a wide variety of opportunities for the development of new centers of economic growth in both rural and urban areas that are currently too far off-line to attract investment in our centralized energy system.

The success of current U.S. industry is also of vital importance to the well-being of our people and of the Nation as a whole. For example, the U.S. auto industry is the largest automotive industry in the world, producing 30% more vehicles than the second largest producer, Japan. For every worker directly employed by an auto manufacturer, there are nearly seven spin-off jobs. America's automakers are among the largest purchasers of aluminum, copper, iron, lead, plastics, rubber, textiles, vinyl, steel and computer chips. The auto industry is also a major exporter, accounting for 12% of all non-agricultural exports. Remaining competitive in the international market is essential to the U.S. economy.

U.S. Department of Energy
1000 Independence Avenue, S.W.
Washington, D.C. 20585-0121

FY 2003

Progress Report for Hydrogen, Fuel Cells, and Infrastructure Technologies Program

Energy Efficiency and Renewable Energy
Office of Hydrogen, Fuel Cells, and Infrastructure Technologies

Approved by Steven Chalk

October 2003

ACKNOWLEDGEMENT

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In addition, we would like to thank all our Program participants for their contributions and all the authors who prepared the project abstracts that comprise this report.

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I. Introduction

Today, after decades of dependence on imported petroleum to fuel the United States' transportation sector, there is a new vision for our nation's future — a form of domestically-derived, clean energy to power not only our vehicles but our industries, buildings, and homes. This form of energy for the future is hydrogen. The President's Hydrogen Fuel Initiative complements the FreedomCAR initiative to reverse America's growing dependence on foreign oil. Together the FreedomCAR Partnership and Hydrogen Fuel Initiative support the development of technology needed for commercially viable hydrogen-powered fuel cells. President Bush committed $1.7 billion for the first five years of a long-term research and development effort for hydrogen infrastructure, fuel cells, and hybrid vehicle technologies.

Hydrogen research at the U. S. Department of Energy (DOE) is being led by the Office of Energy Efficiency and Renewable Energy (EERE). Other DOE Offices carrying out portions of the Initiative are Fossil Energy, Nuclear Energy, and Science. Within EERE, hydrogen and fuel cell technologies are being managed by the Office of Hydrogen, Fuel Cells and Infrastructure Technologies. Hybrid and other advanced vehicle technologies are being developed within the Office of FreedomCAR and Vehicle Technologies.

National Vision

Hydrogen is America's clean energy choice.

Hydrogen is flexible, affordable, safe, domestically produced, used in all sectors of the economy, and in all regions of the country.

The Hydrogen, Fuel Cells and Infrastructure Technologies Program funds research, development, and validation activities linked to public-private partnerships. The government's current role is to concentrate its funding on high-risk, applied research in the early phases of development. As activities progress through the stages of developing technology to validating technical targets, the government's cost share will diminish. The government's role as co-funder will bring technologies to the point where the private sector can make informed decisions on whether or not, and how best to commercialize these technologies, and will define any future policies to promote them.

Program Mission

The mission of the Hydrogen, Fuel Cells & Infrastructure Technologies Program is to research, develop, and validate fuel cells and hydrogen production, delivery, and storage technologies for transportation and stationary applications.

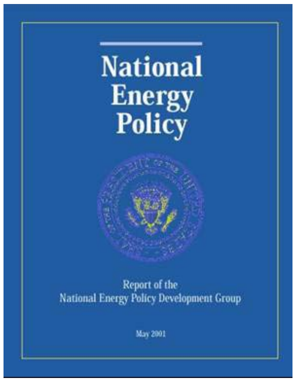
The Hydrogen, Fuel Cells and Infrastructure Technologies Program responds to recommendations in the President's National Energy Policy, the DOE Strategic Plan, and the National Hydrogen Energy Vision and Roadmap. The Program works in partnership with industry, academia, and national laboratories, and in close coordination with the FreedomCAR and Vehicle Technologies Program and other DOE programs, to achieve the four EERE strategic goals:

- Dramatically reduce dependence on foreign oil
- Promote the use of diverse, domestic, and sustainable energy resources
- Reduce carbon emissions from energy production and consumption
- Increase the reliability and efficiency of electricity generation

This report presents a brief overview of DOE's approach to the transition to a hydrogen economy, a description of the fuel cell and hydrogen research conducted by the Hydrogen, Fuel Cells and Infrastructure Technologies Program in fiscal year 2003 (FY 2003), projects to be implemented in FY 2004, and the research priorities for FY 2004.

The Journey Toward a Hydrogen Economy

The transition to a hydrogen economy can be compared to a journey to unknown places, with many challenges to overcome, similar to those which faced our first manned space explorations. DOE has taken the first step toward a hydrogen economy by developing vision, roadmap and long-term planning documents. The planning documents are based on the Administration's National Energy Policy and include input from visionary business leaders and policy makers. The following is a brief description of these documents and other plans that support the President's Hydrogen Fuel Initiative.



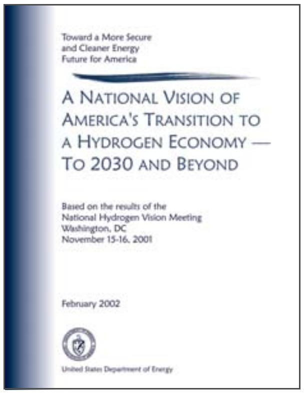
National Energy Policy

Report of the National Energy Policy Development Group

May 2001

The National Energy Policy, released in May 2001, outlines a long-term strategy for developing and using leading-edge technology within the context of an integrated national energy, environmental, and economic policy. It specifically highlighted the potential of hydrogen with the following recommendations:

- Focus research and development efforts on integrating current programs regarding hydrogen, fuel cells, and distributed energy.
- Develop an education campaign that communicates the benefits of alternative forms of energy, including hydrogen.



Toward a More Secure and Cleaner Energy Future for America

A National Vision of America's Transition to a Hydrogen Economy — To 2030 and Beyond

Based on the results of the National Hydrogen Vision Meeting Washington, DC November 15-16, 2001

February 2002

United States Department of Energy

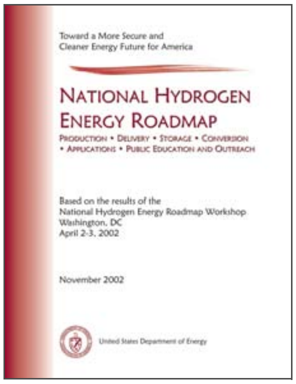
In November 2001, in response to recommendations within the National Energy Policy, DOE organized a meeting of 50 visionary business leaders and policy makers to formulate a National Hydrogen Vision. ***A National Vision of America's Transition to a Hydrogen Economy-to 2030 and Beyond*** was published in February 2002 following the Hydrogen Vision Meeting. This document summarizes the potential role for hydrogen systems in America's energy future, outlining the common vision of the hydrogen economy.

In January 2002, Secretary of Energy Spencer Abraham announced the FreedomCAR Partnership, a cooperative research effort between DOE and USCAR, which is composed of DaimlerChrysler Corporation, Ford Motor Company and General Motors Corporation. FreedomCAR is based upon the following principles:

1. Freedom from petroleum dependence
2. Freedom from air pollutant and carbon dioxide emissions
3. Freedom for Americans to drive where they want, when they want, in the vehicle of their choice
4. Freedom to obtain fuel more affordably and conveniently

The companies of the FreedomCAR Partnership will be at the forefront of development of vehicle technologies for implementation of the hydrogen economy.

In April 2002, DOE followed up with a larger group of over 200 technical experts from industry, academia, and the national laboratories to develop a **National Hydrogen Energy Roadmap**. This roadmap, unveiled by Secretary Abraham in November 2002, describes the principal challenges to be overcome and suggests ways we can achieve our National Vision. To realize this vision, the Nation must develop and demonstrate advanced hydrogen fuel cell and infrastructure technologies. The Roadmap stresses the need for parallel development of model building codes and equipment standards to enable technology integration into commercial energy systems, and outreach programs to effectively educate local government officials and the public, who will determine the long-term acceptance of these technologies.



Toward a More Secure and Cleaner Energy Future for America

National Hydrogen Energy Roadmap

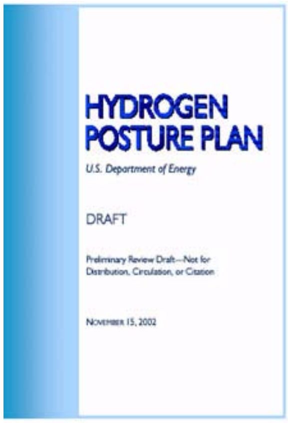
Production • Delivery • Storage • Conversion • Applications • Public Education and Outreach

Based on the results of the National Hydrogen Energy Roadmap Workshop Washington, DC April 2-3, 2002

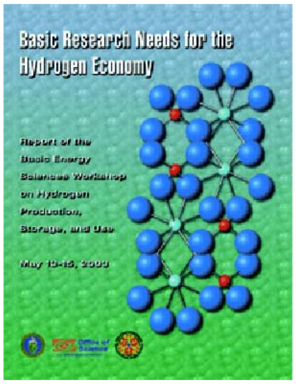
November 2002

United States Department of Energy

In February 2003, DOE completed a draft copy of the ***Hydrogen Posture Plan***. The Hydrogen Posture Plan describes how DOE will integrate its ongoing and future hydrogen R&D activities into a focused Hydrogen Program. It defines four phases of transition to a hydrogen economy (see the following subsection titled *The Road to a Transition* for detailed descriptions of each). The Hydrogen Program will integrate technology for hydrogen production (from fossil, nuclear, and renewable resources), infrastructure development (including delivery and storage), and fuel cells. Successful implementation of the Hydrogen Posture Plan and its activities is also critical to achieving the goals of the FreedomCAR Partnership. A coordinated DOE Hydrogen Program will improve the effectiveness and accountability of DOE's research, development, and demonstration (RD&D) activities and strengthen its contribution to achieving the technical milestones on the road to a hydrogen economy.

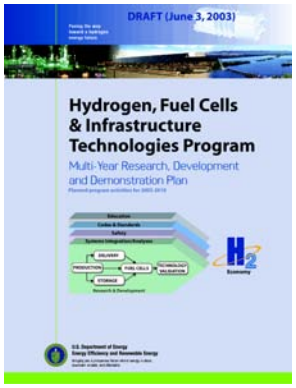


HYDROGEN POSTURE PLAN
U.S. Department of Energy
DRAFT
Preliminary Review Draft—Not for Distribution, Circulation, or Citation
November 15, 2002



Basic Research Needs for the Hydrogen Economy
Report of the Basic Energy Sciences Workshop on Hydrogen Production, Storage, and Use
May 13-15, 2003

The Office of Science hosted a workshop on Hydrogen Production, Storage, and Use, on May 13–15, 2003, to identify fundamental research needs and opportunities to address the enormous gap between our present capabilities for hydrogen production, storage, and use, and those required for a competitive hydrogen economy. More than 120 scientists and engineers from academia, industry, and the national laboratories attended. Participants also included research leaders from abroad and experts from the Offices of Energy Efficiency and Renewable Energy, Fossil Energy, and Nuclear Energy within the U.S. Department of Energy. The detailed findings and research directions (http://www.sc.doe.gov/bes/hydrogen.pdf) address the research challenges for the hydrogen economy. The workshop report concludes that simple improvements of today's technologies will not meet the requirements. Instead, the significant technical barriers need to be overcome with high risk/high payoff basic research that is highly interdisciplinary, requiring chemistry, materials science, physics, biology, engineering, nanoscience, and computational science. It also calls for the seamless integration of basic and applied research to realize the successful transition to a hydrogen economy.



DRAFT (June 3, 2003)
Hydrogen, Fuel Cells & Infrastructure Technologies Program
Multi-Year Research, Development and Demonstration Plan

The Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan was prepared for public review and released on June 3, 2003. The Plan describes the planned research, development, and validation activities for hydrogen and fuel cell technologies through nine key program components through 2010.

Production	Production of hydrogen from domestic resources minimizing environmental impacts
Delivery	Distribution of hydrogen from centralized or from distributed sites of production
Storage	Storage of hydrogen (or its precursors) on vehicles or within the distribution system
Fuel Cells	Provide primary propulsion for fuel cell vehicles, serve as auxiliary power units for vehicles, and provide electrical and thermal power in stationary and portable applications.
Technology Validation	Validation of systems in real-world environments
Safety	Safety assurance in DOE-sponsored R&D activities and in the hydrogen systems developed
Codes and Standards	Development of model codes and standards for domestic and international production, distribution, storage and utilization of hydrogen

Education	Education of key target audiences—including teachers and students, state and local governments, safety and code officials, large-scale end users, and the public—about the hydrogen economy and how it can affect them
Systems Integration	Understanding the complex interactions between components, system costs, energy efficiency, environmental impacts, societal impacts and system trade-offs

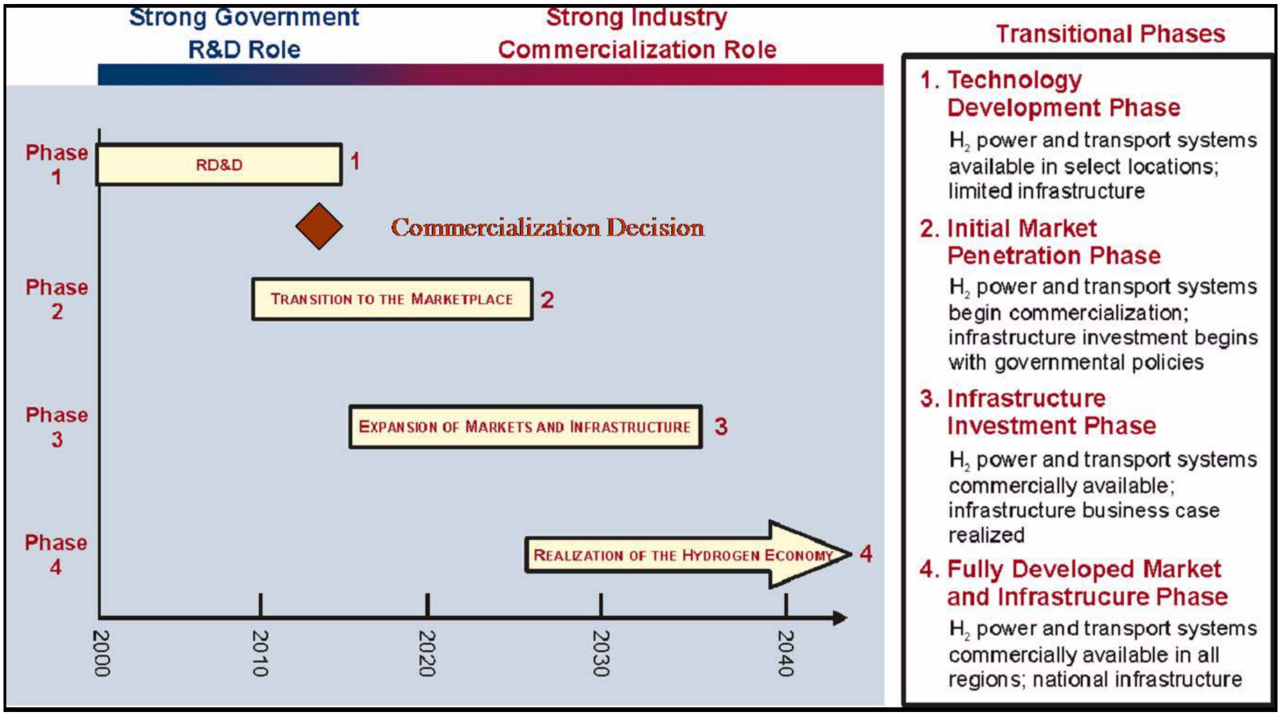
The detailed technical targets and milestones for each element are identified in the Plan.

The Road to Transition

Throughout the planning process, DOE has envisioned four phases in the transition to a hydrogen economy, each of which requires and builds on the success of its predecessor. The transition to a hydrogen economy will take several decades, and this transition will require strong public and private partnerships, commitment, and resolve.

In Phase 1, government and private organizations will research, develop, and demonstrate "critical path" technologies and work to establish comprehensive safety guidelines, codes and standards prior to investing heavily in infrastructure. This phase is now underway, and it will enable industry to make decisions on commercialization by 2015. Following a positive commercialization decision, research will continue on advanced technologies for hydrogen production. Throughout the RD&D phase, exploratory research in materials sciences and engineering, chemistry, geosciences, and molecular biosciences will be carried out in close collaboration with the DOE Office of Science.

Phase 2 is the Initial Market Penetration Phase. This could begin as early as 2010 using existing natural gas and electric grid infrastructure for applications such as portable power and some stationary and transportation applications, and continue as hydrogen-related technologies meet or exceed customer requirements.

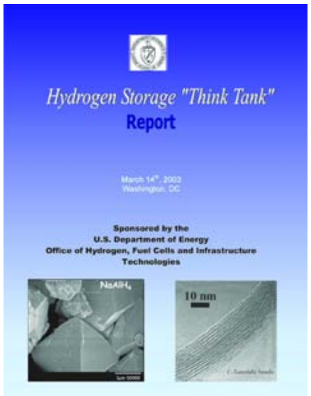


As markets are established, this leads to Phase 3, or the Infrastructure Investment Phase, in which there is expansion of markets and infrastructure. The start of Phase 3 is dependent on a positive commercialization decision for fuel cell vehicles in 2015. A positive decision will attract investment in infrastructure for manufacturing fuel cells and for producing and distributing hydrogen. Government policies still may be required to nurture this infrastructure expansion phase.

Phase 4, which could begin around 2025, is the Fully Developed Market and Infrastructure Phase. In this phase, consumer requirements will be met or exceeded, national benefits in terms of energy security and improved environmental quality will be achieved, and industry will receive adequate return on investment and compete globally. Phase 4 provides the transition to a full hydrogen economy by 2040.

Progress Along the Road to Transition

As discussed, detailed planning for the President's Hydrogen Fuel Initiative was completed during FY 2003. The following is a brief list of accomplishments achieved:



Hydrogen Storage "Think Tank"
Report

March 14th, 2003
Washington, DC

Sponsored by the
U.S. Department of Energy
Office of Hydrogen, Fuel Cells and Infrastructure Technologies

- The Office of Energy Efficiency and Renewable Energy hosted a hydrogen storage "Think Tank" meeting in Washington, D.C., on March 14, 2003, to identify new and potentially promising hydrogen storage technologies. Based on the Think Tank meeting, which included Nobel Prize Laureates, the DOE issued a "Grand Challenge" to the scientific community to solicit applications for research and development of hydrogen storage materials and technologies. The awards made from this solicitation will establish Centers of Excellence.
- The Office of Fossil Energy launched FutureGen, a $1 billion, 10-year verification project that will build the world's first coal-based, near zero-emission electricity and hydrogen plant integrated with carbon sequestration.
- The DOE sponsored a Hydrogen Delivery Workshop in Washington, DC, May 7-8, 2003. Attendees included researchers, government officials, and industry members. This special workshop was held to outline the future technology and research needs for developing cost-effective, reliable, and safe hydrogen delivery systems.
- On June 2-3, 2003, DOE held a Hydrogen and Fuel Cells Coordination Meeting to facilitate communication and coordination among the DOE programs with key roles in achieving the goals of the President's FreedomCAR and Hydrogen Fuel Initiative. The meeting was attended by invited participants from programs in DOE's Offices of Energy Efficiency and Renewable Energy, Fossil Energy, Nuclear Energy, Science and Technology, Science, and the Office of Management, Budget and Evaluation.
- The world's first hydrogen and electricity co-production facility opened in Las Vegas, Nevada, in November 2002. The facility (built by Air Products and Chemicals, Inc., in partnership with Plug Power Inc., the DOE, and the City of Las Vegas) will serve as a "learning" demonstration of hydrogen as a safe and clean energy alternative for vehicle refueling. The facility includes small-scale, on-site hydrogen production technologies, a hydrogen/compressed natural gas blend refueling facility, and a 50-kW PEM fuel cell system that supplies electricity to the grid.

World's First Hydrogen and Electricity Co-Production Facility

- The Office of Energy Efficiency and Renewable Energy released a hydrogen production and delivery technologies solicitation which includes the following topics: biomass gasification and pyrolysis; photolytic processes; distributed natural gas reforming technologies; separation and purification technologies; advanced electrolysis systems; high temperature thermochemical water splitting; hydrogen production infrastructure analysis; and advanced hydrogen delivery technologies. Pre-proposals have been received with proposals due in FY 2004.

- Hosted workshop for education and industry experts to launch a new education program element, December 4-5, 2002.
- The Office of Energy Efficiency and Renewable Energy issued a solicitation for the testing, demonstration, and validation of hydrogen fuel cell vehicles and infrastructure, and the required vehicle and infrastructure interfaces for complete system solutions. The awards will be cost-shared, and each will include a comprehensive safety plan; a program that enhances the development of codes and standards; and a comprehensive, integrated education and training campaign. Awards will be made in FY 2004, and each will be 5 years in length.
- The FreedomCAR Partnership was expanded to include energy companies to focus on hydrogen infrastructure challenges.
- On March 21-22, 2003, DOE sponsored the Non-Platinum Electrocatalyst Workshop to review and identify potential new candidate electrocatalysts that are non-platinum (and non-precious metal). Fifty-five representatives from universities, government agencies, national laboratories, and private industry attended the two-day workshop, held in New Orleans, Louisiana.
- Safety guidelines for DOE Hydrogen Program projects were drafted.
- The Office of Energy Efficiency and Renewable Energy Launched a hydrogen education "campaign" as recommended in the President's National Energy Policy.
  A solicitation was released with proposals due in the beginning of FY 2004.
- Initiated a review by The National Academies of DOE's hydrogen research, development, and demonstration (RD&D) program. An interim letter report was received April 3, 2003, which provides some early feedback and recommendations. A final report is anticipated in FY 2004.
- Energy Efficiency and Renewable Energy conducted a merit review and peer evaluation of all the projects in the Hydrogen, Fuel Cells and Infrastructure Technologies Program. The results of this meeting will be used to guide research activities during FY 2004.
- DOE Awarded a total of $96 million in 24 new awards in support of the President's FreedomCAR and Hydrogen Fuel Initiative. These new projects include research in advanced fuel cell technology for vehicles, buildings and other applications. In particular, the projects on hydrogen storage technologies support DOE's priority to develop methods to safely store hydrogen to enable at least a 300 mile vehicle range—a critical requirement for successful vehicle commercialization. The recipients of these awards have pledged an additional $40 million in cost sharing, bringing the total value of these projects to $136 million.

Stationary/Transportation Awards Announced July 14, 2003

Company	Project Technology
3M Company	MEA and Stack Durability
IdaTech LLC	Stationary Fuel Cell Power System
UTC Fuel Cells LLC	Stationary Fuel Cell Power System & Demo
Plug Power, Inc.	Back-up/Peak Shaving Fuel Cells
Atofina Chemicals, Inc.	Low Cost, Durable Membranes
DuPont	MEA Durability
Plug Power, Inc.	High Temperature Membranes
Texaco Energy Systems	Fuel Cell Fuel Processor
Honeywell International Inc.	Thermal and Water Management
Engelhard Corporation	Platinum Recycling
Ion Power, Inc.	Platinum Recycling
3M Company	Non-Precious Metal Catalysts
Ballard Power Systems Corp.	Non-Precious Metal Catalysts
University of South Carolina	Non-Precious Metal Catalysts
Battelle Memorial Institute	Economic Analysis

Future Plans for Progress Along the Road to Transition

The following are the FY 2004 priorities for the FreedomCAR and Hydrogen Fuel Initiative:

- Establish the International Partnership for a Hydrogen Economy (IPHE). The objective of the IPHE is to efficiently organize, evaluate and coordinate multinational research, development and deployment programs that advance the transition to a global hydrogen economy.
- Establish a fully integrated DOE Hydrogen Program to efficiently manage all DOE hydrogen and fuel cell research and include an innovative systems integration capability to cost effectively execute all aspects of the President's Hydrogen Fuel Initiative.
- Finalize and publish the 5-year hydrogen RD&D plans of the Offices of Energy Efficiency and Renewable Energy, Fossil Energy, and Nuclear Energy based on the peer review by The National Academies.
- Conduct an integrated DOE Hydrogen Program merit review and peer evaluation meeting including the Offices of Energy Efficiency and Renewable Energy, Fossil Energy, Nuclear Energy, and Science.
- Establish three to four Hydrogen Storage Centers of Excellence led by DOE national laboratories including universities, industry, and/or other federal/national laboratories as partners to address the very pressing needs to improve hydrogen storage so that fuel cell vehicles with 300 mile range can become a practical reality.
- Issue solicitation for hydrogen production from coal and award projects.
- Initiate a national Hydrogen Vehicle and Infrastructure Validation Project with three to six consortia (auto/ fuel/ supplier teams) to test vehicles and infrastructure. Data from these "learning" demonstrations will provide feedback to the research program.
- Establish an expert panel to analyze the merits of whether to continue development of on-board fuel processors to reform gasoline and alternative fuels such as methanol, ethanol, and natural gas to produce hydrogen on-board the vehicle.
- Initiate high efficiency polymer electrolyte membrane stationary fuel cell power system projects that will advance and demonstrate the use of fuel cells as an alternative power source to grid-based electricity for buildings.
- Select up to 32 projects to receive up to $80 million of federal funding for development of hydrogen production and delivery technologies.
- Establish and implement a data management plan for the DOE Hydrogen Program.
- Conduct and report on baseline assessment of key target audiences' understanding of hydrogen economy.
- Launch first phase of long-term education strategy by creating hydrogen information clearinghouse to serve multiple audiences and initiating specific education activities focused on teachers and students and state and local governments.
- Conduct a scoping study for a Programmatic Environmental Impact Statement.
- Initiate worldwide commitment for global hydrogen codes and standards as part of on-going IPHE activities.
- Launch the Office of Nuclear Energy Hydrogen Initiative which will demonstrate the economic commercial-scale production of hydrogen using nuclear energy by 2015.

Hydrogen Storage/Sensors Awards
July 14, 2003

Company	Project Technology
Air Products & Chemicals, Inc.	Hydrogen Storage
Cleveland State University	Hydrogen Storage
Intelligent Optical Systems, Inc.	Sensors
Iowa State University	Hydrogen Production
Millennium Cell, Inc.	Hydrogen Storage
Nanomix, Inc.	Hydrogen Storage
QUANTUM Technologies, Inc.	Hydrogen Storage
Safe Hydrogen, LLC	Hydrogen Storage
United Technologies Research Center	Hydrogen Storage
University of California, Irvine	Sensors
UOP, LLC	Hydrogen Storage

- Continue efforts to establish closer relationships with the states through the DOE Regional Offices to execute hydrogen and fuel cell RD&D, especially in the areas of education and codes/standards.

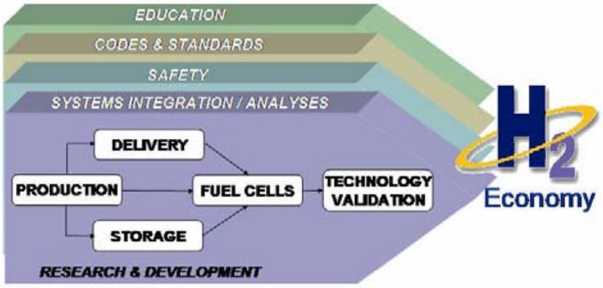
The National Academies Review

The DOE asked The National Academies in December 2002 to evaluate the cost and status of technologies for production, transportation, storage, and end-use of hydrogen and to review DOE's hydrogen research, development, and deployment (RD&D) strategy. On April 4, 2003, The National Academies submitted their interim report offering four recommendations in the following areas:

- Safety: The Committee recommended that DOE make significant efforts to address safety issues.
- Systems Integration and Analyses: The National Academies recommended that R&D successes & failures be analyzed and modeled both as individual technologies and as components of a greater system.
- Exploratory Research: The Committee encouraged DOE to continue funding fundamental, exploratory research for promising, high-risk new technologies.
- Organization: The Committee supports the DOE in its efforts to integrate various hydrogen-related RD&D programs, the Office of Science, and the private sector.

A final report will be submitted during FY 2004. FreedomCAR and the Hydrogen Fuel Initiative are focused on bringing about significant changes to how the country develops and uses its energy resources. The DOE is highly interested in the findings and recommendations of The National Academies so that we can guide the program in a way that achieves the best results for the country. Find more information at www.nas.edu under BEES-J-02-04-A.

Technical Challenges and Mileposts Along the Road to Transition



The EERE Hydrogen, Fuel Cells and Infrastructure Technologies Program has set goals and targets for each of its technical areas. The "core" activities are hydrogen production, delivery, and storage; fuel cell development; and validation technology. Cross-cutting activities of systems integration/analysis, safety, codes and standards, and education are performed in parallel with the technology research and development activities. Following are brief descriptions of the status of these Program activities, the goal for each, pertinent technical targets, current status, and anticipated FY 2004 accomplishments.

Hydrogen Production

Goal: Research and develop low-cost, highly efficient hydrogen production technologies from diverse, domestic sources, including fossil, nuclear, and renewable sources.

Objectives

- By 2010, reduce the cost of distributed production of hydrogen from natural gas and/or liquid fuels to \$1.50/kg (delivered, untaxed) at the pump (without carbon sequestration).

- By 2010, develop and demonstrate technology to supply purified hydrogen (purity sufficient for PEM fuel cells) from biomass at $2.60/kg at the plant gate (projected to a commercial scale 75,000 kg/day).[1] The objective is to be competitive with gasoline by 2015.
- Develop advanced renewable photolytic hydrogen generation technologies. By 2015, demonstrate an engineering-scale biological system that produces hydrogen at a plant-gate cost of $10/kg projected to commercial scale. By 2015, demonstrate direct photoelectrochemical water splitting with a plant-gate hydrogen production cost of $5/kg projected to commercial scale. The long-term objective for these production routes is to be competitive with gasoline.
- By 2010, verify renewable integrated hydrogen production with water electrolysis at a hydrogen cost of $2.50/kg (electrolyzer capital cost of $300/kW$_e$ for 250 kg/day at 5,000 psi with 73% system efficiency). By 2010, verify large-scale central electrolysis at $2.00/kg hydrogen at the plant gate.
- By 2015, research and develop high- and ultra-high-temperature thermochemical/electrical processes to convert hydrogen from high temperature heat sources (nuclear or solar) with a projected cost competitive with gasoline.[2]
- Evaluate other new technologies that have the potential for cost-effective sustainable production of hydrogen and fund appropriate research and development (R&D) in promising areas.

<u>FY 2003 Status</u>

- Cost of distributed production of hydrogen from natural gas: $5.00/kg
- Cost of centralized production of hydrogen from biomass: $4.00/kg (at the plant gate)

<u>Anticipated FY 2004 Accomplishments</u>

- Complete research to enable distributed natural gas reforming technologies delivering 5,000 psi hydrogen at $3.00/kg hydrogen – progress toward achieving 2010 goal of $1.50/kg.
- Accelerate and expand research to reduce the cost of electrolysis for hydrogen production, including high temperature steam electrolysis, and complete an analysis and research on central, integrated, wind-based electrolysis.
- Initiate a geothermal-based electrolysis feasibility study.
- Accelerate and expand research on the production of hydrogen from renewable resources, including biomass gasification/pyrolysis, photobiological and photoelectrochemical production.
- Initiate research on high temperature thermochemical water splitting for hydrogen production.
- Complete a comprehensive techno-economic analysis of the major production options for hydrogen on a consistent and comparable basis.

Hydrogen Delivery

Goal: Develop hydrogen fuel delivery technologies that enable the introduction and long-term viability of hydrogen as an energy carrier for transportation and stationary power.

<u>Objectives</u>

- By 2006, define a cost-effective and energy-efficient hydrogen fuel delivery infrastructure for the introduction and long-term use of hydrogen for transportation and stationary power.
- By 2010, develop enabling technologies to reduce the cost of hydrogen fuel delivery from central and semi-central production facilities to the gate of refueling stations and other end users to <$0.70/kg.
- By 2010, develop enabling technologies to reduce the cost of moving and handling hydrogen within refueling stations and stationary power facilities to a vehicle or stationary power unit to <$0.60/kg.

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1. Collaboration with the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) Biomass Program. Offsets for coproducts not included.
2. Collaboration with DOE’s Office of Nuclear Energy.

- By 2015, develop enabling technologies to reduce the cost of hydrogen fuel delivery from the point of production to the point of use in vehicles or stationary power units to <$1.00/kg in total.

FY 2003 Status

- Cost of gaseous hydrogen compression: $0.18/kg; efficiency of 90%
- Cost of hydrogen liquefaction: $1.11/kg; efficiency of 65%
- Cost of hydrogen trunk pipelines: $1.4 million/mile
- Cost of hydrogen distribution lines: $600,000/mile
- Hydrogen carrier storage capacity: 3 wt.%; efficiency of 80%

Anticipated FY 2004 Accomplishments

- Define and initiate a comprehensive analysis of hydrogen delivery technology and infrastructure options and trade-offs.
- Initiate research projects on hydrogen delivery to support the 2005 and 2010 delivery targets, including lower cost pipelines, compression and liquefaction technology and novel solid and liquid carrier systems.

Hydrogen Storage

Goal: Develop and demonstrate viable hydrogen storage technologies for transportation and stationary applications.

Objectives

- By 2005, develop and verify on-board hydrogen storage systems achieving 1.5 kWh/kg (4.5 wt%), 1.2 kWh/L, and $6/kWh.
- By 2010, develop and verify on-board hydrogen storage systems achieving 2 k Wh/kg (6 wt%), 1.5 kWh/L, and $4/kWh.
- By 2015, develop and verify on-board hydrogen storage systems achieving 3k Wh/kg (9 wt%), 2.7 kWh/L, and $2/kWh.
- By 2015, develop and verify low-cost, off-board hydrogen storage systems, as required for hydrogen infrastructure needs to support transportation, stationary and portable power markets.

FY 2003 Status

- For 10,000 psi tanks: Achieved factor of 10 improvement in cycle life and demonstrated 3-minute fill time.
- For solid state materials: Achieved factor of 10 improvement in kinetics of sodium alanate and identified potential pathway to increased storage capacity

Anticipated FY 2004 Accomplishments

- Demonstrate 10,000 psi tanks achieving 2005 targets of 1.5 kWh/kg and 1.2 kWh/L.
- Complete construction of independent test facility for reversible solid-state storage materials.

Fuel Cells

Goal: Develop and demonstrate fuel cell power system technologies for transportation, stationary, and portable applications.

Objectives

- Develop a 60% efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of $45/kW (including hydrogen storage) by 2010 and $30/kW by 2015.
- Develop a 45% efficient reformer-based fuel cell power system for transportation operating on clean hydrocarbon or alcohol-based fuel that meets emissions standards, a startup time of 30 seconds, and a projected manufactured cost of $45/kW by 2010 and $30/kW by 2015.

- Develop a distributed generation PEM fuel cell system operating on natural gas or propane that achieves 40% electrical efficiency and 40,000 hours durability at \$400-\$750/kW by 2010.
- Develop a fuel cell system for consumer electronics with an energy density of 1,000 Wh/L by 2010.
- Develop a fuel cell system for auxiliary power units (3-30/kW) with a specific power of 150 W/kg and a power density of 170 W/L by 2010.

FY 2003 Status

- Current cost of vehicle fuel cell power systems: \$250/kW (at 500,000 units per year)

Anticipated FY 2004 Accomplishments

- Reduce costs through demonstration of bipolar plate pilot plant production rate of 300 plates/hour.
- Reduce on-board fuel processor start-up time to <1 min. through auto-thermal technology.
- Define requirements and initiate economic analysis/study of stationary fuel cells and their associated markets.

Technology Validation

Goal: Validate integrated hydrogen and fuel cell technologies for transportation, infrastructure, and electric generation in a systems context under real-world operating conditions.

Objectives

- By 2008, validate an electrolyzer that is powered by a wind turbine at a capital cost of \$300/kW$_e$ when built in quantity.
- By 2008, validate hydrogen vehicles which have greater than a 300-mile range, 2,000-hour fuel cell durability, and \$3.00/kg hydrogen production cost (untaxed), and which can be safely and conveniently refueled by trained drivers.
- By 2008, validate stationary fuel cell and hydrogen internal combustion engine (ICE) systems that coproduce hydrogen and electricity from nonrenewable and renewable resources, with a 30,000-hour durability, greater than 32% efficiency, and a price of \$1,250/kW or less (for volume production).
- By 2010, validate an integrated biomass/wind or geothermal electrolyzer-to-hydrogen system to produce hydrogen for \$3.30/kg at the plant gate (untaxed and unpressurized).
- By 2015, validate hydrogen PEM fuel cell vehicles achieving 300+ mile range and 5,000 hours fuel cell system durability, and which can be safely and conveniently refueled by trained drivers.

FY 2003 Status

- Cost of hydrogen production from natural gas: \$5.00/kg
- Fuel cell durability in a systems context of 1,000 hours

Anticipated FY 2004 Accomplishments

- Validate \$3.60/kg hydrogen from natural gas when co-production of electricity is included
- Initiate “learning” demonstrations that emphasize and integrate hydrogen infrastructure and hydrogen powered vehicles to validate technology status and focus future R&D directions.

Codes and Standards

Goal: Facilitate the creation and adoption of model building codes and equipment standards for hydrogen systems in commercial, residential, and transportation applications. Provide technical resources to harmonize the development of international standards among the International Electrotechnical Commission (IEC), the International Organization for Standardization (ISO), and the Global Regulation on Pollution and Energy (GRPE) Program.

Objectives

- Complete the drafting of hydrogen building codes for the National Fire Protection Association's (NFPA's) hearing cycle.
- By 2005, facilitate the adoption of the International Code Council (ICC) codes in three key regions: Northeast, Mid-Atlantic, and Midwest.
- By 2006, support and facilitate the completion and adoption of the ISO standards for hydrogen refueling and storage.
- By 2008, support and facilitate the completion and adoption of the revised NFPA 55 standard for hydrogen storage with data from the technology validation program element activities and the experimental project for underground bulk storage of hydrogen.
- By 2010, support and facilitate U.S. adoption of a Global Technical Regulation (GTR) for hydrogen fuel cell vehicles under the United Nations Economic Commission for Europe World Forum for Harmonization of Vehicle Regulations Working Party on Pollution and Energy under the GRPE program (ECE-WP29/GRPE).

FY 2003 Status

- Developed a plan for international safety standards (currently under review)

Anticipated FY 2004 Accomplishments

- Collaborate with ICC and NFPA to develop first-order continuing education for code officials.
- Establish a coordination plan with education sub-program activity to run workshops for state and local officials.
- Initiate negotiations with critical standards development organizations and develop draft generic licensing agreement and estimate of costs.

Safety

Goal: Develop and implement the practices and procedures that will ensure safety in the operation, handling, and use of hydrogen and hydrogen systems for all DOE-funded projects.

Objectives

- Draft a comprehensive safety plan to be completed in collaboration with industry. The plan will initiate the research necessary to fill safety information gaps and enable the formation of a Safety Review Panel by 2004.
- Integrate safety procedures into all DOE project funding procurements. This will ensure that all projects that involve the production, handling, storage, and use of hydrogen incorporate project safety requirements into the procurements by 2005.
- Publish a handbook of Best Management Practices for Safety by 2010. The Handbook will be a "living" document that will provide guidance for ensuring safety in future hydrogen endeavors.

FY 2003 Status

- Completed draft safety guidelines to be used by all DOE Hydrogen Program projects
- Anticipated FY 2004 Accomplishments
- Assemble panel of experts in hydrogen safety to provide expert technical guidance to funded projects.
- Develop in collaboration with NASA, the U.S. Department of Transportation, and the U.S. Department of Commerce, a search protocol on component and system safety.
- Identify areas of additional study and research for failure modes scenarios.
- Establish annual review criteria for safety.

Education

Goal: Educate key audiences about fuel cell and hydrogen systems to facilitate commercialization and market acceptance of these technologies.

<u>Objectives</u>

By 2010 –

- Achieve a fourfold increase in the number of students and teachers who understand the concept of a hydrogen economy and how it may affect them.
- Achieve a fourfold increase in the number of state and local government representatives who understand the concept of a hydrogen economy and how it may affect them.
- Achieve a twofold increase in the number of large-scale end-users who understand the concept of a hydrogen economy and how it may affect them.
- Launch a comprehensive and coordinated public education campaign about the hydrogen economy and fuel cell technology.

<u>FY 2003 Status</u>

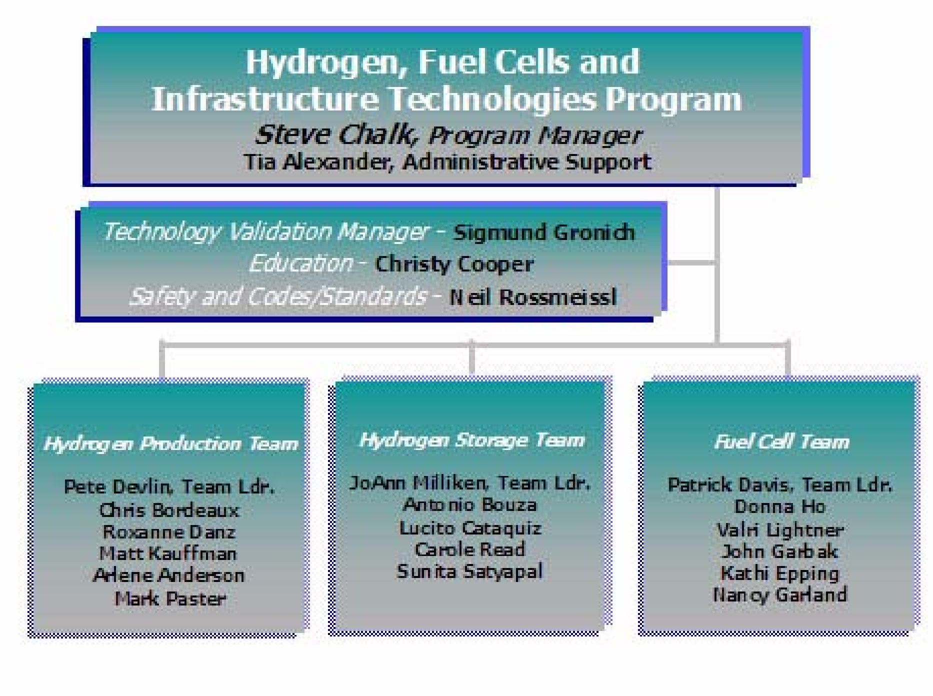
- Developed a comprehensive, long-term plan to educate multiple audiences.

<u>Anticipated FY 2004 Accomplishments</u>

- Launch new middle school and high school hydrogen technology curricula and teacher professional development program.
- Initiate series of hydrogen technology learning workshops for state and local governments.

Hydrogen, Fuel Cells, and Infrastructure Technologies Program Management

This report documents the progress made by the DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program during FY 2003. The following sections of the report contain 161 individual progress reports of projects currently being conducted or newly initiated. These reports provide technical details on the progress being made to achieve the goals and technical targets of the Hydrogen, Fuel Cells and Infrastructure Technologies Program. The following organization chart shows its management structure, and the list of Technology Development Managers provides contact information and shows management responsibilities.



Hydrogen Production Team	
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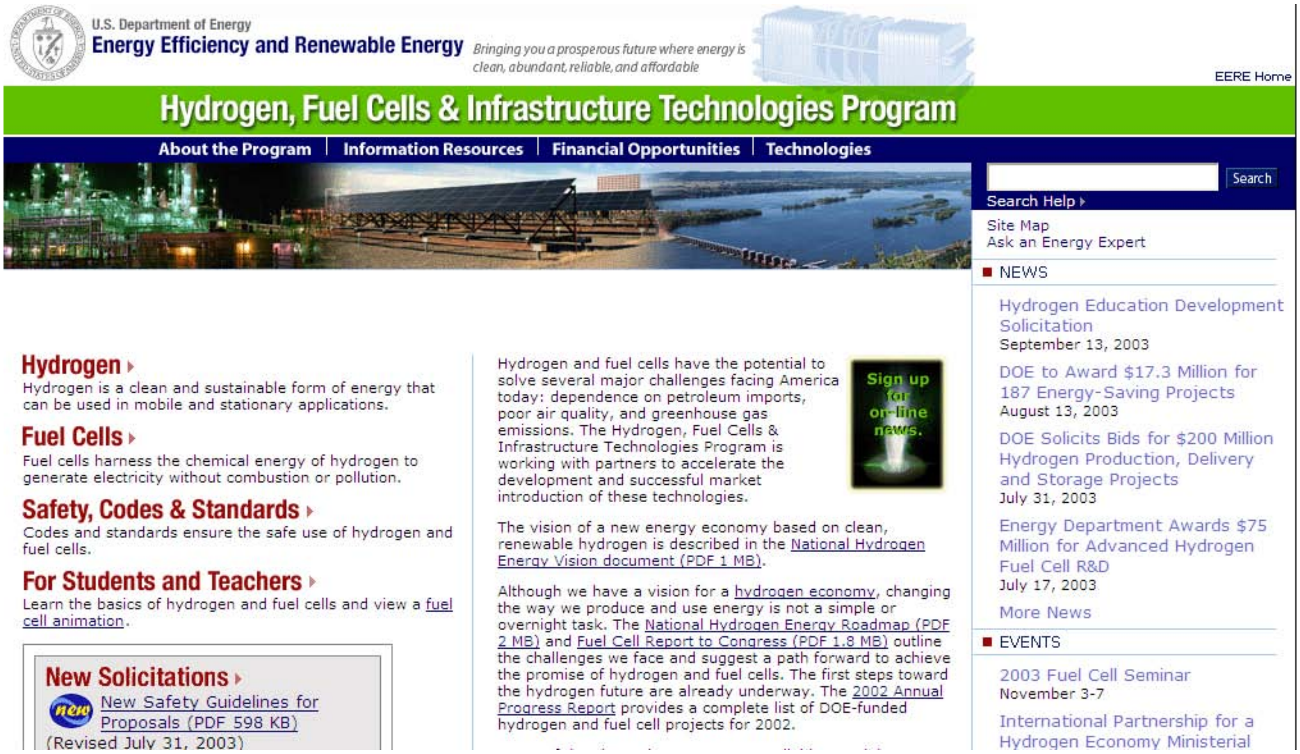
Donna Ho (202) 586-8000 Donna.Ho@ee.doe.gov	• Transportation Fuel Cells • Bipolar Plates • SBIR Program
Valri Lightner (202) 586-0937 Valri.Lightner@ee.doe.gov	• Fuel Processing • MEA R&D • Budget Coordination • Intra-agency Coordination

Updated Website

The website for the Hydrogen, Fuel Cells, and Infrastructure Technologies Program has been updated and expanded to include not only Program information, but information about hydrogen and hydrogen fuel cell vehicles in general.



Hydrogen
Hydrogen is a clean and sustainable form of energy that can be used in mobile and stationary applications.

Fuel Cells
Fuel cells harness the chemical energy of hydrogen to generate electricity without combustion or pollution.

Safety, Codes & Standards
Codes and standards ensure the safe use of hydrogen and fuel cells.

For Students and Teachers
Learn the basics of hydrogen and fuel cells and view a fuel cell animation.

New Solicitations
new New Safety Guidelines for Proposals (PDF 598 KB)
(Revised July 31, 2003)

Hydrogen and fuel cells have the potential to solve several major challenges facing America today: dependence on petroleum imports, poor air quality, and greenhouse gas emissions. The Hydrogen, Fuel Cells & Infrastructure Technologies Program is working with partners to accelerate the development and successful market introduction of these technologies.

The vision of a new energy economy based on clean, renewable hydrogen is described in the National Hydrogen Energy Vision document (PDF 1 MB).

Although we have a vision for a hydrogen economy, changing the way we produce and use energy is not a simple or overnight task. The National Hydrogen Energy Roadmap (PDF 2 MB) and Fuel Cell Report to Congress (PDF 1.8 MB) outline the challenges we face and suggest a path forward to achieve the promise of hydrogen and fuel cells. The first steps toward the hydrogen future are already underway. The 2002 Annual Progress Report provides a complete list of DOE-funded hydrogen and fuel cell projects for 2002.

NEWS

Hydrogen Education Development Solicitation
September 13, 2003

DOE to Award $17.3 Million for 187 Energy-Saving Projects
August 13, 2003

DOE Solicits Bids for $200 Million Hydrogen Production, Delivery and Storage Projects
July 31, 2003

Energy Department Awards $75 Million for Advanced Hydrogen Fuel Cell R&D
July 17, 2003

More News

EVENTS

2003 Fuel Cell Seminar
November 3-7

International Partnership for a Hydrogen Economy Ministerial

The photograph on the next page was taken at the October 8, 2003 DOE program management meeting and includes managers from the Offices of Nuclear Energy (NE), Fossil Energy (FE), Science (SC), and Energy Efficiency and Renewable Energy (EERE), and personnel providing critical support to the program. The Hydrogen Program Merit Review and Peer Evaluation Meeting will be held May 24-27, 2004, in Philadelphia. We hope that you will join us there.

S. Chalk

Steven G. Chalk, Hydrogen Program Manager
Office of Hydrogen, Fuel Cells, and Infrastructure Technologies
Energy Efficiency and Renewable Energy

The Hydrogen Program Team: 1. John Petrovic (LANL); 2. Neil Rossmeissl (EERE); 3. Mark Paster (EERE); 4. Tia Alexander (EERE); 5. John Houghton (SC); 6. Ed Schmetz (FE); 7. Valri Lightner (EERE); 8. Tony Bouza (EERE); 9. David Henderson (NE); 10. Michael Shapiro (TMS); 11. Patrick Davis (EERE); 12. Art Hartstein (FE); 13. Carole Read (EERE); 14. John Garbak (EERE); 15. Lauren Inouye (Sentech); 16. Amy Taylor (NE); 17. Steve Chalk (EERE); 18. Lucito Cataquiz (EERE); 19. Roxanne Danz (EERE); 20. Nancy Garland (EERE); 21. Pete Devlin (EERE); 22. Sunita Satyapal (EERE); 23. Christy Cooper (EERE); 24. Donna Ho (EERE); 25. Rich Bechtold (QSS); 26. Bill Cleary (ANL); 27. Larry Blair (Consultant); 28. Chris Bordeaux (EERE); 29. Matt Kauffman (EERE); 30. Barbara Wolfe (QSS); 31. Reeshemiah Schuler (CSMI); 32. Arlene Anderson (EERE); 33. Lowell Miller (FE); 34. Harriet Kung (SC); 35. Melissa Lott (QSS); 36. Marsha Quinn (EERE); 37. Kristen Rannels (Sentech); 38. Sigmund Gronich (EERE); 39. JoAnn Milliken (EERE); 40. Bobi Garrett (NREL); 41. Kathi Epping (EERE); 42. Tom Morehouse (ETM Strategic Consulting); 43. Peter Alyanakian (DOE Philadelphia Regional Office)

Novel Catalytic Fuel Reforming

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Objectives

The ultimate goal of this research project is to develop technology that will produce pure hydrogen from natural gas and logistical fuels using catalytic steam reforming and membrane hydrogen separation.

Phase III is intended to advance the state of InnovaGen™ fuel processing technology to the point of alpha readiness. This means that the fundamental design of key subsystems will evolve to include:

- Mature configurations (geometry and component placement defined)
- Material specifications
- Value engineering, design for manufacturability
- Reliability engineering and modeling.

Phase III includes considerable research, engineering, analysis, design and testing efforts. The result of these efforts will be prototypes capable of successfully completing a multi-unit test program representative of specified operating conditions.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Fuel Cells

- J. Durability
- L Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration and Efficiency

Production

- A. Fuel Processor Capital Costs

Approach

- Conduct system analyses and generate design specifications.
- Design and fabricate components.
- Test components.
- Design process configurations.
- Evaluate configurations with model simulation.
- Predict component and operational requirements with model simulation.
- Conduct iterative testing of integrated system.

Accomplishments

- Concluded testing of the Phase II 1-kW diesel fuel processor platform.
- Concluded testing of the sulfur tolerance of a 100-W palladium/copper (Pd/Cu) membrane assembly.
- Concluded long-term catalyst testing for natural gas reforming.
- Disassembled and inspected 100-W membrane module after testing.
- Disassembled and inspected 1-kW fuel processor after testing.
- Developed new reactor and burner design concepts. Developed a prototype micro-channel cross-flow combustor.
- Developed membrane module design concepts. Designed and procured components for a membrane/ coupon test fixture.
- Developed improvements to the fuel injector design. Generated an injector nozzle test program. Proceeded with the specification and procurement of equipment for testing the fuel injector and mixer.
- Continued work on heat exchanger design concepts. Established final requirements for heat exchangers.
- Finalized system operating and design parameters.

Future Directions

- Increase system efficiency and reduce system size and weight.
- Further develop hydrogen purification module.
- Improve system packaging.
- Scale up design to at least 60 LPM hydrogen output; enough for a 5-kWe fuel cell.
- Complete micro-channel implementation.
- Automate start-up, operation, and shut-down.
- Perform more complete thermal integration.
- Focus on manufacturability, cost reduction and high-volume production.
- Fully integrate with at least one fuel cell model.
- Thoroughly test reliability.
- Enhance controls - off-site monitoring, data mining, self-diagnostics.
- Complete documentation - drawings, bills of material, manufacturing routers.

Introduction

To be marketable now, fuel cells need to use primary fuel sources from existing production and distribution networks - i.e. natural gas, gasoline, diesel or jet fuels. Fossil fuel-powered fuel cells or refueling stations can form the bridge to a future when renewable resources power fuel cells. When compared to compressed hydrogen, reformed hydrocarbon fuels offer a significant cost advantage in the delivery of power. The high energy density of these fuels will also contribute to increased run times per unit of fuel consumed, and size and weight reductions associated with fuel storage.

To meet this need, InnovaTek is integrating microreactor technology with advanced sulfur-tolerant catalysts and hydrogen membrane technology to create a fuel processor for hydrogen generation. The ultimate goal of this cooperative project is the development of a catalytic reactor heated by the combustion of membrane by-products (raffinate) for the production of clean hydrogen by steam reforming hydrocarbon fuels. Advanced membrane technology is being used to remove CO and CO_2 from the reformate. The fuel processor being developed will provide a pure output stream of hydrogen that can be used without further purification for electrical generation by a PEM fuel cell.

Approach

The ultimate goal of this research program is to develop fuel processing technology that makes it possible for fuel cells to replace internal combustion engines as the power source for electrical generators and auxiliary power units in the 1-5 kW range. The fuel processor developed will produce pure hydrogen from fuels using cost-competitive, highly efficient catalytic steam reforming and membrane separation technology.

The design and optimization of a fuel processing system is complex because of the number of required components and functions (Table 1).

The following objectives (broken down by key subsystems) were identified to achieve our goal.

Overall System Modeling, Analysis and Design

- update model (optimize efficiency, provide design parameters)
- generate and maintain process and instrumentation diagram (P&ID) (revision control and distribution)

Reformer

- burner (convert to diesel start-up)
- vaporizer and superheater (micro-channel alternatives, integration into reactor)
- catalysts (sulfur tolerance, deposition, reforming temperature reduction)
- reformate condensate (recycling, evaporation, disposal)
- reactor design (micro-channel implementation, catalyst deposition, manufacturability)

Fuel Injector

- mixer (develop next generation diesel injector, steam mixer)

Membrane H_2 Purifier

- research contamination causes (investigate Zn, Cd and other contaminants)
- membrane material selection (optimize material form and composition)
- membrane module design (optimize design of membrane module)
- thermal integration (eliminate external heating)

Thermal Management

- condensate cooling/condensing (cooling system design, efficiency improvements)
- other heat exchangers (micro-channel alternatives, integration into the reactor)

Table 1. Primary Components of InnovaTek's Fuel Processor

Component	Function	Product
Catalytic Reactor	Catalytically reforms fossil fuel	Reformate (H_2, CO_2, CO)
Catalyst	Catalyzes the reforming reaction	Reformate
Combustor	Burns raffinate to provide heat for the reforming reaction	Heat, CO_2, H_2O
Fuel injector	Injects and mixes fuel and steam into the reactor	Vaporized steam/fuel mixture
Heat exchangers	Provides the proper temperature for each component	Warmer or cooler gas streams
H-permeable membrane	Converts reformate to pure hydrogen and produces raffinate (membrane reject stream) for combustor	Pure hydrogen, raffinate (H_2, CO_2, CO)

Sulfur Management

- de-sulfurization of reformate (as necessary, preferably re-generative and in-situ)
- desulfurization of fuel (research alternatives)
- thermal integration (eliminate external heating)

Operational Considerations

- safety (failure mode and effect analysis [FMEA], hazard analyses, etc.)
- reliability (reliability modeling, test programs)
- code requirements (research requirements, establish design guidelines)
- manufacturability, maintainability (establish targets, schedule design reviews)

Documentation

- drawings (finalize standards for format, archiving etc.)
- product data management (establish data master, configuration management and other requisite systems)

Physical Layout and Balance of Plant (BoP), including:

- pumping (research and obtain more reliable, less expensive alternatives)
- insulation and shrouds (improve performance and aesthetics)
- valves, orifices, thermocouples, transducers, etc. (integrate control devices)

Sensors and Controls, including:

- metering and flow measurement (eliminate expensive mass flow controllers)
- automation (automated shut-down, start-up and operation)
- hardware, software design (establish requirements for controllers and software)
- diagnostics (implemented as required for troubleshooting)
- data logging (establish requirements, minimize excess data collection)

Results

Catalyst and Membrane Testing

Steam Reforming Catalyst Testing. Over 1,000 hours of catalyst testing was completed using natural gas as a feedstock. The reforming occurs at 850°C with steam/carbon ratio of approximately 3.5. Figure 1 shows the product composition for the last half of the test. Hydrogen concentration is about 75%; the product contains about 1-2% unconverted methane due to the pressure (>80 psig) at which the steam reforming was conducted. This agrees with thermodynamic calculations. The total product flow

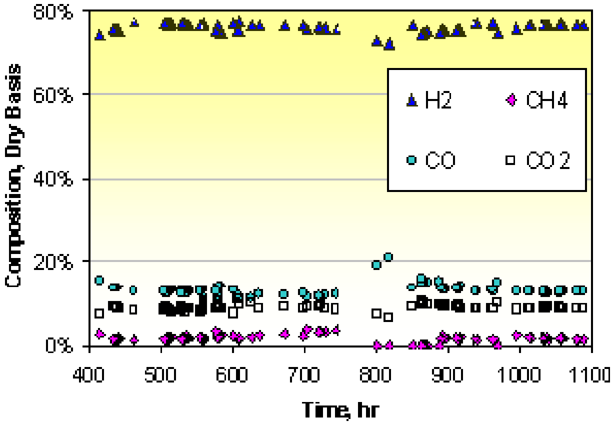

Figure 1. Product Gas (H_2, CO, CO_2, and CH_4) Composition During Steam Reforming of Natural Gas Using InnovaTek's Proprietary Catalyst (ITC #1148); reaction temperature 850°C, water feed rate 1.0 ml/min, natural gas feed rate 380 ml/min, pressure 84.7 psi

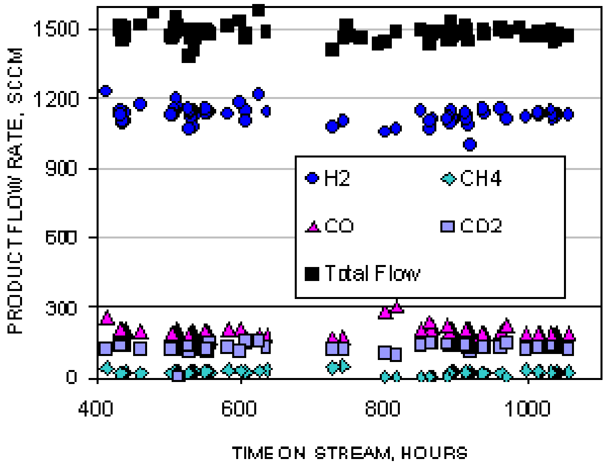

Figure 2. Product Gas (H_2, CO, CO_2, and CH_4) Flow Rates During Steam Reforming of Natural Gas

rate was measured and is plotted in Figure 2 About 1.5 SLM product was produced with a natural gas feed rate of about 380 mL/min, which corresponds to approximately 95% conversion of the natural gas. An 80-hour test with ultra-low sulfur (~5 ppm) diesel, a developmental product obtained from Chevron Phillips Chemical, was also successfully completed (Figure 3).

Membrane Hydrogen Purifier Performance. We designed and fabricated a hydrogen-permeable metal membrane assembly and tested it with simulated reformate with and without sulfur. The 97 ppm concentration of sulfur in the sulfur-containing reformate represents the result of reforming fuel containing approximately 800 ppm sulfur (by weight). Tests were conducted at a pressure of 90 psig. Optimum results were obtained at a membrane temperature of 500°C when sulfur was present and at 400°C without sulfur. Although the sulfur apparently causes some degradation of permeation initially, it appears that performance stabilizes after approximately one hour of run-time. The ultimate recovery with sulfur present is approximately 57% of the recovery without sulfur (Figure 4).The results show promise that a sulfur-tolerant membrane module can be developed but that its surface area will need to be about 1.75 times larger to achieve the same hydrogen permeation rate that is possible when sulfur is not present in the reformate. A visual inspection of the module after disassembly showed no adverse effects from the testing.

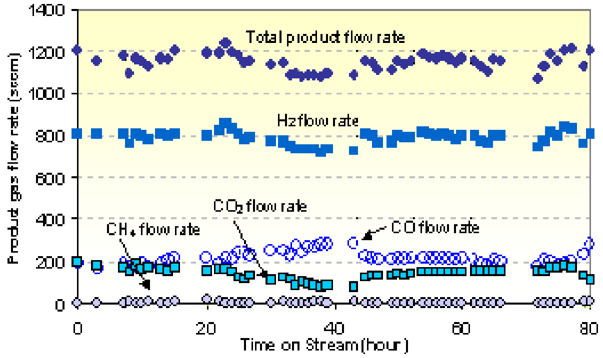

Figure 3. Steam Reforming of Low-Sulfur Diesel Fuel Using InnovaTek's Proprietary Catalyst

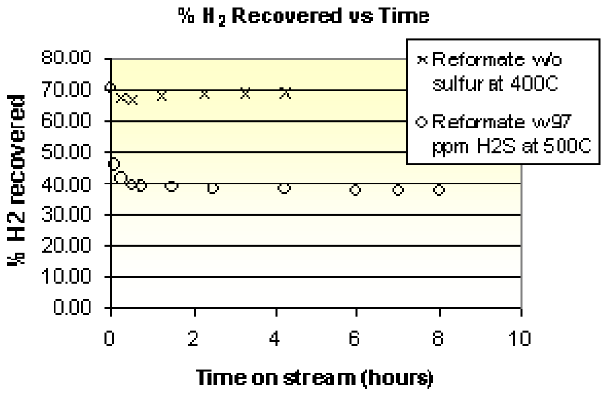

Figure 4. Hydrogen Recovery as a Function of Time and Sulfur Concentration

System Integration

System components were integrated according to the simplified schematic in Figure 5. Table 2 summarizes the operating parameters and system specifications as they currently are defined. We are able to achieve a 49% efficiency using a recuperator to recapture heat from the exhaust to pre-heat combustion air.

Prototype Operation and Testing

We performed continuous testing of the 1-kW prototype using diesel fuel, logging approximately 120 hours of run-time. Over the course of operation, the sulfur content of the fuel was increased incrementally from 50 ppm to 100 and finally to 250 ppm. During these tests, increased understanding was obtained for catalyst and membrane performance in an integrated system. The fuel injector was found to be a critical component that can help eliminate coking, one of the most serious problems associated with reforming heavy hydrocarbon fuels.

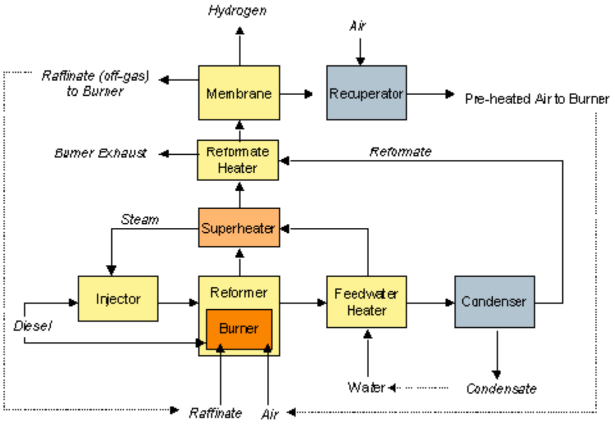

Figure 5. InnovaTek Fuel Processor System Diagram

Table 2. 1-kW System Operating Parameters

Parameter	Value
Diesel Flow Rate to Reactor	3.6 gm/min
Diesel Flow Rate to Burner	2.0 gm/min
Water Feed Rate	23 gm/min
Condensate Collected from Reformate	16 gm/min
Reformer Shell Losses	500 W
Reformate Condensing Temperature	60°C
Reforming Temperature	850°C
Membrane Operating Temperature	400°C
Membrane Surface Area	524 cm^2
Thermal Efficiency	49%

Another finding was that as fuel sulfur content was increased, more frequent catalyst conditioning was required. We also determined that high conversion rates are required during steam reforming to prevent degradation of the membrane system over time.

Hydrogen production of the 1-kW diesel fuel processor was measured over a period of approximately 14 hours of continuous operation at steady-state operating conditions. When compared to the recorded diesel fuel flow rates, an average thermal efficiency was calculated to be at least 36 ±3% (based upon the lower heating values of both the diesel and the hydrogen). This result is short of our target efficiency of 50%, due primarily to higher operating temperatures and steam/carbon ratios, and non-optimized thermal integration. After testing, the prototype fuel processor was disassembled, dissected and inspected. The components were found to be sound and in overall very good condition.

Conclusions

- Our process model was very useful in contributing to the design and establishing the operating parameters of the system.
- Performance tests of InnovaTek's proprietary steam reforming catalyst, conducted in a 100-W test bed and a 1-kW system, indicate that the catalyst can be used for multiple fuel types without the need for prior sulfur removal, although periodic regeneration is required at higher sulfur concentrations.
- A scheme for on-line re-generation of the reforming catalyst has been developed and will be implemented in a modular reactor.
- The hydrogen purification membrane module design is improved, and membrane testing on a custom test fixture indicated that, although the membrane tolerates sulfur, increased surface area is required when sulfur is present in the reformate.
- The fuel injector design continues to improve and is a crucial component to prevent catalyst fouling or reactor plugging during operation.

FY 2003 Publications/Presentations

1. Irving, P.M., T.M. Moeller, Q. Ming, and A. Lee, "Hydrogen Production from Heavy Hydrocarbons Using a Fuel Processor with Micro-Structured Components", presented at the 2002 Fuel Cell Seminar, November 18-21, 2002, Palm Springs, CA.

2. Irving, P.M. "The InnovaGen™ Fuel Processor", presented at the SIRTI Technology Showcase, November 2002, Spokane, WA.

3. Irving, P.M., Q. Ming, and D.R. Stephens, "Development of a Fuel Processor that Generates Hydrogen from Conventional Fuels", In: Proceedings of the 14th Annual U.S. Hydrogen Meeting, March 4-6, 2003, Washington DC.

4. Irving, P.M., "Novel Catalytic Fuel Reforming", Global Climate Energy Project, April 14-15, 2003, Stanford University.

5. Irving, P.M., Q. Ming, T. Dickman, and D.R. Stephens, "The InnovaGen™ Diesel Fuel Processor with Micro-Channel Components", In: Proceedings of the Hydrogen and Fuel Cells 2003 Conference and Trade Show, June 8-11, 2003, Vancouver, BC.

Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels (ITM Syngas)

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Subcontractors:
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Objectives

- Research, develop and demonstrate Ion Transport Membrane (ITM) Syngas ceramic membrane reactor system for the low-cost conversion of natural gas to hydrogen and synthesis gas
- Scale-up the ITM Syngas reactor technology through three levels of pilot-scale testing and precommercial demonstration
- Obtain the technical, engineering, operating and economic data necessary for the final step to full commercialization of the ITM Syngas technology

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- D. Carbon Dioxide Emissions
- AA.Oxygen Separation Technology

This project also addresses DOE Office of Fossil Energy objectives to develop lower cost methods to produce hydrogen from natural gas.

Approach

This project is in Phase 2 of a three-phase program. The approach in Phase 2 includes:

- Task 2.1 Commercial Plant Economic Evaluation
- Task 2.2 Materials and Seals Development and Evaluation
- Task 2.3 ITM Syngas Membrane and Module Design and Fabrication
- Task 2.4 Nominal 24,000 SCFD ITM Syngas Process Development Unit
- Task 2.5 Nominal 330,000 SCFD ITM Syngas Subscale Engineering Prototype

Accomplishments

- Process design and economic evaluation of a 150 million SCFD hydrogen plant with CO_2 separation to provide a carbon-free "clean fuel" showed the potential for 30% capital cost savings in the synthesis gas production step
- Projected hydrogen production costs for a distributed-scale hydrogen process (500,000 SCFD hydrogen, 100 units/year) are more than 25% below the DOE targets for 2005
- Demonstrated good performance stability of tubular membranes and seals at 250 psig and 825°C for 6 month individual test durations
- Achieved the project's Phase 1 oxygen flux targets with catalyzed, supported thin-film planar membranes
- Achieved a three-fold increase in pilot-scale membrane fabrication yields over one year ago
- Selected catalysts for scale-up testing in the Process Development Unit (PDU)
- Demonstrated leak-tight performance of PDU module seals at 425 psig and 850-900°C under static conditions and multiple pressure and thermal cycles
- Tested second-generation pilot-scale membrane modules in the PDU at elevated temperature and pressure with a synthesis gas environment
- Fabricated commercial-size ceramic membranes

Future Directions

- Fabricate multi-wafer membrane module for PDU test
- Test catalyzed planar membranes in PDU
- Fabricate balance of ceramic components for Subscale Engineering Prototype (SEP) module with commercial-size membranes
- Initiate tests to validate commercial-size membrane design
- Conduct tests to determine kinetic parameters for membrane and catalysis performance models

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Introduction

Ion Transport Membranes (ITMs) are a revolutionary platform technology for producing hydrogen and synthesis gas for applications in power generation, transportation fuels, and chemicals. The ITM Syngas process provides a lower-cost method for converting natural gas to hydrogen and synthesis gas by combining air separation and natural gas partial oxidation in a single-step ceramic membrane reactor, with the potential for capital cost savings of over 30%. When successful, this technology will be important to emerging hydrogen markets, such as hydrogen-based fuel cells for transportation and centralized hydrogen production facilities with CO_2 capture.

The new technology utilizes non-porous ceramic ITM membranes fabricated from multi-component metallic oxides that have both high electronic and oxygen ion conductivity at high temperatures (greater than approximately 700°C). In operation, oxygen from a hot air stream is reduced at one surface of the ITM membrane to oxygen ions, which diffuse through the membrane under a chemical potential gradient. At the opposite surface of the membrane, the oxygen partially oxidizes a pre-reformed mixture of hot natural gas and steam to form synthesis gas, a mixture of hydrogen and carbon monoxide. The ratio of hydrogen to carbon monoxide is in part dependent upon the amount of steam. The membrane material must show long-term stability in reducing and oxidizing atmospheres, and long-term compatibility with any oxygen reduction and partial oxidation/reforming catalysts that are in contact with its surface.

Approach

The objective of this program is to research, develop and demonstrate a novel ceramic membrane reactor system for the low-cost conversion of natural gas to hydrogen and synthesis gas: the ITM Syngas process. Through a 9½ year, three-phase program, the ITM Syngas technology will be developed and scaled up to obtain the technical, engineering, and operating and economic data necessary for the final step to full commercialization of the hydrogen and synthesis gas generation technology. Phase 2 of the program was initiated in FY 2000 and will extend for 4½ years. Process concepts and performance will be validated in two stages of scale-up in Phase 2: the Process Development Unit (PDU), which began operation in 2002, and the Subscale Engineering Prototype (SEP), which will operate in 2004-2005.

In Task 2.1, "Commercial Plant Economic Evaluation," advanced ITM Syngas processes will be developed, and the economics of operation at the commercial plant scale will be evaluated based on the results of the Phase 2 program. In Task 2.2, "Materials and Seals Development and Evaluation," membrane materials and seals will be tested at the laboratory scale under process conditions to obtain statistical performance and lifetime data. In Task 2.3, "ITM Syngas Membrane and Module Design and Fabrication," membrane reactors will be designed for the ITM Syngas process at the PDU, SEP and commercial scales. Pilot-scale membrane modules will be fabricated for testing in the PDU. Fabrication of the membrane reactor modules will be scaled up in a Production Development Facility (PDF) to supply the requirements of the SEP.

In Task 2.4, "Nominal 24,000 SCFD ITM Syngas PDU," the components of the ITM Syngas technology will be demonstrated in a laboratory Process Development Unit (PDU). The PDU will operate at an equivalent of 24,000 SCFD of synthesis gas capacity and will performance test pilot-scale planar membranes under commercial process conditions. In Task 2.5, "Nominal 330,000 SCFD ITM Syngas SEP", a Sub-Scale Engineering Prototype (SEP) unit will be built to demonstrate the ITM Syngas technology using commercial-size membranes in sub-scale modules. The SEP will demonstrate the operation of the ITM Syngas process at up to an equivalent of 330,000 SCFD of synthesis gas capacity.

Results

Conventional methods for producing hydrogen from natural gas typically require external sources of heat (e.g. steam methane reformers) or a separate pure oxygen stream (e.g. oxygen-fired autothermal reformers). Steam methane reformers (SMR) use natural gas as fuel in reformer furnaces to generate heat, which is transferred to the reforming catalyst packed in high-pressure tubes, resulting in a significant fraction of the carbon emitted to the atmosphere as CO_2 in the low-pressure flue gas. Oxygen-fired autothermal reformers (ATR) use oxygen to partially oxidize natural gas internally in the reactor and retain nearly all the carbon in the high pressure synthesis gas, thus facilitating removal of CO_2 for carbon capture. However, the ATR requires a separate air separation unit (ASU) to produce high purity, high-pressure oxygen - thus adding complexity and capital and operating cost to the overall process. The ITM Syngas process offers the advantages of partial oxidation of the natural gas and the concomitant retention of carbon in the high-pressure synthesis gas, while simultaneously permeating pure oxygen across the ceramic membrane from a low-pressure air supply (Figure 1).

In an evaluation of advanced process concepts, an ITM Syngas process was developed for a centralized hydrogen production plant with CO_2 removal, producing 150 million SCFD of fuel-grade hydrogen. For this application, the ITM Syngas process was compared to a conventional oxygen-blown ATR with a cryogenic ASU to supply oxygen. Economic evaluation of the ITM Syngas process showed the potential for 30% capital cost savings in

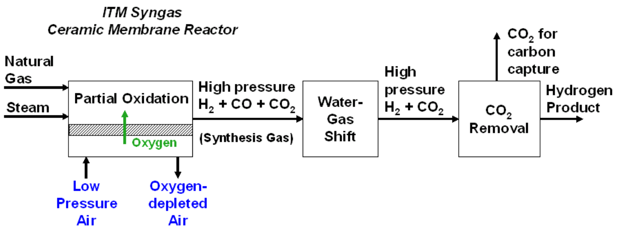


Figure 1. ITM Syngas Process to Produce Hydrogen and Capture CO_2

the synthesis gas generation process area and over 20% capital cost savings for the overall hydrogen and CO_2 production process. The ITM Syngas process also has a higher thermal efficiency of 74% compared to 71% for the oxygen-blown ATR process. The hydrogen product is a "clean" fuel suitable for centralized power generation and for distribution to local stationary or mobile applications, including fuel cells.

Tubular membranes and seal assemblies were tested in high-pressure, high-temperature lab-scale units under commercial process conditions. In these tests, pre-reformed natural gas mixtures at process pressure were passed over the outer surface of the tubular membrane, while air at atmospheric pressure was fed to the inner surface of the tube. Multiple tests, each operated continuously for over 6 months at 250 psig and 825°C under process conditions, were completed, and the membranes demonstrated good performance stability. A long-term test of a tubular membrane at high pressure and temperature is shown in Figure 2.

Sub-scale supported thin-film membranes were also tested at atmospheric pressure for periods of over 1200 hours. Tests of advanced catalyzed membranes demonstrated oxygen fluxes that approach the commercial flux target range and meet the Phase 1 flux target (Figure 3).

Rapid progress has been made in scaling up ceramic membrane fabrication using conventional processing methods (Figure 4). Lab-scale disk membranes were developed in 1999 in conjunction with initial materials development. Pilot-scale membranes were developed in 2000-2001 and have a 30-fold increase in membrane area over the lab-scale membranes. The pilot-scale membranes are being used to demonstrate membrane performance at commercial process conditions in the PDU. Fabrication methods that were developed at the pilot-scale were scaled up for commercial-size membranes, which have a 160-fold increase in membrane area over the lab-scale membranes. Fabrication of commercial-size membranes started in 2002.

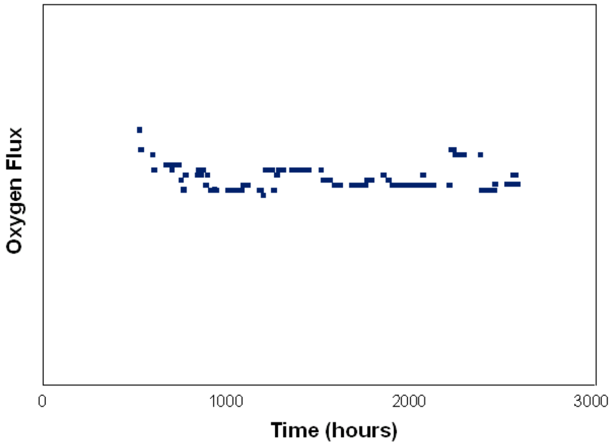


Figure 2. Long-Term High Pressure Test of a Tubular Membrane Shows Stable Oxygen Flux

Pilot-scale membrane modules have been tested in the PDU at elevated temperature and pressure with a synthesis gas environment. The PDU integrates the various components of the ITM Syngas reactor design and is used to confirm the performance of the planar membrane modules and seals under commercial process conditions. Ceramic-to-metal

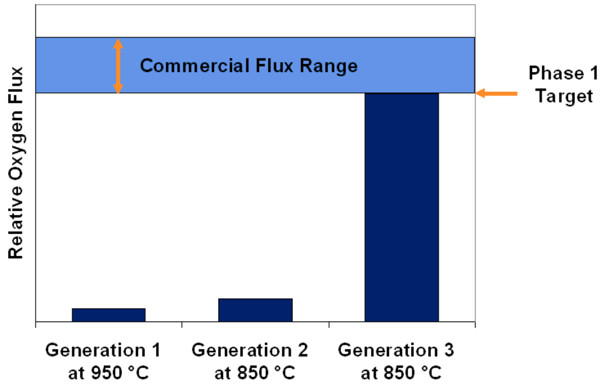
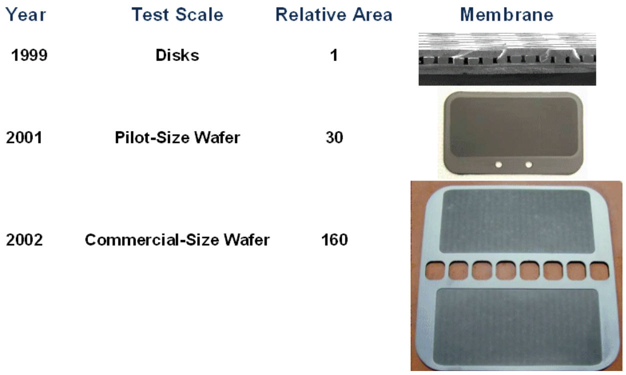


Figure 3. Advanced Catalyzed Membranes Approach Commercial Flux Target



Year	Test Scale	Relative Area	Membrane
1999	Disks	1	
2001	Pilot-Size Wafer	30	
2002	Commercial-Size Wafer	160	

Figure 4. Achieved Rapid Scale-up of ITM Syngas Ceramic Membranes Target

seals are used to connect the ceramic membrane module to metal air feed and vent piping and are a critical element in the membrane reactor system. PDU module seals have demonstrated leak tight performance at 425 psig and 850-900°C under static conditions, and also over 50 thermal cycles and 8 pressure cycles (Figure 5).

Conclusions

Significant progress has been made to develop the ITM Syngas technology. A database is being built of performance data from several six-month duration membrane tests. Membrane modules and seal assemblies have also been fabricated and tested in the PDU at elevated temperature and pressure typical of synthesis gas conditions. Ceramic fabrication scale-up has progressed, and commercial-size membranes are being fabricated. Excellent progress continues to be made against the remaining technical challenges in the demonstration and scale-up of the ITM Syngas technology.

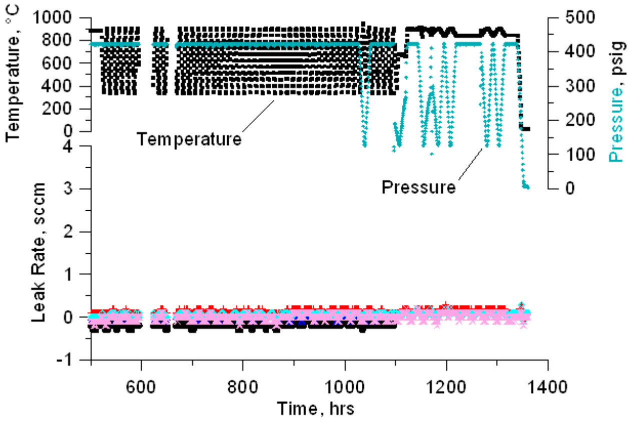


Figure 5. PDU Module Ceramic-To-Metal Seals Demonstrate Leak-Tight Performance at Steady-State and with Thermal and Pressure Cycling

FY 2003 Publications/Presentations

1. "Development of Ceramic to Metal Seals for Ceramic Membrane Applications," 57th Annual Forum of the Pennsylvania Ceramics Association, Sept. 2002

2. "Ion Transport Membranes for Gas Separation," 57th Annual Forum of the Pennsylvania Ceramics Association, Sept. 2002

3. "Development of the Ceramic Membrane ITM Syngas Process," American Chemical Society National Meeting, New Orleans, LA, March 2003

4. "Development of the Ceramic Membrane ITM Syngas Process," American Institute of Chemical Engineers Spring Meeting, New Orleans, LA, March 2003

5. "Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels," US DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Merit Review, Berkeley, CA, May 2003

6. "Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels," US DOE Advanced Synthesis Gas and Clean Fuels Program Merit Review, Houston, TX, June 2003

FY2003 Patents Issued or Applications Filed

1. "Mixed Conducting Membranes for Syngas Production", US Pat #6,492,290

2. Three patent applications filed covering ceramic-ceramic joining methods and the membrane assembly

Integrated Ceramic Membrane System for Hydrogen Production

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Subcontractor: Research Triangle Institute, Research Triangle Park, NC

Objectives

- Develop an integrated ceramic membrane system using an oxygen transport membrane (OTM) in the first stage to produce syngas and a hydrogen transport membrane (HTM) in the second stage to produce hydrogen at a low cost on a scale of 1000-5000 SCFH
- Develop a palladium-based HTM that can meet performance goals for flux, selectivity, life, and cycling on a bench scale
- Develop the substrate materials, coating materials, and appropriate manufacturing technology
- Confirm membrane performance under simulated reactor conditions
- Confirm that the process is cost competitive for distributed hydrogen production

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- E. Control and Safety
- Z. Catalysts
- AA. Oxygen Separation Technology
- AB. Hydrogen Separation and Purification

Approach

- Update literature review
- Develop substrate
- Develop membrane
- Confirm membrane performance through tube testing
- Update process economics

Accomplishments

- Completed Phase I
- Determined that the two-stage integrated ceramic membrane process could be cost competitive if the membranes can be developed

- Identified alloy compositions with suitable resistance to contaminants
- Identified substrate compositions with suitable thermal expansion properties
- Fabricated porous ceramic support tubes
- Coated the porous ceramic support tubes with palladium alloy

Future Directions

- Produce leak-free composite palladium alloy membranes
- Demonstrate membrane performance in simulated reactor conditions
- Determine the cost of hydrogen production using palladium alloy membranes
- Decide whether to continue the project based on membrane performance and projected costs

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Introduction

Hydrogen can be produced from natural gas by mixing it with steam, oxygen, air, or a combination of these to produce syngas, which contains hydrogen. One potentially low cost, efficient way to produce syngas is to use a ceramic membrane to separate oxygen from air. The separated oxygen reacts with natural gas and steam over a catalyst to produce syngas. The membrane, which can be integrated into the syngas generator, eliminates the need for a large, expensive air separation plant. (The work on oxygen membranes is being done in a different project.) Implementing those membranes to produce hydrogen is one of the goals of this project. To produce hydrogen, the product syngas is typically sent to another reactor where most of the CO and some of the steam in the syngas react to produce additional hydrogen. Using conventional existing technology, the hydrogen in the product stream from the second reactor must be purified using additional large, expensive equipment. The goal of the current phase of this project is to simplify hydrogen production by combining the second reactor and the hydrogen purification into a single step in a single vessel, which could significantly reduce the cost of producing hydrogen, and consequently, reduce the price of hydrogen to the consumer. Because of the way that the reaction and separation are combined, it is also possible to produce more hydrogen than would be possible using the conventional two-step approach, providing additional benefit to the consumer.

Phase I of this project analyzed and compared several different processes. Based on projected cost, efficiency, and likelihood of success, a two-stage process wherein each stage was comprised of a membrane reactor was selected. The analysis indicated that this process has the potential to be the least expensive hydrogen production method of those evaluated. Phase II, which began earlier this year, has focused on developing the hydrogen purifier to put this process into practice. Potential materials have been identified, and several attempts have been made toward fabricating the hydrogen purifier. These attempts have shown continuous improvement and provided essential information about what remains to be done to produce an effective purifier.

Approach

The first step in developing the hydrogen purifier was to determine possible materials for the membrane based on available results in the technical literature. Some membrane compositions examined in the past have been unable to resist contamination caused by other materials in the syngas, such as CO or sulfur. Other compositions have failed because they were made of materials with different thermal expansion characteristics so that when the final membrane was heated, the layers separated, destroying the membrane. Possible membrane compositions that are expected to be sufficiently resistant to contaminants and not separate when heated were identified.

The next step in the project is to make and test the membrane to confirm its performance. Porous substrates using ceramic materials have been made based on our expertise in producing ceramic membranes for other applications. These substrates have been coated with palladium, and the resulting membranes have been analyzed. Controlling the pore size and porosity of the ceramic substrate is critical to ensuring that the coating will be leak free and uniform while being sufficiently thin to provide adequate performance at a reasonable cost. The porous substrates have shown continuous improvement because of improved techniques designed to control the pore size and porosity of the substrates. Once sufficient membranes have been produced, they will be tested in a demonstration reactor using simulated syngas.

Provided that the membrane development is successful, the economic assessment performed in Phase I will be revised using the test data. If the integrated ceramic membrane process still appears to be a low-cost hydrogen generation process, we will advance to the next part of the project, which is testing the membrane in an integrated reactor.

Results

In the initial trial, eight porous ceramic tubes were fabricated by isostatic pressing. One of the tubes was activated and plated with palladium alloy layers. The tube was then thermally annealed in argon. Samples of the tube that were analyzed by scanning electron microscope (SEM) before and after annealing indicated the metal film thickness was about 4 µm. SEM analysis indicated that the top surface of this substrate tube was rough with up to 40-50 micron size holes on the surface. Although the plating appeared to go on well and seemed to follow contours into the large holes, it did not appear to bridge the gap at all of the large openings on the surface. A nitrogen leak test confirmed the presence of through holes throughout the surface, as indicated by the SEM analysis of the top surface of annealed films. Figures 1 and 2 show the top of the substrate surface before and after heating, respectively. These pictures clearly show the surface roughness and the size of large 40-50 µm size openings on the surface.

Because of the problems with these tubes, the next group of tubes was made with smaller pores, and thicker plating was used, as shown in Figures 3 and 4. Each of these steps was expected to improve the tube and make it less likely to leak. Tube # 030327-0 was activated and plated with palladium

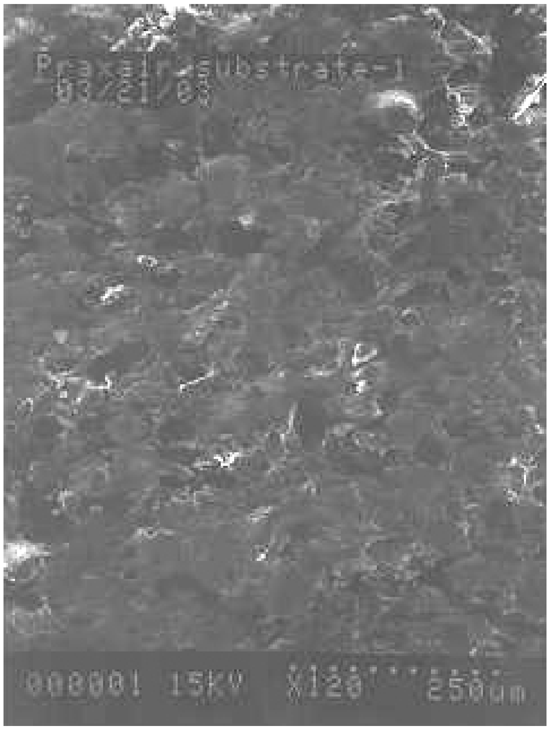

Figure 1. Schematic of Fabricated Tri-layer

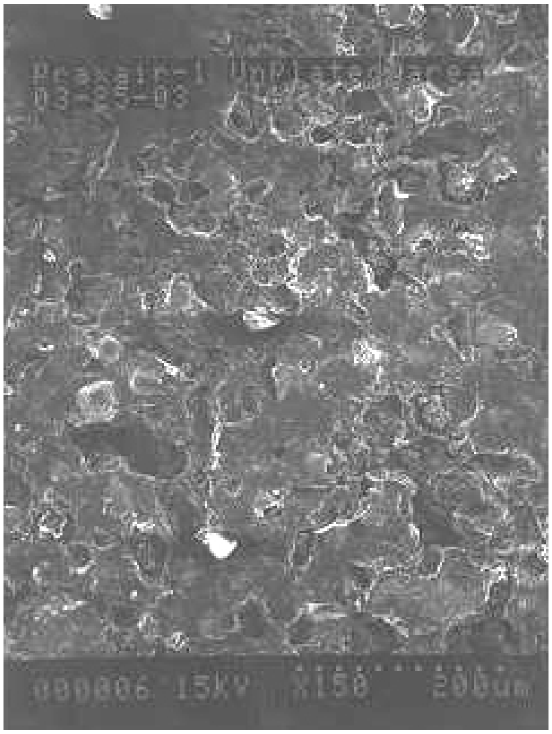

Figure 2. Top of Surface after Annealing

alloy. However, permeation analysis indicated a substantial leak of nitrogen through pinholes throughout the surface. Although the average pore size of the openings on the surface of this tube was smaller than the pores in the first batch, with a finer surface texture, large openings of the order of 50 µm were still evident on the surface (Figure 3). Although the plating appeared to go on the surface well and followed the contours into the large holes, it still did not bridge the gap at all of the large openings on the surface, as seen in Figure 4.

This batch of tubes showed improvement over the first batch, but the substrate surface needs to be smoother with smaller, more uniform openings to obtain a leak-tight metal film. Work on developing improved substrates continues.

Conclusions

- Palladium alloy compositions exist that have sufficient hydrogen flux and resistance to possible contaminants, such as sulfur and CO.
- Low-cost substrate materials exist with proper thermal expansion properties so that thermal cycling of the final membrane is likely to be possible.
- These substrate materials can be fabricated into porous tubes and coated with palladium alloy.
- Control of substrate pore size and porosity is critical.

FY 2003 Publications/Presentations

1. Presentation at the DOE Annual Merit Review Meeting

2. Semi-Annual Progress Report submitted to DOE

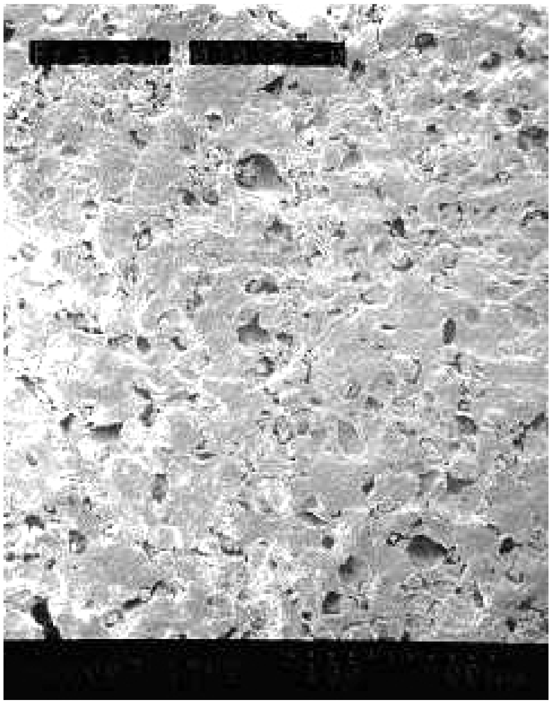

Figure 3. Top of Zirconia Substrate

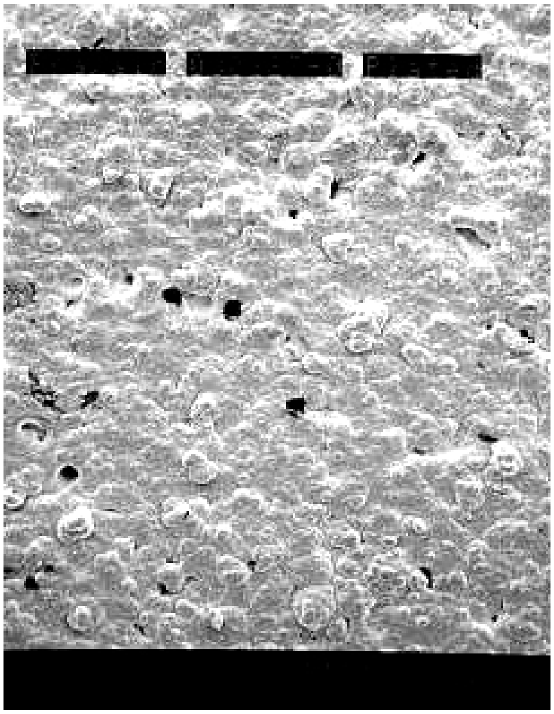

Figure 4. Top of Surface After Plating

Low Cost Hydrogen Production Platform

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Subcontractors:
Boothroyd-Dewhurst Inc, Wakefield RI
Diversified Manufacturing Inc, Lockport, NY

Objectives

- Examine opportunities for on-site production of hydrogen at low cost using existing technologies (steam methane reforming, pressure swing adsorption), with the following parameters:
  - 1,000 - 5,000 scfh
  - Small, compact, single skid system
  - 10-15 year system life
- Establish a benchmark for current technology
- Design and fabricate a prototype on-site hydrogen production system

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- E. Control and Safety

Approach

- Conduct review of existing technologies
- Develop preliminary design and engineering models
- Assess economics versus current and potential future supply options
- Develop and test component prototypes
- Develop final design and verify economics
- Build, install and test complete prototype system

Accomplishments

- Preliminary detail and process design completed
- 3D computer models of components and system completed

- Design for Manufacture and Assembly (DFMA) preliminary analysis completed
- System economic model completed
- Significant hydrogen cost reductions determined to be achievable

Future Directions

- Complete preliminary detail design and engineering models
- Complete DFMA analysis on total system
- Design, construct and test system components
- Verify component performance and overall system life
- Complete final detail design
- Develop, install and test prototype system
- Continue to update business and economic models

Introduction

Steam methane reformer (SMR)-based hydrogen production facilities are highly capital intensive because they are custom-designed and are built using one-at-a-time design and fabrication techniques. Capital costs account for 70-85% of the total per unit hydrogen costs for on-site systems in the 20,000 scfh and below capacity range. As a result, the opportunity exists for very substantial reductions in product hydrogen costs by introducing advanced design optimization technology. The focus of this project is to develop an integrated system for the turnkey production of hydrogen at 1,000 - 5,000 scfh (28-140 Nm^3/hr). The design is based on existing SMR technology and existing chemical processes or technologies to meet the design objectives. Consequently, the system baseline design consists of a steam methane reformer, a pressure swing adsorption (PSA) system for hydrogen purification, natural gas compression, steam generation and all components and heat exchangers required for the production of hydrogen. A process flow diagram of the system is shown in Figure 1. The scope of this project does not include hydrogen compression, storage or fueling station components.

The focus of the project emphasizes packaging, system integration and an overall step change in the cost of capital required for the production of hydrogen at low volumes. To assist in this effort, subcontractors were brought in to evaluate the design concepts and to assist in meeting the overall goals of the project. Praxair supplied the overall system and process design for the concepts and the subcontractors were used to evaluate the designs from a manufacturing and overall design optimization viewpoint. Design for manufacturing and assembly (DFMA) techniques and computer models were utilized to optimize the concepts during all phases of the design development.

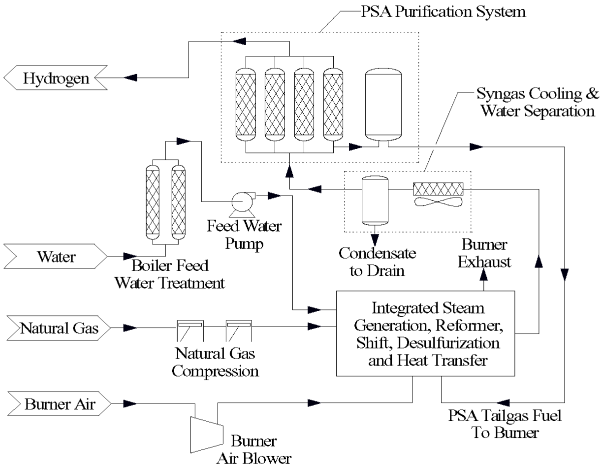

Figure 1. Low-Cost Hydrogen Production Platform Process Flow Diagram

Approach

The means for achieving low hydrogen costs from small systems is through capital cost reductions, integrating components and reducing the number of parts required for an SMR-based hydrogen production system. For conventional small plant designs, more than 75% of the cost of hydrogen is associated with capital costs. The project approach is to apply DFMA design techniques to the component and system designs from the early concept phase of design to the completion of the design effort. The reduction in number of parts and the resulting integration and simplification of the plant layout significantly reduces the capital cost and the overall plant size. Praxair has defined concepts that involve integration of steam generation, reforming, shift reaction and all high temperature components into a single highly integrated package. The PSA purification system as well as the overall skid layout and integration have also been designed using the DFMA approach. This effort shows the potential to significantly reduce the capital cost required for a small hydrogen system and thereby greatly reduce the overall cost to produce hydrogen.

A risk analysis was conducted to identify any design deficiencies related to the potential concepts. The analysis showed that no fundamental design flaw exists with the concepts, but additional simulations and prototypes would be required to verify the design(s) prior to fabricating a production unit. These identified risks will be addressed in detail during Phase II of the development project.

Along with the models of the high-temperature components, a detailed process and 3D design model of the remainder of system, including PSA, compression, controls, water treatment and instrumentation was developed and evaluated. The overall design and specifications were then used to develop accurate hydrogen costs for the optimized system. Potential areas for further cost reductions were also identified and will be investigated in future phases of the program.

A market and business analysis was also conducted as part of Phase I. A study of the current available and potential future hydrogen production technologies was compared with the design concepts developed in this project. An analysis of the potential market, with respect to number of units, feedstocks and capacity was also conducted.

Results

The capital and product costs were estimated for 1,000, 2,000 and 5,000 scfh plants at production rates of 1, 10, 100 and 1,000 units built per year. With the low cost SMR approach, the product hydrogen costs for 1,000 and 2,000 scfh plants at 100 units produced per year were approximately \$24/MMBtu and \$19/MMBtu (HHV), respectively. With increased volume production to 1,000 units per year, the hydrogen costs are reduced by about 12% to \$21/MMBtu for the 1,000 scfh unit and \$17/MMBtu (HHV) for the 2,000 scfh unit. For the 5,000 scfh plant, the cost of hydrogen ranged from \$14 to \$17/MMBtu (HHV) depending on number of units built per year. These costs represent a significant improvement and a new benchmark in the cost to produce small volume on-site hydrogen using existing process technologies. The cost models also show that the utility costs (natural gas @ \$4/MMBtu (HHV), electricity and water) total \$7.50/MMBtu (HHV).

The capital and product costs are based on a skid package designed to be a complete, operationally verified system prior to being shipped to the site for installation. Computer models of the completed system skid assembly are shown in the Figures 2 and 3.

The skid has been designed to easily fit within a standard parking space. All mechanical devices such as valves, pumps, compressors, motors, and controls are located on the periphery of the skid with doors providing easy access to these items. The skid is also designed to be ventilated during operation by using the cooling system fan to provide the required air changes. The electrical enclosure is designed to be isolated from the machinery portion of the skid. Atmospheric analysis for combustible and/or hazardous gases has not been designed into the system. It has been calculated that with sufficient air changes, there is no potential of creating a hazardous or explosive environment within, or in the immediate vicinity of, the skid. The predicted cost to produce hydrogen from this system is shown in Figure 4.

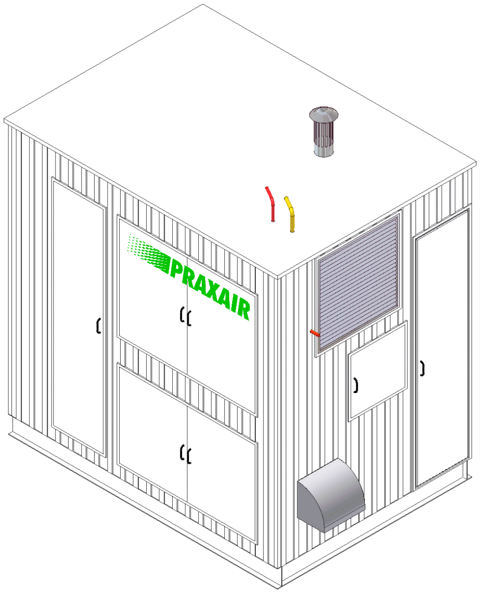

Figure 2. Low-Cost Hydrogen Production Platform Skid Design. (All components and controls necessary for the production of hydrogen using natural gas, city water and electricity as utilities.)

Figure 3. Low-Cost Hydrogen Production Platform - Skid Cover Off

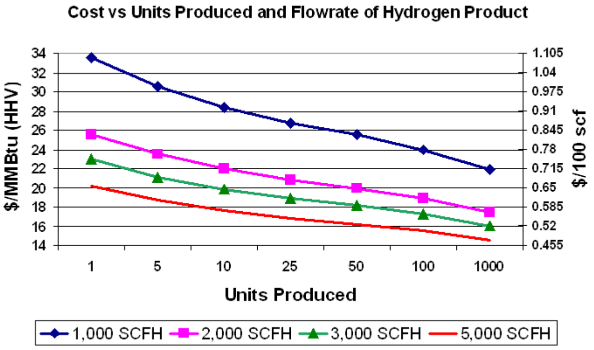

Figure 4. Unit Hydrogen Cost Versus Units Produced and System Capacity

A comparison of fuel costs between internal combustion engine vehicles (ICEVs) and fuel cell vehicles (FCVs) shows that if there is no tax on hydrogen, then the hydrogen must be produced at about $19/MMBtu (HHV) (before compression) to be competitive with fully-taxed gasoline at $1.60/gal. If hydrogen is to be competitive with untaxed gasoline ($1.20/gal), then the cost of uncompressed hydrogen should be $12/MMBtu (HHV). Thus, with a cost of $19/MMBtu (HHV) for 2,000 scfh uncompressed hydrogen with production of hydrogen plants at 100 units/year, FCV hydrogen costs will be nearly equal to ICEV hydrogen costs in early years if there is no tax on hydrogen. With the mass production of hydrogen plants as the FCV market grows throughout the U.S., hydrogen cost will need to decrease to $13/MMBtu (HHV) to make it possible to support a fuel tax. Cost models indicate that $13 to $16/MMBtu hydrogen is not achievable with 1,000 scfh plants, but with production plants of 2,000 scfh and higher, these targets are achievable. The design concepts developed in Phase I of this project show significant progress in decreasing the cost to produce hydrogen in production plants of <5,000 scfh. As the demand for hydrogen increases, the capacity required at each site will grow and units in the production range of 5,000 scfh will be more cost effective. Significant effort will be required to validate the design concepts in the subsequent phases of the project and to develop a working prototype of the system. The total remaining duration of the project is estimated to be three to four years.

The transportation sector is likely to continue to be a primary source for the demand of small-scale hydrogen production systems in the future. Our baseline projections for the number of 2,000-5,000 scfh hydrogen plants that Praxair will have opportunity to build are 30 plants/yr in 2010 and 130 plants/yr in 2020. With the recent modifications to California's zero emission vehicle mandate, the market for FCVs will be slow to develop. The cost of fuel cells also remains a significant barrier for the viability of FCVs. Therefore, this project is structured to develop an optimized SMR-based system and thoroughly test all aspects of the design prior to entering into a production run. Phase I work has demonstrated that significant improvements in cost, plant layout, system integration and overall system optimization are achievable. Therefore, further development efforts will focus on system and component computer modeling and prototype testing. Phase II of the project will focus on demonstrating both the design component testing and economic viability of the concepts developed in Phase I.

Conclusions

1. Applying DFMA principles to the overall design significantly lowered the cost to produce hydrogen at volumes of 1,000 to 5,000 scfh.
2. A complete hydrogen generating system producing up to 5,000 scfh can be packaged in a single skid that is small enough to easily fit into a typical parking space.
3. A new benchmark appears possible for the cost of hydrogen produced from current process technologies (i.e. SMR with PSA purification).
4. Preliminary results from the Phase I study will need to be verified in subsequent phases of the project to ensure that the system is safe, robust and meets the overall project goals.

FY 2003 Publications/Presentations

1. Presentation at the DOE Annual Merit Review Meeting (May 2003)
2. Phase I Final Report (submitted to DOE - June 2003)

Encapsulated Metal Hydride Separation Membrane Development

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Objectives

- Produce a sol-gel encapsulated metal hydride packing material that will absorb hyrogen selectively, will not break down to fines, and will tolerate reactive impurities.
- Evaluate the packing material for hydogen absorption from low concentration streams.
- Develop separation process with the new packing material.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- AB.Hydrogen Separation and Purification

Approach

- Develop formulations and procedures to make silica encapsulated metal hydride composite material.
- Design and install gas manifold for testing encapsulated packing materials for hydrogen absorption from streams of gas mixtures. The tests will generate hydrogen capacity and absorption kinetic data.
- Analyze the encapsulated packing materials before and after repeated hydrogen absorption and desorption to evaluate their physical stability.
- Develop process to use this new hydrogen absorption packing material for efficient hydrogen separation from low concentration gas streams.

Accomplishments

- Produced five variations of encapsulated samples for hydrogen absorption test.
- Conducted hydrogen absorption tests with various samples from gas mixtures that contain nitrogen, methane and carbon monoxide.
- Developed new encapsulation technique that significantly improved the physical stability of the product.

Future Directions

- Increase metal hydride content in the encapsulated product to maximize hydrogen capacity.
- Investigate the encapsulation of metal hydrides of higher equilibrium hydrogen pressure so that the product is better suited for use in pressure swing absorption separation processes.
- Optimize the porosity of the encapsulating matrix to increase the product's resistance to reactive impurities.

- Design and fabricate a pressure swing absorption experimental apparatus to test the encapsulated metal hydride for hydrogen separation.
- Conduct cost analysis.

Introduction

Hydrogen is certainly a clean fuel, but there is no significant quantity of naturally free hydrogen anywhere on earth. Hydrogen exists mostly in combined form with other elements, such as in water and hydrocarbons. Energy is required to free hydrogen from these compounds before it can be used as a fuel. This energy requirement must be minimized to maximize the net useful energy carried by hydrogen. Hydrogen demand today is mostly from the chemical industry and the petroleum refinery industry. This demand for hydrogen is met by steam reforming of natural gas and partial oxidation of hydrocarbon liquids and coal. The cost of hydrogen produced in this way is very low compared to the value of the products made. Many off-gas streams containing up to 50% hydrogen are discarded for economic reasons. Besides, hydrogen produced today is only a few percent of overall energy demand.

A hydrogen economy will bring many changes. First, hydrogen demand will increase many fold. Second, hydrogen will be produced from multiple sources that include renewable and non-renewable. Third, low hydrogen content streams will not be discarded, and the hydrogen must be recovered using cost-effective recovery techniques.

Present technologies for hydrogen separation include pressure swing adsorption (PSA), liquefaction, and membranes. All three processes are efficient for high hydrogen contents and high-pressure feeds but are not efficient for low hydrogen contents and low-pressure feeds. For PSA, the inefficiency is partly due to the fact that the absorbents, including molecular sieves and activated carbons, preferentially absorb the heavy impurities. This is good if the heavy impurities are less than 50%, but is not as good otherwise. When hydrogen content in a gas mixture is less than about 50%, it is more efficient to use an absorbent that absorbs hydrogen instead of the heavier components. A hydrogen absorbent that can be used in a practical separation process is not available today. The objective of this project is to develop such an absorbent and the process to use it.

Approach

Metal hydrides are a very well known group of materials that absorb hydrogen reversibly at moderate conditions. One example is $LaNi_{4.25}Al_{0.75}$:

$$2\ LaNi_{4.25}Al_{0.75} + 5\ H_2 \leftrightarrow 2\ LaNi_{4.25}Al_{0.75}H_5$$

Each bulk liter of this material can absorb up to 18 moles of hydrogen reversibly. The hydrogen can be absorbed and desorbed by changing the hydrogen pressure, the temperature or both. This group of materials would have been well suited for hydrogen recovery from low concentration streams if not for two practical problems. First, metal hydrides in general break down to fines after repeated hydrogen absorption and desorption. The fines are in the micron range that makes them very difficult to use in separation columns. Second, metal hydrides are sensitive to reactive impurities like oxygen and carbon monoxide. Low levels of these impurities can render metal hydrides inactive toward hydrogen. Past efforts to deal with these problems are described by the works of Sandrock et al [1] and Suda et al [2].

In this work, a metal hydride is first broken down to fine particles. The fine particles are then encapsulated in a porous silica matrix to form a composite material. The composite is made in the form of granules or beads for packing separation columns. Each granule is a matrix of porous silica with metal hydride particles uniformly distributed in it. The porosity of the matrix permits hydrogen to reach the metal hydride particles but prevents the larger impurity molecules from penetrating. The porous matrix is strong and has void space for the metal hydride particles to expand and contract so that hydrogen absorption and desorption do not cause breakage of the granules. The composite granules can therefore withstand hydrogen absorption/desorption without generating fines and have good tolerance to reactive impurities.

The encapsulated metal hydride samples are tested for hydrogen absorption first in a batch mode, then in a flow-through mode. In the flow-through mode, a small column is packed with the encapsulated metal hydride granules. Gas mixtures of hydrogen in nitrogen containing methane or carbon monoxide are fed into the column. Hydrogen concentration at the column exit is measured so that breakthrough curves are generated. The breakthrough curves give the capacity and kinetic information of the absorbent at the experimental conditions. The column is regenerated by heat and purging with nitrogen after hydrogen breaks through. After repeated absorption and desorption, the encapsulated granules are inspected for their physical conditions visually and microscopically. Success of a sample is defined by its ability to maintain its hydrogen capacity, absorption kinetics, and physical integrity after repeated cycling. Longer term, a pressure swing separation process using the encapsulated metal hydride (MH) as a packing material will be developed and demonstrated.

Results

Five different encapsulation methods were investigated that generated samples for hydrogen absorption tests: (1) Fumed silica was used for the porous matrix that encapsulated the fine particles of lanthanum-nickel-aluminum ($LaNi_{4.25}Al_{0.75}$); (2) Tetraethyl orthosilicate (TEOS) sol-gel was used as the source of silica for the matrix; (3) Sample in (1) was further treated with TEOS; (4) Method was the same as in (1) except that the La-Ni-Al particles were fluorinated [2] before encapsulation; (5) A method called external gelation that combined fumed silica, TEOS, and pore former to encapsulate the La-Ni-Al powder was used. The samples were tested for hydrogen absorption from different mixtures. Their hydrogen capacities and ability to withstand repeated absorption/desorption cycles are summarized in Table 1. The results show that good resistance to attrition is achieved by most of the samples. The presence of methane does not reduce the hydrogen capacity. The presence of carbon monoxide reduces the capacity significantly. One of the future efforts will be to improve the resistance toward CO.

Figures 1 to 4 show photographs of encapsulated metal hydride samples and the original metal hydride particles before and after hydrogen absorption/desorption cycling. The granules and beads of

Table 1: Summary of Test Results

Method	Resistance to attrition	H_2 capacity from N_2 stream mmol/g MH	H_2 capacity from (N_2+10% CH_4) mmol/g MH	H_2 capacity from (N_2+1% CO) mmol/g MH
Fume silica + $LaNi_{4.25}Al_{0.75}$	good	5	to be tested	to be tested
TEOS sol-gel + $LaNi_{4.25}Al_{0.75}$	poor	2	to be tested	0.45
Fume silica + $LaNi_{4.25}Al_{0.75}$ + TEOS	good	4.5	4.5	1.7
Fumed silica + fluorinated $LaNi_{4.25}Al_{0.75}$	good	4	to be tested	0.45
External gelation + pore former + $LaNi_{4.25}Al_{0.75}$	very good	4	to be tested	to be tested

encapsulated metal hydride stay intact after repeated hydrogen absorption/desorption cycling. On the contrary, metal hydride particles by themselves break down to a fine power after a few cycles.

In flow-through tests, a 40-cc sample is loaded in a ¾-inch diameter, 6-inch long column that is installed on a gas manifold. A feed stream of low concentration hydrogen in nitrogen is delivered to the column. Methane or carbon monoxide is added to the feed depending on the test plan. Hydrogen is absorbed by the encapsulated metal hydride. Nitrogen and other impurities just pass through the column. Hydrogen concentration measured at the exit of the column is very low at the beginning and increases gradually when the metal hydride becomes saturated, producing a breakthrough curve. The breakthrough curve provides information on the performance of the sample. To regenerate, the column is heated to 120°C and purged with nitrogen. From the hydrogen concentration measured at the exit, the partial pressure and quantity of hydrogen recovered can be calculated. A typical set of breakthrough curve and regeneration results are shown in Figure 5. The feed gas contained 12% hydrogen in nitrogen. The feed flow rate was 34 standard cc per minute. The pressure was 1500 torr (29 psia), and the temperature was 22°C. The column absorbed more than about 90% of the hydrogen for about 300 minutes before the hydrogen

Figure 1. Encapsulated La-Ni-Al after 100 Cycles

Figure 2. Encapsulated La-Ni-Al by External Gelation Method

Figure 3. Metal Hydride Particles before Cycling

Figure 4. Metal Hydride Particles after 10 Cycles

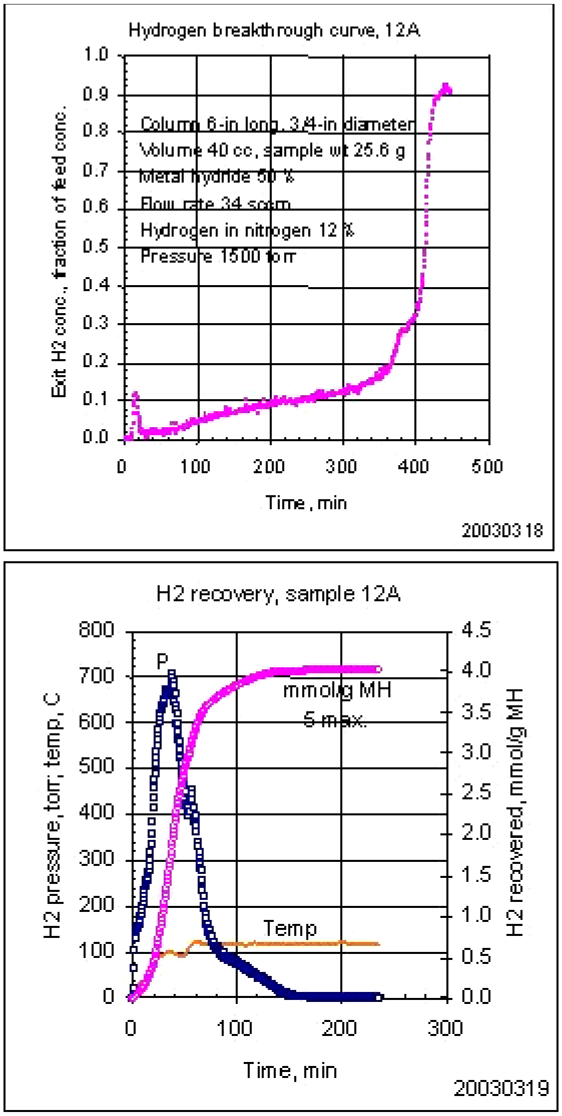

Figure 5. Breakthrough Curve (Top) and Regeneration Results (Bottom) of Hydrogen Absorption by Encapsulated Metal Hydride

broke through rapidly at about 400 minutes into the run. During regeneration, the partial pressure of hydrogen increased with temperature until it reached a maximum of 700 torr. The total hydrogen recovered was about 4 mmol/g of metal hydride compared to a maximum of about 6 at equilibrium.

Conclusions

- Metal hydride powder can be encapsulated in a porous silica matrix using a variety of techniques to produce stable granules suitable for hydrogen separation.
- The encapsulated metal hydride retains its ability to absorb hydrogen readily and has better resistance to reactive impurities.
- The external gelation technique combining the use of a pore former produces the strongest granules. The resistance of these granules to reactive impurities needs to be tested.
- Breakthrough curve data show that an effective pressure swing, temperature swing, or combination swing process for hydrogen recovery from low concentration streams can be developed.

References

1. J. J. Sheridan III et al, Journal of the Less-Common Metals, 89 (1983) 447-455

2. X.-L. Wang et al, Journal of Alloys and Compounds, 231 (1995) 860-864

FY 2003 Publications/Presentations

1. Paper titled "Hydrogen Absorption Property of Encapsulated $LaNi_{4.25}Al_{0.75}$" was accepted for presentation at HYPOTHESIS V (Hydrogen Power - Theoretical and Engineering Solutions International Symposium) to be held 7-10 September, 2003.

Special Recognitions & Awards/Patents Issued

1. U.S. patent number 6,528,441 was issued on March 4, 2003.

Defect-Free Thin Film Membranes for H_2 Separation and Isolation

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Objectives

- Synthesize defect-free thin film zeolite membranes for H_2 isolation and purification.
- Use these as water management membranes in proton exchange membranes (PEMs).
- Replace existing expensive and fragile Pt catalysts.
- Test the separations of light gases (pure and mixtures) through the membranes.
- Demonstrate effective light gas separations and commericalization potential of zeolite membranes.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- D. Durability
- E. Refueling Time
- H. Sufficient Fuel Storage for Acceptable Vehicle Range
- K. Balance-of-Plant (BOP) Components

Approach

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- E. Control and Safety
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
- AB.Hydrogen Separation and Purification

Accomplishments

- Synthesize defect-free thin film zeolite membranes and microporous bulk phases for future membrane applications.
- Model/simulate permeation of light gases through various frameworks/pores for optimized performance.
- Analyze flux and permeation of gases through membranes on unique in-house permeation unit.

- Validate modeling/simulation with actual permeation data to optimize membranes synthesized.
- Foster industrial contacts and collaborations.

Future Directions

- Synthesize and characterize thin films and bulk novel microporous phases including aluminosilicate (Al/Si) zeolite thin films doped and/or ion exchanged with other elements, unsupported aluminosilicate zeolite membranes, and silicotitanate phases (Si/Ti).
- Attempt use of atomic layer deposition of catalytic metals on top of zeolite membrane.
- Synthesize membranes on oxide-coated porous stainless steel (commerically viable) supports
- Model separation values by molecular dynamics calculations for pure and mixed light gases interacting with differing zeolite type membranes (i.e., comparing ZSM-5 to ZSM-W).
- Perform permeation and flux studies of pure and mixed gases through membranes (H_2, CO, CO_2, CH_4, N_2, and SF_6); proceed with unit alterations for H_2S testing.
- Build a partnership with a membrane company. Initiate an agreement for product development with an industrial partner.

Introduction

There is a great need for robust, defect-free, highly selective molecular sieve (zeolite) thin film membranes for light gas molecule separations in hydrogen fuel production from CH_4 or H_2O sources. In particular, we are interested in (1) separating and isolating H_2 from H_2O and CH_4, CO, CO_2, O_2, N_2 gases; (2) water management in PEMs; and (3) replacing expensive Pt catalysts needed for PEMs. Current hydrogen separation membranes are based on Pd alloys or on chemically and mechanically unstable organic polymer membranes. The use of molecular sieves brings a chemically and mechanically stable inorganic matrix to the membrane. The crystalline frameworks have "tunable" pores that are capable of size exclusion separations. The frameworks are made of inorganic oxides (e.g., silicates, aluminosilicates, phosphates) that bring different charge and electrostatic attraction forces to the separation media. The result is materials with high separation abilities plus inherent thermal stability over 600°C and chemical stability. Furthermore, the pore sizes and shapes are defined crystallographically (<1 Å deviation), which allows for size exclusion of very similarly sized molecules. In comparison, organic polymer membranes are successful based on diffusion separations, not size exclusion. We envision impact of positive results from this project in the near term with hydrocarbon fuels, and in the long term with biomass fuels.

Approach

The approach for this project in FY 2003 is the development of defect-free thin film zeolite membranes and new bulk microporous phases for the selective separation of light gases. The development of these membranes includes the synthesis, modeling/simulation, permeation studies, and validation for the separation and isolation of H_2. The permeation studies are of pure and mixed gases through membranes, studied at room temperature and 80°C. The modeling and simulation work helps determine improved pore size and composition for sieving. The validation is the iteration of modeling/simulation data with actual permeation values to improve upon the membranes synthesized.

Previous work at Sandia has successfully shown the ability to grow defect-free aluminosilicate and phosphate-based molecular sieve membranes. The continued focus now is on the enhancement and optimization of the type of molecular sieve for separation, the methodology of film growth, the type of supports upon which to grow membranes (and remain commercially viable). We are studying aluminosilicate frameworks and metal doped frameworks to better determine the relationship between adsorption, sieving and then permeation. To study the effect and preferability of support types, we are studying and comparing unsupported film growth versus film growth on ceramic supports. We are also beginning our studies on newly available ceramic coated stainless steel supports (allowing for phase match on the ceramic, but enhancing durability of stainless steel). With all materials synthesized, we perform characterization in-house to better understand structure-permeability relationships. Characterization methods include X-ray diffraction, thermal analyses, elemental analysis and permeation studies. Our in-house permeation unit is capable of fitting both disk and tubular membrane supports, either of ceramic oxide or stainless steel materials. This unique unit can be run from room temperature to elevated temperatures (= 500°C), though we only plan to go to approximately 80°C. The unit also contains a residual gas analyzer, enabling us to monitor and identify ratios of the permeate mixtures. We are able to leverage end sealant technology we have patented through Sandia. The gases we plan to test for this project include H_2, He, CH_4, CO, CO_2, CH_4, O_2, N_2, H_2S and SF_6, plus mixtures of these gases.

Results

In the area of thin film membranes, we have successfully synthesized micron thick aluminosilicate zeolite membranes on alumina disks (see Figure 1). Our permeation testing (see Figure 2) of the material shows that these membranes are defect-free. Defect free is denoted by permeation selectivity due to size exclusion by molecular sieving through the zeolite pores, and not through crystalline defect sites, pin holes, or crystallite mismatches (pores of this Zeolite are 5.5 Å). Molecules used for this test are He (kinetic diameter = 2.6 Å) and SF_6 (kinetic diameter = 5.5 Å). Pure gas studies are run at room temperature. The only consistent problem has been that our membranes have grown on both sides of the disk support, even when seeding occurs on one side. As a result, our flux through the membrane/support is slightly diminished from what it would be with only one side membranes.

Once the membrane is determined to be defect-free, testing on pure gases vital to the steam reforming cycle for natural gas to hydrogen fuels can begin. In the past years we have shown that the Sandia aluminosilicate membranes have fluxes on the order of 10^{-6} mole/(m^2Pa sec) and separations of H_2/N_2 61, H_2/CO_2 80, $H_2/CH_4 = 7$, CH_4/CO_2 11 [3]. Also, the all-silica Zeolite membranes have superior CO_2 separation from smaller light gases (such as H_2) [3,4]. Lifetime stabilities of the membranes have been undertaken in this project. In over a year of exposure to water vapor, the all silica membranes can be recalcined (to clear the pores of the zeolites) and retested for light gas selectivities. Our studies show good consistency in permeation data plus long-term durability in the actual integrity of the membrane. Furthermore, we have shown a high reproducibility in membrane synthesis procedure yielding consistent permeabilities. (See Figure 1 and Table 1.)

We have expanded our research to include silicotitanate membrane synthesis. In attempts to synthesize ETS-4 and ETS-10 as membranes, we have successfully synthesized both ETS-10 and a completely novel silicotitanate phase. This new phase exhibits initial selectivity toward H_2 and good flux (10^{-8} mole/(m_2Pa sec)), though complete removal of pore-blocking template molecules has not yet been achieved through initial calcination procedures. Further optimization of the calcination procedure will lead to improved results. (See Figure 2.)

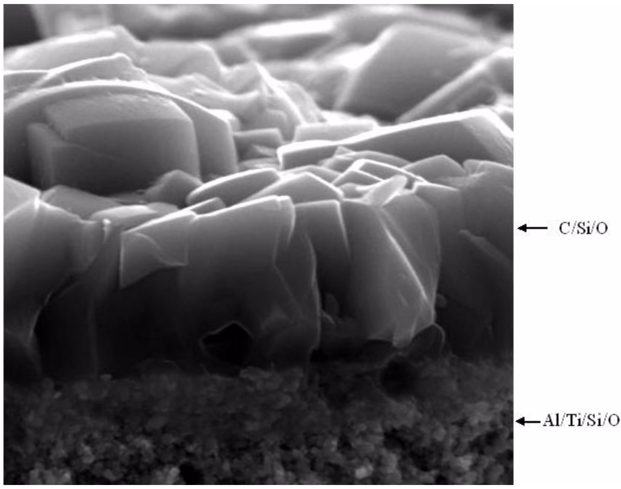

Figure 1. Cross Section View by Scanning Electron Microscope of a 10 Micron Thick Silicalite Zeolite Membrane on an Oxide Coated Stainless Steel Porous Support

We are also studying zeolite W (a 12-ring, 3D pore system) to compare it to the ZSM-5 sinusoidal pathway zeolite. We have successfully synthesized zeolite W crystals on a membrane. However, it is not yet a continuous film. Experiments continue to improve this membrane. (See Figure 3.)

Though not completely understood, these results indicate that we can tune the membrane materials to have selectivity for various light gases. This is even more valuable given that crystalline inorganic zeolite membranes are chemically, thermally and mechanically robust and stable. In comparison to Pd alloy films, the zeolite membranes perform well. According to the literature [5], Pd on alumina had relative ratios of light gas separations of $H_2/N_2 = 110$ at elevated temperature of 350C. The flux was also low (2×10^{-7} mole/m^{2}Pa sec). Furthermore, we have synthesized defect-free aluminosilicate zeolite thin films supported on commercially available oxide coated stainless-steel supports (SS316); industry needs stainless steel to make membranes an economically viable technology.

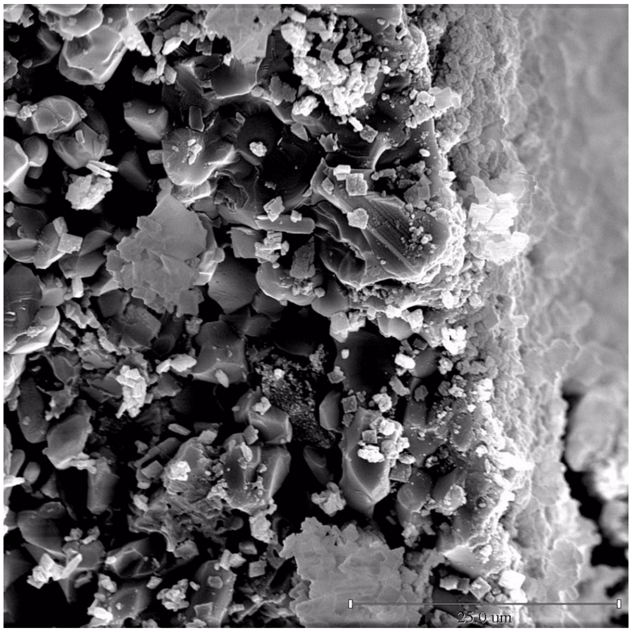

Figure 2. Cross Section of Novel Silicotitanate Crystalline Membrane on an Alumina Support

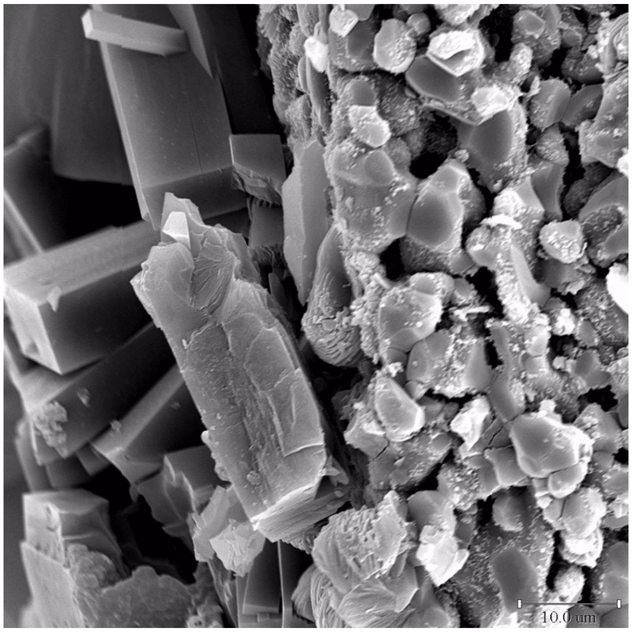

Figure 3. Cross Section of Zeolite W Crystals Grown on an Alumina Support

Table 1. Permeation values for pure gases at room temperature on various silicalite membranes; "regenerated" is calcined after one year exposure to water vapor. Flux = 10-7 mole/m2 s Pa); Trans-membrane pressure = 16 psi.

Gas / (Kinetic ∅ (Å)) Membrane	He (2.6)	SF_6 (5.5)	H_2 (2.8)	CO_2 (3.3)	O_2 (3.5)	CH_4 (3.8)	N_2 (3.6)	CO (3.7)
18A	1.8	< 0.05	2.4	2.9	1.4	-	-	1.6
21A	1.2	< 0.04	1.6	3.0	1.3	1.7	1.1	-
22A	1.5	< 0.02	2.0	5.9	1.2	3.2	1.4	1.4
22B 0	1.5	< .03	2.9	4.9	-	-	-	-
22B regenerated"	1.1	-	1.4	2.9	-	-	-	-
28A	0.8	< 0.03	1.9	5.1	1.3	2.6	1.6	1.6

Conclusions

There is a great need for robust, defect-free, highly selective molecular sieve (zeolite) thin film membranes for light gas molecule separations in hydrogen fuel production from CH_4 or H_2O sources. They contain an inherent chemical, thermal and mechanical stability not found in conventional membrane materials. Our goal is to utilize those zeolitic qualities in membranes for the separation of light gases, and to eventually partner with industry to commercialize the membranes. To date, we have successfully:

- Demonstrated (through synthesis, characterization and permeation testing) both the ability to synthesize defect-free zeolitic membranes and use them as size selective gas separation membranes; these include aluminosilicates, silicates, silicotitanates, and phosphate-based phases.
- Built and operated our in-house light gas permeation unit; we have amended it to enable testing of CO gases, mixed gases, and at high temperatures. We are initiating further modification for H_2S permeation studies.
- Synthesized membranes on commercially available oxide and composite disks (this is in addition to successes we have had in synthesizing zeolitic membranes to tubular supports [6]).
- Synthesized a number of novel bulk and membrane silicotitanate and aluminosilicate phases, including the Si/Ti membrane that exhibits selectivity for H_2.

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FY 2003 Presentations

M. E. Welk, T. M. Nenoff, F. Bonhomme, "Defect-Free Thin Film Membranes for H2 and CO2 Separation and Isolation", Hydrogen and Fuel Cells 2003 Conference and Trade Show, Vancouver, BC, Canada, June 2003.

2. T. M. Nenoff, M. E. Welk, F. Bonhomme, "Defect-Free Thin Film Membranes for H2 and CO2 Separation and Isolation", Spring National ACS meeting, New Orleans, LA, March 2003. Invited Lecture.

3. T. M. Nenoff, M. E. Welk, F. Bonhomme, "Defect-Free Thin Film Membranes for H2 Separation and Isolation", National Hydrogen Association Meeting, Washington, DC, March 2003.

4. T. M. Nenoff, F. Bonhomme, "Defect-Free Thin Film Membranes for H2 Separation and Isolation", 14th World Hydrogen Energy Conference, Montreal, Canada, June 10, 2002.

FY 2003 Publications

1. Mitchell, M.; Gallo, M.; Nenoff, T. M. "Molecular dynamics simulations of binary mixtures of

methane and hydrogen in titanosilicates." J. Phys. Chem., 2003, submitted.

2. Bonhomme, F.; Welk, M. E.; Nenoff, T. M. "CO2 selectivity and lifetimes of high silica ZSM-5 membranes." Micro. & Meso. Materials, 2003, in press.
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Special Recognitions & Awards/Patents Issued

1. Attended HyTeP as SNL speaker/representative in Santa Fe, NM, 4/23/03
2. Invited by Senator Jeff Bingaman (D-NM) for H2 and Fuel Cell Economic Development discussions (included national lab & industry attendees), Albuquerque, NM, 4/25/03

Autothermal Cyclic Reforming Based Hydrogen Generating and Dispensing System

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Objectives

The overall objective of the project is to develop a reformer-based hydrogen refueling station capable of delivering at least 40 kg/day of hydrogen. The specific performance objectives of the refueling system are as follows:

- Produce proton exchange membrane (PEM) fuel cell grade hydrogen (99.99+% purity);
- Achieve fully automated operation during normal, start-up, shut-down and stand-by modes; and
- Achieve 75% hydrogen generator efficiency (HHV - higher heating value basis).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- E. Control and Safety
- Z. Catalysts
- AB.Hydrogen Separation and Purification

Approach

- Design a pre-commercial 40 kg/day hydrogen generating and refueling system to produce fuel cell grade hydrogen from natural gas (NG) based on GE's Autothermal Cyclic Reforming (ACR) process;
- Analyze several process configurations that include ACR reactor, shift reactor, pressure swing adsorber (PSA), and heat exchangers and select the best configuration that has high efficiency, high reliability and lower capital cost;
- Fabricate and operate the ACR-based hydrogen generator;
- Develop a control system for safe operation of the hydrogen generator with low operation and maintenance (O&M) cost; and
- Develop tools to quantify the efficiency, cost and reliability of the system.

Accomplishments

- Assessed the technical feasibility of the design;
- Defined system layout;
- Designed ACR reactors, shift reactors and PSA;
- Operated low-pressure ACR and shift reactors for extended periods of time;
- Operated PSA on simulated reformate;
- Determined the delivered cost of hydrogen based on ACR technology; and
- Determined the competitiveness of the design relative to alternative concepts.

Future Directions

- Modify low-pressure reformer design to operate at high pressure;
- Integrate high-pressure ACR system with Praxair's PSA, hydrogen compressor, and storage system; and
- Safely install and operate the refueling system at a demonstration site.

Introduction

GE is developing a hydrogen generation system designed for vehicle refueling. The hydrogen generation system uses a proprietary reformer to convert hydrocarbon fuels to a hydrogen-rich gas that is purified downstream. The ACR process is a unique technology that can be applied for the production of hydrogen or syngas from different fuels, including natural gas, diesel fuel, and renewable feed-stocks, such as bio-derived fuels. The refueling system also includes a PSA unit to purify the hydrogen, a hydrogen compressor, high-pressure storage tanks, and a dispensing unit to safely deliver the hydrogen from the storage tanks to the vehicle. Praxair will develop the PSA unit. They will also procure the hydrogen compressor, hydrogen storage tanks, and hydrogen dispenser. BP will analyze the refueling station logistics and safety.

ACR is an autothermal cyclic catalytic steam reforming technology for converting hydrocarbons to a hydrogen-rich stream. The ACR process operates in a three-step cycle that involves steam reforming of the fuel in a Ni catalyst bed (Step 1 - Reforming), heating the catalyst bed through oxidation of the Ni catalyst (Step 2 - Air Regeneration), and finally reducing the catalyst to the metallic state (Step 3 - Fuel Regeneration). The heat required for the endothermic reforming step is provided during the exothermic air regeneration step. The ACR process consists of two reactors cycling between the reforming and regeneration (air and fuel) steps to produce a continuous stream of hydrogen. The reformer produces a 70% hydrogen stream that is purified downstream to achieve PEM fuel cell quality. The ACR process represents a significant technological advancement in comparison with autothermal reforming (ATR) and partial oxidation (POX), as the ACR-produced syngas is not diluted with nitrogen and the overall efficiency of the ACR process is higher than that of ATR and POX. When compared to conventional steam methane reforming (SMR), the ACR process has significantly lower capital costs and lower emissions. In addition, the ACR process is fuel flexible and has been successfully demonstrated using high-sulfur fuels.

Approach

The major goal of the ACR-based hydrogen generation and dispensing system project is to deliver PEM fuel cell grade hydrogen for vehicle refueling at the hydrogen cost target of $2.50/kg. The ACR technology promises to reduce the capital cost and improve the efficiency and reliability of the reformer when compared to other reforming technologies (SMR, ATR and POX). The project is broken down into three phases: Phase I - Conceptual Design and Analysis, Phase II - Sub-System Development, and Phase III - Prototype Design, Fabrication, and Operation.

In Phase I, a conceptual design of the entire ACR-based refueling system was developed. The mass and energy balances, process flow diagrams and systems design for the ACR reactors and other components were completed. A market analysis was performed to determine the competitiveness of the design relative to alternative concepts. Finally, an economic analysis of the system was performed to determine if the DOE targets are attainable using ACR technology.

Phase II is sub-system development. The major task in this phase is ACR reactor and catalyst development. The ACR catalyst will be subject to detailed evaluation for fuel conversion efficiency and reliability under different operating conditions. Phase III is prototype design, fabrication and system operation. In this phase, the entire system, including the reformer, PSA, hydrogen compressor, and storage tanks, will be integrated, installed and operated at a demonstration site.

Results

The conceptual design of the ACR system has been finalized. Multiple configurations were evaluated from a standpoint of efficiency, reliability, and capital cost. One major design issue was whether to use high-pressure reforming (150 psig) or low-pressure reforming (5 psig) with a syngas compressor. It was determined that high-pressure reforming was both more efficient and cost effective than low-pressure reforming, as shown in Table 1.

Table 1. Comparison of High-Pressure Reforming and Low-Pressure Reforming

	High-Pressure Reforming (150 psig)	Low-Pressure Reforming (5 psig)
Efficiency (LHV)	75%	71%
Capital Cost	Lower	Higher
Reliability	Higher	Lower, due to syngas compressor

The layout of the selected system is shown in Figure 1. The major subsystems of the refueling system are reformer, shift reactor, PSA, hydrogen compressor, storage tanks, and dispenser. The station will be capable of refueling three vehicles consecutively. The footprint of the refueling system was evaluated. The largest components in terms of size are the storage tanks.

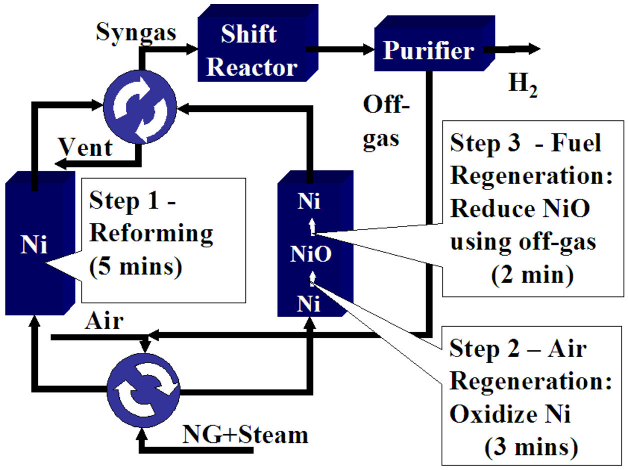

Figure 1. Refueling System Layout

A low-pressure pilot-scale reformer was tested for extended periods of time. The reformer was subjected to several start-stop cycles and operated using automated controls. Figure 2 shows that the reformer operates in a stable manner, and the reformate has about 70% hydrogen.

Praxair has determined the optimal configuration of the PSA for the ACR cyclic process. The PSA will be a 3-bed system designed for low capital cost as well as easy valve maintenance. Praxair performed an extensive evaluation of hydrogen compressors based on capital cost, reliability, and the ability to meet the performance targets. They chose a hydraulically driven compressor. One of the main factors for this choice was its oil-free design that will help prevent contamination of the hydrogen. The compressor has a long, slow stroke that will result in higher reliability. The design allows for quick maintenance that will decrease O&M cost for the system. Praxair is considering both steel and composite tanks for the hydrogen storage system. The major factors in this selection are safety and codes. Multiple methods to fill the vehicle were evaluated, and it was concluded that a cascade system was optimal.

A detailed cost analysis of the entire refueling station was performed to estimate the cost of delivered hydrogen. The model takes into account the system capital cost, O&M cost, and fuel and consumables costs. Figure 3 shows the cost of delivered hydrogen at different system capacities and mass production rates. The plot shows that the refueling system can meet the DOE target at higher capacities (>20,000 scfh) and when mass-produced (>500 units/year).

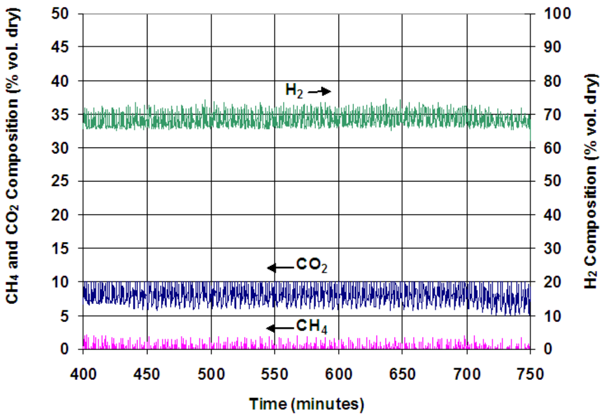

Figure 2. Performance of ACR

A sensitivity analysis was performed on the factors that affect the cost of delivered hydrogen (see Figure 4). The factors that were varied were: NG cost, O&M cost, capital cost, efficiency, and availability. Each of these factors were varied one at a time. Figure 4 shows the cost of delivered H2 at the mean value for each of the factors (center points), as well as the variability in the cost of H2 due to the variability in each of the factors. For example, as shown in Figure 4, the cost of NG has a mean of $4/

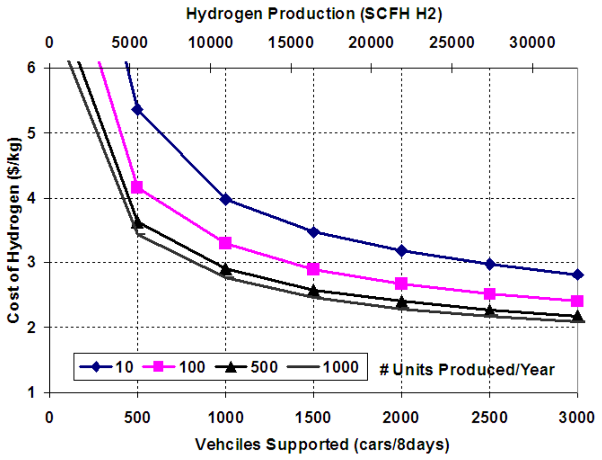

Figure 3. Cost of Hydrogen Estimated for Various System Sizes and Mass Production Rates

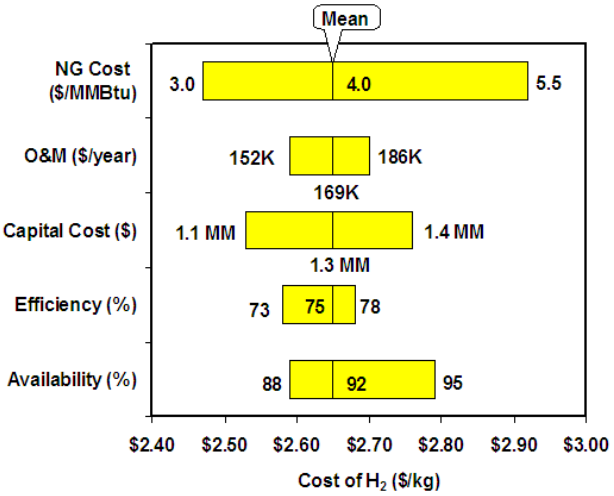

Figure 4. Sensitivity Analysis of Cost of Hydrogen

MMBtu and a variability of \$3.50-\$5.00/MMBtu. This results in a delivered cost of H2 with a mean of \$2.65/kg and a variability of \$2.47-\$2.92/kg. The analysis determined that the variability in cost of hydrogen will be primarily due to variability in NG cost, capital cost, and availability.

Conclusions

The process design of the reformer, shift reactor, and PSA has been completed. The design was optimized to increase efficiency, decrease capital costs, and improve reliability.

The process and economic analysis determined that high-pressure reforming is better than low-pressure reforming for the ACR-based hydrogen generator. A low-pressure reformer was operated for extended periods using automated controls. The reformer operated in a stable manner and delivered a 70% hydrogen stream to the shift reactor. The design of the low-pressure reformer is being modified to allow the reformer to operate at high pressure. The design of the shift reactor has been completed.

After extensive analysis, a three-bed PSA design was chosen over other bed designs in order to reduce capital costs as well as to reduce operation and maintenance costs. Vendors for hydrogen compressor, storage tanks, and dispenser have been identified. Hydro-Pac was chosen for the hydrogen compressor because of their unique slower speed hydraulic drive unit and successful prior experience with Praxair in high-pressure gaseous nitrogen and argon compression. Praxair is considering both steel and composite tanks for the hydrogen storage system. Fueling Technologies Incorporated has been chosen as the vendor for the dispenser. Multiple methods to fill the vehicle were evaluated, and it was concluded that a cascade system is optimal.

The economic analysis indicated that the refueling system will meet the hydrogen cost target of \$2.50/kg at capacities greater than 20,000 scfh and when mass-produced in greater than 500 units/year.

FY 2003 Publications/Presentations

1. Hydrogen Refueling System Based on Autothermal Cyclic Reforming, Kumar, R., International Energy Agency Annexe XV Meeting, Palm Springs, CA, November 17-18, 2002.
2. Hydrogen Refueling Station Based on Autothermal Cyclic Reforming, Kumar, R., Barge, S., Kulkarni, P, Moorefield, C, Zamansky, V., Fuel Cell Seminar, Palm Springs, CA, November 18-22, 2002.

Hydrogen Technical Analysis: Evaluation of Metal Hydride Slurries

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Objectives

- Assess the potential economic, environmental, and other benefits of using metal hydride slurries in a small-scale hydrogen distribution system (H_2 mini-grid) for both hydrogen vehicle fueling (H_2 station) and proton exchange membrane (PEM) fuel cell power systems (FCPSs) for combined building heat and power (cogen).
- Assess the viability of using fluorinated (or otherwise treated) metal hydrides for the purification of carbon monoxide (CO)-containing hydrogen streams.
- Establish R&D objectives for the development of hydrogen purification and H_2 mini-grids using metal hydride slurries.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Production

- AB.Hydrogen Separation and Purification
- AD.Market and Delivery

Delivery

- A. Lack of Hydrogen/Carrier and Infrastructure Options Analysis
- E. Solid and Liquid Hydrogen Carrier Transport

Storage

- V. Life Cycle and Efficiency Analysis

Approach

- Develop conceptual designs and evaluate the cost and efficiency of metal hydride slurry-based purification, storage, and delivery for H_2 stations and direct hydrogen FCPSs and compare to conventional systems (i.e. pressure swing adsorption purification, compressed hydrogen storage/ delivery, and reformate-based FCPSs).
- Determine cost of electricity (COE), hydrogen costs, energy use, greenhouse gas (GHG) emissions, and other emissions for FCPSs and H_2 stations utilizing both conventional and metal hydride slurry technology.
- Perform a molecular-level theoretical evaluation of the long-term feasibility of fluorinated metal hydride purification.

- Search for alternative protection methods or compounds that are even more effective in a practical application.

Accomplishments

- Developed conceptual designs and estimated capital costs for compressed hydrogen (cH_2)-based mini-grids and FCPSs.
- Constructed FCPS performance model with various building load profiles and FCPS efficiency calculations as inputs.
- Developed overall cost assessment and determined preliminary annual costs for reformate and direct hydrogen FCPSs.
- Integrated Phase I conceptual designs and capital costs for cH_2- and metal hydride slurry-based H_2 stations into FCPS performance model and overall cost assessment.

Future Directions

- Develop conceptual designs, evaluate efficiency, and estimate capital costs for metal hydride slurry-based mini-grids and FCPSs.
- Update FCPS performance model for metal hydride slurry-based systems.
- Refine capital cost estimates and evaluate hydrogen distribution costs for both cH_2- and metal hydride slurry-based mini-grids on a $/kg basis.
- Refine capital cost estimates and evaluate COE for cH_2-, reformate-, and metal hydride slurry-based FCPSs.
- Compare hydrogen costs, energy use, GHGs, and other emissions for the FCPS, H_2 mini-grid, and H_2 station utilizing both conventional and metal hydride slurry technologies.
- Evaluate other benefits of distributed generation and H_2 mini-grids.
- Use molecular modeling to describe a fluorinated layer of metal hydride on top of the virgin hydride.
- Establish selectivity of CO/H_2 separation based on energy surface calculation for transport through the fluorinated layer.
- Use the results to determine viability of fluorinated hydrides and develop and test hypothesis for optimization of the barrier layer.

Introduction

In Phase I, completed last year, the professionals at TIAX evaluated the potential cost and performance improvements that alternative and incipient hydrogen purification technologies could have over conventional pressure swing adsorption (PSA). The analysis indicated that the use of fluorinated metal hydrides in slurry form could reduce hydrogen cost and improve safety over conventional PSA purification with compressed hydrogen (cH_2) storage (Lasher et al 2002). In addition, if waste heat could be used to provide the heat for hydrogen desorption, metal hydride slurries could result in efficiency benefits. However, current metal hydrides have low tolerance to impurities typically found in reformate streams, especially oxygen and carbon monoxide. In Phase I, based on research results from Japan (Wang et al 1995a,b), we assumed that fluorinated (or in some other way protected) metal hydrides would be able to demonstrate high tolerance to impurities. However, significant additional research is required to verify these results and develop a stable and effective protective layer on the metal hydride.

Metal hydride slurry is a suspension of a metal hydride in an inert liquid, such as a light mineral oil or liquid alkane. The slurry is assumed to have no impact on the intrinsic hydride performance (e.g.

hydrogen capacity, hydrogen uptake kinetics, thermodynamics), but can result in overall system-level improvements such as higher heat transfer rates, easier transport (i.e. pump-able), and lower risk of impurities poisoning due to the liquid/gas equilibrium constant. A promising application identified for metal hydride slurries was combined purification, storage, and distribution in a small-scale hydrogen distribution system (H_2 mini-grid). Direct hydrogen PEM fuel cell power systems (FCPSs) utilizing H_2 mini-grids could improve reliability, cost, start-up time, emissions, and noise compared to reformate-based systems. In addition, producing hydrogen centrally for both vehicle fueling and FCPSs via a H_2 mini-grid provides an early market and fuel infrastructure for direct hydrogen vehicles.

In the metal hydride slurry mini-grid concept, reformate would be produced at a H_2 station, and hydrogen would be absorbed into the metal hydride slurry while impurities would be stripped out. Then, some of the metal hydride slurry would be pumped through pipelines to local buildings, where pure hydrogen would be desorbed and used to generate power in distributed FCPSs. The spent hydride slurry would then be pumped back to the H_2 station through a separate pipeline (perhaps concentric pipelines) for regeneration. Additional hydrogen capacity would be required at the H_2 station to meet vehicle fueling demands. This application has the potential advantages of being safer and requiring smaller pipe diameters than low pressure (~ 10 atm) cH_2 distribution. In addition, overall system efficiency could be improved provided the FCPSs supply some or all of the heat necessary to desorb hydrogen from the metal hydride.

Approach

In this phase of work, started in June 2002, we are evaluating the feasibility of using metal hydride slurries for purification and the potential benefits of using metal hydride slurries for hydrogen delivery via a H_2 mini-grid.

In order to assess the potential economic, environmental, and other benefits of using metal hydride slurries in the H_2 mini-grid application, we have constructed a FCPS performance model. Annual hourly building load profiles and fuel cell system efficiencies are used in the model to determine hydrogen requirements from the H_2 mini-grid and to optimize fuel cell size. In utility-connected buildings, grid power and natural gas demands are also determined, and annual energy costs are calculated based on utility rates and the cost of hydrogen from the H_2 mini-grid. Annual costs to the building owner and the cost of electricity (COE) are calculated based on the annual energy, maintenance, and capital costs of the FCPSs. Annual greenhouse gas and other emissions can also be determined based on the annual energy demand (i.e. hydrogen, natural gas, and grid electricity). The cost of hydrogen is calculated based on the capital cost of the H_2 mini-grid (i.e. distribution cost) plus the marginal cost of producing hydrogen at the H_2 station (i.e. marginal production cost). Alternatively, hydrogen can be priced at a premium to subsidize hydrogen sales to vehicles.

In order to evaluate the long-term feasibility of fluorinated metal hydride purification, we will perform molecular-level theoretical calculations using first principles and quantum modeling to understand the underlying microscopic mechanism of a fluorinated metal alloy (e.g. La-Ni-Al).

We will test two main hypotheses: (1) fluorination reduces the binding energy of undesired molecular species (e.g. O_2 and CO), and (2) the diffusion barrier created by the fluorinated surface is much lower for hydrogen molecules than for undesired molecules. Based on the calculations, we will generate a general model for surface protection of metal hydrides and formulate general principles for protection techniques. resis.

Results

A summary of our work in progress and some preliminary results and conclusions are presented here. The final results and conclusions will be detailed in a final report, expected to be completed in late fall 2003.

The National Fire Protection Agency (NFPA), the American Society of Mechanical Engineers (ASME), the Compressed Gas Association (CGA), the Code of Federal Regulations (CFR), the U.S. Department of Transportation (DOT), and industry experts were consulted for the design of the cH_2 mini-grid. We assume a delivery pressure equivalent to the output of the PSA (~ 10 atm) can be tolerated in most applications and no boost compressors are required over the short distribution distance (< 2 miles) of the H_2 mini-grid. We have estimated material, construction, "right-of-way", and "right of eminent domain" costs based on vendor quotes and additional cost assessments. Total capital cost for 4-inch pipe is estimated to vary between $250,000 and $600,000 per mile depending on location (rural, suburban, or urban). Right-of-way costs dominate in most cases.

Hourly electric and heat (space and water heating) load profiles for residential and commercial buildings in various locations have been generated for a typical meteorological year (TMY) using DOE EnergyPlus software. The load profiles are used in the FCPS performance model to calculate FCPS power demand (FCPS turns on when the building demand exceeds design power), cogen use (only when fuel cell is on and building heat is needed), and monthly utility demands. Example load profiles are shown in Figures 1 and 2. Note that the electric and space heating demands vary significantly from the winter to summer.

We constructed FCPS models using HYSYS process modeling software to evaluate system parameters that can affect system efficiency and cogen potential. The efficiency and cogen results are used in the FCPS performance model to calculate hydrogen (or natural gas) demand and actual cogen utilization. An example of a system level parametric analysis is shown in Figure 3. Note that low temperature and high pressure FCPS operation increases cogen capabilities because less heat is required for anode and cathode humidification. HYSYS models for the H_2 stations were developed in Phase I.

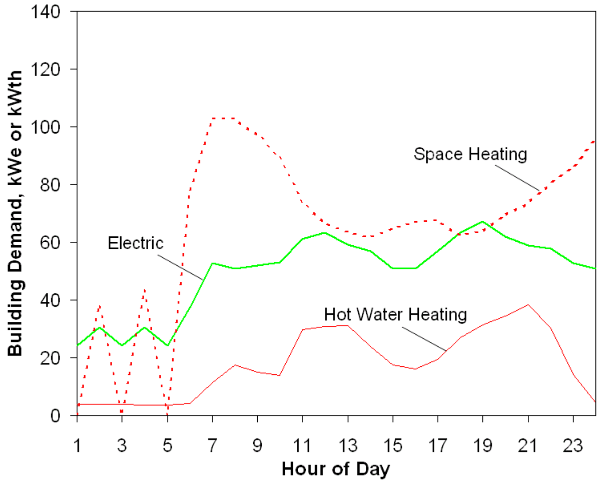


Figure 1. 24-Hour New York City Fast Food Restaurant Load Profile - Winter Day Example

A FCPS performance model has been constructed using the building load profiles and FCPS efficiency and cogen calculations. The model calculates the FCPS and utility energy demands for every hour of a TMY for various building types. We have estimated preliminary annual costs for direct hydrogen and reformate-based FCPSs using the FCPS performance model with typical utility rates and estimates for hydrogen, FCPS capital, and maintenance costs. Examples of the annual cost

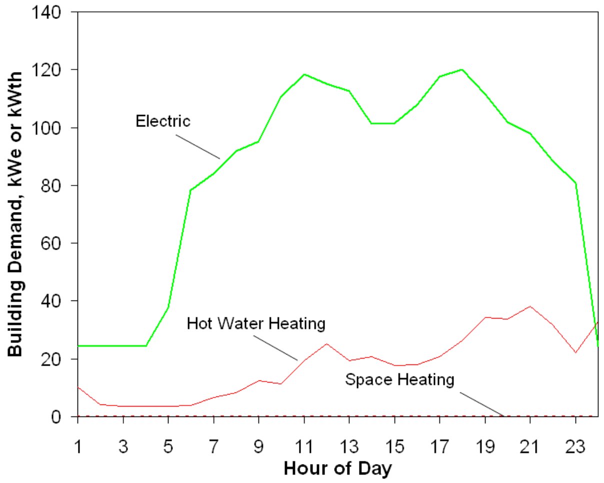
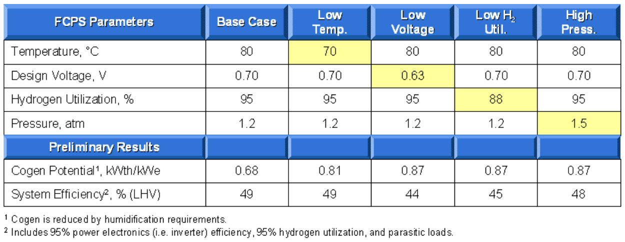


Figure 2. 24-Hour New York City Fast Food Restaurant Load Profile - Summer Day Example



FCPS Parameters	Base Case	Low Temp.	Low Voltage	Low H_2 Util.	High Press.
Temperature, °C	80	70	80	80	80
Design Voltage, V	0.70	0.70	0.63	0.70	0.70
Hydrogen Utilization, %	95	95	95	88	95
Pressure, atm	1.2	1.2	1.2	1.2	1.5
Preliminary Results					
Cogen Potential[1], kWth/kWe	0.68	0.81	0.87	0.87	0.87
System Efficiency[2], % (LHV)	49	49	44	45	48

[1] Cogen is reduced by humidification requirements.

[2] Includes 95% power electronics (i.e. inverter) efficiency, 95% hydrogen utilization, and parasitic loads.

Figure 3. Parametric Analysis using HYSYS Models - Direct Hydrogen FCPS Example

estimates are shown in Figures 4 and 5. Note that in Figure 4, smaller FCPSs suffer from poor economies of scale (more expensive capital on a $/kWe basis) and larger FCPSs suffer from low utilization.

The examples in Figures 4 and 5 assume the following:

- FCPS operates only when the building demand for power meets or exceeds the FCPS design power.
- Low-temperature cogen assumes the FCPS waste heat (i.e. cogen potential) can be used to meet some or all of the building hot water demand (61-74°C) when the FCPS is operating.
- High-temperature cogen assumes some or all of the hot water and space heating demands (74-94°C) can be met when the FCPS is operating.
- Utility stand-by charges are zero.
- The installed capital costs for 50-kWe direct hydrogen and reformate-based FCPSs are $24,500 and $44,500, respectively (assuming high volume manufacturing).
- FCPS stack and fuel processor catalyst bed lives are 40,000 hours.
- Hydrogen is sold to the building owner for just $1.00/kg, representing the marginal cost to produce hydrogen at the H_2 station. This does not include the cost of distribution through the H_2 mini-grid (work in progress).

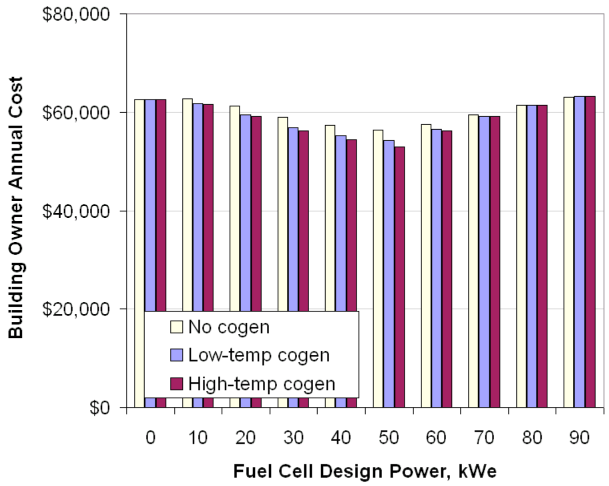


Figure 4. Preliminary FCPS Annual Costs with and without Cogen - Direct Hydrogen Example

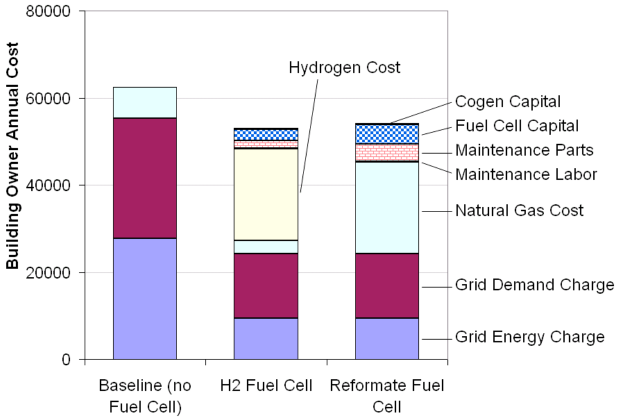


Figure 5. Preliminary FCPS Annual Cost Breakdown - 50 kWe with High-temp Cogen Example

Conclusions

Based on the preliminary results, a few observations can be made:

- There is an optimum FCPS size that will depend on the building load profile (i.e. utilization) and assumed economies of scale (see Figure 4).
- It is not clear whether cogen (high- or low-temperature) will be attractive for distributed FCPSs under the assumed mode of operation and load profiles used in this analysis to date (see Figure 4). The relatively small annual cost savings will have to be weighted against additional system complexity and reliability concerns.
- Fuel costs (hydrogen or natural gas) dominate the annual cost of the FCPSs, assuming capital and maintenance cost estimates for high volume manufacturing (see Figure 5).
- Hydrogen delivery will have to be relatively cheap to maintain competitiveness with reformate-based systems (see Figure 5). However, other benefits of the direct hydrogen FCPSs, such as improved reliability, quick start-up, and quiet and emissions free operation, have not been incorporated into the economic analysis to date.
- In the near-term, when capital and maintenance costs will be high, both direct hydrogen and reformate-based FCPSs will have difficulty competing with the utilities based on energy savings alone. Other benefits of FCPS distributed generation will have to be valued (e.g. power quality, reliability).

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Water-Gas Shift Membrane Reactor Studies

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Objectives

- Evaluate water-gas shift (WGS) reaction kinetics and membrane flux using industrial gas mixtures and conditions
- Test the feasibility of enhancing the WGS reaction at high temperature without added catalysts by using a membrane reactor

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- L. Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration and Efficiency
- N. Cost

Approach

- Complete reverse kinetics and Computational Fluid Dynamics (CFD) modeling to optimize reactor geometry for forward reactions
- Measure forward kinetics in quartz & Inconel reactors to determine reactor wall catalysis
- Measure forward kinetics in reactor packed with membrane material to determine catalytic activity
- Measure membrane H_2 permeability in presence of clean syngas components
- Conduct forward water-gas shift using a membrane reactor at favorable conditions

Accomplishments

- Conducted first-ever high temperature and high pressure reverse WGS reaction kinetics study
- Determined catalytic effect of reactor shell material on WGS reaction
- Conducted CFD simulations to determine effect of reactor geometry on kinetics
- Completed intrinsic kinetics testing of the forward WGS reaction
- Designed and constructed a new hydrogen membrane testing unit with enhanced features for membrane reactor testing

Future Directions

- Evaluate forward WGS reaction kinetics and the catalytic effect of membrane materials
- Design, construct, and test a Pd-Cu alloy membrane reactor to enhance the WGS

- Determine the effect of sulfur poisoning on catalytic reactor materials, membrane materials, and heterogeneous catalyst particles
- Incorporate reaction kinetics results and permeability results into a high temperature, high pressure WGS membrane reactor model

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Introduction

The use of coal as a transition feedstock for a hydrogen economy is likely to be accomplished via gasification, i.e. the conversion of solid coal into a gaseous mixture of CO, CO_2, H_2O, and H_2. The hydrogen yield of such gasifier effluent may be increased by reacting the CO with additional amounts of water, using the so-called water-gas shift (WGS) reaction. Although the WGS reaction is customarily used in industry, the reaction has not been explored at the conditions (temperature, pressure) envisioned in the gasification process, primarily due to non-favorable thermodynamics at those conditions. However, high temperature and high pressure provide a unique scenario to increase the hydrogen yield without the need for an external catalyst, while favoring the overall heat-efficiency of the coal gasification plant. Moreover, the thermodynamics may be enhanced by the use of a membrane reactor, which will allow for continual removal of pure hydrogen through the walls of the reactor (Figure 1). The final products of such a reactor would be a high-pressure, pure CO_2 stream and a pure H_2 stream. This project deals with the study of the membrane reactor in conditions similar to those of a gasifier stream.

Approach

The success of a membrane reactor in increasing the yield of hydrogen will ultimately depend both on a high production rate of hydrogen inside the reactor (fast *kinetics*) and a high rate of flow of hydrogen through the membrane (fast *permeation rate*). The knowledge of the reaction kinetics and membrane permeation is then required to evaluate the suitability of the membrane reactor.

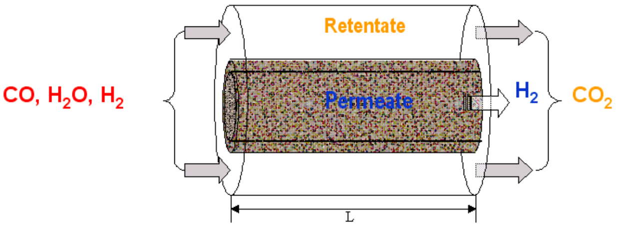

Figure 1. Schematic of a Membrane Reactor for the WGS Reaction

The reaction kinetics of both the *reverse* and *forward* WGS reactions were studied in an inert environment (non-membrane, quartz reactor) to determine the intrinsic kinetics. The effects of high pressure and high temperature were addressed. The influence of the reactor walls was investigated for a high-performance alloy (e.g., Inconel 600®); this is important in order to model the behavior of the reaction in an actual industrial setting.

Pd-Cu alloys, known for their sulfur tolerance (sulfur being one of the main contaminants in the gasifier stream), their good mechanical performance, and their infinite selectivity towards hydrogen, were selected as membrane materials. The membranes were characterized in regard to hydrogen permeance both with sulfur-free and sulfur-laden gases. Current research efforts are focused on the performance of the high-temperature, high-pressure water-gas shift reaction in a Pd-Cu membrane reactor.

Results

The high-pressure, high-temperature *reverse* WGS reaction can be described using an expression of the form

$$r = k_r [H_2]^{1/2} [CO_2]$$

where $[H_2]$ and $[CO_2]$ are the concentrations of hydrogen and carbon dioxide respectively. This suggests that the reaction behaves in a similar way as the low-pressure gas-phase reaction. However, the values for the rate constant (k_r), Figure 2, are somewhat larger for the high-pressure reaction. Figure 2 also presents the experimental and simulation results for the low-pressure reaction. The differences can be explained by considering the chemistry of the reaction, which requires an initial induction period before reaching steady state.

The high-pressure, high-temperature *forward* WGS was then studied. The form of the rate expression, was similar to that predicted from the

$$r = k_f [CO]^{1/2}[H_2O]$$

low-pressure mechanism. In this case, both the low-pressure and high-pressure values of the rate constant (k_f), Figure 3, are in good agreement, as a result of a much shorter induction period.

There is a dramatic increase in the rate of reaction when the reaction is carried out in a metallic (Inconel 600) reactor. Figure 4 indicates that the reaction is 100-fold faster when it takes place in a metallic reactor. This behavior is valid for the low-pressure (Figure 4) and high-pressure (Figure 5) reactions. As a result, the reaction is fast enough that no external addition of catalyst is needed. Surface analysis of the Inconel 600 showed a change in the chemical composition of the alloy in the surface, confirming the catalytic effect brought about by the reactor walls. A long-term study of the consequences of the stability of Inconel 600 under the reaction conditions is required.

Conclusions

- Reaction kinetics of the high-temperature, high-pressure WGS reaction follow the same reaction mechanism as the high-temperature, low-pres-

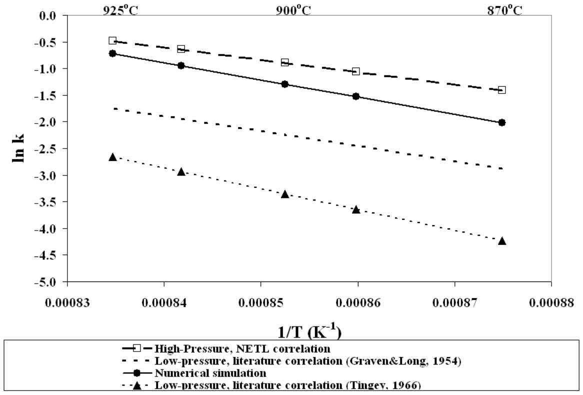

Figure 2. Rate Constant as a Function of Temperature for the Reverse WGS Reaction (Experiments were carried out in a quartz reactor)

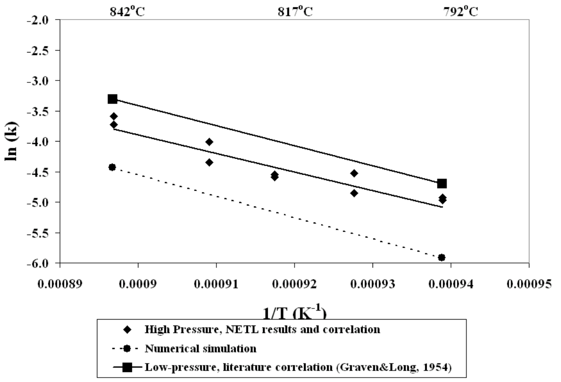

Figure 3. Rate Constant as a Function of Temperature for the Forward WGS Reaction (Experiments were carried out in the quartz reactor)

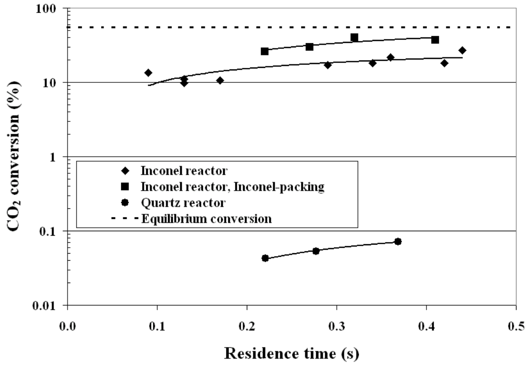

Figure 4. Reactor Wall Effects for the High-Temperature, Low-Pressure Reverse WGS Reaction as a Function of Residence Time

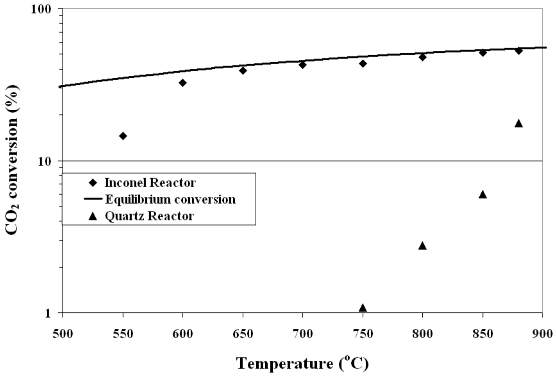

Figure 5. Reactor Wall Effects in the High-Temperature, High-Pressure Reverse WGS Reaction as a Function of Temperature

sure reaction. No significant effect of high pressure in the rate constant was observed.
- Inconel 600 is a strong enhancer of the WGS reaction. As a result, the reaction achieves equilibrium conversions at relatively low temperature.

FY 2003 Publications/Presentations

1. F. Bustamante et al., "Reverse WGS Reaction Kinetics at Elevated Temperature and Pressure in Quartz and Inconel Reactors," AIChE Meeting, Indianapolis IN, November 2002.

2. F. Bustamante et al., "Kinetics of the Homogeneous WGS Reverse Reaction at Elevated Temperature," AIChE Journal, in press summer 2003.

3. M. Ciocco et al., "Hydrogen from Coal: WGS Membrane Reactor Studies," International Coal Utilization Conference, Clearwater FL, March 2003.

4. R. Killmeyer et al., "WGS Membrane Reactor Studies," EE HFCIT Annual Merit Review Meeting, Berkeley CA, May 2003.

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Integrating a Hydrogen Energy Station into a Federal Building

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Objectives

- Evaluate combined fuel cell power/hydrogen production systems (Energy Stations):
  - Analyze energy station systems with 50-kW proton exchange membrane fuel cells (PEMFCs) that are suitable for installation in Federal buildings
  - Analyze options for system components, including direct hydrogen and reformate fuel cells and various storage, power production, and hydrogen usage configurations
  - Determine costs and energy efficiency for different system configurations
- Assess integration with buildings and potential for cogeneration:
  - Analyze potential for heat recovery from fuel cell/hydrogen production systems
  - Identify potential for cogeneration in Federal building applications
- Identify potential fleets for vehicle operation
- Establish partnerships for hydrogen fueling and power sales
- Identify barriers to hydrogen use
- Make recommendations for future development
- Identify potential opportunities to develop fuel cell energy stations

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- Hydrogen Production
  - B. Operation and Maintenance (O&M)
  - E. Control and Safety
- Hydrogen Storage
  - V. Life Cycle and Efficiency Analyses
- Fuel Cells
  - F. Heat Utilization
- Technology Validation
  - C. Hydrogen Refueling Infrastructure
  - I. Hydrogen and Electricity Coproduction

- Education
  - B. Lack of Demonstrations or Examples of Real World Use

Approach

- Analyze integrated power and fueling system
- Explore private and public partnerships
- Identify barriers to hydrogen use

Accomplishments

- Developed list of possible components that will comprise hydrogen generation and dispensing stations
- Developed list of relevant system configurations from possible components, with detailed description and schematics of proposed system configurations
- Selected a baseline system configuration, and initiated a detailed system cost and performance analysis
- Prepared comprehensive list of potential operating configurations
- Surveyed potential public/private fleets and Federal buildings for siting a hydrogen energy station
- Initiated evaluation of building integration and prepared comprehensive list of potential building interfaces
- Determined and contacted sites best suited for hydrogen energy station
- Created general process flow diagram (PFD) representing potential hydrogen energy station fluid/ energy flows for target site system
- Evaluated emissions benefits for hydrogen energy station operation relative to conventional energy sources

Future Directions

- Continue the analysis and identification of energy station applications at target sites
- Analyze the cost, emissions, and energy utilization benefits of integrated power and fueling for specified site
- Identify the key technology, cost, and public perception barriers to hydrogen use
- Make recommendations for future development

Introduction

The purpose of this technical analysis is to evaluate potential synergies between transportation and stationary applications to accelerate development of a hydrogen infrastructure through the installation of 50-75 kW stationary fuel cell-based energy stations at Federal building sites. The various scenarios, costs, designs and impacts of such a station are quantified in a cost-shared project that utilizes a natural gas reformer to provide hydrogen fuel for both the stack(s) and a limited number of fuel cell powered vehicles, with the possibility of using cogeneration to support the building heat load.

Approach

To carry out this analysis project as effectively as possible, TIAX structured it to consist of six major tasks. During the first phase of the project (FY 2002), TIAX completed the first three tasks. During the second phase of the project, TIAX will use the results from the first phase to complete the following three tasks.

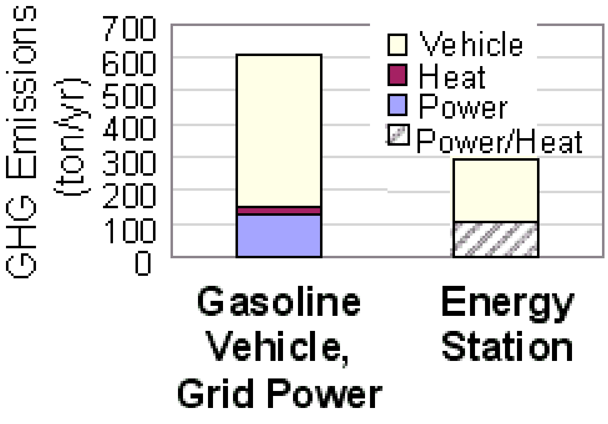
Task 4 — Analyze Integrated Power and Fueling. This task involves a more detailed analysis and modeling of the technologies and system designs that were selected in Task 1. This analysis will evaluate and quantify the costs, emissions, energy flows, number of vehicles to be fueled, and optimal fueling and storage time for each of the selected systems and technologies.

Task 5 — Explore Private and Public Partnerships. This task involves contacting potential public/private partnerships to determine their interest/plans to engage in such ventures. Part of this investigative process will be to determine existing and planned public/private partnerships and undertakings related to the development of a hydrogen fueling infrastructure, and to evaluate their success.

Task 6 — Identify Barriers to Hydrogen Use. TIAX will make an assessment and analysis of the different types of barriers and obstacles with which the development of a hydrogen infrastructure will be faced, including: key technological hurdles, cost obstacles, policy barriers and needed changes, and public perception issues.

Results

During FY 2003, the following items were accomplished under Task 4: Analyze Integrated Power and Fueling Systems. We began to evaluate and quantify the emissions, costs, and energy flows for each of the selected systems and technologies. Figure 1 shows a projection of annual greenhouse gas (GHG) emissions for a hydrogen energy station supporting passenger vehicles and providing electricity and heat for a building. As indicated, the GHG emissions associated with supporting a comparable gasoline vehicle and the equivalent heat and electricity demand for the building using utility gas and electricity are twice that of the emissions from a hydrogen energy station supporting the same energy demand. Figure 2 shows a projection of annual criteria pollutant emissions (i.e., NO_x, CO, and hydrocarbons) for the same cases. Under this comparison, operating a comparable gasoline vehicle and producing the same level of building energy from utility gas and electricity generates 20 times the criteria pollutant emissions generated by a hydrogen energy station.

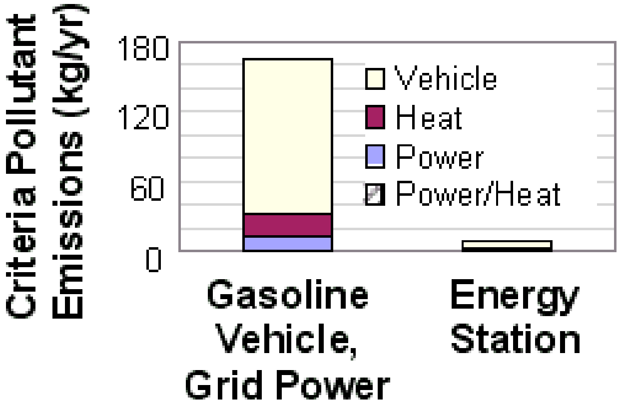


Note:
– Over 50% reduction

Figure 1. Annual Greenhouse Gas Emissions

Figure 3 shows a sample cost curve for fuel cell stacks. These curves indicate the relationship between stack production volume and cost per kilowatt. This and similar cost profiles are being developed to facilitate an overall cost projection of energy stations infrastructure under both small and large volume production scenarios.

Figure 4 provides a sample PFD. PFDs are being generated for the target energy station configurations to model energy flows between major system components. This modeling process facilitates system optimization by indicating component



Note:
–Over 95% reduction
–Criteria pollutants include:
NO_x, CO, and hydrocarbons

Figure 2. Annual Criteria Pollutant Emissions

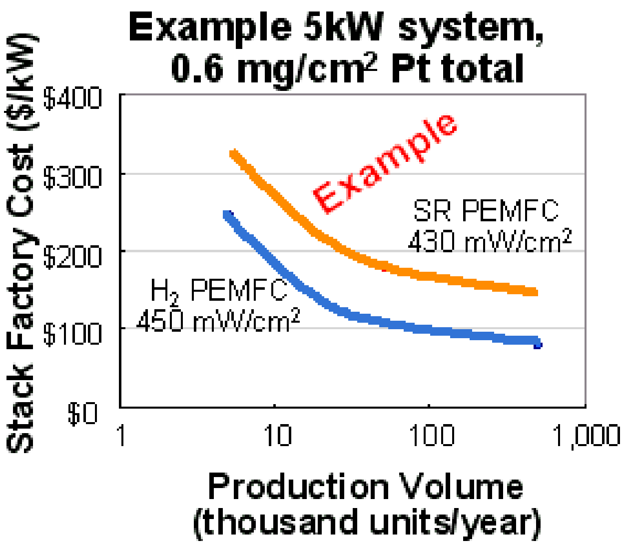


Figure 3. Example Fuel Cell Stack Cost Curves

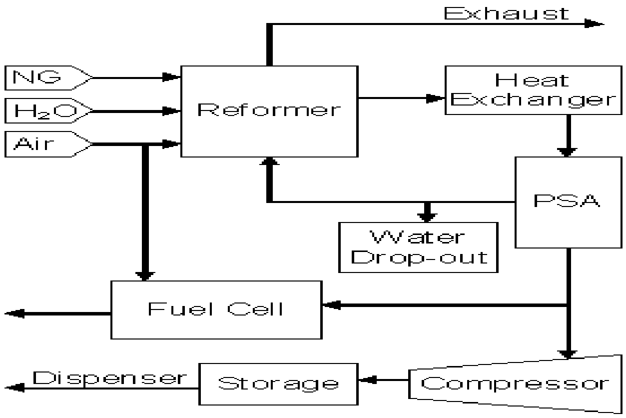


Figure 4. Example Process Flow Diagram

capacity requirements under a desired energy output. Once the system component sizing has been determined, the cost of particular components and of the overall system can be determined.

Conclusions

- TIAX has identified a set of representative technologies and representative operational scenarios that are being analyzed to estimate the size, power output, and cost of a hydrogen energy station at a target site.
- Hydrogen energy stations provide significantly lower GHG and criteria pollutant emissions compared to equivalent conventional vehicle and building operation.
- System optimization of an integrated hydrogen energy station will take into account system operation, capacity, and cost.

Hydrogen from Renewable Energy Sources: Pathway to 10 Quads For Transportation Uses in 2030 to 2050

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Objectives

- Identify a pathway for producing 10 quads of hydrogen per year for transportation uses from renewable sources in the years 2030 to 2050 (1 quad = 10^{15} Btu).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- T. Renewable Integration
- AD.Market and Delivery

Approach

- Determine the total potential hydrogen generation from renewable resources in the U.S. in 2030-2050 to ensure that the production of 10 quads of hydrogen is possible.
- Only the resources that could make a contribution of at least 0.1 quads per year were included: biomass, solar, wind, and geothermal.
- The potential hydrogen generation from each of the four resources was determined on a state-by-state basis.
- The hydrogen demand for a given state in the year 2040 was estimated by assuming that the per capita demand for hydrogen would be proportional to the per capita gasoline usage in that state.
- The cost for hydrogen from each resource was calculated by applying discounted cash flow (DCF) analysis for each step along the hydrogen pathway from production to dispensing into vehicles.
- A simulation was created to generate a hydrogen production scenario for the continental U.S. based on resource availability, cost, and hydrogen demand.

Accomplishments

- Determined that the generation of 10 quads of H_2 from renewable sources is theoretically feasible in 2030-2050.
- Estimated the average cost of the 10 quads of hydrogen in the continental U.S.
- Issued Draft report for review (February 2003).

Future Directions

- Finalize report based on reviewer comments (expected July-August 2003).

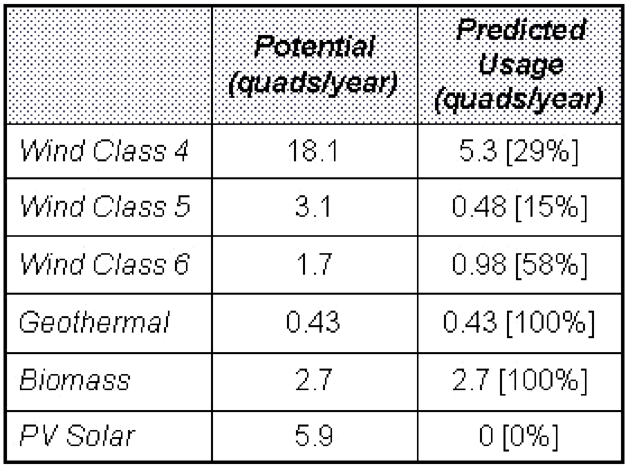
Introduction

This report is the final in a series of studies by Directed Technologies, Inc. of the cost and infrastructure requirements to supply hydrogen for fuel cell vehicles (FCVs). The previous studies have concentrated on the early development of the hydrogen infrastructure to supply a limited number of FCVs. In this study, the focus shifts to future years in which a significant fraction of passenger cars and trucks are FCVs. The goal of the current analysis was to develop a technically feasible pathway to supply 10 quads (one quad = 10^{15} Btu) per year of hydrogen fuel from renewable energy sources for transportation uses in the years 2030 to 2050. [In this report, the lower heating value (LHV) is used when referring to the energy content of a fuel.] The midpoint year 2040 was used for calculations of resource availability and demand that may change over the 20-year period. To put 10 quads of hydrogen energy in perspective, if the passenger vehicles currently on the road were converted to FCVs, 10 quads of hydrogen would be sufficient to fuel all of those vehicles (based on an average 2.2X efficiency gain for FCVs over conventional internal combustion engines).

Approach

We first determined the total potential hydrogen generation from renewable resources in the U.S. in 2030-2050 to ensure that the production of 10 quads of hydrogen is possible. All renewable resources were considered; however, only the resources that could make a contribution of at least 0.1 quads per year were included: biomass, solar, wind, and geothermal. Hydrogen from the biomass resources was assumed to be produced through gasification and steam reforming, and hydrogen from the electricity-generating resources by water electrolysis. (Alternate hydrogen production methods were considered, but the lowest-cost routes to hydrogen were gasification/reforming from biomass and electrolysis from wind, solar, and geothermal electricity.)

The potential hydrogen generation from each of the four resources was determined on a state-by-state basis. The U.S. totals for hydrogen potential in 2040 are listed in Figure 1. The hydrogen potential includes the effect of conversion efficiencies (gasifier or electrolyzer) and line losses in transmission.



	Potential (quads/year)	Predicted Usage (quads/year)
Wind Class 4	18.1	5.3 [29%]
Wind Class 5	3.1	0.48 [15%]
Wind Class 6	1.7	0.98 [58%]
Geothermal	0.43	0.43 [100%]
Biomass	2.7	2.7 [100%]
PV Solar	5.9	0 [0%]

Figure 1. Summary of Hydrogen Availability and Usage for each Resource Predicted by the Model

The hydrogen demand for a given state in the year 2040 was estimated by assuming that the per capita demand for hydrogen would be proportional to the per capita gasoline usage in that state (the per capita gasoline consumption varies considerably from state to state). To calculate the gasoline need for a state in 2040, we multiplied the predicted population by the current per capita gasoline usage, assuming that the relative gasoline use per capita remains the same for each state in the future. The 10 quads of hydrogen was then divided among the states in the same proportion as the projected gasoline consumption.

The cost for hydrogen from each resource was calculated by applying discounted cash flow (DCF) analysis for each step along the hydrogen pathway from production to dispensing into vehicles. The capital costs for equipment were taken from the literature or from projections for future costs for renewable technologies.

A simulation was created to generate a hydrogen production scenario for the continental U.S. based on resource availability and cost. The model strives to simulate an unregulated hydrogen market in which consumers in each state buy hydrogen generated from the least expensive available resource from any other state. In the simulation, hydrogen is purchased in small units (0.0001 quads), with each state purchasing the cheapest available hydrogen in each buying round until all of that state's hydrogen needs are met or the resources are consumed.

Results

The resulting costs of hydrogen at the dispensing site from the various pathways are shown in Figure 2. The hydrogen costs listed on Figure 2 include for comparison purposes the cost for 500 miles of transmission, although the distribution system described below accounts for actual transmission miles.

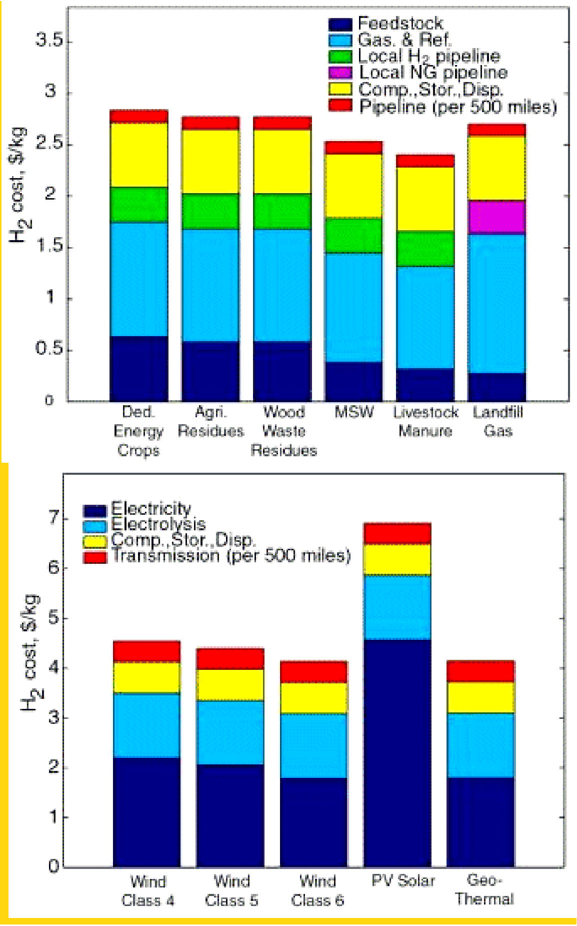


Figure 2. Cost of Hydrogen from Renewable Resources, Including 500 Miles Transmission from Source to Vehicle Dispensing for Reformation Production (top) and Electrolysis (bottom) Methods

Figure 1 shows the simulation results for the annual resource availability and consumption. Consumption of each resource depends both on its availability and on the cost of hydrogen from that resource relative to all other resources. While biomass and geothermal resources represent a small hydrogen potential relative to solar and wind energy, these resources make significant contributions to the national hydrogen demand due to their relatively low cost compared to other renewable resources. Solar energy, however, makes no contribution since it is considerably more costly than the abundant Class 4 wind energy with which it must compete. Of particular note is that 3.34 quads of the 4.8 quads of potential hydrogen from wind classes 5 and 6 goes untapped. Much of this unused wind potential is in the Midwest and Rocky Mountains, where the high transmission cost to the population centers on the coasts prohibits higher-class wind from being cost competitive with Class 4 wind resources at shorter transmission distances.

The distribution of cost of hydrogen in all states is shown in Figure 3, with an average cost of $3.98/kg. Generally, the least expensive hydrogen initially available to all states is from in-state biomass resources, followed by the biomass in neighboring states. Nearly half of all hydrogen from biomass is consumed in-state, with the amount transported out of state (via pipeline) decreasing with increasing inter-state distance. The average inter-state pipeline distance is 259 miles. As states consume their

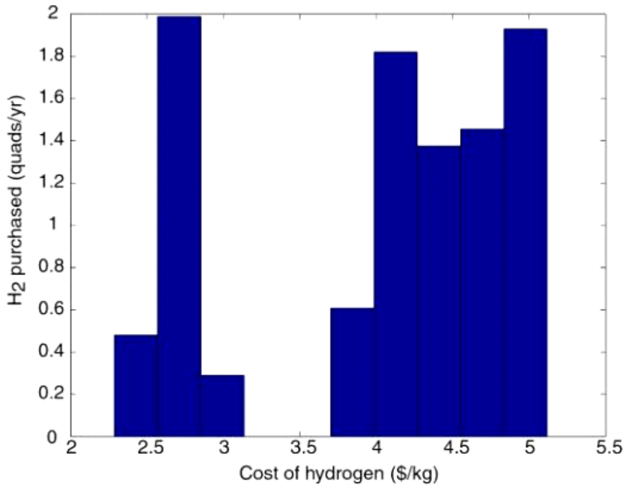


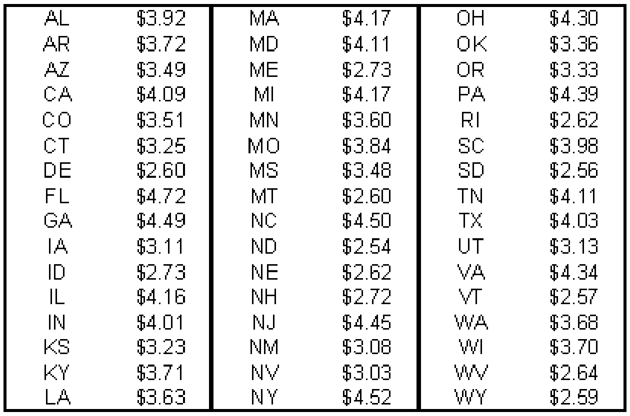
Figure 3. National Hydrogen Cost Histogram (Average is $3.98/kg)

surrounding biomass resources, they are forced to purchase electricity for hydrogen generation, which may be transmitted over longer distances. Only 24% of renewable electricity is used in-state for hydrogen production, and no obvious trend exists for quantity of hydrogen transmitted as a function of transmission distance. The mean distance for renewable electricity transmission is 540 miles. It is interesting to note that no resource is transmitted (via electrical lines or pipelines) more than 1,500 miles, indicating that coastal states reach no further than the middle of the country to meet their hydrogen demand. The resulting state-by-state cost of hydrogen is shown in Figure 4.

Conclusions

The annual generation of 10 quads of hydrogen in the years 2030-2050 from renewable sources for transportation uses in the U.S. is technically achievable and, according to our model, leads to a national average hydrogen cost of $3.98/kg ($33.24/GJ, LHV basis), excluding profits. Wind and biomass are the most significant resources (on an energy supplied basis) for hydrogen production, with geothermal playing a small role due to its limited potential.

Hydrogen from renewable electricity is expensive compared to that from the reformation of biomass for three important reasons. First, most renewable electricity, especially wind and solar, is expensive compared to electricity from fossil fuels due primarily to high capital costs for the wind and solar installations with relatively low capacity factors (all <50%). Secondly, electrolysis incurs large capital expenses and additional inefficiencies. Lastly, transmission of energy as electricity via transmission lines is more costly than hydrogen pipelines.



AL	$3.92	MA	$4.17	OH	$4.30
AR	$3.72	MD	$4.11	OK	$3.36
AZ	$3.49	ME	$2.73	OR	$3.33
CA	$4.09	MI	$4.17	PA	$4.39
CO	$3.51	MN	$3.60	RI	$2.62
CT	$3.25	MO	$3.84	SC	$3.98
DE	$2.60	MS	$3.48	SD	$2.56
FL	$4.72	MT	$2.60	TN	$4.11
GA	$4.49	NC	$4.50	TX	$4.03
IA	$3.11	ND	$2.54	UT	$3.13
ID	$2.73	NE	$2.62	VA	$4.34
IL	$4.16	NH	$2.72	VT	$2.57
IN	$4.01	NJ	$4.45	WA	$3.68
KS	$3.23	NM	$3.08	WI	$3.70
KY	$3.71	NV	$3.03	WV	$2.64
LA	$3.63	NY	$4.52	WY	$2.59

Figure 4. Average Delivered Cost of Hydrogen by State

FY 2003 Publications/Presentations

1. Duane B. Myers at the National Hydrogen Association annual U.S. Hydrogen Conference on March 5, 2003.

2. Duane B. Myers to the DOE H_2 Analysis Working Group on April 23, 2003.

Biohydrogen Production from Renewable Organic Wastes

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Objectives

- Investigate different strategies for selective growth of hydrogen-producing bacteria (e.g., heat selection and pH control, hydraulic loading) in a mixed culture environment.
- Determine the biokinetics parameters of hydrogen-producing microorganisms.
- Identify and quantify hydrogen-producing bacterial population in a complex microbial community background using nucleic acid based technique - terminal restriction fragment length polymorphism (T-RFLP).
- Design and develop improved bioreactor system to favor the growth of hydrogen-producing bacteria.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- H. Fermentative Micro-organisms

Approach

- Develop batch scale and continuous reactor system to evaluate technical and practical feasibility of hydrogen production from synthetic and real waste streams.
- Study the effect of heat treatment of sludge on hydrogen production in a continuous experiment.
- Apply Monod equation to estimate kinetic constants for different types of waste streams.
- Apply nucleic acid based techniques for microbial community identification and quantification.
- Find the correlation between hydrogen yield and the *Clostridium* sp. in the continuous bioreactor.

Accomplishments

- Successfully enriched naturally available mixed seed (e.g. compost, soybean soils, anaerobic digester sludge, etc.) to microbial culture rich in hydrogen-producing bacteria.
- Accomplished a hydrogen yield of 2.2 mole/mole of sucrose by using mixed microbial culture with hydrogen conversion efficiency of 27.5%.
- Developed heat treatment strategy for selective growth of hydrogen producers.
- Evaluated the effect of preheat treatment of seed inoculum at 70-90^{o}C for 15-20 minutes followed by repeat heat treatment of settled sludge on hydrogen yield.
- Determined biokinetics parameters [e.g. specific growth rates (m), half saturation constant (Ks), growth yield (Y)] of hydrogen producers using different substrates.
- Identified and quantified the hydrogen-producing bacteria in a mixed culture environment using nucleic acid based technique known as terminal restriction fragment length polymorphism (T-RFLP).

Future Directions

- Evaluate different reactor configurations and control parameters to obtain higher hydrogen conversion efficiency using real waste streams, e.g. high fructose corn syrup, molasses, food waste, corn processing waste, etc.
- Develop pilot-scale hydrogen production demonstration project using real wastes.
- Continue identification and quantification of hydrogen-producing bacterial population in a complex microbial community background using nucleic acid based techniques.

Introduction

The environmental consequences of extensive use of fossil fuels have already begun to surface. The excessive use of fossil fuels is one of the primary causes of global warming and acid rain, which have started to affect the earth's climate, weather, vegetation and aquatic ecosystems (Hansen *et al*., 1981). Moreover, the U.S. relies heavily on imported petroleum from nations which are politically unstable. Due to global environment and national energy security considerations, a non-polluting and renewable energy source needs to be developed. Hydrogen is a clean energy source, producing water as its only by-product when it burns. Besides, hydrogen can be produced from renewable raw materials such as organic wastes. Therefore, hydrogen is a potential clean energy substitute for fossil fuels.

A new fermentation process that converts negative-value organic waste streams into hydrogen-rich gas has been developed by the Biotechnology Research Group at Iowa State University (Van Ginkel *et al*., 2001). The process employs mixed microbial cultures readily available in nature, such as compost, anaerobic digester sludge, soil, etc., to convert organic wastes into hydrogen-rich gas. An enriched culture of hydrogen-producing bacteria such as *Clostridia* was obtained by heat treatment, pH control and hydraulic retention time (HRT) control of the treatment system. The process not only generates environmentally clean energy - hydrogen, but also stabilizes the waste. Thus, the newly explored hydrogen fermentation technology could curtail the growing energy insecurity and eliminate the global and local pollution problems resulting from excessive use of fossil fuels. The biohydrogen fermentation technology could enhance the economic viability of many processes utilizing hydrogen as a fuel source or as a raw material.

Approach

A series of serum bottle tests were conducted to evaluate the environmental factors (e.g. pH and heat treatment) affecting biological hydrogen production and to investigate the feasibility of biohydrogen production from different substrates. Serum bottle tests were also conducted to determine the biokinetic parameters (e.g. specific growth rate, half velocity constant and growth yield) of hydrogen-producing bacteria for different substrates. Following the batch studies, completely mixed bioreactors were operated for continuous hydrogen production using anaerobically digested sludge that had been heat treated at 100°C for 15 minutes as microbial seed. The experimental set-up employed in this study is shown in Figure 1. Upon successful start-up, the operation of the bioreactor was optimized to maximize hydrogen production. The process

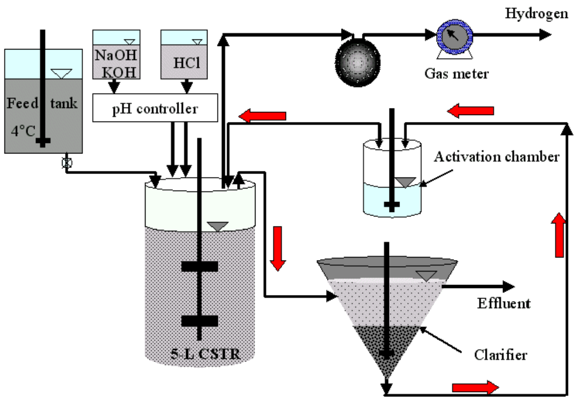

Figure 1. Experimental Setup of Continuous Bioreactor

optimization included determination of optimum operating pH, combination of temperature and duration of heating of settled biomass, frequency of heat treatment, chemical oxygen demand (COD) loading rate and HRT.

A nucleic acid based technique – DNA fingerprinting called terminal restriction fragment length polymorphism (T-RFLP) – was used to identify the abundant populations in a complex microbial community background. This method involves the extraction of DNA from the biomass samples and the amplification of the 16S ribosomal DNA (16S rDNA) gene using the polymerase chain reaction (PCR) with appropriate primers. The forward primer was labeled with fluorescein. The fluorescently labeled PCR products were digested with restriction enzymes *HaeIII, MspI*, and *RsaI*. The fluorescently labeled terminal restriction fragments obtained in this manner were separated by gel electrophoresis.

Results

A series of batch test results showed that a pH of 5.5 was optimum for hydrogen production without any detection of methane as evident from the highest hydrogen conversion efficiency as indicated in Figure 2. This pH was therefore selected for the continuous phase testing. Batch tests also showed that heat treatment of seed inocula at 70-90°C for 15-20 minutes enhanced the hydrogen production by more than five times with respect to control (without heat treatment). Such an increase was likely due to more favorable conditions to spore-forming hydrogen producers by reducing nonspore-forming hydrogen consumers.

Based on biokinetic studies, the specific growth rates (μ) of hydrogen-producing bacteria were found to be 0.10 hr^{-1}, 0.176 hr^{-1} and 0.215hr^{-1} respectively for sucrose, non-fat dried milk (NFDM) and food waste (produce + deli). These values were significantly higher than that for hydrogen-oxidizing bacteria (0.055 hr^{-1}) [Rittmann and McCarty, 2001]. This suggests that a hydrogen-producing bioreactor could be operated at much shorter HRT than the conventional methanogenic reactor. Thus, HRT could be one of the important factors to select the predominance of hydrogen producers in anaerobic reactor. The biohydrogen production rates at various initial substrate concentrations for different substrates are shown in Figure 3.

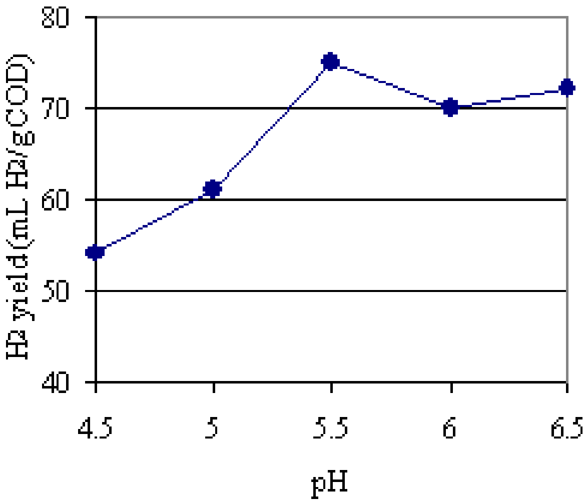

Figure 2. Effect of Ph on Hydrogen Production in Batch Studies

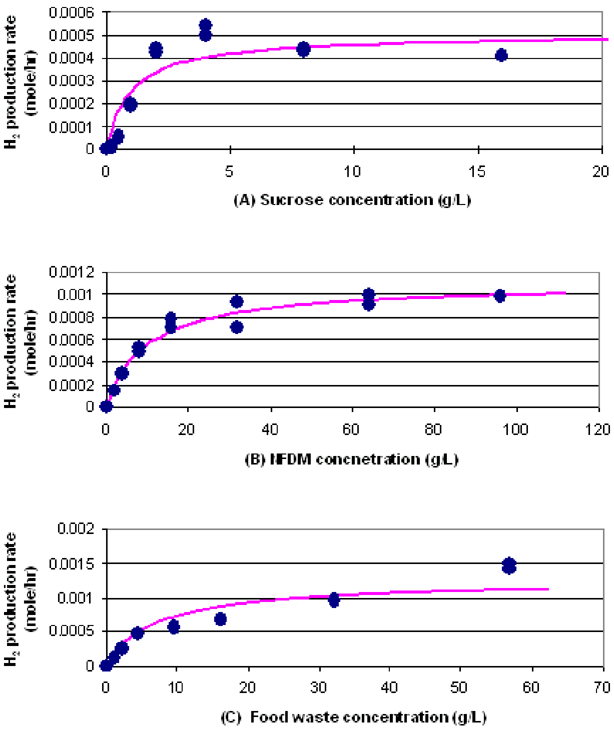

Figure 3. Biohydrogen Production Rates at Various Initial Substrate Concentrations (A) Sucrose; (B) Non-Fat Dry Milk; (C) Food Waste

A continuous bioreactor was operated for about 140 days at a substrate concentration of 20 g/L (sucrose) in a semi-batch feed at an HRT of 24 hr. The seed sludge was preheat-treated at 100°C for 15 minutes followed by a series of heat treatment at 70^{o}C for 20 minutes on day 29 (Phase I), day 113 and day 129 (Phase III). The result is presented in Figure 4. In Phase I, heat treatment was applied to only one-third of total biomass and the reactor showed no significant improvement in hydrogen yield. In Phase III, when all of the biomass was heat treated, the hydrogen production rates increased from 5.0 L/day to 8.3 and 13.0 L/day, respectively on day 113 and day 129. The corresponding hydrogen yields increased from 0.85 mole H_2/mole sucrose to 1.42 and 2.2 mole H_2/mole sucrose, respectively on day 112 and day 130. Thus, the repeated heat treatment was effective in selecting hydrogen producers and activating spore germination.

The microbial community analysis conducted at University of Illinois Urbana-Champaign during the experimental run time is presented in Figure 5. The studies showed that the highest level of H_2 was observed when the populations of *Clostridium* clusters I and II were active in Phases I and III. Thus, repeat heat treatment of all biomass was necessary to achieve sustainable hydrogen production. *Clostridia* are obligate anaerobic acidogenic bacteria that can form spores (endospores) to protect themselves against unfavorable environmental conditions, such as high temperature; however, when the favorable conditions return, they can geminate and become vegetative cells.

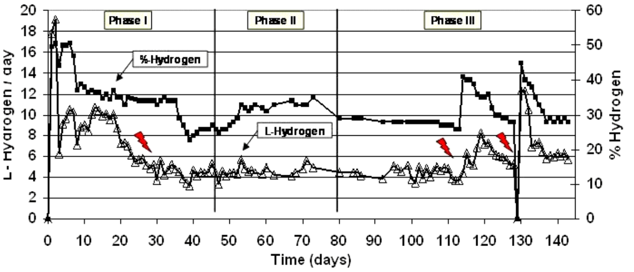

Figure 4. Biohydrogen Production Rate With Periodic Heat Treatment Bioreactor

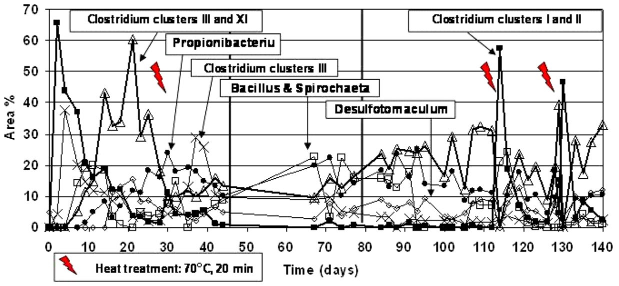

Figure 5. Dominant Microbial Populations in the Reactor as Indicated by T-RFLP Analysis With Restriction Enzyme Msei

A two-stage reactor with the first stage for hydrogen production and the second stage for culturing hydrogen producers is currently being investigated in our laboratory.

Conclusions

- An operational pH of 5.5 was shown to be optimal for hydrogen production.
- Hydrogen-producing bacteria have specific growth rates 2 to 4 times higher than the hydrogen-oxidizing methanogens.
- Both initial heat treatment of the seed inoculum and repeat heat treatments of the biomass during the reactor operation promoted hydrogen production by eliminating non-spore forming hydrogen-consuming microorganisms and by activating spore germination.
- Sustainable hydrogen production was possible with pH control and repeat heat treatment of settled sludge at 70^{o}C for 20 minutes.
- Terminal restriction fragment length polymorphism (T-RFLP) analysis showed that *Clostridium* clusters I and II and *Bacillus* species were dominant populations in the bioreactors.

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3. Simmons J J, Padmasiri S, Duangmanee T, Sung S and Raskin L. Microbial study during hydrogen fermentation in continuous flow bioreactors. *Annual Meeting of the Society for Industrial Microbiology*, August 10-14, 2003, Minneapolis, MN.

Supercritical Water Partial Oxidation

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Objectives

- Develop a gasification technology that can convert biomass wastes of all types into hydrogen and other high-value products.
- Verify that high-pressure supercritical water is an ideal medium for gasification of biomass.
- Show that high hydrogen yields and gasification efficiencies can be reliably achieved with supercritical water partial oxidation (SWPO).
- Confirm competitive hydrogen production costs of ~\$3/GJ (~\$0.35/kg) can be achieved with small-size SWPO gasifiers.
- Demonstrate a 5-ton per day (tpd) reduced-scale gasifier at a small publicly-owned treatment works (POTW).
- Construct a 40-tpd commercial biomass gasifier at a large POTW.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology

Approach

- Build on 20 years experience with supercritical water oxidation (SCWO) of hazardous wastes.
- Exploit the inherent characteristics of supercritical water (SCW) to convert wet biomass into hydrogen:
  - SCW quickly gasifies all organics with minimum char
  - Water-gas shift contributes significantly to hydrogen yields
  - SCW scrubs particulates and acids from hydrogen-rich gaseous products
  - High pressures aid in separation/storage of hydrogen
- Develop supercritical water gasification system in a four-step program:
  - Phase I: Pilot scale testing/feasibility studies (complete)
  - Phase II: Technology development (expect recompete/award in 2003)
  - Phase III: System integration and design
  - Phase IV: Reduced scale demonstration of 5-tpd system
  - Design and construct 40-tpd commercial demonstration system

Accomplishments

- Performed economic analysis showing that competitive hydrogen production costs of ~$3/GJ (~$0.35/kg) can be achieved with small-size SWPO gasifiers.
- Performed pilot-scale conceptual design of SWPO system for Phase II development.
- Prepared a SWPO development plan, including cost and schedule estimates.
- Prepared a business plan to identify SWPO market potential.
- Carried out SWPO market survey in collaboration with San Diego State University (SDSU).
- Defined follow-on activities from preliminary testing through pilot-scale demonstration of an integrated SWPO system.
- Identified improvements to reactor design.
- Submitted Phase I final report in December 2002.

Future Directions

Phase II: Technology Development: (2004)

- Design, fabricate and test advanced pilot-scale SWPO reactor.
- Optimize SWPO operating parameters and H_2 yields during extended-duration tests.
- Revise market, economic and life cycle cost assessments and define scale-up requirements.

Phase III: System Integration & Design: (2005)

- Perform safety, reliability and maintenance, and permitting studies.
- Perform process design and long-lead procurement for Phase IV.
- Update development plan for Phase IV.

Phase IV: Reduced-Scale Demonstration of 5-tpd System: (2006-2007)

- Implement requirements defined during Phase III studies.
- Match reduced-scale SWPO system to industrial H_2 separation and storage systems.

Introduction

General Atomics (GA) is developing supercritical water partial oxidation (SWPO) for the efficient and environmentally advantageous gasification and hydrogen production from low-grade fuels such as municipal wastes, biomass, and high-sulfur coal.

SWPO involves carrying out oxidative reactions in a supercritical water environment - akin to high-pressure steam - in the presence of limited quantities of oxidant, typically pure oxygen or air. Partial oxidation in-situ rapidly heats the gasification medium, resulting in less char formation and improved hydrogen yield. The high-pressure, high-density aqueous environment is ideal for reacting and gasifying organics. The high water content of the medium encourages formation of hydrogen and hydrogen-rich products and is compatible with high water content feeds such as sludges and biomass, and eliminates the need for feedstock drying. The high water content of the medium is also effective for gasification of hydrogen-poor materials such as coal.

Approach

Figure 1 provides a simplified process flow diagram (PFD) for the GA SWPO pilot plant. Pressurized slurry is fed to the preheater, where it is preheated to a temperature of 250°C or other suitable temperature depending on the feed material. It was found during testing that slurry preheating had to be limited to avoid char formation and plugging of the preheater. In addition, the pumpable concentration of biomass slurry was limited, for example to about 10-15 wt% for wood flour. To overcome these limitations, a high organic feed (designated auxiliary fuel in Figure 1) is coprocessed with the slurry. As shown in Figure 1, the high organic feed and oxygen are combined with the preheated slurry at the reactor inlet. The reactor has a volume of about 10 liters and provides a residence time of 60-75 seconds at an operating pressure of 3400 psi and operating temperatures of 650 to 800°C. In the reactor, the feed is converted primarily to CO_2, H_2O, H_2, CH_4 and CO. The gasifier products are cooled after leaving the gasifier and the liquid and gaseous products may then be separated at either high or low pressure. Figure 2 shows a photograph of the SWPO system gasifier skid.

Results for the SWPO pilot-scale testing were reported last year. In the latter half of 2002, the Phase I results were analyzed and used to identify favorable applications for the SWPO technology. An economic analysis was carried out, supported by a market survey of municipal sewage treatment plants in the U.S. All results were then documented in the Phase I Final Report issued in December, 2002.

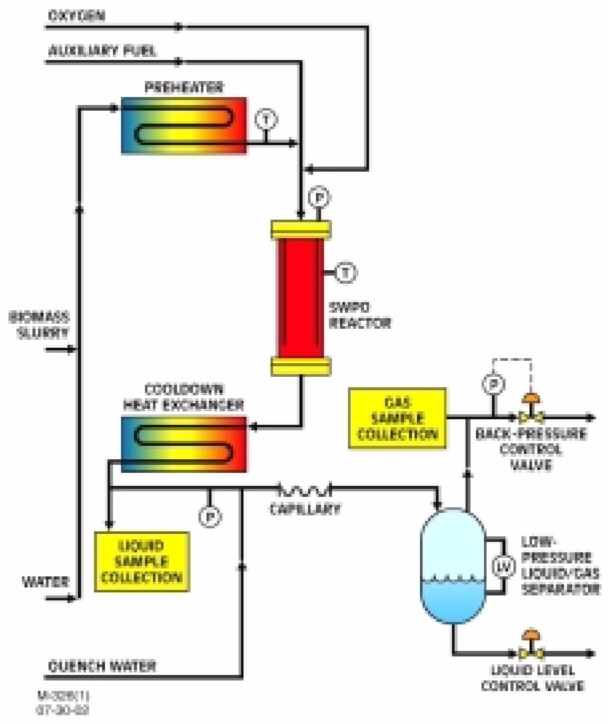

Figure 1. Process Flow Diagram for the SWPO System

Results

The major results for Phase I are as follows:

1. Based on successful Phase I testing, the SWPO pilot-scale conceptual design for Phase II development shall be based on the following:
   - Pumping tests indicate that a biomass slurry feed concentration of about 12 wt% solids is a practical maximum.
   - Feed preheat is typically limited to 260°C to avoid char formation and plugging.
   - A high heating value waste is coprocessed with biomass in order to attain the desired gasifier temperature and still have sufficient feedstock for gasification. Suitable high heating value wastes are trap grease, plastics, rubber, or coal.
   - A vessel-type gasifier rather than a pipe-type gasifier is used to achieve higher gasifier operating temperatures and minimize heat losses.
   - A catalyst-free gasifier is used to enable long-term operation with dirty feed materials without plugging.
   - A high-energy nozzle is used for high dispersion of the incoming feed to improve mixing and attain high gasification yields.
   - A methane-steam reformer is used on the clean SWPO product gas to reform the methane-rich gas to hydrogen.

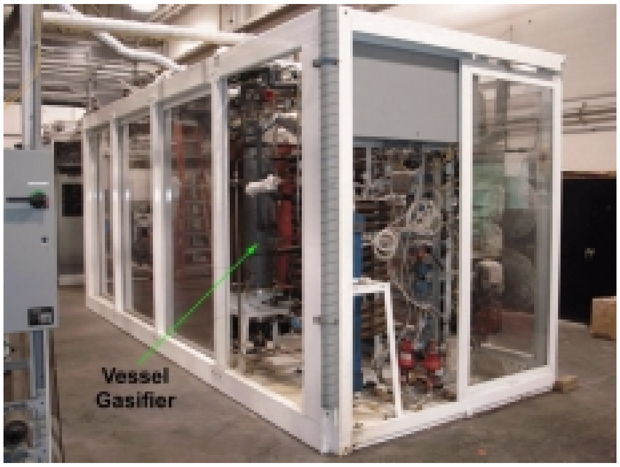

Figure 2. SWPO System Gasifier Skid

- Due to the low level of CO produced in the gasifier, water-gas shift reactors are not necessary.

2. A nationwide web-based survey of municipal sewage treatment plants received over 100 responses. The survey indicates that sludge solids disposal costs are usually above $100 per dry ton and range up to $500 per dry ton.

3. An economic analysis for coprocessing of sewage sludge and waste grease was performed. Results show that competitive hydrogen production costs of ~$3/GJ (~$0.35/kg) can be achieved with small-size SWPO gasifiers. Table 1 shows the key parameters of the analysis. Figure 3 shows how the hydrogen production cost varies with financing terms and revenue received for accepting sludge solids.

Conclusions

The Phase I results indicate that a practical means to overcome limitations on biomass slurry feed concentration and preheat temperature is to coprocess an auxiliary high- heating value material. SWPO coprocessing of two high-water content wastes, partially dewatered sewage sludge and trap grease, yields a scenario for the production of hydrogen at highly competitive prices. It is estimated that there are hundreds if not thousands of potential sites for this technology across the U.S. and worldwide.

The economics for 40 tpd sewage sludge plants augmented with grease trap waste are favorable over a significant range of cost parameters such as sludge revenue and capital financing. Hydrogen production costs for SWPO plants of this size are projected to be about $3/GJ (~$0.35/kg) or less. Economics may be further improved by future developments such as pumping of higher solids content sludges and improved gasifier nozzle designs to reduce char and improve hydrogen yields. The easiest market entry for SWPO is expected to be sales to municipal wastewater treatment plants for use with sewage sludge in conjunction with trap grease, as both of these wastes are ubiquitous and have reasonably well-defined negative value (i.e., the process will receive revenue to accept the feed). Additionally, waste grease is frequently recovered at municipal wastewater treatment plants where it is already contaminated with sewage.

Table 1. SWPO Economic Analysis Basis

Description	Assumption	Reference
Plant size	40 tpd total solids, 30 tpd organic sludge solids (not grease)	Numerous plants of this size in the US and worldwide
Sludge solids revenue	$0-300 per dry ton	SDSU survey
Gasifier residence time	20 seconds	15 seconds for UHM, 1998
Trap grease revenue	$0.08 per gallon	Darling/Al Max telecons
Steam revenue	$3.50 per MMBtu (? 1000 lb)	Yeboah et al., 2002
Cost of liquid oxygen (LOX)	$0.04 per pound	Vendor discussions
Hydrogen purity	99.99%	Typical purity level with pressure swing adsorption
Financing rate	6 to 12%	Current prime interest rate is below 5%
Financing period	Up to 20 years	City of San Diego methane contract is a 20-yr term

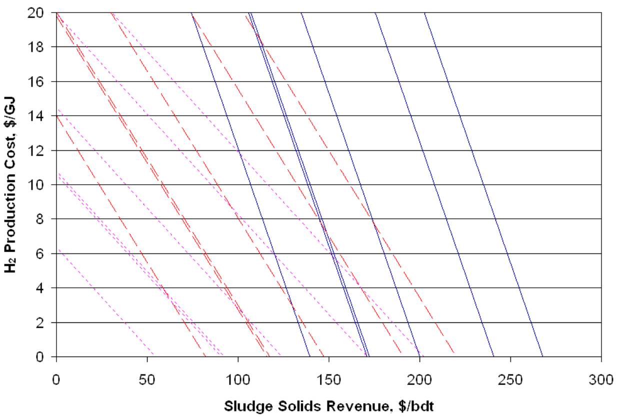

Figure 3. Hydrogen production cost for sewage sludge with trap grease. Solid lines show cases where the amount of grease supplied equals the amount necessary to raise the combined feeds to the final gasifier temperature of 650°C and all of the grease or its equivalent is completely oxidized to H_2O and CO_2. The dashed lines show cases where the amount of grease has been doubled. The dotted lines show cases where the amount of grease has been tripled. For each grease ratio, six different financing arrangements are shown. From left to right, these are 20 years at 6%, 20 years at 12%, 10 years at 6%, 10 years at 12%, 5 years at 6%, and 5 years at 12%.

SWPO should also be favorable to other market applications in which low or negative value, high water content biomass is available in conjunction with a low or negative value fuel material. For biomass slurries, primary candidates are sewage sludge, manure sludge, and shredded and/or composted organic municipal solid waste (MSW) slurries. For the high heating value stream, primary candidates are trap grease, waste plastic or rubber slurries, and coal or coke slurries.

The next phase of the SWPO program will be focused on verifying process improvements identified during the preliminary pilot-scale testing, and then performing extended duration testing with the GA pilot plant. Tests of at least 100 hours duration using sewage sludge and trap grease as simultaneous feedstocks are a primary objective. Follow-on Phases III and IV of the SWPO program will develop and demonstrate a dedicated 5-tpd reduced-scale SWPO facility at a location such as the Encina municipal wastewater treatment plant. Subsequent to this demonstration, the technology will be ready for a commercial-scale demonstration.

While there are clearly technical challenges that must still be addressed, such as demonstration and scale-up of the technology, SWPO represents an outstanding opportunity to further the dual goals of developing a hydrogen economy and practicing environmentally friendly waste disposal. It may well represent one of the few scenarios in which hydrogen may be produced economically from biomass at a relatively small scale. SWPO could thus play a pivotal role in the proliferation of distributed hydrogen generation. As an additional benefit, the high operating pressure of the process presents opportunities for the recovery of high pressure hydrogen product without the high cost of compression.

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Biological Water Gas Shift Development

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Objectives

- Improve biological water-gas shift (WGS) reaction for producing biomass-derived hydrogen, using the photosynthetic bacterium *Rubrivivax gelatinosus* CBS as the biological catalyst.
- Understand the biological machineries governing the CO-shift process in order to improve both CO-shift rates and durability.
- Understand high pressure bioreactor dynamics.
- Design, construct, and operate bioreactor capable of operating at elevated pressure.
- Elucidate CO pressure effects on biological CO-shift reaction.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology

Approach

- Physiology study to determine energy generation during CO shift. If verified, this would assure sustained hydrogen production in darkness.
- Molecular study to clone and characterize genes involved in CO-shift reaction. This would enable us to optimize the CO-shift process.
- Integrated bioreactor engineering and operation to understand high-pressure bioreactor dynamics.

Accomplishments

- Physiological studies have confirmed that adenosine triphosphate (ATP) is generated dur-ing CO shift, which simplifies dark bioreactor operation and maintenance while improv-ing its durability.
- Molecular biology studies have identified 16 genes involved in CO shift, which enables us to manipulate them for over-expression of CO-shift activity.
- Developed a novel recirculating bubble-column reactor which provides good gas-liquid mass transfer.
- Obtained intrinsic CO-shift kinetics of Rubrivivax gelatinosus at various CO concentrations.

Future Directions

- Understand the biochemistry of the hydrogenase enzyme in the CO-shift pathway. The CO-shift hydrogenase is durable and more tolerant to oxygen, unlike most hydrogenases reported in literature. An in-depth investigation could result in insight regarding a structure-function relationship.
- Continue to understand the genetic system of the CO-shift hydrogenase. This knowledge would allow its genetic transfer to other microbial systems for fermentative and photo-lytic hydrogen production.
- Elevated-pressure bioreactor operation with gaseous substrates is a unique research area. Continued development in this area could lead to process improvement and other applica-tions.

Introduction

This project is investigating the use of the photosynthetic bacterium *Rubrivivax (Rx.) gelatinosus* CBS to quantitatively shift and condition crude synthesis gas into a hydrogen-rich stream according to the reaction: $CO + H_2O \leftrightarrow H_2 + CO_2$. In contrast to conventional high-temperature catalytic shift processes, this biologically mediated reaction can operate at ambient temperatures, making it potentially promising for large-scale H_2 production. This project has two different goals: a nearer-term goal to investigate the utility of this biological process as an alternative to conventional shift technology, and a longer-term goal to understand the enzymatic processes involved in the CO-to-H_2 reaction.

The nearer-term goal to determine the utility of this process as a "drop-in" replacement to the conventional high-temperature shift process is important because the process may represent a less-expensive option to the conventional process for certain process streams. The longer-term goal of understanding the enzymatic processes involved may allow the transfer of the hydrogen production system to another organism, which would represent a completely new approach to biological hydrogen production.

Approach

Work on this project is divided into fundamental experiments designed to understand the metabolic CO-shift pathway in *Rx. gelatinosus* CBS, and applied experiments focusing on the scale-up of the overall process.

Our approach to the fundamental experiments is to use both microbiological and molecular biology techniques to help elucidate the overall hydrogen production pathway. Based on evidence from the closely related photosynthetic bacterium Rhodospirillum rubrum, we hypothesize that CO oxidation is catalyzed via a CO dehydrogenase (CODH) enzyme generating reducing equivalents, which are then transferred via a ferredoxin-like iron-sulfur protein to the terminal hydrogenase to yield H_2. Thus, the enzyme complexes responsible for CO oxidation and hydrogen production are distinct and can be studied separately.

Our approach to the scale-up experiments is guided by an independent and very detailed techno-economic analysis of the overall process. This analysis, begun in FY 2001, was refined during FY 2002 and FY 2003. This analysis showed the need to operate the bioreactors at moderate pressures (150-200 psi). Bioreactor operation at these pressures allows significantly higher volumetric hydrogen production rates while incurring no additional reactor costs (conventional reactor materials, e.g., carbon steel, can easily withstand these modest pressures). Our overall approach is to build incrementally larger and higher-pressure bioreactors. At each stage during scale-up, reactor models are developed and compared to actual reactor data to help us fully understand the reactor dynamics.

Results

The goal of our microbiology experiments was to demonstrate that the photosynthetic bacterium *Rx. gelatinosus* CBS could grow solely on CO in the dark. Previous work has shown CO-supported growth in the dark in *Rx. gelatinosus* Strain 1 (Uffen, 1976), in *Rs. rubrum* (Kerby, et al., 1995), and in *Carboxydothermus hydrogenoformans* (Svetlichny et al., 1991). However, all of these experiments used a carbon-containing complex nutrient such as yeast extract or trypticase in the growth medium. Because of this, it is hard to conclude whether CO alone can generate the energy necessary to support cell growth or whether the complex nutrients played a role as well. We have performed a number of experiments to unequivocally demonstrate that bacterium *Rx. gelatinosus* CBS can grow solely on CO in the dark.

Figure 1 shows the results of an experiment in which *Rx. gelatinosus* CBS was grown in minimal medium with CO as the sole carbon substrate. This dark-grown culture has a doubling time of approximately two days in CO, as reflected both by the increase in optical density at 660nm (data in Figure 1), and by an increase in the number of colony-forming units on agar plates (data not shown).

We collected complementary evidence of the ability of *Rx. gelatinosus* CBS to grow solely on CO in darkness by measuring ATP generation during dark growth. Since ATP is a universal energy carrier in biological systems, generation of ATP is generally accepted as proof of growth on a given substrate. We cultured two identical CBS cultures in the presence of CO and light. The two cultures were then placed in darkness, without CO, to exhaust the endogenous ATP levels. After an overnight incubation, the headspace of one culture was filled with 20% CO gas while the other culture headspace was filled with argon gas as a control. At various intervals, aliquots of cell samples were withdrawn and quantified for endogenous ATP levels (Tran and Unden, 1998). Data from Figure 2 clearly indicate that the culture that received CO immediately began to produce ATP over a time period of 15 min, while no net ATP production was measured in the argon gas control. Data from both Figures 1 and 2 therefore indicate that CO supports both cell growth and ATP synthesis in darkness. ATP can be used to generate new cell mass, support nutrient uptake and cell repair, and synthesize new enzymes such as the WGS catalysts, once the existing ones are turned over. These findings therefore have significant implications in that CO shift bioreactor can operate in darkness to sustain long-term hydrogen production, which will greatly simplify the design and operation of the bioreactor.

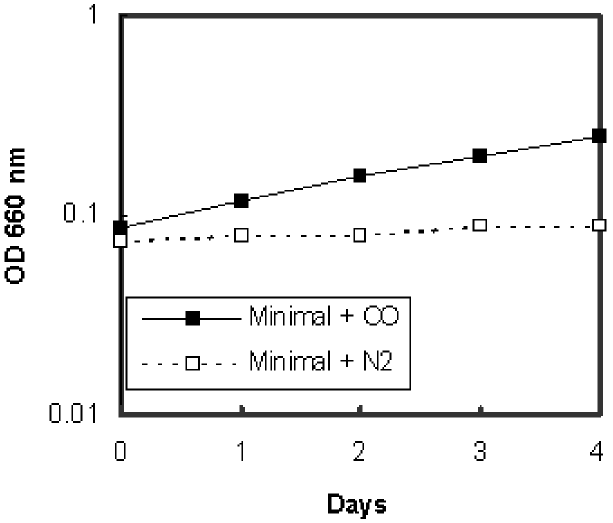

Figure 1. Growth of *Rubrivivax gelatinosus* CBS with CO as the sole carbon substrate in the dark. The culture was bubbled daily with 20% CO (solid line) while the control received N_2 gas (dashed line).

Our work this year in molecular biology was remarkably successful. We have identified 16 putative genes involved in the pathway of H_2 production (Figure 3). Of these 16 genes, four (*hypA, cooF, cooS*, and *cooC*) reside on the same operon and are thought to be involved in the first

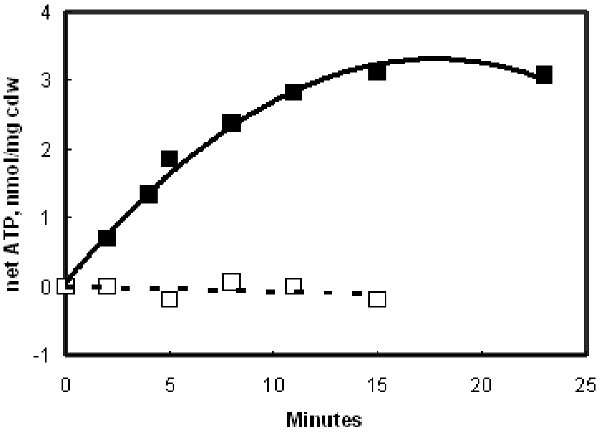

Figure 2. Kinetics of ATP production by *Rubrivivax gelatinosus* CBS in darkness with CO (solid line) or argon gas (dashed line). (cdw = cell dry weight)

enzymatic step of the pathway, the oxidation of CO to CO_2 and the release of protons and electrons from water. The remaining 12 genes are believed to play a role in the hydrogenase reaction, the reduction of protons to H_2. Unlike most other hydrogen-related genes cloned to date, these genes are clustered within the chromosome, encompassing approximately 15 kilobases. The *coo*-genes (for CO-oxidation) all show a high degree of similarity to those found in *Rhodospirillum rubrum*, which also produces hydrogen via the biological WGS (BioWGS) reaction (Fox et al., 1996). Unlike the gene organization in *Rs. rubrum*, *Rx. gelatinosus* CBS contains Hyp (hydrogenase pleiotrophy) genes clustered around the *coo* genes. Hyp genes encode hydrogenase accessory proteins involved in the insertion and co-ordination of Ni^{2+}, Fe, CO, and CN ligands found within the catalytic portion of the hydrogenase. The *hyp* genes are similar to those found in a wide variety of hydrogenase-containing bacteria, including *Chlorobium tepidum*, *Rhodobacter sphaeroides*, *Aquifex aeolicus*, and *Nostoc punctiforme*. Lastly, a putative Ni^{2+} transporter is associated with the BioWGS genes. The translation of this gene sequence predicts that the putative transporter contains an N-terminal signal peptide and six transmembrane domains. Ni^{2+} is an essential component of the *Rx. gelatinosus* CBS hydrogenase, and is also incorporated into multiple enzymes involved in the BioWGS reaction. The putative Ni^{2+} transporter is comparable to those found in *Ralstonia metallidurans*, *Rhodopseudomonas palustris*, and *Bradyrhizobium japonicum*. A *cooS* mutant (termed GV1214) was obtained and analyzed during FY 2002 and determined to be lacking carbon monoxide dehydrogenase (CODH) activity (Vanzin *et al.*, 2002). This mutant was complemented by adding back to the mutant the region of the chromosome containing HypA through *cooC*. This cell line then produced approximate wild-type levels of hydrogen (data not shown).

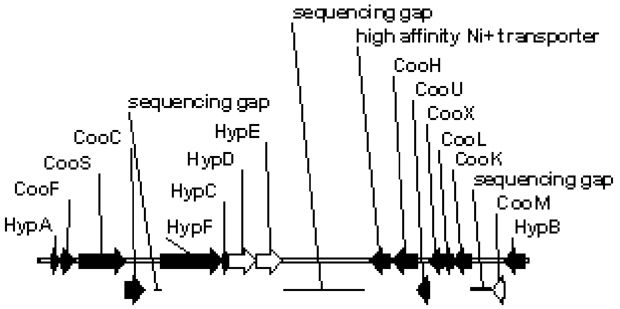

Figure 3. BioWGS gene organization. Filled arrows indicate completed genes, while open arrows indicate partially sequenced genes. The genomic information encompasses approximately 15 kilobases. Scale is approximate.

As mentioned above, the independent techno-economic evaluation of the overall biological water-gas shift process indicated that the bioreactor must be operated at elevated pressures to achieve favorable process economics. Our previous work with pressurized bioreactors has indicated that elevated pressures reversibly inhibit the CO-shift activity of the microorganism. Our current results strongly indicate that the presence of dissolved CO is the major cause of this inhibition.

To verify this, we performed a number of CO conversion rate experiments in agitated shake flasks to determine the effect of dissolved CO concentration on the rate of CO uptake and subsequent H_2 production by the bacterium *Rx. gelatinosus* CBS. While gas-liquid mass transfer often complicates the interpretation of reactor conversion data, we verified that these experimental results were not influenced by mass transfer limitations. The results of these experiments are shown in Figure 4. There is

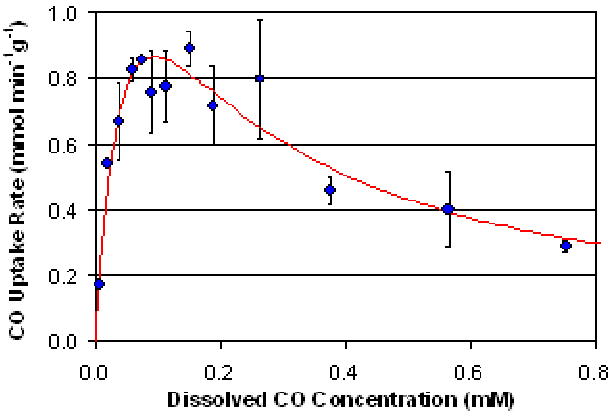

Figure 4. Effect of dissolved CO concentration on the rate of CO conversion by *Rubrivivax gelatinosus* CBS. At concentrations above approximately 0.15 mM, the conversion rate decreases due to substrate inhibition by CO.

considerable scatter in the data, but the overall trend is clear: the rate of CO conversion to H_2 passes through a maximum at approximately 0.15 mM dissolved CO, which corresponds to a gas phase concentration of CO of approximately 20%. These results are consistent with the phenomenon of "substrate inhibition", in which excessive concentrations of a reactant can interfere with the enzyme catalyzing conversion to product. The curve in Figure 4 shows a fit to a substrate inhibition kinetic model.

How does the behavior shown in Figure 4 cause reactor inhibition at elevated pressures? At elevated pressure, the solubility of CO in solution increases, and above a critical pressure (which depends on several factors), the dissolved CO concentration begins to exceed 0.15 mM, which causes a reversible inhibition of reaction rate. Thus, the inhibition can be avoided simply by keeping the dissolved CO concentration below 0.15 mM in the bioreactor. Our preliminary experimental and modeling results (not shown) indicate that elevated cell mass loadings in the bioreactor appear to be effective in keeping the dissolved CO concentration below 0.15 mM, since higher cell mass loadings increase the CO uptake rate per unit bioreactor volume. We are currently performing additional experiments to verify these results.

NREL performed a techno-economic analysis to investigate the relative economics of biological vs. conventional water-gas shift (WGS). Reactor data from our work were used to estimate the size (and therefore cost) of the biological WGS reactor. These results were then compared to the conventional process in the context of an overall system model. The thermodynamics of the biological WGS process are more favorable than the conventional WGS process, but the kinetics are less favorable. Thus, a biological WGS reactor will always be larger (and therefore more expensive) than the corresponding conventional reactor. This difference in reactor cost is balanced by the cost for low-pressure steam production and delivery for the conventional process (the biological process uses liquid water). Thus, the overall cost savings associated with the biological process result from these "balance of plant" savings, and the overall system must be considered when estimating the relative costs of the two different shift technologies. For many biomass-derived synthesis gas streams, the presence of unreacted hydrocarbons (principally methane, CH_4) requires the use of a secondary reformer downstream of the gasifier to convert the unreacted hydrocarbons to additional synthesis gas. Since this reformer requires steam, if the reformer is used, the incremental cost of steam generation for the conventional WGS reactor is minimal, and the lower cost of the conventional WGS reactor makes this technology the preferred option. Thus, it is the amount of methane present in the biomass-derived synthesis gas stream (and not the amount of CO in the stream) that controls which WGS technology is preferred. At lower methane concentrations, no reformer is needed, and the biological WGS process is preferred. At higher methane concentrations, the reformer is necessary, and the conventional WGS process is preferred. The exact methane concentration where this "crossover" occurs depends on a number of factors, but for the assumptions we made in the techno-economic analysis, we believe that the biological WGS process is a promising alternative to conventional process for CH_4 concentrations less than about 3%-5%. The results of this analysis are shown in Figure 5.

Conclusions

- CO can serve both as the carbon and energy substrate to sustain long-term hydrogen production in darkness.

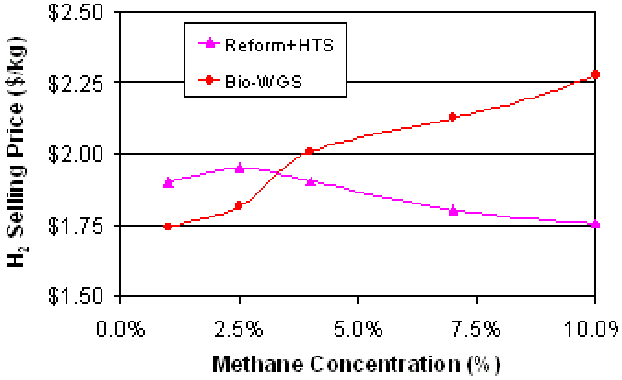

Figure 5. Effect of methane concentration on the cost of hydrogen produced for both conventional and biological WGS processes. Below approximately 3-5%, the biological WGS process appears to be the less expensive option.

- At least 16 genes are required for the CO-to-H_2 reaction in *Rx. gelatinosus* CBS. These genes encode proteins not only involved in catalysis, but also in the transport and assembly of hydrogen-producing enzymes.

- A number of *Rx. gelatinosus* WGS genes are closely related to those known in *Rs. rubrum*, which also produces hydrogen from CO.

- Unlike other hydrogenase-containing microorganisms, *Rx. gelatinosus* CBS contains a large cluster of genes related to hydrogen production. This grouping of genes should facilitate their over-production and/or heterologous expression.

- By restoring wild-type levels of hydrogen production in a CODH mutant, we have demonstrated the ability to make H_2-related proteins of our choosing in CBS. This is a critical step toward the overproduction of microbial catalysts aimed at the production of hydrogen.

- Elevated pressure bioreactor operation is complicated by the inactivation of the WGS pathway by elevated concentrations of dissolved CO. This problem can be avoided by proper bioreactor design.

- The biological WGS reaction appears to be a promising alternative to conventional technology for synthesis gas streams containing low concentrations (<5%) of unreacted hydrocarbons.

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2. Merida, W., P.C. Maness, R.C. Brown, and D.B. Levin. Enhanced hydrogen production from indirectly heated, gasified biomass, and removal of carbon gas emission using a novel biological gas reformer. Accepted for publication in Intl. J. Hydrogen Energy.

3. Maness, P.C., G.V. Vanzin, J. Huang, and S. Smolinski. "The Hydrogen Production Pathway Linked to Carbon Monoxide Oxidation in Rubrivivax Gelatinosus" (Oral Presentation). 12th Western Photosynthesis Conference, Pacific Grove, CO (January 2003).

4. Huang, J., S. Smolinski, G.V. Vanzin, V. Tek, and P.C. Maness. "The Water-Gas Shift Reaction Generates Energy in Darkness" (Poster Presentation). 25th Symposium on Biotechnology for Fuels and Chemicals, Breckenridge, CO (May 2003).

5. Amos, W., Wolfrum, E., Watt, A., "Biological H_2 Production from Synthesis Gas: Preliminary Techno-Economics & Reactor Design Issues" (Poster Presentation). 25th Symposium on Biotechnology for Fuels and Chemicals, Breckenridge, CO (May 2003).

Biomass-Derived Hydrogen from a Thermally Ballasted Gasifier

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Objectives

- Determine whether switchgrass is a suitable fuel for the ballasted gasifier.
- Obtain time-resolved concentrations of important fuel components evolved.
- Identify process conditions that maximize the production of hydrogen.
- Evaluate methods for removing contaminants from the producer gas.
- Evaluate methods for mediating the water-gas shift reaction in the product gas.
- Estimate the economics of hydrogen production from switchgrass.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology

Approach

- Prepare switchgrass fuel and feeder.
- Prepare 5-ton per day bubbling fluidized bed gasifier and a latent heat ballasting system.
- Prepare slipstream for upgrading producer gas.
- Prepare gas sampling and analysis system.
- Perform gasification trials.
- Perform cost estimate of the gasification system.

Accomplishments

- Established analytical methods for accurate and repeatable measurements of H_2S and NH_3.
- Characterized producer gas from gasification of switchgrass.
- Achieved reductions of 95% in total tar and 99% reductions in condensable (heavy) tar by steam reforming.
- Reduced CO in producer gas to less than 0.5 vol-% by water-gas shift reaction.
- Demonstrated operation of ballasted gasifier in production of raw producer gas with hydrogen concentrations averaging 20 vol-% (before gas upgrading).

- Simulated performance of ballast system through thermal modeling.
- Identified technology for separating hydrogen from carbon dioxide.

Future Directions

- Improve the overall cold-gas efficiency of the gasifier.
- Establish methodology for reliable HCl measurements.
- Demonstrate a combined particulate matter/trace contaminant control system.
- Evaluate the feasibility of a combined catalytic reaction/carbon dioxide sorbent system.
- Perform economic assessment of ballasted gasifier system.

Introduction

The goal of this project is to optimize performance of an indirectly heated gasification system that converts switchgrass into hydrogen-rich gas suitable for powering fuel cells. We have developed a thermally ballasted gasifier that uses a single reactor for both combustion and pyrolysis. Instead of spatially separating these processes, they are temporally isolated. The producer gas is diluted neither with nitrogen nor the products of combustion. The heat released during combustion at 850°C is stored as latent heat in the form of molten salt sealed in tubes immersed in the fluidized bed. During the pyrolysis phase, which occurs at temperatures between 600 and 850°C, the reactor is fluidized with steam or recycled producer gas rather than air. Heat stored in the phase change material is released during this phase of the cycle to support the endothermic reactions of the pyrolysis stage.

Because air is not used during the gas-producing phase of the cycle, nitrogen does not dilute the product gas, resulting in relatively high concentrations of hydrogen and carbon monoxide in the producer gas compared to conventional gasifiers. The carbon monoxide, along with steam used to fluidize the reactor, can be shifted to additional hydrogen by the water-gas shift reaction.

Approach

The approach to this project is to employ a pilot-scale (5-ton per day) gasifier to evaluate the thermally ballasted gasifier as a means for producing hydrogen from switchgrass. Gasification at the pilot scale is important for obtaining realistic process data, especially for calculating energy flows through the system and assessing the practicality of feeding switchgrass into the gasifier.

A slipstream from the gasifier is used to evaluate gas cleaning and upgrading options. This slipstream includes: a guard bed designed to remove hydrogen sulfide and hydrogen chloride and some tar; a steam reformer designed to crack the remaining tar and decompose ammonia; and high-temperature and low-temperature catalytic water-gas shift reactors to remove carbon monoxide from the product gas and increase its hydrogen content. A series of gasification trials are being performed to evaluate the effectiveness of these four reactors in removing tar and contaminants, and shifting producer gas towards increased hydrogen and decreased carbon monoxide.

Results

Figure 1 illustrates the slipstream system developed for use with the ballasted gasifier. The slipstream system extracts hot producer gas from the exhaust duct at volumetric flow rates (4.5 – 5.5 L/min) appropriate to isokinetic sampling requirements. This gas sample passes through a heated particulate filter maintained at 450°C to prevent condensation of tars; thus, the collected particulate sample can be used to calculate particulate matter concentrations in the producer gas (typically about 10 g/scm). The particulate-free sample then passes through a guard bed of calcined dolomite that removes hydrogen sulfide and hydrogen chloride prior to passage through metal catalysts that would otherwise be poisoned by these trace contaminants. Steam is added at a level appropriate to steam reforming of tar over a nickel catalyst contained in the second of the four reactors. A high temperature shift reactor and a low temperature shift reactor follow the tar cracker with the purpose of shifting CO and steam to hydrogen and CO_2.

Table 1 summarizes both the operating conditions and results of gas conditioning trials on producer gas generated from air-blown gasification of switchgrass. The "tar cracker" operating in conjunction with the guard bed was able to remove >99% of condensable (heavy) tars from the raw producer gas. Further details of the operation of the tar cracker are found in Reference 1. The combination of water-gas shift reactors reduced CO concentration from 20.1 vol-% to 0.18 vol-%. The outlet concentration of hydrogen was 27.1 vol-%. Further details on the performance of the shift reactors are found in References 2 and 3.

Figure 1 also illustrates the gas sampling system developed for use with the ballasted gasifier, which is separate from the slipstream containing the catalytic reactors. Heated thimble filters remove particulate matter while a tar condenser, operated slightly above 100°C, removes tar without condensing water (an important consideration in accurately sampling water-soluble trace contaminants). The sample stream is split into two streams. One stream goes to a

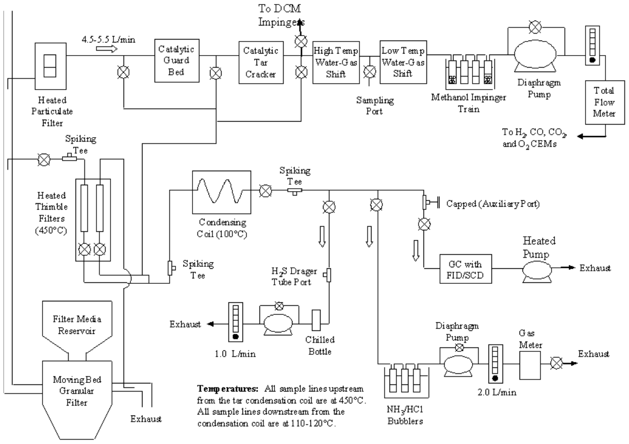

Figure 1. Overall Schematic of Gas Sampling System and Slipstream From Gasifier Effluent

Table 1: Summary of Gas Conditioning Trials on Switchgrass-Derived Producer Gas

Reactor	Guard Bed	Tar Reactor	High Temperature Shift	Low Temperature Shift
Set point temperature of reactor (ºC)	650	800	400	200
Temperature range of reactor (ºC)	600-670	750-850	350-420	180-240
SV (h^{-1})	900	3000	1500	1200
Catalyst	Calcined dolomite	ICI 46-1	Fr-Cr based LB	Cu-Zn-Al based B202
Catalyst volume (ml)	200	60	120	150
Gas Composition*	Inlet gas	Outlet gas	Outlet gas	Outlet gas
H_2	8.5	19.44	23.7	27.1
CO	14.5	8.9	1.37	0.18
CO_2	18.1	20.1	26.8	27.2
CH_4	4.3	3.5	3.4	3.1
C_2H_4	1.5	0.27	0.31	0.13
Tar content (g/Nm^3)	19.5	**	**	**

*Gas composition is dry basis (vol-%) measured by gas chromatography.
** No heavy tar by observation.

heatless drier to produce dry gas for measuring hydrogen sulfide with Draeger tubes. The other stream is partitioned to impinger trains for condensing ammonia and hydrogen chloride in aqueous solutions. Hydrogen sulfide measurements were 190 – 220 ppm, about 50% lower than expected from the sulfur content of the biomass feedstock. This is attributed to absorption by calcined limestone added to the fluidized bed gasifier to control sand agglomeration. Ammonia measurements were 5000 ppm in the raw producer gas.

Since the ballast operates in a cyclic mode, time-resolved gas concentrations are important to assessing the performance of the system. For this purpose, non-dispersive infrared analyzers for CO and CO_2 and an electrochemical cell for O_2 were installed in the gas sampling system (not illustrated in Figure 1). Figure 2 illustrates the continuous data taken during the operation of the ballasted gasifier during the pyrolytic phase of the gasification cycle using these instruments (distinct points are data taken with a gas chromatograph to confirm the continuous measurements). This figure shows how H_2 and CO rapidly increase from virtually zero concentration at the beginning of the pyrolytic phase. Hydrogen peaks almost instantly and gradually declines as the reactor cools while CO continues to climb over most of the pyrolysis phase. Both drop off rapidly after air is readmitted to the reactor (although the persistence of CO in this particular trial indicates that the amount of air added is insufficient for complete combustion of both fresh biomass and residual char in the reactor).

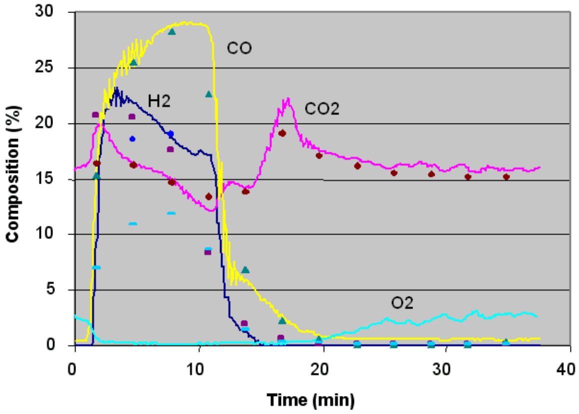

Figure 2. Time Resolved Gas Composition During the Pyrolysis Phase of the Gasification Cycle

Figure 3 illustrates experimental and simulated cooling curves for the ballasted gasifier after an initial combustion heat-up period followed by the admission of steam (but no biomass) to the reactor. The experimental cooling curve shows a distinct inflection as the result of the heat released from the latent enthalpy stored in the ballast tubes. A simple lumped capacitance (LC) model simulates the experimental data reasonably well except during the period of latent enthalpy change, which appears as an isothermal region in the cooling curve. Modeling work proved this to be an artifact of the LC model. Careful accounting of the growth of a solidification zone within the ballast tubes resulted in the receding interface (RI) model, which produces a more realistic cooling curve, as shown in Figure 3. See Reference 4 for additional details.

Conclusions

- Steam reforming of raw producer gas reduced condensable (heavy) tars to undetectable levels.
- Water-gas shift reactors were successful in reducing carbon monoxide to less than 0.2 vol-%.
- Reliable trace contaminant sampling and measurement was established for ammonia and hydrogen sulfide.
- The thermal ballasting system generated raw producer gas with up to 23 vol-% hydrogen.
- An accurate thermal model of the ballasted gasifier was developed.

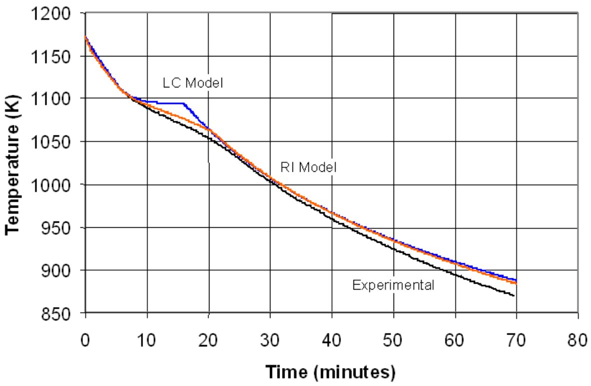

Figure 3. Comparison of Experimental Cooling Curves to Predictions of Thermal Models

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2. Zhang, R., Cummer, K., Suby, A., and Brown, R. C., Biomass-derived hydrogen from an air-blown gasifier," Fuel Processing Technology (submitted).

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Techno-Economic Analysis of Hydrogen Production by Gasification of Biomass

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Objectives

- To determine the economics of hydrogen production by gasification of three biomass candidates: bagasse, switchgrass, and nutshells
- To optimize hydrogen production for use in proton exchange membrane (PEM) fuel cells
- To identify the economic and technical barriers associated with biomass gasification

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
- AB. Hydrogen Separation and Purification

Approach

- Determine the cost and availability of the three candidate biomass feedstocks.
- Design a process scheme for the production of hydrogen.
- Determine optimal hydrogen production through the testing of various simulation cases.
- Analyze research and simulation results to determine technical and economic feasibility.
- Determine the commercialization barriers to the production of hydrogen from biomass.

Accomplishments

- Estimated the cost and availability of all three biomass feedstocks.
- Determined the current technologies available for biomass feeding and hot gas cleanup.
- Simulated and optimized the production of hydrogen through the use of an empirical, GTI proprietary gasifier model and a HYSYS® design and simulation package.
- Performed an economic analysis of the production of hydrogen from the three biomass feedstocks.
- Evaluated current public programs available to reduce the cost of biomass as a feedstock.
- Determined the technical, economic, and psychological barriers to the commercialization of hydrogen from biomass.

Future Directions

The following areas are currently being pursued by GTI, however they are not funded under this project.

- Conduct experimental testing to verify the results obtained in this paper study.
- Evaluate an economical way to clean syngas at reforming temperatures.
- Determine suitable membrane materials that will promote reforming and separation.
- Further evaluate and test pressurized biomass feeding systems on various feedstocks.

Introduction

Biomass represents a large potential feedstock resource for environmentally clean processes that produce power or chemicals. It lends itself to both biological and thermal conversion processes, and both options are currently being explored. Hydrogen can be produced in a variety of ways. The majority of the hydrogen produced in this country is produced through natural gas reforming and is used as chemical feedstock in refinery operations.

In this study, the production of hydrogen by gasification of biomass is examined. Biomass is defined as organic matter that is available on a renewable basis through natural processes or as a by-product of processes that use renewable resources. The majority of biomass is used in combustion processes in mills that produce electricity for end-use product generation. This project explores the use of hydrogen as a fuel derived from gasification of three candidate biomass feedstocks: bagasse, switchgrass, and a nutshell mix consisting of 40% almond nutshell, 40% almond prunings, and 20% walnut shell.

Approach

In this study, an assessment of the technical and economic potential of producing hydrogen from biomass gasification is made. The resource base is assessed to determine process scale potential from information on feedstock costs and availability. Solids handling systems are reviewed. A GTI proprietary gasifier model is used in combination with a HYSYS® design and simulation program to determine the amount of hydrogen that can be produced from each candidate biomass feed. Cost estimations are developed, and government programs and incentives are analyzed. Finally, the barriers to the production and commercialization of hydrogen from biomass are determined. The end-use of the hydrogen produced from this system is small PEM fuel cells for automobiles.

Results

Analysis of the resource base determined bagasse and switchgrass should be analyzed on a scale of 500, 1000, and 2000 tonnes/day and mixed nutshells at 500 tonnes/day. Simulation results were obtained for 500 tonnes/day biomass fed to the gasifier at moisture contents of 20% for bagasse, 12% for switchgrass, and 12.5% for the nutshell mix. A scaling factor of 1 can be used to determine hydrogen production from an increased feed rate (i.e. doubling the feed rate will double the amount of hydrogen produced). Process flow diagrams were developed for all three cases and are very similar with the exception of the need for a dryer for the bagasse case, as shown in Figure 1 (the initial moisture content of the feed is 50% and must be reduced to 20% for feed into the gasifier) [1].

The flow streams and sizes from the process flow scheme were used to adjust the scale and unit

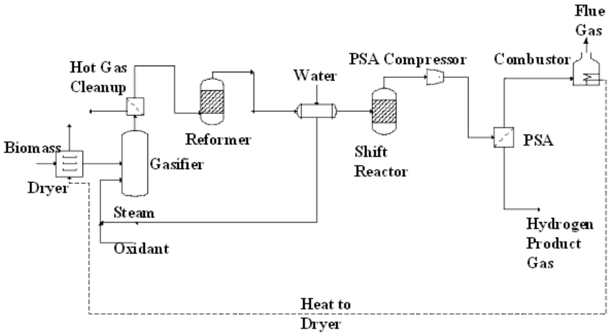

Figure 1. Process Flow Diagram of Bagasse Case with a Dryer (PSA = pressure swing adsorption)

operations that had previously been the subject of cost and design studies by EPRI and GTI. Previous work done for GTI had provided a very detailed breakdown of capital costs, including labor hours on many categories of construction and installation. The work done by EPRI developed cost breakdowns for biomass power systems using biomass feedstocks. Scaling of costs to adjust to the sizes desired for the cases studied here was accomplished according to the following general rule: power law scaling of 0.7 for the solids handling, gasification, gas cleaning, shifting, and purification systems, and 0.8 for the power, steam, balance of plant, general facilities, and overall combined cycle system scaling. Drying and steam turbine components were scaled at a 0.6 power law. Hydrogen production rates and the resulting economics are shown in Table 1 [1].

The economic results achieved in this study are comparable to those from steam methane reforming. For steam methane reforming plants that produce approximately 1.5 million Nm^3/day, the cost of hydrogen production ranges from \$5.85/GJ (\$3.00/GJ natural gas) [2] to \$7.46/GJ (\$4.50/GJ natural gas) [3]. This comparison is shown in Figure 2.

Conclusions

Hydrogen is a valuable fuel that can provide sustainable energy for fuel cell vehicles. The majority of hydrogen is produced by steam methane reforming of natural gas, where average prices of \$5.50 to \$7.50 per gigajoule can be realized for larger facilities. At low natural gas prices, this is the least expensive way to produce hydrogen, but it relies on a non-renewable, fossil fuel.

Biomass gasification represents an alternative means to produce hydrogen. This study evaluated hydrogen production by gasification of three biomass feedstocks: bagasse, switchgrass, and a nutshell mix. The process scheme involved feeding, gasifying, cleaning, reforming, shifting, and purifying to produce a hydrogen stream with better than 99.9% purity. The economics of hydrogen production by gasification of biomass predict that hydrogen can be

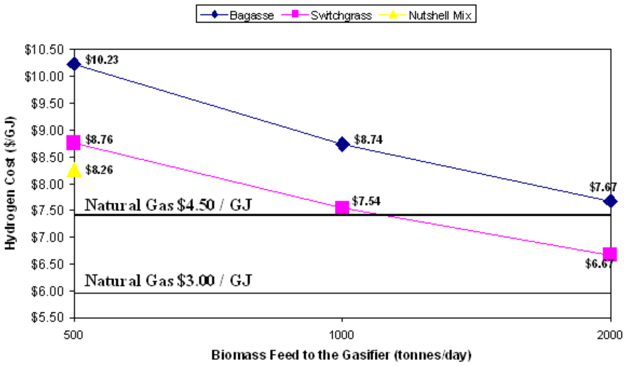

Figure 2. Estimated Cost Comparison of Hydrogen Production

Table 1. Economic Results for Gasification of Three Biomass Feedstocks

	Gasifier Feed Rate	Hydrogen Produced		Feedstock Cost	Capital Cost	H_2 Cost (15% IRR)
Feedstock	Dry Tonnes / Day	Tonnes / Day	Nm^3 / Day	US \$ / GJ	US \$ Million	US \$ / GJ
Bagasse	400	13.2	347,000	1.50	37.0	10.23
	800	62.5	695,000	1.50	61.1	8.74
	1600	125	1,390,000	1.50	100.9	7.67
Switchgrass	440	37.0	412,000	1.50	36.5	8.76
	880	74.0	824,000	1.50	60.6	7.54
	1760	148	1,648,000	1.50	100.9	6.67
Nutshell Mix	438	38.7	488,000	1.50	36.3	8.26

produced economically. Hydrogen prices from $6.50 - $10/GJ can be realized. As technology improves, natural gas prices increase, and government incentive programs evolve, biomass gasification will present an economical way to produce hydrogen for use in PEM fuel cells and other energy consuming systems.

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1. D. Bowen, F. Lau, R. Dihu, S. Doong, R. Remick, R. Slimane, R. Zabransky, E. Hughes, and S. Turn, "Techno-Economic Analysis of Hydrogen Production by Gasification of Biomass." Final Report to U.S. Dept. of Energy, Contract DE-FC36-01GO11089, June 2003.

2. D. Bowen, F. Lau. Poster presentation at the May 2003 US DOE Hydrogen and Fuel Cell Program Merit Review.

3. D. Bowen, F. Lau, R. Dihu, S. Doong, R. Remick, R. Slimane, R. Zabransky, E. Hughes, and S. Turn, "Hydrogen from Biomass Gasification." Canadian Hydrogen Association and Fuel Cells Canada Conference, Vancouver, BC, Canada, June 2003.

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Hydrogen from Biomass - Catalytic Reforming of PyrolysisVapors

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Objectives

- Demonstrate the production of hydrogen from biomass pyrolysis integrated with catalytic steam reforming and prepare for scale-up of the system to greater than 500 kg H_2/day by 2009.
- Improve the efficiency of the system, including the reformer, and the use of appropriate catalysts to reduce the cost to below $2.90/kg H_2 by 2009.
- Demonstrate the use of a variety of feedstocks so that significant quantities of hydrogen can be made from biomass.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Control and Safety
- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
- Z. Catalysts
- AD.Market and Delivery

Approach

- Support DOE funded partners to demonstrate the integrated pyrolysis/reforming process using agricultural residues (peanut shells) as feedstock; document mass balance and catalyst performance in a long-duration test.
- Validate the yields and throughputs obtained in the bench-scale system so that information can be used for technoeconomic analysis of the process and for the design of the future scale-up of the process, which will begin in FY 2004 at a scale of 250 kg H_2 produced/day.
- Facilitate the addition of unit operations for use in a demonstration that will use H_2 to produce electricity and fuel vehicles such as buses.
- Work with interested parties to extend the applicability of the work to other geographical locations.
- Contribute state-of-the-art chemical analysis and process control so that the small-scale systems can be run with high confidence of safety and reliability.

Accomplishments

- Developed gas filtration unit operation that solved the problem of plugging the distribution plate with entrained char.
- Provided technical support of the reformer installation in Blakely, Georgia, where the system was run for 100 hours.
- Filed a provisional patent that incorporates biomass conversion to hydrogen with a co-product of carbon-based soil amendment system.
- Supported partnership development in other areas of the country so that the results can be deployed when ready.

Future Directions

- Develop the Phase 3 system design that will include better heat management in the pyrolyzer and reformer and will add a condenser, compressor, and pressure swing adsorption (PSA) system to the gas conditioning system.
- Initiate tests necessary to develop a circulating fluidized bed reforming process.
- Develop process control systems that will facilitate the cost-effective development of safety engineering for small-scale biomass-to-hydrogen systems.

Introduction

The goal of this work is the production of renewable hydrogen from agricultural residues at a comparable cost to existing methane-reforming technologies by 2015. Near-term production of renewable hydrogen from biomass requires a co-product strategy to compete with conventional production of hydrogen from the steam reforming of natural gas. The processing of pyrolysis co-products from the production of activated carbon is one possible path to demonstrate such a strategy.

The original concept was that the pyrolysis oil could be separated into two fractions based on water solubility. The water-soluble fraction would be used for hydrogen production, and the water insoluble fraction could be used in adhesive formulations. The bio-oil can be stored and shipped to a centralized facility for conversion to hydrogen via catalytic steam reforming and shift conversion. Although the adhesive byproduct option remains viable, commercial deployment opportunities are still not near-term. Hence, other opportunities had to be developed based on the co-product strategy. The conversion of biomass to activated carbon is an alterative route to hydrogen with a valuable co-product, as outlined in Figure 1. A third option is converting the charcoal into carbon-based fertilizers. In those two options, the volatiles produced in the pyrolysis step can be converted to hydrogen. This is a near-term possibility for deployment. Slow pyrolysis is used in the first step of the activated carbon process to optimize the yield of charcoal and organic vapors.

Approach

A schematic of the system is shown in Figure 2. Pelletized peanut shells were fed to a cross-draft,

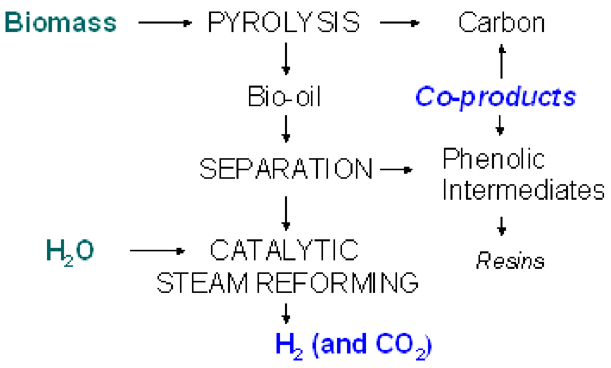

Figure 1. Biomass to Hydrogen Based on Pyrolysis with a Co-Products Strategy

moving-bed pyrolysis reactor heated by propane combustion gases. Superheated steam was used to educe a fraction of the vapors through a bag-house filter to remove char fines and then to a preheater before the reformer. Pelletized peanut shells were fed at a rate of 50 kg/hr to the pyrolysis reactor, which was controlled so the exit gas temperature was 500°C. Using a helium tracer, it was determined that 20% of the total gaseous products from the pyrolyzer were educed in the steam flow to the reformer. Before reforming, the steam/vapor stream entered a preheater that raised the gas stream temperature to 650°-700°C.

The catalytic fluid bed reformer was fed with up to 5 kg/h of pyrolysis vapor. The maximum allowable operating temperature and pressure are 900°C and 140 kPa, respectively. The reformer is equipped with internal and external cyclones for disengaging catalyst particles, instrumentation, data acquisition, and safety features (alarms). Commercial nickel-based catalyst ground to particle sizes of 300-500 mm was used in the reactor. The catalyst is fluidized using superheated steam, which is also a reactant in the reforming process. The cyclones capture both fine catalyst particles and solid carbon generated by gas-phase pyrolysis of the vapors that may occur in competition with the catalytic steam reforming. The Inconel reactor with a perforated distribution plate is placed inside a three-zone electric furnace to maintain the reactor at the desired temperature during the endothermic steam reforming operation. The reformed products flow through the spray scrubbers and a cold wall condenser before passing through a coalescing filter to remove aerosols.

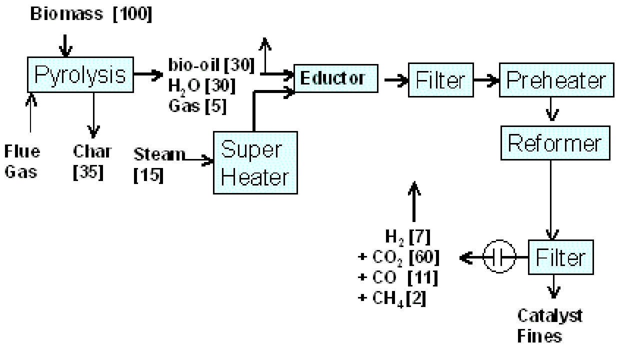

Figure 2. Diagram of Process as Performed for the 100-hour Duration Run

Results

The purpose of the 100-hour run was to reform the whole pyrolysis vapors in the 30-cm catalytic steam reforming fluid bed reactor. The more chemically stable, lignin-derived phenolics are more likely to coke on the nickel catalyst. Prior runs in the 5-cm reformer have used only the aqueous carbohydrate-derived fraction of pyrolysis oil.

Figure 3 shows the product gas composition (H_2, CO_2, CO and CH_4) and the differential pressure (DP) across the reformer bed over the first 70 hours of the 86 hours that the reformer was on line. Periods where the reformer was taken off line, a total of 16 hours, are not included in the figure. The final 16 hours are not shown in Figure 3, since the plugging of the filter before the eductor made the system unstable. The build-up of char across the filter also caused the gradual decrease in DP across the reformer bed, as shown in Figure 3. The composition of the gas indicates that the yield of hydrogen from this agricultural residue feedstock is approximately 90% of maximum. Additional optimization of process conditions should result in somewhat higher yields (note that, in a commercial operation, the remaining CO could be converted to CO_2 and additional hydrogen using conventional water-gas shift processing). In these tests, the gas product stream was flared. No breakthrough of pyrolysis products was noted, and the methane level, which is a sensitive indicator of catalyst activity, did not increase. The significant finding here is that the lignin-derived pyrolysis products were reformed completely. The changes in product gases were due

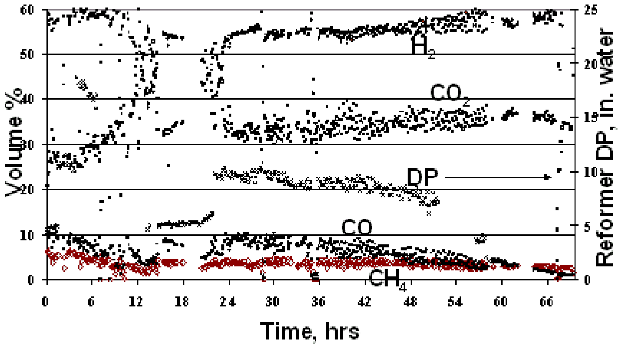

Figure 3. Product Gas Composition (H_2, CO_2, CO and CH_4) and Differential Pressure (DP) Across the Reformer Bed

to a systematic decrease in mass flow to the bed due to an increase in pressure drop across the hot gas filter. This build-up of particulate matter was unexpected, but the change in product gas composition indicates better performance. The increase in hydrogen yield and decrease in relative yield of both CO and CH_4 were the results of effectively decreasing the weight hourly space velocity and increasing the steam-to-carbon ratio. We achieved a higher rate of conversion most likely by allowing more time for carbon gasification from the catalyst surface.

Conclusions

- The steam reforming of biomass pyrolysis vapors and liquids, when integrated with the production of high value products, is a promising near-term approach to the production of renewable hydrogen. This approach will be applied in Georgia at a plant that makes activated carbon from peanut shells and has pyrolysis by-products available for conversion. The key technical goal for the run is to obtain preliminary performance data on the catalyst, especially physical attrition and deactivation.
- In the next phase, the reactor will be run for 1000 hours with additional gas stream processing included. The hydrogen that is produced will be separated from CO and CO_2 using pressure swing adsorption. The purified hydrogen will be mixed with natural gas and used in engine demonstrations. Other agricultural residues and deployment logistics are being evaluated for cost and co-product potential.

FY 2003 Publications/Presentations

"Renewable hydrogen production by catalytic steam reforming of peanut shells pyrolysis products." Robert J. Evans, Esteban Chornet, Stefan Czernik, Calvin Feik, Richard French, Steven Phillips, Yaw D. Yeboah, Danny Day, Shivayam Ellis, Dennis McGee, and Matthew J. Realff. Preprints, ACS Fuel Chemistry Symposium, Boston MA, 2002.

Special Recognitions & Awards/Patents Issued

Provisional Patent, Danny Day and Robert J. Evans, "A process for the combined production of hydrogen, sequestered carbon and a slow release fertilizer from biomass."

Production of Hydrogen from Post-Consumer Residues

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Objectives

- Explore feasibility of producing hydrogen from low-cost, potentially high-hydrogen-yield renewable feedstocks that could complement biomass feedstocks, increase flexibility, and improve economics of the biomass-to-hydrogen process.
- Determine efficiency of pyrolysis/reforming technology in application to readily available post-consumer wastes: plastics, trap grease, mixed biomass and synthetic polymers.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology

Approach

- Pyrolysis or partial oxidation of biomass, plastics, and other solid organic residues in the post-consumer waste stream.
- Catalytic steam reforming of the resulting pyrolysis gases and vapors.
- Catalytic steam reforming of biomass-derived liquid streams (trap grease).

Accomplishments

- Demonstrated production of hydrogen from polypropylene (PP) by fluidized bed pyrolysis/reforming process with the yield: 34 g H_2/100 g PP, which is 80% of the stoichiometric potential.
- Demonstrated efficiency of fluidizable, attrition-resistant catalyst developed at NREL for trap grease reforming; average yield: 22 g H_2/100 g grease (60% of the stoichiometric potential).

Future Directions

- Identify the nature of catalyst deactivation and improve performance of the production of hydrogen from waste grease.
- Test and optimize pyrolysis/reforming process for complex feedstocks (textiles, mixed plastics) using commercial and NREL developed catalysts.
- Demonstrate production of hydrogen by co-processing renewable (solid and liquid biomass and wastes) and fossil (natural gas) feedstocks.

Introduction

The environmental concerns and instability of the prices of natural gas make the use of renewable biomass and wastes an attractive alternative for the production of hydrogen. In recent years, we developed a production method that combines two stages: fast pyrolysis of biomass to generate bio-oil, and catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide. Because of the low cost of storage and transport of bio-oil, pyrolysis and reforming can be carried out at different locations to improve the overall process economics. Such a concept helps overcome the barrier of high feedstock cost for producing hydrogen from biomass.

This research further addresses the challenge of feedstock cost by expanding the feedstock base to other renewable low-cost materials that could be processed separately or in combination with biomass. This year we adapted the technology developed for biomass to two types of post-consumer waste materials: plastics and "trap grease". Plastics, which account for 8%-9% of today's U.S. waste stream, or about 15 Mt annually, are mostly landfilled. Potentially, the waste plastics could be used to generate 6 Mt of hydrogen per year. Waste grease is largely available throughout the country and so far is mostly discarded (i.e., not recycled or reused). The amount of grease collected in traps installed on the sewage lines of restaurants and food processing plants, and from wastewater treatment plants is about 6 kg/person/year, which has the potential for producing 0.5 Mt of hydrogen annually.

Approach

The concept proposed for plastics is a two-stage process: fast pyrolysis or gasification to convert polymers to a gas/vapor stream of monomers and other low-molecular weight compounds followed by catalytic steam reforming of this gas to yield hydrogen and carbon oxides. "Trap grease" does not require a depolymerization step and can be directly steam reformed to produce hydrogen.

Results

The production of hydrogen from plastics (polypropylene) was carried out in a two-reactor system shown in Figure 1. Polypropylene was fed to the fluidized bed pyrolyzer, where it depolymerized to gases and vapors that reacted with steam in the second reactor – a fluidized bed catalytic reformer – to produce hydrogen, carbon oxides, and minor amounts of hydrocarbons. During a 10-hour operation, the hydrogen concentration in the product gas was above 70%, and its yield was 80% of the stoichiometric potential (complete conversion to CO_2 and H_2) as shown in Figures 2 and 3.

The production of hydrogen from "trap grease" was carried out in the single-step fluidized bed catalytic steam reforming process (liquid grease fed to the reformer). During the first year of the project, we used a commercial catalyst that did not have sufficient mechanical strength, which resulted in significant catalyst losses due to attrition and entrainment from the

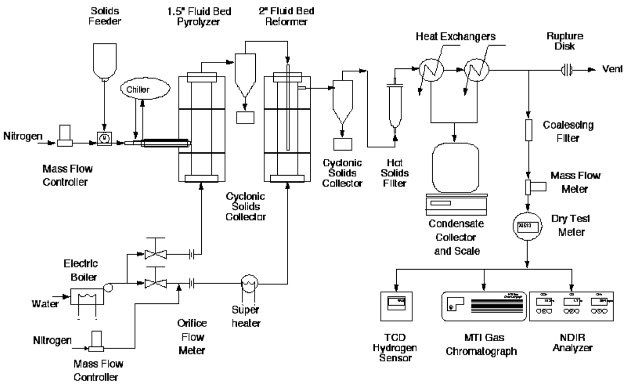

Figure 1. Fluidized Bed Integrated Pyrolysis/Reforming System

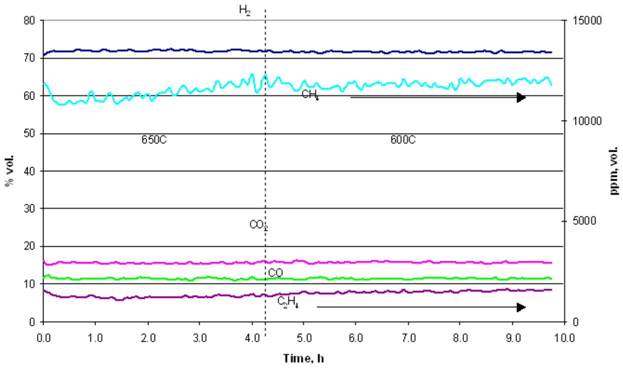

Figure 2. Product Gas Composition from Pyrolysis/ Reforming of Polypropylene

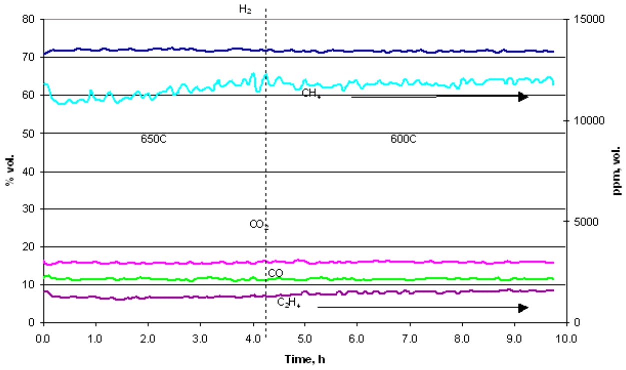

Figure 3. Yield of Hydrogen from Pyrolysis/Reforming of Polypropylene

reactor. As shown in Figures 4 and 5, the NREL developed catalyst used in this year's tests showed a satisfactory performance for 120 hours on stream, producing hydrogen with a yield greater than 60% of the stoichiometric potential, and then deactivated, probably because of the contaminants in "trap grease". The used catalyst is analyzed to identify the reason and the nature of deactivation.

Conclusions

- Using a two-reactor pyrolysis/reforming system, we demonstrated that hydrogen could be efficiently produced from plastics; 34 g hydrogen was obtained from 100 g of polypropylene, which is 80% of the stoichiometric potential.
- Reforming of "trap grease" resulted in 25 g hydrogen per 100 g grease for 115 hours of catalyst time on stream. After this time, the process performance significantly decreased due to the catalyst deactivation.

FY 2003 Publications/Presentations

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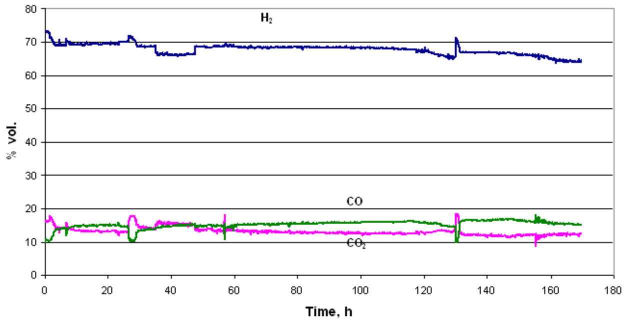

Figure 4. Product Gas Composition from Reforming of Trap Grease

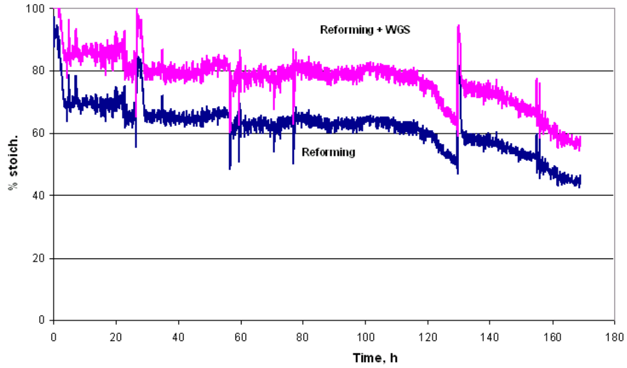

Figure 5. Yield of Hydrogen from Reforming of Trap Grease (WGS = water gas shift)

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3. 3.Czernik, S., French, R., Feik, C., Chornet, E., Hydrogen from Biomass-derived Liquids, in Proceedings of 14th World Hydrogen Energy Conference, Montreal, Canada, June 10-14, 2002.

Special Recognitions & Awards/Patents Issued

1. Record of Invention filed with U.S. DOE.

Fluidizable Catalysts for Hydrogen Production from Biomass Pyrolysis/Steam Reforming

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Subcontractor: Yves Parent (Chemical Engineering Consulting Services)

Objectives

- Develop attrition resistant supports and multi-functional, multi-component fluidizable catalysts from these supports for efficiently reforming pyrolysis vapors and liquids derived from biomass.
- Develop fluidizable catalysts for reforming feedstocks derived from post-consumer waste (trap grease, waste plastics).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
- Z. Catalysts

Approach

- Develop and optimize fluidizable reforming catalysts using CoorsTek. Inc. specialty aluminas as supports.
- Evaluate catalytic reforming performance with gas and liquid phase feedstocks derived from biomass and post-consumer wastes.
- Design and fabricate a micro-scale reactor for rapid screening of catalysts.

Accomplishments

- Optimized catalyst composition for reforming the aqueous fraction of liquids derived from biomass pyrolysis.
- Developed a catalyst for waste grease reforming.
- Designed and fabricated a rapid catalyst test system.

Future Directions

- Develop catalysts for other renewable feedstocks.
- Improve support materials for bubbling and circulating bed systems.
- Understand and overcome deactivation mechanisms (coking, sulfur and phosphorous poisoning).
- Develop non-nickel reforming catalysts.

Introduction

Commercial naptha reforming catalysts are used to process heavy crude oils in packed bed configurations, and they are the most likely industrial catalysts available for reforming biomass-derived pyrolysis liquids. These catalysts cannot withstand the harsh reaction conditions used in a fluidized bed for producing hydrogen from pyrolysis liquids. Fluidization is preferred in such a case to optimize the contact of catalyst with the feedstock and minimize coke formation. In a typical commercial fixed bed reactor, the pyrolysis liquids tend to form coke instead of being reformed. The commercial backed bed catalysts, which generally consist of nickel coated onto alumina supports, attrit significantly when fluidized and yield consistent losses of 10-20 wt% per day. Because process economics cannot tolerate such catalyst loss, we needed to identify and/or develop an attrition-resistant support that can withstand fluidized reforming conditions.

Numerous support screening experiments showed that commercially available specialty alumina materials produced by CoorsTek Ceramics could have the necessary strength to withstand fluidizing conditions. Catalysts made from these supports have been used to reform pyrolysis liquids, and the generated performance data have been used to refine subsequent catalyst compositions. This year we report results from continued development of catalysts for reforming aqueous pyrolysis liquids and preliminary results from testing our catalysts with other renewable feedstocks including biomass gasification vapors and waste trap grease. These feedstocks require fine-tuning of the catalyst composition to handle sulfur impurities in trap grease and tars contained in gasification vapors. The challenge now is to design novel catalysts with improved reforming activity, gasification activity (gasify coke deposits on the catalyst surface), and poison tolerance (sulfur and phosphorous contained in trap grease) for these new feedstocks.

Approach

We have developed robust nickel-based reforming catalysts from strong alumina particles produced by CoorsTek Ceramics. These materials, which can withstand the harsh conditions required for reforming pyrolysis liquids, produce hydrogen with efficiencies as good or better than those of the best commercial catalysts. Our best original catalyst composition, compared to the composition of a commercial reforming catalyst, provided good activity and performance for reforming aqueous pyrolysis liquids. Our work this year focused on refining that base composition to further improve catalyst performance for reforming the liquids. Additionally, we began testing the basic catalyst with other renewable feedstocks and assessing how feedstock changes impact catalyst performance. The overall goal is to design cost efficient feedstock-flexible reforming catalysts.

All catalysts were evaluated with the aqueous fraction of pyrolysis oils from pine or mixed hardwoods for a 24-hour period in a two-inch fluidized bed laboratory scale reactor equipped with in-line gas analyzers and process controllers. Inlet and outlet gas compositions at steady state conditions were used to calculate hydrogen, carbon dioxide, carbon monoxide, and methane yields. We used the CO_2/CO ratio (from the reformed gas mixture) as a general measure of selectivity for water-gas shift (WGS) and coke gasification, and we used the H_2/CH_4 ratio to measure reforming selectivity. Overall activity is measured by the H_2 yield, which is the ratio of actual yield to theoretical yield x 100. Theoretical yield is the amount of hydrogen produced if reforming and WGS reactions convert all carbon in the feedstock to CO_2. Performance data were then correlated with catalyst compositions to guide the next choice of catalyst "recipe" to test.

Results

Table 1 shows catalyst and performance data for four catalyst compositions compared to the commercial reforming catalyst C 11 NK. Our goal this year was to improve hydrogen yields (reforming activity) and to improve feeding of the pyrolysis liquids into the fluidized catalyst bed. The H_2/CH_4 ratio shows that we can meet or exceed commercial catalyst selectivity for hydrogen production though WGS performance, measured by CO_2/CO, is still less than that of the commercial material. Note as well that our catalysts use significantly smaller quantities of Ni, Mg, and K than does the commercial material. The implication of this result is that we can now consider using other reforming metals like platinum and palladium since required amounts are less.

Figure 1 compares performance data for several catalysts and lists the composition data. Catalysts 10-12 all contain about the same amount of potassium oxide (K_2O), and feeding upsets are clearly seen as spikes in the hydrogen content. We think the spikes are caused by solid chunks of feedstock, located at the injection nozzle, breaking up in the fluidized catalyst bed. The commercial catalyst and catalysts 14-15 do not exhibit feedstock spiking, and we think this is attributable to the increased amount of K_2O contained in these materials. Potassium promotes gasification, the formation of volatile carbon oxides from solid carbon, and seems to inhibit the formation of carbonized feedstock chunks at the injection nozzle. Improving feeding behavior of a complex, difficult to feed material is a significant accomplishment that will allow routine use of aqueous pyrolysis liquids in fluidized reactors.

Figure 2 compares performance of one of our best catalysts with that of the commercial material for pyrolysis liquid reforming. Our catalyst produces hydrogen in higher yield than the commercial catalyst though our WGS activity is lower. Our catalyst also produces more methane though the commercial catalyst likely reaches the same methane concentration for extended reaction time. The WGS reaction, which produces H_2 and CO from catalytic reaction of H_2O and CO_2, is also catalyzed by nickel.

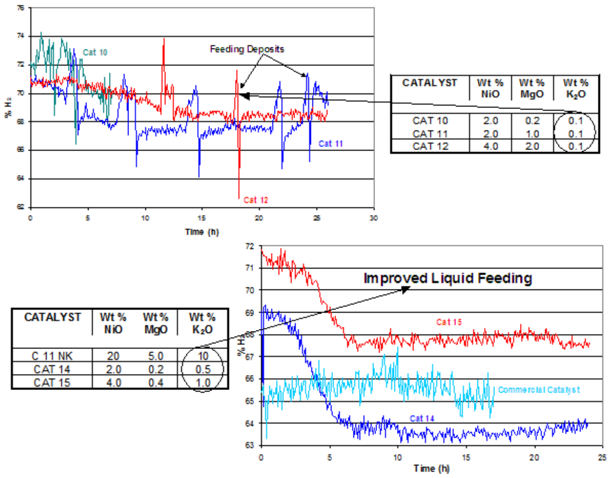

Figure 1. Catalyst Performance for H_2 Production from Reforming Aqueous Pyrolysis Liquids at 850°C in a 2-inch Fluidized Bed Reactor; Feeding Deposits Are Related to Catalyst K_2O Content

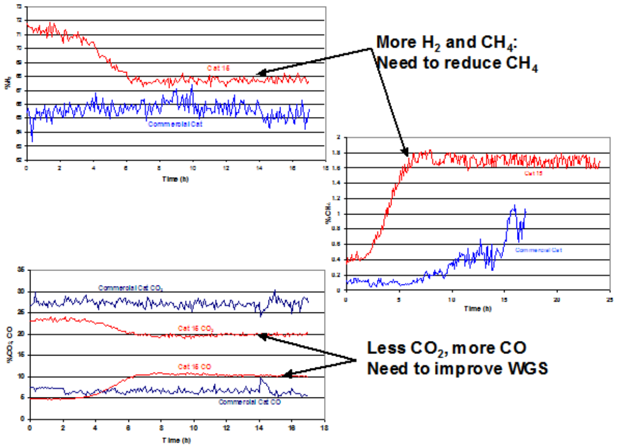

Figure 2. Catalyst Performance of our Catalyst #15 and the Commercial Catalyst C 11 NK for Pyrolysis Liquid Reforming at 850°C in a 2-inch Fluidized Bed Reactor

Table 1. Catalyst Selectivity Data for Reforming Aqueous Pyrolysis Oil Extracts Calculated During the Interval 20-23 Hours of On-Stream Reaction

CATALYST	Wt % NiO	Wt % MgO	Wt % K_2O	SUPPORT % Al_2O_3	CO_2/CO	H_2/CH_4	H_2 YIELD
C 11 NK	20	5.0	8.0	MIX	4.1	39.6	91
CAT 11	2.0	1.0	0.1	90	1.4	54.0	84
CAT 12	4.0	2.0	0.1	90	1.8	57.1	87
CAT 14	2.0	0.2	0.5	90	1.0	30.0	79
CAT 15	4.0	0.4	1.0	90	2.1	39.9	83

We continue to work on improving WGS activity through composition changes.

We evaluated the performance of catalyst 15 with two feedstocks: pyrolysis liquids and liquid trap grease (waste restaurant grease). The trap grease was washed with several volumes of hot water to remove soluble impurities like sodium chloride prior to use. The trap grease is less chemically complex than the pyrolysis liquids and should be easier to reform. Figure 3 verifies that assumption by showing a slightly better hydrogen yield from trap grease. Initial WGS activity was better for trap grease, but it began to decline after three hours of reaction. WGS activity for pyrolysis liquids never reached that of trap grease though the decline came later at six hours of reaction and reached a steady state. Methane production was the same for both feedstocks. Preliminary surface analysis of the fresh and used catalysts (all composition 15) showed that trap grease catalyst contained about 150 ppm of surface phosphorous, which had to come from the feedstock as neither the fresh catalyst nor the catalyst used for pyrolysis liquids contained any phosphorous. It is possible that phosphorous impacted WGS activity though it did not appear to affect hydrogen production. This result demonstrates the impact that feedstock will have on overall reaction performance.

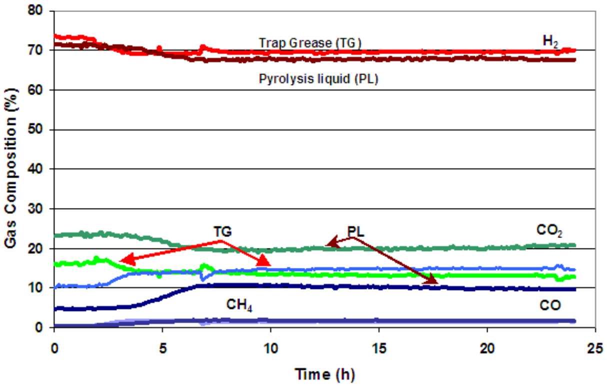

Figure 3. Catalyst #15 Performance Data for H_2 Production by Reforming Aqueous Pyrolysis Liquids and Waste Grease at 850°C in a 2-inch Fluidized Bed Reactor

Conclusions

- Developed novel, attrition-resistant fluidizable reforming catalysts with CoorsTek Specialty Ceramics.
- Evaluated performance of 16 catalysts for 24 hrs with pyrolysis oil-derived feedstocks in a small pilot scale reactor. This provides steady state comparison of catalyst performance with different feedstocks and varied catalyst compositions.
- Improved reforming activity (compared to commercial catalyst) for pyrolysis oils with reduced nickel content catalysts though WGS activity remains slightly less than that of the commercial catalyst.
- Improved pyrolysis oil feeding to the fluidized catalyst bed by increasing potassium oxide (K_2O) content.
- Developing sulfur- and phosphorous-tolerant catalyst compositions for reforming waste grease.

FY 2003 Publications/Presentations

1. K. Magrini, SC. Czernik, R. French, Y. Parent, E. Chornet, "Fluidizable Catalyst Development for Steam Reforming Biomass-Derived Feedstocks", in preparation.

Special Recognitions & Awards/Patents Issued

1. Record of Invention on fluidizable catalysts filed with DOE.

Hydrogen from Biomass for Urban Transportation

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Subcontractors:
Scientific Carbons Inc, Blakely, GA
Georgia Institute of Technology, Atlanta, GA
Enviro-Tech Enterprises Inc, Matthews, NC

Objectives

- Undertake the engineering research and pilot-scale process development studies to economically produce hydrogen from biomass such as peanut shells.
- Educate and train underrepresented minorities to enhance diversity in the nation's workforce in the energy area.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis and Reforming Technology

Approach

- Develop feedstock supply, process economics and deployment strategies.
- Design, construct, integrate and test pyrolysis-reformer pilot reaction unit.
- Undertake long term (1,000 hours) testing of the performance of the catalyst.
- Design, construct and test the hydrogen separation and storage unit.
- Develop an environmental and technical evaluation method based on analytical monitoring of process streams.
- Develop partnerships, collaborations and education and training programs.

Accomplishments

- Continued developing a model of network process steps to account for feedstock, location, process, and the uncertainties in these factors.
- Collected bio-oil and determined solubility parameters and physical property estimation methods of the components of the bio-oil product of peanut shell pyrolysis.

- Completed system modifications, integration and 100-hour pyrolysis-reformer run for long term catalyst testing.
- Completed analysis of the data for the 100-hour long term catalyst testing.
- Identified potential agricultural uses of the carbon product from the pyrolysis unit.
- Developed plans for 1,000-hour long term testing of the catalyst and process for Phase 3.
- Initiated partnership and collaboration with the University of Georgia, Athens, to move the pyrolysis-reformer pilot unit to their Bioconversion Center facilities in Athens, GA.
- Initiated evaluation of approaches to hydrogen separation and storage, including pressure swing adsorption (PSA) and Quantum's technology for hydrogen storage.
- Held Phase 3 project review meetings at Clark Atlanta University and the University of Georgia, Athens.

Future Directions

- Complete development of models and solutions.
- Perform solubility and physical property measurements and estimations.
- Complete extraction studies and the evaluation of phenolates as co-products for adhesives.
- Modify pyrolyzer, reformer, analysis and other process units for long term testing.
- Design, install and test preheater and PSA units.
- Install new sensors and process control system software in pilot unit.
- Move and integrate units at the University of Georgia Bioconversion Center.
- Perform shakedown run of the integrated system.
- Complete the proposed 1,000 hours of long term operation.
- Complete the engine tests for stationary applications.
- Complete all partnership arrangements.

Introduction

Biomass can be converted to hydrogen by two distinct strategies: 1) gasification followed by shift conversion and 2) pyrolysis of biomass to form a bio-oil that can be subsequently converted to hydrogen via catalytic steam reforming and shift conversion. This project uses the latter approach, which has the potential to be cost competitive with current commercial processes for hydrogen production [1]. The process has been demonstrated at the bench scale at the National Renewable Energy Laboratory (NREL) using model compounds and the carbohydrate-derived fraction of bio-oil [2,3]. The concept has several advantages over the traditional gasification technology. Bio-oil is easily transportable, so the second step (steam reforming) can be carried out at a different location, close to the existing infrastructure for hydrogen use or distribution. The second advantage is the potential for production and recovery of higher-value co-products from bio-oil that could significantly impact the economics of the entire process.

The project focuses on the use of agricultural residues such as peanut shells to produce hydrogen for urban transportation using the pyrolysis-reforming technology. Specifically, a pilot-scale reactor on site at Scientific Carbons Inc.-a small company in Blakely, Georgia, that produces activated carbon by pyrolysis of densified peanut shells-is being used to test the concept. The primary focus of Phases 1 and 2 of the project was to undertake the process development studies in the use of the large quantities of peanut shells produced in Georgia as feedstock for the proposed pyrolysis-steam reforming process. Phase 1 designed, constructed and tested the reformer unit. In Phase 2, Scientific

Carbons's pilot-scale pyrolyzer, which has a feed rate of 50 kg/hour, was integrated with the reformer and used to perform a demonstration of the process to convert the off-gas of the peanut-shell carbonization process to hydrogen. The integrated pilot process was successfully tested for 100 hours. Phase 3 will make further modifications and perform a 1,000-hour long term performance testing of the catalyst and pilot system. The process could be modified and expanded to run a variety of other feedstocks and to make a range of alternative products.

Approach

The approach used to conduct the study is based on six main tasks:

1. Feedstock supply, process economics, and deployment strategies (modeling, extraction and property estimation): Literature data and thermodynamic models were employed to evaluate a large number of organic solvents for the extraction of phenol from aqueous bio-oils. Several good solvents were identified, and extractions were carried out on bio-oil samples provided by NREL. Process models for feedstock supply and deployment strategies were developed.

2. Reactor modifications and shakedown: Modifications in the pyrolyzer and reformer were made, and the entire system, including the pyrolyzer, reformer, and analytical instruments, was integrated and tested. The pyrolyzer unit achieves its heat requirements through the use of a rich burning natural gas burner. A computer is used to track the temperature and pressure drops across the reactors.

3. Long term catalyst testing: The pilot unit was operated in Phase 2 for 100 hours for the long term catalyst testing.

4. Hydrogen separation, storage and utilization: The effort in hydrogen separation is focused on the use of pressure swing adsorption (PSA) for the separation of the hydrogen from carbon dioxide. After the baghouse and condenser, the reformer gas will be dried and compressed before being sent to the PSA system. The current plans are to use an accumulator to store the hydrogen before sending it into an engine for performance testing.

5. Environmental and technical evaluation: A hydrogen analyzer and a gas chromatograph were set up to continuously monitor on line the gas composition and the performance of the reformer bed.

6. Partnership building and outreach: The project team initiated discussions with the University of Georgia (UGA) to move the pilot unit from Blakely, Georgia, to the Bioconversion Center facilities at UGA. The idea was enthusiastically received by UGA. Several meetings were held among the project partners and UGA at Clark Atlanta University and UGA. The current plans are to move the unit to the Bioconversion Center facilities in the summer of 2003.

Results

Figure 1 shows photographs of the pilot unit, its components and the flares from the pyrolyzer and reformer units. The temperature and pressure profiles across the reformer and orifice plate are depicted in Figure 2. The figure indicates that the 100 hours operation was fairly stable without any plugging in the plate or flow lines. No hot spots developed within the fluidized bed reactor.

The composition profile of the effluent gas from the reformer is given in Figures 3 and 4. Figure 3 gives the profile over the entire run period, and

Figure 1. Pictures of the Pilot Plant Unit, Components and Flares

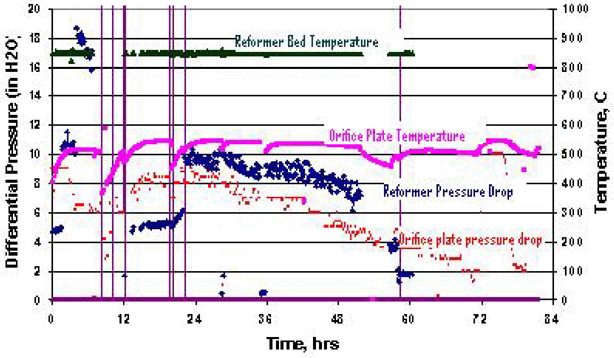

Figure 2. Temperature and Pressure Profiles of Reformer and Orifice Plate

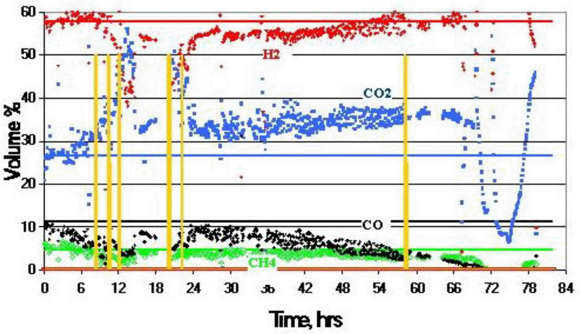

Figure 3. Composition Profile of the Reformer Gas over the Long-Term Run Period

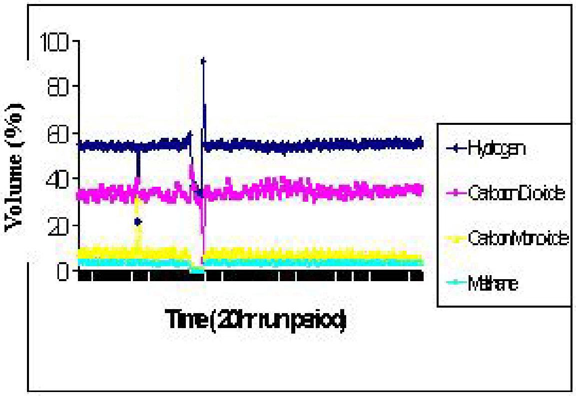

Figure 4. Gas Composition over a 20-hr Period During the Long-Term Catalyst Test

Figure 4 gives the profile of a 20-hour section. The average gas composition (volume % on dry and nitrogen-free basis) over the run period is summarized in Table 1. Also shown in Table 1 are the yields of char, water, bio-oils and gas obtained in the pyrolysis unit. The results show about 60% hydrogen, 25% carbon dioxide, 10% carbon monoxide and 5% methane in the reformer gas. The pyrolysis resulted in about 30% char, 30% water, 30% bio-oils and 5% gases.

Table 1: Yields and Gas Composition for the 100-hour Run

Pyrolyzer (Yields %)		Reformer Gas Product Composition, (% Dry N_2-free basis)	
Char	32	Hydrogen	57
Water	32	Carbon Dioxide	26
Bio-Oils	31	Carbon Monoxide	12
Gases	5	Methane	5

Conclusions

- Demonstrated successfully pyrolysis-reformer concept for 100 hours operation.
- Discovered agricultural uses and carbon sequestration strategy via novel carbon slow release sequestered fertilizer.
- Identified economical co-product options for bio-oils, e.g., adhesives.
- An engine will be run successfully with the product gas with significant reduction of NO_x.
- Further R&D: over 1,000 hours operation and higher hydrogen production rate could lead to economically competitive hydrogen and a viable integrated bioconversion process.

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2. Wang, D., S. Czernik, D. Montané, M. Mann, and E. Chornet, 1997, I&EC Research, 36, 1507-1518.

3. Wang, D., S. Czernik, and E. Chornet, 1998, "Production of Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oil", *Energy&Fuels*, 12, 19-24.

FY 2003 Publications

1. Annual Project Review Presentation made at the Hydrogen, Fuel Cells and Infrastructure Review Meeting at Berkeley, CA, May 18-22, 2003

2. Semiannual report on project submitted to the Department of Energy in April 2003

3. Evans, R; E Chornet, S. Czernik, C. Feik, R. French, S. Philips, J. Abedi, Y. Yeboah, D. Day, J. Howard, D. McGee and M. Realff (2002), *Renewable hydrogen production by catalytic steam reforming of peanut shells pyrolysis products,* American Chemical Society (ACS) Paper presented at the Annual ACS Meeting, Boston, MA

Reformer Model Development for Hydrogen Production

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Objectives

- Research and develop low cost, highly efficient hydrogen production from renewable sources
- Reduce the cost of distributed production of hydrogen from liquid fuels such as diesel and biomass oils

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance
- C. Feedstock and Water Issues
- D. Carbon Dioxide Emissions
- E. Control and Safety
- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis and Reforming Technology

Approach

- Develop a two-part database that is the benchmark for developing and testing the elements of the reformer model, called submodels
- Derive submodels from one part of the database to be used for the reformer simulation
- Use the complement of the database to test the derived submodels
- Validate the entire model using experimental data
- Utilize the validated model to optimize and scale up reformers

Accomplishments

- Created a two-part database portraying the evaporation and mixing of a large number of single-chemical-species-liquid drops in a turbulent flow
- Used one part of the database to develop computationally efficient models (called submodels) of the small scale interaction of the drops and flow
- Tested the submodels on the complement of the database to assess the interaction of the submodels with the large scales; found a model that is stable and accurate and reduces computational costs by a factor of 300

- Tested a model of multicomponent-liquid (i.e. mixture of many chemical species, as in diesel and biomass oils) drop existing in the literature and found that it has serious limitations
- Developed a computationally efficient improved model of the evaporation of a multicomponent-liquid drop when the fuel is a mixture of hundreds of chemical species

Future Directions

- Validate the single-chemical-species-liquid model with experimental data for an evaporating spray
- Create a database of the evaporation and turbulent mixing of multicomponent-liquid drops to enable the extraction of submodels for complex-mixture liquids
- Extract submodels for complex-mixture liquids evaporation and turbulent mixing
- Test the interaction of the submodels for complex-mixture liquids evaporation and turbulent mixing with the large flow scales
- Validate the multicomponent-liquid model with experimental data for an evaporating spray
- Create a two-part database of the reforming reactions in turbulent flows in the presence of evaporating multicomponent-liquid drops to enable the extraction of submodels for the chemistry/turbulent-flow interaction
- Use one part of the database to extract submodels of the interaction between chemistry and turbulence
- Test these submodels on the complement of the database to assess the interaction between the submodels and the database
- Validate the reformer model (i.e. turbulent, reactive flow laden with evaporating drops) by comparing with experimental data

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Introduction

Reforming is a chemical process wherein a hydrocarbon feedstock reacts with water to form H_2 and other gaseous chemical species. These reactions are induced in a container, called the reactor. In this reactor, the feedstock is introduced in the form of a spray of drops. Atomization of a liquid (i.e., the formation of drops) enlarges the surface area of the liquid, thereby promoting evaporation. The evaporated species reacts with steam in the presence of catalysts which enhance the reaction. The reactor operates at a temperature of 700°C to 850°C and pressures of 3 to 25 atmospheres, which favor the output of the reaction [1]. Concerns encountered with reforming for H_2 production are the efficiency of the process (e.g. optimization of the parameters for maximum yield), which must be high enough to render H_2 economically viable; the presence of coking reactions, which build carbon on the catalysts, thereby deactivating them; and reactor scale-up to industrial sizes.

The present study addresses all concerns of the process with the goal of understanding the details of the physical/chemical processes involved, so as to enable changes of the present operation that are based on physics/chemistry rather than circumstantial empirical correlations. This understanding will also be vital in proposing reactor scale-up.

Approach

The approach is based on numerical simulations that are experimentally validated. The idea is that just as the aircraft industry uses simulations to design aircraft (and no longer performs costly wind-tunnel testing), the hydrogen industry can eventually design reformer reactors using simulations as well. However, in many ways the situation in a reformer is considerably more challenging to model than for the aircraft; in the reformer one has a turbulent two-phase (liquid drops and gas) reacting flow with phase change (drop evaporation). Moreover, the feedstock is invariably a complex mixture of hydrocarbons that cannot be effectively treated as a single chemical species because different components of the mixture are responsible for different aspects of the process.

The methodology uses the contemporary direct numerical technique called DNS to achieve a transitional state, defined as a state displaying turbulent features. The DNS is performed in a domain much smaller than that of interest because currently and in the foreseeable future there is no large enough computer to simulate turbulent flows of practical interest; even with the small domain size, these DNS calculations are very computationally intensive, lasting thousands of computer hours. However, neither the small DNS domain size nor the costly computations are of concern because this simulation is supposed to be only a tool for model development. The models extracted from DNS are Subgrid Scale (SGS) models, and they represent the small-scale behavior of the flow. This small-scale behavior cannot be computationally resolved for flows of practical interest; therefore, SGS modeling is used. The simulations wherein the large scale of engineering interest are computed, and the small scales, all of which have a major impact on large scales, are modeled, is called Large Eddy Simulation (LES). These LESs are intended to be computationally much cheaper than the DNS, so as to be able to use them on a routine basis for engineering design. The goal is here to create DNS databases, develop SGS models, and ultimately perform LES. The predictive ability of LES crucially depends on the quality of the SGS models.

Results

We have created DNS databases of transitional states both for gaseous flows and for flows containing millions of drops. For drop-laden flows, we have used in the computation either single-component (SC) or multicomponent (MC) drops. To model MC drop evaporation, we used a model already existing in the literature, which we showed contained limitations when exercised for drops evaporating in mixtures of air and hydrocarbon vapor. The limitations motivated us to develop a more robust model of MC drop evaporation, which was validated in its predictive capability [2].

SGS models were developed using one part of the DNS database and then tested on the complement of the database. The results showed that currently used SGS models are inherently incorrect, in that they are unable to reproduce the DNS database [3]. Particular deficiencies are mostly seen in their inability to predict the correct drop distribution in the flow and the correct mixture fraction, which is essential for predicting reforming reactions. From the analysis of the database, we have developed accurate SGS models that are as computationally inexpensive as those incorrect ones that are currently used. This comparison is presented in Figures 1-6, which also include in the captions the computational times necessary to achieve these states starting from two segregated gaseous streams moving with respect to each other, where the bottom stream is laden with drops that may evaporate (the initial gas temperature is larger than the initial drop temperature). The initial mass loading with liquid drops is 50%. The results show that Figure 2 is only a caricature of Figure 1, rather than a replicate, and the same can be said of Figure 5 with respect to Figure 4. In contrast, Figure 3 replicates reasonably well Figure 1, and Figure 6 compares very favorably with Figure 4, and this at only a fraction of the computational time of the original simulation.

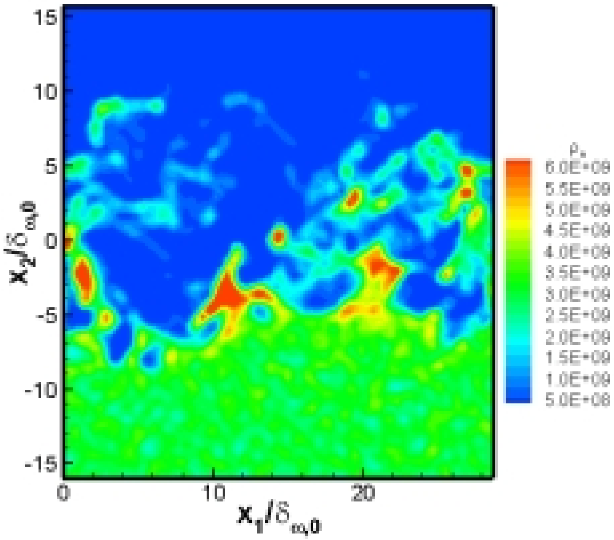

Figure 1. Drop number density (in m^{-3}) obtained from a DNS. The figure illustrates the results from a computation that lasted 2981 hours of computer time. In the figure, the small scales are removed, and only one out of 8 drops is shown, in order to have an appropriate comparison with LES.

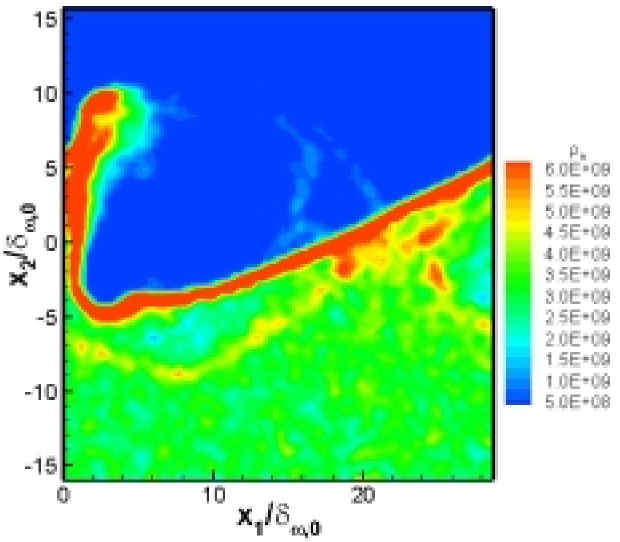

Figure 2. Drop number density (in m^{-3}) obtained from a LES using currently used SGS models. The simulation lasted 37 hours of computer time.

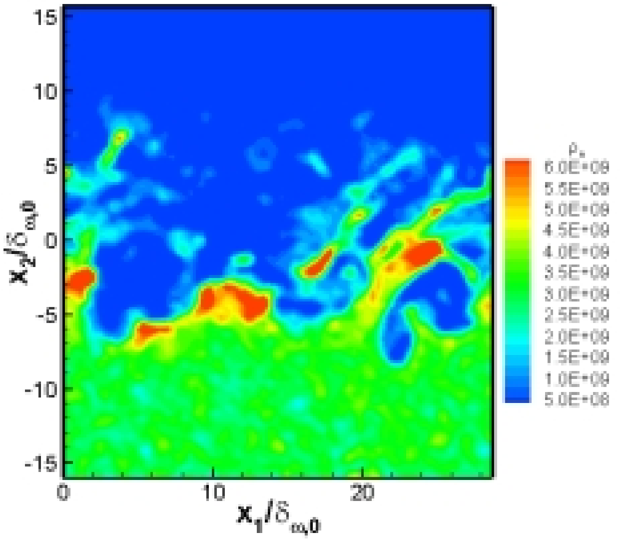

Figure 3. Drop number density (in m^{-3}) obtained from a LES using the best SGS model developed in this program. The simulation lasted 37 hours of computer time (same number of hours as in Figure 2).

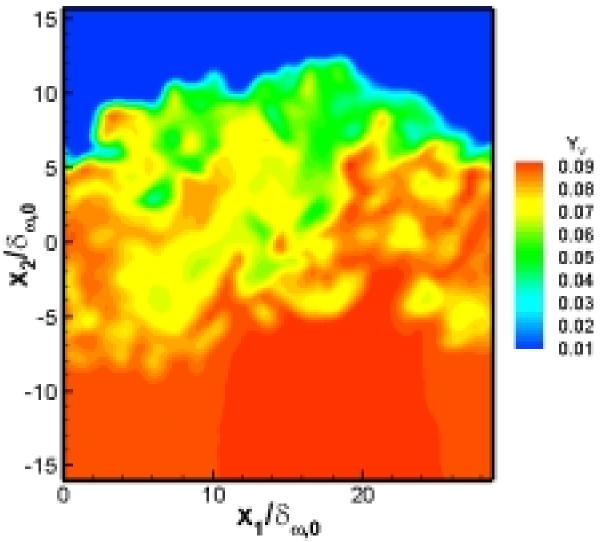

Figure 4. Vapor mass fraction obtained from the same DNS as in Figure 1. Just as in Figure 1, the small scales are removed, and only one out of 8 drops is shown, in order to have an appropriate comparison with LES.

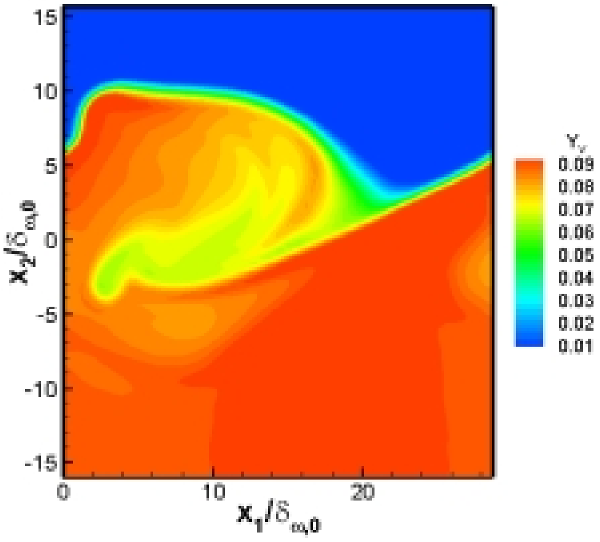

Figure 5. Vapor mass fraction obtained from a LES. The figure illustrates the results from the same computation as in Figure 2.

Conclusions

It is now apparent that current models are highly deficient in their portrayal of turbulent mixing and drop evaporation in a turbulent flow. The same can be stated about the modeling of evaporating drops of complex hydrocarbon mixtures. Models developed in this project have the ability to remedy these deficiencies and will thus be used in further computationally efficient simulations.

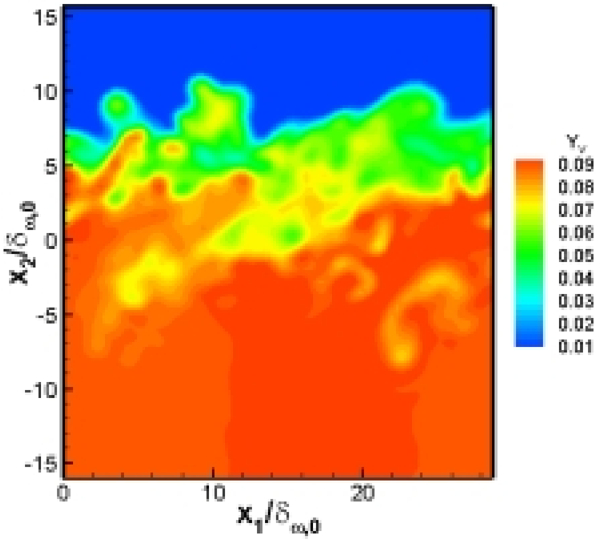

Figure 6. Vapor mass fraction obtained from a LES. The figure illustrates the results from the same computation as in Figure 3.

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8. "*A priori* study of models for large eddy simulations of drop-laden flows", (N. Okong'o and J. Bellan), presented at the Joint Meeting of the US Sections of the Combustion Institute, March 17-19, 2003; also ILASS 2003, Monterey, CA, May 18-21, 2003
9. "*A posteriori* study of models for large eddy simulations of drop-laden flows", (A. Leboissetier, N. Okong'o and J. Bellan), ILASS 2003, Monterey, CA, May 18-21, 2003

Special Recognitions & Awards/Patents Issued

1. NASA Certificate of Recognition for each one of the papers above
2. Invited publication (appeared July 2002) by the Chemical Propulsion Information Agency Bulletin, sponsored by the DoD Information Analysis Center

Maximizing Photosynthetic Efficiencies and Hydrogen Production in Microalgal Cultures

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Objectives

- Minimize, or truncate, the chlorophyll (Chl) antenna size in green algae to maximize photobiological solar conversion efficiency and hydrogen production.
- Demonstrate that a truncated Chl antenna size would minimize absorption and wasteful dissipation of sunlight by individual cells, resulting in better light utilization efficiency and greater photosynthetic productivity by the green alga culture.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Light Utilization Efficiency

Approach

- Employ DNA insertional mutagenesis, screening, biochemical and molecular genetic analyses for the isolation of "truncated Chl antenna size" strains in the green alga *Chlamydomonas reinhardtii.*
- Clone and characterize the gene(s) that affect the "Chl antenna size" in *Chlamydomonas reinhardtii.*
- Apply such genes to generate a "truncated Chl antenna size" in this green alga.

Accomplishments

- First-time cloning of *Tla1*, a 'Chl antenna size regulatory gene' (30-year breakthrough).
- DNA, mRNA and protein sequences were deposited in the GenBank (GenBank Accession No. AF534570 and AF534571).
- Manuscript on this gene and its application to this project was published in the peer-reviewed international journal 'Planta'.
- The DOE's Joint Genome Institute validated the sequence information on the Tla1 gene and credited our work regarding the function of this gene.
- Results from this work apply directly to green alga hydrogen production, biomass accumulation, and carbon sequestration efforts.

Future Directions

- Identify additional *Tla*-type genes.
- Functionally characterize these genes (how do they work?).
- Perform genetic crosses to combine different tla-type properties and phenotypes.
- Establish transformation protocols with Tla-type genes to downregulate the Chl antenna size in *Chlamydomonas reinhardtii.*

Introduction

The goal of the research is to generate green algal strains with enhanced photosynthetic productivity and hydrogen production under mass culture conditions. To achieve this goal, it is necessary to optimize the light absorption and utilization properties of the cells (Kok 1953; Myers 1957; Radmer and Kok 1977). A cost-effective way to achieve this goal is via a reduction in the number of chlorophyll (Chl) molecules that function in photosynthesis. Thus, efforts are under way to isolate microalga mutants with a **truncated chlorophyll antenna size**.

The rationale for this R&D is that a truncated light-harvesting Chl antenna size in green algae will prevent individual cells at the surface of the culture from over-absorbing sunlight and wastefully dissipating most of it (Figure 1). A truncated Chl antenna size will permit sunlight to penetrate deeper into the culture, thus enabling many more cells to contribute to useful photosynthesis and hydrogen production (Figure 2). It has been shown that a truncated Chl antenna size will enable up to ~3 times greater solar energy conversion efficiency and photosynthetic productivity than could be achieved with fully pigmented cells (Melis et al. 1999). The research seeks to develop *Chlamydomonas reinhardtii* strains having a permanently truncated Chl antenna size, and to isolate and characterize the genes and proteins that confer this property to the green algae. This information will find direct application in hydrogen production, biomass accumulation and carbon sequestration.

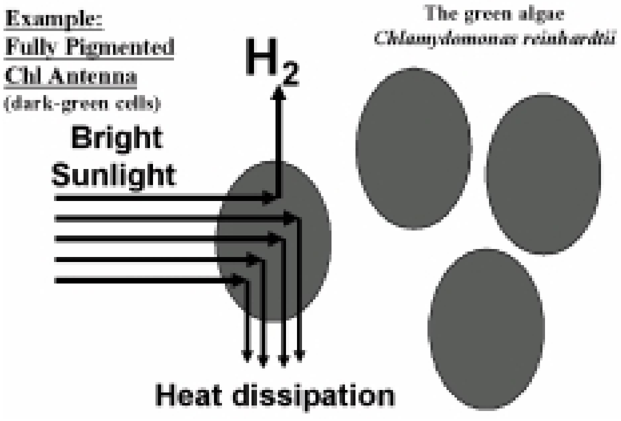

Figure 1. Schematic of the fate of absorbed sunlight in fully pigmented (dark green) algae. Individual cells at the surface of the culture over-absorb incoming sunlight (i.e., they absorb more than can be utilized by photosynthesis), and 'heat dissipate' most of it. Note that a high probability of absorption by the first layer of cells would cause shading, i.e., would prevent cells deeper in the culture from being exposed to sunlight.

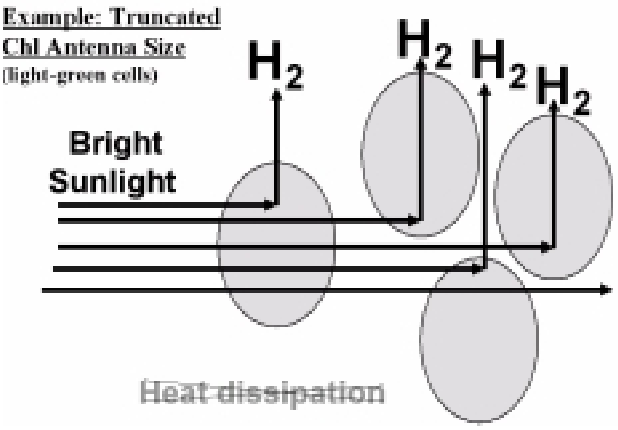

Figure 2. Schematic of sunlight penetration through cells with a truncated chlorophyll antenna size. Individual cells have a diminished probability of absorbing sunlight, thereby permitting deeper penetration of irradiance and hydrogen production by cells deeper in the culture.

Approach

The immediate objective of the research is to identify genes that control the Chl antenna size of photosynthesis, and further, to manipulate such genes so as to confer a truncated Chl antenna size in the model green alga *Chlamydomonas reinhardtii.* Identification of such genes in *Chlamydomonas* will permit a subsequent transfer of this property, i.e., "truncated Chl antenna size", to other microalgae of interest to the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program.

This objective is currently being approached through DNA insertional mutagenesis/screening and biochemical/molecular/genetic analyses of *Chlamydomonas reinhardtii* cells.

Results

In FY 2003, work described the molecular, genetic and functional properties of tla1, a *Chlamydomonas reinhardtii* DNA insertional transformant having a **t**runcated light-harvesting chlorophyll **a**ntenna size. The plasmid insertion into the nuclear DNA of this transformant interrupted *Tla1*, a newly identified gene, which is apparently responsible for the regulation of the Chl antenna size in green algae (Polle et al. 2003). To the best of our knowledge, this is a first-time cloning and genomic-proteomic characterization of a Chl antenna size regulatory gene in photosynthesis. A summary of the results obtained is given in bullet form, below:

- 6,500 DNA insertional transformants were generated and screened (Polle et al. 2003). Only one mutant with a 'truncated Chl antenna size' could be identified.
- Genetic crosses and mapping of the DNA around the insertion site confirmed that the exogenous plasmid interfered with a novel gene, termed by us as *Tla1*.
- DNA, mRNA and protein sequences of *Tla1* were elucidated and deposited in the GenBank (GenBank Accession No. AF534570 and AF534571).
- Absorbance-difference kinetic spectrophotometry (Dspec) revealed that interference with the *Tla1* gene expression resulted in a truncated photosystem II (PSII) Chl antenna size, down to 50%, and a photosystem I (PSI) Chl antenna size, down to 67% (Table 1).

Table 1. C. *reinhardtii* cellular chlorophyll content and photosystem chlorophyll antenna size in wild type and tla1 mutant as determined by Dspec analysis (n = 5, ±SD).

	wild type	***tlaI***	**% change**	**Long-term goal**
Chl/cell-mol x10^{-15}	2.4 ±0.5	0.9 ±0.06	38%	
Chl-PSII	222±26	114±36	51%	37
Chl-PSI	240±4	159±12	66%	95

- Sodium-dodecyl-sulfate polyacrylamide gel electrophoresis (SDS-PAGE) analysis revealed lack of specific light-harvesting complex proteins from the antenna of the *tla1* (Polle et al. 2003).
- A light-saturation curve of photosynthesis measurements revealed a greater light intensity for the saturation of photosynthesis in the *tla1* mutant than in the wild type, revealing a minimized ability to absorb light and less wasteful dissipation of excitation energy as heat.
- The *tla1* mutant showed enhanced light utilization efficiency and greater photosynthetic productivity under mass culture conditions (Figure 3).

Conclusions

- The partially truncated chlorophyll antenna size of the *tla1* mutant alleviates the over-absorption of incident sunlight by individual cells and the wasteful dissipation of over-absorbed irradiance.
- A truncated light-harvesting chlorophyll antenna size in the *tla1* mutant diminishes the severe cell shading that occurs in normally pigmented wild type and permits a more uniform illumination of the cells in a mass culture.
- A truncated light-harvesting chlorophyll antenna size in the tla1 mutant leads to better solar conversion efficiencies and greater photosynthetic productivity of the algae under bright sunlight conditions.

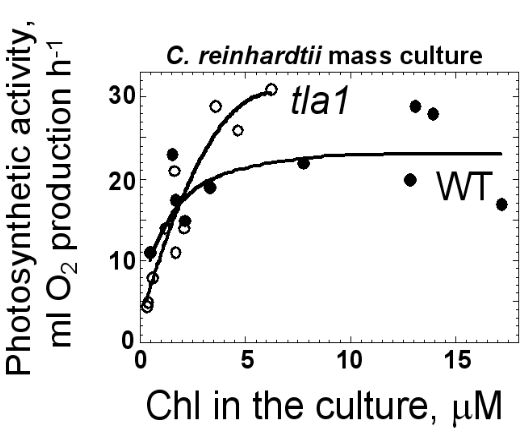

Figure 3. Photosynthetic productivity measurements were conducted with wild type and the *tla1* mutant of *Chlamydomonas reinhardtii* as a function of chlorophyll concentration in a mass culture (Polle et al. 2003). Measurements were conducted in the greenhouse at a solar incident intensity (photosynthetically active radiation) of about 1,500 µmol photons m^{-2} s^{-1}.

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Algal H_2-Production Systems: Creation of Designer Alga for Efficient and Robust Production of H_2

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Objectives

Develop advanced renewable photolytic hydrogen generation technologies through creation of a designer alga by genetic insertion of a proton channel into the photosynthetic thylakoid membrane. By 2015, demonstrate an engineering-scale biological system that produces hydrogen at a plant-gate cost of $10/kg projected to commercial scale.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- J. Rate of Hydrogen Production

Approach

Creation of designer alga for efficient and robust production of H_2 through genetic insertion of a proton channel into the thylakoid membrane.

Accomplishments

This is a new project. Because of the Congress and DOE budget situation under the "Continuing Resolution," this project did not receive any funding until April 2003. In April 2003, the DOE authorized $50K for J. Lee (1) to attend the Merit Review and (2) to make preparation for a full start of the project on October 1, 2003. So, the following are the results of our preliminary studies and the project preparation work.

- Identified the technical variables (problems) needed to optimize algal H_2 production.
- Designed a method—genetic insertion of a proton channel into the thylakoid membrane—to solve the identified technical problems.
- Demonstrated the proof of principle through preliminary studies.

Future Directions

Since this is a new project that is yet to be fully started, its proposed milestones represent the future directions. If funding support is fully provided, the project objective could be achieved within 4-5 years with the following milestones.

- Year 1—Design and construction of DNA sequence coding for polypeptide proton channel

- Year 2—Genetic transfer of hydrogenase promoter-linked polypeptide proton-channel DNA into algal strain DS521
- Year 3—Characterization and optimization of the polypeptide proton-channel gene expression
- Year 4—Demonstration of efficient and robust production of H_2 in designer alga (ready for next phase: scale-up and commercialization)

Introduction

This R&D project will create algal H_2-production systems by a new and novel approach that has recently been developed at ORNL. In this approach, a "designer alga" for efficient and robust H_2 production will be created by genetic insertion of hydrogenase promoter-programmed polypeptide-proton channels into photosynthetic thylakoid membranes.

Approach

We have recently developed a systematic approach to create a "super" photosynthetic organism—a "designer alga" that is specifically designed for production of molecular hydrogen through photosynthetic water splitting (ORNL Invention Disclosure ID 0981).[1] This designer alga will be able to overcome the four major physiological problems that currently challenge researchers and investors in the field of photosynthetic H_2 production: (1) restriction of photosynthetic H_2 production by accumulation of a proton gradient, (2) competitive inhibition of photosynthetic H_2 production by CO_2, (3) requirement of bicarbonate binding at photosystem II (PSII) for efficient photosynthetic activity, and (4) newly discovered O_2 sensitivity in algal H_2 production.

The key element of our proposed approach is creation of a designer alga for efficient and robust production of H_2 through genetic insertion of a programmable polypeptide proton channel into the thylakoid membrane. The genetic insertion of programmable thylakoid-membrane proton channels is proposed to be achieved by transformation of a host alga with a genetic vector that contains a polypeptide proton-channel gene linked with a hydrogenase promoter. The envisioned super alga that can be created by the proposed work should be able to perform autotrophic photosynthesis using ambient-air CO_2 as the carbon source and grow normally under aerobic conditions such as in an open pond. When the algal culture is grown and ready for H_2 production, the proton-channel gene will then be expressed simultaneously with the induction of the hydrogenase enzyme under anaerobic conditions because of the use of the hydrogenase promoter. The expression of the proton-channel gene should produce polypeptide proton channels in the thylakoid membrane, thus dissipating the proton gradient across the thylakoid membrane without adenosine triphosphate (ATP) formation.

As illustrated in Figure 1, our recent experimental studies with the proton uncoupler carbonyl cyanide m-chlorophenylhydrazone (FCCP) have already demonstrated that insertion of a proton-conductive channel in the thylakoid membrane could significantly enhance H_2 production by eliminating the problems of both the proton-gradient accumulation and the newly discovered alternative O_2 sensitivity that is dependent on the proton gradient.[2] Furthermore, the cessation of photophosphorylation (ATP formation) caused by action of the proton channels can, in turn, switch off the Calvin cycle activity (CO_2 fixation), which requires ATP and competes with the ferredoxin (Fd)/hydrogenase H_2-production pathway for the photosynthetically generated electrons. As a result, the competitive inhibition of H_2 production by CO_2 will now be eliminated, and photosynthetic H_2 production in the designer alga will be able to occur in the presence of CO_2. Since photosynthetic H_2 production in a successful designer alga no longer requires a CO_2 (HCO_3^-)-free environment, the requirement for HCO_3^- binding at photosystem II (PSII) for efficient photosynthetic activity will also no longer be a problem. The requirement can now be

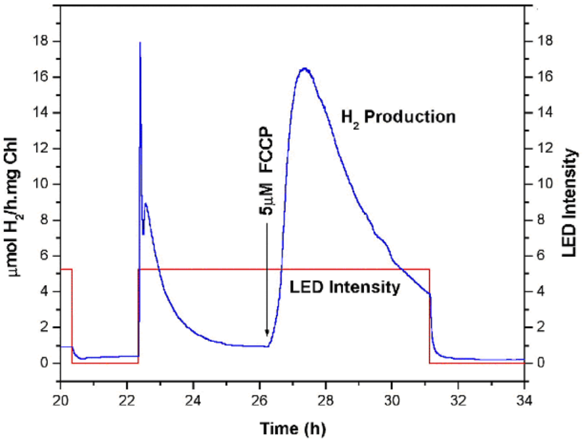

Figure 1. Stimulation of photosynthetic H_2 production in C. reinhardtii 137c following addition of the proton uncoupler FCCP in a background atmosphere of 1000-ppm O_2. Addition of 5 μM FCCP produced a dramatic increase in H_2 production, followed by a slow decay. The slow decay is due to a side effect of FCCP, known as ADRY,[3] in which FCCP gradually inhibits PSII activity. This ORNL experimental result indicates that use of a polypeptide proton channel that does not have the ADRY effect could enhance H_2 production by eliminating the problems of both the proton-gradient accumulation and the newly discovered alternative O_2 sensitivity.

satisfied by leaving some CO_2 in the medium. In conclusion, the use of polypeptide proton channels in the thylakoid membrane can provide four advantages for H_2 photoevolution: (1) the accumulation of a proton gradient that impedes the photosynthetic electron transport from water to Fd/hydrogenase will be prevented; (2) the competitive inhibition of photosynthetic H_2 production by CO_2 (Calvin cycle activity) will be eliminated; (3) the requirement for bicarbonate binding at PSII for efficient photosynthetic activity will be satisfied; and (4) the newly discovered O_2-sensitive pathway that competes with the H_2-production pathway for photosynthetically generated electrons could also be avoided by the dissipation of the proton gradient with the switchable proton channel.

Results

The proof-of-principle experimental results from our preliminary studies were also presented in a poster presentation at the May 2003 DOE Merit Review Meeting. We are now making preparations for a full start of this project on October 1, 2003. Because of the current funding limit, the technical lab work of this project will not be able to start until the arrival of the FY 2004 funding support.

Conclusions

Creation of designer alga by genetic insertion of a proton channel into the thylakoid membrane is one of the key R&D tasks that are required for the photobiological H_2-production system to work. We have already developed a systematic approach to achieve the proposed work. The proof of principle for this designer alga H_2-production R&D project has been demonstrated through preliminary studies.

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Algal Systems for Hydrogen Photoproduction

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Objectives

- Generate algal hydrogenase mutants with higher O_2 tolerance to function with aerobic H_2-production systems being developed in collaboration with Oak Ridge National Laboratory (ORNL) and University of California (UC) Berkeley.
- Optimize the rates of H_2 production using an anaerobic production system discovered by UC Berkeley and NREL.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- K. Continuity of Photoproduction

Approach

<u>Subtask 1 (Hydrogenase Function and Molecular Engineering):</u>

- Apply different mutagenesis techniques to generate O_2-tolerant algal hydrogenases.
- Select transformants that express recombinant hydrogenases and study their H_2-production capability in the presence of varying amounts of added O_2.
- Genetically combine the O_2-tolerance phenotype with truncated antenna (UC Berkeley) and proton channel (ORNL) mutants.

<u>Subtask 2 (Biochemical and Process Characterization):</u>

- Develop a sulfur-deprived system for continuous H_2 photoproduction.
- Optimize engineering and biochemical parameters.
- Demonstrate continuous H_2 production for a total of 800 hours by 2008.

Accomplishments

- By homology modeling, identified residues in algal hydrogenase HydA1 that form the 5.5-7.0 Å diameter gas channel and mapped them to three regions: close to the catalytic site, mid-way to the surface, and close to the surface (subtask 1).
- Mutagenized one of the residues located next to the catalytic site (valine 240) and demonstrated H_2 production with increased tolerance to O_2 (subtask 1).
- Developed a system for continuous H_2 production based on a two-reactor, sulfate-chemostat design (subtask 2).

- Demonstrated continuous H_2 production for a total of 480 hours using the new photobioreactor system (subtask 2).

Future Directions

- Perform molecular dynamics simulation to validate our results with the O_2-tolerant mutant and guide further site-directed mutagenesis work.
- Generate and test multiple algal hydrogenase mutants by a variety of mutagenesis techniques (e.g., site-directed, random *in vitro*, and gene shuffling).
- Accelerate the identification of O_2-tolerant clones by developing new high-throughput assays.
- Use spectroscopic and biochemical techniques to investigate and correct or circumvent the rate limitations inherent to the sulfur-deprived system.
- Examine alternative photobioreactor designs.
- Increase the duration of H_2 production (1,500 h at >2 ml/h in 2010) using a mutant that incorporates the best properties of the NREL, UC Berkeley and ORNL individual mutants.

Introduction

The green alga, *Chlamydomonas reinhardtii*, has the biochemical machinery necessary to efficiently photoproduce H_2 from water. However, under normal conditions where O_2 is a by-product of photosynthesis, sustained algal H_2 photoproduction cannot be maintained for more than a few minutes (Ghirardi et al., 1997). Oxygen is a powerful inhibitor of algal [Fe]-hydrogenase (the catalyst that releases H_2 gas) function, and H_2 photoproduction stops abruptly if O_2 is present. Oxygen inactivation is thought to occur by the direct binding of O_2 to one of the iron species (with an unoccupied coordination site) located at the catalytic center (Adams, 1990). Our current project addresses two different strategies for surmounting the O_2-sensitivity problem. These include (a) molecular engineering of the hydrogenase to remove the O_2 sensitivity (subtask 1) and (b) development of physiological means to separate O_2 and H_2 production (subtask 2).

Our early work for the DOE Hydrogen Program involved the cloning and sequencing of two algal hydrogenase genes (Forestier et al., 2001, 2003), and this provided us with the tools and background knowledge to make rapid progress in the molecular engineering area. The work on subtask 1 has focused on a knowledge-based approach and is addressing regions in one of the algal hydrogenases (HydA1) that could be involved in access of O_2 to the catalytic site. This annual report describes the method that we used to (a) identify this region and (b) design, generate and test the first site-directed mutant targeted to improved O_2 tolerance.

In the absence of an O_2-tolerant hydrogenase, we demonstrated (with UC Berkeley) that it is possible to physiologically manipulate *C. reinhardtii* to generate anaerobic conditions, induce the hydrogenase gene and photoproduce H_2 sustainably for about 3-4 days (Melis et al., 2000; Ghirardi et al., 2000). This method was based on the partial inactivation of photosynthetic O_2 evolution resulting from depriving the cultures of sulfate. Although technically successful, the sulfur-deprivation process is currently too expensive. In order to address the cost issue, we describe here the development of a continuous system that decreases the cost of H_2 production.

Approach

Subtask 1 (Hydrogenase Function and Molecular Engineering): There are a number of mutagenesis approaches to molecular-engineer enzymes for altered catalytic activity. Some of these approaches involve random changes in the enzyme's gene sequence (either by *in vitro* error-prone polymerase chain reaction or gene shuffling), followed by high-throughput screening for the desired mutants. However, it is also possible to alter an enzyme's activity by applying a knowledge-based approach. In attempting to confer O_2 tolerance to algal hydrogenases, we chose the latter. Our approach is based on the hypothesis that inactivation of a hydrogenase depends on the access of O_2 to the enzyme's catalytic site. We assumed that this access occurred through a gas channel, a hydrophobic pathway identified in other hydrogenases by X-ray structure analyses (Montet et al., 1997; Nicolet et al., 1998) and identified by our group in algal [Fe]-hydrogenases (King et al., patent pending). According to a hypothesis presented for NiFe hydrogenases (Bernhard et al., 2001; Volbeda et al., 2002), a narrower channel might discriminate between the reaction product, H_2, and the inhibitor, O_2. We designed mutants in which residues with bulkier side chains are substituted for some of the small residues that line the gas channel. We report here the generation of the first site-directed hydrogenase mutant specifically designed to demonstrate increased tolerance to O_2 exposure. Future work will involve the generation of mutants with multiple amino acid substitutions in the gas channel, and it may also address the complementary use of random mutagenesis to target protein sequences that we cannot rationally relate to O_2 tolerance.

Subtask 2 (Biochemical and Process Characterization): The use of sulfur deprivation to metabolically shift the algal cultures from an O_2- to a H_2-production process was reported by UC Berkeley and NREL in 2000 (Melis et al., 2000). As originally conceived, the method involved cycles of O_2 production (in sulfur-replete medium) followed by cycles of H_2 production (in sulfur-deprived medium) [Ghirardi et al., 2000]. This temporal-separation batch process was studied by NREL and found to be too costly (Amos, 2000). Among the variables responsible for the high cost were the use of centrifugation to cycle the cultures from one phase to the next and the limited time during which the cultures photoproduce H_2. We investigated two approaches to remove the centrifugation step: (a) the use of judicious dilution of the sulfur-replete cultures to deprive them of sulfate (Laurinavichene et al., 2002) and (b) the design of a new two-photobioreactor system, based on cell growth under a sulfate chemostat in one reactor, followed by H_2-production under sulfur-deprived conditions in a second reactor. The cultures in the second bioreactor should produce H_2 continuously in the light but at limited rates.

Results

Subtask 1 (Hydrogenase Function and Molecular Engineering): The putative amino acid sequences of the two cloned algal hydrogenases, HydA1 and HydA2, were derived from their gene sequences. The amino acid sequences were then used to generate homology models of the respective protein structures, using the Swiss-Model program and further refinements by GROMOS (Forestier et al., 2003; King et al., submitted). Modeling was based on the known X-ray structure of another [Fe]-hydrogenase, CpI, found in the anaerobic bacterium *Clostridium pasteurianum* (Peters et al., 1998). Figure 1 shows the resulting structures of CpI, HydA1, and HydA2. The core regions of HydA1 and HydA2 exhibit a very high degree of structural similarity between each other and CpI, and the locations of the H-cluster catalytic sites overlap closely with those from CpI. The catalytic site consists of a 2Fe2S center linked by a cysteine residue to a 4Fe4S center, which is bound to the protein structure by three other cysteine residues (Peters et al., 1998; Nicolet et al., 1998). Moreover, the 2Fe2S center was shown to be ligated by unusual molecules such as CO, CN, and di(thiomethyl)amine (Nicolet et al., 2002). The main differences between the bacterial and the algal hydrogenases are (a) the presence of extra sequences in the N-terminal portion of CpI that bind additional FeS centers (Happe et al., 2002; Forestier et al., 2003), which serve as an electron relay from a soluble donor bound to the surface of the protein to the catalytic site, and (b) the presence of loops L1 and L2 in HydA1 and HydA2 that correspond to intervening gene sequences present only in the algal hydrogenases. Speculation suggested that the loops could be involved in the docking of ferredoxin (Winkler et al., 2002). We propose that their function could be related to regulating catalysis by transferring regulatory signals from the surrounding medium to the catalytic site.

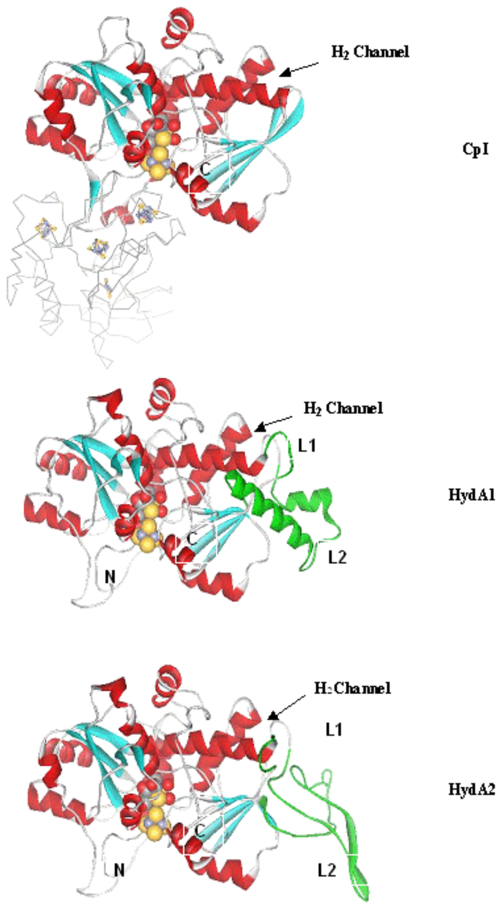

Figure 1. Model of the X-ray Structure of the *Clostridium pasteurianum* CpI and Homology Models of the Two Algal Hydrogenases, HydA1 and HydA2

The catalytic H-clusters in the three proteins are located in close proximity to a solvent-accessible area, termed the gas channel. Small, hydrophobic residues were identified as components of the channel wall. Homology modeling done at NREL suggested that mutating amino acid residues along the gas channel could narrow the channel in the region next to the catalytic site and in turn lower the access of O_2 (King et al., submitted). One of those residues, valine 240, was replaced by molecular engineering techniques with a bulkier counterpart, tryptophan. Table 1 shows that the H_2-production activity of the mutant (measured by two different assay methods, see legend) is more resistant to O_2 inactivation than the wild-type strain. This result confirms our initial hypothesis and justifies future molecular engineering techniques to further improve O_2 tolerance by modifying gas-channel residues.

Table 1. Effect of O_2 exposure on the rates of H_2 photoproduction by the WT and V240W strains of *Chlamydomonas reinhardtii*. Assay I measures the initial rate of light-induced H_2 production measured with a Clark electrode; assay II measures the rate of H_2 production induced by the addition of dithionite-reduced methyl viologen and is measured over a period of 10-15 min. The samples were exposed to the indicated concentrations of O_2 for 2 min preceding each assay.

O_2 concen-tration, %	% Uninhibited H_2-production rate			
	Assay I (light)		Assay II (MV_{red})	
	WT	V240W	WT	V240W
0	100	100	100	100
0.1	42	-	-	-
1	12	100	19	88
1.5		48	-	-
2	0	12	2.4	45
3	0	5		-
4	-	-	1.5	24

Subtask 2 (Biochemical and Process Characterization): Sulfur deprivation of algal cultures selectively inactivates photosynthetic O_2 evolution and creates an anaerobic environment. Anaerobic conditions are sufficient to induce the hydrogenase gene, initiate synthesis of the hydrogenase protein, and promote subsequent H_2 photoproduction. The latter cannot be sustained for more than 3-4 days, however, due to pleiotropic effects of sulfate deprivation on the algae at later times. We conducted a detailed study of the relationship among the different metabolic pathways under sulfur-deprived conditions and concluded that the initial rate of H_2 photoproduction is limited by the rate of reductant utilization. This results in an over-reduced plastoquinone pool (Antal et al., 2001 and in preparation). The limitation is not due to low hydrogenase activity (Ghirardi et al, submitted), but is possibly related to regulatory mechanisms associated with the non-dissipation of a proton

gradient, as suggested for anaerobic, sulfur-replete cultures (Lee and Greenbaum, 2002).

Since the initial rate of H_2 photoproduction cannot be increased easily by biochemical or engineering manipulations (Kosourov et al., 2003), we attempted to develop a system in which the cultures produce H_2 at a similar fixed rate but for much longer periods of time. Figure 2 shows the concept. In the first photobioreactor, the algal cells are grown in a chemostat mode (by continuous dilution with medium containing sufficient amounts of sulfate). The cultures in the second photobioreactor are initially sulfur-deprived and allowed to start photoproducing H_2. At that point, the second photobioreactor is connected to the first, and the H_2-producing cultures are continuously replaced by photosynthetically-competent cells from the first photobioreactor. The two main objectives of the above design are to continuously (a) replace sulfur-deprived cells with fresh cultures to avoid the long-term inhibitory effects of sulfur deprivation on H_2 photoproduction and (b) remove accumulated fermentation products from the H_2-photoproduction reactor.

The performance of the two-photobioreactor system was tested over a period of three weeks to meet our milestone for FY 2003. Figure 3 demonstrates that the system works as expected and is able to photoproduce H_2 at a rate that is constant during the first two weeks but decreases during the third week. Preliminary economic analyses indicate that the expected cost of the system is almost four times lower than that of the corresponding batch system (from $760 to $200/kg [Amos, unpublished]). Further improvements both to the system and to the organism by NREL, UC Berkeley and ORNL will be crucial to continuing to lower the cost of H_2 photoproduction.

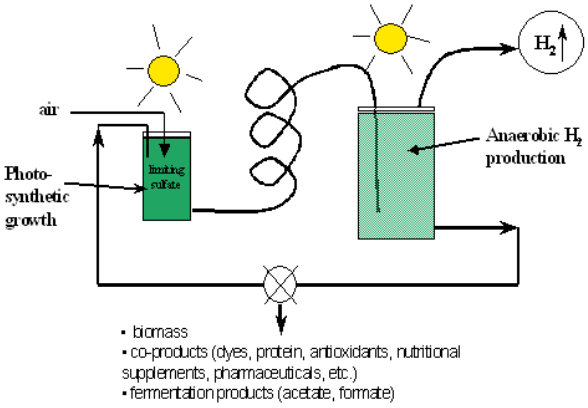

Figure 2. Schematic Diagram of the Two-Photobioreactor, Continuous Algal H_2 Photoproduction System

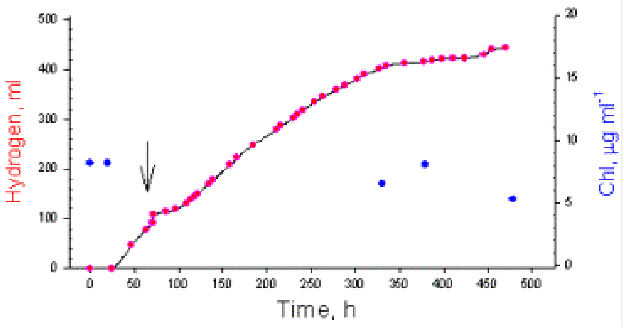

Figure 3. Accumulation of H_2 by illuminated, sulfur-deprived algal cultures in the continuous mode. The arrow indicates the time point at which the second photobioreactor was connected to the first. Notice that the cell density, indicated by the Chl concentration, decreased towards the end of the experiment.

Conclusions

- The generation of the first successful algal hydrogenase mutant (V240W) validates our knowledge-based mutagenesis approach to improve the O_2 tolerance of the enzyme and justifies our hypothesis that direct O_2 access to the catalytic site both inactivates enzyme activity and limits H_2 photoproduction.
- Algal H_2 photoproduction can be extended for much longer periods of time using the sulfur-deprivation method to physically (rather than temporally) separate O_2 and H_2 production activities; this approach currently lowers the cost of the process by about a factor of four when compared to the batch system.

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1. Laurinavichene, T., Tolstygina, I.V., Galiulina, R.R., Ghirardi, M.L., Seibert, M. and Tsygankov, A. (2002) Dilution methods to deprive *Chlamydomonas reinhardtii* cultures of sulfur for subsequent hydrogen photoproduction. Int. J. Hydrogen Energy 27, 1245-1249.
2. Flynn, T., Ghirardi, M.L. and Seibert, M. (2002) Accumulation of O_2-tolerant phenotypes in H_2-producing strains of *Chlamydomonas reinhardtii* by sequential applications of chemical mutagenesis and selection. Int. J. Hydrogen Energy 27, 1421-1430.

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7. Hahn, J.J., Ghirardi, M.L. and Jacoby, W.A. The effect of process variables on photosynthetic algal hydrogen production. Submitted.

8. King, P., Forestier, M., Zhang, L., Ghirardi, M.L. and Seibert, M. Molecular engineering of a *Chlamydomonas reinhardtii* hydrogenase for increased O_2 tolerance. Proceedings of the Boden Conference in Artificial Photosynthesis, Sydney, Australia. Submitted.

9. Ghirardi, M.L., Kosourov, S. and Seibert, M. Artificial photosynthetic systems for algal hydrogen production. Proceedings of the Boden Conference in Artificial Photosynthesis, Sydney, Australia. Submitted.

FY 2003 Presentations/Posters

1. Invited presentation at Oak Ridge National Laboratory, October 2002. "Photosystem II, the Engine for Algal Hydrogen Production", M. Seibert.

2. Invited Mechanical Engineering Departmental Seminar, University of Colorado, Boulder, November 2002. "Algal H_2 Production—Physiology, Molecular Genetics and Process Development", P. King, S. Kosourov, M.L. Ghirardi and M. Seibert (MS presented).

3. Invited presentation at the Boden Conference on Artificial Photosynthesis, Sydney, Australia, January 2003. "Modifying Photosynthesis for Continuous Algal Hydrogen Photoproduction", M.L. Ghirardi, S. Kosourov and M. Seibert (MLG presented).

4. Invited presentation at the Boden Conference on Artificial Photosynthesis, Sydney, Australia, January 2003. "Cloning and Molecular Engineering of *Chlamydomonas* [Fe]-hydrogenases for Oxygen Tolerance", M. Seibert, P. King, L. Zhang, M. Forestier, S. Schwartz, T. Happe and M.L. Ghirardi (MS presented).

5. Invited seminar in the Research School of Biological Sciences, Australian National University, January 17, 2003. "Algal H_2 Production—Physiology, Process Development, and Molecular Genetics", P. King, S. Kosourov, M.L. Ghirardi and M. Seibert (MS presented).

6. Presentation at the University of Colorado's Super Microbiology Group, April 2003. "Cloning of a Second Putative [Fe]-Hydrogenase from the Green Alga *Chlamydomonas reinhardti*i", M. Forestier, P. King, L. Zhang, M. Posewitz, S. Plummer, S. Smolinski, M. Ghirardi and M. Seibert (MLG presented).

7. Invited presentation at the U.S. Air Force AFOSR workshop on Biohydrogen and Artificial Photosynthesis, Denver, CO, April 2003. "Algal Hydrogen Photoproduction", M.L. Ghirardi.

8. Poster at the Symposium on the Biotechnology for Fuels and Chemicals, Breckenridge, CO, May 2003. "Algal Hydrogen Production – Physiology and Process Development", M. Seibert, L. Zhang, V. Makarova and M.L. Ghirardi (MS presented).

9. Invited presentation at the Bio2003 conference in Washington D.C., June 2003. "Algal Hydrogen Photoproduction", M.L. Ghirardi, A. Fedorov, P. King, S. Kosourov, M. Posewitz, S. Smolinski, L. Zhang and M. Seibert (MLG presented).

Patents

1. Kosourov, S., Ghirardi, M. and Seibert, M. "Multi-stage microbial system for continuous hydrogen production". Patent application filed October 2002.

2. King, P., Ghirardi, M.L. and Seibert, M. "Oxygen-tolerant hydrogenases and methods for designing and making same". Provisional patent application filed April 18, 2003.

FY 2003 Videos

1. City in a Pyramid, Discovery Channel, April 2003

2. Video for KLTV Channel 8, Lakewood, CO, March 2003

Photoelectrochemical Systems for H_2 Production

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Objectives

- Identify and characterize new semiconductor materials that are capable of splitting water using sunlight as the only energy input.
- Improve the durability (stability) of semiconductor materials in aqueous solutions.
- Develop multijunction high-efficiency water-splitting systems to meet the 2015 target of 14% solar-to-hydrogen efficiency.
- Apply basic science understanding for control of the energetics of the semiconductor in solution (band edge engineering).
- Develop techniques for the preparation of transparent catalytic coatings and their application to semiconductor surfaces.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Material Durability
- O. Photoelectrochemical Efficiency

Approach

- Discover, research and develop semiconductor materials for improved photoelectrochemical (PEC) systems.
- Optimize and control energetics, developing a fundamental understanding of semiconductor surface interactions with aqueous solutions.
- Identify materials for protective coatings and materials for catalysis.

Accomplishments

- First PEC study of $In_xGa_{1-x}N$ ($0<x<0.14$) material.
- First PEC study of GaAsPN material.

- First synthesis of CuInGaSSe material with band gaps in the range 1.6-2.0 eV.
- First study of the surface modification of $GaInP_2$ with water soluble metallo-porphyrins.

Future Directions

- Evaluate nitride materials as longer lifetime water splitting systems.
- Develop multijunction systems for high efficiency.
- Explore thin film materials as low-cost water splitting systems.
- Develop protective coatings that reduce corrosion and provide catalysis.
- Explore approaches for control of surface energetics.

Introduction

The direct PEC splitting of water is a one-step process for producing H_2 using solar irradiation; water is split directly upon illumination. This type of direct conversion system combines a photovoltaic material and an electrolyzer into a single monolithic device. For this one-step process to be viable, two basic criteria must be met: the light harvesting system must have the correct energetics to effect the decomposition of water, and the system also must be stable in an aqueous environment. Direct conversion photoelectrochemical systems not only eliminate most of the costs of an electrolyzer, but they also have the possibility of increasing the overall efficiency of the process (as compared to photovoltaie (PV)/electrolysis), leading to a further reduction in the cost of delivered hydrogen.

Approach

PEC hydrogen production is in an early stage of development, and it depends on a breakthrough in materials development. The primary effort in this project is to synthesize a semiconducting material or a semiconductor structure with the necessary properties. For the direct PEC decomposition of water to occur, three key energetic conditions and the criteria of stability for the semiconductor must be met. For the energetic conditions, the semiconductor's band gap must be sufficiently large to split water and yet not too large as to prevent efficient absorption of the solar spectrum (ideally 1.8-2.2 eV), the band edges of the semiconductor must overlap the hydrogen and oxygen redox potentials, and the charge transfer across the semiconductor/liquid interface must be fast enough to prevent band edge migration. In addition, the semiconductor's surface must be stable against corrosion both in the dark and under illumination. Our study of PEC direct-conversion systems involves two areas of research: semiconducting materials and surface treatments. Semiconducting materials can be divided into two types based on their solid state structure: single photon absorbers and multiphoton devices. Surface treatments include coatings to address energetic issues, corrosion problems, and catalysts for the water splitting reactions.

Materials research in this area is progressing on two fronts: 1) working on the high efficiency materials in order to apply basic scientific understanding to lower efficiency, low-cost materials, and 2) working on the durability of low-cost materials in order to apply basic scientific understanding to higher efficiency, lower durability materials. Currently, the highest efficiency systems have the shortest lifetimes, and the lower efficiency systems have the longest lifetimes. The optimal system will likely be a compromise between efficiency and lifetime.

Results

As part of our search for semiconductor materials with inherently greater stability, we have been studying the group III-nitrides for use as PEC materials. Earlier work in our group has shown that GaN can split water and is stable under certain operating conditions. While it is known that GaN is chemically very stable, its band gap is too large (~3.4 eV) to be an efficient PEC device. We have also shown that adding indium to the material can lower the band gap and that it appears that the composition of $In_xGa_{1-x}N$ can be adjusted to produce a band gap suitable for solar water-splitting applications. Our best $In_xGa_{1-x}N$ material currently synthesized has a band gap of 2.71 eV (Figure 1). To be a useful material for water splitting, this band gap must be lowered further by increasing the amount of indium. Work is continuing in this area.

Another material that shows excellent stability in aqueous solution and has a bandgap in the appropriate range for good solar absorption (2.25 eV) is gallium phosphide (GaP). Unfortunately, this is an indirect band gap, leading to low solar absorption efficiency and low conversion efficiency. Recent work has shown that adding a small amount of nitrogen to the GaP lowers the band gap and creates a direct transition. The combination of a smaller band gap and a direct transition would produce a much more efficient system. The $GaP_xN_{(1-x)}$ material is being synthesized at NREL as part of their work for the DOE Solar Energy Program, which makes it particularly interesting for an initial study. Figure 2 shows our data on measurement of the band gap. As expected, there is a direct transition and a nearly ideal band gap of 1.9 eV. Further characterizations are necessary to determine if this material can function as a water-splitting device.

Thin-film copper indium gallium diselenide (CIGS) devices are well known for their high conversion efficiency when prepared as polycrystalline thin films. Electrodeposition is a potentially scalable technique for large area thin film fabrication at reduced costs. In fact, CIGS films have been successfully prepared from electrodeposited precursors to yield solar energy conversion devices with an efficiency of 15.4%. Sulfur incorporation has also been used in CIGS solar energy materials to increase device performance and to provide a graded band gap structure. Our effort in this area was to incorporate sulfur throughout the entire film, to obtain a material exhibiting a higher band gap that is suitable for water splitting. The combination of lower system manufacturing cost (from electrodeposition) and a high efficiency material represents an important area of research for hydrogen production systems. In addition, indium in the film may provide some protection against corrosion. In aqueous solution, indium can form a conducting oxide layer that stabilizes the interface and may protect the underlying material. In this initial effort, $Cu(In,Ga)(Se,S)_2$ thin semiconducting films were made from electrodeposited $Cu(In,Ga)Se_2$ precursors, followed by physical vapor deposition of In_2S_3, Ga, and Se. The band gaps of these materials were found to be between 1.6 and 2.0 eV (Figure 3), which spans the optimal band gap necessary for application for the top junction in PV multijunction devices and unassisted water photolysis. Note also that this research demonstrates the ability to synthesize materials with a full range of band gaps from a single material set.

In the area of bandedge engineering, gallium indium phosphide ($GaInP_2$) surfaces were modified with metallo-porphyrin compounds in order to shift

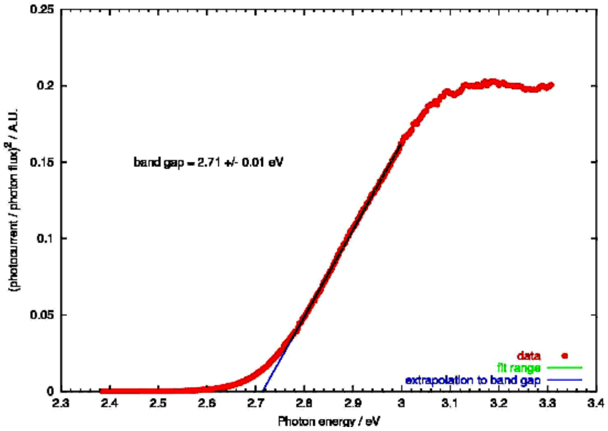

Figure 1. Band Gap Analysis of the Photocurrent Spectrum for Sample $In_{0.14}Ga_{0.86}N$

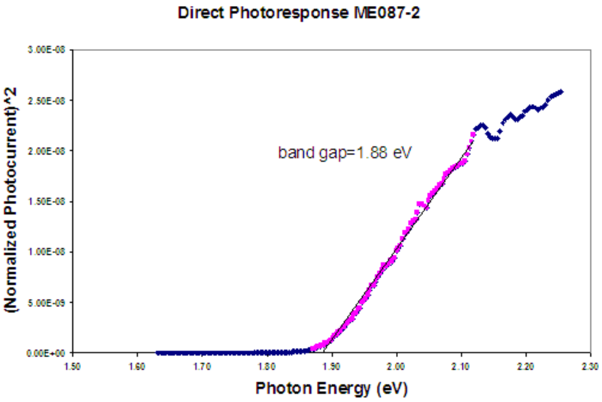

Figure 2. Band Gap Analysis of GaPN Material

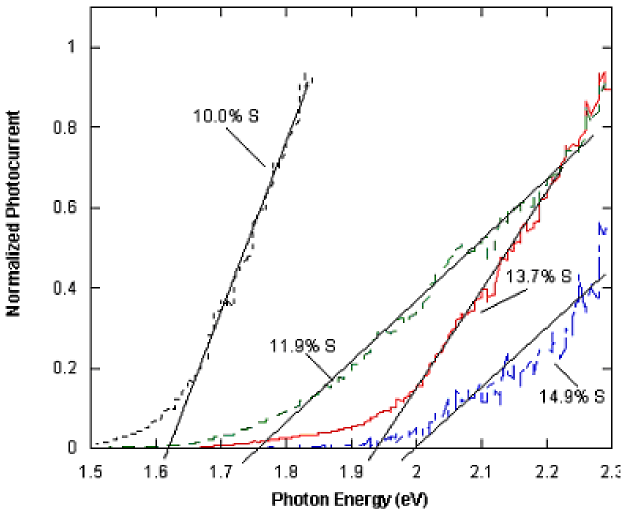

Figure 3. Photoresponse Measurements of Thin Films With Varying Composition (Atomic percent sulfur in each film is shown)

the semiconductor's band edges. Compounds used included Nickel(II)-Tetra(N-Methyl-2-pyridyl) porphyrin chloride [NiTMPyP(2)], Fe(III)TMPyP(2), and VO(IV)TMPyP(4). Sample treatments using these water-soluble compounds were applied by immersion of the semiconductor in a solution of the porphyrin for varying lengths of time. The position and movement of $GaInP_2$ band edges were monitored by capacitance measurements, and shifts of up to 1 volt were observed after some surface treatments. While a shift of 1 volt should be sufficient to allow $GaInP_2$ to split water, no water splitting was observed. Work is continuing to determine what is preventing the system from operating as we expected.

Conclusions

- Nitride materials based on GaInN are possible high-efficiency, water-splitting materials, showing good stability and the correct energetics.
- Initial studies on nitride materials based on GaPN showed that achieving the necessary band gap was possible.
- Surface studies of water-soluble, porphyrin-modified $GaInP_2$ showed that it is possible to affect the energetic position of the semiconductor band edges.
- Work on the thin-film CuInGaSSe system showed that it is possible to synthesize material with band gaps in the range 1.6-2.0 eV.

FY 2003 Presentations

- Presentation for the Chemistry Department of the Colorado School of Mines entitled "Photoelectrochemical Direct Water Splitting Systems."
- Presentation for North Carolina State University entitled "Photoelectrochemical Systems for Hydrogen Production via Direct Water Splitting."
- Presentation at the American Institute of Chemical Engineers' Spring meeting, speaking in a session on climate change.
- Presentation at the American Physical Society's Spring meeting, speaking in a session on climate change.
- Presentation at the U.S. DOE Hydrogen Program's first Quarterly Program Performance and Results Briefing, for upper DOE management.
- Lecture on renewable energy and hydrogen at the University of Colorado for a class on energy and the environment.
- Banquet speaker at the Northwest regional American Chemical Society meeting in Spokane, Washington.
- Presentation at the California Alternative Energy Retreat in Bishop, California, speaking on the general topic of hydrogen.
- Presentation at the California Hydrogen Business Council, speaking on the NREL Hydrogen Program research.
- Presentation at the Georgia Tech "Blue Skies" symposium speaking on the hydrogen economy.
- Two talks at the XII International Materials Research Congress, Mexico, "Band edge Engineering of p-GaInP2 Electrodes with Porphyrins, Pthalocyanins and other Organic Molecules," and "Corrosion Studies of Stainless Steels for Bipolar Plate Material in Polymer Electrolyte Membrane Fuel Cells."

- Presentation at the National Hydrogen Association meeting entitled "Hydrogen and Energy Security: Key Issues and Potential" with Jim Ohi.
- Presentation on the hydrogen economy at the ASM International Oak Ridge Chapter, Oak Ridge, Tennessee.
- Two presentations at Ashland University, Ashland, Ohio, one entitled "Renewable Energy Systems, Energy Storage and Hydrogen," and a second one for local high school students entitled "Energy and Hydrogen, Today and Tomorrow."
- Presentation on fuel cells and hydrogen to the Clean Energy States Alliance Spring 2003 Meeting.
- Presentation at GE Central Research on photoelectrochemical water splitting.
- Presentation at the International Electrochemical Society meeting (invited) entitled "Integrated Multijunction Photovoltaic/Electrolyte System for Water Photoelectrolysis."

FY 2003 Publications

1. V. M. Aroutiounian, V. M. Arakelyan, G. E. Shahnazaryan, G. M. Stepanyan, J. A. Turner, and O. Khaselev, "Investigation of Ceramic Fe2O3 <Ta> Photoelectrodes for Solar Energy Photoelectrochemical Converters," International Journal of Hydrogen Energy, 27, p 33 (2002).
2. Scott Warren and J. Turner, "Increasing the Efficiency in Photoelectrochemical Hydrogen Production," USDOE Journal of Undergraduate Research, p 75 (2002).
3. J. D. Beach, H. Al-Thani, S. McCray, R. T. Collins, and J. Turner, "Bandgaps and Lattice Parameters of 0.9 um Thick InxGa1-xN Films for 0<x<0.140," J. Appl. Phys, Vol 91, No. 9, (2002).
4. X. Mathew, A. Bansal, J. Turner, R. Dhere, N. Mathews and P. Sebastian, "Photoelectrochemical Characterization of Surface Modified CdTe for Hydrogen Production," J. New Mat. For Electrochemical Systems, Vol 5 149-154 (2002).

Special Recognitions & Awards/Patents Issued

1. Outstanding Mentor Award from the Office of Science, U.S. Department of Energy.

Photoelectrochemical Hydrogen Production

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Objectives

- Develop low-cost, thin-film metal-oxide materials with suitable properties for use in "Hybrid Photoelectrodes" (*HPE*) for solar water splitting.
- Develop optimized *HPE* designs based on best available thin-film metal-oxide and photovoltaic-grade semiconductor materials.
- Demonstrate stable water splitting using *HPEs* based on best available materials systems.
- Demonstrate 7.5% solar-to-hydrogen (STH) efficiency with 1000 hour life by 2005; demonstrate 9% STH with 2000 hour life by 2010.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Material Durability
- N. Materials and System Engineering
- O. Photoelectrochemical Efficiency

Specific technical issues for durability and efficiency in the UH hybrid designs include the development of 'low-temperature' (<300°C) processes which yield photoactive and stable metal-oxide films compatible with hybrid photoelectrode fabrication, and continued development of optimized materials and device designs are needed to meet program goals.

Approach

Materials Research: Current focus on developing low-temperature reactive sputtering process to produce photoactive and stable metal-oxide films including Fe_2O_3 and WO_3

- *Partnership Support (Duquesne University & others):* to develop further understanding of structure and composition of photoactive metal oxides for the engineering of new, process-compatible materials.

Photoelectrode Testing: Current focus on incorporating best available materials into "Hybrid Photoelectrode" structures to evaluate performance and stability

- *Partnership Support (University of Toledo):* to design and fabricate multi-junction amorphous-silicon alloy devices with specified voltage and current characteristics.

Photoelectrode Optimization: Continued development of optimized materials and device designs for use in high-performance / low-cost "Hybrid Photoelectrodes ."

Accomplishments

Fe_2O_3 films successfully deposited using low-temperature sputter process:

- Ability to engineer key film properties successfully demonstrated.
- Excellent film adhesion and stability in alkaline media achieved.
- Photocurrents up to 0.1 mA/cm^2 achieved under 1-sun (typical outdoor sunlight without concentration) in films deposited to date.

WO_3 films successfully deposited using low-temperature sputter process:

- Ability to engineer key film properties successfully demonstrated.
- Excellent film adhesion and stability in acid media achieved.
- Photocurrents up to 1.2 mA/cm^2 achieved under 1-sun in films deposited to date.

Stable operation of “Hybrid Photoelectrode” demonstrated:

- Structure: amorphous silicon alloy tandem (University of Toledo) with sputtered indium tin oxide (ITO) and low-temperature sputtered WO_3 (UH) - 2.5 cm^2 area.
- Stable hydrogen production in 1 N H_2SO_4 measured for over 10 hours.
- Photocurrents up to 0.5 mA/cm^2 in 1-sun outdoor tests (0.7% STH).
- Performance consistent with measured properties of the WO_3 material and the tandem silicon cell.
- Analysis indicates significant efficiency enhancement possible with improved metal-oxide properties.

Future Directions

- Continued development of the "Hybrid Photoelectrode" using in-house and partnership resources.
- Expand efforts to optimize hybrid-compatible materials for efficiency and long-life.
- Design, fabricate and test "Hybrid Photoelectrodes" incorporating optimized materials.

Introduction

Under the sponsorship of the U.S. Department of Energy (DOE), the Thin Films Laboratory at the Hawaii Natural Energy Institute of the University of Hawaii (UH) has been developing high-efficiency, potentially low-cost, photoelectrochemical (PEC) systems to produce hydrogen directly from water using sunlight as the energy source. The main thrust of the PEC systems research at UH has been the development of integrated multi-junction photoelectrodes based on low-cost semiconductor, catalytic, and protective thin films [1].

Figure 1 shows a generic planar photoelectrode structure, where sunlight absorbed in photoactive regions produces electricity to drive the hydrogen evolution reaction (HER) and the oxygen evolution reaction at opposite surfaces. In order to meet the DOE’s goals, the photoelectrode system must be

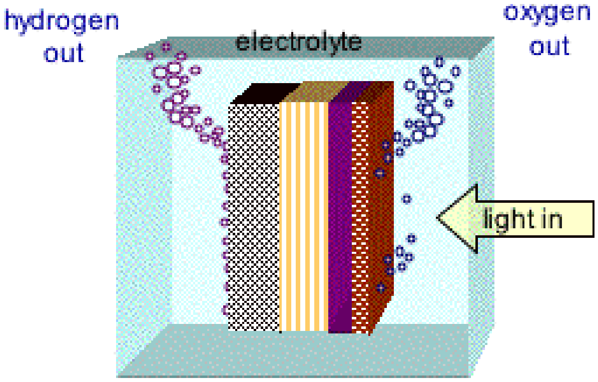

Figure 1. Generic Planar Photoelectrode Structure With Hydrogen and Oxygen Evolved at Opposite Surfaces

low-cost, and it must be capable of operating stably in corrosive aqueous electrolyte environments with solar-to-hydrogen (STH) conversion efficiencies greater than 7.5% by 2005, 9% by 2010 and greater than 10% by 2015 [2]. In an attempt to meet the cost and performance goals, UH has been concentrating on the development of a "Hybrid Photoelectrode" (*HPE*) which incorporates low-cost metal-oxide and photovoltaic-grade semiconductor thin films, as described in the following section.

Approach

The basic "Hybrid Photoelectrode" structure developed at UH is shown in Figure 2. This multi-junction device combines thin-film solid-state with PEC junctions to meet the voltage, current and stability requirements for hydrogen production. The design approach has relied on continued use of integrated models for photoelectrode design [3], establishment of industry and university partners with thin-film materials expertise, and fabrication and evaluation of photoelectrode test devices. Significant advantages of the *HPE* design over other structures investigated at UH [4] include elimination of lateral current collection; simplification of device geometry for ease of fabrication; and improved stability based on the thick, seamless outer metal-oxide layer.

The primary focus of our current work has been the development of *HPE*s based on low-cost solid-state junction materials such as amorphous silicon (a-Si) and copper-indium-gallium-diselenide (CIGS) coated with photoactive nano-structured metal oxides such as iron oxide (Fe_2O_3) and tungsten trioxide (WO_3). There has been extensive investigation into these metal-oxide films for their PEC water splitting properties; Figure 3, for example, shows hydrogen-production characteristics for Fe_2O_3 films deposited by spray-pyrolysis at Duquesne University [5] and for pyrolytic WO_3 films developed at the University of Geneva [6]. It can be seen that hydrogen currents can be quite high in the metal-oxide PEC junctions, but only at sufficient levels of voltage bias. In the *HPE* configuration, the necessary voltage bias is automatically generated in the buried solid-state junction utilizing low-energy photons not absorbed at the PEC interface.

Unfortunately, fabrication of hybrids using pyrolytic oxides is not possible at this time, since substrate temperatures for the established pyrolysis

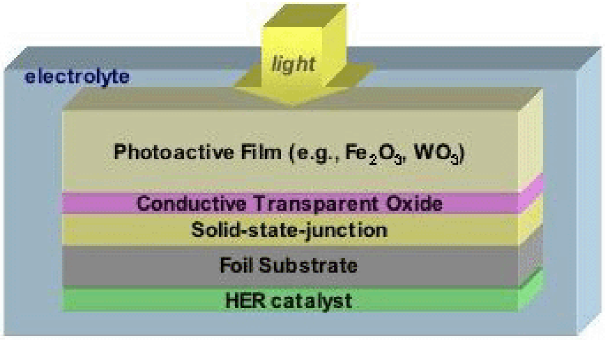

Figure 2. The Multi-Junction "Hybrid Photoelectrode" Structure, Showing Constituent Thin-Film Layers (Photons are absorbed both at the metal-oxide/electrolyte interface and at the buried solid-state junction.)

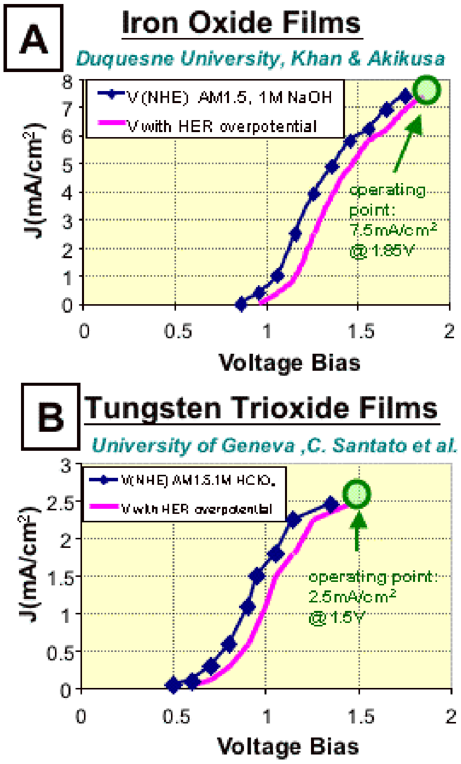

Figure 3. Published Photoelectrochemical Hydrogen Production Characteristics of Metal-Oxide Thin Films: A. Fe_2O_3 film (Duquesne University); B. WO_3 film (University of Geneva)

processes, generally exceeding 400°C, are high enough to damage the underlying solid-state junction. It has therefore been an important part of our research approach to develop low-temperature (<300°C) processes yielding photoactive and stable metal-oxide films. Specific emphasis has been on developing low-temperature reactive-sputter processes for Fe_2O_3 and WO_3 films, along with fabrication and testing of *HPE* prototypes using amorphous silicon solid-state junctions (fabricated at the University of Toledo) with the best available sputter-deposited oxide films.

Results

Significant progress was made this year in the development of low-temperature reactively-sputtered metal-oxide films for use in water-splitting "Hybrid Photoelectrodes", and in the demonstration of operational devices using these materials. Importantly, all project milestones in materials research and photoelectrode development have been met to date.

A key milestone in our materials research was the successful fabrication of photoactive Fe_2O_3 and WO_3 films using low-temperature reactive sputtering processes. Reactive sputtering is a vacuum deposition technique [7] where a range of process parameters, including substrate temperature, ambient gas partial pressures, and sputtering power, can influence film characteristics. We found, for example, that structural, electronic and photoelectrochemical properties of sputtered Fe_2O_3 and WO_3 films could be significantly altered by varying oxygen partial pressure and substrate temperature.

Figure 4 demonstrates the range of variations in grain structure (Figure 4a) and electronic conductivity (Figure 4b) observed in the sputtered iron-oxide films. It was found that the films deposited at the high end of our 'low-temperature' range (200°C) with low oxygen percentages (5%) exhibited the best conductivities (attributable to large grain structure and oxygen vacancy levels). Unfortunately, although they exhibited excellent stability in electrolyte, the hydrogen photocurrents in these films were limited to 0.1 mA/cm^2 in outdoor tests. In contrast, photocurrents up to 1.2 mA/cm^2 were readily achieved in the sputtered WO_3 films investigated to date, as seen in Figure 5a for a sample deposited at 200°C with 12% oxygen. Similar to the iron-oxide samples, the tungsten-trioxide films were stable in electrolyte, and also exhibited a process-dependent range of property variations. Figure 5b, for example, shows the WO_3 films' conductivities, again with the highest observed in films deposited at 200°C with low oxygen percentages.

A critical milestone in our photoelectrode development effort was the successful demonstration of functional "Hybrid Photoelectrodes" using sputtered materials. The operational devices were fabricated using tandem amorphous silicon junctions (fabricated by the University of Toledo) coated with reactively-sputtered WO_3 films (1.0-2.0 µm). Ten photoelectrodes with an active area of 2.5 cm^2 have been fabricated to date and evaluated using the test structure shown in Figure 6a. All ten exhibited hydrogen photocurrent during outdoor testing, and importantly, the observed performances were consistent with analyses based on behavior of the silicon and tungsten-trioxide films used. Figure 6b

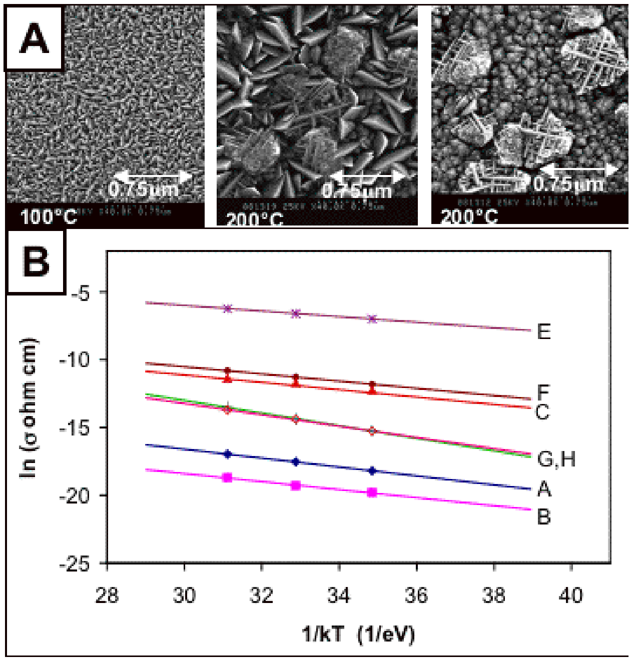

Figure 4. Measured Property Variations in Low-Temperature Sputtered Iron-Oxide Films: A) Grain Structure Dependence on Deposition Parameters; B) Large Variations in Electrical Conductivity

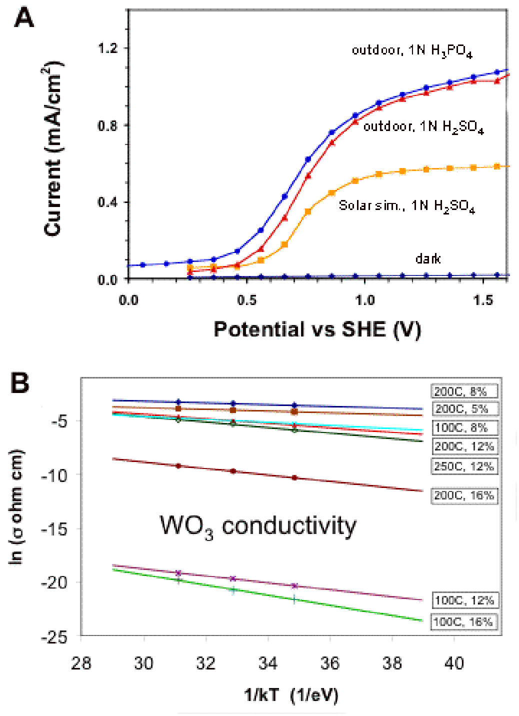

Figure 5. Properties of Low-Temperature Sputtered Tungsten-Trioxide Films: A) Photocurrents in Acid Media; B) Electrical Conductivity as a Function of Deposition Parameters

shows the predicted 1-sun operating point of 0.45 mA/cm^2 for one of the test devices, consistent with the measured performance shown in the inset. The best devices tested to date have generated hydrogen at up to 0.8% STH without serious degradation over a 10-hour operating period. Although the efficiency is low in these initial prototypes, there is clear room for improvement by enhancing the WO_3 photocurrent levels, as seen in Figure 6b. On this basis, future plans must include heavy emphasis on the further materials development of metal-oxide films.

Conclusions

- The optical/electronic properties of present hybrid-compatible metal oxides have been identified as the *key limiting factor* to hydrogen-production efficiency in *HPE*s at this time, clearly defining the primary focus for continued research efforts.
- Expanded efforts to optimize hybrid-compatible materials for efficiency and life are needed.

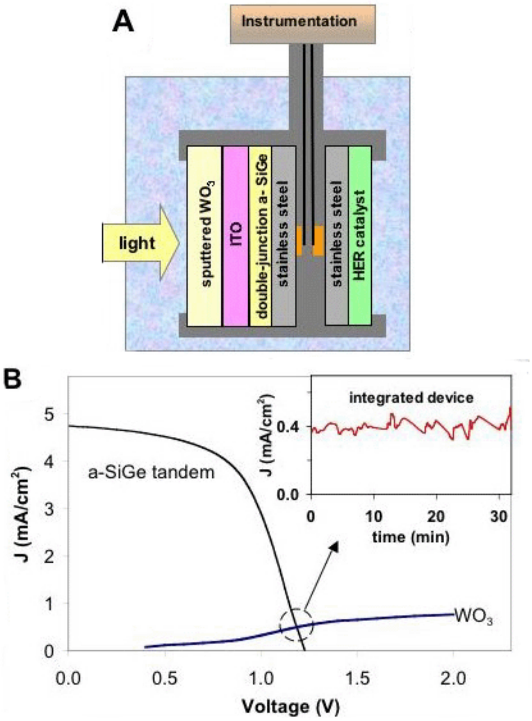

Figure 6. Successful "Hybrid Photoelectrode" Demonstration: A) Test Structure; B) Analysis Based on Performance of Component Films, and Measured Performance of the Integrated Device

- We are confident that with continued development and testing of *HPE*s based on best available materials from both in-house and partnership resources, we will be able to *meet the 2005 and 2010 program goals.*

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1. E. L. Miller, R. E. Rocheleau, X. M. Deng, "Design Considerations for a Hybrid Amorphous Silicon/Photoelectrochemical Multijunction Cell for Hydrogen Production." International Journal of Hydrogen Energy, 28 (6) (2003) 615-623.

2. E. L. Miller, R. E. Rocheleau, S. Khan, "A Hybrid Multijunction Photoelectrode for Hydrogen Production Fabricated with Amorphous Silicon/Germanium and Iron Oxide Thin Films." International Materials Research Congress XI, Cancun, Mexico (2002).

Special Recognitions & Awards/Patents Issued

1. E. L. Miller & R.E. Rocheleau, "Hybrid Solid-State/Electrochemical Photoelectrode for Hydrogen Production": provisional patent with the UH *Office of Technology Transfer and Economic Development.*

Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

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Objectives

- Continue synthesis and screening of libraries designed in year 1 and follow promising (lead) materials as they are identified.
- Explore the composition-function relationship of dopants in ZnO hosts.
- Investigate metal oxide libraries for electrocatalytic hydrogen production and expand our high-throughput screening to include relative electrocatalytic overpotential as a routine screen.
- Develop a high-throughput optical screening system to measure the effective bandgap of metal oxides in libraries.
- Synthesize and screen model libraries optically for bandgap as a primary screen; create secondary libraries of compositions with solar spectrum adsorption and subsequently screen the derivate libraries for appropriate redox/flatband levels and finally for H_2 production.
- Investigate library design for synthesis of semiconductor heterostructures utilizing two-photon absorption processes.
- Continue to expand our investigation of nanoporous materials with emphasis on the ZnO, WO_3 and TiO_2.
- Participate as a member of the USA Annex-14 Expert Group in the International Energy Agency's (IEA's) Hydrogen Implementing Agreement on photoelectrolytic hydrogen production.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Material Durability
- N. Materials and System Engineering
- O. Photoelectrochemical Efficiency

Approach

- Using new and existing high-throughput synthesis and screening technology, create and screen suitable new mixed metal oxide materials for electrochemical/photoelectrochemical hydrogen production.
- Improve and expand the chemical synthesis routes developed for automated high-throughput experimentation.
- Utilize the automated synthesis systems to create libraries of potential hydrogen electrocatalysts/photocatalysts.

- Rapidly screen libraries for potential materials with electrocatalytic and/or photoelectrocatalytic activity.
- Synthesize, using conventional routes, selected materials identified in libraries for detailed structural and electronic analysis.

Accomplishments

- Designed and fabricated combinatorial chemistry systems for synthesis and screening of hydrogen production photocatalysts (Figures 1a, 1b).
- Demonstrated that compositional and preparative modifications of known metal oxide hosts may improve their photoelectrocatalytic properties (Figure 2).
- Achieved first electrochemical synthesis of ordered nanoporous metal oxides (Figure 5).
- Discovered nanoparticulate Pt/WO_3, which is photoactive and resistant to CO poisoning.
- Developed methods for and demonstrated controlled electrosynthesis of high-activity Au nanocluster catalysts.
- Identified H intercalation as a critical component of poisoning resistance of metal oxide electrocatalysts.

Future Directions

- Expand the exploration of new materials with the parallel synthesis and screening systems with particular emphasis on expanding the exploration of the composition-function relationships of quartenary ZnO systems.
- Develop an automated spray pyrolysis methodology and system as a means of high-throughput synthesis and demonstrate the system for dopants in iron-based hosts.
- Expand the search for improved photoelectrochemical performance from nanoporous/nanoparticulate morphologies of known hosts.
- Using calibrated standards, obtain quantitative values of the efficiencies of the materials under investigation in terms of electrons per photon and power efficiency.
- Begin definition and design of photoelectrochemical reactor systems which can incorporate the new materials, and perform preliminary process design calculations on a large-scale hydrogen plant to establish cost estimate models.

Introduction

The overall project objective is to utilize combinatorial material science to expedite the discovery of an efficient, practical, and economically sensible material for the photoelectrochemical production of hydrogen from water and sunlight. This represents a shift in the research paradigm from conventional serial chemical research to a combinatorial approach that features systematic and high-speed exploration of new metal-oxide based solid-state materials. By investigating large arrays of diverse materials, we are working to improve the understanding of the fundamental mechanisms and composition-structure-property relationships within these systems while discovering new and useful energy-producing photocatalysts.

Approach

As we have developed automated chemical synthesis and screening systems during the first two years of the program, in the second year we have focused on the preparation and analysis of diverse metal-oxide libraries with semiconducting and other properties suitable for photoelectrocatalysis. Diversity has included (1) variations in composition (by variable doping, electrochemical synthesis conditions, and surface redox catalysts) and (2) variations in structure (by deliberate and diverse ionic and non-ionic templating agents, synthesis conditions, and doping). The libraries are primarily screened by photoelectrochemical methods, including zero-bias photocurrent and cyclic photovoltammetry.

Results

Task 1. We created tungsten-molybdenum mixed oxide libraries ($W_{1-x}Mo_xO_3$) using a parallel synthesis method. The film compositions were readily controlled by varying the ratios of the two metals in the electrolyte. By X-ray diffraction patterns and Raman spectroscopy, atomically-mixed metal oxides were confirmed to exist rather than simply mixed phases of pure tungsten oxide and pure molybdenum oxide (Figure 2). Zero-bias photocurrents of the mixed oxides were strongly dependent on the film composition. The maximum photoresponse was observed with $W_{0.5}Mo_{0.5}O_3$, and photoactivity decreased as film composition approached either pure oxide. The photoresponse of the $W_{0.5}Mo_{0.5}O_3$ mixed oxide film, 18.5 μA/cm^2, was 50.4% higher than that of the pure tungsten oxide film. Cation intercalations were carried out for

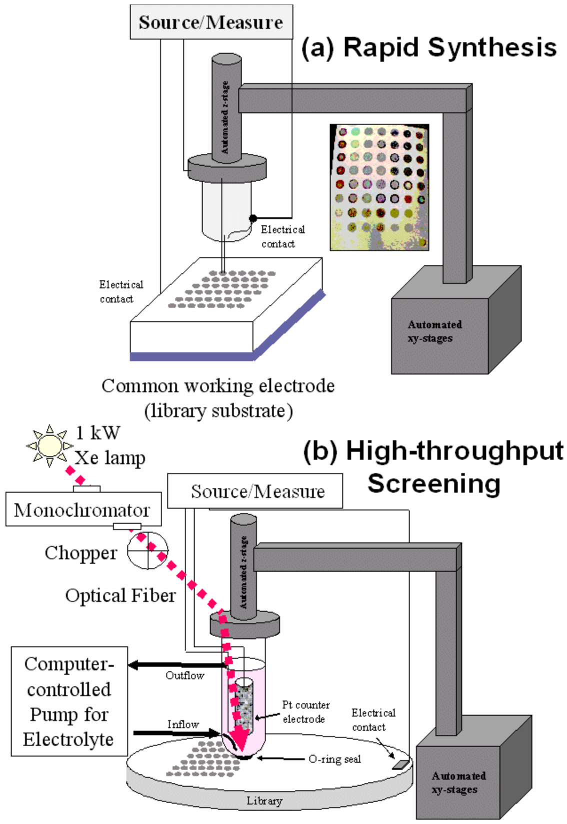

Figure 1. Automated Electrochemical Synthesis and Screening: (a) Rapid synthesis - a perforated polypropylene block with 63 independent o-rings is sealed upon a substrate, allowing for 63 distinct electrolyte compositions. A probe with reference and counter electrodes are automatically dipped into each bath, and a potentiostat conducts electrodeposition of each sample. (b) High-throughput screening - a scanning photoelectrochemical cell traverses a library, illuminating each sample with a chopped light source, and photocurrent is measured.

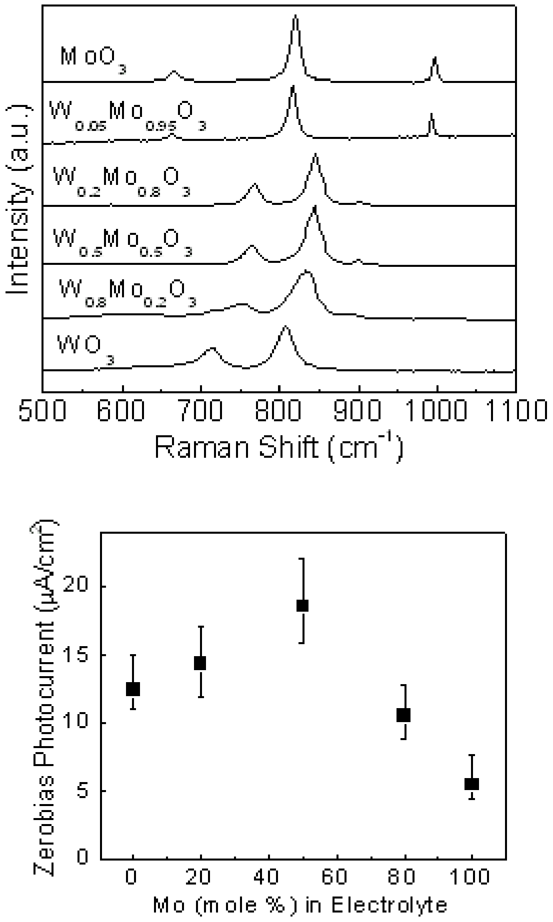

Figure 2. (top) Raman spectroscopy of tungsten-molybdenum mixed oxides with respect to film compositions and (bottom) Zero-bias photocurrent of tungsten-molybdenum mixed metal oxide films. All samples were n-type semiconductors. Illumination was provided by a 150-W Xe lamp.

the tungsten-molybdenum mixed oxide library using H^+, Li^+, Na^+, and K^+. Interestingly, as the ratio of tungsten to molybdenum approaches unity, electrochromic properties improve. Compared to either pure tungsten oxide or pure molybdenum oxide, the mixed oxides show considerably enhanced intercalation properties, with the $W_{0.5}Mo_{0.5}O_3$ film exhibiting the highest intercalation properties of all. Metal oxide libraries were also successfully synthesized by electroless deposition on copper substrates from metal peroxo electrolytes (WO_3, MoO_3, ZrO_2, Nb_2O_5). The reducing electrons were provided by the copper substrate as it was oxidized to CuO.

Task 2. Several hundred samples of different ZnO-based materials have been synthesized and screened for zero-bias photocurrent. All materials were binary systems consisting of ZnO and a single other element – typically a transition metal – and a range of dopant concentrations was explored for each element. The aim of the dopant is to improve upon the photocatalytic activity of ZnO, particularly under visible illumination, and to increase the stability of the material. Table 1 has been constructed to qualitatively indicate the impact of the dopants on the material properties vs. pure ZnO ("very poor", "poor", "average", "good", and "excellent"). Cobalt showed the greatest improvements in terms of visible light photocurrent, and the photoactivity of cerium samples remained high for several minutes, as opposed to pure ZnO, whose photocurrent decayed to 15% of its initial value after the same amount of time. Iron, nickel, ruthenium, and manganese also showed improvements to ZnO. After having explored 24 different binary ZnO systems, of different concentrations, we are looking forward to focusing on the best materials to begin our investigation of ternary and quaternary libraries.

Task 3. Diverse compositions of cobalt-iron-nickel oxide materials supported on 304 stainless steel have been synthesized by combinatorial spray pyrolysis. These samples have been studied for water oxidation electrocatalysis by tafel slopes and exchange current in basic electrolytes (KOH 20% w/w). Different precursor solutions were used to create compositional differences. The best electrocatalysts found to date in this study were synthesized with iron or nickel at 10-20% of the cobalt concentration in solution. Ternary libraries will be explored in the near future.

Tasks 4 & 5. We are currently completing our infrastructure for the automated measurement of bandgap of combinatorial libraries. The system is shown schematically in Figure 3. In this design, an integrating sphere is affixed to our x-y-z combinatorial stages. In a fully automated fashion, the integrating sphere steps down upon each sample independently, and each sample is illuminated by a 1-kW Xe lamp (ThermoOriel). An optical fiber carries the diffuse reflectance of the sample to an Ocean Optics S2000 detector, which measures the spectra and allows for bandgap calculation. This combinatorial method for bandgap measurement will be the first screening conducted on libraries.

Task 6. Heterostructures of Cu_2O/TiO_2 have been synthesized and screened for photocatalytic activity.

Table 1. Qualitative impact (excellent, good, average, poor, very poor) of 24 different elements when co-deposited with ZnO as compared to pure ZnO.

Co-deposited species with ZnO	Visible Photocurrent	UV-Vis Photocurrent	Stability
Ag	Poor	Poor	Average
Al	Good	Average	Good
Au	Poor	Poor	Average
Ce	Average	Average	Excellent
Cd	Poor	Poor	Average
Co	Excellent	Poor	Good
Cr	Poor	Poor	Average
Cu	Poor	Poor	Average
Eu	Poor	Poor	Average
Fe	Good	Good	Average
Mn	Average	Average	Good
Mo	Poor	Poor	Poor
Ni	Excellent	Excellent	Average
Nb	Poor	Average	Good
Pd	Very Poor	Very Poor	N/A
Pt	Poor	Poor	Poor
Rh	Poor	Poor	Aveage
Ru	Excellent	Excellent	Average
Sb	Poor	Poor	Average
Sn	Average	Average	Good
Ti	Very Poor	Very Poor	N/A
V	Poor	Poor	Average
W	N/A	N/A	N/A
Zr	Average	Average	Good

The Cu_2O/TiO_2 heterojunction scheme can be viewed in Figure 4. Cu_2O is a photocatalyst that benefits from a small bandgap (2.0 eV), which allows for excellent solar absorption. It is limited, however, by photocorrosion which degrades the material rapidly. TiO_2, on the other hand, is a robust photocatalyst that is stable for long periods of time (ca. thousands of hours); however, it is limited by poor visible photon absorption (bandgap 3.0 eV). By creating a heterojuction of Cu_2O covered with TiO_2, a photocatalytic system (which operates as a photocathode) results which absorbs more visible light than pure Cu_2O and is as stable as pure TiO_2.

Task 7. We have been developing a general method for the production of high surface area nanostructured films by utilizing electrochemically-driven self-assembly of surfactants. We have successfully electrodeposited mesoporous WO_3, TiO_2 by controlling deposition conditions (Figure 5). Mesoporous tungsten oxide films with lamellar structure were successfully synthesized by electrodeposition using sodium dodecylsulphate (SDS) as a templating agent. Nanophases can be varied by changing the deposition potential, which directly affects the surface charge densities of the electrode and, therefore, the surface assembly patterns of the inorganic-surfactant aggregates. Compared to nonporous tungsten oxide prepared with isopropanol, lamellar phase mesoporous tungsten oxide showed higher photocatalytic activity and greater current density for hydrogen intercalation. Functional improvements are most probably due to the larger surface area of mesoporous tungsten oxide and facilitated charge transport.

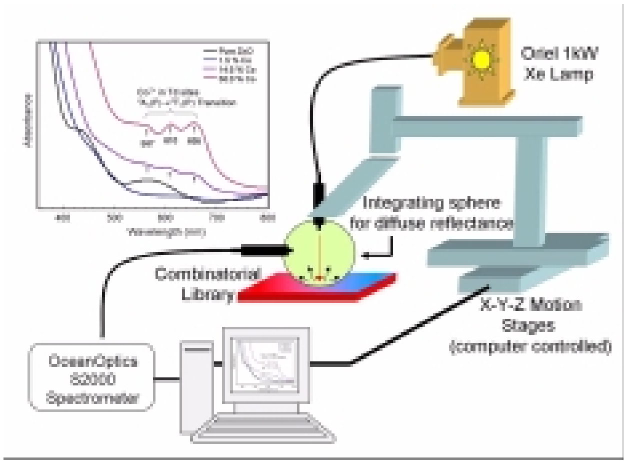

Figure 3. Schematic design of combinatorial measurement of diffuse reflectance for ultraviolet-vis spectroscopy and bandgap calculation.

Task 8. We have actively contributed to the Annex 14 of the IEA, including attendance and participation in the expert meeting in Paris, France, April 27-28. Results were presented to the Annex working group from our laboratory, and we shared ideas concerning the future of international collaboration in the area of photoelectrochemical water splitting.

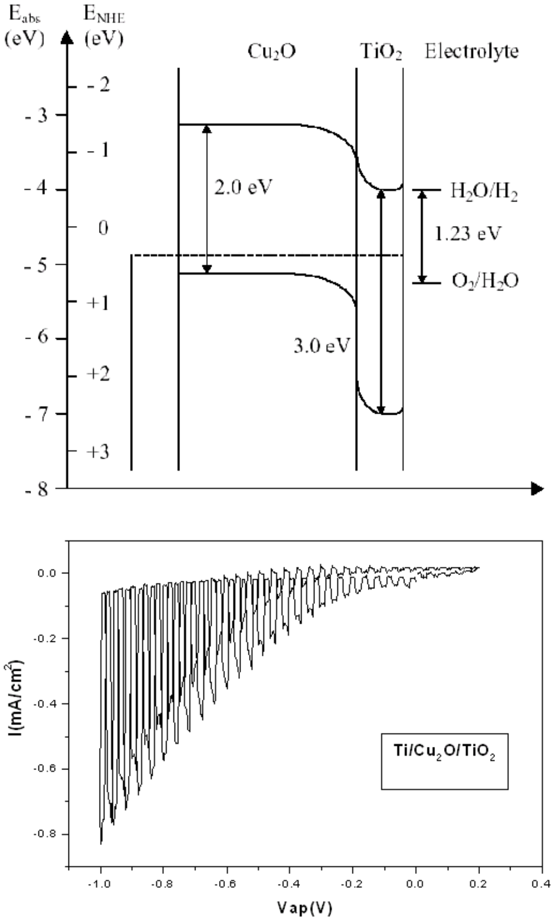

Figure 4. Cu_2O/TiO_2 Heterojunction on Ti Foil: (top) The Cu_2O functions as a light absorber and the TiO_2 overlayer protects against corrosion. The band diagram demonstrates why the device operates as a photocathode despite n-type TiO_2 on the surface. (bottom) The device produces nearly 1 mA/cm^2 of photocurrent at –1 V bias vs. Ag/AgCl under 1 sun illumination.

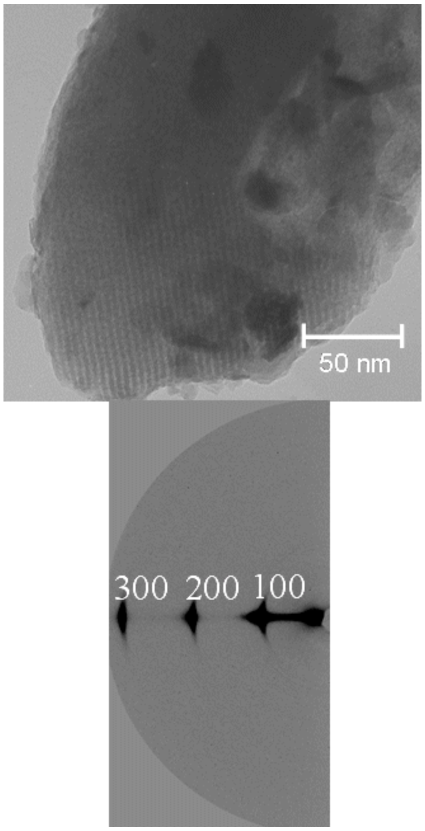

Figure 5. Nanoporous Metal Oxide Photocatalyts: (top) Transition electron microscopy images of tungsten oxide films deposited in the presence of SDS and (bottom) 2D-grazing incidence x-ray diffraction pattern of lamellar tungsten oxide on indium tin oxide coated glass.

Conclusions

As we complete the second year of the project in the fall of 2003, we will have developed combinatorial methods for high-throughput synthesis and screening of new mixed-metal oxides active for photoelectrochemical production of hydrogen. Mixed WO_3-MoO_3 has shown improvements over the pure oxide components, and binary ZnO:Me (Me = Co, Ni, Fe, Ru, Ce, Mn) have demonstrated improved photocatalytic performance compared to pure ZnO. A new means of nanoporous metal oxide synthesis has been demonstrated and Pt and Au nanoparticles created electrochemically which show promise as new surface electrocatalysts.

FY 2003 Publications/Presentations

1. S.-H. Baeck, T. Jaramillo, G. Stucky, and E. McFarland, "Controlled Synthesis of Nanoparticulate Tungsten Oxide", Nano Letters, 2(8), 831-834(2002).

2. S.-H. Baeck, C. Brandly, T. Jaramillo, and E. McFarland, "Combinatorial Electrochemical Synthesis and Characterization of Tungsten based Mixed Metal Oxide", Journal of Combinatorial Chemistry, 4(6), 563-568 (2002).

3. S.-H. Baeck, T. Jaramillo, and E. McFarland, "Influence of Composition and Morphology on Photo and Electrocatalytic Activity of Electrodeposited Pt/WO_3", Abstracts of Papers of American Chemical Society, 224: 062-FUEL Part 1 (2002).

4. S.-H. Baeck and E. McFarland, "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-Molybdenum Mixed Oxides," Korean Journal of Chemical Engineering, 19 (4), 593-596 (2002).

5. K.-S. Choi, H. Lichtenegger, G. Stucky, and E. McFarland, "Electrochemical Synthesis of Nanostructured ZnO Films Utilizing Self-Assembly of Surfactant Molecules at Solid-Liquid Interfaces", Journal of the American Chemical Society, 124(42), 12402-12403 (2002).

6. W. Siripala, A. Ivanovskaya, T. Jaramillo, S.-H. Baeck, and E. McFarland," A Cu_2O/TiO_2 Hetrojuction Thin Film Cathode for Photoelectrocatalysis", Solar Energy Materials & Solar Cells, 77(3), 229-237 (2003).

7. T. Jaramillo, S.-H. Baeck, B.R. Cuenya, and E. McFarland, "Catalytic Activity of Supported Au Nanoparticles Deposited From Block Co-polymer Micelles", Journal of the American Chemical Society, 125(24), 7148-7149 (2003).

8. K.-S. Choi, E. McFarland, and G. Stucky, "Electrocatalytic Properties of Thin Mesoporous Platinum Films Synthesized Utilizing Potential-

Controlled Surfactant Assembly", Advanced Materials, Accepted and in Press (2003).

9. S.-H. Baeck, K.-S. Choi, T. Jaramillo, G. Stucky, and E. McFarland, "Enhancement of Photocatalytic and Electrochromic Properties of Electrochemically Fabricated Mesoporous WO_3 Thin Films", Advanced Materials, Accepted and in Press (2003 August).

10. S.-H. Baeck, T. Jaramillo, G. Stucky, and E. McFarland, "Synthesis of Tungsten Oxide on Copper Surfaces by Electroless Deposition", Chemistry of Materials, Accepted and in Press (2003 August).

Discovery of Photocatalysts for Hydrogen Production

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Objectives

- To design and construct tools for the high throughput screening of the properties of photocatalysts relevant to the photoelectrochemical generation of hydrogen.
- To use the high throughput screening tools to identify materials with the appropriate energetics for water splitting.
- To use the industrially relevant laser pyrolysis materials production capability of our partner, NanoGram Corp., to produce commercial scale quantities of photocatalysts.
- Demonstrate that materials issues that are a hindrance to the commercialization of photoelectrochemical water splitting can be addressed through a materials discovery process.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Materials Durability
- N. Materials and Systems Engineering
- O. Photoelectrochemical Efficiency

Approach

- Develop tools for the high throughput analysis of material properties relevant to photoelectrochemical hydrogen generation.
- Work with existing nanoparticulate powder manufacturer to test materials with existing technology to produce kg/hr scale quantities.
- Identify candidate materials for further study via high throughput screening.

Accomplishments

- Constructed Solar Simulator.
- Designed and constructed 25-cell photolysis analysis module.

- Acquired diffuse reflectance instrument employing Ocean Optics Spectrometer.
- Initiated evaluation of NanoGram NPM^{TM} produced nanoparticulate titania.

Future Directions

- Modify stable metal oxide semiconductors to shift bandgap to increase utilization of the solar spectrum and increase solar to hydrogen efficiencies.
- Complete 25-cell module for electrochemical analysis of materials to provide band edge energy and photoaction spectrum analysis.
- Incorporate hydrogen sensor technology developed for fuel cell safety applications into analysis modules for direct hydrogen determination.
- Increase level of collaboration between other DOE funded laboratories via establishment of mutual database.

Introduction

The process whereby semiconductor materials absorb light and convert that light to electricity has been known for some time and is the cornerstone of the photovoltaic (PV) industry. As an alternative to generating electricity, the electron/hole pair generated by the absorption of light by a semiconductor could be used to facilitate a chemical transformation, thereby storing the energy for later use. This is the basis for the photoelectrochemical (PEC) generation of hydrogen from sunlight, water and a semiconductor-based photocatalyst. In this process, electrons generated by the absorption of light are used to reduce water, generating hydrogen, and the holes are used to oxidize water, generating oxygen. The hydrogen produced could then be used as a fuel in either electrolytic or combustion processes. It is more efficient to generate hydrogen using PEC directly than to use a PV array to feed an electrolyzer.

The key materials requirements for efficient PEC hydrogen production are: A) a semiconductor with a bandgap relevant to the solar spectrum so as to maximize solar utilization, B) band edge energies relevant to the reduction and oxidation potentials of water to minimize energy mismatch, C) fast interfacial electron transport to minimize recombination and D) stability in the presence of an aqueous electrolyte. The key technical barriers to the implementation of PEC hydrogen production relate to the fact that materials that satisfy all of these requirements, simultaneously, have not been found. This is not due to a conflict with these requirements and known laws of physics (there are none), but rather reflects the immature stage of this technology. In the earliest work on this technology, semiconductor materials developed for the PV industry were analyzed and found to be unsuitable due to their poor stability in aqueous electrolytes. Current work is under way with respect to the identification of materials specifically for the purpose of photoelectrochemical generation of hydrogen.

Approach

The use of high throughput techniques to speed the discovery process has been in place for a number of years; pharmaceutical companies were the first to invest heavily in the combinatorial synthesis and high throughput analysis concept. The key to the concept is to test as many samples as possible as quickly as possible for a specific property rather than to do a complete characterization on a specific material or class of materials. In this manner, candidates for further study can be culled from very large sample sets. In our approach to develop tools for the high throughput screening of materials for properties relevant to PEC hydrogen production, we have designed and built a 25-cell module to analyze the photolysis products generated upon illumination of samples with a simulated solar spectrum. The basic design incorporates a vacuum sealed sample module with a pressure transducer to monitor the pressure as a function of photolysis time, see Figure 1. The pressure transducer data is computer monitored, and at set pressure intervals, a Gillson sample handler (top right of Figure 1) that has been modified is triggered to sample the head space gas and feed it to a gas chromatograph for analysis. The vacuum seal component of this design ensures that each cell is isolated, and the quick release and seal capabilities make loading quick and easy.

In the Hydrogen, Fuel Cells and Infrastructure Technologies Program (HFCIT) Multi-Year Program Plan, the need to have processes for the commercially relevant production of PEC materials is identified. Part of the sample lots that we are investigating are produced by NanoGram Corp. using their nanoparticle manufacturing technology, NPMTM. NanoGram has the process technology to produce these materials at rates of kilograms per hour and higher should a demand for these materials arise.

Results

To date, the key results involve the design and construction of the 25-cell photolysis analysis module, which we have now fully engaged in the initial screening of sample sets of nanoparticulate titania provided by our partner, NanoGram Corp. The photolysis setup delivers a photon flux on the order of 80 mW/cm^2 to the sample cells as determined by actinometry. An interesting observation is that the pressure transducer response factor is slowly changing. This was noticed during the course of a routine pressure testing in which we had initially observed very a very narrow distribution of pressure responses; however, after a number of experiments, the distribution of response factors appeared to increase, see Figure 2. As such, we now routinely collect a calibration curve for the pressure transducers. As shown in Figure 3, while the response factors of the various pressure transducers does vary considerably, the response of any given transducer is very linear over pressure ranges encountered during the normal course of operation.

A sample data set collected during the course of a photolysis experiment is shown in Figure 4. Contained with the 25 sample cells are 6 TiO_2 samples in triplicate, one Niobate in triplicate and four blanks containing a similar particulate that is known to be inactive. The data set has been corrected for the photon flux for each specific cell and for the pressure transducer response. From this

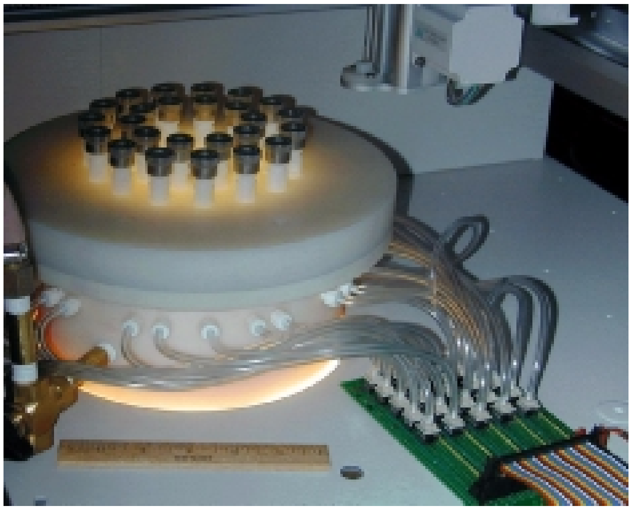

Figure 1. Picture of 25-Cell Photolysis Analysis Module

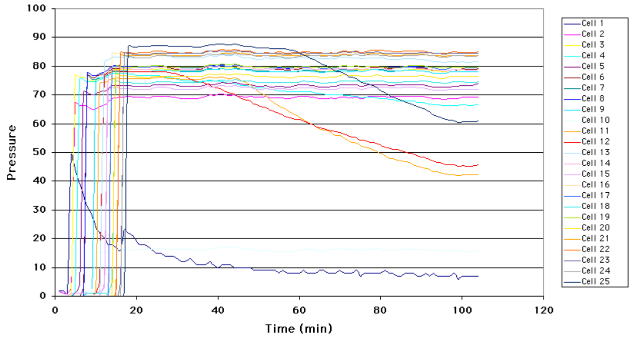

Figure 2. Leak Test Results Indicating Range of Pressure Transducer Response Factor

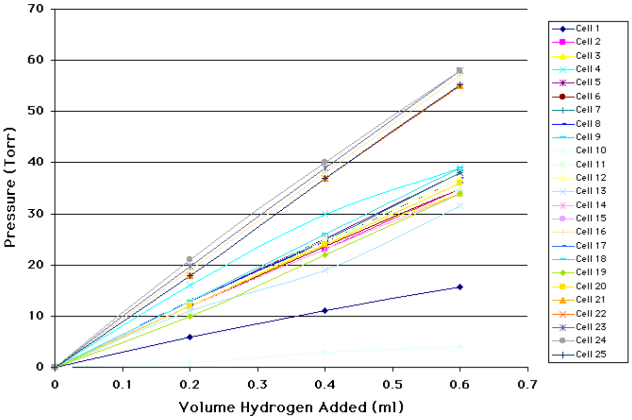

Figure 3. Results of Calibration of Pressure Transducer Response Factor

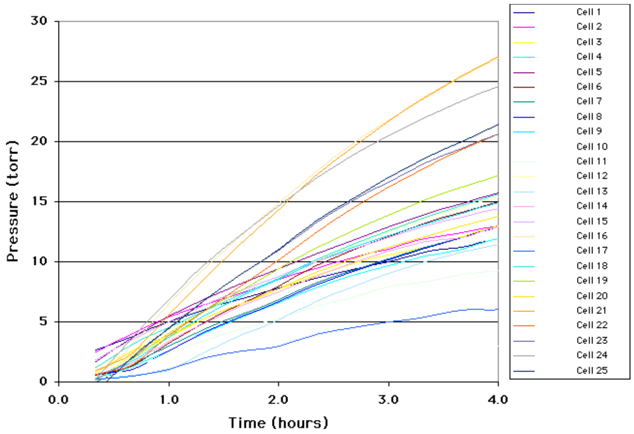

Figure 4. Time Versus Pressure Results

experiment, the niobate sample resulted in the best efficiency and the highest pressure versus time plots, followed by an oxygen-deficient phase of titania which does extend the absorption spectrum into the visible. The niobate, while still exhibiting efficiencies of less than 1%, is a material that we will be investigating further in various modified forms. To date, we have received over 50 different samples from NanoGram, with the majority of them being titania samples prepared over a significant range of particulate sizes, see Table 1.

In our initial screen of the TiO_2 samples, a platinum catalyst was deposited onto the particle sets via the photoreduction of a platinum salt. Samples have also been prepared using chemical reduction of impregnated platinum salts; however, these to date have not been screened. In the titania series prepared with the photoreduced platinum catalyst, we see no statistical variation in the efficiency of hydrogen generation as a function of particle size, and in all cases efficiencies were in the range of 0.1% solar photons to hydrogen. Interestingly, there does appear to be a trend developing with respect to the hydration of the titania. These results are very premature, and considering the overall rather disappointing performance of these materials to date, it is doubtful that time will be spent analyzing them further with the platinum catalyst. We are currently evaluating these materials with other catalysts. We are also currently expanding the materials we are looking at to include some niobate structures. These materials have shown evidence of water splitting in the past and the extension of their absorbance spectra into the visible relative to the titania samples, see Figure 5.

Table 1. Partial TiO_2 Sample List Indicating Particle Size and Surface Area

Sample	median diameter, µm	Surface area, m2/gm
TDX-25	0.11	20.9
TDX-33	0.10	20.1
TDX-30	0.08	22.8
TDX-101	0.08	27.9
TDX-37	0.07	26.2
TDX-51	0.07	25.3
DIM76	0.07	38.0
TDX-50A	0.06	29.4
TDX-55	0.06	29.0
TDX-110	0.06	33.6
TDX-24	0.05	32.8
DIM57	0.04	52.5
DIM113	<0.03	56.0
DIM82	< 0.03	55.6

Conclusions

Our initial results, while far from complete or conclusive, indicate that the nanoparticulate titania samples provided by NanoGram Corp. exhibit very poor efficiencies for the conversion of photons of solar relevance to hydrogen. In no case were conversion efficiencies greater than 0.3% observed in any of the titania samples. This clearly indicates that we need to expand the composition of materials being explored. With the relocation of one of NanoGram Corporation's laser pyrolysis instruments to the SRI campus, we will be able to facilitate this expansion of material candidates considerably.

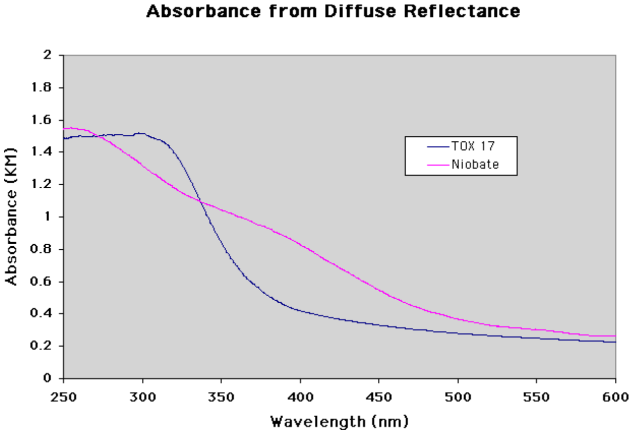

Figure 5. Absorbance spectra generated from diffuse reflectance data for a titania, TOX 17, and a niobate semiconductor sample.

FY 2003 Publications/Presentations

1. Brent MacQueen, "Photoelectrochemical Hydrogen Production", Invited Lecture, Hydrogen Workshop of the Global Climate Energy Project, March 2003, Stanford University, Palo Alto CA.

Low Cost, High Efficiency Reversible Fuel Cell Systems

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Objectives

- Improve performance of reversible solid oxide stacks (capable of operating in both fuel cell and electrolysis modes) by reducing polarization and rate of degradation.
- Demonstrate an integrated fuel cell hot subassembly with a stack of about 50 reversible type cells operating on natural gas.
- Evaluate the economic impact of reversible solid oxide fuel cell/electrolyzer systems and consider applications where a competitive advantage may be achieved.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance (O&M)
- Q. Cost
- R. System Efficiency
- S. Grid Electricity Emissions
- T. Renewable Integration
- U. Electricity Costs

Approach

- Evaluate alternate materials and cell geometry parameters to reduce cell polarization.
- Reduce operating temperature to improve stack life.
- Test a stack of up to 50 reversible cells in a new integrated system assembly.
- Perform cost and environmental evaluations of alternative equipment and system configurations.

Accomplishments

- Optimized cell geometry by modeling the stack and system.
- Designed, fabricated, and evaluated reversible stack performance over a range of temperatures and operating conditions.
- Demonstrated stable operation for >1200 hours in small reversible stacks at acceptable efficiency.
- Met all stack performance targets.
- Completed preliminary economic analysis and identified applications where reversible electolyzer/fuel cell systems may have a competitive advantage.

Future Directions

- Fabricate and test a stack of up to 50 reversible cells using standardized processes.
- Complete evaluation of alternative stack operating conditions.
- Complete cost and environmental assessment of alternative system configurations.
- Complete present project in Fall of 2003.

Introduction

The Technology Management, Inc. (TMI) reversible (fuel cell - electrolyzer) system employs a stack of high temperature solid oxide cells to electrochemically produce either electricity (from fuel and air or fuel and oxygen) or hydrogen (from water and supplied electricity). A fuel cell version of the system operating at atmospheric pressure could operate on natural gas (or other carbon-containing fuel) and air. A high-pressure reversible electrolyzer version would make high-pressure hydrogen and oxygen from water and also operate in reverse (on demand) to generate electricity from these gases. The novel reversible stacks require simpler and more efficient auxiliary equipment than conventional fuel cell systems. Calculations have shown that the proposed systems could achieve higher efficiencies in both fuel cell and electrolysis modes than existing alternatives.

During the current phase of the project, TMI has demonstrated reversible cells and stacks which bettered the quantitative performance targets set for polarization voltage, operating efficiency, rate of performance loss, and seal leakage rate. This success resulted from a cell and stack development program that studied the effects of component dimensions and fabrication details, assembly procedures, startup procedures, and operating conditions. A complete test system for stacks up to 50 cells has been designed, built, and operated (with stacks up to 19 cells thus far). Cost and engineering studies were extended significantly to identify cases where vehicle-grade, high-pressure hydrogen could be produced at the refueling point from natural gas at costs below DOE targets. The use of the proposed reversible electrolyzers for energy storage also appears to offer sizeable advantages over the expected cost, size, and weight of known rechargeable batteries.

Approach

The overall goals for reversible stack performance are (a) high efficiencies at selected power levels and (b) low degradation rate (power loss over time at constant flows). High efficiencies, in turn, require low polarization voltages and low seal leakage rates. Low polarization voltages in solid oxide stacks result from low concentration polarization and low resistive polarization, the latter being quantified by area specific resistance (ASR, expressed in Ohm-cm^2). Seal leakage rates may be computed as a valve coefficient (C_v, a relative measure of flow through an orifice). Simulations and prior experiments have shown that achieving the desired performance of TMI's reversible stacks is significantly more difficult in fuel cell mode than in electrolysis mode. The current phase uses the following goals in fuel cell mode.

- ASR < 1.00 Ohm-cm^2
- $Cv < 10^{-5}$
- Degradation rate < 5% per 1000 hours

Fabrication improvements, materials substitution, temperature optimization, and assembly improvements were evaluated to reduce ASR. Dimensional optimization and startup details are being used to minimize seal leakage. A lower degradation rate is achieved via improvements in fabrication details and seal leakage. Concentration polarization was reduced by combining increased porosity, improved dimensional stability, and adjusted component dimensions.

The design of a larger system for operation with up to 50 cells is based upon prior work by TMI on other test systems augmented by additional system-specific engineering calculations.

Cost and engineering studies build on work performed during the prior phases of this project as well as cost studies by TMI for other projects. Data on natural gas and electricity pricing are from the Energy Information Administration. Hydrogen cost targets are taken from public DOE hydrogen and fuel cells documents.

Results

Reversible Stack Development. At the start of the present phase, measurements of reversible cell performance were poor and insufficient to achieve targets. There were also considerable variations from cell to cell. Concentration polarization was initially high, thereby limiting maximum possible current densities to only about 100 mA/cm^2. Major improvements have been the result of increased porous layer thicknesses and improved dimensional stability, thereby maintaining higher effective porosities.

Early ASR measurements ranged from about 2.2 to over 3.0 Ohm-cm^2, which were in excess of the goal of 1.00 Ohm-cm^2. ASR was improved by reducing seal leakage, optimizing electrical contact between cell layers, and by slightly increasing temperature. Studies have found that ASR varies with both fuel utilization (fuel oxygen potential) and current density. Recent ASR measurements have ranged from 0.84 to about 1.4 Ohm-cm^2 in single cells and stacks, increasing at high fuel utilization.

Early seal leakage rates varied, sometimes being more than ten times the target C_v of 10^{-5}. Improvements in dimensional tolerances, assembly procedures, and startup procedures have resulted in measured C_v values below the target, with the best values being less than 10^{-6}.

Early degradation rates were highly variable, sometimes exceeding 20% per 1000 hours. One 19-cell stack operated for over 360 continuous hours on natural gas with less than 2% per 1000 hours degradation. However, if a stack has one or more significant leaks, considerably higher rates are still seen. The temperature dependence of degradation rate has not yet been quantified.

A limited number of cells and stacks were tested in electrolysis mode, with the results confirming those from earlier work. Measured ASR in this mode equaled that in fuel cell mode. In projected commercial solid oxide electrolyzers, allowable ASRs are higher than those for highly efficient fuel cell systems due to electrolyzer heat balance considerations.

Cell and Stack Fabrication. Evolutionary improvements and modifications were made to existing TMI materials specifications, fabrication methods, and cell dimensions to accommodate the reversible cell and stack design. Minor modifications of standard TMI fabrication procedures were sufficient to produce thicker fuel and oxygen electrodes. Larger diameter, thicker seals were made using methods from internally funded programs. Over one hundred reversible cells have been fabricated for this project thus far.

Integrated System Demonstration. An important objective of this phase is to demonstrate a complete working system containing a sizeable reversible stack because stack performance is strongly dependent upon the system variables.

Figure 1 shows the test system for stacks up to 50 cells. This system has been designed, built, commissioned, and operated with stacks up to 19 cells thus far. The cylindrical assembly includes the reversible stack, heat exchanger, fuel processing, air blower, startup heater, electrical connections, thermocouples, stack mounting assembly, and insulation. The rectangular enclosure contains test instrumentation, active electrical load circuit, detachable startup systems, and fuel control valve.

Figure 1. Laboratory System Assembly

The best performance parameters measured to date on this system (with 9- to 19-cell stacks) are shown in Table 1 (seal orifice coefficient was estimated from open-circuit voltage: up to 1.12 V/cell).

Table 1. Best Performance Parameters for Reversible Stack System

Parameter	Units	Goal	Measured
Area specific resistance	Ohm-cm^2	< 1.00	0.96
Power degradation rate	per 1000 hrs	< 5%	< 2%
Seal orifice coefficient		$< 10^{-5}$	$< 10^{-6}$

Cost and Engineering Studies. The installed and operating costs of systems producing hydrogen for vehicles are critical. The ultimate widespread use of hydrogen vehicles will only occur if and when affordable hydrogen is readily available. Vehicular hydrogen must also be very pure and available at pressures up to about 80 MPa (11,600 psi) for refilling vehicle tanks rated at about 69 MPa (10,000 psi). Hydrogen production processes that result in the lowest delivered-to-vehicle costs are expected to eventually dominate the market.

TMI believes it may have a candidate technology for achieving very low delivered hydrogen costs. Configured as shown in Figure 2 and sited at vehicle refueling sites, TMI reversible stack and system technology would be employed for both fuel cell system modules (using natural gas or other carbonaceous fuel) and the reversible electrolyzer subsystem, capable of producing 80 MPa pure hydrogen for vehicles as well as performing energy storage (battery replacement). The calculated projected energy conversion efficiencies in fuel cell, electrolyzer, and energy storage modes, as well as the overall natural gas to high-pressure pure hydrogen mode, can be shown to be superior to known competing technologies.

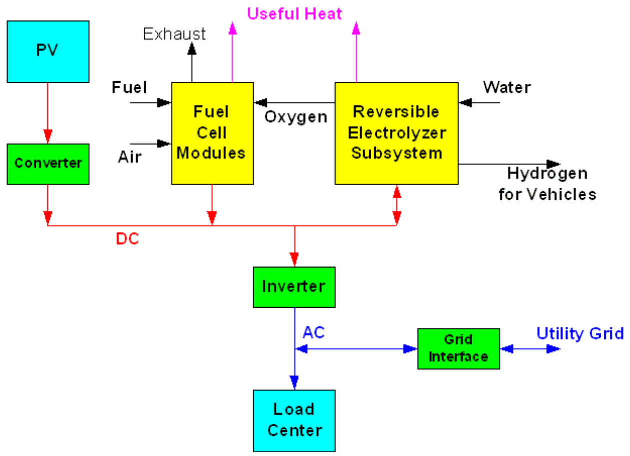

Figure 2. System Concept

TMI cost studies to date show that the lowest vehicle-delivered costs (below $1.50 per kg hydrogen) are projected for residential systems which can co-produce vehicle hydrogen, AC power, and hot water.

Conclusions

- Improved reversible solid oxide stack performance has been achieved.
- Sizeable reversible solid oxide fuel cell/ electrolyzer stacks and a complete test system have been demonstrated.
- Projected cost (at the refueling nozzle) of vehicle hydrogen from natural gas has been computed to be as low as $1.50 per kg hydrogen.
- Projected solid oxide electrolyzer efficiencies near 95% have been achieved.
- Highly versatile system concepts using reversible electrolyzers and fuel cells have been proposed.

FY 2003 Publications/Presentations

1. "Low Cost, High Efficiency Reversible Fuel Cell Systems", R. C. Ruhl, DOE Hydrogen and Fuel Cells Annual Merit Review, Berkeley CA, May 20, 2003

High-Efficiency Steam Electrolyzer

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Objectives

- Develop a highly efficient steam electrolyzer for distributed hydrogen production
- Utilize natural gas as an anode depolarizer to reduce electricity consumption
- Demonstrate prototype electrolyzers with successively higher hydrogen production capacities in the laboratory
- Demonstrate a 5-kW electrolyzer for proton exchange membrane (PEMFC) vehicle refueling in the field

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- Q. Cost
- R. System Efficiency
- U. Electricity Costs

Approach

- Optimize cathode and anode materials for enhanced electrochemical kinetics and obviate carbon deposition problems
- Study the effect of microstructure on electrode performance
- Develop tubular electrolyzer stack for pressurized operation
- Develop tube fabrication and ceramic-to-metal seal processes
- Optimize system components and engineering design and perform long-term durability testing on components and systems
- Engineer pressure vessel and electrolyzer components to maximize unit safety and lifetime
- Design, build, and demonstrate prototype electrolyzers with successively higher hydrogen production capacities and demonstrate in the laboratory (to 5 kW)
- Perform a field demonstration of a 5-kW electrolyzer for PEMFC vehicle refueling

Accomplishments

- Improved performance of anode and cathode materials by optimizing composition and coating techniques
- Explored tube fabrication techniques to develop scalable production method
- Built and demonstrated laboratory-scale electrolyzer capable of producing 700 sccm of hydrogen

- Designed new electrolyzer system targeting 1-kW hydrogen production
- Confirmed tube assembly seals in test sample withstand thermal cycling between ambient and 700°C
- Initiated collaboration with the Connecticut Global Fuel Cell Center for tube fabrication
- Completed construction of 1-kW electrolyzer engineering test bed system and pressure tested to 150 psi at 700°C (tube assemblies will be delivered in August for September test)

Future Directions

- Assemble and test 1-kW electrolyzer
- Evaluate and optimize 1-kW electrolyzer
- Perform long-term testing of components and system
- Evaluate improved anode formulations to minimize carbon deposition
- Design and build 5-kW electrolyzer
- Field test 5-kW system

Introduction

A hydrogen economy will require readily available and affordable hydrogen fuel. Current methods of hydrogen production do not fulfill these requirements. We are working on an electrolyzer system that can provide distributed hydrogen production while taking advantage of the nation's existing natural gas infrastructure. Electrolysis is a promising hydrogen production technology both because of its ability to produce pure hydrogen from water and because it does not require large, centralized plants. Unlike other technologies, the cost of hydrogen production scales well from larger to smaller systems. Electrolysis units could be widely distributed and scaled to meet the hydrogen requirements of different users such as individual households, local fueling stations and industrial facilities. A significant drawback to traditional electrolysis is the large electricity consumption required to convert water to hydrogen and oxygen. The electricity requirements mean such systems are expensive to operate. In addition, if the electricity is provided from coal or gas-fired power plants, electrolytic hydrogen production does not mitigate greenhouse gas emissions.

The concept described in this report is intended to resolve some of the problems associated with electrolytic hydrogen production. By utilizing natural gas in place of air in the anode compartment in a solid oxide electrolyzer, the electricity requirements of the system are greatly reduced. The system has the capability to produce pure hydrogen or hydrogen humidified to levels appropriate for direct use in a PEM fuel cell. With inherent electrochemical compression, the requirement for external compression for pressurization could be reduced. This technology offers numerous advantages for distributed hydrogen production for stationary and transportation hydrogen fuel cells. Our preliminary calculations indicate that using this concept, hydrogen could be produced at a cost competitive with gasoline (on a per gallon equivalent basis) while also lowering carbon dioxide emissions.

Approach

As mentioned above, natural gas is used to depolarize the anode in our solid oxide-based Natural-Gas-Assisted Steam Electrolyzer (NGASE), reducing electricity usage and therefore leading to lower cost operation. We are currently pursuing a system operating in total oxidation mode in which the steam at the cathode is reduced to hydrogen and oxide anions while the methane is oxidized at the anode to carbon dioxide and water. In this mode, hydrogen is produced on the cathode side and is easily converted to a pure hydrogen stream by condensation of the accompanying water vapor. The system could also be modified to operate in partial oxidation mode in which additional hydrogen is produced on the anode side by water-shifting the carbon monoxide produced by methane partial oxidation.

Our approach is to improve system efficiency by the judicious choice of materials and by engineering the system components to maximize durability and safety. In 2003, we are building and testing an experimental system of 1 kW hydrogen production capacity. We plan to utilize this system as a test bed for future systems while also working to optimize materials performance. We are also conducting component durability testing.

Results

Past accomplishments include demonstrating the effectiveness of the use of natural gas in the anode chamber for lowering electricity consumption. It was shown that methane provided a reduction from 1.5 volts with a conventional system (with air in the anode compartment) to 0.5 volts at 1 A/cm^2 current density. An initial test system utilizing a four-tube array was demonstrated that produced 700 sccm of hydrogen at 750°C and 35 psi of steam. Results from this system were used to generate an improved design.

In FY 2003, the continuing resolution caused delays in component procurement and system construction, and the project also experienced some personnel shifts. We have worked to design a new system that should avoid some of the problems encountered in the previous prototype while offering greater flexibility. For example, the last system was limited to operating pressures of 35 psi due to leaks in the pressure vessel. Our current engineering test bed consisting of all necessary system components minus tube assemblies (Figure 1) has been built and tested to 150 psi at a temperature of 700°C and has proven to be leak free. This system is designed to accept arrays of four tubes up to 18 inches long and can be readily modified to accept higher numbers of tubes. Thus, with minimal cost and effort, our hydrogen generating capacity could be increased without the need to build an entirely new system.

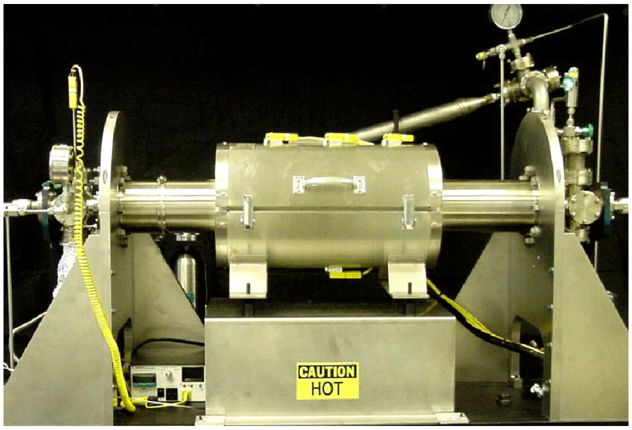

Figure 1. Electrolyzer Engineering Test Bed

In order to address the issue of carbon deposition at the anode, we have begun examining potential improved anode materials. Candidate materials with compositions approximating that of the cermet anode are screened by temperature programmed oxidation-mass spectrometry by placing powders in a quart tube and passing methane through the powder as the temperature is ramped up to 700°C. The gaseous reaction products are analyzed by a residual gas analyzer mass spectrometer. The telltale sign of carbon deposition is the evolution of hydrogen as the methane is converted to carbon and hydrogen. Materials that display reduced carbon deposition tendencies will be further evaluated by single cell testing to mimic actual electrolyzer operating conditions.

We have initiated a collaboration with the Connecticut Global Fuel Cell Center for the fabrication of tubes by an extrusion technique. The Connecticut group has more than ten years experience in tube extrusion, and this will accelerate system development efforts. After the application of electrolyte and cathode coatings, the tubes will be brazed into specially designed flexible electrical isolators (Figure 2). In the previous system, the tubes were connected in parallel, resulting in resistive losses; the new design will allow the tubes to be connected in series to allow reduced current operation. We are working with an industrial vendor to optimize these components.

Conclusions

- We have designed a new electrolyzer system that shows promise for economically attractive distributed hydrogen production.
- The electrolyzer engineering test bed has been assembled and pressure tested to 150 psi at 700°C, and we have confirmed both the pressure vessel seals and the tube assembly seals can

Figure 2. Drawing of Flexible Electrical Isolator

withstand repeated temperature cycling between ambient and 700°C.

- Our new system is designed to be flexible and scalable, allowing increased hydrogen generating capacity without the need to build a new system from the ground up.
- We have initiated a collaboration with the Connecticut Global Fuel Cell Center for fabrication of anode-supported tubes and are working with an industrial vendor for component assembly.
- Carbon deposition at the anode remains a potential challenge that we believe can be solved in the near-term by slight humidification of the methane along with applying a potential to the tubes. We are also carrying out materials studies to evaluate potential improved anode materials.
- We expect to complete the assembly of the current 1-kW electrolyzer system by late August with system testing to commence in September.
- Our system is designed to allow easy scale-up to 5 kW of hydrogen generating capacity.

FY 2003 Publications/Presentations

1. DOE Hydrogen and Fuel Cells 2003 Annual Merit Review, Oral Presentation, A.L. Vance, J.W. Trent, E.F. See, L.P. Martin, R.S. Glass "High-Efficiency Steam Electrolyzer" May 20, 2003.

High-Temperature Solid Oxide Electrolyser System

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Objectives

- Develop and test energy-efficient, regenerative, solid oxide electrolyser cells (SOECs) for hydrogen production from steam using a high temperature heat source
  - Reduce ohmic losses to improve energy efficiency
  - Increase SOEC durability and sealing with regard to thermal cycles
  - Minimize electrolyte thickness
  - Improve material durability in a hydrogen/oxygen/steam environment
- Demonstrate cell performance and associated equipment operation in a flexible test loop
- Optimize stack configuration for incorporation into a full-scale plant
- Test integrated SOEC stacks operating in the electrolysis mode
- Specify and test hydrogen-permeation-resistant materials for high-temperature heat exchangers

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- Q. Cost
- R. System Efficiency
- U. Electricity Costs
- W. High Temperature Materials
- X. Policy and Public Acceptance

Approach

- Develop solid oxide electrolyte, electrode, and catalyst materials optimized for high-temperature steam electrolysis
- Develop a flexible test loop at INEEL for performance testing of single electrolysis cells and cell stacks and for hydrogen permeation testing
- Test single solid oxide electrolysis cells for performance over a range of operating temperatures, gas compositions, and current densities both at Ceramatec and at INEEL
  - Initial testing will be performed on baseline cells, fabricated using existing Ceramatec solid oxide fuel cell (SOFC) technology (Yttria-stabilized zirconia electrolyte-supported cells)

  - Subsequent testing will be performed on cells developed with different electrolyte compositions, electrode-supported cells, various catalysts, etc.
- Develop a high performance electrolysis stack configuration based on the results of the single-cell tests, including high-performance bi-polar plates
- Perform electrolysis testing in realistic cell stacks over a range of operating conditions and system pressures
- Perform high-temperature hydrogen permeation testing of candidate heat exchanger materials

Accomplishments

- Test loop designed, passed safety approvals and placed in operation January 21, 2003
- Single "button" cells tested for performance in electrolysis and fuel cell modes at Ceramatec and at INEEL
- Initial parameters incorporated in conceptual full-scale plant design
- Planning for multi-cell stack testing begun
- Numerical analysis by Argonne National Laboratory under way

Future Directions

- Evaluate alternative electrolytes and catalysts in single-cell testing
- Develop multi-cell stacks and stack testing capability
- Conduct test of multi-cell stacks
- Analyze operation of cells and overall plant with numerical techniques

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Introduction

Of the many methods proposed for hydrogen production, water-splitting is considered ideal because it avoids CO_2 emissions. Two types of water-splitting technologies have been studied: thermochemical and electrolysis. Chemical-reaction-based water-splitting processes are hindered by the extremely corrosive process environment (for example, in the iodine-sulfur process, H_2SO_4 is produced and then dissociated at 850°C). Conventional low-temperature electrolysis of steam results in an unsatisfactory thermal efficiency.

This work is an experimental research project being conducted via a collaboration between the INEEL and Ceramatec, Inc. of Salt Lake City, Utah, to test the high-temperature, electrolytic production of hydrogen from steam using a reversible, solid oxide cell. The research team is designing and testing solid oxide cells for operation in the electrolysis mode, and evaluating materials for the high-temperature heat exchanger, condenser, and other components necessary for producing hydrogen using a high-temperature process heat source plus electrical power. This high-temperature process heat and the electrical power requirement could be supplied simultaneously by a high-temperature nuclear reactor. Operation at high temperature reduces the electrical energy requirement for electrolysis and also increases the thermal efficiency of the power-generating cycle. The high-temperature electrolysis process will utilize heat from a specialized secondary loop carrying a steam/hydrogen mixture. It is expected that with this combination of a high-temperature reactor and high-temperature electrolysis, the process will achieve a thermal conversion efficiency of 40 to 50% while avoiding the challenging chemistry and corrosion issues associated with the thermochemical processes. Planar solid oxide cell technology is being utilized because it has the best potential for high efficiency due to minimized voltage and current losses. INEEL and Ceramatec scientists have been developing planar solid oxide cell technology for the past 20 years.

Approach

Solid oxide cells will be developed and tested for operation in the electrolysis mode. Initial testing will document the performance of single "button" cells, such as the cell shown in Figure 1. Subsequent testing will document the performance of multiple-cell stacks operating in the electrolysis mode. Testing will be performed both at Ceramatec and at INEEL. A logical progression is being followed in the test project. The first cells to be tested were single cells based on existing materials and fabrication technology developed at Ceramatec for production of solid oxide fuel cells. These cells use a relatively thick (~175 µm) electrolyte of yttria- or scandia-stabilized zirconia, with nickel-zirconia cermet anodes and strontium-doped lanthanum manganite cathodes. Additional custom cells with lanthanum gallate electrolyte have been developed and tested. During the second phase of this project, multiple-cell stacks will be developed using the most promising materials identified through the single-cell testing.

In order to carry out the initial phase of the test project at INEEL, a new test loop has been developed for testing of single solid oxide electrolysis cells. A photograph of the setup is shown in Figure 2. It will be modified later for testing of multiple-cell stacks. The test loop is designed for cell operation in the 700-1000ºC temperature range. The following parameters are measured and controlled during testing: cell temperature, anode-side gas flow rate and composition (Ar, H_2, H_2O), inlet and outlet dewpoint temperature, applied cell voltage (±0-1 V differential from open-cell voltage), cell current, area-specific resistance, and hydrogen production rate. This facility is more heavily instrumented (52 channels of instrumentation) than the test facility used at Ceramatec for single-cell testing.

The scope of corrosion / permeation work to be performed in the second and third years of this project will focus on testing of various candidate high-temperature heat exchanger materials over a wide range of temperatures and partial pressures. Effects of permeation barrier treatments such as calorizing, oxide layers, and/or coatings will also be assessed. Candidate materials include Inconel and Hastelloy alloys, as well as ceramics. Permeation test materials will be characterized before and after testing using Scanning Electron Microscopy and Auger Electron Spectroscopy. Rates of permeation will be measured using techniques such as hydrogen permeation current, ultrasonics, and direct measurement of hydrogen leakage by capture of escaping hydrogen (using a containment envelope and carrier gas) and subsequent on-line gas analysis.

Results

Initial testing has been performed using single electrolyte-supported (thick) button cells fabricated by Ceramatec. Results of several representative "button" cell tests are presented in Figures 3 – 6. Figure 3 shows the open-cell potential measured across the reference electrodes of a button cell during heat-up in the INEEL test furnace. The measured values are compared to a prediction obtained from the Nernst equation, which quantifies the ideal open-

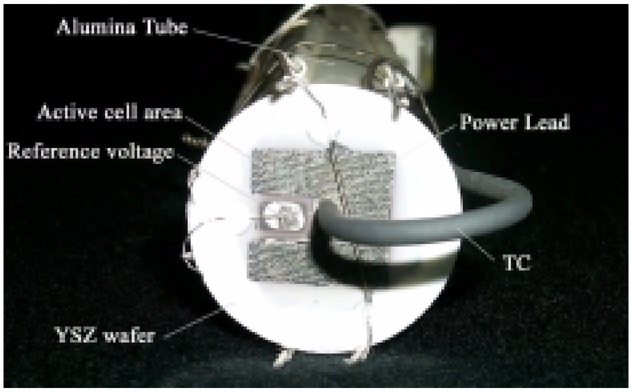

Figure 1. Details of Solid-Oxide Button Cell Fabricated by Ceramatec (TC = thermocouple, YSZ = yttria-stabilized zirconia)

Figure 2. High-Temperature Single-Cell Steam Electrolysis Test Setup at INEEL

circuit potential from thermodynamic principles as a function of cell temperature, gas composition, and system pressure. Agreement between the measured values and the predictions is excellent, instilling confidence in the experiment design. The INEEL test loop is instrumented with precision dewpoint sensors located upstream and downstream of the electrolysis cell, allowing for direct measurement of steam consumption or production in electrolysis or fuel-cell modes, respectively. Figure 4 provides a plot of dewpoint change as a function of electric current for a single-cell test performed at INEEL in both electrolysis and fuel-cell modes. The figure shows both the measurements and a prediction, revealing good agreement. Figure 5 displays the results of a direct current (DC) potential sweep test performed on a scandia-stabilized zirconia-electrolyte cell at INEEL in which a power-supply voltage is applied to the cell in order to force operation over a range of voltages. The results shown in the figure demonstrate reversible operation between the fuel-cell and electrolysis modes of operation. The slope of the potential sweep is highest for large negative current densities where the effects of steam starvation begin to have an effect. A similar figure representing a DC potential sweep test performed at Ceramatec on a lanthanum gallate-electrolyte cell is presented in Figure 6. The figure

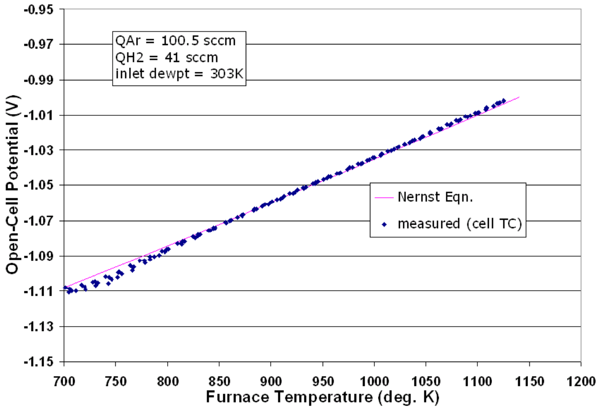

Figure 3. Open-Cell Electrical Potential Measured Across a Button Cell as a Function of Cell Temperature During Heat-up

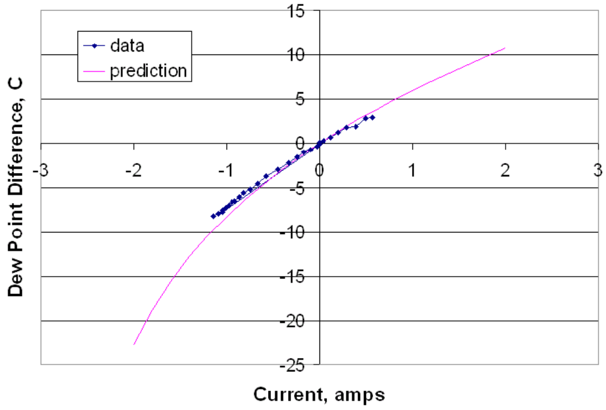

Figure 4. Dew Point Change as a Function of Cell Electric Current, Measurements And Theory

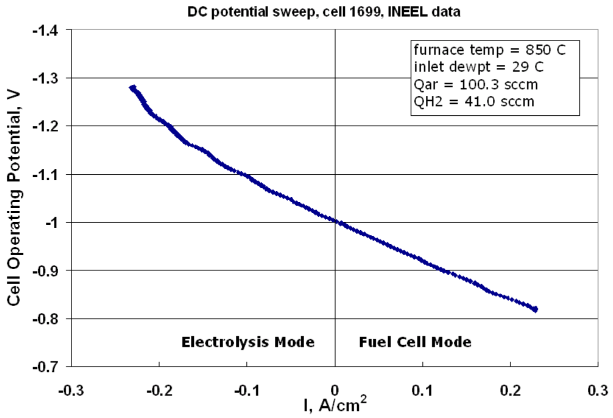

Figure 5. DC Potential Sweep Showing Reversible Operation of a Scandia-Stabilized Zirconia Button Cell Tested at INEEL in Both Fuel-Cell and Electrolysis Modes at 850ºC

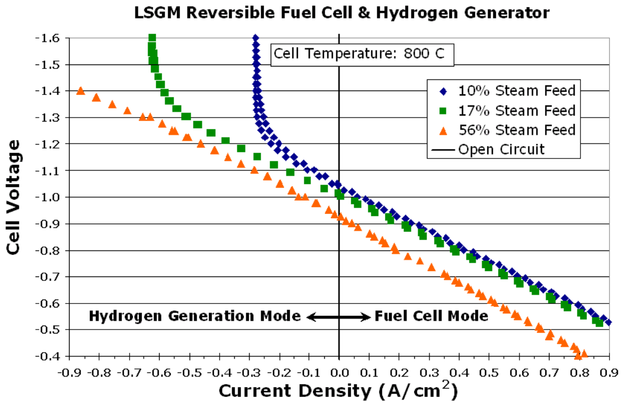

Figure 6. DC Potential Sweep Showing Reversible Operation of a Lanthanum-Gallate Button Cell Tested at Ceramatec in Both Fuel-Cell and Electrolysis Modes at 800ºC (LSGM = lanthanum strontium gallium magnesium oxide)

again demonstrates reversible operation between the fuel-cell and electrolysis modes of operation. It also clearly demonstrates the effects of steam starvation in the electrolysis mode at low steam concentrations. This cell exhibited excellent performance with an area-specific resistance (ASR) of 0.57 Ω-cm^2, indicating low ohmic losses.

Initial results of these single-cell tests are very promising in terms of demonstrating high efficiency high-temperature steam electrolysis using solid oxide cells. Subsequent testing will be focused on testing cells fabricated from alternate materials optimized for the electrolysis application. Long-duration performance tests will also be performed. Stack configurations will be developed and tested.

Conclusions

- High-temperature steam electrolysis using a high-temperature heat source is a viable near-term strategy for large-scale hydrogen production.
- Solid oxide cells represent a logical choice for high-temperature steam electrolysis due to their high operating temperature and high efficiency.
- INEEL and Ceramatec have initiated a research project that is showing promising initial results on the thermoelectric efficiency issues related to the high-temperature electrolysis process.

FY 2003 Publications/Presentations

1. O'Brien, J. E., Herring, J. S., Lessing, P. A., and Stoots, C. M., "High Temperature Steam Electrolysis from Advanced Nuclear Reactors Using Solid Oxide Fuel Cells," presented at the First International Conference on Fuel Cell Science, Engineering and Technology, Rochester, NY, April 21-23, 2003

Thermocatalytic CO_2-free Production of Hydrogen from Hydrocarbon Fuels

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Objectives

- Develop an economically viable process for centralized and distributed production of hydrogen from hydrocarbons with minimal CO_2 emissions
- Improve the catalytic activity of carbon catalysts and process sustainability
- Increase the yield of high-value carbon products and reduce the cost of hydrogen production

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- D. Carbon Dioxide Emissions

Approach

- Produce hydrogen-rich gas via thermocatalytic decomposition of hydrocarbons utilizing a part of the carbon product as a catalyst for the process
- Improve the catalyst activity and process efficiency by continuous activation of carbon particulates in presence of activating agents
- Design, fabricate and test 3-kW_{th} thermocatalytic reactor for CO/CO_2-free production of hydrogen-rich gas and a carbon product from hydrocarbon fuels

Accomplishments

- Demonstrated that the catalyst activity and the process sustainability could be improved by activation of carbon particulates in the presence of small amounts of steam and/or CO_2
- Determined the effect of impurities potentially present in commercial hydrocarbon feedstocks (e.g., H_2S, N_2, moisture, high hydrocarbons) on the process efficiency and the catalyst activity and stability
- Demonstrated the efficient removal of small amounts of CO/CO_2 and olefins from the hydrogen gas via catalytic hydrogenation processes
- Designed, fabricated and tested 3-kW_{th} thermocatalytic reactor using commercial hydrocarbon fuels (pipeline natural gas, commercial propane)
- Conducted reactor modeling and scaling-up studies (in cooperation with industry)
- Evaluated potential markets and new application areas for carbon products

Future Directions

- Optimize the performance of a pyrolytic reformer for distributed production of hydrogen gas with the CO and H_2S content below 10 ppm using commercial hydrocarbon fuels
- Increase the yield of high-value carbon products (>$0.3 per kg) and reduce the cost of hydrogen production (for distributed production applications)
- Conduct system integration studies to increase power density of the pyrolytic reformer and reduce its capital cost

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Introduction

Conventional hydrogen production processes (e.g., steam methane reforming) produce large amounts of CO_2 emissions. One alternative to conventional processes is a single-step thermocatalytic decomposition (TCD) (or pyrolysis) of natural gas (NG) or other hydrocarbon fuels into hydrogen and carbon:

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H^o = 75.6 \text{ kJ/mol } (CH_4)$$

Due to the absence of oxidants (e.g., H_2O and/or O_2), no carbon oxides are formed during the process, thus obviating the need for water gas shift and CO_2 removal stages, which significantly simplifies the process. Pure carbon is produced as a valuable byproduct that can be marketed, thus reducing hydrogen production cost. The technical goals of this research effort are to (1) determine efficient carbon catalysts for methane decomposition process; (2) conduct process engineering development studies, including reactor modeling and scale-up; and (3) characterize carbon byproducts of the process and evaluate their market value.

Approach

The approach is based on TCD of hydrocarbon fuels over high surface area carbon catalysts. The important feature of the process is that the reaction is catalyzed by carbon particulates produced in the process (no external catalyst is required, except for the start-up operation). Carbon catalyst particles circulate between a reactor and a heater, both operating in a fluidized bed regime (similar to industrial fluid coking process). Carbon catalysts exhibit high temperature and sulfur resistance. Due to low endothermicity of the process, the overall CO_2 emissions from the process could be drastically reduced (compared to conventional processes).

Results

The effect of carbon catalyst activation (with small amounts of steam) on the rate of methane decomposition was determined. Figure 1 illustrates the effect of steam treatment of carbon catalyst on its catalytic activity toward methane decomposition. It is evident that the steam treatment of carbon particles resulted in a drastic increase in both catalyst surface area and methane decomposition rate.

It was determined that the presence of small amounts of impurities (H_2S/CH_3SH, CO_2, nitrogen and moisture) potentially present in industrial hydrocarbon fuels is not detrimental to the catalyst activity and process efficiency. These impurities may result in contamination of hydrogen with trace

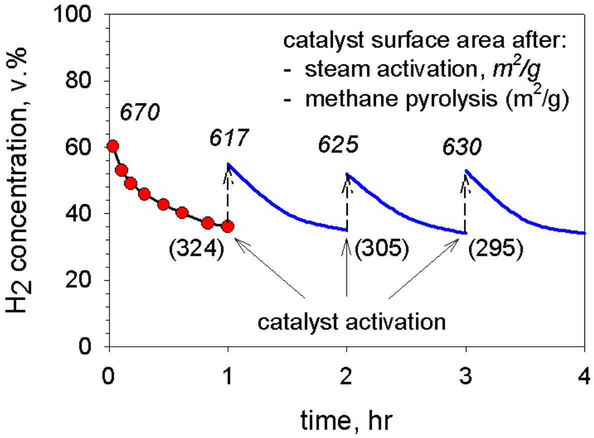

Figure 1. TCD of Methane over Carbon Catalyst in Cyclic Pyrolysis-Activation Process. $T_{pyr.}$=850°, $T_{act.}$=900°C (*x*-axis shows pyrolysis time only)

amounts of CO and H_2S that can be efficiently removed from hydrogen gas via catalytic methanation and ZnO scrubbing techniques.

A 3-kW_{th} thermocatalytic reactor for production of hydrogen-rich gas and carbon from industrial-grade feedstocks (pipeline NG and commercial propane) was fabricated and tested (Figure 2). The average concentration of hydrogen in the pyrolysis gas was 45-72 v.% (the balance, predominantly methane), depending on the feedstock and temperature. After methanation, CO/CO_2 concentrations in H_2 dropped to <10 ppm level.

The studies on modeling and scale-up of the fluidized bed reactor were conducted (in cooperation with Reaction Engineering International—REI). A three-phase model to describe bubbling fluidized bed reactor containing carbon particles was developed (Figure 3). The model predictions were in reasonable agreement with the experimental measurements.

Collaborative efforts with industry (MER Corporation, Universal Oil Products—UOP) and national labs (Lawrence Livermore National Laboratory—LLNL) in evaluating markets and identifying potential application areas for carbon products were conducted. The market for carbon products was estimated at 4-5 million ton/year level with carbon selling price at approximately $300/ton.

Figure 2. Experimental Set-up with 3-kW_{th} Thermocatalytic Reactor

Conclusions

It was demonstrated that the catalyst activity toward methane decomposition and process sustainability could be significantly improved via continuous activation of carbon catalysts in the presence of small amounts of steam (the activation occurs outside the pyrolyzer). The process was designed where carbon particulates circulate between a hydrocarbon pyrolyzer and a catalyst heater, both operating in fluidized bed regime (similar to industrial fluid coking process). The impurities (CO_2, H_2S/CH_3SH, moisture) present in commercial hydrocarbon fuels are not detrimental to catalyst activity and process efficiency, and could be efficiently removed from hydrogen gas. A 3-kW_{th} thermocatalytic reactor for CO/CO_2-free production of hydrogen-rich gas was designed, fabricated and tested using pipeline NG and commercial propane as feedstocks. The market for carbon products was estimated at 4-5 million ton/year level with carbon selling price at approximately $300/ton. FSEC participated in several collaborative research efforts with industry, national labs and universities (MER

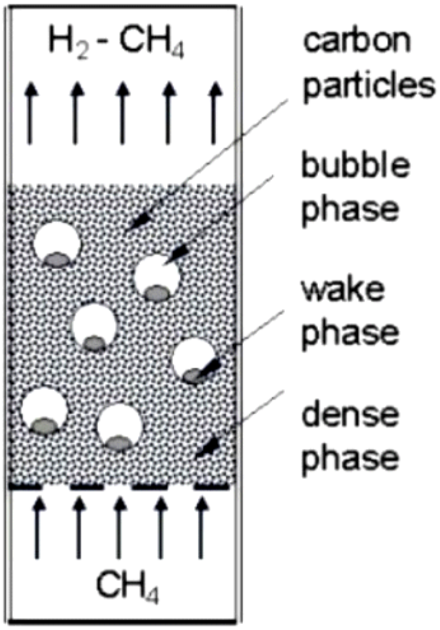

Figure 3. Modeling of Three-Phase Bubbling Fluidized Bed Reactor Containing Carbon Particles

Corporation, REI, National Renewable Energy Laboratory, UOP, LLNL, Florida Institute of Technology).

FY 2003 Publications/Presentations

1. Muradov, N. "Emission-free Fuel Reformers for Mobile and Portable Fuel Cell Applications", *Journal of Power Sources*, v.118, 1-2, 320-324 (2003)
2. Muradov, N. "On-site Production of Hydrogen from Hydrocarbon Fuels with Minimal Greenhouse Gas Emissions", *Symposium: Hydrogen Energy for 21st Century, Amer. Chem. Soc. Meeting*, New Orleans, 2003
3. Muradov, N. "Catalytic Conditioning of Sulfurous Hydrocarbon Fuels for Fuel Cell Applications", *Symposium: Fuel Clean-up Considerations for Fuel Cells, Amer. Chem. Soc. Meeting*, New Orleans, 2003
4. Muradov, N., T-Raissi, A. "Hydrogen Production via Catalytic Reformation of Low-quality Methane Containing Feedstocks", *HYPOTHESIS*, Italy, 2003
5. Muradov, N., Smith, F. "Thermocatalytic Hydrogen Production from Natural Gas with Drastically Reduced CO_2 Emissions", *HYPOTHESIS*, Italy, 2003
6. Muradov, N. and Schwitter, A. "Formation of Conical Carbon Structures on Vapor-grown Carbon Filaments", *Nano Letters*, v.2, 673 (2002)
7. Muradov, N. "Low-emission Fuel Reformers for Fuel Cell Applications", *14th World Hydrogen Energy Conference*, Montreal, Canada, 2002
8. Muradov, N. "Emission-free Fuel Reformers for Fuel Cell Applications", *Fuel Cells, Science and Technology 2002*, Amsterdam, Netherlands, 2002
9. Muradov, N. "Thermocatalytic CO_2-free Production of Hydrogen from Hydrocarbon Fuels", *DOE Annual Hydrogen Prog. Rev. Meeting*, Golden, 2002

Special Recognitions & Awards/Patents Issued

1. University of Central Florida Research Incentive Award, 2003
2. Muradov, N. *U.S. Patent Application No. 60/194,828* "Thermocatalytic Process for CO_2-free Production of Hydrogen and Carbon from Hydrocarbons" (2002)
3. Linkous, C., Muradov, N. *U.S. Patent No. 6,572,829 B2* "Closed Cycle Photocatalytic Process for Decomposition of Hydrogen Sulfide to its Constituent Elements" (2003)

Analysis of Solar Thermochemical Water-Splitting Cycles for Hydrogen Production

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Objectives

- Analyze thermochemical water-splitting cycles (TCWSCs) suitable for solar interface from the viewpoint of thermodynamics, chemical process engineering, costs and their potential environmental impact.
- Develop a more precise method for determining the thermal efficiency of TCWSCs.
- Build chemical process engineering flowsheets for prospective solar-driven TCWSCs.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- V. High- and Ultra-High-Temperature Thermochemical Technology
- W. High-Temperature Materials
- Y. Solar Capital Cost

Approach

- Review all published papers, reports, patents, etc. in the past 25^+ years that relate to thermochemical water-splitting cycles, in general, and solar driven cycles, in particular.
- Use FactSage^{TM} program to perform chemical equilibrium calculations.
- Employ HYSYS/ASPEN Plus chemical process simulation (CPS) program for developing process flowsheet, process analyses and optimization.
- Compare the performance characteristics and costs of the University of Tokyo-3 (UT-3) and sulfur-iodine (S-I) TCWSCs.
- Identify processes that especially benefit from the solar interface.
- Use chemical process flowsheet analysis to identify new processes/cycles or modifications of the existing cycles that improve performance and facilitate better interface with solar heat source.

Accomplishments

- Examined cycle efficiency calculation methods and developed a technique based on chemical process simulation flowsheet (see list of publications).
- Used HYSYS CPS to analyze the sulfuric acid decomposition process of a solar driven sulfur-iodine TCWSC.

- Developed two new flowsheets for decomposing sulfuric acid in the solar based S-I cycle (see list of publications).
- Completed flowsheet simulation of sulfuric acid purification and decomposition using HYSYS steady-state processor.
- Evaluated kinetic models for sulfur trioxide decomposition using HYSYS simulation tool.
- Performed thermodynamics analyses of the decomposition of sulfuric acid and sulfur trioxide at various temperatures and pressures (see list of publications).
- Developed a new Sulfur-Ammonia (S-A) TCWSC based on sulfuric acid decomposition.

Future Directions

- Develop and optimize a completed flowsheet for the S-I cycle and precisely determine its thermal efficiency and costs.
- Analyze purification process of aqueous hydroiodic acid (HI) solution.
- Carry out Aspen Plus process flowsheet analysis of separation of HI and H_2SO_4 and investigate the possibility of a newer and simpler process scheme.
- Perform thermodynamic calculations involving HI decomposition and the $SO_2 + I_2$ reaction.
- Determine phase equilibrium involving HI and H_2SO_4.

Introduction

In the course of the past several decades, many thermochemical cycles have been devised for production of hydrogen from water. It has been shown that thermochemical water splitting cycles (TCWSCs) have potential to deliver overall system efficiencies in excess of 40%. Among the most studied TCWSCs are sulfur-halogen cycles. Figure 1 depicts a simple schematic diagram of the sulfur-halogen TCWSCs. Presently there are two potential high temperature heat sources available for use with thermochemical processes. They are solar thermal concentrator and central receiver systems, and nuclear reactors (i.*e.* high temperature gas-cooled reactors, HTGR). The U.S. DOE, under the Nuclear Energy Research Initiative (NERI) Program, has funded several efforts aimed at hydrogen production using nuclear power.

One major program is underway at General Atomics (GA) Corp., in collaboration with the University of Kentucky (UK) and Sandia National Laboratories (SNL), to assess the technoeconomics of H_2 production using HTGR. GA/UK/SNL reports provided a starting point for this evaluation of thermochemical water-splitting cycles suitable for solar interface and capable of providing efficient and cost-effective means of H_2 production from water. After analyzing more than 100 different thermochemical water splitting cycles, the GA/UK/SNL study narrowed the prospective cycles to two; namely, the University of Tokyo's UT-3 and GA's Sulfur-Iodine cycle. At FSEC, we have selected and analyzed, in detail, three thermochemical processes. They are 1) sulfur family cycles, especially GA's S-I cycle; 2) the UT-3 cycle; and 3) the SynMet process developed at the Paul Scherrer Institute (PSI), Switzerland.

Approach

Our approach was to develop detailed flowsheets of the candidate TCWSCs and processes. We have considered the following systems:

i. Bunsen reaction involving iodine and thermal decomposition of HI. As depicted in Figure 1, in addition to the sulfuric acid decomposition step, the following reactions are employed:

$$SO_2 + I_2 + 2H_2O = 2HI(aq) + H_2SO_4\,(aq)$$

followed by thermal decomposition of hydroiodic acid:

$2HI = H_2 + I_2$

This is the General Atomics process with the revised cycle having improved energetics and an overall efficiency of about 50%. A variation of this TCWSC is the so-called Bowman-Westinghouse cycle that employs a reaction involving bromine (instead of iodine) and electrolysis of hydrobromic acid (in lieu of thermal decomposition of HI). The electrolytic decomposition of HBr requires a cell voltage of about 0.80 V (for acid concentration of 75 wt%).

One problem with the Westinghouse cycle involves the pH effects during electrolysis of sulfur dioxide in aqueous solution. At low solution pH, sulfur forms instead of hydrogen. To avoid sulfur formation, one has to maintain a high solution pH that requires a reduction in acid concentration in the solution. Low acid flow rates translate into low hydrogen evolution rates. In summary, we note that the hydrogen production rate depends on the solution pH, while pH is dependent on sulfur dioxide concentration. To avoid sulfur formation, the electrolytic process has to maintain low acid concentration levels to keep pH levels high. This in turn leads to a decrease in H_2 production rate. Low sulfuric acid concentration will also require a more intensive and costly acid separation and concentration step, reducing the efficiency of H_2SO_4 decomposition to sulfur dioxide and oxygen (see Figure 1). The acid decomposition step consumes a major portion of the input energy to the cycle.

ii.UT-3 thermochemical cycle. This thermochemical hydrogen production cycle has been developed by Kameyama and Yoshida (at the University of Tokyo). The UT-3 process is one of the most studied thermochemical hydrogen production cycles in the world. It should be noted that the UT-3 process is being developed for coupling to nuclear power reactors. The reported cycle efficiency is in the range of 40 to 50%. The cycle involves the following four gas-solid reactions:

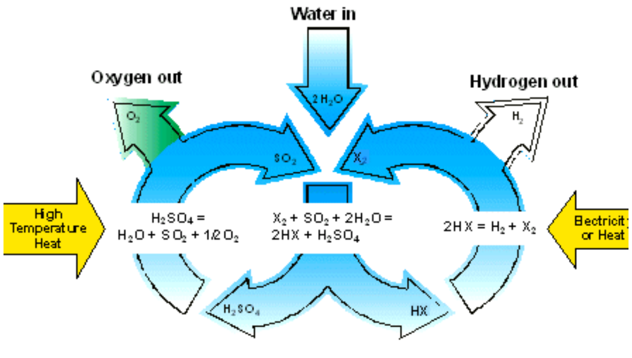

Figure 1. Schematic Diagram of Sulfur-Halogen Cycle (X= iodine or bromine)

$CaBr_2 (s) + H_2O (g) = CaO (s) + 2HBr (g)(1170 K)(1)$

$CaO (s) + Br_2 (g) = CaBr_2 (s) + ½ O_2 (g)(700 K) (2)$

$Fe_3O_4 (s) + 8HBr (g) = 3FeBr_2 (s) + 4H_2O (g) + Br_2 (g)(130 K) (3)$

$3FeBr_2 (s) + 4H_2O (g) = Fe_3O_4 (s) + 6HBr (g) + H_2 (g)(810 K) (4)$

Reaction (1) has been the slowest step, kinetically, amongst the four reactions; thus, it is rate-limiting for the whole cycle. Since it is necessary that all of the reactions proceed at the same rate for continuous operation of the cycle, the slow rate of hydrolysis of calcium bromide adversely affects the whole process efficiency. Another undesirable feature of the UT-3 cycle is that it is a gas-solid type process consisting of a pair of hydrolysis (endothermic) and Br reduction (exothermic) reactions that occur in four series reactors. In order to conduct these processes as in fixed bed reactors, the gases must alternatively flow in opposite directions. In other words, a given reactor must run an endothermic reaction in one direction for about two hours and then an exothermic one in the opposite direction for the next two hours, and so forth.

The UT-3 cycle has been investigated extensively for almost 25 years since it was first proposed in 1978. It has also been fully detailed in flowsheets, and many issues related to the reaction chemistry and kinetics of individual processes, as well as the process separation issues, have been studied in detail. The overall efficiency of the improved adiabatic UT-3 process has been reported as 40% to 50%. However, difficulties remain with UT-3 cycle requiring further improvements. Examples include 1) heat-transfer and temperature control - reactions 1 and 4 are hydrolytic reactions, which require energy input, while reactions 2 and 3 are exothermic, requiring heat removal from the reactors; 2) steady-state operation - circulation time period for the UT-3 cycle has been reported to be two hours; 3) separation issues - to cool down exothermic reactors and sweep the reaction products out of reaction zones, excess steam is needed; 4) packed reactor design; 5) process lifetime issues; etc.

iii. Zn/ZnO process. This is the so-called "SynMet" process developed at PSI. The process combines ZnO-reduction and CH_4-reforming within a solar reactor. It consists of a gas-particle vortex flow confined to a solar cavity receiver that is exposed to concentrated solar irradiation. A 5-kW reactor has been built at PSI and subjected to tests in a high-flux solar furnace. Natural gas is used as a reducing agent to process ZnO according to the following overall reaction:

$ZnO + CH_4 = Zn + 2H_2 + CO$(5)

The process reforms methane in the absence of catalysts and is being optimized to produce syngas especially suited for methanol synthesis, and co-production of Zn and syngas avoids CO_2 emissions in the traditional carbothermal reduction of ZnO. Even though the PSI process is the only system developed for direct solar interface, it is not, however, a typical TCWSC, per se.

Results

In order to mitigate problems discussed above, a new sulfur-ammonia cycle has been conceived that is a better fit to solar power source and does not suffer from acid solubility issues. A schematic diagram of the cycle is depicted in Figure 2. A flowsheet of the cycle is given in Figure 3. Ammonium sulfite is fed to a photocatalytic reactor, where sulfite ions are oxidized into sulfate ions while water is reduced to H_2. Ammonium sulfate is then decomposed into ammonia gas and, at the same time, water also boils off. Through the decomposer, liquid sulfuric acid is introduced into the acid vaporizer to generate gaseous sulfur trioxide and water. The product sulfuric trioxide is then reduced to produce sulfur dioxide gas and oxygen in a reduction reactor. Small amounts of sulfuric acid remaining can be separated from the gaseous mixture containing sulfur dioxide, oxygen and water with an acid separator. Sulfuric acid so separated is then recycled, and sulfur dioxide and oxygen are mixed with ammonia and chemically adsorbed to produce ammonium sulfite, which is then fed into the photocatalytic reactor to begin a new cycle.

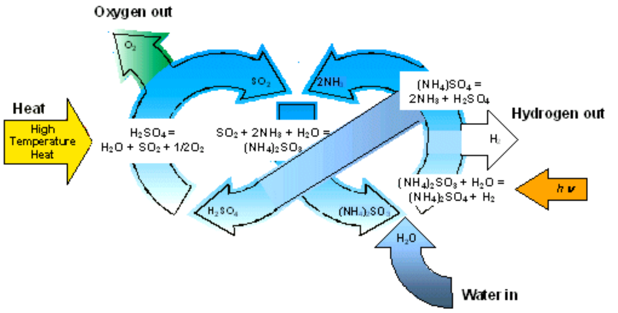

Figure 2. Schematic Diagram of Sulfur-Ammonia Cycle

In the adsorption unit, oxygen is separated from the stream. The chemical reactions involved in the proposed sulfur-ammonia cycle are:

$(NH_4)_2SO_3(a) + H_2O$Æ $(NH_4)_2SO_4(a) + H_2(g)$ 80°C
(photocatalytic step)(6)

$(NH_4)_2SO_4(a)$ Æ $2NH_3(g) + H_2SO_4(l)$ 350°C
(thermochemical step)(7)

$H_2SO_4(l)$ Æ $SO_3(g) + H_2O(g)$400°C
(thermochemical step)(8)

$SO_3(g)$Æ $SO_2(g) + 1/2O_2(g)$850°C
(thermochemical step)(9)

$SO_2(g)+2NH_3(g) + H_2O$ Æ $(NH_4)_2SO_3(a)$ 25°C
(chemical adsorption)(10)

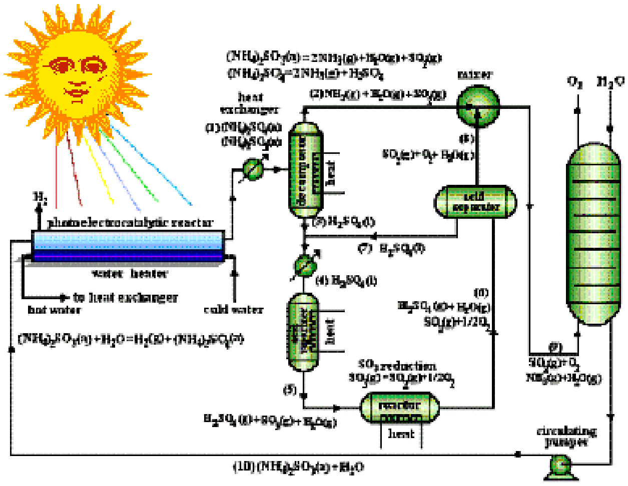

Figure 3. Process Flowsheet for the Proposed Sulfur-Ammonia Cycle

Among these reactions, Reactions (6), (7) and (10) are unique to this new cycle. Reactions (8) and (9) are common to all sulfur family cycles.

If reaction (6) is carried out at a temperature of 80 ~ 90°C, the concentration of ammonium sulfate is about 50 wt% (assuming complete conversion of sulfite to sulfate ions). This concentration is six times higher than in the Bowman-Westinghouse cycle. Since pH in ammonium sulfate or ammonium sulfite solutions is higher than that of pure sulfuric acid or sulfurous acid at the same concentration of anions, sulfite ion oxidation can be conducted in a higher concentration solution without elemental sulfur repercussion. Furthermore, higher sulfuric acid concentration will ease acid separation and concentration as well as improve process energetics. Moreover, increased acid concentration will increase the sulfite ion oxidation rate. Interestingly, the solubilities of sulfite and sulfate ions are comparable at 30°C. However, at temperatures higher than 30°C, ammonium sulfite has higher solubility in water than ammonium sulfate. If reaction (6) is operated at 80°C, the concentration of sulfite ions becomes higher than sulfate ions, thus increasing the oxidation rate.

The energy required to separate the products of reaction (7), i.e. ammonia and sulfuric acid, can be provided by reaction (10), so there is no net energy input. This is not, however, the case with the S-I cycle that requires energy input for HI decomposition. The S-A cycle is well suited to solar input as a heat source and ultraviolet (UV) light. The UV part of solar spectrum is of great value for the photolytic and/or photocatalytic redox reactions. In the photocatalytic reactor, sulfite ions are oxidized to sulfate ions while hydrogen is generated. The photoreactor consists of two segments. The first layer adsorbs UV light, promoting a redox reaction. Because neither sulfite nor sulfate can adsorb visible light, a second under-layer can be used to adsorb concentrated long wavelength light, heating and decomposing sulfur trioxide to sulfur dioxide.

Conclusions

TCWSCs employing solar energy as a heat source can be attractive due to their relatively higher efficiency. The UT-3 cycle is a pure thermochemical process that has been under investigation for close to 25 years. Bowman-Westinghouse sulfur is a hybrid cycle in which an electrolytic process and a thermal decomposition of sulfuric acid are combined to co-produce hydrogen and oxygen. The main drawback of the Bowman-Westinghouse cycle is that the electrolysis step requires low concentration of sulfuric acid, leading to higher energy consumption in the acid concentration and separation process. A new sulfur-ammonia thermochemical cycle was proposed for decomposing water into hydrogen and oxygen. The cycle consists of three steps: 1) photocatalytic oxidation of ammonium sulfite to generate ammonium sulfate while water is reduced to hydrogen utilizing both thermal and UV portion of the solar spectrum; 2) ammonium sulfate decomposition into ammonia and sulfuric acid, with the latter undergoing the same reduction process as that in the Bowman-Westinghouse sulfur cycle; and 3) chemical co-adsorption of ammonia and sulfur dioxide to produce ammonium sulfite, which is then recycled to produce H_2 and ammonium sulfate.

The new cycle has the potential for achieving high overall efficiency by using readily available and inexpensive chemicals. Solar energy is used as a heat source, and UV portion is utilized for a photocatalytic redox reaction. Prior experimental results obtained at FSEC indicate that photolytic and/or photocatalytic oxidation of sulfite ions occurs at acceptable rates with no occurrence of side reactions.

FY 2003 Publications/Presentations

1. Muradov, N.Z. and A. T-Raissi, "Hydrogen Production via Catalytic Reformation of Unconventional Methane Containing Feedstocks," Paper submitted for presentation and publication at the HYPOTHESIS Symposium held in Porto Conte, Italy, September 7-10, 2003.
2. T-Raissi, A. "Photocatalytic Oxidation of Terpenic VOCs," Invited paper submitted for presentation at the 2nd AOP (II EPOA) International Conference held at Campinas, Brazil, August 25-27, 2003.
3. T-Raissi, A. " Hydrogen Storage in Ammonia and Aminoborane Complexes," Presentation at the 2003 Hydrogen Program Annual Review, Berkeley, CA , May 21, 2003.

4. T-Raissi, A. "System Analysis of H_2 Production and Utilization at KSC," Presentation at the NASA Hydrogen Review Meeting at Tampa, FL, January 15, 2003.

5. T-Raissi, A. "Analysis of Alternate Hydrogen Production Processes," Presentation at the NASA Hydrogen Review Meeting at Tampa, FL, January 15, 2003.

6. T-Raissi, A. "Hydrogen Storage in Amine Borane Complexes," Presentation at the NASA Hydrogen Review Meeting at Tampa, FL, January 15, 2003.

7. T-Raissi, A. and C. Huang, "Technical Analysis of Hydrogen Production," A semi-annual contract report to U.S. DOE under DEFC3600GO10603, February 2003.

8. T-Raissi, A., et al. "Task IV-2, System Analysis of Hydrogen Production and Utilization at KSC," Interim contract report on NASA NAG3-2751, January 2003.

9. Huang, C. and A. T-Raissi, "Task IV-6, Analysis of Alternative Hydrogen Production Processes," Interim contract report on NASA NAG3-2751, January 2003.

10. T-Raissi, A., et al. "Task III-3, Hydrogen Storage in Amine Borane Complexes, Part II - Molecular Modeling of Hydrogenation of Borazine to Cyclotriborazane," Interim contract report on NASA NAG3-2751, January 2003.

11. T-Raissi, A. "Cryogenics Tasks, NASA KSC Update and System Analysis, and Analysis of Alternate Hydrogen Production Processes," Presentation at the NASA-GRC Program Review Meeting, Cleveland, OH, September 3-4, 2002.

12. T-Raissi, A. "Chemical Storage - Overview," Keynote speech at the DOE Hydrogen Storage Workshop, Argonne National Laboratory, Argonne, IL, August 14, 2002.

13. T-Raissi, A. "System Analysis of H_2 Production Concepts - Overall System Analysis," Presentation at the NASA-Hydrogen Research at Florida Universities Program Review Meeting held at FSEC, July 16-17, 2002.

Special Recognitions & Awards/Patents Issued

1. T-Raissi, A., et al. "Apparatus for decoupled thermo-photocatalytic pollution control," U.S. Patent No. 6,551,561, April 22, 2003.

2. T-Raissi, A., et al. "Apparatus and method for low flux photocatalytic pollution control," U.S. Patent No. 6,531,035, March 11, 2003.

3. Recipient of 2002-03 I&C Award for Excellence in Research, UCF.

4. Director of the FSEC's Hydrogen R&D Division as of August 31, 2002.

Hydrogen Composite Tank Project

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Objectives

- Develop and validate 5,000 psi storage tanks - tank efficiency: 7.5 - 8.5 wt%
- Validate 5,000 psi in-tank pressure regulators - system efficiency: 5.7 wt%
- Develop and validate 10,000 psi storage tanks - tank efficiency: 6 - 6.5 wt%
- Develop and validate 10,000 psi storage systems - system efficiency: 4.5 wt%
- Optimize designs and processes to achieve the DOE cost targets

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- D. Durability
- E. Refueling Time
- H. Sufficient Fuel Storage for Acceptable Vehicle Range
- K. Balance-of-Plant (BOP) Components

Approach

- Learn from the successful 100-year history of pressure vessels (industrial, aerospace, CNG)
- Optimize materials, design, and process to improve weight efficiency (5,000 psi tanks)
- Develop & validate volumetrically efficient storage systems (10,000 psi tanks)
- Improve system efficiency (in-tank regulator, balance-of-plant components)
- Validate and certify components (codes & standards, regulatory approvals)
- Work towards cost reduction (technology, economies of scale)

Accomplishments

- Designed industry's first hydrogen 10,000 psi (700 bar) tanks
- Successfully completed validation per European Integrated Hydrogen Project (E.I.H.P.) (Draft 7) and obtained certification (TÜV German Pressure Vessel Code DBV P.18)
- Designed and developed industry's first hydrogen 10,000 psi (700 bar) in-tank pressure regulation system, pressure relief device, manual valve and other balance-of-plant components

- Delivered fully-validated 10,000 psi hydrogen storage systems for automotive original equipment manufacturer (OEM) use
- Demonstrated fast refueling at the rate of 1 kg/minute

Future Directions

- Perform further structural optimization of 10,000 psi tanks in view of improving gravimetric and volumetric efficiencies
- Evaluate lower cost materials to reduce cost
- Evaluate the application of integrated sensors for in-situ structural monitoring
- Evaluate other means of improving volumetric efficiency

Introduction

Possible approaches to hydrogen storage include compression, liquefaction, chemical storage, metal hydrides, and adsorption. Although each storage method has desirable attributes, no approach currently satisfies all the efficiency, size, weight, cost, durability and safety requirements for transportation use. Research continues in these areas, with progress being made in all approaches. Improvements in the energy densities of hydrogen storage systems, reductions in cost, and increased compatibility with available and forecasted systems are required before viable hydrogen energy use will be realized.

The objective of this hydrogen composite tank project was to design, develop, validate, fabricate, and manufacture hydrogen fuel tanks and in-tank regulators along with vehicle integration brackets and isolators and have them delivered to Virginia Tech University and Texas Tech University in support of the Future Truck competition. The 5,000 and 10,000 psi systems developed in this project provide an attractive near-term and possibly medium-term solution for hydrogen storage. The currently validated QUANTUM "TriShield" tank technology meets the usable specific energy, usable energy density, cycle life, refueling rate and limit of loss of hydrogen targets of the DOE for 2005 and approaches the targets for 2010. While cost remains challenging, significant cost reductions are possible with further optimization coupled with economies of scale.

Approach

The QUANTUM advanced composite tank technology incorporates a "TriShield^{TM}" design philosophy. The QUANTUM Type IV TriShield^{TM} cylinder, as illustrated in Figure 1, is comprised of a seamless, one piece, permeation resistant, cross-linked, ultra-high molecular weight polymer liner that is over wrapped with multiple layers of carbon fiber/epoxy laminate and a proprietary external protective layer for impact resistance. TriShield^{TM} hydrogen tanks feature a single-boss opening to minimize leak paths. The path to achieving high gravimetric efficiency is optimization in materials, design and processes.

The TriShield^{TM} hydrogen tank is designed to accommodate QUANTUM's patented in-tank regulator, which confines high gas pressures within

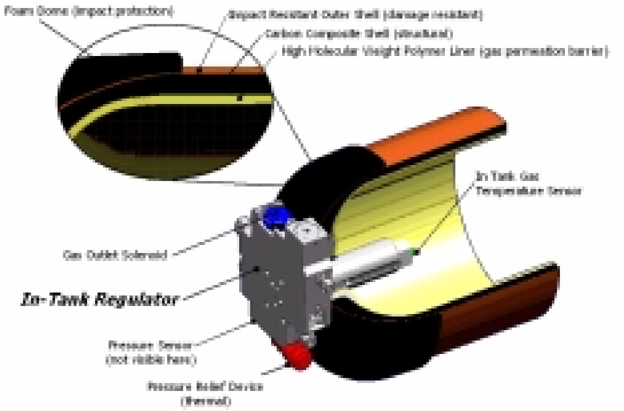

Figure 1. QUANTUM Compressed Hydrogen Storage

the tank and, thus, eliminates high-pressure fuel lines downstream of the fuel storage subsystem. The system cost can be significantly reduced by combining a check valve to assist tank filling, fuel filtering, fuel tank pressure and temperature monitoring, pressure relief device and tank lock-off in the regulation module. Figure 2 shows a complete storage system including storage tanks and balance-of-plant components.

Results

The 5,000 and 10,000-psi tanks developed by QUANTUM Technologies have been validated to meet the requirements of DOT FMVSS304, NGV2-2000 (both modified for hydrogen) and draft E.I.H.P standard. To ensure safety and reliability in an automotive service environment, a number of performance tests have been completed: Burst Tests (2.35 safety margin), Fatigue (45,000 pressure cycles at ambient temperature), Extreme Temperature, Hydrogen Cycling, Bonfire, Severe Drop Impact Test, Flaw Tolerance, Acid Environment, Gunfire Penetration, Accelerated Stress, Permeation and Material Tests. The developed "in-tank regulators" meet the requirements of NGV3.1 and E.I.H.P.

Figure 3 shows the relevance of various components to system-level efficiencies at 5,000 and 10,000 psi storage pressure. It is clear that optimization of the balance-of-plant components is critical to achieve system-level gravimetric efficiency, especially when multiple tanks are utilized. Storage at 10,000 psi provides important volumetric advantages without significant energy penalty (see Figure 4).

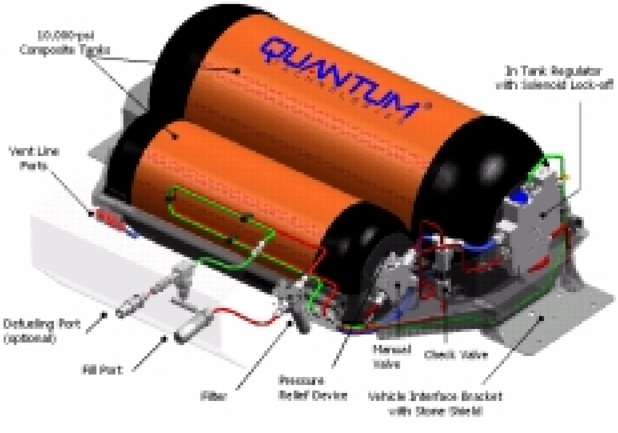

Figure 2. Compressed Hydrogen Storage System

Table 1 shows the DOE FreedomCAR targets for 2005 and 2010, in relation to the current status of 10,000 psi storage. It can be seen that the biggest challenge is cost, which needs to be reduced by a factor of 20. It is anticipated that cost reduction will include optimization through technology (50 to 75% reduction), followed by economies of scale (factor of 10).

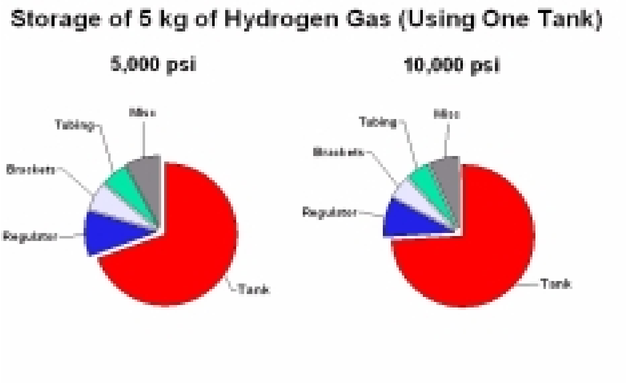

Figure 3. System-Level Weight Efficiency

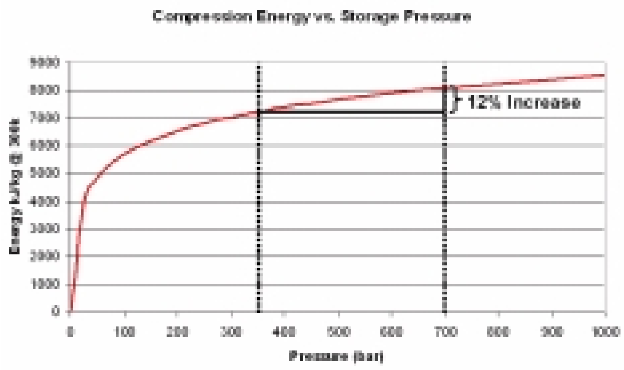

Figure 4. Volumetric Efficiency: 5,000 psi vs 10,000 psi Storage

Table 1. DOE FreedomCAR Targets vs. Status

Parameter	2005	2010	Status
Usable Specific Energy (kWh/kg)	1.5	2	1.9
Usable Energy Density (kWh/L)	1.2	1.5	1.3
Cost ($/kWh)	6	4	114
Cycle Life (1/4 to full Cycles)	500	1,000	15,000 - 45,000
Refueling Rate (kg H_2/min)	0.5	1.5	1
Loss of Usable Hydrogen (grams)	1	0.1	0.0006

Conclusions

- The 5,000 psi and 10,000 psi compressed hydrogen storage systems developed and validated in this project provide a convenient near-term solution, and are currently available and successfully deployed on fuel cell vehicles.
- DOE 2005 performance targets are achievable.
- Storage is a significant cost factor in overall fuel cell system cost.
- Carbon fiber and stainless steel hardware costs represent over 90% of the costs.
- Design and process improvements to address storage tank costs are on-going.

FY 2003 Publications/Presentations

1. Andris R. Abele, "Advanced Hydrogen Storage Systems", Hydrogen and Fuel Cells 2003 Conference and Trade Show, Vancouver (June 2003).
2. Brian Jenkins, "Advanced Hydrogen Fuel Systems for Fuel Cell Vehicles", 1st International Conference on Fuel Cell Science & Energy Technology (April 2003).

Development of a Compressed Hydrogen Gas Integrated Storage System (CH2-ISS) for Fuel Cell Vehicles

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Subcontractor: General Dynamics Armament & Technical Products (GDATP), Lincoln, Nebraska

Objectives

Advance the technology elements required to develop a semi-conformal, Compressed Hydrogen Gas Integrated Storage System (CH2-ISS) for light-duty fuel cell electric vehicles (FCEV) by conducting engineering research as follows:

- Develop materials and treatments to reduce hydrogen gas permeation through tank liners
- Develop an optimized carbon fiber/epoxy resin tank overwrap to support storage tank design with improved gravimetric energy density construction
- Determine alternative methods and materials for manufacture of the integrated storage system

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- H. Sufficient Fuel Storage for Acceptable Vehicle Range
- I. Materials
- K. Balance-of-Plant (BOP) Components

Approach

- Develop baseline CH2-ISS design consistent with packaging and driving range requirements
- Develop tank liner materials and surface treatments and measure hydrogen gas permeation
- Build and performance test all-carbon overwrap tanks with alternative toughened epoxy resin formulations
- Evaluate alternative materials and designs for production of the ISS shell and unitary gas control module
- Develop CH2-ISS vehicle packing interface design for notional FCEV applications

Accomplishments

- Continued evaluation of low permeation tank liner materials and developed a test unit for accurately measuring gas permeation

- Continued work on improving tank gravimetric energy density through development of toughened epoxy resins
- Continued evaluation of alternative materials for constructing the CH2-ISS outer shell; purchased material coupons and developed preliminary design of test fixture
- Continued work on the unitary gas control module (UGCM); downselected one of two alternative designs for prototype development
- Initiated storage system-vehicle interface technology task; developed idea of storage-to-vehicle attachment system (Crash Management System) that both preserves vehicle "crumple zone" while reducing impact load to the storage unit; established CH2-ISS size and operating pressure to support FCEV with 300+ mile driving range

Future Directions

- Build and evaluate performance of storage tanks with improved gravimetric energy density
- Conduct flammability and impact tests on alternative CH2-ISS outer shell materials; select optimum
- Design, build, test and evaluate unitary gas control system
- Design the CH2-ISS with sufficient fuel storage for 300+ mile driving range
- Detail storage-to-vehicle interface Crash Management System design

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Introduction

The storage of compressed hydrogen gas (CH2) poses challenges in the areas of relatively low energy density, system cost, crashworthiness, and vehicle packaging. A solution to these challenges is offered by the Integrated Storage System (ISS) technology (U.S. Patent No. 6,257,360 issued July 2001) jointly developed by Johns Hopkins University Applied Physics Laboratory (JHU/APL) and General Dynamic Armaments and Technical Products (GDATP) (formerly Lincoln Composites). Under DOE Cooperative Agreement DE-FC36-01G011003, the ISS technology is being advanced to support development of a 5,000 and/or 10,000 psi service pressure semi-conformal gas storage system that provides sufficient fuel storage for 300+ mile driving range without impacting passenger and cargo space or compromising vehicle safety, and that is able to be mass produced at DOE target storage cost.

Approach

ISS uses Type IV all-composite tanks constructed with a high-density polyethylene (HDPE) thermoplastic liner structurally overwrapped with carbon fiber and epoxy resin. The tanks are encapsulated within a high-strength outer shell unitizing the individual cylinders into a single container and providing protection from environmental exposure. Additional physical protection of the tanks is provided by urethane foam surrounding the tank dome region (location of highest stress concentration during impact). A unitized gas control module (UGCM) is incorporated into the ISS package and provides all necessary gas flow control and safety features. Figure 1 is a

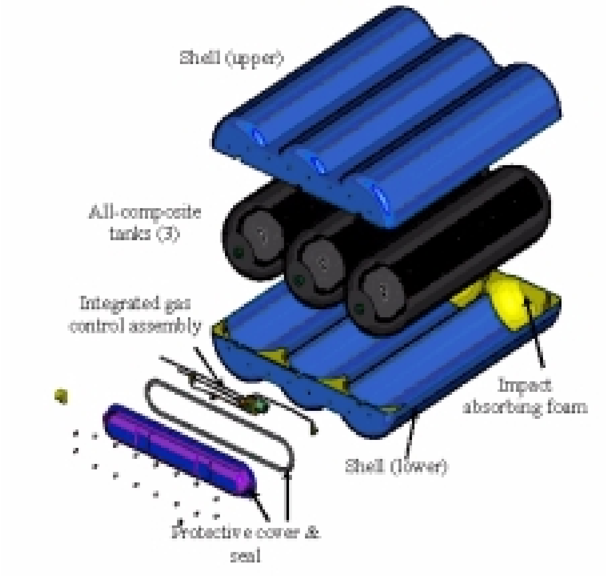

Figure 1. Assembly View of the CH2-ISS

computer-aided design (CAD) image of the CH2-ISS design. The objective of the DOE Cooperative Agreement is to advance the technologies needed to support developing and safety certifying a CH2-ISS.

There are five specific tasks: (1) HDPE treatment and alternative tank liner materials for hydrogen gas permeation reduction; (2) epoxy resin toughness enhancement to improve tank gravimetric energy density; (3) materials and process evaluation for manufacturing the ISS protective shell; (4) engineering of an optimized unitary gas control module; and (5) development of vehicle interface technologies to support storage system packaging requirements and system crashworthiness objectives. Within the timeframe covered in this report, JHU/APL had only received 35% of DOE committed FY 2003 funding. The progress reported herein therefore represents only approximately 35% of the plan activities. As a result of the delayed commitment of funds, the completion date for FY 2003 tasks was negotiated to March 31, 2004.

Results

Task (1): ISS uses Type IV high-pressure gas storage tanks constructed with a thermoplastic liner overwrapped with carbon fiber and epoxy resin. The liner serves as a permeation barrier, mechanical interface to aluminum bosses, and a stable mandrel for the filament winding process. The main focus of the permeation task has been to quantify and control the hydrogen gas permeation rate through the thermoplastic liner. In addition, two alternative secondary seal designs at the plastic liner/metal boss interface were explored. To accurately measure gas permeation, GDATP developed a test unit. This unit utilizes a hydrogen mass spectrometer in combination with a 2500 L vacuum chamber. A mass spectrometer as the instrument of measurement provides real-time data acquisition and evaluation. Permeation testing to date has been performed using a non-flammable 5% H_2 / 95% N_2 (by volume) gas composition. A proprietary surface treatment on the existing HDPE (High Density Polyethylene) lined tanks reduced permeation by 80% compared to the untreated HDPE. Two alternative proprietary liner materials were also tested, and they showed a 90% reduction in the permeation rate over untreated HDPE. More materials have been prepared but had not been tested at the time of this report.

Task (2): Decreasing tank weight (to improve gravimetric density) and reducing tank fabrication cost are key technology advancement goals. In FY 2002, GDATP established that increasing epoxy resin toughness with toughening agents formulated into GDATP's standard resin led to successful gunfire test for an all-carbon fiber overwrap at a 2.25 factor of safety (FOS) design. However, the specific toughening agents tested also modified the resin by lowering its glass transition temperature (impacting tank service temperature) and increasing its viscosity (impacting the tank winding process). Despite these shortcomings, the work was very encouraging and led to the hypothesis that if the right additive(s) was found, tanks could be manufactured without any loss in performance or higher fabrication cost. In addition, further tank weight reduction might be achieved if built with a factor of safety less than the regulatory 2.25 minimum. Current federal and international standards for Type IV tanks dictate the minimum allowable factor of safety 2.25. The minimum FOS was derived by industry and the government for natural gas vehicle tanks and accounts for material and manufacturing variations and physical/environmental abuse tolerance. In the ISS application, the tanks are fully protected by an unstressed outer shell and impact protection foam; consequently, the 2.25 FOS may not be needed to field a fully safe system. To explore this, we are embarking on a systematic examination of modern epoxy resin toughening agents and screening them for their effect on toughness, tank service temperature, the tank winding process, cost and other factors. During this reporting period, plans have been developed to have Dr. Giuseppe Palmese at Drexel University perform the resin screening study. There was insufficient DOE funding, in the timeframe covered by this report, to initiate the resin study.

Task (3): The ISS uses a high-strength, lightweight shell/cover in conjunction with flexible urethane impact-absorbing foam to encapsulate and protect the individual tanks into a single unitized container. In FY 2002, a manufacturing study was performed addressing alternative means for constructing, at low-cost and in high volume, the CH2-ISS outer shell and protective cover. The study identified a number of candidate materials and manufacturing processes used for high volume automotive reinforced plastic parts. These included compression molding with sheet molding compound

(SMC), structural reaction injection molding (SRIM), injection molding, and resin transfer molding (RTM). Both SMC and SRIM were determined to be good candidates. There remained, however, issues of part strength in the required bonfire test and impact strength for the drop test, that needed to be fully answered before making the final selection. To that end, material coupon tests are planned, and representative SMC and SRIM coupons were purchased. A special coupon test fixture is being devised that incorporates a load applied to the shell coupons under the conditions of the bonfire test simulated with heat lamps. Load bearing capability and qualitative condition of the coupons will be used to assess the results of the test for each sample. There was insufficient DOE funding, in the timeframe covered by this report, to initiate the test panel testing.

Task (4): The CH2-ISS is treated as a single, inseparable container, requiring only one manual service valve, one solenoid, and one thermally activated pressure relief device (PRD), all incorporated into a unitary gas control module (UGCM). The added cost and complexity of redundant components when using multiple separable tanks in a vehicle installation is avoided by this approach. The gas control system is safeguarded from physical damage with impact absorbing foam within a high-strength protective cover. In FY 2002, two alternative UGCM notional designs were developed with differing approaches to transferring heat, from a potential under-vehicle fire, to the thermally activated PRD. In FY 2003, work continued with particular focus on system crashworthiness, and the heat pipe option of heat transfer was selected as the safest design. For added safety, the UGCM design was refined to eliminate hard-mounting to a tank for added crashworthiness isolation. A non-disclosure agreement was established between JHU/APL and Circle Seal Inc. to allow interface information to be shared for commercial off-the-shelf component integration into the UGCM. There was insufficient funding available over the timeframe covered by this report to start work on finalizing the UGCM design and building a prototype unit for service, safety and reliability testing.

Task (5): With the need to develop FCEVs with driving ranges comparable to today's ICE (internal combustion engine) vehicles, work began on a vehicle interface technology task to explore options to increase hydrogen capacity at practical temperatures and pressures without compromising cargo and passenger space. The focus of this work has been a point design on a class of light-duty vehicles (i.e., car-based sport utility vehicles) to increase space in the vehicle under chassis to house a larger capacity CH2-ISS unit, without impacting passenger or cargo volume or reducing ground clearance, all while notionally meeting vehicle crashworthiness goals. The point design study led to the idea of a breakaway, four-bar linkage Crash Management System (CMS) to secure the CH2-ISS and to tip and guide the unit into the under carriage in the event of a high-speed rear end collision. This is done to preserve the all-important vehicle "crumple zone," thus protecting the passengers, and to control the impact energy imparted to the CH2-ISS to reduce the likelihood of physical damage. A patent disclosure for the CMS concept was developed and filed. A scaling analysis was performed that included the parameters of storage unit size and service pressure. The analysis showed that the 300+ mile driving range goal is possible with a properly sized and packaged CH2-ISS unit while meeting all other vehicle utility and safety objectives.

Conclusions

Some progress has been made in developing a high energy density, near-rectangular, safety-certified and affordable container for the onboard storage of compressed hydrogen gas for use in fuel cell electric vehicles. The work has focused on hydrogen tank gravimetric energy density improvement and permeation reduction, refining the design of a unitary gas control module and exploring means of achieving driving ranges comparable to today's vehicles without compromising vehicle utility or safety. Due to the slow dispersion of DOE funding, the FY 2003 planned work will not be completed until the revised phase completion date of March 31, 2004.

FY 2003 Publications/Presentations

1. "Development of a Compressed Hydrogen Gas Integrated Storage System (CH2-ISS) for Fuel Cell Vehicles - Peer Review Presentation CD/ROM Report", May 20, 2003

Next Generation Hydrogen Storage

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Objectives

- Adapt derivative technology from today's tanks to reduce cost by ~50%
- Improve performance of tanks by incorporating new high-strength materials
- Improve useable density of physical hydrogen storage through conformability
- Develop fundamental understanding of structural storage in various geometries
- Demonstrate safety innovations as components in ongoing burst experiments
- Contribute expertise to regulatory processes reflecting the results of research

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- F. Codes and Standards
- H. Sufficient Fuel Storage for Acceptable Vehicle Range
- J. Lack of Tank Performance Data

Approach

- Gain theoretic understanding of models that combine mass, volume, and cost
- Conduct scholastic research in University libraries seeking ultra-strong materials
- Construct test equipment capable of safely burst testing small prototypes
- Develop mechanical interface that enables assembled (not wound) tanks
- Adopt Statistical Process Control and Statistical Qualification analyses
- Collect suitable data to enable statistical engineering of burst probabilities

Accomplishments

- Established fundamental new dimensionless formalism that combines mass, volume, and cost
- Performed first statistical qualification on pressure vessel structural component
- Adopted Weibull statistical distribution identification method to tank failure
- Discovered new geometries capable of carrying structure loads through replicates
- Explored new structural geometries ideal for mass production with composites

Future Directions

- Prototype new structural geometries ideal for mass production with composites
- Extend statistical methods to burst testing of small pressure vessel prototypes
- Match dimensionless theory to actual burst performance of replicated structures
- Acquire data on the unexplored tensor debonding waves in "turn to dust" bursts
- Learn to engineer tailored elasticity and self-destruction for better crash safety

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Introduction

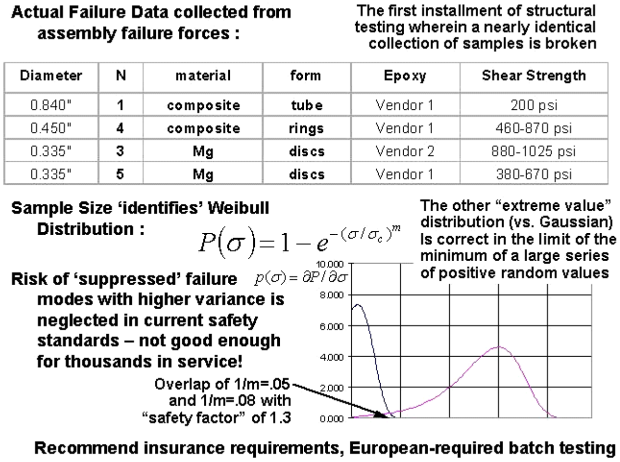
Physical containment of hydrogen has been accomplished successfully by tanks for the past few decades. Compressed hydrogen gas at ambient temperature as a means of storing hydrogen is already available and getting better. So compressed hydrogen storage provides a near-term solution based on already-solved problems, with well understood limitations. Current and next-generation hydrogen tanks are on track to achieve the 2005 and 2010 targets in the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan. The relative absence of further technical risks in these two generations of tanks provides near-term opportunities to reduce their costs significantly by taking calculated risks on new ways to build them.

The most advanced (Type IV) hydrogen tanks built with current technology have potential cost reduction of roughly a factor of two. That potential formed the basis for planning advanced tank development experiments at LLNL. On the way to those experiments, fundamental discoveries emerged which foretell several directions for expansion of the frontiers of physical containment. Tanks are not the only structures suitable for physical storage of compressed hydrogen - some of the newly discovered containment geometries could do the same job better, providing greater range, shape-ability, and lower cost. Taking the risks required to depart from the prior art in advanced hydrogen tanks can make physical containment of hydrogen a strong contender for the 2015 Program Plan Objectives.

Approach

LLNL advanced tank development efforts followed a deliberate plan intended to reduce the cost of hydrogen storage tanks twofold. Most of those savings are expected to derive from a change in qualification methods applied after manufacture. Replacing arbitrary safety factors with real failure statistics (using a discipline called Statistical Process Control, or SPC) can save roughly 30% of costly structural mass. Such SPC is applied routinely in mass-produced high-technology products like tires and semiconductors, and its first application to tank components was made in this year's research at LLNL (illustrated in Figure 1).

The composite structural components that were tested to failure form the critical assembly interface of several new kinds of hydrogen containers (shown in Figure 2), which LLNL expects to prototype in the next fiscal year as an attractive alternative to conventional (wound composite) tanks. These new kinds of assembled tanks carry most of the structural loads through the internal volume of the container. The limitations of physical storage are no longer imposed by a highly developed prior art in advanced (wound composite) tanks, and must be replaced by



Actual Failure Data collected from assembly failure forces :

The first installment of structural testing wherein a nearly identical collection of samples is broken

Diameter	N	material	form	Epoxy	Shear Strength
0.840"	1	composite	tube	Vendor 1	200 psi
0.450"	4	composite	rings	Vendor 1	460-870 psi
0.335"	3	Mg	discs	Vendor 2	880-1025 psi
0.335"	5	Mg	discs	Vendor 1	380-670 psi

Sample Size 'identifies' Weibull Distribution :

$$P(\sigma) = 1 - e^{-(\sigma/\sigma_c)^m}$$

The other "extreme value" distribution (vs. Gaussian) Is correct in the limit of the minimum of a large series of positive random values

Risk of 'suppressed' failure modes with higher variance is neglected in current safety standards – not good enough for thousands in service!

Overlap of 1/m=.05 and 1/m=.08 with "safety factor" of 1.3

Recommend insurance requirements, European-required batch testing

Figure 1. Statistical Research Based on the Weibull Distribution and Real Failure Force Data

models based on raw materials structural properties and feasible, mass-producible component geometries.

Results

Attractive geometries and materials options for such non-tank hydrogen containers were the target of considerable investigation this year. Packing replicated structural components together (as illustrated in Figure 3) was found to offer statistical advantages, comparable mass, and nearly-arbitrary conformability. The versatility of shapes into which such 'macro-lattices' could be assembled provides a route to 'ultra-conformability' that could roughly halve the volume penalty of storing compressed hydrogen aboard motor vehicles.

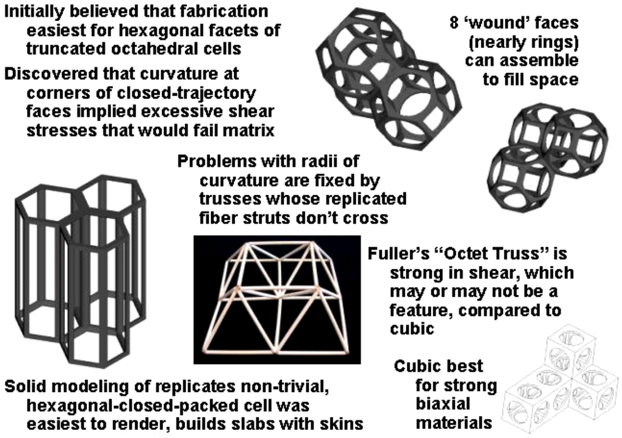


Figure 2. Various 'Non-Tank' Geometries Assemble into 'Macro-Lattices' to Enable Mass Production of Nearly-Arbitrary, Ultra-Conformable Shapes

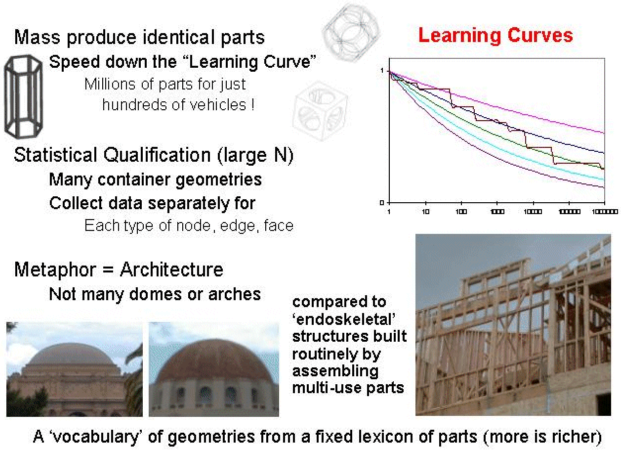


Figure 3. Mass Production Advantages of Macrolattices, Including a Metaphor to Architectural Structures

The mass and volume of tanks and non-tanks can be modeled as feasible-technology curves in a volume vs. mass plot (shown in Figure 4). A fundamental theoretical innovation was developed to enable calculation of the performance consequences of novel non-tank geometries. Its formulae allow designers to trade off mass, volume, and cost, while constraining vehicle range, proceeding with full rigor to combine dissimilar dimensioned performance measures. Figure 4 (volumetric vs. mass density of hydrogen storage) forecasts that progress will follow calculable paths to the right of the 2005 and 2010 objectives of DOE's Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan.

Conclusions

- The frontier of performance for physical hydrogen storage has been re-opened.
- Statistical Process Research has been initially demonstrated for hydrogen storage.
- Statistical methods can limit probabilities of failure to required levels (Pfail<10^{-7}).
- Mass production and innovative non-tank structures can provide copious statistics.

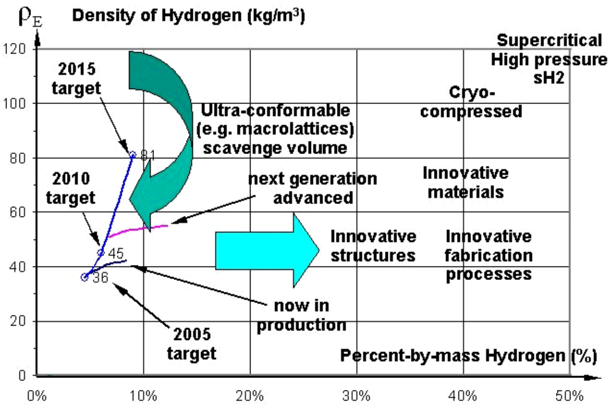


Figure 4. Advanced Type IV Pressure Vessels on Track for Hydrogen Storage Objectives - With Lots of Room for Progress

FY 2003 Publications/Presentations

1. Hydrogen Storage Using Light Weight Tanks, DOE Annual Hydrogen Fuel Cells and Infrastructure Program Review, Berkeley, CA, May 20, 2003.

Hydrogen Storage in Insulated Pressure Vessels

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Objectives

- Demonstrate the advantages of insulated pressure vessels in terms of improved packaging, reduced evaporative losses and reduced costs.
- Demonstrate safety of insulated pressure vessels by conducting certification tests.
- Write standards for assuring the safety of insulated pressure vessels.
- Demonstrate insulated pressure vessel technology in two pickup trucks.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability
- E. Refueling Time
- F. Codes & Standards
- G. Life-Cycle and Efficiency Analyses
- H. Sufficient Fuel Storage for Acceptable Vehicle Range
- J. Lack of Tank Performance Data
- K. BOP Components
- L. Hydrogen Boil-Off

Approach

- Conduct experiments to verify safety of insulated pressure vessels.
- Conduct analysis to verify safety of insulated pressure vessels.
- Study existing standards for hydrogen storage in vehicles.
- Test performance of two insulated pressure vessels on pickup trucks.

Accomplishments

- Performed SAE cryogenic drop and bonfire tests. The insulated pressure vessels successfully passed both tests.

- Signed a contract with the South Coast Air Quality Management District (SCAQMD) for $800,000 in complementary funding to conduct a demonstration.
- Generated an overall fuel system design for a truck at SunLine Transit.
- Studied current standards for hydrogen tanks. We have generated a preliminary list of tests for insulated pressure vessel certification based on current standards for hydrogen tanks.
- Tested 5000-psi vessels at cryogenic temperature. The pressure vessels were burst tested after cycling, and they met the required burst pressure criterion.
- Prepared a preliminary procedure for insulated hydrogen pressure vessel certification and submitted it to Structural Composites Industries (SCI) and the SCAQMD (our industrial and state government project partners).
- Wrote a comprehensive summary of hydrogen storage technologies to be published in the "Encyclopedia of Energy."

Future Directions

- Conduct a demonstration project at SunLine Transit where the insulated pressure vessels will be installed in two trucks.
- Conduct a fundamental study of conformal cryogenic compatible pressure vessels and analyze desirable shapes as well as desirable pressure ratings.
- Build conformal cryogenic compatible pressure vessels with optimum characteristics as identified in the fundamental study.

Introduction

The goal of this project is to develop a hydrogen storage technology that can satisfy light-duty vehicle storage needs in a cost-effective way. This high pressure, low temperature vessel has the packaging advantages of liquid hydrogen tanks (low weight and volume), with much reduced evaporative losses, infrastructure flexibility, lower energy consumption, lower cost, enhanced user convenience, and safety.

For reduced cost and complexity it is desirable to use commercially available aluminum-fiber pressure vessels for insulated hydrogen pressure vessels. However, commercially available pressure vessels are not designed for operation at cryogenic temperature.

We plan to demonstrate insulated hydrogen pressure vessels that have packaging characteristics similar to liquid hydrogen (LH2) tanks and are superior to ambient temperature pressure vessels. Compared with liquid hydrogen tanks, insulated hydrogen pressure vessels give increased flexibility to the fueling infrastructure, since the vehicle can be fueled with liquid hydrogen for long trips, or with less-energy-intensive ambient temperature hydrogen for daily driving. The high-pressure capability of the pressure vessel and the thermodynamic properties of hydrogen result in virtually zero boil-off losses for insulated hydrogen pressure vessels. Finally, due to their high-pressure capability, insulated hydrogen pressure vessels never run out of hydrogen after a long period of parking. This may be a major issue for liquid hydrogen tanks that can lose all their hydrogen due to evaporation.

Approach

We are conducting experiments and analysis to verify that insulated hydrogen pressure vessels are a safe technology for vehicular storage of hydrogen. We have conducted a long list of Department of Transportation (DOT), International Standards Organization (ISO) and Society of Automotive Engineers (SAE) tests, and our pressure vessels have successfully met the passing criteria for all of them.

We are planning a demonstration to prove the feasibility of insulated hydrogen pressure vessels in vehicles. To accomplish this task, we have secured

$800,000 of complementary funding from the South Coast Air Quality Management District, SCI and SunLine Transit.

Results

During this year, we completed the two final certification tests for insulated hydrogen pressure vessels. These are the SAE cryogenic drop test (Figure 1) and the SAE cryogenic bonfire test (Figure 2). These tests were successfully conducted, and our vessels met the required passing criteria.

We are also working on demonstrating the safety and advantages of insulated hydrogen pressure vessels by installing two of these vessels in pickup trucks owned by SunLine Transit. As a part of our work for demonstrating the insulated hydrogen pressure vessels in the pickup trucks, we have designed a system for fueling the truck engine with hydrogen from the vessel. We have selected and purchased all required components (valves, regulators, connectors, and safety devices). These components will be mounted into the pickup trucks in the near future.

Figure 1. Insulated Hydrogen Pressure Vessel Being Subjected to the SAE Cryogenic Drop Test

We have also designed a computerized control system that will operate our fueling system for the pickup trucks. This system uses a MatLab-based program that runs on a laptop computer that will be carried in the vehicle.

We have prepared a draft certification procedure for insulated hydrogen pressure vessels. This procedure is considered to be guidance to manufacturers who may want to commercialize this technology in the future. The certification procedure includes 28 tests that have been selected from existing standards for ambient temperature pressure vessels (DOT, ISO) and for cryogenic vessels (SAE, European Integrated Hydrogen Program).

We wrote a comprehensive summary of hydrogen storage technologies. This will be published in the "Encyclopedia of Energy." This paper offers a new perspective on the characteristics of hydrogen storage technologies, including weight, volume, cost, safety and energy required for fuel processing.

Figure 2. Insulated Hydrogen Pressure Vessel Being Subjected to the SAE Cryogenic Bonfire Test

Conclusions

Insulated hydrogen pressure vessels are being developed as an alternative technology for storage of hydrogen in light-duty vehicles. Insulated hydrogen pressure vessels can be fueled with either liquid hydrogen or compressed hydrogen. This flexibility results in advantages compared to conventional hydrogen storage technologies. Insulated hydrogen pressure vessels are lighter than hydrides, more compact than ambient-temperature pressure vessels, and require less energy for liquefaction and have less evaporative losses than liquid hydrogen tanks.

A series of tests have been carried out to verify that commercially available pressure vessels can be operated at cryogenic temperature with no performance losses. All analysis and experiments to date indicate that no significant damage has resulted. Future activities include a demonstration project in which the insulated hydrogen pressure vessels will be installed and tested on two vehicles. Future work will address the possibility of optimum space utilization inside the vehicle through the use of cryogenic-compatible conformal pressure vessels.

FY 2002 Publications/Presentations

1. **Certification Testing and Demonstration of Insulated Pressure Vessels for Vehicular Hydrogen and Natural Gas Storage**, Salvador M. Aceves, Joel Martinez-Frias and Francisco Espinosa-Loza, Randy Schaffer, William Clapper, Proceedings of the 8th International Conference and Exhibition on Natural Gas Vehicles, Washington, DC, October 8-10, 2002.

2. **Hydrogen Storage and Transportation**, Gene Berry, Joel Martinez-Frias, Francisco Espinoza-Loza, Salvador Aceves. Invited article submitted to the Encyclopedia of Energy, 2003.

Special Recognitions & Awards/Patents Issued

Project will be featured in a 4-page article in "Science and Technology Review" magazine in June 2003.

Low Permeation Liner for Hydrogen Gas Storage Tanks

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Subcontractor: University of California at Los Angeles (UCLA), Los Angeles, CA

Objectives

- Develop a polymer liner that greatly limits hydrogen losses from commercial, light-weight, composite, high-pressure hydrogen tanks

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- C. Durability
- I. Materials

Approach

- Select and fabricate polymeric materials with the necessary electron and proton conducting properties to form an electrochemical tri-layer barrier to hydrogen permeation through polymer tank-liners
- Fabricate "bench-top" models of the tri-layers on polymer substrates
- Demonstrate the successful functioning of the bench-top model devices at low and high pressures
- Demonstrate a successful prototype of an active, electrochemical hydrogen barrier system within a high-pressure, polymer-lined, composite hydrogen storage tank

Accomplishments

- Filed U.S. Patent Application on concept (# 10,253,265 in Sept. 2002)
- Negotiated and signed Cooperative Research and Development Agreement (CRADA) (No. 03-CR-07) with a major manufacturer of composite, high-pressure gas storage tanks
- Fabricated initial tri-layer coatings, overcame wetting problems, and began electrical characterization of the individual layers and tri-layers
- Synthesized Pt/Au nanoparticle catalyst that will be added into the poly-3,4-ethylenedioxythiophene (PEDOT) electrodes

- Designed and built a low-pressure hydrogen permeability device at UCLA
- Designed a high-pressure hydrogen permeability device at INEEL

Future Directions

- Test tri-layers on coupons of polymers within low-pressure permeability device
- Conduct further electrical characterization of the tri-layers
- Test tri-layers with various catalysts at electrode interfaces using the low- pressure permeability device and select successful combinations
- Fabricate the high-pressure permeability device
- Test successful tri-layers on coupons within the high-pressure permeability device
- Test perfected tri-layers within commercial high-pressure composite gas storage tanks

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Introduction

State-of-the-art high-pressure gas storage tanks consist of an inner liner, made from a polymer such as cross-linked polyethylene or nylon, overlaid with a continuous graphite fiber/epoxy reinforcement layer. These tanks have successfully stored high-pressure methane gas. It is desired to extend the application of this type of tank to high-pressure hydrogen. However, hydrogen has a significantly higher permeability rate through these polymer liners than methane. Permeation not only leads to a gradual loss of hydrogen pressure, but the hydrogen is thought to damage and weaken the reinforcement layer which could lead to cyclic fatigue or other failures of the tank.

This project was recently begun to develop a hydrogen diffusion barrier that can be applied to the interior of the polymer liner. The barrier will have the following attributes: (1) low permeability of hydrogen, (2) adhere well to the polymer liner, (3) stiffness (modulus) of the coating should match the underlying polymer to avoid cracking when the tank is pressurized, (4) the application method should allow for coating inside a tank with a narrow neck and result in hermetic (gas-tight) coatings that are devoid of pin-holes, (5) the material and coating method should not appreciably add to the overall cost or weight of the tank.

Approach

An electrochemically "active" hydrogen barrier, fabricated from polymers, is being developed. A schematic of this barrier is shown in Figure 1. The hydrogen partial pressure established by the voltage is extremely low at the underlying polymer interface. The hydrogen partial pressure can be calculated using the Nernst equation, as shown in Figure 1. An appropriate level of voltage will be calculated and experimentally verified.

The development plan includes the following:

1. The barrier is to be constructed of three layers of polymers consisting of a proton-conducting electrolyte (electronic insulator) sandwiched in-between electronically conductive polymer electrodes. Candidate polymer compositions were selected based upon existing knowledge. If this

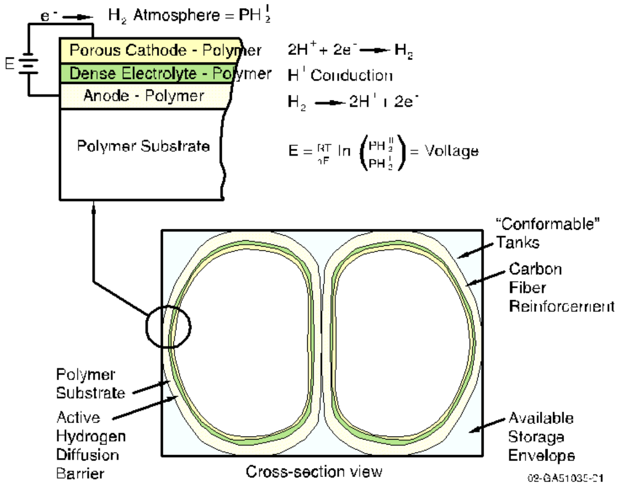

Figure 1. Schematic Showing Tri-layer Hydrogen Barrier Concept

knowledge is not sufficient, new or modified compositions will be developed. Appropriate catalyst materials will be added at the electrolyte/electrode interfaces.

2. The methods to manufacture the layers are being adapted from existing techniques or developed during the project. This could include dip coating or spraying of monomers followed by polymerization. Other possibilities will be explored, and successful manufacturing technologies will be developed.
3. The device is designed as a galvanic-type device that functions to prevent hydrogen permeation through application of a small direct current (dc) voltage using small currents. Methods to provide attachment of the dc voltage are being developed.

Results

Significant progress was made in all four task areas: selection of materials, fabrication of tri-layer coatings, characterization of coating layers, and experimental verification of hydrogenation protection.

The first set of candidate materials were fabricated as a tri-layer prototype barrier. The material selected for the electrodes was highly-conductive H-PEDOT polymer (PEDOT + a small amount of alcohol). The addition of an alcohol (e.g., ethylene glycol) has been shown to increase the electronic conductivity of ordinary PEDOT by up to three orders of magnitude. The material selected for the electrolyte layer was PAMPAS [Poly (2-acrylamino-2-methyl-1-propanesulfonic acid-co-styrene)]. Tri-layers of these materials were first made by spin-coating on glass. Later, the layers were spin-coated on polymer substrates. However, the non-polar surface of the PAMPAS electrolyte resulted in a high contact angle while spin-coating the second layer of PEDOT. To avoid this problem, the PAMPAS film was subjected to an ultraviolet-ozone treatment to modify the surface. The contact angle was greatly reduced, and a good second layer of PEDOT was then obtained.

Electrical characterizations were then conducted on the tri-layer devices shown as a schematic diagram in Figure 2. These included I-V (current/voltage) characteristics of the device and complex impedance measurements. Aluminum layers of 100 nm thickness were evaporated on the two H-PEDOT layers to form electrical contacts. I-V tests showed that the device was a good electronic insulator because of the insulating PAMPAS electrolyte. The device showed a very low current (< 10^{-8} mA) under an applied bias (0-3 Volts), as shown in Figure 3. The complex impedance results will be reported in later reports or papers.

Figure 4 shows the completed low-pressure permeability apparatus. Figure 5 shows an initial permeability test without a barrier and with a barrier (biased and unbiased). Significant reduction in permeation was shown with addition of the tri-layer

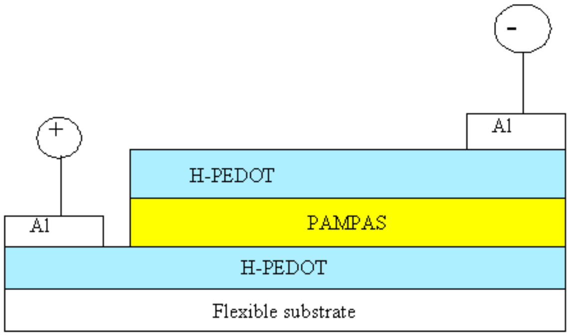

Figure 2. Schematic of Fabricated Tri-layer

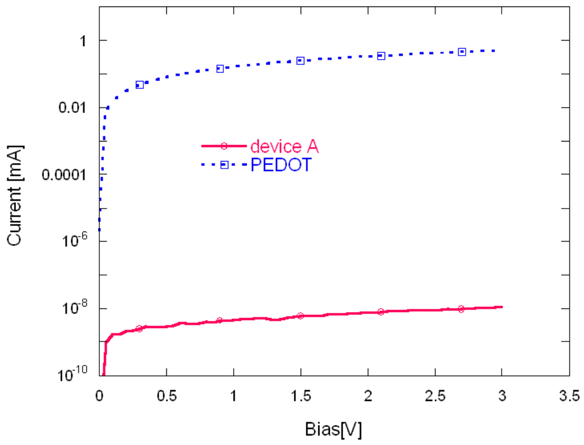

Figure 3. I-V Characteristic Plot for the Tri-layer Barrier

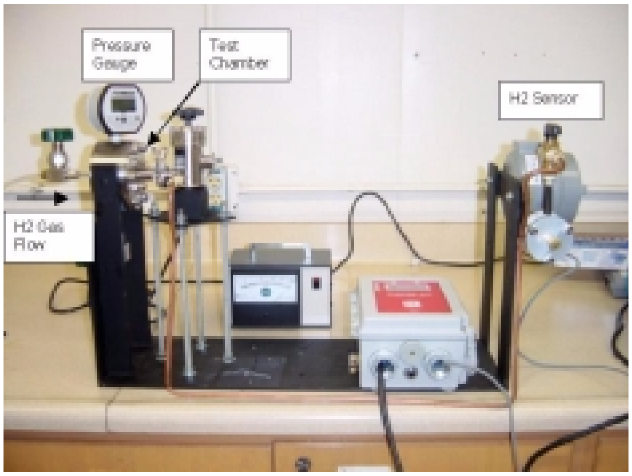

Figure 4. Low-pressure Hydrogen Permeability Apparatus Fabricated at UCLA

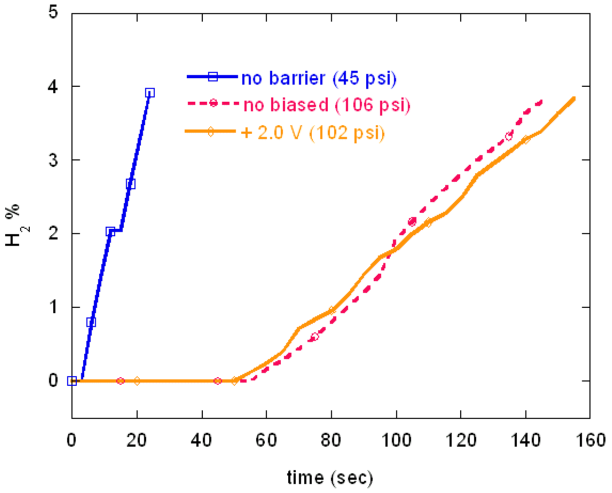

Figure 5. First Permeability Tests Using Low-Pressure Hydrogen

barrier. However, there is little difference between the biased and unbiased cases. Therefore, as previous planned, a catalyst will be necessary (as with proton exchange membrane type low-temperature fuel cells) to enable hydrogen reduction/oxidation at the electrode/electrolyte interfaces.

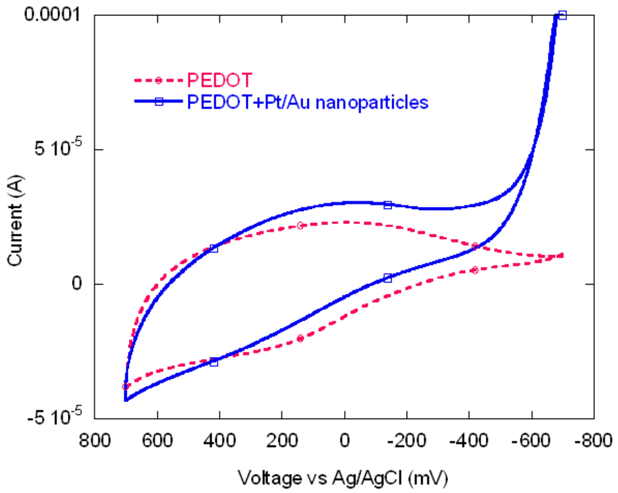

Figure 6. Cyclic Voltammetry of PEDOT Electrodes plus Pt/Au Nano-particles (Electrodes in 1 M HCl + 1 M NaCl solution)

Platinum/gold (Pt/Au) is being investigated as a catalyst. This material was synthesized as nano-particles in our laboratories. The material shows good catalytic reduction of hydrogen as shown in Figure 6. The nano-catalyst will be incorporated into PEDOT electrodes to enable the hydrogen reduction and oxidation reactions at the electrolyte interface, and additional hydrogen permeability tests will be conducted.

Conclusions

- Good progress has been made toward the final goal of developing a polymer liner that greatly limits hydrogen losses from commercial, light-weight, composite, high-pressure hydrogen tanks.
- All of the milestones that were set for this time period have been achieved. Materials were selected, and prototype tri-layer electrochemical barriers have been fabricated and characterized for electrical properties.
- Preliminary testing indicated that fine catalyst particles will be necessary at the electrode/electrolyte interfaces to reduce the high free energy of the hydrogen oxidation and reduction reactions.
- Nanoparticles of Pt/Au catalyst have been synthesized, and good catalytic reduction of hydrogen has been observed. Therefore, we are well positioned to test the tri-layer barriers (with catalyst) in the low-pressure permeability apparatus that was designed and fabricated.

FY 2003 Publications/Presentations

1. "Low Permeation Liner for H_2 Gas Storage Tanks", Paul A. Lessing, Y.Yang, L.P. Ma, F.C. Chen, V. Shrotriya, N. Sirosh, M.J. Warner, Hydrogen, Fuel Cells & Infrastructure Technologies Program, 2003 Merit Review and Peer Evaluation Meeting, May 19-22, 2003, Berkeley, California.

Special Recognitions & Awards/Patents Issued

1. U.S. Patent Application: Paul A. Lessing, "Polymeric Hydrogen Diffusion Barrier, High-Pressure Storage Tank so Equipped, Method of Fabricating a Storage Tank, and Method of Preventing Hydrogen Diffusion", September, 2002.

Low Cost, High Efficiency, High Pressure Hydrogen Storage (New FY 2004 Project)

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Objectives

Deliver a cost-effective and safe high-pressure hydrogen storage system that will meet all of the DOE goals for compressed hydrogen storage

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- E. Refueling Time
- H. Sufficient Fuel Storage for Acceptable Vehicle Range
- I. Materials

Approach

QUANTUM will develop and test an advanced, cost-effective, and safe high-pressure hydrogen storage system. The first task will be to choose the most appropriate fiber from which to construct the tank. The 3-dimensional or tri-axial composite material strength values will be generated for the baseline material. Small composite test bottles will be fabricated and burst tested. Strain gages will be mounted on the bottles to correlate burst pressure and composite wall stresses and strains. A detailed axisymmetric finite element analysis of each test bottle will be completed to correlate to the strain gage data obtained from the bottle burst tests. Composite specimens will be fabricated and tested to obtain the cross-ply compressive strength of the material.

A representative tank will be designed for 10,000 psi service pressure. A detailed finite element model that includes the metallic parts will be completed to assess the stress/strain state in the composite shell and metallic parts. Up to three tanks will be fabricated and burst tested to finalize the tank design for 10,000 psi. Three tanks will be fabricated and tested to demonstrate the scale-up capabilities of the material characterization and optimization. One tank will be burst tested, and two tanks will be cycle tested and burst tested at the end of cycle testing.

QUANTUM will work with Oak Ridge National Laboratory to identify a robust and cost-effective stress sensor technology that is suitable for integration on tanks. This sensor will allow the tank to operate at reduced stress ratios with the benefit of lighter weight.

A review of current tank Design Failure Modes and Effects Analysis will be completed to assess the critical issues and validation tests of a tank. Three tests will be specified to demonstrate the strength and life capabilities of the tanks. The three tests will be completed, and it is anticipated that the tests will include pressure cycling at ambient and elevated temperatures.

Tests will be conducted to better understand the thermodynamics of the tank charging and discharging process and to capitalize upon that understanding by optimizing fuel temperature and pressure and how that relationship is affected by additional insulation on the tank, on-board refrigeration, heat-sink technologies, fuel consumption rate and thermal load.

The analysis portion of the project will establish a working foundation upon which the development of a refueling refrigeration system design, on-board refrigeration system design, heat-sink system design, and tank insulation system design will be made. The analysis is meant to serve as both a guide for development as well as a means by which the fundamental thermal characteristics of the fuel and tank system can be understood and predicted. Most of the analysis will be built from first-principles.

Catalytically Enhanced Hydrogen Storage Systems

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Objectives

- Determination of the chemical nature of the titanium species responsible for the enhanced kinetics of Ti-doped $NaAlH_4$.
- Determination of the mechanism of action of the dopants in the dehydrogenation and re-hydrogenation processes.
- Development of hydrogen storage materials based on complex aluminum hydrides that meet the FreedomCAR hydrogen storage targets of cost, specific energy, and energy density.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan.

- B. Weight and Volume
- C. Efficiency
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

- Determination and quantification of effective dopant through electron paramagnetic resonance (EPR) and magnetic susceptibility studies.
- Elucidation of the effects of doping directly on hydrogen by neutron diffraction, inelastic neutron scattering (INS), solid state nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy.
- Determination of the dependence of plateau pressure on doping level.
- Synthesis and evaluation of advanced alanates suggested by the insight gained by fundamental studies.

Accomplishments

- Verification that doping $NaAlH_4$ with Ti dopant precursors generates Ti(III) dopants that persist through dehydrogenation and repeated hydrogen cycling.
- First accurate determination of the location of the hydrogen atoms in $NaAlH_4$ through a neutron diffraction study of $NaAlD_4$.
- Observation of the bulk perturbation of the $[AlH_4]^-$ anion upon doping through ^2H NMR and IR spectroscopy studies.

- Measurement of changes in plateau pressure resulting upon variation in level of Ti substitution in $NaAlH_4$.
- Development of a method for the removal of sodium salt by-products from doped $NaAlH_4$.

Future Directions

- Continue characterization and quantification of titanium species in doped $NaAlH_4$ by combination of EPR and magnetic susceptibility and determine whether kinetic enhancement is due to Ti(III) or Ti(IV) species.
- Continue IR, NMR, and INS spectroscopic studies and obtain Raman spectra to elucidate the influence of doping on the dynamics of the $[AlH_4]^-$ anion and their relationship to hydrogen cycling kinetics.
- Determine the hydrogen cycling properties of doped $NaAlH_4$ from which doping by-product(s) have been removed.
- Probe whether the purification method can be extended to hydride containing high (>10 mol %) doping levels and Li- and Mg-based alanates.

Introduction

We have developed methods of doping sodium aluminum hydride, $NaAlH_4$, with titanium and/or zirconium that give rise to state-of-the-art hydrogen storage materials. During the initial dehydrogenation reaction seen in equation 1, $NaAlH_4$ rapidly evolves

$$3\ NaAlH_4 \ \text{---------->}\ Na_3AlH_6 + 2\ Al + 3\ H_2 \quad (1)$$

temperatures upon doping with 2 mole percent $Ti(O^nBu)_4$ by our methods. At 100°C, hydrogen flow rates of 0.01 g H_2/s per kg under a constant pressure of 1 atm have been observed. This performance is adequate to meet the demands of a fuel cell operating under practical conditions. We have also found that NaH and Al doped with 2 mole percent Zr absorbs 4.4 weight percent hydrogen within 15 minutes at 120°C under 125 atm of hydrogen pressure. However, despite this progress in enhancing the dehydrogenation and re-hydrogenation processes, it has not yet been demonstrated that ~5 weight percent hydrogen can be reversibly released from these materials under conditions that are required for the practical operation of an onboard fuel cell. Most notably, the rate and equilibrium plateau pressures of the second dehydrogenation reaction, seen in equation 2, are

$$Na_3AlH_6 \ \text{---------->}\ 3\ NaH + Al + 3/2\ H_2 \quad (2)$$

impractical for hydride that is doped with titanium, and improved variations of this material must be produced to achieve commercial viability. To guide our development of advanced alanates, we have sought to gain a fundamental understanding of the nature of the dopants and the structural effects they exert on the hydride.

Approach

It was initially speculated that the remarkable enhancement of the hydrogen cycling kinetics in doped $NaAlH_4$ was due to surface-localized catalytic sites. However, we obtained X-ray crystallographic data that revealed that the doping of the hydride results in bulk lattice distortions. These observations have led us to develop a new model of the doped hydrides in which Na^+ ions are substituted by M^{4+} and/or M^{3+} dopant ions and the generation of the requisite number of Na^+ vacancies in the hydride lattice to maintain charge neutrality. Spin isolated Ti(III) has been identified in the EPR spectroscopy. This finding is consistent with the presence of the Ti^{3+} cations in the doped hydride as predicted by our "substitution model" of doped $NaAlH_4$. It also raises the question of whether the enhanced hydrogen cycling kinetics in the doped hydride are the result of substitution of Na^+ by M^{3+} or M^{4+} or both. In a collaborative study with Dr. Sandra Eaton of the University of Denver, we are endeavoring to resolve this ambiguity through further EPR studies in conjunction with quantification of the density of the paramagnetic M^{3+} through magnetic susceptibility experiments.

Although x-ray diffraction and EPR studies showed that the doping of $NaAlH_4$ results in bulk structural changes, these techniques cannot yield reliable information about the structural environment of the hydrogen atoms. Thus, in order to determine what changes occur in the structural environment of the hydrogen atom upon doping the hydride, neutron diffraction, INS, solid state NMR, and infrared spectroscopic studies are being conducted. We have established collaborations with Dr. Hendrick Brinks and Dr. Bjorn Hauback, Institute for Energy Technology, Kjeller, Norway (neutron diffraction); Terry Udovic, National Institute of Standards and Technology (INS); Dr. Juergen Eckert, Los Alamos National Laboratories (INS); and Prof. Klaus Yvon and Dr. Sandrine Gomes, University of Geneva (IR) for these efforts.

The doping process generates by-products that constitute "dead weight" in the kinetically enhanced hydride. For example, doping with $TiCl_3$ or $TiCl_4$ results in the formation of segregated NaCl by-product. Thus, the increased kinetic enhancement at higher doping levels results in a capacity loss due to the weight of **both** the Ti dopant and the by-product. Additionally, the earlier "redox" model of the doped hydride predicts a 3-4 equivalent loss in hydrogen-carrying Al upon doping. By contrast, our "substitution" model of the doped hydride predicts all Al remains available for hydrogen binding. This is an important distinction as only the newer model suggests that removal of "dead weight" doping by-product might lead to materials having both increased hydrogen capacity as well as the highly acceptable kinetics that are achieved at high doping levels. Additionally, the "substitution" model, unlike the redox model, predicts that plateau pressure, a thermodynamic property, should be significantly altered at high doping levels. Thus, we are probing the effect of doping on the equilibrium plateau pressures of the hydride. We are also developing methods of removing the inert, "dead weight" by-products that are generated in the doping process and are measuring the hydrogen cycling capacities and kinetics of these purified materials.

Results

Electron Paramagnetic Spin and Magnetic Susceptibility Studies: Preliminary electron paramagnetic resonance studies were conducted in collaboration with Dr. Sandra Eaton, University of Denver, and Dr. Karl Gross and Eric Majoub, Sandia National Laboratory. The EPR spectrum of a sample $NaAlH_4$ doped with 2 mol % $Ti(OBu)_4$ is seen in Figure 1. The very sharp, singlet signal that dominates the spectrum can be readily assigned to spin isolated Ti(III). Very similar spectra were obtained from a variety of samples that were doped with either Ti(III) or Ti(IV) precursors. This finding lends strong support for our "substitution" model of doped $NaAlH_4$. Continuing collaborative studies with the University of Denver group have shown that the spin isolated Ti(III) dopants persist through dehydrogenation and in repeated hydrogen cycling of the material. While the EPR studies provide strong support for the substitution of Ti^{3+}, into the bulk hydride lattice, it does not preclude the possibility that EPR silent, diamagnetic Ti^{4+} is also present. In order to explore this possibility, we have begun efforts to quantify the amounts of Ti(III) present in Ti doped hydride through magnetic susceptibility measurements. At this point we have completed the measurement of χ (magnetic susceptibility) values for a series of standards containing known amounts of Ti(III) and generated a standard plot of χ vs. moles Ti(III)/cc. Quantification of the amount of Ti(III) present in samples of the doped hydride can now be accomplished by comparison of their measured χ

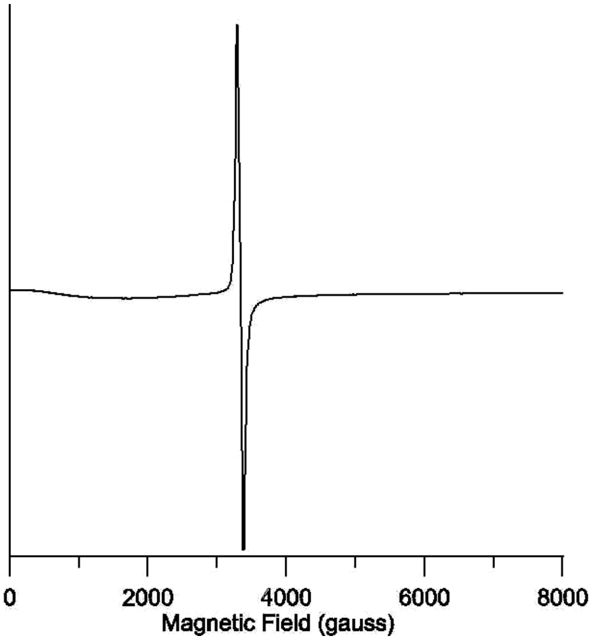

Figure 1. EPR Spectrum NaAlH4 Doped with 2 mol % $Ti(OBu)_4$

values to the standard plot. If the level of Ti(III) present is less than the Ti doping level, it can be inferred that the unaccounted titanium is present as diamagnetic, Ti(IV). Determination of the amounts of Ti(III) and Ti(IV) in the doped hydride will allow us to determine if the kinetic enhancement resulting upon doping tracks the level of substitution of Na^+ by Ti^{3+}, Ti^{4+}, or both.

Neutron Diffraction: In order to undertake a neutron structure determination, we had to develop a method for the synthesis of high purity $NaAlD_4$. This was accomplished through the reaction of $LiAlD_4$ with NaF in the presence of an aluminum alkyl catalyst. Neutron diffraction data were collected at the Institute for Energy Technology in Kjeller, Norway, from a sample of $NaAlD_4$ that was prepared through this method. Final refinement of this data gave the structure of the hydride seen in Figure 2. The deuterium atoms were well located, giving a structure with two unique Al-D distances of 1.627(2) and 1.626(2) Å, and two unique D-Al-D angles of 107.30(1) and 113.90(1).

Infrared Spectroscopy: Preliminary infrared spectroscopic studies have been carried out. No new vibrational modes or changes in absorption frequencies can be detected upon comparison of doped and undoped samples of $NaAlH_4$. However, there is a dramatic broadening of the infrared absorptions in the samples of the doped hydride. This finding indicates that while the bonding in the $[AlH_4]^-$ anion is unperturbed upon doping, the changes that occur upon bulk Ti^{3+} substitution in the lattice result in a broader allowable range of orientation of the anions in the lattice.

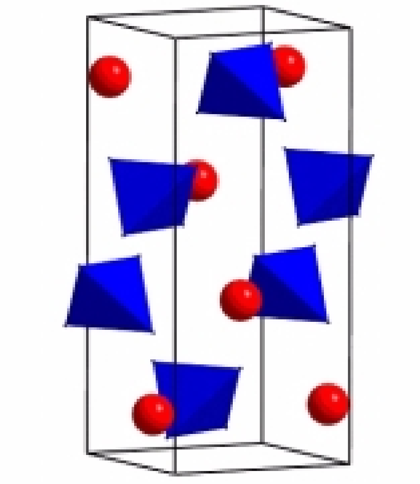

Figure 2. Crystal Structure of $NaAlD_4$

Solid State Nuclear Magnetic Resonance Spectroscopy: Comparison of the solid state ^2H spectra of doped and undoped samples of $NaAlD_4$ show a significant broadening of the dipolar doublet upon doping. This finding is in agreement with our interpretation of the IR studies: the changes that occur upon bulk Ti^{3+} substitution in the lattice result in a broader allowable range of orientation of the anions in the lattice.

Effect of Doping Level on Plateau Pressures: The equilibrium hydrogen pressure has been determined for samples of $NaAlH_4$ that were doped with 1.3 – 2.0 mole % $Ti(OBu)_4$. The plateau pressure was seen to increase linearly from 3.0(2) to 4.7(2) Mpa over the range of doping levels.

Purification of Doped Materials: A proprietary method has been developed for the removal of the contaminant sodium salts resulting upon Ti doping of $NaAlH_4$. X-ray diffraction has shown that the removal of the by-products is >95% complete.

Conclusions

We have, for the first time, accurately determined the location of the hydrogen atoms in $NaAlH_4$ through a neutron diffraction study of $NaAlD_4$. Our EPR, IR, and NMR studies provide additional support for our "substitution" model of doped $NaAlH_4$ that was initially proposed on the basis of x-ray diffraction data. The ERP studies lend strong support to our hypothesis that Ti doping of the hydride results in the substitution of Ti^{3+} into the bulk hydride lattice that persists through repeated cycles of dehydrogenation/re-hydrogenation. The IR and solid state ^2H NMR studies also provide clear evidence that bulk changes occur in the hydride upon doping. Moreover, the changes in the equilibrium plateau pressures that are predicted by the "substitution" model have been verified. Thus, prospects seem bright for the possibility of tailoring an alanate material with thermodynamic properties well suited for utilization as an onboard hydrogen carrier for PEM fuel cell applications. Furthermore, we have developed a method for the removal of the "dead weight" by-products that result from the doping process. Thus, it may be possible to obtain mixed Na/Ti alanates that contain up to 6 wt % available hydrogen and exhibit superior hydrogen cycling kinetics.

Publications (5/02-6/03)

1. D. Sun, H.T. Takeshita, T. Kiyobayashi, N. Kuriyama, and C.M. Jensen, "X-ray Diffraction Studies of Titanium and Zirconium Doped $NaAlH_4$: Structural Basis of the Enhanced Hydrogen Storage Properties Resulting Upon Doping", *J. Alloys Compd.* **2002**, *337*, 8.
2. K.J. Gross, C.M. Jensen, and G.J. Thomas, "Catalyzed Alanates for Hydrogen Storage", *J. Alloys Compd.* 2002 *330-332*, 683.
3. G. Sandrock, K. Gross, G. Thomas, C. Jensen, D. Meeker, and S. Takara, "Engineering Considerations in the Use of Catalyzed Sodium Alanates for Hydrogen Storage", *J. Alloys Compd.* **2002**, *330-332*, 696.
4. G.J. Thomas, K.J. Gross, N.Y.C. Yang, C.M. Jensen, "Microstructural Characterization of Catalyzed $NaAlH_4$ ", *J. Alloys Comp.* **2002**, *330-332*, 702.
5. B.C. Hauback, H. W. Brinks, C.M. Jensen, K. Murphy, and A.J. Maeland, "Neutron Diffraction "Structure Determination of $NaAlD_4$" *J. Alloys Comp.* **2003**, *358,* 142.
6. S.S. Eaton, K. Gross, E. Majzoub, K. Murphy, and C.M. Jensen, "EPR Studies of Titanium Doped $NaAlH_4$: Fundamental Insight to a Promising New Hydrogen Storage Material", *Chem. Commun.*, in press.
7. T. Kiyobayashi, S.S. Srinivasan, D. Sun, and C.M. Jensen, "Kinetic Study and Determination of the Enthalpies of Activation of Titanium and Zirconium Doped $NaAlH_4$ and Na_3AlH_6" *J. Phys. Chem.*, in press.

Invited Presentations (May 2002 – June 2003)

1. 5/13/02 Symposium on Hydrogen Storage Materials and Hydrogen Generators, 201st meeting of the Electrochemical Society, Philadelphia, PA.
2. 8/13/02 Universal Oil Products Research Center, Des Plaines, Illinois.
3. 9/05/02 International Symposium on Metal Hydrogen Systems, Annecy, France.
4. 9/13/02 California Institute of Technology.
5. 3/18/03 Research Association for the Development of Advanced Metal Hydrides meeting, Osaka, Japan
6. 6/11/03 European Materials Research Society 2003 Meeting, Symposium on Nanoscale Materials for Energy, Strasbourg, France.

FY 03 Patents

1. Craig M. Jensen and Ragaiy. A. Zidan, "Hydrogen Storage Materials and Method of Making by Dry Homogenation", **2002**, US patent 6,471,935.

Hydride Development for Hydrogen Storage

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Objectives

- Develop new complex hydride materials with >6 weight percent system hydrogen capacity at below 100°C.
- Improve the kinetics of absorption and desorption and thermodynamic plateau pressures of Ti-doped sodium alanate metal hydrides.
- Improve processing and doping techniques of Ti-doped sodium alanate to lower cost.
- Help develop state-of-the-art hydrogen storage/delivery systems by determining important materials engineering properties of these complex hydrides.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

<u>On-Board Hydrogen Storage</u>

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability
- E. Refueling Time
- F. Codes and Standards
- G. Life Cycle, and Efficiency Analyses

<u>Reversible Solid-State Material Storage Systems (Regenerated On-Board)</u>

- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption
- O. Test Protocols and Evaluation Facilities
- P. Dispensing Technology.

Approach

We employ a parallel approach through work in each of the following areas:

- Investigate new complex hydrides to achieve higher capacities.
- Develop new doping process to improve both rates and capacity.

- Experimentally characterize the material properties using analytic techniques such as X-ray and neutron diffraction, electron spin resonance (ESR), nuclear magnetic resonance (NMR), etc.
- Determine the hydriding mechanisms through experimental analysis and modeling.
- Determine important engineering materials properties of the alanates to ensure that complex hydrides are on track for eventual commercialization.

Accomplishments

- Ti-doped Mg_2FeH_6 has been investigated as an analog to the alanate system.
- Preliminary investigation of Li-based complex hydrides has been performed.
- Using Sandia's direct synthesis and doping approach, it was found that Ti-halides (Cl, F, Br) all successfully enhance kinetics with $TiCl_2$ providing the best results.
- It was also determined that non-reactive precursors (TiH_2 and pre-reacted halides) improve kinetics, opening up new routes to improve capacity.
- Through collaborations with universities and other labs, we have performed in-depth NMR, neutron diffraction, and ESR measurements studies. These have aided in furthering our understanding of the Ti-doping mechanism.
- Pressure composition temperature isotherm (PCT) measurements have been performed on Na alanate. These measurements indicate that Ti-doping modifies the thermodynamic stability of the materials as well as the kinetics of hydrogen sorption.
- Detailed pressure- and concentration-dependent kinetics measurements have been made. This provided the basis for a more complete kinetics model that now allows the calculation of hydrogen sorption behavior over a broad range of conditions.
- Instrumentation has been completed and experimental work has been started to measure engineering materials properties of the complex hydrides, including thermal and electrical conductivity, volume expansion, and porosity. This work is critical for the ultimate commercialization of this technology.

Future Directions

- New complex hydrides: Continue work to achieve higher hydrogen storage capacities with reasonable kinetics compared with current sodium alanates.
- Search for new AlH_6-based alanates: Achieve higher hydrogen storage capacities by discovering new highly coordinated aluminum-hydrogen compounds.
- Structure properties and mechanisms of Ti-doped sodium alanates: Continue work to fully understand how transition metal doping affects the bulk structure properties that lead to enhanced kinetics of sodium alanates.
- Materials synthesis improvements and scale-up: Improve materials synthesis processes for the scale-up and commercialization of the state-of-the-art alanates.
- Effect of contaminants on performance of complex hydrides: Determine the degree to which low-level contaminants in a hydrogen gas supply will impact the performance of complex hydride storage materials.
- Materials compatibility and safety studies: Ensure materials compatibility of the complex hydride storage systems.
- Engineering material properties characterization: Experimentally investigate and report material properties of current state-of-the-art Ti-doped sodium alanates to enable engineering design solutions for hydrogen storage systems.

- Complex hydride systems life cycle analysis: Investigate the technology scale-up effects of potential systems used for solid-state hydrogen storage.

Introduction

The purpose of this project is to develop and demonstrate the next generation of practical hydrogen storage materials. This task will focus on complex metal hydrides with high reversible hydrogen storage capacities and novel approaches to on-board hydrogen storage.

This research is based on achievements that Sandia has made in developing advanced Ti-doped Na alanates [1]. The discovery of enhanced hydrogen sorption by Ti-doped alanates opened up an entirely new prospect for lightweight hydrogen storage [2-3]. These materials have nearly ideal equilibrium thermodynamics, high capacities, and moderate kinetics. However, while the hydrogen capacity is 2 to 3 times better than commercial low-temperature hydrides, it does not meet the DOE/FreedomCAR storage capacity targets. Thus, other higher capacity reversible complex hydrides must be developed. At the same time, Na alanates continue to provide a good working model to better understand reversible hydrogen sorption in complex hydrides. Sandia's direct synthesis process and new Ti-doping methods have led to a dramatic improvement in the reversible hydrogen capacity and hydrogen absorption and desorption rates. These methods will be employed to seek out advanced complex hydrides with larger hydrogen storage capacities and better performance.

Approach

Ti-doped alanate samples were prepared by direct synthesis from NaH and Al powders doped with 4 mol.% of $TiCl_3$. These powders were mechanically milled for 30 minutes in an argon atmosphere. Samples were prepared, transferred and measured without exposure to air.

Thermodynamic measurements were performed on a fully automated commercial PCT instrument. Absorption and desorption kinetics measurements were obtained volumetrically using manual Sieverts' apparatus and a cylindrical 316 SS reactor (1.3 cm outer diameter by 0.12 cm wall thickness and length of 12 cm) containing about 1.5 g of catalyzed samples. A thermocouple well in the center of the vessel allows for accurate temperature measurements during cycling. Data were recorded via computer, and measurements lasted from minutes to several days, depending on the $TiCl_3$, level test pressure, and temperature conditions.

Results

Thermodynamics of Ti-doped alanates. Our most recent measurements of the thermodynamic properties of the current generation of 4 mol.% Ti-doped alanates were performed using an automated PCT instrument (Figure 1). These measurements show the two plateau regions associated with the formation and decomposition of the $NaAlH_4$, the Na_3AlH_6 phases. Absorption and desorption measurements of the $NaAlH_4$ phase were made at 135, 150 and 170°C. These clearly show two distinct regions. One portion has a flat pressure plateau and the other is sloping. These results suggest that sample is composed of an inhomogeneous distribution of material with dissimilar kinetic and thermodynamic properties. One hypothesis is that

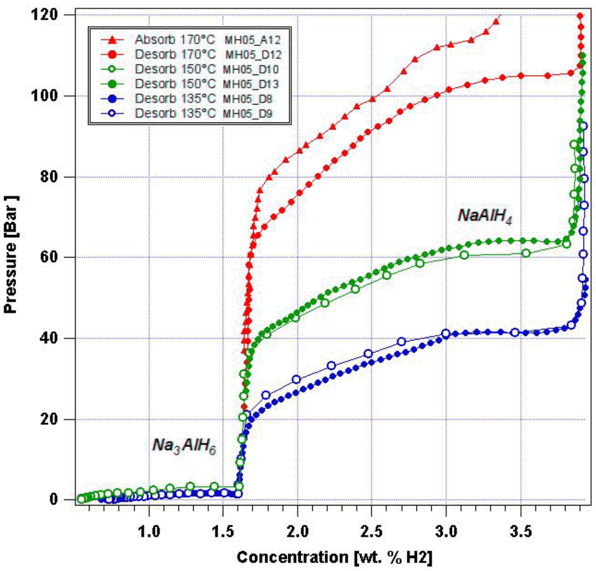

Figure 1. PCT measurements of Hydrogen Absorption and Desorption of $NaAlH_4$ and Na_3AlH_6 at 135, 150 and 170°C

the Ti is not homogeneously distributed in the sample. If that is the case, then there is a direct link between the presence of Ti and a change in the thermodynamics of alanate formation. Thermodynamics being a bulk property, this could only happen through introduction of Ti into the crystal lattice. Knowing whether Ti is at the surface or present in the bulk is fundamental to solving the mystery of the mechanism of the Ti-enhanced sorption properties. These preliminary results are being followed up with a more detailed analysis.

Kinetics of Ti-doped alanates. Hydrogen sorption rates of Ti-doped Na-alanate were measured at various temperatures, pressures, and hydrogen concentrations. Rate equations have been derived from this data to calculate the formation and decomposition kinetics of both $NaAlH_4$ and Na_3AlH_6. It was found that, in addition to temperature, the pressure differential (applied pressure vs. equilibrium pressure) and composition have a strong impact on the sorption rates. These equations provide important information that is needed for alanate performance modeling. Using these equations, the optimum temperature can be estimated for hydrogen absorption at a given applied pressure. For example, the best temperature for hydrogen absorption using 100 bar of hydrogen is 140°C, not 160°C (Figure 2). These equations can also be used to estimate the lowest temperature needed for desorption at a given rate and pressure. We intend to extend this approach to the kinetics of other hydrogen storage materials.

Fundamental studies of Ti-doped alanates. The structure of Ti-doped sodium aluminum deuteride has been determined using Rietveld refinement of X-ray and neutron powder diffraction data and compared to that of undoped $NaAlD_4$ and $NaAlH_4$. Neutron powder diffraction data were taken at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) with T. Udovic (Figure 3). Refinement of the diffraction data for deuterium atom positions of $NaAlD_4$ was complicated due to the four phases present in the sample: the tetra-deuteride $NaAlD_4$, the hexa-deuteride Na_3AlD_6, NaCl, and Al. Due to the small level of Ti-doping (4 at.%), the presence of Ti-Al compounds could not be conclusively determined, and no attempt was made to include any Ti-Al phases in the refinements [6]. The refined lattice parameters for the tetragonal $NaAlD_4$ structure are found to be a=5.010 angstroms and c=11.323 angstroms. Results of first-principles calculations of the lattice parameters are within a few percent of the Rietveld-refined values. The generalized gradient approximation (GGA) is found to produce significantly better agreement with the experimental data than the local-density approximation (LDA), which is attributed to a very inhomogeneous distribution of electronic density in the alanates. The Rietveld refinement, LDA, and GGA results for the

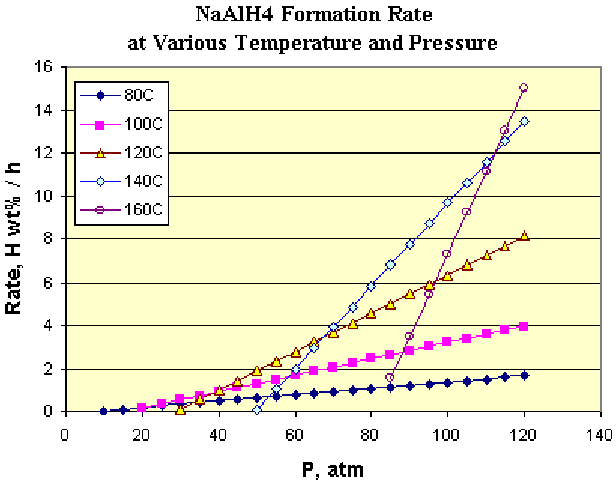

Figure 2. Calculated Hydrogen Absorption Rates for NaAlH4 as a Function of Pressure at Different Temperatures

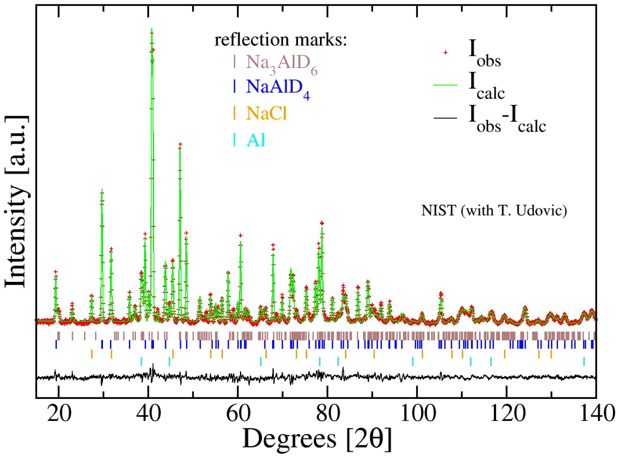

Figure 3. Rietveld Refinement of Powder Neutron Diffraction Data of a Ti-doped Alanate Sample

Al-H bond length in $NaAlD_4$ are 1.626, 1.634, and 1.631 angstroms, respectively. Refined values of the Al-H bond lengths in Na_3AlD_6 are in agreement within 2% of earlier work on undoped Na_3AlD_6 [5].

Improvements in materials synthesis. Our previous work raised questions about the importance of the Ti halide to Na halide decomposition reaction on the overall Ti-induced enhanced kinetics. It is this reaction that is responsible for most of the hydrogen capacity loss on Ti-doping the alanates. For this reason, an indirect doping process was tested. A sample was prepared in which $TiCl_2$ was pre-reacted with LiH by mechanical milling. The resulting powder was then milled in a 6 mol.% ratio with NaH and Al to form a pre-alanate mixture in which the Ti-halide had not been directly reacted with NaH. From a mechanistic point of view, this method should indicate whether or not the Ti halide and Na reaction is necessary for Ti-enhanced kinetics. From a practical perspective, this method may also provide an incremental improvement in capacity at higher doping levels due to the formation of the lighter LiCl byproduct rather than NaCl. The mixture was subjected to a series of hydriding / dehydriding cycles. The measurements showed an activation process that is much more profound than in the direct Ti halide doped materials. An Arrhenius plot (Figure 4) of desorption rates vs. temperature indicates similar activation energies for both the direct and the indirect doping methods. Thus, directly reacting Ti halides with sodium (hydride or metal) is beneficial for initially rapid kinetics, but not necessary for long cycle-life materials.

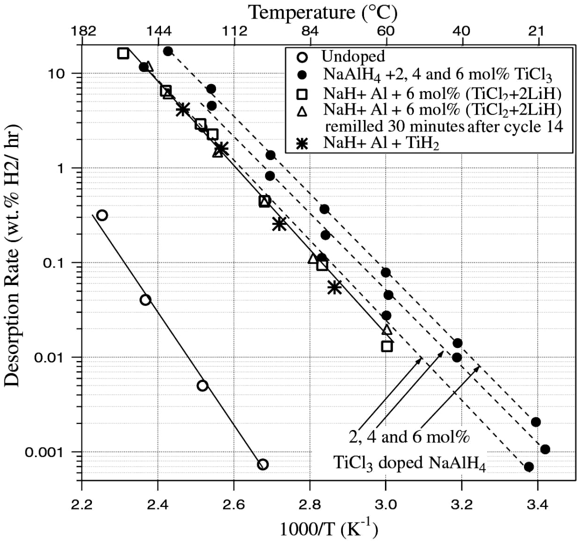

Figure 4. Arrhenius Plot Comparing $NaAlH_4$ Desorption Rates of Generation II, III-D, and III-E Alanates (rates: II on a total weight basis, III-D and III-E on a NaH + Al weight basis)

Extending the above notion that Ti-diffusion/substitution may be possible without using a Ti halide or organic precursor, a sample was tested using only TiH_2. Once again, the desorption rates are nearly identical to those of the indirect doped material and the 2 mol.% $TiCl_3$-doped alanates. From an applications perspective, TiH_2 as a dopant precursor should overcome the problem of capacity loss associated with the formation to Na halides when using Ti halide precursors.

New complex hydrides. We have been investigating other complex hydrides besides the Na alanates. These include Li alanates and Mg alanates. So far, neither system could be made to reversibly absorb hydrogen under moderate conditions (100 bar and up to 300°C). We have also investigated the Mg-Fe-H system through our International Energy Agency task 17 collaboration with the University of Geneva, Switzerland. Using our direct synthesis approach, we started with MgH_2 and Fe powders, which were mechanically milled together. The second absorption cycle showed activity beyond the formation of MgH_2. X-ray diffraction measurements showed both MgH_2 (about 41 wt%) and Mg_2FeH_6 (about 15 wt%) along with Fe (about 44 wt%) (Figure 5). We also tested the material prepared in the same manner but doped during the milling process with 4 mol.% $TiCl_3$. This preparation appears to have an effect on the rehydriding kinetics. Notably, there is rapid hydrogen absorption associated with the formation of MgH_2 even below 100ºC. The study of the Mg-Fe-H system is important because it is an analog to the Na alanate system. Demonstration of doping-enhanced reversibility in the Mg-Fe-H system will provide more clues as to the role of Ti and other transition metal dopants. In addition, it will demonstrate the possibility that a wider class of complex hydrides can be modified through doping. Detailed measurements are being performed at this time.

Engineering material properties. Engineering material properties investigations of Ti-doped sodium alanates is currently underway. The selection of the properties and the associated parameter space

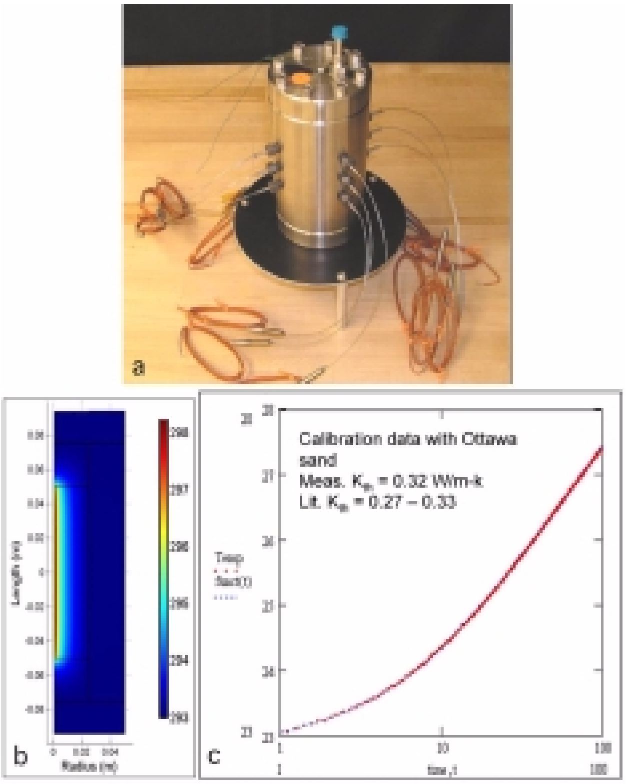

Figure 4. X-ray Diffraction Patterns of MgH_2 + Fe Before and After Hydriding Showing Presence of Mg_2FeH_6

focuses on hydrogen-storage application needs. For example, the characterization of the thermal conductivity of complex hydrides is critical for advanced design and modeling of hydride-based hydrogen storage systems. The thermal conductivity test hardware has been built and calibrated. A finite element model was used to determine optimum instrument design geometry as well as to validate the experimental method used to determine thermal conductivity. The model helped to minimize the mass of sodium alanate necessary to achieve accurate and measurable results. Testing on various calibration materials has provided consistent and repeatable results. Thermal properties testing of sodium-alanate as a function of phase composition and hydrogen gas pressure is in progress. In addition, a test cell has been constructed that can measure the pressure exerted on a wall by constraining the sodium aluminum hydride, and an electrical-properties cell has been built for measuring DC and AC response of the alanate material. All instrumentation has been designed to be used in the future to characterize new hydrogen storage materials as they are developed.

Conclusions

The results presented above demonstrate that solid progress is being made on the development of light-weight complex hydrides for hydrogen storage applications.

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6. "New Reversible Complex Hydrides for Practical Hydrogen Storage", K.J. Gross, E. Majzoub, World Hydrogen Energy Conference, 2002, Montréal, Canada

Special Recognitions & Awards/Patents Issued

1. Sandia National Laboratories internal funding through Laboratory Directed Research and Development grants: 1) Alanate-hydride fuel cell demonstration project (Gross), 2) Transition metal catalyzation of sodium aluminum hydrides (Majzoub)

Complex Hydrides for Hydrogen Storage

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Objectives

- Identify complex hydrides containing greater than 6 wt% hydrogen
- Obtain or prepare target compounds
- Investigate hydrogen release and reversibility of target compounds
- Maximize kinetics and reversible content of most promising materials

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Weight and Volume
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

- Select target compounds with greater than 6 wt% hydrogen
- Purchase or synthesize target compounds
- Determine hydrogen release/uptake characteristics of pure compounds
- Determine effects of ball milling on hydrogen release/uptake characteristics of pure compounds
- Determine effects of catalysts on hydrogen release/uptake characteristics

Accomplishments

- Identified alanates and borohydrides with greater than 6 wt% hydrogen
- Obtained or synthesized most promising compounds
- Studied solvent-free synthetic procedures
- Identified lithium alanate as a promising candidate
- Completed in-depth study of hydrogen release characteristics of lithium alanate
- Identified ball milling as the cause of lowered dehydriding temperature
- Studied effects of incorporation of Ti, $TiCl_3$, $TiCl_4$, TiH_2 $AlCl_3$, Ni, Fe, $FeCl_3$, C, and V on lithium alanate hydrogen release
- Found that Ti and TiH_2 caused minimal decrease in hydrogen content
- Discovered that elemental titanium, ball milled with sodium alanate, facilitates rehydriding

Future Directions

- Complete investigation of exothermic decomposition of lithium alanate
- Study the reversibility of catalyzed lithium alanate
- Synthesize solvent-adduct free magnesium alanate
- Investigate decomposition products and reversibility of borohydrides

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Introduction

Studies involving complex hydrides of aluminum so far reported in the literature have been primarily restricted to sodium aluminum hydride with a smaller amount of work reported involving lithium aluminum hydride. While these studies are important from a fundamental and mechanistic point of view, they do suffer two serious limitations. One limitation is that the reversible hydrogen capacity of sodium aluminum hydride falls short of the hydrogen content required for practical application. A second limitation arises from the very complex nature of the alanates. Progress in understanding the mechanisms of hydrogen uptake and release and catalyst function in these systems is hampered by data interpretation based on questionable chemistry. For example, in one study,[1] it was reported that the ball milling of $TiCl_3$ with $NaAlH_4$ resulted in the reduction of titanium by the Na in $NaAlH_4$. This conclusion was supported by the comparison of the $TiCl_3$-$NaAlH_4$ system to an industrial process in which $TiCl_4$ is reduced by hot elemental Na. These two systems are not comparable. In $NaAlH_4$, Na is in the Na^+ form and is incapable of reducing anything. The industrial process utilizes elemental sodium, an excellent reducing agent. This form of sodium is capable of functioning as a reducing agent because it has an electron to lose, forming Na^+ in the process. The work described in that report is excellent from a physics, solids, and materials point of view. However, the mechanistic error punctuates the need for multidisciplinary teams, including chemists as well as physicists and materials scientists, to solve the hydrogen storage problem.

While the recent advances in hydride storage by the research groups of Bogdanovic,[2] Jensen,[3] Zaluski,[4] and Gross[5] have illustrated the reversibility of select complex hydrides, none have been shown to contain the required amount of hydrogen. Additionally, some of the contradictions and inaccuracies in the published work illustrate the need for more in-depth investigations from a chemical viewpoint. Because of the low reversible hydrogen content in the compounds that others are studying, this work has purposely targeted complex hydrides that theoretically contain hydrogen at a higher level than does the sodium aluminum hydride.

Approach

The literature was surveyed for known complex hydrides of aluminum and boron that contain greater than 6% hydrogen. Of the compounds revealed, those that were commercially available were purchased. Those with reported literature syntheses were prepared according to those methods. For those without reported syntheses, procedures were developed. Both wet chemical and solvent free synthetic procedures were investigated.

The compounds were subjected to a baseline study to determine the onset temperatures and rates of hydrogen release, and the reversibility of the process in the uncatalyzed form. This part of the work revealed the need for additional study of lithium alanate due to its unusual characteristic of exothermic dehydrogenation and large hydrogen content.

Following the baseline study, the effects of catalysts on the reversibility of the dehydrogenation were studied. Because the catalysts were incorporated using a high-energy ball milling, the effects of ball milling alone were also investigated.

Results

The primary goal of this project was to investigate a series of complex hydrides of aluminum and/or boron, with large hydrogen contents, as hydrogen storage media. The compounds originally considered contain a minimum of 7.5% hydrogen by mass. While some of these hydrides have been reported to decompose to compounds that still contain one or more hydrogens, the numbers shown below reflect total hydrogen content. A secondary goal was to identify a catalyst for each hydride that facilitates decomposition while enabling rehydrogenation.

The hydrides originally considered were $NaAlH_4$ with 7.5% H, $Ca(AlH_4)_2$ with 7.7% H, $Zr(BH_4)_3$ with 8.8% H, $Ti(AlH_4)_4$ and $Mg(AlH_4)_2$ both with 9.3% H, $NaBH_4$ and $LiAlH_4$ both with 10.5% H, $Ca(BH_4)_2$ with 11.4% H, $Fe(BH_4)_3$ with 11.9% H, $Ti(BH_4)_4$ with 12.9% H, $Mg(BH_4)_2$ with 14.8% H, $LiAlH_4(BH_4)_4$ with 15.2% H, $LiBH_4$ with 18.2% H, and $Al(BH_4)_3$ with 20.0% H.

Because dehydriding is typically endothermic, we decided to investigate the observed exothermic dehydrogenation of $LiAlH_4$. The thermogram for $LiAlH_4$, Figure 1, shows that three exothermic events, with onset temperatures of 139°C, 157°C, and 169°C, respectively, were associated with the decomposition of $LiAlH_4$. The pressure data indicate that gas release, most likely hydrogen, began at approximately 110°C but reached a maximum rate at a temperature corresponding to the onset temperature of the first exothermic event in the thermogram. This release continued until approximately 4% of hydrogen was released. Then, the hydrogen release sharply slowed at approximately 170°C, corresponding to the onset temperature of the third exothermic event in the thermogram. This slower hydrogen release continued until approximately 6.3% hydrogen was lost. The first and third exothermic events in the thermogram were thus associated with hydrogen release, and the second event was most likely a phase change that occurs with no gas release.

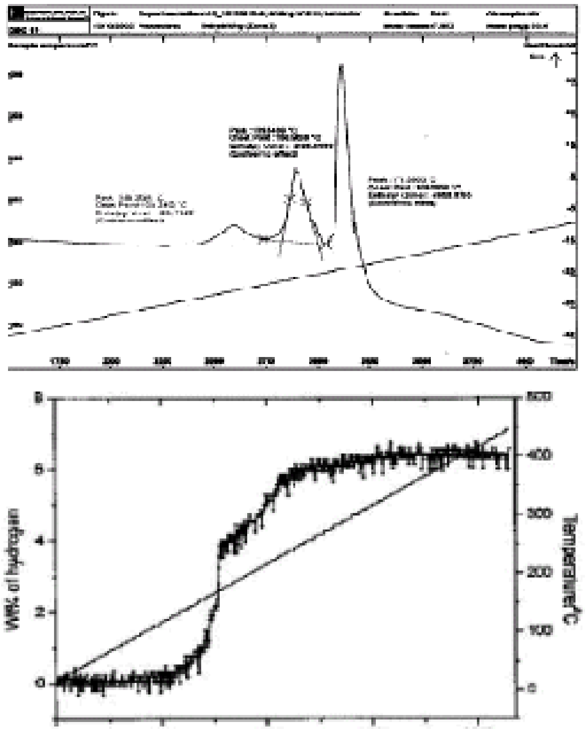

Figure 1. Thermogram (top) and Pressure Plot (bottom) for the Thermal Decomposition of $LiAlH_4$

Catalyst studies were begun with titanium using the mechanical incorporation method suggested by Jensen, et al.[3] Ball milling $LiAlH_4$ with $TiCl_4$ did decrease the temperature required for dehydrogenation, as was reported by Jensen in his study of $NaAlH_4$. As was also reported by Jensen in his work with $NaAlH_4$, the hydrogen content was significantly decreased due to the fact that the Ti^{4+} was reduced during the ball milling process, causing loss of a portion of the stored hydrogen. The reducing agent for this process must have been the alanate ion, AlH_{4-}, since neither Li^+ nor Na^+ is capable of such a reaction. The resulting NaCl was a difficult-to-remove, non-hydriding contaminant, further decreasing hydrogen capacity.

The pressure plots obtained by dehydriding undoped $LiAlH_4$, $LiAlH_4$ milled alone, and $LiAlH_4$ samples doped with Ti, $TiCl_3$, $TiCl_4$, and TiH_2 can be seen in Figure 2. Doping with titanium(III) chloride and with titanium(IV) chloride both result in a greatly decreased hydrogen release due to the loss of the first hydrogen release step. Doping with TiH_2 or with elemental titanium causes only a slight decrease in the amount of hydrogen released and does not eliminate the first step of hydrogen release. Thus, it is hoped that incorporation of either of these catalysts will result in allowing lithium alanate to reversibly bind hydrogen while retaining a large hydrogen content.

Ball milling alone results in about the same decrease in the amount of hydrogen released as doping with either TiH_2 or Ti. Most interesting is the fact that ball milling alone causes the same reduction in the temperature of hydrogen release as does doping.

Figure 3 shows the differential scanning calorimetry (DSC) pressure data for the thermal decomposition of $LiAlH_4$ samples that were ball milled with $AlCl_3$, Ni, Fe, $FeCl_3$, carbon black, and with V. Nickel caused a small decrease in the amount of hydrogen released, while vanadium caused a larger decrease. The effect of nickel appeared to be limited to the first step of hydrogen release, while vanadium appears to have decreased the amount of hydrogen released from both steps of the decomposition. Incorporation of aluminum chloride or elemental iron produced the same effect on the temperature of hydrogen release. However, the iron also appears to have caused a decrease in the amount of hydrogen released in the first step. Iron(III) chloride caused a reduction in the hydrogen release temperature. However, this temperature decrease was accompanied by a significant decrease in the amount of hydrogen released in both decomposition steps.

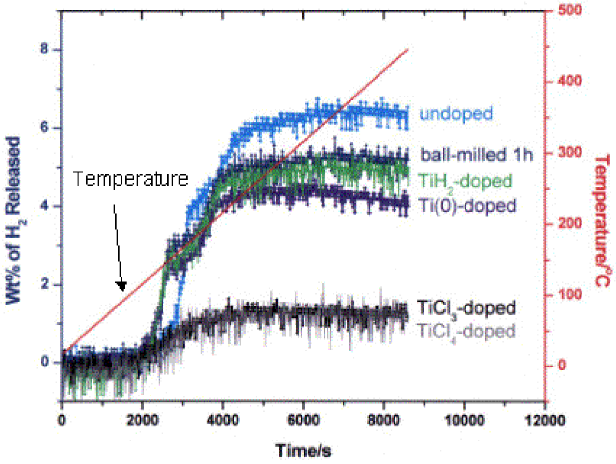

Figure 2. DSC Pressure Data for Dehydriding of $LiAlH_4$ Doped with Ti, $LiAlH_4$ Doped with $TiCl_3$, $LiAlH_4$ Doped with $TiCl_4$, $LiAlH_4$ Doped with TiH_2, and $LiAlH_4$ Ball Milled without Doping

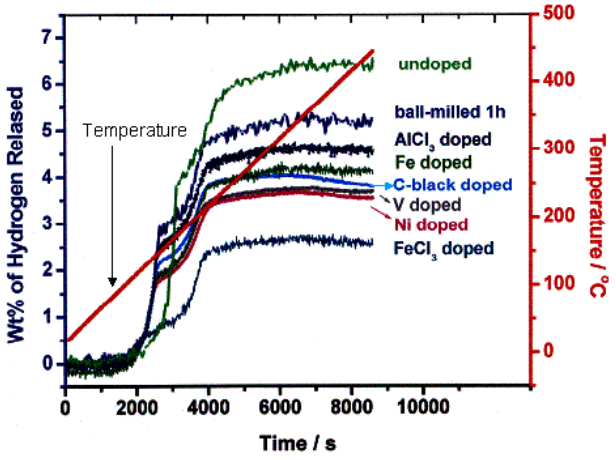

Figure 3. DSC Pressure Data for the Thermal Decomposition of $LiAlH_4$ Samples That Were Ball Milled with $AlCl_3$, Ni, Fe, $FeCl_3$, Carbon Black, and with V

Conclusions

- Synthesis of a number of alanates and borohydrides investigated
  - Wet chemical methods used for synthesis of magnesium alanate, magnesium borohydride, and calcium borohydride
  - Solvent free methods used for $Mg(AlH_4)_2$, $Mg(BH_4)_2$, a magnesium hydride/titanium hydride mixture, $Ti(AlH_4)_4$ and $Ti(BH_4)_4$
  - Synthesis of $Mg(AlH_4)_2$ solvent adduct accomplished
  - Wet chemical methods yielded solvent adducts that decomposed upon solvent removal
  - Solvent free synthetic methods identified as having greatest potential
- Lithium alanate is a potentially viable hydrogen storage compound
  - Large hydrogen capacity
  - Decomposition is exothermic
  - Decomposition mechanism varied with material manufacturer
  - Decomposition of ball milled Lancaster sample resembles Aldrich sample
  - Improved kinetics and reduced dehydriding temperature result from ball milling
- Effects of catalysts on dehydrogenation of lithium alanate studied
  - Addition of $TiCl_3$, $TiCl_4$, or $FeCl_3$ results in large reduction of hydrogen content

  - Addition of V results in the same decrease in hydrogen release temperature but with smaller loss in hydrogen capacity
  - Addition of Fe, $AlCl_3$, Ni, C, Ti, or TiH_2 results in a decrease in the temperature of hydrogen release without a significant loss of H_2 capacity
    - Temperatures similar to those of undoped, ball milled material

- Mechano-chemical synthetic procedures for complex hydrides studied

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High Density Hydrogen Storage System Demonstration Using $NaAlH_4$ Based Complex Compound Hydrides

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QuesTek, LLC, Evanston, IL

Objectives

- Improve the charging and discharging rates of the $NaAlH_4$ based hydrogen storage medium. Specifically, in collaboration with other efforts:
  - Increase the reversible weight fraction of hydrogen stored to 7.5% from the current 5.5%
  - Enhance the hydrogen evolution rate from 0.1 wt%/hr at 80°C to 0.55 wt%/hr to meet fuel cell demands
  - Increase the regeneration rates from the documented 0.5 wt%/hr to 90 wt%/hr to achieve the five minute refill requirement
- Determine the safety and risk factors associated with enhanced compositions
- Design, develop and evaluate a hydrogen storage system having a 5 kg hydrogen capacity and installation capability in a fuel cell powered mid-size sedan

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Weight & Volume
- D. Durability
- E. Refueling Time
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

- Create combined atomistic/thermodynamic models of the $NaAlH_4$ system to determine catalyzed compositional ranges, sorption mechanisms and the effects various catalyst additions have on these mechanisms.
- Cyclically evaluate selected Complex Compound Hydride (CCH) compositions to determine degradation mechanisms and ameliorations as well as compatibility with construction materials.
- Conduct standardized safety testing related to the classification of hazardous materials.

- Develop preliminary designs through the evaluation of existing systems, generation of weight/volume/cost improvements, and high level optimization to balance automotive demands.
- Perform heat and mass flow modeling for detailed optimization of the required system volume, mass and hydrogen sorption characteristics. Evaluate methods to enhance heat conduction into the CCH powder.
- Fabricate and evaluate 1 kg H_2 and 5 kg H_2 capacity hydrogen supply systems.
- Conduct preliminary system performance modeling analyses of the combined proton exchange membrane fuel cell (PEMFC)/H_2 storage system under steady state and transient conditions to establish system optimization and dynamic control requirements.

Accomplishments

- Applied atomistic/thermodynamic modeling to complex compound hydrides successfully.
- Completed safety experiments resulting in no change in transportation packing class for these materials from their unmodified condition.
- Characterized two alanate compositions for sorption kinetics.
- Identified preliminary design and materials of construction based on volume, mass and cost estimates.
- Completed sub-component models and trials.

Future Directions

- Complete design of the first 1 kg hydrogen storage system designated CCHS#1.
- Identify catalyzed $NaAlH_4$ media composition from characterized compositions.
- Complete fabrication, media catalyzation and loading of CCHS#1.
- Evaluate system operating characteristics, hydriding and dehydriding rates, and system volumetric and gravimetric densities utilizing laboratory supplied heat and hydrogen.
- Initiate system modeling efforts based on previously understood fuel cell and balance-of-plant models.

Introduction

One of the most significant barriers to the widespread application of hydrogen-based propulsion is the development of on-board storage systems which can provide the needed quantity of hydrogen with acceptable volume, weight, cost and safety risk. The major classes of established hydrogen storage methods - compressed gas, liquid, metal hydrides and chemical hydrides - all have advantages and disadvantages, but none is clearly superior for automotive transportation. In particular, a disadvantage of metal hydrides is their low hydrogen capacities of less than 2 wt% for alloys with discharge temperatures such that the waste heat of a PEMFC (~ 90 °C) can be used to release the hydrogen. Many chemical hydride materials, while having high capacities, are classified as irreversible, which requires that the entire material be replaced during refueling rather than simply charged with hydrogen gas. This project is focusing on the reversible chemical hydride, $NaAlH_4$, with a theoretical hydrogen capacity of 5.5 wt%, and seeks to enhance the material for improved charging and discharging rates as well as increased capacity. Safety studies of the enhanced material will be conducted to support the technology as it is driven toward commercialization.

The project also seeks to apply this material in the development of a system which will reversibly store a high wt% of hydrogen at low pressure for an indefinite amount of time. The storage system which contains the CCH powder must serve two primary functions: (1) exchange heat between the powder and a working liquid to drive the absorption/desorption of hydrogen; (2) support elevated hydrogen pressure during refueling. These functions must be performed with a minimum of weight, volume and cost. In addition, there are other secondary characteristics such as (i) allowing for significant volumetric change of the powder, (ii) exchanging hydrogen without the loss of the fine CCH powder particles, (iii) maintaining chemical compatibility with the CCH powder and hydrogen, (iv) producing minimal impurities going to the PEMFC, and (v) fitting into a conformable volume.

Approach and Results

Atomistic models were created utilizing the Vienna Ab-initio Simulation Package (VASP) of $NaAlH_4$, Na_3AlH_6 and NaH using known lattice parameters and atomic occupation sites. Full volume and site relaxations were allowed with resulting structures nearly identically replicating literature values. Catalyst substitutions of Ti^{+3}, V^{+3}, Zr^{+4} and Li^{+1} were made in both the $NaAlH_4$ and Na_3AlH_6 structures with transition metal substitution for Al^{+3} cations and alkaline metal substitutions for Na^{+1} cations showing the lowest lattice energy, by far (see Figure 1). Lattice enthalpy (DH) calculations were performed on various "compositions" of catalysts from which thermodynamic calculations utilizing ThermoCalc were able to determine free energy of formation, DG. From the free energy determinations, the vant Hoff plots for various compositions of catalyst were calculated, see Figure 2. The results of these calculations indicate catalyst additions modify the thermodynamics of hydrogen sorption and thus play a far more significant role than simple heterogeneous catalysis as referred to in the literature.

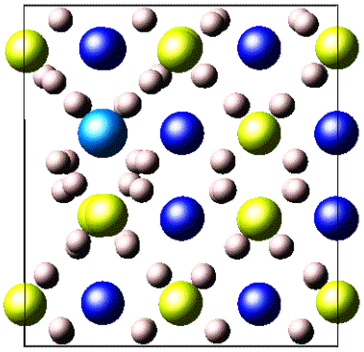

Figure 1. Atomistic Model Depicting Insertion of Ti^{+3} Cation into $NaAlH_4$ Super-Cell Substituting for Al^{+3} Cation after Volume and Energy Relaxation

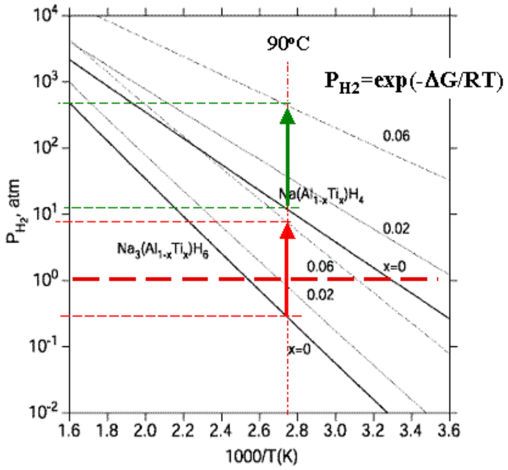

Figure 2. Vant Hoff Plot of Calculated Pressure Equilibria for 2 & 6 m% Ti^{+3} Substituted $NaAlH_4$ and Na_3AlH_6

An equation depicting the rate of a chemical reaction as a function of temperature, pressure and composition taken from Reference 1 which was first implemented in modeling of LaNi5 hydrogen storage beds is defined as:

$$\left(\frac{dC_1}{dt}\right)_{r1} = A_1 \exp\left(-\frac{E_1}{RT}\right) * \left(\frac{P_{e,1} - P}{P_{e,1}}\right) * (C_2)^{\chi_1}$$

where Ci is the composition; Pe,i is the plateau pressure for composition i; Ai, Ei and Ci are experimentally determined constants for reaction i; and t, R, T and P are the time, gas constant, temperature, and pressure, respectively. Figure 3 depicts the modeled rates of reaction and experimental verification of the model with very good agreement resulting. These equations can be solved simultaneously for the sorption rates of $NaAlH_4$ and Na_3AlH_6 respectively. Given these rates of reaction and the heats of reaction developed elsewhere, a spatially resolved temperature distribution can be modeled utilizing a finite element method (FEM) code. These calculations were carried out using various preliminary system designs, heating fluid temperatures, etc. Figure 4 shows the results of three such simulations for differing numbers of heat transfer fluid conduits.

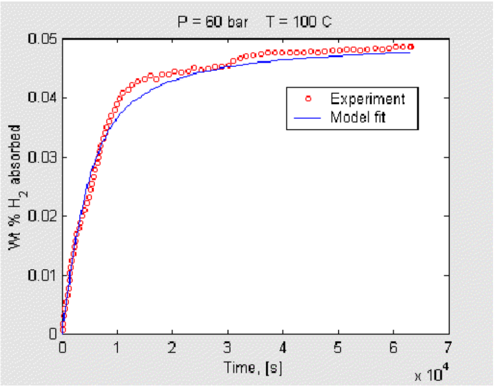

Figure 3. Comparison of Calculated and Measured Hydrogen Absorption and Desorption

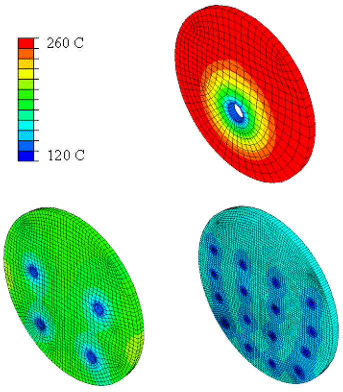

Figure 4. Temperature Distribution at 1400 sec. after Charging at 100 Bar H_2

A series of experiments were conducted to measure the reactivity of the catalyzed CCH media in contact with either water or air. Experimental details were taken from two sources: DOT/UN Doc., Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria [Reference 2], and from ASTM E1226, Dust Explosion Testing. Tests were conducted in three materials states: fully charged, primarily $NaAlH_4$; partially discharged, composed of a mixture of Na_3AlH_6 and Al^o powder; and fully discharged, composed of NaH and Al^o powders. Various combinations of water and air contact and ambient and elevated temperatures were included in the testing protocols. The results of these tests confirmed that these compounds are water and humidity reactive, but their packaging and handling classifications do not change with the addition of catalysts. The hexa-hydride materials were somewhat more reactive in spontaneous ignition and burn rate testing than either of the other compositions.

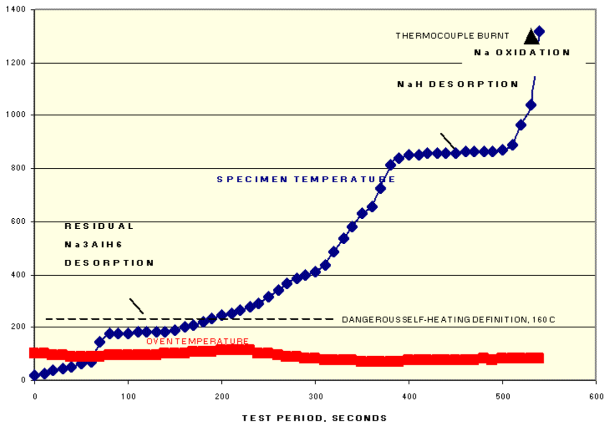

Figure 5. Time/Temperature Plot of Partially Discharged Material Heated to 100°C in Air Showing Various Oxidation Events

The results of one test are depicted in Figure 5 where the partially discharged material was packed into a 25 cm^3 cube, loaded into a furnace and heated in air to 100°C. The temperature vs. time plot given in Figure 5 shows the development of oxidation reactions in which a thermocouple is inserted into the powder. Two reactions are clearly observed, one initiating at approximately 200°C which is thought to be dehydrogenation of the Na_3AlH_6 compound, and the other initiating at ~850°C thought to be dehydrogenation of NaH. Oxidation of Na^o and Al^o metals proceeds exothermically to temperatures greater than 1200°C where the thermocouple failed.

Conclusions

1. Numerous experiments were carried out on catalyzed $NaAlH_4$ in various phases of decomposition. The results indicate these materials to be flammable when in contact with water or water vapor in the air. The partially discharged material containing a mixture of Na_3AlH_6 and aluminum powder was found to be somewhat more reactive than the fully charged material, but in all cases, the packing classification did not change.

2. Significant advances have been made in modeling of the media utilizing a combination of atomistic and thermodynamic methods which has proven to be state-of-the-art in its methodology and enlightening in its results. If the catalytic additions can be made to stay within the host structure, upon repeated sorption cycles, the full 5.5 wt% of hydrogen should be accessible at pressures above 1 bar.

3. An analytical expression for hydrogen sorption rates was identified in the literature and utilized in conjunction with known thermodynamic values to predict temperatures in simulated hydrogen storage systems.

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2. DOT/UN Doc., *Recommendations on the Transport of Dangerous Goods*, Manual of Tests and Criteria, 3rd Revised Ed., ISBN 92-1-139068-0, (1999).

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1. D.L. Anton, High Density Hydrogen Storage System Development, IEA Task XVII, Fall 2002, Geneva.

2. D.L. Anton, High Density Hydrogen Storage System Development, IEA Task XV, Spring 2003, Stockholm.

3. D.L. Anton, *Hydrogen Desorption Kinetics in Transition Metal Modified* $NaAlH_4$, MH2002, Annecy, France, Sept. 2002.

4. S.M. Opalka, *First Principles Study of Sodium-Aluminum-Hydrogen Phases*, MH2002, Annecy, France, Sept. 2002.

5. D.L. Anton, *Hydrogen Desorption Kinetics in Transition Metal Modified* $NaAlH_4$, J. Alloys & Compounds, (in press).

6. S.M. Opalka and D.L. Anton, *First Principles Study of Sodium-Aluminum-Hydrogen Phases*, J. Alloys & Compounds, (in press).

Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods (New FY 2004 Project)

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Objectives

To discover complex metal hydrides for hydrogen storage that contain 6% or more of hydrogen and can reversibly desorb hydrogen between -40 and 90ºC

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- M. Hydrogen Capacity and Reversibility

Approach

The objective of the proposed project is to discover complex metal hydrides for hydrogen storage which contain 6% or more of hydrogen and can reversibly desorb hydrogen between -40 and 90ºC. The project will combine molecular modeling with high-throughput combinatorial material synthesis, testing and characterization, large-scale materials testing, and system engineering studies to produce prototype commercially viable hydrogen storage systems.

The focus of the first project year is to establish, validate and demonstrate the combinatorial tools and molecular modeling approach, while initiating materials discovery experiments. Specific first year objectives include:

- Refine technical requirements
- Develop and validate medium-throughput (parallel) synthesis, screening and characterization tools
- Design and implement the high-throughput solution and solid-phase synthesis, screening and characterization tools
- Develop theoretical methods to predict equilibrium structures of complex hydrides
- Finalize material classes for the second year screening studies
- Begin screening experiments on complex metal hydrides in the medium-throughput system

The focus throughout the second year will include screening studies of candidate hydrogen storage materials. Screening will continue in the medium-throughput system while validating the high-throughput system, after which both systems will be used. Detailed modeling and characterization studies will guide screening toward materials likely to have thermodynamics required to meet the DOE technical targets. Modeling and characterization and the results from the screening studies will be used to identify mechanisms of action in new materials. Specific second year objectives include:

- Validate the high-throughput synthesis and testing system
- Perform screening studies (medium and high throughputs) on expanded classes of complex metal hydrides
- Perform modeling studies to predict the thermodynamics of novel complex hydrides
- Conduct detailed characterization studies on promising candidates
- Advance mechanistic understanding of new complex metal hydrides
- Evaluate and select most promising classes/candidates for optimization studies in the third year

The goal of the third project year is to produce an economical hydrogen storage system by optimizing hydride catalyst combinations, scaling them up for commercial testing, and performing analyses to assess the economic value of the resulting hydrogen storage system. Specific third year objectives include:

- Predict phase diagrams of candidate materials from empirical data and theoretical predictions
- Optimize hydride/catalyst combinations
- Demonstrate successful scale-up and design prototype hydrogen storage systems
- Conduct engineering analyses to verify suitability to meet DOE technical targets
- Analyze economic factors to establish commercial viability

Sub-Nanostructured Non-Transition Metal Complex Grids for Hydrogen Storage (New FY 2004 Project)

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Objectives

To grow sub-nanostructured metal grids for hydrogen absorption in storage applications

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Hydrogen Capacity and Reversibility

Approach

The primary goal of this project is to grow sub-nanostructured metal grids for hydrogen absorption in storage applications. Sub-nanostructuring will:

1. Increase hydrogen molecule dissociation rate on the active sites
2. Increase hydrogen atom transport rate into the metal
3. Decrease performance degradation by cycling caused by decrepitation
4. Increase heat transfer in the metal matrix
5. Increase hydrogen uptake

This novel approach involves electrochemically growing the metal phase, an atom at a time, in a sub-nanostructured “mold.” The mold will be made from known zeolites including the recently discovered titanium silicate, which has unique structural characteristics. The energy required for the growth is minimal; it is equal to the electron charge (times the valence) per metal atom.

The major tasks involved in this project are: 1) zeolite growth and treatment, 2) cathode preparation, 3) electrochemical growth, 4) physical characterization, 5) chemical characterization and performance evaluation.

Task 1. Zeolite Growth and Treatment: It is necessary to grow zeolite crystals with the required morphology to obtain a uniform film on the cathode. Normal growth of zeolites involves hydrothermal synthesis between 150-300^{O}C under autonomous pressure in autoclaves. The crystal morphology is controlled by the solution chemistry (which may include inert additives) and time-temperature combination. The alumina/silica ratio of zeolites is controlled during synthesis to optimize the density of exchangeable cations. In addition to morphology, the formulations must be optimized for optimum cation density and for ease of zeolite mold removal after the metal grids are grown.

Task 2. Cathode Preparation: Cathode preparation is the most significant technical hurdle in this project. The cathode coated with zeolites must not have any macroscopic pathway for cations to diffuse. This requires mechanical compacting and/or polymer patching and/or in-situ growth of the zeolite around the electrode. We will start with readily available powders in our labs to gain experience in cathode preparation. Later, we will switch to specially grown powders in Task 1 to minimize the macropores.

Task 3. Electrochemical Growth: This is the heart of the process, where the metal grid is electrochemically grown in the zeolite micropores one atom at a time. We will start electrochemical growth with electrodes prepared by mechanical compaction with readily available powders to gain experience with electrochemical growth. Later, we will switch to specially prepared electrodes. In all cases, the growth kinetics will be closely monitored.

Task 4. Physical Characterization: The metal grids will be first physically characterized by using standard techniques such as optical and scanning electron microscopy for morphology, x-ray fluorescence for non-destructive and wet-chemistry including atomic absorption as destructive elemental analysis, atomic force mocroscopy/scanning tunneling microscopy for nano-structure analysis, and simple density measurements. Only samples that show acceptable nano-structure will be chemically characterized after zeolite mold removal.

Task 5. Chemical Characterization and Performance Evaluation: Analysis of equilibrium and kinetic data coupled with physical property data enable hydrogen storage performance calculations including mass balances, energy balances, estimated charge/discharge times (under isothermal conditions), etc. The performance calculations will be based on the packing material rather than the overall system. The performance will be compared to available data for other approaches and to the target values.

During the first year of the project, it will be determined whether pure metal grids can be grown that have equilibrium and/or kinetic performance better than the same metal in bulk phase. In the second year, the cathode preparation method will be finalized, and sub-nanostructured non-transition metal complex grids will be grown. In the third year, anode preparation and electrolyte chemistry will be finalized, an analysis will be completed of projected hydrogen storage, and an evaluation/cost estimate will be completed.

III.B.7. Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity (New FY 2004 Project)

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Objectives

- Develop a reversible, 7.5 hydrogen wt.% capacity complex hydride with the kinetics required for automotive PEM fuel cell operation, which can be cyclically discharged and recharged for 500 cycles.
- Prepare such a storage media in sufficient quantities to enable evaluation in a subscale hydrogen storage system.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Weight and Volume
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

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Approach

The goal of the project is to develop a new complex hydride compound capable of reversibly storing hydrogen with capacity greater than 7.5 wt.% for 500 regeneration cycles with 100% efficiency. The project will develop, prepare and deliver such a storage media in sufficient quantities to enable evaluation in a sub-scale hydrogen storage system being developed under the DOE contract "High Density Hydrogen Storage System Demonstration Using $NaAlH_4$ Based Complex Compound Hydrides."

The objective of this project is to discover new reversible high hydrogen content complex hydride compounds of the structure $Na_yM_{+ix}(AlH_4)_{y+ix}$, in the quaternary phase space between sodium hydride (NaH), alane (AlH_3), transition metal or rare earth (M) hydrides (MH_z, where z= 1-3) and molecular hydrogen (H_2). This project will encompass all of the technology development stages for identifying, developing and commercializing complex hydride compound hydrogen storage media to meet the DOE technical targets. The team will accelerate the discovery of new complex hydride compounds and guide experimentation with first principles modeling. Simultaneously, the team will apply multiple synthetic methodologies to isolate new hydrides, and couple thermodynamic predictions and structural characterizations to verify structures of newly identified phases. The team will conduct three levels of performance evaluations to select compositions for further development, optimize dehydrogenation and hydrogenation catalysis with spectroscopic mechanistic studies and first-principles screening simulations, develop manufacturing processes to reduce cost and scale-up production, and develop business analyses for the commercialization of hydrogen storage systems integrated with fuel cell power plants.

The following tasks are planned for year 1.

Task 1.0 First Principles Modeling

- Predict new quaternary complex hydride compositions to recommend for synthesis targets
- Evaluate the theoretical phase stability and reversible hydrogen content of the best quaternary complex hydride candidates, and identify new catalyzed quaternary compositions with decreased dehydrogenation activation barriers.
- The compilation of a candidate structure list for ground state screening simulations from the structural and thermodynamic parameters of analogous compounds will be completed.
- Present compositional section phase diagrams and pressure-composition-temperature diagrams established to evaluate the phase stability and reversible hydrogen content of high capacity systems

Task 2.0 Synthesis

- Materials will be synthesized via three distinct processing routes: solid state processing, molten-state processing and solute based processing. Synthesis attempts will be performed on lithium and titanium alanate compounds and mixed sodium/lithium/titanium compounds. Following identification and synthesis of such phases, 5-10 g samples will be synthesized for performance evaluations.
- Synthesis attempts will be performed on compounds and mixed sodium compounds, which are hypothesized to exist based on high catalytic activity and solubility in $NaAlH_4$
- Initial samples will be analyzed and processing iterated to synthesize 5-10 g samples for performance evaluation.
- Analyses will yield data on the temperature and preliminary thermal properties of dehydrogenation reactions

Task 3.0 Analysis

- Thermodynamic variables will be determined for a selected number of compounds, which hold promise for enhanced hydrogen storage capability. This information will be used for ab-initio model verification.
- Once a new phase has been identified and a process developed to synthesize it in reasonable purity, it will be tested using a Sievert's apparatus specifically designed to measure solid/gas reaction kinetics. Each sample will be prepared identically to yield a comparative base between current state-of-the-art $NaAlH_4$ compounds under development and the new high hydrogen capacity materials being developed in this project.
- Thermodynamic variables will be determined for a selected number of compounds, which hold promise for enhanced hydrogen storage capability. This information will be used for ab-initio model verification.

Task 4.0 Performance

- Measure solid/gas reaction kinetics; confirm capacity

Hydrogen Storage in Carbon Single-wall Nanotubes

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Objectives

- Develop reproducible hydrogen capacity measurements and sample preparation methods.
- Meet the DOE hydrogen storage goals of 4.5 wt% H_2, 1.2 kWh/L by 2005.
- Optimize scalable methods for the production and purification of carbon single-wall nanotubes (SWNTs) and other nanostructured carbons for hydrogen storage.
- Gain better understanding of the hydrogen adsorption mechanisms for carbon nanotube/metal composites, particularly the importance of how, and in what form, the metal is incorporated into the SWNTs.
- Develop new methods for controlled metal incorporation in purified, cut SWNT samples.
- Probe other carbon systems for potential high hydrogen storage capacities at near ambient conditions.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- C. Durability
- D. Refueling Time
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Physisorption and Chemisorption
- O. Test Protocols and Evaluation Facilities
- P. Dispensing Technology

Approach

- Establish Carbon Materials Working Group (CMWG) to develop sample handling and measurement protocols and improve reproducibility of capacity measurements.
- Improve purification technique to efficiently remove graphite-encapsulated metal particles present in SWNT materials generated by a wide variety of techniques.
- Develop a low-cost, gas-phase, continuous process for carbon nanotube production employing hot wire chemical vapor deposition (HWCVD).
- Fabricate carbon nanotube samples containing iron particles of differing sizes and occurring at different but specific sites and determine the hydrogen storage properties of these highly specific samples.

- Employ TiI_4 vapor transport to deposit small Ti particles in purified, cut SWNT samples. Employ thermal evaporation of Ti to deposit thin metallic films on purified, cut SWNT samples.
- Analyze the hydrogen storage properties of conducting carbon polymers supplied by Prof. Alan MacDiarmid at the University of Pennsylvania.
- Analyze the hydrogen storage properties of HWCVD generated nano-crystalline graphite doped with iron nanoparticles.

Accomplishments

- Incorporated a CO_2 oxidation step in the purification process to remove graphite-encapsulated metals more completely.
- Developed a low-cost, scalable HWCVD technique for the continuous production of carbon multi-wall nanotubes (MWNTs) and demonstrated the potential of the same technique for SWNT production.
- Discovered that the activation of hydrogen storage on carbon nanotubes at near ambient conditions is dependent on the incorporation of small metal particles in highly intimate contact with the tube structure.
- Determined barriers to Ti incorporation via both vapor transport and evaporation, but gained significant knowledge to focus on efforts with higher likelihood of success in future investigations.
- Discovered unanticipated hydrogen storage capacities on HWCVD generated nano-crystalline graphite doped with iron nanoparticles.
- Performed preliminary assessment of the adsorption of hydrogen on conducting polymer samples provided by Prof. Alan MacDiarmid of the University of Pennsylvania.

Future Directions

- Establish, contingent upon DOE's approval, a DOE-sponsored Virtual Center of Excellence for the study and advancement of carbon-based hydrogen storage materials. The Center plans to bring together experts from national labs, universities and industry, including Nobel Laureate, Prof. Richard Smalley of Rice University, and Dr. Guido Pez of Air Products and Chemicals, Inc.
- Gain a better understanding of the mechanistic processes associated with hydrogen binding on nanostructured carbon materials.
- Develop reproducible methods to activate materials to high, room-temperature capacities (>4 wt%).
- Utilize computational chemistry to provide a link to and guidance for experimental efforts.
- Establish high-throughput experimental methods to rapidly evaluate nanostructured carbon hydrogen storage materials.
- Use knowledge obtained from this year's research to establish a better method for the controlled incorporation of metal into nanostructured carbon materials.
- Continue exploring alternative nanostructured carbon materials for room-temperature hydrogen storage, including aromatic cage compounds containing transition-metal ions.

Introduction

The decreasing fossil fuel supply and the growing number of densely populated metropolitan cities with poor local air quality have spurred an initiative to develop an alternative to petroleum motor fuels. Hydrogen, which may be produced from renewable sources, has emerged as one of the most promising candidates for the replacement of the current carbon-based energy services. Although hydrogen could supply all of the world's vehicular energy demands[1], a major impediment to the implementation of this new fuel is the lack of a convenient, cost-effective on-board storage system.

Compact, lightweight carbon adsorbent materials have become potential candidates for use in a hydrogen storage system. Of particular interest are the "engineered" nanostructured carbons such as carbon single-wall and multi-wall nanotubes (SWNTs and MWNTs) and graphitic nanoparticles or cages. Interestingly, the presence of small quantities of transition metals has been shown to enhance the hydrogen adsorption capacities of graphitic materials[2]. The long-term goal of the project is to enable efficient adsorption of hydrogen at ambient temperature and pressure on nanostructured carbon materials at system energy densities specified by DOE (4.5 wt% H_2, 1.2 kWh/L by 2005).

Approach

Laser-vaporization[3] and a simple purification technique[4] have been employed to generate SWNTs for hydrogen storage applications. However, the current purification process is not effective for the removal of graphite-encapsulated metals. Also, the laser process is not scalable for industrial production of carbon nanotubes. A CO_2 oxidation step has been added to the purification process in order to aid in the removal of graphite-encapsulated metals. Also, a continuous and potentially scaleable HWCVD technique has been developed for the production of carbon nanotubes.

Building on past research, which has shown that transition metal catalysts lead to enhanced hydrogen storage capacities on graphitic nanostructured materials[2], experiments were performed to understand the nature of the metal/carbon interaction as well as to control the incorporation of metal into cut, purified carbon SWNT samples. Finally, hydrogen storage properties of non-nanotube carbon materials were explored in detail.

Results

Improvements in SWNT Purification and Development of HWCVD Process for Continuous Carbon Nanotube Production. Graphite-encapsulated metals are not removed via our current purification process (16-hr reflux in 3 M HNO_3 followed by air oxidation at 550°C)[4]. By employing oxidation in CO_2 prior to the dilute acid reflux, a reduction in the analysis metal content in the final purified materials is observed. Figure 1 shows thermal gravimetric analysis (TGA) curves for air oxidation of a SWNT material following the 3 M HNO_3 reflux and the same material subjected to CO_2 oxidation prior to the acid reflux. The weight of the material remaining in both TGA curves corresponds to the presence of a metal oxide residue. The metal oxide residue has been reduced by approximately a factor of two in the material that was oxidized in CO_2 prior to the acid reflux. Apparently, this oxidation cracks the graphite- encapsulation, allowing for better digestion of the metal during the acid reflux.

If nanostructured carbons are to be employed in vehicular hydrogen storage applications, continuous and scalable production techniques must be developed[5]. Hot wire chemical vapor deposition (HWCVD) has been adapted to be a continuous growth process for high-density carbon multi-wall nanotubes (MWNTs). MWNT growth is optimized in 1:5 CH_4:Ar at 150 Torr with reactor temperatures of 400 and 550°C for static and flowing gases, respectively. Ferrocene is employed to provide a gas-phase catalyst. Highly graphitic nanotubes can be continuously deposited with iron content as low as 15 wt.% and carbon impurities below TGA detection

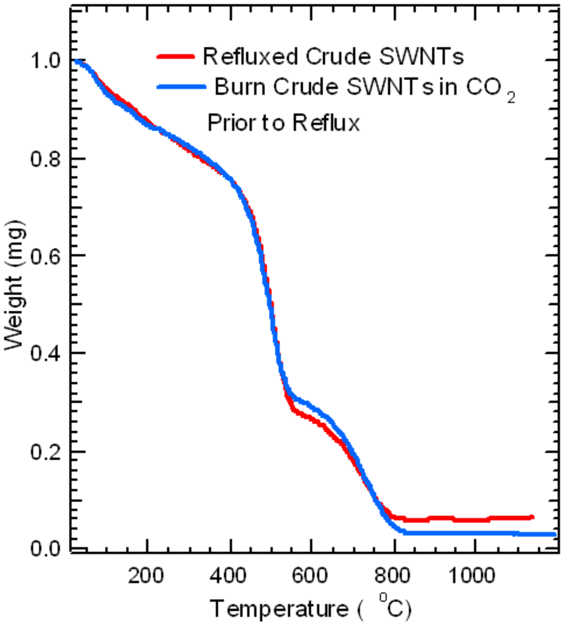

Figure 1. TGA Spectra for Air Oxidation of an SWNT Material Following the 3 M HNO_3 Reflux and the Same Material Subjected to CO_2 Oxidation Prior to the Acid Reflux

limits. The MWNTs are simply purified to >99.5 wt.% with minimal structural damage and with a 75 wt.% yield[6]. Figure 2 (top) shows a matt of high purity MWNTs produced by this technique. The production of isolated SWNTs[7] and small bundles of SWNTs have also been achieved with a similar HWCVD technique without employing an external furnace to increase the reactor temperature. Figure 2 (bottom) shows isolated SWNTs produced by the HWCVD method. Increases in SWNT yields are anticipated when a dual catalyst mixture is employed.

Understanding the Metal/Carbon Interaction Required to Observe Hydrogen Adsorption at Near Ambient Conditions. Hydrogen adsorption is observed at near ambient temperatures on the as-synthesized HWCVD MWNTs containing iron nanoparticles. No hydrogen adsorption, however, is observed at near ambient temperatures for the purified MWNTs containing <0.5 wt.% iron. Figure 3 (top) shows temperature programmed desorption (TPD) curves of crude and purified MWNT materials following a room temperature H_2 exposure at 500 Torr with subsequent cooling to ~190 K and evacuation to ~5 x10^{-8} Torr. Iron nano-particles purchased from Alpha Asaer were then incorporated in purified MWNTs as well as in µm-sized particles of graphite via sonication.

Figure 3 (bottom) shows TPD curves of these sonicated materials following the same hydrogen dosing procedure. No hydrogen adsorption was observed at near ambient temperatures when iron nano-particles were incorporated via sonication.

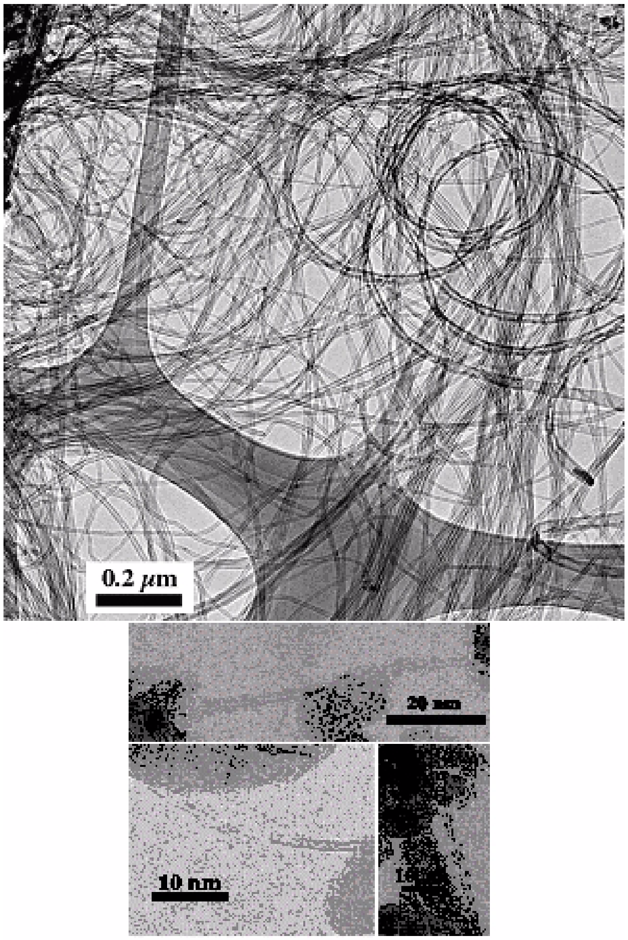

Figure 2. TEM Images of Crude HWCVD-Generated MWNTs (top) and Isolated SWNTs (bottom)

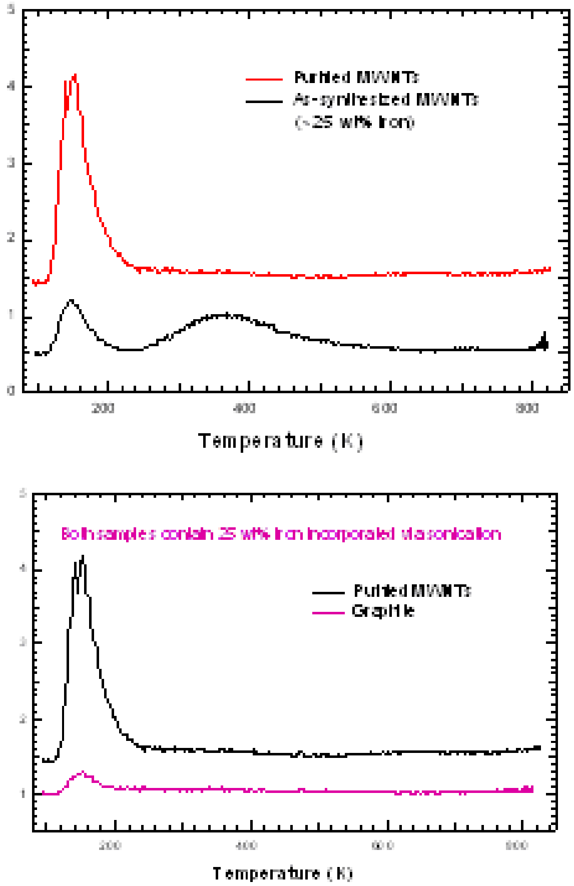

Figure 3. TPD H_2 Desorption Signals of As-Synthesized and Purified HWCVD-Generated MWNTs (top) and Purified MWNTs and Graphite with Iron Nano-Particles Incorporated via Sonication (bottom)

Figure 4 shows high resolution transmission electron microscope (TEM) images of the as-synthesized MWNTs (top) and the purified MWNTs following metal incorporation via sonication (bottom).

Note that in the as-synthesized materials, the iron nano-particle is located at the MWNT tip, while in the sonicated materials, the iron nano-particle randomly overlaps several nanotubes. These results, for the first time, conclusively demonstrate that small metal nano-particles must be in highly intimate contact with carbon nanotubes in order to observe hydrogen adsorption at near ambient conditions[8].

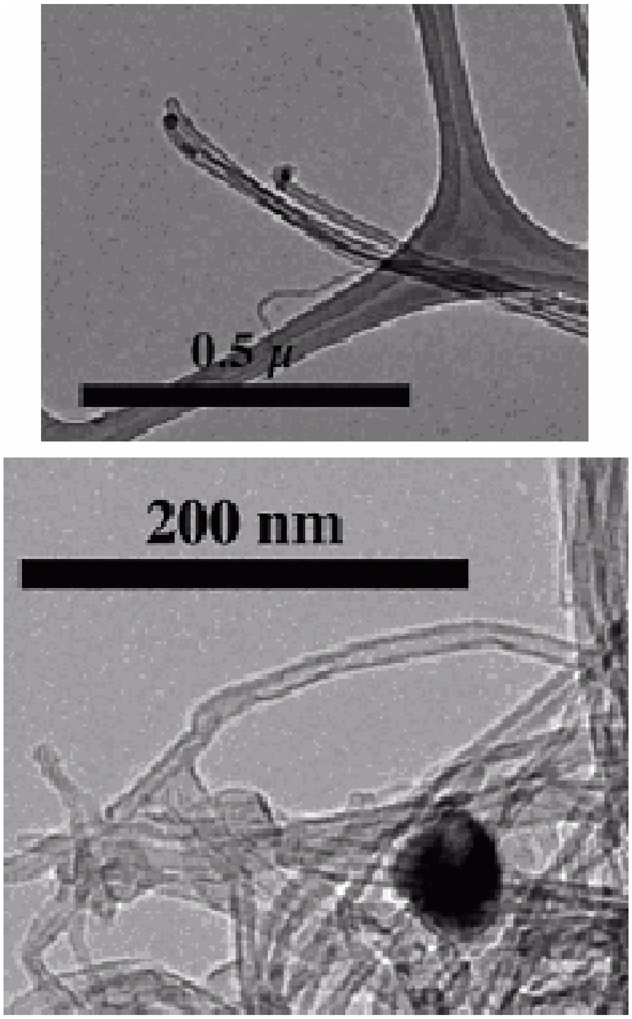

Figure 4. TEM Images of As-Synthesized HWCVD MWNTs (top) and Purified MWNTs with Iron Nano-Particles Incorporated via Sonication (bottom)

Controlled Incorporation of Ti into Purified, Cut SWNTs. Single-wall carbon nanotubes were produced via laser vaporization and subsequently cut by an oxidative process that does not introduce a metal hydride. The transport of Ti via TiI_4 is well known ($Ti + 2I_2 <--> TiI_4$). TiI_4 evaporates at 377°C (1 atm) and decomposes at higher temperatures. TiI_4 was vapor transported to purified, cut SWNTs at a higher temperature in the presence of H_2 in an effort to incorporate small particles of TiH_2. Unfortunately, the formation of TiC is thermodynamically favored over the formation of elemental Ti or C at all temperatures. Even in the presence of H_2, the titanium carbide was always formed, as shown by x-ray diffraction (XRD) measurements. No unusual hydrogen adsorption properties were observed for the SWNT samples containing titanium carbide.

Evaporation of thin films of Ti was also employed to establish a controlled method of metal incorporation in purified, cut SWNTs. Again, however, enhanced hydrogen adsorption was not observed for these samples. This behavior was attributed to the rapid oxidation of the Ti films. In the future, Pd evaporation will be explored since Pd is not susceptible to air oxidation at ambient conditions. Iron evaporation may also be employed since oxidation of the iron nano-particles is not detected with XRD in the as-synthesized MWNTs, even after several weeks of exposure to air.

Hydrogen Adsorption on Conducting Polymer and Non-Nanotube Nanocarbons. The hydrogen adsorption properties of several conducting polymers supplied by Prof. Alan MacDiarmid were explored. Figure 5 (top) shows the TPD spectrum of a PANI-CSA polymer treated with Triton-x that was degassed to 100°C and exposed to hydrogen at 760 Torr. For comparison, a TDP spectrum of a SWNT sample that was degassed to 1000°C and exposed to hydrogen at 500 Torr is also shown. In both cases, the sample was cooled to ~190 K while the H_2 gas was evacuated. For the SWNTs, the low-temperature "peak" is most likely the tail of a larger peak that would dominate if the sample could be cooled to a lower temperature while still in the presence of 500 Torr H_2. However, for the polymer sample, a peak with two shoulders is clearly observed above the minimum temperature to which the sample is cooled. These results indicate that unique, higher-temperature hydrogen adsorption sites exist on this conducting polymer sample. Adsorption experiments conducted with a hydrogen overpressure could shift the H_2 desorption temperatures for the polymer to higher temperature, and these will be explored.

The hydrogen storage properties of nano-carbon samples produced by the decomposition of ferrocene in the HWCVD chamber were also examined. The sample was shown with TGA to contain 42 wt.% iron. An H_2 TPD curve for this sample following degassing in vacuum to 550°C and exposure to 500 Torr H_2 is shown in Figure 5 (bottom). For comparison, a TPD spectrum of as-synthesized HWCVD generated MWNTs containing 25 wt% iron is also shown following the same dosing procedure. The nano-carbon sample actually displays a hydrogen adsorption capacity at near ambient conditions that is ~ 10x greater than that of the MWNT sample. Iron is not anticipated to store hydrogen at near room temperature. Further, the results of Figure 3 (bottom) clearly show that iron nanoparticles do not uptake hydrogen under the dosing conditions employed here. These results, therefore, conclusively show that non-nanotube carbons may also be promising candidates for vehicular hydrogen storage applications.

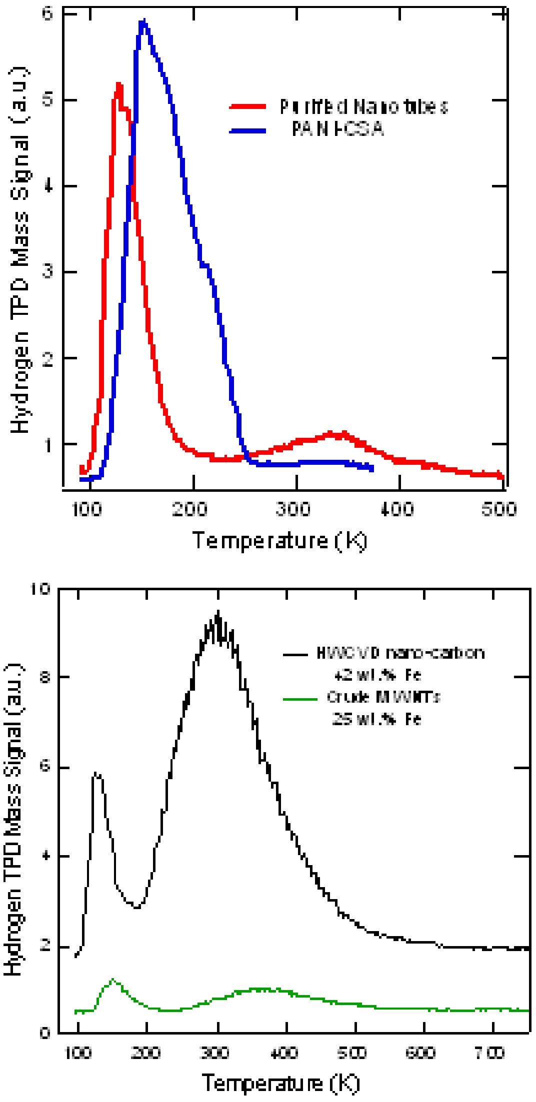

Figure 5. Hydrogen TPD Spectra of a Conductive Carbon Polymer Compared to Purified SWNTs (top) and HWCVD-Generated Nano-Carbon and Nano-Iron Particles Compared to HWCVD MWNTs (bottom)

Conclusions

- Graphite-encapsulated metals are more easily removed from crude SWNT materials if CO_2 oxidation is employed prior to the conventional purification process.
- HWCVD has been developed as a continuous and scaleable technique for the production of MWNTs at high density. HWCVD has also been demonstrated for continuous production of SWNTs.
- Metal assisted hydrogen adsorption at near ambient conditions on carbon nanotubes only occurs when small metal nano-particles are in intimate contact with the tubes.
- The evaporation of Pd instead of Ti onto carbon nanotube materials will likely be more effective in hydrogen adsorption catalysis since Pd is not oxidized in air at room temperature.
- Both conducting carbon polymers and HWCVD-generated Fe-doped nano-carbons are promising candidates for vehicular hydrogen storage materials.

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Special Recognitions & Awards/Patents Issued

1. Patent continuation-in-part application: PCT/01-19 CIP "Hot Wire Production of Multi-Wall and Single-Wall Nanotubes." Dillon, A.C., Mahan, A.H. and Alleman J.L., March, 2003.
2. "Hot Wire Chemical Vapor Deposition of Isolated Carbon Single-walled Nanotubes", published in Appl. Phys. Lett. 81 (2002) 4061, was selected for the November 25, 2002, issue of the Virtual Journal of Nanoscale Science & Technology. The Virtual Journal is an edited compilation of links to articles from participating publishers, covering a focused area of frontier research.

Doped Carbon Nanotubes for Hydrogen Storage

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Objectives

Develop reversible high-capacity hydrogen storage material to meet the DOE goals for a hydrogen storage system:

- Hydrogen capacity greater than 6 wt.%
- Favorable thermodynamic and kinetics suitable for transportation applications
- Stable with hydriding/dehydriding cycling

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption
- O. Test Protocols and Evaluation Facilities
- P. Dispensing Technology

Approach

- Produce large quantities of consistent structure carbon nanotube material
- Attempt to create a weak covalent hydrogen bond, dihydrogen
- Dope carbon nanotubes with transition metals and alloys
- Dope carbon nanotubes with other elements and metal clusters
- Tune material for hydrogen sorption to occur at desired temperature and pressure

Accomplishments

- Synthesis of material was achieved with:
  - Different dopants
  - Different quantities of dopants
  - Different diameters and configurations
- Thermodynamic and material characterization were conducted by:
  - Setting up a high pressure thermovolumetric (TVA) system

  - Measuring the hydriding and dehydriding of material
  - Examining nanotubes with cycling
  - Spectroscopic analysis of product was performed

Future Directions

- Continue production of nanotubes with different dopants
- Determine thermodynamic characteristics of hydrogen uptake and release
- Identify the type and size of nanotubes and clusters that result in a reversible, high hydrogen capacity material
- Tune conditions to result in a high yield of material possessing favorable characteristics
- Utilize theoretical modeling to guide the experiment

Introduction

The absence of a practical means for hydrogen storage has been a major obstacle in the transition to a hydrogen economy. Developing a solid-state hydrogen storage system that meets the DOE objectives has been the goal of researchers for years. Unfortunately, the extensive work in the area of conventional metal and intermetallic hydrides did not result in materials suitable for on-board hydrogen storage. Carbon nanotube technology represents a new direction for solid-state hydrogen storage, especially if these materials can be altered to store large amounts of hydrogen at room temperature. Persistent research activities, worldwide, have been exploring the use of carbon nanotubes for hydrogen storage [1-5].

This research is taking into account the barriers that face the development of a hydrogen storage system in general as well as taking into account problems that are inherent to carbon nanotube technology. This research is focused on modifying carbon nanotube systems in an attempt to enhance and tune the hydrogen storage capabilities of the nanotubes. The objective of this research has been to introduce transition metals and hydrogen bonding clusters into the nanotubes. The intent is aimed at producing consistent size dopants and structures of carbon nanotubes to avoid inconsistency in measurements. The success of making doped carbon nanotubes with transition metals and alloys can allow for a weak covalent bond similar to cases of dihydrogen bond that is not restricted to pure physisorption or chemisorption bond [6,7]. Controlling the type and size of tubes and dopant is expected to tune the product for hydrogen sorption to occur at desired temperature and pressure.

Approach

Our research is focused on modifying carbon nanotubes by doping them with different atoms and encapsulating metal clusters inside the tubes to make them suitable for hydrogen storage. Relying on physisorption alone will lead to a bond that is too weak, and chemisorption will lead to a bond that is too strong. Therefore, our objective is to establish a weak covalent bond where the electron donation from the (s) orbital of hydrogen to the doped tubes weakens but does not break the hydrogen-hydrogen bond.

The method of producing doped carbon nanotubes with controlled characteristics is a method developed at SRTC and is in the process of being patented. Thermodynamic characterization of hydrogen uptake and release will be conducted. Different spectroscopic methods are applied to identify the type and size of nanotubes and clusters that could result in a reversible high hydrogen-capacity material. Collaboration with academia and other government laboratories has been established.

Results

The synthesis of different doped carbon nanotubes has been achieved using SRTC technique that allowed for controlling the type and amount of dopants in the tubes. It was possible to produce large quantities of consistent structure carbon nanotube systems (see Figures 1 and 2). Preliminary results of hydrogen sorption showed 1% by weight hydrogen uptake and release. A thermogravimetric (TGA) system capable of operating at a wide range of temperatures was used to measure hydrogen uptake and release. Nitrogen doped carbon nanotubes, with average nitrogen content of about 5 wt. %, were also synthesized (see Figure 3).

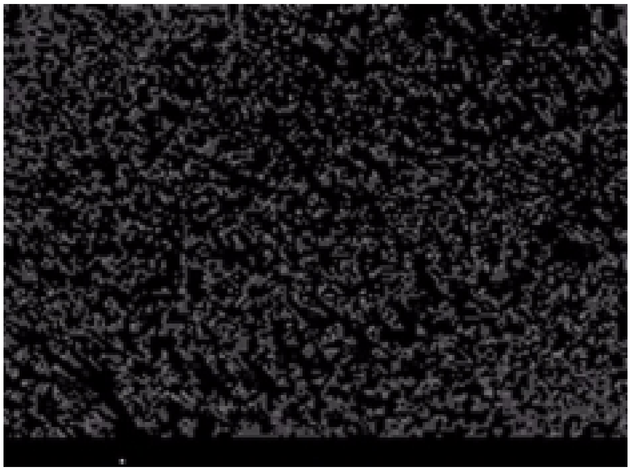

Figure 1. Consistent Structure Doped Carbon Nanotubes

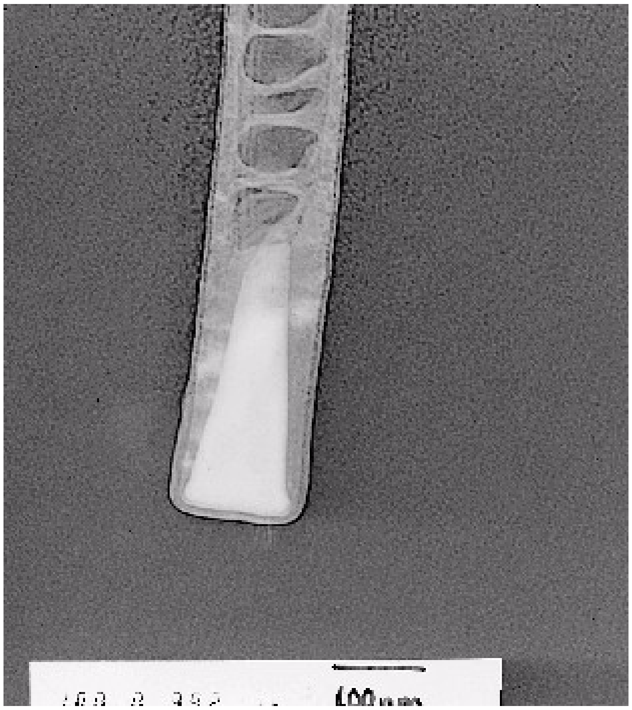

Figure 2. Tip of a Nanotube with Encapsulated Metal Particle

Conclusions

Although more investigation is needed to identify the type of hydrogen bond with the carbon nanotubes, the preliminary results look encouraging. One of our goals has been to synthesize nanotubes containing other elements such as boron or nitrogen, largely due to the possibility of fabricating nanotube materials with tailored electrical and mechanical properties. This goal was achieved as nitrogen doped carbon nanotubes were synthesized [8].

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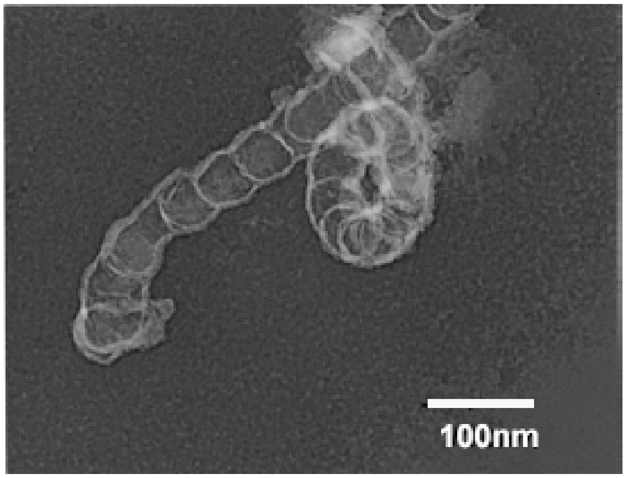

Figure 3. Nitrogen-doped Carbon Nanotube

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1. "Synthesis and Thermoelectric Power of Nitrogen Doped Carbon Nanotubes"
2. B.Sadanadan a, T. Savage a, S. Bhattacharya a, T. Tritt a, Alan Cassell b, M. Meyyappan b, Z.R. Dai c, Z. L. Wang c, R. Zidan d and A. M. Rao a, J. nanoscience and nanotechnology, Volume: 3 Number: 1, 99 - 103 (2003).

Special Recognitions & Awards/Patents Issued

1. Patent disclosure has been submitted, on producing and controlling the characteristics of doped carbon nanotubes

Hydrogen Storage in Metal-Modified Single-Walled Carbon Nanotubes

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Objectives

- Alter adsorption enthalpy of hydrogen on single-walled nanotubes (SWNTs) by use of a potassium intercalant.
- Increase number of adsorption sites in SWNTs by increasing the surface area through the use of intercalant.
- Improve the hydrogen storage capacity of SWNTs.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

- Investigate potassium intercalation synthesis procedures and measure sorption behavior of flaked graphites.
- Apply synthesis "recipes" to SWNT intercalation.
- Measure hydrogen sorption isotherms using Sieverts apparatus

Accomplishments

- Optimized synthesis procedures for KC24 and KC8 intercalated graphites.
- Determined synthesis procedures for K intercalated SWNTs, including CNI HiPco synthesized SWNTs.
- Determined purification routes for commercial Carbolex SWNTs.
- Carried out initial single point isotherm measurements and Raman and x-ray diffraction measurements for structural characterization.
- Produced K-intercalated SWNTs with room temperature sorption comparable to activated carbons.

Future Directions

- Further purification and intercalation of SWNTs.
- Optimization of K intercalation into SWNTs.
- Complete volumetric hydrogen adsorption measurements of SWNTs.

Introduction

The abundance of carbon and its relatively low molecular weight make it an attractive possibility as a hydrogen sorbent for fuel tank applications, where a high gravimetric density (mass ratio of hydrogen to carbon) is required. Graphite is the most commonly available form of carbon and consists of stacked graphene sheets. However, the interaction of graphite with hydrogen molecules is very weak, and the carbon layers are stacked too closely together for hydrogen molecules to fit between the layers, a necessity if a high density of hydrogen molecules is to be absorbed by the graphite.

The addition of potassium as an "intercalant" improves the ability of graphite to absorb hydrogen. When processed under controlled conditions, potassium atoms can separate the graphite layers and form an open hexagonal structure.

It has been known for over thirty years that KC_{24} potassium-intercalated graphite can readily absorb and desorb hydrogen but that this occurs most readily at 77 K [1]. The overall level of absorption in KC_{24} is ~1.2 wt% at this temperature. The limitation of 1.2 wt% can be understood on the basis of a space filling argument. Potassium atoms form an open hexagonal structure on alternating graphene layers, and four hydrogen molecules can fit within the open hexagon, defining the upper absorption limit. The lattice separation that potassium atoms induce within the graphitic layers can better accommodate the size of molecular hydrogen.

Adopting the approach of increasing the adsorption enthalpy for graphites should have a similar effect for SWNTs, and also have the effect of increasing the surface area of SWNTs. SWNTs have effectively high surface areas (~1600 m^2/gm outer surface area and ~1000 m^2/gm inner surface area) that are well beyond normal graphitic carbon. However, nanotubes typically form rope structures due to van der Waals interactions which promote rope formation, limiting the surface area to ~300 m^2/gm (interior and exterior surface areas for a SWNTs should be above 2600 m^2/gm). Potassium intercalation of SWNTs will separate the individual tubes. Computational work on SWNTs shows that under certain conditions, increasing the van der Waals gap will increase the amount of hydrogen that can be adsorbed [2].

Approach

We have been exploring 2-zone furnace procedures for the synthesis of KC_{24} and KC_8 and nanotube materials. Following 35-year-old synthesis techniques, we have used Madagascar graphites (from Superior Graphite in Chicago), which are generally recognized as the best graphites for intercalation. We have also used Carbon Nanotechnologies (CNI) HiPco nanotubes in addition to nanotubes originally acquired from the group at Rice University.

We have also obtained SWNTs from Carbolex. CNI no longer manufactures laser-oven synthesized SWNT material, which tends to have a narrower size distribution (typically with a 13 Å diameter) than the HiPco material (8-13 Å diameter range) that they presently synthesize and sell. Part of our goal in this work is to synthesize a well-defined structure on the basis of the well-packed rope structure we have seen previously in laser-oven material from Rice.

Our structural characterization tools include x-ray diffraction, transmission electron microscopy (TEM) and Raman spectroscopy.

We are having a 2nd generation Sieverts apparatus constructed at the Jet Propulsion Laboratory (JPL) that will enable us to obtain both adsorption and desorption isotherms. In the meantime, we have been collaborating with Dr. John Vajo of HRL Laboratories, who has been measuring single point adsorption isotherms for us.

Results

Figure 1 shows an overlay of intercalation synthesis behavior for stage formation of graphite compared to staging behavior for SWNTs. At Δt values of 0 to ~100°C, we can expect Stage 1 compounds to appear, while Δt values of 110 to 150°C are required to form Stage 2 compounds. For SWNTs, values of Δt up to 170°C only yield compounds of between KC_8 and KC_9 stoichiometry. Δt values above 170°C indicate no compound formation occurs. The solution to the problem of yielding the correct stoichiometry is to limit the amount of potassium in the reactor assembly to match the desired final stoichiometry.

X-ray data is shown in Figure 2. The trace in the upper right shows low angle data from a laser over synthesized nanotube from Rice and shows the periodic structure associated with tube packing to form ropes. The lower left trace shows the result of condensing potassium onto this material as part of our initial attempt to induce intercalation into nanotubes. The upper right trace shows that we have been able to disrupt the periodicity of the rope structure by using a Δt of 10°C. The lower right trace shows our processing attempts to de-intercalate the sample onto which potassium had been condensed.

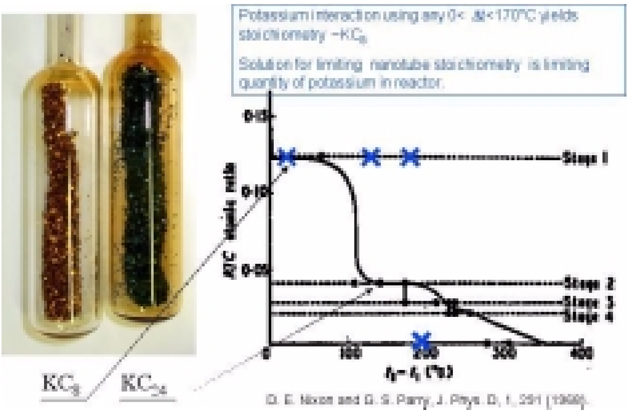

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Figure 1. Phase Diagram for Staging in Graphite Overlayed with Our Observed Uptake of Potassium in Nanotube

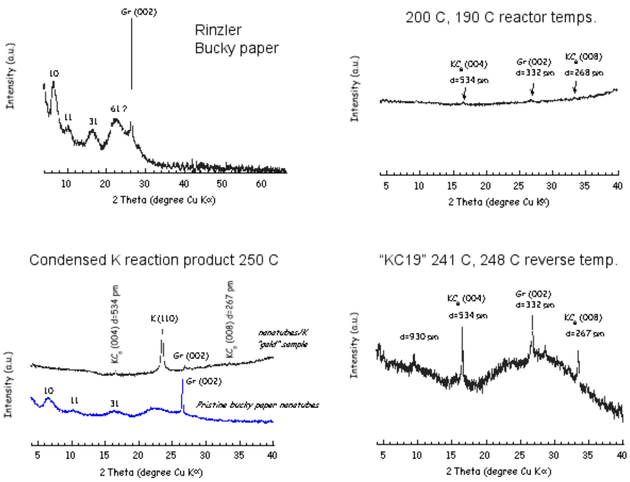

Figure 2. X-ray Data for Unprocessed and Intercalated "Bucky" Paper Using Processing Conditions as Noted

Transmission electron micrographs summarizing our processing procedures for purification of an alternative laser-oven synthesized material from Carbolex are shown in Figure 3.

In Figure 4, a summary of the improvements to room temperature sorption behavior of potassium-modified nanotubes is plotted. We can clearly see

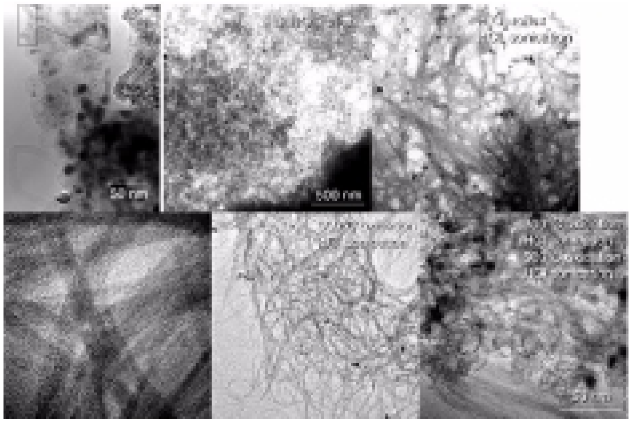

Figure 3. TEM micrographs showing the microstructural evolution as a function of processing for as-prepared Carbolex nanotubes. Starting from the upper left and going clockwise is the as-prepared material, HNO_3 refluxed, H_2O_2 refluxed and HCL sonicated, 2-step oxidation treated and high temperature oxidation treated and a high magnification micrograph.

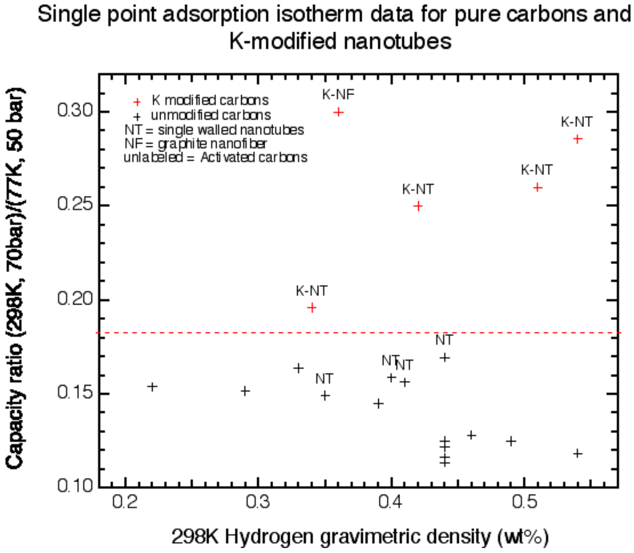

Figure 4. Ratio of Room Temperature to Liquid Nitrogen Temperature Gravimetric Densities for Pure and Potassium Intercalated Carbons

that unmodified carbons in the lower part of the plot have room temperature sorption that is 1/6 to 1/8 of the 77 K gravimetric density. Potassium intercalation can improve this ratio by nearly a value of two, indicating that the adsorption enthalpy is being altered. Even though the absolute values for gravimetric density are ~0.5 wt%, we have been able to effect improvements to the room temperature adsorption of nanotubes so that they are now comparable to the best activated carbons, which also have hydrogen gravimetric densities of ~0.5 wt%. We have accomplished this, even though we have not yet optimized the processing or structure of the intercalated nanotubes.

Conclusions

Our potassium modification to carbon nanotubes yields room temperature hydrogen gravimetric densities that are now comparable to the best activated carbons. This indicates that we have now succeeded in altering the chemical potential for hydrogen physisorption in nanotubes. We plan to continue to optimize the structure of these materials by expanding or swelling the structure, to improve the surface area in a way that preserves the packing or rope symmetry. We anticipate that this will further improve the room temperature hydrogen storage capacity of these materials.

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Carbon-based Sorbent Systems for an Effective Containment of Hydrogen (New FY 2004 Project)

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Objectives

- Develop a new hydrogen storage technology using novel reversible H_2-sorbent materials
- Deliver a packaged hydrogen storage system which will hold 6.0 wt.% hydrogen

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Weight and Volume
- M. Hydrogen Capacity and Reversibility

Approach

Air Products will develop a hydrogen storage technology using reversible H_2-sorbent materials that will be contained in suitable robust, lightweight, low-cost containers. We propose to design and develop materials and processes for sorption-based hydrogen storage systems in support of DOE's FreedomCAR program and other portable-power initiatives.

Our goal is to devise hydrogen-containment systems of 6 wt.% H_2-deliverable capacity at volumetric densities that range from 0.45 to 0.81 kg H_2/L, that are operable with fast filling rates (<5 min.) within a specified (-40 to 90^{o}C) operating temperature range and that achieve total reversibility over 500 cycles. The system's cost is limited to $10/kg, which corresponds to $833 for a fuel tank that carries 5 kg of usable hydrogen.

Our systems are to consist of a pressure/temperature H_2-reversible solid sorbent material that is packaged in a lightweight container under a modest pressure of hydrogen. The critical performance parameters are gravimetric and volumetric deliverable hydrogen capacity at specific loading and delivery process conditions. The sorbent's hydrogen capacity must actually exceed 6.5 wt.% in order to realize the ultimate goal of a hydrogen storage system which contains 6 wt.% H_2.

Goals include designing reversible H_2-sorbent materials: solid-state compositions that can take up hydrogen and release it by only varying the system's externally variable parameters of temperature and H_2 pressure, without the introduction or release of any other substances. Our ultimate goal of Phase I is to deliver to DOE a small prototype (0.1-1 kg sorbent) of a packaged hydrogen storage system that operates by temperature- or pressure-swing adsorption and utilizes a hydrogen sorbent material that has a reversible capacity, by total package weight, of 6.0% hydrogen in the specified temperature range (-40 to 90^{o}C) and under moderate pressure of hydrogen (<1000 psia).

If successful in Phase I, we intend to submit to DOE a proposal for research and development towards an adsorbent production process (at a target cost of <$5/kg) and continuation of the packaged system prototype development, including integration of the packaged system with a commercial fuel cell stack.

Process for the Regeneration of Sodium Borate to Sodium Borohydride for Use as a Hydrogen Storage Source (New FY 2004 Project)

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Subcontractors: Air Products and Chemicals, Inc.; Princeton University

Objectives

- To develop an electrolysis process for the reduction of borates to borohydrides
- To conduct preliminary engineering studies of the electrolysis process developed

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- Q. Regeneration Processes for Irreversible Systems

Approach

Under this project, Millennium Cell will collaborate with Air Products and Chemicals, Inc., a recognized industry leader in hydrogen technology, as well as Professor Andrew Bocarsly of Princeton University. This project provides a solution to the storage of hydrogen through cost effective use and production of a chemical hydride, sodium borohydride ($NaBH_4$). The team proposes to develop a novel $NaBH_4$ production process and pilot the process at a size suitable for engineering scale-up.

Chemical hydrides, particularly $NaBH_4$, have been proposed as effective hydrogen storage methods for a wide variety of applications in both distributed power generation and transportation applications. The hydrogen storage densities of sodium borohydride and its aqueous solutions meet the technical target of 6% hydrogen capacity set by DOE. The demonstrated advantages and benefits of $NaBH_4$ are known; however, regeneration and production systems warrant further study in order to bring $NaBH_4$ to widespread commercialization. Therefore, it is the goal of this project to determine the technical feasibility of a new synthetic method for producing $NaBH_4$ that improves significantly upon the current process. It is expected that an improved process will lead to $NaBH_4$-based hydrogen fuel systems being economically competitive with hydrocarbon-based fuels.

The storage capacity of $NaBH_4$ and the relative simplicity of its hydrogen delivery methodology make it possible to construct a hydrogen fuel system that allows a vehicle to achieve a 400+ mile range on a single fill-up without sacrificing conventional passenger space inside the vehicle. Sodium borohydride can be stored as an aqueous solution, adding to its advantage as a safe and convenient carrier for hydrogen. Its performance characteristics on hydrogen delivery have been validated by Millennium Cell's proprietary Hydrogen on Demand^{TM} technology. Prototype testing indicated that the load following characteristics of hydrogen delivered from borohydride is essentially non-distinguishable from that of compressed hydrogen.

An important barrier to overcome in commercializing this technology is the current cost of sodium borohydride. The key to lowering the cost is the technical feasibility of a more energy efficient $NaBH_4$ synthetic process. The regeneration of $NaBH_4$ from sodium borates requires the input of a substantial amount of energy. In the existing commercial process, this energy input is manifested as the energy input required to produce sodium metal, which is used in large quantities in a subsequent chemical process to yield $NaBH_4$. In this proposal, we intend to explore the concept of hydrogen-assisted electrolysis for the reduction of sodium borates or both sodium borates and sodium hydroxide. Electrochemical reactions involving hydrogen often have the advantage of low overpotential and single step process operations; therefore, they are able to achieve higher overall energy efficiencies. If this project is successful, it will significantly advance hydrogen storage technology for transportation and other potential markets by lowering the cost while meeting the specific energy and density criteria set by the DOE.

Chemical Hydride Slurry for Hydrogen Production and Storage (New FY 2004 Project)

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Objectives

- Develop a MgH_2 slurry system with a gravimetric density >11 wt% H_2
- Develop a MgH_2 slurry system with a gravimetric capacity of >1.5 kWh/kg
- Develop viable methods to recycle by-products and produce MgH_2 from Mg and H_2 to meet DOE cost targets

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- Q. Regeneration Processes for Irreversible Systems

Approach

Safe Hydrogen, LLC is developing a new hydrogen storage medium using chemical hydride slurry, which is made by mixing chemical hydride with mineral oil and dispersants. The oil coats the hydride particles and protects them from inadvertent contact with water while also moderating the reaction rate of the hydride with water when desired. The slurry itself will store 5 kg of hydrogen in less than 52 L of volume. The by-product of the reaction will be stored in the same container as the hydride slurry but will be separated by a baffle or barrier.

The primary purpose for developing the slurry is to create energy-dense chemical hydrides that can be transported, pumped and metered as a liquid. Additionally, the slurry storage medium enhances safety by eliminating the need to transport hydrogen gas. Hydrogen gas is produced as needed by mixing the chemical hydride slurry with water. Unlike hydrogen gas, possible slurry seepage can be identified and contained quickly.

A project focused on lithium hydride indicated that magnesium hydride slurry could provide additional safety and cost benefits. Magnesium hydride slurry reacts very slowly at room temperatures. As a result, if the slurry is spilled into a pool of water, only a few bubbles of hydrogen are produced each minute. The by-product of the reaction is quite safe (magnesium hydroxide, sometimes called “milk of magnesia,” is used as an antacid or laxative). It is also expected that magnesium hydride would cost less to manufacture than lithium hydride.

The proposed project focuses on:

1. Slurry development
2. Mixer development
3. Recycle system development

In the slurry development, Safe Hydrogen plans to develop magnesium hydride slurry as demonstrated with lithium hydride slurry. In the mixer development, Safe Hydrogen will improve the mixer design for slurries of magnesium hydride or lithium hydride. We will reduce the size, weight, and production cost of the mixing system while increasing its robustness.

The majority of the work planned for this project is development of the recycle system. The economics of the system depend on the recycle costs. By using the metal several times a year, the amount of hydrogen carried by each unit of metal is increased and the cost of hydrogen is decreased. By operating large-scale plants, we reduce the cost of the metal production. We expect recycle costs to be less than production costs from ore because the front end and back end of the recycle process are much simpler and lower cost than those of the production process.

There are two currently-used methods of reducing magnesium. The most common method electrolytically separates magnesium from magnesium chloride. The other is a metallothermic method that uses ferrosilicon as a reductant. A potentially lower cost carbothermic method was used in the 1940s and 1950s by the Permanente Metals Company. One of its intermediate products was powdered magnesium that would be particularly attractive for making magnesium hydride slurry.

A new method of producing magnesium from magnesium oxide being developed by Boston University has the potential to reduce costs and simplify the process. We intend to evaluate and compare the various methods of reducing magnesium and lithium. The evaluations will begin with process design and analyses to estimate the cost of production by each method. Experimental activities are coupled with the process analyses to provide additional process understanding of the Boston University process and new carbothermic reduction technology.

Novel, Light-Element Nanostructured Materials for Hydrogen Storage (New FY 2004 Project)

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Objectives

To demonstrate the operation of a nanostructure-based hydrogen storage tank which meets the DOE cost goals of $5/kW-hr

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- M. Hydrogen Capacity and Reversibility

Approach

This project will develop and prototype a new hydrogen storage technology based on low-temperature physisorption of hydrogen on nanostructured materials based on light elements. The Nanomix team will develop and test new materials and scale them up to prototype testing. The materials will be the heart of a simple storage system that takes advantage of the inherent thermodynamic properties of hydrogen and promises to surpass competing technologies in overall system performance. Starting with activated carbon, Nanomix will design and construct a pilot-scale prototype to define and study critical operating parameters such as temperature, pressure, refueling time, and dormancy. The research and development effort will identify new materials with appropriate heats of adsorption using computational tools, synthesize and test both known and new candidate materials, develop high surface area forms, construct a storage tank prototype, and test the tank with quantities of candidate materials that emerge successfully from the preceding materials development project.

This three-year project includes seven separate tasks:

Task 1. Planning and Management: Prepare a project management plan that addresses organization, schedule budget, procurement, health & safety, data quality and reporting. Participate in DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program meetings, etc.

Task 2. Computational Design and Screening: Identify new candidate materials for hydrogen adsorption; conduct screening level ab initio calculations of the binding energy of hydrogen; perform density functional calculations on promising candidates; and predict composition, structure and stability and project cost of production and toxicity. Complete analysis of two groups in the first year and identify at least 2 new materials.

Task 3. Experimental Verification: Procure or synthesize small quantities of nanostructured materials for screening; characterize hydrogen storage properties - binding energy and coverage over a range of temperatures; and select high potential materials. Complete verification of at least two new materials in the first year.

Task 4. Optimize Material for Hydrogen Storage: Synthesize very high surface area samples and conduct engineering measurements of hydrogen storage properties. Complete synthesis of B_2O_3 and at least one new material in the first year.

Task 5. Pilot Material Synthesis / Production: Evaluate pilot-scale and larger process feasibility and production costs; synthesize B_2O_3 or another material for testing in the first year.

Task 6. Prototype Testing: Design and construct a prototype H_2 storage tank to test material and operating parameters; test high surface area carbon structures in the first year.

Task 7. Reporting and Deliverables: Submit quarterly and annual project reports.

Standardized Testing Program For Emergent Chemical Hydride And Carbon Storage Technologies

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Subcontractors:
Teledyne Energy Systems, Hunt Valley, MD
The National Hydrogen Association, Washington, D.C.
Energy Conversion Devices, Inc., Troy, MI

Objectives

- Develop and operate a standard testing and certification program specifically aimed at assessing the performance, safety and life cycle of emergent complex metal hydrides and carbon adsorption/desorption hydrogen storage materials and systems.
- Work with industry and the U.S. government to develop an accepted set of performance and safety evaluation standards.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Test Protocols and Evaluation Facilities
- M. Hydrogen Capacity and Reversibility
- F. Codes and Standards
- B. Weight and Volume
- D. Durability

Approach

- Task 1: Perform a comprehensive review of the current accepted practices for testing the performance of complex metal hydride and carbon storage media.
- Task 2: Define the equipment and test protocols that will be used in the standardized testing program.
- Task 3: Design and construct the test facilities for characterizing the performance of complex metal hydride and carbon storage media.
- Task 4: Evaluate the operation of the test facility with actual sample materials to verify that all components operate correctly pursuant to the test protocols developed in Task 2.

- Task 5: Analyze emergent complex metal hydride and carbon storage materials in accordance with the protocols established in Task 2.
- Task 6: Work for the adoption of the test protocols developed in this program by a recognized national or international standards organization.

Accomplishments

- Completed literature review of current measurement state-of-the-art.
- Developed preliminary facility and equipment design.
- Completed visits to leading laboratories involved in hydrogen adsorption/desorption measurements.
- Submitted document specifying the equipment to be used for characterization of solid-state hydrogen storage materials.

Future Directions

- A testing facility equipped to perform gravimetric, volumetric and thermally programmed desorption (TPD) measurements on small quantities of solid-state hydrogen storage materials has been defined (2Q, 2003).
- The design of the facility to test full-scale storage systems will be finalized (3Q, 2003).
- Construction of the facility for testing small quantities of solid-state hydrogen storage materials will be completed (2Q,2004).

Introduction

The choices of viable hydrogen storage systems at this time are limited to compressed hydrogen gas (CH_2) storage tanks, cryogenic liquid hydrogen (LH_2) storage tanks, chemical hydrides, and solid-state materials, including complex metal hydrides and carbon. While each of these enabling storage technologies has specific advantages and disadvantages, the solid-state storage systems may offer advantages in terms of storage capacity and, most importantly, safety.

The realization that storage systems utilizing solid-state storage materials may most efficiently meet the storage capacity and safety requirements of a hydrogen-based infrastructure has led to significant interest and monetary investment to accelerate the development of complete hydrogen adsorption storage systems. However, there are no standard guidelines, dedicated facilities, or certification programs specifically aimed at testing and assessing the performance, safety and life cycle of these emergent systems. The development of a standardized protocol and testing system would allow both DOE and the R&D organizations to assess the potential performance of the wide array of materials and systems and focus their efforts on those that show the most promise.

Approach

In anticipation of the availability of many new materials and technologies for hydrogen storage, the purpose of the present effort is to develop an evaluation facility with established evaluation protocols and standards for the testing and assessment of these emergent solid-state storage materials and systems. Upon thorough validation of the experimental apparatuses and associated protocols, the testing facility and the technical staff that supports it will be available as the focal testing center to any prospective innovator of complex metal hydride or carbon hydrogen storage materials or systems. Although the final form of the test protocol and equipment is still being defined, it is anticipated that the test system will be centered around hydrogen sorption/desorption measurements of small quantities of storage materials. These measurements may be performed using a trio of devices, including a magnetically coupled thermogravimetric analyzer (TGA), as shown in Figure 1, a Sieverts apparatus, as shown in Figure 2, and a thermally programmed desorption apparatus. An ability to test complete storage systems will also be included.

The performance characteristics of candidate materials will be determined through a comprehensive materials characterization and systems testing approach. This approach will encompass the elements described below.

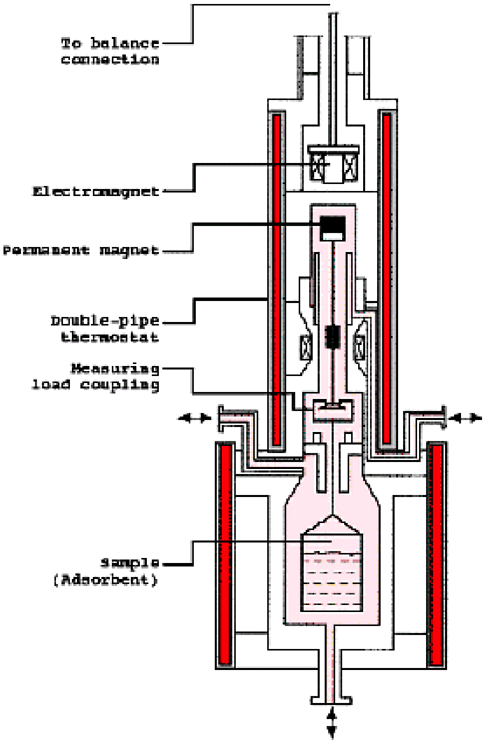

Figure 1. Magnetically Coupled Thermogravimetric Analyzer

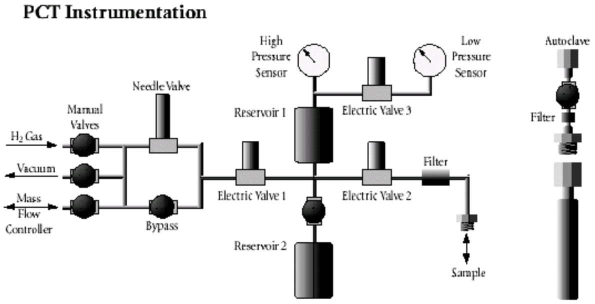

Figure 2. Schematic of Sieverts Apparatus

Certification of Chemical Composition and Crystallographic Properties. Materials selected for evaluation will be analyzed to determine or verify their elemental composition and crystallographic properties using appropriate analytical capabilities: atomic adsorption spectroscopy (AAS), X-ray fluorescence (XRF), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and powder X-ray diffraction.

Evaluation and Certification of Performance Parameters. The intrinsic thermodynamic characteristics of candidate storage materials, where existing data is not available, will be evaluated by modulated differential scanning calorimetry (MDSC). Data of this sort that has already been generated by others will be used to the extent that it is relevant to the specific goals of the present study. The intrinsic thermodynamic characteristics that will be derived from the MDSC analysis include the following:

- Determination of first and second order phase transitions
- Heat of transition
- Transition temperature
- Non-reversible transitions (such as in decomposition)
- Decomposition temperature
- Decomposition exotherm
- Crystalline versus amorphous compositions

Once the intrinsic thermodynamic characteristics are firmly established, the storage materials will be subjected to the performance assessment test protocols. The performance parameters and conditions that will be derived from the testing regime are as follows.

- Specific energy contained in storage system
- Sorption/desorption cycle life
- Resistance to exogenous contaminates
- Average refueling time
- Most favorable thermal-cycle conditions
- Impact resistance (only applicable to complete hydrogen storage container technologies)

- Vibration resistance (only applicable to complete hydrogen storage container technologies)
- Fire resistance (only applicable to complete hydrogen storage container technologies)

Results

The first phase of the current project involved a review of the current state-of-the-art in measurement equipment and protocol for characterization of hydrogen storage behavior of small quantities of solid-state materials. The review involved a review of the pertinent literature and visits to a number of leading laboratories. Specifically, General Motors Research, Air Products, the National Renewable Energy Laboratory and Sandia National Laboratories were visited. The general findings of the review of the current state-of-the-art are summarized below.

1. The wide range of materials currently under investigation results in a wide range of measurement conditions, e.g., sample quantities ranging from 1 mg to 1g and environments ranging from vacuum to 100 atm.

2. Three prominent techniques are being used to measure hydrogen storage capacity: gravimetric (TGA), volumetric (Sieverts) and thermally programmed desorption (TPD).

3. Errors in measurement results have generally been related to the indirect nature of the techniques (TGA and Sieverts) and/or operating near the sensitivity limits of the equipment.

4. Single walled nanotubes (SWNTs) are currently the most challenging material to measure due to a combination of very small mass and high pressure. However, one laboratory depends on hydrogen desorption measured in a vacuum environment.

Proposed Analytical Equipment. The storage capacities of solid-state materials are best understood through the use of phase diagrams, which are often constructed from pressure concentration temperature (PCT) measurements. The PCT measurements are isothermal measurements of the equilibrium hydrogen concentration as a function of the surrounding hydrogen pressure. Two methods are in use for the determination of sorption isotherms: a volumetric method using a Sieverts P-V-T (Pressure-Volume-Temperature) system and a gravimetric method that uses a microbalance for determination of weight changes. It has been proposed that both volumetric and gravimetric capabilities be included in the facility. A brief description of each is provided in separate sections that follow.

In addition to the volumetric and gravimetric capabilities, the inclusion of a thermally programmed desorption (TPD) apparatus has also been proposed. The TPD is in use in a number of laboratories and has been reported by one of the leading SWNT R&D groups to yield the most accurate measure of SWNT desorption. Inclusion of the TPD will allow comparisons of all three primary techniques in one laboratory and offers the possibility to reproduce measurements performed at any laboratory using the same technique in use at that laboratory. Inclusion of the TPD will not involve a major investment of project funds since a Thermal Desorption and Recoiling Mass Spectrometry (TDARMS) system in place at SwRI can be converted to a TPD for minimal cost. The TDARMS/TPD is described in a subsequent section.

High Pressure TGA. A high pressure TGA has been proposed for the gravimetric measurements. The proposed TGA incorporates a Rubotherm magnetic suspension balance and a mass spectrometer for gas speciation during desorption measurements. The accuracy of the instrument will be dependent upon sample mass and system pressure. Accuracy for a 300 mg sample at 1 atm is estimated to be 3×10^{-4} wt.%.

Sieverts Apparatus . It has been proposed that a PCT Pro-2000 be employed for volumetric sorption/desorption measurements. The PCT Pro-2000 is a fully automated, state-of-the-art Sieverts instrument for measuring gas sorption properties of materials. The instrument is designed for high precision measurements on small samples. Measurements can be made at pressures between 0.001 and 200 atm and at temperatures up to 400°C. This instrument has an estimated accuracy of 0.2 wt.% for a 300 mg sample measured at 100 atm.

TPD Apparatus . As the name implies, a TPD instrument is used primarily for hydrogen desorption measurements. It is not effective for generating PCT or kinetic data. Nonetheless, TPDs are in use in a number of laboratories and have produced the most accurate measures of hydrogen storage capacity for SWNTs. Inclusion of a TPD instrument in the facility would broaden capabilities and allow, along with the TGA and Sieverts instruments, for replication of any measurements made by a material developer.

SwRI has a TDARMS system, which is being converted to a TPD instrument for minimal cost to the project. The SwRI instrument has a quadrupole mass spectrometer with axial ion source and 90° off-axis secondary electron multiplier detector. It utilizes a high-pressure orifice dual gate-valve interface between the mass spectrometer and the sample chamber. The sample chamber is Summa® passivated and evacuated by cryosorption roughing pumps and high vacuum turbo molecular pumps. The sample stage and heating are being modified for hydrogen desorption measurements.

Conclusions

The following conclusions have been drawn from the results of the review.

1. No single measurement technique will be appropriate for all of the materials that are currently being considered for hydrogen storage.

2. A comprehensive testing facility will need to have multiple techniques to cover the full range of materials.

3. The presence of multiple techniques will provide higher confidence in results by enabling cross checks of storage capacity using more than one technique.

4. Whenever possible, gas speciation should be included in the measurement of storage capacity.

FY 2002 Publications/Presentations

1. Project overview presented at FreedomCAR Tech Team Meeting, September 19, 2002, Detroit, MI.

2. Project overview presented at Sandia National Laboratories, November 18, 2002, Livermore, CA.

3. Project overview presented at IHIG H2 Storage Working Group Meeting, February 13, 2003, Chicago, IL.

4. Project overview presented at 2003 Hydrogen and Fuel Cells Merit Review Meeting, May 20, 2003, Berkeley, CA.

Fuel Cell Systems Analysis

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Objectives

- Develop a validated model for automotive fuel cell systems and periodically update it to assess the status of technology.
- Conduct studies to improve performance and packaging, to reduce cost, and to identify key R&D issues.
- Compare and assess alternative configurations and systems for transportation and stationary applications.
- Support DOE/FreedomCAR automotive fuel cell (FC) development efforts.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Compressors/Expanders
- D. Fuel Cell Power System Benchmarking
- F. Heat Utilization
- H. Start-up Time
- I. Fuel Processor Start-up/Transient Operation
- M. Fuel Processor System Integration and Efficiency
- R. Thermal and Water Management

Approach

- Develop, document and make available an efficient and versatile system design and analysis tool.
- Validate the model against data obtained in laboratory and at Argonne's Fuel Cell Test Facility.
- Apply model to issues of current interest.

Accomplishments

- Supported revision of compressor-expander module (CEM) targets by analyzing power consumed by the air management subsystem on standard drive cycles for direct H_2 and gasoline reformed FC vehicles.
- Supported setting of H_2 storage targets by analyzing the fuel economy of FC vehicles.
- Developed dynamic models of compressor, expander and motor on a single shaft; ram-air cooled condenser and radiator; catalytic water gas shift (WGS) and auto-thermal reactor (ATR) on microlith supports; and monolith-supported preferential oxidation (PrOx).
- Proposed and analyzed fuel cell systems for hybrid vehicles.

- Analyzed data for Nuvera system obtained at Argonne's Fuel Cell Test Facility.
- Evaluated FC systems for combined heat and power.

Future Directions

- Perform drive cycle analyses of direct hydrogen and reformed FC systems.
- Analyze FC systems for combined heat and power for stationary applications.
- Support fuel processor engineering projects at Argonne National Laboratory.
- Continue to support DOE/FreedomCAR development efforts.

Introduction

While different developers are addressing improvements in individual components and subsystems in automotive fuel cell propulsion systems (e.g., cells, stacks, fuel processors, balance-of-plant components), we are using modeling and analysis to address issues of thermal and water management; design-point and part-load operation; and component-, system-, and vehicle-level efficiencies and fuel economies. Such analyses are essential for effective system integration.

Approach

Two sets of models are being developed. GCtool is a stand-alone code with capabilities for design, off-design, steady state, transient and constrained optimization analyses of FC systems. GCtool-ENG has an alternate set of models with a built-in procedure for translation to the MATLAB/ SIMULINK platform commonly used in vehicle codes such as PSAT (vehicle simulation software package developed at Argonne).

Results

One of the major activities in FY 2003 was to model and analyze pressurized direct hydrogen fuel cell systems for hybrid vehicles. The modeled system, shown in Figure 1, uses compressed hydrogen fuel and operates at 2.5 atm, 80ºC, and a cell potential of 0.7 V at the rated power point. It is humidified to 90% relative humidity at the stack temperature using process water and heat from the stack coolant, as is the cathode air discharged from the compressor. Process water is recovered from spent air in an inertial separator just downstream of the stack, in a condenser and in a demister at the turbine exhaust. The waste heat transferred to the coolant in the stack is either used for humidifying the anode and cathode streams or rejected in a radiator.

Our interest is in a load-following fuel cell system (FCS) coupled to an energy storage device operated in a charge-sustaining mode. For this type of hybrid system, the FCS alone must be capable of meeting the vehicle power demand under all sustained driving conditions. The minimum size of the FCS is then determined by the power demand at the top sustained speed, taken as 100 mph, or the power necessary to maintain the vehicle at 55 mph at 6.5% grade for 20 min. With battery assist, the FCS must have the response time to allow the vehicle to accelerate from 0 to 60 mph (Z-60) in a specified time, taken as 10 seconds. To be competitive with its internal combustion engine counterpart, the FCS must have 1-s transient response time for 10% to 90% power and be able to reach maximum power from cold start in 15 s at 20^{o}C ambient temperature and in 30 s at -20^{o}C ambient temperature. We further require that the FCS be 50% efficient at the rated power and be water balanced for all rated loads at 50% oxidant utilization and ambient temperatures up to 42^{o}C.

Our analyses show that the air management system, i.e., the compressor, expander and motor, must be oversized to meet the cold start-up time targets. To meet the 1-s transient time target, over short time periods, the electric motor has to be overloaded and the maximum oxidant utilization, generally limited to 50%, is allowed to rise to 60%.

FCS for Hybrid Mid-Size SUV. With the requirements and approach defined above, Table

1 lists the attributes of three FCSs for a hybrid mid-size SUV. The minimum rating of the FCS is 80 kW; it is determined by the sustained top speed rather than the gradeability criterion. The minimum power rating for the energy storage system (ESS) is the difference between the maximum power demand at Z-60 and the rating of the FCS. FCS-1 is a 100-kW system without an expander. It needs a rather large 27-kW motor for the air management system. FCS-2 is a 100-kW system with an expander and a motor which is one-third the size of the motor in FCS-1. FCS-3 is a 160-kW system with an expander. It can potentially power the SUV without battery assist. Under all conditions, FCS-3 has the highest efficiency and FCS-1 the lowest efficiency.

Stack Performance. Figure 1 shows the behavior of the stack for FCS-2, the 100-kW system with an expander. Under warm conditions, it produces about 105 kWe at the rated power point. With the air management system oversized to satisfy the cold start-up time requirement, it can generate 120 kWe at a cell voltage of 0.65 V. At 20°C, the power is 20% lower with the cell voltage decreasing to 0.55 V. At -20°C, the stack is derated by 35% and the cell voltage goes down to 0.45 V. With the oversized CEM, the net derating is only 10% at 20°C and 25% at -20°C.

Table 1. FCS for Hybrid Mid-Size SUV (AWD = all wheel drive, GVW = gross vehicle weight)

	Mid-Size AWD SUV			
GVW with FCS	2400 kg	Frontal Area	2.46 m^2
Coef. Rolling Fraction	0.0084	Drag Coef.	0.41
	Traction Power Requirement		
Z-60	160 kWe		
Top Speed (100 mph)	80 kWe		
6.5% Grade (55 mph)	70 kWe		
	FCS - 1	FCS - 2	FCS - 3
Rated Power at 0.7 V	100 kWe	100 kWe	160 kWe
Air Management System	w/o Expander	with Expander	with Expander
CEM M/C Power	27.3 kW	9.5 kW	15.1 kW
FCS Efficiency			
@ Rated Power	47%	54%	54%
@ 25% of Rated Power	61%	63%	63%
@ 80 kWe	52%	56%	59%
@ 20 kWe	62%	63%	64%

Heat Rejection System. Our analyses show that the size of the heat rejection system for the SUV is determined by the gradeability condition rather than the top sustained speed. Shown in Figure 3 are the heat duties and the heat rejection capabilities as a function of vehicle speed. For FCS-3, the 160-kW system with an expander, the heat duty is zero at speeds less than 60 mph, implying that the stack cannot be maintained at 80°C at low speeds. A radiator sized for heat duty at 6.5% grade at 55 mph can meet the heat rejection requirements at all speeds. Because the maximum heat rejection is greater than the heat duty, a thermostatic control is required.

The trends of heat duty and heat rejection are similar for FCS-2, the 100-kW system with an expander, but with one important difference. The

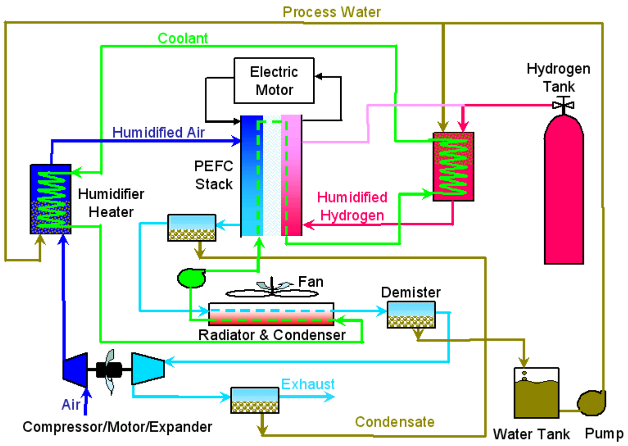

Figure 1. Pressurized Direct H_2 Fuel Cell System

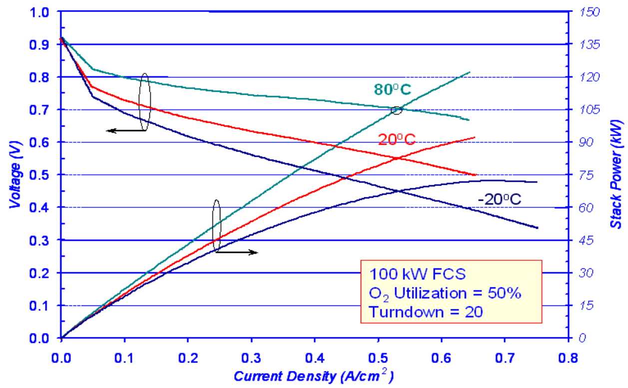

Figure 2. Stack Behavior with Oversized CEM

heat duty at the gradeability condition is nearly twice as large even though the FCS is 60% smaller.

Water Management System. The results in Figure 4 indicate that the criterion for sizing the water management system changes with FCS rating. For FCS-3, the 160-kW system, the maximum heat duty levels off after 80 mph. A condenser sized for heat duty at 6.5% grade at 55 mph can meet heat rejection requirements at all speeds.

For FCS-2, the 100-kW system, the heat duty peaks at about 75 mph. Heat load at grade is no longer the design point, nor is the speed at which the heat load is highest. Instead, the design point is at an intermediate speed of about 70 mph. Unlike the radiator, the condenser for a 100-kW system is smaller than one for a 160-kW system.

CEM Idle Speed. Our work on the air management system has looked at the issues of idle speed and maximum turndown. For reference, idle speed is the minimum rpm at which the air management system can provide sufficient cathode air to enable the FCS to generate the power needed by the CEM if it was overloaded to meet a sudden surge in power demand. Idle speed is an important parameter that affects the system efficiency at part load as well as oxygen utilization and water recovery. It is determined by the motor power, the motor/controller algorithm and the physical design of the rotating turbomachinery.

For a high speed, matched, turbo compressor/expander set, we have determined that with an expander, the maximum turndown can be as high as 20. Without an expander in the system, the maximum turndown can be as low as 5.

FCS Efficiency. Figure 5 shows the effect of CEM turndown on FCS efficiency over the Federal Urban Driving cycle (FUDS) for FCS-2, the 100-kW system with an expander. Results are presented for CEM turndowns of 5 and 20. Differences in efficiency are clearly evident at low loads. Both give efficiencies in excess of 60% over FUDS, but with a turndown of 20, the peak efficiency can exceed 70% at low loads. However, the scatter in dynamic efficiency is wider at a maximum turndown of 20.

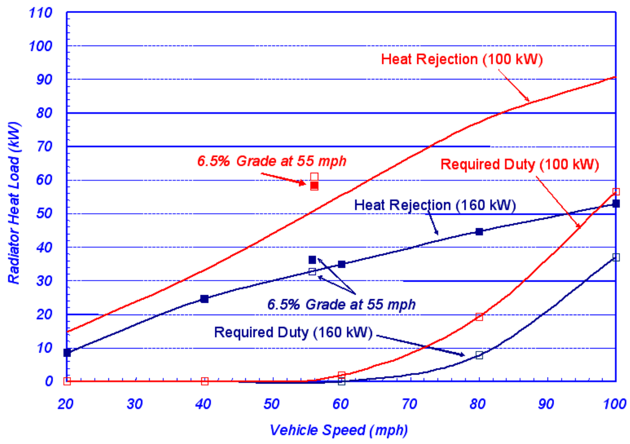

Figure 3. Heat Loads on the Stack Radiator

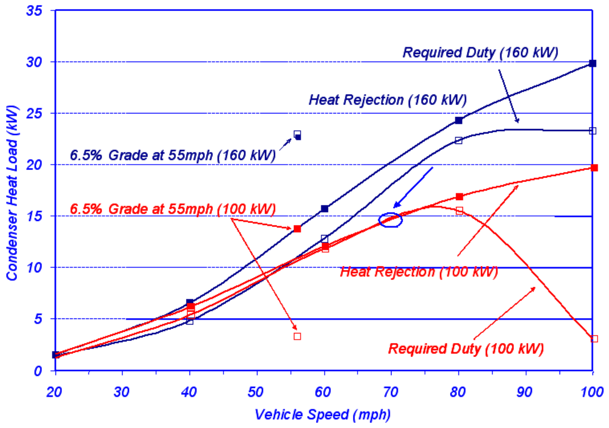

Figure 4. Heat Loads on the Water Recovery Condenser

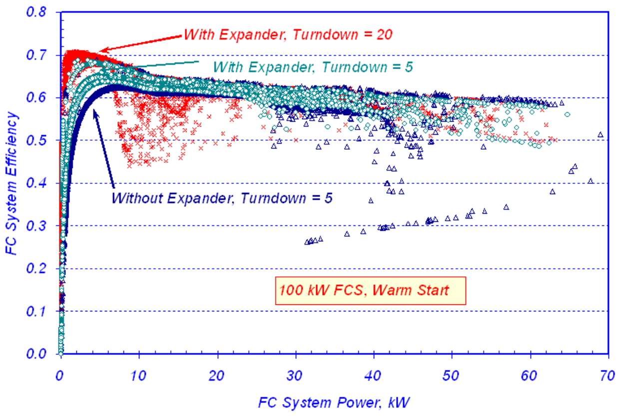

Figure 5. Effects of CEM Turndown and Expander on FCS Efficiency over FUDS

This scatter is largely due to acceleration demand near idling speeds.

Also shown in Figure 5 is the contribution of the expander to FCS efficiency over FUDS. Comparing the results for FCS-2 and FCS-1, the 100-kW systems with and without an expander, differences in efficiency at high loads are due to the additional power generated by the expander and at low loads due to the larger turndown obtainable with an expander in the system. Without an expander, the dynamic fluctuations in efficiency are minor at low loads but can be substantial at high loads.

Oxygen Utilization. Figure 6 shows that in a load-following FCS, oxygen utilization cannot be held constant over driving cycles. This is because of the inertia of the rotating components comprising the air management system and the finite turndown. In particular, oxygen utilization is close to zero during idling conditions and is low during deceleration. The system cannot be water-balanced at low O_2 utilization. In our dynamic simulations, we attempt to maintain the water tank at a constant level by recovering excess water at high loads to compensate for water being consumed at low loads.

Conclusions

- The air management system plays an important role in determining the transient response, cold start-up and part-load performance of a pressurized FCS.

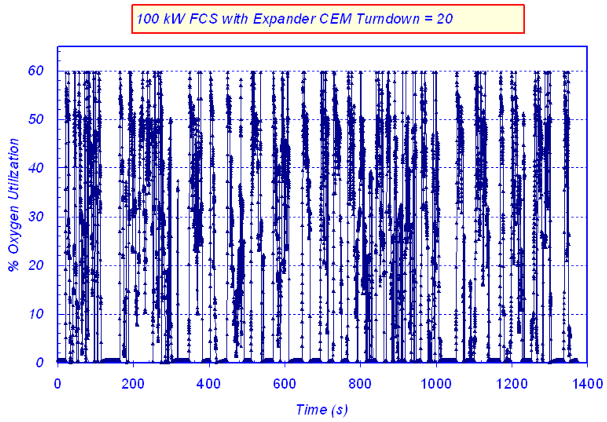

Figure 6. Oxygen Utilization over FUDS

- The size of the heat rejection system for a hybrid mid-size SUV is determined by the gradeability condition rather than the top sustained speed.
- The efficiency at part load and the dynamic fluctuations in efficiency depend on the maximum CEM turndown and the presence of an expander in the system.
- In load-following FCSs, oxygen utilization cannot be held constant over driving cycles. Although it is not possible for the FCS to be water balanced during periods of low oxygen utilization, it can be water neutral over a driving cycle.

FY 2003 Publications/Presentations

1. Ahluwalia, R. K., Deville, B., Rousseau, A., Doss, E. D., Zhang, Q., and Kumar, R., "Performance of Hydrogen Fuel Cell Systems and Vehicles," Third IEA Annex XV Meeting, Düsseldorf, Germany, June 28, 2002.

2. Ahluwalia, R. K. and Milliken, J., "Hydrogen, Fuel Cells and Infrastructure Technologies," World Renewables Energy Congress, Cologne, Germany, July 1-5, 2002.

3. Ahluwalia, R. K., Wang, X., and Rousseau, A., "Direct Hydrogen Fuel Cell Systems for Transportation," Fourth IEA Annex XV Meeting, Palm Springs, CA, November 17-18, 2002.

4. Ahluwalia, R. K., Wang, X., and Rousseau, A., "Direct Hydrogen Fuel Cell Systems for Hybrid Vehicles," Fifth IEA Annex XV Meeting, Stockholm, Sweden, June 17-18, 2003.

5. Ahluwalia, R. K., Doss, E. D., and Kumar, R., "Performance of High-Temperature Polymer Electrolyte Fuel Cell Systems," Journal of Power Sources, 117, 45-60, 2003.

Fuel Cell Vehicle Systems Analysis

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Objectives

- Provide DOE and industry with technical solutions and modeling tools that accelerate the introduction of robust fuel cell technologies.
- Quantify benefits and impacts of the Hydrogen, Fuel Cells & Infrastructure Technology (HFC&IT) Program development efforts at the vehicle level (current status evaluation).
- Understand sensitivity of fuel cell technical target values and provide recommendations to DOE technology development managers (future goal evaluation).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- D. Fuel Cell Power System Benchmarking
- I. Fuel Processor Startup/Transient Operation
- P. Durability
- R. Thermal and Water Management

Approach

- Develop component and vehicle models and link to existing models to enhance systems analysis capabilities.
- Work with industry to apply robust design techniques, optimization tools, and computer-aided engineering (CAE) tools to overcome technical barriers.
- Study benefits of fuel cell system and vehicle design scenarios and transfer to industry.
- Assess impact of various technical team targets at component level.

Accomplishments

- Analyzed and published "Fuel Economy Impacts of Gasoline Reformer Warm-up."
- Integrated two new detailed fuel cell system models into ADVISOR, expanding the range of complexity of modeling capabilities.
- Published technical paper on fuel cell system water management over typical drive schedules.
- Applied robust design methods to fuel cell stack design with Plug Power to understand manufacturing and durability sensitivities.
- Developed Technical Targets Tool for tracking and analyzing the national fuel consumption impacts of DOE research programs.

- Completed initial sensitivity analysis of vehicle fuel economy to fuel cell program technical targets using Technical Targets Tool.

Future Directions

- Perform fuel cell hybrid vehicle system optimization - work with FreedomCAR fuel cell, energy storage, and vehicle systems technical teams to develop energy storage system targets for fuel cell hybrid vehicles.
- Assess sensitivity of fuel consumption to fuel cell technical targets applied across multiple vehicle platforms using Technical Targets Tool.
- Continue water and thermal management analyses for fuel cell vehicles under real driving conditions.
- Transfer robust design techniques to industry to address fuel cell stack cost and durability technical barriers.

Introduction

The Fuel Cell Vehicle Systems Analysis activity at the National Renewable Energy Laboratory is a continuation and expansion of previous efforts in this area. Previous efforts focused on the application of ADVISOR [1], a complete vehicle systems modeling tool, to understanding fuel cell hybrid vehicle design barriers and opportunities. The Office of Hydrogen, Fuel Cells & Infrastructure Technologies has used the simulation results from ADVISOR in the past to assess and revise component and system technical targets. Primary financial support for the development and maintenance of ADVISOR has been through the Office of FreedomCAR and Vehicle Technologies, and the Office of Hydrogen, Fuel Cells & Infrastructure Technologies has been able to leverage this significant investment.

Recent efforts build upon and expand the capabilities of this activity. A new Technical Targets Tool was developed and introduced to automate the technical targets analysis process. It links directly to ADVISOR for vehicle performance estimates and rolls these results up to predict national fuel consumption impacts of DOE research efforts across multiple light-duty vehicle platforms. Additionally, we integrated and applied two new detailed fuel cell system models to understand the water management issues of fuel cell vehicle operation over typical drive cycles. Future studies will include analysis of thermal management characteristics during vehicle operation. Finally, we have developed collaborative relationships with industrial partners and have applied robust design methods to stack and reformer systems to address cost and durability technical barriers.

Approach

It has been our approach to develop component and vehicle models and link them to existing models to enhance our systems analysis capabilities. We work with industry to share and apply robust design techniques, optimization tools, and CAE tools to address the issues of durability, cost, and efficiency. Any results that we derive that are non-proprietary typically form the basis for a publication. Publication and public presentation of our study results have been effective means for transferring knowledge on simulation results and design sensitivities to industry. Finally, we support DOE's effort to set reasonable and challenging technical targets by assessing the impacts of various technical team targets at vehicle system and fleet levels.

Results

Using the existing models in ADVISOR, we estimated the fuel economy impacts on EPA drive cycles of gasoline reformer warm-up. Test data is not yet available as to how long the warm-up process may take or how much energy it may require; however, in our study, we swept the duration and fueling rate over reasonable ranges. We predicted that for long duration and high fueling rates, the fuel consumption for an urban drive cycle could increase by as much as 90% (Figure 1). If the DOE programs are successful in meeting their targets for warm-up, the fuel economy penalty would be 15%-30% in comparison to a hot start fuel cell scenario. In comparison, a typical internal combustion engine (ICE) vehicle incurs a 6%-8% fuel economy penalty for cold-starts. The results of this small study were published at the 2003 Society of Automotive Engineers (SAE) Future Transportation Technologies Conference.

We have also integrated two new fuel cell system models into ADVISOR. The first, a fuel cell model developed by Virginia Tech, based on their contributions to the FutureTruck competition, allows us to model systems with variable pressure operating strategies and performs a complete thermal and water balance on the system. The second is a model developed at the Swedish Royal Institute (KTH). This model is based on the Springer et al. stack model and focuses on complete thermodynamics for the balance of plant system. The models were applied to assess the water balance of a fuel cell hybrid vehicle over typical drive cycles. Results of this study were published at the 2003 American Society of Mechanical Engineers (ASME) First International Conference on Fuel Cell Science, Engineering and Technology.

The results of a study with Plug Power looking at the application of robust design techniques for fuel cell stack design were also published at this same conference. The study reviewed the sensitivity of pressure and pressure distribution within the membrane electrode assembly (MEA) due to variability in mounting bolt loading, MEA thickness, bipolar plate thickness, and material properties (Figure 2). Understanding how tightly these manufacturing variabilities must be controlled is critical to reducing production costs and improving durability.

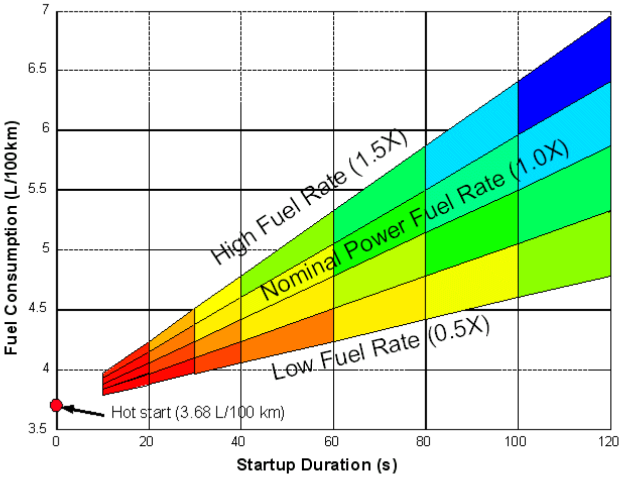

Figure 1. Estimated Fuel Consumption Impact Based on a Range of Startup Durations and Fueling Rates

As a result of our efforts this year, we completed the first version of the Technical Targets Tool. This new tool provides a means for tracking and assessing the impacts of DOE program technical targets. The tool contains a database of technical targets that are applied across multiple vehicle platforms. The tool uses ADVISOR to predict the performance characteristics of vehicles based on the technical targets. A time-based penetration curve and vehicle class specific sales predications are used to estimate the potential fuel consumption savings of the DOE technology programs. Future results are expected to

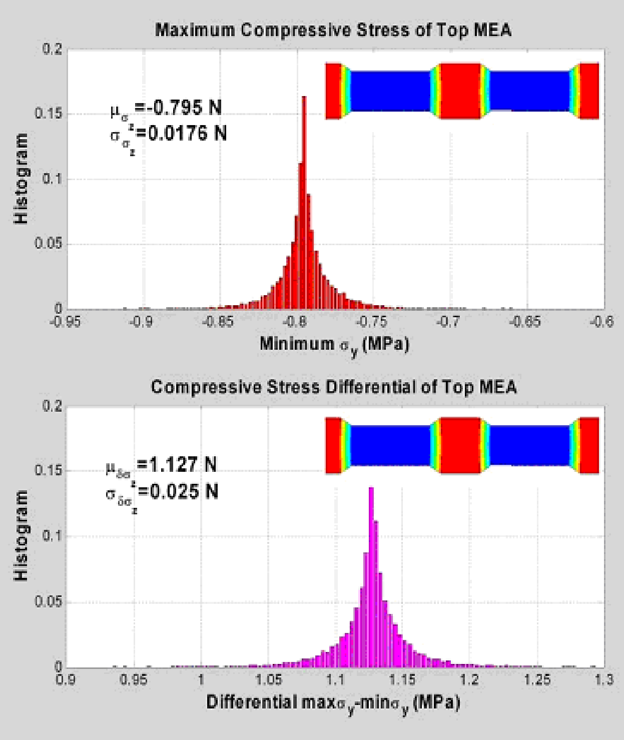

Figure 2. Histograms of maximum maxδ_{ztop} and differential compressive stress $\Delta\delta_{ztop}$ in the top MEA

help ensure that the existing program technical targets lead to applicability across multiple platforms and provide the greatest impact from the DOE efforts.

Conclusions

The following conclusions can be drawn from the Fuel Cell Vehicle Systems Analysis efforts:

- Our analysis showed that the fuel economy impacts of gasoline reformer warm-up may be substantial. The DOE program targets are focused on minimizing this impact.
- Our study on fuel cell system water management over typical drive schedules highlighted capabilities of the new fuel cell system models integrated into ADVISOR. Results of the water balance study showed that condenser and reservoir sizing decisions should consider both the drive cycle requirements and the operating conditions.
- The application of robust design methods to fuel cell stack design provided our industry partner, Plug Power, with a process and a better understanding of the sensitivities that several design variables have on stack pressure distribution. This information could lead to less expensive, more durable fuel cell stacks.
- We demonstrated that the new Technical Targets Tool could be used to predict impacts on national fuel consumption resulting from DOE research program efforts applied across multiple vehicle platforms. As expected, the initial sensitivity results using the Technical Targets Tool indicate the fuel cell system and motor efficiencies have a significant impact on vehicle fuel economy.

FY 2003 Publications/Presentations

1. Markel, Tony; Wipke, Keith; Haraldsson, Kristina; Kelly, Ken; Vlahinos, Andreas. "Fuel Cell Vehicle Systems Analysis." Presented at Hydrogen, Fuel Cells and Infrastructure Technologies Annual Program Review. Berkeley, CA. May 20-23, 2003.
2. Wipke, K. B.; Markel, A.; Haraldsson, K.; Davis, P. "Predicting the Fuel Economy Impact of "Cold-Start" for Reformed Gasoline Fuel Cell Vehicles." SAE Publication 2003-01-2253. Presented at SAE Future Transportation Technologies Conference. Costa Mesa, CA. June 23-25, 2003.
3. Markel, Tony; Zolot, Matthew; Wipke, Keith B.; Pesaran, Ahmad A. "Energy Storage System Requirements for Hybrid Fuel Cell Vehicles." 3rd International Advanced Automotive Battery Conference. Nice, France. June 10-13, 2003.
4. Haraldsson, Kristina; Markel, Tony; Wipke, Keith. "An Analysis Of Water Management for a PEM Fuel Cell System in Automotive Drive Cycles." ASME First International Conference on Fuel Cell Science, Engineering and Technology. Rochester, New York. April 21-23, 2003.
5. Willis, Gordon; Weller, Rick; Wipke, Keith. "An Engineering System for Automated Design and Optimization of Fuel Cell Powered Vehicles." ASME First International Conference on Fuel Cell Science, Engineering and Technology. Rochester, New York. April 21-23, 2003.
6. Vlahinos, Andreas; Kelly, Kenneth; D'Aleo, Jim; Stathopoulos, Jim. "Effect of Material and Manufacturing Variations on Membrane Electrode Assembly Pressure Distribution." ASME First International Conference on Fuel Cell Science, Engineering and Technology. Rochester, New York. April 21-23, 2003.
7. Kelly, Kenneth; Vlahinos, Andreas; Rodriguez, Pablo; and Bharathan, Desikan. "Innovative Thermal Management of Fuel Cell Power Electronics." ASME First International Conference on Fuel Cell Science, Engineering and Technology. Rochester, New York. April 21-23, 2003.
8. Haraldsson, Kristina; Wipke, Keith. "An Evaluation of Select PEM Fuel Cell System Models." The 202nd Electrochemical Society Symposium. Salt Lake City, Utah. October 23, 2002.

9. Markel, Tony; Wipke, Keith; Nelson, Doug. "Vehicle System Impacts of Fuel Cell System Power Response Capability." SAE Publication 2002-01-1959. Presented at FutureCar Congress. June, 2002.

References

1. Markel, T., Brooker, A., Hendricks, T., Johnson, V., Kelly, K., Kramer, B., O'Keefe, M., Sprik, S., Wipke, K., "ADVISOR: a systems analysis tool for advanced vehicle modeling" Journal of Power Sources Volume 110, Issue 2, 22 August 2002, pp. 255-266.

Cost Analyses of Fuel Cell Stack/Systems

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Objectives

To develop an independent cost model for proton exchange membrane (PEM) fuel cell systems for transportation applications and to assess cost reduction strategies for year 2000 to 2004 development projects

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- N. Cost (Fuel-Flexible Fuel Processor)
- O. Stack Material and Manufacturing Cost

Technical Targets

System	Efficiency	Cost	
		2010	2015
Direct Hydrogen Fuel Cell Power System (including hydrogen storage)	60%	$45/kWe	$30/kWe
Reformer-based Fuel Cell Power System - clean hydrocarbon or alcohol based fuel - 30 second start-up - satisfies emissions standards	45%		

Approach

- In the first two years, develop a baseline system configuration and cost estimate based on best available and projected technology and manufacturing practices, and assess the impact of potential technology developments on system cost reduction
- In the subsequent four years, annually update the baseline cost model and system scenarios based on assessments of developments in PEM fuel cell system technologies and manufacturing processes.

Accomplishments

- Evaluated status of bipolar plate technology for PEM fuel cells (Table 1)
- Compared cost and performance of graphite and metallic bipolar plates
- Examined performance impact of using graphite bipolar plates instead of metallic bipolar plates

Table 1. Overview of Bipolar Plate Technologies Considered in this Analysis

Substrate Material	Coating Material	
Aluminum	**Non-Metal**	**Metal-Based**
Stainless Steel	Graphite	Noble Metals (gold, silver)
Ni-Cr alloys	Conductive Polymer	Metal Carbides
Metal/polymer composite		Metal Nitrides
		Cladding

Future Directions

Develop projections of future system performance and cost based on continued industry feedback, alternative system scenarios, and projected technology developments

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Introduction

In 1999, a baseline cost estimate for a 50-kW PEM fuel cell system for passenger vehicles was developed based on technology available in the year 2000, but using a high production volume scenario (i.e., 500,000 units per year). In 2000, we solicited feedback from system and component developers on the system configuration, design and performance parameters, and manufacturing process and costing assumptions. The impacts of alternative system design approaches were also assessed: specifically, what would be the impact of sizing the stack at the high power point rather than 0.8 volts, and what would be the impact of hybridization, i.e., reducing or increasing rated power, on the fuel cell system power cost ($/kW). In 2001, we focused on the development of future costs based on projected technology. In 2002, an electrochemical model for the relationship between catalyst loading, temperature, pressure, and power density was combined with the cost model to understand the tradeoffs between catalyst loading and cost of the stack. The cost model was used to develop projections for direct hydrogen fueled systems. In 2003, we evaluated the impact of replacing graphite bipolar plates with metallic bipolar plates.

The potential benefits of metallic bipolar plates that we analyzed were reduced plate thickness and weight and improved thermal and electrical conductivity. Higher electrical conductivity increases the efficiency of the system by decreasing parasitic loss, which enables the formation of smaller stacks. Similarly, lighter weight increases power density [kW/kg]. Thinner plates decrease the thermal management and the packaging requirements, which increases the applicability of PEM fuel cells in the automotive industry. All of these benefits may lead to lower cost (Figure 1). Finally, recyclability and consistency of metal forming technologies were considered as additional benefits of metallic bipolar plates.

Approach

The assessment of bipolar plate technology for PEM fuel cells was started with the initial hypothesis

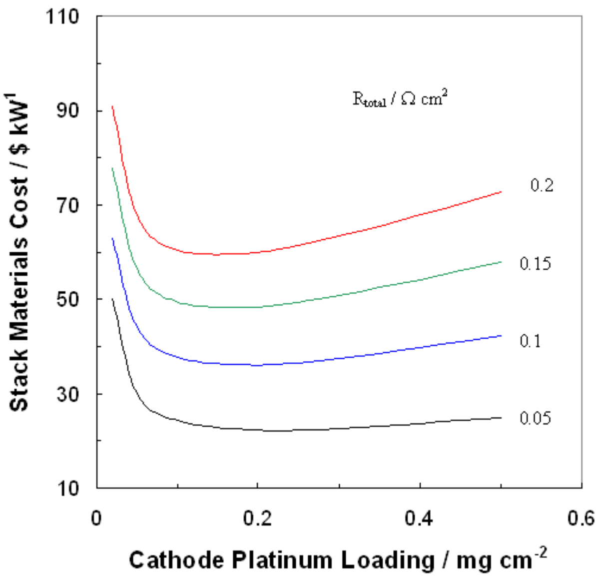


Figure 1. QUANTUM Compressed Hydrogen Storage

Table 2. Benefits and Drawbacks of Graphite, Composite and Metallic Bipolar Plates

	Graphite (machined)	Metal (SS, Al, Ti)	Graphite Composite
Benefits	Stability Low specific density Low contact resistance with electrodes Corrosion resistance	High Thermal conductivity Recyclable Consistent product	Lower contact resistance Corrosion resistance
Drawbacks	Expensive to machine Brittle Thick	Needs coating Membrane poisoning Formation of insulating surface oxides	Low bulk conductivity

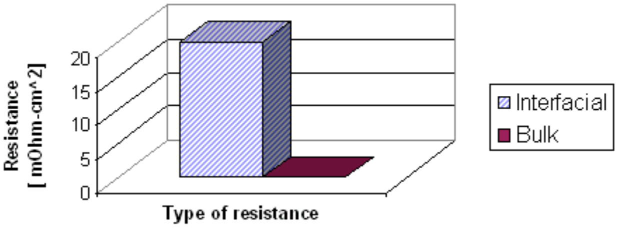


Figure 2. Bulk and Interfacial Contact Resistance for Stainless Steel Alloy SS 904 L Bipolar Plates

that metallic bipolar plates may lower stack cost by reduction of ohmic losses, and that increased volumetric power density would enhance integration into vehicles. The following comparative parameters were considered:

- thickness (and its impact on volumetric density)
- weight
- thermal conductivity
- electrical conductivity (bulk and interfacial resistance)
- material and processing cost

Metallic bipolar plates were analyzed by evaluating the alternatives for substrate material and coating technology. Thermal and electrical properties and feasible dimensions were studied.

Industry representatives from the bipolar plate and coating industries and material suppliers were contacted to identify benefits and drawbacks of metallic and graphite bipolar plates (Table 2).

Results

Interfacial resistance between the bipolar plate and the electrode dominates bulk resistance for both graphite and metal bipolar plates. There was no evidence indicating that the interfacial resistance for metallic plates was lower than graphite's. Therefore, metal's smaller bulk resistance (9.5×10^{-3} mΩ-cm^2 vs. 9 mΩ-cm^2) is not a clear advantage (Figure 2).

The cost of thinner and highly corrosion resistant metallic plates (i.e. SS 904 L) is not lower than thicker graphite-based plates. As an example, the cost per plate (1 mm thick, 603 cm^2) made of 904L was calculated to be $10.31, compared to $2.75 per graphite-based plate (3.75 mm thick, 603 cm^2), as shown in Table 3. Application of the conductive coating further increases the cost of the substrate.

A three-fold decrease in the thickness of the bipolar plate (e.g. 3.75 to 1 mm) decreases the stack volume by at least 50% and the overall system volume by at least 10%. However, graphite plate thickness is approaching values of 1 mm, similar to metallic bipolar plates. Flow field requirements and mechanical robustness set minimum dimensions, regardless of manufacturing feasibility. Therefore, although thinner plates have a significant effect on

Table 3. Metallic and Graphite Plate Costs (all costs are in U.S. dollars)

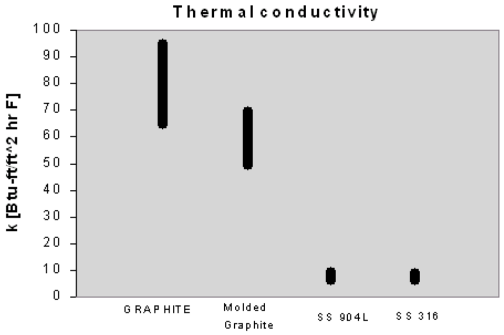
Plate Type	**Graphite Baseline**	**Metallic – SS 316**	**Metallic - SS 904**
Substrate Material Cost [$/plate]	2.24	2.22	5.42
Substrate Material Cost [$/m^2]	37	37	90
Processing Cost [$/plate]	0.51	1.07	1.07
Processing Cost [$/m^2]	8	18	18
Coating Cost [$/plate]	No	3.79	3.79
Coating Cost [$/m^2]	No	63	63
TOTAL [$/plate]	2.75	7.08	10.31
TOTAL [$/m^2]	46	117	171
TOTAL STACK COST for BIPOLAR PLATES [$/kW]	21	53	78
Weight [kg]	179	228	225

volumetric density, they can be achieved by using both graphite and metal.

Thermal conductivity of metallic bipolar plates based on stainless steel is not superior to molded graphite (Figure 3).

Conclusions

- Metallic bipolar plates do not offer a clear performance or cost advantage over graphite-based bipolar plates.
- Cost of bipolar plates could increase 23-40% relative to graphite plates depending on the stainless steel alloy used.
- Metallic bipolar plates do not result in significantly higher volumetric density.
- Thermal management requirements for metallic bipolar plates are not more favorable than requirements for graphite plates.
- Development of effective coatings are critical to the viability of metallic bipolar technology.



Note: The thermal conductivity for molded graphite was assumed to be the weighted average of the properties of vinyl ester polymer (31.2%) and pure graphite (65%).

Figure 3. Thermal Conductivity of Different Materials

FY 2003 Publications/Presentations

1. *Fuel Cell Cost Issues.* SAE TOPical TEChnical Symposium. April 8-9, 2003. Dearborn, Michigan.
2. 2003 Annual Hydrogen, Fuel Cells & Infrastructure Technologies Program Merit Review and Peer Evaluation in Berkeley, California.

Precious Metal Availability and Cost Analysis for PEMFC Commercialization

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Objectives

The project objectives include:

- Assessment of current and projected demand for platinum group metals (PGMs) exclusive of fuel cell applications
- Estimation of the relationships between supply capacity/reserves and long-term growth in demand for PGMs
- Development of an econometric model to simulate the impact of fuel cell market growth scenarios on PGM supply and pricing
- Analysis of supply and pricing sensitivity to critical parameters in the model related to fuel cell markets and technology advances
- Solicitation of critical feedback from the important participants in the PGM value chain on the model assumptions and projections
- Development of a cost projection for the economics of recycling PGMs from fuel cells and the impact on PGM supply and price

The overall goal is not only to develop projections of PGM availability and cost, but also to identify and quantify the industry and market drivers influencing these parameters. On the demand side, we will break down the demand between existing markets and the potential applications of fuel cells. We will identify underlying trends in the industrial/chemical and lifestyle markets with attention to growth of demand and potential for substitution of alternative materials. In the fuel cell markets, the impact of technology on PGM demands will also be considered.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- N. Cost
- O. Stack Material and Manufacturing Cost

The overall DOE platinum target for reformate based-systems is 0.2 g Pt/kW.

Approach

The project has been broken into five tasks as follows:

1. Collection of historical PGM supply/demand/pricing and resource data
2. Development of fuel cell market commercialization scenarios
3. Development of a PGM recycling scenario, including a high level PGM proton exchange membrane fuel cell (PEMFC) recycling cost model
4. Development of an econometric model for the simulation of the impact of fuel cell introduction on PGM supply and price
5. Solicitation of feedback from PGM industry and automotive original equipment manufacturers (OEMs)

Tasks 1 and 4 were scheduled for the fiscal years 2001 and 2002. The balance of the tasks will be completed in year 2003.

Accomplishments

- Econometric analysis of historical platinum price, supply, and demand data completed
- Platinum resource and market data compiled
- Results of econometric analysis presented to Johnson-Matthey and International Platinum (IPA) for feedback
- Market demand scenarios developed for fuel cell vehicles and platinum catalyst out to 2050; scenarios presented to South African mining companies, IPA, and automotive OEMs to obtain feedback on market projections, potential supply responses, resource projections, and technology assumptions

Future Directions

- The platinum and automotive industry feedback will be integrated to develop conclusions on the potential impact of PEMFC commercialization on price and availability of platinum
- Final report will be issued

Introduction

Platinum group metals (PGMs) are critical to the commercialization of fuel cells because of their role in supporting critical levels of performance (power density and efficiency), but they also represent a significant contribution to overall system cost. Depending on operating design parameters, platinum would represent between 10 and 20% of the system cost of a gasoline fuel cell system produced in high volume. PGMs (primarily platinum and some ruthenium) are critical to catalyzing reforming/shift reactions in the fuel processor and electrochemical oxidation and reduction in the fuel cell, with the fuel cell requirements presently dominating the demand. Successful adoption of fuel cells in transportation applications in the long term could create markets on the order of ten million vehicles, leading to significant pressure on PGM suppliers to increase production capacity and supply. Consideration of stationary and portable applications for fuel cells further increases the demands on PGM supplies. Clearly, the combination of stationary, portable and transportation markets for fuel cells will create pressure on the PGM industry to increase supplies and might cause skyrocketing prices (thereby threatening fuel cell market viability) unless action is taken to guide the process. In addition to price, the commercialization of fuel cells will also depend on the amount of economically mineable PGM resources and the ability of the PGM value chain to supply the PGM materials in the needed forms and at reasonable markups above the London Metals Exchange (LME) price.

Econometric analysis and modeling were applied to understand and simulate the relationships between supply, demand, and price for historical markets. An understanding of the basis for platinum resource projections was developed and used to compile a future platinum resource estimate. Inputs from the platinum and automotive industries are being obtained to project future fuel cell vehicle platinum demand and the ability of the mines to respond to these demands. The impact on price of platinum will be assessed using the econometric model.

Approach

The modeling approach starts with construction of an econometric model based on historic supply, demand, and price data. A simulation will then be run to study the impact of introduction of fuel cell vehicles on the supply and price of platinum. Automotive catalysts and jewelry are the two dominant markets for platinum (approximately 80%); hence, they will be important elements in the econometric model. The investment industry consumes a minor amount of material but can exert significant influence on short-term price. However, over long periods of time, investment should have zero impact on supply and demand.

After completion and validation of the econometric model, future demand scenarios will be input into the econometric model to project the impact of fuel cell commercialization on supply and pricing. The scenarios for stationary, portable, and transportation applications of fuel cells will range from optimistic to pessimistic and contain volume and time estimates. Economic growth, catalyst technology development, and shifts in automotive powertrain technology will be some of the factors considered in development of the demand scenarios. The model and the scenarios can be used to conduct sensitivity analyses to the various factors. Recycling will play a significant role as platinum consumption increases further. The high value of recycled platinum drives a high level of recovery today.

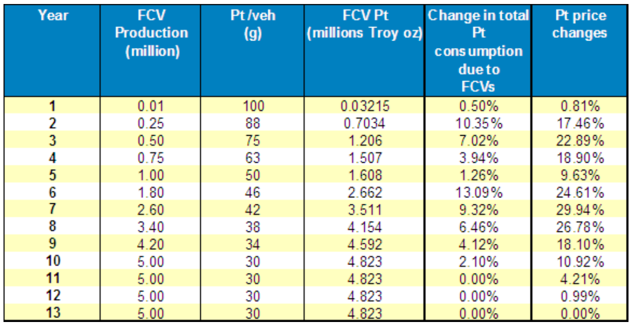
Inputs from the platinum and automotive industries have been and are being solicited to obtain data, feedback on assumptions, and reactions to projections of fuel cell technology and commercialization. The two industries worked together to introduce platinum-based catalytic converters in the 1970's, and similar efforts of even larger scale (e.g., expansion in mining capacity and capital investments) will be called for in the commercialization of fuel cells. Consequently, input from the industry drivers is essential to development of conclusions.

Results

Use of the econometric model to simulate the impact of fuel cell vehicle commercialization indicates that the platinum price will increase in the short-run until increased production restores balance between supply and demand. As production catches up to demand, the platinum price will return to its long-term mean price. Table 1 contains an illustrative case of fuel cell vehicle (FCV) introduction and platinum demand. Figure 1 illustrates the results from the simulation model for short-run and longer-run price.

The total platinum demand projection was built up from total vehicle projections for the U.S., Japan, Western Europe, China, and India; fuel cell vehicle market penetration scenarios; and a vehicle platinum requirement scenario. The selected countries represent approximately 80% of worldwide vehicle

Table 1. Illustrative Fuel Cell Vehicle Introduction Scenario and Simulated Impact on Platinum Price



Year	FCV Production (million)	Pt /veh (g)	FCV Pt (millions Troy oz)	Change in total Pt consumption due to FCVs	Pt price changes
1	0.01	100	0.03215	0.50%	0.81%
2	0.25	88	0.7034	10.35%	17.46%
3	0.50	75	1.206	7.02%	22.89%
4	0.75	63	1.507	3.94%	18.90%
5	1.00	50	1.608	1.26%	9.63%
6	1.80	46	2.662	13.09%	24.61%
7	2.60	42	3.511	9.32%	29.94%
8	3.40	38	4.154	6.46%	26.78%
9	4.20	34	4.592	4.12%	18.10%
10	5.00	30	4.823	2.10%	10.92%
11	5.00	30	4.823	0.00%	4.21%
12	5.00	30	4.823	0.00%	0.99%
13	5.00	30	4.823	0.00%	0.00%

sales. Vehicle projections were based on population projections for the respective countries and assumed vehicles per capita. For the mature markets in the developed countries, the vehicles per capita have reached asymptotic values, while for the emerging transportation markets in developing countries, the vehicles per capita will show significant growth. For this reason, we developed vehicle per capita scenarios for the latter regions. We also assumed a time lag for fuel cell vehicle introduction into the emerging markets. In the developed countries, a moderate to declining population growth leads to a modest vehicle sales increase driven by the U.S. Large populations along with increasing vehicles per capita in China and India lead to significant new vehicle markets. In 2050, we estimated sales in the developed countries would be 47 million vehicles, while the developing countries would add an additional 25, 46, or 86 million vehicles depending on the market growth scenario (i.e., slow, moderate, or high).

Preliminary fuel cell market introduction scenarios are shown in Figure 2. The ANL (Argonne National Laboratory, Ref 1) penetration curve was used to estimate fuel savings in the U.S. from fuel cell vehicle commercialization. In the ANL scenario, used as our bounding case, commercialization starts with rapid adoption in 2018 and a market penetration of 100% by 2037. The more moderate scenarios assume a slower adoption and penetrations of 80% and 50%. Overlaying these scenarios, we assume technology advances that result in reduced platinum loadings per vehicle of 20 grams in 2015 and 15 grams by 2025.

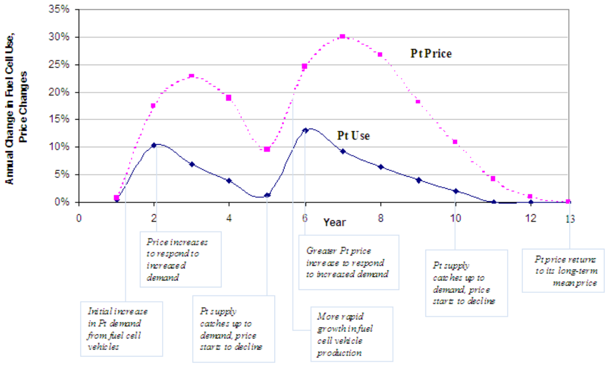


Figure 1. Simulation of platinum price response to increased platinum demand from fuel cell vehicle introduction.

Combining the vehicle projections, fuel cell vehicle market projections, platinum loading assumptions, and growth in traditional platinum markets leads to the primary platinum curves shown in Figure 3 for the moderate and slow growth fuel cell vehicle scenarios. Figure 4 highlights the critical role that recycling will play in reducing the demand for primary platinum. In the moderate growth

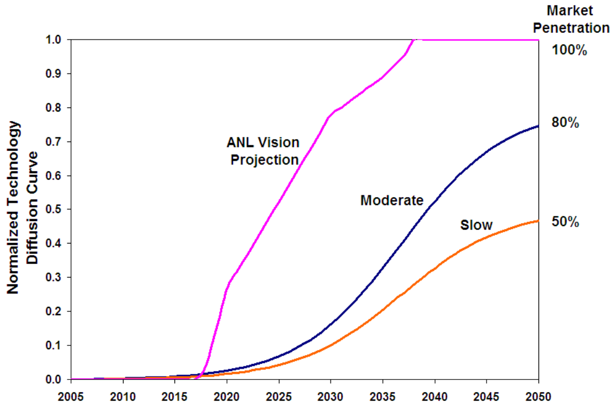


Figure 2. Fuel cell vehicle market penetration scenarios for developed and developing countries. The latter countries have 10- and 15-year time lags for the moderate and slow scenarios.

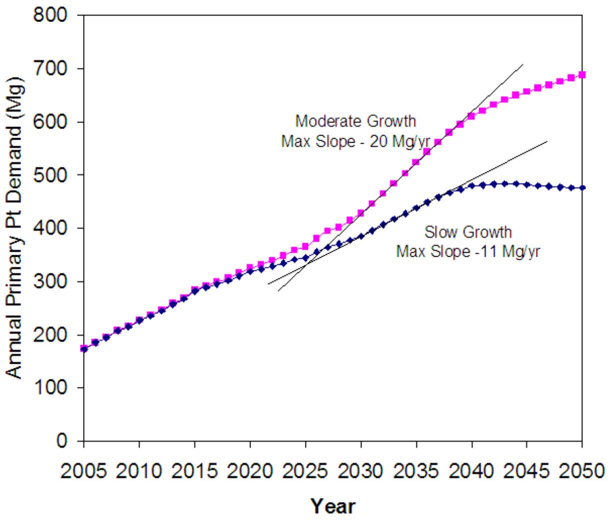


Figure 3. Total primary platinum demand needed to supply vehicle and other platinum market needs. The vehicle demand includes both the developed and developing countries.

scenario, recycled platinum used in fuel cell vehicles exceeds primary platinum after 2045. Figure 5 shows the platinum demand for the moderate commercialization scenario relative to historical platinum production data. The integration of the primary platinum demand out to 2050 shows the cumulative production represents approximately 30% of projected resources.

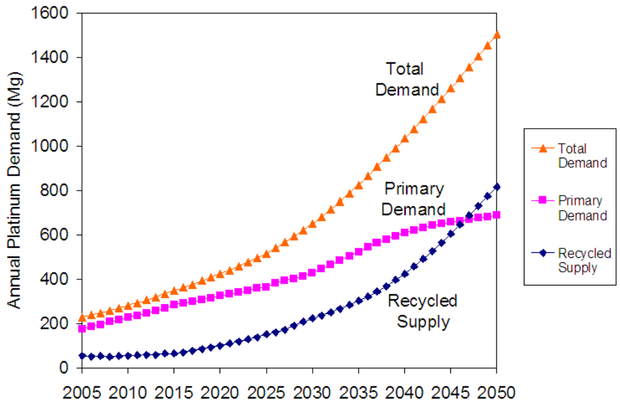


Figure 4. Overall annual platinum demand for the moderate growth scenario with the primary and recycled supply shown. Platinum from recycling exceeds primary supply after 2045.

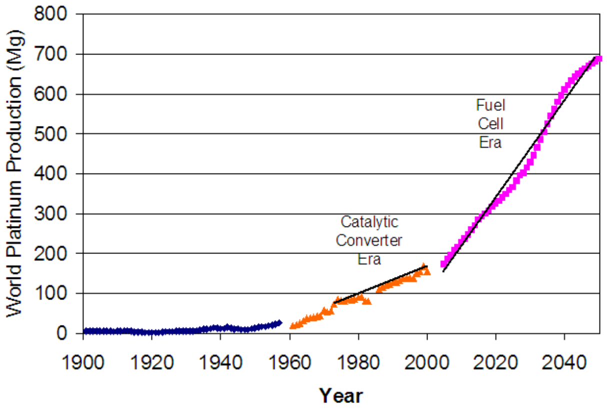


Figure 5. Moderate vehicle and fuel cell commercialization scenario platinum demand plotted relative to historical growth in platinum production.

Conclusions

The results presented in this report still require the final feedback from the platinum and automotive industries.

- Short-run spikes in platinum price may occur, dependent on the balance between demand and supply. Traditionally, the platinum industry has tried to maintain a constant real price to sustain traditional markets for PGMs while promoting growth of new applications. The expectation is that the platinum industry will continue to increase production to keep supply and demand in balance.
- The platinum industry will have to increase their rate of new production capacity to satisfy increased demand.
- High levels of recycling will be critical to reducing demands on primary platinum and are expected to exceed primary production.
- The combination of recycling and advances in mining technology to economically recover deeper sources of PGM ore will be needed to maintain reserves of platinum.

References

1. M.K. Singh, "VISION: a spreadsheet energy use model developed by ANL for the U.S. DOE", ANL, December 2002 run for DOE/OHFCIT2

FY 2003 Presentations

1. 2003 U.S. DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Merit Review and Peer Evaluation in Berkeley, California.

2. 2002 Fuel Cell Seminar in Palm Springs, California.

DFMA Cost Estimates of Fuel-Cell/Reformer Systems at Low/Medium/High Production Rates

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Objectives

- Develop realistic and internally consistent detailed designs for automotive gasoline fuel processor/proton exchange membrane (PEM) fuel cell systems and direct hydrogen PEM fuel cell systems by using current-year technology.
- Apply Design for Manufacture and Assembly (DFMA) design and costing techniques to compare system designs at low, medium, and high annual production rates.
- Develop a roadmap to lower system cost by performing a sensitivity study of the major components in the fuel processor and fuel cell systems.
- Determine the impact on cost, volume, and mass of replacing the fuel processor unit operations with microchannel-type components.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Hydrogen Production

- A. Fuel Processor Capital Costs

Hydrogen Delivery

- A. Lack of Hydrogen/Carrier and Infrastructure Options Analysis

Fuel Cells

- D. Fuel Cell Power System Benchmarking

Approach

- Conduct annual updates of design, manufacturing methods, and costs for the four 50-kW_{net} PEM fuel cell systems previously examined:
  - reformer/fuel cell system operating at 0.7 V/cell peak-power
  - reformer/fuel cell system operating at 0.6 V/cell peak-power
  - direct hydrogen fuel cell system operating at 0.7 V/cell peak-power

  - direct hydrogen fuel cell system operating at 0.6 V/cell peak-power
- Perform cost sensitivity analysis for material costs and system performance parameters.
- Analyze weights, volumes, and costs of microchannel device substitutes for reformer components and compare to baseline design.

Accomplishments

- Performed annual update to cost estimates of baseline and three alternative systems with more detailed estimates of peripheral components.
- Conducted a sensitivity study to quantify the overall fuel cell cost reductions that could result from cost reductions and technological improvements in major fuel processor and fuel cell system components.
- Compared microchannel designs for the major fuel processor components (catalytic reactors and heat exchangers) with the existing baseline designs, with a focus on component mass and volume.

Future Directions

- Update baseline reformer and fuel cell cost estimates to reflect advances in technology and additional manufacturing and design improvements.
- Construct a roadmap to lower system cost based on the results of the sensitivity study.
- Analyze potential cost reductions resulting from gas purification technologies.
- Examine feasibility of alternate fuel cell designs and operations, such as stack construction, voltage and/or pressure pulsing, and air compression technologies.
- Identify feasible manufacturing techniques and costs for microchannel fuel processor components.

Introduction

Directed Technologies Inc. (DTI) has performed a DFMA-style cost estimation for an onboard gasoline reformer and fuel cell system at several annual production volumes. The Design for Manufacture and Assembly (DFMA) technique is a rigorous design/redesign and cost estimation methodology developed by Boothroyd and Dewhurst (1) and adapted by DTI. DTI has previously analyzed the cost of a 50-kW_{net} baseline system and compared it to an alternate reformer/fuel cell system and two direct hydrogen fuel cell systems.

The current report provides updates to the estimated costs for these four systems, a sensitivity analysis aimed at identification of cost reduction options in the baseline system, and a summary of the evaluation of microchannel technology for possible use in the fuel processor system. Microchannel component design takes advantage of the high specific heat transfer area that can be achieved through the use of reaction and heat exchange devices that have flow channels with critical dimensions of less than 1 millimeter.

Approach

System Cost Updates. Using information gained over the past year related to the cost of fuel cell (FC) materials and components as well as interactions with industry, the cost of the baseline 0.7 V/cell reformer-FC system, the 0.6 V/cell reformer-FC system, and both the 0.6 and 0.7 V/cell direct hydrogen systems have been updated. While the newest cost estimates are slightly different than previous ones, the trends and conclusions drawn in previous years remain unchanged.

Cost Sensitivity Analysis. With the intent of developing a roadmap to lower system cost, we examined the sensitivity of system cost to various material costs and performance parameters for both the reforming system and the fuel cell stack. The relative cost contribution of the following materials was examined:

- Stack components: ionomer, gas diffusion layer (GDL), and bipolar plates
- Precious metal (PM) catalysts in the fuel cell stack, reforming and gas-cleanup sections
- Reformer shell materials
- Reformer catalyst support and application

Using a component-by-component parametric model, the sensitivity of system cost to the following parameters was evaluated:

- Stack power density
- Overall system efficiency
- Reformer, water gas shift (WGS), and preferential oxidation (PrOx) bed volumes
- Gasoline sulfur levels

Microchannel Technology Assessment. We have considered microchannel devices as replacements for the following fuel processor subsystems:

- Autothermal reformer/steam reformer (ATR/SR)
- High-temperature water gas shift (HTS)
- Water boiler/vaporizers (2 items)
- Low-temperature water gas shift (LTS)
- Preferential oxidation (PrOx)

The subsystems listed above were screened through discussions with Pacific Northwest National Laboratory (PNNL) and by preliminary design calculations to determine which processing steps could benefit by the substitution of microchannel devices.

Results

System Cost Updates. The system cost breakdowns for the 0.7 V/cell reformate and direct hydrogen systems are shown in Figure 1. In both systems, the fuel cell stack contributes roughly half the cost of the complete system.

Cost Sensitivity Analysis. In a fixed system design, material costs for various components provide an estimate of the relative potential for system cost reductions through material cost reductions. The results of the materials cost analysis are shown in Figure 2, where membrane ionomer, membrane catalyst, GDL, and bipolar plate are shown to be the largest cost-contributing materials.

Figure 3 is a tornado plot for several system performance parameters, indicating that fuel cell stack power density (and, hence, active area) is the most significant performance parameter affecting system cost. The data shown correspond to the 0.7 V/cell reformer-FC system at a manufacturing rate of 500 units per year but are nearly identical at a manufacturing rate of 500,000 units per year.

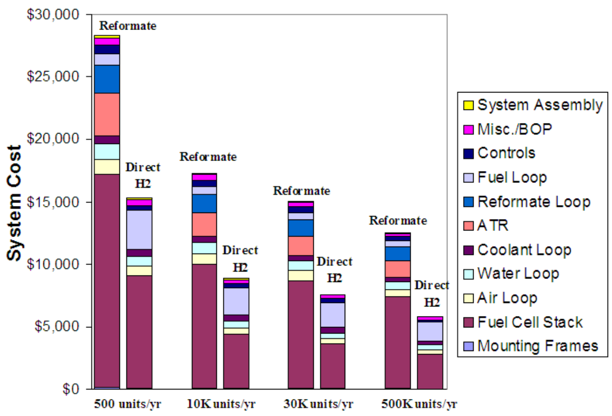

Figure 1. Cost Breakdown for 0.7 V/cell Reformer-Fuel Cell and Direct Hydrogen Systems

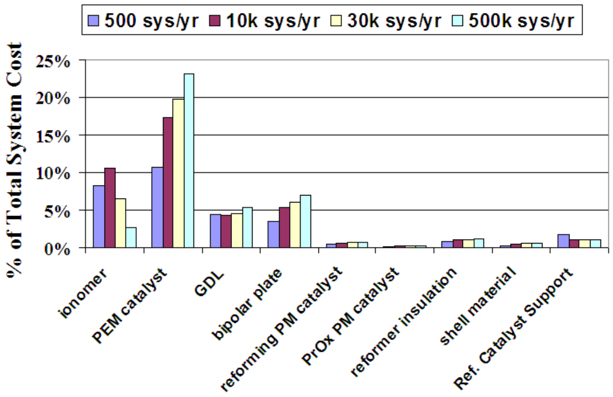

Figure 2. Contribution of Material Costs to System Costs for Baseline Reformer-Fuel Cell System

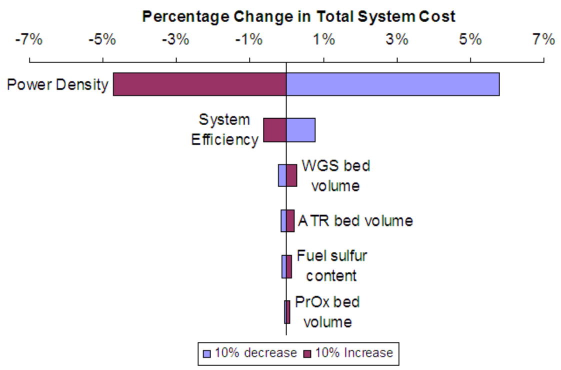

Figure 3. Effect of Operational Parameters on System Cost at Production Rate of 500 Systems/Yr

Microchannel Technology. The autothermal reformer (ATR) was eliminated as a potential application for microchannel components due to the high temperatures involved (>800°C) that would require thick metal walls and because the adiabatic operation of the ATR is well-suited to using a ceramic monolith reactor. Additionally, design calculations indicate there is at most a 10% improvement in reactant mass transfer through the catalyst matrix in a microchannel with 750 mm flow paths compared to a monolith with 1 mm cells.

More substantial volumetric reduction is potentially achievable through conversion of the water vaporizer to a microchannel design. Such a design was prepared using 480°C reformate as the heating fluid to vaporize the water as in the baseline design. The core of the microchannel design achieved an 82% reduction in volume compared to the baseline design; however, when fluid manifolding is included, the volume reduction shrinks to 32% (669 cm^3 vs. 991 cm^3). This indicates, sensibly, that imaginative integration of components will be required to achieve maximum volumetric reduction, since manifolding can quickly erase much of the gains.

The microchannel water gas shift (WGS) reactor design combines the high temperature shift bed, water vaporizer, and low temperature shift bed from the baseline design into a single device. The integration of heat exchange and reaction allows the WGS reaction to trace the equilibrium curve from 400°C down to 300°C, resulting in a reduced catalyst volume compared to the baseline. Preliminary calculations show that a reduction in system volume of 68% is possible by using the microchannel design (4.2 liters vs. 13.0 liters). (The PNNL staff is in the process of reviewing the design for the microchannel WGS, and their comments will be considered before finalizing the design.) However, due to the addition of the metallic heat exchange elements, the mass of the microchannel core and the mass of the baseline system are estimated to be almost identical (12.6 kg vs. 12.7 kg).

Conclusions

The baseline design for this study was developed using DFMA-style techniques applied to the stack and fuel processing components to achieve low cost. In the resulting system, the fuel cell stack represents roughly half the system cost at all production rates. This fact is emphasized by both the material and performance parameter sensitivity analyses, in which fuel cell stack materials and power density are shown to be the most significant cost contributors. Substantial cost reductions in the system can only be achieved by addressing issues with the potential to reduce stack size, either directly through improved stack performance or indirectly through fuel processor improvement to deliver higher purity hydrogen to the stack. These approaches can be summarized as follows:

- Lower stack material and fabrication costs
    - lower catalyst loading
    - less expensive stack materials
- Increased stack power densities
    - improved membrane performance
    - improved stack operation
    - improved gas processing for pure hydrogen

Microchannel devices are potentially attractive for fuel processor subsystems that benefit from combined reaction and heat exchange. The water gas shift and preferential oxidation steps, therefore, are potential applications for microchannel technology, while the adiabatic autothermal reforming is not. An integrated microchannel WGS heat exchanger/ reactor can potentially achieve a nearly 70% volume reduction compared to the baseline non-integrated unit. Analysis to date suggests negligible, if any, mass reduction for the microchannel system compared to the baseline. The next step in the analysis is to use DFMA-style techniques to identify the most practical and cost efficient manufacturing processes and thereby determine the resulting system cost for the microchannel water gas shift reactor.

References

1. Boothroyd, G., Dewhurst, P., and Knight, W. Product Design for Manufacture and Assembly, Second Edition. Marcel Dekker, Inc. New York, 2002.

FY 2003 Publications/Presentations

1. Brian D. James at the FreedomCAR Fuel Cell Tech Team on September 18, 2002.
2. Brian D. James at the FreedomCAR Storage Tech Team on October 16, 2002.
3. Brian D. James at the SAE Congress in Detroit on March 5, 2003.
4. Brian D. James at the 2003 Merit Review and Peer Evaluation Meeting of the US DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program on May 20, 2003.

Atmospheric Fuel Cell Power System for Transportation

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Objectives

The objectives of this project are to demonstrate, through testing, the following:

- One fully integrated, gasoline fueled 25-50 kW proton exchange membrane (PEM) power plant.
- Two-phase approach using catalytic partial oxidation (CPO) fuel processing system (FPS).
  - Phase one, Fuel Processor One (FP1): focus on start time, steady state and transient operation of the FPS and generation of quality reformate. Testing conducted in FY 2003.
  - Phase two, Power Plant One Reformate (PP1R): focus on demonstrating full integration of PEM fuel cell power plant. Testing to be conducted in FY 2004.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Start-up/Transient Operation
- J. Durability
- K. Emissions and Environmental Issues
- L. H_2 Purification/CO Cleanup
- M. Fuel Processor System Integration and Efficiency
- N. Cost

Approach

- Build FP1, integrated FPS assembly.
- Test CPO based FPS, FP1.
- Build PP1R power plant from FP1.
- Test PP1R assembly, fully integrated PEM power plant.
- Tear down and analyze PP1R test article.

Accomplishments

- Built and tested integrated fuel processing system, FP1.
- Analyzed data and presented results at the DOE annual merit review meeting.
- Started building fully integrated PEM power plant.

Future Directions

- Test PP1R assembly, fully integrated PEM power plant.
- Analyze and present PP1R test data.
- Tear down and analyze PP1R assembly.

Introduction

UTC Fuel Cells (UTCFC) is committed to the commercialization of PEM fuel cell power plants for transportation applications. UTCFC has in place a program addressing the technology development and verification of each of the necessary components, subsystems and fully integrated power plant. The focus of the program is an ambient PEM power plant operating on gasoline liquid fuel capable of delivering 25-50 kW net DC power using a CPO-based fuel processor.

Approach

Figure 1 provides a schematic of the gasoline fuel cell power plant showing the distinction between FP1 and PP1R. The major subsystems include the Fuel Processing Subsystem, the Power Subsystem and the Balance of Plant (BOP). The BOP includes the Thermal Management Subsystem, the Air and Water Subsystems and the Controller and associated electrical equipment.

A photograph of the FPS is shown in Figure 2. This is a fully assembled FPS that includes the CPO reformer, low and high temperature shift converters and CO cleanup. Figure 3 is a photograph of the FP1 assembly with the FPS integrated.

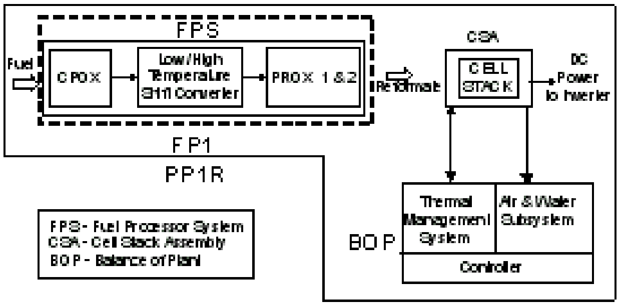

Figure 1. System Schematic

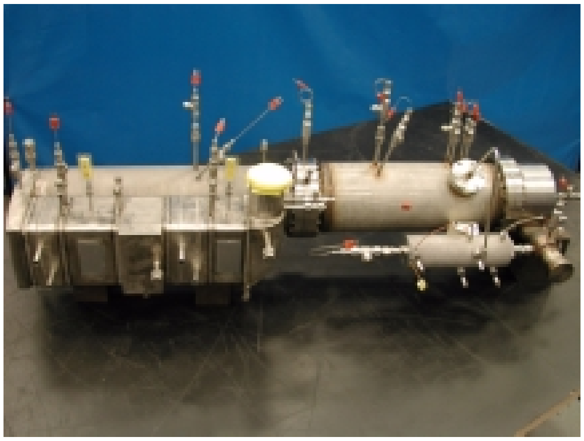

Figure 2. FPS Assembly

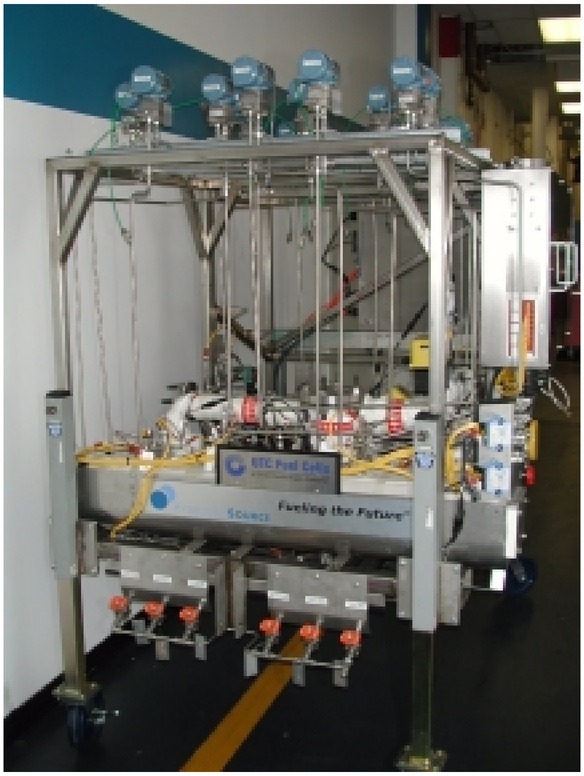

Figure 3. FP1 Assembly

Results

The FP1 test article was tested at UTCFC's facilities in South Windsor, Connecticut. The fuel used for this testing was California Phase II desulfurized reformulated gasoline (RFG) liquid fuel. Table 1 provides the FP1 test data summary compared against industry target values.

Table 1. FP1 Data Summary (LHV = lower heating value, NMHC = non-methane hydrocarbon, ppm$_{VW}$ = parts per million by volume on a wet basis)

FP1 Summary	Target	FP1 Test Data
FPS Volume, liters	75	78
Heat up time, s	165	171
Number of start/stops	500	111
Duration of operation (total hrs) - Longest single run, hrs	2000	232 hrs 10 hrs
Range of equivalent power, kWe	10-50	10-50
LHV efficiency, % at rated LHV efficiency, % below rated	≥75 ≥70	69% 69-72%
Emissions (ppm$_{vw}$) - Start (NMHC, CO, NO$_x$) - Run (NMHC, CO, NO$_x$, CO$_4$) - Transient (CO, NH$_4$, Aromatics)	 <34, 1791, 21 <22, 15. 1.6, 700 <100	5, 1.7, 9.1 20, 14, <1, 630 TBD

Figure 4 provides data that show the FPS was able to start up in approximately 5 minutes.

Figures 5 and 6 show the FP1 steady state and transient CO levels. CO levels during steady state and transient operation were in the 20 ppm range, which is the desired limit for acceptable PEM fuel cell operation. These results show that the CPO-based FPS is capable of producing reformate acceptable for PEM fuel cell operation.

Following FP1 testing, the test article was removed from the UTCFC test stand and started its build to the PP1R power plant, in preparation for phase two of testing.

Conclusions

The FP1 test results showed significant improvements over the previous generation gasoline reformate system (S200). Start time and CO levels coming out of the FPS and into the cell stack are critical areas for on-board reforming to be promising for commercial transportation applications. FP1 start time of approximately five minutes and CO levels in the 20 ppm range are very encouraging and provide a good baseline for the fully integrated power plant testing scheduled for next year.

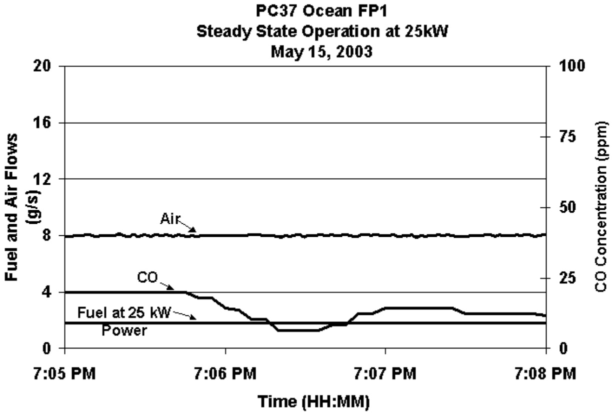

Figure 5. FP1 Steady State Data

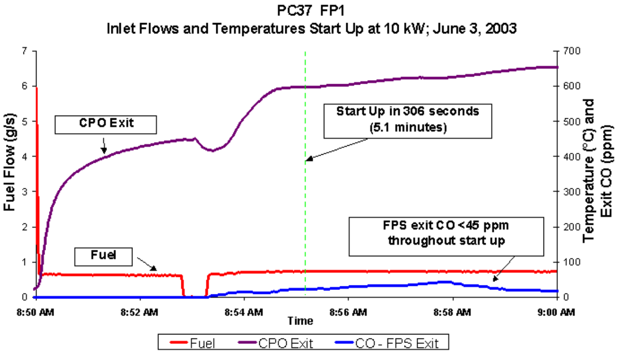

Figure 4. Start Time Demonstration

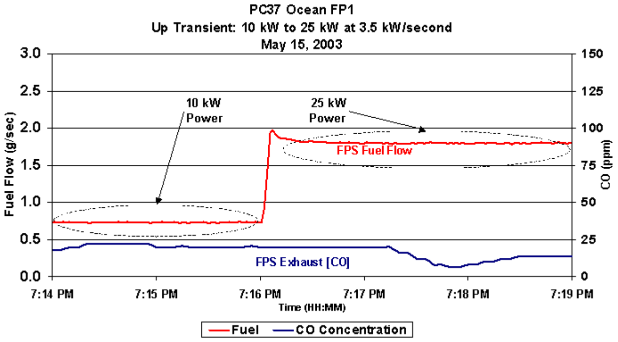

Figure 6. FP1 Transient Data

UTCFC is committed to the commercialization of PEM fuel cell power plants for transportation applications and will test the fully integrated PEM power plant (PP1R) next year along with Argonne National Laboratory (ANL).

FY 2003 Publications/Presentations

1. M. Tosca, "Atmospheric Fuel Cell Power System for Transportation", DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program 2003 Annual Merit Review, Berkeley, CA (May 2003).
2. M. Steinbugler, "Progress and Challenges in PEM Automotive Fuel Cells with Gasoline Reformers", The 3rd International Advanced Automotive Battery Conference, June 10-13, 2003, Nice, France.

Platinum Recycling Technology Development (New FY 2004 Project)

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Objectives

- Develop technology for the recycling and/or re-manufacture/reuse of catalyst-coated fuel cell membranes and catalyst-coated fuel processing components that are used in fuel cell systems.
- Recover valuable platinum group metals and NAFION™ fluorine-containing polymer.
- Develop comprehensive understanding of the failure mechanisms of fuel cell catalysts and membranes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability

Approach

The overall objective of this project is to develop technology for the recycling and/or re-manufacture of catalyst-coated fuel cell membranes and catalyst-coated fuel processing components that are used in fuel cell systems. A novel feature of our approach is the recovery of the active ionomer as well as the precious metals. Currently, platinum is the most viable catalyst for proton exchange membrane (PEM) fuel cell systems. However, if the potential of this technology is to be realized, the long-term availability of platinum group metals may become a serious limitation. As platinum reserves are depleted, this will lead to an increase in the cost of fuel cells. Hence, platinum recycling is critical to the long-term economic sustainability of PEM fuel cells. In addition, the value of the ionomer component in catalyst-coated membranes currently exceeds that of the precious metals; thus, recovery of the ionomer is also warranted. Future cost estimates using projected annual fuel cell vehicle production volumes of 500,000 per year demonstrate that cost of the ionomer will continue to be a major cost contributor to fuel cell power plants relative to the platinum required. Furthermore, it is the presence of the NAFION™ fluorine-containing polymer in the fuel cell recycle stream that greatly complicates conventional recycling methods, which are ill-suited due to the toxic and corrosive HF gas released during these processes. We will therefore develop a process that enables the extraction and reuse of both the precious metals and the ionomer in current fuel cell components.

We will also demonstrate the feasibility of a novel vapor phase extraction process to reclaim precious metals from fuel processing components. We will recover the platinum group metals in an environmentally benign manner as well as the valuable NAFION^{TM}.

This project brings together large and small industrial partners with a strong group of university faculty researchers to develop a novel method of recovering all of the valuable materials of PEM fuel cell systems. Ion Power and DuPont have an existing long-term business relationship dedicated to the promotion of the NAFION^{TM} polymer in all applications. Ion Power, Inc. is a small business working on developing high performance catalyst coated membranes for fuel cell and electrolyzer applications. The faculty members from the Department of Chemical Engineering at the University of Delaware provide world-recognized expertise in the technical areas of vapor phase extraction and deposition of platinum group metals (PGM), characterization and evaluation of PGM electrocatalysts, physical characterization of ionomers, and separation science.

In this project, we propose to develop a process that will allow for the re-manufacture of new catalyst coated membranes (CCMs) from used CCMs extracted from failed fuel cell stacks. This will be accomplished by removing the CCM from the stack, decontaminating the CCM to remove impurities, and then dissolving the CCM in an autoclave reactor to form a slurry of dissolved NAFION™ together with the Pt/C catalyst particles. We will develop a technology that will then separate these two valuable ingredients and allow the NAFION™ solution to be re-processed into a new fuel cell membrane. Ideally, the recovered catalyst (Pt/C) will be re-deposited on the re-manufactured membrane so that a completely re-manufactured CCM is the final deliverable. As a result of our multifaceted industrial and academic team, an important byproduct of this project will be fundamental research that will help determine the failure mechanisms that are currently hampering the performance of state-of-the-art catalyst coated membranes.

Platinum Group Metal Recycling Technology Development (New FY 2004 Project)

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Objectives

- Develop environmentally friendly processes for recovering and recycling the platinum, palladium, rhodium and ruthenium present in fuel reformers and proton exchange membrane (PEM) fuel cell stacks.
- Investigate leaching, industrial microwave, supercritical carbon dioxide, and pyrometallurgical processes, and select the preferred processes for recovering precious metals from the various types of catalysts present in PEM fuel cell systems.
- Build and operate pilot equipment to demonstrate process viability.
- Estimate the economics of viable processes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

<u>Fuel Flexible Fuel Processors</u>

- N. Cost

<u>Component</u>

- O. Stack Material and Manufacturing Cost

Approach

The primary objective is to develop and demonstrate the viability of processes for recovering and recycling the platinum, palladium, rhodium, and ruthenium present in fuel reformers and PEM fuel cell stacks. For the viable processes, pilot scale equipment will be built and operated to gather information needed to estimate process economics.

Several different types of catalysts are present in PEM fuel cell systems. The fuel reformers that are used to make hydrogen have catalyzed ceramic or metal substrates. Fuel cell stacks are sandwich structures made from membrane assemblies (typically composites of carbon cloth, catalysts and fluoropolymers) and bipolar plates. Different processes are required to recover and recycle the precious metals present in the different components of a PEM fuel cell system.

An environmentally friendly process will be developed for recovering precious metal from membrane electrode assemblies (MEAs). Simple combustion of MEAs produces a Pt-rich ash that is hard to handle. This process also gives off significant amounts of toxic and corrosive hydrogen fluoride (HF) gas. Several new processes will be investigated including industrial microwave technology, conventional leaching, microwave-assisted leaching, and supercritical carbon dioxide leaching. The leaching processes are unlikely to generate HF, thus solving the HF emissions problem, and, at the same time, present an opportunity for recovering the fluoropolymer. Following the leaching, pyrometallurgical reprocessing will be used to increase precious metal yield and sequester the fluoride as an insoluble slag.

New processes will also be developed for recovering precious metal from the catalyzed ceramic and metal substrates present in a reformer. At present, ceramic-supported catalysts are ground up, and the precious metal is separated and concentrated using a pyrometallurgical process. A modified version of the currently used process will be developed to treat the slag and thereby increase precious metal yield. Pyrometallurgy is not well suited to recover the precious metal from reformer catalysts that are coated on metal supports such as metal monoliths, foams, and heat exchangers. A new process will be researched that delaminates the wash coat and treats the delaminate by conventional refining technology to recover precious metals.

In the third year of the project, the most promising processes will be designated for scale up. In the final three years of the project, pilot equipment will be built and operated to demonstrate process viability and gather information to estimate process economics.

The above work will take place over a 5-year period.

Cost and Performance Enhancements for a PEM Fuel Cell System

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Objectives

- Develop an optimum turbocompressor configuration by working with fuel cell system manufacturers and continuing the work currently performed
- Reduce turbocompressor/motor controller costs while increasing design flexibility
- Develop and integrate the turbocompressor/motor controller into a fuel cell system

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Compressors/Expanders

Approach

- Use automotive and aerospace turbomachinery technology for low cost and low weight/volume
- Build upon previous turbocompressor experience
- Use VNT® (variable nozzle turbine) inlet geometry for improved performance across the desired flow range
- Use a mixed flow type compressor for improved low flow performance
- Use contamination/oil-free and zero maintenance compliant foil air bearings
- Use a modular approach to improve design flexibility
- Use a high efficiency, low cost two pole motor
- Use a low-cost variable speed motor-controller topology design that does not require sensors

Accomplishments

- Requirements established from various developers' inputs
- Analysis and design of the reduced cost and enhanced performance turbocompressor, motor and motor controller are underway

Future Directions

- Complete testing of the turbocompressor VNT® variable nozzle turbine
- Complete analysis, design, and fabrication of a reduced cost and enhanced performance turbocompressor

- Complete analysis, design, and fabrication of a reduced cost and enhanced performance motor
- Complete analysis, design, and fabrication of a reduced cost and enhanced performance motor controller with no sensor requirements

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Introduction

The objective of this work is to develop an air management system to pressurize an automotive fuel cell system. The turbocompressor is a motor-driven compressor/expander that pressurizes the fuel cell system and recovers subsequent energy from the high-pressure exhaust streams. Under contract by the U.S. Department of Energy, Honeywell designed and developed the motor driven compressor/ expander and evaluated performance, weight and cost projection data. As compared to positive displacement technology, the turbocompressor approach offers potential for high efficiency and low cost in a compact and lightweight package.

Approach

The turbocompressor design currently underway for the 'Cost and Performance Enhancements for a PEM Fuel Cell Turbocompressor' project consists of a mixed flow compressor impeller, a VNT® variable nozzle turbine, and a motor magnet rotor incorporated onto a common shaft operating up to a speed of 110 krpm on compliant foil air bearings. A motor controller drives and controls the motor, which is capable of driving the turbocompressor to the maximum design speed. The air bearings are lubrication free in addition to being lightweight, compact, and self-sustaining; no pressurized air is required for operation.

The turbocompressor will operate by drawing in ambient air, compressing it, and then delivering it to the fuel cell stack, fuel processor if available, and to the motor and bearing cavities for cooling. The exhaust streams will then be expanded through the turbine to aid in the overall turbocompressor/fuel cell system efficiency. The design will be modular to enhance system developer flexibility. The motor, which will be of the two pole toothed type, and the motor controller, which will incorporate controls that do not require separate sensors for operation, will be conducive to low cost and improved packaging.

Both the mixed flow compressor impeller and the VNT® variable nozzle turbine improve system performance by improving the flow, pressure ratio and power characteristics of the turbocompressor over the flow range. The mixed flow compressor impeller design (coming from various aerospace applications) and the VNT® variable nozzle turbine (from the Garrett Engine Boosting Systems automotive turbocharging division) make the design low cost.

Results

The existing turbocompressor with a mixed flow compressor and a VNT® variable nozzle turbine, shown in Figures 1, 2 and 3, is scheduled to be tested in late 2003. The mixed flow compressor showed improved low flow performance with an improved surge line; however, the VNT® variable nozzle turbine, which would have further improved

Figure 1. Honeywell Fuel Cell Turbocompressor with Mixed Flow Compressor and VNT® Variable Nozzle Turbine

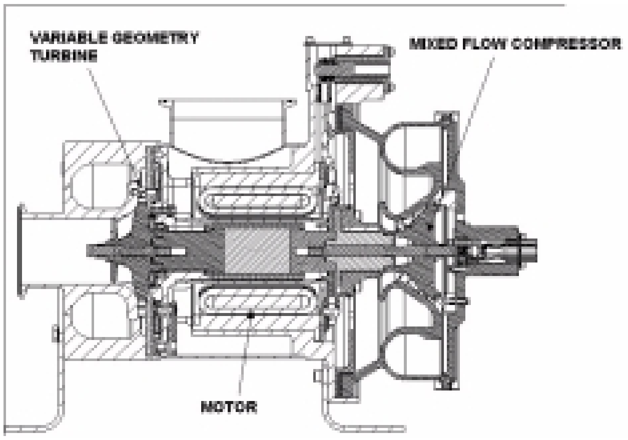

Figure 2. Cross Section of Honeywell Fuel Cell Turbocompressor with Mixed Flow Compressor and VNT® Variable Nozzle Turbine

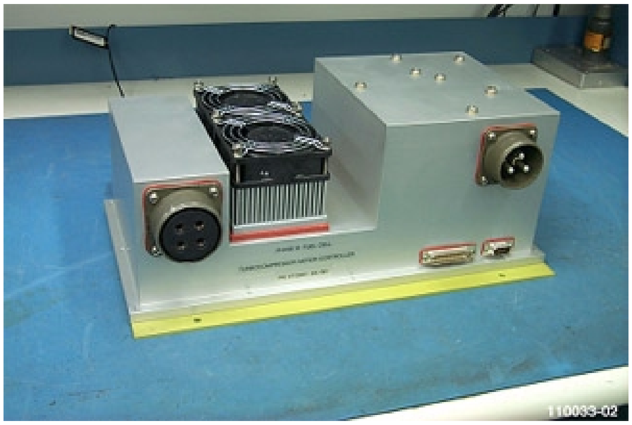

Figure 3. Fuel Cell Turbocompressor Motor Controller

performance and, consequently, lowered overall power consumption, was not tested due to project constraints. The test data noted above will be used in the 'Cost and Performance Enhancements for PEM Fuel Cell Turbocompressor' project. Predicted and tested performance of the turbocompressor and motor/controller with the mixed flow compressor test results are presented in Figure 4.

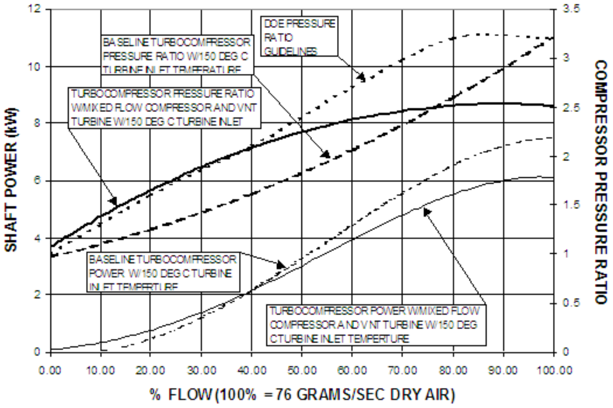

Figure 4. Turbocompressor Shaft Power/Compressor Outlet Pressure Ratio vs. Percent Flow (Baseline curves are based on actual data; mixed flow and VNT® curves are predicted.)

Table 1. Fuel Cell Turbocompressor Physical Parameters

DOE Parameters	DOE Targets	Honeywell Turbocompressor
Weight	3 kg total (w/o heat exchangers)	Turbocompressor and motor: 6.0 kgController: 5.0 kg
Volume	4 L total (w/o heat exchangers)	Turbocompressor and motor: 4.0 LController: 6.0 L

After working with the various system developers and the DOE, a set of specifications was completed for the 'Cost and Performance Enhancements for a PEM Fuel Cell Turbocompressor' project. Work on the reduced cost and enhanced performance turbocompressor, motor and motor controller layout and analysis is underway with preliminary weight and volume shown in Table 1. The design is scheduled to be completed in 2003.

Conclusions

- The turbocompressor concept using self-sustaining compliant foil air bearings has demonstrated low power consumption and good pressure ratio at low flow rates in a compact, lightweight package.
- Testing and subsequent analysis has predicted positive effects of the mixed flow compressor to the fuel cell system performance, with improved efficiency and pressure ratio across the flow range.
- Analysis has predicted positive effects of the VNT® variable turbine nozzle across the flow and temperature range, with efficient recovery of energy from the fuel cell exhaust.

- Working with the various fuel cell system developers and the DOE, a complete set of specifications has been generated.
- The turbocompressor, motor and motor controller layout and analysis are underway.

FY 2003 Publications/Presentations

1. Air Management Systems, SAE TOPTEC; April 9, 2003
2. Fuel Cell Turbocompressor, DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program; May 22, 2003

Development and Testing of a Toroidal Intersecting Vane Machine (TIVM) Air Management System

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Objectives

- Develop a Toroidal Intersecting Vane Machine (TIVM) air management system that satisfies DOE's automotive fuel cell system requirements and is readily adaptable to alternate user requirements.
- Select and demonstrate design features to assure adequate sealing, minimum porting pressure loss, and low friction operation.
- Develop the TIVM design methodology to allow efficient application to alternate user requirements.
- Develop manufacturing processes for low-cost high-volume production.
- Measure the performance of the TIVM compressor/expander across the operating range.
- Fabricate and deliver a compressor/expander/motor prototype for independent testing.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Compressors/Expanders

Approach

- Demonstrate the basic performance of the TIVM concept as a compressor/expander.
- Test candidate materials for friction and wear using standard laboratory tribilogical methods.
- Test candidate seal and port designs as well as low friction materials in simplified test configurations to select the best performing options for the TIVM compressor/expander.
- Optimize the vane surface solution methodology to provide a more efficient design process.
- Fabricate a TIVM compressor/expander prototype using seals, porting, and materials selected from the simplified feature tests and evaluations.
- Conduct performance tests of the prototype covering the full operating range.
- Refine the prototype features as necessary to obtain optimal performance.
- Develop cost efficient manufacturing methods for high volume production.
- Integrate a high efficiency motor with the TIVM prototype and test the combined unit across the operating range.

- Deliver a TIVM compressor/expander/motor (C/E/M) prototype to Argonne National Laboratory (ANL) for testing.

Accomplishments

- Friction and wear tests with the primary material pair for the TIVM vanes have shown that these materials will meet the operating and lifetime requirements. Testing has been performed at two independent laboratories.
- A simplified single vane test (SVT) rig has been designed, fabricated and operated to screen seal design concepts and low friction materials.
- Computational Fluid Dynamics (CFD) calculations were performed to guide seal designs.
- Several seal design concepts were developed and tested ; three of them met both leakage and friction requirements.
- Design optimization has reduced maximum speed from 4800 rpm to 3200 rpm with no increase in volume.
- Experimental expander vanes are being fabricated to potentially qualify a unique powder metallurgy process that provides net shape, finish, and hardness without secondary operations.
- A theoretical mathematical analysis of the surface solution methodology has been used to provide a significantly improved surface definition.
- Initial thermal analyses have been performed to evaluate geometric changes caused by differential thermal expansion.

Future Directions

- Complete seal measurements for combined leakage and friction characteristics and confirm satisfactory performance of at least one design.
- Perform porting feature measurements to confirm satisfactory performance.
- Complete investigation of the additional TIVM innovation with potential to reduce the required shaft power by >1kW.
- Build a fully operational prototype with selected seals and ports and measure the integral performance.
- Integrate a high efficiency motor and measure performance of the combined C/E/M unit; deliver to ANL for testing.

Introduction

The Toroidal Intersecting Vane Machine (TIVM) is an innovative mechanical concept, invented and patented by Mechanology, which can be configured as an integrated, positive displacement compressor/expander or compressor/compressor. In FY 1999, DOE investigated the TIVM concept for potential application to automotive fuel cell systems and determined that the inherent efficiency, compactness and thermodynamic attributes of this concept might be of significant benefit. Mechanology developed a design specifically for the 50 kWe automotive system and evaluated its potential performance. Based on the encouraging results obtained, a first generation compressor/expander prototype was built and tested. Figure 1 illustrates this prototype partially assembled to show the compressor and expander. The compressor/expander prototype tests indicated that the TIVM runs smoothly with no mechanical problems; however, improvements are required to limit air leakage. Additional tests using the generic prototype with temporary seals demonstrated the capability of the TIVM to produce the necessary flow and pressure. Based on these observations, the TIVM compressor/expander development plan is focused on development and demonstration of seals, ports and low friction materials. These are necessary

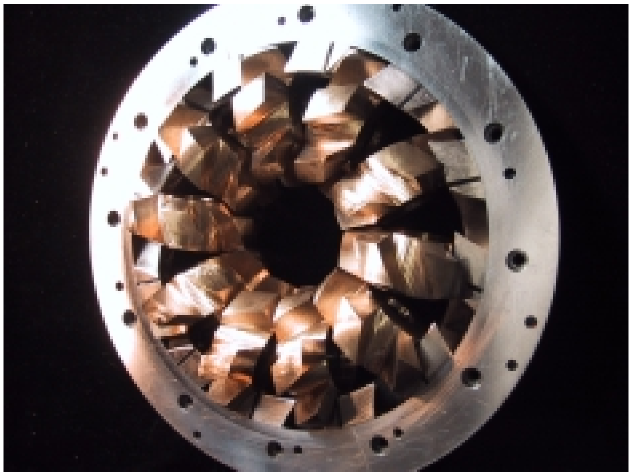

Figure 1. Partially Assembled First Generation TIVM Compressor/Expander Prototype

to satisfy the functional performance requirements with low parasitic power. Although not the main focus of the current development project, the requirements for air management system packaging, noise, and cost are considered as critical for a successful TIVM based system and are carefully considered as development progresses.

Approach

The basic functions of the TIVM compressor/expander (kinematics, pressure, flow) have been demonstrated; however, development and qualification of specific seals, flow ports and low friction materials are required to meet the performance requirements.

During 2003, Mechanology has focused on the use of simplified feature tests to allow rapid, efficient characterization of a broad range of design options for later inclusion in a full TIVM device. The initial simplified tests use a single vane test (SVT) device to measure the leakage and friction characteristics of candidate vane seal designs. Computational Fluid Dynamics (CFD) analyses of the vane/housing/air interactions have been used to guide the design and testing of these features. Additional tests will be performed using the SVT device to finalize the seal designs to be used in the next TIVM compressor/expander prototype.

Definition of the vane surface configurations required for a specific TIVM can be accomplished through an iterative process developed by Mechanology. With sufficient iterations, a very good meshing surface solution can be obtained, as evidenced by the generic TIVM prototype vanes. However, this process is quite time consuming. Mechanology has explored alternate mathematical approaches to develop a more efficient surface design methodology.

Low friction materials are necessary for the intersecting vanes to realize the predicted energy efficiency of the TIVM compressor/expander. Additionally, these materials must have sufficiently low wear under the TIVM operating conditions to perform acceptably during a 6,000 hour lifetime. Several candidate material pairs and potential coatings have been identified based on published data. To qualify materials for the TIVM, standard laboratory friction and wear tests are being performed. Successful materials are being tested in the single vane test rig, and subsequently, the best materials will be used in a TIVM prototype.

In parallel with the specific technology development for the TIVM, Mechanology continues to evolve the overall design to reduce the operating speed and increase the efficiency. The improved design features will be incorporated into the subsequent prototypes.

One or more full TIVM compressor/expander prototypes will be fabricated by Mechanology and tested across the full operating range. Modifications will be made as necessary to optimize performance. Subsequently, a high efficiency electric motor will be integrated with the TIVM to form a complete compressor/expander/motor component. This unit will be tested by Mechanology and then delivered to ANL for independent testing.

Results

ANL has constructed a tribology test rig that operates at the speed and interface pressure of the TIVM compressor/expander vanes at full power. During 2003, ANL resolved vibration problems with the test rig and performed friction and wear tests with stainless steel and low friction engineered polymer samples provided by Mechanology under both dry and high humidity conditions. These measurements have indicated an acceptable friction coefficient at the TIVM operating conditions and wear rate consistent with the lifetime requirement.

A simplified single vane test rig has been designed, fabricated and made operational for screening of seal designs and testing of low friction materials with vanes traveling at speeds in the planned operating range. Figure 2 illustrates the single vane test device design with the pressure cover removed. This device permits parametric variation of clearances and seal preloads as well as rapid change-out of materials and seal designs. The computer control and data acquisition program allows testing at specified speeds and pressure differentials with automated data logging.

CFD calculations were performed by ANL using Mechanology's single vane test configuration. These analyses have been used to understand the interaction of the vane/seal/air system as a function of operating conditions and to guide seal designs. Based on these results, non-contact seals were eliminated from the design concept options, and compliant contact seals have been selected.

Figure 2. Single Vane Test Equipment

Mechanology has analyzed all of the potential leakage paths for both the compression and expansion cycles and has developed time histories of the pressure differentials across each path throughout the cycle. These data quantify the driving potential for leakage from the compression and expansion chambers.

Mechanology reviewed the development of state-of-the-art seals relevant to the TIVM requirements. We found that the brush seals developed for jet engine and turbine applications will more than meet our requirements for some locations. Based on the seal study, new configurations were developed for the remaining TIVM seal locations, and samples were prepared for testing in the SVT rig. Tests were performed for leakage and friction individually to give accurate measurement of the very small values, and combined dynamic tests were performed for the combined behavior. Several design concepts were eliminated because of excessive leakage or friction. Figure 3 illustrates an example of the pressure vs. time data from a seal dynamic test. Pressures in excess of 7 atm have been generated at relatively low speeds, indicating the effectiveness of the seals. Three design concepts met both the leakage and friction requirements.

Detailed analysis of the TIVM operation and the sources of inefficiency have shown the potential for a modified TIVM geometry that has significantly reduced friction. Patent disclosures are being prepared prior to release of the details of this additional innovation.

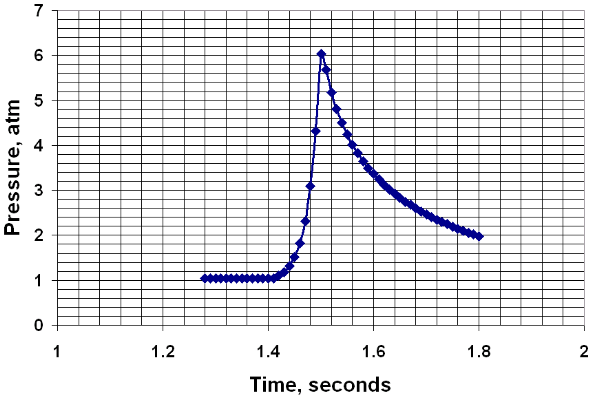

Figure 3. SVT Pressure vs. Time Example Data

Conclusions

Design and analysis of the first generation TIVM compressor/expander has shown that this concept has the potential to meet the DOE requirements for automotive fuel cell applications with significantly better performance than other options. Testing of the compressor/expander and generic TIVM prototypes has demonstrated correct kinematic functioning and the capability to produce the required pressure and flow. These tests have also highlighted the need for efficient seals and flow ports in the TIVM. Laboratory tribology measurements have shown acceptably low friction and wear for the preferred material pair candidate for the intersecting vanes. The ongoing development program is focusing on selection of seals, porting, and material options through simplified feature tests and then sequentially more prototypic TIVM tests. The single vane test results indicate that there are multiple seal design concepts that meet both leakage and friction requirements. Using the leakage and friction characteristics of one option tested, the expected power required to drive the TIVM compressor/expander at full flow is approximately 6 kWe, as shown in Figure 4. A fully prototypic TIVM compressor/expander/motor will be fabricated and tested to measure actual performance with the selected options. Subsequent work will include development and qualification of cost efficient manufacturing methods for high volume production and development of features to assure compliance with noise requirements. Additional testing will focus on operating environment and reliability/endurance issues.

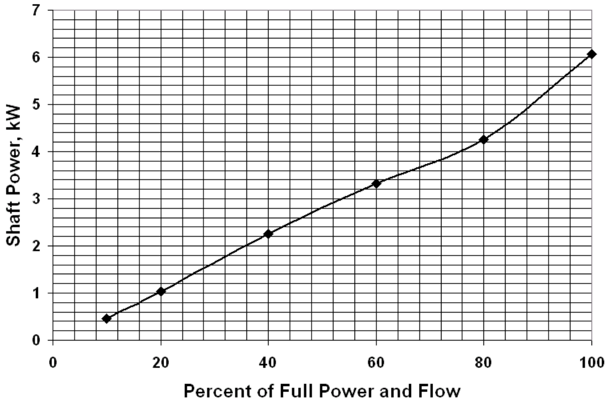

Figure 4. Expected TIVM Power for 50 kWe System

FY 2002 Publications/Presentations

1. “Toroidal Air Management System Development and Testing Status”, presented to the FreedomCAR Technical Team, April 16, 2003.

2. “Development of a Toroidal Intersecting Vane Machine Air Management System for Automotive Fuel Cell Systems”, presented at the DOE Hydrogen and Fuel Cells 2003 Annual Merit Review, May 22, 2003.

4. “TIVM Compressor/Expander/Motor Development and Demonstration, Cooperative Agreement DE-FC04-02AL67626, Annual Technical Progress Report - November 2001 to December 2002 and Quarterly Progress Report – October 2002 to December 2002”, submitted January 30, 2003.

Motor Blower Technologies for Fuel Cell Automotive Power Systems

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Subcontractors: Phoenix Analysis and Design Technologies, Phoenix, AZ; R&D Dynamics, Bloomfield, CT

Objectives

- Develop small, lightweight, motor driven blowers to provide cathode air and reformer air for a near ambient fuel cell operating on gasoline.
- Identify and/or develop manufacturing methods that will allow the blowers to be produced at low cost in large production volumes.
- Demonstrate blower performance via integration into a power plant.
- Evaluate both reformer air blower approaches, regenerative vs. centrifugal, and identify superior technology.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Compressors/Expanders

Approach

- Define performance requirements, flows, pressures, temperatures as well as cost and life targets for an ambient pressure based fuel cell system.
- Phoenix Analysis and Design Technologies (PADT) will develop and build a mixed flow type blower to meet requirements for cathode air and a regenerative type blower to meet reformer air requirements. Prototypes will be used to evaluate aerodynamic performance as well as life and durability.
- R&D Dynamics will develop and build a high-speed centrifugal machine supported by air bearings as an alternate approach to the reformer air application.
- UTC Fuel Cells will demonstrate operability and performance of both approaches by integrating the units into a power plant or conducting subsystem testing.

Accomplishments

- Requirements for both the cathode air blower and reformer air blower have been defined and documented.
- PADT has tested the mixed flow cathode air machine to 100% design speed and achieved greater than 60% overall efficiency at rated flow and pressure rise.

- The R&D Dynamics high-speed compressor was down-selected as the preferred reformer air blower over the PADT proposed regenerative machine.
- R&D Dynamics has tested the high-speed centrifugal machine to 85% of design speed. Demonstrated flow and pressure maps agree well with the predicted values, and a peak overall efficiency of 50% has been demonstrated.
- PADT has completed a cost study which predicts production costs of $83 per blower in quantities of 100,000 units/year.

Future Directions

- Continue testing of R&D Dynamics compressor to 100% of design speed.
- Deliver both blowers to UTC Fuel Cells for evaluation in subsystems.
- Continue off-design testing to evaluate robustness of designs under high ambient and process inlet temperature conditions.
- Continue to refine designs for low cost manufacturing processes and ease of assembly.
- Investigate lower cost motor and motor drive technologies.

Introduction

Near ambient pressure fuel cells running on gasoline require two sources of air, one for the fuel cell cathode and one for the gasoline reformer, which generates hydrogen. Due to the relative pressure differences required by the two applications, it is not energy efficient to fulfill the two air requirements with a single blower/compressor as is commonly utilized in pressurized type fuel cell systems. This project will develop two different types of machines to meet each air supply requirement independently.

Blowers to meet these two applications are not commercially available in the size and volume required for packaging into a vehicle. Thus, this project aims to utilize high speed technology which will allow the blowers to develop the required flow and pressure rise in a small package size. Increasing the rotational speed presents several technical challenges, namely bearing life and motor heating. The motor heating issue is further compounded by the fact that we are able to reduce the size of the motor by running at higher speeds, yet the amount of shaft power required to be output by the motor remains the same. This results in a much higher than typical power density motor, and with the reduction in surface area, a much higher heat flux is required to maintain stator temperatures. This problem can be resolved in one of two ways: increase the efficiency of the motor and reduce the amount of heat generated by it, or increase the heat transfer capability of the stator and motor housing.

Approach

The approach for this project was to first define and document the blower requirements for an ambient pressure fuel cell system. The requirements issued by DOE in 2000 focused on targets for pressurized systems that were not directly applicable to the UTCFC ambient pressure system. New targets for blower performance, efficiency, cost, weight and volume were defined by UTCFC and documented in 2001, and the air flow requirements were separated into two distinct applications: the cathode air blower, a high flow low pressure application, and the reformer air blower, a higher pressure low flow type application.

Using these requirements for the two applications mentioned above, we identified three types of machines with possible benefits to the two applications, one for the cathode air blower and two types for the reformer air blower. The types of machines considered were restricted to what could be classified as mature air moving technology and thus would allow us to focus on reducing size, weight and cost rather than doing fundamental aerodynamic development. For the cathode air blower application, a mixed flow axial machine was selected. The aerodynamics for these types of machines are well understood; thus, we were able to limit our scope of aerodynamic development to minor variations of the basic design to achieve optimum efficiency.

For the reformer air blower, we considered two types of machines, each with its own unique set of advantages. The first machine was a very high speed, 140,000 rpm, radial centrifugal machine supported by air bearings. Because of the high speed, this type of machine is capable of delivering high pressure air in a very small package size with good overall efficiency. However, the very high speeds also required some technology development to minimize risks associated with the bearings and very high-speed motors and controllers. Thus, a regenerative type machine was evaluated as a potential second reformer air blower technology. Regenerative type machines are typically very good at developing higher pressures at low flow rates and lower speeds than typical centrifugal devices, which makes this technology attractive. The flow and pressure could be developed at speeds consistent with the use of grease packed ball bearings, which are desirable due to their low cost. However, regenerative type machines are typically lower efficiency as compared to other centrifugal machines; thus, a key task was to perform basic aerodynamic research into variations of the traditional regenerative wheel and housing design to optimize for peak efficiency.

Results

The cathode air blower and controller designs have been completed and are shown in Figures 1 and 2. The blower and motor drive have been tested to 100% of design speed, and performance is shown in Figure 3. Please note that efficiency shown in this figure is overall efficiency and accounts for all losses in the motor/motor drive and all frictional losses and is a true representation of the total parasitic load to the fuel cell system associated with providing cathode air. It is calculated by dividing the isentropic power by the direct current power input to the motor drive.

The blower has been designed for low cost, high volume production, and several of the parts used in the prototype blowers were actually manufactured using injection molding techniques which will yield very low per piece cost in production volumes. Additionally, much of the effort this year focused on reducing effort and precision required to assemble the components, thereby reducing the cost associated with final assembly of the blower. A detailed cost study was conducted for each part of the blower and the final assembly effort, during which manufacturers were asked to quote production prices in volumes of 100,000 per year. A total cost for the blower and motor drive of $83 is predicted, which compares favorably with our initial cost target of $75 per blower.

The high-speed reformer air blower and controller, developed by R&D Dynamics, are shown

Figure 1. PADT Cathode Air Blower

Figure 2. PADT Cathode Air Blower Controller

in Figures 4 and 5, respectively. At the time of this writing, they have been tested to 120,000 rpm. Approximately 85% of design speed and performance, as shown in Figure 6, is inline with predicted values. Unfortunately, rotor heating and motor controller issues have prevented us from running to 100% of design speed thus far. This past year was heavily focused on reducing the severity of motor rotor heating effects with solutions concentrated in two areas: 1) increasing the amount of cooling air supplied to the motor cavity and 2) experimenting with rotor magnets and rotor materials to reduce heating caused by eddy current losses. A new motor cooling scheme that taps into process air from the blower exit, rejects heat through finned tubing and directs it through the motor cavity has shown good results and enabled us to achieve 120,000 rpm. We believe this technique will allow us to reach 100% design speed. In addition to improving the current motor and controller designs, we have purchased a new motor and controller which have been designed from the ground up to minimize rotor heating due to eddy currents. We expect that these new motor and controller designs will allow us to run speeds in excess of 100% design speed, and combined with the improved cooling scheme, should give us acceptable thermal margins even with elevated blower inlet air temperatures.

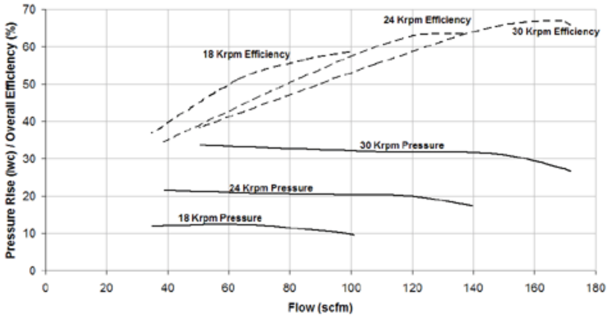

Figure 3. PADT Cathode Air Blower Performance (iwc = inches water column)

Figure 4. R&D Dynamics Reformer Air Blower

Figure 5. R&D Dynamics Reformer Air Blower Controller

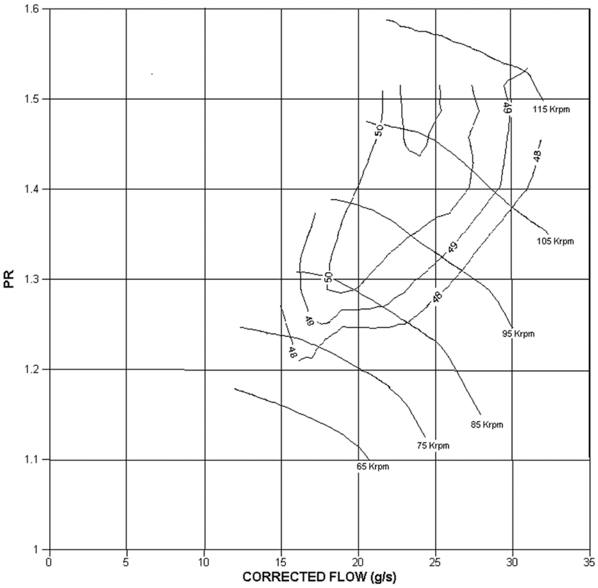

Figure 6. R&D Dynamics Reformer Air Blower Performance (PR = pressure ratio)

The regenerative technology reformer air blower development effort has not produced the results we had hoped for and the aforementioned task to achieve significantly improved aerodynamic efficiencies. To assist us in this task, a fluidic model was developed and calibrated with actual test data and has allowed us to easily and accurately predict wheel efficiencies for a variety of wheel configurations. Unfortunately, the model has shown that the traditional regenerative wheel design is very difficult to improve upon, as numerous wheel design variations were modeled and the best one increased pump head efficiency by only 2 percentage points over the traditional design. As a result of this inherently low wheel efficiency, the increased shaft power required from the motor resulted in a severe heating problem for both the motor and pump head in addition to low overall efficiency. For this reason, we have decided to terminate the regenerative blower effort and redirect our efforts to more meaningful technical challenges in other areas within the program.

Conclusions

- The cathode air blower is a very efficient way to move air at low pressure ratios. Work in the coming year will focus primarily on increasing blower reliability and durability in high temperature and high vibration applications.
- The high-speed, centrifugal reformer air blower design has produced predicted aerodynamic performance in a very compact package. Future work will focus on the achievement of 100% design speed, redesigning the unit for low cost, high volume production and achieving motor controller durability.
- When working with compact, high-speed motors, the number one issue is motor rotor heating. The motor controller and motor rotor must be designed as a package to minimize this effect.
- Regenerative type machines are inherently inefficient and are best suited for applications requiring a pressure ratio less than 1.3.

FY 2003 Publications/Presentations

1. Freedom Car Annual Review, April 16, 2003, Detroit, MI
2. DOE Merit Review, May 22, 2003, Berkeley, CA

Hybrid Compressor/Expander Module

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Subcontractors: Concepts NREC, White River Junction, VT; Scroll Corporation, Carlisle, MA

Objectives

- Based on the experience of two previous generations of scroll-based Compressor/Expander Modules developed with DOE, design and build a hybrid compressor/expander combining turbomachinery and positive displacement scroll compression.
- Deliver a system with equivalent thermodynamic performance, at significantly lower weight and volume, when compared to previous generations of scroll Compressor/Expander Modules.
- Develop the algorithms and hardware to ensure stable and effective control of the hybrid system.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Compressors/Expanders

Approach

- In the first phase, develop system architecture and subsystem designs consistent with the overall goals of maintaining thermodynamic performance while reducing weight and volume relative to previous generations.
- In the second phase, complete detailed engineering and initiate fabrication of brassboard and final subsystem components, and develop the control system hardware and algorithms.
- In the third and final phase, complete fabrication of components and conduct subsystem assembly and test, followed by system integration and performance verification.

Accomplishments

- Completed detailed system design tradeoff study, resulting in specific definition of requirements for both the turbocompressor and scroll compressor subsystems.
- Completed detailed subsystem design tradeoff studies for turbocompressor and scroll compressor subsystems, resulting in selection of design configurations for both subsystems.
- Completed preliminary detailed design of both major subsystems, including component identification and sizing, cost estimation and performance estimates.

- Identified specific opportunities for performance enhancement through the use of limited exhaust gas recirculation.
- Initiated preliminary brassboard system testing of scroll compressor drive configuration to evaluate bearing performance and lubricant management.

Introduction

Most current automotive fuel cell systems are designed for pressurized operation in order to reduce system size, boost stack efficiency, and improve water management. Because of the aggressive efficiency goals driving fuel cell development, the compressor must operate efficiently over a wide flow range, and efficient waste energy recovery in an expander is required to offset the compression load. Traditionally, high-speed turbomachine technology, such as that used in automotive turbochargers, has resulted in a compact package that delivers high efficiency at the design point, but with performance that falls off dramatically under off-design conditions. Scroll technology, a type of positive displacement machinery, provides high compressor and expander efficiencies across a broad range of operating conditions, but results in a package that is significantly larger and heavier than that of high-speed centrifugal technology.

The objective of this project is to develop a hybrid compressor/expander module, based on both scroll and high-speed turbomachine technologies, which will combine the strengths of each technology to create a concept with superior performance at minimal size and cost. The resulting system will have efficiency and pressure delivery capability comparable to that of a scroll-only machine, at significantly reduced system size and weight when compared to scroll-only designs. In addition, this configuration offers the advantage of applying the required external power to the scroll compressor, a relatively low-speed device, eliminating the need for a high-speed motor to supply mechanical power to a turbomachine.

Approach

The design approach for the Hybrid TurboScroll Compressor/Expander Module (CEM) exploits the experience of developing the first two generations of scroll Compressor/Expander Modules, in combination with the substantial experience of our turbomachine subcontractor, Concepts NREC. (Figure 1 shows the Second Generation Scroll CEM on its test stand). By combining the performance attributes of a positive displacement scroll compressor (electrically driven) with those of a turbocharger (driven by fuel cell exhaust gases), we expect to be able to very closely match the pressure/flow requirements of the DOE guidelines in a package that is smaller and lighter than previous generations. Figure 2 tabulates several key design goals for the project; they show dramatic improvement over the Second Generation performance noted.

A novel approach to the development of an appropriate system architecture resulted in the block diagram shown in Figure 3.In this configuration, the turbocompressor draws in atmospheric air and compresses it to an intermediate pressure. In order to reduce both the size and operating temperature of the scroll compressor, an intercooler is provided to reject part of the heat of compression to atmosphere. The partially compressed gas, now cooler and denser, is then fed into the scroll compressor, which uses electrical power to achieve the final compression of the gas. Finally, the compressed air is fed into the

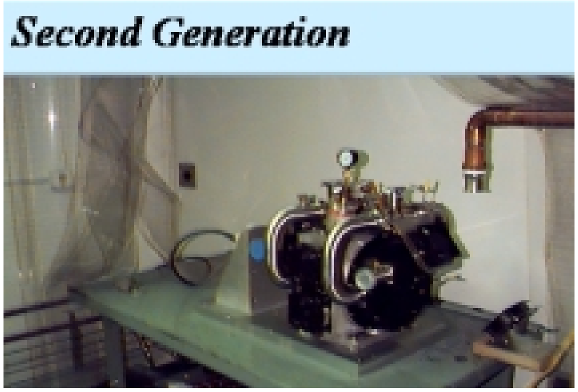


Figure 1. Second Generation Scroll Compressor/ Expander Module

fuel cell, which increases its temperature and reduces its pressure slightly. The exhaust gas from the fuel cell drives the turbine and, the bulk of its energy extracted, is exhausted to atmosphere. The turbine provides the shaft power to drive the turbocompressor by direct coupling. This operating mode is used up to a selectable fraction of maximum flow, currently set to approximately 80-90%, at which point a relief valve opens, permitting a small fraction of the discharge gas mass flow to bypass the turbine and be fed directly into the intercooler inlet. With this system feature, the turbomachine is dramatically simplified by eliminating the controllable inlet guide vanes, and its operating range is substantially reduced, thereby improving its overall efficiency profile.

This architecture offers some important advantages:

- The turbocompressor provides stack operating pressure control by purely passive means, eliminating the need for an active control element and its associated parts, actuator and control logic;
- The bypass valve permits recapture of a significant fraction of the discharge enthalpy without passing through the turbomachine;
- A fraction of the waste water in the discharge stream is recirculated into the inflow stream; and
- The scroll compressor provides pressure/flow characteristics that enable efficient operation across a broad range of flow rates.

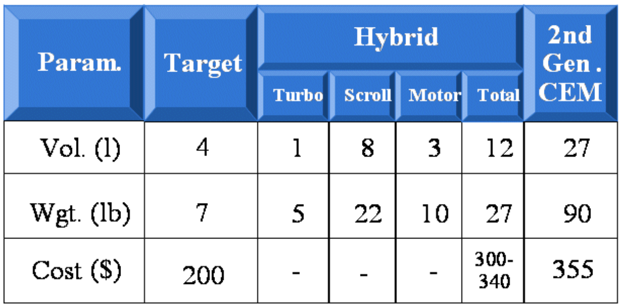
Capturing these advantages entails, of necessity, overcoming certain risks:

- Overcoming a small oxygen deficit in the inflowing process gas that results from recirculating a small amount of discharge gas, and
- Managing any possible stack toxins in the discharge stream.

Starting with the turbocharger, pictured in Figure 4, the design approach involved balancing competing elements.; Over a dozen different turbomachine configurations were considered, exploring the potential for multiple stage and controllable geometry designs to address the performance requirements. Although ultimate performance can only be achieved with controllable guide vanes for the expander and/or compressor, these features add substantially to the cost and complexity of the turbomachine. By exploiting the opportunity to recirculate a small fraction of the discharge gas, a fixed geometry turbomachine can be made to cover the full required performance range. For the scroll, the design approach has involved the detailed evaluation of three competing configuration options and the selection of a single conventional design approach, as shown in Figure 5. This design represents a low-risk approach, incorporating new and stringent lubricant management features into well-proven design configurations. A brassboard working model of the drive mechanism currently under construction will prove the utility and functionality of the preliminary design.

Results

A novel system architecture has been developed that exploits a simple pressure-operated relief valve to permit a fixed-geometry turbine to provide stack



Param.	Target	Hybrid				2nd Gen. CEM
		Turbo	Scroll	Motor	Total	
Vol. (l)	4	1	8	3	12	27
Wgt. (lb)	7	5	22	10	27	90
Cost ($)	200	-	-	-	300- 340	355

Figure 2. Key Hybrid TurboScroll Performance

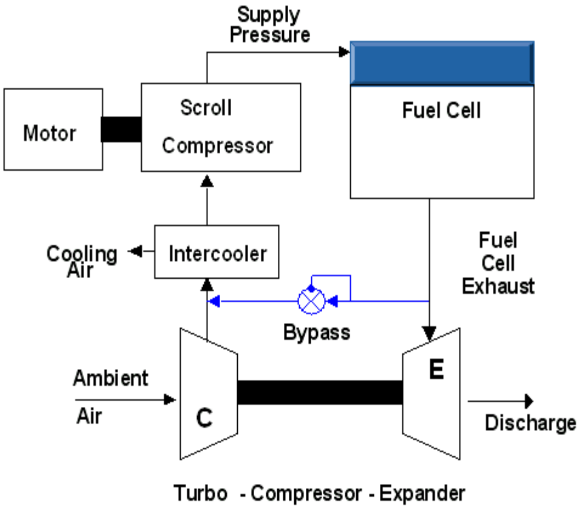


Figure 3. Hybrid TurboScroll System Architecture

pressure control tailorable to a wide variety of possible pressure-flow profiles. The system feeds both the turbocompressor output and any bypass gas into an intercooler for rejection of heat and densification of the process gas prior to compression to final operating pressure through the scroll compressor. Based on detailed preliminary designs, substantial improvements in system weight and volume, relative to previous generation machines, have been achieved by the hybridization of turbo-compression and positive displacement scroll compression in this system. Manufacturing costs based on these preliminary designs have also improved.

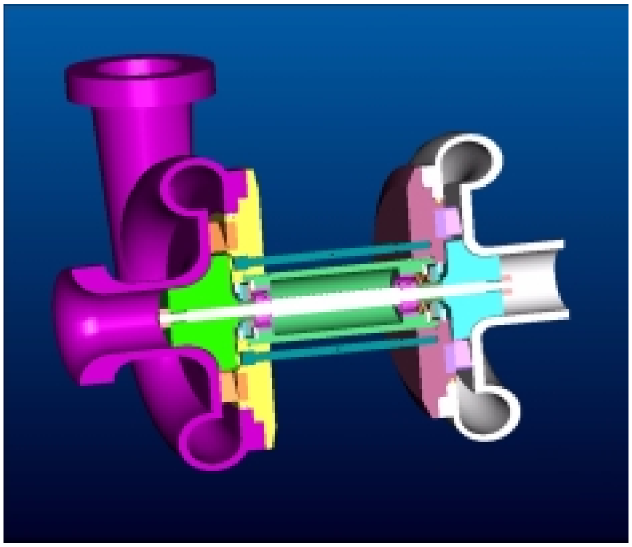


Figure 4. TurboCompressor Preliminary Design

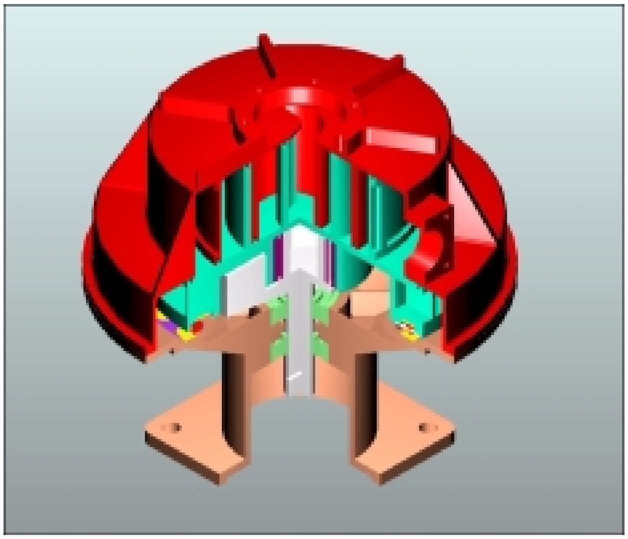


Figure 5. Scroll Compressor Preliminary Design

Preliminary design of the turbocompressor has been completed. In the turbocompressor, conventional grease-lubricated ball bearings have been identified and selected. Lubricant management is simplified by the relatively low vapor pressure of the selected grease, as well as the physical and pressure-gradient isolation provided in the design of the turbocompressor. Aluminum wheels and housings have been designed, and the rotordynamics configured to provide "stiff," or below-resonance, operation over the whole operating range. Estimated maximum turbine efficiencies of 86%, and compressor efficiencies up to 75%, closely approach the targets defined in the DOE guidelines. The intercooler has conventional performance requirements, and, indeed, the selected approach is to use an available automotive intercooler of the appropriate size and integrate it into the system.

Preliminary design of the scroll compressor has been completed. The selected scroll compressor design uses a conventional crank-driven orbiting scroll, supported on a roller-Oldham thrust bearing system, grease lubricated. This configuration has the substantial advantage of conventionality, enabling the direct utilization of knowledge gained in dozens of scroll compressor design programs. The most highly stressed machine element, the crank bearing, has been selected and will be tested in a full-scale brassboard drive mechanism demonstration device. This roller bearing will be of conventional design and grease lubricated. The lubricant for both the crank and thrust bearings will be isolated from the process gas by three means: (1) the high viscosity and low volatility of the grease itself, (2) mechanical sealing of the process gas space from the lubricant space, and (3) pressure gradient isolation of any tramp lubricant from entering the process stream. Estimated compressor peak efficiencies of 70% are comparable with the efficiencies demonstrated in previous generations of scroll compressors and indicate that the overall net shaft power consumption of the system will be approximately 5-6 kW.

Conclusions

Based on detailed preliminary designs of the critical system elements, the Hybrid TurboScroll Compressor/Expander Module concept will deliver significant improvements in weight, volume and manufacturing cost relative to previous generation systems. Further, based on analysis of the preliminary designs, the parasitic power requirements of the system are also expected to improve. A novel system architecture substantially simplifies the overall system, permits flexible pressure/flow tailoring of the system behavior, and provides important improvements in manufacturability with minimal performance penalty provided that the small decrease in oxygen concentration in the feed gas is well tolerated by the fuel cell.

FY 2003 Publications/Presentations

1. DOE Compressor/Expander Module Development Program, Tech Team Meeting, April 16, 2003.

2. DOE Compressor/Expander Module Development Program, Merit Review Meeting, May 22, 2003.

Carbon Foam for Fuel Cell Humidification

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Objectives

- To fabricate a compact, efficient humidification system to recover water and heat from the exhaust of a polymer electrolyte membrane (PEM) fuel cell to humidify the inlet air.
- Utilize carbon foam as heat and mass transport medium.
- Optimize carbon foam density, window and pore size to maximize efficiency in heat and water transport.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- R. Thermal and Water Management

Approach

- Design test rig to evaluate the carbon foam's ability to absorb water, provide humidification, and provide heat rejection.
- Determine the ability to pass water through the carbon foam.
- Evaluate the structure of the carbon foam and how it pertains to its ability to function as a water and heat transfer medium.
- Analyze data to determine how the carbon foam could be used to develop an improved humidification system in order to reduce energy requirements, size and cost of a recovery unit.

Accomplishments

- Demonstrated the carbon foam's ability to absorb water and reject heat while humidifying air.
- Demonstrated the ability to pass water through the foam, proving that once water condenses on the foam, it will pass through.
- Demonstrated that the structure and window/pore size of the carbon foam are directly related to its ability to transfer heat and water.

Future Directions

- Tailor the window/pore opening size so that the wicking capability of the carbon foam is optimized to deliver saturated air at 80°C, at required flow rates, to the inlet air stream of a PEM fuel cell.
- Determine the effects of tailoring the window/pore opening size to the heat transfer capability of the carbon foam.

- Interface with a manufacturer of recovery units for fuel cell technology so that all aspects of a recovery unit are considered.
- Design a full-scale recovery unit to evaluate the carbon foam's ability to recover water from the exhaust side of the fuel cell.
- Demonstrate reduced need for ancillary equipment (no need for water pumps, heaters, etc…).
- Work alongside a fuel cell manufacturer to field test a carbon foam recovery unit on PEM fuel cells.

Introduction

The efficiency of the automotive polymer electrolyte membrane (PEM) fuel cell depends on many factors, one of which is the humidification of the inlet air. If the inlet air is not sufficiently humid (saturated), then the stack can develop dry spots in the membrane, and efficiency and voltage will drop. Therefore, it is necessary to ensure that humid inlet air at the proper elevated temperature is supplied to the stack. Current methods involve using a spray nozzle to atomize water droplets onto a cloth or wire mesh substrate. As the inlet air passes over the cloth, it gains moisture and becomes more humid; however, since the air is not preheated, the actual level of humidification (percent humidity) drops as the air is heated in the fuel cell. If heat could be supplied to the water efficiently, the system would become independent of the ambient conditions, the inlet air could become more humid at the proper temperatures, and the overall stack could maintain a high level of efficiency. Carbon foam has been demonstrated to be very efficient in heat transfer in previous work with power electronic heat sinks and automotive radiators. Using the carbon foam in the PEM fuel cell may solve the inlet air humidification problems.

This unique carbon foam (Figure 1) has a density between 0.2 and 0.6 g/cm^3 and a bulk thermal conductivity between 40 and 187 W/m·K. The ligaments of the foam exhibit a thermal conductivity higher than that of artificial diamond. Additionally, in combination with a very accessible surface area (>4 m^2/g), the overall heat transfer coefficients of foam-based heat exchangers can be up to two orders of magnitude greater than those of conventional heat exchangers (in some designs).

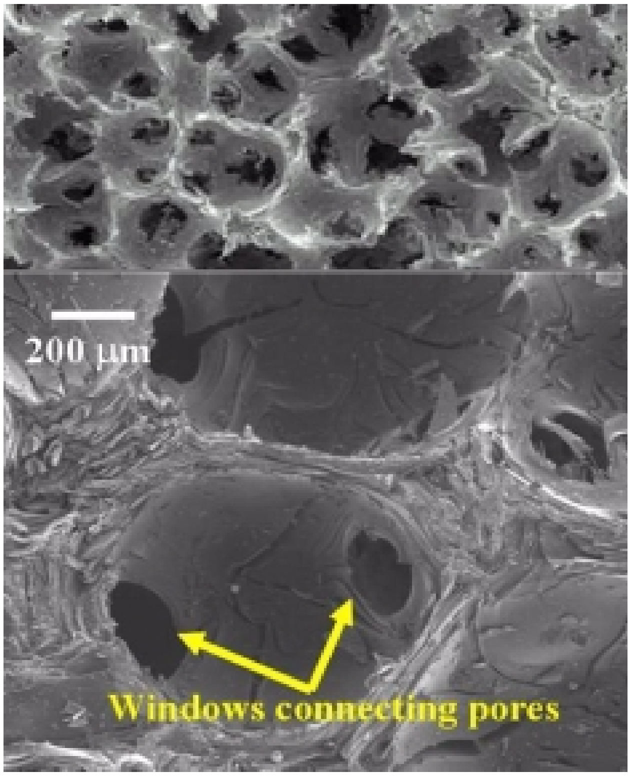

Figure 1. Oak Ridge National Laboratory's Carbon Foam Showing the Pore and Window Sizes

The high thermal conductivity, combined with a very high specific surface area, permits the carbon foam to use waste heat from power electronics, cooling fluids, and exhaust gases to vaporize water on the pore surfaces more efficiently than other media, thus enhancing humidification. The high conductivity of the foam will also permit heating of the inlet air, thereby supplying hot, humid inlet air to the fuel cell stack, regardless of the ambient conditions.

Approach/Results

To characterize the behavior of the foam as a humidifier, a test chamber (Figure 2) was modified to quantify its ability to saturate air with water. The system is designed with no gap around the foam

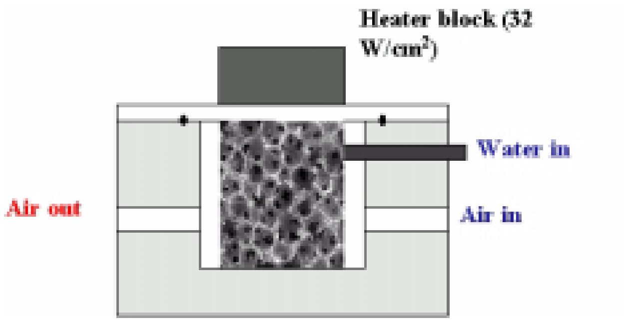

Figure 2. Schematic of the Humidification System

thereby forcing the fluid to pass through the windows and pores of the foam. A tube was inserted into the chamber to supply water directly to the foam, so it saturates the foam completely. As the air is forced through the foam, it forces the water over the surfaces of the foam, leading to efficient evaporation. As the water evaporates, it removes significant amounts of heat while simultaneously saturating the air. A simulated power inverter (cartridge heaters in a 5x5x2 cm aluminum block) is mounted to the aluminum plate and is capable of generating up to 800 W (32 W/cm^2). Refer to Table 1 and Figure 3 for the complete data set.

Table 1. Results of Humidification Tests at a Power Density of 19 W/cm^2

Water flow rate (cm^3/min)	0	10	20
Air flow rate (kg/min)	0.17	0.17	0.17
Electronics temperature (°C)	162	151	136
Outlet air temperature (°C)	103	73	58
RH% outlet air	<0.5	24	87
RH% @ 60°C	1.17	43.5	79
RH% @ 80°C	0.5	18.3	33

As seen in Table 1, the carbon foam reduced the electronics temperature with dry air alone. However, when the water was added to the foam for evaporation, the electronic temperature dropped. Because the latent heat of vaporization of water is several orders of magnitude greater than the sensible heat capacity of water and air, only small amounts of water are needed to effect a large absorption of energy. The relative humidity of the outlet air (inlet to the fuel cell) can be modified easily by changing the amount of water added to the foam. The problem will be to balance the heat rejection from the power electronics of the coolant with the volume of inlet air and water needed to humidify the inlet air.

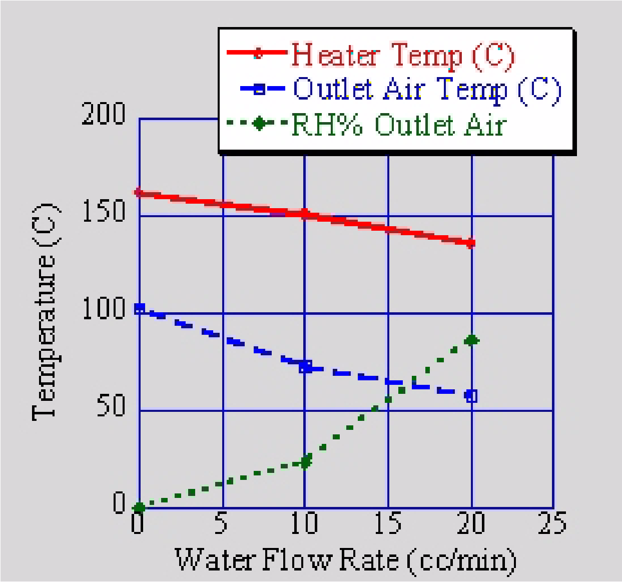

Figure 3. Heater Temperature as a Function of Power Density for Various Water Flow Rates for Humidification

Water flow experiments through the foam were conducted by passing a specified amount of water through a funnel with a piece of carbon foam placed at the base of the funnel. The carbon foam piece measured 10 mm in diameter and 10 mm in length. There were three different densities utilized, thus with varying pore and window sizes. Refer to Table 2 to review the data for the experiments. As can be seen, the low-density foam had lower thermal conductivity, larger window size (more open structure), thus higher water flow rates than the higher density foams.

A heat flow resistance model designed for carbon foam radiators has been helpful in further development of heat exchangers utilizing the carbon foam. It has shown that the highest resistance to heat flow is convective heat transfer at the foam/air surface. Therefore, there is a need to allow more air to pass through the foam in order to take advantage of the tremendous amount of surface area available. This leads to examining more open structured carbon

Table 2. Results of Water Flow Experiments Utilizing a 10 mm Diameter by 10 mm Long Piece of Carbon Foam with Three Different Densities

Density (g/cm^3)	0.403	0.492	0.556
Thermal conductivity (W/m·K)	26.56	71.62	90.72
Window size (mm)	0.195	0.148	0.147
Pore size (mm)	0.381	0.382	0.501
Water flow rate (cm^3/sec)	0.259	0.072	0.049

foams which lead to higher water flow rates and high heat transfer.

Conclusions

Carbon foam is an ideal medium for a recovery unit to humidify and heat the inlet air of a fuel cell. While it has been demonstrated to be able to humidify inlet air to near-saturation levels, several problems exist. First, the volume of water needed is enormous, and it is anticipated that the water will have to be captured in the exit stream of the fuel cell. By cooling the exit stream while humidifying the inlet air, the dew point of the exit gas can easily be reached, and water will condense, allowing the water to be recycled.

Second, while the fuel cell inlet air will be required to operate at several atmospheres above ambient for proper fuel cell application, this pressure will be sufficient to force the air through the foam. With less dense carbon foams, the pressure drop across the foam will be significantly less. Other future work of this project will be to collaborate with a fuel cell manufacturer to develop a prototype humidifier and test it in a real system. Because the water balance on the system will be the most difficult task to overcome, several different designs will be desired to optimally achieve the humidification while recovering excess water from the fuel cell.

Proton Exchange Membrane Fuel Cell Power System on Ethanol

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Subcontractors:
Nuvera Fuel Cells, Cambridge, Massachusetts
Aventine Renewable Energy, Inc. (formerly Williams Bio-Energy), Pekin, Illinois

Objectives

Caterpillar, Nuvera Fuel Cells, and Aventine Renewable Energy have teamed up to develop and demonstrate a 10-15 kWe ethanol-fueled proton exchange membrane (PEM) fuel cell system. The primary objectives of this project are to:

- Demonstrate performance, durability & reliability via field demonstration
- Remove technical uncertainties
- Understand correlation and reduce gaps between stationary and transportation applications
- Collect data to evaluate economic feasibility
- Assess commercial viability of the total system

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Durability
- G. Power Electronics
- K. Emissions and Environmental Issues

Approach

- Nuvera will assess and modify advanced fuel cell power module (processor and fuel cell stack) designs that are now under development in separate projects to develop the power module for this project.
- Caterpillar will design the power converter module and will integrate the system.
- Aventine will supply the ethanol and the host site to test the unit and conduct endurance testing.

Accomplishments

- The fuel cell power module accumulated 200 hours at various fuel cell power levels, while the fuel processor had been operating in idle mode for more than 600 hours.

- The power converter (laboratory direct current [DC] power supply to alternating current [AC] into utility grid) has operated in the range 8 to 16 kW for over 300 hours.
- The Aventine site in Pekin, Illinois has been prepared for system installation.
- The data acquisition system has been run with real-time field data.
- The web site for external reporting of field operation is 90% complete.
- The safety review of operations is complete, and all permits have been approved.
- The response plan for field operations and supportability is close to completion.

Future Directions

- Operate the power module at rated power (>5 kWe) for 250 hours with full automation (Nuvera in 3Q, 2003).
- Following above, operate integrated power module and power converter with full automation and complete acceptance testing (Nuvera and Caterpillar in 3Q, 2003).
- Ship the functional unit to the test site and start the endurance-testing phase (Nuvera, Caterpillar, and Aventine starting in 4Q, 2003).

Introduction

Nuvera will design, build, test, and deliver a 10-15 kWe DC fuel cell power module that will be specifically designed for stationary power operation using ethanol as a primary fuel. Two PEM fuel cell stacks in parallel will produce 250 A and 60 volts at rated power. The power module will consist of a fuel processor and CO clean-up, fuel cell, air, fuel, water, and anode exhaust gas management subsystems. A state-of-the-art control system will interface with the power system controller and will control the fuel cell power module under start-up, steady state, transient, and shutdown operation. Temperature, pressure, and flow sensors will be incorporated in the power module to monitor and control the key system variables under these various operating modes. The power module subsystem will be integrated with the power converter, tested at Nuvera and subsequently delivered to the Aventine site in Pekin, Illinois.

Approach

Nuvera plans to modify advanced fuel cell power module designs that are now under development in separate projects for use in this project. They will start with a power module that is a multi-fuel design for transportation (light-duty vehicle) applications. The purpose of using this design baseline is twofold.

- By using an existing design, Nuvera will avoid much of the design effort and technical risk associated with a completely new power module design.
- By using a transportation-based design, this demonstration will simultaneously illustrate that renewable ethanol can be used in fuel cell power systems applied to stationary power generation as well as transportation.

Caterpillar will design, build, test and deliver a power converter module that converts the DC output of the power module into AC power. Caterpillar will also provide system level control to ensure all major subsystems work in harmony and provide constant power to the industrial load on site. The fuel cell system will deliver power to the grid at the Aventine ethanol production site in Pekin, Illinois.

The power converter design will rely on Caterpillar's experience with state-of-the-art solid-state power converters that employ switches, inverters and pulse width modulation to shape a sinusoidal voltage and current in time with the existing power source on site.

Caterpillar also aims to demonstrate technology to the greatest extent possible that can meet the dual requirements of the transportation industry and the stationary electric power generation industry. In addition to low levels of emissions, we intend to demonstrate high efficiency, durability, and reliability. These technical objectives will enable us to calculate the cost of electricity ($/kW-hr) for transportation and stationary power applications.

Aventine will host the industrial site for this demonstration. Aventine provided site electrical load

Figure 1. Power Converter at Caterpillar Technical Center

and ethanol fuel requirements. They have prepared the site to ensure the fuel cell system links to their power network, supply of ethanol fuel and other utilities. During the demonstration, Aventine's personnel will monitor and service (general maintenance and where feasible, troubleshoot and repair) equipment and permit visitors to witness the demonstration in comfort and safety.

Results

The cooperative team has achieved several milestones to date since project inception and commencement. The results are highlighted below for the two major subsystems.

Power Converter. The power converter has been built and tested. Figure 1 shows the unit at Caterpillar's Technical Center, and Table I summarizes the test data to date.

Power Module. The power module has been built and continues to be tested. Figure 2 shows the unit at Nuvera Technical Center, and Table II summarizes the test data to date.

Industrial Demonstration Site. Aventine has completed the site preparation at their plant in Pekin, Illinois, where the integrated power system will be tested for endurance. Figure 3 shows the fully prepared site ready for system installation.

Table I. Summary of the Power Converter Laboratory Test Results

Description	Physical Units	Numerical Value	Comments
Maximum DC input power (230 A, 70 V)	kW	16	
Maximum AC output power	kW	13.5	Into local utility grid
Energy efficiency at rated power (15 kW)	%	90	
Total Harmonic Distortion at rated power (15 kW)	%	2	Meets UL 1741 & IEEE 519
Total laboratory time operating above 4 kW	hours	85	Design & Packaging are complete, 2nd unit under construction as spare

Table II. Summary of the Power Module Laboratory Test Data

Criterion	Specification	Status
Power	Idle to 15 kWe	Idle to 11 kWe
Start-up time	60 min	Less than 60 min
Efficiency	>25%	29%
Laboratory Hours	500 hours for Factory Acceptance Testing	145 hours at various power levels
Start-up	Afterburner free	Afterburner free
Controls Automation	Unattended operation	Combination of manual and automated operation

In addition, Nuvera, Aventine, and Caterpillar have worked together to generate data collection and retrieval. Table III summarizes accomplishments related to data collection, data display, and field operation with remote control.

Figure 2. Power Module at Nuvera Test Laboratory

Figure 3. Aventine Industrial Site for 4000-hour Demonstration

Table III. Summary of Data Collection, Data Display, and Remote Control

Utility grid interactive connections are installed at test site.
Ethanol storage and handling is installed at test site.
Data acquisition system running on laboratory data is 90% complete.
Remote monitoring, data backup and Internet viewing is 90% complete.
Visitor parking and observation amenities are installed.
Hazardous operations procedures are complete.

Conclusions/Future Work

A Final Design Review was hosted by and held at Nuvera in Cambridge on June 10, 2003, with DOE and Caterpillar focusing on critical issues and plans for resolution while refining the project plan with milestones, targeting critical test and review dates. The plan identified critical paths and methodologies to follow them in order to stay on track within budget and time. Also reviewed were the power converter and module integration plans and acceptance criteria to allow shipment. A facility tour to witness the on-going factory acceptance testing of the power module was provided by Nuvera.

Nuvera will continue the automation of the controls and factory acceptance testing and prepare for the shakedown integrated testing (power module and power converter). Caterpillar has completed the second (spare) power converter and will test it, while fine-tuning the first one and also preparing it for integration. Aventine will finalize and fine-tune all installed equipment to date on site in preparation for the endurance testing.

The team expects to commence field demonstration of possibly the nation's first ethanol-powered PEM fuel cell unit in 4Q, 2003.

FY 2003 Publications/Presentations

1. Midwest Regional Hydrogen Infrastructure Forum, 10 October 2002, Chicago, Illinois
2. Renewable Fuels Association Booth, Fuel Cell Seminar, 18 to 21 November 2002, Palm Springs, California
3. Illinois Coalition Meeting, 17 April 2003, Des Plaines, Illinois
4. DOE Merit Review, 21 May 2003, Berkeley, California

New Proton Conducting Solid Sulfide Membranes for Intermediate Temperature Fuel Cells

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Objectives

- Investigate a new class of inorganic sulfide-based proton conducting membranes for hydrogen fuel cell applications.
- Produce anhydrous solid membranes having minimal fuel crossover capability and address many of the problems associated with current hydrogen fuel cell technologies.
- Optimize membrane materials to yield high proton conductivities (10^{-3} to 10^{-1} S/cm) in the intermediate temperature range of 125^{o}C to 300^{o}C.
- Demonstrate performance, thermally stability, and chemical stablility to H_2O and O_2 in a typical fuel cell setup at operating temperatures.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- F. Heat Utilization
- O. Stack Material and Manufacturing Cost
- R. Thermal and Water Management

Approach

- Synthesize new protonated sulfides (thio-acids).
- Synthesize membrane materials from thio-acids; final product may be a glass, glass/ceramic, or ceramic material with stable sulfur-hydrogen bonds.
- Measure the proton conductivity between –70^{o}C and 500^{o}C.
- Determine the thermal stability.
- Determine the chemical stability with respect to H_2O and O_2.
- Determine electrochemical properties, including reduction and oxidation potentials, and cyclic voltammetry.
- Cooperatively fabricate and test membrane electrode assemblies (MEAs) using the most promising membranes. This is to be done in partnership with an external company specializing in fuel cells.

Accomplishments

- The hydrosulfides of potassium, rubidium, cesium, and barium have been synthesized. Proton conductivity of 10^{-9} to 10^{-6} S/cm has been acheived in the temperature range of 25^{o}C to 200^{o}C.

- Mixed hydrogen alkali thiogermanates have been synthesized with the adamanatane-like $Ge_4S_{10}^{4-}$ anion. Proton conductivity of 10^{-10} to 10^{-5} S/cm has been acheived in the temperature range of 50°C to 225°C.
- A new class of anhydrous proton conducting materials has been recently synthesized (patent protection pending). These materials acheive fast proton conductivity (10^{-3} to 10^{-2} S/cm) from 65°C to 270°C.

Future Directions

- Test the recently developed fast proton conducting anhydrous membrane materials (patent protection pending) under relative humidity (RH) conditions as subject by a fuel cell environment. Build MEAs using these membrane materials in cooperation with UTC Fuel Cells. Continue to sythesize and characterize structurally similar membrane materials.
- Synthesize pervoskite and distorted pervoskite type ABS_3 (A = Ca, Sr, Ba, etc.; B = Zr, Ce, etc.) precursor materials. These materials may then be doped with trivalent anions (Y, La, etc.) and reacted with liquid H_2S to produce proton conducting membranes.
- Synthesize adamantane-like $A_xGe_4S_{10}$ ($1.5 \le x < 2$) and $M_yGe_4S_{10}$ (M = K, Rb, Cs; $3 \le y < 4$) precursor materials. These materials may then be reacted with liquid H_2S to produce proton conducting membranes.

Introduction

Hydrogen-based fuel cells are becoming increasingly popular as an alternative energy source for automobiles. This is evident by the recent presidential Hydrogen Fuel Initiative to reverse America's growing dependence on foreign oil by developing the technology needed for commercially viable hydrogen-powered fuel cells. At the heart of the fuel cell is the proton exchange membrane (PEM), which transports protons from the anode to the cathode while providing electronic insulation between them. Currently, there are many types of electrolyte materials for application as PEMs. However, each material has specific limitations restricting its usefulness for application to fuel cells.

With these current fuel cell membrane materials, there remains a temperature region between 125°C and 300°C in which currently no one membrane can provide optimum performance. In this regime, we propose the use of sulfide-based proton conducting membranes. In general, these membranes are being developed to be anhydrous in nature, thermally stable up to 300°C, and chemically stable with respect to H_2O and O_2. Being solid in nature, these membranes are not expected to exhibit fuel cross-over problems. Additionally, proton conductivities of these membranes are expected to be orders of magnitude higher than their oxide counterparts, assuming they follow the trend exhibited by monovalent cations such as Li and Ag in chalcogenide verses oxide host materials (Angell 1992). Well-ordered crystalline structures exhibiting fast proton conductivity may also be developed for sulfide materials analogous to those previously reported for various oxide materials (e.g. Huang 1995, Haile 2001).

Approach

Various precursor materials, including oxides, hydroxides, sulfides, fluorides, chlorides, bromides, and iodides, that are capable of forming thio-acids in liquid H_2S solutions have been identified. As an example, the reaction of GeO_2 or GeS_2 with liquid H_2S at room temperature produces the thio-acid $H_4Ge_4S_{10}$. Membranes may be produced by tailoring precursor materials to obtain structural ordered reaction products with high proton conductivities. Taking various alkali or alkaline earth modified glassy or crystalline materials and reacting them in a liquid H_2S solution is one way to accomplish this.

Proton conductivity in the protonated reaction products, i.e. membrane materials, is being determined through impedance measurements as a function of temperature and frequency. Direct current polarization experiments have been used to determine the electronic verses ionic conductivity of these materials. Physical properties of the protonated materials have been determined, including decomposition, sublimation, and crystallization. Structural comparisons have been used to examine stability with exposure to H_2O and O_2.

Conductivity measurements under RH environments are underway. Additionally, a cooperative effort to fabricate and test MEAs using our most promising membranes is being carried out in partnership with UTC Fuel Cells.

Results

Many protonated sulfide materials have been produced from liquid H_2S reactions with various precursor materials. The conductivities of these protonated materials have been measured with reference to alkali and/or electronic base conductivity. Figure 1 illustrates proton conductivity for alkali hydrosulfides of K, Rb, and Cs. These materials have low conductivities (< 10^{-6} S/cm) and average thermal stability (< 200°C). Additionally, the alkali hydrosulfides readily react with H_2O and CO_2 under atmospheric conditions, precluding them from being successful candidates for MEAs.

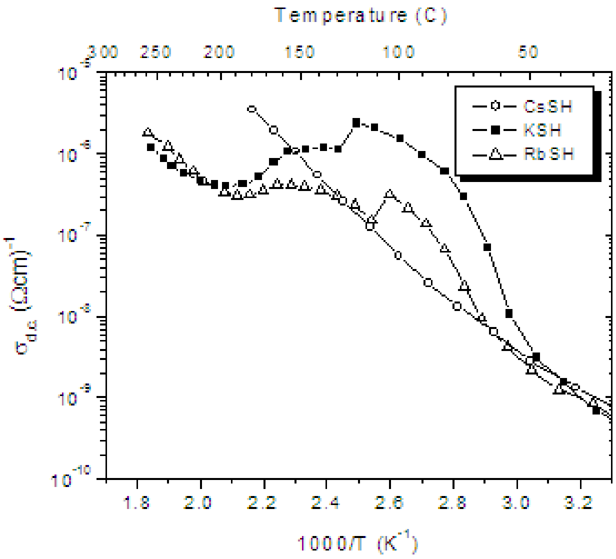

Figure 1. Proton Conductivity of Alkali Hydrosulfides of KSH, RbSH, and CsSH

Another class of protonated materials is based on the crystalline $Ge_4S_{10}^{4-}$ anion. Figure 2 shows the infrared (IR) vibrational spectra illustrating mixed hydrogen and alkali terminal units. Peaks observed below 550 cm^{-1} represent vibrational modes of the $Ge_4S_{10}^{4-}$ structural unit cage, whereas the peaks around 2500 cm^{-1} represent the S-H stretching mode. The broad mode ~2250 cm^{-1} for the hydrogen cesium systems indicates the presence of intercalated H_2S; this is analogous to intercalated H_2O as required for many fast proton conducting materials (e.g. Nafion®). Figure 3 shows typical conductivity spectra of these hydrogen alkali thiogermanate phases. For the phases with higher alkali content (x ≥ 2), a discontinuity from Arrhenius behavior is typically observed with higher proton conductivity (~10^{-5} S/cm), suggesting a well-ordered structure capable of effective proton transport. At higher temperatures (> 175°C), these phases start decomposing by losing mobile proton species, and as a result, the conductivity decreases. Further work is underway to optimize these materials for proton conductivity and thermal stability.

Figure 4 shows examples of proton conductivity for some of the recently designed anhydrous membrane materials (patent protection pending).

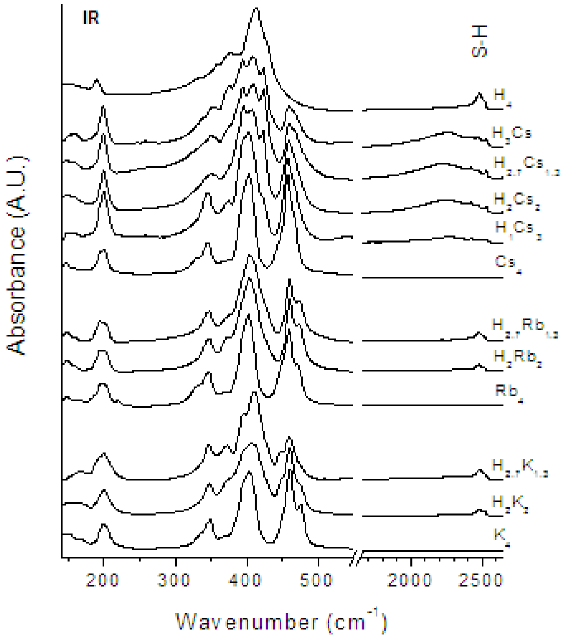

Figure 2. IR Spectra of Hydrogen Alkali Thiogermanates

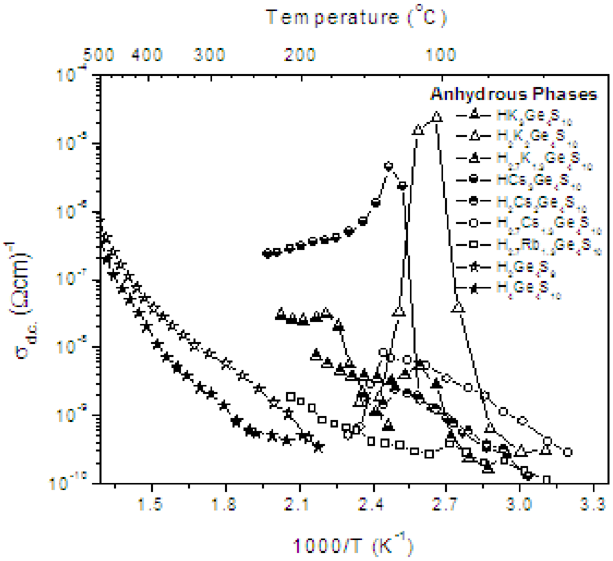

Figure 3. Typical Proton Conductivity for Hydrogen Alkali Thiogermanates

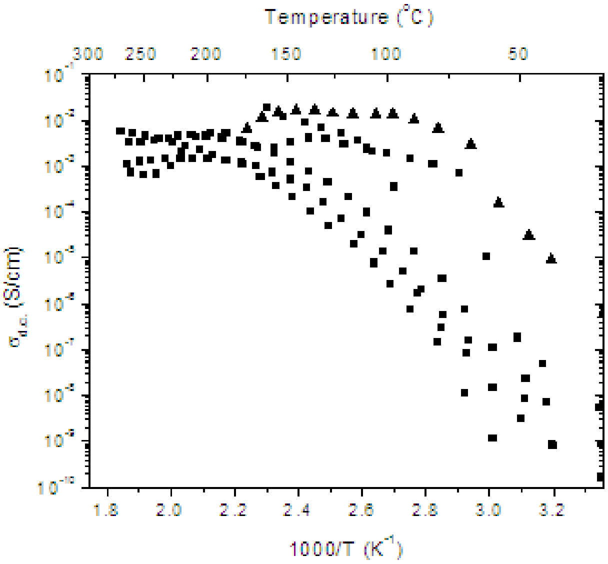

Figure 4. Fast Proton Conductivity for Recently Developed Anhydrous Membrane Materials

Fast proton conductivity is observed (10^{-3} to 10^{-2} S/cm) from 65°C to 270°C. These new protonated materials illustrate the viability and promise of alternative proton conducting membrane materials for the intermediate temperature range of 125°C to 300°C. RH testing and MEA fabrication and testing are currently underway with these new anhydrous proton conductors.

Conclusions

- A new synthesis route for producing thio-acids, hydrosulfides, and sulfides has been identified and patented.
- The structure, conductivity, thermal and chemical stability of many protonated materials have been investigated; many more are being pursued.
- Structurally ordered membrane materials have been identified as potential fast proton conductors, and effort is underway to produce these new protonated materials.
- Recently, one of these new classes of fast proton conducting materials have been identified and synthesised for the first time (patent protection pending).
- Preliminary ionic conductivity values as high as 10^{-3} to 10^{-2} S/cm have been realized from 65°C to 270°C; these materials are thus classified as fast proton conductors.

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1. Martin, S.W., Poling, S.A., Sutherland, J.T., Design and Development of New Glass-Ceramic Proton Conducting Membranes. *DOE Hydrogen Program Annual Review, Proceedings (2002)*: NREL/CP-610-32405.

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1. S.A. Poling, C.R. Nelson, and S.W. Martin, "Anhydrous proton conductivity in hydrogen

alkali thiogermanates," submitted to Solid State Ionics (2003), talk presented at the 14th International Conference on Solid State Ionics (2003)

2. J.T. Sutherland, S.A. Poling, C.R. Nelson, and S.W. Martin, "Formation reaction routes for the thiogermanic acids with GeO_2 and GeS_2 precursors," to be submitted to Solid State Ionics, poster presented at the 14th International Conference on Solid State Ionics (2003)

3. C.R. Nelson, S.A. Poling, and S.W. Martin, "Synthesis and characterization of potassium, rubidium, and cesium thiogermanate glasses," to be submitted to the Journal of Non-Crystalline Solids

4. J.T. Sutherland, S.A. Poling, R.C. Belin, and S.W. Martin, "Exploration of the H_2S-GeS_2 system," to be submitted

5. J.T. Sutherland, S.A. Poling, C.R. Nelson, and S.W. Martin, "H_2S synthesis route for high purity L.T. 3-D a-GeS_2," in press, Material Science Letters (2003)

6. S.A. Poling, C.R. Nelson, J.T. Sutherland, and S.W. Martin, "Crystal structure of thiogermanic acid $H_4Ge_4S_{10}$," in press, Inorganic Chemistry (2003)

7. S.A. Poling, C.R. Nelson, J.T. Sutherland, and S.W. Martin, "Proton conductivity in anhydrous and hydrous thiogermanic acids," submitted to Solid State Ionics (2003)

8. S.A. Poling, C.R. Nelson, J.T. Sutherland, and S.W. Martin, "Synthesis and characterization of the thiogermanic acids $H_4Ge_4S_{10}$ and $H_2Ge_4S_9$," Journal of Physical Chemistry B 107 (2003) 5413-5418

Special Recognitions & Awards/Patents Issued

1. Synthesis and uses of Thio Acids, Steve W. Martin, Steven A. Poling, Jacob T. Sutherland, Iowa State University, ROI ISURF 2894, February 8, 2002. Provisional filing date of July 26, 2002.

2. Record of invention for fast proton conductors, Iowa State University, ROI ISURF, July, 2003.

3. Invited talk, 14th University Conference on Glass, "Preparation and Characterization of New Proton Conducting Glasses and Ceramics," Rensselaer Polytechnic Institute, Troy, NY, August 13-15, 2003.

Fuel Cell Distributed Power Package Unit: Fuel Processing Based on Autothermal Cyclic Reforming

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Objectives

- Design, fabricate and operate an integrated pre-commercial fuel processor to produce a continuous proton exchange membrane (PEM) fuel cell grade hydrogen-rich stream.
- Assess the reliability, potential cost and performance of the fuel processor.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Cost
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- D. Carbon Dioxide Emissions
- E. Control and Safety

Approach

- Design a pre-commercial 50-kWe fuel processor to produce PEM fuel cell grade hydrogen-rich gas from natural gas based on GE's Autothermal Cyclic Reforming (ACR) technology.
- Analyze several process configurations that include ACR reactors, shift reactors, preferential oxidation reactors (PrOx) and heat exchangers, and select the best configuration with high efficiency, high reliability and low capital cost.
- Design, fabricate and operate the ACR-based fuel processor.
- Develop a control system for safe operation of the fuel processor with low O&M cost.
- Develop tools to quantify the efficiency, cost and reliability of the fuel processor.

Accomplishments

- Designed, fabricated and operated a pre-commercial 50-kWe fuel processor that includes the ACR, shift and PrOx reactors and heat exchangers to produce a continuous hydrogen-rich stream with less than 50 ppm CO.
- Developed a control system for safe operation of the fuel processor.

- Developed a cost analysis model to estimate the delivered electricity cost from the ACR and PEM fuel cell based power system as a function of capacity and mass production rate.
- Developed tools (Failure Reporting, Analysis and Corrective Action System {FRACAS} and Reliasoft) to track and quantify the reliability of the fuel processor.

Future Directions

- Optimize the ACR-based fuel processor to get <10 ppm CO in the product stream.
- Integrate the fuel processor with a PEM fuel cell.
- Develop an ACR catalyst that is active and durable for over 5,000 hours to reduce the O&M costs further.

Introduction

GE is developing a proton exchange membrane (PEM) fuel cell based distributed power generation unit that uses a proprietary fuel processor to convert fossil fuels to a hydrogen-rich gas for use in the PEM fuel cell. The target application is commercial and residential buildings with electric demand in the 20-200 kWe range and with cogeneration needs. The goal of this project is to design, develop, and demonstrate an integrated unit for generating electric power in buildings. Phase II is a demonstration of the integrated fuel processor to continuously generate PEM fuel cell grade hydrogen. This integrated unit will be used to generate data needed in the design of a prototype power generation package. The unit promises high efficiency, low emissions and low cost by utilizing a novel process called autothermal cyclic reforming (ACR).

ACR is an autothermal cyclic catalytic steam reforming technology for converting hydrocarbons to a hydrogen-rich stream. The ACR process operates in a three-step cycle that includes steam reforming of the fuel in a Ni catalyst bed (Step 1 - Reforming), heating the reactor through oxidation of the Ni catalyst (Step 2 - Air Regeneration), and finally reducing the catalyst to the metallic state (Step 3 - Fuel Regeneration). The heat required for the endothermic reforming step is provided during the exothermic air regeneration step. The ACR process consists of two low pressure reactors cycling between the reforming and regeneration (air and fuel) steps to produce a continuous stream of hydrogen-rich gas. The fuel processor produces a 70-80% hydrogen stream that can be purified downstream for PEM fuel cell quality using a shift and a PrOx reactor. The ACR process is a unique technology that can be applied for the production of hydrogen from different fuels, including natural gas, diesel fuel, and renewable feedstock, such as bio-fuels. The ACR process represents a significant technological advancement in comparison with autothermal reforming (ATR) and partial oxidation (POX), as the ACR-produced syngas is not diluted with nitrogen, and the overall efficiency of the ACR process is higher than ATR and POX. When compared to conventional steam methane reforming (SMR), the ACR process has significantly lower capital costs and lower emissions. In addition, the ACR process is fuel flexible and has been successfully demonstrated using high-sulfur fuels.

Approach

A major goal in the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan is to reduce the cost of H_2 or electricity produced from natural gas or other fossil fuels. The ACR technology promises to reduce the capital cost and improve the efficiency and reliability of the fuel processor as compared to other reforming technologies (SMR, ATR and POX). The final process configuration for the ACR-based fuel processor was selected after detailed process analysis of several configurations to achieve the desired performance targets including capital cost and efficiency.

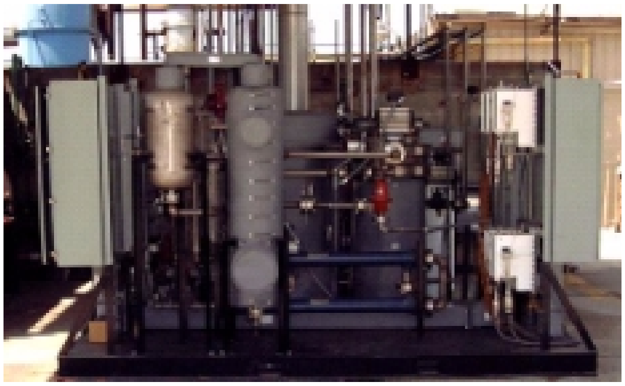


Figure 1. ACR-based 50-kWe Fuel Processor

A 50-kWe fuel processor was designed and fabricated. The integrated fuel processor consists of ACR reactor, shift reactor, PrOx reactor and heat exchangers. Figure 1 shows the picture of the fuel processor. A control system was developed for automatic and safe operation of the fuel processor. A detailed safety review, including preliminary hazard analysis (PHA), hazardous operations review (HAZOP) and accident scenario review (ASR) of the fuel processor, was carried out before operating the fuel processor. The integrated fuel processor was operated to produce a continuous hydrogen-rich stream.

Process analysis tools were developed to quantify the efficiency, cost and reliability of the fuel processor. The efficiencies of several ACR-based process configurations were calculated and compared with efficiencies of existing reforming technologies. An economic model was developed to calculate the capital and O&M costs for the fuel processor under different scenarios of capacity and mass production. The reliability of the fuel processor is being tracked and quantified by using GE's tools, such as FRACAS and Reliasoft.

Results

The ACR unit produces a continuous hydrogen-rich stream (70-80% hydrogen on a dry basis) through cyclic operation of two reactors. Methane slip from the ACR reactors is less than 5%. Figure 2 shows the typical dry gas composition of the product gas from the ACR reactors. The reformate stream contains 8-10% carbon monoxide.

The shift reactor reduces the concentration of CO in the product gas to less than 0.5% via water gas shift reaction ($CO + H_2O \Rightarrow H_2 + CO_2$). The PrOx reactor further reduces the CO concentration below 50 ppm via selective oxidation of CO to CO_2. Further optimization of PrOx reactor operating conditions will result in reducing the CO concentration in the product below 10 ppm. Figure 3 summarizes the typical product dry composition after ACR, shift and PrOx reactors.

The cost analysis model was developed to estimate the cost of electricity produced by the ACR fuel processor integrated with a fuel cell. The model takes into account the capital cost, O&M costs, fuel cost and consumable cost. Figure 4 shows the relationship between the cost of electricity and the

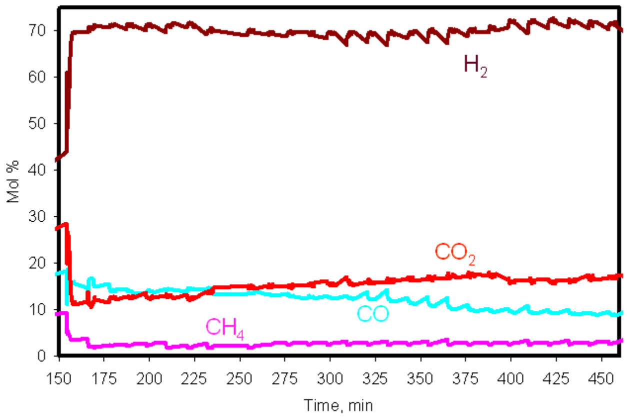
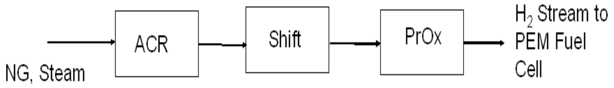


Figure 2. Composition of the Product Gas (Dry Basis) from the ACR Reactors



Reactor	H_2	CO	CO_2	CH_4
ACR	69%	9%	19%	3%
Shift	73%	0.6%	23%	3%
PrOx	72%	< 50 ppm	25%	3%

Figure 3. Composition at the Outlets of ACR, Shift and PrOx Reactors (Dry Basis)

fuel processor/fuel cell capacity at different mass production rates based on the cost analysis model. The plot shows that the fuel processors will be cost effective at higher capacities (> 300 kWe) and when mass-produced (> 5,000 units/year).

Figure 5 shows the cost of electricity as a function of catalyst life for a 200-kWe fuel processor. If the catalyst life is over 2,000 hours, the fuel processor becomes cost effective. Nearly 30 different reforming catalysts were studied in a related project funded by the California Energy Commission. A catalyst that is active and durable for 2,000 h has been identified.

The reliability of the fuel processor is currently being tracked in the failure reporting, analysis and corrective action system (FRACAS). Once the FRACAS system is populated with statistical failure data, the reliability of the entire fuel processor will be calculated using a software tool called Reliasoft. Reliasoft links the reliability of individual components through a block diagram to calculate the reliability of the integrated fuel processor.

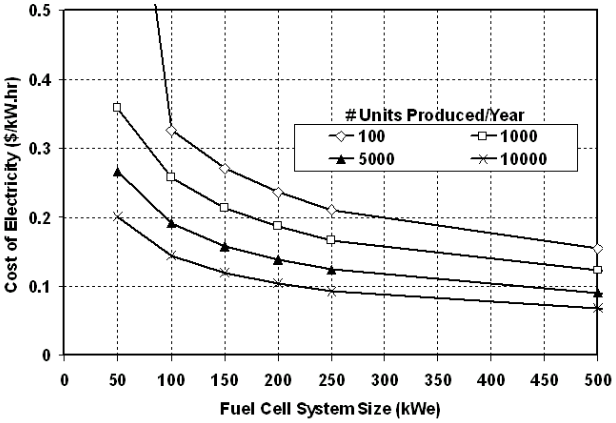


Figure 4. Relationship Between the Cost of Electricity and the Fuel Processor Capacity at Different Mass Production Rates

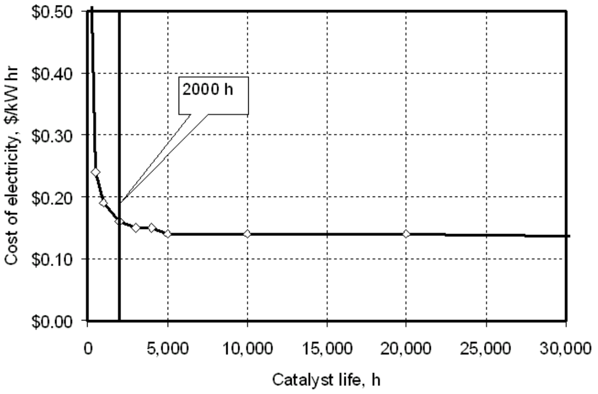


Figure 5. Cost of Electricity as a Function of Catalyst Life

Conclusions

- The ACR-based fuel processor produces a continuous hydrogen-rich stream (70-80% hydrogen on a dry basis) through cyclic operation of two ACR reactors. The heat required for the endothermic reforming process is generated by exothermic oxidation reaction of the nickel catalyst followed by its regeneration.
- The shift and PrOx reactors reduce the CO concentration in the product stream below 50 ppm, thus generating a PEM fuel cell grade hydrogen-rich stream (further optimization of the PrOx reactor will reduce the CO concentrations below 10 ppm).
- Optimization of the ACR-based fuel processor will improve the efficiency and reliability of the system and will result in cost reduction.

FY 2002 Publications/Presentations

1. Hydrogen Refueling System Based on Autothermal Cyclic Reforming, Kumar, R., International Energy Agency Annexe XV Meeting, Palm Springs, CA, Nov 17-18 2002.

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Advanced Buildings PEM Fuel Cell System (New FY 2004 Project)

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Objectives

- Validate and deploy an advanced, integrated 50-kilowatt (kW) proton exchange membrane (PEM) fuel cell system for hotel systems and follow-on applications.
- Develop the fuel cell stack and associated balance of plant by scaling up an existing 25-kW stack design and employing advanced membrane electrode assemblies (MEA).
- Develop the fuel processor and associated balance of plant by scaling up an existing 10-kW equivalent steam reformer and integrating a pressure swing adsorption (PSA) hydrogen purification module for generating hydrogen fuel with purity consistent with a targeted 40,000-hour life system.
- Develop approach for seamless and affordable grid interconnectivity.
- Characterize hotel systems and follow-on market requirements for distributed cogeneration fuel cell systems, and establish a commercialization strategic plan.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Distributed Generation

- E. Durability
- F. Heat Utilization
- H. Startup Time

Fuel Flexible Fuel Processor

- J. Durability
- N. Cost

Components

- O. Stack Material and Manufacturing Cost
- P. Durability

Approach

The overall objective of this project is to develop an advanced 50-kW PEM fuel cell system. The CM-50 power plant will deliver both electricity and thermal energy. It will serve hotel systems initially, and follow-on segments including multi-family dwellings, prison systems, hospital/medical care facilities, office buildings, and similar defense market applications. An Integrated Product Team comprised of IdaTech, LLC; Hydrogenics Corporation; Southern California Gas; San Diego Gas & Electric; Puget Sound Energy; Marriott International; and the California Hotel & Lodging Association, as supported by W. L. Gore & Associates and R4 Energy, Inc., will perform this work.

An assessment of building systems by the utility partners has revealed that the targeted market segments will effectively use 50 kW of electricity and 65 kW of thermal energy, saving energy costs while reducing environmental emissions. These on-site baseload generators will employ developed and scaled-up fuel cell stack and fuel processing technology, leveraging existing U.S. and Canadian federal investments. The PEM system will reduce baseload electricity and thermal energy expense for mid-sized and large hotel systems through single unit and ganged fuel cell configurations.

The key to the CM-50 fuel cell system solution is a blend of advanced fuel cell technology developed by Hydrogenics, and proven fuel processing technology consisting of steam reforming of natural gas and pressure swing adsorption purification integrated by IdaTech. Hydrogenics will use the latest membrane electronic assembly componentry developed by W. L. Gore & Associates in its low-pressure fuel cell stack. Low pressure is a key to achieving long lifetimes and higher system efficiencies.

Sempra Energy (with members Southern California Gas and San Diego Gas & Electric) and Puget Sound Energy will each site one field trial power plant in their service territories in the 2005 timeframe. Marriott International will select a third field trial site at one of its West Coast properties. The utility and hotel systems will supply grid interconnection solutions as well as manage the overall siting and field trial projects. The California Hotel & Lodging Association will provide guidance regarding hotel systems energy requirements, including buildings integration and expected performance parameters. R4 Energy will provide building and follow-on markets consultation services and recommendations for compliance with federal, state and local buildings codes and standards.

The fuel cell system gross electrical efficiency is projected to be 38% using the DOE definition for efficiency: direct current power at the fuel cell electrodes divided by the total energy of the fuel metered into the fuel cell system based on the lower heating value of natural gas. Overall system efficiency is projected at 71% for installations recovering useful heat down to 50°C. The power and thermal ratings are directly driven by the targeted hotel requirement.

The proposed fuel cell system incorporates the ability to operate in stand-alone uninterrupted power supply mode, displacing for example more than 1,000 emergency diesel gensets deployed in San Diego alone. A diesel genset emits approximately 3 lbs NO_x per megawatt hour (MWh), while the proposed system will emit a virtually undetectable level of NO_x, CO and CO_2. Since sulfur is trapped during fuel processing, fuel cell SO_x emissions will be in the low parts per billion range.

Forty percent of over 13,000 domestic hotel properties could use the forthcoming CM-50 power plant as their source of primary power. The Team will develop the CM-50 fuel cell system, conduct three comprehensive demonstration field trials along West Coast markets from California to Washington state, and proceed to commercial deployments throughout North America.

The Team is committed to deploying the CM-50 commercially at the conclusion of the proposed project. Given the high potential for achieving performance, cost, reliability and durability objectives, early market deployment is achievable. Additionally, applications for a 50-kW system are evolving, indicating a broader market appreciation for their utility.

150-kW PEM Fuel Cell Power Plant Verification and Regional Demonstration of 150-kW PEM Fuel Cell Power Plant (New FY 2004 Project)

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Objectives

- Verify the specification, durability, and reliability of a 150-kW natural gas fueled proton exchange membrane (PEM) power plant
- Verify multiple power plants can be connected to a distribution feeder with no adverse interconnection effects
- Confirm that integration of power plant heat with a liquid desiccant dehumidification system increases warm weather heat utilization
- Demonstrate market viability and expedite commercial application of large PEM fuel cell power plants in the distributed generator (DG) market
- Validate grid interconnectivity compliance with UL1471 and IEEE1547 at utility sites throughout the U.S.
- Demonstrate high power plant availability in utility generation service

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year RD&D Plan:

<u>Distributed Generation Systems</u>

- E. Durability
- F. Heat Utilization
- G. Power Electronics

<u>Fuel-Flexible Fuel Processors</u>

- J. Durability

<u>Components</u>

- P. Durability
- R. Thermal and Water Management

Approach

UTC Fuel Cells (UTCFC) is in the process of developing a 150-kW PEM power plant whose planned specifications will meet the DOE targets for fuel cells.

As part of this project, the prototype power plant operated in Task 1 is dedicated to verifying the specification and capability to operate in climate extremes. In Task 2, the plan is to field three evaluation power plants that demonstrate power plant reliability. Cell stack and fuel processor catalyst durability testing and accelerated stress testing of mechanical components in Task 2 will complement the power plant data. Field evaluation power plants will provide an experience base in order to demonstrate high reliability. Task 3 addresses concern with heat utilization in commercial buildings. Integration between the power plant and liquid desiccant dehumidification will be evaluated by the United Technologies Research Center. Liquid desiccant dehumidification appears to be a good use of power plant heat to address 30 to 50 percent of the air conditioning load. Task 4 seeks to verify that a power plant certified for interconnection to UL1741 can be installed with minimum cost or delay and provides data measured by a distribution utility (Connecticut Light and Power) on interconnection effects of multiple power plants on a single distribution feeder. The Electric Power Research Institute will conduct analysis to extend these results to the U.S. as a whole.

The team assembled to verify the 150-kW PEM fuel cell power plant includes UTCFC, Hydrogen Source (HYS), United Technologies Research Center (UTRC), Connecticut Light and Power (CL&P) and the Electric Power Research Institute (EPRI).

As part of the regional demonstration portion of this project, UTCFC will use four 150-kW PEM natural gas fueled power plants to demonstrate grid connectivity, high power plant availability, low emissions and high efficiency to utilities, owners/ operators and the investment community.

A Team of UTCFC, New York Power Authority, Austin Energy, San Francisco Public Utilities Commission/Hetch Hetchy Water and Light, and EPRI has been formed to provide expertise in the area of grid interconnectivity.

Use of the 150-kW PEM power plant will assess the readiness of the technology for these initial field demonstrations. The team has defined the work of the project to broadly address grid interconnectivity issues. The issues include 1) participation in developing and reviewing interconnectivity standards, e.g., UL1471 and IEEE1547 and individual State standards and regulations for grid interconnection; 2) selecting utility test sites in load intensive areas with a diversity of grid characteristics, e.g., generating mix, load composition, equipment and generator age, and geographical, regional and climatic variation; 3) confirming applicability of standards to all sites and situations and establishing appropriate field test protocols for confirmation; and 4) resolving specific technical issues, e.g., islanding, fault clearing capability, personnel safety considerations, reactive power support, and power quality including flicker, voltage sag and harmonics.

The regional demonstration project technical work is conducted in three tasks. In Task 1, the Team will select a diversity of sites throughout the U.S. for installation and testing of power plants. UTCFC will fabricate, acceptance test and deliver power plants to the sites for installation. The host utility will install the power plant. In Task 2, host utilities will perform tests to determine power plant availability, emissions, efficiency and grid connectivity characteristics. UTCFC will provide field support to demonstrate a power plant availability of more than 95%. UTCFC also will evaluate two alternative strategies for cost effectively achieving availabilities of more than 95% in commercial service. In Task 3, EPRI and UTCFC will establish protocols for grid connectivity testing. EPRI and UTCFC will analyze the grid connectivity data collected by host utilities and the remote data center to validate the use of standards UL1471 and IEEE1547 for grid connectivity certification and grid connection.

Backup/Peak Shaving Fuel Cell Systems - Design and Development of the GenCore™ II (New FY 2004 Project)

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Objectives

- Develop a cost-reduced, polymer electrolyte membrane (PEM) fuel cell stack tailored to hydrogen fuel use
- Develop an advanced electrical energy storage system
- Develop a modular, scalable power conditioning system tailored to market requirements
- Design a scaled-down, cost-reduced balance of plant (BOP)
- Certify design to Network Equipment Building Standards (NEBS), Underwriters Laboratories (UL) and European Conformity (CE) requirements

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Durability
- G. Power Electronics
- H. Start Up Time

Approach

Plug Power Inc. is conducting a 30-month project to advance the state-of-the-art of fuel cell technology with the development of a new generation of commercially viable, stationary, back-up/peak-shaving fuel cell systems.

The GenCore™ II (GCII) backup fuel cell system, to be designed, developed and tested by Plug Power in this project, will be the first mass-manufacturable implementation of Plug Power's GenCore (GC) platform targeted for battery and small generator replacement applications in the telecommunications, broadband and uninterruptible power supply markets. The GCII will be a standalone, H_2-in-DC-out battery and small generator replacement system.

In designing the GCII specifically for the telecommunications market, Plug Power's efforts will be greatly enhanced by our teaming arrangement with BellSouth Telecommunications, Inc., a leading industry end user.

The final GCII system, to be fielded in 2005, will represent a market-entry, mass-manufacturable and economically viable design. Phase I of the project employs Plug Power's Technology Delivery Process to develop the technology initiatives of the design. This structured process uses rigorous testing and evaluation methods in order to minimize the risks inherent in bringing new technologies into commercial designs. The technology development effort for the GCII has two major tasks that essentially run in parallel: system technology development and module technology initiatives. As module technology innovations are completed, they will be integrated and verified in the system. Phase II uses Plug Power's New Product Delivery process to introduce the technology initiatives as hardware modules for integration. Phase III also employs the New Product Delivery Process to bring the hardware from a set of technology modules to an integrated system through field-testing and certification. Phase III culminates in the system demonstration at DOE. The project will follow the schedule below:

- Q3, 2003 – Q4, 2004: Collect field data for GenCore II development on certification testing and field deployment of prototypes
- Q2, 2004 – Q1, 2005: Design and develop GenCore II
- Q4, 2004: Build confirmation and life test systems
- Q2, 2005 – Q1, 2006: Conduct field testing with BellSouth and NEBS, UL and CE testing
- Q4, 2005 – Q1, 2006: Demonstrate GenCore II at DOE's Argonne National Laboratory

Economic Analysis of PEMFC Systems (New FY 2004 Project)

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Objectives

- **Task 1:** Perform a study focusing on fuel cell technology, market, economic, and environmental analyses. The objective will be to develop a complete understanding of fuel cell technology, potential fuel cell capacity, the energy market, market size and potential in a wide range of possible stationary building applications, supply curves for promising fuel cell markets, and government policies and impacts. This knowledge will enable analyses of the economics and national impacts of the technology.
- **Task 2:** Employ the Interactive Future Simulations (IFS™) software to generate alternative scenarios to determine the commercial viability of fuel cells by the year 2020. (IFS™ software is commercial computer software owned by Battelle.) The future economic viability and impacts of fuel cells in the U.S. are highly uncertain and based on widely diverging market conditions. Anticipating these diverging market conditions is indispensable for understanding and influencing the actions required to encourage the successful commercialization of fuel cells.
- **Task 3:** Develop a stakeholder's forum for:
  - Focused investigations of critical issues and identification of foremost industry, government, and other consumer needs;
  - Identification of critical success factors and principal barriers;
  - Development of strategies and partnerships for addressing barriers;
  - Development of training modules and communications tools.
- **Task 4:** Establish the PEM Fuel Cell Center (***One-Stop Information Center for PEM Fuel Cells*** website). There is a considerable amount of research being conducted by federal laboratories and the private sector, as well as a number of university research centers. Presently, there is no single repository for proton exchange membrane (PEM) fuel cell information. The information center will inventory or link to information and educational resources that presently exist, while augmenting the information with the results from other work completed as part of this project. The Center's website will have several access areas that will be tailored to meet the information demands of distinct stakeholder groups. Public policy will impact both time-to-market and the speed of market penetration of PEM fuel cells. Battelle will provide expertise to support policy development and analysis. This will include, as demanded by policy-makers, forums and seminars on targeted aspects of the PEM fuel cell policy environment.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Fuel Cells

- D. Fuel Cell Power System Benchmarking

Education

- B. Lack of Demonstrations or Examples of Real World Use
- C. Institutional Barriers and Access to Audiences
- D. Regional Differences

Approach

Battelle will complete a comprehensive four-task action plan/process that includes technology-economic, contingent valuation, and forecasting assessments to identify critical success factors in the commercialization of fuel cells. Battelle will also initiate a formal stakeholder involvement process to govern our assessments and to share information critical to promoting user acceptance of this technology.

In Task 1, Battelle will evaluate the economic variability of stationary PEM fuel cells of different sizes (1, 5, 25, 100, and 250 kW), operated as stand-alone, distributed generators (DGs) and as combined heat and power (CHP) systems. Battelle will solicit extensive stakeholder involvement, specifically from industry, academia, and research institutes, to gather accurate information on systems, technology performance, developmental status, applications, and economics.

In Task 2, since the future of PEM fuel cells is highly uncertain, Battelle will use a proven, computer-based method to generate alternative futures or scenarios. In each scenario, we will identify defined alternative outcomes, such as rapid market penetration of PEM fuel cells in the application of stationary power. Each scenario will be different, which will allow us to see the total sets of conditions associated with the rapid market penetration. Battelle will identify the most important trends, issues, and factors to be included in the scenarios.

In Task 3, a stakeholder group will be formed that represents a balance among interests in the fuel cell industry, academia, government, non-profit organizations, consumers, and, as they are identified, target markets such as electric power generators. Battelle will solicit and carefully manage the involvement of technology developers or vendors to provide an unbiased opinion of technology commercialization options. Developers and vendors may act as members of the stakeholder group to the extent that they represent the general technology area, or an association of developers or users. The collaboration among stakeholder group members also will enrich the development of effective communications tools for educating the broader stakeholder community.

In Task 4, Battelle will focus on three key objectives in facilitating the commercialization of PEM fuel cells:

- Improving understanding of the technology in target markets. Providing information and tools to target markets will enable informed decisions about the uses and applications of PEM fuel cells.
- Enhancing the technology's competitiveness. PEM fuel cells will compete with other energy technologies on a mix of attributes that will include the pure economics of cents/kW. Battelle will provide information to the PEM fuel cell industry to enhance understanding of other factors important to develop for and convey to promising target markets.
- Collecting data on emerging technologies. Battelle will actively search for technologies that could reduce the cost of fuel cells, thereby improving their competitiveness in the marketplace. These innovations will be communicated to the PEM fuel cell industry.

Water-Gas Shift Catalysis

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Objectives

Develop water-gas shift (WGS) catalysts for on-board fuel processing that meet the DOE targets for performance [gas-hourly space velocity (GHSV) $\geq$30,000 h^{-1}, CO conversion $\geq$90%, CO selectivity $\geq$99%], durability [lifetime >5000 h], and cost [<\$1/kW_e]. Eliminate the drawbacks of commercial WGS catalysts, CuZn and FeCr oxides, for on-board fuel processing, including the need for well-controlled in situ activation, the loss of activity due to temperature excursions, and the need to sequester the catalysts during shutdown to prevent deactivation.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- N. Cost

Approach

- Explore metal/metal oxide combinations that exhibit the bifunctional mechanism where the metal adsorbs CO, CO is oxidized by the metal oxide, and the metal oxide is then reoxidized by water.
- Metals (e.g. Pt, Ru, Co, Cu) that have CO adsorption energies of 20-50 kcal/mol
- Metal oxides that exhibit redox activity under WGS reaction conditions

Accomplishments

Pt Catalysts

- Improved the activity and stability of Pt/doped ceria catalyst with a bimetallic formulation.
- Identified Zr and Gd as dopants for ceria that can improve WGS activity at temperatures >300°C compared to undoped Pt/ceria.
- Demonstrated that 5 ppm H_2S does not enhance deactivation of Pt/doped ceria catalyst at 300°C but does promote deactivation at 400°C.

Cu Catalysts

- Investigated Re, Ni-Re, and Mn as promoters to enhance the activity of Cu catalysts.

Future Directions

Pt Catalysts

- Optimize bimetallic formulation to increase activity while decreasing Pt loading to achieve DOE cost target.
- Retard Pt sintering.
- Address H_2S poisoning at 400°C.
- Evaluate catalyst performance on monolith.

Cu Catalysts

- Increase low temperature (230-300°C) activity.
- Reduce Cu sintering through the addition of promoters to improve stability.
- Improve sulfur tolerance.
- Conduct characterization studies (SEM/TEM and EXAFS/XANES) to improve activity and reduce deactivation.

Introduction

On-board reforming of hydrocarbon fuels for H_2 generation for fuel cell-powered vehicles produces reformate containing ≤10% CO. The CO content in reformate must be reduced to <100 ppm because it poisons the polymer electrolyte fuel cell (PEFC). The water-gas shift (WGS) reaction ($CO + H_2O = CO_2 + H_2$) converts CO to CO_2. Commercial WGS catalysts, CuZn and FeCr oxides, have a number of drawbacks, including the need for a well-controlled in situ activation process, the loss of activity due to temperature excursions, and the need to sequester the catalysts during shutdown to prevent reoxidation. All of these factors make the commercial WGS catalysts undesirable for use in on-board fuel processing. The goal of this project is to develop new WGS catalysts that overcome these drawbacks and meet the DOE performance, durability, and cost targets.

Approach

Metal/metal oxide combinations that exhibit bifunctional mechanisms are being explored where the metal active sites adsorb CO and the oxide support provides the oxygen for CO oxidation and is reoxidized by water. Pt and Cu are being studied because their CO adsorption energies are 20–50 kcal/mol, which is considered to be optimal for WGS catalysts [1]. Gadolinia and zirconia doped ceria are being investigated as supports because they exhibit redox chemistry under WGS reaction conditions. Kinetic studies on Pt/ceria catalysts have shown that the rate is zero order in CO and one-half order in H_2O (i.e., the CO conversion rate is proportional to $P_{CO}^{0} P_{H2O}^{0.5}$) [2,3], suggesting that the Pt surface is saturated with CO and the reaction is controlled by the reoxidation rate of ceria by water, the oxygen transfer rate from the ceria to the metal interface, or the metal dispersion and surface area. Our approach is to improve ceria redox/oxygen transfer rates by cation doping, improve water dissociation on the Pt surface by addition of a second metal, and stabilize Pt against sintering.

WGS rates were measured in a microreactor using synthetic reformate (6.9% CO, 10.4% CO_2, 31.1% H_2, 31.0% H_2O, and 20.7% N_2) on powder samples at a catalyst temperature of 250–400°C. High space velocities were used (GHSV=200,000–1,500,000 h^{-1}) to maintain differential reactor conditions (i.e., conversion ≤15%) at the lower temperatures (250–300°C).

Results

The effect of Pt loading on WGS activity was investigated. The WGS activity (per gram catalyst) increased with Pt loading (0.87–2.86%) while the CO conversion rates (per mole Pt) were nearly identical

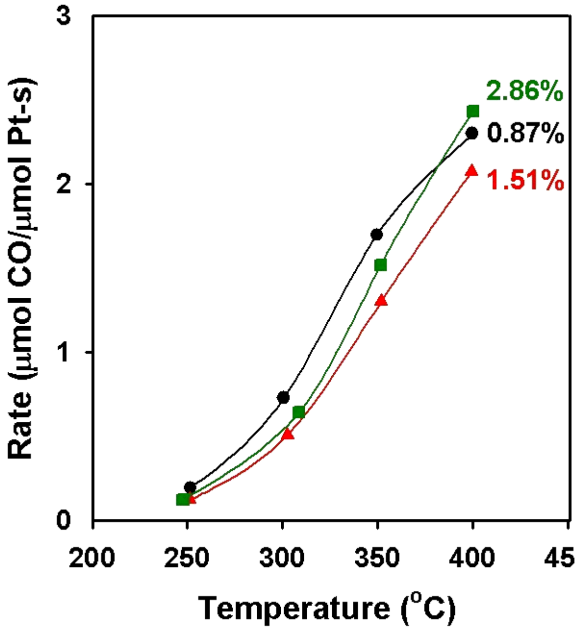

Figure 1. Effect of Pt Weight Loading on WGS Activity (per mole of Pt) of Pt Supported on Doped Ceria

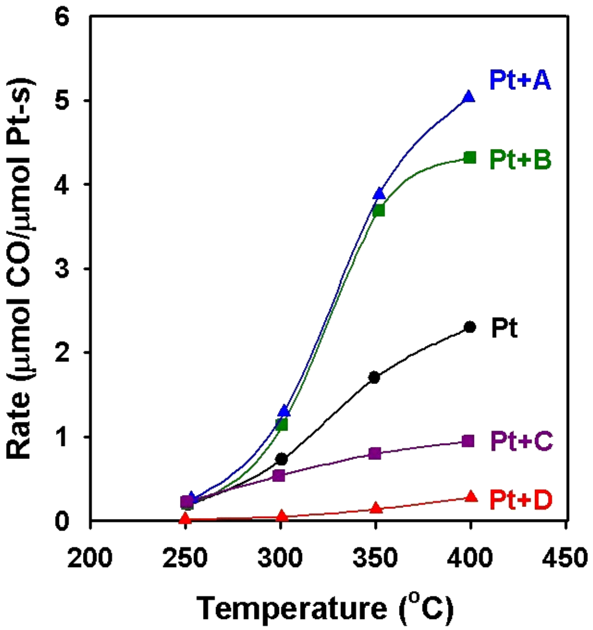

Figure 2. Water-Gas Shift Activity of Pt and Pt+M Supported on Doped Ceria

(Figure 1), indicating that WGS rates (per mole Pt) are independent of Pt loading. Therefore, the CO conversion per unit volume of reactor can be increased by increasing the Pt loading to achieve the volume/weight targets.

Pt bimetallic formulations were investigated in an attempt to reduce the amount of Pt while enhancing its activity. Bimetallic formulations were selected on the basis of theoretical studies of the energetics of H_2O dissociation and reactions between CO_{ads} + OH_{ads} on Pt-mixed metal clusters [4]. The WGS activities (per mole Pt) of different Pt bimetallic formulations (Pt+M) are compared to Pt in Figure 2. Pt+A and Pt+B showed higher rates than Pt, indicating that the addition of A and B is favorable for promoting the WGS reaction. On the other hand, the addition of C and D seemed to have inhibiting effects on WGS because lower rates were observed on Pt+C and Pt+D than with Pt. The activities of Pt+A and Pt+B are compared to Pt at 300°C with time on stream in Figure 3. Pt lost half of its activity after ~40 hours and Pt+B deactivated more rapidly than Pt and lost half of its activity after ~2 hours. Pt+A was more stable than Pt and had a half life of ~217 hours. Wang *et al.* reported that deactivation observed during WGS on Pt/ceria and Pd/ceria catalysts is caused by metal surface area loss [5]. The Pt+A bimetallic formulation may inhibit the sintering of Pt, resulting in enhanced stability.

Co, Sn, Ni, Re, and Mn promoters were added to Cu-based WGS catalysts to try to improve the air stability. The activity decreased when Co and Sn were added, and these were subsequently dismissed as potential promoters. Rhenium was selected because it improved the air stability of Co-based WGS catalysts. Rhenium and copper do not form a solid solution or alloy of definitive stoichiometry. Nickel forms a solid solution with both Cu and Re and was used to increase their interaction. The Cu-Re catalyst is significantly more active than the Cu-Ni-Re catalyst (Figure 4). The selectivity to H_2 is considerably reduced with the presence of Ni because nickel is a very efficient methanation catalyst, particularly under WGS conditions. As shown in Figure 4, the Cu-Mn catalyst showed higher activity than the Cu catalyst at temperatures >275°C. However, the air stability of the Cu-Mn catalyst was poor; 10–20% of the initial activity was lost after a single exposure to dry air at 400°C. The promoted samples were more active than Cu at the higher temperatures (>375°C) after exposure to air. Preliminary powder x-ray diffraction studies were

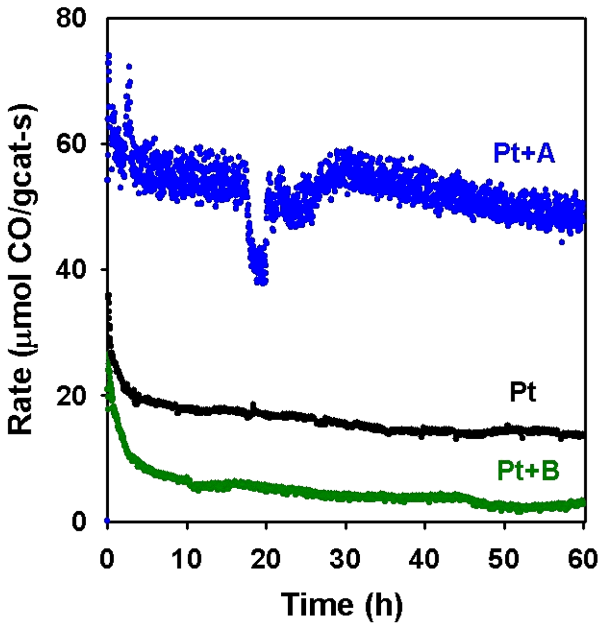

Figure 3. Water-Gas Shift Activity of Pt and Pt+M Supported on Doped Ceria

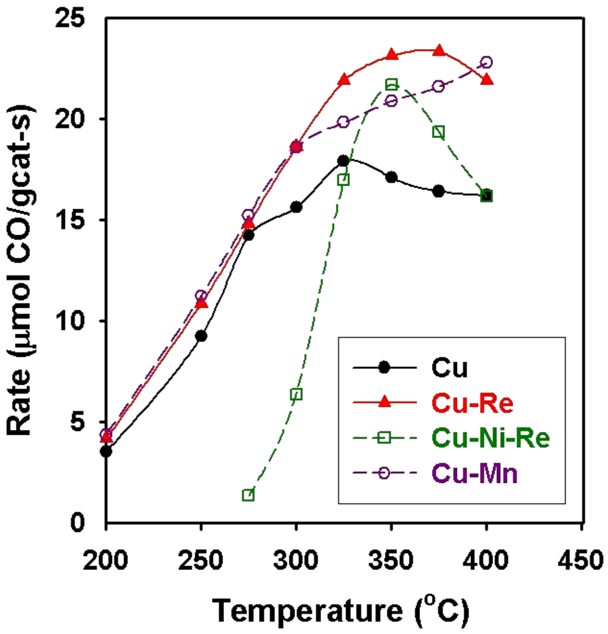

Figure 4. Effect of Promoters on WGS Activity of Cu/γ-Al_2O_3

inconclusive regarding the extent of interaction of the promoters (Re, Mn) with Cu in these catalysts. Manganese is expected to form a spinel phase with Cu, based on available CuO-Mn_2O_3 phase diagrams.

Conclusions

- WGS activity (per gram catalyst) increased with Pt loading while CO conversion rates (per mole Pt) were similar, indicating that rates (per mole Pt) are independent of Pt loading (0.87–2.86 wt%).
- Activity and stability of Pt/doped ceria catalysts increased with bimetallic formulations.
- Ni, Re, and Mn promoters enhanced WGS activity of Cu/γ-Al_2O_3, but promoted samples were less stable after air exposure.

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Catalysts for Autothermal Reforming

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Objectives

- Develop advanced autothermal reforming (ATR) catalysts that meet DOE targets for fuel-flexible fuel processors, i.e., fuel efficiency ≥99.9%, H_2 selectivity ≥80%, gas-hourly space velocity (GHSV) ≥200,000 h^{-1}, durability ≥5000 h, and cost ≤$5/kWe.
- Develop a better understanding of reaction mechanisms to increase catalytic activity, reduce deactivation, and improve sulfur tolerance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Start-up/Transient Operation
- J. Durability
- K. Emissions and Environmental Issues
- N. Cost

Approach

- Building on past experience, we are investigating two classes of materials, transition metals supported on mixed-oxide substrates and perovskites containing no precious metals.
- Determine catalyst performance (i.e., yields of H_2, CO, CO_2, and CH_4) as a function of catalyst formulation, fuel composition (including sulfur content), and operating parameters (e.g., O_2:C and H_2O:C ratios, temperature, and GHSV).
- Conduct catalyst characterization and mechanistic studies to gain insight into reaction pathways.
- Work with catalyst manufacturers to optimize catalyst structure and performance.

Accomplishments

For transition metals on mixed oxide supports

- Optimized catalyst formulation to improve performance of monoliths.
- Demonstrated 54.6 vol% H_2 (dry, N_2-free) from sulfur-free (<450 ppb S) gasoline at GHSV of 110,000 h^{-1} with Rh catalyst on a monolith.
- Identified Pt sintering as a major cause for catalyst deactivation.
- Identified oxide formulation that does not lose surface area during reforming.

For the Ni-based perovskites

- Identified $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ as a composition with improved structural stability compared to $LaNiO_3$ under ATR conditions.
- Demonstrated <50% loss in activity with benchmark fuel with 50 ppm S.

Future Directions

- Evaluate catalyst performance on a larger scale using 1-5 kWe adiabatic reactors to confirm microreactor results, better evaluate long-term and startup performance, and determine optimal geometry for structured support.
- Work to decrease precious metal loading while improving catalyst stability and sulfur tolerance.
- Work to improve catalyst activity and sulfur tolerance of perovskite catalysts.
- Address the effect of rapid startup on catalyst stability.
- Increase our fundamental understanding of reaction processes and mechanisms for deactivation and sulfur poisoning.

Introduction

Catalytic autothermal reforming (ATR) of hydrocarbon fuels to generate H_2 has been widely accepted as the most promising route to meet the efficiency, weight and volume, durability, and cost goals for on-board fuel processors for automotive fuel cell systems. Argonne National Laboratory is developing new reforming catalysts tailored to meet the unique operating requirements for reforming complex fuel mixtures, such as gasoline. Two different classes of materials are being examined: Group VIII transition metals (e.g., platinum, rhodium, or nickel) supported on an oxide ion-conducting substrate (e.g., gadolinium-doped ceria (CGO)), and mixed non-noble metal oxides with the ABO_3 stoichiometry and the perovskite structure. The transition metal-based catalysts have demonstrated near-equilibrium yields of H_2 from a number of fuels, including gasoline, diesel, and natural gas, exhibiting high catalytic activity and resistance to coking. Süd-Chemie, Inc., of Louisville, Kentucky, currently produces this catalyst under a licensing agreement.

Approach

Catalyst samples as powders and coated on monoliths are evaluated for H_2 yield, fuel conversion, and resistance to coking and sulfur poisoning as a function of operating parameters (such as the type of fuel, its sulfur content, O_2:C and H_2O:C ratios, and reaction temperature) in a microreactor system. Fuels tested include sulfur free (<450 ppb S) and low sulfur (~30 ppm S) gasolines, isooctane (2,2,4-trimethylpentane), and a benchmark fuel mixture[1]. Catalyst characterization techniques such as extended X-ray absorption fine structure spectroscopy (EXAFS) are used to understand changes in catalyst morphology during ATR and to help improve catalyst performance and stability.

Results

Transition Metals Supported on an Oxide-Ion Conducting Substrate. Monoliths coated with Rh-containing catalysts, Rh-CGO or Rh-Pt-CGO, produced reformates from sulfur-free gasoline with a higher H_2 yield, 8.7 and 9.3 moles of H_2 per mole of gasoline, respectively, than the monolith coated with a catalyst containing only Pt (2.5 moles of H_2 per mole of gasoline) as shown in Figure 1. The methane yield was 0.4 moles of CH_4 per mole of gasoline for both Rh-CGO and Rh-Pt-CGO. Non-methane hydrocarbons included C_2-C_6 paraffins and the aromatics benzene, toluene, and xylenes. For Rh-CGO, the H_2 yield increased to 9.3 moles of H_2 per mole of fuel when the reaction temperature was increased from 700 to 750°C. For Pt-CGO, the H_2 yield increased from 2.5 to 8.4 moles of H_2 per mole of gasoline as the reaction temperature was increased from 700 to 800°C. For ATR, the steam reforming component of the reaction produces the H_2, and the higher H_2 yields observed with the Rh-containing catalysts are consistent with various studies which have shown that Rh is the most active Group VIII transition metal for steam reforming.[2] As the GHSV was increased from 27,500 to 110,000 h^{-1}, the H_2 yield decreased slightly from 8.7 to 8.4 moles of H_2 per mole of gasoline for Rh-CGO as shown in Figure 2. On a concentration basis, the H_2 concentration decreased from 55.4 to 54.6 vol% (dry, N_2-free) as the GHSV was increased from 27,500 to 110,000 h^{-1}. Tests are in progress to determine if modifying the structured support can reduce hydrocarbon breakthrough.

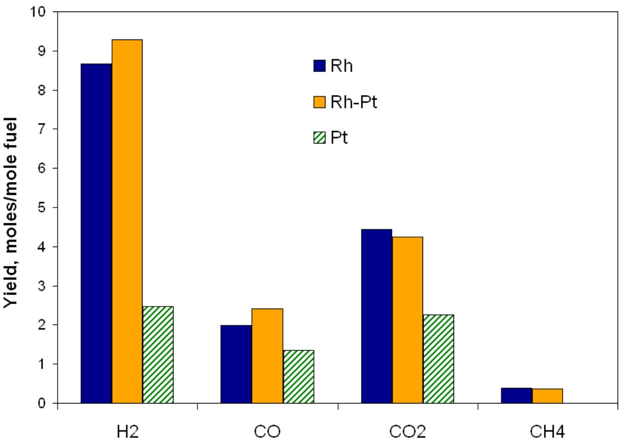

Figure 1. Comparison of the H_2, CO, CO_2, and CH_4 Yields Produced from <450 ppb S Gasoline Catalyzed by Rh-, Rh-Pt, or Pt-CGO at 700°C

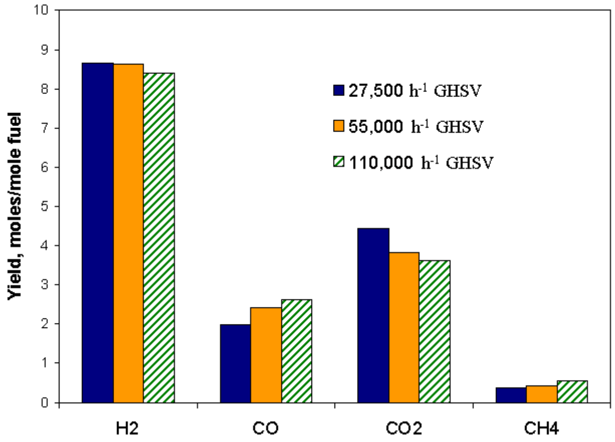

Figure 2. Effect of GHSV on H_2, CO, CO_2, and CH_4 Yields Produced from <450 ppb S Gasoline Catalyzed by Rh-CGO at 700°C

Previous studies have shown that Pt-CGO is more sulfur tolerant than Rh-CGO.[1] The sulfur tolerance of Rh-Pt-CGO was evaluated by reforming two gasolines, one which contained <450 ppb S and the other which contained 30 ppm S. As shown in Figure 3, the H_2 concentration decreased from 58.2 to 54.8 vol%, representing a 6% decrease, during the first 48 h with sulfur-free gasoline. The fuel was then switched to the 30 ppm S gasoline. The H_2 concentration decreased further to 49.8 vol%, which represents a 10% decrease, over the next 48 h, indicating that sulfur in the fuel was poisoning the catalyst. EXAFS analyses showed that Pt is highly dispersed on Pt-CGO before ATR but undergoes sintering during ATR. Sulfur in the fuel appears to enhance the sintering of Pt. Similar studies are in progress for the Rh and Rh-Pt.

Mixed Metal Oxides with the Perovskite Structure. We have previously reported that for the lanthana-based pervoskites containing first-row transition metals (i.e., $LaCrO_3$, $LaMnO_3$, $LaFeO_3$, $LaCoO_3$, and $LaNiO_3$), the highest H_2 yields are observed with the least stable complexes, $LaCoO_3$ and $LaNiO_3$, which decompose into La_2O_3 and metallic Co and Ni, respectively, under ATR conditions.[3] The stability of $LaNiO_3$ under ATR was increased by replacing some of the Ni with Cr, termed "B-site" doping. This resulted in a slight decrease in the H_2 yield, which could be recovered

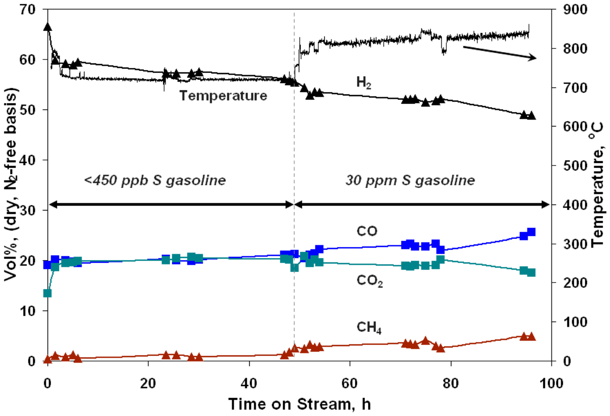

Figure 3. Comparison of vol% of H_2, CO, CO_2, CH_4, and Total Hydrocarbons (HCs) in Reformate Produced from <450 ppb S and 30 ppm S Gasolines Catalyzed by Rh-Pt-CGO/ Monolith

by replacing some of the La with Sr, termed "A-site" doping. $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ was identified as the optimal composition.

The sulfur tolerance of $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ was evaluated by comparing the H_2 yield from reforming benchmark fuel containing two different S contents, 5 and 50 ppm, added as benzothiophene. $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ is susceptible to sulfur poisoning with the decrease in the H_2 yield being greater and more rapid at the higher sulfur content. Attempts to improve the sulfur tolerance by replacing Cr with metals such as Mn or Fe were not successful, as shown in Figure 4.

Conclusions

Transition Metal(s) Supported on an Oxide-Ion Conducting Substrate

- Showed that formulations containing Rh are the best-performing ATR catalysts.
- Demonstratedthat Rh-CGO on a monolith can produce a reformate containing 54.6 vol% H_2 (dry, N_2-free) from a <450 ppb S gasoline at a GHSV of 110,000 h^{-1}.
- Using EXAFS, showed that Pt sinters under ATR conditions and that S may enhance sintering.

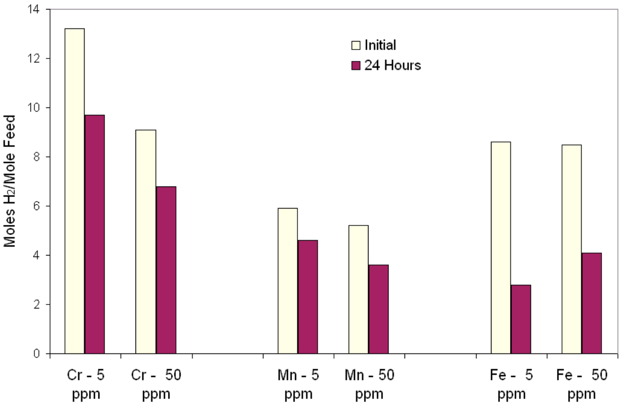

Figure 4. Comparison of the Effect of 5 and 50 ppm S on H_2 Yield Produced from Benchmark Fuel Catalyzed by $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$, $La_{0.8}Sr_{0.2}Mn_{0.9}Ni_{0.1}O_3$, and $La_{0.8}Sr_{0.2}Fe_{0.9}Ni_{0.1}O_3$

Mixed Metal Oxides with the Perovskite Structure

- Identified $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ as a composition with improved structural stability compared to $LaNiO_3$ under ATR conditions.
- Determined that deactivation due to sulfur poisoning depends on the sulfur content in the fuel; however, complete loss of activity was not observed.

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3. J. R. Mawdsley, T. R. Krause and J. P. Kopasz, "Perovskite Catalysts for Producing Hydrogen Using Gasoline Fuel," Presented at the 2003 American Ceramic Society Annual Meeting, Nashville, TN, April 28-30, 2003.

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Development of Novel Water-Gas-Shift Membrane Reactor

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Objectives

- Synthesize and characterize CO_2-selective membranes for the novel water-gas-shift (WGS) membrane reactor.
- Use the membrane data obtained in the mathematical model developed to show the feasibility of achieving H_2 enhancement via CO_2 removal and CO reduction to 10 ppm or lower and to elucidate the effects of system parameters on the reactor from the modeling study.
- Develop the membrane reactor for achieving H_2 enhancement and <10 ppm CO.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- L. Hydrogen Purification/Carbon Monoxide Cleanup

Approach

- Synthesize and characterize CO_2-selective membranes containing amino groups.
- Use the membrane data obtained in the modeling work to study membrane reactor performance and to guide/minimize experimental work.
- Incorporate the membrane synthesized in the reactor to demonstrate H_2 enhancement via CO_2 removal and CO reduction to 10 ppm or lower.

Accomplishments

- Synthesized membranes with high CO_2 permeabilities and high CO_2/H_2 and CO_2/CO selectivities.
- Elucidated the effects of system parameters including CO_2/H_2 selectivity on the membrane reactor for synthesis gases from autothermal reforming.
- Showed the feasibility of achieving H_2 enhancement via CO_2 removal, CO reduction to $\leq$10 ppm, and high H_2 recovery based on the modeling study using the membrane data obtained.
- Obtained <10 ppm CO in the H_2 product in initial WGS membrane reactor experiments using the synthesis gas feed with 1% CO.

Future Directions

- Continue to synthesize and characterize improved membranes for the reactor.
- Complete the proof-of-concept demonstration using the lab membrane reactor.
- Conduct the prototype membrane reactor demonstration for a fuel cell.

Introduction

A water-gas-shift (WGS) reactor for the conversion of carbon monoxide (CO) and water to hydrogen (H_2) and carbon dioxide (CO_2) is widely used in chemical and petroleum industries. The reactor is also critically needed for the conversion of fuels, including gasoline, diesel, methanol, ethanol, natural gas, and coal, to H_2 for fuel cells. Since the WGS reaction is reversible, it is not efficient, resulting in a high concentration of unconverted CO (~ 1%) in the H_2 product and a bulky, heavy reactor. This reaction can be enhanced significantly through a CO_2-selective membrane, which removes the reaction product, CO_2, to beat the reaction equilibrium and shift the reaction towards the product side. The CO_2-selective WGS membrane reactor has advantages including (1) a high-purity H_2 product is recovered at the high pressure (feed gas pressure) and (2) air can be used as the sweep gas to remove the permeate, CO_2, on the low-pressure side of the membrane to have a high driving force for the separation. These advantages are especially important for fuel cell vehicles. The first advantage eliminates the need for an unwanted compressor. With the second advantage, the high driving force created by the air sweep can result in low CO concentration and high H_2 purity and recovery.

Approach

We have synthesized novel CO_2-selective membranes by incorporating amino groups in polymer networks. The membranes synthesized were characterized in a gas permeation unit to determine their CO_2 permeabilities and CO_2/H_2 and CO_2/CO selectivities. We have used the selectivity and flux data obtained as the input to the mathematical model developed [1] to show the feasibility of achieving H_2 enhancement, CO reduction to $\leq$10 ppm, and high H_2 recovery; to study the effects of system parameters on the reactor; and to guide/minimize experimental work. In the model, the low-temperature WGS reaction kinetics for the commercial catalyst ($Cu/ZnO/Al_2O_3$) reported by Moe [2] and others [3] was used. In addition, we have incorporated the membrane synthesized in the laboratory WGS membrane reactor to show CO reduction to 10 ppm or lower in the H_2 product in initial reactor experiments using the synthesis gas feed with 1% CO.

Results

Synthesis and Characterization of Novel CO_2-Selective Membranes. Figure 1 shows the CO_2 permeability and CO_2/H_2 selectivity results as a function of temperature from 100°C to 180°C for the feed gas pressure of 2.1 atm and the sweep gas (air or nitrogen) of atmospheric pressure. As shown in this figure, the CO_2 permeability was about 4000 Barrers [1 Barrer = 10^{-10} cm^3(STP)-cm/cm^2-s-cmHg] or higher for the temperatures ranging from 100°C to 150°C. However, the permeability decreased to about 2000 Barrers as the temperature increased to 180°C. This was due to the reduction of water retention in the membrane as the temperature

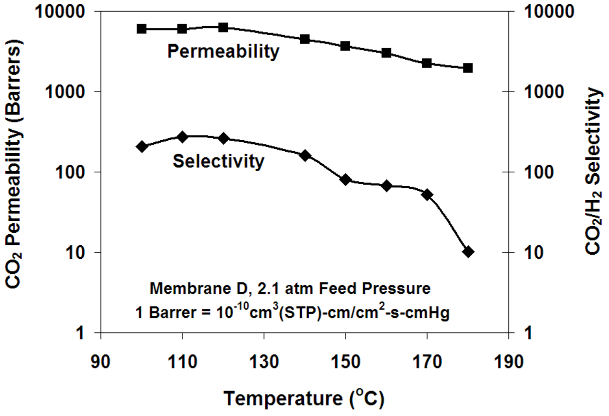

Figure 1. CO_2 Permeability and CO_2/H_2 Selectivity Results as a Function of Temperature

increased. Also shown in this figure, the CO_2/H_2 selectivity was about 100 or higher for the temperatures ranging from 100°C to 150°C. However, the selectivity decreased slightly as the temperature increased to 170°C. This was a result of the CO_2 permeability decrease due to the reduction of water retention in the membrane as described above. At 180°C, the selectivity decreased significantly to slightly greater than 10 due to the significant swelling of this membrane at this high temperature. Nonetheless, the selectivity of 10 is still good enough to give a high H_2 recovery of about 90%, which will be described in the following modeling work.

Figure 2 gives the CO_2 permeability results as a function of feed pressure from about 2 atm to about 4 atm at 150°C. As shown in this figure, the permeability did not change significantly with the feed pressure.

Figure 3 shows the CO_2/CO selectivity results as a function of temperature from 100°C to 160°C for the feed gas pressure of 2.1 atm. The CO_2/CO selectivity results were greater than 215, which is very good. However, the selectivity decreased as the temperature increased. This was a result of the CO_2 permeability decrease due to the reduction of water retention in the membrane as described above.

Modeling of Membrane Reactor Using Membrane Data Obtained. The CO_2/H_2 selectivity of 40 and the CO_2 permeability of 4000 Barrers were used in the modeling work. We have investigated the performance of the countercurrent membrane reactor for the synthesis gases from the autothermal reforming of gasoline with air. The three synthesis gases investigated at 3 atm contained CO at concentrations of 10%, 5%, and 1%. Figure 4 illustrates the profiles of the CO concentration in the H_2 product for a total reactor length of 61 cm for these three feed CO concentrations. As shown in this figure, a H_2 product with less than 10 ppm CO was obtained from each of these synthesis gases. In the membrane reactor, for each of these synthesis gases, the syngas flow with an inlet temperature of 140°C was countercurrent to the flow of hot air sweep with an inlet temperature of 140°C, the molar flow rate ratio of the air sweep to the syngas (γ) was 1.5, and

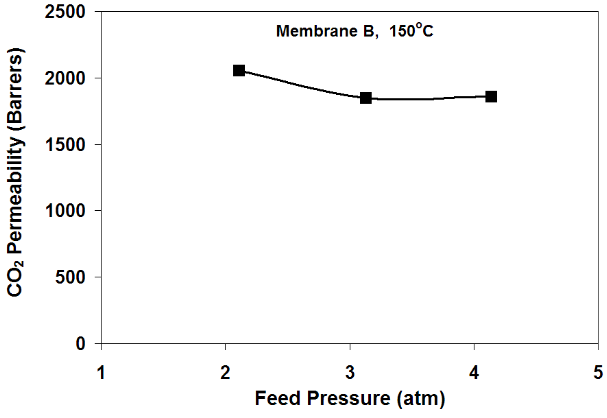

Figure 2. CO_2 Permeability Results as a Function of Feed Pressure at 150°C

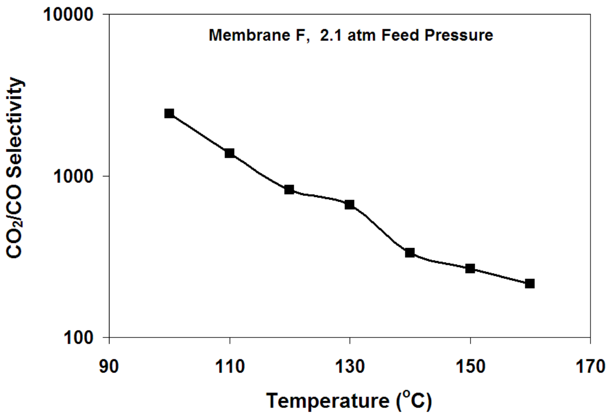

Figure 3. CO_2/CO Selectivity Results as a Function of Temperature

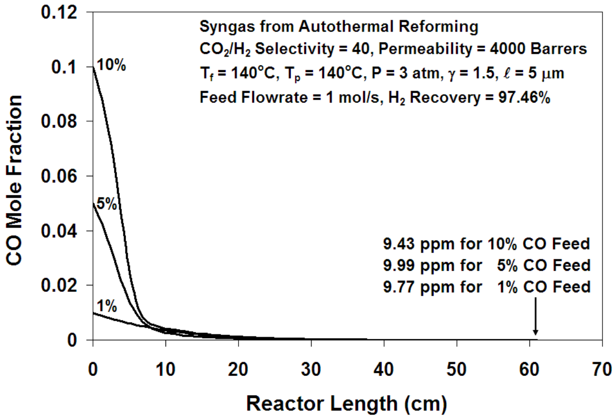

Figure 4. Profiles of Carbon Monoxide Mole Fractions in the Hydrogen Products along the Membrane Reactors for 10%, 5%, and 1% CO Feed Gases

the catalyst was the commercial Cu/ZnO supported on alumina.

For each of these synthesis gases, significant H_2 enhancement was achieved via CO_2 removal. For example, the H_2 concentration was increased from 41% in the inlet 1% CO feed gas to 48.5% in the outlet H_2 product on the wet basis (from 45.3% to 53.6% on the dry basis). Similar significant H_2 enhancement was also achieved for the 5% and 10% CO feed gases. In addition, a high H_2 recovery of greater than 97.4% was obtained for these synthesis gases, as indicated in Figure 4.

We have also investigated the effects of CO_2/H_2 selectivity on exit CO concentration and H_2 recovery for these synthesis gases through the modeling. For the CO_2/H_2 selectivity ranging from 10 to 80, the exit CO concentration of less than 10 ppm was achievable. A lower selectivity actually resulted in a slightly lower exit CO concentration as a lower selectivity (higher H_2 loss) enhanced the WGS reaction. However, the selectivity had a significant effect on H_2 recovery as depicted in Figure 5 for the 1% CO feed gas. A selectivity of 10 gave a H_2 recovery of about 90%, which is still quite good. As the selectivity increased, the H_2 recovery increased significantly. At the selectivity of 40, the H_2 recovery was greater than 97.4%, as mentioned earlier. For the selectivity of 60 or greater, the H_2 recovery was greater than 98.3%.

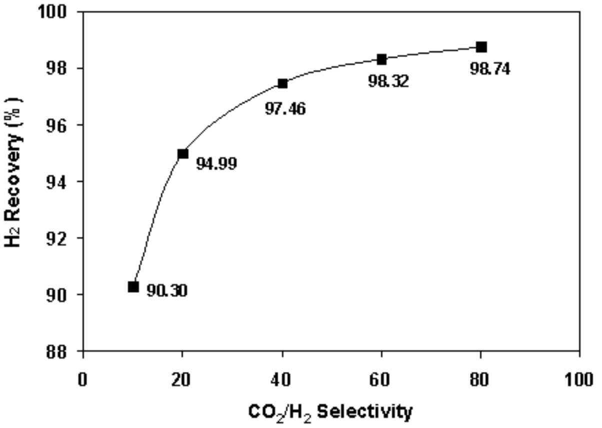

Figure 5. Effect of CO_2/H_2 Selectivity on H_2 Recovery for 1% CO Feed Gas

Initial Membrane Reactor Experiments. We began to incorporate the membrane synthesized in the laboratory WGS membrane reactor to conduct the proof-of-concept demonstration. In initial membrane reactor experiments, the commercial Cu/ZnO catalyst supported on alumina was placed on the top of the membrane, the operating temperature was 150°C, and the synthesis gas (from autothermal reforming) containing 1% CO was used. The rationale for using this synthesis gas was that it could be readily made from the commercial WGS reactor. In the initial membrane reactor experiments, a CO concentration of 10 ppm or lower in the H_2 product was obtained. This membrane reactor work is in progress.

Conclusions

We have synthesized membranes with high CO_2 permeabilities and high CO_2/H_2 and CO_2/CO selectivities. The membranes showed a high CO_2 permeability of about 4000 Barrers, a high CO_2/H_2 selectivity of greater than 40, and a high CO_2/CO selectivity of greater than 215 at 100 – 150°C. These membranes could be operated to about 180°C. Based on the modeling study using the membrane data obtained, we showed the feasibility of achieving H_2 enhancement via CO_2 removal, CO reduction to ≤ 10 ppm, and high H_2 recovery. In addition, we obtained <10 ppm CO in the H_2 product in initial WGS membrane reactor experiments using the synthesis gas feed with 1% CO.

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5. W. S. W. Ho, "Engineering Membranes for Environmental and Energy Applications", Invited Talk at University of California, Riverside, CA, December 6, 2002.

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Patent Pending

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On-Board Vehicle, Cost Effective Hydrogen Enhancement Technology for Transportation PEM Fuel Cells

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Subcontractors:
UTC Fuel Cells, South Windsor, Connecticut
HydrogenSource, South Windsor, Connecticut

Objectives

Develop technology based on an integrated water gas shift (WGS) reactor/Pd membrane H_2 separator for a fuel processor that is capable of producing on-board high purity hydrogen for 50 kWe gasoline-based proton exchange membrane (PEM) fuel cell transportation power plants. This fuel processor design should satisfy DOE’s 2005 technical targets for system efficiency, volume, weight, cost, life, start-up time, transient response time and emissions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Startup/Transient Operation
- N. Cost

Approach

- Develop a WGS/H_2 separator reactor design integrated into a 50 KWe gasoline-based fuel processing system (FPS) and assess FPS and overall PEM fuel cell (FC) system performance using proprietary, physics-based, validated reactor mathematical models and system level mathematical models.
- Perform trade studies between differential operating pressure, inlet temperature, number of tubes, tube diameter, length and Pd effective layer thickness for the Pd membrane modules to identify optimum reactor design and operating conditions for maximum H_2 recovery efficiency and minimum reactor size/cost.
- Use the models to analyze different reactor and system designs and integration schemes to identify best system efficiency and minimum size/cost.
- Synthesize and assess performance (H_2 permeance, selectivity) of advanced, thin, low cost, long-life, Pd-based, supported (on porous metal supports) membranes.
- Test best Pd membranes under WGS conditions and assess their performance as a function of operating time and number of start up/shut down events (future task).

Accomplishments

- Identified, through reactor models, optimum WGS reactor configuration and operating conditions. H_2 recovery efficiencies up to 96% demonstrated for a membrane reactor operating pressure not higher than 6 atm. Identified best FPS design and Pd membrane reactor integration scheme.
- Demonstrated, through system level models, that a PEM FC power plant with a Pd membrane-based FPS could achieve ~6 points higher efficiency than the conventional system that does not employ a Pd membrane WGS reactor.
- Demonstrated, through system level models, that the FC power plant is in water balance with a ~20% smaller size Energy Recovery Device (ERD) and ~10% smaller radiator and accumulator sizes relative to the baseline power plant.
- Estimated an FPS volume of 1140 W/L, weight of 1100 W/kg, start-up time of <1 minute for 50% of full rated power, transient response time of ~5 seconds and cost of $16/kWe+0.4x (Cost of Baseline FPS).
- Synthesized, by electroless plating and appropriate surface treatment conditions, a ~15 micron, “defect-free” Pd membrane over a porous metal support with H_2 permeance of ~15 m^3/m^2-hr-$atm^{0.5}$ and H_2/N_2 selectivity of 1,100 at 350°C. No membrane performance deterioration was observed in 250 hours of testing and under 10 thermal cycles. Identified the critical characteristics of the porous metal supports for robust and thinner (< 5 microns) Pd membranes.

Future Directions

- Assess capability for Pd deposition on the internal tube surface by electroless plating.
- Obtain porous metal supports with narrower pore size distribution and lower surface roughness on the surface where the Pd phase will be deposited.
- Down select Pd membrane manufacturing process from the critical evaluation of two candidates (electroless plating and UTRC proprietary process).
- Synthesize and characterize low thickness (<5 microns), “defect-free”, Pd-Ag alloy membranes with H_2 permeance and selectivity targets of 30-45 m^3/m^2-hr-$atm^{0.5}$ and 2,000 at 350°C, respectively by optimizing porous metal supports.
- Evaluate membrane performance (H_2 permeance and selectivity) and percent H_2 recovery under first stage WGS reformate test conditions.
- Evaluate best membrane performance under an aggressive number of thermal cycling tests (~100 cycles).
- Develop mathematical models from lab-scale tests that predict performance of the reactor under specified life (4,000 hrs for automotive) and start up/shut down events (1,000 for automotive) targets.
- Design, build and test an integrated WGS Pd membrane reactor hardware prototype.

Results

Figure 1 highlights the significant fuel processing system (FPS) simplification that can be achieved with an integrated WGS Pd membrane reactor by comparing this system (Figure 1b) to the conventional one (Figure 1a). Figure 2 (plots (A) through (C)) illustrates some of the trade studies performed to access the optimum WGS Pd membrane reactor operating conditions. H_2 concentration profiles were generated as a function of the reactor length in the high pressure tube side (where the WGS catalyst is located) and in the ambient pressure shell side (where the separated H_2 product and the steam sweep gas flows) to access the changes of the differential H_2 partial pressure

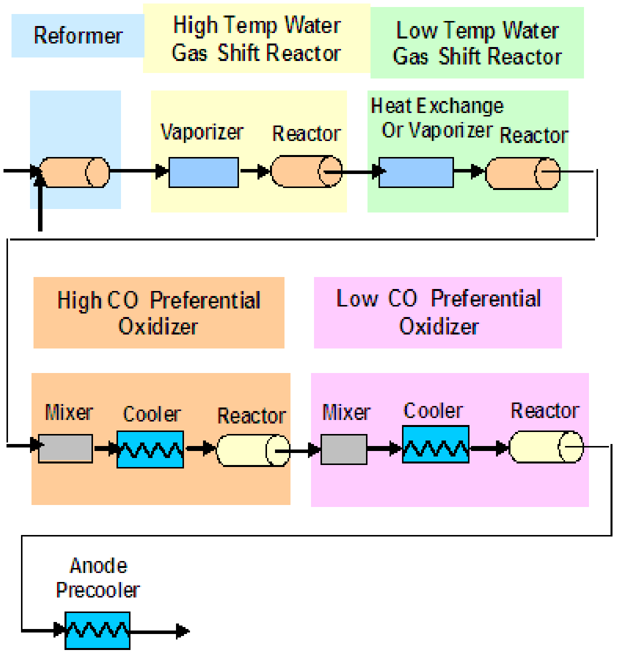

Figure 1A. Schematic of a Conventional Fuel Processing System

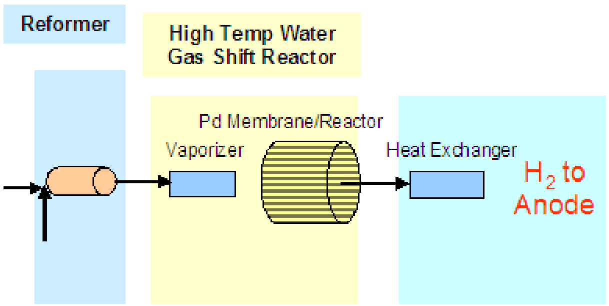

Figure 1B. Schematic of a Pd Membrane-Based Fuel Processing System

(process driving force). It was determined that the amount of WGS catalyst does not account for more than one third of the required reactor volume, while the reactor volume and H_2 separation efficiency depend on the differential operating pressure, membrane thickness, and number and length of membrane tubes. A multi-criteria type of optimization approach was applied to identify the optimum FC system efficiency for a specified operating inlet pressure in the membrane reactor (6 atm). For this system that employs a compressor/expander in order to improve system mechanical efficiency and reduce parasitic power, it was found that with a 7 liter membrane reactor, ~31% FC system efficiency is possible with a ~67% FPS efficiency. The membrane reactor was operated at 85% H_2 recovery efficiency. The results of this simulation are summarized in Figure 3 and imply that a maximum FC power plant efficiency does not necessarily imply a maximum FPS efficiency. However, we recommend this design, since the overall FC system efficiency rather than the FPS efficiency should be maximized. The effective Pd thickness for the Pd membrane reactor that was used in this simulation was ~4 microns, resulting in a H_2 permeance of ~45 $m^3/m^2\text{-hr-atm}^{0.5}$ at 350°C.

Table 1. FPS System Characteristics

Metric	DOE Target	Conventional System	Pd Membrane System
FPS Efficiency	78%	67%	67%*
FPS Power Density (W/L)	> 700	570	1140
FPS Power Density (W/kg)	> 700	550	1100
FPS Cost ($/kWe)	25	C	0.4xC+16
FPS Start Up Time (min)	< 1 min for 33% Full Power (FP)	~3 min for < 50% FP (non optimized)	< 1 min for 50% FP
FPS 10%-90% Transient Response Time	> 5 sec	N/A	~5 sec
PEM FC System Efficiency	N/A	~25%	30.80%

* 77.7% FPS Efficiency can be achieved, but with lower overall PEM FC efficiency

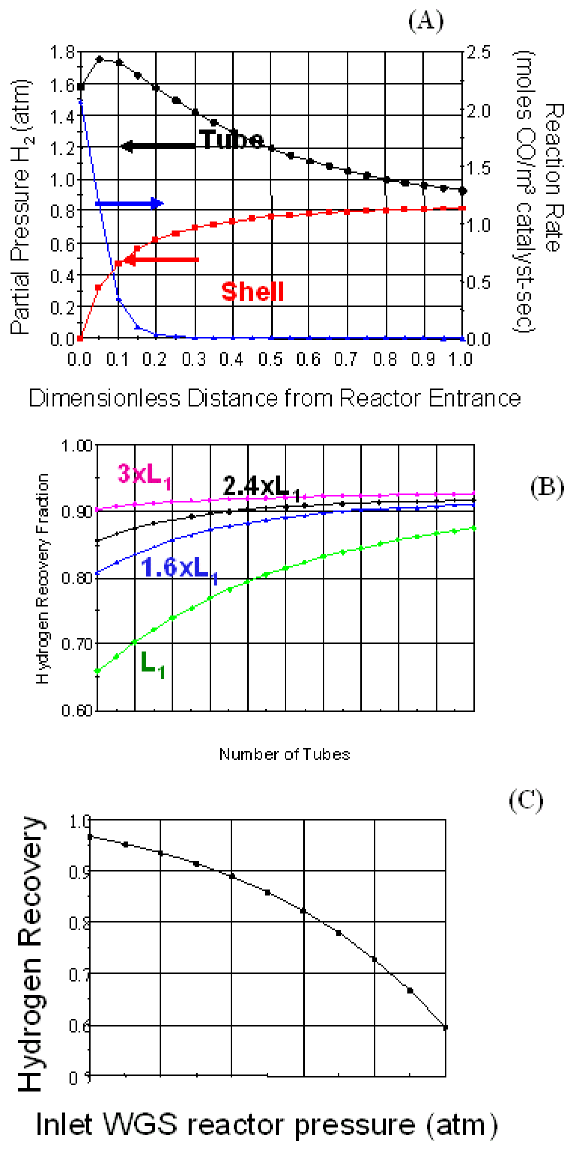

Figure 2. Impact of Operating and Physical Parameters on Performance of the WGS Pd Membrane Reactor

The simulation results for system start-up, shown in Figure 4, illustrate a less than one minute start up time for the FPS for 50% of the full rated power and <5 sec transient response time. This achievement is significant and is due to the elimination of a large number of components from the FPS. In addition, the FPS provides the cells stack with ~100% purity H_2 right from the start. The estimated FPS performance characteristics in comparison to DOE targets are shown in Table 1. As this table illustrates, the proposed system design promises excellent progress towards the desirable system targets.

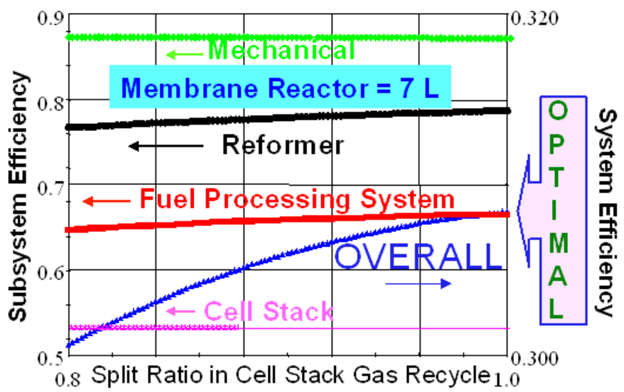

Figure 3. Subsystem and Overall PEM FC System Efficiencies

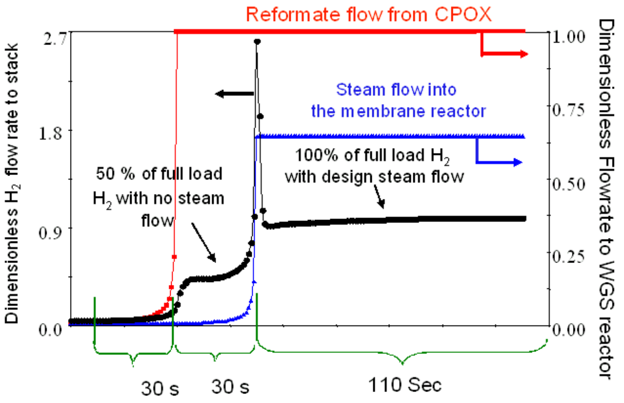

Figure 4. Model Simulation Shows that the Pd Membrane-Based FPS Achieves 50% Power within ~30 Seconds (CPOX = catalytic partial oxidation)

Conclusions

- The FPS design incorporating an integrated WGS Pd membrane reactor satisfies DOE's efficiency, size, start up and transient response targets. Furthermore, the predicted FC power plant efficiency is ~6 points higher than the current system design.
- This design will reduce balance-of-plant volume and cost (ERD, radiator, accumulator), while the significantly simplified system will be easier to control under transients.

- Surface treatment approaches and required support characteristics have been identified that will yield high performance membranes.

FY 2003 Publications/Presentations

1. Mallika Gummalla, Benoît Olsommer, Nikunj Gupta, and Zissis Dardas. "Physics-Based Simulations of Water Gas Shift Membrane Reactor for Prediction Reactor Volume and Performance", Presentation, Abstract, and Presentation Record, American Institute of Chemical Engineers, 2003 Spring Meeting, Fuel Processing Session II, New Orleans, LA, March 2003

Plate-Based Fuel Processing System

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Objectives

- Develop reactor designs and catalyst systems for the direct steam reforming of gasoline to a hydrogen-containing stream adequate for a proton exchange membrane (PEM) fuel cell.
- Develop computer simulation models of these systems to predict and optimize performance.
- Develop and test prototype reactors in a 1 to 10 kW(e) size range and demonstrate DOE target performance, especially fast startup and load change.
- Demonstrate integrated fuel processor system operation.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Startup/Transient Operation
- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration
- N. Cost

Approach

- Develop conceptual plate reactor designs for steam reforming, water gas shift and preferential CO oxidation. Assemble detailed computer simulation models for these designs.
- Develop catalyst washcoat compositions with the required activity, selectivity and initial durability consistent with the catalyst performance requirements specified by the simulations. As required, measure detailed reaction kinetics for these catalyst compositions.
- Design and fabricate prototype plate reactor mechanical designs in the 1 to 10 kW(e) size range.
- Demonstrate plate reactor performance including startup, transient operation, efficiency and other performance factors.

Accomplishments

- Completed structural analysis of plate reactor system and established design criteria for required cyclic durability (startup and transient) and developed prototyping strategy for an initial laboratory demonstration directed at transient and efficiency criteria. Proceeding with multiple parallel paths with future down-select to one or two final prototype units for demonstration.

- Developed and demonstrated a steam reforming catalyst with the required performance using the Argonne National Laboratory (ANL) Benchmark Fuel I with 10 ppm sulfur. Global kinetics have been measured for use in the plate reactor simulation model.
- Developed a base metal, non-pyrophoric water gas shift catalyst that is air stable and does not require pre-reduction. Demonstrated stability to 500 hours and activity meeting the DOE target performance.
- Developed a preferential CO oxidation catalyst that can achieve the required reactor performance for a plate configuration operating at 150°C. Demonstrated stability to 800 hours.

Future Directions

- Using measured kinetics for the best catalysts, complete simulation modeling for the target steam reforming plate reactor system. Complete prototype plate reactor designs for this reactor and fabricate at least one and possibly two prototype designs at the 1 to 10 kW(e) size for demonstration testing. Modify test rig facilities to accommodate the prototype units to accomplish testing including startup and transient operation over the required load range. Demonstrate startup to full load in less then 60 seconds and, if possible, less then 30 seconds, and demonstrate rapid transient load variation.
- Develop computer simulation models of the water gas shift reactor and preferential CO oxidation reactor designs using measured kinetics and design results from reformer prototype tests. Develop prototype plate reactor designs for these processes and fabricate prototype hardware for demonstration testing.
- Develop a transient simulation to demonstrate full fuel processor startup and transient operation consistent with DOE targets.

Introduction

The major obstacles to on-board reforming of liquid fuels to provide hydrogen for fuel cell applications are 1) time required for startup from a cold start; 2) ability to handle fast output transients; and 3) general complexity, size, weight and cost. These obstacles are being addressed in a number of DOE projects through development, integration and optimization of existing fuel processing system designs. This project is directed at investigating and developing plate reactor concepts where the catalytic function is integrated into a primary surface heat exchanger. The catalyst is coated onto the surface of a thin walled plate heat exchanger. For example, in the case of the steam reforming reactor, a reforming catalyst driving the endothermic reaction is coated on one side of the thin plate and a catalytic oxidation catalyst is coated onto the other side to drive the exothermic reaction, with the heat transferred efficiently between these catalysts by the thin metal plate. These structures can provide fast transient operation, compact reactors, very good temperature control and optimized operation. This project is directed at developing and demonstrating these reactor systems for processing gasoline to PEM-quality hydrogen.

Approach

The development of plate reactor designs for conversion of gasoline to hydrogen requires the integration of the detailed reactor design with details of the catalyst performance. To integrate all of these aspects and optimize the design, this project makes extensive use of reactor modeling that includes all important aspects of the system, e.g. convective gas flow, diffusion, catalyst layer structure, heat transfer throughout the structure and detailed kinetics of the catalytic reaction. Since in many cases reaction kinetics are not available, initial work was directed at developing catalyst materials with activity in the desired range that could be applied as a thin washcoat layer onto the plate surface. The kinetics of the catalytic reaction were then measured in sufficient detail to allow adequate modeling of the plate reactor design using in-house developed computer codes for each reactor design. In many cases, improved catalysts were required and were developed.

The resulting target reactor design and catalyst system were then used to develop mechanical designs for a plate reactor to be used in laboratory demonstration at the 1 to 10 kW(e) size. Some early work was directed at understanding the effect of rapid temperature transients (startup, shutdown and loading) on the plate reactor design, and design aspects were identified that would lead to good cyclic life, particularly for the steam reformer reactor where the temperature transients are most severe.

Results

Steam Reforming: The defined approach is to directly steam reform gasoline in a plate reactor configuration using combustion on the opposite side of the plate to provide the endothermic heat of reaction. A catalyst has been developed that shows good activity and stability. Some test results are shown in Figure 1. Test conditions were:

- Temperature: 825°C, Pressure: 3.0 atm
- Space velocity (SV): 21.0 g fuel per g catalyst-hour
- Steam to carbon ratio: 3.8
- Fuel: ANL Benchmark Fuel I with 10 ppm sulfur
- Tube wall coated test reactor that simulates the required flow conditions, catalyst washcoat layer and catalyst temperature

While pressure variation causes some fluctuations in the H_2 yield, the catalyst performance is relatively stable. The amount of catalyst required for a 50-kW(e) reactor is 0.42 kg, assuming the catalyst activity is stable at this performance level. Measurements are in progress to obtain a global kinetic expression for use in developing a detailed simulation of the plate reformer system. This catalyst will be incorporated into the demonstration prototype plate reformer described later.

Water Gas Shift Reactor: Catalytica Energy Systems Inc. (CESI) has developed an improved water gas shift catalyst (WGS) formulation with highly desirable characteristics such as 1) no pre-conditioning requirement, 2) no air sensitivity, 3) non-precious metal based, and 4) low sensitivity to condensed water. This catalyst has shown good durability (Figure 2) in reactor runs up to 500 hours. For this level of activity, 5 kg of catalyst would be required for a 50-kW(e) fuel processor, which meets the DOE WGS catalyst performance targets.

Durability data for WGS catalysts is very important due to the high sensitivity of this system to thermal degradation and past experience that durability is highly dependent on composition and operating conditions. For this reason, a static aging system is being developed to age the catalyst materials for long times, e.g. up to the target durability of 5000 hours, with minimum effort and cost. The strategy is to age a large batch of the target material at conditions that simulate water gas shift

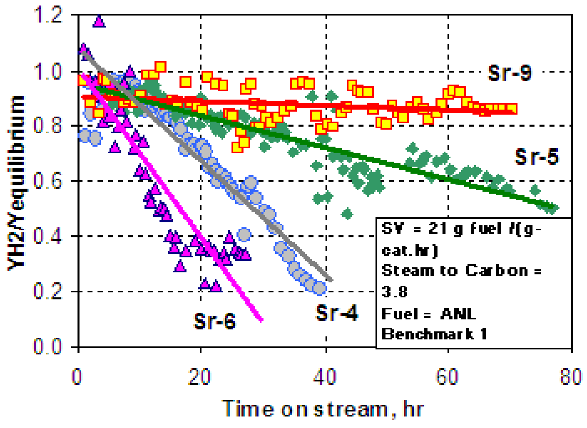

Figure 1. Steam Reforming of ANL Benchmark Fuel I with 10 ppm Sulfur on 4 Different Catalyst Materials under Plate Reactor Conditions

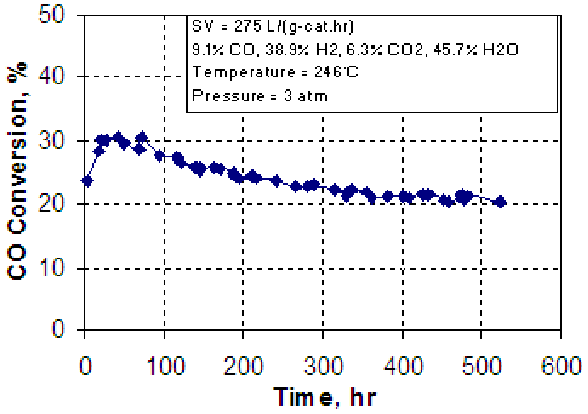

Figure 2. Water Gas Shift Reaction Durability Run with Base Metal Catalyst

reactor operation and periodically remove samples for characterization and activity testing. CESI has shown this to be a cost effective strategy for obtaining catalyst durability data. Work is currently in progress to validate this system by comparison of static aged catalyst materials with materials aged in the laboratory bench-scale test reactor as presented in Figure 1. New catalyst compositions will be similarly aged to determine long-term durability.

Detailed kinetics have been measured for these stable base metal water gas shift catalysts, and these data are being used to model plate reactor designs for optimum operation. As an example, the plate reactor configuration using countercurrent air as the temperature control media with the catalyst materials developed in this program provides greater then 90% CO conversion with a typical steam reformer outlet composition and a catalyst loading of 3 kg, as shown in Figure 3. While this shows the potential performance of such a system, catalysts with durability at higher temperatures (340 to 380°C) must be developed.

Preferential Oxidation: The plate reactor approach allows the close control of catalyst temperature during reaction. This is especially important for the preferential oxidation of CO, where the selectivity of the reaction is highly temperature dependent. Testing with a packed bed reactor was unsuccessful due to this temperature dependence, and work was shifted to a wall coated test reactor design where the catalyst temperature could be controlled. Preliminary catalyst development is complete, and kinetics have been obtained over a wide range of operating conditions. Durability test results are shown in Figure 4, where a fresh catalyst and an aged catalyst are compared. The catalyst was aged by operation in preferential oxidation reaction, including kinetic measurements and long-term runs at conditions simulating low load to high load and low conversion to high conversion. Test conditions are:

- Inlet gas composition: 1% CO, 1% O_2, 64% H_2, 18% H_2O, 16% CO_2
- Gas space velocity: 118 liters/gcat-hr

The performance of the aged catalyst is essentially identical to the fresh material. One unusual aspect of this catalyst is the observation that the selectivity for oxidation of CO compared to oxidation of H_2 was observed to vary from 50 to 60% over most conditions. The amount of catalyst required for a 50-kW(e) preferential oxidation reactor in the plate configuration is about 600 g when operated at 150°C and achieving 20 ppm CO in the outlet gas stream.

Demonstration Prototype Plate Reformer: One of the major issues in the design of a plate reactor

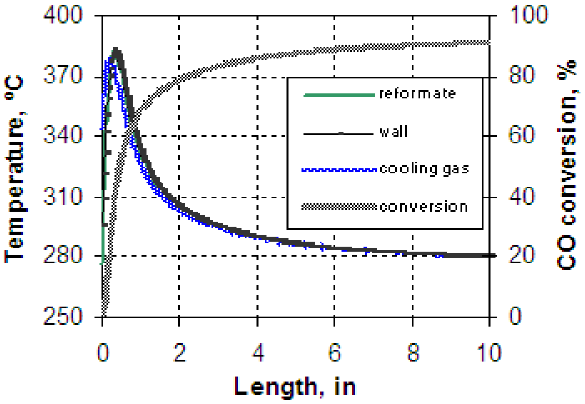

Figure 3. Model simulation of water gas shift plate reactor design with countercurrent cooling gas flow. CO conversion of 90% achieved with 3 kg of catalyst if activity can be maintained over these conditions.

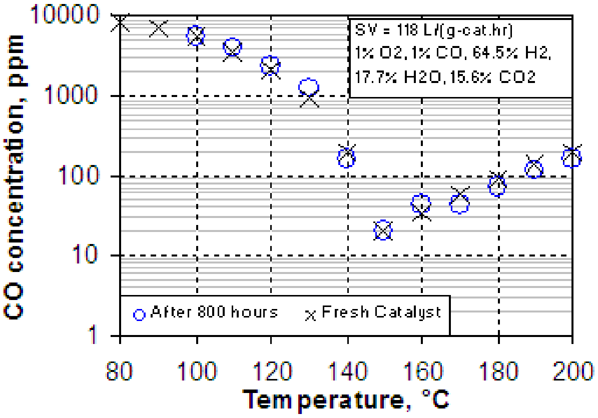

Figure 4. Catalyst durability demonstration for the preferential oxidation of CO. CO conversion as temperature was varied from 80 to 200°C for a fresh and 800 hour aged catalyst. No catalyst deactivation was observed.

system is the high stress level arising from the startup and transient cycles that produce large temperature transients and large thermal gradients. Previously reported work described extensive finite element structural analysis of the plate reactor concept and examined numerous reactor design approaches. A design approach was developed that resulted in a calculated maximum strain of 0.28%, close to the target value that would provide the required cyclic fatigue life for the rapid thermal transients occurring during startup and load following. This design approach was used to develop three approaches to a prototype reactor mechanical design for fabrication and demonstration testing. Typical design aspects of the prototype will be:

- Primary surface plate thickness: 0.15 mm
- Catalyst washcoat layer thickness: 20 to 50 microns
- Gas flow channel dimensions: 0.6 to 1.5 mm diameter by 100 mm

The manifolds supplying the feed (fuel and air to the combustion side, fuel and steam to the reformer side) are sized to ensure uniform distribution (within 4%) of the feed to all of the plates. The plates and manifold are assembled in a manner to minimize thermally induced stresses.

The new design is being taken to prototype fabrication through 3 parallel approaches: (1) using pre-existing heat-exchanger plates that provide most of the required functionality, (2) using soft-tooled plate stamping to produce an a priori design and (3) using a fin-folding technique to produce a design derived from gas turbine heat exchangers that show good transient performance. At least one but most likely two of the fabrication approaches will be selected to produce a prototype unit in the 1 to 10 kW(e) range for demonstration testing.

Conclusions

- Computer simulation has demonstrated that plate reactor designs provide very efficient reactor performance for steam reforming, water gas shift and preferential CO oxidation arising from the ability to control the catalyst temperature to a desired range.
- Catalyst systems have been developed that can be applied as a washcoat onto heat exchange surfaces and can provide the required performance for plate reactor fuel processor systems.
- Direct steam reforming of gasoline with 10 ppm sulfur has been demonstrated. The gasoline plate reformer would be the first reactor in a fuel processor, and a design approach has been developed to demonstrate startup including fast startup and transient operation. Design and fabrication of prototype plate reactors is in progress.

FY 2003 Publications/Presentations

1. J. M. Zalc, H. Liu, R. Dalla Betta; "System Integration Issues for a Plate Reactor-Based Automotive Fuel Processor", Am. Institute of Chemical Engineers Meeting, 8 November 2002, Indianapolis, IN.

2. "Plate Based Fuel Processing System", FreedomCAR Technical Team Review, 19 March 2003, Detroit, MI.

3. V. Sokolovskii, J. Zalc, D. Poojary, T. Ho, D. Taube, G. Malukhin, R. Dalla Betta; "Non-noble Metal Water-Gas Shift Catalysts for Automotive Fuel Cell Application", American Chemical Society Meeting, April 2003.

4. "Plate Based Fuel Processing System", 2003 DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Review Meeting, 19-22 May 2003, Berkeley, CA.

Quick-Starting Fuel Processors - A Feasibility Study

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Objectives

- Determine the feasibility of starting a practical fuel processor in 60 seconds or less.
- Identify technical barriers that limit the fast-start capabilities of fuel-flexible fuel processors.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Startup/Transient Operation
- M. Fuel Processor System Integration and Efficiency
- L. Hydrogen Purification/Carbon Monoxide Cleanup

Approach

- Working with multiple national laboratories, universities, and commercial organizations, design a gasoline fuel processor that can meet DOE's performance targets.
- Develop a start-up strategy that will enable the fuel processor to deliver >90% of its rated hydrogen production capacity in 60 seconds or less.
- Demonstrate start-up performance of key fuel processor components and the performance of the integrated fuel processor in laboratory tests.
- Analyze test results to evaluate performance.

Accomplishments

- Designed a laboratory-scale (10 kWe) fuel processor.
- Provided project partners with component specifications for fuel processor fabrication.
- Modeled fuel processor, demonstrating the feasibility of an 84% steady-state efficiency and a 60-sec start-up time.

Future Directions

- Demonstrate 60-sec start-up in a fuel processor that delivers 90% of rated hydrogen capacity.
- Demonstrate greater than 80% fuel processing efficiency under steady-state operation.
- Analyze data for processor performance, start-up fuel consumption, and process limitations.

Introduction

To be capable of start-and-go driving, all propulsion power components must be operational shortly after the driver turns the key. For a fuel cell vehicle with an on-board fuel processor, this means that the fuel processor must produce and deliver sufficient hydrogen to the fuel cell on this basis. This requirement is relaxed somewhat in a hybrid vehicle operated by a fuel cell and a battery, since the battery can provide initial traction power while the fuel cell system warms up to its operating temperatures.

For the on-board fuel processor, the Department of Energy has targeted start-up times of 60 seconds and 30 seconds (from ambient temperature of 25°C) for the years 2005 and 2010, respectively. Considering the significant mass of the fuel processor, some of which must be heated to several hundred degrees centigrade, the start-up process warrants attention at the early design stage. Reducing the thermal mass will reduce the energy needed (fuel consumption) during start-up, and a consistent, reproducible, and durable fuel processor that can meet the start-up time targets can be ensured through suitable heating strategies.

Approach

A subscale (10-kWe) fuel processor system will be designed, fabricated, and tested in the laboratory to demonstrate that it can convert gasoline and deliver 90% of its hydrogen production capacity in 60 seconds. The fuel processor will be designed for a steady-state fuel processing efficiency (defined as the lower heating value of hydrogen produced divided by the lower heating value of the gasoline feed) greater than 80%. The experimental unit will be thermally integrated and will include several heat exchangers and air and water injection ports.

This is a collaborative project with contributions from Los Alamos National Laboratory (LANL), Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), and a number of universities and private organizations. The fuel processor will be assembled and tested at Argonne National Laboratory (ANL).

Results

A laboratory-scale 10-kWe fuel processor has been designed to operate at an efficiency of greater than 80%. The fuel processor (see Figure 1) consists of an autothermal reformer (ATR) followed by a 4-stage water-gas shift (WGS) reactor and a 3-stage preferential oxidation (PrOx) reactor. A total of 6 heat exchangers are located in the reformate flow path to cool the reformate gases. The cooling needed before the fourth WGS stage is achieved by injecting liquid water. The higher steam concentration improves the low-temperature shift conversion. HE1, the heat exchanger between the ATR and WG1, is a microchannel heat exchanger designed and fabricated by PNNL to handle a heat load of 3.6 kW. The five other carbon foam heat exchangers are designed and fabricated by ORNL. The preferential oxidation reactor zones are designed and fabricated by LANL.

Table 1 lists some of the key design and operating parameters of the fuel processor. At the rated capacity

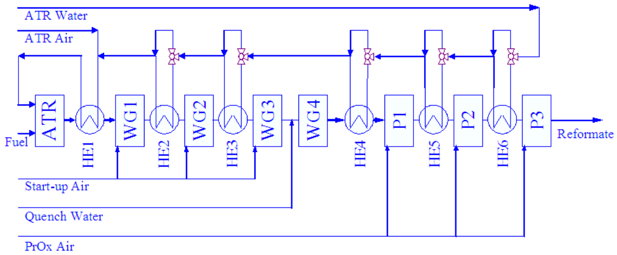

Figure 1. A Simplified Schematic of the Fuel Processor

Table 1. Design and Operating Point for the 10-kWe Fuel Processor to be Studied

	ATR	WG1	WG2	WG3	WG4	P1	P2	P3
GHSV, per hr	74K	66K	41K	22K	13K	37K	37K	37K
Inlet Temperature, °C		375	350	300	280	140	140	100
Exit Temperature, °C	775	440	367	310	287	220	188	113
O/C Ratio (at Inlet)	0.75							
S/C Ratio (at Inlet)	2.1				2.3			
H_2 at Exit, %-wet	31.8	37.5	39.1	39.9	39.7	38.7	37.7	37.5
CO at Exit, %-wet	9.7	4.0	2.5	1.6	1.0	0.3	0.1	10 ppm
H_2O at Exit, %-wet	23.9	18.1	16.6	15.8	16.9	16.9	17.2	17.2

of 10 kWe, the overall gas hourly space velocities (GHSVs) in the ATR, WGS (combined), and PrOx (combined) are 74000, 6200, and 12300 per hour, respectively. With these catalyst loadings and operating conditions, the model predicts a fuel processing efficiency of 84%. This value assumes no heat loss and that sufficient heat is available from the anode gas burner to vaporize and heat fuel vapor to 150°C and supply liquid water at 90°C.

Table 2 lists the mass of each of the catalyst zones and the heat exchangers in the 10-kWe experimental fuel processor and their respective average temperatures at the steady-state design point. Based on these masses and temperatures, the minimum fuel energy that will be needed to heat up the fuel processor components during start-up from 25°C is 1.5 MJ.

The start-up strategy relies on the ATR component reaching its operating temperature very quickly. Assuming this can be achieved by operating at a high O/C ratio [ratio of oxygen (from air) to carbon in the ATR feed stream] without damaging the catalyst, the resulting reformate (containing combustible gases H2, CO, and light hydrocarbons) will be oxidized just ahead of WG1, WG2, and WG3 by injecting controlled amounts of air, as shown in Figure 1. The start-up strategy requires that only the ATR and the first three zones of the shift reactor are brought up to temperature. The PrOx units have been sized to compensate for the higher CO (up to 4%) from the shift reactor during start-up.

Table 2. **Masses of Components in the Experimental Fuel Processor (10-kWe) and the Minimum Energy Needed to Reach Operating Temperatures**

Component	Mass, g	Average Temperature, °C
ATR	150	725
WGS-1	235	400
WGS-2	375	360
WGS-3	690	300
WGS-4	1150	285
PrOx-1	290	180
PrOx-2	290	165
PrOx-3	290	110
HE-1	1100	575
HE-2	586	395
HE-3	586	334
HE-4	943	214
HE-5	943	180
HE-6	943	144
Minimum Fuel Energy Needed per Start from 25°C, MJ		1.5

Figure 2 shows the temperature progression predicted from the simulation of a start-up algorithm. The ATR temperature reaches 800°C in less than 2 seconds, and temperatures in WG1, WG3, and P3 are close to their design temperatures in 60 seconds. The sharp rise in ATR temperature seen in this simulation is considered somewhat risky for catalyst durability. Even though the strategy does not call for heating HE1, the high-temperature reformate from the ATR does contribute to its warm-up. Figure 3 shows that the hydrogen production rate reaches ~90% of capacity within 60 seconds. Experimental measurements

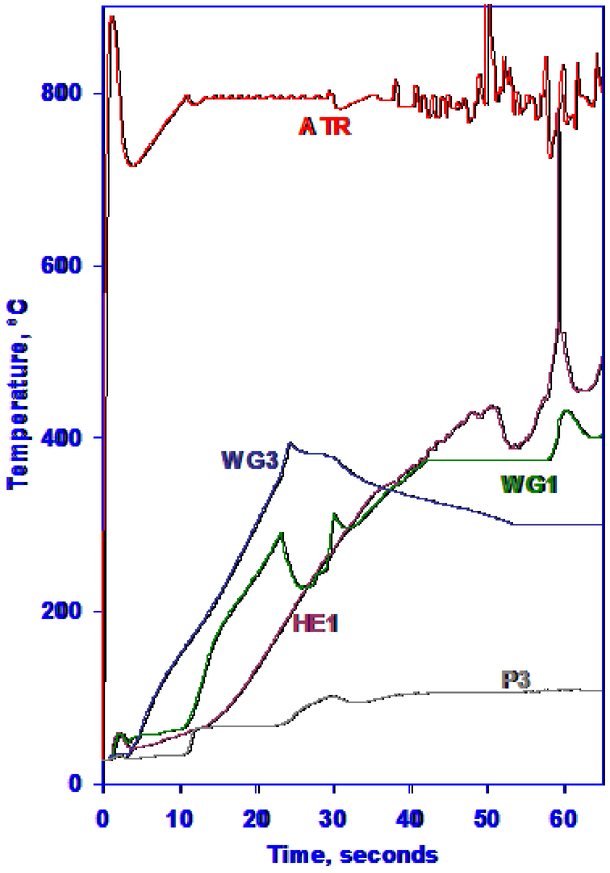

Figure 2. Simulation of a Start-Up Algorithm Showing Temperature Progression of Selected Components (at exit)

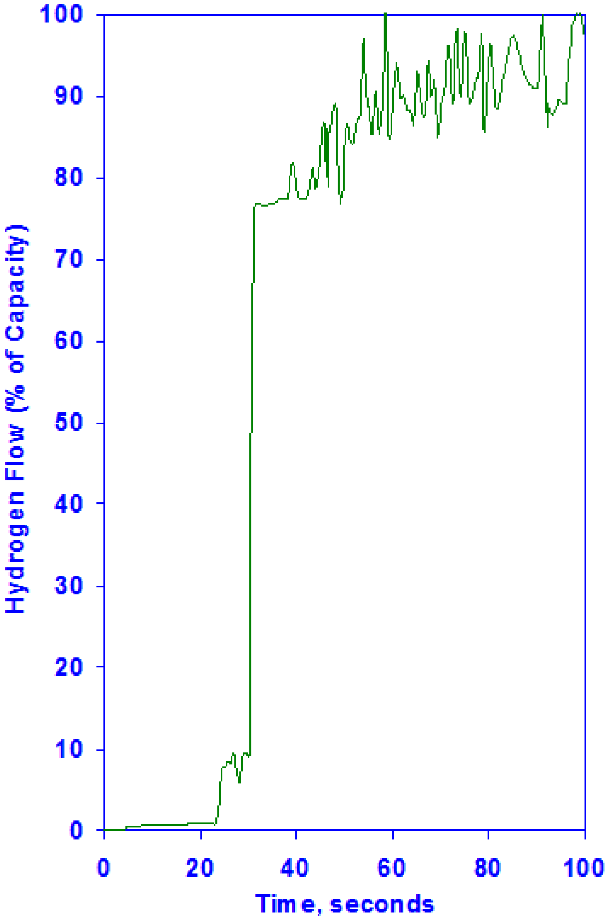

Figure 3. Simulation of a Start-Up Algorithm Showing Hydrogen Production During the Start-Up Period

will be used to develop an acceptable fast-start algorithm.

Conclusions

Argonne National Laboratory is leading a collaborative effort to study the feasibility of fast-starting a fuel processor. A fuel processor has been designed to deliver 90% of its rated capacity for hydrogen in 60 seconds. A model of the fuel processor projects that the targeted start-up goals can be met and that the fuel processor will operate at a steady-state efficiency of greater than 80%. These calculated results will be validated experimentally with the fuel processor being fabricated, and the results will be analyzed to identify technical barriers that limit the fast-start capabilities of fuel processors.

FY 2003 Publications/Presentations

1. C. Pereira, S. Ahmed, S.H.D. Lee, and M. Krumpelt, "Integrated Fuel Processor Development," 2002 Future Car Congress Proceedings, SAE Paper No. 02FCC-161, Arlington, VA (2002).

Special Recognitions & Awards/Patents Issued

1. R. Ahluwalia, S. Ahmed, and S.H.D. Lee, "Method for Fast Start of a Fuel Processor," Invention Disclosure filed with Argonne National Laboratory (2003).

2. S. Ahmed, R. Ahluwalia, and S.H.D. Lee, "Fuel Processor for Producing Hydrogen from Hydrocarbon Fuels," Invention Disclosure filed with Argonne National Laboratory (2003).

Fast Start Reformer Components

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Objectives

- Support the development of the Argonne National Laboratory (ANL) FASTER fuel processor project with the expertise developed at PNNL, ORNL, and LANL.
- Design and fabricate a highly effective recuperator with low pressure drop to recuperate incoming steam and air with autothermal reformer (ATR) reformate.
- Design and fabricate a microchannel mixer to uniformly add air to reformate ahead of the water gas shift (WGS) catalyst to accelerate heating of the WGS catalyst.
- Design and fabricate a lightweight heat exchanger that meets system constraints and operational performance requirements.
- Optimize heat exchanger assembly for insertion into the FASTER system.
- Demonstrate a heat duty of at least 1 kW with a pressure drop of <0.1 psi.
- Investigate and develop a preferential oxidation (PrOx) reactor component design for integration into the FASTER fuel processor.
- Deliver these components as part of a compact assembly for installation into the FASTER reactor system.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Start-up/Transient Operation
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration and Efficiency

Approach

- Design and fabricate a highly effective, low pressure drop recuperator.
- Design and fabricate micro-channel mixer for introducing air into reformate during startup.
- Deliver a compact recuperator/mixer assembly for installation into the FASTER experimental system.
- Design a prototype heat exchanger (HX) meeting original specifications for Tier 1; fabricate a test rig to validate HX design.
- Test prototype HX under operational constraints and measure all inlets and outlets, i.e., pressure, temperature, flow, etc.
- Analyze the data to determine heat duty as a function of water flow rate at a given inlet gas temperature.
- Identify and measure the performance of PrOx catalysts for use in a PrOx reactor component.
- Collaborate on PrOx component design and fabricate PrOx components.
- Measure PrOx component response to simulated startup conditions and events.

Accomplishments

- Design work on recuperator, mixer, and assembly complete.
- Both microchannel units are currently being diffusion bonded.
- Modeled design concept to estimate pressure drop and heat transfer of the graphite foam heat exchanger at all sizes specified by project lead, ANL.
- Designed a prototype heat exchanger approximately 3-inch inner diameter and 5-inch outer diameter with a machined channel into which a cooling jacket was press fit.
- Tested prototype and met or exceeded all specifications. Improvements in design of the prototype HX were made and a second iteration prototype was fabricated.
- Delivered all of Tier 1 heat exchangers at the end of June, 2003. Fabrication of Tier 2 heat exchangers is on schedule; anticipated delivery date is the end of July, 2003.
- Measured kinetic parameters of PrOx catalysts for reactor design.
- Investigated performance of PrOx reactor under simulated startup conditions.
- Obtained catalyst substrates for unique PrOx component design and started fabrication.

Future Directions

- Complete fabrication and deliver assembly to ANL for inclusion in FASTER prototype.
- Evaluate performance as part of the FASTER experimental effort.
- Test Tier 1 HX at higher gas inlet temperatures; measure heat duty as a function of water flow rate at higher inlet temperature(s).
- Evaluate different avenues for further reducing the weight of the graphite foam heat exchanger assembly while maintaining heat transfer and pressure drop.
- Verify design performance in multi-stage PrOx experiments.

Introduction

The major technical challenge for the development of a successful onboard fuel processor for fuel cell systems is the 2010 technical target for startup in less than 30 seconds. Overcoming this technical challenge is the objective of the FASTER (Feasibility of Acceptable Start Time Experimental Reactor) project led by Argonne National Laboratory (ANL), whose goal is to design, build, and test an experimental fuel processor to demonstrate concepts for rapid startup. The FASTER project is a collaborative effort which includes the contributions of three additional national laboratories that have developed significant expertise for the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program. Pacific Northwest National Laboratory (PNNL) has expertise in the development of microchannel heat exchanger technology for reforming components, Oak Ridge National Laboratory (ORNL) has expertise in the development of graphite foam heat exchanger technology, and Los Alamos National Laboratory (LANL) has developed preferential oxidation (PrOx) technology for the removal of carbon monoxide. The contributions of these three national laboratories are reported here.

Recuperator/Mixer Assembly - Between the outlet of the autothermal reformer (ATR) and the entrance to the water gas shift (WGS) reactor is an assembly being provided by PNNL. The assembly is designed to fit within the FASTER geometry and contains a recuperator and a mixer. The recuperator will recover heat from the ATR reformate to preheat the air and steam feed to the ATR. This cools the reformate to a temperature suitable for the WGS catalyst. The effective recovery of heat from the hot reformate allows the system to be energy efficient. The micro-channel mixer is positioned at the reformate outlet of the recuperator. During startup, it will mix air into the reformate, causing oxidation of reformate on the WGS catalyst to accelerate heating of the WGS catalyst. A uniform reformate/air mixture is required to prevent local hot or cold spots on the WGS catalyst during startup.

Graphite Foam Heat Exchangers – Within the WGS and PrOx reactors, temperature control is paramount to efficient operation. Heat exchangers (HXs) must be lightweight and capable of handling a heat duty of 1 kW at low pressure drops. These heat exchangers must meet the operational and physical constraints of the FASTER system design for effective catalysis downstream. ORNL is providing these HXs to facilitate fast start.

PrOx - The preferential oxidation (PrOx) reactor component is typically the last component of the fuel processor, and its function is to control the outlet carbon monoxide to levels below 10 ppm. LANL is using its experience in PrOx research and design to develop a PrOx reactor to enable fast start. This includes reducing the thermal mass of the catalysts and components in contact with the flow, identifying a catalyst with a low light-off temperature for CO oxidation that also maintains CO selectivity over a wide temperature range, and identifying strategies to oxidize high concentrations of CO at startup before the WGS reactors become operational. The goal is to incorporate these features into PrOx reactor components to be fabricated and delivered for assembly into the FASTER fuel processor.

Approach

Recuperator/Mixer Assembly - The micro-channel components are made by etching metal sheets, stacking them in sequence, and then sealing contacting surfaces by diffusion bonding. The recuperator and portions in contact with hot reformate are being fabricated in Inconel 600. Within the recuperator, the fluids exchange heat in a series of counterflow, laminar channels. Lower temperature components including the mixer are being fabricated in 316L stainless steel. The microchannel mixer divides the reformate and air into numerous channels, interleaves them, and then allows them to exit the downstream face of the panel. Actual mixing occurs as the flows exit the closely spaced interleaved channels. Features are included to maintain uniform mixing despite temperature differences between the fluids.

Graphite Foam Heat Exchangers - The approach to designing graphite foam heat exchangers capable of handling the heat duty and pressure drop requirements was to first use computational fluid dynamics (CFD) to model the foam under these constraints. From the model results, a corrugated design was fabricated. The model of the graphite foam capabilities was validated experimentally. Copper was chosen as the coolant jacket material due to its high bulk thermal conductivity and its ability to spread the heat in all directions, aiding in heat transfer. Initially, the inlet and outlet for the cooling water for the jacket were on the same side of the jacket. Infra-red (IR) imaging showed symmetric cooling about the jacket; however, this IR imaging also showed that the coolant two-phase flow could be improved. Thus, in the second iterative prototype, the flow is now bi-furcated, with the inlet and outlet 180° from one another (Figure 1). This should increase the two-phase flow and therefore enhance heat transfer in the assembly.

PrOx - The approach to developing a PrOx reactor component has been to first identify PrOx catalysts that have desirable characteristics for startup performance. Laboratory PrOx reactor hardware is used to measure the kinetic parameters of the catalysts under simulated steady-state operating conditions and to measure the PrOx component response to simulated startup conditions and events. Kinetic parameters are supplied to ANL for use in the fuel processor design calculations. Based on the design, catalyst substrates are obtained, catalyzed, and fabricated into the reactor components for the FASTER fuel processor.

Results

Recuperator/Mixer Assembly – The thermal performance requirements for the recuperator are shown in Figure 2. In addition, a number of spatial requirements were placed on the design to allow the assembly to connect to the ATR, match desired connection locations, and fit within the 6-inch diameter core of the FASTER reactor system. The recuperator and mixer are designed and fabrication is under way. A key feature of the recuperator is turndown performance. The recuperator is predicted to maintain >85% effectiveness as the flow is decreased from 100% of design capacity to 10% of capacity. This feature prevents excessively high reformate temperatures (which could damage the WGS catalyst) under the normal range of operating rates. The weight of the components is estimated to be ~800 g for the recuperator, ~176 g for the mixer and ~1100 g for the total assembly. The assembly to be delivered to ANL is shown in Figure 3.

Figure 1. Tier 1 Graphite Foam Heat Exchangers for FASTER

Graphite Foam Heat Exchangers - Tests indicate that the heat duty is relatively constant for a given inlet gas temperature. Further, tests reveal that heat transfer through the graphite foam may be insensitive to water flow (Figure 4). This will allow for more flexibility in the control of the overall FASTER system; it may be possible to maintain critical

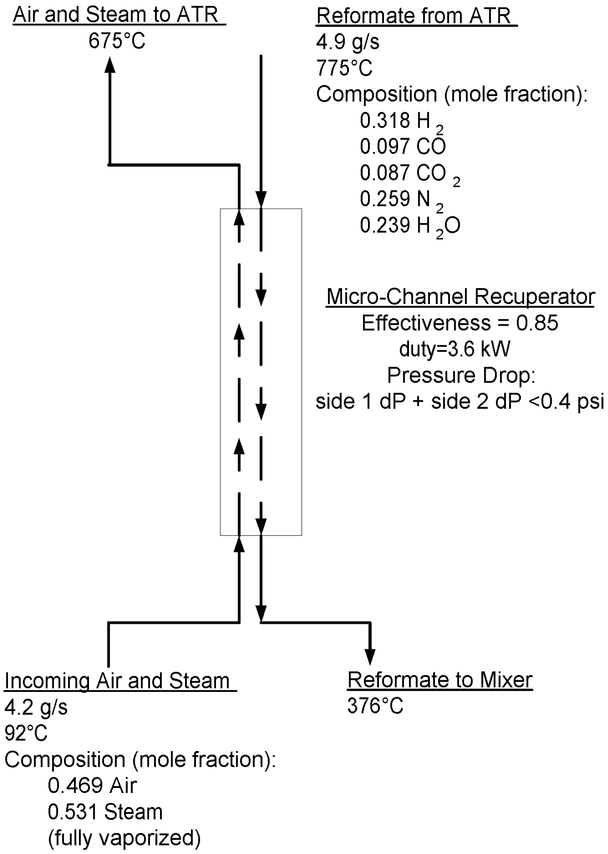

Figure 2. Design Requirements for Recuperator Thermal Performance

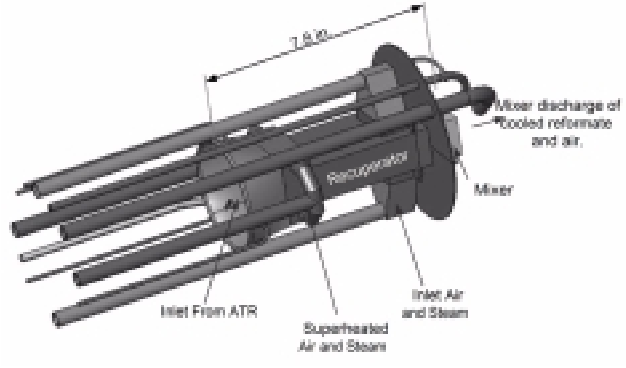

Figure 3. Recuperator/Mixer Assembly for Incorporation into FASTER ATR

temperature regimes for each catalyst while using supply water at low flow rates. Feedback may be used to more efficiently control the water flow rates to increase the overall system efficiency.

PrOx - PrOx catalysts were obtained from various manufacturers on monolith, ceramic foam, and metal foam substrates. Based on preliminary testing, a catalyst was identified with low light-off temperature and good selectivity. The performance of the catalyst was measured over the range of expected operating conditions, and the data was provided to ANL for their fuel processor model and evaluation of kinetic parameters.

A three-stage PrOx design was chosen to permit greater flexibility in removing higher CO concentrations (>1%). The first and second stages will operate to bring the outlet CO to 2000 to 1000 ppm. The third stage will operate to bring the outlet CO to <10 ppm with a small temperature rise to avoid the reverse WGS reaction. Foam substrates were obtained for the unique geometry of the PrOx component dictated in the fuel processor design.

Single-stage startup experiments were conducted to investigate the startup response of a PrOx catalyst monolith from room temperature. For these experiments, a primary gas flow consisting of 46.4% H_2, 32.9% N_2, 19.0% CO_2, and 1.2% CO at a temperature of 20ºC was established at a gas hourly space velocity (GHSV) ≈31,000 hr^{-1} through a 600cell/in^2, 3-inch diameter, 5-inch long PrOx catalyst monolith. Air injection was started, and the resulting outlet CO concentration and monolith temperature profile were measured as a function of time. Figures 5 and 6 show the outlet CO concentration response and monolith temperature response as a function of time, respectively. The outlet CO decreases rapidly to its steady-state values in less than 30 seconds, while the temperature response takes longer to reach steady-state. The low

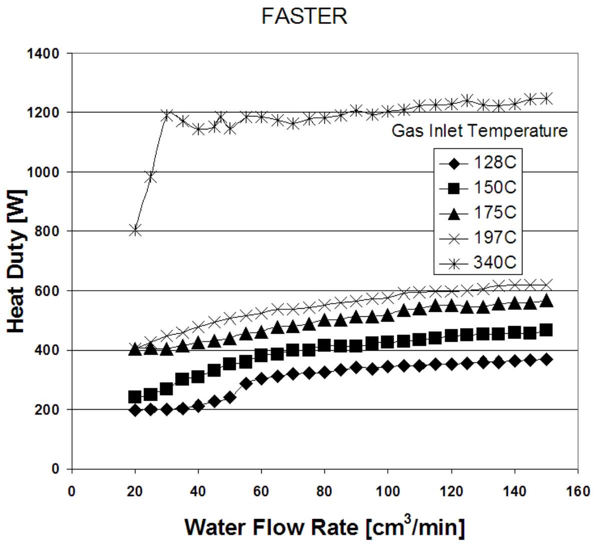

Figure 4. Performance of Tier 1 Graphite Foam Heat Exchanger

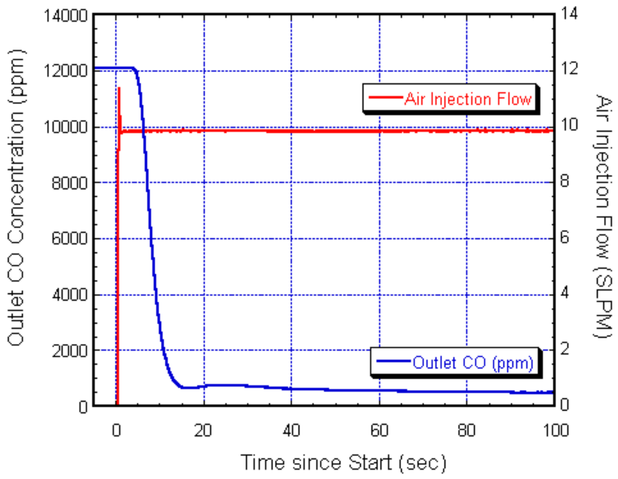

Figure 5. PrOx Outlet CO Response as a Function of Time

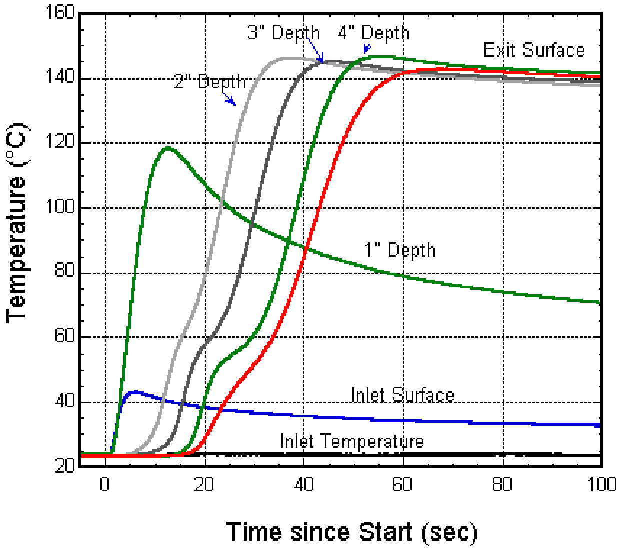

Figure 6. PrOx Monolith Temperature Response as a Function of Time

light-off temperature of the catalyst is evident from the response. Similar responses were obtained for both higher (2.2%) and lower (2350 ppm) inlet CO concentration. Based on these experiments, fast startup of the PrOx reactor component appears feasible.

Conclusions

- A compact, lightweight and efficient microchannel recuperator meeting the desired thermal performance, pressure drop and spatial requirements is possible.
- A microchannel mixer provides a method to uniformly mix air into reformate during startup to accelerate heating of the WGS catalyst.
- Graphite foam has met or exceeded specifications for performance in the FASTER system.
- Graphite foam heat exchangers appear to be relatively insensitive to water flow, especially at higher gas inlet temperatures.
- Further decreases in weight of the heat exchanger assembly may be possible.
- PrOx catalysts have been identified and characterized, and a three-stage PrOx design is being fabricated.
- Outlet CO concentrations could be reduced to steady-state values in less than 30 seconds in PrOx single-stage startup experiments.

FY 2003 Publications/Presentations

1. Whyatt, G. A., Poster: Micro-Channel Recuperator and Mixer for FASTER (Feasibility of Acceptable Start Time Experimental Reactor) Autothermal Reformer. Presented at the Hydrogen, Fuel Cells and Infrastructure Technologies Program 2003 Merit Review and Peer Evaluation Meeting, May 19-22, 2003, Berkeley CA.
2. Inbody, M. A., R. L. Borup, et al. (2002). Transient Control of Carbon Monoxide with Staged PrOx Reactors. 224th National Meeting of the American Chemical Society, Boston, MA, American Chemical Society.
3. Inbody, M. A., R. L. Borup, et al. (2002). Transient PrOx Carbon Monoxide Measurement, Control and Optimization. 2002 Fuel Cell Seminar.
4. McMillan, A.D., Romanonski, G.R., Klett, J.W., Armstrong, T., and Stinton, D., Annular Graphite Foam Heat Exchangers Were Developed for FASTER. Presented at the Hydrogen, Fuel Cells and Infrastructure Technologies Program 2003 Merit Review and Peer Evaluation Meeting, May 19-22, 2003, Berkeley, CA.

Special Recognitions & Awards/Patents Issued

1. Patent Application: Greg A. Whyatt, #60-471,130, Microchannel Mixing Device, 5/16/03

Reformate Cleanup: The Case for Microchannel Architecture

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Objectives

The overall objective of the effort at PNNL is to apply microchannel architectures where appropriate in fuel processing systems for transportation, stationary, and portable applications to reduce size and weight, improve fuel efficiency, and enhance operation. Specific objectives for this project are focused on CO cleanup and balance of plant, including

- Demonstrating 90% conversion of CO in a single-stage water-gas shift (WGS) reactor that scales to less than three liters at full-scale (50 kWe),
- Evaluating the potential importance of microchannel architectures in reducing the size and weight and improving performance of preferential oxidation (PROX) reactors,
- Exploring the ability to improve H_2S adsorption with conventional sorbents through improved temperature control, and
- Developing compact microchannel heat exchange technology for the recovery and recycle of water in fuel processor/fuel cell systems.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- R. Thermal and Water Management

Approach

- Demonstrate a compact differential-temperature microchannel water-gas shift reactor
  - Select and characterize a high activity shift catalyst
  - Calculate the optimal temperature profile
  - Design and test a multi-channel microreactor with integrated heat exchange to demonstrate the advantage of the approach
  - Demonstrate lifetime and durability of the engineered catalyst
  - Integrate with a steam reforming fuel processor
- Investigate approaches for PROX reactor enhancements with microchannels
  - Evaluate industrial PROX catalysts for fast kinetics
  - Confirm favorable operational characteristics with effective temperature control at the 2-kWe scale

  - Investigate weight reductions through use of low-density alloys
  - Investigate transient and startup characteristics
  - Integrate with a steam reforming fuel processor
- Explore effectiveness of controlling temperature profile to enhance H_2S removal in conventional adsorbent materials
  - Quantify H_2O sorption kinetics as a function of temperature for commercial sorbent materials
  - Calculate optimal temperature profile for differential temperature adsorber
  - Construct microchannel unit and obtain experimental performance data under differential temperature conditions
  - Compare results with isothermal performance
- Integrate microchannel heat exchange and phase separation technology to recover and recycle water in fuel processor/fuel cell systems

Accomplishments

- Performed extended operation and thermal cycle testing of precious metal water-gas shift catalyst in engineered form
- Continued efforts toward demonstrating differential temperature WGS operation in a multi-channel counter-flow reactor
- Designed and built a prototype first-stage microchannel PROX reactor at the 2-kWe scale and demonstrated effective operation up to 4 kWe
- Demonstrated a multi-channel air-cooled partial condenser with integrated phase separation on a simulated cathode effluent at the 1.5-kWe scale

Future Directions

- Continue catalyst development with focus on durable engineered forms of commercial WGS catalyst
- Design, build and test a second generation differential temperature microchannel reactor
- Evolve PROX reactor concepts for higher productivity and improved thermal control
- Demonstrate differential temperature H_2S sorption
- Integrate WGS, PROX, and sulfur removal in an integrated steam reforming fuel processor
- Pursue fabrication alternatives to facilitate low cost manufacturing targeting low temperature components

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Introduction

A critical aspect of attaining size and weight objectives for on-board fuel processors is achieving rapid heat and mass transfer rates, which is made possible by microchannels. This has been demonstrated in the past for the highly endothermic steam reforming reaction in microchannel reactors having integrated heat exchange to supply the necessary heat. This project extends the effort to the areas of reformate cleanup and balance-of-plant, in order to identify other elements of a fuel processing/ fuel cell system that can benefit from the microchannel architecture.

The water-gas shift (WGS) reaction is the conventional processing step after the fuel reformer to convert carbon monoxide to carbon dioxide, thereby reducing CO as a poison for PEM fuel cells while increasing hydrogen yield. The WGS reaction is exothermic, so that high temperature operation favors kinetics but equilibrium is more favorable at low temperature. The conventional approach is to operate a high temperature shift (HTS) reactor above 400°C, followed by a low temperature shift (LTS) reactor operating below 300°C to achieve the necessary conversion, with a heat exchanger in between to cool the reformate. A more optimal temperature profile could reduce the size of the shift subsystem and reduce the amount of catalyst required. The preferential oxidation (PROX) reactor is used to reduce carbon monoxide to levels that can be tolerated by PEM fuel cells by selectively oxidizing CO with air. Typically, PROX catalysts have a relatively narrow temperature window where CO conversion and selectivity are high. Microchannel approaches for integrating heat exchange within a PROX reactor offer potential improvement in PROX reactor performance.

The conventional approach for removing hydrogen sulfide, a poison for downstream catalysts and the fuel cell, from the reformate stream is adsorption using zinc oxide. H_2S adsorption also exhibits a temperature trade-off between sorption equilibrium and increased mass transfer rates, so improved localized temperature control is expected to improve performance. Finally, because fuel processors and fuel cells require water, recovery and recycle of water is necessary, and partial condensation is an appropriate topic for microchannel heat exchange as a means for achieving water balance. Each of these topics represents opportunities for applying microchannels to CO cleanup and balance-of-plant needs, which are under investigation in this project.

Approach

The general approach is a logical sequence of steps designed to demonstrate feasibility and potential benefits for overcoming programmatic technical barriers. This typically involves selecting a catalyst material from available sources through a screening process. The selected material is then characterized in an engineered form suitable for microchannel reactors through a series of tests over a range of operating conditions. A kinetic model may be developed from detailed finite element analysis of the reactor to support subsequent reactor engineering and design. The next step is to build and test a prototype microchannel reactor as a concept demonstration and to provide experimental data for scale-up and system integration. Finally, a microchannel reactor is designed and built based on integrated system specifications and tested within an integrated fuel processor to validate system performance.

Water-gas shift and hydrogen sulfide adsorption have similar temperature trade-offs that suggest performance can be enhanced by monotonically decreasing the temperature as the process proceeds. For these applications, the approach is to utilize integrated microchannel heat exchange to actively cool the reformate stream as it passes through a microchannel reactor. For example, theoretical calculations suggest the amount of water-gas shift required can be reduced by up to half with this approach. For PROX, a two-stage reactor approach is adopted with at least the first stage actively cooled to remove heat generated by the reactions and control the temperature of the catalyst within a range where high conversion and high selectivity are obtained.

Results

Water-Gas Shift Reactor – Efforts in water-gas shift microchannel reactor development have included continuing catalyst characterization, lifetime testing, and deactivation investigations, and progress has been made in demonstrating a multi-channel WGS reactor with a decreasing reaction gas temperature profile. Two new formulations of Sud-Chemie precious metal catalysts were tested as possible improvements over the PMS5 catalyst adopted by the project in FY 2002.

The 7-channel reactor shown in Figure 1 was tested in FY 2002, and the results showed significantly lower catalytic activity than found previously in single-channel testing. This catalyst was removed from the reactor, and individual catalyst pieces were tested in an isothermal single-channel reactor. Single-channel results confirmed 20 times lower activity than expected, and issues with loading the catalyst into the reactor were identified as possible causes.

A second attempt was made to demonstrate differential temperature operation in a multi-channel counter-flow microreactor, and the results are summarized in Figure 2. Most significantly, the ability to maintain the activity of the catalyst was demonstrated. In one test at 107,000 GHSV, with the feed end temperature at 375°C and the outlet end at 325°C, 79% conversion of the CO was achieved, decreasing the dry gas CO concentration from 12.4% to 2.6%. However, differential temperature performance did not provide the advantage over isothermal operation that was expected, as illustrated in Figure 2. When the reactor was operated with the feed end at 375°C and a decreasing temperature profile, greater CO conversion and a lower outlet CO concentration was achieved when compared to isothermal operation at the colder outlet temperature. However, when compared to isothermal operation at the feed temperature of 375°C, performance was diminished. Flow maldistribution between the channels in the multi-channel reactor was identified as the cause of unexpected performance. Future efforts will target improving flow distribution while also optimizing catalyst loading and reactor configuration.

Preferential Oxidation -- Commercially available catalysts were characterized in engineered form in a single-channel microreactor, including both precious metal and non-precious metal catalysts. Based on these results, a 2-stage approach was adopted, with a lower cost, non-precious metal catalyst selected for the first stage capable of achieving 97% conversion of CO from 1% to 300 ppmv with high selectivity when operated within a 20°C temperature range centered at 200°C. A precious metal catalyst is anticipated for the second stage to further reduce the CO level to 10 ppmv.

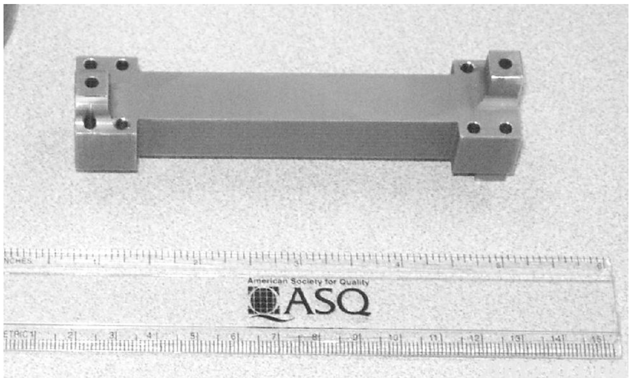

Figure 1. Seven-Channel WGS Reactor with Interleaved Counter-Current Heat Exchange Microchannels for Isothermal and Differential Temperature Operation

A prototype reactor was designed and built for first stage PROX at the 2-kWe scale. The reactor shown in Figure 3 has four chambers, each with separate air addition. A microchannel heat exchanger within the reactor removes the heat generated from the reaction. Quasi-isothermal conditions are maintained within the PROX catalyst by the heat exchanger and by modulating air addition to each chamber. The operational characteristics of this reactor were determined by varying the reformate flow rate, operating temperatures, O_2/CO ratios in each chamber, and inlet CO concentration (between 1-2% on a dry basis). The flow rate range corresponded to between 2 and 4.7 kWe equivalent fuel cell power output. Conversion profiles through the reactor are shown in Figure 4 for four power levels. Over 97% CO conversion was achieved at the

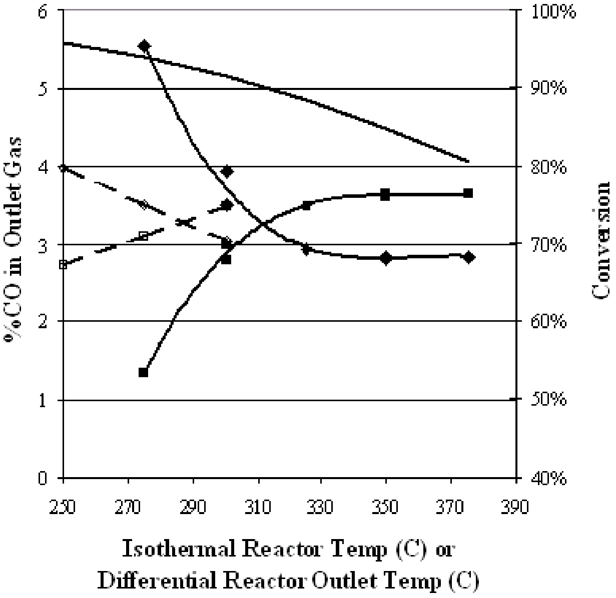

Figure 2. Comparison of Isothermal and Differential Temperature Operation with Steam Reformate Feed (12.4% CO and 14.3 CO_2, dry gas) at 100,000 GHSV and 0.65 Steam to Dry Gas Showing CO Conversion (■) and CO Concentration (□) under Isothermal Operation and CO Conversion (◆) and CO Concentration (✧) under Differential Mode with the Reformate Feed at 350°C with the Equilibrium CO Conversion Line Shown at the Top

4-kWe power level, which was twice the design objective.

Desulfurization – Development of microchannel desulfurization technology was initiated in FY 2003, and efforts to date have been focused on developing experimental and analytical capabilities to support testing. Initial studies are underway to characterize CO uptake onto zinc oxide materials as a function of temperature to support calculations of optimal temperature profile to balance kinetics and sorption equilibrium.

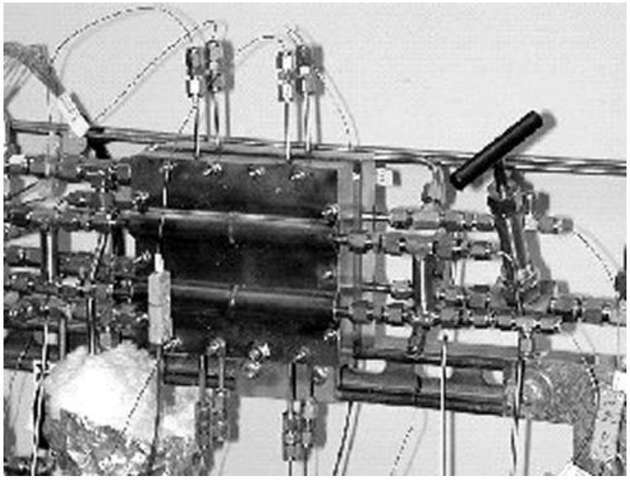

Figure 3. Prototype PROX Reactor with Microchannels for Quasi-Isothermal Operation and Multiple Compartments for Staged Air Injection

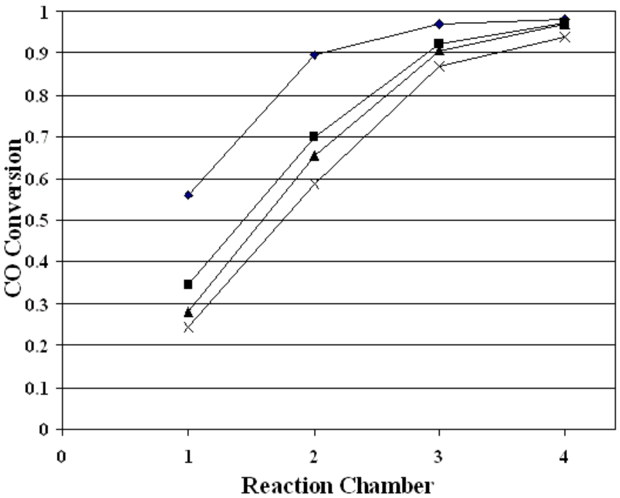

Figure 4. Carbon Monoxide Conversion Profiles through the Prototype First-Stage PROX Reactor Operated with an Overall O_2/CO Ratio of 1.0, Feed CO Concentration of 1.14% (dry), 0.3 Steam to Dry Gas Ratio, and Reformate Flow Rates Corresponding to 2 kWe (◆), 3 kWe (■), 4 kWe (▲), and 4.7 kWe (**X**)

Partial Condensation with Phase Separation – A prototype multi-channel partial condenser with phase separation was tested over a range of flows, water content and temperatures. The cross-flow, air-cooled device was designed to recover water from the effluent stream from the cathode of a PEM fuel cell at approximately the 1.5-kWe scale. Design conditions include hot feed at 80°C, coolant air at 30°C, and air-side pressure drop of 2.2 inches of H_2O that would require an estimated 14 W of parasitic load at full scale. The aluminum device is extremely lightweight and includes a phase separator to remove the condensate separate from the gas effluent. The device is shown in Figure 5, and the results of testing are compiled in Figure 6, including comparison to theoretical prediction. Actual performance exceeds predicted performance, and specific power exceeded 2000 Wt/kg at 74% water recovery. Water separation efficiency was 90-100%, and the coolant side pressure drop was about 4 inches of H_2O, which was about twice the design value.

Conclusions

- Although additional work remains in demonstrating 90% conversion in a single-stage water-gas shift reactor using the differential temperature microchannel reactor concept, the approach remains valid for achieving a WGS

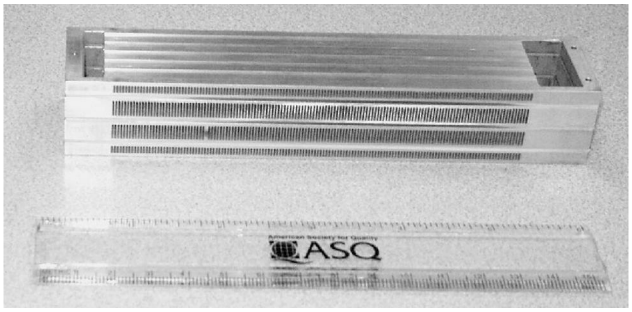

Figure 5. Aluminum Microchannel Partial Condenser Containing 3 Sets of 0.020-inch Condensing Microchannels Interleaved with Cross-Flow 0.024-inch Cooling Channels

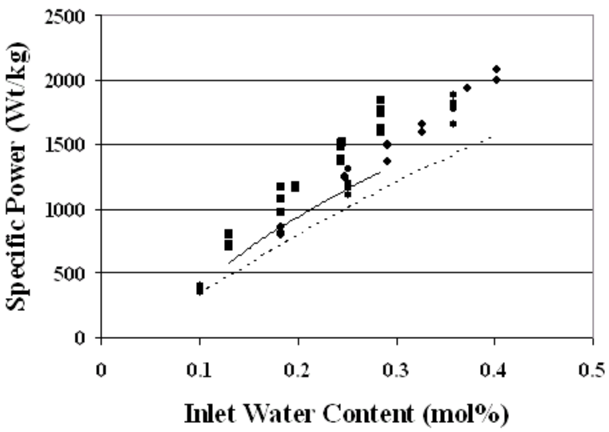

Figure 6. Specific Power versus the Water Content of the Prototype Microchannel Partial Condenser at Condensing Stream Air Flows of 32 SLPM (●) and 48 SLPM (■) with Trend Lines Shown through the Predicted Performance Values at the Same Operating Conditions that Produced the Experimental Data for Both 32 SLPM Air Flow (- - -) and 48 SLPM Air Flow (——).

reactor that is less than 3 liters at the 50-kWe scale.

- A prototype first-stage PROX having integrated microchannel heat exchange has been shown to have excellent thermal control and high productivity.
- Improving desulfurization using conventional sorbent materials is viable by optimizing thermal profiles using microchannels.
- Lightweight, high thermal conductivity metals, such as aluminum, can be used in fabricating microchannel devices having high specific power for lower temperature components, including microchannel partial condensers for water management in fuel processors and fuel cell systems.

FY 2003 Publications/Presentations

1. TeGrotenhuis, W.E., K.P. Brooks, D.L. King, R.S. Wegeng, "Optimizing the Water Gas Shift Reaction in Microchannel Reactors by Trading-Off Equilibrium and Reaction Kinetics through Temperature Management", poster presentation at the **2002 Fuel Cell Seminar**, November 18-21, Palm Spring, California.

2. TeGrotenhuis, W.E. and V.S. Stenkamp, "Testing of a Microchannel Partial Condenser and Phase Separator in Reduced Gravity", presented at **First International Conference on Microchannels and Minichannels**, April 24-25, 2003, Rochester, New York, USA (proceedings in print).

Microchannel Steam Reformation of Hydrocarbon Fuels

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Objectives

- Evaluate the increase in productivity of steam reforming at temperatures greater than 650°C.
- Evaluate increase in sulfur tolerance at temperatures >650°C.
- Design and build low-pressure drop reactor, vaporizer and air recuperator that can maintain efficiency while exhibiting very low air side pressure drop.
- Test rapid start strategy for steam reforming reactor and associated heat exchangers.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Start-Up/Transient Operation
- J. Durability
- M. Fuel Processor System Integration and Efficiency

Approach

- Assemble high temperature reforming components including an Inconel 625 reactor and recuperator to allow testing of microchannel steam reforming at reformate outlet temperatures >650°C.
- Measure reforming capacity as a function of temperature for methane, isooctane and benchmark fuel at ~1 kWe scale. Evaluate capacity at conversion levels of ~99.9% and >99.995% (no detectable non-methane hydrocarbons).
- Evaluate reformer performance with up to 30 ppmw sulfur in the fuel.
- Design and build low pressure drop microchannel reactors and associated heat exchangers to enable testing of an approach to rapid startup.
- Perform initial testing of the rapid start approach.

Accomplishments

- Completed measurement of reformer capacity vs. temperature above 650°C for reforming methane, isooctane and benchmark fuel.
- Measured productivity vs. temperature above 650°C while reforming benchmark fuel with no detectable non-methane hydrocarbons in the reformate (conversion > 99.995%).
- Completed preliminary testing using sulfur spikes.
- Completed initial testing of combustor (atomized gasoline) to provide heat to fast-start system.

- Microchannel components for low pressure drop reforming system (reactors, water vaporizer, air recuperator, reformate recuperator) are designed and fabricated through the diffusion bonding step.

Future Directions

- Continue sulfur tolerance and carbon formation testing at elevated temperatures.
- Evaluate reforming performance of low pressure drop reactor design.
- Evaluate a potentially improved (lower-cost, increased durability) reforming catalyst which is now available.
- Evaluate fast-start approach using stainless steel fast-start components.
- Once data collection for high temperature sulfur tolerance and carbon deposition testing is complete, revise fast-start design to utilize smaller, lighter high-temperature reformer.
- Integrate fast start reformer system with water gas shift (WGS) and preferential oxidation (PrOx) reactors at 2 kWe scale.

Introduction

This project is applying the rapid heat and mass transfer attainable in microchannels to the development of a highly compact and efficient steam reformer. Once developed, the steam reformer will fit on-board a highly efficient fuel cell vehicle and provide hydrogen to a proton exchange membrane (PEM) fuel cell, which in turn will produce electricity to power the vehicle. By reforming to produce hydrogen on-board the vehicle, the fuel can be gasoline, providing vehicle range, and the need to purify and compress hydrogen is eliminated. Also, an automobile with on-board reforming could be fueled using the existing gasoline infrastructure, an important advantage if a hydrogen refueling infrastructure is not available.

In past work, this project demonstrated that steam reforming, normally considered a slow reaction, can achieve rapid kinetics in a microchannel reactor. In addition, it was demonstrated that this technology could be scaled up (10-25 kWe equivalent) and that the reforming reactor along with an integrated network of highly efficient microchannel heat exchangers could be highly compact and yet efficient. An approach to build water vaporizers having very low air side pressure drops was developed and demonstrated. A water vaporizer using this design sized for a 50-kWe fuel processor was delivered to McDermott as part of a fuel processing demonstration. Evaluation of microchannel reforming data indicated significant increases in reformer capacity might be available at higher temperatures than initially tested. The potential increase was judged to be sufficient in magnitude that the reduction in reactor mass might justify use of higher-priced alloys in place of stainless steel. In addition, the reactor tolerance for sulfur, a contaminant found in gasoline which must be removed prior to the PEM fuel cell, was expected to improve at higher temperature. Reforming the fuel and removing the sulfur from reformate is expected to be easier than removing the sulfur from liquid fuel. The current work examines the extent to which the reformer productivity and sulfur tolerance improve at temperatures above 650°C. In addition, work to develop a rapid-start capability, critical for an on-board automotive application, is being pursued (an earlier prototype required ~15 minutes for a cold start). The effort is aimed at assembling and testing a steam reforming system including the reformer and its associated heat exchangers that can cold start within ~30 seconds. Once demonstrated, the system will be expanded to include the WGS and PrOx reactors.

Approach

Reforming Capacity at High Temperature - The testing of reforming productivity was performed on an ~1 kWe test stand which has been shown to relate well to performance obtained in larger scale reactors. The reforming reactor shown in Figure 1 was integrated into a system of heat exchangers and tested at temperatures above 650°C. In a typical reforming test, the temperature and flow of the combustion stream were held constant. The feed rates of hydrocarbon and steam were then increased (or decreased) while maintaining a fixed 3:1 steam to carbon ratio until there was a small but easily measurable residual of non-methane hydrocarbon in the reformate. For isooctane and benchmark fuel, this translated to a conversion level of 99.7% to 99.9%. When reforming methane, the approach to equilibrium methane content was used, and the approach was 96% to 99%. After operating at each point for sufficient time to assure short-term stability, the combustion side temperature was changed and flows readjusted to obtain another point on the productivity vs. temperature curve. After completing the curve for benchmark fuel, an additional curve was generated in which the flows were reduced until there were no detectable non-methane hydrocarbons in the reformate (>99.995% conversion).

Sulfur Tolerance at High Temperature - The same reactor and test system used for the productivity vs. temperature experiments is now being used to test the sulfur tolerance at temperatures above 650°C. Sulfur spikes equivalent to 30 ppmw sulfur in the liquid fuel are being introduced by adding H2S to the vaporized fuel and steam and by spiking the liquid fuel with benzo-thiophene and thiophene.

Fast Start Reformer - Calculations were performed to define a steam reforming system, including the reforming reactor and associated heat exchangers, which would be able to start up within 30 seconds. The design is based on maintaining a very low pressure drop through the heat exchangers and reactors. During startup, the combustion gases flow through the reactors and vaporizer in parallel so that the high air flow does not result in a high pressure drop. The flow during normal operation is then changed to pass through reactors in series to reduce the total air flow and maintain efficiency. The low pressure drop during the startup period results in the fan required to provide the air flow being relatively less expensive. In addition, the electrical power requirement is low enough to be within the reach of a conventional automotive battery. The low pressure drop during normal operation reduces the cost of the fan but, perhaps more importantly, significantly reduces the parasitic power associated with air compression compared to either a steam reformer with higher pressure drops or an autothermal reformer operating at multiple psi pressures.

Results

Reforming Productivity vs. Temperature - The test reactor used to explore high temperature reforming rates is shown with the reformate recuperator and combustor attached to it in Figure 1. Reforming results are shown in Figure 2. Dramatic increases in processing rate were observed as the reformate outlet temperature was increased from 650°C to 875°C. The reforming rate of benchmark fuel increases exponentially as temperature is increased with no indication of leveling off due to heat or mass transfer limitations. This translates into the potential to significantly reduce reactor size if reforming at higher temperature.

Sulfur Tolerance vs. Temperature - Preliminary results of the improvement in sulfur tolerance with increased temperature are shown in Figure 3. Reforming at a temperature of 800°C or more significantly increases the ability of the catalyst to

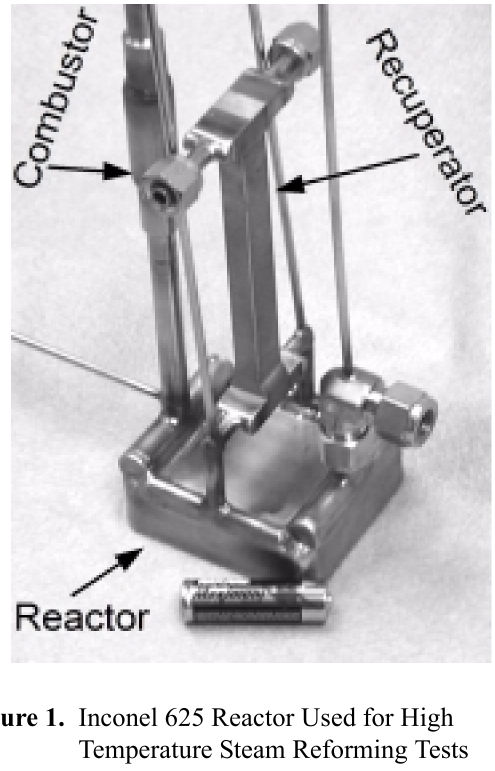

Figure 1. Inconel 625 Reactor Used for High Temperature Steam Reforming Tests (Reformate recuperator and combustor are shown attached.)

process the sulfur containing fuel without losing activity. Additional testing with spikes up to 30 ppmw S in the fuel introduced as hydrogen sulfide (added as gas to vaporized steam/fuel), thiophene and benzothiophene have confirmed the ability of the catalyst to process this level of sulfur with moderate reduction in activity for short periods of time. However, an increase in pressure drop over time across the reactor when reforming sulfur-spiked benchmark fuel has been observed. The increase in pressure drop is halted if the spike is removed. It is believed that this is an interaction between the high-nickel alloy Inconel 625 used to fabricate the high temperature reformer and the sulfur content in the fuel. This issue is being investigated further.

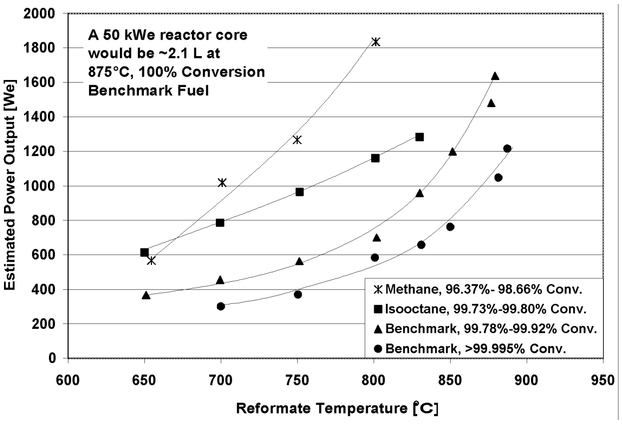

Figure 2. Throughput of Inconel 625 Reactor as a Function of Reformate Outlet Temperature (Throughput is expressed as electrical output. This could support assuming 90% conversion of CO in a WGS reactor, 50% selectivity in a PrOx reactor and a PEM fuel cell operating at 44% efficiency.)

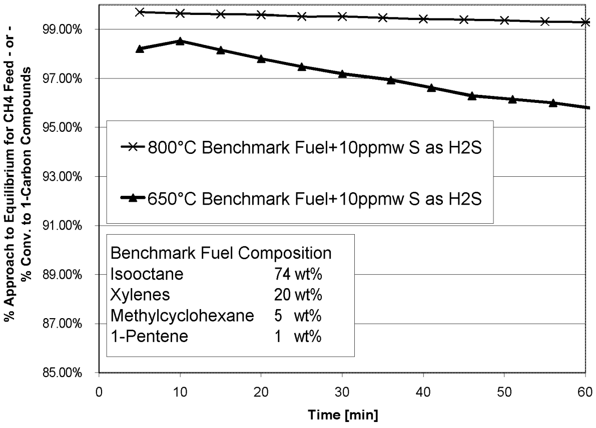

Figure 3. Increase in Sulfur Tolerance While Reforming Benchmark Fuel at 800°C vs. 650°C

Fast Start Reformer - The microchannel hardware required for testing the rapid start approach has been designed, and individual components have been fabricated through the diffusion bonding step. The microchannel components are shown in Figure 4. During normal operation, the 2-kWe system will require about 100 slpm of air flow with a pressure drop of 6.0 inches of water. During startup the system will utilize ~4000 slpm at a pressure drop of 5.2 inches of water. The pressure drop is maintained low by routing combustion gases in parallel through components during the startup period. A startup combustor was tested and demonstrated to provide the required flow of 800°C combustion gas in ~2 seconds.

Conclusions

- The exponential gain in steam reformer productivity with temperature while reforming benchmark fuel implies a reactor operating at 850°C can be less than 1/3 the size of a reactor operating at 650°C.

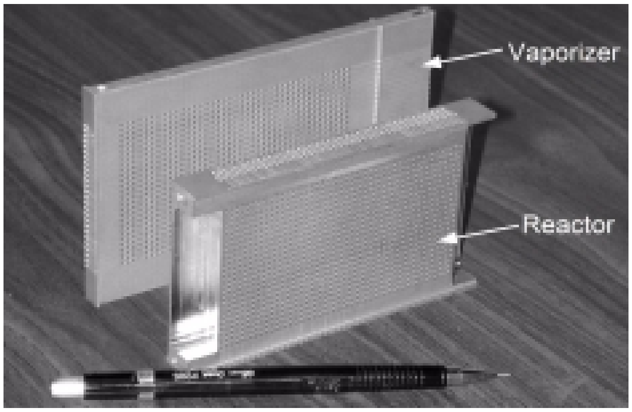

Figure 4. Low Pressure Drop Reactor System Components to be Used in Rapid Start Testing (The reactor weighs 400 g and supports ~500 We at 650°C. If produced in high temperature alloy and operated >850°C, the reactor would be capable of 2 kWe. The vaporizer weighs 325 grams and supplies steam for 2 kWe reforming capacity.)

- The steam reformer can provide reformate with no detectable non-methane hydrocarbons over the temperature range tested.
- The sulfur tolerance of the catalyst is significantly improved by operating at temperatures >800°C.
- The addition of a sulfur to benchmark fuel resulted in increases in pressure drop over time across the Inconel 625 steam reformer. This is being investigated.
- The approach to achieving rapid start of the steam reformer appears feasible.

FY 2003 Publications/Presentations

1. Whyatt, G. A., K. Brooks, J. Davis, C. Fisher, D. King, L. Pederson, S. Stenkamp, W. Tegrotenhuis, B. Wegeng. Progress in Microchannel Steam Reformation of Hydrocarbon Fuels. Presented at the Hydrogen, Fuel Cells and Infrastructure Technologies Program 2003 Merit Review and Peer Evaluation Meeting, May 19-22, 2003 Berkeley CA.

Special Recognitions & Awards/Patents Issued

1. Patent Application: System for Rapid Cold Startup of Microchannel Steam Reformer. #60-471,286, G. A. Whyatt.

Fuel Processors for PEM Fuel Cells

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Objectives

- Demonstrate high performance desulfurizer, catalyst, micro-reactor and microcombustor/ microvaporizer concepts that will enable production of compact fuel processors for proton exchange membrane (PEM) fuel cells
- Design, fabricate and evaluate a 1-kWe fuel-flexible fuel processor during the first 36 months (one of the fuels capable of being reformed will be EPA Phase II reformulated gasoline)
- Design, fabricate and evaluate a fuel-flexible fuel processor capable of producing up to 10 kWe hydrogen (one of the test fuels will be EPA Phase II reformulated gasoline)

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Startup/Transient Operation
- J. Durability
- M. Fuel Processor System Integration and Efficiency
- N. Costs

Approach

- Tasks devised to accomplish the project objectives include:
- Design and model components and systems that would meet power density targets;
- Develop high capacity sorbents capable of removing sulfur to target levels;
- Develop better performing autothermal reforming (ATR), water gas shift (WGS) and preferential oxidation (PrOx) catalysts and associated microreactors;
- Fabricate highly efficient microcombustors/microvaporizers;
- Fabricate microchannel reactors and system;
- Evaluate components and fuel processing system;
- Estimate cost for fuel processor.

Accomplishments

- Modeled several of the microchannel reactors (FEMLAB and FLUENT) and entire fuel processor system (ASPEN and Matlab Simulink);
- Demonstrated Cu-Y zeolite sorbents that significantly out-performed other available sorbents;
- Demonstrated ceria/zirconia-based ATR, carbide-based WGS and sol-gel derived PrOx catalysts that out-performed available commercial catalysts;
- Developed methods to scale up production of carbide-based catalysts;
- Designed fuel and water microvaporizers;
- Fabricated and tested metal, ceramic and silicon-based micro-reactors;
- Designed and began construction of prototype 1-kWe fuel processor system.

Future Directions

During this coming year, our goal is to fabricate at least two 1-kWe fuel processor systems. The first design is a hybrid system that includes micro- and conventional reactor technologies. The second design will be based primarily on ceramic micro-reactors. Specific tasks will include:

- Fabricate highly efficient microcombustors/microvaporizers,
- Fabricate microchannel reactors and system,
- Evaluate components and fuel processing system.

Introduction

Fuel cells are being developed to power cleaner, more fuel efficient automobiles. The fuel cell technology favored by many automobile manufacturers is proton exchange membrane (PEM) cells operating with H_2 from liquid fuels like gasoline and diesel. A key challenge to the commercialization of PEM fuel cell based powertrains is the lack of sufficiently small and inexpensive fuel processors. Improving the performance and cost of the fuel processor will require the development of better performing catalysts, new reactor designs and better integration of the various fuel processing components. These components and systems could also find use in natural gas fuel processing for stationary, distributed generation applications.

Approach

Prototype gasoline fuel processors will be produced and evaluated against the Department of Energy technical targets. Significant improvements over the present state-of-the-art will be achieved by integrating low-cost microchannel systems, high activity catalysts, π-complexation sorbents, and high efficiency microcombustor/microvaporizers being developed at the University of Michigan. The microchannel system will allow (1) more efficient thermal coupling of the fuel processor components and minimization of the heat exchanger requirements, (2) improved catalyst performance due to optimal reactor temperature profiles and increased heat and mass transport rates, and (3) better cold-start and transient responses.

The project will be accomplished in 3 phases. The Phase I effort will focus on demonstrating compact desulfurizer, micro-reactor and microcombustor/microvaporizer components for a 1-kWe fuel processor, and developing low-cost methods for the production of microchannel systems. The components will be third-party tested and will provide the basis for design and fabrication of an integrated 1-kWe ethanol or gasoline fuel processor during Phase II. We will scale up the smaller processor to up to 10 kWe during Phase III.

Results

Design and modeling. The modeling activities have been at three levels: detailed component modeling, modeling for simplified component integration and thermal management, and system integration and optimization modeling. FLUENT is being applied to develop detailed computational fluid dynamics (CFD) models of the internal reacting flow process for the prototype reactor components. The results are being used to design the ATR, WGS and PrOx reactors. A general 1-D counterflow heat exchanger model has been formulated into a non-dimensional model to facilitate systematic thermal management studies over a wide range of operating conditions. One of the key design issues is to maintain good temperature control. Finally, based on the systematic detailed and 1-D modeling studies, an integrated system optimization tool was developed. Based on the counterflow heat exchanger model as a canonical unit to represent individual components, a first-order reaction model has been implemented to calculate accurate reaction and heat generation rates. Matlab Simulink is being used to integrate a network of the various components including the ATR, WGS, and PrOx reactors, to predict the system behavior and to optimize the overall performance. The detailed component models and the 1-D models described will continue to provide submodels for individual blocks that constitute the system integration model.

Sorbent development. Cu-Y zeolite based sulfur sorbents have been developed and evaluated. Breakthrough curves for desulfurization of diesel for these sorbents are compared to those for several benchmark sorbents in Figure 1. Selexsorb CDX is an activated alumina specially formulated by Alcoa for the adsorption of polar organic compounds including sulfur-based molecules (mercaptans, sulfides, disulfides, thiophenes). The $CuCl/\gamma\text{-}Al_2O_3$ sorbent was prepared by dispersing $CuCl_2$ on an activated alumina surface with the aid of a dispersing agent followed by reduction of Cu^{2+} to Cu^{+}. The AC/Cu-Y sorbent is a layered bed of 15 wt% activated carbon followed by Cu-Y. The highest adsorption capacity was achieved for AC/Cu-Y. Approximately 82% of its original capacity was recovered after treatment with air at 350°C. The capacity loss could be due to modification of the carbon during calcination.

Catalyst development. High activity ATR, WGS, and PrOx catalysts have been demonstrated. A material consisting of 10 wt% Ni on a $Ce_{0.75}Zr_{0.25}O_2$ support was identified as the best performing octane ATR catalyst. This catalyst yielded high H_2 production rates under the following conditions: O/C = 1.0, H_2O/C = 2.0, space velocity (SV) ~290,000 hr^{-1} (iso-octane flow ~ 0.2 mol/hr or 100 We).

Carbide-supported WGS catalysts (M/Mo_2C) were synthesized that significantly exceed important targets established by the DOE. In particular, at 240°C, conversions exceeding 90% with H_2 selectivities greater than 99% were achieved at gas hourly space velocities in excess of 50,000 hr^{-1} (reactant contained 38% H_2, 16% N_2, 10% CO, 6% CO_2 and 30% H_2O). Rate laws for the carbide-based catalysts are also conducive for use at low CO contents and high product concentrations. Assuming high activities, low reaction orders for the reactants and products are preferred. Table 1 compares power law reaction orders for commercial Cu/Zn/Al catalysts, two oxide supported precious metal catalysts, high surface area Mo_2C and the carbide-supported catalyst.

Table 1. Reaction Orders for the Following Power Law: Rate = $k \bullet P_{CO}{}^{m} P_{H2O}{}^{n} P_{CO2}{}^{o} P_{H2}{}^{p}$

Catalyst	M	n	o	P
Mo_2C	0.55±0.05	0.19±0.07	-0.02±0.06	-0.01±0.07
M/Mo_2C	0.13±0.04	0.48±0.05	0.01±0.04	-0.24±0.04
Cu/Zn/Al	0.94±0.05	0.72±0.12	-0.38±0.10	-0.42±0.06
Cu/Zn/Al (1)	1.0	1.4	-0.7	-0.9
Cu/Zn/Al (2)	1.07±0.16	0.55±0.18		
Pd/CeO_2 (3)	0.0	0.5	-0.5	-1.0
Pt/Al_2O_3 (4)	-0.21±0.03	0.75±0.04		

Rate data for the carbide-based catalyst were adequately described by the following Langmuir-Hinshelwood rate law where r is the rate, k is a rate constant, P_i are the partial pressures and K_i are the adsorption constants:

$$r = \frac{kP_{H_2O}}{(1 + K_{H_2O}P_{H_2O} + K_{H_2}P_{H_2})^2}$$

This rate law is consistent with a dual-site reaction with H_2O dissociation being the rate

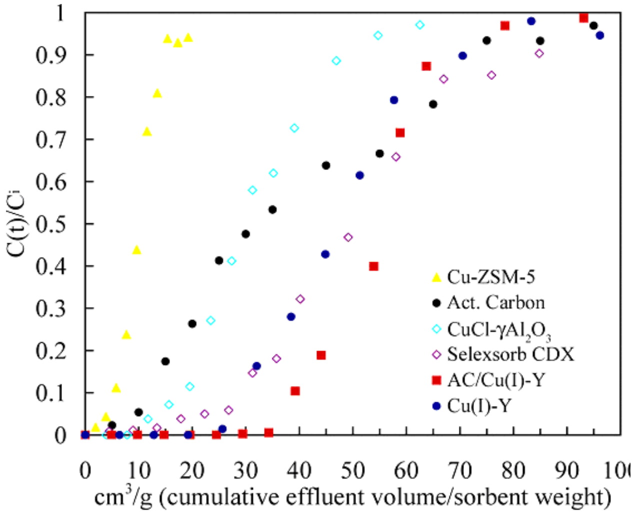

Figure 1. Breakthrough Curves for Desulfurization of Diesel (measurements at room temperature and atmospheric pressure)

determining step. Osram Sylvania has scaled up production of the carbide catalysts to nearly 1-kg batches.

We identified two catalysts for use in the PrOx reactor: 5% Pt/15% ceria-85% alumina and 1% Au/Fe_2O_3. The Pt catalyst gives greater than 98% conversion with 50% CO oxidation selectivity at high temperatures (120-180°C), and the Au catalyst gives 99% conversion with 58% selectivity at 50°C. These catalysts were wash-coated onto monoliths and silicon and aluminum micro-reactor structures. We also built honeycomb and microchannel reactors for PrOx. The honeycomb reactor was capable of reducing the CO content of ~10 L/min of reformate to less than 10 ppm.

Microchannel System Development. The heat required from the burner is directly coupled to the degree of heat recuperation achieved by component integration throughout the rest of the system. As a result, detailed burner/vaporizer requirements were developed based on results from the integration simulations. On a 1-kW basis, the total heat needed for vaporization and stream heating to target temperatures is 948 W, while the total heat available from the ATR and WGS reactions is 1001 W. An additional 300 W is available from combustion of the anode tailgas. A tailgas burner thus suffices for steady-state operation and is being developed. The fuel vaporizer is being developed which derives heat directly from the tailgas burner. The water vaporizer recovers heat first from the reactors and then derives additional heat from the tailgas burner or from a non-catalytic fuel burner.

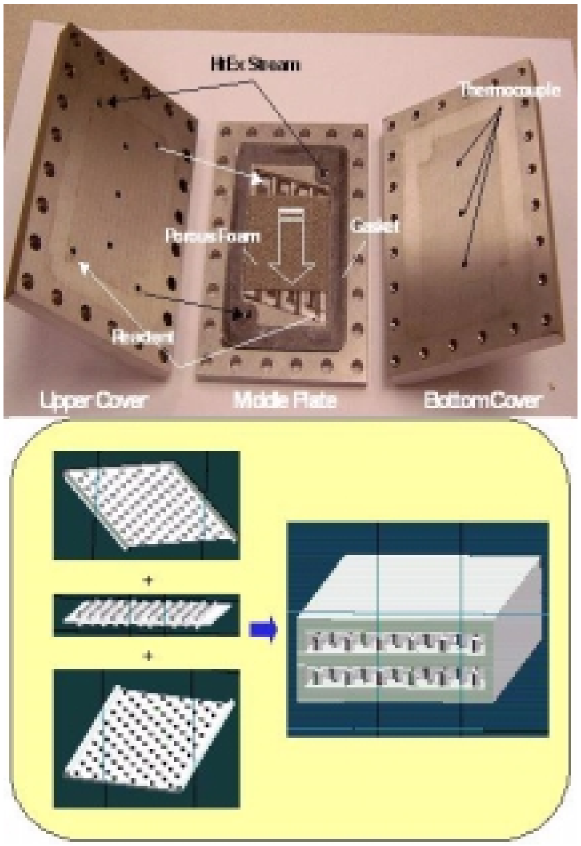

Figure 2. Illustrations of (top) Experimental Test Micro-Reactor and (bottom) Target Design Based on Simulations Results

Cost-effective manufacturing methods have been developed to mass produce the fuel processor components. A semi-solid forming process has been identified as one of the most promising candidate processes. This process has good capability for creating the complex micro/meso-scale geometries required for the reactor components.

Conclusions

Significant progress was made last year. Several better performing fuel processing materials were developed. The deployment of these sorbents and catalysts should result in significant reductions in the fuel processor size, weight and cost. Novel reactor geometries were also demonstrated. (See Figure 2.) Efforts for the coming year will focus on fabricating an integrated, 1-kWe gasoline fuel processor with characteristics that exceed key Department of Energy performance targets.

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1. "Autothermal Reforming of Isooctane Over Supported Nickel Catalysts", Tadd, A., Saraf, V., Schwank, J., Jundee, T., and Rirksomboom, T., Preprints, AIChE Annual Meeting, Indianapolis, IN, November 3-8, 2002.
2. "Supported Nickel Catalysts for Autothermal Reforming of Hydrocarbons", Tadd, A., Saraf, V., Schwank, J., Jundee, T., and Rirksomboom, T., North American Catalysis Society Meeting, Cancun, June 2003.
3. "High Throughput Evaluation of Novel Autothermal Reforming Catalysts for Fuel Cell Applications", Schwank, J., Tadd, A., Saraf, V., and Gould, B., EuropaCat-VI, Innsbruck, Austria, August 31- September 4, 2003.
4. "Deactivation Mechanisms for Supported Gold WGS Catalysts", Kim, C. H., Bej, S. K., and Thompson, L. T., AIChE Annual Meeting, Indianapolis, IN, November 2002.
5. "Function and Performance of Carbide Catalysts for the Water Gas Shift Reaction," Patt, J. J., and Thompson, L. T., AIChE Annual Meeting, Indianapolis, IN, November 2002.
6. "Function of Carbide and Nitride Water Gas Shift Reaction Catalysts," Patt, J. J., Bej, S. K., and Thompson, L. T., Materials Research Society Fall Meeting, Boston, MA, December 2002.
7. "Deactivation Mechanisms for Supported Gold WGS Catalysts", Kim, C. H., Bej, S. K., and Thompson, L. T., MRS Fall Meeting, Boston, MA, December 2002.
8. "Deactivation of Supported Water Gas Shift Gold Catalysts", Kim, C. H. and Thompson, L. T., ACS Spring Meeting, New Orleans, LA, March 2003.
9. "Deactivation and Regeneration of Nanocrystalline Gold WGS Catalysts," Kim, C. H., Bej, S. K., and Thompson, L. T., North American Catalysis Society Meeting, Cancun, June 2003.
10. "Desulfurization of Transportation Fuels with Zeolites Under Ambient Conditions," R. T. Yang, A. J. Hernandez-Maldonado and F. H. Yang, Science, 301, 79 (2003).
11. "Desulfurization of Commercial Liquid Fuels by Selective Adsorption via p-Complexation with Cu(I)-Y Zeolite," A. J. Hernández-Maldonado and R. T. Yang, Ind. Eng. Chem. Res., 42, 3103 (2003).
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13. "Desulfurization of Transportation Fuels with Zeolites Under Ambient Conditions," Yang, R. T., ACS Spring Meeting, New Orleans, LA, March, 2003, Award Address of ACS Award for Separation Science and Technology.

Sulfur Removal from Reformate

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Objectives

Develop a sulfur removal process for on-board fuel processing to meet DOE targets for hydrogen sulfide (H_2S) removal to <10 ppbv H_2S in reformate by 2010, a reactor volume of <0.06 L/kW$_e$ and weight of <0.06 kg/kW$_e$, and operation at a gas-hourly space velocity (GHSV) of 50,000 h^{-1}.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup

Approach

- Identified Cu oxides as candidate materials based on the H_2S equilibrium partial pressure for candidate adsorbents (metal sulfide-H_2S equilibrium).
- Synthesize mixed metal oxides consisting of CuO/Cu_2O and another transition metal oxide to stabilize copper in its oxide forms.
- Conduct experimental studies in a microreactor system to evaluate the H_2S concentration in the effluent as a function of temperature, flow rate, water content, and the gas composition for candidate mixed metal oxides.

Accomplishments

- Synthesized various mixed metal oxides consisting of CuO/Cu_2O and screened them for H_2S uptake in a microreactor system.
- Determined the effects of operating temperature, flow rate, water content, and gas composition on the performance of H_2S removal by a copper oxides-based composition.
- Demonstrated that a copper oxides-based composition reduced H_2S concentration from 10 ppmv to <50 ppbv from a simulated reformate.

Future Directions

- Evaluate H_2S uptake for the materials supported on the structured form.
- Characterize materials to improve performance and address stability issues.
- Optimize the composition and materials processing and work with industrial collaborator.

Introduction

On-board reforming of gasoline is one option being considered for supplying H_2 for polymer electrolyte fuel cell (PEFC) powered propulsion systems for automobiles and light-duty vehicles. Under reforming conditions, the sulfur present in gasoline is converted to H_2S. Although new Environmental Protection Agency (EPA) regulations will reduce the sulfur content of gasoline to <80 ppmw beginning in 2006, reformate produced from these gasolines will still contain ~10 ppmv H_2S. Concentrations of H_2S as low as 50 ppbv have been shown to irreversibly poison the PEFC catalysts.[1] As a consequence, DOE has established a target of <10 ppbv H_2S in reformate by 2010.

Two different approaches, liquid-phase desulfurization of the fuel prior to reforming[2] and gas-phase desulfurization of reformate after reforming, are being considered for on-board sulfur removal. There is a concern with liquid-phase desulfurization that H_2S will still need to be removed from reformate. Gas-phase desulfurization requires that the reforming catalyst be sulfur-tolerant. Our focus is on developing adsorbents for gas-phase desulfurization.

Zinc oxide (ZnO) is used for sulfur removal in the production of H_2 from natural gas for ammonia and methanol synthesis. For on-board fuel processing using ZnO, thermodynamic equilibrium predicts that a temperature of <250°C is required to reduce the H_2S concentration to <10 ppbv. We have observed that the concentration of H_2S in reformate increased as the temperature decreased below 300°C due to unfavorable kinetics, making ZnO unsuitable for on-board fuel processing.[3] Copper oxides (CuO and Cu_2O) have among the highest sulfidation equilibrium constants for metal oxides and can potentially achieve parts-per-billion concentrations of H_2S in reformate. However, under fuel processing conditions, Cu_2O/CuO are reduced to metallic Cu. The sulfidation equilibrium for metallic Cu is significantly less than that of Cu oxides, resulting in reduced desulfurization efficiency. Research has focused on combining CuO/Cu_2O with other metal oxides to stabilize the oxide form,[4] which is the approach that we are investigating.

Approach

Compositions consisting of Cu and a second transition metal oxide dispersed on a high surface area support, such as γ–Al_2O_3, were prepared by either co-impregnation or successive impregnation methods using nitrate salts as precursors. The H_2S desulfurization performance of these compositions was evaluated in a microreactor system. In a typical test, a sample of up to 2 mL was exposed to a synthetic reformate (10-40 ppmv H_2S, 29% H_2, 20% H_2O, 6% CO, 6.1% CO_2, 0.2% CH_4, balance N_2) at temperatures ranging between 200-400°C and at GHSVs ranging between 2000-50,000 h^{-1}. The H_2S concentration in the effluent from the reactor was measured using a gas chromatograph (GC) equipped with a flame photometric detector (FPD) with a detection limit of 200 ppbv H_2S and an on-line lead-acetate based H_2S analyzer with a detection limit of 20 ppbv H_2S.

Results

Figure 1 shows a typical H_2S breakthrough curve (i.e., H_2S concentration in the effluent as a function of time) for these sorbents at 350°C and a GHSV of 2000 h^{-1} with a feed H_2S concentration of 40 ppmv. All compositions tested, including Cu alone, exhibited two stages of H_2S breakthrough. During the first stage, they reduced the H_2S concentration below detection limit of the FPD. During the second stage, they reduced the H_2S concentration to ~10 ppmv. The second stage is believed to be associated

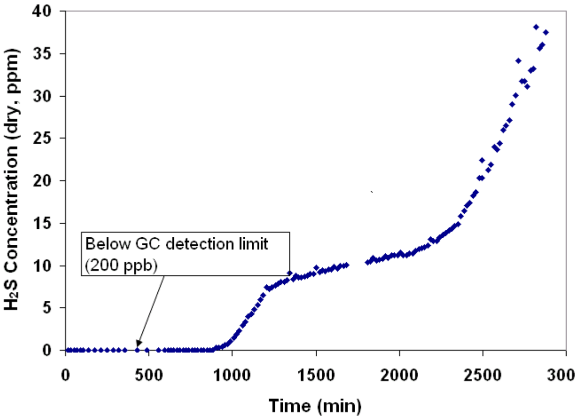

Figure 1. The H_2S Breakthrough Curve for Cu+B at 350°C and a GHSV of 2000 h^{-1}

with the sulfidation of metallic copper since the observed H_2S concentration of 10 ppmv is close to that predicted by thermodynamic equilibrium (7.2-10.6 ppmv at 350-380°C) for metallic Cu; however, this has not been experimentally confirmed. These materials did show different sulfur uptake capacities as shown in Table 1. The highest sulfur uptake capacities were shown by compositions identified as Cu+B and Cu+C.

The Cu+C system was chosen for further study to determine the effect of various operating parameters including temperature, GHSV, and the water content in reformate on H_2S removal. Temperature significantly affected H_2S removal performance, as shown in Figure 2. The H_2S concentration was reduced from 10 ppmv to <50 ppbv at 200 and 300°C; however, a longer breakthrough time was observed at 200°C, indicating a higher H_2S uptake capacity. At 200°C, the reduction of copper oxides to metallic Cu is less favorable, suggesting more of the Cu may be in the oxide form, which would favor desulfurization.

The effect of GHSV at 200°C is shown in Figure 3. Although breakthrough time decreased significantly as the GHSV was increased from 10,000 to 50,000 h^{-1}, similar sulfidation efficiencies (~20 ppbv) and Cu utilizations (~60%) were observed at both GHSVs. When the temperature was increased to 350°C, the performance decreased significantly at the higher GHSV. The sulfidation efficiency was 25 ppbv and the Cu utilization was 15% at a GHSV of 10,000 h^{-1}, which decreased to 200 ppbv and 5%, respectively, at a GHSV of 50,000 h^{-1}. This implies that lower operating temperatures are desirable if the GHSV target is to be met.

Table 1. Copper Utilization for Sulfidation of Binary Oxides of Copper and a Second Transition Metal

Sorbent formulation	Surface area (m²/g)	Sulfur uptake (%, based on Cu content)[a]
Cu+A/Al_2O_3	197.9	37.3
Cu+B/Al_2O_3	199.5	57.9
Cu+C/Al_2O_3	211.3	53.9
Cu+D/Al_2O_3	201.5	44.0
Cu+E/Al_2O_3	202.3	32.8
Cu/Al_2O_3	258.8	36.3

[a] Calculated based on H_2S uptake until breakthrough occurs (1 ppmv H_2S).

The effect of the H_2O concentration in the reformate on H_2S removal performance is shown in Figure 4. The pre-breakthrough H_2S concentration increased as the H_2O concentration increased from 11 to 30 vol%, consistent with the reaction equilibrium (e.g., $Cu_2O + H_2S(g) = Cu_2S + H_2O(g)$). Since H_2O is a product of the sulfidation reaction, increasing the H_2O concentration in the reformate shifts equilibrium towards the reactants, leading to a higher H_2S concentration.

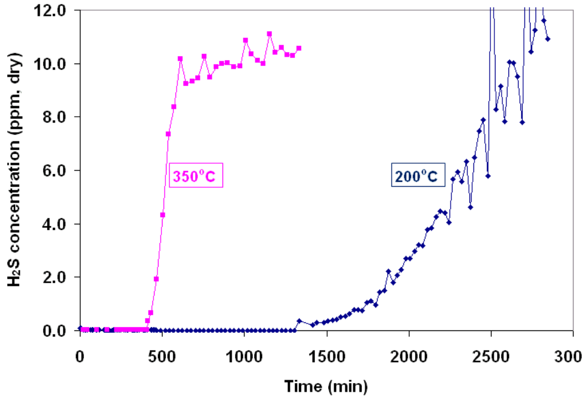

Figure 2. The Effect of Temperature on H_2S Breakthrough for Cu+C at a GHSV of 10,000 h^{-1}

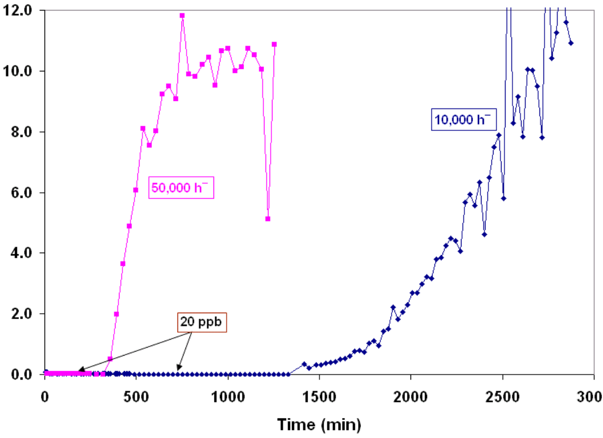

Figure 3. The Effect of GHSV on H_2S Breakthrough for Cu+C at 200°C

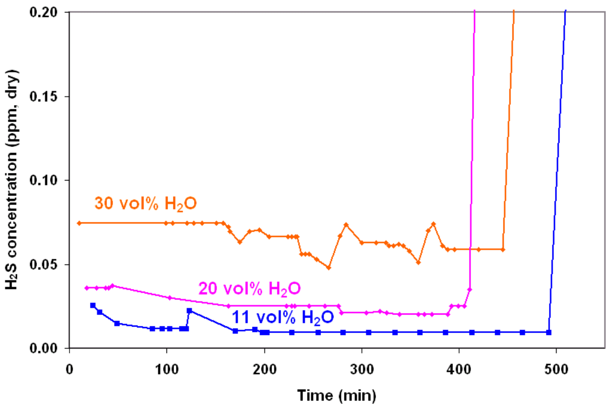

Figure 4. The Effect of H_2O Concentration in the Reformate on H_2S Breakthrough for Cu+C at 350°C and a GHSV of 10,000 h^{-1}

Conclusions

- Binary oxides containing Cu are capable of reducing the H_2S concentration from 10 ppmv to <50 ppbv in reformates containing 30% H_2 and 20% H_2O at temperatures ranging from 200-350°C and GHSVs ranging from 10,000-50,000 h^{-1}.
- Lower operating temperatures, lower H_2O concentrations, and lower GHSVs are desirable to meet DOE targets.

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Selective Catalytic Oxidation of Hydrogen Sulfide

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Objectives

- Develop activated carbon catalysts with controlled microstructures for selective oxidation of H_2S to elemental sulfur.
- Identify key microstructural and surface chemistry features of activated carbons that promote hydrogen sulfide removal.
- Characterize the catalytic performance and reaction kinetics of commercial and laboratory-created activated carbons in model reformate gas streams.
- Understand reaction mechanisms, and explore the key microstructural features of activated carbons and the key reaction mechanisms for H_2S removal to the ppb level.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Fuel-Flexible Fuel Processors Barriers

- J. Durability

Component Barriers

- P. Durability

Approach

- Produce activated carbons for hydrogen sulfide removal that have various pore size distributions, functional groups, and inorganic impurity levels.
- Characterize the structure of commercial and laboratory-created activated carbons to be tested for catalytic oxidation of hydrogen sulfide.
- Perform catalysis tests on commercial and laboratory-created activated carbons in model reformate gases and isolate the effects of activated carbon structure and pertinent gaseous species on H_2S removal.
- Use in-situ analytical techniques and molecular modeling to determine the dependence of reaction mechanisms on activated carbon structure.

Accomplishments

- Characterized the pore structure and carbon structure of several commercial and laboratory-synthesized activated carbons.

- Preliminary results imply that using in-situ techniques such as diffuse reflectance mid-infrared Fourier transform spectroscopy (DRIFTS) holds promise in studying catalytic removal of H_2S.
- Designed and constructed a catalysis test system for catalytic oxidation of hydrogen sulfide in model reformate gas streams.
- Used Reverse Monte Carlo analysis of diffraction data to simulate the structure of activated carbon.

Future Directions

- Isolate the importance of surface functionality and impurities on pertinent reactions for hydrogen sulfide removal using catalysis experiments and in-situ analytical techniques.
- Synthesize several typical carbon-based catalysts from different sources under controlled activation processes.
- Establish processes for modifying the functional group content and impurity level of activated carbons.
- Determine optimal pore size distribution for maximum sulfur removal capacity.
- Evaluate the effect of reaction conditions on the activity and selectivity of selected catalysts.
- Study catalytic reaction kinetics and explore reaction mechanisms.

Introduction

Hydrogen is commonly produced by reforming natural gas; however, reformate contains impurities, such as hydrogen sulfide (H_2S), which can poison shift catalysts and fuel cell electrodes. Even a low concentration (a few ppm) of hydrogen sulfide dramatically shortens the life of fuel cell catalysts. Major ongoing research efforts are seeking to develop fuel cell catalysts that are more sulfur tolerant. The mission of this research project is to develop an oxidative process to reduce sulfur levels to the parts per billion range using low-cost carbon-based catalysts. This project is a new start in FY 2003, starting in March.

Selective oxidation of hydrogen sulfide to elemental sulfur on an activated carbon catalyst has been identified as a highly promising approach for the purification of fuel cell feedstocks [1]. While activated carbons are commercially used for hydrogen sulfide removal from gas streams, the key mechanisms for hydrogen sulfide removal and the critical features in an activated carbon catalyst are not well understood. Research efforts often have relied solely on commercial activated carbons, and none of the past development efforts have evaluated the use of carbon as a catalyst. In addition, the results reported by various investigators are often diverse and contradictory, especially concerning kinetics and reaction pathways. This project will emphasize the design and development of low-cost, regenerative, carbon-based catalysts that meet the required characteristics for reducing sulfur in fuel cell feedstocks to desired level. A variety of activated carbons from different sources of carbon and different activation processes will be synthesized and evaluated. The effect of operating parameters on the activity and selectivity of catalysts will be evaluated using DRIFTS (diffuse reflected infrared Fourier transform spectroscopy) (Figure 1). Based on the achievement of carbon materials with the

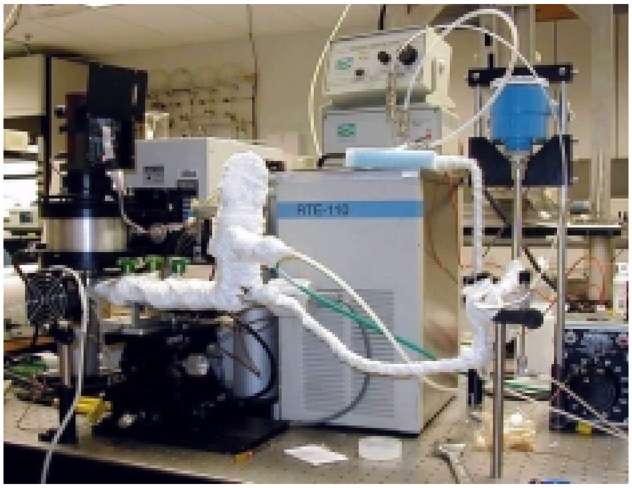

Figure 1. Picture of DRIFTS System

desired structure and surface chemistry, new insights will be provided to clarify the reaction mechanisms.

Approach

The assembled research team allows for a processing-to-product approach to tackle the timely issue of hydrogen sulfide removal from reformate feedstocks of hydrogen. The feedback between materials processing, molecular modeling, reaction mechanism studies, and engineering evaluation provides a synergistic approach for the development of an activated carbon catalyst.

Different precursors and variations in activation conditions can produce dramatically different microstructures in carbon materials. A focused effort to identify their relationships and the influence of the resultant pore structure (pore volume, pore size and distribution) on the performance of carbon catalyst is necessary. Surface functional groups play an important role in the catalytic activity of the catalyst [2]; thus, it is important to identify the initial surface functional groups and then develop techniques to modify or alter surface functionality. To produce an optimal activated carbon catalyst, the functional group content should be tailored to optimize hydrogen sulfide adsorption and minimize side reactions, such as adsorption of CO and H_2O, that could result in the formation of sequestered hydrogen sulfide products.

Inorganic impurities have also been shown to strongly catalyze hydrogen sulfide oxidation [3]. In order to understand the influence of catalytic impurities on the reactions of interest, highly pure carbons will need to be synthesized to isolate their effects. Inorganic impurities must also be added to activated carbons in order to elucidate their role in adsorption and catalysis. It is commonly accepted that metal impurities in activated carbons play important roles in catalytic performance. Key issues that must be clarified include 1) identification of the reaction mechanisms associated with specific impurities, 2) the activity and selectivity of those impurities, and 3) the efficacy of these impurities after extensive sulfur deposition and catalyst regeneration.

Reaction mechanisms will be determined using a combination of catalytic reactor experiments on simple gas mixtures, in-situ analytical techniques (such as DRIFTS), and molecular modeling. Together, these techniques can isolate individual gas-carbon reactions, explore competition between gases for reaction sites, determine the mechanisms for deleterious side reactions, and predict ideal carbon structures for H_2S removal. This combination of analysis methods provides multiple perspectives of catalyst reactions, ranging from idealized thermodynamic reaction predictions to measured catalyst surface interactions to an overall perspective of downstream gas composition. Key reaction parameters include temperature, pressure, oxygen concentration, H_2S concentration, water content, and the concentration of other impurities.

Ultimately, an activated carbon catalyst is only successful for hydrogen sulfide removal if it can perform to required concentrations in an actual reformate gas stream for a reasonable time period using a practical reactor geometry. A catalyst must remove and retain hydrogen sulfide in the presence of the wide range of impurities found in reformate feedstocks. Optimized activated carbon catalysts will be tested on simulated reformate feedstocks of hydrogen. The potential of promising catalyst candidates for regeneration also needs to be explored. Partnering with laboratories and industry will be explored as a means to evaluate down-selected catalysts on actual reformed gas streams.

Results

The porosity and carbon structure of several commercial and laboratory-created activated carbons have been determined. Typical results are listed in Table 1 and Table 2. The activated carbons are derived from different precursors (pitch-derived carbon, coconut shell carbon, coal, and low-ash charcoal) in order to determine the effects of common inorganic impurities. Also, preliminary experiments have sought to accurately determine their functional group content.

An in-situ study has been initiated to understand the interaction of gas species such as H_2S, O_2 and

Table 1. X-ray Diffraction Parameters of Assorted Commercial and Laboratory Activated Carbons

	Precursor	Interplanar spacing (nm)	Crystallite height (nm)	Crystallite diameter (nm)
Anshan 1000 m^2/g	pitch fiber	0.3667	1.127	1.775
Anshan 1500 m^2/g	pitch fiber	0.3660	1.134	1.803
Calgon Centaur 4x6	coal	0.3574	1.157	1.813
Calgon OLC 12x40	coconut shell	0.3662	1.080	1.810
Calgon OVC 4x10	coconut shell	0.3764	1.107	1.847
ORNL SMM-19	carbon fiber monolith	0.3742	1.058	1.757
ORNL SMS-48	carbon fiber monolith	0.3743	1.081	1.736
PICA G55C-1	coconut shell	0.3737	1.037	1.821
PICA VA507	coconut shell	0.3767	1.053	1.886
Westvaco Ultramicroporous	wood	-	-	1.720

Table 2. Pore Structure Characterization of Assorted Commercial and Laboratory Activated Carbons from Nitrogen Adsorption Analysis

	BET surface area (m^2/g)	D-R micropore volume (cc/g)	D-A average pore diameter (Å)
Anshan 1500 m^2/g	1393	0.756	22.3
Calgon Centaur 4x6	1144	0.506	21.3
Calgon OLC 12x40	1110	0.506	21.3
Calgon OVC 4x10	884	0.391	19.7
ORNL SMM-19	1730	0.895	22.8
ORNL SMS-48	1404	0.619	20.7

CO with carbon surface and interpret the reaction mechanisms of H_2S oxidation and undesired side reactions for the formation of COS and SO_2. A DRIFTS reactor which is capable of in-situ measurement up to 500°C is being used to identify the change of carbon surface chemistry in various gas atmospheres. A preliminary study on the interaction of CO with activated carbon has provided positive support for this approach, and typical results are shown in Figure 2.

Reverse Monte Carlo modeling has been applied to diffraction data to produce a theoretical activated carbon microstructure. By introducing select modifications to theoretical microstructures, carbon microstructural variables can be kept constant except for a specific feature of interest (functional group content, pore size, carbon structural order, etc.), and the effect of specific feature changes on the thermodynamics and kinetics of H_2S removal can be predicted. Slight modifications of these theoretical microstructures will later be used to model the behavior of actual activated carbons by incorporating the measured microstructural features of activated carbons.

A catalytic reactor system for hydrogen sulfide has been designed and is being constructed. A schematic representation of the system is shown in Figure 3.

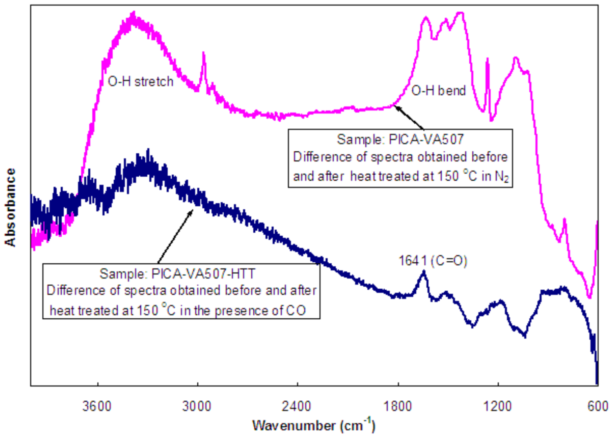

Figure 2. Preliminary Results on the Interaction of CO with Activated Carbon Observed by DRIFTS

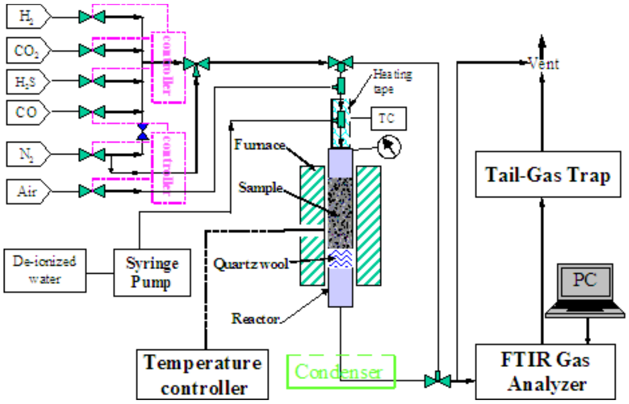

Figure 3. Schematic Representation of the Experimental Setup for Testing Carbon-Based Catalyst (FTIR=Fourier transform infrared)

Conclusions

- The microstructures of several activated carbon materials have been characterized for subsequent correlation to catalysis results.
- Preliminary results imply a promise of using *in-situ* techniques such as DRIFTS in studying catalytic removal of H_2S.
- Reverse Monte Carlo methods have been applied to diffraction data to create a theoretical model of the microstructure of activated carbon in order to identify reaction sites.

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Effects of Fuel Constituents on Fuel Processing Catalysts

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Objectives

- Determine the effects of the major constituents, additives, and impurities in petroleum fuels on fuel processor performance and durability.
- Collaborate with major oil companies on the development of future fuels for fuel cell vehicles.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Durability
- K. Emissions and Environmental Issues
- M. Fuel Processor System Integration and Efficiency
- N. Cost

Approach

- Investigate reforming the major components of gasoline under controlled conditions in a microreactor.
- Determine the dependence of product gas composition on temperature and space velocity.
- Test simple mixtures of components, impurities, and additives to determine their synergistic or poisoning effects.
- Test complex refinery blends to determine which streams are most attractive for on-board reforming.
- Conduct long-term (1000-h) tests to determine catalyst poisoning and other degradation effects over time.

Accomplishments

- Determined that antioxidant additives have little or no effect on reforming at temperatures $\geq$750ºC and gas-hourly space velocities (GHSVs) $\leq$50,000 h^{-1}; however, they can decrease hydrogen yield at lower temperatures or higher GHSVs.
- Discovered that pyridine decreases the rate of isooctane reforming, even at 800ºC.
- Examined reforming refinery streams and refinery blends supplied by major oil companies.
- Investigated the long-term effects of detergent additives on reforming.
- Developed an understanding of reforming binary mixtures in terms of the effects of competition for the limited number of active sites on the catalyst.
- Demonstrated that aromatics and naphthenes decrease the rate of reforming of isooctane on advanced bimetallic catalysts, as well as on Pt-based catalysts.

Future Directions

- Investigate the long-term effects of antioxidant additives and heterocyclic impurities.
- Develop a reforming model that can predict the performance of complex fuel mixtures.
- Investigate reforming binary/ternary mixtures and additives with advanced catalysts.

Introduction

Fuel cell vehicles offer the potential for very low emissions and high fuel economies. Efficiency and emissions, however, are affected by the fuel used. With hydrogen as the on-board fuel, the lowest vehicle emissions (zero) and the highest fuel economy can be obtained. In the absence of a hydrogen production, delivery, and marketing infrastructure, on-board reforming of hydrocarbon fuels (e.g., gasoline) is a potential transitional solution for the near-term introduction of fuel cell vehicles. The goals of this project are to identify the desirable and undesirable constituents of gasoline and develop specifications for a hydrocarbon fuel especially suitable for fuel cell vehicles.

Our previous work indicated that there are significant differences in how readily the major types of hydrocarbons in gasoline (paraffinic, aromatic, naphthenic, and olefinic) can be reformed.[1,2] Tests on refinery blends indicated that fuels high in aromatic content were more difficult to reform and that aromatics affected the rate at which paraffinic species could be reformed.[2] We have expanded our study to investigate the effects of gasoline additives and impurities on reformer performance.

Approach

The reformability of various fuel mixtures was measured at Argonne National Laboratory (ANL) under autothermal reforming conditions. These studies were conducted at 600-800°C and GHSVs between 15,000 and 150,000 h^{-1} (corresponding to reactor residence times of approximately 200 to 20 milliseconds) and involved various blends of isooctane with aromatic, naphthenic, N-containing heterocycle, and oxygenate compounds, as well as surrogates for the additives used in gasoline.

Results

Antioxidants. We investigated the reforming of isooctane-phenol solutions over a Pt-ceria-based catalyst to determine the effects of phenol-based antioxidants. The phenol concentration was ~100 ppm, an order of magnitude higher than in gasoline, to accelerate catalyst degradation. A comparison of the product gas compositions from reforming these solutions at 800ºC and various space velocities is shown in Figure 1. The hydrogen content of the product gas decreased with the addition of phenol for GHSV >50,000 h^{-1}. In addition, CO levels decreased throughout the GHSV range. Hydrogen yields for pure isooctane and isooctane + phenol were close to the theoretical maximum yields at 750 and 800ºC and GHSVs below 50,000 h^{-1}, but dropped off with decreasing temperature. The decrease accelerated with the phenol additive.

A plot of the difference in the H_2 yield between isooctane and isooctane + phenol as a function of

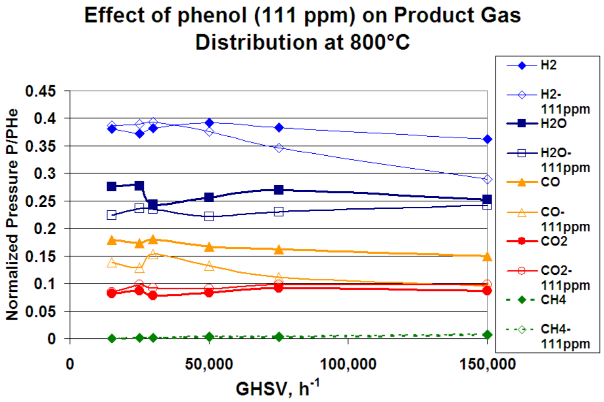

Figure 1. Product Gas Compositions from Reforming Isooctane and Isooctane + 111-ppm Phenol over a Pt Catalyst at 800ºC for Various Space Velocities

temperature and GHSV is shown in Figure 2 (% difference = $(P_{H2(C8+phenol)} - P_{H2(C8)})/P_{H2(C8)} \times 100$).

This plot shows that the additive had no effect on hydrogen yield at 750 to 800ºC and 15,000 to 50,000 h^{-1} GHSV. However, the phenol additive decreased the hydrogen yield at higher space velocities or lower temperatures. This is partly due to a decrease in the rates of feed hydrocarbon breakdown. With pure isooctane, no hydrocarbons higher than C6 were observed in the product gas, whereas with phenol present, fragments as large as C_7H_{15} were observed.

Heterocyclic impurities. The effect of pyridine, a nitrogen heterocyclic impurity in gasoline, was investigated by reforming mixtures containing 50-ppm pyridine in isooctane. The difference in hydrogen yield with and without pyridine is shown in Figure 3. The hydrogen yield decreased substantially over most of the operating space, even at high temperatures and low space velocities.

Fuel composition. Our previous work had shown that aromatic and naphthenic constituents decreased the rate of reforming isooctane over a Pt-ceria-based catalyst.[2,3,4] To determine if this is true for autothermal reforming in general, we investigated the reforming of isooctane-xylene and isooctane-methylcyclohexane mixtures over a bimetallic Pt-Rh catalyst. This bimetallic catalyst has substantially higher activity than the Pt catalyst, yielding 80–90% of the theoretical maximum hydrogen yield at 600°C and 150,000 h^{-1} GHSV. In comparison, the Pt catalyst yielded less than 60% of the theoretical maximum hydrogen at 650°C and the same GHSV. The bimetallic catalyst was tested for reforming isooctane, isooctane + xylene (20%), and isooctane + methylcyclohexane (20%).

The addition of xylene decreased the hydrogen yield at high GHSVs (≥75,000 h^{-1}) and low temperatures, as shown in Figures 4(a) and 4(b). Hydrogen yields fall below 90% of the theoretical maximum at 750ºC and a GHSV of 150,000 h^{-1}. This decrease is believed to be due to competitive reactions at the catalyst sites. Aromatics interact more strongly with the metal centers and decrease the number of available reaction sites for the less strongly adsorbing paraffins. The naphthenes dehydrogenate to form aromatics, which then compete with the paraffins for the catalytic sites.

Conclusions

- Antioxidant additives in gasoline have been found to decrease hydrogen yield in the reformate, but only at high GHSVs and/or low reforming temperatures.
- Pyridine decreased hydrogen yield, even at low GHSV and high temperature.
- Aromatic and naphthenic components decreased the rate of paraffin reforming, even when using advanced bimetallic catalysts.

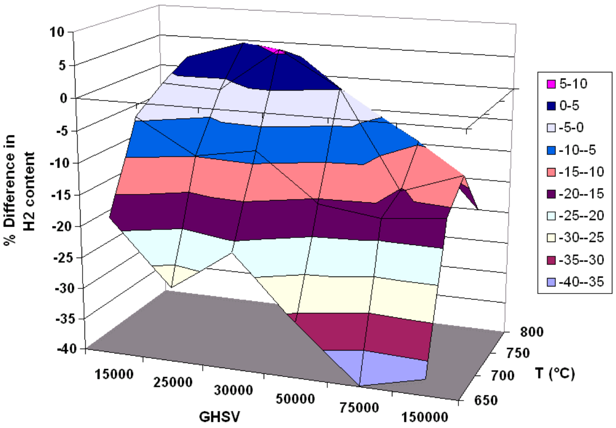

Figure 2. Difference in the H_2 Yield between Isooctane and Isooctane + Phenol as a Function of Temperature and GHSV

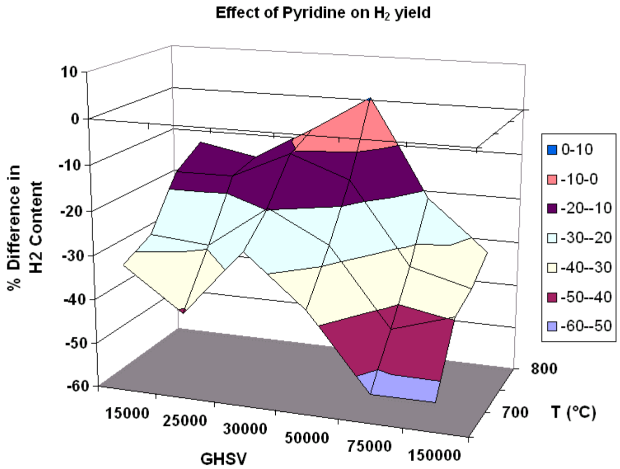

Figure 3. Difference in the H_2 Yield between Isooctane and Isooctane + 50-ppm Pyridine as a Function of Temperature and GHSV

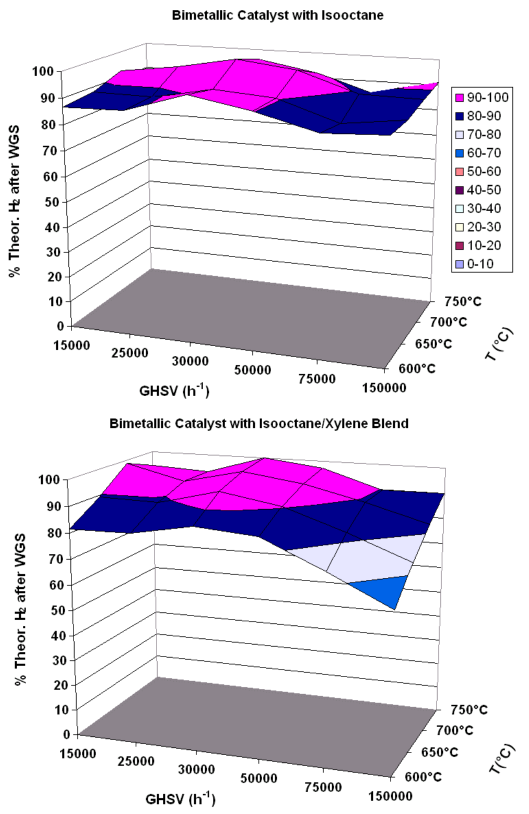

Figure 4. Hydrogen Yield as a Percentage of the Maximum Theoretical Hydrogen Yield Obtainable from Reforming (a) Isooctane and (b) Isooctane + 20% xylene over an Advanced Bimetallic Catalyst

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1. J. P. Kopasz, S. Ahmed, M. Krumpelt, and P. Devlin, "Challenges in Reforming Gasoline: All Components Are Not Created Equal," SAE Technical Paper Series, 2001-01-1915 (2001).

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1. S. Ahmed, J. Kopasz, R. Kumar, and M. Krumpelt, "Water Balance in a Polymer Electrolyte Fuel Cell System," J. Power Sources, 112, 519-530 (2002).

2. M. Pacheco, J. Sira, J. Kopasz, and S. Ahmed, "Reaction Kinetics and Reactor Modeling for Fuel Processing of Liquid Hydrocarbons for Fuel Cell Applications: Isooctane Reforming," Applied Catalysis, accepted for publication.

3. J. P. Kopasz, L. Miller, and D. Applegate, "Effects of Additives and Impurities on the Reforming of Gasoline," 2003 AIChE Spring National Meeting, 2nd Topical Conference on Fuel Cell Technology, New Orleans, LA (2003).

4. J. P. Kopasz, L. E. Miller, and D. V. Applegate, "Effects of Multicomponent Fuels, Fuel Additives, and Fuel Impurities on Fuel Reforming," SAE Future Transportation Technology Conference (2003).

5. J. P. Kopasz, L. E. Miller, and D. V. Applegate, "How Fuel Composition Affects On-Board Reforming for Fuel Cell Vehicles," SAE Powertrain and Fluid Systems Conference and Exhibition (2003).

Testing of Fuels in Fuel Cell Reformers

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Objectives

- Quantify fuel effects on fuel processor performance and durability
  - Measure fuel component, impurity, additive effects
  - Examine fuel effects on fuel processor start-up
- Understand parameters that affect fuel processor and stack lifetime and durability
  - Measure fuel processor catalyst stability and activity
  - Evaluate fuel effect and start-up effect on carbon formation
  - Identify chemical species limiting durability
  - Test durability to evaluate long term performance

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Start-up/Transient Operation
- J. Durability
- M. Fuel Processor System Integration and Efficiency
- N. Cost

Approach

- Examine fuel effects on fuel processing by testing fuels in catalytic and gas phase oxidation and reforming reactors
  - Examine individual fuel components, component blends
  - Examine 'real' fuels (reformulated gasoline, naphtha)
  - Examine fuel additives (anti-oxidants, detergents, impurities)
- Examine fuel effect on fuel reformer light-off and start-up
  - Measure fuel light-off temperature
  - Measure carbon formation during fuel processor light-off
- Model and measure carbon formation
  - Model carbon formation equilibrium
  - Measure carbon formation during fuel vaporization

  - Measure carbon formation during start-up of fuel processor
- Examine reforming of fuels at low temperatures for portable power applications

Accomplishments

- Measured carbon formation during vaporization process of hydrocarbon fuels
- Measured carbon formation during start-up of fuel processor
- Examined effect of fuel components on light-off temperature and start-up
  - Delineated straight-chained hydrocarbons vs. branched chains and aromatic compounds
  - Oxygenated fuel components
  - Additives and impurities such as detergents and sulfur
- Compared gas phase oxidation and catalytic oxidation with different fuel components
- Examined the reforming of fuels at low temperatures for portable power applications

Future Directions

- End task on Testing of Fuels in Fuel Cell Reformers
  - Summarize and publish final results
- Focus on H_2 durability of PEM Fuel Cells
  - Single cell MEA durability
  - Short stack Durability
  - Drive cycle testing of MEAs
  - MEA and GDL evaluation and characterization
  - Off-line and accelerated durability testing

Introduction

The goal of this research is to explore the effects of fuels, fuel constituents, additives and impurities on the performance of on-board hydrogen generation devices and, consequently, on the overall performance of a PEM fuel cell system using a reformed hydrocarbon fuel. Understanding the performance of fuels and their effects on the durability of PEM fuel cell systems is key for their commercial introduction and use. A fast start-up time of the fuel processor systems is crucial for their use in automotive fuel cell applications. Energy consumption, carbon formation, start-up time and limits on durability are all potential effects of fuel composition on the fuel processor during the start-up and light-off of fuel processors.

Approach

To examine the effect of fuel on hydrogen generation devices, various fuel components, mixtures, and real fuels have been tested in automotive-scale autothermal (ATR) fuel reformers. The focus of the testing is to examine fuel effects on start-up performance and factors that limit durability. Start-up time and durability are critical aspects of reformer performance for onboard vehicle operation. Carbon formation can significantly limit durability. Fuel effects on carbon formation were examined by measuring carbon formed during fuel vaporization of various fuel components and mixtures and by measuring carbon formed in the start-up of an ATR fuel reformer. The carbon formed was measured by physical collection and by in situ laser scattering-extinction measurements in the ATR experiments.

The light-off temperature of the ATR catalyst is a significant factor in its start-up performance. Thus, light-off temperatures were measured for fuel components, component blends, and real fuels in an isothermal catalyst test reactor.

The effect of fuel composition on fuel processor operating temperature and stability was compared between a catalytic partial oxidation reactor and a gas-phase partial oxidation reactor, both automotive-scale. Fuel composition effects were delineated by matching performance of real fuels with blended component mixtures.

Results

In autothermal reforming, proper fuel/steam/air mixture preparation is critical to avoid hot/cold spots, carbon formation, and catalyst degradation and to obtain proper conversion of hydrocarbons. Vaporization is one method to introduce fuel into a reformer, however it may lead to fuel pyrolysis, thus forming particulates or carbon during vaporization. Figure 1 compares the carbon formation measured during vaporization and refluxing of fuels and fuel components. In general, pure hydrocarbons did not show carbon formation, while real fuels did show carbon formation during the vaporization. The higher hydrocarbon streams such as kerosene and diesel fuel had more carbon formation than reformulated gasoline (RFG) or kerosene and diesel fuel in which sulfur had been removed. To suppress carbon formation with these fuels that pyrolyze, direct fuel injection into the authothermal reformer may be required instead of prior fuel vaporization.

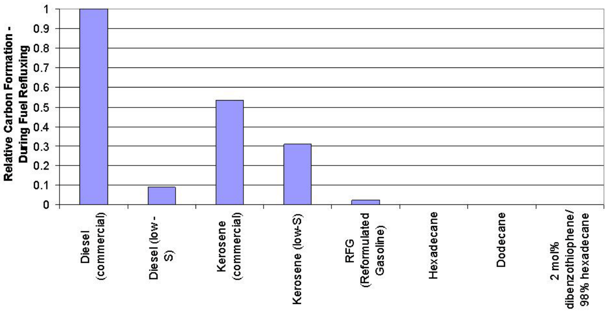

Figure 1. Carbon Formation Measured During Fuel Vaporization and Refluxing of Fuel Components

The start-up of the fuel processor system is critical for commercialization. During the start-up process, water may not be available. Without water it is impossible to light off a fuel processor at rich operating conditions and avoid regimes where carbon formation is favored by chemical equilibrium. Fuel effects on carbon formation during start-up were quantified for different fuel compositions using an ATR reactor. These measurements were made at steam/carbon ratios of 0.0 and 0.5, simulating low water light-off of the reactors. The carbon formed is summarized in Figure 2. Ethanol addition to iso-octane and RFG helps suppress carbon formation, while the addition of aromatic compounds or longer-chained hydrocarbon (dodecane) leads to increased carbon production.

Under rich operating conditions, catalysts require pre-heating before the oxidation reaction lights off, creating a self-sustaining exothermic reaction. The amount of preheat required is a factor in the start-up time and energy. Figure 3 shows measured light-off temperatures for various hydrocarbon fuel constituents. Straight-chained hydrocarbons are observed to light off at lower temperatures than similar branched-chained hydrocarbons. Aromatics, such as xylene and methylnaphthalene, increased the light-off temperature.

Figure 4 shows the change in the light-off temperature by the addition of oxygenated hydrocarbons and sulfur-containing hydrocarbons to iso-octane. The addition of oxygenated hydrocarbons, such as ethanol or methanol, to either

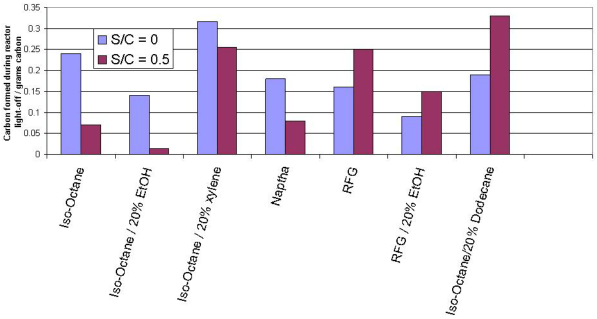

Figure 2. Fuel Composition Effect on Carbon Formation During Start-Up of ATR Reactor

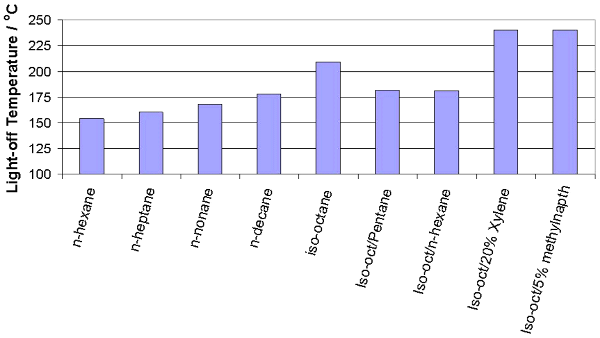

Figure 3. Fuel Composition Effect on ATR Light-Off Temperatures by Straight-Chained Aliphatic, Branched-Chained Aliphatic and Aromatic Hydrocarbons

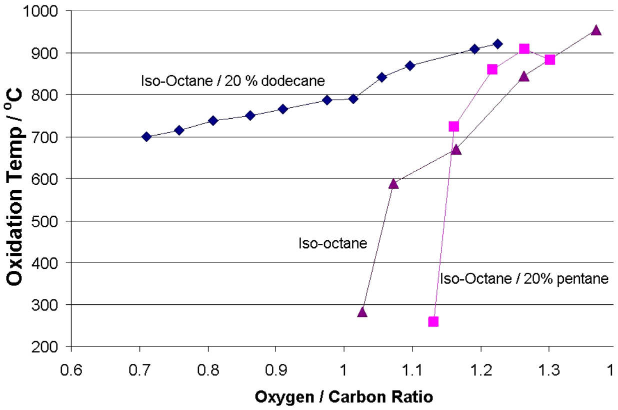

Figure 5. Comparison of Fuel Composition Effect of Heavy And Light Straight-Chained Hydrocarbon on Gas Phase Partial Oxidation

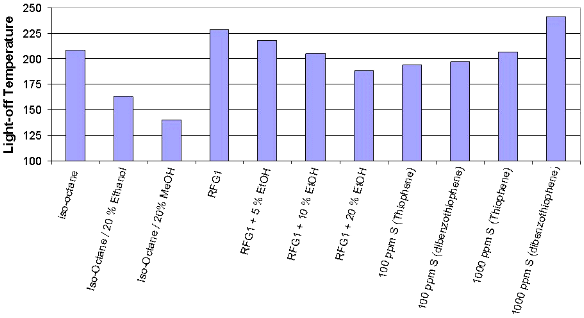

Figure 4. Fuel Composition Effect on ATR Light-Off Temperatures by Oxygenated Hydrocarbons and Sulfur Containing Hydrocarbons

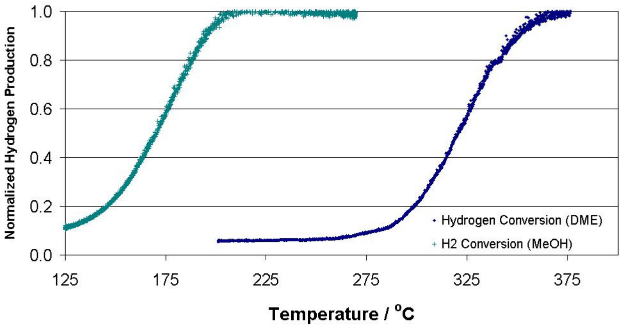

Figure 6. Comparison of Low-Temperature Reforming Fuels, Methanol And Dimethylether

iso-octane or RFG reduced the light-off temperature, with greater concentrations reducing the light-off temperature to a greater extent. The addition of sulfur-containing hydrocarbons at low concentrations (100 ppm S) reduced the light-off temperature, while higher concentrations (1000 ppm S) increased the light-off temperature.

In FY2002, we observed that during gas phase partial oxidation, real fuel blends operated stably at lower oxygen-to-carbon (O/C) ratios than pure components, such as iso-octane, opposite to the trend for catalytic partial oxidation. To delineate this effect, pentane (short-chained) and dodecane (long-chained) hydrocarbons were added to iso-octane and tested over a range of O/C ratios in the gas phase partial oxidation reactor. Figure 5 shows that the addition of dodecane increased the range of O/C ratio at which the gas phase partial oxidation reactor could operate, while pentane did not. Thus the long-chain hydrocarbons in real fuels increase the range of O/C ratio for gas phase partial oxidation, which is reflected in the relative cetane number of the fuel, a measure of the ignition delay.

Fuels such as gasoline and diesel fuel require high temperature reforming reactions. For portable power applications, there is interest in developing lower temperature reformers. Figure 6 shows a comparison of two fuels that reform at low temperature, methanol and dimethylether (DME). Full conversion of methanol was observed by about 205°C, while 360°C was required for DME. While DME requires a higher operating temperature, it does not have the toxicity issues that methanol has, and it still reforms at a significantly lower temperature than hydrocarbons containing carbon-carbon bonds.

Conclusions

Fuel effect on catalytic light-off has been measured for a large number of different components. Straight-chained hydrocarbons have a lower light-off temperature than similar carbon number branched-chained hydrocarbons. Aromatics require higher light-off temperatures, while oxygenated compounds lower the light-off temperatures.

Carbon formation was measured for various hydrocarbon compositions and operating conditions. Carbon formation was also measured during the fuel processor start-up transient. Aromatics show the highest tendency for carbon formation, while oxygenates help suppress carbon formation during light-off.

Fuel composition effects have been measured for their relative kinetics during catalytic and gas phase oxidation and reforming. Gas phase oxidation favors real fuel mixtures with longer-chained hydrocarbons over gasoline-sized hydrocarbons such as iso-octane. Steam concentration has a large effect on gas phase oxidation, while its effect on catalytic oxidation is not large. Catalytic oxidation favors short-chained aliphatic hydrocarbons, while aromatics and long-chained hydrocarbons have lower catalytic kinetics.

FY 2002 Publications/Presentations

1. 2002 American Chemical Society Meeting, Boston, Massachusetts, August 18-22.
2. 2002 Fuel Cell Seminar Poster, Palm Springs, California, Nov. 17-21.
3. Department of Defense Logistic Fuel Reforming Conference, Panama City Beach, Florida, August 27.
4. Spring 2003, American Institute of Chemical Engineers, New Orleans, Louisiana, March 30-April 3.
5. Hydrogen Production and Northwest Transportation Meeting, Seattle, Washington, June 16.
6. 2003 SAE Powertrain & Fluid Systems Conference, October 27-30, Pittsburgh, Pennsylvania, SAE paper 2003-01-3271.

Development of Reaction Kinetics for Diesel-Based Fuel Cell Reformers

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Objectives

Develop reaction kinetics, predictive models, and test methods for diesel fuel reforming and provide necessary tools and information to fuel reforming developers and fuel cell system integrators for technology development, performance optimization, and system control.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Fuel Processor System Integration and Efficiency

Approach

- Conduct process optimization study for the diesel autothermal reforming.
- Carry out kinetic measurements of representative model compounds.
- Develop a level-1 kinetic model with a benchmark fuel (diesel).
- Build liquid hydrocarbon characterization capability.

Accomplishments

- Tested three model compounds from the major representative functional groups in diesel fuel.
- Developed surface response maps for steam reforming, partial oxidation and autothermal reforming (ATR) using Pt/γ-alumina catalysts for n-tetradecane, 1-methylnaphthalene, and decalin.
- Built liquid hydrocarbon characterization capability.

Future Directions

- Evaluate other fuel compounds within a classification to examine if similar reforming behavior exists.
- Conduct combinatorial fuel compound studies.
- From response mapping, develop intrinsic reaction models for particular catalyst types.
- Collaborate with Las Alamos National Laboratory to provide carbon deactivation kinetics.
- Collaborate with Argonne National Laboratory to obtain experimental reactor performance data to validate reaction models and provide for fuel reactant mixing modeling capability suitable for computational fluid dynamic (CFD) modeling codes.
- Develop a detailed kinetic model that incorporates CFD.

Introduction

The fuel processor is a critical component of fuel cell systems. The processor must be able to provide a clean, tailored synthesis gas to the fuel cell stack for long-term operation. Key characteristics desired for the processor (and the system) include low cost, high efficiency, maximum thermal integration, low maintenance intervals, and acceptable startup and transient response. There are also several barrier issues that must be overcome to achieve these characteristics. Carbon formation, particularly upon startup, must be minimized to avoid coking of the catalysts in the reformer and downstream fuel cell. Fuels containing sulfur can poison both the reforming catalysts and the fuel cell anode. High thermal mass components (some of which may have heat-ramp restrictions) can limit startup times and transient response. And finally, cost targets must be achieved to ensure commercial success.

Fundamental understanding for design and operation of reformers is important for successful technology development. One of the most fundamental engineering design parameters that can be measured in the laboratory is the intrinsic kinetics of a catalyst system. Once established for a particular feedstock and catalyst system, it can be coupled with computational fluid dynamics (CFD) code to effectively design, optimize, and minimize hydrocarbon slip in autothermal reformer systems. In principle, the kinetics of NO_x formation, sulfur poisoning, carbon formation and catalyst aging can be added to allow for a complete predictive model for reformer performance and operation.

However, modeling of reforming systems is extremely complicated. Diesel fuel consists of a complex variable mixture of hundreds of hydrocarbon compounds containing mainly olefins, saturates and aromatics. Empirical expressions for space velocity or simple power law-type models are typically used to design reformers. Unfortunately, these tend to be limited to a specific catalyst, fuel composition, and operating point. Therefore, the development of validated predictive models that can account for variations in these parameters is necessary.

For the autothermal reforming of diesel with steam and oxygen, a complex reaction network is expected. Elucidation of this network and the development of a generalized complex network model for platinum catalysts will be the initial focus of this project. The overall kinetic approach employed will balance the level of detail that can accurately be accommodated by CFD code with the ability to easily update kinetic parameters for a new catalyst system.

Approach

To select an appropriate model, it is necessary to understand the reaction mechanisms and pathways for the chemical system. One approach to gaining that understanding is surface response mapping. This is a statistical technique used to map characteristic responses (e.g. yield, conversion, carbon buildup, etc.) to input variables (O_2/C, H_2O/C, temperature, space velocity, etc.) over a defined region. It identifies the significance of parameters and their interactions. Also, it provides data that can lead to validation of kinetic models and can test the statistical significance of proposed reaction pathways. As the most important mechanisms and reaction pathways are defined, appropriate models will be selected to develop the model. Kinetic measurements of single component or individual reaction systems will be developed and used to validate the model. This will initially be done for a platinum catalyst and extended to other catalyst systems as needed to complete the model.

A fixed bed reactor system was used to conduct the experiments. The reactor was operated continuously at steady state. γ-Alumina supported platinum (0.611 wt%) catalyst (surface area 103 m^2/g) was used in this study as a base catalyst. A summary of reaction conditions is given in Table 1.

Individual model compounds representing each organic class in diesel were subjected to autothermal, partial oxidation, and steam reforming at the temperatures and space velocities given in Table 1. Tetradecane, decalin, and 1-methylnaphthalene were identified as model compounds to represent paraffins, naphthenes, and aromatics, respectively, found in diesel.

Table 1. Experimental conditions

		Paraffin	Aromatic	Naphthene
Model Compound		**n-Tetradecane**	**1-methyl naphthalene**	**Decalin**
O_2/C	POX	0.5	0.5	0.5
	SR	0	0	0
	ATR	0.3	0.3	0.3
H_2O/C	POX	0	0	0
	SR	3.0	3.0	3.0
	ATR	1.5	1.5	1.5
T (°C)		750 - 900	750 - 850	750 - 850
GHSV (h^{-1})		50,000 - 200,000	22,000 - 66,000	50,000 - 150,000

Gas chromatography was used to identify and separate the reaction products. The gases (N_2, O_2, CO, CO_2, and CH_4) were analyzed using a thermal conductivity detector (TCD), and the gaseous hydrocarbons were analyzed using a flame ionization detector (FID). Gas chromatography (Perkin Elmer's AutoSystem XL) coupled with mass spectrometry (Perkin Elmer's TurboMass Gold) was used to quantify and identify the complex liquid hydrocarbon product mixture that formed at various hydrocarbon conversions. Product yield is reported as a percentage of the theoretical yield based on moles of carbon in hydrocarbon fed to the reactor. For example, the yield of product A (H_2, CO, and CO_2) can be defined as

$$\text{Yield of A (\%)} = \frac{\text{Moles of A produced}}{\text{N} \times \text{moles of hydrocarbon fed to the reactor}} * 100$$

where N is the number of carbons in hydrocarbon fuel used in this study. In some cases, H_2 yields may be higher than 100% since steam reforming and the water gas shift reaction also contribute to H_2 production apart from hydrocarbons.

Results

Statistical Analysis of Reforming Process

The yields of individual species from hydrocarbon reforming, z, which depend on the space velocity (x) and reaction temperature (y), can be described by the equation

$$z = b_0 + b_1x + b_2y + b_{11}x^2 + b_{22}y^2 + b_{12}xy \quad (1)$$

where z = the yield of individual species after completion of the reaction, x = gas hourly space velocity (hr^{-1}), y = temperature (°C), and $b_0 \ldots b_{22}$ are the coefficients of the model. The coefficients of Equation 1 were estimated by making use of the responses of experiments for the standardized values of x and y which varied in the range given in Table 1. A relationship between yields (z) and two quantitative variables x (space velocity) and y (reaction temperature) is represented by response surface curves as shown in Figures 1-5. Coefficients of quadratic Equation 1 are summarized in Table 2 for H_2 and CO yields from autothermal reforming of various types of raw materials used in this study. Quadratic fit of data from response surface mapping was excellent (>90%).

Analysis of a response surface curve can be helpful in establishing the hypothetical kinetic schemes of the process. The effect of different parameters on the course of a process may vary from one organic class to another. That is why we decided to study each organic class separately.

Model compounds representing each homologous series present in diesel were evaluated to develop surface response maps for steam reforming, partial oxidation and autothermal reforming over Pt catalysts. Each model compound behaved differently upon reforming under the same conditions. Aromatics were less active than aliphatics and required relatively higher contact time to convert into synthesis gas. The hydrogen production rates at the same conditions were observed in this order: Aromatics << Naphthenes < Paraffins.

Table 2. Coefficients of Quadratic Equations for Autothermal Reforming of Model Components

Fuel	X	Coefficients						R^2
		b_0	b_1	b_2	b_{11}	b_{12}	b_{22}	
Tetradecane	H_2	1313.8	$-6.0e^{-4}$	-2.36	$1.4e^{-9}$	$-1.4e^{-7}$	$1.2e^{-3}$	0.96
	CO	283.8	$2.9e^{-4}$	-0.62	$7.4e^{-10}$	$-6.3e^{-7}$	$3.9e^{-4}$	0.98
1-Methylnaphthalene	H_2	1155.9	$1.9e^{-3}$	-2.36	$4.7e^{-9}$	$-2.4e^{-6}$	$1.2e^{-3}$	0.98
	CO	521.8	$1.7e^{-3}$	-1.14	$-6.1e^{-10}$	$-1.6e^{-6}$	$6.2e^{-4}$	0.96
Decalin	H_2	627.4	$-2.6e^{-4}$	-1.47	$2.7e^{-9}$	$-4.2e^{-7}$	$8.7e^{-4}$	0.97
	CO	1975.2	$-1.2e^{-3}$	-3.67	$1.7e^{-9}$	$-6.7e^{-7}$	$1.7e^{-3}$	0.87

Hydrocarbon product distributions depended greatly on the model compound, the type of reforming performed, and the process parameters (space velocity and reaction temperature). Generally, in addition to desired products (H_2 and CO), the gas product streams also include CO_2, C1 to C7 n-alkanes, ethylene, propylene, iso-butane, iso-pentane, and benzene. Methane and CO_2 were the major by-products present in significant amounts in the gas product streams. Furthermore, a series of oxygenated products such as aldehydes and ketones were observed in liquid product from partial oxidation of n-tetradecane, particularly at higher space velocities and lower temperatures.

Figures 1-3 show the effect of temperature and space velocity on the yields of H_2, CO, and CO_2 from the autothermal reforming of n-tetradecane (paraffin). Figures 4-5 show the yields of H_2 from the autothermal reforming of 1-methylnaphthalene (aromatic) and decalin (naphthene), respectively. Generally, the yields of H_2 and CO increased with increasing reaction temperature and decreasing space velocity. However, the yields of CO_2 from autothermal reforming of n-tetradecane and decalin decreased with increasing temperature because the lower temperatures favor the water-gas-shift reaction, while the reverse of water-gas-shift reaction is facilitated at higher temperatures.

Higher yields of methane (1-10%) were observed in the product gas from autothermal reforming of different feedstocks. Methane is not thought to be produced from the methanation reactions because those reactions are not thermodynamically favored at the temperature studied. It is probable that CH_4 is formed by successive α-scission of the hydrocarbons on the metal catalysts,

$$C_nH_m => CH_4 + C_{n-1}H_{m-4} \quad (2)$$

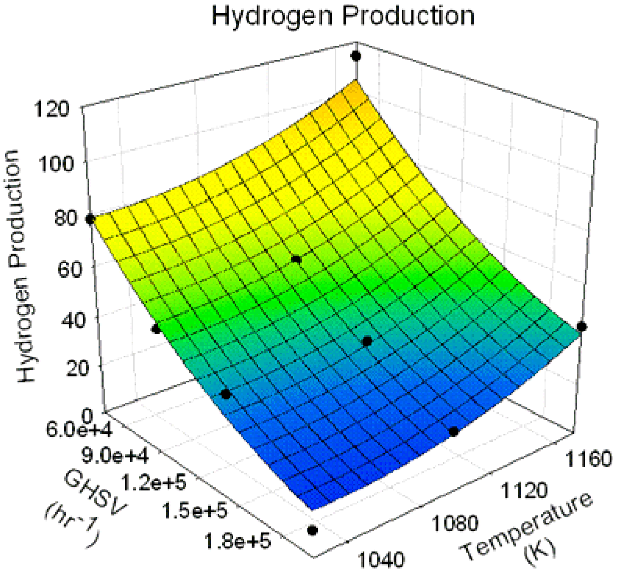

Figure 1. Yield of H_2 from ATR of n-Tetradecane ($O_2/C = 0.3$ and $S/C = 1.5$)

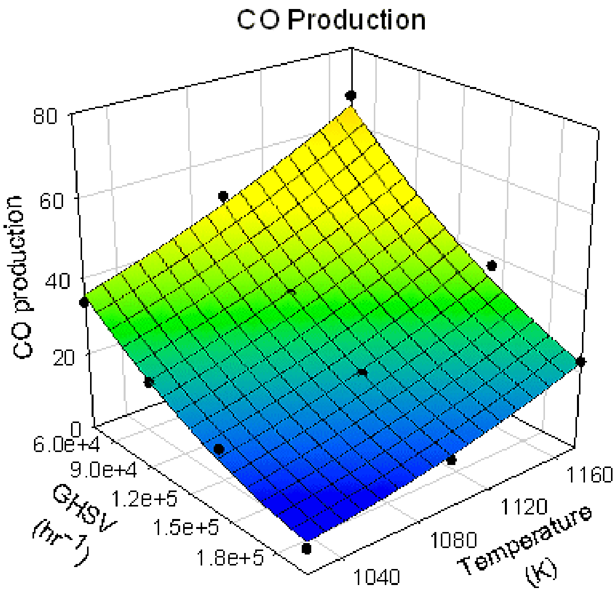

Figure 2. Yield of CO from ATR of n-Tetradecane ($O_2/C = 0.3$ and $S/C = 1.5$)

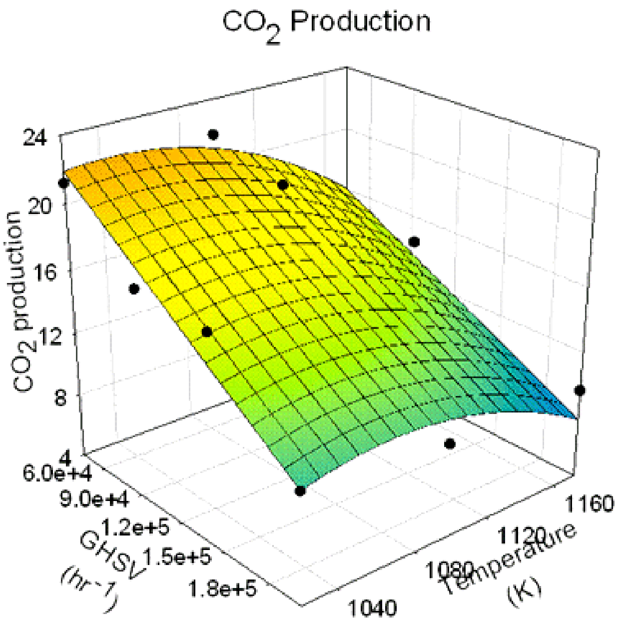

Figure 3. Yield of CO_2 from ATR of n-Tetradecane (O_2/C = 0.3 and S/C = 1.5)

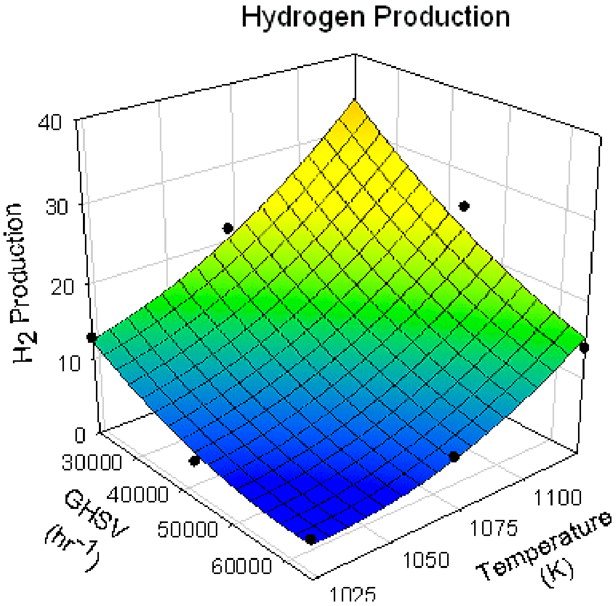

Figure 4. Yield of H2 from ATR of 1-Methylnaphthalene (O2/C = 0.3 and S/C = 1.5)

Higher yields of methane compared to negligible other hydrocarbons coupled with the significant concentrations of naphthalene in the product stream from autothermal reforming of 1-methylnaphthalene suggests that the reforming of aromatics starts with a dealkylation reaction.

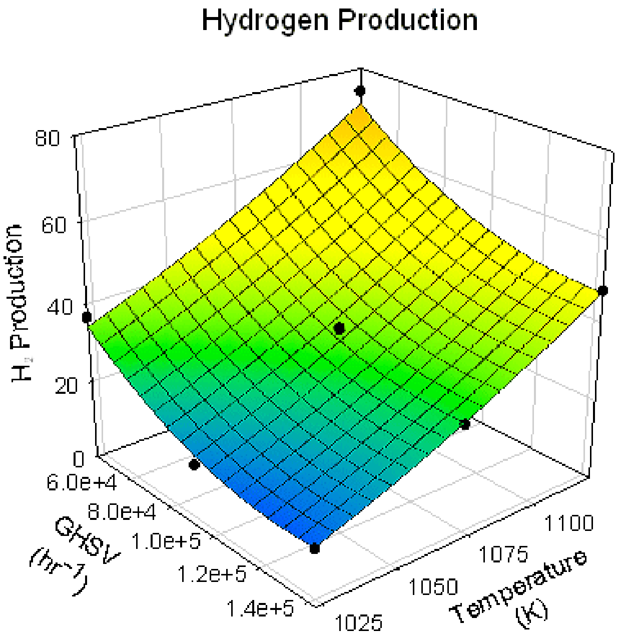

Figure 5. Yield of H_2 from ATR of Decalin (O_2/C = 0.3 and S/C = 1.5)

Yields of cracking products, lower paraffins and olefins, decrease as temperature increases or space velocity decreases. Higher temperature facilitates the cracking reaction, but at the same time, it also increases the rate of reforming reaction. Increasing the residence time would increase the contact time between the catalyst and reactants, thereby increasing the conversion of cracking products into syngas and reducing the yield of cracking products.

Isoparaffins or branched olefins were not observed, which suggests that isomerization reactions are not taking place during reforming of diesel fuel components. Also, naphthenes were not detected from the autothermal reforming of paraffins or aromatics. However, a series of olefins (alkenes, dienes, trienes, alkynes, etc.) formed from reforming of n-tetradecane, particularly at higher space velocities and lower temperatures.

Production of olefins and aromatics was significant from autothermal reforming as well as partial oxidation of n-tetradecane at higher space velocity and temperature. Formation of compounds such as n-octyl benzene, but no naphthenic compounds from the paraffin reforming, suggests that the aromatics are produced primarily by cyclization reactions of poly-enes rather than cyclization of paraffins to naphthenes and then dehydrogenation to aromatics. Reforming of decalin also produced significant concentration of aromatics, presumably via dehydrogenation reaction.

Reforming of 1-methylnaphthalene at elevated temperatures (~900°C) produced significant coking on the catalyst and resulted in higher pressure drops and eventually reactor plugging. Aromatics contribute significantly to the catalyst deactivation compared to paraffins and cycloparaffins present in the diesel fuel.

Conclusions

Single component reforming studies were conducted on tetradecane, decalin, and 1-methylnaphthalene. These model compounds represented the major organic classes found in diesel fuel (paraffins, naphthenes, and aromatics) and, studied individually, aided in analyzing the reforming characteristics and tendency of each species. Use of a surface response mapping technique was helpful in assessing the impact of space velocity (residence time) and temperature on reforming of the various compounds. Hydrogen, carbon monoxide, and carbon dioxide production were measured as a function of temperature, space velocity, and reforming type for a platinum-based catalyst. Intermediate species formation of various hydrocarbons including olefins and aromatics were observed during reforming. Carbon formation at various operating points and with certain fuel compounds point to the importance of understanding the mechanism or route for both reformer operation and catalyst design. Additional studies, including combinatorial fuel reforming, are needed to ensure successful development of this technology area.

FY 2003 Publications/Presentations

1. Rogers, W., Shi, S., Berry, D. A., Gardner, T. H., Shekhawat, D., "Modeling of Reformers for Fuel Cell Applications", First International Conference on Fuel Cell Science, Engineering and Technology, Rochester, NY, April 21-23, 2003.
2. Shi, S., Rogers, W., Berry, D. A., Gardner, T. H., Shekhawat, D., "Numerical Simulation of Partial Oxidization Processing of Diesel for Fuel Cells", Fourth ASME/JSME Joint Fluids Engineering Conference, Honolulu, HI, July 6-11, 2003.
3. Zinn, A. N., Gardner, T. H., Berry, D. A., James, R. E., Shekhawat, D., "Investigation of a Novel Reciprocating Compression Reformer for Use in Solid Oxide Fuel Cell Systems", First International Conference on Fuel Cell Science, Engineering and Technology, Rochester, NY, April 21-23, 2003.
4. Berry, D. A., James, R. E., Gardner, T. H., Shekhawat, D., "Systems Analysis of Diesel-Based Fuel Cells", First International Conference on Fuel Cell Science, Engineering and Technology, Rochester, NY, April 21-23, 2003.
5. Berry, D. A., Gardner, T. H., Shekhawat, D., "Development of Predictive Models for Diesel-Based Fuel Processors", 2003 Annual Merit Review Meeting of Hydrogen, Fuel Cells & Infrastructure Technologies Program, DOE Office of Energy Efficiency and Renewable Energy, Berkeley, CA, May 18 - 22, 2003.

Reforming of Diesel Fuel for Transportation Applications

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Objectives

- Verify feasibility of diesel autothermal reforming (ATR) in engineering-scale reformer
- Demonstrate operation with liquid fuel injection
- Reduce H_2O:C ratio needed to prevent coking

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- J. Durability
- M. Fuel Processor Integration and Efficiency
- N. Cost

Approach

- Perform computational fluid dynamics (CFD) modeling of reactors to guide reactor design
- Investigate reforming chemistry to determine how diesel fuel formulations, H_2O:C ratio, and O_2:C ratio affect reforming efficiency, coking, and catalyst lifetime
- Optimize reactor engineering based on results from modeling and reforming chemistry

Accomplishments

- Demonstrated successful operation of liquid fuel injector
- Determined effect of O_2:C and H_2O:C ratios on reforming efficiency for several different diesel components
- Demonstrated that di-aromatic components are more difficult to reform than mono-aromatics

Future Directions

- Determine how fuel composition affects catalyst durability
- Investigate reforming under partial oxidation (POX) conditions and in low H_2O:C regimes
- Provide data for National Energy Technology Laboratory (NETL) model development and validation

Introduction

Diesel fuel is widely distributed and has a high energy density. This makes diesel reforming an attractive option for hydrogen production on-board vehicles. The hydrogen-rich reformate gas produced from diesel reforming can be used to produce power with fuel cells or used to reduce NO_x emissions from combustion engines using reformate feed to selective catalytic reduction units. Diesel reforming poses several unique technical challenges, however. These challenges result from the physical and chemical properties of diesel fuel. To better understand diesel reforming and the chemistry involved, we have investigated the autothermal reforming of several major diesel constituents in a kilowatt-scale reactor.

Major technical challenges in reforming diesel fuel include preventing coking while maintaining high reforming efficiencies and extending the catalyst lifetime/durability. We have found that delivering the fuel and obtaining a well-mixed stream of fuel, steam, and air before the fuel begins to decompose thermally can affect catalyst durability and coking. Due to the high boiling point of diesel fuel, vaporizing the fuel and using gas-phase mixing prior to the reactor is not a viable option. Poor mixing leads to oxygen-starved regions, regions where the reactant ratios favor coke formation, and hot spots that accelerate catalyst degradation. To overcome this problem, we developed and tested an injection nozzle of a new design. This injector design led to well-mixed reactants that allowed us to reform diesel surrogates and obtain reformate compositions that closely match those predicted by equilibrium thermodynamic calculations. In addition to the reactant vaporization and mixing issues, the complex nature of diesel fuel also leads to several challenges in reforming. To understand better the chemistry of diesel reforming, we have investigated the reforming of representative compounds from the different classes of hydrocarbons present. Experiments were performed at gas hourly space velocities (GHSV) of 10,000 to 100,000 h^{-1} with varying oxygen-to-carbon ($0.15<O_2/C<0.5$) and steam-to-carbon ($1<H_2O/C<3$) ratios to determine the influence of these parameters on product gas composition and on reformer efficiency.

Approach

Computational fluid dynamics (CFD) modeling was utilized to study mixing of reactants and to guide improvements in a liquid injector system to deliver fuel to the reactor. The spray behavior of the new liquid injector nozzle was characterized with the help of a nonintrusive, laser-based phase Doppler particle analyzer (PDPA). After testing, the injector was installed in an engineering-scale reactor for the reforming tests.

Model compounds of different types of hydrocarbon species found in diesel fuel were tested under autothermal reforming conditions in the engineering-scale reactor. No external heating was supplied to the reactor. The product gas compositions were determined with various steam-to-carbon and oxygen-to-carbon ratios.

Results

We have performed CFD modeling studies that indicate that mixing of reactants is critical in avoiding hot spots and cold spots. The results also indicate that substantial variations occur in the H_2O:C and O_2:C ratios across the catalyst. The H_2O:C ratio is critical in controlling coking. To address this problem and provide well-mixed reactants to the catalyst bed, we have developed an innovative injector nozzle that produces small droplets of diesel fuel with low air-side pressure drops. It intimately mixes the fuel, steam (or water at startup), and air prior to the catalyst bed. In tests with hexadecane, the corrected and fitted mass median diameter (MMD) determined from PDPA over the central 1.5" of the spray was 8.3±2.7 µm at high-flow conditions (10 ml/min hexadecane) and 8.0±2.3 µm at low-flow conditions (3 ml/min hexadecane).

We have initiated a study of reforming of the various types of chemicals found in diesel fuel using liquid injection. Reforming of species found in diesel fuel indicate that there are differences in how the different species react. The product gas composition from reforming dodecane, hexadecane, and xylene as a function of O:C ratio (oxygen coming from O_2 in air) is shown in Figure 1. The hydrogen yield increases with increasing O:C to a

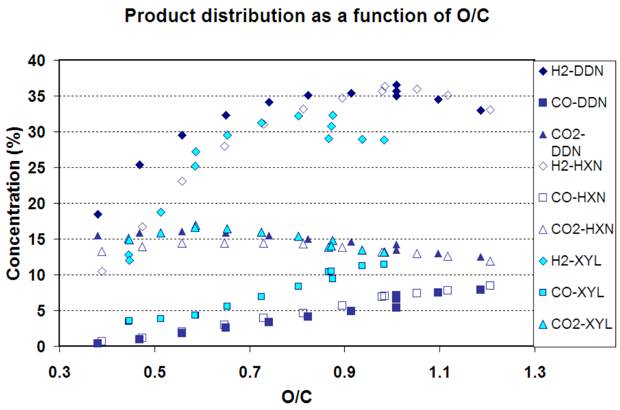

Figure 1. Effect of the O:C Ratio on the Product Gas Distribution from Autothermal Reforming of Dodecane (DDN), Hexadecane (HXN) and Xylene (XYL) in an Engineering Scale Reactor

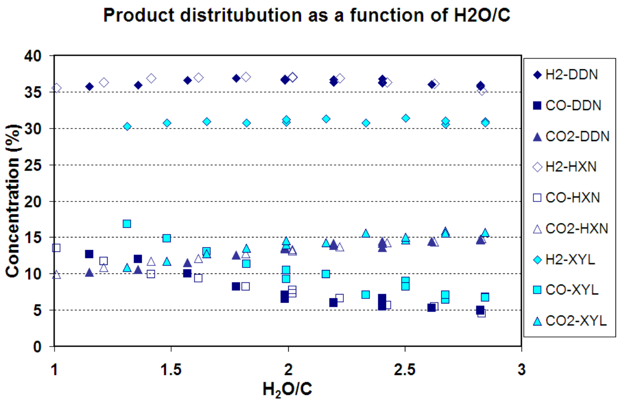

Figure 2. Effect of the H_2O:C Ratio on the Product Gas Distribution from Autothermal Reforming of Dodecane (DDN), Hexadecane (HXN) and Xylene (XYL) in an Engineering Scale Reactor

maximum at an O:C of approximately 1.0 for dodecane and hexadecane and 0.8 for xylene, then decreases. The increase occurs more rapidly for the shorter chain length dodecane than for hexadecane or xylene. Reforming efficiency also increases with O:C, reaching a maximum where the H_2 concentration maximizes, then levels off. Reforming efficiency is defined as:

$$\eta_{ref} = \{Ct_{H2}\Delta Hc_{H2} + Ct_{CO}\Delta Hc_{CO}\}/Ct_{fuel}\Delta Hc_{fuel}$$

$Ct_{,i}$ = Molar flow rate of i
ΔHc_i = *Heat of combustion of i*

The effect of the H_2O:C ratio on reforming is shown in Figure 2. As the H_2O:C ratio increases, the hydrogen content increases slightly, while the CO concentration decreases. This leads to an overall decrease in efficiency with increasing H_2O:C ratio. The decrease is likely the result of the increased thermal load from the additional steam, which results in lower reactor temperatures.

Xylene was more difficult to reform than the paraffinic species, providing lower hydrogen content and resulting in higher catalyst temperatures at similar O:C and H_2O:C ratios. Methylnaphthalene was reformed to determine how the multi-ring aromatic species present in diesel fuel react during reforming. Reforming of the methylnaphthalene was more difficult than the reforming of xylene. Reforming efficiencies were lower, and coke deposits were more likely to form.

Conclusions

- Proper delivery and mixing of reactants are needed to obtain high efficiencies and avoid hot spots and areas of non-uniform H_2O:C and O:C ratios.
- The new liquid injector nozzle provided small (<10 micron) droplets of fuel under relevant reactor operating conditions.
- Substantial differences were found and documented in how the major different diesel fuel constituents are reformed.
  - Aromatics result in higher maximum reforming temperatures and lower energy conversion efficiencies.
  - Di-aromatics are more difficult to reform than mono-aromatics.
- Increasing H_2O:C ratio reduces coking but decreases overall efficiency.

FY 2003 Publications/Presentations

1. "Characterization of Kilowatt Scale Diesel Autothermal Reformer With Surrogate Fuels", Di-Jia Liu, Hsiu-Kai Liao, Laura Miller and Shabbir Ahmed, presented at 2003 AIChE Spring National Meeting, New Orleans, LA, March 30 - April 3, 2003.

2. "Diesel Reforming for Fuel Cell Application in a 1- to 5-Kilowatt ATR Reformer", Di-Jia Liu, Hsiu-Kai Liao, Laura Miller and Shabbir Ahmed, presented at 18th North American Catalysis Society Meeting, Cancun, Mexico, June 2 - June 6, 2003.

3. "Diesel Reforming in a Kilowatt Scale Autothermal Reformer with Liquid Injection", Di-Jia Liu, Hsiu-Kai Liao, Laura Miller and Shabbir Ahmed, presented at 2003 Future Transportation Technology Conference, June 23-25, 2003, Hilton, Costa Mesa, California.

4. "Diesel Reforming in a Kilowatt Scale Autothermal Reformer with Liquid Injection", Di-Jia Liu, Hsiu-Kai Liao, Laura Miller and Shabbir Ahmed, SAE publication 03FTT-6.

Advanced High Efficiency Quick Start Fuel Processor for Transportation Applications

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Engelhard Corporation
Worcester Polytechnic Institute
Calnetix

Objectives

With the STAR (Substrate-based Transportation Autothermal Reformer) and HiQ (High Efficiency Quick Start Transportation Fuel Processor) projects, Nuvera's goal is to develop an advanced fuel processing system for transportation applications. The HiQ concept combines a fuel processor, a fuel cell, and a turbogenerator for power generation and is also useful for stationary applications where high efficiency is critical. This is a combined report for both the STAR and HiQ projects.

<u>STAR</u>

- Develop technologies needed to improve the power density, specific power, and start-up time of fuel processors. These technologies include lightweight advanced low thermal mass catalysts, substrates, compact heat exchangers, and desulfurization media.
- Design and test the STAR fuel processor to ensure that it meets or exceeds FreedomCAR targets. Identify areas of improvement.
- Prove reliable operation of the fuel processor via integration with a proton exchange membrane (PEM) fuel cell.
- Increase system durability via fuel purification, reformate clean-up, catalyst advances, and mechanical design iterations.

<u>HiQ</u>

- Design, develop, and test a high power density, multi-fuel processor system that enables high efficiency and quick start operation of an integrated fuel cell power system for automotive applications. The concept will combine a low thermal mass catalytic fuel processor with a turbogenerator, leading to a hybrid system.
- Develop low-cost, high space velocity water-gas shift catalysts with subcontractors.
- Demonstrate rapid startup to low power and high net system efficiency.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Start-Up/Transient Operation
- J. Durability
- L. Hydrogen Purification/CO Clean-Up
- M. Fuel Processor System Integration And Efficiency
- N. Cost

Approach

STAR

- Perform automotive system analysis and identify strategies to meet FreedomCAR targets.
- Work closely with sub-contractors to develop key technologies and sub-components.
- Design, build, and test a compact integrated multi-fuel processor to investigate efficiency, power density, emissions, and reformate purity.
- Integrate the STAR fuel processor and a fuel cell, investigate the performance of the power system, and identify system level integration issues.
- Deliver the integrated fuel processing system to Argonne National Laboratory for testing.

HiQ

- Integrate STAR-type fuel processor with a turbo-generator system to recover waste energy from the fuel cell stack and provide capability for rapid start (less than one minute) to partial power levels.
- Design and build proof-of-concept fuel processor and turbo-generator system using conventional pelleted catalyst technologies.
- Demonstrate rapid start-up and high-efficiency operation on proof-of-concept system.
- Design and build high power density automotive multi-fuel fuel processor combining STAR and HiQ technologies.
- Deliver the integrated fuel processing system to Argonne National Laboratory for testing.

Accomplishments

STAR

- Continued to advance the compact fuel processor design using substrate-based catalysts, custom heat exchangers and burners, and innovative mechanical design.
- Fuel processor achieved automotive volume (75 liters), power density (2.1 kW-H_2/liter of fuel processor), and aspect ratio (<9 inch height).
- Tested the complete compact fuel processor on gasoline, ethanol, and natural gas.
- Achieved 200 kWth on gasoline with 80% hydrogen efficiency and CO < 50 ppm.
- Evaluated STAR operation on natural gas at 175 kWth feed rate with 74% hydrogen efficiency and CO < 50 ppm.
- Demonstrated STAR operation on ethanol at 180 kWth feed rate with 75% hydrogen efficiency and CO < 50 ppm.

- Integrated the fuel processor with a fuel cell to achieve 35 kWe and a gross efficiency of 31% (31 kWe from 100 kWth).
- Pushed the limits of the STAR design through durability testing and made significant advances in hours, thermal cycles, and mechanical design. The durability test results guided research into sub-component tests that are now ongoing.

HiQ

- Modeled, designed and constructed a proof-of-concept fuel processor system incorporating the key new technologies for the Nuvera HiQ combined-cycle process.
- Tested the HiQ proof-of-concept fuel processor in the laboratory with a stack simulator and a standard automotive turbocharger.
- Demonstrated less than 60 second start-up time to net power availability.
- Demonstrated fuel processor performance consistent with 40% net system efficiency.
- Demonstrated low exhaust emissions over entire start-up transient, as well as at steady state.
- Designed low cost integrated turbine-compressor-motor-generator system with sub-contractor and started development program.

Future Directions

STAR

- Complete testing on ethanol and natural gas.
- Continue fuel processor performance optimization on gasoline operation.
- Continue sub-component development with sub-contractors.
- Deliver fuel processor system to Argonne National Laboratory, complete STAR project, and submit final report.

HiQ

- Demonstrate proof-of-concept system over full load range.
- Demonstrate proof-of-concept system integrated with turbine-compressor-motor-generator subsystem.
- Design and build automotive fuel processor incorporating STAR technology advances.
- Demonstrate start-up, efficiency, and emissions characteristics of automotive fuel processor in conjunction with turbine-compressor-motor-generator.
- Deliver fuel processor with turbine-compressor-motor-generator to Argonne National Laboratory.

Introduction

Nuvera Fuel Cells, Inc. (Nuvera) is a leading developer and supplier of fuel cells, fuel processors, and integrated power systems for the stationary, industrial, and transportation markets. Nuvera is working with the U.S. Department of Energy (DOE) to develop efficient, low emission, on-board multi-fuel processors for the transportation application. The fuels of interest are gasoline, methanol, ethanol, and natural gas.

Approach

With the STAR and HiQ programs, Nuvera is addressing the goal of developing a high power density, quick start fuel processing system that also provides very high net direct current (DC) efficiencies when coupled with an appropriate fuel cell. The STAR project is focused on development of high power density substrate reforming technology, while the HiQ project to date has developed new system integration and power cycle technology to enable quick start and high efficiency. The STAR project will end in 2003; the HiQ project will continue by incorporating the STAR technology into a novel system integration scheme, capitalizing on the benefits of both.

Results

STAR. Based on catalyst, burner, and heat exchanger technologies produced in previous years, Nuvera built and tested several iterations of the compact STAR fuel processing system. The design, which has a total volume of ~75 L, contains all the catalytic reaction zones, the steam generation system, and heat exchangers (Figure 1). This fuel processor also has the shape factor necessary for installation in the fuel cell vehicle.

During this reporting period, Nuvera tested the STAR fuel processor on gasoline, ethanol, and natural gas. The design focus was gasoline, and the majority of the effort was spent on optimizing gasoline performance. The gasoline results exceeded targets, with a hydrogen efficiency of 80% and CO of less than 50 ppm at up to 200 kWth (Figure 2 shows 180 kWth data) feed rate. The STAR fuel processor also showed successful operation on ethanol and natural gas, processing both fuels with less than 50 ppm CO and hydrogen efficiencies of ~75%. Natural gas and ethanol testing focused on proving the fuel flexibility, and efficiencies were lower than gasoline only because time constraints prevented full optimization.

The STAR fuel processor also underwent durability testing to investigate the limits of the design. Mechanical durability has been improved significantly - over five enhancements in the longevity (hours) and 100% improvement in thermal cycle capability as compared to the previous compact fuel processors (Figure 3). The durability results suggested areas of sub-component research, which are currently underway both at Nuvera and sub-contractors.

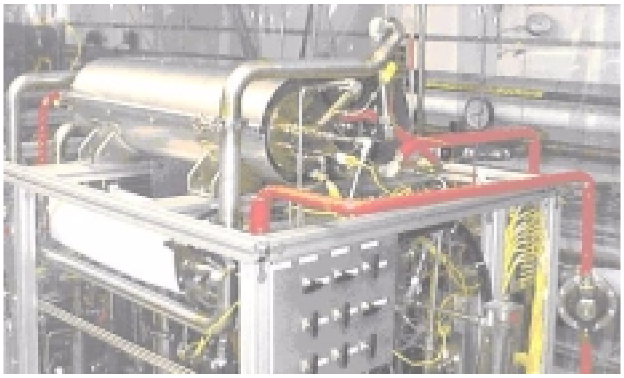

Figure 1. STAR Fuel Processor on Test Cart

To ensure high quality of STAR reformate, the fuel processor was integrated with a fuel cell (Figure 4). The integration was successful and produced 35 kWe and was limited only by the laboratory air supply system. The gross efficiency achieved was 31%, i.e. the system produced 31 kWe from the fuel cell with 100 kWth of gasoline fed to the fuel

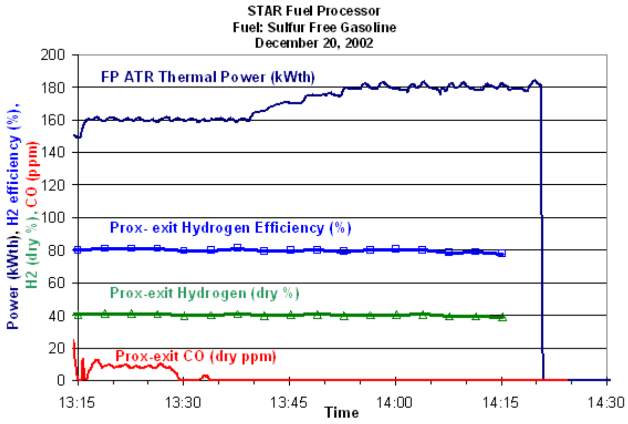

Figure 2. STAR Fuel Processor Operation on Gasoline (160-180 kWth)

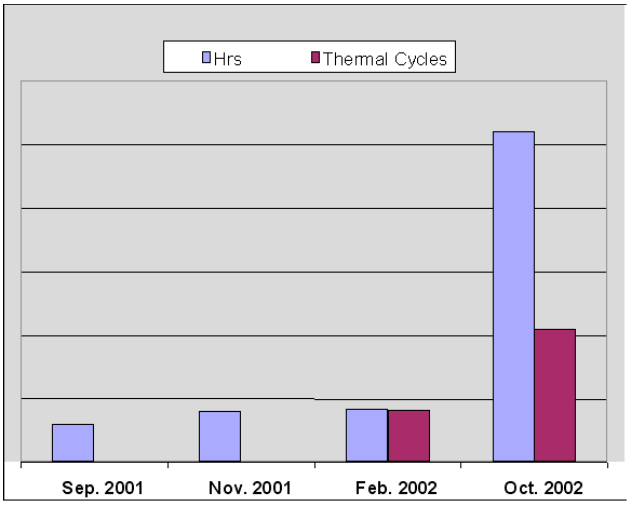

Figure 3. Durability Improvement of Nuvera STAR Fuel Processor

processor. There is significant room for improving the system efficiency; however, this is beyond the scope of the current project. The integration and fuel processor performance results indicate that the STAR fuel processor has the minimum rating of 62 kWe, exceeding the program target of 50 kWe.

The STAR fuel processor program represents a culmination of four years of intensive R&D and design efforts. Nuvera started with basic component testing of the catalysts and developed custom heat exchanger and burner designs. Today, Nuvera has combined these components to produce an advanced automotive fuel processor that finally achieves the volume, power, efficiency, hydrogen production, and reformate quality targets for onboard fuel processors.

HiQ. The focus of the HiQ project in the past year has been on proving the feasibility of increasing system efficiency and decreasing startup time via novel system integration strategy. The block diagram shown in Figure 5 outlines the HiQ system configuration. High system efficiency is achieved by using the waste heat from the stack to evaporate water into the cathode air. The resulting flow of water vapor is heated to an appropriate temperature in the combustor and passed through the turbine, where it generates mechanical power. The integrated generator on the turbine shaft converts this mechanical power into electrical output. Thus, the system converts heat that is ordinarily wasted into useful electrical power, which improves the overall system efficiency.

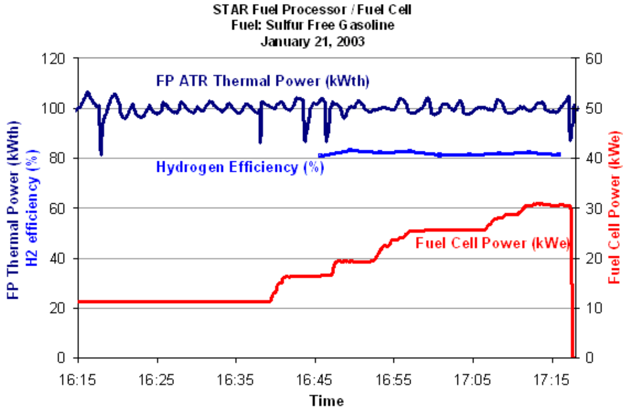

Figure 4. STAR Fuel Processor/Fuel Cell Integration

The technical challenges involved include combustor, heat exchanger, and fuel processing improvements to enable this heat-to-power conversion to take place. A key aspect of the process is that the combustor technology developed by Nuvera in this project allows the use of high-temperature automotive turbine technology. Not only does this reduce cost, but it also allows quick start-up; the combustor and turbo-generator can be operated as a micro-turbine at start-up, allowing for some power production even before the fuel processor is warmed up and the fuel cell is producing power.

The feasibility demonstration was successfully carried out using a proof-of-concept fuel processor, stack simulator, and automotive turbocharger.

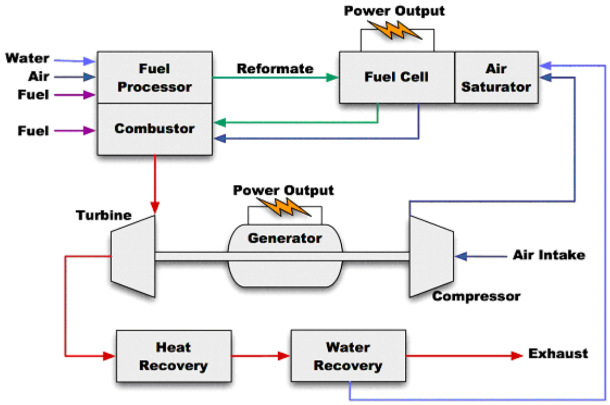

Figure 5. HiQ System Integration Concept

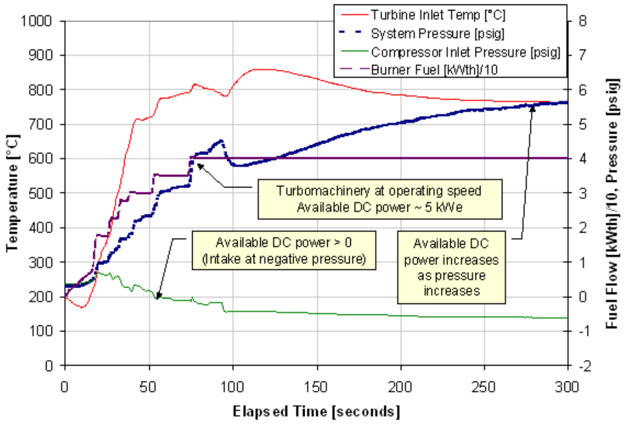

Figure 6. Plot of HiQ system startup with automotive turbocharger used as placeholder for turbine/compressor/motor/generator system. The system reaches a state that will correspond to net power output from the turbo-generator in less than 60 seconds from start-up.

Computational models were used to project fuel cell and turbo-generator power output levels based on the observed laboratory data. As shown in Figure 6, the start-up time to the low power micro-turbine mode has been demonstrated to be less than 60 seconds.

Conclusions

STAR

- The substrate-based STAR fuel processor meets the volume (75 L), power (200 kWth), hydrogen efficiency (80%), and CO (<50 ppm) targets for onboard fuel processors.
- Durability testing of the STAR fuel processor showed great improvements in mechanical design and suggested areas of research that are currently ongoing.
- A STAR fuel cell/fuel processor integration proved high reformate quality with successful operation of the fuel cell.

HiQ

- A proof-of-concept fuel processor system has been developed and has demonstrated the feasibility of the HiQ system integration scheme.
- Laboratory results support projections of start-up times of less than 60 seconds to partial power levels.

FY 2003 Publications/Presentations

1. Jian L. Zhao, William Northrop, Timothy Bosco, Brian Bowers, *On-Board Gasoline Fuel Processor ---- STAR.* AIChE 2003 Spring National Meeting – Topical Conference on Fuel Cell Technology, Session 99, New Orleans, LA, 30 March-3 April 2003.

2. Lawrence Clawson, James Cross, Christopher O'Brien, *Development and Analysis of a 50 –100 kW Hybrid Cycle Integrated PEM Fuel Cell and Fuel Processor System with High Efficiency and Rapid Start-up*, presented at "Fuel Cell Advances 2002," Amsterdam, The Netherlands, 25-26 September 2002.

Development of a 50-kW Fuel Processor for Stationary Fuel Cell Applications Using Revolutionary Materials for Absorption-Enhanced Natural Gas Reforming (New FY 2004 Project)

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Objectives

- Develop and test a fuel processor capable of producing a high hydrogen concentration (>98%) reformate containing inconsequential levels of carbon dioxide and carbon monoxide.
- Develop high durability CO_2 absorbents containing both high temperature water gas shift (WGS) and steam reforming catalysts.
- Perform process design, system efficiency, and cost estimate studies.
- Design, construct, and test a "stand alone" natural gas fed 50-kW fuel processor which will meet these performance targets: efficiency >85%, CO concentration <10 ppm, H_2S concentration <50 ppb, system life >40,000 hours.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Start-Up Time
- J. Durability
- K. Emissions/Environmental Issues
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- N. Cost

Approach

ChevronTexaco will develop a natural gas fueled 50-kW fuel processor capable of producing a high hydrogen concentration (>98%) reformate containing inconsequential levels of carbon dioxide and carbon monoxide. This capability will be achieved using a new catalyst powder manufacturing technique which promises to breathe new life into an old fuel processing concept, adsorption-enhanced reforming (AER). ChevronTexaco will use a unique spray-based powder manufacturing approach to develop and produce powders that have been specifically designed for absorption-enhanced reforming using logical materials design concepts. The spray-based powder manufacturing approach allows the creation of materials with unique microstructures and compositions that cannot be achieved by competing powder manufacturing approaches. Initial results indicate that this approach may lead to a major breakthrough in the development of high capacity, highly reversible CaO-based CO_2 absorbents. The combination of Cabot Superior Micropowders' (CSMP) unique powder manufacturing capabilities, ChevronTexaco's refining catalyst experience, and Texaco Energy System LLC's (TES) natural gas reforming/fuel cell experience presents the opportunity for higher fuel cell power plant efficiencies, reduced capital costs, and long term environmental benefits.

The ChevronTexaco team will develop a single catalyst bed composed of high durability CO_2 absorbents, high temperature water gas shift catalysts and steam reforming catalysts. Process design, system efficiency, and cost estimate studies will be performed leading to the design, construction, and testing of a "stand alone" natural gas fed 50-kW fuel processor. This approach is in contrast to the high capital and operating costs associated with pressure swing adsorption or membrane separation.

The major benefits of this approach are the reduced cost combined with an increase in performance and reliability of the whole fuel cell system. The production of a high purity hydrogen feed stream based on the reaction $CH_4 + 2H_2O + CaO \rightarrow 4H_2 + CaCO_3$ leads not only to a lower cost, highly efficient fuel processor, but also reduces the cost (higher H_2 content = less precious metal in the membrane electrode assembly) and improves the durability of the fuel cell stack through reduction of CO (poison) and CO_2 (reverse WGS and acidity enhancer). The system will comprise two or more AER beds, some of which are recycled while one is used to reform the natural gas. In addition to the reactor, the system will contain heat exchangers, a methanation unit, a desulfurization unit and a tail gas oxidizer. We estimate this system will achieve at least 85% energy efficiency with less than 10 ppm CO and less than 50 ppb H_2S in the reformate and with durability of more than 40,000 hours. Our current estimate of the reactor volume is about 80 liters with three reactors required.

Past work has proven the concept, but commercialization has failed due to the poor durability of the carbon dioxide absorption material. Materials that were produced in a cooperative program between CSMP and ChevronTexaco researchers have shown the feasibility of greatly improved durability. The extrudates made with powders manufactured by CSMP's spray technology retain their original CO_2 absorption capacity and carbonation/de-carbonation kinetics through many cycles. Tests of the process in TES's automated small scale reactors confirm the ability of the process to produce >98% purity H_2 with inconsequential levels of CO_2 and CO.

Integrated Manufacturing for Advanced Membrane Electrode Assemblies

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Subcontractors:
DuPont Company, Wilmington, DE
Nuvera Fuel Cell, Cambridge, MA
Northeastern University, Boston, MA

Objectives

- Create improved cathode structures and catalysts for proton exchange membrane fuel cells (PEMFCs) at temperatures less than 100^{o}C that allow a significant reduction of precious metal (PM) without loss in performance
- Develop a durable membrane for fuel cell operation at higher temperature and low water vapor pressure (>120^{o}C, <25% relative humidity, >5000 hrs)
- Incorporate the advances of (1) and/or (2) with advanced membrane electrode assembly (MEA) fabrication processes that are amenable to mass production

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

- Fabricate highly controlled fine gradient gas diffusion layers through machine coating methods; exploit a new structure-function approach to designing improved catalysts and catalyst alloys; combine the gas diffusion layers and the improved catalysts to create enhanced electrode structures

- Synthesize and evaluate small-molecule organic electrolytes to test functional groups; incorporate promising functional groups into polymeric electrolytes and evaluate
- Develop new machine-based or ion beam coating methodologies to create ultra-low loaded precious metal MEAs

Accomplishments

- Introduced a lower-cost method for preparing a more active platinum on carbon black compared to standard commercial preparations
- Elucidated details on the structure-activity relationship behind the platinum alloy's enhanced activity for oxygen reduction
- Demonstrated proof-of-principle of the fine gradient ELAT® gas diffusion electrode (GDE) fabricated on a developmental coating machine (20% increase in current density at 0.6 V)
- A combination of new catalyst and improved control of gradient on an experimental carbon cloth has shown a 50% decrease in cathode platinum needed per kilowatt power output in machine fabricated structures
- Verified 10-30% increase in power density of new improved cathode materials in a Nuvera short stack
- Determined specific organic electrolyte functionalities that provide conductivity at low relative humidity (RH)
- Synthesized ionomers with conductivity significantly improved vs. benchmark Nafion® and evaluated their thermal stability

Future Directions

- Achieve lower total PM loadings through ion beam assisted deposition (IBAD) on membrane
- Use new GDE structures to lower metal load
- Adapt new understanding on conductivity and thermal stability to increase the number of candidate ionomers; develop membranes from these candidate ionomers

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Introduction

A continuing challenge for PEMFC technology is precious metal thrift and creating new ion exchange membranes that are capable of stable operation at temperatures exceeding 120°C and, preferably, 150°C. The greatest barrier to reduction of platinum metal in the MEA is due to the cathode half reaction, which can be addressed through both improved catalysts and the electrode structure around the catalyst. In addition, there is a significant incentive to increase the operating temperature, the advantages being a) smaller radiators in transportation applications, b) more efficient use of by-product heat in stationary applications (e.g. hot water generation), c) potential for faster oxygen reduction kinetics at the cathode, d) increased tolerance to CO in reformed-hydrogen feed streams, and e) better kinetics for methanol oxidation in direct methanol fuel cells (DMFCs). For higher temperature operation, the need to limit the total stack pressure to 1 to 1.5 bar places a limit of ~0.5 bar on the water partial pressure, which corresponds to only 25% RH at 120°C – a significant challenge in designing new membrane materials.

During this report period, we have focused on new platinum catalysts, elucidation of structure-activity relationships for alloys, new GDE structures, and new high temperature polyelectrolytes. Our work on new electrolytes that provide the requisite conductivity at high temperature and low RH has identified candidates with improved conductivity over the benchmark.

Approach

In the last report, we identified a series of innovative catalyst preparation techniques and described linking electrochemical activity to detailed bulk structural information derived from spectroscopic determinations. During this report period, we have focused on the most promising preparation methodologies and exploited these methodologies to produce highly active platinum on carbon black, as well as prepare alloy structures that led to additional insights on the structural properties that control catalytic oxygen reduction.

Our program proposed the "fine gradient" ELAT® as a new design for the GDE or gas diffusion layer (GDL) that would facilitate both gas and proton transport to the catalyst. By reducing undesired variations in coating quality, we were able to create fine gradients of architectural features such as pore size distribution and hydrophobicity within the gas diffusion layer structure. All these structures are fabricated on a sophisticated developmental coating machine so they are readily assessed for suitability towards high volume manufacturing. Lastly, the most promising structures were advanced to Nuvera Fuel Cell for short stack testing/verification.

For higher temperature membranes, a wide variety of organic functional groups were explored and small molecule model compounds synthesized. The model electrolytes were examined for their ability to conduct protons at low RH, by dint of either "holding on" to more water than Nafion®, or by having a different conduction mechanism that does not require as much water in the electrolyte. The scope at this point included some seven different types of acid groups with aromatic or fluorinated substrates. After discovering/identifying promising small-molecule electrolytes, the next step was to prepare polymeric electrolytes that "tie-down" the molecules, a necessity to reach the goal of no leachable components. At this point the thermal stability of the new polymers is evaluated using a thermo-gravimetric method. As of June 2003, we are about 60-80% finished with making the candidate polymers and evaluating conductivity and stability. The next step is to fabricate membranes from the new polyelectrolytes. We anticipate using cross-linking and/or composite membrane approaches to improve their mechanical properties and control water swelling and hydrogen crossover. Finally, MEAs will be fabricated and tested in single cells. In parallel with these efforts are smaller ones to benchmark the fuel cell performance of Nafion® and Nafion® inorganic composites at 120°C.

Results

Progress on developing higher power catalysts is summarized in Table 1. Generally, catalysts with smaller crystallite sizes are preferred. This preference is due to the much higher surface area inherent in what are essentially nanoparticles. However, electrochemical activity is more important than surface area, and the actual electrochemical surface area is a more effective measure of

Table 1. Comparison of Commercial Platinum Catalyst to New Platinum Catalyst

	Crystallite Size (X-ray diffraction, nm)		**Electrochemical Surface Area (CO stripping, m^2/g)**	
%wt Pt/C(on Vulcan XC-72)	**Commercial Catalyst (E-TEK^{sm})**	**New Catalyst**	**Commercial Catalyst (E-TEK)**	**New Catalyst**
10	2.0	-	-	-
20	2.5	2.2	-	-
30	3.2	2.5	32	53
40	3.9	2.8	-	39
60	8.8	3.7	-	28
80	25	4.9	-	-

electrochemical activity. In comparing our findings for 30% Pt, one sees not only a significant decrease in crystallite size, but a large gain in electrochemical surface area. The commercial prep has 36% of the total platinum area electroactive, while the new prep has 47% of total area electroactive. Thus, we have created a catalyst with a greater proportion of active crystal faces.

Extensive research of the oxygen reduction reaction (ORR) on platinum has shown that water activation by platinum produces surface species such as metal-OH that inhibit the ORR (1). Through efforts at Northeastern University, we have shown that the inhibition is highly dependent on structural features within a single alloy. These structural features are strongly determined by the method of preparation. Evaluation of the alloy's performance for ORR in electrolyte solvents that contain low amounts of water helps mimic how these catalysts would perform in high temperature fuel cells. In analytical experiments, we show there is very little difference between platinum and platinum alloys for ORR in low water environments.

Having established more facile control of deposition of the microporous layer, and applying this methodology to building the electrode layer, we systematically varied the porosity and hydrophobicity throughout the structure during a multi-layer build. We established a true fine gradient of porosity, whereby the total range of porosity (gas feed to electrode) was three orders of magnitude. For example, this contrasts with intermediate structures that achieved a porosity range of just under two orders of magnitude. The initial proof-of-principle for machine-made fine gradient ELAT® structures demonstrated a 25% increase in current under mass transport limited conditions (0.6 V, 70^{o}C, H_2/air, 1.5 atm total).

The fine gradient approach has also allowed us greater flexibility in converting new web materials such as carbon cloth. Table 2 summarizes results formalized as the key technical target "grams of platinum per kilowatt of power," whereby a combination of different carbon cloth webs, new improved catalyst, and more facile control of the gradient demonstrates our current status for reducing platinum content at the cathode. For comparison, a standard assembly containing commercially available components uses 1.8 g platinum at the cathode per kW of power when operating at 400 mA/cm^2. By changing the underlying carbon cloth and incorporating a high definition microporous layer, we are able to reduce the amount of platinum needed per kilowatt power output to 1.29 g/kW. Our current best is 0.89 g/kW, whereby we gain the greater activity of the new platinum catalyst plus aspects of the fine gradient structure on a new carbon cloth substrate. Samples of various structures and improved catalyst have been evaluated at Nuvera Fuel Cell in short stacks (each MEA>200 cm^2, 70^{o}C, 1.5 atmospheres total). Relative gains in performance from 10-30% were realized, depending on the operating current density, thus verifying single cell test results.

Table 2. Impact of Base Material and More Facile Control of the Gradient

Cloth Web	**Cathode**	**Cathode**	**Total Pt**	**Total Pt**
	@ 100mA/cm^2	**@ 400mA/cm^2**	**DOE goal 2005**	**DOE goal 2010**
	g/kW	**g/kW**	**g/kW**	**g/kW**
Standard (st. Pt/C)	6.40	1.80	0.6	0.2
Type 1 (st. Pt/C)	3.73	1.29		
Type 2 (new Pt/C)	3.11	0.89		
Type 3 (st. Pt/C)	6.69	2.50		

(single cell, 70^{o}C, 1.5 atm. absolute, Air/C 1.5/2 stoich., Nafion 112)

During the investigation of different types of organic acid electrolytes, the attempts to synthesize water-less electrolytes mostly failed to exceed mS/cm conductivity. Only one electrolyte functionality was discovered which, when incorporated in two different compounds (candidates U and AB), gave 20 - 40 mS/cm proton conductivity at 125 to 180°C with either no water or at RH < 10%. Though promising, this electrolyte type had inferior conductivity to several others which still relied on water. Thus, several other *small-molecule* compounds were identified that had better conductivity relative to Nafion. In the last year, these electrolyte groups have now been successfully incorporated into *polymeric* electrolytes. The ionic conductivities of three of these candidate polymers are compared with that of benchmark Nafion in Figure 1. The conductivity is still decreasing with relative humidity, though the “rapid drop-off cliff” has been pushed to lower RH. Note that the mechanical properties of these polymers must be improved, e.g. by crosslinking or making composites, to arrive at thin membranes suitable for fuel cells.

New polymer electrolytes are being screened for thermal stability using a thermal gravimetric analysis (TGA) kinetic method (2). TGAs are performed under air humidified at 22°C and heating rates between 1 and 10°C/min. From this data, the activation energy for the first stage of thermal decomposition may be determined, and an upper limit on the lifetime of the polymer at the intended use temperature of 120°C could be extrapolated (Table 3).

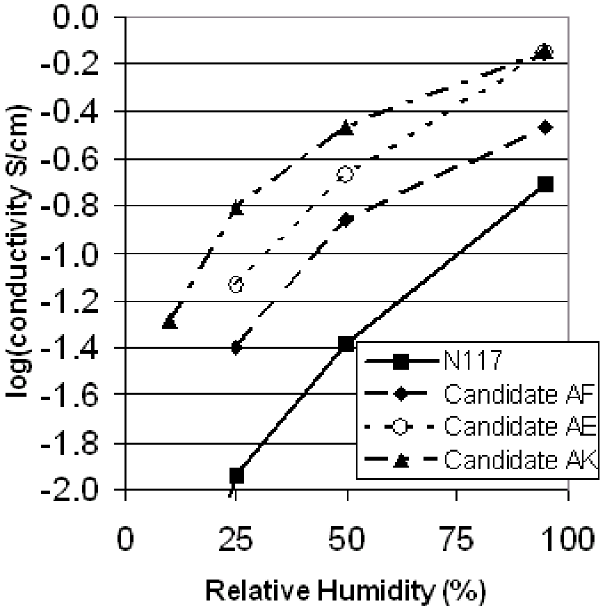

Figure 1. Ionic Conductivity of Benchmark Nafion® N117 and Three Experimental Ionomers at 120°C vs. Relative Humidity

Table 3. Thermal Stability for Nafion® and Experimental Polymer Electrolytes; Activation Energy, Preexponential Factor, and an Upper Limit to Life, in hours, Extrapolated to 120°C, Based on 10% of the First Stage of Decomposition to Be Completed

Sample	Activation Energy (Ea) (kJ/Mol)	Log (A min^{-1})	Upper Limit to Life @ 120°C (hr)
Candidate AE	290	24.3	4.0×10^{11}
Candidate AN	210	16.1	3.0×10^{9}
Candidate AM	190	17.3	1.8×10^{5}
Nafion® N112	160	12.9	1.3×10^{5}
Candidate AF	40	14.0	1.4×10^{2}
Candidate Z	80	7.4	2.0 X 100

Caveats are that this test does not address electrochemical stability, nor does it detect degradation which does not result in weight loss (e.g. backbone scission), and the effect of the very low RH used has not yet been determined. The test can only alert one to a potential problem with the new polymers. Nafion® N112 has a predicted upper limit due to thermal degradation at 120°C of 1.3×10^5 hr, which exceeds the lifetime goals of 5 to 40 $\times 10^3$ hr. Experimental polymers have been found to have a wide range of upper limits, with examples significantly higher, and several lower, than that of Nafion.

Conclusions

- Approach to structure-activity has yielded a more active platinum catalyst on carbon black with smaller platinum crystallite sizes and greater electrochemical surface areas.

- Full potentials of the alloy catalysts are not realized in the "low temperature" fuel cell with the current electrode structure; under conditions of temperature above 100°C (low water), the ability for an alloy to inhibit poisoning due to absorption of oxygenates is no longer relevant, and these alloys may not realize the gain observed at lower temperature (high water) conditions.
- The fine gradient ELAT® methodology provides a pathway to construct structures previously not attainable and will be used to recover some of the unrealized platinum alloy activity; this approach has also aided in reduction of the precious metal content in the cathode.
- Using functional groups different from perfluorosulfonic acid ionomers, it is possible to make ionomers with significantly increased conductivity over that of Nafion® at 25% RH.
- Ionomers can be made that pass a screening test for thermal stability.
- Achieving both conductivity and thermal stability in the same ionomer is even more challenging, but is likely possible also.

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1. S. Mukerjee, S. Srivanasan, M.P. Soriaga and J. McBreen, Electrochem. Soc. 142(1995) 1409 and references therein.

2. J.H. Flynn and L.A. Wall, Polymer Letters, 4 (1966) 323.

FY 2003 Publications/Presentations

1. "Integrated Manufacturing for Advanced Membrane Electrode Assemblies," E.S. De Castro and M.G. Roelofs, DOE 2003 Merit Review and Peer Evaluation Meeting, May, 2003, Berkeley, CA.

2. "Reducing Overpotential Losses for Oxygen Reduction Reaction with Pt Based Alloys: a RRDE Investigation" - V. Srinivasamurthi, C. Urian, and S. Mukerjee (Northeastern University), 203rd Electrochemical Society Meeting, Paris, France, 2003. Abstract No.1208.

3. "Oxygen Reduction Kinetics on Pt and Pt Alloys under Lower Humidity, Rotating Disk Electrode Experiments," V. Srinivasimurti and Sanjeev Mukerjee; in preparation for the Journal of the Electrochemical Society.

4. "A Systematic Investigation of the Shift of H_2O Binding Energy of Pt and Pt Alloys; Changes in the On-Set Potential of Oxygen Reduction," A. F. Gullá and Sanjeev Mukerjee; in preparation for the Journal of the Electrochemical Society.

Development of High Temperature Membranes and Improved Cathode Catalysts

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Subcontractors:

High Temperature Membrane:
Virginia Polytechnic Institute and State University, Blacksburg, VA
Pennsylvania State University, University Park, PA
Stanford Research Institute International, Menlo Park, CA
IONOMEM, Marlborough, CT
Princeton University, Princeton, NJ

Cathode Catalysts:
Northeastern University, Boston, MA
University of South Carolina, Columbia, SC
United Technologies Research Center (UTRC), East Hartford, CT
Case Western Reserve University, Cleveland, OH

Objectives

- Develop and demonstrate an advanced polymeric membrane able to operate at near ambient (1-1.5 atm.) pressure in the temperature range of 120~150×C that is able to meet DOE goals for performance.
- Develop and demonstrate improved Pt cathode catalysts that will enable the reduction of Pt loading to 0.05 mg/cm^2 and meet DOE goals for performance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

- **Phase 1:** High temperature membranes (HTMs) and improved Pt catalysts will be synthesized, characterized and compared with issued specifications. [In progress]
- **Phase 2:** Laboratory-scale catalyst-coated membranes (CCMs) will be fabricated, optimized and tested using the Phase 1 down-selected membranes and catalysts.
- **Phase 3:** Full-size CCMs with the down-selected and optimized HTMs and catalysts will be fabricated and tested in 2 individual multi-cell stacks.

Accomplishments

This project was initiated during the first quarter of 2002. The down-selection to retain promising catalysts and HTMs is scheduled for Q3 of 2003. All subcontractors are working towards optimizing their respective catalyst and HTM systems.

- Four membrane systems with proton conductivity on the order of 10 mS/cm at 120°C and 50% relative humidity (RH) were synthesized:
  - Biphenyl sulfones (BPSH) from Virginia Tech,
  - Modified sulfonated polyetheretherketone (S-PEEK) from Stanford Research International,
  - Fluorinated polyether sulfone (FPES) from Penn State, and
  - Heteropolyacid (HPA) filled NafionÒ from IONOMEM.
- IONOMEM has established a baseline for HTM performance of 0.6 V at 0.4 A/cm^2 (120°C, 30% RH).
- Slab band calculations using Vienna ab-initio slab program (VASP) project have provided insight into binary alloy skin effect.
- Higher activity and more stable binary Pt alloys were synthesized using the colloidal-sol, carbothermal, and pulse electrodeposition routes.
- Reproducible and state-of-the-art (SOA) CCMs were fabricated using the decal transfer process.
- All the requisite details and infrastructure for the catalyst and membrane down-selection process have been established. The down-selection process will commence during Q3 of 2003 and will be completed by the end of Q1 of 2003.

Future Directions

- Further optimize membrane systems and/or fillers required to improve conductivity at practical RH.
- Develop a generalized stability template for HTMs.
- Continue Pt-alloy synthesis using the various routes and optimize for activity and stability.
- Investigate several methodologies to reduce Pt loading (e.g., ionomer gradient, etc.).
- Initiate catalyst and HTM down-select process.

Introduction

Two main challenges in the proton exchange membrane (PEM) fuel cell arena are the reduction of cathode Pt loading and development of membranes that can operate over 120°C. Surmounting these two challenges will directly affect the cost, performance and the size of PEM fuel cell stacks. On the HTM project, new polymeric materials with negligible thermal degradation and acceptable proton conductivity in the 120-150°C range are required. On the improved catalyst project, a combination of higher activity catalysts and thinner catalyst layers is required to achieve the aggressive DOE performance targets.

Approach

To develop HTMs, UTCFC has teamed with research groups that possess competencies in the field of polymer chemistry and engineering. The subcontractors on the project are investigating modified Nafion® and new non-Nafion based membrane systems (see Table 1). The subcontractors on the improved catalyst project and their individual approaches are given in Table 2. More details on both the approaches can be found in Reference.

Results

This project was initiated in June of 2002. Since then, all the subcontractors on the project have set up the necessary infrastructure and have reported significant progress in the areas of catalyst and polymer synthesis. New catalyst systems with improved activity and stability relative to commercial pure Pt carbon supported systems have been identified. Under the HTM program, UTCFC has stressed the importance of developing polymers capable of conducting protons under practical relative humidity (RH) conditions. The HTM subcontractors are optimizing their polymeric materials for acceptable proton conductivity at 120°C and 50% RH. A number of polymer systems whose proton conducitivities are on par with or exceed that of Nafion® have been identifed. Salient progress details are presented below.

High Temperature Membrane: On the HTM project, four of the five subcontractors have successfully synthesized polymer systems that yield finite proton conductivities at 120°C and 50% RH. One issue faced by most of the polymer subcontractors has been poor conductivity for their membrane systems at practical RH conditions. Prior to Q2 of 2003, polymer membranes solely constituted by a blend of the basic sulfonated monomer showed excellent proton conductivity at 120°C and saturated conditions. However, the conductivity dropped off steeply as the RH was lowered below 100%. To overcome this issue and to minimize the dependence of the membrane proton conductivity on the humidity, all the subcontractors have tested the addition of hydrophilic conductivity enablers. These hydrophilic additives improve the water retention capability of the polymers at low RH. The types of fillers investigated to date include a wide variety of inorganic heteropolyacids and proprietary hydrophilic polymeric blends. With the aid of the the above types of fillers, the HTM subcontractors have consistently measured a proton conductivity greater than or equal to 0.03 S/cm (reference point of Nafion 117) at 120°C and 50% RH.

An example of one class of filled polymers that shows good promise is the fluorinated sulfonated polythetheretherketone (FSPEEK) from SRI International (see Figure 1 for a schematic of the basic polymer). The sulfonated polymer is blended with a basic polymer to generate pseudo-crosslinking through an acid-base interaction, thus providing

Table 1. High Temperature Membrane Project Approach

Group	Principal Investigator	Approach
IONOMEM	Mr. Leonard Bonville	Hygroscopic solid ion conductor (e.g., zirconium phosphate,etc) filled Nafion®
Penn State University	Prof. Digby Macdonald	Sulfones and sulfoxides of aromatic PPBP and aliphatic PVA. Covalent sulfonic acid bonded PEEK, PBI and PPBP
Princeton University	Prof. Andrew Bocarsly	Layered sulfonated Polystyrene/ Fluoropolymer system
Stanford Research Institute	Dr. Susanna Ventura	Sulfonated PEEK-PBI-PAN
Virginia Tech	Prof. James McGrath	Sulfonated Poly(arylene ether sulfone)

Table 2. Advanced Cathode Catalyst Project Approach

Group	Principal Investigator	Approach
North Eastern University (NEU)	Prof. Sanjeev Mukerjee	Micellar Pt nano cluster synthesis, colloidal sol synthesis of binary Pt alloys.
University of South Carolina (USC)	Prof. Branko Popov	Pulse electro-deposition of Pt and Pt alloys on Carbon. [Pt and Pt-X, X=Fe, Ni, Co, Mn and Cu]
UTC Fuel Cells (UTCFC)	Mr. Michael Perry	Carbothermal synthesis of ternary Pt alloys. [Pt-Ir-X and Pt-Rh-X, [X =Ni, Co and V]]
Case Western Reserve University (CWRU)	Prof. Alfred Anderson	Quantum chemical modeling of Pt alloys and ORR.
UT Research Center (UTRC)	Dr. Ned Cipollini	Reproducible and stack size CCM fabrication.

conducting polymer membranes with good mechanical stability. To minimize the dependence of the membrane proton conductivity on the humidity, SRI has tested two classes of hydrophilic polymers. Figure 1 illustrates the proton conductivity of several SRI polymer membranes at 120°C as a function of the RH. The conductivity of Nafion 117 (blue diamond) is shown as a reference line. The black line (hollow squares) shows the proton conductivity of the first-generation SRI membrane, where no additive was used in the polymer blend of the acidic/basic polymer. The conductivity of this membrane drops quite significantly at RH lower than 80%. On the other hand, membranes containing hydrophilic polymer additives (14210-21c, 14210-25, and 14210-53) showed significantly higher conductivity at low RH than the correspondent membrane without any additives. In particular, the conductivity at low RH for these membranes was found to be higher for additives with higher hydrophilic character. The SRI membrane 14210-53 was found to have the highest conductivity at 30 and 50% RH. For this membrane, proton conductivity values were 0.011 S/cm at 120°C and 30% RH and 0.038 S/cm at 120°C and 47% RH. These conductivities were higher than any other SRI membranes, as well as higher than Nafion 117.

A summary of proton conductivities of other membrane systems developed under this project is shown in Figure 2. The 120°C and 50% RH proton conductivity metrics for biphenyl sulfones (BPSH) filled with hetero-polyacid from Virginia Tech., FSPEEK from SRI International, fluorinated polyethersulfones (FPES) from Penn State and Nafion filled with hetero-polyacid from IONOMEM are presented in the figure. The conductivity values of the membranes are compared to that of Nafion 117. As seen from the figure, the conductivities of all the membrane systems on the project are higher than the corresponding Nafion value. It is also important to note that the glass transition temperatures of the membranes shown in Figure 2 are higher than Nafion. Prior to the down-select process, the membrane subcontractors are further optimizing the thermal, mechanical and chemical stability of the membranes.

Reproducible and SOA high temperature fuel cell performance has been established by IONOMEM. The IONOMEM technical approach for high temperature catalyzed membranes integrates, on a molecular level, the proton-conducting Nafion® polymer with hygroscopic hetero-polyacids such as phosphotungstic acid, or zirconium hydrogen phosphate. This nano-composite material maintains low water vapor pressure, provides more water-independent proton conduction, and holds promise of satisfying DOE

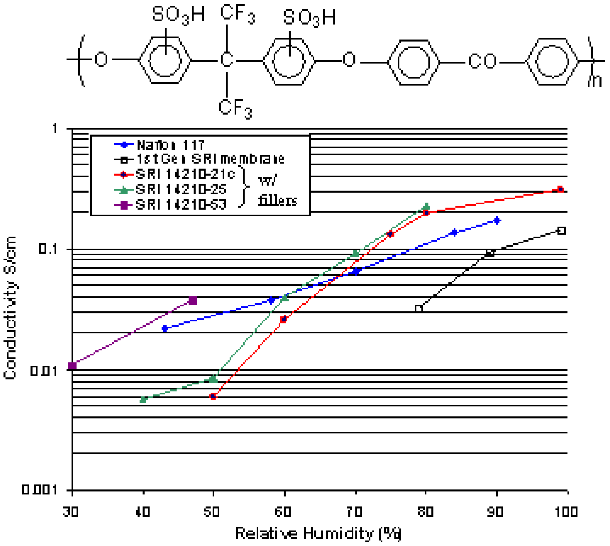

Figure 1. Conductivity Measured at 120°C as a Function of RH for Polymer Membranes with Variable Composition (blue [diamond] line: Nafion 117)

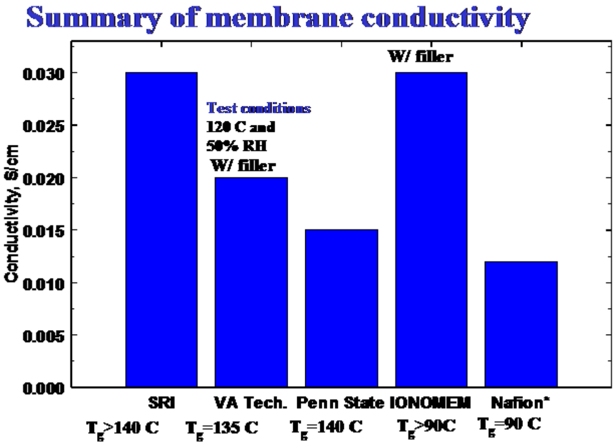

Figure 2. Summary of Proton Conductivities Measured at 120°C and 50% RH by the Various Subcontractors on the HTM Project (see Table 1, SRI: FSPEEK, VA Tech.: BPSH, Penn State: FPES, IONOMEM: Nafion filled with hetero-polyacid)

performance requirements. At the project initiation, IONOMEM's high-temperature membrane electrode assembly (MEA) demonstrated a consistent performance level of 0.454 volts at 400 mA/cm^2, operating at 120°C and ambient pressure on hydrogen and air both saturated near 90°C. The performance under the above-mentioned conditions was further enhanced to 0.6 V at the same current density during 2003. Polarization curves at 120°C and 35% RH for the IONOMEM membrane are shown in Figure 3. As seen from the Figure, the 400 mA/cm^2 performance at 120°C and 35% RH (albeit at low fuel and air utilizations) is 600 mV. The corresponding ohmic resistance at 120°C and 35% RH is 0.18 ohm-cm^2.

Advanced Cathode Catalysts: The advanced catalyst project is set up with three of the four subcontractors (Northeastern University, University of South Carolina, and UTCFC) synthesizing more active Pt alloy catalysts. Case Western Reserve University (CWRU) is supporting the catalyst synthesis task with fundamental molecular level simulations, and UTRC is fabricating and testing MEAs using the catalysts synthesized on the project.

CWRU's main goal on this project is to gain understanding of structure and electronic factors in oxygen electroreduction over platinum alloyed with transition metals. Their approach has been to predict, using quantum mechanical calculations, the reversible potentials for water oxidation on platinum alloys to form adsorbed OH, the surface species that is believed to block oxygen from reaching the electrode surface (Reference 2). During Q2 of 2003, Case completed calculations of H_2O and OH bonding to various sites on the four layer slab models of the (111) Pt_3Cr surface with and without a monolayer Pt surface "skin" which is found to form on supported alloy particle catalysts and on single crystal alloy surfaces (Reference 3). They found that their predictions for the Pt skin effect were in good agreement with the shift in overpotential for O_2 reduction and the apparent shift in onset potential for H_2O(ads) oxidation to OH(ads) seen in the literature for Pt_3Cr and other Pt alloys with metals from the first transition series. These results are currently being applied by UTCFC to develop novel shell-core structures for superior oxygen reduction activity.

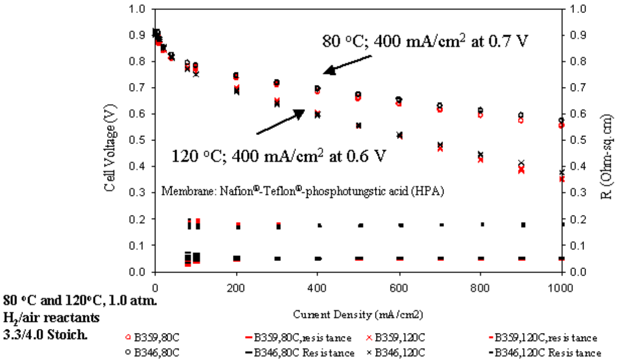

Figure 3. IONOMEM's High Temperature Fuel Cell Performance at 120°C and 35% RH (The performance is compared to performance under 80°C and saturated conditions.)

At UTCFC, in the ternary alloy area, we have completed the preparation and screening of $Pt_{75}Ir_{12.5}X_{12.5}$ (X=Co, Ni, V) alloy systems using the carbothermal synthesis route (Reference 4). Electrochemical surface areas of the synthesized catalysts were in the 50-60 m^2/g range with particle size in the 2-5 nm range. Half-cell activity measurements indicate that the catalyst activities of Pt alloys are in the order of $Pt_{75}V_{25} > Pt_{75}Ir_{12.5}V_{12..5} > Pt_{75}Co_{25} > Pt_{50}Ir_{25}V_{25} > Pt_{75}Ir_{12.5}Ni_{12.5}$. The activity of $Pt_{50}Ir_{25}V_{25}$ was 1.7 X greater than pure Pt catalyst. This could result in a kinetic improvement of 15 mV at 65°C. X-ray diffraction analysis confirms that $Pt_{50}Ir_{25}Co_{25}$ and $Pt_{50}Ir_{25}V_{25}$ are ordered, face-centered cubic structures with reduced Pt-Pt near-neighbor distance, which might be the reason that their activities are superior to pure Pt catalyst. The path forward for UTCFC is to scale up the best catalysts in a large quantity (>20 g) for further evaluation in subscale cells.

In the binary alloy area, UTCFC has tested ca. 50% weight loading Pt-Co catalysts and compared the performance, endurance and cyclic durability with pure Pt. Figure 4 contains the comparison of the Tafel plots obtained in a subscale cell for Pt-Co and Pt. Analysis of the Tafel plots shows that the ratio of the volumetric exchange current densities of Pt-Co and Pt is 1.25. The ratio of the surface area of the Pt and Pt/Co catalysts is approximately 1.75 (obtained using cyclic voltammetry). Therefore, the ratio of the true catalyst activity is approximately 2.2. The increased catalytic activity translated to an increase of ca. 10 mV at all current densities on the polarization curve. The stability of Co in the Pt-Co catalyst was investigated using electron microprobe analysis (EMPA) after 4000 cycles between 1.2 and 0.8 V. In Figure 5, the scans are compared to those obtained with pure Pt cycled under the same conditions as above. The EMPA scans show no migration of Co into the membrane or to the anode side. The absence of Co migration is a strong benefit for the Pt/Co alloy system.

Also, comparing the Pt dissolution fronts for Pt and Pt-Co catalysts shows that the Co incorporated into the catalyst stabilizes the Pt and reduces the rate of migration of the dissolved Pt.

At the University of South Carolina (USC), Pt/C electrodes were fabricated by using pulse current electrodeposition methods. With the use of current pulses rather than direct current, a higher deposition current density could be used, and Pt deposits with a higher surface area and activity are possible. Figure 6 compares the performance of USC's electrodeposited catalyst with a loading of 0.15 mg/cm^2 to commercial ETEK catalyst of 0.4 mg/cm^2. The kinetic enhancement with the USC catalyst is on the order of 20 mV at all current densities.

USC has identified the optimum current density and the duty cycle for the electrodeposition of higher activity Pt and Pt alloys and is currently fabricating subscale MEAs for testing at UTCFC.

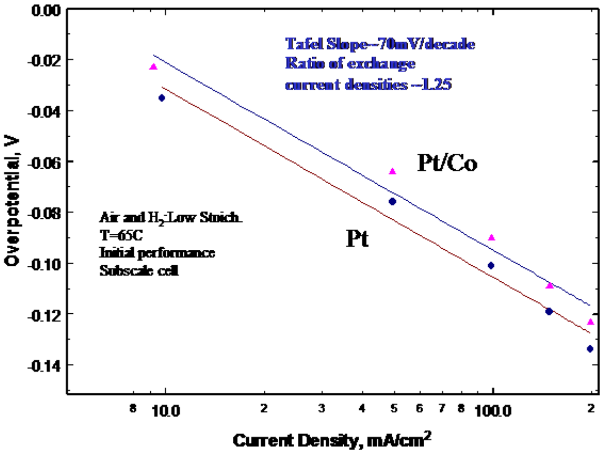

Figure 4. Comparison of the Tafel Behavior for Pt-Co and Pt Catalyst Systems (The kinetic enhancement obtained with Pt-Co is ca. 10 mV at all current densities.)

At UTRC, reproducible and SOA MEAs are being fabricated to aid in the catalyst down-selection process. Performance of some of the sample MEAs fabricated at UTCRC are presented in Table 3. As seen in the table, the air/H_2 performance of the

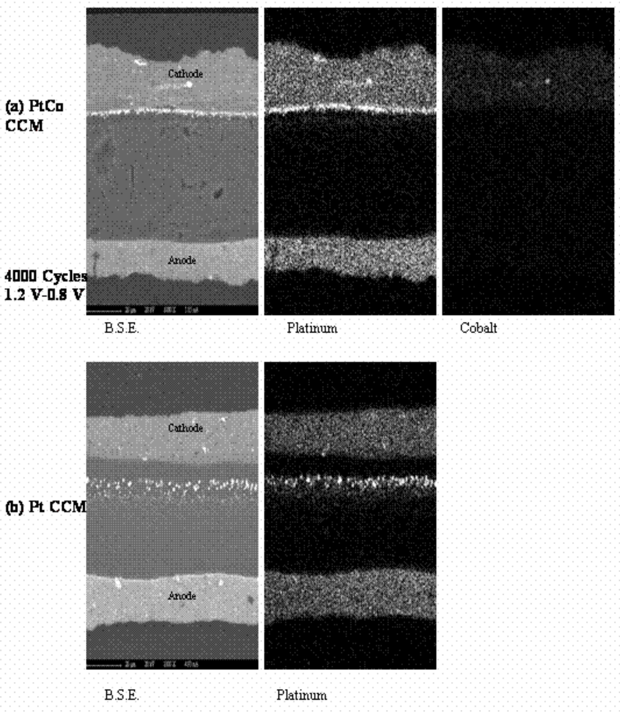

Figure 5. EMPA Images for Pt-Co and Pt Catalysts after 500 hours of Endurance Hold at 0.5 A/cm^2

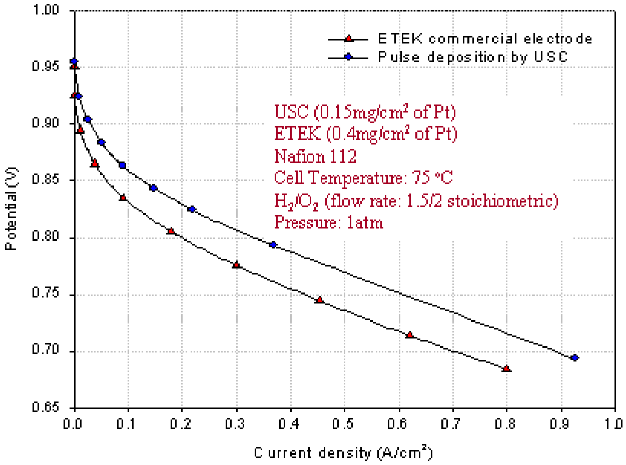

Figure 6. Performance of USC's Electrodeposited Catalyst with a Loading of 0.15 mg/cm^2 Compared to Commercial ETEK Catalyst of 0.4 mg/cm^2 (The kinetic enhancement with the USC catalyst is on the order of 20 mV at all current densities.)

UTRC MEAs is comparable to the commercial MEAs, and the performance reproducibility is excellent. Also shown in Table 3 are the DOE targets for the reduced loading. Once the going forward catalyst systems are identified, UTRC will optimize the catalyst layers and aid in the reduction of the Pt loading.

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3. Stamenkovic, V., Schimdt, T. J., Ross, P. N. and Markovic, N. M., J. Phys. Chem. B, 106, 11970-11979, 2002.
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Table 3. Performance Comparison of UTRC MEAs

CCM ID	V, mV @ 400 mA/cm^2		V, mV @ 100 mA/cm^2		ECA, m^2/g Pt		Comments
	H_2/O_2	H_2/Air	H_2/O_2	H_2/Air	Cathode	Anode	
DOE target	0.80		0.85		N/A		Membrane thickness 15µm
REM 411 Commercial	0.824	0.786	0.885	0.857	-	-	Membrane thickness 15µm
REM 404	0.800	0.760	0.875	0.848	46	54	Membrane thickness 15µm
REM 413	0.795	0.757	0.879	0.845	44	69	Membrane thickness 15µm
REM 414	0.790	0.748	0.880	0.848	-	-	Membrane thickness 15µm
REM 415	0.810	0.767	0.887	0.854	54	65	Membrane thickness 15µm
REM 416	0.798	0.756	0.886	0.854	69	44	Membrane thickness 15µm

IV.E.3. Advanced MEAs for Enhanced Operating Conditions

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Objectives

Develop high performance, lower cost membrane electrode assemblies (MEAs) that

- meet demanding system operating conditions of higher temperature with little or no humidification,
- use less precious metal than current state-of-the-art constructions, and
- are made by processes amenable to high volume manufacturing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

- Develop advanced cathode catalysts that have less precious metal and can be made by high volume compatible processes, building on the knowledge gained in the preceding 3M/DOE Cooperative Agreement, DE-FC02-99EE50582.
- Develop membranes that are stable at operating conditions of $85 < T < 120°C$, based on 3M's hydrophilic ionomers that have shown greater stability at these temperatures than current commercial membranes. Optimize matching MEA components, flow field, and air management for these operating conditions.
- Develop high temperature non-aqueous electrolyte membranes, stable catalyst constructions, optimized catalyst/membrane interfaces, and matching gas diffusion layer and flow field components for an operating range of $120 < T < 150°C$ and nearly dry operation.
- Scale up and optimize MEA component fabrication processes amenable to high volume, high quality, low cost production for selected components from the above tasks.
- Characterize selected MEAs in full-scale, short stacks.

Accomplishments

- Demonstrated reduced F- ion generation and longer lifetime of 3M's perfluorinated sulfonic acid ionomeric membrane compared with standard proton exchange membrane (PEM) ionomer.
- Developed a "liquid H-pump" technique to measure the proton conductivity of ionic liquids and acids.
- Developed liquid mixtures with no added water having proton conductivities of 40 mS/cm at 120ºC with no water, which is 100 to 1000 times greater than anhydrous acids.
- Demonstrated a membrane additive that reduces membrane weight loss occurring during a peroxide soak test by over a factor of 100 compared to a standard ionomer control.
- Developed cathode catalyst compositions and structures having higher performance at a Pt loading of 0.1 mg/cm^2 than the baseline, using 3M nanostructured catalyst processes amenable to high volume manufacture.
- Demonstrated higher chemical oxidative stability of the 3M nanostructured film supported catalysts compared with commercial carbon black supported Pt catalysts.
- Demonstrated higher electrochemical stability of surface area and double layer capacitance of nanostructured ternary catalysts under either highly oxidative thermal or electrochemical potential conditions compared to carbon black supported catalysts.

Future Directions

- Continue the membrane and cathode catalyst development and screening and the fabrication and testing of integrated catalyst coated membranes (CCMs).
- Optimize gas diffusion layers, flow fields, and air management to match the CCMs for higher temperature operation, building on previously developed computational models and test results.

Introduction

Poroton exchange membrane fuel cells (PEMFCs) have been developed sufficiently to demonstrate their feasible use for automotive and distributed stationary applications. However, several issues must be addressed to demonstrate commercial viability, including efficiency, durability, and cost. Overall, system efficiency is the critical factor affecting fuel usage and operating costs. The efficiency of a fuel cell is directly related to the cell operating voltage. The higher the voltage, the higher the efficiency, but the current density and power available are then lower, which affects stack size and cost. These factors are primarily affected by polarization of the cathode catalyst and stability of catalyst activity and surface area. Therefore, higher performing and more stable cathode catalysts are required to achieve the goals of increased performance with less precious metal catalyst. From a system perspective, operation at higher temperatures reduces thermal management constraints, thereby increasing overall efficiency. Greater tolerance of fuel impurities at high temperatures can also contribute to performance increases and, potentially, to lower costs of fuel processing components. However, the humidification requirements for higher temperature operation are significant. Designing an MEA to operate under hot, dry, pressurized conditions requires development of new membranes, catalysts and gas diffusion layers that are stable and durable at those conditions. The components must be matched to each other and integrated with a flow field design and air management strategy. In addition, the processes for making the MEA components must be consistent with high volume production. This project is directed toward development of MEAs that meet demanding system operating conditions of higher temperature and little or no humidification, use less precious metal than current state-of-the-art constructions, and are made by processes amenable to high volume manufacturing.

Approach

The approach to higher temperature MEAs on this project involves the development of components for two sets of temperature ranges: $85 < T < 120^{o}C$ and $120 < T < 150^{o}C$. For the lower temperature range, proton exchange membranes are being developed based on modifications of existing perfluorinated sulfonic acid (PFSA) type membranes that still rely on water for proton conduction, such as Nafion™ or 3M's PFSA ionomeric membrane. These modifications include incorporation of functionalized additives to facilitate peroxide decomposition for better oxidative stability and enhanced water retention for higher conductivity under low humidification. For the higher temperature range, new membrane materials and non-water based proton conduction methods are being investigated, which utilize 3M perfluorinated acids, various proprietary liquids, and various inorganic additives. Work includes understanding how to incorporate those materials into polymer matrices to form effective membranes. The polymer matrices and process methods include both new and existing materials and methods.

The approach to the development of advanced cathode catalysts that have less precious metal than current state-of-the-art constructions builds on the knowledge gained in 3M/DOE Cooperative Agreement DE-FC02-99EE50582. Cathode catalysts that significantly outperformed pure Pt were made using a 3M nanostructured, thin film catalyst support system and catalyst deposition process, which easily generates new compositions and structures via a dry, roll-goods process (roll-goods are made by a semi-continuous process and stored on a roll) amenable to high volume manufacturing. (See FY 2003 Progress Report on the above contract and also References 1 and 2.) The catalyst structures and PtAB ternary materials developed under that contract exhibit unique electronic features and increased surface area. The 3M nanostructured thin film supports (carbon free) show less susceptibility to oxidation and loss of catalyst surface area under highly oxidative conditions than commercially available carbon supported dispersed catalysts. Methods for generating new catalyst constructions include pilot-line production of large area catalyst formulations and a combinatorial method for generating and characterizing a wide latitude of ternary and quaternary compositions and structures using similar thin film catalyst deposition methods (with subcontractor Dalhousie University). Conventional dispersed catalysts with improved oxidatively stable carbon supports are also being investigated.

For all the enhanced membrane and catalyst materials and process development work, a suite of critical property measurements is employed to guide development and down-selection of approaches. These include methods to measure the ionic and proton conductivity of the membranes, electrochemical impedance spectroscopy, chemical stability, PEM physical and mechanical properties, catalyst electrochemical surface areas and activities, and fuel cell tests under various protocols. Finally, methods to form effective interfaces of the catalysts with the new membranes for both operating temperature ranges are necessary for optimum MEA performance.

Results

As part of the effort to develop a more stable PEM for the range of $85^{o}C < T < 120^{o}C$, a series of nearly 60 composite membranes was fabricated based on addition of inorganic dispersions to Nafion™ in order to enhance water uptake. Extensive resistance testing by hydrogen pump and high frequency impedance at 120°C, ambient pressure and 80°C dew point showed the effect of the majority of these additives was to make the resistance worse than the Nafion™ control. Two of the additives made slight improvements under these challenging conditions. More recently, some of these same additives have been incorporated into the 3M ionomeric membrane. As shown in Reference 3, under identical test conditions of 80ºC cell, 0.35 A/cm^2, and H_2/air at 27%/27% relative humidity (RH), 3M roll-good fabricated membranes using 3M's own PFSA ionomer had an 80% increase in lifetime over 3M fabricated membranes made with Nafion™ 1000 ionomer. It is expected that incorporation of the right functionalized additives to the 3M ionomer should further enhance these stability properties and maintain conductivity with less humidification. This work will now focus on this new ionomer.

Peroxide generated at the anode in PEMFCs due to oxygen crossover is a serious mode of membrane degradation at high temperatures and dry conditions (Reference 4). Significant progress has been made developing and applying methods to evaluate the activity of membrane additives for peroxide decomposition. The key method uses weight loss measurements of membranes soaked in peroxide solutions for prolonged periods of time. Using literature and proprietary approaches, additives have been identified and screened for addition to the PFSA ionomers which, in addition to reducing weight loss in these accelerated tests, must not negatively impact ionic conductivity, electronic resistance, or fuel cell performance of the resulting MEAs. Figure 1 illustrates the membrane mass loss of various additives versus controls, showing that Additive C can reduce the mass loss from the -10% seen for the non-additive control to zero within the ±0.1% error of the measurement. Fuel cell performance and F^- ion release rates are being evaluated.

A total of 53 different Pt based ternary cathode catalysts have been fabricated on large area, roll-good capable pilot-line equipment and evaluated by various fuel cell tests. The catalysts, all made on the 3M nanostructured support films, differ by composition, non-noble metal type, and a structure factor tied to the catalyst deposition process. All have 0.1 mg/cm^2 of Pt or less and for screening purposes are tested with standard PFSA membranes. Figure 2 (top) illustrates comparative polarization curves under a pressurized oxygen test protocol for comparing the activity of the various catalysts, showing many performing better than pure Pt. Figure 2 (bottom) illustrates the range of precious metal loadings under investigation and the effect on H_2/air fuel cell performance for one PtA_xB_y construction. The anode catalyst is 0.14 mg Pt/cm^2 in each case of Figure 2 (bottom). A four-fold

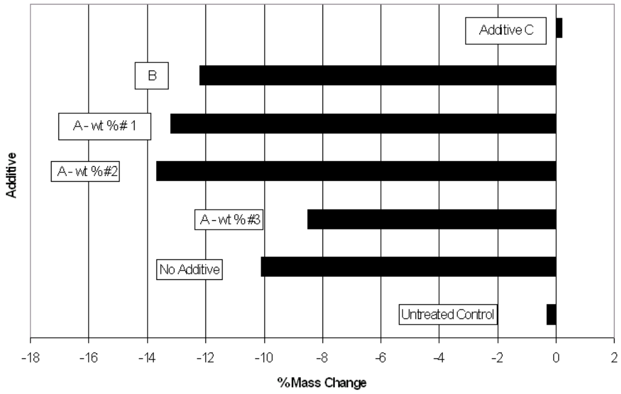

Figure 1. Comparison of the effect of various additives on PFSA membrane mass loss upon exposure to 1 M H_2O_2 at 90ºC for 120 hours (refreshed every 24 hours), showing that one, Additive C, can reduce the mass loss from -10% seen for the non-additive control to zero within the ±0.1% error of the measurement.

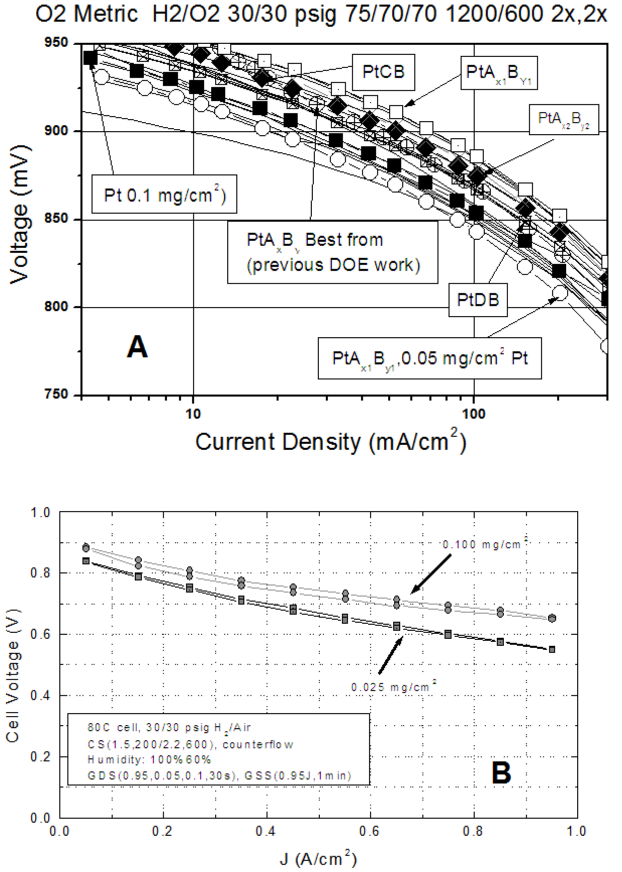

Figure 2. (A) Comparison of high pressure oxygen metric polarization curves from various nanostructured thin film ternary catalysts with 0.1 mg/cm^2 of Pt, unless noted.
(B) Comparison of pressurized, constant stoichiometry (CS), constant current, polarization curves for two PtAB cathode catalyst constructions having 0.100 and 0.025 mg Pt/cm^2, with 0.14 mg/cm^2 of pure Pt on the anode. Cell T = 80ºC, 30/30 psig, 1.5/2.2 H_2/air stoichiometry, galvanodynamic scans (GDS), 100%/60% anode/cathode inlet RH, 50-cm^2 quad-serpentine flow field.

reduction in cathode loading has cost approximately 50 – 100 mV of cell performance over the 0.1 to 0.9 A/cm^2 current range and illustrates the challenge of the DOE targets of 0.05 mg/cm^2 total per MEA producing 0.5 A/cm^2 at 0.8 V.

Significant progress has been made with our Dalhousie University subcontractor in applying combinatorial methodology for fabricating 50-cm^2 sized arrays of continuously varying catalyst compositions and structures, applied to the 3M nanostructured support films. A dozen of these catalyst arrays have been fabricated in triplicate and characterized by scanning X-ray diffraction and electron microprobe, formed into MEAs at 3M and tested using combinatorial and segmented cell screening methods as well as larger fuel cell tests. Baseline data have been obtained to establish the degree of correlation between the subcontractor's and 3M's deposition processes and identify issues with the combinatorial and segmented cell screening analyses that need to be resolved in order to usefully reveal catalyst activity differences seen in single cell constructions.

Under high temperature and dry conditions, stability of all the MEA components is a challenge. The catalyst activity, its surface area and its support particle must all be stable, both chemically and electrochemically, particularly against oxidation. The thermal stability of the 3M nanostructured film supported catalysts was shown to be significantly greater than commercially available carbon supported Pt catalysts, using highly sensitive thermal gravimetric analysis weight-loss profiles over 20 hours at 170ºC in air (see Reference 3). *In-situ* fuel cell measurements of catalyst electrochemical surface area (ECSA) before and after 90 hours under 120ºC, 30 psig H_2/air, and constant current conditions have shown a negligible loss in surface area for the 3M ternary catalysts, compared to a 42% loss in 70 hours from carbon supported Pt catalysts. More recent characterization of oxidative stability was completed by voltammetric polarization of cells to 1.2 V for 5 hours at 80ºC under saturated H_2/N_2, followed by complete cyclic voltammetry scans for ECSA measurements. As shown in Figure 3, over approximately 50 hours, the conventional dispersed carbon supported catalysts' ECSA decreased significantly and progressively after each 5 hour period while its double layer capacitance increased, indicating carbon oxidation. In contrast, the 3M nanostructured film supported Pt catalysts' ECSA progressively increased, consistent with catalyst clean-up, and the double layer capacitance was essentially unchanged, consistent with the increased thermal stability of the 3M catalyst support system. The loss of surface area is shown to be directly related to fuel cell performance, and the rate of surface area loss is temperature dependent.

Good progress towards development of a high temperature membrane (120 < T < 150ºC) that does not rely on water for proton conduction has been

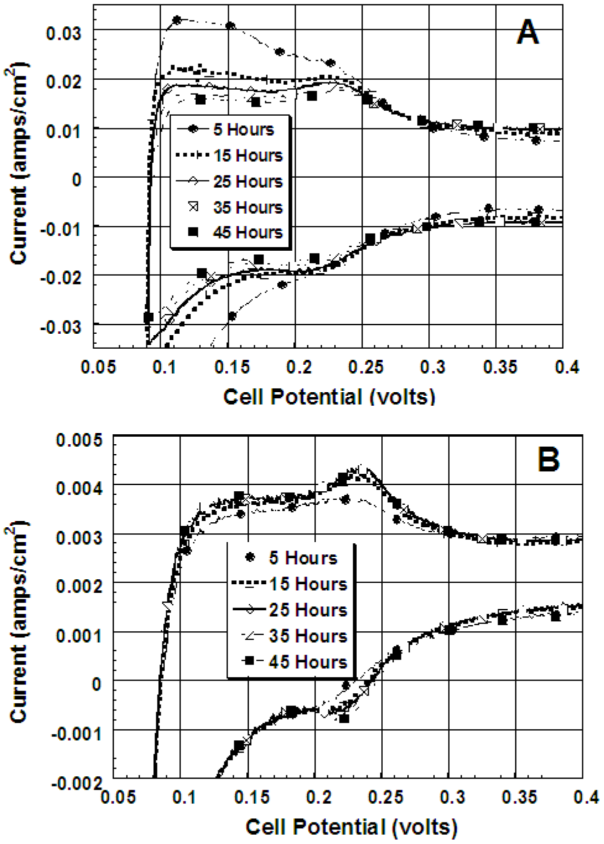

Figure 3. Comparison of cyclic voltammograms from (A) carbon supported Pt and (B) 3M nanostructured film supported Pt, taken every five hours during which the cell was polarized to 1.2 V at 80ºC under saturated H_2/N_2. The ECSA of the C/Pt catalyst decreased with time, and its double layer capacitance increased. The opposite is true for the 3M nanostructured film supported catalyst.

realized through both development of critical characterization techniques and new materials synthesis. High proton conductivity, as opposed to a more general ionic conductivity measured by AC impedance techniques, in the absence of water is a first requirement for such materials, and a methodology was developed to measure the proton conductivity of liquid based cells containing the new electrolyte candidates. Figure 4 compares the proton conductivity as a function of temperature in the absence of water of five different combinations of fluorinated acids and liquid additives, none of which involves phosphoric acid. As seen, the combination of acid D with liquid X has already at 120ºC produced conductivity sufficient for acceptable fuel cell performance at lower temperatures with standard PEMs. Work has recently begun on incorporating these proton conductive materials into useable solid polymer membranes and addressing the issues of forming effective catalyst/ionomer interfaces. More conventional high frequency impedance measurements of these membranes agree with the liquid cell proton conductivity measurements.

Conclusions

The 3M PFSA ionomeric membrane has shown longer lifetime and improved mechanical properties over membranes made with current commercial PEM ionomers for operation in the temperature range 85 < T < 120°C. There is the opportunity for further improvement with key additives. For the range 120 < T < 150°C, the approach to development of new membranes using perfluorinated acids plus liquid additives is promising, based on actual proton conductivity results. Key issues will revolve around forming useful membranes and effective catalyst/electrolyte interfaces with these new materials. The oxidative chemical stability and high temperature electrochemical surface area stability of 3M nanostructured catalysts and supports appear to be better than those of commercial carbon black supported Pt catalysts. The 3M nanostructured catalyst process and combinatorial approach to development of new catalysts are continuing to yield catalyst constructions having improved performance with lower loadings.

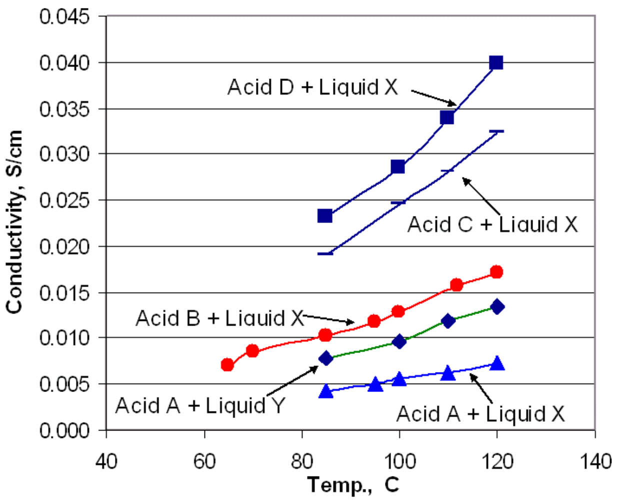

Figure 4. Illustration of the proton conductivity, measured in a special liquid cell with proton injection, of five different electrolyte combinations of perfluorinated acids and liquid additives, with no water in the system. The target range for adequate proton conductivity is ≥ 0.030 S/cm.

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3. 2003 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, May 19 - 22, 2003, Berkeley, CA, Project 72.

4. A. B. Laconti et al., "Mechanisms of membrane degradation," in Handbook of Fuel Cells, Fundamentals, Technology and Applications, Vol. 3, eds. W. Vielstich, A. Lamm and H. Gasteiger, John Wiley and Sons, p. 647.

FY 2003 Publications/Presentations

1. 2003 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, May 19 - 22, 2003, Berkeley, CA, Project 72.

Ultra-Thin Composite Membrane-Electrode Assembly For High-Temperature Proton Exchange Membrane Fuel Cells

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Subcontractor: Ion Power, Inc., Bear, DE

Objectives

- Develop an ultra-thin (< 75 µm), durable membrane capable of operation at 100-140°C
- Achieve <0.2 Ωcm^2 membrane ohmic resistance and <1% crossover
- Attain high ionic conductance with negligible electronic conductivity
- Attain high mechanical strength
- Demonstrate >0.6 V performance at 400 mA/cm^2 under ambient reformate/air operation at 120°C

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Durability
- F. Heat Utilization
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- R. Thermal and Water Management

Approach

Develop a solid superacid-Nafion® composite membrane electrode assembly (MEA):

- Solid superacids as high-temperature proton conductors and moisture retainers
- Nafion® phase as proton conducting binder phase
- Stable support phase added to enhance strength

Accomplishments

- Developed an understanding of MEA performance-controlling factors
- Demonstrated MEA performance of ~0.6 V at 400 mA/cm^2 and membrane ohmic resistance of <0.2 Ωcm^2 under system operating conditions [atmospheric, low relative humidity (RH), hydrogen/air stoichs 1.2/2.0] at 120°C

- Achieved >750 mV performance at 400 mA/cm^2 under 30 psig operating pressure
- Successfully scaled up MEA to 300 cm^2

Future Directions

- Understand MEA decay mechanisms in detail
- Further enhance mechanical durability
- Enhance catalyst utilization by further increasing proton conductivity in cathode

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Introduction

Fuel cells are inherently very efficient and clean, and they offer the best alternative to conventional power generation technologies. For fuel cells to be commercially competitive, issues such as cost, size, and functionality need to be addressed. A desired commercial distributed/stationary fuel cell system is an atmospheric-pressure natural gas-fueled proton exchange membrane fuel cell (PEMFC) system with >35% higher heating value (HHV) efficiency, >100°C operation for cogeneration, simple construction, >40,000 h reliable life, and <$1000/kW system cost. For the PEMFC to be commercially viable, the performance of critical components, such as the polymer electrolyte membrane in particular, needs to be enhanced. At present, the operating temperature of the state-of-the-art PEMFC is approximately between 60 and 80°C. Carbon monoxide poisoning of the PEMFC anode's precious metal catalyst is a major technical barrier for utilizing hydrocarbon feedstock. Since the poisoning by CO weakens considerably with temperature, one mitigation approach is to operate the PEMFC at higher temperatures. Many other advantages can also be realized, such as faster electrode kinetics, higher quality waste heat for cogeneration, cathode flooding mitigation, and greater ability to remove waste heat.

The baseline Nafion® membrane is deficient in terms of ionic conductivity above 100°C and at low relative humidity (RH), conditions desired for atmospheric-pressure stationary applications. Such conditions tend to dry out the membrane, drastically reducing membrane proton conductivity. Furthermore, the loss of water causes membrane embrittlement, resulting in membrane cracking, reactant cross-leakage and poor electrode-membrane contact. Therefore, a cost-effective membrane, with proton conductivity that is less sensitive to change in water content, is needed. Another important issue for >100°C operation is significantly reduced cell voltage loss. Only a minor portion of cell voltage loss is caused by the membrane ohmic resistance increase. The majority of the voltage loss increase is due to the increase in cathode polarization.

Approach

The overall objective is to operate a PEMFC at 100-140°C to improve CO tolerance, mitigate water and thermal management challenges and reduce membrane cost. The basic approach is to develop a composite membrane consisting of mechanical support and high-temperature proton conduction phases. In order to improve cathode performance, incorporating promising solid superacids into the cathode is also pursued.

Results

A number of ultra-thin composite membranes and MEAs have been developed to improve water retention and proton conduction at 120°C (Figure 1). Additives/modifiers with specific properties have been synthesized. The performance of the fabricated MEAs in laboratory-scale cells has been characterized to screen promising formulations. About 0.6 V performance and <0.2 Ωcm^2 resistance at 120°C and 400 mA/cm^2 under system operating conditions (atmospheric, low RH, high utilizations) have been achieved (Figure 2). The anode polarization loss is negligible (~10 mV) under these conditions. The MEA Pt loading was 0.4 mg/cm^2 for each electrode. This represents one of the best cell performances ever reported in the literature under these conditions. Greater than 750 mV performance at 120°C was also achieved under pressurized operating condition (30 psig) (Figure 3). The promising MEA has been successfully scaled up to nominal 300 cm^2 (Figure 4). The AC-impedance data revealed that the cathode is under mixed ohmic-kinetic control, while mass-transfer loss is minor (Figure 5). Therefore, enhancing proton conductivity in the cathode is expected to further improve cathode performance. This project was completed on June 30, 2003.

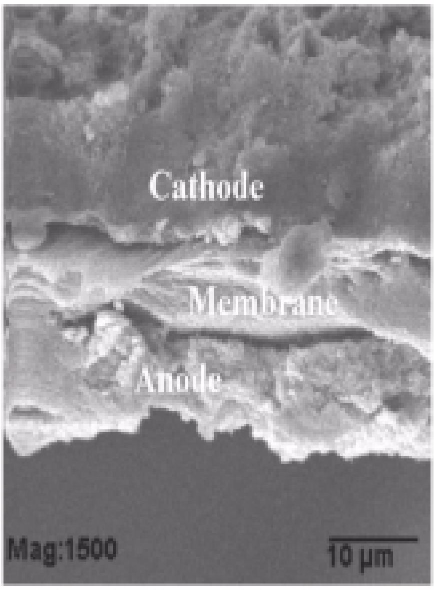

Figure 1. High-performing Ultra-thin MEA (<75 µm)

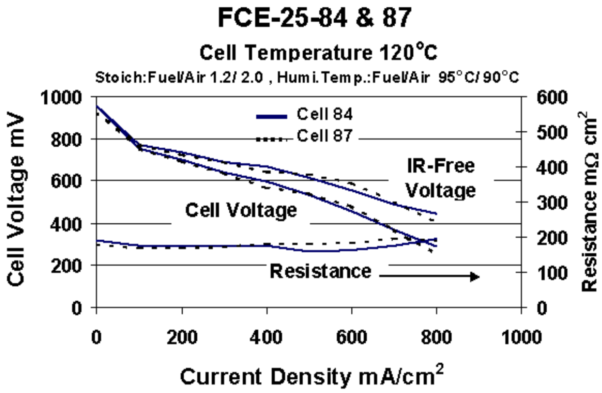

Figure 2. About 0.6 V Performance and <0.2 Ωcm^2 Resistance at 120°C and 400 mA/cm^2 under System Operating Conditions (atmospheric, low R.H., high utilizations) Have Been Achieved

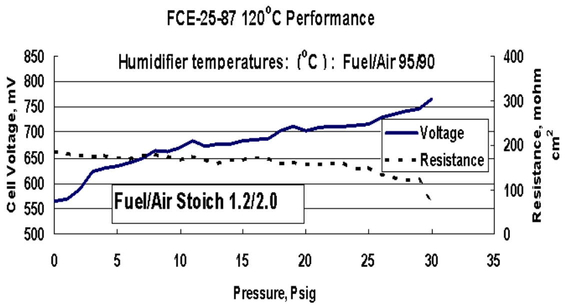

Figure 3. Performance of >0.75 V at 400 mA/cm^2 under Pressurized Operating Conditions Ha Been Achieved

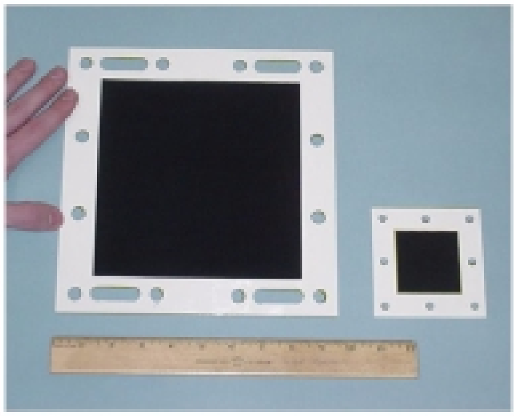

Figure 4. Promising MEA Has Been Successfully Scaled Up to 300 cm^2

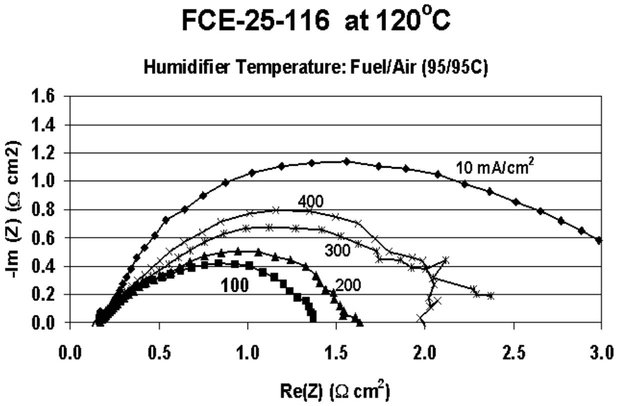

Figure 5. AC-impedance Data Show That the Cathode Is Under Mixed Kinetic-Ohmic Control at 120°C

Conclusion

An MEA performance of ~600 mV at 400 mA/cm^2 under system operating conditions has been demonstrated, representing a major milestone towards developing a viable atmospheric PEMFC system. To further enhance cell performance (to a desired 0.8 V at 400 mA/cm^2), optimization of cathode structure and formulation to enhance proton conduction and cathode catalyst utilization is required.

FY 2003 Publications/Presentations

1. Yuh, P. Patel, R. Kopp, and L. Lipp, "Membrane-Electrode Assembly for High-Temperature PEMFC," The American Chemical Society 226th Meeting, New York City, NY, September 7-11, 2003.

2. Yuh, "R&D on an Ultra Thin Composite Membrane for High-Temperature Operation in PEMFC," 2003 Hydrogen and Fuel Cells Merit Review Meeting, Berkeley, CA, May 19-22, 2003.

3. Yuh, "R&D on an Ultra Thin Composite Membrane for High-Temperature Operation in PEMFC," Annual Report to US DOE, for the Period of September 2000 to August 2001.

4. Yuh, "R&D on an Ultra Thin Composite Membrane for High-Temperature Operation in PEMFC," Annual Report to US DOE, for the Period of September 2001 to August 2002.

Development of High-Performance, Low-Pt Cathodes Containing New Catalysts and Layer Structure

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Subcontractors: DuPont Fuel Cells, Wilmington, DE; CFDRC, Huntsville, AL

Objectives

- Develop and apply combinatorial powder synthesis platform based on spray pyrolysis for discovery of high-performance, low-Pt cathode electrocatalysts.
- Develop engineered cathode layer structures containing the new electrocatalysts.
- Demonstrate enhanced performance of membrane electrode assemblies (MEAs) with low Pt content towards the DOE goals of 0.6 g Pt/kW in automotive applications for the year 2005.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- Q. Electrode Performance
- P. Durability

Approach

- Design and build a Combinatorial Powder Synthesis System (CPSS) capable of generation of large numbers of electrocatalyst powders with variable composition and microstructure.
- Design and build rapid ink formulation and electrode deposition equipment to screen electrocatalysts generated by the CPSS for their activity in oxygen reduction reaction (ORR) in half-cell configuration.
- Establish baseline for performance of Pt electrocatalysts in ORR based on rapid screening; establish go/no-go criteria for binary and ternary alloy electrocatalysts synthesized in the combinatorial system.
- Continue optimization of the MEA structure with benchmark Pt-based supported catalysts with various Pt loadings in the catalysts and in the cathode layer.
- Model the electrode structure to reveal effects of layer porosity and gas humidification levels at different fuel cell operating conditions (temperature and pressure).

Accomplishments

- The assembly of the CPSS was completed, fully automated and integrated to achieve the initial planned rates of electrocatalyst samples production (between 100 and 150 samples per week).

- The assembly of the rapid ink formulation and electrode deposition equipment was completed, and testing rates are compatible with electrocatalyst production rates.
- Baseline performance of Pt electrocatalysts was evaluated for a broad range of Pt loadings. Go/no-go criteria were established for newly synthesized alloy electrocatalysts. The half-cell rapid screening technique is exclusively used for screening electrocatalysts for their ORR activity.
- Combination of the best ternary alloy catalyst (Effort 1) and the best MEA structure/printing approach (Effort 2) delivers single MEA performance of less than 1 g Pt/kW at 0.8 V (100% improvement compared to best results of 2002, 2 g Pt/kW), see Figure 1.
- Modeling of cathode layer porosity and pore size distribution provides guidance for electrocatalyst structure modification.

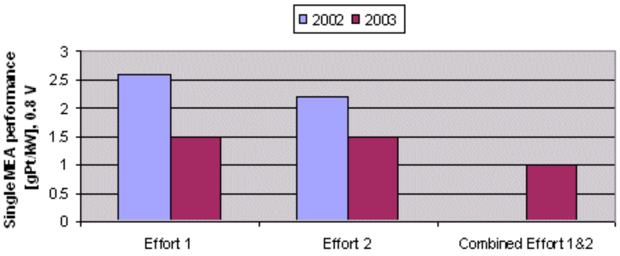

Figure 1. Summary of Performance Achievements in FY 2003 Compared to FY 2002

Future Directions

- Apply the CPSS and rapid screening equipment to the production and screening of a large number of electrocatalyst powders with variable compositions and microstructures.
- Characterize electrocatalysts by structural and electrochemical techniques to provide further focus of the combinatorial workflow and choice of compositions.
- Perform single MEA testing at various fuel cell operating conditions (gas utilization, humidification and pressure).
- Perform long-term testing.
- Demonstrate performance of best-performing electrocatalyst and the optimal MEA structure in a short stack fuel cell.
- Design and start assembly of rapid screening equipment in MEA configuration.
- Complete modeling of ionomer distribution within the cathode layer structure.

Introduction

The overall project goals, as stated previously, are to significantly improve both the kinetic performance of the electrocatalyst powder at low noble metal loadings (Effort 1: *Combinatorial discovery of low-Pt compositions with microstructure optimization using spray-based catalyst manufacturing)* and its utilization in the cathode layers through layer structure development (Effort 2: *Development of engineered particles and layers)*.

Approach

The approach relies on the integration of combinatorial synthesis of ORR electrocatalysts by spray conversion and optimized electrode structures enabled by the unique morphology of these electrocatalysts. The majority of the second year's effort was focused on the design, assembly and benchmarking of the combinatorial equipment for electrocatalyst synthesis and the high-throughput equipment for testing in half-cell configuration.

These equipment additions will allow for a significant increase in the number of compositional and micro-structural electrocatalyst variations that can be screened during Year 3 of the project. In parallel, the correlation between rapid half-cell screening test data and MEA performance for multi-component (alloys and mixed oxides) electrocatalysts was addressed.

The combined progress of both Effort 1 and Effort 2 were demonstrated in a single 50 cm^2 MEA. Stack testing criteria have been established and include stability testing of alloys in acidic media and long-term testing in a single MEA. Testing in the MEA configuration was expanded to cover broader variations of the operating conditions recommended by the fuel cell manufacturers in addition to the standard testing conditions.

Results

Combinatorial Synthesis. The assembly and testing of the Combinatorial Powder Synthesis System (CPSS) was completed in March 2003, and the CPSS is currently being used for combinatorial electrocatalyst synthesis (Figure 2). The CPSS was designed based on an R&D platform that leverages SMP's knowledge base of system scale-up, which ensures a pathway to high-volume manufacturing once promising candidates have been identified from an experimental campaign. The CPSS system is highly automated; an operator is required only to prepare feedstock precursor solutions (which are combined on-the-fly in controlled amounts) and to respond to operating excursions. To execute a run, the CPSS reads a database containing the physical data of the precursor solutions and the critical operating parameters (including processing temperature, gas flow rates, precursor feed rates and elemental composition of the target materials). For each individual run, the CPSS maintains and monitors the set points for all critical parameters. Graphical, numerical and statistical data for each run are presented in real-time charts and spreadsheets. Individual powder samples are isolated in the collection system to prevent cross-contamination and losses. The powders can be easily removed from the collection system and packaged for characterization, storage or shipment.

Figure 2. Combinatorial Powder Synthesis System (CPSS)

The CPSS has been engineered to accommodate up to four metal sources and two carbon sources for each campaign. As a result, a wide variety of compositions can be explored with minimal downtime for system cleaning or re-configuration. Depending on testing requirements and material systems, 100 to 150 samples per week can be produced, with a potential to further increase the number of samples to 300 per week. Furthermore, the CPSS greatly reduces the volume of paperwork, man-hours and quantity of raw materials required to accomplish a rigorous study while providing a higher level of data quality. Baseline performance of the system was evaluated against the conventional unit. Specifically, physical characteristics (e.g. metal crystallite sizes, particle sizes, morphology) of test powders were examined, and it was determined that the combinatorial system can reproduce results from the scale-up units for benchmark Pt-based catalysts. Long-term testing of the system demonstrated that the CPSS operates consistently and accurately with minimal input from the operator. Data (with statistical analysis) are automatically collected and reported by the supervisory control and data acquisition (SCADA) system to ensure reproducibility and accountability.

Rapid screening of the electrochemical performance. DuPont Fuel Cells designed and completed the assembly of the rapid ink formulation and electrode deposition equipment in June 2003. The new equipment can automatically mix and deposit electrode inks with rates comparable to those of the electrocatalyst synthesis achieved by the CPSS at Cabot Superior MicroPowders (Cabot SMP). The samples are then tested in half-cell 3-electrode configurations in parallel using a variety of electrochemical techniques. Between 75 and 150 electrocatalysts can be screened per week, and test results are presented as current density normalized by the amount of Pt in the electrocatalyst (Figure 3). In parallel, cyclic voltamograms are recorded to facilitate a more detailed understanding of the active phase structure, such as active surface area and type and uniformity of surface features formed. The preparation of electrode inks was further optimized for electrocatalysts with different Pt and alloy compositions. An excellent correlation was established between the half-cell screening data and the performance of alloy electrocatalysts in MEA configuration.

Based on extensive testing of Pt baseline catalysts supplied by Cabot SMP, a go/no-go criteria for the mass activity of the electrocatalyst was established for each group of electrocatalysts (10, 20, 30, 40, 50, 60 wt.% Pt in combination with various carbon supports). The main goal of establishing adequate go/no-go criteria for this primary screen of newly synthesized electrocatalysts was to minimize the more time-consuming testing in MEAs and the number of false negative (or marginally positive) results. Currently, in order to qualify for testing in an MEA configuration, the specific mass activity of a new multi-component electrocatalyst needs to exceed that of the best pure Pt catalyst by at least 20% (Figure 3). The go/no-go criteria could be further increased to ensure that the testing in the MEA configuration will be focused mainly on electrode layer optimization.

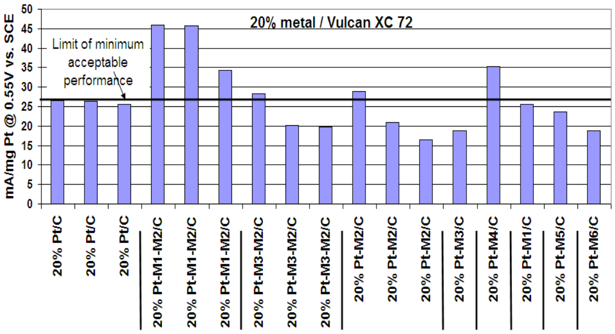

Figure 3. Test Results from Half-Cell Rapid Screening for Mass Activity of 20 wt.% Pt and Alloys Supported Electrocatalysts (SCE = saturated calomel electrode)

Binary and ternary Pt alloys. In order to establish and improve the combinatorial approach methodology, the spray pyrolysis processing of several binary and ternary compositions supported on Vulcan XC-72 was further optimized. The efforts were directed towards variations of metals loading (20, 40, 60 wt.%) and types of carbon support. The effect of spray processing and post processing conditions on the metal crystallite size and degree of alloying were also evaluated. Post processing of the electrocatalysts was further optimized, and testing of the stability of the alloys in acidic media is underway. For the best-performing 20 wt.% metal ternary alloy catalyst, an increase of the mass activity of up to 70% (in terms of mA/mg Pt) was observed when alloyed catalysts were compared to pure Pt in the rapid half-cell testing (supported alloys close to 2 times more active than pure Pt, Figure 3). Figure 4 compares the MEA performance of 20 wt.% PtM_1M_2/Vulcan XC-72 electrocatalyst compared with 20 wt.% Pt/Vulcan XC-72 at identical total Pt loadings of 0.13 mg Pt/cm^2. At 0.8 V, the performance of the ternary alloy catalyst is 220 mA/cm^2, as compared to 100 mA/cm^2 for the pure Pt electrocatalyst. If compared at constant current density of 0.2 mA/cm^2, the alloy catalyst delivers approximately 30 mV higher potential. Initial

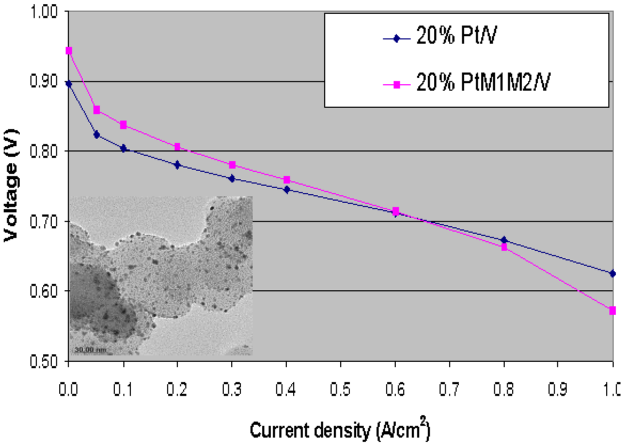

Figure 4. Polarization Curves for MEA with Total Loading of 0.13 mg Pt/cm^2 (Comparing performance of 20 wt.% PtM_1M_2 ternary alloy catalysts and 20 wt.% Pt/ Vulcan XC 72, test conditions described in the text; bottom left, TEM image of alloy catalyst.)

structural analysis of the ternary alloy electrocatalysts demonstrates excellent dispersion of the active phase (Figure 3).

MEA test conditions. Test MEAs (50 cm^2) were used for the evaluation, using Nafion 112 (DuPont) membranes. The MEAs were tested at 80ºC, with flows corresponding to 1 A/cm^2 at 1.5 stoichiometry for hydrogen and 2.5 stoichiometry for air on the anode and cathode, respectively. H_2 and air (100% humidified) were used at 30 psig pressure on both the anode and cathode.

MEA structure development. The development of the electrode structure was focused on optimization of the electrode deposition method with Pt and Pt-alloy electrocatalysts that demonstrated best performance in the rapid half-cell screening. Figure 5 shows charts for the MEA performance in terms of current and power density and in g Pt/kW at 0.8 V for 50 wt.% Pt/C and 20 wt.% ternary alloy catalyst as a function of the total Pt loading in the MEA. For the 50 wt.% Pt/high surface area carbon electrocatalyst, the performance in terms of current density at 0.8 V for the whole range of Pt loadings (0.55 to 0.35 mg Pt/cm$_2$) is above 400 mA/cm^2, and it achieves 1 g Pt/kW for 0.35 mg Pt/cm^2 loading. The ternary alloy catalyst supported on Vulcan XC-72 demonstrates 300 mA/cm^2 at 0.8 V with 0.2 mg Pt/cm^2 total Pt loading and below 1 g Pt/kW. These results demonstrate significant improvement in the overall MEA performance compared to last year's benchmarked MEA performance of 2 g Pt/kW (over 100% improvement).

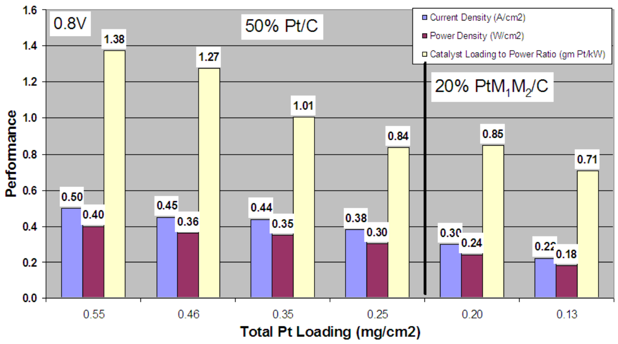

Figure 5. Summary of MEA Performance Characteristics

Modeling effort. During the past year, CFDRC developed models to address the impacts of pore size distribution and active phase placement within various pore sizes on the overall performance of the fuel cell. These models are based on detailed reaction-diffusion balance of species at various length scales and include such effects as Knudsen diffusion. The models were used for parametric studies involving variation of catalyst fractions within four different pore sizes of interest to Cabot SMP. The results clearly demonstrate the sensitivity of the MEA performance to the distribution of the active phase in various pore sizes and provide valuable guidance for modification of porosity of the electrocatalysts and electrode layer. CFDRC also performed several parametric studies to address the effects of global parameters such as temperature, pressure, relative humidity and gas stochiometries on cell performance. These studies showed good correlation to the experimentally observed trends and provided guidance on the optimization of fuel cell operating conditions and/or MEA structure.

Conclusions

During the second year of the project, several significant milestones were met, and progress was demonstrated on all main tasks. In Effort 1: *Combinatorial discovery of low-Pt compositions with microstructure optimization using spray-based catalyst manufacturing*, two critical tools for the combinatorial workflow were designed and their assembly completed: Combinatorial Powder Synthesis System (Cabot SMP) and Rapid Ink Formulation and Electrode Deposition Equipment (DuPont Fuel Cells). In Effort 2: *Development of engineered particles and layers*, further improvement in the MEA performance was achieved due to optimization of the cathode structure and deposition method. Most importantly, it was demonstrated that a combination of the best-performing ternary Pt alloy catalysts (Effort 1) and the best electrode layer structure (Effort 2) had an additive effect and delivered MEA performance of less than 1 g Pt/kW at 0.8 V, representing over 100% improvement over last year's benchmarked performance of 2 g Pt/kW (Figure 1). In addition, the synthesis of best-performing ternary Pt alloy catalyst was scaled to commercial powder production levels.

FY 2003 Publications/Presentations

1. P. Atanassova, D. Dericotte, P. Napolitano, R. Bhatia, J. Brewster, M. Hampden-Smith, C. Lundgren, L. Wang, S. Mazumder, Hydrogen, Fuel Cells and Infrastructure Technologies FY 2002 Progress Report, p.423

2. P. Napolitano, D. Dericotte, R. Bhatia, P. Atanassova, M. Hampden-Smith, T. Kodas, "Combinatorial Synthesis of Oxygen Reduction Electrocatalysts by Spray Pyrolysis", presentation, 2002 ECS Meeting, October 20-24, 2002, Salt Lake City, Utah, Meeting abstracts, p.729

3. P. Napolitano, D. Dericotte, B. Apodaca, R. Bhatia, P. Atanassova, M. Hampden-Smith, T. Kodas, "A New Focused, Scaleable Combinatorial Synthesis and Discovery Platform: Applications to Fuel Cell Electrocatalysts", presentation, 5th Annual International Symposium on Combinatorial Approaches for New Materials Discovery, February 10-21, 2003, San Jose, CA

4. M. Hampden-Smith, P. Atanassova, P. Atanassov, T. Kodas, "Manufacture of Electrocatalyst Powders by a Spray-based Production Platform", Handbook of Fuel Cells, 2003 John Wiley & Sons, Eds. W. Vielstich, H. Gasteiger, A. Lamm, Vol.3, p. 497

Design and Installation of a Pilot Plant for High-Volume Electrode Production

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Subcontractors:
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W.L. Gore & Associates, Inc., Elkton, MD

Objectives

- Significantly reduce overall membrane electrode assembly (MEA) cost by developing vacuum catalyzation methods that can meet DOE precious metal loading targets of 0.2 g/rated kW by 2010.
- Improve prospects for practical implementation of fuel cell technology in high-volume applications by demonstrating scalable, high-throughput manufacturing technologies.
- Evaluate performance of materials under relevant fuel cell operating conditions to confirm process viability.
- Complete process development and qualification of a pilot manufacturing plant.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost

Approach

- Determine the impact of large-scale catalyzation methods on MEA performance, if any, and develop approaches to minimize them.
- Establish in situ process control methods for catalyst deposition and demonstrate high-efficiency metal recovery approaches.
- Benchmark MEAs fabricated at SwRI against commercially available products.
- Incorporate SwRI-manufactured MEAs into two "short stack" fuel cells built by General Motors (GM) and deliver to Argonne National Laboratory for testing and evaluation.

Accomplishments

- Continued work with pilot manufacturing system, catalyzing over 3000 linear feet of electrode material as part of ongoing process optimization and production yield studies.
- Completed assembly and initial testing of hydrogen-air and reformate-air fuel cell stacks at GM.
- Conducted single-cell durability testing over 500+ hours in conjunction with Gore.

Future Directions

- Deliver stacks to Argonne National Laboratory for further testing and evaluation.
- Continue process development and optimization in anticipation of transitioning technology to full-scale production.
- Adapt vacuum deposition methods to fabrication of ultra-thin Pd alloy membranes for hydrogen purification (new DOE project).
- Examine feasibility of vacuum deposition methods in development of reversible fuel cells and non-precious metal catalysts.

Introduction

Progress in the adoption of fuel cell technology in the automotive area will depend to a large extent on the economics of catalyst utilization, the MEA production system, and the resultant performance in a fuel cell system. Recent cost analyses have suggested that MEAs can constitute as much as 80% of the cost of a fuel cell stack. Hence, improvements in the inherent performance of MEAs while substantially reducing the catalyst content per unit area will contribute significantly to lowering the cost of producing fuel cell generated power. The development of manufacturing concepts permitting the continuous and high-speed catalyzation of electrodes should have a significant beneficial impact on the cost of the MEAs and the dollars per kilowatt of power produced by the fuel cell.

Until recently, most MEAs were produced in time-consuming, batch-type processes. This situation has existed because of generally low volume purchases of MEAs and the large variety of MEA sizes and configurations required by the various fuel cell systems manufacturers. In effect, the industry is in a "chicken and egg" situation where low-price components, including MEAs, are required for high-volume commercialization of fuel cells, yet component suppliers need high volumes to attain low prices. Without a large present market, the investment risk is considerable and may be beyond the means of any industrial entity.

High-volume, continuous operations capable of producing sub-components such as electrodes should dramatically reduce the cost of the finished product. Southwest Research Institute (SwRI) is investigating this proposition by developing large-area, vacuum-based electrode substrate coating technologies to reduce overall material content of the finished part. Specifically, "ultra-low" precious metal loaded electrodes with loadings of 0.10 mg/cm^2 or less have been fabricated using state-of-the art polymer electrolyte membranes and electrode substrates procured from Gore. The best-performing MEAs have been delivered to General Motors for the construction and supply of two fuel cell "short stacks" to Argonne National Laboratory (ANL).

Approach and Results

Activities in the past year have focused on further investigations of optimal materials processing conditions using the vacuum roll coater. Several thousand linear feet of additional intermediate electrode material has been supplied by Gore over the past year for use with this system. Pilot quantities of catalyzed electrode material (Figure 1), up to 500 linear feet per run, have been prepared and

Figure 1. Vacuum-Catalyzed Intermediate Electrode Material

evaluated using standardized test methods. These materials have in turn been used to fabricate full-scale MEAs utilizing state-of-the-art GORE-SELECT® membranes (Figure 2).

A small number of fuel cell "short stacks", each typically 803 cm^2 active area and consisting of 14 cells using composite plates, have been assembled and tested at GM. Each stack contains both baseline and experimental MEAs that can be individually monitored for "side-by-side" testing and comparison. The hydrogen-air stack utilizes a total precious metal loading of 0.2 mg/cm^2 and has generated a peak power of approximately 5 kW operating at 220 kpa pressure with hydrogen and air stoicheometries of 1.2 and 2.0, respectively. In laboratory tests, smaller single cells (25-100 cm^2) were fabricated with total loadings of ~0.1 mg/cm^2 and have generated power densities of more than 1.0 A/cm^2 at 0.6 V running at similar pressures and stoicheometries. In an effort to more fully characterize the performance of ultra-low load electrodes, the effects of cathode humidification, gas diffusion media, cell compression, and cell assembly have been investigated. In support of this effort, W.L. Gore and Associates has also been conducting performance and durability life testing of samples fabricated at SwRI. The results to date have suggested that, while durability goals may be even more challenging with low loading electrodes compared to high loading samples independent of the catalyst deposition method used, this particular technology has significant value in enabling low-loading MEAs to meet the required power density targets.

Figure 2. Full-Scale MEA for GM Test Stack

Conclusions

A pilot manufacturing facility has now been completed that has the capability to catalyze more than 100,000 square meters of electrode material on a three-shift basis - enough to facilitate the production of MEAs for tens of thousands of fuel cell-powered automobiles. Pilot quantities of catalyzed electrode material, up to 500 linear feet per run, have been prepared, with small scale (25-100 cm^2 active area) and full scale (up to 800 cm^2 active area) MEAs fabricated using the prepared electrode materials. Selected examples have been provided to W.L. Gore and GM for testing, evaluation, and, incorporation into two fuel cell stacks. The first hydrogen-air stack has generated a peak power of approximately 5 kW and is being prepared for delivery to ANL. The second stack, configured to run on reformate, is scheduled for final test and shipment before the end of the fiscal year.

Scale-Up of Carbon/Carbon Composite Bipolar Plates

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Subcontractor: UTC Fuel Cells, Inc., South Windsor, CT

Objectives

- Develop carbon/carbon composite materials for bipolar plates that meet or exceed targets
- Evaluate the performance of the bipolar plate materials through fuel cell stack testing
- Design and construct a research-scale production line for materials development efforts
- Design and construct a pilot-scale production line to demonstrate high-volume, low-cost bipolar plate manufacturing

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost

Approach

Phase I

- Design, construct and install material forming, pressing and thermal treatment equipment
- Systematically investigate material forming techniques and composition ingredients
- Systematically investigate material processing variables and test material properties
- Perform fuel cell testing to evaluate plate performance at UTC Fuel Cells
- Investigate forming techniques aimed at rapid, low-cost production

Phase II

- Design, construct and install pilot-scale production line for 300 plates per hour capacity
- Design and implement quality assurance system for pilot line
- Evaluate pilot line performance and estimate pilot and mass bipolar plate production costs
- Evaluate pilot line bipolar plates for fuel cell performance and deliver fuel cell stack

Accomplishments

- Completed numerous fuel cell tests at UTC Fuel Cells, gathering invaluable information regarding material design and functionality
- Completed installation and demonstration of Phase I development line
- Expanded line to manufacture materials in higher volumes to meet near-term demands for product

- Developed extensive quality assurance system to complement near-term product manufacturing (quality system audited by UTC Fuel Cells)
- Began investigation into Phase II pilot production line processes; identified key process bottleneck areas in Phase II line
- Developed detailed timeline and organized plan for Phase II line implementation
- Continued development of improved bipolar plate materials

Future Directions

- Continue fuel cell testing at partner site
- Continue product development activities
- Initiate Phase II line process investigations to address specific process bottlenecks
- Accelerate Phase II line design and installation activities
- Continue to develop materials and processes to increase product yield and product sensitivity to raw material and process variation

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Introduction

In April 2001, Porvair Fuel Cell Technology, Inc. (PFCT) licensed a carbon/carbon composite bipolar plate formation technology from Oak Ridge National Laboratory. The goal of PFCT is to transfer this technology from the laboratory to full-scale, low-cost mass production to meet the emerging need of the rapidly developing fuel cell industry. This project is directed at further developing the carbon/carbon bipolar plate material to meet the performance, durability and cost demands of the fuel cell industry, and demonstrating a pilot-scale manufacturing line to produce this material in reasonable pilot quantities (300 plates per hour) at low cost.

Approach

The path to final production demonstration is split into two major parts in this project. Phase I focuses upon material and composition refinement to satisfy the fuel cell property and performance requirements. Phase II focuses upon the design, installation and operation of a fully functional bipolar plate production line capable of demonstrating high speed, low cost plate manufacturing.

The approach taken in materials development utilizes information fed back to PFCT by our customers following product property and fuel cell testing. Specific needs and concerns of our customers are evaluated relative to the current state of the product or process development to guide improvements leading toward a better bipolar plate. Internally, materials development efforts are guided through the performance of statistically designed experiments. Key product or process variables are evaluated in an orthogonal array of experiments. Results are measured and analyzed to determine the degree of influence each variable has on the measured property. A statistical model is then built to aid in moving subsequent experiments into a near-optimum range of investigation.

The approach utilized in planning the Phase II production line utilizes external contract engineering assistance along with internal process development activities. A local engineering house has been contracted to assist with Phase II project planning and execution. The execution plan schedules specific milestone events, including the development of an overall project outline, the development of key Process Instrumentation and Control, Process Flow and Plant Layout Diagrams, the development of the governing quality system and the basics of plant layout and construction (tear-down and clear-out, utility plan, environmental permitting, equipment specifications and bids, etc.).

Results

Phase I of the project has been completed in the past year. Our Phase I objectives were met, including development of materials with properties that exceed DOE targets and successful fuel cell testing through our commercial partner, UTC Fuel Cells. Further, because of the strong interest in the product, activities were performed to expand the Phase I development line, and quality system development activities were implemented for this line. PFCT and our customers provided the funds used to expand the Phase I line.

Figures 1 and 2 show some of the expanded Phase I equipment. The accelerated manufacturing of the product enabled PFCT to accelerate the learning associated with product and manufacturing issues. These include raw material specification fit to the product, impurities and supply capability, and process variability and its effect on product properties and product yields. Much of this experience will transfer directly to the Phase II line and enable faster implementation of that line.

Figure 1. Expanded Development Equipment Used In Bipolar Plate Manufacture - Forming

Figure 2. Development Equipment Used in Bipolar Plate Evaluation - Laboratory

Materials development activities continued in 2003 with the goal of continued materials properties improvement and cost reduction. Through materials development efforts, electrical conductivity was increased while maintaining flexural strength, formability and low hydrogen permeability. Table 1 shows the properties relative to DOE targets. Conductivity, strength and material purity (all carbon product) are the key advantages of the material developed at PFCT. Figures 3 and 4 show the range of conductivity and strength achieved versus final

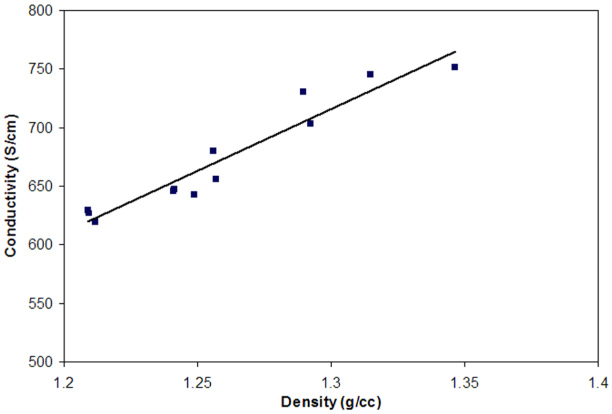

Figure 3. Product Conductivity as a Function Of Density

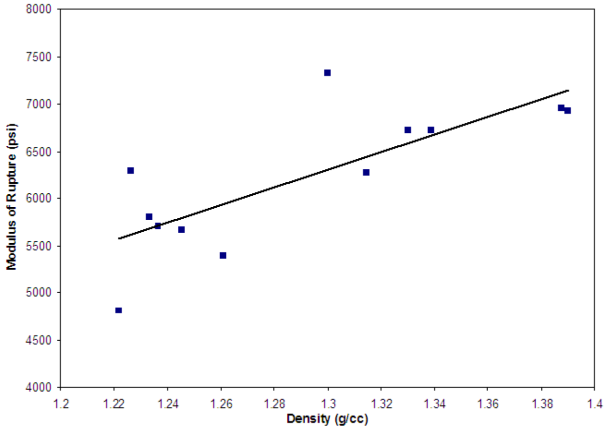

Figure 4. Product Strength as a Function of Density

Table 1. Carbon/Carbon Material Properties

Property	Value	DOE Target
Electrical Conductivity (S/cm) (ASTM C611)	> 600	> 100
Density (g/cc)	1.00 - 1.30	-
Flexural Strength (psi)	>5000	> 600 (crush)
Flexibility (%)(deflection at mid-span)	1.5 - 3.5	3-5
Hydrogen Permeability (cc/cm^2/sec) (ASTM D1434)	<2x10^{-6}	<2x10^{-6}

product density, respectively. The conductivity of the product greatly exceeds that of competitive low-cost bipolar plate materials. Different bipolar plate designs have been fully embossed using the developed materials with good success, demonstrating the potential of this material in the manufacture of low-cost plates.

In manufacturing products, sealing against hydrogen occurs through the chemical vapor infiltration process. In this process, carbon is deposited from a hydrocarbon gaseous precursor such that a hermetic skin is formed on the surfaces of the product. This yields a product that is sealed at a much lower overall density than competitive bipolar plates. Figure 5 is a micrograph of the sealed region of the product.

Numerous fuel cell tests have been performed at UTC Fuel Cells to date. The goals have been focused at both investigating the product for basic performance and evaluating aspects of the product for acceptable fuel cell performance and durability. Both single cell and multiple cell testing has occurred. Much of this testing has been funded by UTC Fuel Cells, independent of this development project. Positive test results have led to a strong demand for the product, but specific data are proprietary. The chart shown in Figure 6 shows qualitatively the performance improvements that PFCT products have been able to achieve over the course of the project. In general, the number following Porvair in the chart is chronological. Later products performed well against the bill of material machined graphite. Specific test results have been used by UTC Fuel Cells to evaluate product performance relative to competitive products and plate design. Specific feedback to PFCT has been used to guide product design and process changes to yield a better performing and more consistently manufactured product.

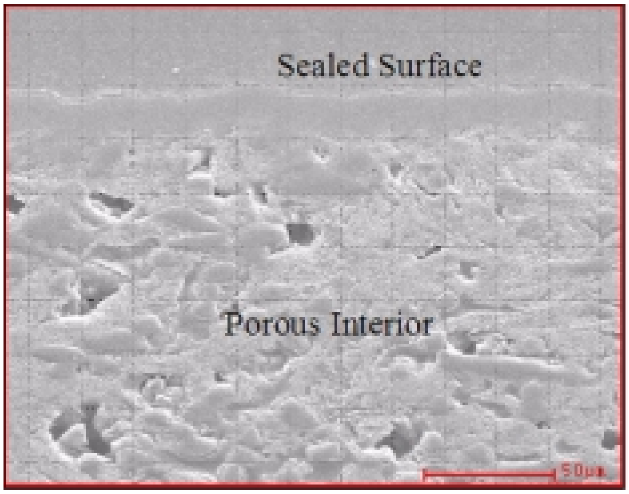

Figure 5. SEM Micrograph of a Molded Carbon/Carbon Composite Material (Figure shows thin skin coating on plate exterior to provide plate sealing.)

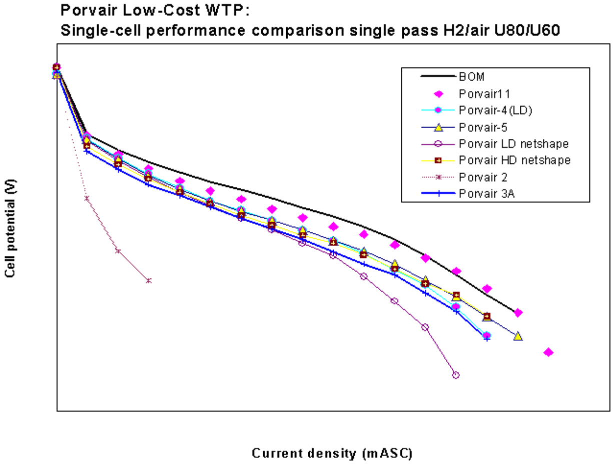

Figure 6. Polarization Curve Showing PFCT Materials in UTC Fuel Cells Testing Relative to Bill of Material (BOM) Target (Numbers in chart reference product trials in approximate chronological order.) WTP = water transport plate; LD = low density; HD = high density; ASC = a/cm^2

Specific work has been done toward the Phase II line, including up-front planning and process scale-up development. Specific portions of the process, where equipment cost is prohibitive or where line bottlenecks exist, are receiving attention to simplify the required equipment and increase the processing time for that portion of the manufacturing cycle. A plan has been developed to investigate these processes to yield equipment specifications so that the necessary equipment can be ordered and installed for Phase II.

The Phase II line will be semi-automated, where key processes are monitored and controlled with calibrated electronic equipment. Component transfer will be through use of conveyors or simple robotics where such operations are not complex. Initial cost analyses have been performed to evaluate the cost-effectiveness of the line. As with any manufacturing process, final product cost depends greatly on the yield of the manufacturing line. The line implementation plan anticipates low yields to start, increasing to optimum levels over the first 4-6 months of line operation.

Conclusions

Porvair Fuel Cell Technology has continued to develop materials and manufacturing processes to supply high quality bipolar plates to the fuel cell industry. Advancements in the past year have included continued mass manufacturing process investigation and Phase II production line planning.

In addition, due to product demand, the laboratory system has been expanded, and a complete quality assurance system has been developed and implemented for this development line. The quality system will serve as the backbone for the Phase II production line.

Fuel cell tests of PFCT's bipolar plate products have continued at a rapid rate at UTC Fuel Cells, as the products are evaluated for beta and pre-production units. Tests have taken place in single-cell, multi-cell and full stack arrangements.

Special Recognitions & Awards

1. Federal Laboratory Consortium for Technology Transfer, Excellence in Technology Transfer Award

Carbon Composite Bipolar Plates

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Objectives

- Develop a slurry molded carbon fiber material with a carbon chemical vapor infiltrated sealed surface as a bipolar plate.
- Collaborate with manufacturer/licensee with regard to testing and manufacturing of such components.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan

- O. Stack Material and Manufacturing Cost

Approach

- Fabricate fibrous component pre-forms for the bipolar plate by slurry molding techniques using carbon fibers of appropriate lengths.
- Fabricate hermetic plates using a final seal with chemical vapor infiltrated carbon.
- Develop commercial-scale components for evaluation.

Accomplishments

- In coordination with licensee, have reduced thickness of plates from 2.5 mm to 1.5 mm. Determined influence of chemical vapor infiltration (CVI) temperature on depth of infiltration.
- Further characterized and measured mechanical properties of carbon composite plate material.
- Determined electronic properties, including effect of surface roughness on resistance.
- Developed initial model of chemical vapor infiltration process that is scalable to production. The model was utilized to improve the flow pattern of gas used to deposit carbon on the plate.

Future Directions

- Support continued scale-up of the licensee's operation through modeling of fabrication processes.
- Optimize mechanical properties through combination of pre-form material and CVI conditions.

Introduction

The challenges for PEMFC technology for automobiles lie in reducing the cost and weight of the fuel stack, an impediment to which is the cost and weight of the bipolar plate. The bipolar plate is the electrode plate that separates individual cells in a stack. A stack is formed when multiple cells are aligned one after another so as to work in series, with the bipolar plate providing an electrode for the cells on either side. The reference material for the bipolar plate is high-density graphite with machined flow channels. Both material and machining costs for graphite, however, are prohibitive for many fuel cell applications, and this has led to substantial development efforts to replace graphite. The requirements for a bipolar plate are stringent, including low-cost materials and processing, light weight, thin (<3mm), sufficient mechanical integrity, high surface and bulk electronic conductivity, low permeability (boundary between fuel and oxidant), and high corrosion resistance (in the moist atmosphere of the cell).

The bipolar plate approach developed at Oak Ridge National Laboratory (ORNL) uses a low-cost, slurry-molding process to produce a carbon-fiber pre-form. The molded, carbon-fiber component could have an inherent volume for diffusing fuel or air to the electrolyte surface or impressed flow-field channels. The bipolar plate is made hermetic through chemical vapor infiltration (CVI) with carbon. The infiltrated carbon also serves to make the component highly conductive.

The work during FY 2003 included efforts to reduce the thickness of the bipolar plate. Other research focused on determining the properties of bipolar plates prepared from pre-form material supplied by Porvair Fuel Cell Technology (the licensee) as well as ORNL, as a function of processing. This includes strength and fracture toughness, the depth of penetration of infiltrated carbon, and the effect of surface roughness on conductivity/resistivity. Also developed during this period was a first-order model of the CVI process based on the ORNL CVI system. These efforts were in cooperation with and in support of the work at Porvair to scale up and commercialize the technology.

Approach

At Porvair Fuel Cell Technology, pre-forms were produced that were reduced from 2.5 mm in thickness to 1.5 mm through an increased concentration of particulate material in the pre-form that resulted in a higher green density (density before infiltration with carbon). The effect of this higher green density on infiltration was investigated through intercomparisons with ORNL material, which did not contain particulates and was of lower density. Void volume as a function of through-thickness position was determined by digital analysis of images of polished cross-sections. The effect of processing conditions (CVI temperature) on density gradients through the plates were similarly investigated.

The mechanical properties of the plates were determined through notch sensitivity. Holes of differing sizes were machined in plate specimens and tested under tension to failure. The characterization of the variation of strength with hole size provides information on fracture toughness. Ultimate strength is found from the zero intercept of the strength versus the ratio of hole diameter to sample width.

The electrical properties as a function of surface roughness may be an issue in fuel cell stacks. This was investigated by producing samples with differing surface roughnesses due to different CVI temperatures, and by also evaluating polished and uninfiltrated samples. Two-point and four-point measurements were obtained which provide contact resistance and bulk conductivity, respectively.

In order to allow efficient scale-up of the CVI process, a computational fluid dynamics model of the process, coupled with chemical kinetic information, was developed. This used the existing CVI system geometry and conditions at ORNL.

Results

Porvair has successfully reduced the thickness of the bipolar plates through a high particulate content giving high green strength (strength before infiltration with carbon). Determination of the through-thickness density gradient of the infiltrated Porvair material reveals that little carbon is deposited within the material and that the overcoating and sealing of the surface happens early during infiltration (Figure 1). This is in contrast to the original ORNL pre-form material that consists entirely of fiber and carbonized phenolic, and has more than twice the uninfiltrated void volume. Thus, after infiltration, especially at higher temperatures where the ORNL material is overcoated and sealed relatively rapidly, the ORNL component has a large density gradient, whereas the infiltrated Porvair pre-form has a high-density outer coating and fairly uniform internal density. Lower temperature and longer infiltration times do not modify this behavior for the Porvair material, but do result in higher density, more uniform ORNL plates. All infiltrated plates are hermetic.

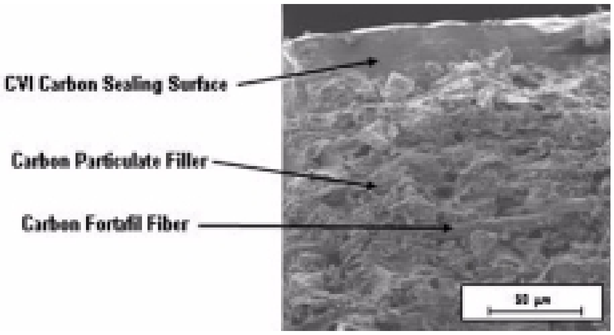

Figure 1. Fracture Surface of a Sealed Bipolar Plate Produced with Porvair Pre-Form Material Showing the Particulate Filled Interior and the CVI Carbon Coating on the Surface

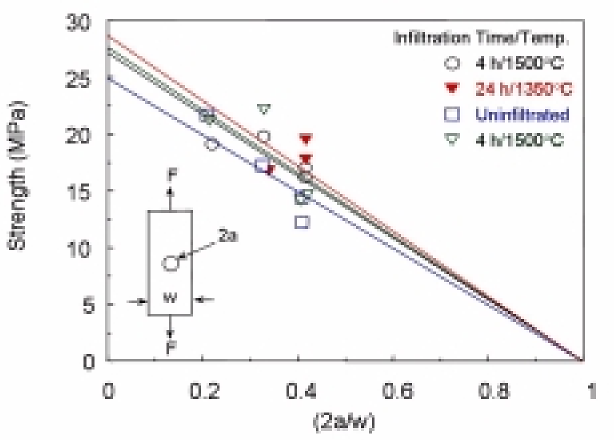

Figure 2. Plot of Measured Strength Versus the Ratio of Hole Size to Sample Width Illustrating Ultimate Strength and Notch-Insenstivity

The strength and fracture toughness of the bipolar plate material were evaluated using the variable hole tensile test. The results of the tensile curves (Figure 2) reveal that the material is relatively notch insensitive. The strengths indicated by the zero intercepts (Figure 2) range from 25 to 28 MPa.

Measurements of contact resistance show a weak dependence on surface roughness. Table 1 shows the results where only the polished samples indicate a measurably lower contact resistance, with the exception of the uninfiltrated material which had fewer interfaces that could contribute to ohmic losses. High bulk conductivity is also indicated.

The computational fluid dynamics modeling revealed flow patterns within the CVI reactor. This included differences in the flow above and below the bipolar plate. This information was used to modify the inlet geometry so that the flow was significantly more uniform, and therefore deposition rates on the top and bottom of the plates were more uniform. Figure 3 illustrates the effect of improving the flow geometry.

Conclusions

- Increasing the particulate content of the pre-form allows a reduction in bipolar plate thickness, more uniform density, and easier/more rapid sealing via CVI.
- Mechanical property measurements indicate the bipolar plate material is notch-insensitive, and therefore relatively tough, and has good strength.
- Electrical measurements indicate low contact resistance and high bulk conductivity, with a weak dependence on surface roughness.

Figure 3. Computed Flow Pattern of Reactive Gases Around a Bipolar Plate in the ORNL CVI Reactor

Table 1. Two- and Four-Point Probe Electrical Measurements

Infiltration Treatment	Sourface Roughness Rz µm	Resistance 2 Probe DC ohms	Conductivity 4 Probe V/I σ S/cm
4 hours at 1500°C	8.83	1.86	365
24 hours at 1350°C	12.9	1.37	417
Uninfiltrated	13.5	0.86	369
4 hours at 1500°C	10.2	2.16	386
24 hours at 1350°C	14.3	1.57	383
24 hours at 1350°C	2.9	0.84	408

- Computational fluid dynamics applied to the CVI process at ORNL indicated means for increasing plate infiltration uniformity.

FY 2003 Publications/Presentations

1. T. M. Besmann, J. J. Henry, Jr., J. Klett, D. Haack, and K. Butcher, "Optimization of a Carbon Composite Bipolar Plate For PEM Fuel Cells," Proc. Materials Research Society, Vol. 756

Special Recognitions & Awards/Patents Issued

1. Year 2002 National Federal Laboratory Consortium “Excellence in Technology Transfer Award.”

2. Year 2002 Southeast Region of the Federal Laboratory Consortium “Excellence in Technology Transfer Award.”

Cost-Effective Surface Modification for Metallic Bipolar Plates

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Objectives

- Develop a low cost metallic bipolar plate alloy that will form an electrically conductive and corrosion resistant nitride surface layer during thermal nitriding to enable use in a proton exchange membrane (PEM) fuel cell environment.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost.
- P. Durability

Approach

- Conduct a study of the nitridation behavior of a series of model Ni/Fe-X base alloys (X = nitride forming elements such as Cr, Nb, Ti, V) that can potentially meet DOE bipolar plate cost goals.
- Identify the most promising combination of X additions, ternary and higher order alloying elements, and nitriding conditions that result in the formation of an adherent, protective nitride surface layer.
- Evaluate the corrosion, electrical properties, and fuel cell behavior of the thermally nitrided alloys.
- Characterize the nitride layer microstructure and composition by x-ray diffraction, electron probe microanalysis, scanning electron microscopy, and transmission electron microscopy. Use this information in a feedback loop to modify alloy chemistry and nitridation processing conditions to optimize the protectiveness of the nitride surface layer.

Accomplishments

- Nitridation of a model Ni-50Cr alloy was optimized to form a dense, protective CrN/Cr_2N surface layer.
- The nitrided model Ni-50Cr alloy exhibited very low levels of metal-ion dissolution and negligible increase in contact resistance in a 1000-hour single-cell, fuel cell test using 50 cm^2 active area anode and cathode plates and in a 4100-hour bipolar coupon corrosion test.

- A United States patent disclosure was submitted in April 2003 for nitrided Ni/Fe-Cr and related base alloys thermally nitrided to form a protective CrN/Cr_2N surface layer.
- Collaboration was established with DANA Corporation, Tennessee Technological University, and the University of Minnesota to evaluate sealing and manufacturability issues of nitrided Ni-Cr alloys and to demonstrate technological viability of the approach by a 5-cell stack test.

Future Directions

- Continue in-cell evaluation of nitrided Ni-50Cr to fully characterize and optimize the protectiveness of the CrN/Cr_2N surface layer. This testing will include single-cell and stack testing with Los Alamos National Laboratory (LANL) and fuel cell manufacturers.
- Modify alloy composition/nitriding conditions to form a corrosion-resistant CrN/Cr_2N surface layer on Ni/Fe-Cr base alloys that are comparable to conventional stainless steels in terms of manufacturability and cost in order to meet DOE bipolar plate cost goals. Establish partnerships with alloy producers and fuel cell manufacturers.

Introduction

The bipolar plate is one of the most expensive components in PEM fuel cells. Thin metallic bipolar plates offer the potential for significantly lower cost than currently-used machined graphite bipolar plates and reduced weight/volume and better performance than developmental polymer/ carbon fiber and graphite composite bipolar plates. However, inadequate corrosion resistance can lead to high electrical resistance and/or contamination of the polymer membrane, both of which can significantly degrade performance. Metal nitrides offer electrical conductivities up to an order of magnitude greater than that of graphite and are highly corrosion resistant. Unfortunately, most conventional coating methods (for metal nitrides) are too expensive for PEM fuel cell stack commercialization or tend to leave pin-hole defects, which result in accelerated local corrosion and unacceptable performance.

Approach

The goal of this effort is to develop a bipolar plate alloy that will form an electrically conductive and corrosion resistant nitride surface layer during thermal (gas) nitriding. There are three advantages to this approach. First, because the nitriding is performed at elevated temperatures, pin-hole defects are not expected because thermodynamic and kinetic factors favor complete conversion of the metal surface to nitride. Rather, the key issues are nitride layer cracking, adherence, and morphology (discrete internal subsurface precipitates vs. continuous external scales), which can potentially be controlled through proper selection of alloy composition and nitridation conditions. Second, the alloy can be formed into final shape by inexpensive metal forming techniques such as stamping prior to thermal nitridation. Third, thermal nitridation is an inexpensive, well-established industrial technique.

Results

A nitrided Ni-50Cr model alloy coupon was exposed for 4100 hours (h) under simulated PEM fuel cell anode and cathode bipolar plate conditions using the corrosion test cell developed at LANL [1]. The test environment was a pH 3 solution of H_2SO_4 containing 2 ppm F^- at 80°C. Hydrogen and air at 1 atmosphere were supplied to the anode and cathode faces, respectively, of the flat (no flow field features) test coupon. Platinum screens passed 1 A/cm^2 electrical current to the ELAT® electrode/carbon backing paper/bipolar test coupon assembly, and the electrical potential was recorded in-situ to monitor resistive surface phase (e.g. oxide) growth. In the corrosion test cell, the nitrided Ni-50Cr bipolar coupon exhibited a voltage change of only 2 mV/ 1000 h at the anode and 2.7 mV/1000 h at the cathode over the course of the 4100 h exposure. The anode face of the coupon effectively experienced ~ -0.31 V vs standard hydrogen electrode (SHE) and the cathode face +0.56 V. Ni levels of only 0.85,

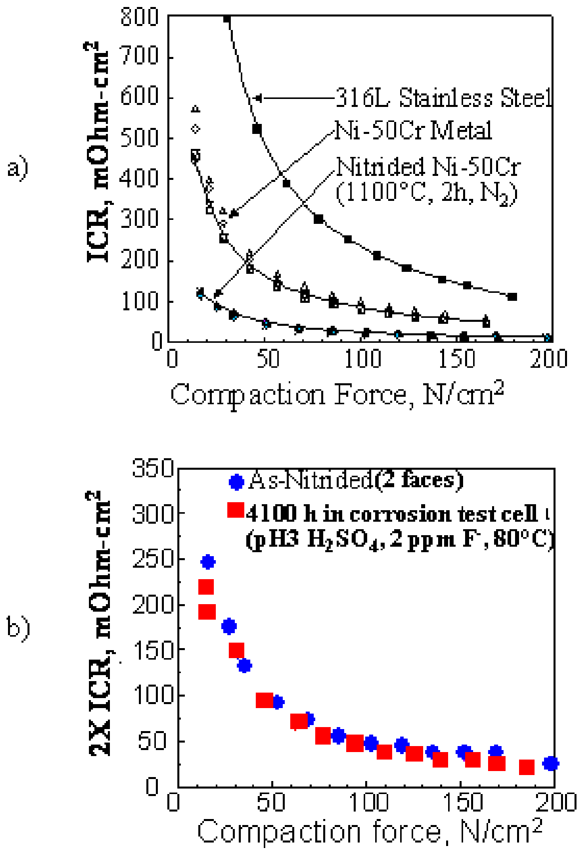

Figure 1. Interfacial contact resistance data a) as-nitrided b) after 4100 h in corrosion test cell. Note that the data for the bipolar coupon from the corrosion test cell include both anode and cathode faces; the as-nitrided comparative data from Figure 1a was therefore doubled.

0.56, and 2.4 ppm were measured in the anode-face exposed solutions and 0.034, 0.019, and 0.027 ppm Ni in the cathode-face exposed solutions, respectively, for 0-1500, 1500-3400, and 3400-4100 hours of exposure. Cr was not detected. Interfacial contact resistance (ICR) data as a function of compaction pressure are shown in Figure 1. The Ni-50Cr alloy (no nitridation treatment) had a lower contact resistance than 316L stainless steel, shown for comparative purposes. Subsequent nitridation of Ni-50Cr significantly lowered contact resistance (Figure 1a). ICR measurements of the 4100 h exposed bipolar test coupon (Figure 1b) showed no increase in ICR relative to as-nitrided Ni-50Cr. Back scattered electron (BSE) images of a nitrided Ni-50Cr control coupon, the 4100 h cathode-environment exposed face, and the 4100 h anode-environment exposed face, are shown in Figure 2. The external nitride scale consisted of three layers: a ~1 micron thick semi-continuous outer layer of CrN (not visible in the figure); an intermediate, 3-5 microns thick continuous layer of Cr_2N; and an inner layer of the ternary Ni-Cr-N π phase. The microstructure of the nitride on the cathode-exposed face (Figure 2b) and the anode-exposed face (Figure 2c) appeared essentially the same as the archival, as-nitrided material, with no evidence of significant attack or surface oxide formation (based on transmission electron microscopy cross-sections).

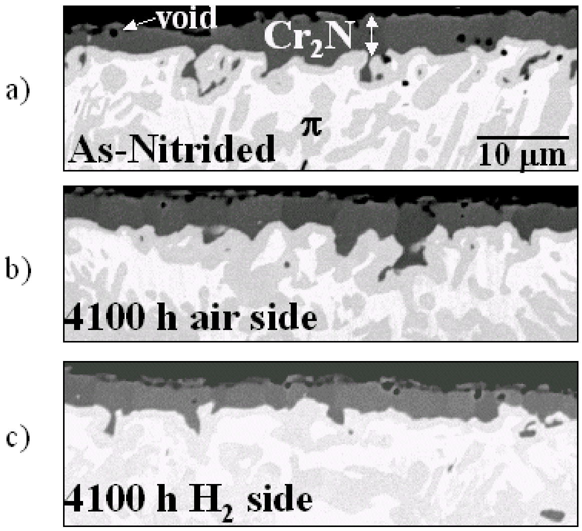

Figure 2. Back Scattered Electron Cross-Sections of Nitrided Ni-50Cr a) as-Nitrided b) 4100 h Air (cathode face) Exposure in Corrosion Test Cell, c) 4100 h H_2 (anode face) Exposure in Corrosion Test Cell

A single-cell fuel cell test was subsequently conducted using 50 cm^2 active area anode and cathode plates of nitrided Ni-50Cr with a simple serpentine flow-field groove pattern (Figure 3). The membrane electrode assembly (MEA) was Nafion® 112 with anode and cathode loadings of ~ 0.20 mg Pt/cm^2. The gas diffusion layers (backings) were uncatalyzed ELAT®. Double-sided ELAT® was used on the anode sides and single-sided on the cathodes. The cells were operated at 3 atmospheres (absolute) and at 80°C. Purified hydrogen was introduced to the cell at 0.3 standard liters per minute (SLPM) and compressed room air at 1.8 SLPM. The fuel cell was operated continuously at 0.7 V

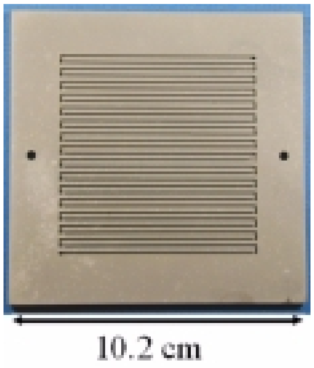

Figure 3. Nitrided Ni-50Cr Cathode Plate from Single-Cell Fuel Cell Test

.An inadvertent cutoff in the supply of hydrogen to the cell during the test resulted in membrane damage and performance degradation such that the test was halted after 500 h, and the damaged MEA was replaced. A second MEA was prepared with anode/cathode loadings of 0.23/0.37 mg Pt/cm^2 on a thicker membrane, Nafion® 1135. It was operated for 500 h, for a total of ~1,000 h of in-cell testing of the nitrided plates. Cell resistance, an indicator of membrane contamination, did not increase a discernable amount over the second 500 h (resistances were measured with the initial MEA but were untrustworthy due to the damaged MEA). The baseline interfacial resistance contributions between the nitrided plates and the adjacent gold-coated current collector plates were 5 mΩ-cm^2 at the cathode plate and 1 mΩ-cm^2 at the anode (the total-cell resistances were on the order of 130 mΩ-cm^2).

X-ray fluorescence indicated only trace levels of Ni and Cr in the MEAs after the single-cell fuel cell test, in the range of only 0.01 to 0.3 x 10^{-6} g/cm^2. This level of contamination is extremely low and consistent with the stable, inert, and protective behavior of the CrN/Cr$_2$N surface. Some stagnant liquid was observed in one of the alignment pin ports on disassembly of the cell and was subsequently found to be Cr-rich. However, little Cr or other contamination was observed in the membrane in the area surrounding this alignment pin. A local casting flaw and/or compositional inhomogeneity (e.g., inclusion) in the alloy is suspected to have led to poor nitridation at this spot, making it vulnerable to attack.

Conclusions

The results of the 4100 h corrosion test and the 1000 h single-cell fuel cell test demonstrate the potential of thermally grown CrN/Cr$_2$N surface layers on Cr-bearing alloys to:

1 prevent significant metal-ion membrane contamination,

2 maintain low contact resistance, and

3 effectively cover and protect flow-field groove features under PEM fuel cell bipolar plate operating conditions.

Future work will focus on the formation of corrosion-resistant CrN/Cr$_2$N surface layers on Ni/Fe-Cr base alloys that are comparable to conventional stainless steels in order to meet DOE bipolar plate cost goals.

References

1. K. Weisbrod, U.S. Patent 6,454,922 "Corrosion test cell for bipolar plates" September 24, 2002.

FY 2002 Publications/Presentations

1. M.P. Brady, K. Weisbrod, I. Paulauskas, R.A. Buchanan, K.L. More, H. Wang, M. Wilson, F. Garzon, L.R. Walker, "Protection of Metallic Bipolar Plates in PEM Fuel Cells", submitted for journal publication June 2003.

2. M.P. Brady, I. Paulauskas, R.A. Buchanan, K. Weisbrod, H. Wang, L.R. Walker, L.S. Miller, "Evaluation of Thermally Nitrided Metallic Bipolar Plates for PEM Fuel Cells", to be published in Proceedings of the 2nd European PEFC Forum, Lucerne, Switzerland, June 30-July 4, 2003.

3. M.P. Brady, K. Weisbrod, C. Zawodzinski, I. Paulauskas, R.A. Buchanan, and L.R. Walker, "Assessment of Thermal Nitridation to Protect Metal Bipolar Plates in Polymer Electrolyte

Membrane Fuel Cells", Electrochemical and Solid-State Letters, 5, 11 2002.

4. M.P. Brady, K. Weisbrod, C. Zawodzinski, I. Paulauskas, R.A. Buchanan, L.R. Walker, K.L. More, D.F. Wilson, and P.F. Tortorelli, "Thermal Nitridation to Protect Metal Bipolar Plates in PEM Fuel Cells", presented at the Fall 2002 Meeting of The Materials Research Society, December 2002.

5. I. Paulauskas, M.P. Brady, R.A. Buchanan, "Thermally Nitrided Alloys As Materials For Bipolar Plates In PEM Fuel Cells", poster presented at the 2002 Gordon Research Conference of Fuel Cells, Roger Williams University, RI, July 28-August 2, 2002.

Special Recognitions & Awards/Patents Issued

1. "Metallic Bipolar Plate Alloys Amenable to Inexpensive Surface Modification for Corrosion Resistance and Electrical Conductivity", M.P. Brady, J.H. Schneibel, B.A. Pint, and P.J. Maziasz, United States Patent Disclosure, April 2003.

High-Performance, Matching, PEM Fuel Cell Components and Integrated Pilot Manufacturing Processes

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Objectives

- Develop a set of high-performance, matched proton exchange membrane (PEM) fuel cell components and pilot manufacturing processes to facilitate high-volume, high-yield stack production.
- Demonstrate the matched component performance in a 1-kW fuel cell stack.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- Q. Electrode Performance

Approach

Phase 1

- Utilize the 3M-patented, nanostructured thin film catalyst support system and catalyst deposition process to easily generate new compositions and structures of (a) binary and ternary catalysts for higher cathode performance and (b) binary anode catalysts and electrode structures for higher reformate tolerance with a non-precious metal replacement for Ru.
- Develop carbon electrode backing/gas diffusion layer (EB/GDL) media optimized for performance with the catalyst system and flow field.
- Optimize the fuel cell flow field design for optimized water management and air bleed utilization with the catalyst and EB/GDL components.
- Define pilot manufacturing scale-up of the processes for fabrication of catalysts, catalyst-coated membrane (CCM) assemblies, and EB/GDL.

Phase 2

- Optimize pilot-scale manufacturing of roll-good fabricated (made by a semi-continuous process and stored on a roll) catalyst support films and catalyst deposition.

- Specify membrane electrode assembly (MEA) component parameters and conduct final pilot-scale runs to generate process statistics.
- Fabricate, test, and provide a 1-kW stack to subcontractor for evaluation using optimized flow field and matched MEAs fabricated by pilot processes.

Accomplishments

- Completed multiple pilot-scale roll-good fabrication runs and statistical evaluation of nanostructured catalyst support films with multiple lots of cathode (PtAB) and anode (PtM) catalyst depositions on the substrates.
- Completed multiple pilot-scale fabrication runs and statistical evaluation of multiple lots of roll-good fabricated CCM assemblies, using multiple lots of PEMs and catalyst roll-goods.
- Completed fuel cell testing and statistical analyses of roll-good fabricated EB/GDL materials and CCMs having matched properties for optimum performance.
- Fabricated and tested two air-cooled and one liquid-cooled stack designs (> 1 kW) with unique compression, manifolding, and cooling features for evaluating 200-cm^2 MEAs.
- Completed successful liquid-cooled stack testing of MEAs made with roll-good fabricated, nanostructured, thin film catalysts and matching components at subcontractor and 3M facilities. Obtained 1.9 kWe + 2.25 kW heat at 62% air utilization under “Vehicle Test Conditions” with ~0.34 mg Pt/cm^2/MEA total. Results meet DOE 2005 target of 0.6 g Pt/peak kW.

Future Directions

- Contract period of performance ended April 30, 2003.
- New work on high-performance, lower-cost MEAs, which utilizes the accomplishments of this contract, is being conducted under DE-FC04-02AL67621, "Advanced MEAs for Enhanced Operating Conditions."

Introduction

The MEA is the core component set of a PEM fuel cell stack. An MEA consists of five basic components: anode and cathode catalysts, ion exchange polymer membrane, and anode and cathode electrode backing/gas diffusion layers (EB/GDL). The functions of these basic components are intimately related, and their properties must be matched for optimum performance. For large-scale volume fabrication at the costs and quality targets required by transportation applications, very high yields and in-line process control of integrated processes based on cost-effective materials are required. To realize the full performance of the MEAs in a stack, the stack design must be optimized so as not to compromise the single-cell performance of the MEA. This requires understanding how to design the coolant and gas manifolds and compression control scheme and match the flow fields to the EB/GDL to obtain uniform reactant, temperature and current density distributions. This contract was directed towards demonstrating high-performance, matching PEM fuel cell components manufacturable by integrated pilot processes in a 1-kW sized stack.

Approach

The approach to the development of high-performance MEAs involved the development of components that were individually optimized and then matched for best overall performance at a particular set of operating conditions. It included the development of new anode and cathode catalysts directed at increasing performance and stability and reducing precious metal loading, using the 3M nanostructured, thin film catalyst support system and catalyst deposition process, which easily generates new compositions and structures via a dry, roll-goods process. The approach also included development of roll-goods EB/GDL media optimized for performance with the catalyst system and flow field and of a flow field design for optimized water management and air and fuel utilization. Evaluation of each component involved a variety of characterization techniques and single-cell fuel cell performance measurements under a broad range of controlled conditions. Pilot-scale, roll-goods manufacturing processes were optimized for fabrication of catalyst support films and catalyst depositions, CCM assemblies, and EB/GDL media. Process statistics were gathered in pilot-scale runs to assess the potential for high-volume manufacturing. Stack development was carried out to optimize uniformity of the stack reactant flows, compression, and temperature distributions over the MEA. Finally, performance of the matched components was demonstrated in short stacks (>1 kW), which were assembled at 3M and evaluated at the subcontractor's facilities and at 3M.

Results

In the FY 2002 Annual Progress Report for this contract (Ref. 1), results were presented for Pt binary and ternary cathode catalyst constructions that outperformed pure Pt. In particular, MEAs made with a ternary cathode designated as PtAB-2 and a Pt anode were highlighted. The single cell performance with lab-scale fabricated roll-good MEAs corresponded to the DOE 2005 target of 0.6 g/kW at 0.8 V and 0.3 g/peak kW of precious metal. During Phase 2, the nanostructured thin film catalyst support system and the PtAB catalyst deposition process were successfully scaled up on pilot line equipment, and the same fundamental performance enhancements of the ternary were maintained. A new binary anode catalyst, "PtM," having a non-precious metal replacement for Ru had shown promise in Phase 1, and its scale-up was started in Phase 2 along with testing of MEAs made with PtM/PtAB. However, it did not perform as well with the PtAB cathode catalyst as PtRu. Also, changing from the lab to the pilot-scale process affected its performance. Because optimizing the PtM construction and process would have required more time than was available on the contract, the PtRu anode was selected for scale-up. Both the PtRu and the PtAB nanostructured catalysts were successfully scaled up in a pilot production facility. Multiple lots were fabricated by roll-good processes on pilot production equipment and used in pilot scale-up experiments for the CCM assembly process. Characterization of the down-web and cross-web catalyst composition and loading verified a high level of uniformity.

The CCM process experiments, in which the anode and cathode catalyst layers were transferred from the customized nanostructured substrate to the PEM, were run on pilot-scale, roll-goods equipment using multiple lots and types of catalyst and PEM (3M fabricated) roll-goods. This included catalyst lots that had been coated on reused substrate as a way to reduce costs. Extensive characterization of the roll-good fabricated CCMs to validate properties such as precious metal loading and to investigate variability indicated that the processes had been successfully scaled up and also that the reuse of the substrate was successful. The CCMs used in the stack tests discussed below were fabricated in the final pilot-scale runs.

The EB/GDL component was developed and the processes scaled up in Phase 1, and preliminary results were reported in Ref. 1. During Phase 2, statistical analyses of the process variability for key response variables were completed, and a nested design of experiments was designed and completed for fuel cell response variables. The fuel cell response was less sensitive than the EB/GDL off-line physical property responses, which indicated that good process control for those key responses is sufficient for low variability in the EB/GDL fuel cell performance. Overall, the assessment indicated good potential for meeting anticipated process capability requirements in high-volume production.

Cost projections were made using a detailed proprietary cost model for the MEA components and roll-goods processes. Different production scenarios were evaluated beginning with the processes and facilities currently used and then calculating improvements in areas identified with significant cost reduction potential. The final scenario utilized hypothetical values of process, labor, and material costs that might be realized when a high-volume market size is reached. Under the final scenario using the detailed cost model, the MEA cost is not inconsistent with currently projected high-volume, long-term automotive pricing requirements.

The performance of the matched components was successfully demonstrated in stacks developed at 3M with consultation from the subcontractor. The stack design goal was to optimize the uniformity of the compression and the reactant and coolant flows for the MEA well enough to realize the same performance as obtained in single-cell testing. This was achieved using a 3M proprietary flow field design (discussed in Ref. 1), a unique modular compression control and gasket scheme, and computational fluid dynamic and thermal modeling designed gas and coolant flow manifolds. Bipolar plate development was not part of the scope, so gold-plated Al was used based on fabrication ease for small quantities, electrical conductivity, and corrosion resistance. Three 1.4-kW (nominal) designs (two air-cooled and one liquid-cooled) were fabricated and tested at 3M. One air-cooled design was targeted at reformate/air operation, with the other air-cooled design and the liquid-cooled design targeted for H_2/air. The liquid-cooled stack, “Beta-1,” was then fully evaluated by the subcontractor at the General Motors Fuel Cell Activities facility under various protocols designed to demonstrate different aspects of the stack and MEA characteristics, including automotive test conditions. The stack contained fourteen 200-cm^2 MEAs made with the pilot-scale roll-good processes. The nanostructured Pt/PtAB CCMs had ~0.34 mg Pt/cm^2/MEA total. Under automotive (vehicle simulation and compressor load following) test conditions, the stack achieved a mean cell voltage within 11 mV of the subcontractor’s target of 680 mV at 0.8 A/cm^2 under pressurization conditions at 80ºC and stoichiometric flow ratios of 3.0 anode and 1.6 cathode with sub-saturated anode and dry cathode reactant streams. The required anode and cathode pressure drops across the stack were demonstrated. Cell-to-cell uniformity was excellent (23 mV spread, 6 mV standard deviation @ 1 A/cm^2). In other tests, fuel and air utilization was also shown to be very good: the stability at very low stoichiometric flow ratios greatly exceeded expectations, achieving 95% hydrogen utilization and 77% air utilization at ambient pressure. The vehicle polarization test results exceeded design expectations, producing 1.9 kWe peak actual with 62% air utilization versus the 1.4 kWe with 45% air utilization expected. The stack was subsequently operated for 400 hours with no substantial change in performance. The values of 0.34 mg Pt/cm^2 and 1.9 kW represent 0.50 g Pt/peak kWe, which meets the DOE 2005 target of 0.6 g Pt/peak kW. Results from a subset of the tests conducted at the subcontractor’s facilities are shown in Figures 1-4.

Figure 1 compares the “Beta-1” stack output under ambient and pressurized constant flow conditions. The stack results match well with single-cell test results (not shown) using a 3M protocol. The up and down scans are both included, so 28 curves are superimposed for each pressure condition, illustrating the tight uniformity of the response, including hysteresis, of the 14 MEAs, which were

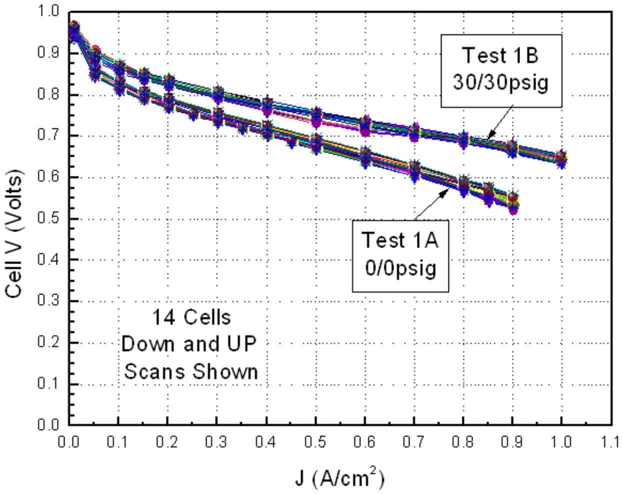

Figure 1. Comparison of ambient and pressurized operation of the 3M "Beta-1" stack at the subcontractor's facilities under a 3M test protocol for comparison with single-cell tests. The roll-good fabricated MEAs have 0.34 mg precious metal/cm^2/MEA. Test 1A: 75ºC stack, 70/70ºC dew points, 25/72 standard liters per minute (SLM) H_2/air, galvanodynamic scanning, 1 min. per point. Test 1B: 85ºC stack, 70/70ºC dew points, 30/90 SLM H_2/air, galvanodynamic scanning, 1 min./point. Both up-scan and down-scan curves are shown for the 14 MEAs in both the ambient and pressurized conditions.

taken at 1-foot intervals along the CCM and MEA roll-goods.

Figure 2 shows the "Baseline High-Pressure Polarization Curve" under the subcontractor's protocol. At 1 A/cm^2, the standard deviation from the average cell voltage among the 14 MEAs is only 6 mV.

In Figure 3, the stack response under the "Vehicle Polarization Test Conditions" is shown. The stack inlet pressures and dew points (proprietary) are varied with current density. The stack and MEAs yielded good cell-to-cell uniformity over a majority of the current density range. At 1.2 A/cm^2, the spread in voltage among the 14 cells was only 42 mV for a relatively low cathode stoichiometry of 1.6. The voltage spread appears to be largest, 49 mV, at 0.4 A/cm^2, but, excluding cells 1 and 2, it reduces to only 22 mV. At the maximum tested current density, a peak power of 1.9 kWe is produced with 2.25 kW of heat.

Figure 4 compares the stack/MEA response under Test 7 (see Figure 3) with Test 3B, the subcontractor's compressor-load following protocol.

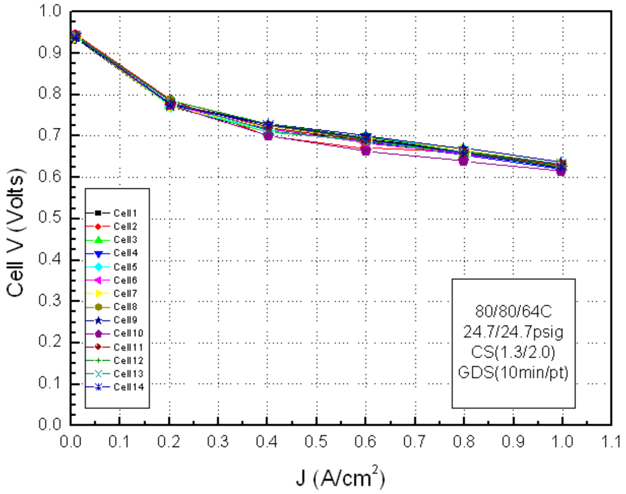

Figure 2. Test 4: "Baseline High-Pressure Polarization Curve," 80ºC stack, 80/64ºC anode/cathode dew points, 1.3/2.0 H_2/air constant stoichiometry (CS), 24.7/24.7 psig inlet pressure, galvanodynamic scanning (GDS), 10 min./point.

The pressure-load profile was the same, but the stack temperature, reactant humidification, and flow stoichiometries differed. Even though Test 3B had a higher cathode flow stoichiometry (2.0) than Test 7 (1.6), the humidification was somewhat greater than under Test 7, indicating that the MEAs and stack perform better under hotter and drier conditions.

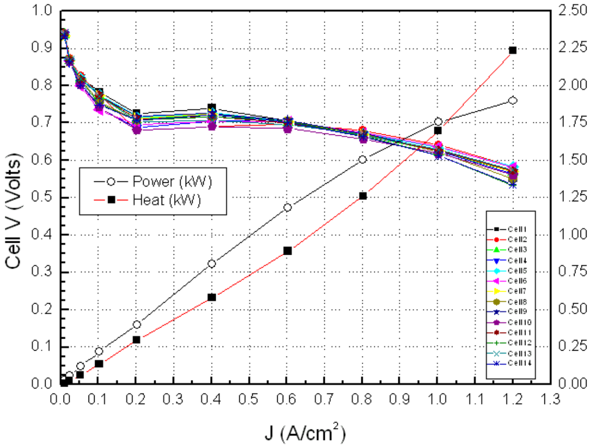

Figure 3. Test 7: "Vehicle Polarization Test Conditions," 61-84ºC stack, variable (proprietary) dew points, 3.0/1.6 H_2/air stoichiometry, 2.9-24.7 psig inlet pressure, galvanodynamic scans, 10 min./point.

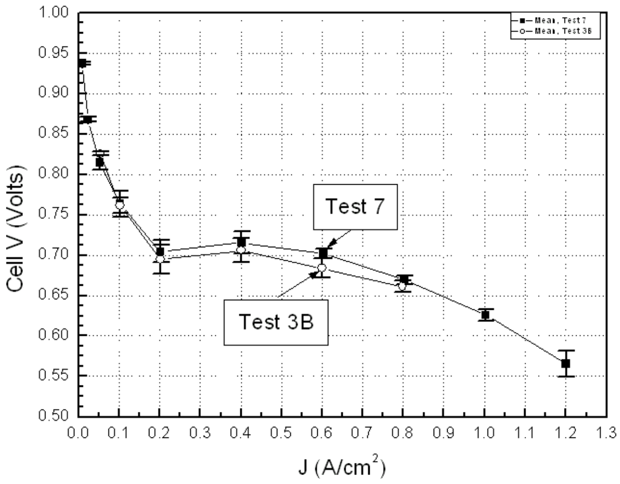

Figure 4. Comparison of the stack/MEA response under Test 7 (see Figure 3) and Test 3B, the subcontractor's "Compressor-Load Following" protocol. Even though the cathode stoichiometry for Test 3B is higher than that of Test 7, the conditions are hotter and drier for Test 7, and this gives better performance in the mid-current range.

Conclusions

The development and roll-goods fabrication of a set of high-performance, matched PEM fuel cell components was completed and successfully demonstrated in stack testing at the subcontractor's facilities. The results under H_2/air correspond to 0.50 g Pt/peak kWe, which meets the DOE 2005 target of 0.6 g Pt/peak kW. The MEA components used in the stack testing were produced by roll-good, pilot-scale processes that have the potential for meeting projected high-volume automotive requirements.

References

1. Hydrogen, Fuel Cells, and Infrastructure Technologies FY 2002 Progress Report, page 379.

High-Temperature Membranes

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Objectives

Develop new membranes and membrane electrode assemblies (MEAs) for operation at temperatures substantially in excess of 120°C.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

Simultaneously carry out R&D on:

- Physical chemistry of polymer electrolytes
- New polymeric electrolytes
- New approaches to proton transport in polymer electrolytes

Develop MEAs based on new polymer electrolytes

Accomplishments

<u>New Membranes</u>

- Synthesized new hybrid organic/inorganic membranes
- Synthesized new materials to implement strategies targeting 'water replacements'

<u>Catalyst Coated Membranes (CCMs)/Electrodes</u>

- Showed performance limitation associated with low humidity operation relying on water
- Elucidated effect of imidazole adsorption on electrode reactions

<u>Industrial and Other Collaborative Interactions</u>

- Evolved team model for project

- Completed Roadmap for High Temperature Polymer Membranes
- High-Temperature Polymer Membrane Working Group continues to expand with increased industrial interaction

Future Directions

Computational Studies

- Perform more extensive work on novel systems designed to identify approaches to maintain water content at 120oC

Membrane Development

- Provide new materials from each partner
- Implement battery of methods for screening membranes; new electrolytes to be tested in 4-month cycle starting in fall

CCMs/Electrodes

- Start developing MEAs from new materials (CWRU)
- Expand initial tests on oxygen reduction reaction (ORR) at high temperature/low humidity and on adsorption of imidazole, with intent to provide solutions
- Develop understanding of interactions at buried interfaces within electrodes
- Provide means for scale-up of polymers, film-making and CCM production to modest scale

Industry and Other Collaborations

- Next round of new start funding: increased emphasis on 120oC solutions
- Begin to distribute 'lessons learned' info via website

Introduction

The need to operate at temperatures exceeding 100°C presents difficult new challenges for the electrolytes used in fuel cells. This difficulty stems from the decrease in water content of the polymer electrolytes in the desired temperature range. There is a need for detailed understanding of the impact of poor or zero hydration on membrane and electrode processes in the fuel cell. Water plays a key facilitating role in proton transport, and lower water content thus leads to lower conductivity. Lack of water also has important negative consequences for electrode behavior.

Approach

At this point, we do not know which of several approaches is most promising. Thus, our membrane development efforts include: (1) a full-fledged effort to explore approaches involving polymer synthesis and development, as well as implementation of new "carrier" media to replace the function of water in Nafion; and (2) a study of proton transfer dynamics to inform the synthetic efforts. We are using theory to explore specific possibilities for new acid group types or for acid-base interactions that could lead to progress in proton transfer media and to assess the possibility of holding useful water in electrolytes at high temperature. We are increasing our understanding of the energetics of proton transfer to inform synthetic efforts. We are working to incorporate new polymers in fuel cells by developing catalyst-coated membranes from new materials. Finally, we also have extended our range of polymer electrolyte development efforts by including several different universities and significant industrial input. Our goal is to engage the polymer community to the maximum extent possible, harvesting the best new ideas for development.

Results

Physical Chemistry. We are extending our computational studies to provide insight into the following processes: (i) tailoring bases to mimic water using substituted imidazoles or other proton carriers; and (ii) continuous water transport pathways at low relative humidity. This work augments experimental studies on water uptake by polymers and additives of various types.

New Membranes. Many new materials are presently being prepared and tested. These are: (i) polymers and inorganic materials with controlled pore size modified with acid groups lining pores or by inclusion of proton conducting subunits; (ii) polymer matrices filled with surface-modified inorganic particles; (iii) polymeric systems with intrinsically stronger acid groups; and (iv) polymer systems swollen or imbibed with tailored proton acceptors including imidazole and ionic liquids. These are useful both intrinsically and as test or model systems. Summarized below are approaches being explored by some of the partners in the High Temperature Membrane project:

CWRU: inorganic/organic hybrid systems; new polymers; strong acid groups; electrode studies at high temperature; making MEAs; polymer scale-up and film processing; computational studies; and fuel cell testing (working on both temperature ranges).

University of Texas/Dallas: inorganic scaffolds with added conducting polymers (primarily high temperature range)

Arizona State University: molten salts (primarily high temperature range)

NASA Jet Propulsion Laboratory: proton conducting salts (primarily high temperature range)

Virginia Commonwealth University: strong acid groups; advanced MEA processing method (low temperature range)

CCMs. In work this year, we focused on basic studies of the problems that arise in the high temperature regime. Specifically, we used impedance spectroscopy on fuel cells operating under conditions of subsaturation. We found additional features in the spectrum under these conditions. This is illustrated in Figure 1. We are presently working to understand the precise mechanistic reasons for existence of these features.

Several approaches to high temperature conduction involve the use of imidazole or modified imidazoles. In Figure 2, a cyclic voltammogram shows the impact of imidazole on basic electrochemistry at Pt. It appears that the oxide

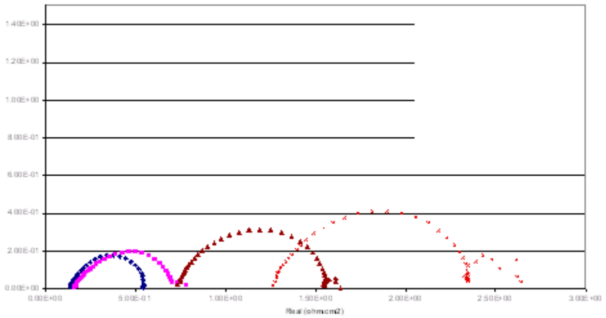

Figure 1. Impedance Spectrum of Fuel Cell Under Sub-Saturation Conditions (<u>Operating conditions:</u> Current density: 0.1 A/cm^2; Pressure: ambient; Fuel: H_2; Oxidant: oxygen; Gas utilization: 10%; Cell temperature: 70°C to 100°C; Dew point: 70°C)

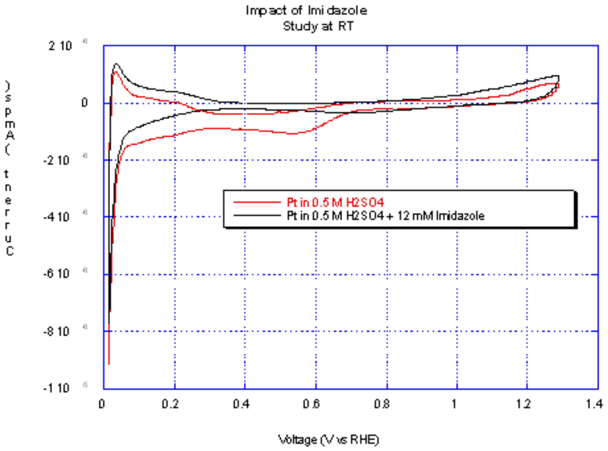

Figure 2. Cyclic Voltammogram of Pt Electrode Exposed to Imidazole

formation region is strongly impacted by the presence of imidazole in solution.

Industrial and Other Collaborative Interactions. We are engaged in a series of collaborative efforts with industry, national laboratories, and universities to facilitate efforts to achieve the targets for high-temperature polymer membranes. We have organized the High-Temperature Polymer Membrane Working Group, which has met four times to date. Bi-annual meetings allow us to assess progress and to communicate issues and needs to the high-temperature membrane community.

Conclusions

The development of new polymer electrolytes for operation at elevated temperature is under way. However, this is a long-term project. Replacement of water is the most difficult problem, but adequate stability and cathode activity are not trivial objectives to achieve. We have developed several different approaches to address this problem. Fundamental work is guiding the process via useful insights into the conduction process to guide synthetic efforts. The first polymers geared for temperatures in excess of 100°C are emerging, and testing is showing that, although promising, there are definite shortcomings. Work on making viable new materials continues.

Electrodes for Polymer Electrolyte Membrane Operation on Hydrogen/Air and Reformate/Air

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Objectives

- Improve tolerance to carbon monoxide (CO) and study the effect of other fuel and air impurities.
- Improve the efficiency of the fuel cell electrodes while lowering the dependence on Pt loadings.
- Improve overall polymer electrolyte membrane (PEM) fuel cell operating efficiency.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- Q. Electrode Performance

Approach

- Investigate the use of reconfigured anodes to improve fuel cell performance in the presence of trace levels of CO impurities.
- Evaluate new anode catalysts for CO tolerance.
- Investigate porosity and fuel cell performance as functions of the ionomer content in the catalyst layer.
- Evaluate new cathode catalyst materials for higher operating efficiencies at lower precious metal loadings.
- Investigate the effect of potential ambient air impurities on cathode performance.

Accomplishments

- Demonstrated increased tolerance to 500 ppm CO/reformate using the reconfigured anode.
- Demonstrated 1000 hrs of operation of the 1 wt% Pt-10 wt% Ru anode catalyst running on H_2 /air with 50 ppm CO and 4% air bleed.
- Demonstrated the performance degradation of a Pt-Cr cathode catalyst after 500 hours of operation.
- Demonstrated how the catalyst layer porosity and fuel cell performance correlate with catalyst layer Nafion content.
- Established the negative effects of SO_2 and NO_2 on cathode performance.

Future Directions

- Investigate alternative catalyst materials for use in reconfigured anodes.
- Continue the evaluation of new potential CO tolerant catalysts.
- Screen new potential cathode catalyst materials, particularly with low Pt content.
- Continue to develop improved membrane electrode assembly (MEA) fabrication protocols.
- Investigate methods to mitigate the effects of SO_2 and NO_2 on fuel cell performance.
- Investigate the effect of other potential ambient air impurities on fuel cell performance.
- Investigate strategies for recovering the performance of fuel cells whose catalysts have been poisoned by H_2S and SO_2.

Introduction

The reforming of hydrocarbon fuels is one of the leading processes under consideration for producing hydrogen to power PEM fuel cells. However, the hydrogen stream generated by the reforming process can contain volatile chemical compounds that significantly diminish fuel cell performance. Two approaches to solving this problem are to improve the efficiency of the reformation process to lower the levels of harmful impurities, or to modify the fuel cell itself to be more tolerant toward those compounds. This study has taken the latter approach, where ways were investigated to improve the anode performance in the presence of anticipated reformate impurities.

Fuel cell operation depends not only on hydrogen oxidation at the anode but also on oxygen reduction at the cathode. The oxygen reduction reaction plays a very significant role in limiting the operating efficiency of the fuel cell and is very dependent on high precious metal loadings in the catalyst layer. Improving the efficiency of the oxygen reduction reaction while lowering the precious metal loading is critical to commercialization of fuel cell technology for transportation applications. Also, recent awareness that impurities in the air stream can affect fuel cell performance has led to a more detailed investigation of some potentially harmful compounds commonly found in air.

Approach

The impurity in the reformate stream expected to have the largest adverse affect on fuel cell performance is carbon monoxide (CO). This gas is more strongly adsorbed on the surface of the catalyst than hydrogen, effectively blocking the sites where hydrogen oxidation would normally occur. One method to prevent this from happening is to remove the CO by oxidizing it to carbon dioxide, which does not adsorb on the catalyst, before it can reach and react with the anode surface. This can be accomplished by using the reconfigured anode developed by Los Alamos National Laboratory (LANL). The reconfigured anode has an outer, non-precious metal catalyst layer added to the standard MEA. Bleeding a low level of oxygen into the fuel stream results in preferential oxidation of CO at this outer layer. A second approach to solving the CO problem is to use an anode catalyst that is intrinsically more CO tolerant. For example, platinum/ruthenium alloys have been shown to be more CO tolerant than platinum alone and have the added advantage of containing a lower percentage of the expensive platinum metal component. Many new potential catalysts are submitted to LANL on a regular basis from both commercial and non-commercial sources. These materials are fabricated into MEAs using an established protocol, and then tested in fuel cells under standard operating conditions.

A third approach to identifying improved fuel cell anodes is to develop a better understanding of the kinetics and mechanisms associated with reactions of suspected impurities in the reformate stream with various catalyst materials. This information can potentially lead to alternative mitigation schemes. The mechanism for CO poisoning of platinum-based anode catalysts is fairly well understood; for other potential poisons and catalyst combinations, that may not necessarily be the case. During this past review period, we have focused on catalyst interactions with hydrogen sulfide and ammonia, two very likely by-products in reformed fuels initially containing sulfur and nitrogen compounds.

A similar list of activities was undertaken to improve fuel cell cathode performance and can be summarized in the following outline:

- Develop new MEA fabrication methods to improve catalyst utilization.
- Work with catalyst suppliers to develop/test new catalyst formulations.
- Study the effect of catalyst layer structure on performance.
- Study the effects of suspected impurities present in air (sulfur dioxide, nitrogen oxides, particulates) on cathode performance.

Results

Anode catalysts consisting of Pt-Ru alloys have been shown to be more tolerant to CO in the fuel stream than platinum alone. However, the commercially available materials are still expensive due to their high Pt contents. R. Adzic and co-workers from Brookhaven National Laboratory submitted a new catalyst for evaluation, with much lower platinum loading. This material contained only 1% platinum and 10% ruthenium, on a carbon support. A 1000-hour performance test was carried out using this catalyst in a fuel cell anode with a loading of 17 µg Pt/cm^2, approximately 1/10 that of a normal loading. The results are shown in Figure 1. The voltage losses after 1000 hours of operation at fixed current were only 40 mV when the cell was operated on clean H_2, and 60 mV when operated with H_2 containing 50 ppm CO and 4% air. This is an extremely promising result that could have a major impact on lowering fuel cell costs and bringing the technology closer to commercialization.

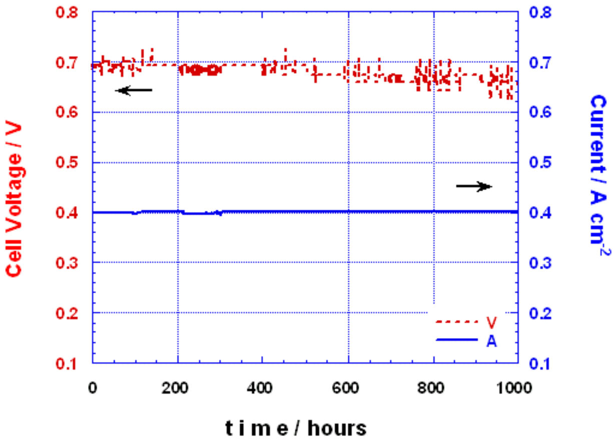

Figure 1. Low Pt Content Anode Durability Test at Constant Current

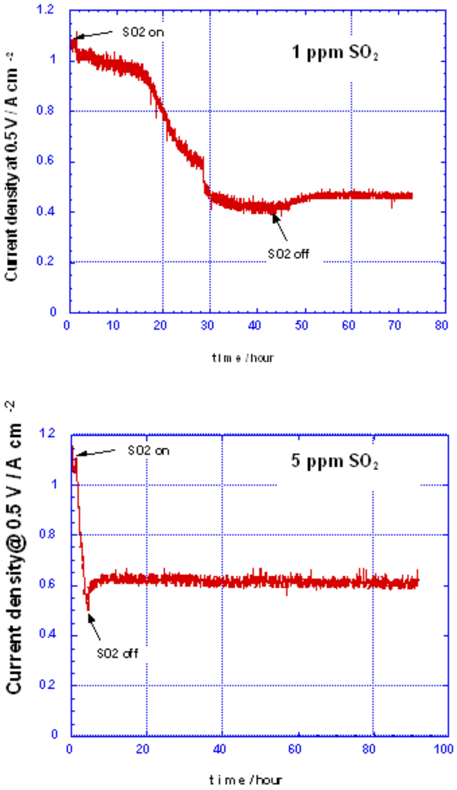

Figure 2. Effect of Sulfur Dioxide on Fuel Cell Performance

On the cathode side, the effects of two common air impurities were investigated: sulfur dioxide (SO_2) and nitrogen dioxide (NO_2). Figure 2 shows the performances of fuel cells whose cathodes are exposed to 1 ppm and 5 ppm of SO_2, respectively. Both levels of impurity degraded the fuel cell performance, and, as expected, the effect with the higher concentration was faster and more acute. In both cases, the cathode performance degradations were irreversible; the fuel cell did not recover after the SO_2 was shut off and it was allowed to operate on clean air for many hours. Further characterization by cyclic voltammetric measurements showed the SO_2 (or a related species) was strongly adsorbed on the Pt catalyst surface.

Nitrogen oxide has a similar negative effect on cathode performance, as shown in Figure 3. Performance degradation was less severe than with sulfur dioxide, but still significant. The degradation upon exposure to 5 ppm of NO_2 for about 15 hours was reversible as the cell recovered its original performance when operated again with clean air. Long-term exposure to 0.4 ppm NO_2 produced a slower negative effect on fuel cell performance that did not recover on operation with clean air. This data is still preliminary, and there is still no conclusive evidence to suggest the mechanism by which this impurity degrades performance. However, it is clear that the quality of the air stream entering the fuel cell is as important as the quality of the fuel stream and must be of reasonably high purity to guarantee performance optimization and durability.

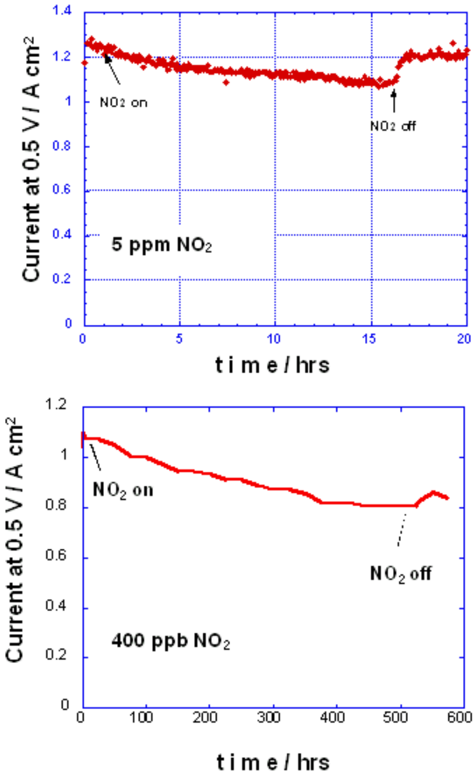

Figure 3. Effect of Nitrogen Dioxide on Fuel Cell Performance

Further characterization of the catalyst layers of the MEA was also conducted with an aim toward optimizing fuel cell performance. For example, a measure of the porosity of the catalyst layer formed from recast Nafion showed that maximum porosity corresponded with optimum performance at a Nafion content of approximately 30%. It was also discovered that varying the fabrication materials and method could alter the surface morphology of the catalyst layer. Under certain conditions, a thin ionomer film formed on the outer surface of the catalyst layer. This film inhibited transport of reactant gases to the active catalyst sites and the removal of water formed at the cathode. The decrease in mass transport resulted in a drop in performance at high current densities.

Conclusions

- We have shown that a level of 50 ppm CO in the fuel stream could be tolerated with a Pt/Ru catalyst at relatively low loading (17 µg Pt/cm^2) when combined with air bleed. This catalyst was also shown to be quite stable under normal operating conditions, exhibiting a minimal drop in performance over 1000 hours.
- Some common air impurities, SO_2 and NO_2, were also found to have a deleterious effect on fuel cell performance when admitted to the cathode air stream. These compounds will have to be removed prior to use in a fuel cell system to ensure continued performance and durability.
- The preparation method and materials affect the morphology of the catalyst layer in an MEA. The optimal performance observed at a Nafion loading of approximately 30% in the MEA correlates with a maximum in catalyst layer porosity. Under certain preparation conditions, a thin skin that inhibits molecular transport forms on the outer catalyst layer. This skin affects the fuel cell performance in the high current region of the operating curve.

FY 2003 Presentations

1. K. Sasaki, Y. Mo, J. X. Wang, F. A. Uribe and R. R. Adzic. "Pt Submonolayer Electrocatalysts for H_2 Oxidation and O_2 Reduction". 203rd Meeting of The Electrochemical Society Meeting, Paris, France. April 2003. Abstr. 2679.

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New Electrocatalysts for Fuel Cells

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Objectives

- Conduct research on the kinetics and mechanism of electrode reactions in low temperature fuel cells.
- Develop new electrocatalysts using a materials-by-design approach.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- Q. Electrode Performance

Approach

- Study the kinetics of fuel cell electrode reactions on well-characterized model electrodes and high surface area fuel cell electrocatalysts using modern electroanalytical methods.
- Study the mechanisms of the reactions using state-of-the art in-situ spectroscopes.
- Use ultrahigh vacuum (UHV) methods of surface preparation and surface analyses to form tailored surfaces.
- Synthesize nanoclusters to have the tailored surface.
- Characterize the microstructure of the nanoclusters by high-resolution electron microscopy.
- Transfer technology to catalyst developers/vendors.

Accomplishments

- Proof-of-principle experiments demonstrated that a Au-Pd alloy with <50 wt. % Pd can replace Pt as the hydrogen electrode catalyst without any loss in performance.
- Proof-of-principle experiments demonstrated that "Pt skin" structures with a non-precious metal core can be stable under proton exchange membrane fuel cell (PEMFC) air cathode operating conditions.

Future Directions

Cathode side:

- Create "skin" nanostructures of Pt on non-noble substrates and determine activity and stability as a novel low-Pt air cathode electrocatalyst. Select the most promising substrate for synthesis as high surface area catalyst.
- Develop and optimize a new class of non-Pt model catalysts. Synthesize and test new non-Pt high surface area catalysts at fuel cell conditions.

Anode side:

- Synthesize and characterize Pd-Au bimetallic nanoparticles and conduct preliminary testing as anodes in PEMFC hydrogen-air cells.
- Determine CO-tolerance of tailored electrodes consisting of thin films (1-10 monolayers) of Pd on the close-packed single crystal surfaces of Ta, Re, and W.

Introduction

It is known from the theory of surface segregation in bimetallic alloys that in certain systems, preferential surface enrichment in one element is so strong that it leads to a "skin" structure, i.e. the outermost layer is a "skin" of one element. Theoretically, for nanoparticles, such a segregating alloy system could form particles having a "grape" microstructure, a skin of one element over a core of the other. In principle, one could use this thermodynamic property to replace the "buried" atoms in Pt nanoparticles with a non-precious metal, e.g. Fe or Co, resulting in 100% Pt dispersion (all Pt atoms are surface atoms) without the need to create extremely small particles, e.g. <2 nm. For example, if a standard pure Pt catalyst consists of particles having on average a dispersion of 20%, replacement of the buried atoms in those particles with a base metal would enable the Pt loading to be reduced by a factor of 5, all other factors being the same. This is the basic strategy we are currently pursuing to reduce Pt loading in PEMFC cathodes.

Approach

Pt_3Ni and Pt_3Co are classical examples of alloys of Pt having a skin surface structure, a pure Pt skin. In this case, enrichment occurs by interchange of Pt and Co atoms between the first two atomic layers, the subsequent layers having the bulk composition (75% Pt). The thermodynamic driving force in this case is for the larger atom to be at the surface, since in face-centered cubic metals the surface is generally relaxed outward and the second layer contracted. The Pt_3Ni and Pt_3Co systems do not represent cases of the extreme segregation we need for replacing buried Pt atoms, but they do serve as a useful test case for the concept of a skin structure, and there appears to be a beneficial electronic effect for the Pt skin. Importantly, the Pt skin structure in $Pt_3Co(Ni)$ was stable when used as an oxygen reduction electrode under PEMFC conditions. The current approach is to extend the concept to Pt-refractory metal alloys, such as Pt-Re, Pt-W, or Pt-Ta. In these systems, the segregation is more extreme, driven by both the strain energy (Re and W are smaller atoms than Pt) and the surface tension; hence, the skin structure can be achieved with a lower bulk Pt concentration, replacing more buried Pt atoms with a non-Pt atom.

Results — Model Cathode Catalysts

Pt_3Re solid electrodes were prepared using conventional metallurgy and pre-treated in a surface analytical UHV chamber equipped with various instruments for surface preparation and analysis. As with $Pt_3Co(Ni)$, for each alloy, either a pure Pt skin or a 75 at. % Pt surface could be prepared and tested as an oxygen reduction catalyst. The resulting activity for oxygen reduction as a function of composition is shown in Figure 1. The Pt skin structure on all three alloys is more active than the pure Pt reference surface, suggesting there is an

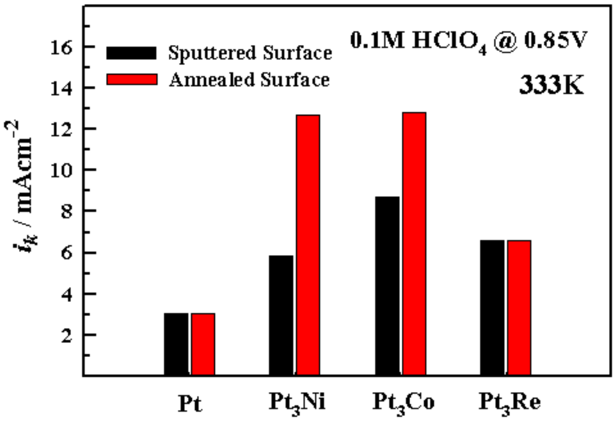

Figure 1. Steady-state current densities (per unit geometric area) at 0.85 V (vs. reversible hydrogen electrode—1 bar H_2, 333 K) for six different alloy electrodes vs. pure Pt: Pt skin on Pt_3Ni, Pt_3Co, and Pt_3Re (the annealed surfaces); and the 75% Pt surfaces on Pt_3Ni and Pt_3Co (the sputtered surfaces)

electronic effect that is generally beneficial for oxygen reduction kinetics. Importantly, the results represented in Figure 1 were obtained under the extreme conditions of use as an oxygen reduction electrode, e.g. continuous cycling between 0.1 – 1.0 V under 1 bar O_2 in acid electrolyte at 60°C produced no change in the cyclic voltammetry curves for the surfaces.

Epitaxial thin films of Pd on Pt(111) and Re(0001) single crystals were deposited either in UHV by a vapor deposition method or in-situ by purely electrochemical methods. The morphology was studied by a combination of ex-situ UHV surface analytical tools (low-energy electron diffraction, low-energy ion scattering—LEIS) and in-situ soft x-ray spectroscopy and Fourier transform infrared spectroscopy. Photoelectron spectroscopy (PES) results depicted in Figure 2a show that in the surface electronic density of states of the valence band, the position of the d-band center relative to the Fermi level is slightly lower for the pseudomorphic monolayer of Pd on Pt(111) than on bare Pt(111). The monolayer thickness was determined by LEIS (Figure 2b). Interestingly, such a small change in the surface electronic structure has a dramatic effect on the kinetics of the oxygen reduction reaction (ORR). In 0.1 M KOH, the general form of current vs. Θ_{Pd} relationship for the ORR has a volcano shape (Figure 2c), with the maximum catalytic activity exhibited by a surface modified with 1 monolayer (ML) of Pd. When the Pd deposit exceeds 1 ML, the catalytic activity is decreased linearly, with the Pd multilayer less active than unmodified Pt(111). This is strikingly similar to the “volcano relation” we reported here last year for the hydrogen oxidation reaction (HOR) on the same surfaces. For either the ORR or the HOR, there is no clear explanation for the volcano relation. On the side where $\Theta_{Pd} > 1$, the higher activity of the Pd monolayer versus the multilayer cannot be attributed to the effect of strain on the reactivity of metal surfaces proposed by Norskov and co-workers (Phys. Rev. Lett. 81(1998) 2819), since the strain is too small (+0.65% increase in the interatomic spacing). On the side where $\Theta_{Pd} < 1$, the increase in activity from the addition of an intrinsically less active metal is surprising and unexplained.

However, for the Pd film deposited on Re(0001), we were able to find a clear and compelling

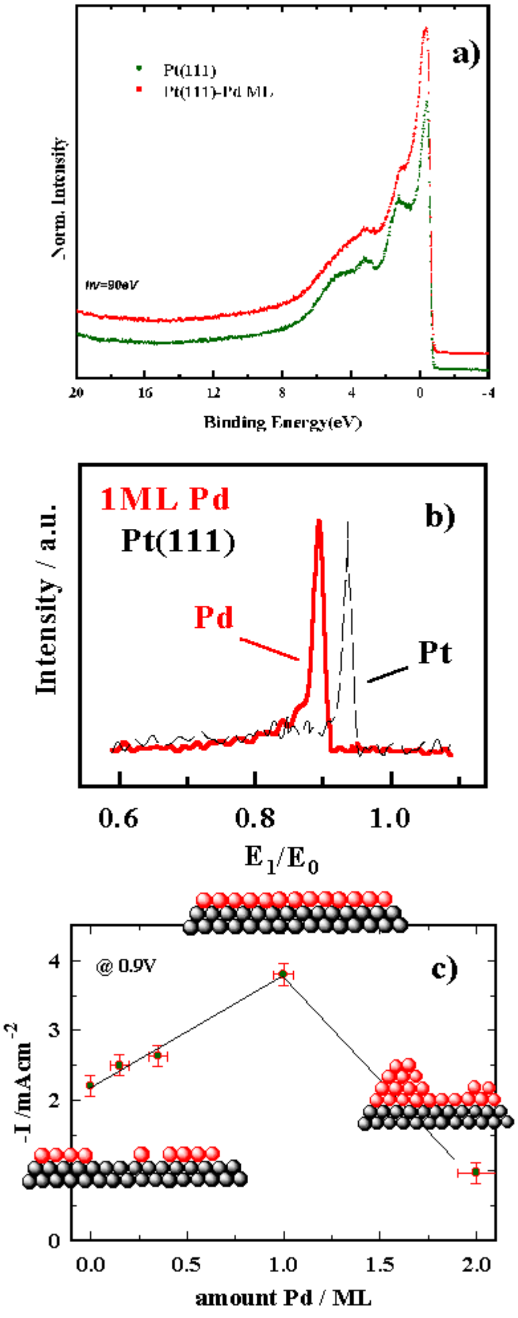

Figure 2. (a.) High-resolution UV (hυ = 90 eV) photoelectron spectra in the valence band region for a Pd monolayer film on Pt(111) and the clean Pt(111) surface; (b.) LEIS spectra for the same surfaces showing the Pd layer is one atomic layer thick; (c.) Kinetics of ORR as a function of Pd coverage of Pt(111)

correlation between the electronic interaction of the Pd overlayer with the Re substrate and the resultant catalytic properties. The strong electronic interaction causes a significant narrowing of the d-band for the *surface* metal atoms (Figure 3a difference curve) with two relatively sharp peaks strikingly similar to the d-band of Ag(111). The d-band center, as defined by Norskov, is located ca. 1 eV below that of a Pd multilayer and/or that of the Pd deposited on Pt(111).

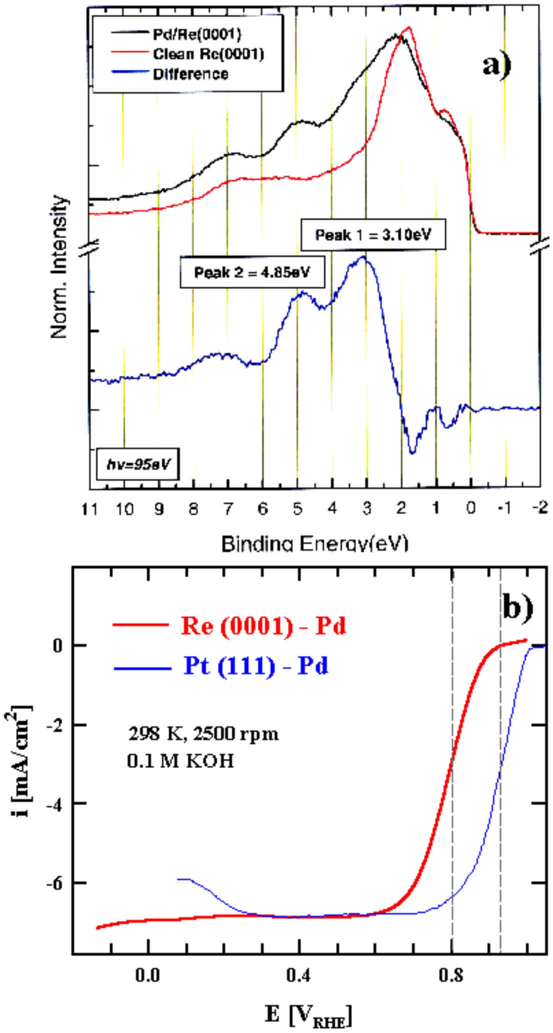

Figure 3. (a.) High-resolution UV (hυ = 90 eV) photoelectron spectra in the valence band region for a Pd monolayer film on Re(0001) surface and the clean Re(0001) surface; (b.) Comparison of the polarization curves for ORR on the two different Pd monolayer films showing the dramatic effect of the electronic interaction with the substrate on the electrocatalytic properties of the Pd film

First principles density functional theory calculations by Norskov and co-workers for Pd/Re(0001) (Phys. Rev. B 60 (1999) 6146) predicted a shift of 0.72 eV due to filling of the d-band by electrons from the Re substrate. This d-band filling, in turn, has the expected effect on oxygen reduction kinetics, lowering chemisorption energy for O_{2-} and thus the kinetics of the ORR, as shown by the kinetic results in Figure 3b. While the results with the model Pd/Re(0001) system are not of practical interest, the clear correlation to electronic properties of the surface, which can be accurately calculated for nearly any surface one can conjure up, is extremely significant and encouraging.

Conclusions

Proof-of-principle experiments indicate that synthesis of Pt as a "skin" on bimetallic nanoparticles could enable Pt loadings in the PEMFC air cathode to be lowered by as much as a factor of 5 from present (optimized) levels, e.g. from 1 g per kW to 0.2 g per kW. Comparable experiments with Pd thin films indicate an even greater reduction in Pt group metal (PGM) loading is possible for the hydrogen electrode, comparable to the PGM content of the catalytic converter in current typical internal combustion engine vehicles.

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Low-Platinum Catalysts for Oxygen Reduction at Proton Exchange Membrane Fuel Cell Cathodes

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Objectives

- Decrease the platinum content of the oxygen reduction catalysts in fuel cell cathodes to meet the DOE 2010 precious-metal-loading goals of 0.2 g/rated kW and electrode costs of $5/kW.
- Achieve catalyst loadings of 0.02 mg Pt/cm^2 and stability greater than 5000 hours.
- Optimize catalyst performance for low overpotentials.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance

Approach

- Disperse platinum on selected hydrous-oxide and hydrous-phosphate supports to enhance the proton transport to and catalytic activity of the platinum sites.
- Evaluate the electrochemical performance of the low-platinum catalysts in standardized half-cell and fuel-cell measurements.
- Perform stability studies of the catalysts in aggressive chemical solutions, in the presence of gaseous poisons, and in operating fuel cells.
- Identify the structure-property relationships of the active materials by studying nanoscale features with various characterization tools, including pair density function analysis of X-ray diffraction.
- Collaborate with industry and university contacts for independent evaluation of the catalysts.

Accomplishments

- Identified stable platinum/hydrous iron phosphate catalysts that have approximately 10× less platinum than the platinum/Vulcan carbon catalysts.
- Observed lack of adsorption of carbon monoxide on Pt-FePO$_x$ catalysts in half-cell measurements.

- Developed new, stable platinum/hydrous tin-oxide catalysts that exhibit excellent electrochemical performance at 10× lower platinum loadings compared to a standard platinum/Vulcan carbon catalyst.
- Improved electrochemical testing methods (half cell and fuel cell) by internal developments and collaborations with industry.
- Operated fuel cells having cathode catalysts of either platinum iron phosphate or platinum tin oxide.
- Characterized nanoscale structure and platinum oxidation state of active phosphate and oxide catalysts.

Future Directions

- Continue to identify optimum platinum loadings of catalysts for maximum performance.
- Develop methods to make high surface-area, nanoscale particles of the phosphate and oxide catalysts.
- Test tolerance of the catalysts to poisons such as carbon monoxide and sulfur dioxide in the air streams of proton exchange membrane fuel cells (PEMFCs).
- Improve methods for the preparation of fuel cell cathodes having the new oxide and phosphate catalysts via research at the Naval Research Laboratory (NRL) and collaboration with industry.
- Test new catalysts in PEMFCs at NRL and with collaborators, and evaluate long-term stability.

Introduction

The cost of the fuel cells and imports of noble metals can be drastically reduced by using little or no Pt in fuel cell electrodes, thereby improving the commercialization potential of fuel cells. Researchers recognized years ago that the Pt content of PEMFC electrodes could be reduced by dispersing nanoscale Pt particles on a porous, electronically conductive media (Vulcan carbon) and adding a proton conducting media (a perfluorosulfonic membrane, Nafion®)(1). When surrounded by Vulcan carbon and Nafion, the Pt serves more effectively as an electrocatalyst for hydrogen oxidation and oxygen reduction because there are ample transport paths for protons and electrons. Whereas the catalytic activity of the Pt is critical, the electrode reactions are mediated by the rate of the transport of the gases, protons, electrons and water to and from the Pt surfaces.

We are investigating three types of catalyst that may be able to serve as low-cost, stable electrodes in fuel cells: Pt-$FePO_x$, Pt-$NbPO_x$, and Pt-SnO_x. Selected hydrous phosphate and oxides can serve as catalytic supports for Pt because of their innate activity and their microporous or open-framework structures that enhance proton conduction (2). Hydrous iron phosphates are known as corrosion barriers, paint additives and friction coatings; anhydrous phosphate-based catalysts can be used for direct conversion of methane into oxygenates and oxidative dehydrogenation (3); and lithiated $FePO_4$ is also being tested as a positive electrode in Li-ion batteries (4). Anhydrous Pt-SnO_x materials have been previously investigated for use in PEMFC anodes by other researchers (5), but proved to be unstable under reducing conditions.

Approach

Hydrous phosphates and oxide catalysts are made in aqueous solutions from commercially available chemicals, filtered, air dried, and then heated from 150 to 200°C. By heating below 200°C, the materials retain >0.2 mole % water in their structure. The powdered materials are mixed with 50 to 80 weight % Vulcan carbon to improve their electronic conductivity and for fabrication into electrodes.

The Pt-doped phosphate and oxide materials are evaluated for their performance in PEMFCs using a modified recipe for a rotating disk electrode (RDE) for platinum electrocatalysts (6). They are also formed into membrane electrode assemblies for testing in PEMFCs using the procedures developed and optimized by Los Alamos National Laboratory (7). The stability of the catalysts is evaluated by heating the powdered catalysts (without carbon) in 1.0 M sulfuric acid at 90°C for 1 to 12 h and then testing the electrochemical performance of the recovered powders. A key criterion is that the acid has no evidence of metal dissolution.

The physical properties of the catalysts are characterized using a variety of approaches, including surface area measurements, thermal analysis, transmission electron microscopy, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy. The materials are generally amorphous to conventional X-ray diffraction, so their structure is characterized by the pair-density-function analysis of high-energy X-ray diffraction patterns. The pair-density-function analysis has been particularly useful for this group of catalysts because it is able to resolve the local and medium-range structure of the materials from 0.2 to 1.5 nm, or the size region that has the greatest impact on the ensuing catalytic results.

Results

Nanoscale Pt-$FePO_x$ particles dispersed on Vulcan carbon have excellent electrocatalytic activity for oxygen reduction, as shown in the cyclic voltammetry plot in Figure 1. The activity is exemplified by the precipitous drop in the activity between 1.0 and 0.7 V vs. a real hydrogen electrode (RHE), giving a half-wave potential of 0.91 V, as shown in the Tafel plot in Figure 2. By comparison, a standard 20% Pt/Vulcan carbon catalyst has a half-wave potential of 0.89 V. The active Pt-$FePO_x$ catalysts have ~0.3 nm micropores, and the Pt is dispersed throughout the phosphate tetrahedra and is lodged in interstitial sites throughout the structure, creating disorder and opening micropores. X-ray photoelectron and absorption spectroscopies indicate that the Pt is oxidized, most likely in a 2+ or 4+ state. An advantage of Pt^{x+} catalyst sites is that they are poisoned less easily than Pt-metal sites. In fact, Pt^{2+}/Pt^{4+} is not poisoned by sulfur, but rather catalytically oxidizes it to benign sulfate species (8). Because the Pt is an oxidized form in these phosphate catalysts, they appear to be unpoisoned by carbon monoxide. Typically, carbon monoxide adsorbs on the surface of platinum and blocks it from further catalysis, but these phosphate catalysts show no evidence of carbon monoxide adsorption and/or poisoning when tested in a half cell. These Pt-$FePO_x$ materials have been successfully fabricated into membrane electrode assemblies and tested in a PEMFC at NRL. The ultimate test of these materials' viability will be their long-term performance in a PEMFC, as trace iron will degrade Nafion (9).

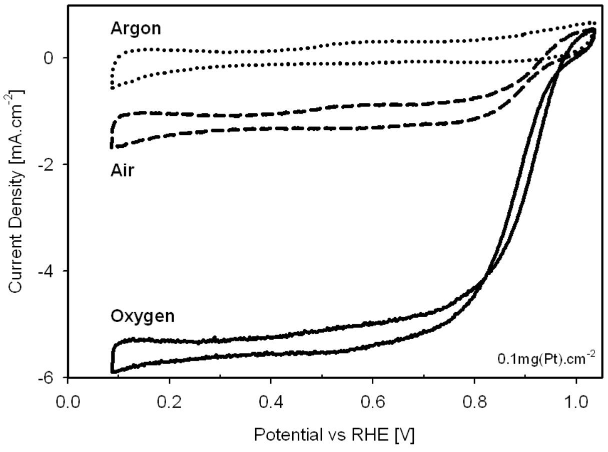

Figure 1. Cyclic voltammetry of a rotating disk electrode of 10% Pt-$FePO_x$ mixed with Vulcan carbon under Ar, air and oxygen. The RDE is prepared using the method in reference 7. The data shown is in 0.1 M $HClO_4$ at 60°C at a rotation rate of 1600 rpm and at a scan rate of 5 mV/s using a Pd/H reference electrode that is corrected to RHE. The Pt loading of the RDE is approximately 0.1 mg Pt/cm^2.

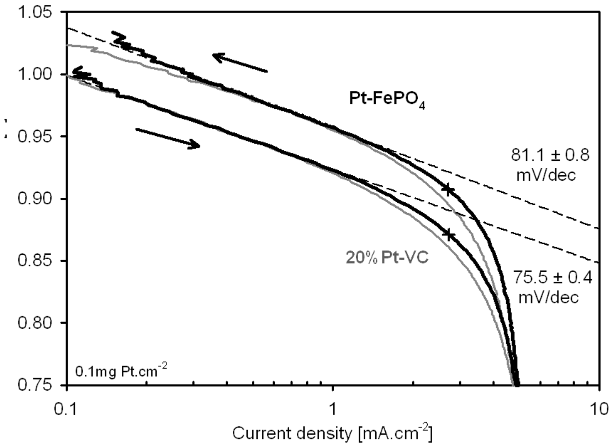

Figure 2. Tafel plots of Pt-$FePO_x$ on Vulcan carbon vs. a 20% Pt/Vulcan carbon standard as calculated from cyclic voltammetry experiments carried out using the conditions described in the caption for Figure 1. The Pt loading is 0.1 mg Pt/cm^2 in both RDEs. Crosses indicate the half-wave potentials of the catalysts.

The Pt-$NbPO_x$ materials are attractive because of their high stability in acid, and they perform well for oxygen reduction when doped with Pt. However, the materials have relatively low open circuit potentials (OCPs) that are 0.8 V vs. RHE, compared to the expected 1.0 V for Pt/Vulcan carbon. These low OCPs are a detriment to PEMFCs, as they cut down on the cell voltage and therefore the power. Because of this drawback, these catalysts have not yet been tested in PEMFCs, but efforts are underway to increase the OCP via doping with other transition metals.

The Pt-SnO_x materials also have excellent electrochemical performance. The performance of the catalysts in a PEMFC is shown in Figure 3. In this experiment, the Pt loading of the cathode is 0.02 mg Pt/cm^2 of Pt-SnO_x/Vulcan carbon, and the anode is 0.2 mg Pt/cm^2 of 20% Pt/Vulcan carbon. When normalized to current, these Pt-SnO_x catalysts outperform the Pt/Vulcan carbon standard by a factor of 3.5, per weight Pt. Further improvements are anticipated as the Pt loading of the SnO_x is optimized and the particle size is reduced. The Pt-SnO_x catalysts are stable to heating in sulfuric acid; however, we also observe that the catalysts are not stable at fuel cell anodes. Like the phosphate materials above, these SnO_x-based materials are microporous, as shown in Figure 4.

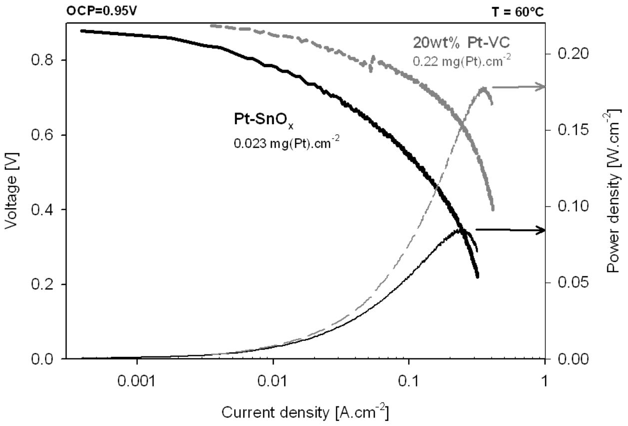

Figure 3. Comparison of PEMFCs having cathodes of 0.023 mg Pt/cm^2 of Pt-SnO_x/Vulcan carbon and 0.22 mg Pt/cm^2 of 20 wt% Pt/Vulcan carbon at 60°C, under humidified H_2/O_2 at atmospheric pressure, and using Nafion 112 membranes. Both anodes have loadings of 0.2 mg Pt/cm^2 of 20-wt% Pt/Vulcan carbon. The standard PEMFC has a power of 0.18 W/cm^2 at a current density of 0.34 A/cm^2, while the Pt-SnO_x PEMFC has a maximum power 0.09 W/cm^2 at a current density of 0.26 A/cm^2, despite having 10× lower Pt at the cathode.

Conclusions

- Hydrous metal oxides and phosphates doped with platinum may be viable candidates as high-activity, inexpensive oxygen reduction catalysts for PEMFC cathodes.
- The microporous structures of the catalysts appear to influence the performance of the catalysts.
- The catalysts are stable under aggressive acid treatment, and therefore are likely to have long-term stability under the operating conditions of a PEMFC cathode.
- The catalysts can be successfully fabricated as stable cathodes for PEMFCs.
- These phosphate and oxide catalysts may prove to be more stable than Pt metal over long-term tests because their platinum is in an oxidized state (Pt^{2+}/Pt^{4+}) and therefore is less prone to poisoning.

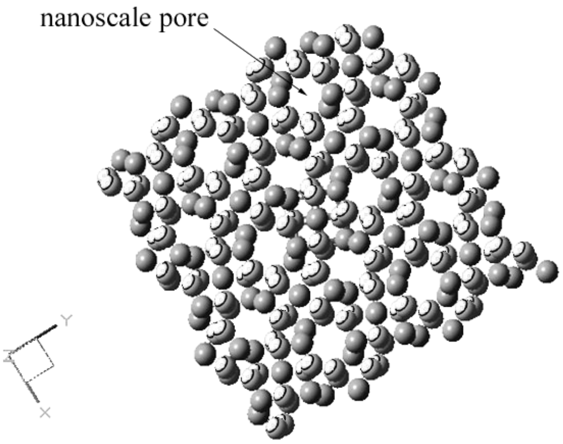

Figure 4. Schematic of the microporous structure of Pt-doped hydrous SnO_x. The nanoscale pores are conducive to proton conduction.

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FY 2003 Publications/Presentations

1. N. P. Ugarte, K. E. Swider-Lyons, "Low-Platinum Tin-Oxide Electrocatalysts for PEM Fuel Cell Cathodes," in the Proceedings of the Symposium on Polymer Fuel Cells, Electrochemical Society Proceedings Series, October 2002, in press.

2. N. P. Ugarte, K. E. Swider-Lyons, "Low-Platinum Metal-Oxide Electrocatalysts for PEM Fuel Cell Cathodes," Third International Symposium on Proton Conducting Membrane Fuel Cells, 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, 20-25 October 2002.

3. P. J. Bouwman, J. A. Stanley, G. B. Cotten, K. E. Swider-Lyons, W. Dmowski, T. Egami, "Low-Platinum, Oxide-Based Electrocatalysts for Oxygen Reduction in PEM Fuel Cells," Gordon Research Conference on Electrochemistry, Ventura, California, 12-16 January 2003.

4. K. E. Swider-Lyons, P. J. Bouwman, N. P. Ugarte, W. Dmowski, "Amorphous Hydrous Metal Oxides as Electrocatalysts for Fuel Cell Cathodes," American Chemical Society Symposium on Advances in Materials for Proton Exchange Membrane Fuel Cells, Monterey, California, 23-26 February 2003.

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9. ~~K. E. Swider Lyons, P. J. Bouwman, N. P. Ugarte, W. Dmowski, "Low Platinum, Oxide-based Electrocatalysts for Oxygen Reduction in Proton Exchange Membrane Fuel Cells," ASM International Symposium on Fuel Cells: Materials, Processing and Manufacturing Technologies, Pittsburgh, Pennsylvania, 13-16 October 2003.~~ delete

Special Recognitions & Awards/Patents Issued

1. Patent disclosure: K. S. Lyons, P. J. Bouwman, "Hydrous phosphate catalysts with low platinum," Navy Case No. 84,631, 26 March 2003.

2. Patent disclosure: K. S. Lyons, N. P. Ugarte, "Platinum-impregnated hydrous tin oxide catalysts," Navy Case No. 84,632, 26 March 2003.

Low Platinum Loading Catalysts for Fuel Cells

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Objectives

- Further improve the new catalyst consisting of a submonolayer of Pt on carbon-supported Ru nanoparticles (1%Pt/10%Ru/C) to come close to the DOE's 2010 target of 100 $\mu g/cm^2$ noble metal loading.
- Further elucidate the inhibition mechanism of CO on H_2 oxidation on Pt.
- Reduce Ru loadings in Pt-Ru electrocatalysts.
- Explore monolayer-level-supported Pt electrocatalysts for O_2 reduction.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- Q. Electrode Performance

Approach

- Synthesize and characterize the electrocatalyst having a submonolayer of Pt on Ru nanoparticles and determine its CO tolerance.
- Test the new electrocatalyst in a membrane electrode assembly (MEA) at the Los Alamos National Laboratory.
- Use an in situ surface x-ray diffraction technique to follow the adsorption of CO on Pt during H_2 oxidation.
- Synthesize and test a non-noble metal alloy and early transition metal nanoparticles as support for Pt to reduce Ru loading.
- Prepare Pt monolayer/multilayer deposits on Au (111) and Au nanoparticles using our new method for depositing Pt monolayers and test these surfaces as O_2 reduction electrocatalysts.

Accomplishments

- The CO tolerance of the 1%Pt /10%Ru/C catalyst for oxidizing H_2 containing 1000 ppm CO at 2500 rpm was more than doubled compared with the last year's value. MEA stability tests at Los Alamos National Laboratory, conducted by Francisco Uribe and coworkers, showed a small loss in activity after 1000 hours of operation with combined H_2 and H_2 + 50 ppm CO + 4% air-bleed fuels. This catalyst has 1/10th (17 $\mu g/cm^2$) of the Pt loading of standard catalysts. For Pt, the loading of the new catalyst is below the DOE's target (150 $\mu g/cm^2$) for precious metals for 2004. For Ru, it is at the present level of state-of-the-art catalysts.

- The (√19 x √19)13CO phase was determined for the first time by x-ray diffraction technique on Pt(111): a fast (2 x 2) ↔ (√19 x √19) phase transition was found. The oxidation of H_2 with 2% CO is inhibited by the formation of an ordered CO (2 x 2) adlayer.
- Pt on C-supported Au nanoparticles can be an efficient catalyst for reducing O_2. A Pt mass specific activity 2.5 times higher than that of Pt10%/C was achieved. Its stability needs to be investigated.
- Pt on C-supported W nanoparticles may be a promising catalyst for H_2 oxidation.

Future Directions

- Optimize a Pt/Ru electrocatalyst, and conduct final tests at LANL and industrial laboratories.
- Investigate the possibilities of reducing Ru loading by non-noble metals, such as W.
- Explore Au-non-noble metal alloy nanoparticles as supports for a Pt monolayer for O_2 reduction.
- Investigate several low d-band vacancy metals as support for a Pt monolayer for O_2 reduction.

Introduction

We investigated a new catalyst consisting of a submonolayer of Pt on carbon-supported Ru nanoparticles (1%Pt/10%Ru/C) with the goal of improving its properties and further understanding the origins of its activity. Its catalytic activity was determined using a rotating thin-film disk electrode. The long-term stability and CO tolerance of this catalyst was tested in a fuel cell electrode (membrane electrode assembly) at Los Alamos National Laboratory. Several preliminary experiments were aimed at reducing the Ru loading. We also obtained new insights into the mechanism of poisoning the catalytic activity of a Pt(111) surface by CO.

The possibility of making an active catalyst for O_2 reduction consisting of Pt monolayers on metal nanoparticles on carbon support was explored. The initial results for Pt on Au indicate that very active catalysts can be obtained by this approach.

Approach

A new method for preparing Pt/Ru catalysts involving spontaneous deposition of Pt on Ru nanoparticles was further studied with the goal of optimizing it to increase the activity of the catalysts. In contrast to the Pt-Ru alloys catalysts, all the Pt atoms in this new one are available for the catalytic reaction. Therefore, the interaction of the Pt atoms with Ru, and the state of the Ru surface, are of utmost importance for the catalyst's activity. Ru-Ni and Ru-Co nanoparticles were deposited on carbon using an impregnation method, while a Pt submonolayer was deposited on these nanoparticles spontaneously. The activity for H_2 oxidation and the CO tolerance were determined. The tests also were conducted with Pt clusters obtained by electroless deposition on polycrystalline W and carbon-supported W nanoparticles. Tungsten nanoparticles were obtained using BNL's new method of sonication solvolysis of W salts.

We employed an in situ x-ray diffraction technique using synchrotron radiation to follow the formation of ordered CO adlayers on Pt(111) during H_2 oxidation, monitoring the process as a function of time. The inhibition of H_2 oxidation was clearly related to the adlayers' structure.

Obtaining Pt monolayer catalysts for O_2 reduction is important for several reasons, including the possibility of reducing Pt loading, and of improving the activity of the catalysts. The initial results, obtained with a Pt monolayer deposited on Au using our new method of galvanic replacement of an adsorbed Cu monolayer, show the high activity of such surfaces.

Results

A thin-film rotating disk electrode (RDE) was used to determine catalytic activities and CO tolerance. Figure 1 shows the results of an accelerated test of CO tolerance of the $PtRu_{20}$ catalyst based on measuring the current at 0.05 V as a function of time for the oxidation of H_2 containing 1000 ppm CO at

60ºC. For comparison, we include the results showing a smaller CO tolerance for two commercial catalysts, along with the results for $PtRu_{20}$ from the last review. A considerable improvement has been achieved; the CO tolerance of the $PtRu_{20}$ catalyst increased in this test from < 3 h to > 6 h.

Figure 2 shows the life test in MEA with an earlier version of the catalyst synthesized a year and a half ago. Clean H_2 and H_2 with 50 ppm CO and 4% air bleed were used as fuel. The losses after 1000 hours are 40 mV when the cell operates on clean H_2, and 60 mV with the H_2+50 ppm CO+4% air mixture. The cell was run with the latter fuel composition for a third of the total time. The test still is in progress. This result clearly shows that Pt submonolayers on Ru nanoparticles are stable during the fuel cell's operation and that this system represents a real catalyst. In addition to the high activity for H_2 oxidation and a weak CO bonding, the strong segregation of Pt and Ru is a key factor that determines this catalyst's stability. The data provide a powerful illustration of the possibility of nanoparticle surface modification by Pt monolayers as a method of obtaining low noble-metal loading of catalysts.

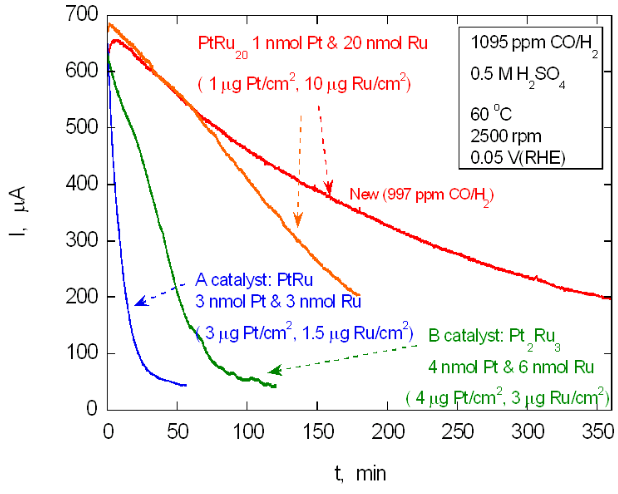

Figure 1. The CO tolerance of the improved $PtRu_{20}$ catalyst (top curve) compared with an earlier sample and two commercial catalysts. The current at 0.05 V is plotted as a function of time for the oxidation of H_2 containing 1000 ppm CO at 60ºC; 2500 rpm. The catalyst loadings are given in the graph. RHE = reversible hydrogen electrode.

The $(\sqrt{19} \times \sqrt{19})^{13}CO$ phase was determined for the first time on Pt(111) by *in situ* x-ray diffraction technique. We found that the (2 x 2) ↔ $(\sqrt{19} \times \sqrt{19})$ phase transition occurs in several seconds. The oxidation of H_2 with 2% CO is inhibited by formation of the ordered CO (2 x 2) adlayer. Incomplete removal of CO disorders the phase, but the inhibition of H_2 oxidation remains unchanged.

To reduce the Ru loadings, RuNi and RuCo nanoparticles were deposited on XC-72 by wet impregnation, followed by spontaneous deposition of Pt. The activity of these catalysts for H_2 oxidation is somewhat lower than that of $PtRu_{20}$, while their CO tolerance is similar. Pt/Wpoly and Pt/W/C catalysts have a considerable activity for H_2 oxidation but poor CO tolerance.

Figure 3 displays rotating ring-disk electrode (RRDE) measurements of O_2 reduction on the Pt monolayer on an Au(111) surface, showing its very high activity ($E_{1/2}$ = 0.830 V) and practically no H_2O_2 generation. Two Tafel slopes, usually observed with Pt electrodes, can be obtained from kinetic currents determined by the Koutecky-Levich plots. O_2 reduction on the Pt adlayer (9 µg Pt/cm^2) on Au/C has $E_{1/2}$ = 0.820 V. X-ray absorption

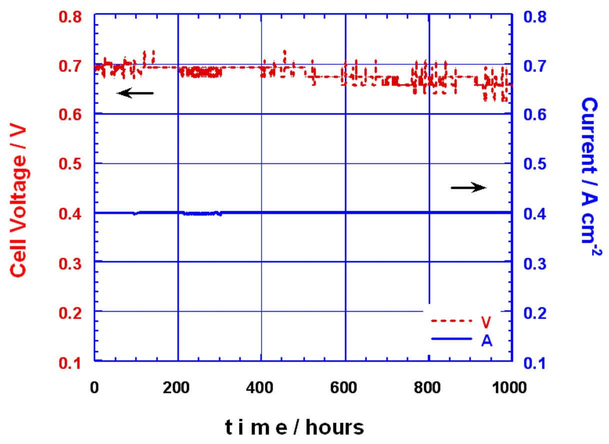

Figure 2. The long-term test in a cell conducted at LANL by F. Uribe and coworkers. Anode: 0.19 mg total metal/cm^2 (10%Ru, 1%Pt) **17 µg Pt/cm^2**; Cathode: 0.23 mg Pt (20% Pt/C, ETEK)/cm^2; Electrode areas=50 cm^2; T= 80ºC; Pressures A/C = 30/30 psig. Total run time = 1000 hours at constant current (710 hours of operation with clean H_2 and 290 hours with H_2 + 50 ppm CO + 4 % air bleed).

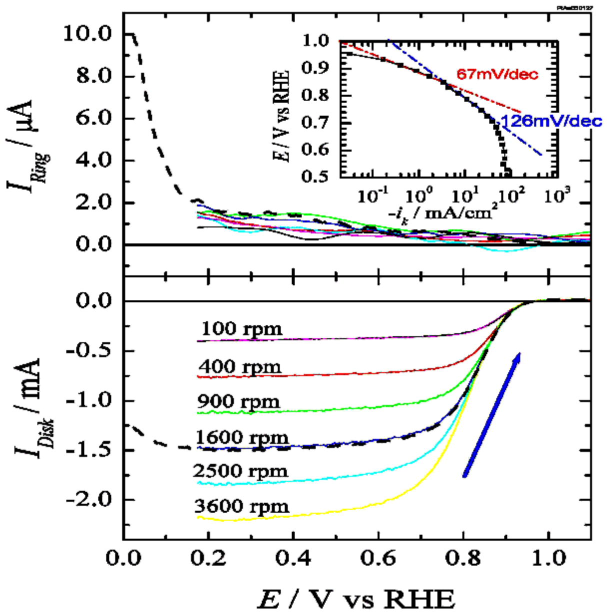

Figure 3. RRDE measurements of O_2 reduction on a Pt_{1ML}/Au(111) surface. The insert shows the Tafel plot with kinetic currents obtained from the Koutecky-Levich plots.

spectroscopy measurements and voltammetry curves indicate that PtOH formation on Pt/Au/C and Pt/Au(111) shifts to more positive potentials than those of Pt/C and Pt(111) surfaces, respectively. This property may be very important for the function of these catalysts since PtOH inhibits O_2 reduction. The long-term stability of the Pt/Au catalyst is questionable since this system is anti-segregated. These results, however, illustrate the important possibility that a Pt monolayer on metal nanoparticles can be an active catalyst for O_2 reduction.

Figure 4 is a histogram of the Pt-mass-specific activities of several bimetallic catalysts that we have tested so far. It shows that all the adlayer Pt deposits on Au nanoparticles have a higher Pt mass-specific activity than a standard 10%Pt/C catalyst. A mixed $Pt_{0.75}Pd_{0.25}$ catalyst performs the best.

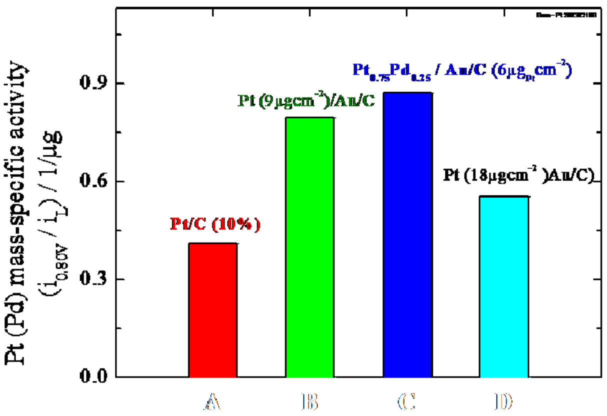

Figure 4. Histogram of the Pt-mass-specific activities of several bimetallic catalysts at E=0.8 V; 1600 rpm.

Conclusions

The performance of the 1%Pt10%Ru catalyst was considerably improved and a two-fold increase in CO tolerance achieved according to the accelerated test with a rotating disk electrode. The long-term testing of the earlier version of the catalyst in MEA at LANL has reached 1000 hours in the oxidation of H_2 and H_2 + 50 ppm of CO and 4% of air with only a minor loss of performance. The test is still in progress. For Pt, the loading of the new catalyst is below the DOE's target (150 μg/cm^2) for precious metals for 2004. For Ru, it is at the present level of the state-of-the-art catalysts. As illustrated by the data for Pt on Au, Pt monolayers on metal nanoparticles can be active catalysts for O_2 reduction.

Publications

1. H. Inoue, S.R. Brankovic, J.X. Wang, R.R. Adzic, Oxygen Reduction on Bare and Pt Monolayer-Modified Ru(0001), Ru(101-0) and Ru Nanostructured Surfaces, Electrochim. Acta, 47 (2002) 3777.

2. S.R. Brankovic, N.S. Marinkovic, J.X. Wang, R.R. Adzic, Carbon Monoxide Oxidation on Bare and Pt-modified Ru(101-0) Single Crystal Electrodes, J. Electroanal. Chem., 532 (2002) 57

3. J.X. Wang, S.R. Brankovic, Y. Zhu, J.C. Hanson, and R.R. Adzic, Kinetic Characterization of H_2 Anode Catalysts Made by Spontaneous Deposition of Pt on Ru Nanoparticles, J. Electrochem. Soc. in press.

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Patents

1. Patent application submitted. The U.S. Patent Office serial number 09/812246.

Direct Methanol Fuel Cells

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Objectives

Develop materials and components and optimize operating conditions of the direct methanol fuel cell (DMFC) for maximum power density and fuel conversion efficiency at a minimum cost. In particular:

- Design and optimize membrane-electrode assemblies (MEAs) to enhance cell performance.
- Advance electrocatalysis of methanol oxidation and oxygen reduction to increase power density and lower total precious metal loading.
- Characterize and optimize non-Nafion polymers with reduced crossover and improved performance.
- Model, develop and demonstrate practical viability of advanced cell components.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- D. Fuel Cell Power System Benchmarking
- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

- Build, operate and test performance of DMFCs with different anode and cathode catalysts, membranes and MEAs.
- Through experimentation, develop thorough understanding of the key factors impacting cell performance and durability.
- Maximize efficiency, power and energy density of DMFCs by creative designing of stack components and experimental verification of the hardware performance.

Accomplishments

Cathode Research

- Carbon-supported Pt catalysts optimized for performance at a loading of 0.6 mg cm^{-2}.
- Respectable performance demonstrated at an air stoichiometric ratio between 2 and 3.

Electrocatalysis

- Alternative carbon-supported cathode catalyst demonstrated for over 200 hours with power density ~15% better than that of a reference Pt catalyst.
- Key factors affecting the performance of Pt-Ru anode catalysts determined by a combination of electrochemical ("in fuel cell"), x-ray diffraction (XRD), thermogravimetric analysis (TGA) and CO-stripping techniques.

Performance Durability

- Effect of Pt oxide formation on short-term DMFC performance determined; a method of regaining cathode activity developed and successfully implemented in life testing.
- Ruthenium crossover through Nafion® membrane and its effect on the cathode activity demonstrated for the first time; other reasons for long-term MEA degradation identified.

Membrane Research

- Significant selectivity improvement over non-fluorinated bi-phenol sulfone (BPSH) polymers achieved with two fluorinated poly(arylene ether sulfone) polymers: 6F [hexafluorinated (biphenol A) sulfonated poly(arylene ether sulfone)] and 6F-CN [hexafluorinated / nitrile-functional sulfonated poly(arylene ether sulfone)].
- Low-resistance 6F-CN MEAs prepared and successfully tested in a DMFC for several hundred hours with tolerable performance degradation.

Stack R&D

- Three generations of 11-W stacks for a 20-W DMFC system for portable power designed, built and tested.
- Four latest-generation stacks delivered to Ball Aerospace for system integration.
- Design of all components for the 500-W auxiliary power unit (APU) DMFC stack completed; excellent performance demonstrated with a six-cell short stack operating at zero cathode backpressure and air stoichiometry ratio below three.

Future Directions

- Investigate the mechanism and design methods for controlling degradation of the Nafion® and non-Nafion MEAs.
- Optimize performance and improve durability of systems based on novel alternative membranes, such as 6F and 6F-CN.
- Perform theoretical and practical study of the impact of catalyst layer structure on the rate of methanol oxidation and oxygen reduction.
- Investigate novel carbon-supported catalysts for low-loading DMFC operation.
- Improve DMFC performance by understanding and optimizing hydrophilic/hydrophobic properties of the cathode.
- Demonstrate for at least 100 hours sustained operation of a large-surface area stack with air stoichiometry ratio below two.

Introduction

Direct methanol fuel cell research at Los Alamos National Laboratory (LANL) has focused on developing materials and designing optimum operating conditions for DMFCs to be used in portable power applications (commercial electronics, battery replacement for the military) and transportation (on-board APUs). The main objective of LANL's research effort in the DMFC area has been to demonstrate that methanol-based systems can meet power-density, energy-conversion efficiency and cost targets.

Results

In our FY 2003 research, we continued our effort to optimize carbon-supported catalysts for the main purpose of reducing the precious metal loading in DMFCs. Five cathode Pt/C catalysts with Pt content ranging from 30 wt% to 80 wt% were tested at a target catalyst loading of 0.6 mg_{Pt} cm^{-2}. Experiments revealed that 56% Pt/C and 60% Pt/C are not only the most active for oxygen reduction, but are also more immune to methanol crossover effects. DMFC performance recorded with the 80% Pt/C was not as good as that of 56% Pt/C and 60% Pt/C, yet was much above that of the 40% Pt/C and 30% Pt/C.

Last year, we introduced a new binary cathode catalyst, Pt-X/C (patent application pending), with higher activity towards oxygen and improved methanol tolerance compared to the Pt/C reference catalyst. In FY 2003, we demonstrated superior performance of that catalyst in a 200-hour life test. The Pt-X performance at the end of the life test, 15% better than that of a reference Pt/C catalyst, would have been even better had it not been for its relatively poor long-term stability. Future research will focus on improving the stability of this catalyst, which could lead to as much as 50% improvement in the cell performance. An attempt will also be made to obtain the Pt-X catalyst in an unsupported form, more suitable for portable DMFC use.

Progress in cathode and cell-component research has led to significant lowering of the airflow required to maintain good cell performance. In FY 2003, we demonstrated single cells and prototype stacks that, in addition to showing good performance and high efficiency, can operate on ambient air and with an air stoichiometry ratio of ~2.3. This low stoichiometry exceeds the airflow reduction milestone of the DMFC project at LANL.

The current year marks a very significant increase in the DMFC durability research at LANL. We developed a setup for the parallel durability testing of several MEAs as well as techniques for detecting performance losses of different MEA components. We have extensively used carbon monoxide probing for determining the number of active catalyst sites and atomic composition of the anode and cathode surfaces at various times of the life test. All durability research was carried out under practical cell operating conditions, at low flow and pressure of the cathode air and high cell operating voltage. As indicated by the life-test data in Figure 1, most of the short-term DMFC performance losses occur in the first 24 hours of the life test. This loss has been attributed to the surface oxidation of the platinum catalyst at its operating potential of 0.80-0.85 V. It can be regained by reducing the catalyst surface, for example, by stopping the cathode airflow for a few seconds (Figure 2).

In addition to short-term performance loss caused by oxidation of the Pt surface, DMFCs also suffer from long-term (generally irreversible) performance degradation. This performance loss is most likely due to changes in the hydrophobic/hydrophilic properties of the cathode, loss of the

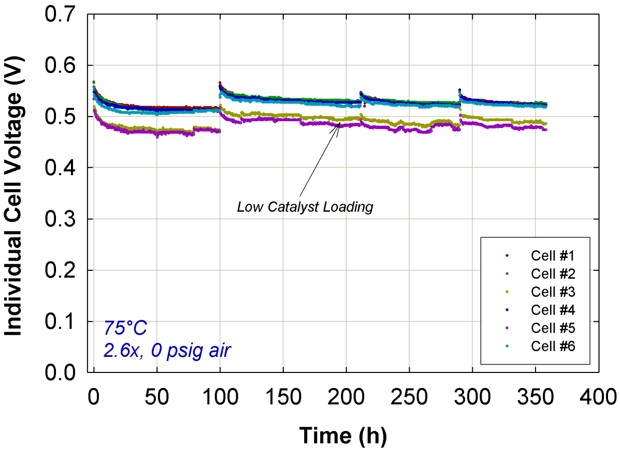

Figure 1. A 350-hour Parallel Life Test of Six Cells Operated at a Constant Current Density of 0.08 A cm^{-2} at 75°C

ionomer from the electrodes (cathode in particular), and lowering of the cathode activity as a result of ruthenium crossover and its re-deposition at the Pt surface. Ruthenium crossover was first demonstrated at LANL in FY 2003 by using the carbon monoxide probe technique. This research will continue in FY 2004, focusing on the methods of stabilizing Ru in the DMFC anode.

In the past year, we developed alternatives to standard Nafion® MEAs that for the first time promise considerable improvement in DMFC membrane technology. This research, carried out in close collaboration with Virginia Polytechnic Institute, led to the demonstration of two new polymers from the poly (arylene ether sulfone) family: 6F and 6F-CN. Changes in the physicochemical properties of the non-fluorinated BPSH polymer brought about by the presence of -CF_3 (lower water uptake and better adhesion) helped to significantly reduce the interfacial resistance between the membrane and the electrodes while preserving good selectivity. Consequently, the initial DMFC performance of the two new membranes was found to be better than that of Nafion® 117 under the same test conditions (Figure 3). Unlike non-fluorinated BPSH membranes, which suffer from irreversibly reduced performance after only 100 hours, 6F-CN-35 showed no degradation in the first 200 hours of life testing and only a slight performance drop after 700 hours. 6F-CN-35 exhibited no increase in high-frequency resistance over the time of the life test, suggesting a good and stable membrane/electrode interface. This result represents a significant achievement in alternative DMFC membrane research.

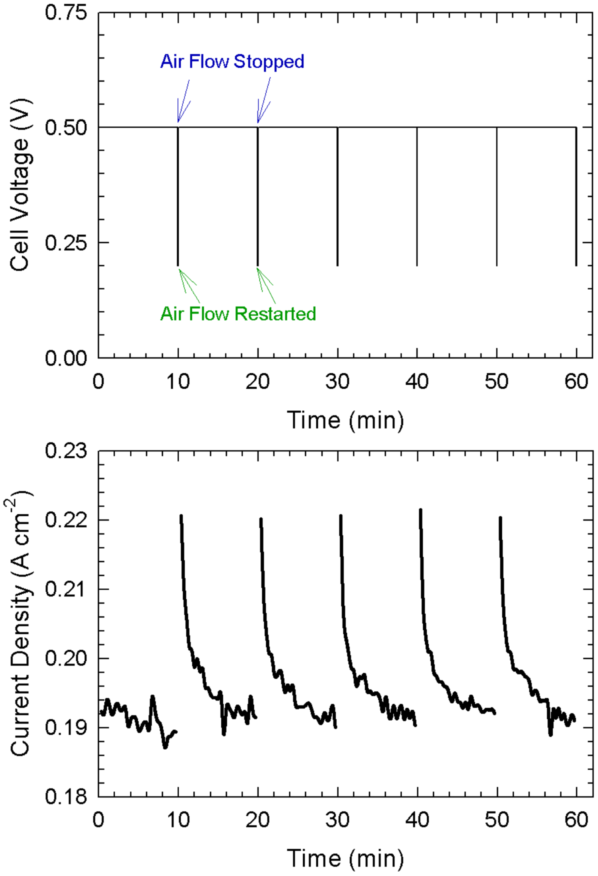

Figure 2. Effect of Cell Voltage (Cathode Potential) Pulsing on the DMFC Operation at 80°C

In parallel with the fundamental research in catalysis, membranes and MEAs, which has remained the focal point of the direct methanol fuel cell program at LANL, we also made substantial progress in the design and prototyping of DMFC stacks for portable and auxiliary power applications. Three generations of highly efficient and lightweight 11-W stacks were developed for the operation at a design voltage of 0.55/cell. Four units from the last generation were supplied to our system partner, Ball Aerospace & Technologies Corporation, for integration into two 20-W system prototypes for the military (a DARPA-sponsored project).

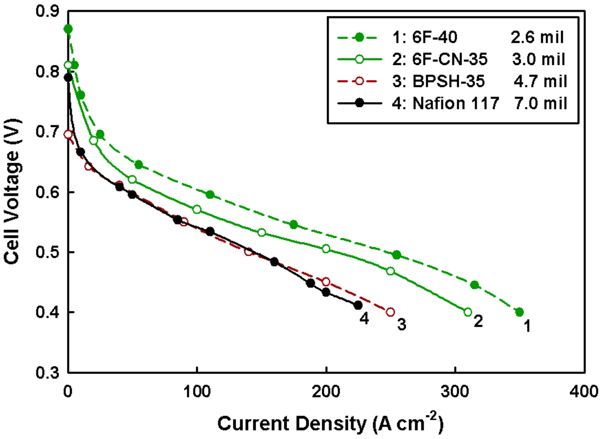

Figure 3. DMFC Polarization Plots Obtained with Four Different membranes: Nafion® 117, 6F-40, 6F-CN-35 and BPSH-35 (Plots recorded at 80°C and an ambient cathode air pressure of 0.76 atm in Los Alamos)

All key components for the 500-W APU stack were designed and tested in a six-cell stack, which preceded the construction of the actual stack deliverable scheduled in a few months. The short stack was assembled using 100-cm^2 active area cells. All six cells in the short stack exhibited uniform and good performance when operated at ambient cathode pressure and an air stoichiometry ratio of 3.0. The maximum power generated by the stack under these conditions was measured at 140 W (Figure 4), with negligible penalty on a scale-up from the single cell to the stack. As a result, the number of cells in the full stack required to generate the design power of 500 W is estimated at approximately 50, significantly lower than the originally planned 100.

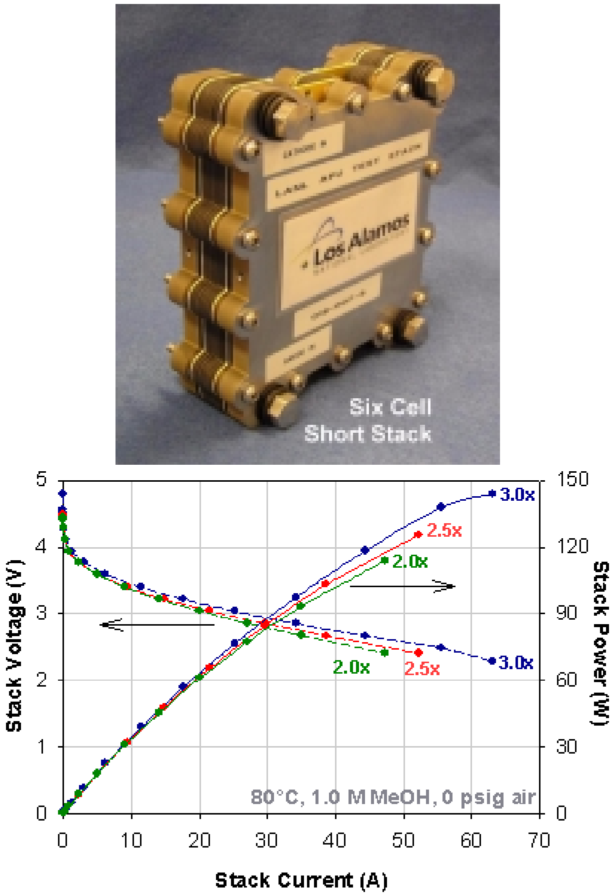

Figure 4. Development of 500-W DMFC Stack for Auxiliary Power System: Polarization and Power Plots for Six-Cell Stack at 80°C

Conclusions

The main conclusions from the DMFC research performed at LANL in the past year can be summarized as follows:

- The use of carbon-supported Pt catalyst with a Pt-to-C ratio of 50 - 60 wt% significantly reduces the catalyst loading at only a moderate performance penalty. Careful optimization of the cathode structure allows for continuous cell/stack operation at an air stoichiometric ratio as low as two.
- DMFC cell/stack suffers from short- and long-term performance loss. The short-term loss is predominantly caused by the oxidation of the cathode Pt. This loss can be reversed by intermittent reduction of the catalyst. Long-term performance degradation results from irreversible changes to the structure of the electrode and the hydrophobic/hydrophilic properties of the cathode, as well as from Ru crossover. Mitigating the long-term durability issues will require modifications to the MEA components and methods of cell fabrication.
- Thanks to low impedance of the membrane-electrode interface and preserved high selectivity, two new membranes from the BPSH family, 6F and 6F-CN, exhibit superior DMFC performance to Nafion® 117. Based on the life test data for 6F-CN-35, the membranes also promise good durability.
- Significant practical potential of DMFC technology was demonstrated with the 11-W stack prototypes operating at low flow and ambient pressure of the air. The stack power density, already measured at 130 W kg^{-1}, is expected to exceed 300 W kg^{-1} soon, both for low power (11-W) and high power (500-W) stacks.

FY 2003 Publications

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2. "A Six-Cell 'Single-Cell' Stack for Stack Diagnostics and Membrane Electrode Assembly Evaluation," B. Pivovar, F. Le Scornet, C. Eickes, C. Zawodzinski, G. Purdy, M. Wilson, and P. Zelenay, in Proton Conducting Membrane Fuel Cells III, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.

3. "The Effect of BPSH Post Treatment on DMFC Performance and Properties," M. Hickner, Y. Kim, J. McGrath, P. Zelenay and B. Pivovar, in Proton Conducting Membrane Fuel Cells III, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.

4. "Optimization of Carbon-Supported Platinum Cathode Catalysts for DMFC Operation," Y. Zhu, E. Brosha and P. Zelenay, in Proton Conducting Membrane Fuel Cells III, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.

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6. "Processing Induced Morphological Development in Hydrated Sulfonated Poly(arylene ether sulfone) Copolymer Membranes," Y. S. Kim, L. Dong, M. Hickner, B. Pivovar, and J. McGrath, Polymer, accepted for publication June 13, 2003.

FY 2003 Presentations

1. W. L. Gore, Elkton, Maryland, June 20, 2002. Title: "Direct Methanol Fuel Cells"; P. Zelenay* (invited lecture).

2. Gordon Research Conference on Fuel Cells, Bristol, Rhode Island, July 28 - August 2, 2002. Title: "DMFC Research at Los Alamos: Towards Better Performing Cells and Stacks" P. Zelenay* (invited/keynote lecture).

3. 202nd Meeting of the Electrochemical Society, Salt Lake City, UT, October 20-24, 2002. Title: "A Six-Cell 'Single-Cell' Stack for Stack Diagnostics and Membrane Electrode Assembly Evaluation," B. Pivovar*, F. Le Scornet, C. Eickes, C. Zawodzinski, G. Purdy, M. Wilson, and P. Zelenay.

4. 202nd Meeting of the Electrochemical Society, Salt Lake City, UT, October 20-24, 2002. Title: "The Role of Membrane Thickness and Interfaces on DMFC Properties," M. Hickner and B. Pivovar*.

5. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "The Effect of BPSH Post Treatment on DMFC Performance and Properties"; M. Hickner*, B.S. Pivovar, Y. Kim, J. McGrath and P. Zelenay.

6. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "Modeling the Direct Methanol Fuel Cell Anode"; C. Diniz*, R. Moore, P. Badrinarayanan and P. Zelenay.

7. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "Understanding the Cathode of A Direct Methanol Fuel Cell"; P. Badrinarayanan*, R. Moore, C. Diniz, J. Cunningham and P. Zelenay.

8. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "Optimization of Carbon-Supported Platinum Cathode Catalysts for DMFC Operation"; Y. Zhu*, E. Brosha and P. Zelenay.

9. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "Electrochemical and XRD Characterization of Pt-Ru Blacks for DMFC Anodes"; C. Eickes*, E. Brosha, F. Garzon, G. Purdy, P. Zelenay, T. Morita and D. Thompsett.

10. The International Battery Association and 5th Hawaii Battery Conference, Ernest B. Yeager Memorial Symposium, Waikoloa, Hawaii, January 7-10, 2003. Title: "Electrocatalysis in Direct Methanol Fuel Cells"; P. Zelenay (invited lecture).

11. Workshop on "Advances in Materials for Proton Exchange Membrane Fuel Cell Systems," Asilomar, California, February 23-27, 2003. Title: "Direct Methanol Fuel Cell Research at Los Alamos: From Fundamentals to Stacks"; P. Zelenay (plenary lecture).

12. Workshop on "Advances in Materials for Proton Exchange Membrane Fuel Cell Systems," Asilomar, California, February 23-26, 2003. Title: "The Influence of Polymer Structure on Fuel Cell Electrolyte Properties"; B. S. Pivovar (invited talk).

13. Columbia University, Department of Chemical Engineering, New York, NY, April 22, 2003. Title: "Effect of Polymer Structure on Fuel Cell Properties"; B. S. Pivovar (invited talk).

14. 203rd Meeting of the Electrochemical Society, Paris, France, April 27 - May 2, 2003. Title: "Methanol Crossover in Direct Methanol Fuel Cell Systems"; B. Pivovar*, G. Bender, P. Piela and P. Zelenay.

15. 203rd Meeting of the Electrochemical Society, Paris, France, April 27 - May 2, 2003. Title: "State of the DMFC Cathode During Prolonged Cell Operation"; C. Eickes, P. Piela and P. Zelenay*.

16. Seminar "Electrocatalysis in PEM Fuel Cells", Trondheim, Norway, May 5, 2003. Title: "Electrocatalysis in Direct Methanol Fuel Cells"; C. Eickes, P. Piela and P. Zelenay* (invited lecture).

17. Annex XI Meeting of International Energy Agency Meeting, May 6 - 7, 2003, Trondheim - Bergen, Norway. Title: "20 W DMFC System Development at LANL"; P. Zelenay*.

Development of Advanced Catalysts for Direct Methanol Fuel Cells

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Objectives

- Reduce catalyst cost for direct methanol fuel cells
- Demonstrate the feasibility of reducing noble metal catalyst loading to less than 0.5 mg/cm^2
- Develop a low-cost manufacturing technique for membrane electrode assembly (MEA) fabrication
- Identify potential non-noble metal catalytic systems

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost

Approach

- Prepare multi-component thin film catalyst layers by direct current and radio frequency magnetron sputtering
- Identify a corrosion-resistant non-noble metal system
- Exploit nanophase properties of sputtered thin films based on Ni/Zr, Co/Zr, and other valve metal combinations
- Devise ways to control composition, microstructure, and electrochemical performance
- Characterize catalyst layers in half-cells and full cells
- Characterize catalyst layers by X-ray diffraction (XRD) and scanning electron microscopy (SEM) for structural and electronic properties

Accomplishments

- Prepared multicomponent combinatorial samples with unique non-equilibrium nanophase structure by sputter deposition
- Identified novel corrosion-resistant non-noble nanophase thin film catalyst layers based on nickel and zirconium
- Nickel/zirconium intermetallics with compositions less than 70% nickel found to be corrosion resistant under fuel cell conditions
- Nickel/zirconium layers have been found to protect base metal surfaces such as nickel in sulfuric acid
- Quaternary composition consisting of Pt-Ru-Ni-Zr enhances noble metal utilization in catalysts for methanol oxidation

Future Directions

- Continue to study composition, morphology and electrochemical performance of Ni/Zr coatings
- Evaluate quaternary compositions of Ni-Zr-Pt-Ru to lower the amount of Pt-Ru and to tune electronic interactions
- Evaluate Co-Zr sputtered layers for methanol oxidation activity; Co has higher catalytic activity compared to Ni for many organic transformations
- Exploit morphological modification using ion-beam techniques for improving activity
- Correlate electronic properties of materials from extended X-ray absorption fine structure (EXAFS) and X-ray photoelectron spectroscopy (XPS) with catalytic properties

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Introduction

Fuel cells offer the possibility of reduced emissions and high efficiency for transportation applications. Of the various fuel cells being considered, the direct methanol fuel cell (DMFC) is very attractive due to the key advantages of system simplicity and good transient response compared to reformate-air fuel cell systems. However, DMFCs currently require unsupported noble metal catalysts at high loadings of 2.5-4.0 mg/cm^2, leading to a high catalyst cost of $100-150/kW. Also, to keep the overall fuel cell cost low, the preferred method of catalyst application must be designed for manufacturing. Thus, cost presents a major obstacle to commercialization of DMFCs for transportation applications. Enhancement of the overall fuel cell efficiency is also necessary to meet the weight and volume requirements for transportation applications. The present research effort aims at addressing these key issues of cost and efficiency. The overall objective of the effort is to develop new low-cost electrocatalyst materials and new methods of preparing fuel cell electrodes that will reduce the amount of noble metal used and lead to overall cost reduction and improved performance of direct methanol fuel cells.

Approach

Using sputter-deposition, mixed compounds and multi-component alloys of virtually any composition can be readily deposited [1]. Specifically, non-equilibrium phases have unique properties compared to phase-separated intermetallics. Although non-noble metals such as nickel and cobalt are excellent for catalysis of hydrogenation and dehydrogenation of organics, they are not stable in acidic media. Therefore, the possibility of creating multi-component alloys containing some mixture of Ni, Co, Zr, Pt, and Ru that are catalytically active and stable in the fuel cell environment has been investigated. The first studies conducted were on co-sputtered Ni-Zr films. Structure, corrosion resistance in acid, and electrochemical activity for methanol oxidation were then studied. A series of quaternary Ni-Zr-Pt-Ru samples were also fabricated and tested to examine the possibility of lower Pt/Ru loadings in the catalyst.

Results

Investigations at JPL on sputter-deposited nanocrystalline Ni-Zr have shown that these bimetallic phases exhibit excellent corrosion resistance in 1 M sulfuric acid. Figure 1 contains results of X-ray diffraction from a series of combinatorially deposited Ni-Zr alloys with Ni/Zr atomic ratios ranging from 45/55 to 75/25. These data suggest that a single-phase nanocrystalline solid solution is obtained. Scherrer peak-broadening analysis indicates that the average grain size in these films is less than 2 nm. Based on the literature, such an amorphous/nanocrystalline type of structure is anticipated to be more corrosion resistant than similar materials with a polycrystalline microstructure.

Figure 2 shows an image of a series of samples consisting of Ni-Zr of varying composition deposited on carbon foil and immersed in a 1 M H_2SO_4 solution for 24 hours. The photograph is visible evidence that films with Ni/Zr atomic ratios less than 70/30 remain intact and shiny, while those films with

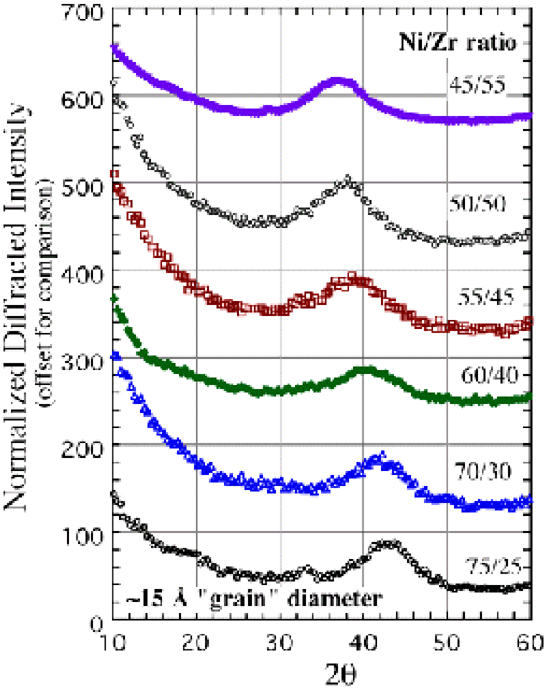

Figure 1. X-ray diffraction from a series of Ni/Zr films as deposited onto a Si wafer substrate. The data are consistent with that expected from a nanocrystalline Ni/Zr solid solution.

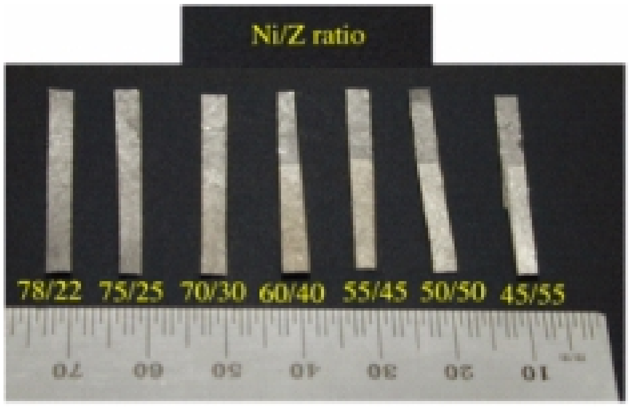

Figure 2. Image of Ni/Zr films sputtered onto carbon foil and immersed in 1 M H_2SO_4 solution for 24 hours. The films with Ni/Zr atomic ratios less than 70/30 are still visible, while those films with higher Ni contents appear to have dissolved.

higher Ni content dissolve and leave behind a substrate with no coating.

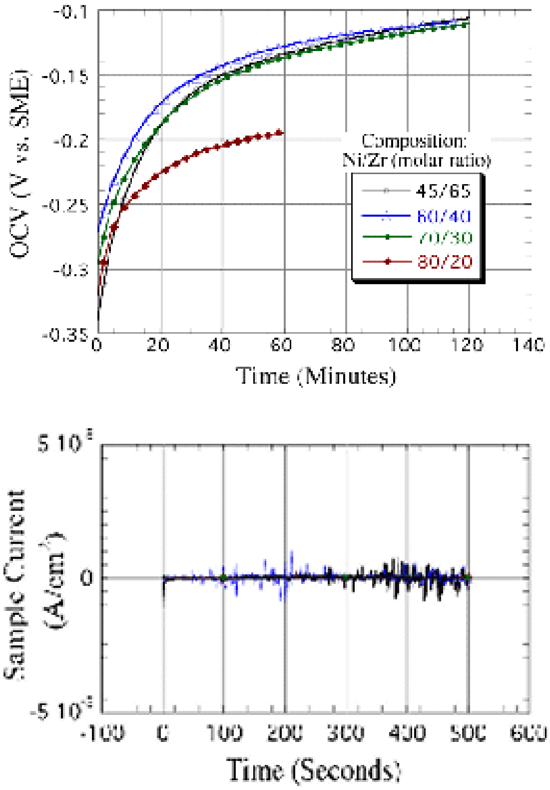

Figure 3. (top) Plot showing Voc vs. time for Ni/Zr on C foil. Those with a Ni/Zr ratio lower than 70/20 had a higher potential vs. MSE compared to that observed from pure Ni, indicating chemical stability. (bottom) Potentiostatic current vs. time plots for a 40/60 Ni/Zr film under potentials ranging from 0.05 to 0.74 V vs. NHE. No measurable currents were detected.

Figure 3 (top) shows plots of open circuit potential (Voc) of various Ni/Zr film electrodes as a function of time in de-aerated solutions of 1 M sulfuric acid. The open circuit potential values attained with all the compositions is much greater than 0.6 V vs. the mercury/mercurous sulfate reference electrode (MSE), suggesting that the surface is not evolving hydrogen and is extremely passive in contact with sulfuric acid. Also, data in Figure 3 (bottom) shows that there is essentially no cell current induced upon cell biasing with potentials ranging from 0.05 to 0.75 V vs. normal hydrogen electrode (NHE), confirming the corrosion resistance and absence of any significant faradaic process under applied anodic potentials. A film consisting of 40/60 Ni/Zr was used in a fuel cell anode as an under-layer for a sputtered Pt/Ru DMFC anode layer.

In this test, the anode structure consisted of a Torayâ carbon paper substrate, a 150-nm thick layer of Ni/Zr, and a 200 nm thick layer of Pt/Ru (50/50). This anode was combined with a Nafionâ membrane and a Pt-black cathode to form a membrane-electrode assembly that was tested as a direct methanol fuel cell. Figure 4 shows the performance of the fuel cell. The fuel cell performance was stable over several days of testing with no evidence of degradation, showing that the Ni/Zr was robust in the acidic fuel cell environment.

The results in Figure 4 also indicate that the Ni/Zr was sufficiently electrically conductive - an important criteria that needs to be satisfied by a corrosion-resistant layer to be considered for this type of application.

It is also possible for this new class of materials to be used to minimize the Pt/Ru loading by creating quaternary alloy systems that contain very small amounts of noble metal and are primarily composed of non-noble metals. One such possible system is co-sputtered Pt/Ru/Ni/Zr.

Results of polarization experiments in solutions of methanol/1 M sulfuric acid are shown in Figure 5. These results indicate that a catalyst layer that contains just 17% Pt exhibits the same current as that with 50 atomic % Pt, confirming the possibility of significantly lowering the noble metal content using non-noble metal additives such as Ni and Zr. Investigation of the electrochemical oxidation activity of these films, consisting of Pt-Ru-Ni-Zr, at elevated temperatures show that activity levels exceed those expected from plain sputtered PtRu (without Ni/Zr). The mechanisms driving this effect will be investigated in FY 2004.

Conclusions

- Thin film corrosion-resistant and electrocatalyst layers consisting of non-noble metal combinations have been prepared by sputter deposition.
- As-deposited Ni-Zr films were found to be nanocrystalline in nature, with average grain sizes less than 2 nm in diameter.
- Ni/Zr films with nickel content greater than 40% were found to be corrosion-resistant in sulfuric acid and in the fuel cell environment.
- A direct methanol fuel cell comprising of a sputtered Pt/Ru (50/50) anode catalyst layer with an underlayer of 150 nm thick Ni-Zr was found to be stable over multiple days of testing.

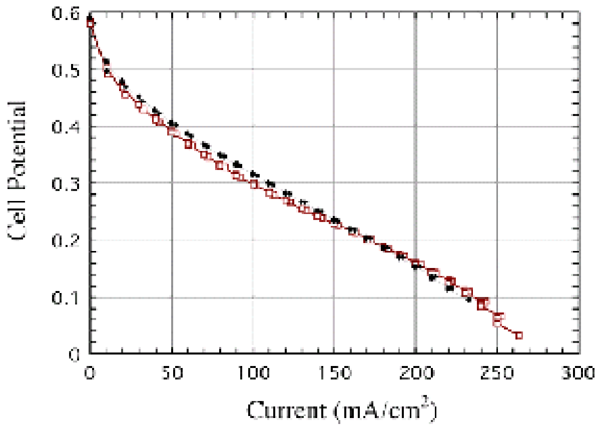

Figure 4. Multiple current-voltage sweeps of a DMFC made using a Ni-Zr support layer on the anode. Though the Pt-Ru layer was not optimized for best performance, this test showed that a Ni/Zr support layer was compatible with a full fuel cell environment.

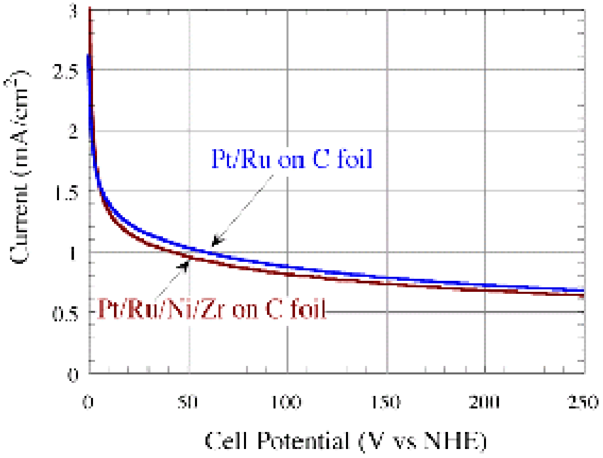

Figure 5. Potentiostatic data showing half-cell current vs. time for a $Pt_{50}Ru_{50}$ film and a $Ni_{16}Zr_{36}Pt_{17}Ru_{31}$ film sputtered on carbon foil. When held at 0.7 V vs. NHE in 1 M methanol, 1 M sulfuric acid at about 25°C, the observed current levels are very similar.

- Quaternary alloy mixtures of Pt-Ru-Ni-Zr have been found to have properties similar to Pt-Ru films with over three times the Pt content. This new class of alloy catalyst that consists of a large amount of non-noble metal with very small amounts of Pt seems to be extremely promising.

References

1. DOE Labs Annual Report 2001.

FY 2003 Publications/Presentations

1. S. R. Narayanan, J. Whitacre and C.K. Witham, "Advanced Catalysts for Direct Methanol Fuel Cells", Presentation at the DOE Lab Annual Merit Review, May 2003, Berkeley, CA.

2. "Nanocrystalline Corrosion-Resistant Layers Via Sputter Deposition." Manuscript in preparation, to be submitted to Journal of Power Sources in September 2003.

3. "Minimizing Pt Loading in Methanol Fuel Cells Using A Quaternary Pt-Ru-Ni-Zr Catalysis Layer." Manuscript in preparation, to be submitted to Journal of Electrochemistry in September 2003.

Special Recognitions & Awards/Patents Issued

1. New Technology Report # 40415 titled "Corrosion resistant materials for fuel cells based on nanophase Nickel-Zirconium alloys", S.R. Narayanan, Jay Whitacre and T. I. Valdez, May 2003.

2. New Technology Report #20250: Sputter-deposited fuel cell electrodes and membranes with high performance and low-cost: A new technique for commercialization of fuel cells", B. Jeffries-Nakamura, W. Chun, S.R. Narayanan, R. Ruiz, August 1997.

Novel Approach to Non-Precious Metal Catalysts (New FY 2004 Project)

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Objectives

- Reduce the dependence of proton exchange membrane (PEM) fuel cell catalysts on precious metals.
- Achieve performance comparable to precious metal catalysts used in currently commercialized membrane electrode assemblies (MEAs) at a cost 50% less compared to a target of 0.2 g Pt/peak kW.
- Target demonstrated durability of greater than 2,000 hours with less than 10% power degradation.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability

Approach

The objectives of this project are to reduce the dependence of PEM fuel cell catalysts on precious metals in order to reduce the cost of the fuel cell stack as well as the overall system cost without loss of current performance or durability. The target is to develop catalysts that perform at least as well as the conventional precious metal catalysts currently in use in commercialized MEAs and that cost 50% less compared to a target of 0.2 g Pt/peak kW. The target for catalyst durability is greater than 2,000 hours with less than 10% power degradation.

The proposed work is directed at meeting these objectives while taking into account that the total costs of the catalysts include the processing costs for their synthesis and integration into an MEA. Several innovative technology approaches will be combined for synthesizing new non-precious metals and their support particles by process methods that also simultaneously disperse and coat the catalysts onto high-volume compatible substrates for low-cost integration into MEAs. The proposed candidate non-precious metal catalysts are based on the latest advances in fundamental understanding of the most promising areas of cathode catalyst development in the world. Sound scientific evidence from published data has been used to identify a new class of potentially active multi-element chemical centers for oxygen reduction. Two process methods, new for this purpose, will be investigated for synthesizing these new materials and applying them onto a 3M proprietary, high surface area, catalytic support system, compatible with high-volume roll-good processing of MEAs. The approach takes advantage of recent advances in 3M cathode catalyst development, which have significantly reduced the precious metal content of Pt-based ternary catalysts.

The proposed work is divided into two principal tasks. The first task is focused on development of the required new material properties. This will be accomplished through extensive catalyst fabrication and performance screening to obtain correlations of the material composition and structure characteristics with the desired electrochemical properties on the one hand and the various process parameters on the other. The second task is focused on scale-up of the materials and processes to demonstrate the feasibility for high-volume production and generate large area MEAs for PEM fuel cell stack testing. The proposed work covers a 3-year period.

Novel Non-Precious Metals for PEMFC: Catalyst Selection Through Molecular Modeling and Durability Studies (New FY 2004 Project)

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Objectives

- Construct and test membrane electrode assemblies (MEAs) with different non-precious metallic nanoclusters.
- Demonstrate the potential of non-precious metal catalysts to perform at least as well as the conventional Pt catalysts currently in use in MEAs and cost at least 50% less while meeting a target of 0.2 g (Pt loading)/peak kW.
- Optimize the catalyst composition for durability of >2000 hours operation with less than 10% power degradation.
- Perform slab band surface calculation of H_2O and OH adsorption on novel catalysts. Based on this, we will identify promising catalysts and optimize their compositions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Manufacturing Cost
- P. Durability
- Q. Electrode Performance

Approach

The goal of the proposed work is to construct and test membrane electrode assemblies (MEAs) with different non-precious metallic nanoclusters. The objective is to demonstrate the potential of non-precious metal catalysts to perform at least as well as the conventional Pt catalysts currently in use in MEAs and cost at least 50% less while meeting a target of 0.2 g (Pt loading)/peak kW. Apart from activity, optimization of catalyst composition will be based on durability of >2000 hours operation with less than 10% power degradation. Performance (activity and stability) of the following three different types of metallic nanoclusters will be extensively studied: (i) metal carbon nanoclusters; (ii) non-precious chalcogen compounds and (iii) binary transition metal microcycles. The approach takes advantage of recent accomplishments in USC cathode catalyst development which have drastically reduced the thickness of the catalyst layer and the precious metal content of Pt-based binary catalysts.

Theoretical studies will be conducted to determine the electronic, geometric, and thermodynamic factors that determine catalytic and electrocatalytic behavior as observed from the experimental characterization. Theoretical studies will comprise a series of high level *ab initio* investigations on representative clusters as well as on extended systems focusing on fundamental interactions relevant to adsorption and reaction processes.

The proposed work is divided into five tasks. The first task is focused on molecular modeling of novel catalysts. The work will include Vienna ab Initio Simulation Program (VSAB) slab band calculation to model surface adsorption of H_2O and O_2 reduction intermediates for the purpose of estimating their reversible potentials of formation. The second task is focused on synthesis of novel catalysts, which will include: (i) synthesis of metal carbon nanoclusters; (ii) synthesis of non-precious chalcogen compounds and (iii) synthesis of binary transition metal microcycles. The third task targets the material characterization of the catalysts. The fourth task focuses on electrochemical characterization, including electrochemical characterization of thin film membrane assemblies and optimization studies of nanostructured electrode/ electrolyte interface. The fifth task will optimize the stability of the catalysts. The objective of this task is to evaluate the long-term performance of the composite electrodes. Tafel and linear polarization (LP) technique and conventional three-electrode setup will be used to estimate the corrosion rates of the electrocatalysts in sulfuric acid. To test the long-term performance of the electrocatalyst under real environmental conditions, a single test cell will be used coupled with the test station. The infrared polarization test will be performed as a function of time (300 hours) at constant potential of 0.8 V.

This work will be done in collaboration between University of South Carolina (USC); Case Western Reserve University (CWRU), Cleveland, Ohio; and Northeastern University, Boston, Massachusetts.

Development of a Thermal and Water Management System for PEM Fuel Cells (New FY 2004 Project)

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Objectives

Develop an integrated thermal and water management (TWM) system that efficiently uses the fuel cell waste heat and water to minimize overall system weight and volume without compromising overall system efficiency

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- C. Thermal Management
- F. Heat Utilization
- R. Thermal and Water Management

Approach

For automotive applications, it is essential to develop a low-cost, high-performance thermal and water management (TWM) system for proton exchange membrane (PEM) fuel cells. The objective of this project is to develop an integrated TWM system that efficiently uses the fuel cell waste heat and water to minimize overall system weight and volume without compromising overall system efficiency. Water consumption and production will be balanced to eliminate the need for makeup water.

Waste heat generated by the PEM fuel cell cannot be easily removed from the system because it is supplied with a relatively low temperature. This requires heat exchangers with high effectiveness to achieve compact systems. Compact, lightweight heat exchangers of this type, having advanced heat transfer extended surfaces, have been developed for aerospace applications, where a premium is placed on size, weight, and performance. This heat transfer technology will be transitioned to Honeywell's automotive division, where high-volume manufacturing processes will be utilized to reduce costs of the equipment.

Some of the advanced technologies to be evaluated for accomplishing the objectives of the project include:

- An enthalpy wheel developed by Emprise Corporation, a member of the Honeywell team, utilizing latent heat transfer methods to greatly improve recovery of water and fuel cell waste heat.
- A membrane-based water management system developed by Isotronics, a member of the Honeywell team, that can be used to transfer water vapor from the hot and humid exhaust

stream from the fuel cell to the cooler and drier stream entering the fuel cell as reactant.
- A cathode recycle approach to avoid water condensation and revaporization.
- Microchannel thermal heat transfer equipment, an evolving technology that may lead to savings of 30 percent volume in the thermal management system over current technologies.

The analytical and test results of this study could have a dramatic impact on water and thermal management systems for PEM fuel cells for automotive applications. The project will be conducted over a three-year period in two phases.

Development of Polybenzimidazole-based, High-Temperature Membrane and Electrode Assemblies for Stationary and Automotive Applications (New FY 2004 Project)

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Objectives

- Select the appropriate polymer chemistry for polybenzimidazole (PBI) proton exchange membrane materials optimized to fuel cell requirements.
- Demonstrate the long-term performance of the PBI membrane, including mechanical, electrochemical, and operating properties, in cells and stacks.
- Provide a cost analysis of a low-cost membrane manufacturing process with projected costs consistent with meeting the specified high-volume targets.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Transportation Systems Barriers

- C. Thermal Management
- E. Durability
- F. Heat Utilization

Component Barriers

- P. Durability
- Q. Electrode Performance
- R. Thermal Management

Approach

The goal of this project is to optimize a high-temperature PBI membrane to meet the performance, durability, and cost targets required for stationary and automotive fuel cell applications. The ultimate result will be a low-cost PBI membrane material and a corresponding manufacturing process that will meet the DOE targets for a membrane that operates at greater than 120°C at pressures up to 3 atm with a projected design lifetime in excess of 40,000 hours. The corresponding membrane electrode assembly (MEA) cost targets are <$10/kW for 500,000 automotive fuel cell stacks per year and <$1,500/kW for 1,000 stationary fuel cell stacks per year. In this project, the Plug Power team will conduct extensive testing and verification of candidate PBI materials under automotive and stationary operating conditions, followed by selection of the best chemical composition and manufacturing process that will yield a highly reliable, low-cost membrane.

The proposed work covers a three-year period and is divided into three principal parallel and integrated technology focuses. The first focus addresses screening of candidate polymers and membrane fabrication processes. Film properties will be measured, and their relationship with polymer structure will be determined; the parameters that control film fabrication and manufacturing scale-up will be defined.

In the second focus, MEAs will be screened for numerous performance characteristics, followed by in-depth parametric studies for both short- and long-term applications. Scaled-up MEAs with active areas of at least 250 cm^2 will be assembled into and evaluated in short stacks.

The third focus is the development and demonstration of hardware optimized for PBI-based MEAs. Specifically, membrane/electrode interfaces, flow fields and acid management strategies will be investigated. Cathode performance improvements will be sought by optimizing standard electrode architectures and by investigating unique solutions such as nanotechnologies. The coupling of hardware and MEA performance will be a significant aspect of this work. A key deliverable will be a model to quantify the manufacturing cost of the selected PBI membrane.

The Plug Power team includes two university partners, Rensselaer Polytechnic Institute (RPI) in Troy, New York, and Albany NanoTech (ANT) at the State University of New York (SUNY) in Albany. The third partner is Celanese Ventures (GmbH), a polybenzimidazole (PBI) manufacturer.

Development, Characterization, and Evaluation of Transition Metal/Chalcogen Based Cathode Catalysts for PEM Fuel Cells (New FY 2004 Project)

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Objectives

Develop a non-precious metal cathode catalyst for proton exchange membrane (PEM) fuel cells which is as active and as durable as current platinum group metal (PGM) based catalysts at a significantly reduced cost.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost

Approach

The objective of this project is to develop a non-precious metal cathode catalyst for PEM fuel cells which is as active and as durable as current PGM based catalysts at a significantly reduced cost. The catalytic surfaces of interest are based upon non-precious transition metals such as Co, Ni, Cr and Fe in structures with non-stoichiometric amounts of chalcogens (S and Se) to produce the active sites in an oxygen containing environment.

The partnership Ballard Power Systems has with several universities, including the University of British Columbia and Case Western Reserve University, links together for the first time fundamental research on electrocatalysis and evaluation of catalysts in real fuel cell stacks. This project brings together scientific knowledge and innovation with commercial considerations and technological verification, giving an opportunity to deliver an application-ready material.

This work will study well defined surfaces to determine not only the magnitude of the activity but also the nature of the active site and the mechanism involved. The project will then proceed to develop a commercially viable, environmentally friendly process for the production of high surface area fuel cell catalysts for demonstration in fuel cell stacks.

The major advantages of this project are not just cost related, as the development of catalysts that are more specific for oxygen reduction than platinum leads to catalysts that are more robust and less sensitive to air-borne contaminants. The lower cost of a major component of fuel cell technology will significantly advance the fuel cell technology towards the marketplace in commercial products such as vehicles and portable power applications.

PEM Stack Durability (New FY 2004 Project)

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Objectives

- Develop a detailed understanding of the membrane electrode assembly (MEA) failure process
- Develop perfluorosulfonic acid (PFSA) membranes with extended lifetimes
- Model membrane failure modes
- Perform extended stack tests with the optimized membranes and characterize structure and degradation mechanisms
- Elucidate failure mechanisms and develop technologies to meet the design lifetime target of proton exchange membrane (PEM) fuel cells (40,000 hours operation with <10% degradation in performance for stationary applications in 2010)
- Perform research, development and demonstration of membrane/catalyst systems that address transportation and/or stationary applications

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Durability
- O. Stack Material and Manufacturing Cost

Approach

Proton exchange membrane fuel cell companies need a more durable, longer-lived, cost effective membrane technology. PEM systems based on PFSA membranes are better understood than their high temperature counterparts. This project focuses on risk reduction of previously identified PFSA membrane degradation mechanisms and validation of promising mitigation strategies.

DuPont has enlisted the unique experience and capabilities of the University of Connecticut and the University of Southern Mississippi to realize our goals. Our combined extensive experience, understanding of degradation mechanisms and proprietary membrane stabilization technology will provide a significant improvement in PFSA membranes that will achieve the DOE 2010 stack durability target of 40,000 hours for stationary fuel cells.

DuPont Fuel Cells, in partnership with United Technologies, will deliver a fuel cell system with a 40,000 hour PEM stack at an affordable price at the conclusion of this three-year project.

MEA and Stack Durability for PEM Fuel Cells (New FY 2004 Project)

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Subcontractors:
Plug Power Inc., Latham, NY
Case Western Reserve University, Cleveland, OH

Objectives

- Develop an understanding of membrane electrode assembly (MEA) failure mechanisms encountered under real world operating conditions.
- Develop a high performance MEA and matched system operating conditions having enhanced durability (targeted for 40,000 hours operation with <10% performance degradation in stationary applications).
- Characterize life expectancy and performance degradation of the MEA in extended testing (>2000 hours) in a field-ready fuel cell system using reformate fuel.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability

Approach

Proton exchange membrane (PEM) fuel cells are poised to change the landscape of power generation over the next ten years. Applications for portable power, back-up power, automotive power, and stationary power generation are being developed around the world. Estimates for the size of the fuel cell industry range as high as $50 billion by 2010. For this to be realized, however, considerable technical challenges still remain. The most significant of these challenges are those of cost and system lifetime, where 40,000 hours of operation with less than 10% decay is desired. In order to address these issues, we have assembled a team consisting of 3M, a materials and MEA manufacturer in the PEM fuel cell industry; Plug Power, a fuel cell stack and system manufacturer; and Case Western Reserve University, an electrochemical research institute with extensive knowledge of fuel cell technology.

In order to achieve the desired lifetime goals, the team will focus on (1) determining the root causes of MEA failure modes – membrane failure, catalyst activity losses, mass-transport losses, electrode losses (structural changes) and interfacial losses, and (2) using the information garnered from part one in the development of new materials and system designs to improve durability. The project plan has several innovative approaches, namely: (a) use of new perfluorinated sulfonic acid ionomers; (b) development of ex-situ component aging tests designed to separate out effects of individual material degradation mechanisms and correlation with real-time and accelerated in-cell performance tests; (c) assembly and testing of MEAs using virgin and aged components to identify how those aged components affect cell performance; (d) use of novel experimental approaches for determining the loci of degradation within the cell; (e) use of computational modeling of non-uniformities within a cell to characterize how non-uniformities affect failure modes and to design out the non-uniformities; and (f) system and materials perspective to understand the interactions of the stack design and operation on MEA performance and durability. Throughout this work, it is our intent to develop technologies that can accelerate the introduction of PEM fuel cell technology into a wider variety of applications that demand longer lifetimes. To accomplish this, Plug Power will evaluate the approaches and technologies identified to ensure that they are economically feasible in terms MEA cost and durability vs. a cost of energy model. The proposed work covers a three-year period.

Development of a Low-Cost, Durable Membrane and Membrane Electrode Assembly for Stationary and Mobile Fuel Cell Applications
(New FY 2004 Project)

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Objectives

- Develop low-cost, high-durability membranes and membrane electrode assemblies (MEAs) for polymer electrolyte membrane (PEM) fuel cells.
- Improve the Kynar® polyvinylidenefluoride (PVDF) based membrane, particularly regarding conductivity and water management. The result of this work will be an optimized composition of Atofina's polymer alloy yielding a high-conductivity/low-cost membrane at the laboratory scale.
- Prepare suitable electrodes for the Kynar® PVDF membrane.
- Develop manufacturing processes for polyelectrolyte ionomer, membranes, and high-performance MEAs.
- Run long-term endurance tests in fuel cells, evaluate possible degradation and degradation mechanisms and, in parallel, develop accelerated tests to provide faster feedback to the synthetic effort related to the membrane and the polyelectrolyte ionomer.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost

Approach

The objective of this project is to develop low-cost, high-durability membranes and membrane electrode assemblies (MEAs) for polymer electrolyte membrane (PEM) fuel cells. The team members, lead by Atofina, are Johnson Matthey Fuel Cells, UTC Fuel Cells, the Georgia Institute of Technology and the University of Hawaii.

The technical approach is based on technology developed by Atofina exploiting the unique properties of its Kynar® polyvinylidenefluoride (PVDF). Kynar® offers a unique combination of exceptional chemical and electrochemical stability, excellent mechanical properties, low flame and smoke properties, and recyclability at a low cost. Atofina turned to its own fluoropolymers technology to seek cost-effective solutions, which also could offer several other significant benefits in terms of improved mechanical properties and high-temperature performance. These membranes and MEAs have the potential to operate at higher temperatures than conventional fluoroionomers (of the Nafion® type) and offer high durability.

The mechanical characteristics of membranes prepared from Kynar® PVDF are excellent. The films are sturdy; they show very good tear resistance and negligible creep at all temperatures tested (as high as 120°C). Johnson Matthey Fuel Cells reported permeability to hydrogen on the order of 1/3 of that of Nafion, a very desirable property. The combination of excellent mechanical properties and low gas permeability offers the exciting prospect to make high-performance, thin membranes. In this respect, it is noteworthy that it is the resistance of the membrane/MEA which dictates proton conductivity – not the intrinsic conductivity (i.e., thinner membranes have a lower resistance than thicker membranes).

The project's technical work is divided into three major tasks. Task 1 is membrane development led by Atofina in collaboration with Georgia Tech, particularly on high-throughput membrane composition screening and characterization. The deliverables of Task 1 are a high-conductivity, low-cost membrane (lab scale). Task 2, MEA development, is led by Johnson Matthey Fuel Cells, with substantial input from Atofina for the polyelectrolyte ionomer. The deliverable of Task 2 is a high-performance, low-cost MEA produced on a pilot line featuring high durability. Task 3, cell and stack development and verification, is led by UTC Fuel Cells with the help of the University of Hawaii. The product of Task 3 will be a multiple-cell stack meeting DOE's goals. The three tasks will be conducted in sequence with substantial overlap for feedback loops. The total duration of the project is anticipated to be 36 months.

Atofina is the fourth largest chemical company in the world. It has a major focus on thermoplastics polymers, and it is the largest producer of PVDF. The project will be conducted in its state-of-the-art Research Center located in King of Prussia, Pennsylvania. Johnson Matthey Fuel Cell (JMFC) is a business unit of Johnson Matthey PLC, a specialty chemicals company and a leader in platinum and platinum catalysts. JMFC is a leading developer of fuel cell components, particularly catalysts and MEAs. The work will be carried out primarily in West Chester, Pennsylvania. UTC Fuel Cells (UTCFC) is a unit of the United Technologies Corporation and is a leader in the development, manufacturing, and operations of fuel cell power plants. Their part of the project will be conducted partly in South Windsor, Connecticut, and partly at the University of Hawaii. The University of Hawaii, in collaboration with the Hawaiian Electric Company, UTCFC and the Office of Naval Research, has established a first class facility for testing and evaluating full-size single-cell and multi-cell fuel cell stacks. Georgia Tech has very special expertise in the field of high-throughput and combinational techniques. Atofina will utilize these techniques to screen and optimize large numbers of compositions in an efficient manner.

Neutron Imaging Study Of the Water Transport Mechanism in a Working Fuel Cell

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Objectives

- Quantify water content in fuel cell.
- Quantify water dynamics in fuel cell.
- Optimize neutron imaging spatial and temporal resolutions.
- Demonstrate neutron imaging as a tool for analyzing water management and performance of operational fuel cells.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- R. Thermal and Water Management
- P. Durability

Approach

- Stage 1. Based on previously established design parameters and goals, the facility was designed and the components manufactured. Careful radiation safety analysis was performed to ensure the effectiveness of radiation protection at the facility.
- Stage 2. Parallel discussions were held with fuel cell developers to evaluate a realistic fuel cell system in-situ. This included the use of a fuel cell and a fuel cell controller to monitor the operation of a fuel cell during operation on the neutron beam line.
- Stage 3. Assembled facility is extensively tested for radiation protection.
- Stage 4. Fuel cell experiments are run to observe the flow field dynamics and water build-up and clogging in the gas diffusion layer (GDL).

Accomplishments

- Designed and built a neutron imaging facility.
- Demonstrated real time neutron imaging method.
- Examined operational fuel cells for fuel cell component developers.

Future Directions

- Evaluate coded source imaging as a method for high-resolution real time imaging.
- Provide license-free distributable software for fuel cell developers to independently analyze fuel cell operation data.

- Upgrade detector systems to allow both:
  - oreal time frame rate (30 fps) and
  - ohigh spatial resolution.
- Conduct both non-proprietary and proprietary imaging experiments to improve knowledge of how water management systems function in fuel cells.
- Develop neutron imaging methods to accurately measure water gradients across a fuel cell proton exchange membrane (PEM).
- Determine diffusion coefficient and hydrophobic characteristics of the GDL.
- Characterize the two-phase flow mechanism in the fuel cell flow field.
- Conduct a time-dependent study of the membrane-catalyst-GDL interface integrity.

Introduction

In a fuel cell, water is formed as a byproduct of the reaction between hydrogen and oxygen. If the water does not drain quickly and efficiently, then fuel cells will not work properly. Water formation is also a signature of activity in a fuel cell, so the lack of water formation demonstrates a defective area of the fuel cell.

Since fuel cells are not transparent to visible light, other forms of penetrating radiation (example: x-rays, neutrons) must be used to analyze the operation of the fuel cell. X-ray imaging is unsuitable because hydrogen is nearly invisible to the high-energy x-rays required to penetrate the metallic encasement of the fuel cell. Neutrons, which are massive, neutrally charged particles, can easily penetrate metals and still be extremely sensitive to water in quantities less than a microgram. The reason for this is best illustrated by a comparison of the relative cross sections shown in Figure 1. The large x-ray cross section of Al compares to a small neutron cross section. Conversely, the x-ray cross section for hydrogen is small compared to the neutron cross section. This makes neutrons ideal for sensing microgram quantities of water.

Approach

A new Neutron Imaging Facility (NIF) has been constructed at the BT6 high intensity thermal beam line at the NIST Center for Neutron Research (NCNR) nuclear reactor (Figure 2) to non-destructively characterize water transport mechanism in single or multi-stack PEM fuel cells. The facility features a very high uniform neutron flux and high spatial resolution over area (Figure 3). The high neutron flux will allow attaining a time resolution of less than 1 second and a spatial resolution as low as 10-30 mm with an appropriate neutron detector.

Experimental tests of the facility have been performed in collaboration with various fuel cell

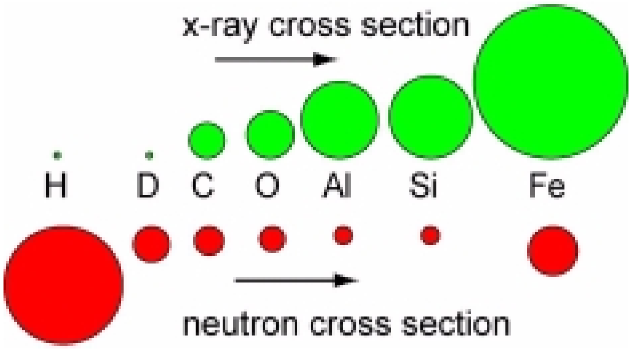

Figure 1. Comparison of X-Ray Cross Sections to Neutron Cross Sections (The neutron cross section for hydrogen is much larger than the higher Z elements. The converse is true for x-ray cross sections.)

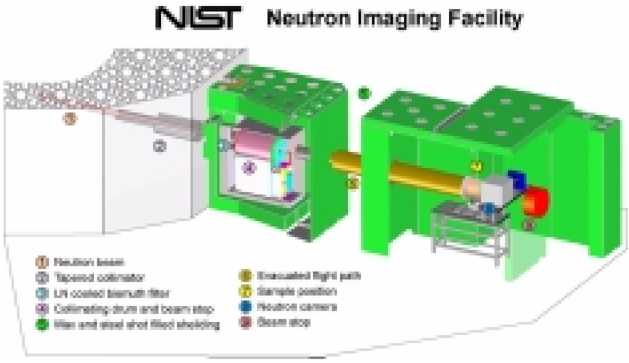

Figure 2. New Neutron Imaging Facility Online at NIST

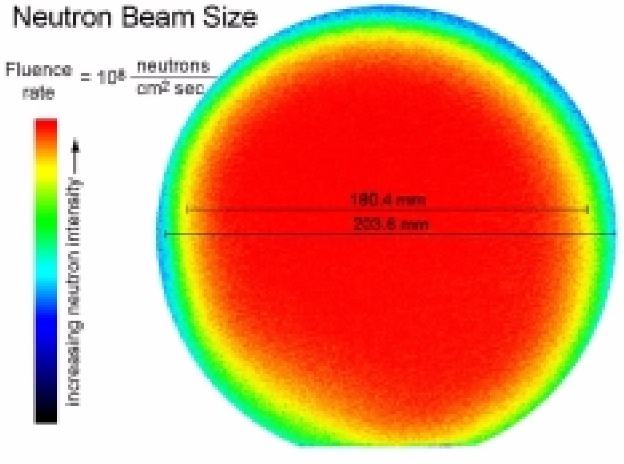

Figure 3. Neutron Beam Size and Intensity Distribution (Beam diameter in the uniform region is about 18 cm.)

developers. The results of these tests are currently being evaluated for the design of future tests. Currently, the facility provides hydrogen (currently 1.2 liters/minute), air and nitrogen gasses for users of the facility. Users are required to provide a fuel cell controller to match the fuel cell used in the facility. We shall incorporate a generic single cell fuel cell controller to the setup in the very near future.

Results

An example neutron image is shown in Figure 4. In the image, the gas distribution system of a fuel cell shows up as the serpentine race tracks. The purpose of these channels is to distribute gas evenly to the membrane and to act as a drain for water coming out. In these images, the neutrons easily penetrate the fuel cell when dry. As the fuel cell runs, water builds up and appears as a darker shadow region. Computer analysis, shown as the colorized (bottom) image in Figure 4, allows the dry cell to be removed, revealing only the water formation in both the flow channels and the gas diffusion media. In Figure 4, large amounts of water appear as red, and dry regions appear as black.

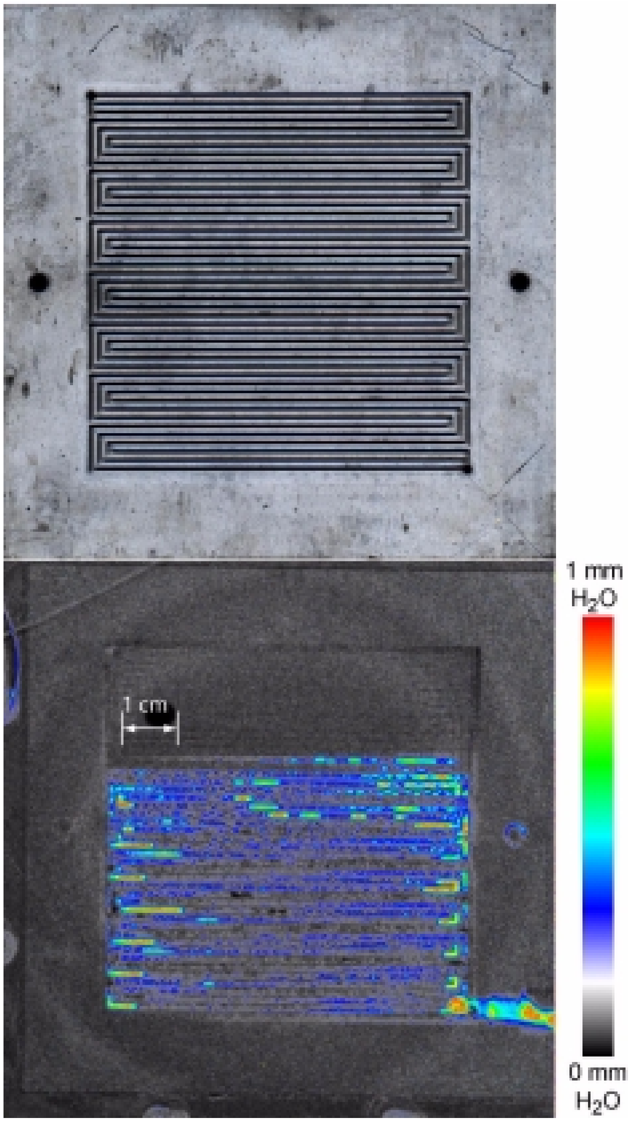

Figure 4. (Top) Photo of the Graphite Flow Channels; (Bottom) Processed Neutron Image of the Water Formed During Operation of the Cell

At the imaging station, the largest fuel cell that can be imaged is about 20 cm x 20 cm. A sample of larger length can be imaged section by section through translation of the sample. The fuel cells also can be single-stack or multi-stack. The facility will operate as a user facility where proposals submitted will be required to be reviewed for merit before allocating beam time. A generic fuel cell test station will be available for general use, but users will be free to bring their own if needed.

Conclusions

- A neutron imaging facility now exists at NIST.
- High neutron flux of about 10^8 $sec^{-1}cm^{-2}$ has been achieved.

- High spatial resolution of 20 µm - 200 µm has been achieved.
- In-situ analysis of fuel cell water management using neutron imaging is now possible.
- Near real time analysis of fuel cell operation is now possible.

FY 2003 Publications/Presentations

1. Invited talk at 'Plug Power', Albany, NY, March 2002. 'Investigation of fuel cell water transport using thermal neutron imaging techniques.'
2. Presentation at DOE fuel cell conference, Denver, CO, May 2002. 'High flux thermal neutron imaging station for fuel cell research.'
3. Invited talk at Argonne National Laboratory, Argonne, IL, June 2002. 'Neutron imaging technique to determine diffusion co-efficient of Li ions in Li ion conductors.'
4. Invited talk at Dupont, Wilmington, DE, February 2003. 'NDE of fuel cell via neutron imaging.'
5. "In-situ neutron imaging techniques for evaluation of water management systems in operating PEM fuel cells", Submitted to "Journal of Power Sources."

Low-Friction Coatings and Materials for Fuel Cell Air Compressors

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Objectives

Develop and evaluate the friction and wear performance of low-friction coatings and materials for fuel cell air compressor/expander systems. Specific goals are:

- 50 to 75% reduction in friction coefficient
- One-order-of-magnitude reduction in wear
- Transfer of the developed technology to DOE industrial partners

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Compressors/Expanders

Approach

- Identify critical compressor components requiring low friction.
- Apply Argonne's near-frictionless carbon (NFC) coatings to the components where appropriate and evaluate.
- Develop polymer composite materials containing boric acid solid lubricant and evaluate.
- Develop tribological mechanism-based material selection methodology for various compressor/ expander components.

Accomplishments

- Identified the radial air bearings and thrust bearings of Meruit's turbocompressor as components that require both low friction and low wear rate for satisfactory performance.
- Thrust washer wear tests showed that Argonne's NFC coating reduced friction by about four times and wear rate by two orders of magnitude. Both exceeded the project goals.
- NFC coatings increased the scuffing resistance of a steel surface about 10 times.
- NFC-coated air bearing hardware components are currently undergoing durability testing.
- Completed initial friction and wear testing of Nylon-12 polymer with B_2O_3 addition. Significant reduction in wear was observed with the addition of B_2O_3, especially under high relative humidity.
- Achieved 50% reduction in friction for application in Variex-variable displacement compressor/ expander using Hitco C/C composite and anodized Al contact pairs.
- Designed and constructed a new high-speed friction and wear test rig for evaluating materials for Mechanology's torroidal intersecting vane machine (TIVM).

- Evaluated high-speed frictional performance of several candidate materials and coatings for TIVM vanes.

Future Directions

- Develop a tribology-based material selection methodology for compressor and blower components.
- Compile a database of pertinent candidate material and coating properties.
- Conduct a detailed tribological performance evaluation of TIVM select candidate materials based on high-speed frictional behavior.
- Optimize NFC coating for TIVM vane application.
- Coat TIVM components with optimized NFC for rig testing at Mechanology.
- Initiate efforts to address tribological issues in AD Little and UTC Fuel Cells, Inc. compressor/ expander programs.

Introduction

A critical need in fuel cell systems for vehicles is an efficient, compact, and cost-effective air management system to pressurize the fuel cell systems to about 3 atmospheres. Pressurization of fuel cells will result in higher power density and lower cost. Because no off-the-shelf compressor technologies are available to meet the stringent requirements of fuel cell air management, several compressor and blower systems are currently being developed for DOE by different contractors. The efficiency, reliability and durability of compressors depend on effective lubrication or friction and wear reduction in critical components such as bearings and seals. Conventional oil or grease lubrication of compressor components is not desirable because such lubricants can contaminate and poison the fuel cell stack. The objective of this project is to develop and evaluate low-friction coatings and/or materials for critical components of air compressor/expanders being developed by various contractors for DOE vehicular fuel cell systems. The work this year focused on evaluation of materials and coatings for Mechanology's TIVM, as well as the development of generalized material selection methodology for compressor components.

Approach

For various air compressor/expanders being developed, we will identify the key critical components that require low friction coefficient and wear resistance. Over the years, the tribology group at Argonne has developed low-friction and low-wear coatings and materials. Most notable is the discovery of an amorphous carbon coating with extremely low friction coefficients (<0.001 in dry nitrogen) and very low wear. Where appropriate, the NFC coating will be applied to the critical component(s). Other commercially available low-friction coatings will be evaluated for various applications. In some cases, alternative low-friction polymeric materials and other low-friction coatings will be evaluated.

Results

Mechanology TIVM. The primary sources of friction in the TIVM are the vane sliding interface, the housing compressor seal and expander bearings. Design analysis shows that overall system friction coefficient less than 0.3 is required to meet the DOE program target for efficiency. The most critical of the three TIVM friction sources is the vane sliding interface because of its high sliding speed of 60-75 m/s. Selection of appropriate vane material is critical for successful operation of the TIVM compressor/ expander. As reported last year, preliminary frictional behavior as a function of sliding speed was evaluated for several material and coating (including NFC) combinations. Some material combinations with adequate friction behavior at high sliding speeds were identified.

More detailed tribological evaluations were conducted for potential TIVM vane materials. The three-ball-on-disc high speed test rig was refurbished to make it more robust. The normal and tangential forces are now measured by a three-axes load cell (Figure 1). This will allow more accurate measurement of friction coefficient as the variation in the normal force is taken into account. The test rig is also now equipped with an environmental coated chamber, allowing the variation of relative humidity. Friction and wear tests were conducted as a function of sliding speed for candidate vane materials and coatings at ambient room relative humidity (~30% RH) and at 100% relative humidity. Figure 2 shows the variation of the friction coefficient with sliding speed for various materials and coatings meeting the friction requirement of 0.3 under ambient room air. The lowest friction coefficient was obtained when both the disc and the ball surfaces were coated with NFC. Steel on polyetheretherketone (PEEK) shows friction coefficients less than 0.15 for the speed range evaluated. Under 100% relative humidity, the friction coefficients for all the materials evaluated were lowered (Figure 3). This may be due to hydrodynamic lubrication by the presence of water at the sliding interface. At the very high sliding speed, the friction coefficients for all material pairs were approaching the same value. This is consistent with the possibility of hydrodynamic lubrication by water. Figure 4 shows the wear on balls of various materials sliding on PEEK and NFC-coated discs. Minimal wear was observed on the balls sliding on PEEK, except for brass (Figure 4, top). Due to higher hardness of the NFC coating, it produced more wear on the balls slid against it (Figure 4, bottom).

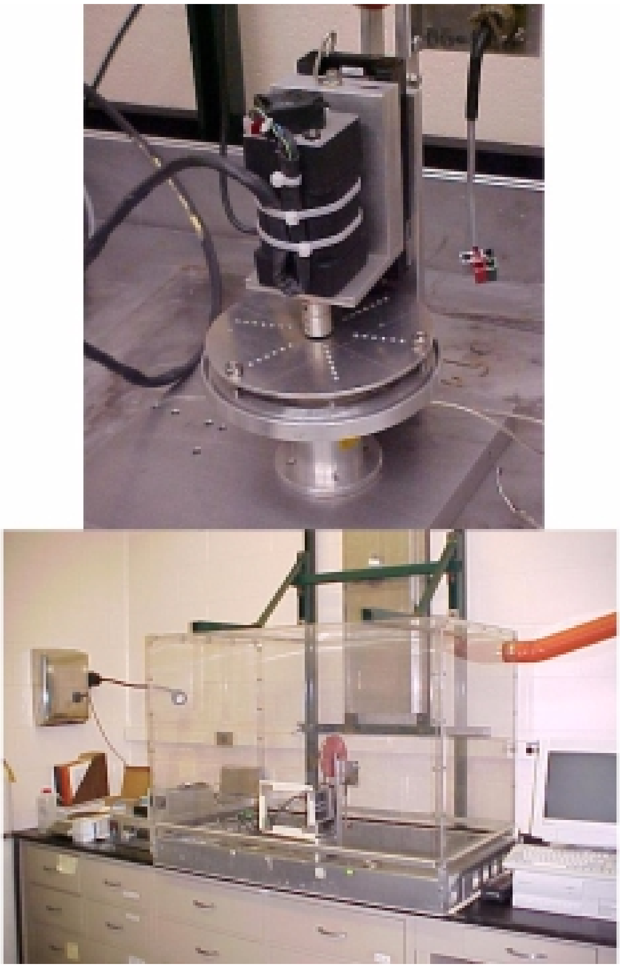

Figure 1. Picture of Modified High Speed Friction and Wear Test Rig With 3-Axes Load Cell and Environmental Chamber for Humidity Control

Conclusions

More detailed friction and wear evaluation of candidate materials and coatings for Mechanology TIVM vanes showed that humid air will not have adverse effects on the friction behavior of these materials, at least for a short duration of time. Long-

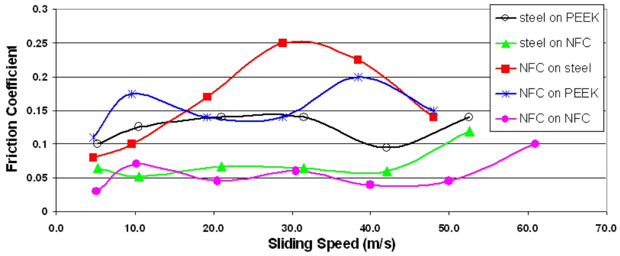

Figure 2. Variation of Friction Coefficient with Sliding Speed for TIVM Vane Candidate Material and Coating Combinations in Ambient Room Air (30% RH)

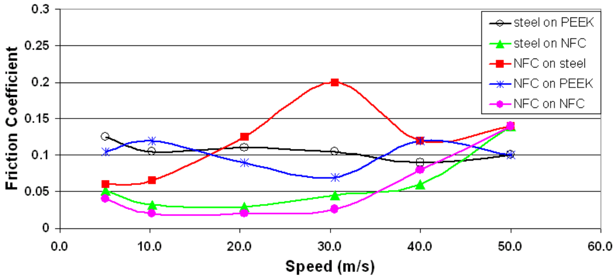

Figure 3. Variation of Friction Coefficient with Sliding Speed for TIVM Vane Candidate Materials and Coatings under 100% Relative Humidity

term effect of humidity must be assessed as part of future efforts.

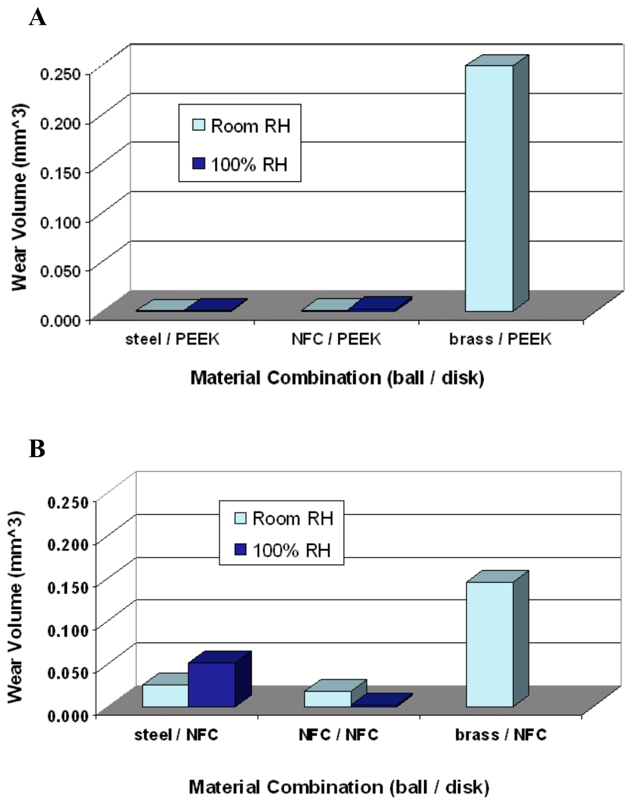

Figure 4. Wear Volume in Various Balls Slid Against (top) PEEK Disc and (bottom) NFC-Coated Steel Disc

FY 2003 Publications/Presentations

1. O. O. Ajayi, A. Erdemir, and G. R. Fenske, "Low Friction Coatings and Materials for Fuel Cell Compressor & Blowers," 2003 Merit Review and Peer Evaluation Meeting, May 19-22, 2003. Berkeley, California.

Bipolar Plate-Supported Solid Oxide Fuel Cell

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Objectives

Develop an improved solid oxide fuel cell (SOFC) for auxiliary power units (APUs).

- Improve mechanical properties (i.e., vibration and shock resistance).
- Improve cell power output by eliminating the contact resistance between cell and interconnect layers.
- Reduce materials costs.
- Develop a low-cost fabrication method.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- D. Fuel Cell Power System Benchmarking
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration And Efficiency
- O. Stack Material And Manufacturing Cost
- P. Durability
- Q. Electrode Performance

Approach

- Support a SOFC on a metallic bipolar plate rather than a ceramic layer.
- Reduce the thickness of the anode layer.
- Fabricate cell components using powder metallurgy processing.
- Sinter cell components in one high-temperature processing step.

Accomplishments

- Achieved sintered laminate of flow fields, bipolar plate, anode, and electrolyte.
- Demonstrated that the bipolar plate-supported SOFC has four times the strength of an anode-supported cell.
- Achieved an open-circuit voltage of 1.14 V (>99% of theoretical value).
- Achieved a single-cell power output >260 mW/cm².

Future Directions

- Design and fabricate a short stack (2 cells) to achieve an open-circuit potential that is >90% of the theoretical value on hydrogen/air.

- Test two-cell stack on simulated reformate/air.
- Test startup time, cyclability, and durability.
- Investigate improved materials for the metallic support, anode, and cathode.
- Improve fabrication procedure.
- Collaborate with universities, industry, and other national laboratories.

Introduction

Solid oxide fuel cells (SOFCs) are attractive power sources for vehicular auxiliary power applications because they exhibit high power densities and efficiencies, have simplified fuel-reforming requirements, and are fuel-flexible. However, their high operating temperature and the brittle nature of their ceramic cell components have precluded their use. SOFCs have traditionally been operated at ~1000°C because the cell support was a thick doped-zirconia electrolyte layer. Recently, the operating temperature has been lowered to 650-800°C by supporting the cell on a thick ceramic-metal (cermet) anode layer and decreasing the thickness of the electrolyte layer to <20 µm, thus decreasing its resistance. The lower operating temperatures have made SOFCs more viable for transportation applications, allowing better thermal integration with the fuel reformer (operating at ~700°C), the use of metallic flow fields and interconnects, and shorter startup times. However, there are still barriers to the use of SOFCs for these applications, including (1) susceptibility to cracking due to vibration, impact, and thermal shock; (2) contact resistance between the cell components; and (3) high materials and manufacturing costs. The bulk of the materials costs of the anode-supported SOFC lies in the large amount of zirconia in the thick anode support and the cost of expensive alloys in the bipolar plate. The use of a cermet layer to support the cell also makes the cell fragile and susceptible to damage by thermal shock.

Approach

Argonne researchers are developing a design concept, called the TuffCell, to address the issues facing the use of SOFCs in APU applications. The objective of the Argonne effort is to improve mechanical properties, eliminate contact resistance between the cell and interconnect layers, reduce materials costs, and use low-cost fabrication methods. In the TuffCell concept, the brittle electrolyte and anode layers are co-sintered with the metallic gas flow fields and bipolar plate, forming an integrated repeat unit for stacking. The metallic bipolar plate serves as the cell's support, which increases the mechanical strength and thermal cyclability of the cell. The bulk of the bipolar plate can be made of inexpensive stainless steels, with thin passivating layers at the surfaces exposed to the corrosive fuel and oxidant atmospheres. Materials costs are reduced by using thin layers of electrolyte, anode, and metal alloys on an inexpensive metallic support. In contrast to state-of-the-art SOFC fabrication, which includes several high-temperature sintering steps, this method uses a single-step powder metallurgy process carried out in a programmed atmosphere. Eliminating multiple high-temperature processing steps reduces fabrication costs.

Each component layer of the cell is formed using tape-casting or slurry-coating methods and laminated with other components to form a single stack unit. Laminates containing the electrolyte, anode, fuel flow field, bipolar plate, and air flow field are sintered together in a controlled-atmosphere tube furnace. The cathode is applied and sintered *in situ* during the initial heating of the cell or stack. Figure 1 shows a schematic and photo of the TuffCell stacking unit.

Results

Several cells varying in thickness have been fabricated using the TuffCell approach. Figure 2 is a scanning electron micrograph of a laminate cross section prior to application of the cathode. This particular laminate consists of a 10-µm electrolyte, 120-300-µm anode, 600-µm flow fields, and a 200-

µm bipolar plate. All of the layers were well bonded, and the electrolyte and bipolar plate were gas-impermeable. The flow fields have 70-80% porosity, and the overall thickness of the laminate is 1.5 mm.

Figure 3 illustrates the improvement in fracture strength of a bipolar plate-supported SOFC over a pre-reduced conventional anode-supported SOFC. The first inflection in the metal-supported SOFC curve marks the fracture of the electrolyte. Further displacement shows the effects of metal ductility. The anode-supported cells fracture in a brittle failure, showing one-quarter of the strength of the bipolar plate-supported SOFC.

Figure 4 shows the improvements in single-cell polarization and power density achieved since the FY 2002 Annual Report. These improvements were realized by improving the microstructure of the nickel-yttria-stabilized zirconia cermet anode to enhance the electrical conductivity (August 2002), and by using a doped-cobaltite cathode with a doped-ceria interlayer (November 2002) rather than the doped-ferrite cathode used in the past.

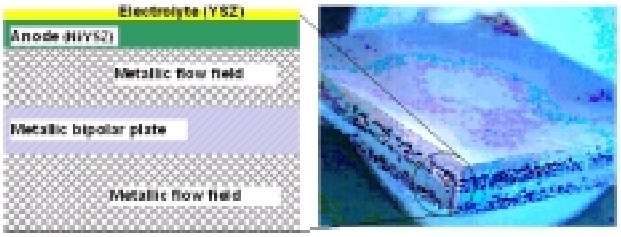

Figure 1. Schematic and photograph of the bipolar plate-supported SOFC stacking unit.

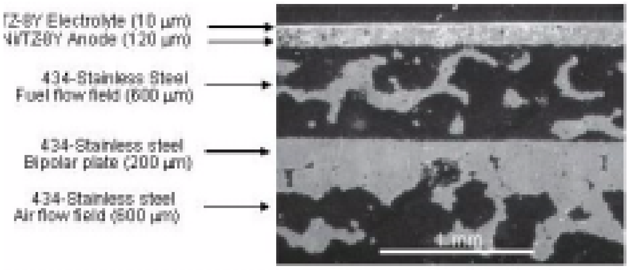

Figure 2. Scanning electron micrograph of a sintered bipolar plate-supported SOFC laminate. The laminate contains a dense electrolyte and bipolar plate as well as a porous anode and flow fields. The flow fields are continuously connected below the plane of the figure, achieving a well-bonded monolithic unit.

One of the bipolar plate-supported cells was cycled between room temperature and 800°C at 10°C/min to determine the tolerance of the cells to temperature cycling. Figure 5 shows that there is no degradation in the electrochemical performance of the cell after two temperature cycles (the test was terminated after two cycles).

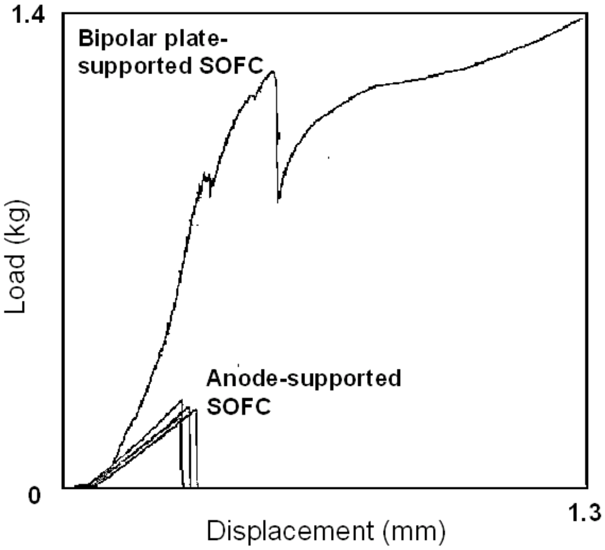

Figure 3. Load vs. displacement results of a 4-point bend test comparing the strength of the metal-supported SOFC with the conventional anode-supported SOFC.

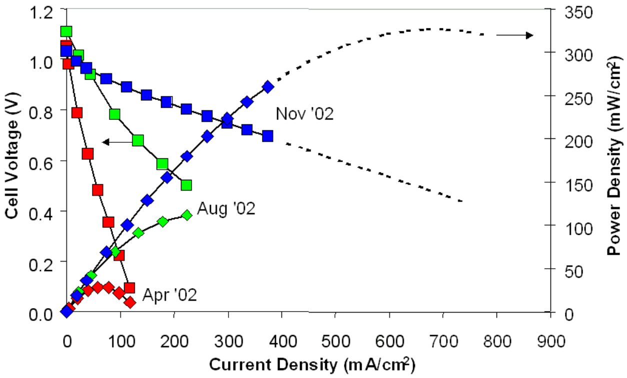

Figure 4. Improvement in the single-cell polarization and power density of the bipolar plate-supported SOFC. Cells were tested at 800°C with hydrogen anode gas and oxygen cathode gas.

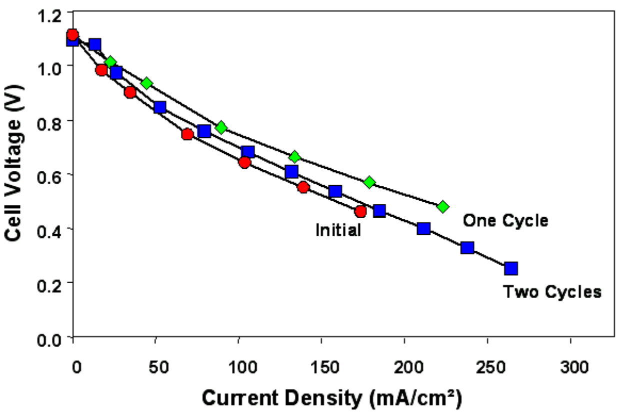

Figure 5. Single-cell polarization curves after cycling the cell temperature between 800°C and room temperature at 10°C/min. The cell was tested at 800°C with hydrogen anode gas and air cathode gas.

Conclusions

A new design and fabrication concept is being developed for the SOFC to address the shortcomings of current designs for portable applications. The design supports the cell on a metallic bipolar plate, and fabrication uses ceramic and powder-metal processing to construct a monolithic unit bonding the flow fields, bipolar plate, anode, and electrolyte in one high-temperature sintering step. Results of four-point bending tests showed that the sintered laminates have four times the load-to-failure capabilities of conventional anode-supported cells. This means that handling and stacking these cells should be easier, and the stacks should be more mechanically robust. Single-cell electrochemical tests at 800°C on hydrogen and air achieved a power density of >250 mW/cm^2. With proper refinements to the design and electrode layer compositions, significant improvements in the power density are expected.

Future work will also focus on increasing the individual cell size; building short stacks of cells; testing these stacks using hydrogen and simulated reformate; and determining start-up time, the ability to cycle the temperature, and cell durability. The ultimate goal of this research is to develop rugged, high power density, low-cost stack units made by a commercially viable manufacturing process.

FY 2003 Publications/Presentations

1. T. A. Cruse, J.-M. Bae, J. D. Carter, R. Kumar, and M. Krumpelt, "A Novel Approach to Making Metallic Interconnects for Planar Solid Oxide Fuel Cells," 2002 Fuel Cell Seminar, Palm Springs, CA (2002).

2. J. D. Carter, J. M. Ralph, J.-M. Bae, T. A. Cruse, C. Rossignol, M. Krumpelt, and R. Kumar, "Improved Materials and Cell Design for Mechanically Robust Solid Oxide Fuel Cells," 2002 Fuel Cell Seminar, Palm Springs, CA (2002).

3. J. D. Carter, T. A. Cruse, J.-M. Bae, J. M. Ralph, D. J. Myers, M. Krumpelt, and R. Kumar, "Bipolar Plate-Supported Solid Oxide Fuel Cells for Auxiliary Power Units," Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA (2002).

4. J. D. Carter, T. A. Cruse, J.-M. Bae, J. M. Ralph, C. Rossignol, D. J. Myers, R. Kumar, and M. Krumpelt, "Application of Cathode Materials to Co-Sintered Metal Supported SOFC," American Ceramic Society 105th Annual Meeting, Nashville, TN (2003).

5. J. D. Carter, T. A. Cruse, J. M. Ralph, and D. J. Myers, "Powder Metallurgy and Solid Oxide Fuel Cells," 2003 International Conference on Powder Metallurgy and Particulate Materials, Las Vegas, NV (2003).

Special Recognitions & Awards/Patents Issued

1. J. D. Carter, J.-M. Bae, T. Cruse, J. M. Ralph, R. Kumar, and M. Krumpelt, "Solid Oxide Fuel Cell with Improved Mechanical and Electrical Properties" (2002).

Assessment of Fuel Cell Auxiliary Power Systems for On-Road Transportation Applications

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Objectives

- Assess the viability of the use of proton exchange membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs) as auxiliary power units (APUs) for on-road vehicles.
- Identify major technical issues and key risk areas and determine research and development (R&D) needs and possible DOE roles.
- Project potential fuel cell APU benefits to the nation.
- Assess how fuel cell APUs may accelerate market introduction of fuel cells for propulsion and hybrid transportation applications.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- D. Fuel Cell Power System Benchmarking

Approach

- Determine PEMFC and SOFC performance parameters.
- Identify and select three promising near-term and future fuel cell APU applications.
- Develop design concepts and evaluate benefits and cost impacts for the three selected APUs.
- Perform an R&D gap analysis, determining gaps among fuel cell cost and technical performance/market needs.

Accomplishments

- Identified direct hydrogen PEMFCs as the most attractive near-term fuel cell technology and diesel-fueled partial oxidation (POX) fuel processor with planar anode-supported SOFCs as the most attractive longer-term fuel cell technology for on-road transportation APU applications.
- Characterized fuel cell/APU applications including medium- and heavy-duty trucks and light-duty vehicles.

- Solicited data and feedback for promising APU applications and completed inventory of data gaps (e.g. capacity, fuel capability, duty cycle).
- Selected three APU applications for conceptual design and vehicle integration analysis including diesel-fueled POX/SOFC APUs for long-haul trucks and transit buses, and direct hydrogen PEMFC APUs for law enforcement vehicles.
- Estimated APU versus idling engine efficiency and emissions at rated power and part load for the three selected applications.
- Projected annual fuel and emissions savings using fuel cell APUs in three selected applications.

Future Directions

- Evaluate the benefits of a truck refrigeration unit (TRU) and perform a detailed analysis if appropriate.
- Finalize vehicle integration layouts and cost analysis for three fuel cell APU systems.
- Finalize comparisons of conceptual systems with competing technologies.
- Determine R&D gaps among fuel cell cost and technical performance/market needs.

Introduction

Over the last five years, interest in the use of fuel cells for auxiliary power units (APUs) in vehicles has risen, particularly for truck idling and truck refrigeration unit (TRU) applications, driven by increasingly stringent idling and TRU regulations. Fuel cell powered APUs have the potential to reduce emissions, noise, vibration, fuel consumption, and size relative to conventional, internal combustion engine (ICE) APUs. In this work, the DOE has commissioned TIAX to assess the viability of the use of proton exchange membrane fuel cells and solid oxide fuel cells as APUs for on-road vehicles.

Approach

After determining the fuel cell APU performance parameters, we selected three promising fuel cell APU applications, developed conceptual designs, and assessed the potential benefits of the systems. We concentrated on PEMFC and SOFC technologies and applications likely to be attractive at the present time and extending to 2010. We addressed applications that use the existing fuel infrastructure (namely gasoline and petroleum diesel), alternative fuels (e.g. propane), and future fuels (hydrogen). We considered passenger cars, class 1 and 2 light-duty trucks and sport utility vehicles (SUVs), class 3-8 trucks, recreational vehicles, transit buses, and specialized vehicle applications. Military applications are not part of the current scope of work.

The project involves five tasks: project kick-off, identification and selection of APU systems, development of design concepts and evaluation of potential benefits, analysis of R&D gaps, and analysis update after delivery of the draft final report.

Results

The key factors that influence fuel cell APU technology selection are cost, weight (i.e. power density), efficiency, and system volume. Other important factors are technology maturity, fuel capability/flexibility (and associated complexity of a fuel reformer), startup time, and fuel cell stack life. A high-level ranking showed that direct hydrogen PEMFC was the most attractive near-term technology and diesel-fueled partial oxidation (POX) fuel processor with planar anode-supported SOFC was the most attractive longer-term technology for fuel cell APUs.

Two types of screens were used to identify three applications for detailed analysis. The initial screening criteria focused on application characteristics:

- Duty cycle - vehicle accessory duty cycle (i.e. load profile) should be suited to APU use (e.g. hotel loads during idle times)

- Market size - market potential must be adequate to support investment in APU technology
- Vehicle cost - initial vehicle cost must be high enough that an APU would likely represent a relatively small portion (<15 %) of the total cost

The second screening criteria focused on both the short- and long-term benefits related to:

- Energy savings
- Emissions savings
- Cost savings
- Acceleration of fuel cell technology commercialization

Vehicle applications meeting both screening criteria were long-haul truck cabs, transit buses, and law enforcement vehicles. Both long-haul trucks and the transit bus applications are attractive longer-term SOFC APU applications because they have potential to reduce fuel use and emissions significantly at relatively modest additional capital cost. As designed, both the truck and bus APU applications process the on-board diesel fuel in a POX reformer to generate fuel for the SOFC. Law enforcement vehicles are an attractive near-term PEMFC APU application because they are often centrally refueled and maintained by a fleet operator, mitigating alternative fuel infrastructure problems. They have the potential to accelerate fuel cell introduction by employing direct hydrogen fueling and storage, as well as to reduce fuel use and emissions. Law enforcement vehicles are also attractive because of their relatively low cargo needs, leaving space available for compressed hydrogen fuel tanks. For the purposes of this analysis, we assume the law enforcement vehicle has a hydrogen ICE powertrain and a direct hydrogen PEMFC APU.

Accessory duty cycle and fuel cell system efficiency are used in a modified drive cycle model to estimate fuel consumption, emissions, and fuel cell sizing for the APU. Figure 1 illustrates the conceptual framework of the modified ADVISOR drive cycle model. Representative vehicle duty cycle(s), fuel cell performance data, and engine-specific emissions and fuel consumption maps are input, and fuel and emissions estimates are output.

Long-Haul Truck Cab. The accessory duty cycle for a long-haul truck sleeper cab was estimated using industry-supplied data. The fuel cell system energy conversion efficiency was determined at various loads and design capacities using detailed thermodynamic and fuel cell performance models. The SOFC stack part load efficiency was optimized by choosing the appropriate combination of cell voltage and fuel utilization at each point (TIAX, 2002). The analysis shows that there is not a large difference in efficiency with rated capacity in the range of 5 to 9 kW, especially near full load (see Figure 2). Using the accessory duty cycle and fuel cell system efficiencies in the modified drive cycle model, a 4-kW APU system was found to minimize fuel consumption. Estimated annual fuel savings and

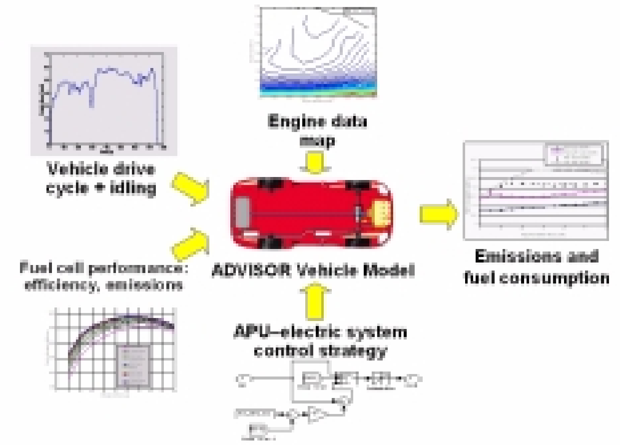

Figure 1. Conceptual Framework of ADVISOR-based Vehicle System Model

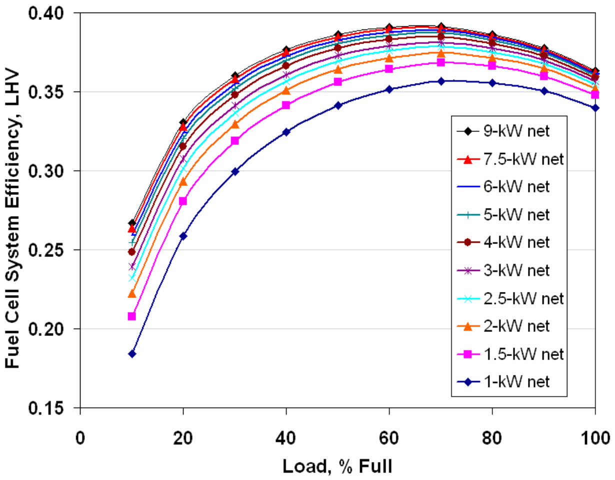

Figure 2. SOFC System Efficiency as a Function of Load

emissions benefits per truck are shown on Figure 3 for a 4-kW SOFC APU. Savings will depend on engine idling speed, or rotations per minute (rpms), which in turn depends on the engine design. Savings will also depend on the duty cycle, which varies over a wide range. Approximately 15-20% of the market idles <2 hours/day, 60-70% idles 2-10 hours/day, and 15-20% idles >10 hours/day.

Transit Bus. The accessory duty for transit buses was estimated to be 11 kW to run the air conditioner (A/C) in warm weather operation and a 3-kW baseload to run other accessories all the time. We evaluated two cases, one where the APU supplies power for the baseload only (3 kW), and one where it supplies both the baseload and A/C load (14 kW). The fuel cell system energy conversion efficiency was similar to the truck cab application. Estimated fuel savings and emissions benefits per bus are shown on Figure 4 for a 14-kW SOFC APU. Fuel savings are negative (i.e. more fuel is consumed) for the transit bus APU application because it is never practical to turn off the main engine during normal stop and go operation. Since engine idling is required in the typical drive cycle, it is more efficient to use the engine to supply all accessory power. While the SOFC is more efficient than the ICE, idling the ICE with no load plus operating the APU is less efficient than idling the engine to supply 3-14 kW of accessory power with no APU. Annual emissions are reduced only slightly.

Law Enforcement Vehicle. The accessory duty cycle for law enforcement vehicles was developed from a survey of police fleet operators. An APU for this application would require up to 5 kW for lights, radio, etc. during idling situations (e.g. traffic surveillance). The fuel cell system energy conversion efficiency was determined at various loads using detailed thermodynamic and fuel cell performance models (see Figure 5). The PEMFC system pressure and stack cell voltage are assumed to

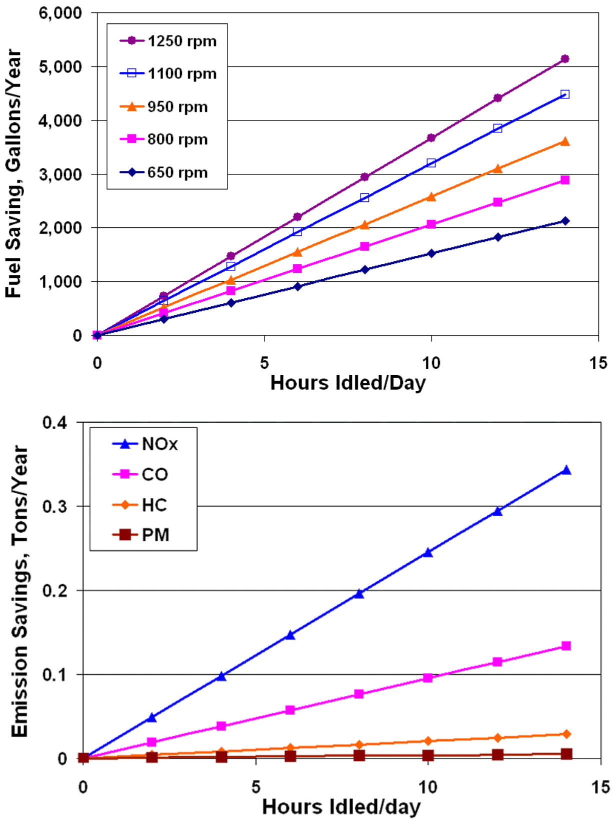

Figure 3. SOFC APU Annual Diesel Fuel and Emissions Savings - Long-Haul Truck Cab

	Engine Only	SOFC	Engine w/SOFC	Engine+SOFC	Reduction
Fuel Use	**gal/hr**	**gal/hr**	**gal/hr**	**gal/hr**	**%**
Base load	3.5	0.2	3.4	3.6	**-2.1**
A/C full time	4.2	0.9	3.4	4.3	**-1.2**
NO_x Emissions	**g/mile**	**g/mile**	**g/mile**	**g/mile**	**%**
Base load	24.6	0	23.2	23.2	5.8
A/C full time	31.5	0	23.2	23.2	27
PM Emissions	**g/mile**	**g/mile**	**g/mile**	**g/mile**	**%**
Base load	0.3	0	0.3	0.3	1.1
A/C full time	0.3	0	0.3	0.3	1.9

Figure 4. SOFC APU Diesel Fuel and Emissions Savings - Transit Bus

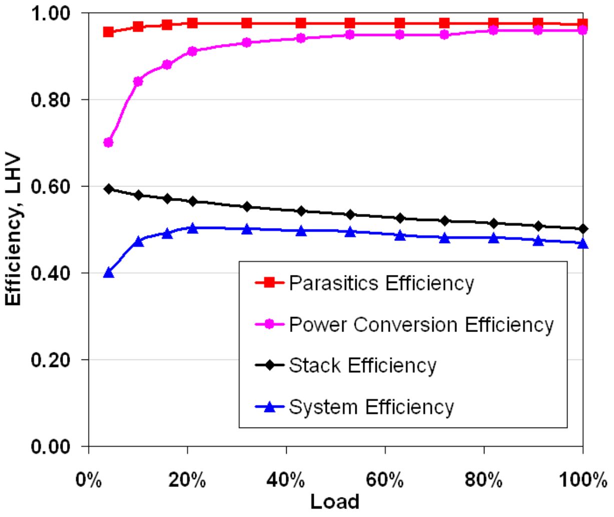

Figure 5. Direct Hydrogen PEMFC Efficiency as a Function of Load

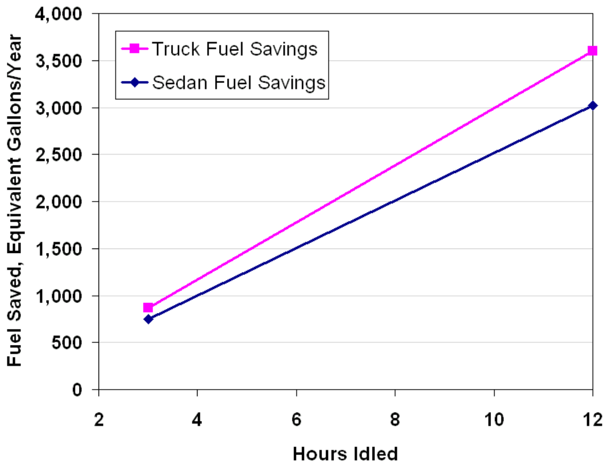

Figure 6. Direct Hydrogen PEMFC APU Annual Fuel Savings - Law Enforcement Vehicle

vary with load (pressure decreases and cell voltage increases at lower load). Estimated annual fuel savings per vehicle are shown in Figure 6 for a 5-kW PEMFC APU. Savings will depend on idling time, which varies significantly. Emissions savings were not evaluated because it is assumed that the engine utilizes clean-burning hydrogen (i.e. hydrogen ICE powertrain).

Conclusions

Introduction of APUs for long-haul truck and law enforcement vehicle applications can provide significant fuel and emissions savings proportional to the amount of abated idling time. Transit bus applications, however, are unlikely to result in significant benefits due to the necessity for engine idling even with an APU. In place of a detailed vehicle integration and cost analysis of the transit bus application, we will instead evaluate the benefits of a TRU and perform a detailed analysis if appropriate.

References

1. TIAX, “Grid-Independent, Residential Fuel-Cell Concept Design and Cost Estimate”, *Final Report to DOE NETL in Subcontract to Parsons,* Subcontract Number 73622-30005, October 18, 2002

FY 2003 Publications/Presentations

1. Presentation to 21st Century Truck Industrial Working Group in conjunction with SAE Government & Industry meeting, Washington, DC, May 15, 2002

Evaluation of Partial Oxidation Fuel Cell Reformer Emissions

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Objectives

- Measure the emissions from a partial oxidation/autothermal reformer (POx/ATR) fuel processor for a proton exchange membrane fuel cell (PEMFC) system under both cold-start and normal operating conditions
- Assess the feasibility of meeting emissions standards for automobiles and light-duty trucks through the use of a fuel cell vehicle with a flexible-fuel reformer

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- K. Emissions and Environmental Issues

Approach

- Define a representative test cycle consisting of both startup and normal operating conditions
- Use the established test cycle to quantify emissions from a POx reformer before and after anode gas burner (AGB) treatment
- Measure emissions with continuous emissions monitoring (CEM) measurements supplemented with laboratory analyses of speciated hydrocarbons and particulate matter (PM)
- Use reasonable approximations and estimates to convert emissions data from a grams/unit fuel basis to a predicted grams/mile basis

Accomplishments

- Measured emissions from a gasoline-fed fuel processor (without fuel cell) over several operating conditions
- Measured emissions from an ethanol-fed fuel processor with fuel cell over several operating conditions (analysis pending)
- Speciated total hydrocarbon (THC) data before and after the AGB
- Assessed the sensitivity of monitoring equipment over a range of operating conditions
- Analyzed data to report emissions on a g/kg fuel basis

Future Directions

- Perform extensive emissions testing of a fuel cell/reformer system to include particulate, formaldehyde, and ammonia as well as NO_x, hydrocarbons, and CO
- Sample and analyze emissions from Nuvera Fuel Cells fuel processor-fuel cell system in 2003
- Project on-road emissions from fuel cell vehicles with on-board reformers

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Introduction

Fuel reformer operation is generally divided into two operating modes: startup and normal partial oxidation. During startup, the fuel processor burns fuel at near stoichiometric conditions until critical system temperatures and pressures stabilize to target values. Once the target conditions are reached, the reformer operates in normal mode in which the fuel processor burns fuel at very rich conditions. Since these modes are comprised of considerably different operating conditions, it follows that the emissions associated with each of these modes are also considerably different.

The combustor is typically cold under startup conditions, generating emissions during this brief period (target times are under 30 seconds) that can be substantially higher than those produced during the remaining, much longer portion of the driving cycle. The pollutant emissions produced during startup operation include NO_x, CO, formaldehyde, and organic compounds. These organic compounds, including hydrocarbons, alcohols, and aldehydes, are regulated in California and referred to as non-methane organic gases (NMOG). Under normal, fuel rich operating conditions, virtually no NO_x is formed, although the formation of ammonia is possible. Most hydrocarbons are converted to carbon dioxide (or methane and/or hydrogen if the reaction is incomplete); however, trace levels of hydrocarbons can pass through the fuel processor and fuel cell. The shift reactors and the preferential oxidation (PrOx) reactor reduce CO in the product gas, with further reduction in the fuel cell. Thus, of the criteria pollutants (NO_x, CO, and hydrocarbons [NMOG]), NO_x and CO levels are generally well below the most aggressive standards. NMOG concentrations, however, can exceed emissions goals if these are not efficiently eliminated in the catalytic burner.

Approach

In this study, a gasoline fuel processor and an ethanol fuel processor were operated under conditions simulating both startup and normal operation. Emissions were measured before and after the AGB in order to quantify the effectiveness of the burner catalyst in controlling emissions. The emissions sampling system includes CEM for O_2, CO_2, CO, NO_x, and THC. Also, integrated gas samples are collected in evacuated canisters for hydrocarbon speciation analysis via gas chromatography (GC). This analysis yields the concentrations of the hydrocarbon species required for the California NMOG calculation. The PM concentration in the anode burner exhaust is measured through the placement of a filter in the exhaust stream.

Emissions data will be used to project on-road emissions for fuel cell vehicles with reformers. Emissions data will be characterized in terms of startup or reforming modes. Although current fuel processor technologies are not configured to follow a typical vehicle load profile, hybrid vehicle power management strategies may facilitate using such fuel processors. For this project, the fuel processor is operated at several steady-state points while emissions are monitored for the steady-state conditions and transients between load changes. The data collected during startup, different loads, and transients serve as inputs to a vehicle emissions model. Using these data, this vehicle emissions model then predicts the emissions for each second in a driving cycle based on load. Startup emissions are considered along with the total driving emissions.

Results

During FY 2003, we performed two series of emissions tests: one gasoline ATR system tested without a fuel cell and one ethanol ATR system tested with a fuel cell. The emissions tests involved sampling criteria pollutants and CO_2 from each of these systems at various operational load points, as described in the previous section. Concentrations of the aforementioned species are obtained using the emissions sampling system shown in Figure 1. Although emissions data have been collected for both the gasoline and ethanol systems, only the gasoline system data have been sufficiently analyzed to allow presentation of results at this time.

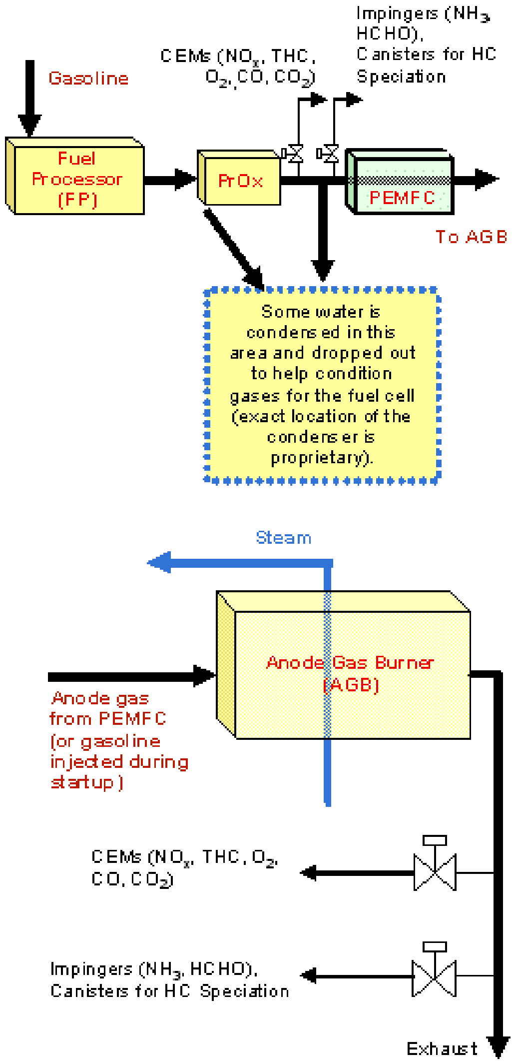


Figure 1. Emissions Testing Setup for the Fuel Processor and Fuel Cell System

In general, testing did not attempt to follow a vehicle driving cycle, but rather followed a series of steady-state conditions with load changes. Figure 2 shows emissions levels at the AGB for the beginning of a gasoline reformer testing series. This series of operating load points was started at low load conditions after a hot start (about 6 kWe or 12% load) and brought to steady state at 12 kWe. THC emissions at the AGB outlet were below the monitor detection limit throughout the testing period. CO emissions were highest at the lower load points and dropped when the power was increased above 10 kWe, or 20% full power. NO_X emissions stabilized at about 20 ppm for operation above 10 kWe.

In order to determine how current emissions performance would compare to existing vehicle standards, these emissions levels were converted to a gram per mile basis using the system power input and typical vehicle efficiencies. The results of this conversion are given in Figure 3 along with the corresponding California super ultra low emission vehicle (SULEV) passenger vehicle standards. For the series shown in Figure 2, CO and THC emissions are much lower than the SULEV standard. For the same test series, the NO_X emissions are on the same order of magnitude as the SULEV standard, indicating that the reformer system may require additional optimization to meet the SULEV NO_X standard.

The PM concentrations for both tests correspond to emissions levels below California SULEV vehicle emissions standards. These PM concentrations were determined by passing the entire exhaust stream

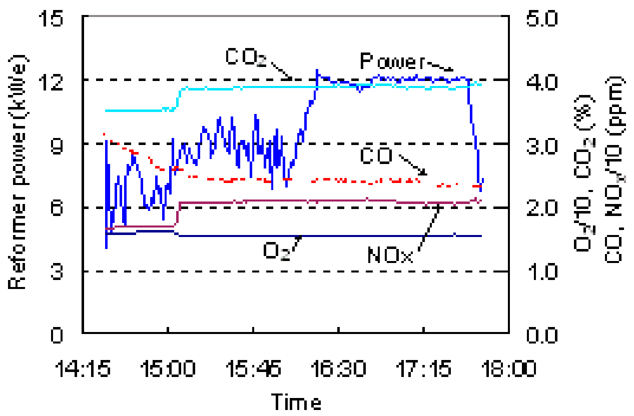
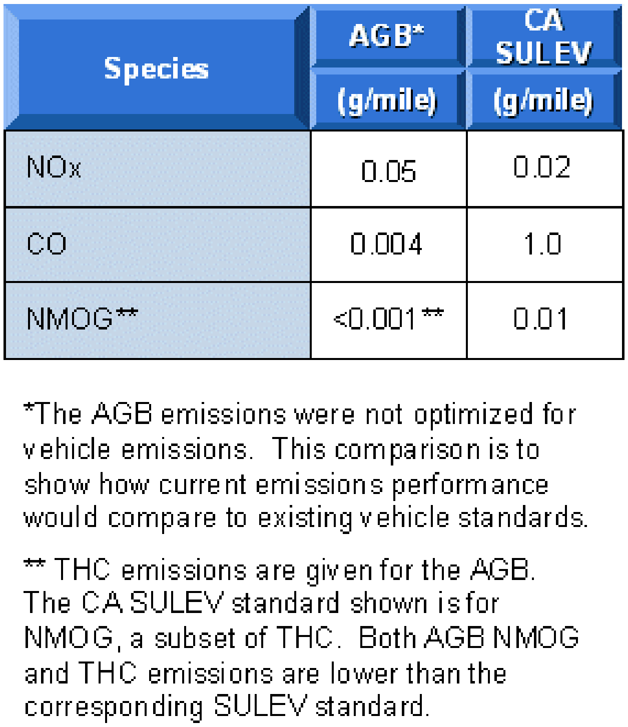


Figure 2. CEM Emissions Test Results at the AGB Outlet (partial)

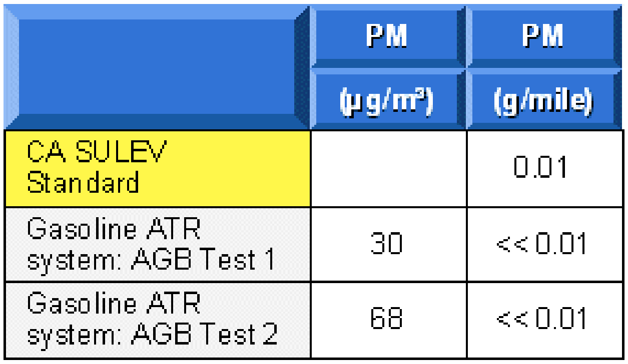


Species	AGB* (g/mile)	CA SULEV (g/mile)
NOx	0.05	0.02
CO	0.004	1.0
NMOG**	<0.001**	0.01

*The AGB emissions were not optimized for vehicle emissions. This comparison is to show how current emissions performance would compare to existing vehicle standards.

** THC emissions are given for the AGB. The CA SULEV standard shown is for NMOG, a subset of THC. Both AGB NMOG and THC emissions are lower than the corresponding SULEV standard.

Figure 3. Projected Vehicle Emissions at the AGB Outlet (unoptimized)



	PM (μg/m³)	PM (g/mile)
CA SULEV Standard		0.01
Gasoline ATR system: AGB Test 1	30	<< 0.01
Gasoline ATR system: AGB Test 2	68	<< 0.01

Figure 4. PM Emissions Results at the AGB Outlet

through the PM filter and averaging the integrated PM sample over the total flow that passed through the filter. Figure 4 shows PM concentrations at the AGB determined for steady-state gasoline ATR system operation and the corresponding SULEV standard.

Conclusions

The combustion of reformer products at the AGB did not represent an optimized fuel cell vehicle configuration. Even with these limitations, the following conclusions can be drawn from the data.

- NO_X emissions from an AGB averaged about 20 ppm for the load points tested. These emissions levels would correspond to approximately 0.05 g/mile of NO_X for operation. In order to meet stringent emissions standards, further optimization will be required. Also, other power loads will need to be tested to ensure that emissions are acceptable for all operating modes.
- In-use THC and CO emissions were under 0.2 ppm and 3 ppm, respectively, which would correspond to on-road emissions well below the SULEV standards. More data on startup with an optimized fuel processor is required before startup on-road NMOG and CO emissions can be estimated.

Modeling and Control of a Solid Oxide Fuel Cell Auxiliary Power Unit

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Objectives

- Task 1: Develop a dynamic system model of a solid oxide fuel cell (SOFC) based auxiliary power unit (APU) and design a system controller to minimize diesel fuel consumption, maximize operating lifetime and satisfy electrical load requirements for Class VIII truck applications.
- Task 2: Develop analytical models and perform testing to determine the dynamic structural response and vibrational limits of SOFC-based APU systems in a Class VIII truck operational environment.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- C. Thermal Management
- D. Fuel Cell Power System Benchmarking
- H. Startup Time
- P. Durability

Approach

Task 1

- Create a dynamic, electro-chemical model of the SOFC stack.
- Create dynamic balance of plant component, operational models using theoretical first principles and experimental data.
- Create a system functionality model by combining component models.
- Design controllers using the model to optimize fuel efficiency and lifespan.
- Verify models through experimental testing and collaboration. Collect actual Class VIII truck electrical load profiles with PACCAR and test APU systems with Delphi.

Task 2

- Develop a lumped parameter model to determine the vibration amplitude of the SOFC stack due to base excitation of the APU.
- Perform stress analysis on a detailed finite element model of a multiple-cell planar SOFC stack using the stack loading history.
- Develop failure models for Positive-Electrolyte-Negative (PEN) cell fracture and seal interfacial separation to define APU vibrational limits and isolation requirements for stack durability.

- Collect data in collaboration with PACCAR for actual vibration loads of a truck-mounted APU.
- Perform dynamic testing of an APU and components for fundamental material data and model validation.

Accomplishments

Task 1

- Creation of APU system and component models: electro-chemical model of the SOFC stack, diesel fuel reformer, exhaust gas combustor and heat exchangers.
- Completion of a dynamic model of a truck heating and air-conditioning system, including inrush current at startup and driver heat input.
- Assembly of controllers to regulate cathode air temperature during heat-up phase to prevent thermal shock to SOFC and fuel flow rate control under varying electrical load.

Task 2

- Reviewed standards for shock and vibration testing and electronic equipment design for heavy trucks to establish a basis for the dynamic loading environment.
- Created lumped parameter model in ANSYS to determine influence of APU components on stack dynamic response.
- Detailed finite element model of SOFC stack to determine resonant frequencies and dynamic stresses due to harmonic excitation.
- Identified method to define a vibrational limit spectrum to prevent stack failure.

Future Directions

Task 1

- Create high level, optimized controllers to maximize fuel efficiency and device lifespan.
- Improve dynamic models. Focus on the SOFC stack response to dynamic inputs (such as fuel flow rate changes and temperature changes) through collection of experimental data on single cell SOFCs.
- Model un-measurable inner parameters of SOFC stack.
- Improve power conversion electronics modeling through collaboration with University of Illinois, Chicago.
- Collect actual electrical system load profiles in Class VIII trucks with PACCAR.
- Test realism of control strategies for APU system in partnership with Delphi.

Task 2

- Complete failure model development for PEN fracture and interfacial separation.
- Incorporate spectral solution methods.
- Develop procedure to analyze shock and impact loading of the APU.
- Perform parametric analysis for various SOFC and APU designs.
- Collect actual truck shock and vibration data in collaboration with PACCAR.
- Determine fundamental properties for cell materials under dynamic loading.
- Perform experimental testing of SOFC and APU components in collaboration with Delphi.

Introduction

Long-haul trucks require electrical power to operate hotel loads (lights, heating/air conditioning and televisions) while parked for the operator to rest. Typically, these loads are powered by idling the engine or, less commonly, with a dedicated diesel generator based auxiliary power unit (APU). Fuel cell based APUs hold the promise of greater energy efficiency, lower operating costs, lower emissions, and quiet operation. A solid oxide fuel cell (SOFC) is expected to be the choice for transportation applications because 1) it has higher power density than other designs to minimize stack mass and volume and 2) it offers fuel flexibility due to its high operation temperatures and toleration of impurities.

This project looks at modeling of SOFC APUs to understand how design choices impact efficiency and durability. This work is the first step towards full electrification of the truck when the engine is used solely for propulsion and today's belt driven pumps and fans are run off electricity from the APU. Task 1 investigates operational models of APU components and the entire system to show how the devices interact, and different configurations are investigated for increased fuel efficiency. The operational models allow the creation of effective control strategies to optimize fuel efficiency and long lifespan. Task 2 provides modeling tools to evaluate the dynamic thermal-mechanical stresses in the stack. The high temperature and dissimilar materials make SOFC structural robustness challenging when it must also withstand the rigorous dynamic loading of a heavy truck. The models will allow designers to define appropriate materials, cell design, physical layout, and isolation components to minimize vibrational loads to acceptable levels for increased durability in real applications.

Approach

Task 1: The approach to creating operational models of the APU components and system has been to combine theoretical operation with experimental data, keeping the models broadly applicable but realistic. Electrical load profiles from Class VIII trucks will be collected with PACCAR to understand how APUs are used in practice. Models for components such as the diesel partial oxidation (POX) reformer, heat exchangers and SOFC stack are created in a modular environment that allows them to easily be connected in different configurations. This allows different fuel and thermal management strategies to be tested. Work on the controller has begun, with independent control of individual components. This will be followed by higher level controllers, coordinating all components and increasing fuel efficiency. Finally, as the model matures, it will be possible to optimize control to minimize fuel consumption, maximize lifespan and meet electrical load requirements.

Task 2: The commercial finite element code ANSYS was used to model the APU system response at three levels. For the first model, the APU was simplified to a small number of major components. Based on mass and stiffness properties of the components and connections, the dynamic loading imparted to the stack due to base excitation of the APU could be calculated across the frequency range of interest. This was used as input to a detailed model of the SOFC stack, which computes the deformation and stresses of the cells due to harmonic excitation. Stress analysis results can be compared to strength of the constituent materials to determine allowable excitation amplitudes. Fracture must be considered for brittle materials like the ceramic PEN and rigid seals. Finite element models to study anode cracks and interfacial seal separation are under development and will be similarly used to determine allowable excitation amplitudes. Parametric analysis will then be performed to identify critical elements in APU and stack design. Collection of actual excitation loads and experimentally testing of the SOFC components and APU will benchmark the models to ensure they are usable in real truck and transportation applications.

Results

The scope of this research project is to create models and controllers that provide design guidelines for SOFC-based APU applications. The models provide information about what conditions the SOFC APU will be subject to in operation and how it behaves. Models and controls are verified and augmented through experimental testing.

Task 1: To date, this research has produced operational models of the following APU components: POX reformers (both diesel and gasoline), combustor, heat exchangers and the SOFC stack. These models compute the chemical and thermal reactions inside each component. An example of the voltage-current (VI) output of the SOFC model for various stack temperatures is shown in Figure 1. Models of electrical loads such as the heating and air-conditioning system have also been created. These models have been connected to form a complete system for simulation of operations.

Using the component models, initial controllers have been developed. Currently, control is divided into two phases: startup and operating. The startup controller regulates the temperature of air blown over the stack to heat it to operating temperatures (around 700°C). The rate of temperature increase must be strictly regulated to prevent undue thermal stress to the stack that would shorten its operational lifespan. The operating controller ensures that sufficient fuel is reaching the stack to produce enough electricity to match the electrical load. As electrical load requirements decrease, fuel flow to the stack should also decrease, preventing waste and increasing fuel efficiency. An example of this controller is shown in Figure 2.

Task 2: Work for this year is exclusive to predictive model development and study of dynamic loading effects. Modal results for a planar stack indicate the fundamental frequency is due to out-of-plane vibration of the frame-supported PEN and the interconnect plate, depending on the interconnect stiffness as shown in Figure 3. Fundamental frequencies from thin plate theory and modal results for a stack model are shown in Figure 4, and they are much greater than typical engine speeds of 700-2100 rpm (12-35 Hz). An example curve for the permissible harmonic excitation of a five-cell stack is shown in Figure 5. Superposition of the elastic solutions for thermal-mechanical and dynamic stresses was used to predict the maximum amplitude based on a single criterion that the Mode I stress intensity factor for a 5 or 25 mm semicircular flaw at the anode surface be less than a critical stress intensity of 1.0 MPa-m1/2. The results indicate that a stack vibration of 1-4 G's can be critical, although this assumes that the flaw is at the location of maximum stress. The union of all potential failure

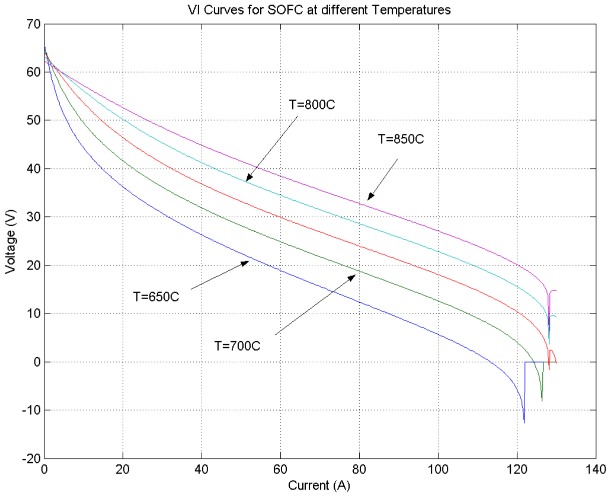


Figure 1. SOFC Voltage-Current Curves for Various Temperatures

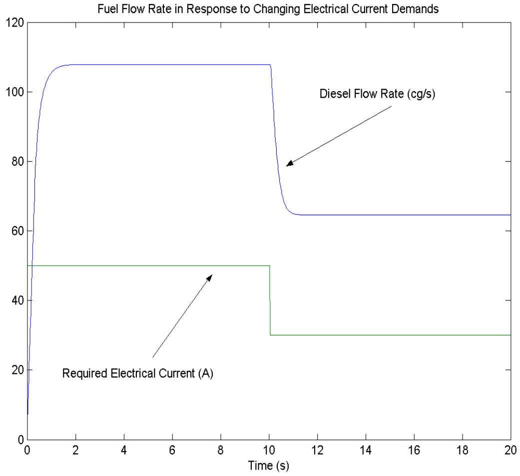


Figure 2. Fuel Flow Rate Response to Electrical Current Change

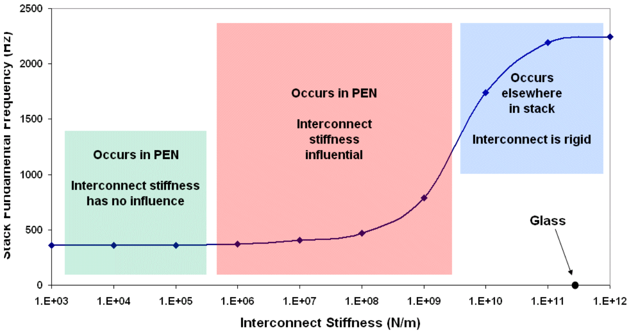
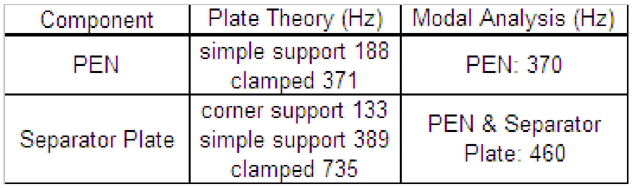


Figure 3. Variation of PEN Fundamental Frequency with Interconnect Stiffness



Component	Plate Theory (Hz)	Modal Analysis (Hz)
PEN	simple support 188 clamped 371	PEN: 370
Separator Plate	corner support 133 simple support 389 clamped 735	PEN & Separator Plate: 460

Figure 4. Fundamental Frequencies for SOFC Components from Thin Plate Theory and Modal Analysis

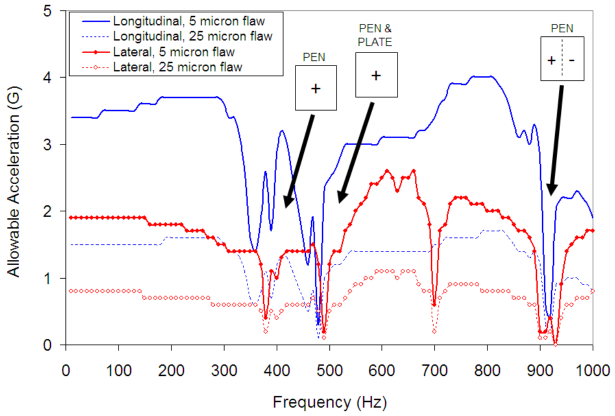


Figure 5. Permissible Longitudinal and Lateral Vibration Amplitudes for a Planar SOFC Stack

criteria with consideration of defect density would define the actual critical response curve. Interfacial separation of the PEN and seals is expected to be an important failure mechanism due to coefficient of thermal expansion mismatches. Interfacial fracture of dissimilar materials is inherently mixed mode (Mode I and Mode II are coupled), and stress intensity factors depend on material properties which depend on anode porosity and nickel content. Relations to determine elastic properties and stress intensity factors as a function of porosity and composition have been developed using the Mori-Tanaka method as shown in Figure 6 for the properties of the NiO/YSZ anode.

Conclusions

- Task 1: State-of-the-art models of an SOFC APU system and components were developed to describe the operational behavior of the APU. The models were used to develop controllers to regulate fuel utilization under varying electrical loads and prevent thermal shock during heat up. Performance will be improved by creating higher level, optimized controllers and incorporating the results of experimental tests on single cell SOFC and APU systems in partnership with Delphi. Electrical load use profiles will be collected from real trucks with PACCAR, and detailed power electronic models will be made with University of Illinois, Chicago. Further models to describe full truck electrification will be done in collaboration with an engine manufacturer such as Caterpillar.

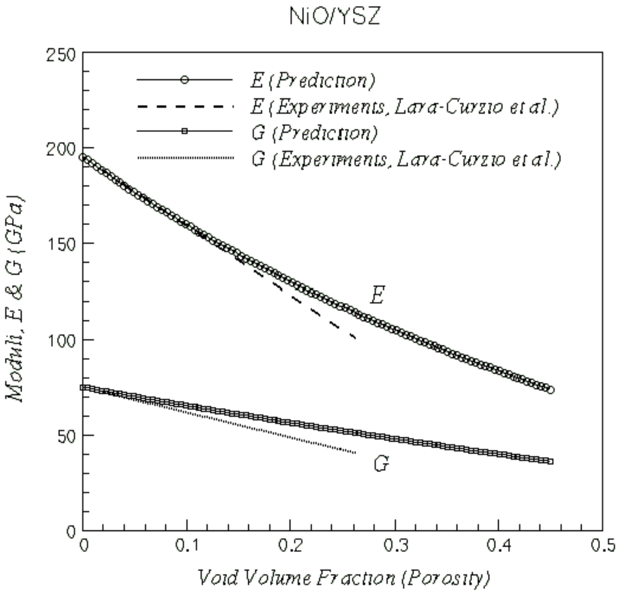


Figure 6. Comparison of Model and Experimental Results for Elastic Moduli of the NiO/YSZ Anode as a Function of Porosity

- Task 2: Finite element models constructed for dynamic analysis of a lumped parameter APU system and stress analysis of a detailed SOFC stack were used with a simple failure criterion to predict permissible vibration load as a function of frequency. For the future, continued improvement of the finite element analysis and failure models will provide wider applicability, truck dynamic loads will be determined with PACCAR to ensure realistic loading conditions, and APU/SOFC component testing will be done with Delphi to validate modeling efforts.

FY 2003 Publications/Presentations

1. M.A. Khaleel, B.J. Koeppel, and S.J. Moorehead, "Solid Oxide Fuel Cell Auxiliary Power Units for Long-Haul Trucks: Modeling and Control", Hydrogen, Fuel Cells & Infrastructure Technologies Program 2003 Merit Review and Peer Evaluation Meeting, Berkeley, CA (2003). Poster No. 96.

Montana PEM Membrane Degradation Study, Year 1 Report

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Objectives

- Develop a system capable of measuring current and voltage performance for each membrane in a proton exchange membrane (PEM) fuel cell stack and record the performance of each individual cell.
- Develop a single-cell PEM fuel cell to allow in situ synchrotron X-ray measurements of the cell in operation.
- Perform initial magnetic resonance microimaging experiments on membrane materials.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Distributed Generation Systems

- E. Durability
- G. Power Electronics

Components

- P. Durability

Approach

- Design a system to capture individual cell performance in real time (current, voltage, temperature points taken every 0.5 milliseconds).
- Test the stack response as it is subjected to load transients. Monitor each cell in the stack for its entire lifetime.
- As failures occur, analyze the cell using X-ray techniques, including methods that provide spatial resolution and chemical composition information.
- As failures occur, analyze the membrane material using magnetic resonance imaging (MRI) microimaging techniques to get information about membrane permeability.
- Search electrical records of failed membranes to see if mode of failure or an electrical signature of failure can be discerned.

Accomplishments

- A fuel cell monitoring system has been constructed and undergone initial testing.
- An individual synchrotron-compatible fuel cell has been constructed and tested at the National Synchrotron Light Source (NSLS).
- Initial MRI microimages of membranes have been obtained.

Future Directions

- Modify the fuel cell monitoring system; then, run and monitor fuel cells under transient load change conditions.
- Perform further X-ray analysis of membrane electrode assemblies (MEAs) on new cells to get baseline information before degradation occurs.
- Start construction of an electrophoretic MRI probe so mobility in membranes under field testing can be measured.
- Perform X-ray work on any degraded membranes.
- Perform MRI work on any degraded membranes.

Introduction

The Montana State University PEM Membrane Degradation project is geared towards determining how and why membranes in fuel cells degrade and fail. By monitoring every individual membrane in a fuel cell 2000 times/sec while the cell is subjected to real-world use, we hope to: 1) cause the types of degradation users typically see, but in a controlled environment; 2) determine an electrical signature that will identify what causes failure, or at least warns of impending failure; 3) perform advanced X-ray and MRI characterization of the degraded membranes to provide information that may result in improvements of the membrane material; and 4) perhaps allow design of electronic control systems that will prevent fuel cells from operating under conditions where damage is likely to occur.

Approach

The Montana State University PEM Membrane Degradation project has three interdependent components: 1) Fuel Cell Electrical Characteristics Monitoring, 2) Synchrotron Based X-Ray Characterization of Membranes, and 3) Nuclear Magnetic Resonance (NMR) Microscopy of Polymer Electrolyte Membranes. The project will involve continuous, comprehensive monitoring of PEM fuel cell electrical performance while the cell is being subjected to real-world types of loads and transients. A fuel cell enclosure will contain 80 membranes housed in 8 cartridges. Each side of the cartridge (5 membranes) will contain an analog-to-digital (A/D) converter that will measure voltage for each individual membrane, current and temperature at a 2000 Hz rate. This total of 224,000 data points per second will be stored to provide a permanent record of performance of each individual membrane over its entire life span. This comprehensive set of data has promise of yielding an electrical signature of impending failure. Membranes in various states of degradation and failure will be extracted for characterization using the two analytical techniques in the project.

X-ray characterization will be used to investigate the catalyst and possible poisoning of the catalyst, via X-ray Photoelectron Spectroscopy. In addition, a synchrotron-compatible fuel cell has been constructed to perform measurements during operation. If the electrical monitoring program identifies load conditions that generate degradation, in situ measurements can be performed under these conditions to determine chemical changes in the catalyst, and possibly in the membrane material itself. These measurements can be performed with 10 mm or better spatial resolution so localized effects and spreading of damage can be studied, which may provide insight into the mechanism of failures. NMR microimaging techniques will also be utilized to investigate membrane performance. Rather than imaging the membrane itself, this technique will provide images that contain information about water and hydronium ion mobility within the membranes. These imaging experiments will be performed on membranes in various states of degradation.

Results

Fuel Cell Electrical Characteristics Monitoring. We have designed, built, and tested three prototypes of a USB serial interface, 14-bit, 280,000 sample/sec analog-to-digital converter board. This unit features an AD7856 converter, a 50 MIPS Ubicom SX28 controller, and a DLP design USB interface module. The timebase stability is 50 ppm. The measured noise variance is typically less than 1.5 LSB, or about .009 percent of full-scale. In addition to superior signal performance, our custom solution is better than commercial alternatives because its small size allows us to locate the analog-to-digital conversion physically closer to the fuel cell cartridges. Most data collection alternatives would require us to route hundreds of wires carrying sensitive analog measurements in close proximity. This would lead to cross-talk and noise pickup between the leads that would likely degrade the measurements far beyond the inherent capabilities of commercial products.

The data acquisition module is useful for other research at CTA. In addition, the Massachusetts Institute of Technology (MIT) and Woods Hole Oceanographic Institute (WHOI) have expressed considerable interest in the hardware. Both groups are interested in the novel capabilities and small size of our design relative to commercial offerings. MIT student Jim Paris is presently rewriting the Linux kernel driver for the USB interface and working with Greg Linus Torvalds and Kroah-Hartman (creators of Linux, and the Linux USB drivers, respectively) to ensure that the MSU/MIT enhancements are incorporated in future releases of Linux. WHOI is interested in using the board for next-generation instrument packs that are affixed to marine animals, where small size and low power are obvious concerns.

We are presently designing an analog instrumentation-grade front end that goes between the USB data acquisition board and the fuel cell cartridges. We've identified a wiring scheme for each fuel cell cartridge, where voltage and temperature measurements are carried from the cartridge to the analog board via CAT5e twisted pairs. The fuel cell modules plug into the front-end instrumentation using modular connectors so that the modules are easy to swap out when the membranes fail. A key part of the front-end instrumentation is a new Analog Devices high-common mode range amplifier with integrated, trimmed, precision front end resistors. This unit features common mode rejection exceeding the rails, which is needed to isolate individual membrane potentials from the stack. The Analog Devices unit also comes with an auxiliary amplifier to adjust the voltage output range to that of the A/D converter. The cost of this instrumentation from Tektronix, for example, would exceed $100,000 for the number of channels we are considering.

The storage server is at the highest level of the data acquisition hierarchy. We have assembled an SMP (simultaneous multi-processing) AMD Athlon based machine with two 1.4 Terabyte RAID-5 hot-swap arrays. These have a combined capacity of 2.8 Terabytes. In addition to disk hot-swap capability, the server has a redundant hot-swapable power supply system. All fans and other moving parts are also hot-swap. We project that this will be sufficient for approximately the first year of measurements with appropriate compression.

A major contribution of the project is that we will expose membranes to realistic transient load conditions. Creating these conditions requires a transient capable DC active load. We've purchased a set of these from Agilent and are presently testing them. We have also designed and built our own active load. Testing for this device has been postponed in the interest of proceeding to the measurement stage as quickly as possible.

Synchrotron Based X-Ray Characterization of Membranes. For this fiscal year, the following accomplishments were made. A graduate student (Alex Lussier) and a Research Experience for Undergraduates (REU) participant built a synchrotron-compatible fuel cell for in-situ X-ray characterization of the catalytic materials of the fuel cell during operation to identify performance degradation mechanisms. Chemical state and local structure information by X-ray absorption spectroscopy (XAS) and by X-ray absorption fine structure (XAFS) will identify the environment of the catalytic materials. These results will be compared to X-ray characterization of fuel cell components that have shown performance degradation to identify the failure mechanism. We will be able to identify catalytic poisoning and map out the poisoning element with good spatial resolution (a few microns resolution).

From the support of this program, MSU is now a Participating Member in two beamlines at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory. The first is the soft X-ray MSU Nanoscale Materials X-ray Characterization Facility at U4B (Spokesperson Y.U. Idzerda), and the second is a hard X-ray Absorption Fine Structure beamline at X23B (spokesperson Bruce Ravel). Both are open facilities for any research programs, but we now have guaranteed access.

For preliminary work, we are characterizing the small fuel cell power output as a function of the hydrogen gas flow, air flow, and the load. We can compare these measurements to the performance curves for a commercial fuel cell measured elsewhere at MSU. This commercial cell is not compatible with the synchrotron techniques, although disassembly of the fuel cell and characterization of the catalytic and membrane materials will be a part of this research project.

In addition to the in-situ X-ray characterization, we have initiated a project of modeling diffusion in fuel cells to identify failure modes. Finite element modeling of hydrogen ion and heat diffusion in PEM fuel cells has identified a possible mechanism for thermal failure of the membrane due to membrane thickness variations. This modeling will also assist us in understanding the performance degradation due to diffusion barriers at interfacial regions (from structural modifications or alloying) and due to catalytic poisoning.

NMR Microscopy of Polymer Electrolyte Membranes. To date, we have focused on obtaining PEM samples, establishing the wet lab experimental protocol for sample preparations following prior NMR work[1] and establishing the NMR microscopy methods for imaging of PEMs. Before investigation of the PEM membrane, polymer hydrogel samples were used to establish the NMR methods. Figure 1 shows NMR microscopy data for a 500 μm thick sample of hydrogel material. The hydrogel is cut into a 5 mm diameter disk and placed into a 6 mm diameter 500 μm thick Teflon (PTFE) sample holder with supernatant distilled H_2O. The images are of calculated NMR parameters-T_1 relaxation (Figure 1a), T_2 relaxation (Figure 1b) and translational diffusion coefficient (Figure 1c)-and have an in-plane spatial resolution of 78 μm/pixel. The NMR signal is being obtained from the (^1H) protons on the water molecules within and external to the hydrogel. Spin-lattice, or T_1, relaxation depends on the mechanisms available for energy transfer between the spins and thermal energy repositories such as translations, vibrations and rotations of the lattice. In a polymer gel matrix (or a polymer membrane such as a PEM), the presence of paramagnetic impurities or electron rich elements such as oxygen are a source of relaxation which depends on the chemistry of the matrix. The physical structure of the matrix-for example, the extent of cross linking in a gel-also impacts the relaxation by affecting the molecular motion of the water within the matrix and the resulting fluctuation rate of the magnetic fields. Hence, both the matrix mobility and chemical composition impact the T_1 relaxation behavior in the sample. The T_1 value for the water in the hydrogel, shown in light blue in Figure 1a, is measured to be 2 s, while that of the free water, shown in purple in Figure 1a, is 2.2 s. This indicates enhanced relaxation rate $1/T_1$ of the water within the gel due to the restricted motion of the water molecules.

Spin-spin, or T_2, relaxation is due to interactions between the nuclear magnetic moments of the sample. The relaxation is due to the fluctuations in magnetic field from the dipole interactions due to molecular mobility [2, 3]. T_2 values in solids are very short, indicating the fast magnetic relaxation rate, $1/T_2$, due to strong coupling of the dipole moments. In liquids, T_2 is much longer since the motion of the spin generates motional averaging of the relaxation mechanism that results in a slow relaxation rate. The T_2 of the water within the hydrogel, shown in light blue in Figure 1b, is 122 ms, while that of the free water surrounding the sample, shown in purple, is 165 ms. The restricted mobility

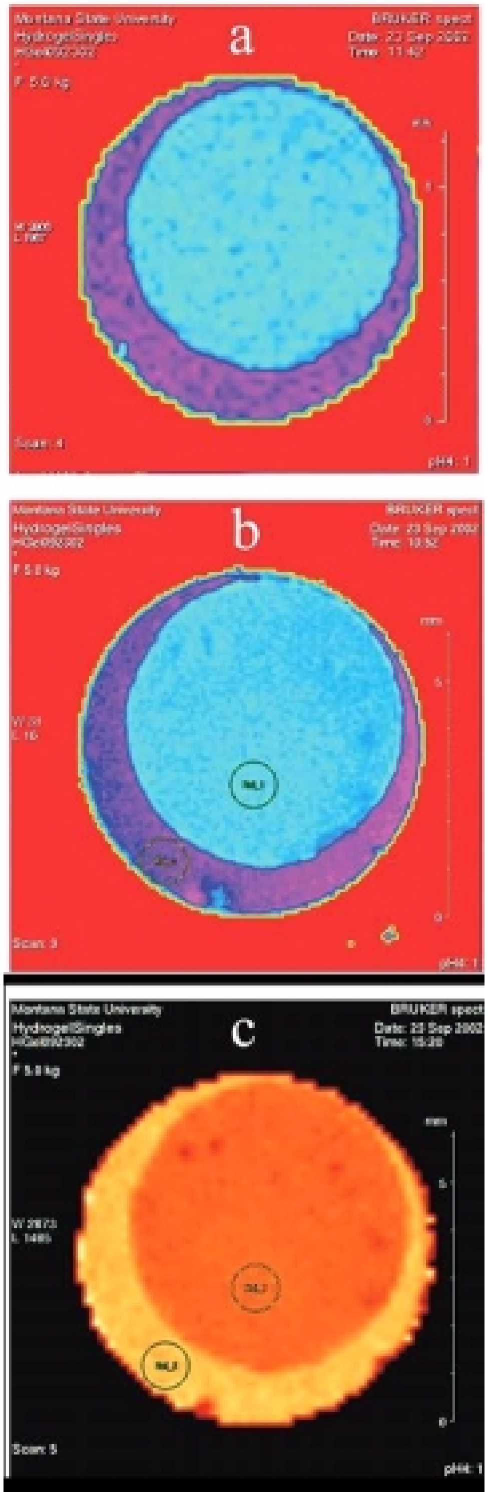

Figure 1. MRI microimages of a) T_1 relaxation, b) T_2 relaxation and c) diffusion coefficient of the water constrained within the matrix of a polymer hydrogel. The images are a top view of a 5 mm disk (light blue in a0 and b0) in a 6 mm diameter sample cell.

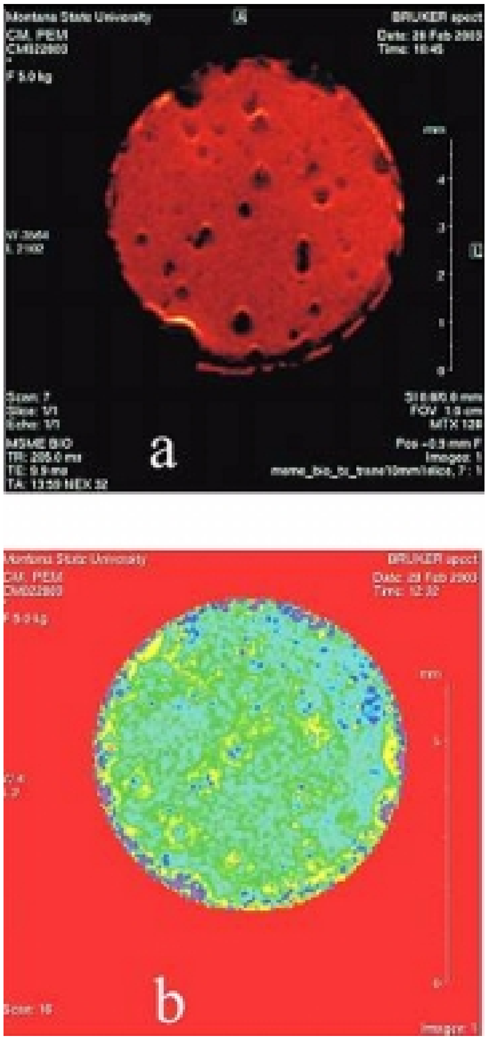

Figure 2. a) MRI microimages of the T_1 weighted water concentration within a 178 µm thick disk of Dupont Nafion 117. The image intensity is proportional to water concentration weighted by T_1 relaxation so that the free water surrounding the disk appears as black. Thus, the black regions within the disk indicate regions where water mobility is similar to free water. b) MRI map of the spatial T_2 distribution within the sample.

within the hydrogel reduces the motional averaging of the spin-spin interactions, resulting in enhanced relaxation rate $1/T_2$. Consistent with the spatially resolved T_1 and T_2 data is the molecular translational self-diffusion coefficient of the water shown in Figure 1c. The orange region shows the slower self-diffusion of the water within the hydrogel, 1.95×10^{-9} m^2/s, relative to the free water of brighter yellow with a diffusion coefficient of 2.45×10^{-9} m^2/s.

These values of self-diffusion coefficient are in excellent agreement with those found from bulk NMR measurements without spatial resolution [4].

Preliminary images of Dupont Nafion117 PEMs have been acquired. While *bulk* NMR measurements of electroosmotic mobility [1] and molecular self-diffusion of water [5] within PEMs have been reported, to our knowledge the images in Figure 2 are the first *spatially* resolved *images* of water within a PEM. The sample cell and in-plane spatial resolutions are the same as those used in Figure 1, 78 mm/pixel, with the data averaged over the 178 µm sample thickness. The image in Figure 2a is of the water concentration within the PEM weighted by the T_1 relaxation behavior, in contrast to the calculated T_1 value maps in Figure 1a where the intensity of the image is directly the calculated T_1 value. The T_1 weighting is such that the signal from free water is completely relaxed and gives no signal. Figure 2b is a T_2 map of the PEM, with red indicating small T_2 values with increasing T_2 through yellow, green, blue and purple. Comparison of Figure 2b and Figure 1b indicates the significant heterogeneity of the magnetic relaxation behavior within the PEM. The holes in Figure 2a could be the result of either highly mobile water or water in contact with strong chemical relaxation centers. Interpretation of these images will require significant experimental and theoretical analysis, including combining NMR measurements of T_1, T_2 and time dependent self-diffusion, and is ongoing.

Conclusions

The three-pronged approach shows promise for yielding insights to degradation mechanisms and the changes in materials properties that result.

FY 2003 Publications/Presentations

1. Joseph D. Seymour, Sarah L. Codd, James C. Mabry, Scott C. Busse and Eric S. Peterson. "NMR microscopy of water and methanol distribution and dynamics in polymer electrolyte membranes." North American Membrane Society, 14th Annual Meeting, Jackson Hole, WY, May 17-21, 2003.

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Microstructural Characterization of PEM Fuel Cells

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Objectives

- Use transmission electron microscopy (TEM) characterization techniques to observe the distribution of precious metal catalyst, pore space and ionomer in proton exchange membrane (PEM) electrodes
- Understand the processing/structure/property relationship for membrane electrode assembly (MEA) electrodes to allow for optimization of the electrode structure for higher performance
- Characterize/quantify microstructural changes and their relation to the performance loss in PEM MEAs upon use in a fuel cell system to understand issues relating to durability and lifetime

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance

Approach

- Prepare thin cross-sections of PEM MEAs via diamond knife ultramicrotomy
- Using TEM techniques, characterize the structure of the electrodes (e.g. size of catalyst particles, amount and location of ionomer, spatial distribution of supported catalyst) and relate to performance and/or processing
- Investigate the electrode/membrane interfaces for evidence of microchemical degradation of the ionomeric membrane after extended use in a fuel cell

Accomplishments

- Successfully prepared cross-sections of MEAs provided by Los Alamos National Laboratory (LANL)
- Improved the sectioning technique to routinely achieve 100 nm thick sections (vs. former 300 nm thicknesses) for greatly improved electron transparency and structural detail
- Characterized the electrode structure effect of boiling the MEA in sulfuric acid
- Characterized the as-prepared catalyst distribution for an advanced MEA design

Future Directions

- Investigate the effects of ionomer content on the structure of the electrodes
- Characterize the microstructural changes which occur between standard decal painting of the electrodes and tape casting
- Study the role the catalyst composition plays in the development of the overall electrode structure
- Suggest modifications to the electrode forming process to optimize the use of the precious metal catalyst

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Introduction

Proton exchange membrane (PEM) fuel cells hold great promise for use as an environmentally friendly power source for automobiles. One of the key requirements in making PEMs commercially viable is to reduce the cost by reducing the amount of precious metal catalyst necessary to provide high power density operation at low temperature. In order for efficient catalysis to occur, gas molecules must be able to easily interact with the surface of the catalyst particles. A pathway for diffusion of protons must exist in close proximity to the active sites on the catalyst, and an electrically conductive pathway from the catalyst to the electrodes is required for electron transport. Finally, water (the by-product of the fuel cell reaction) has to be transported away from the catalyst for continuing reaction to occur. These requirements show the complexity of building an efficient PEM fuel cell and clearly indicate the opportunity for atomic-scale microstructural and chemical characterization to provide feedback on the geometry and distribution of the various components for optimum performance.

PEM fuel cells are well known to "age" upon application as a power source. Over time, the performance of both individual cells and the overall system degrades. By examining the structure and composition of the MEAs before and after use in a fuel cell environment, the changes which may have occurred can provide valuable information on the mechanism(s) of performance loss. Understanding the primary degradation mechanisms is the first step to successfully engineering an improved MEA with less performance loss.

Approach

Cross-sections of PEM MEAs were prepared for transmission electron microscopy (TEM) by techniques of ultramicrotomy. Small sections from the MEAs, approximately 3 mm by 8 mm, were selected for sample preparation. The samples were placed into silicone embedding molds, and an Araldite epoxy resin was added to the molds to embed the sample. The resin was polymerized at least 16 hours at 60°C in order to produce a solid epoxy piece with the MEA sample embedded. The epoxy embedded sample was trimmed initially using a Leica EM Trim tungsten carbide trimming tool. A tungsten carbide tip was used to rapidly remove excess epoxy from around the MEA sample to produce a small, flat area suitable for ultramicrotomy. The nature of the MEAs dictated a narrow (0.25 to 0.5 mm), long (1-2 mm) area for ultramicrotomy. The epoxy-embedded MEA was then secured into the cutting arm of a Leica Ultracut UCT Ultramicrotome. A 45° diamond knife was used to slice several sections of various thicknesses from each sample. The goal is always to produce the thinnest possible slice for TEM examination. Slice thicknesses were typically 100 nm or less under room temperature microtomy conditions, facilitated by proper development of the appropriate resin mixture. The thin slices were floated off the diamond knife edge onto distilled water and then collected onto copper mesh grids.

The thin samples were observed in either a Hitachi HF-2000 field-emission transmission electron microscope (FE-TEM) or in a Hitachi HD-2000 dedicated scanning transmission electron microscope

(STEM, also a field emission instrument). Both high resolution TEM imaging of individual catalyst particles and their carbon support and atomic number (or "Z-contrast") STEM imaging of the electrode structure were performed. The structure of the electrodes is key for good performance. The "three phase boundary" where porosity, ionomer and catalyst particles come together is where effective catalysis occurs. Both imaging and chemical composition analysis are provided by TEM at the length scale which is appropriate for understanding the details of the electrode structure. Additionally, the boundary between the electrode and the membrane is of great interest to the fuel cell community. A number of indirect electrochemical measurements suggest that the interface between the electrode and the membrane is a weak point in the durability of the overall system. Analysis of the structure and composition of this area for both freshly prepared MEAs and MEAs which have been used in a fuel cell for a number of hours provides a first step towards reducing the degradation of PEM fuel cells over time.

Results

Advances in room temperature ultramicrotomy this fiscal year have allowed us to prepare MEA cross-sections which are below 100 nm in thickness. Figures 1 and 2 are Z-contrast micrographs of sections from the same MEA electrode illustrating the benefits of the thinner section. Z-contrast imaging is a technique in the STEM which forms an image from the electrons, which are scattered to large angles by the atoms of the sample (1). Atoms with a larger atomic number (Z) scatter electrons to high angles more strongly than atoms with lower atomic number. In the case of PEM fuel cell electrodes, the high atomic number catalyst particles (typically Pt) scatter electrons to a much greater degree than the surrounding ionomeric material and therefore appear as bright specks in the image. The sample shown in Figure 1 is 300 nm thick, which is sufficiently thin for successful imaging and microanalysis of the electrode. Transmission electron microscopy always involves the projection of a three-dimensional microstructure onto a two-dimensional image. In this case, significant overlap of the catalyst particles is observed with a thickness of 300 nm. Significant data can be extracted from images such as Figure 1, including the size distribution of the catalyst particles and the gross electrode structure. However, details of the spatial distribution of the ionomer and the porosity are obscured by the thickness of the section shown in Figure 1. Figure 2 is a Z-contrast micrograph from a 100 nm thick section of the same MEA. The individual catalyst particles are more easily seen in Figure 2 versus Figure 1. Additionally, the porosity of the electrode is seen in the dark area in the lower section of the micrograph. Evidence of the carbon black support of the catalyst particles is seen in the grayscale difference between the background of the image and the brighter areas around the catalyst particles. The catalyst particles are seen to coat the surface of the carbon black

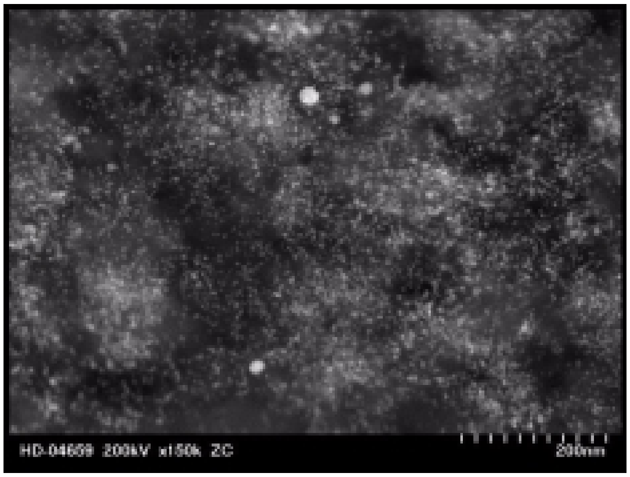

Figure 1. Z-contrast Micrograph of a 300 nm Thick Section of an MEA Electrode

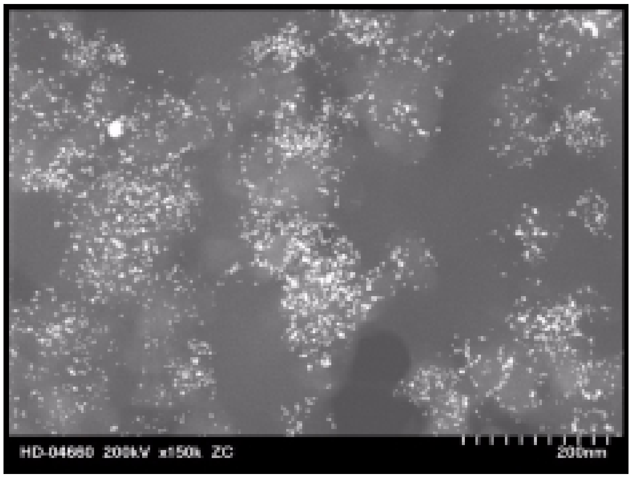

Figure 2. Z-contrast Micrograph of a 100 nm Thick Section of an MEA Electrode

support. A much more thorough understanding of the detailed structure of the electrode is possible from the image in Figure 2 as compared to the image in Figure 1. The thicker specimen allows for the characterization of the catalyst particles and the gross spatial distribution of the catalyst, while the thinner specimen allows, for the first time, a direct observation of the spatial distribution of all three phases of an MEA electrode: catalyst and support, ionomer and porosity.

The effect of boiling the MEA in sulphuric acid on the initial microstructure of the electrode was also investigated this fiscal year. Figures 3 and 4 are TEM micrographs of electrode for sections ~100 nm thick. Bright-field TEM images are formed from unscattered and low-angle scattered electrons. At low resolution, the bright areas of the image correspond to porosity and/or low scattering parts of the sample. The MEA shown in Figure 3 did not undergo the boiling step during the preparation process for the MEA. The section was sufficiently thin that the porosity, catalyst and support and ionomer are clearly distinguishable. The small black specks are the individual catalyst particles, while the larger circular features are the carbon black support. The ionomer is the overall light grey background, while the porosity is visible as the white areas in the micrograph. The catalyst clusters are very close together in Figure 3, with very little ionomer-only area visible. Figure 4 illustrates the electrode structure on an MEA which was boiled in sulphuric acid as part of the fabrication process. The section thickness and micrograph magnification are the same as in Figure 3. The catalyst clusters are better separated, with obvious areas of ionomer visible in the image. Catalyst particles in PEM fuel cell MEAs have previously been shown to coarsen with time during fuel cell use. The microstructure in Figure 3, where the catalyst particles start off much closer together than the corresponding structure in Figure 4, is much more susceptible to catalyst coarsening and the subsequent performance loss.

Conclusions

- Room temperature ultramicrotomy is capable of producing MEA cross-sections 100 nm thick.
- Sections that are 100 nm thick allow for the characterization/analysis of **all** the components of a PEM fuel cell electrode, while thicker sections do not.
- Boiling in sulphuric acid has a great effect on the initial microstructure of the electrode in a PEM fuel cell MEA.

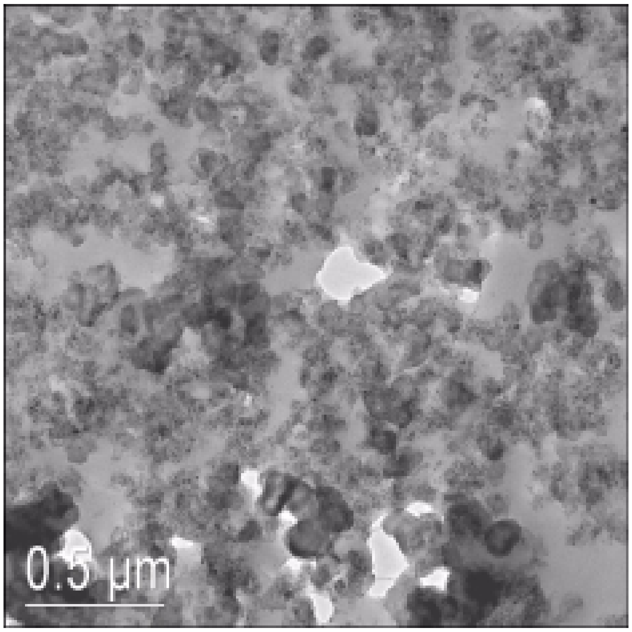

Figure 3. TEM Micrograph of an MEA Electrode not Boiled in Sulphuric Acid

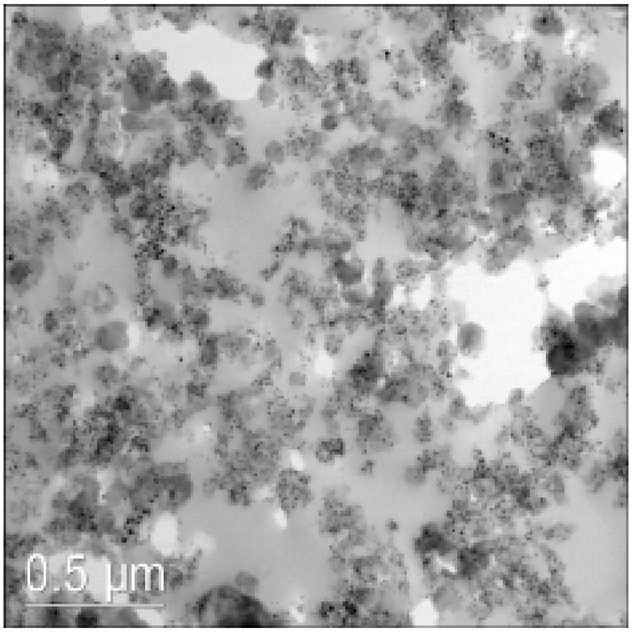

Figure 4. TEM Micrograph of an MEA Electrode which was Boiled in Sulphuric Acid

- The boiling process is expected to improve the durability of the electrode by increasing the distance between catalyst particle regions.

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2. D. A. Blom and L. F. Allard, "TEM Characterization of PEM Fuel Cells", 2003 DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Merit Review and Peer Evaluation Meeting.
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Validation of an Integrated System for a Hydrogen-Fueled Power Park

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Objectives

- Determine the optimal natural gas to proton exchange membrane (PEM) power system
  - Central reformer or local reformers
  - Central PEM or local PEM
  - Waste heat utilization
  - Operating mode
- Determine the ideal site for a power park
  - Total peak power
  - Power profile
  - Commercial or industrial
  - Utilization
- Optimize the system for lowest total power price
- Demonstrate a prototype natural gas to PEM power park at a suitable site

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Durability
- F. Heat Utilization
- G. Power Electronics
- H Startup Time

Approach

- Investigate and estimate the cost for each system configuration
- Determine the optimal (lowest cost of power) system configuration
- Provide the best cost of power today and in the future
- Determine building types that are amenable
- Determine the optimal operating mode (baseload, peakshave, backup, island)
- Investigate fuel cell capabilities today vs. optimal operating requirements and DOE targets

Accomplishments

- Modeled the cost of power as a function of fuel cost, efficiency, maintenance, fuel cell and reformer costs, return on investment, and overhead
- Determined the required fuel cost, efficiency, and capital costs to provide 10% return on investment at \$0.10/kWh cost of power
- Determined the amenable building types
- Determined the unit costs of hot water piping, hydrogen piping, and electrical wiring
- Estimated the impact of waste heat utilization on the cost of power
- Examined current state-of-the-art reformer, purification, power conditioning, and fuel cell systems
- Studied various distributed generation projects to identify the factors that contributed to the decision to install distributed generation

Future Directions

- Hydrogen energy stations (fueling and power generation concurrently)
- Other system cycles that are more efficient

Introduction

The goal of this project is to develop an optimized power generation system with natural gas as the fuel and PEM fuel cells providing the conversion to electricity. The first step of this project was to identify all possible processes that could be used to produce power from natural gas. Construction and capital costs were then collected from all available vendors of reformers, purification, and fuel cells. A cost of power model was built to provide rapid calculations while changing inputs. The selection of the optimal process was then completed based on the cost of power.

The next step involved a reverse calculation to determine what fuel cost, utilization, capital costs, and efficiency were required to achieve a target electricity cost of \$0.10/kWh. These answers determined the target size, operating mode, costs, and efficiencies for the system to meet DOE targets. The optimal system did not meet the DOE targets, so we continue to look into hybrid systems, such as the Hydrogen Energy Station (joint fueling and power production).

Approach

Each process was modeled using ASPEN Plus (modeling software) to determine system efficiency and potential waste heat. The construction costs were estimated by our construction estimating group using Penn State as the site with three buildings located 200 yards (each) away from a central location. The capital cost of reformers, purification systems, and fuel cells were determined by obtaining quotations from all identified manufacturers. The cost of power model was developed from our standard cost of gas model. Building power profiles were provided by Joe Huang, Lawrence Livermore National Laboratory (LLNL).

Results

There are a number of improvements that are required to achieve \$0.10/kWh power cost. These include:

- 25% increase in overall efficiency
- 4000% increase in fuel cell life
- 500% increase in power output
- 95% reduction in cost of PEM fuel cell and 75% reduction in cost of reformer system

The most effective use of PEM power both in terms of power cost and environmental impact would be in a baseload power application.

Combined heat and power has a minor effect on the cost of power, as the reformers already utilize the majority of the waste heat. The remaining waste heat is low grade and is most likely only amenable to supplementing hot water requirements.

Conclusions

- Today's cost of power from natural gas fueled PEM fuel cells is $0.45/kWh.
- Pressurized steam methane reforming with pressure swing adsorption (PSA) purification is the optimal system.
- Requirements to reduce cost to $0.10/kWh include:
  - 40% total efficiency (31% best today)
  - $3,300/kW capital cost ($14,000/kW today)
  - 15 year life or 131,400 hrs (1,000 hrs today)
  - $3.37/MMBTU natural gas price ($5.65/ MMBTU at smaller sizes)
- Size of the system needs to be above 800 kW to achieve industrial natural gas rates.
- Hydrogen energy station or other complex cycles could provide better utilization or efficiencies.

References

1. Joe Huang (LLNL) - building power profiles
2. Vendors - Reformer, PSA, metal membrane, and fuel cell costs and performance data.

FY 2003 Publications/Presentations

1. Poster Session at 2003 Annual Program Review and Peer Evaluation

Novel Compression and Fueling Apparatus to Meet Hydrogen Vehicle Range Requirements

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Objectives

- Develop or identify components suitable for 700 barg hydrogen refueling
- Develop an isothermal compressor for low cost, gaseous compression
- Demonstrate a prototype compressor at a suitable site

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. High Costs of Hydrogen Compression

Approach

- Develop a compression cycle that utilizes low cost components
- Test fluids for use in the compression cycle
- Develop components for 700 barg fueling
- Test various components in service

Accomplishments

- Developed a compression cycle that is low cost
- Built a test skid for testing of fluid properties at various hydrogen pressures
- Developed new components with leading vendors for 700 barg fueling
- Initiated testing of high pressure components for durability and life

Future Directions

- Build a prototype compressor with a capacity of approximately 1 nm3/hr
- Test alternate working fluids

Introduction

The goal of this project is to develop a low cost, isothermal gaseous compressor. The first step of this project was to identify all possible processes which could be used to compress gaseous hydrogen. Construction and capital costs were then estimated, and the design was refined based on the target costs.

A parallel effort was begun to develop high pressure fueling components that have the desired cost, life, and performance.

Approach

Each process was modeled using ASPEN Plus (modeling software) to determine system efficiency and to determine component sizing. Local fabricators with relevant experience estimated the construction costs.

We approached Air Products preferred vendors and began co-development of a number of valves and instruments to support 700 barg fueling.

Results

We have tested a number of components and fitting types in hydrogen fueling service. Based on this experience, we have determined that medium pressure cone and thread fittings are the most robust fittings for these pressures.

We have also found that a number of hydrogen fueling components require additional refinement. Permeation of softgoods or diaphragms and explosive decompression are two common issues.

High pressure storage is the most difficult area as no cost-effective options exist today. Steel vessels at 14,000 psig maximum allowable working pressure, required for cascade filling, are very expensive. Stainless steel machined vessels are also very expensive. Composite storage vessels hold the most promise. Composite storage vessels have currently been granted Department of Transportation exemptions for specific tanks of specific design. No American Society of Mechanical Engineers (ASME) exemptions or certifications exist for a stationary application like fueling.

We have just begun testing various fluids to determine their impact on the thermodynamics of isothermal compression of hydrogen.

Conclusions

- An isothermal compressor is feasible.
- Thermodynamics of process fluids with hydrogen are unavailable at 700 barg, so we will develop our own data.
- High pressure components can be developed at reasonable prices for 700 barg fueling.
- Storage is the most difficult component as it must be rated at 135% of the fueling pressure.
- Composite cylinders could one day provide a viable storage solution with lowered costs and ASME approval.

References

1. Vendors - Compressor components, instruments, fittings, and valves.

FY 2003 Publications/Presentations

1. Poster Session at 2003 Annual Program Review and Peer Evaluation

Special Recognitions & Awards/Patents Issued

1. Patent application is pending on the compressor cycle.

Hawaii Hydrogen Power Park

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Implementing Partner: Hawaii Natural Energy Institute, Honolulu, HI
Principal Investigator: Richard E. Rocheleau
Project Manager: Mitch Ewan

Objectives

- Demonstrate an integrated hydrogen power park comprised of the following:
  - Electrolyzer powered by a renewable energy source,
  - Hydrogen storage and distribution system,
  - Proton exchange membrane (PEM) fuel cell connected to the grid & building, and
  - Optional hydrogen-fueled vehicle dispensing system;
- Demonstrate hydrogen as an energy carrier;
- Investigate interface issues with grid and buildings;
- Identify codes & standards required to site a power park;
- Identify barriers to a hydrogen infrastructure;
- Educate local authorities on hydrogen technologies;
- Prepare an economic analysis of hydrogen infrastructure development;
- Generate public interest and support.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Hydrogen Production

- T. Renewable Integration

Off-Board Hydrogen Storage

- U. Codes and Standards
- V. Life Cycle and Efficiency Analysis

Technology Validation

- B. Hydrogen Storage
- C. Hydrogen Refueling Infrastructure
- E. Codes and Standards

- H. Hydrogen from Renewable Resources
- I. Hydrogen and Electricity Co-production

Education

- A. Lack of Awareness
- B. Lack of Demonstrations or Examples of Real World Use
- C. Institutional Barriers and Access to Audiences

Approach

Sequence of steps used to conduct the research:

Phase 1

- Design the Hawaii Power Park System proceeding from conceptual design, to detailed design, to final design;
- Map out the permitting processes and develop a permitting plan;
- Educate the local permitting authorities and prepare a community outreach plan;
- Procure and test the individual system components at the Hawaii Fuel Cell Test Facility ("FCTF") located in Honolulu, including use of a UTC single-cell PEM fuel cell;
- Procure initial fuel cell module;
- Procure and install the data acquisition system;
- Develop the Power Park systems model.

Phase 2

- Procure additional fuel cell power system modules;
- Obtain all necessary permits to relocate to the Natural Energy Laboratory Hawaii Authority (NELHA) Distributed Energy Resources (DER) Center;
- Complete necessary site improvements to receive equipment;
- Ship system from FCTF to NELHA DER Center;
- Interface the system with the commercial building and the utility grid;
- Add new systems, high pressure storage, renewable electrolyzer systems as funding allows;
- Conduct community education & outreach program;
- Conduct initial engineering cost & performance analysis.

Phase 3

- Prepare test plans & procedures;
- Conduct experiments, analyze the data and prepare reports;
- Develop a business case for hydrogen;
- Prepare an overall project Final Report.

Accomplishments

- Permits for FCTF system development site issued;
- Electrolyzer delivered, installed and commissioned at the Hawaii FCTF;
- Prototype hydrogen gas distribution panels designed, installed and operated;
- Candidate site selected subject to negotiation of a satisfactory lease agreement;

- Negotiations initiated for procurement of first 5-kW PEM fuel cell module from UTCFC;
- Interactive project management web site developed.

Future Directions

- Continue in accordance with the project plan;
- Seek new partners to expand test bed capabilities for hydrogen technologies.

Introduction

Distributed power generation is increasingly viewed as an important component of the future electrical energy supply in the United States. A "Hydrogen Power Park" is a distributed power system comprised of locally available energy sources such as natural gas or renewable electricity generated by wind, geothermal or solar. The natural gas is reformed to produce hydrogen. The renewable electricity powers an electrolyzer to produce hydrogen. The hydrogen is stored and then used in a fuel cell or an environmentally acceptable hydrogen or hydrogen/natural gas internal combustion engine (ICE) to generate electricity to power a building complex or industrial facility. The hydrogen could also be used to fuel automobiles equipped with fuel cells or hydrogen internal combustion engines. As hydrogen technologies become competitive with conventional energy technologies, the "Hydrogen Power Park" concept is considered by the DOE to be an important step towards developing the viability of using hydrogen as an "energy carrier" in distributed power generation applications.

In addition to the technical barriers being addressed through RD&D in laboratories for specific components of a hydrogen system, there are obstacles to successful implementation of fuel cells and the corresponding hydrogen infrastructure that can only be addressed by integrating the components into complete systems. To have confidence in these technologies, they must work as designed in "real world" systems. Power Park projects are part of the validation process. They are comprised of the most current technologies and operated in a real-world environment. A by-product of this approach to technology validation is that technical and system problems are revealed, and component requirements can be better evaluated.

Approach

Our project approach was to first assemble a very strong public/private team whose members support the Power Park's objectives and have relevant hydrogen expertise to bring to the project.

Our project team organization is illustrated in Figure 1. Our project partners include those companies that are responsible for supporting infrastructure for conventional fuels, electricity, and utility gas. Their participation will ensure that issues critical to integrating hydrogen systems within the existing fuels and electricity delivery infrastructure are considered. The roles and interests of the team members are as follows:

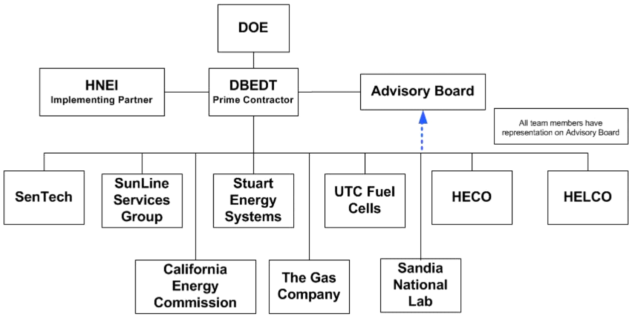

Figure 1. Project Team & Organization

State of Hawaii - Hawaii Department of Business, Economic Development and Tourism (DBEDT):

- DBEDT provides state leadership to the introduction of a hydrogen infrastructure in the State of Hawaii and to bringing hydrogen systems into the marketplace. Through the implementation of this project, the state envisions the creation of a "living laboratory" that will allow the state to address a number of issues to overcome impediments for the utilization of DER systems and hydrogen development.

- DBEDT is the Prime Contractor.
- DBEDT provides overall program coordination and is a cost share partner.

Hawaii Natural Energy Institute, University of Hawaii (HNEI):

- HNEI, a research unit within the School of Ocean & Earth Science & Technology (SOEST) at the University of Hawaii Manoa, has been an active participant in DOE's Hydrogen Program since 1986 and, in 1996, was named a DOE Center of Excellence for Hydrogen Research & Education.
- HNEI is the Implementing Partner to execute the project on behalf of DBEDT.

Sentech:

- SenTech is a Washington DC consulting company that provides technical and economic analysis, education and outreach, and project management support to the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program.

UTC Fuel Cells (UTCFC):

- UTCFC has a long history of commercializing fuel cells and is considered by many to be the premier U.S. fuel cell company in both stationary and transportation applications.
- UTCFC will supply fuel cell systems and engineering support for installation and evaluation.

Stuart Energy Systems:

- Stuart is a major developer and supplier of electrolyzers and has an extensive program to develop electrolyzers powered by renewable energy sources. This project provides a venue for testing and demonstrating their products in a real world environment.
- Stuart is providing significant cost share.

Hawaii Electric Light Company (HELCO):

- HELCO is the electric utility on the Big Island. HELCO is a subsidiary of HEI, which is the holding company for the electric utilities on Oahu, Maui and the Big Island.
- HELCO shall provide engineering and staff expertise in the permitting process and design of the interconnections between the grid, the electrolyzer, the fuel cell power system and the commercial test building.
- HELCO shall utilize the existing utility consumer education programs to provide an outreach medium for the Power Park project.

Hawaiian Electric Company (HECO):

- HECO is the electric utility for the island of Oahu and is the largest of the Hawaiian electric utilities.
- As part of its ongoing interest in and support of renewable energy projects, HECO has agreed to participate in the Power Park project and is providing engineering and staff time to review system designs on a cost share basis.

The Gas Company (GasCo):

- GasCo is the gas utility for Hawaii. It supplies Synthetic Natural Gas (SNG) to parts of Oahu and propane to the remainder of Oahu and the neighbor islands;
- GasCo is supplying low pressure hydrogen storage tanks and related engineering and permitting expertise.

SunLine Services:

- SunLine is providing engineering and staff time to transfer its expertise in the permitting process, community outreach programs, and design of a hydrogen infrastructure.
- Participation in design review meetings to be conducted on the Big Island to provide valuable "Lessons Learned" and technology transfer from the SunLine experience.

California Energy Commission (CEC):

- CEC has an interest in supporting the introduction of hydrogen infrastructure and DER in California. The Hydrogen Power

Park provides the opportunity to leverage CEC resources in a dedicated test bed that is available to conduct projects of specific interest to CEC and California utilities at a fraction of the cost of establishing a similar facility.

Sandia National Laboratory Livermore (SNLL):

- SNLL is a recent addition to the Hawaii Hydrogen Power Park team.
- SNLL is developing flexible systems that can be quickly adapted to provide engineering analysis of advanced power parks for production of both hydrogen and electricity.

The complete Power Park Project spans three years and is divided roughly into three 1-year phases which closely match the expected cash flow. The design of the system shall provide the flexibility to add components and new technologies as desired by existing and new partners. The "Hawaii Hydrogen Power Park" conceptual design is illustrated in Figure 2. The diagram shows an optional wind hydrogen system, an optional reformer system and an optional fuel dispensing system for transportation systems. While the initial project called for the testing of a PEM fuel cell system, an internal combustion engine running on hydrogen or a hydrogen rich mixture is an option of interest to the CEC and GasCo. The optional systems are subject to the availability of additional project funding.

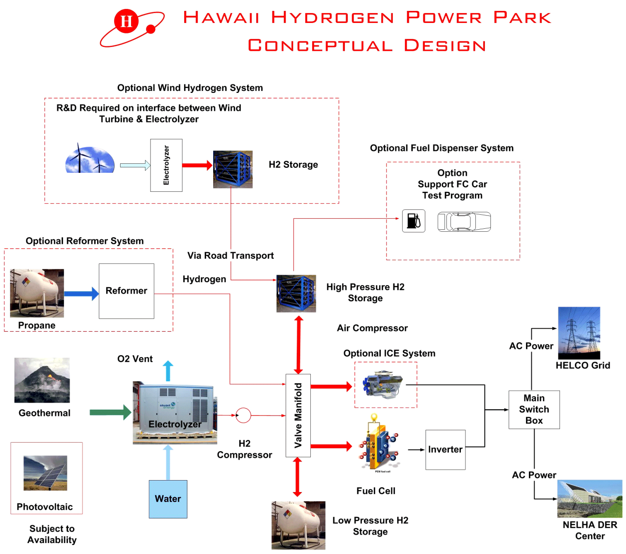

Figure 2. Hawaii Power Park Conceptual Design

Project Implementation. Due to funding cash flow availability, Phase 1 was subdivided into two phases 1A & 1B. Phase 1A constitutes the design phase of the project and extends until October 2003. Phase 1B constitutes the procurement and assembly of the hydrogen production and storage systems and the first fuel cell module. Phase 1B extends until approximately June 2004 and overlaps with Phase 1A. In Phase 1A, the overall Power Park system shall be designed, starting with a conceptual design and going through progressively more detailed iterations resulting in a final design. The hydrogen production and storage system required to support the fuel cell and systems testing will be assembled and tested in Phase 1B at the Hawaii Fuel Cell Test Facility (FCTF) site in Honolulu. The hydrogen during this initial phase will be produced from a grid-connected Stuart Energy Systems electrolyzer. The first fuel cell module will also be procured and integrated into the hydrogen system at the FCTF site during Phase 1B. Identifying and resolving safety and permitting issues are also critical Phase 1 tasks. Analytical tasks in Phase I will focus on defining the power requirements for the Power Park and calculating the costs of hydrogen from the various primary energy options (solar, wind, geothermal etc.).

In Phase 2, the primary emphasis will be on installing and demonstrating the hydrogen and fuel cell systems at the Gateway Center facility. Funding permitting, we will expand and diversify the hydrogen production technologies by adding a second electrolyzer connected directly to a wind turbine at a Big Island wind farm and transport the hydrogen by means of high pressure tanks to the Power Park site. The system will be modular (trailer or skid-mounted) and portable so that it can be moved to other renewable energy source sites on the Big Island and to other Hawaiian islands.

Phase 3 will consist of a series of system experiments for system optimization, market development activities and an expansion of the education and outreach program. A series of studies and analyses will be performed to evaluate system

Figure 3. Stuart Energy Systems Electrolyzer at the FCTF

design differences between automotive and stationary applications.

Results

The project is in the early stages of designing and assembling the system. To date we have prepared a conceptual design of the Power Park and are working on the detailed design. The electrolyzer, a long lead item, has been delivered to the FCTF and has been commissioned. The electrolyzer is pictured in Figure 3. We have also gone through the process of permitting the FCTF site and have received the permits. This experience will help in the permitting process required by the County of Hawaii on the Big Island. We have assembled a high pressure gas storage system and connected the electrolyzer hydrogen output. Negotiations are currently underway for the supply of the first PEM fuel cell module, which will be tested at the FCTF.

Conclusions

- This project is in the formative stage and no conclusions can be drawn at this time.

FY 2003 Publications/Presentations

1. Poster presentation at the 2003 Hydrogen & Fuel Cells Merit Review Meeting - 19-22 May 2003 at Berkeley California

Hydrogen Power Park

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Objectives

Discover and document whether the power park concept is technically and economically viable as a clean energy system, and if so, under what operating and market conditions. Specific objectives include:

- Identify the drivers of economic performance for multi-use hydrogen energy systems including energy sources (renewable & conventional fuel sources), capital costs, operation and maintenance (O&M) costs, and emissions (cost benefit analysis vis-à-vis pollution non-attainment areas).
- Determine conditions for system optimization and cost reduction for hydrogen systems, including design footprint and multi-use energy station applications.
- Identify the characteristics of an economically viable hydrogen-based energy system designed for peak shaving and vehicle fueling applications.
- Accelerate the development of technology delivery, system operations, and applications experience in hydrogen energy systems.
- Collect and evaluate operational, durability, and efficiency information for an integrated renewable/electrolyzer system.
- Contribute to development of relevant safety standards and protocols for hydrogen-based power systems.
- Evaluate the market for integrated hydrogen energy systems: develop a business plan for distributed hydrogen energy systems, as appropriate; test potential for "green power" customers.
- Educate the public: promote awareness of hydrogen-based energy systems through development of educational materials and group sponsored events.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- C. Hydrogen Refueling Infrastructure
- D. Maintenance and Training Facilities
- E. Codes and Standards
- H. Hydrogen from Renewable Resources
- I. Hydrogen and Electricity Coproduction

Approach

- Develop, install, and operate a hydrogen co-production facility capable of delivering ~500 kWh/day of on-site electricity and ~15 kg/day of compressed hydrogen for vehicle refueling.
- Integrate renewable energy into an end-to-end hydrogen energy station concept that utilizes solar & biomass power combined with electrolysis and stationary PEM fuel cell technology to take advantage of power during off-peak hours to generate hydrogen for on-peak power generation and vehicle fueling.
- Using the latest hydrogen generation, storage, regeneration and control technologies, evaluate opportunities to reduce overall system cost and maximize performance through optimization of system design & operation, practical approaches to permitting, and integration of power and transportation applications using a common hydrogen infrastructure.
- Obtain permits and install an integrated electrolytic hydrogen production, storage, on-site power generation, and vehicle refueling facility in the State of Michigan.

Accomplishments

- Selected team
- Established optimal technologies and sources
- Developed work plan & budget
- Established codes & standards framework
- Selected system site
- Began system design & permitting - 20% complete
- Procured equipment - 75% complete

Future Directions

- Install & commission system
- Develop education & outreach program
- Operate, monitor, and maintain system
- Develop project technical report
- Assess economics & develop business plan, as appropriate
- Document and publish project results

Introduction

Given the potential for the commercialization of hydrogen as a replacement energy carrier for fossil fuels, this demonstration project, which models a complete renewable hydrogen system, from biomass/solar power to hydrogen generation and storage to electrical generation and vehicle fueling, will provide meaningful information to overcoming the technical and economic challenges of realizing a hydrogen-based economy.

The project develops, installs, and operates a hydrogen co-production facility capable of delivering ~500 kWh/day of on-site electricity and ~15 kg/day of compressed hydrogen for vehicle refueling (Figure 1). By incorporating the most commercially representative units into a complete system operated under realistic scenarios, this approach can provide data necessary to validate component technical targets and feedback for efficient Department of Energy R&D program management.

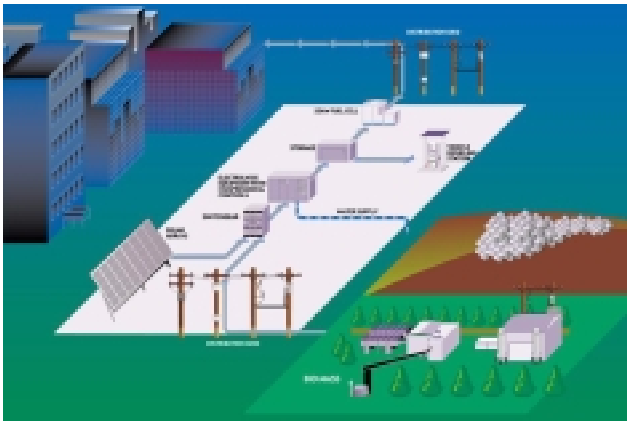

Figure 1. DTE Energy Hydrogen Power Park, Southfield, MI

Approach

This project integrates renewable energy into an end-to-end hydrogen energy station concept that utilizes solar & biomass power combined with electrolysis and stationary PEM fuel cell technology to take advantage of power during off-peak hours to generate hydrogen for on-peak power generation and vehicle fueling (Figure 2).

Using the latest hydrogen generation, storage, regeneration and control technologies, the project will evaluate opportunities to reduce overall system cost and maximize performance through optimization of system design and operation, practical approaches to permitting, and integration of power and transportation applications using a common hydrogen infrastructure.

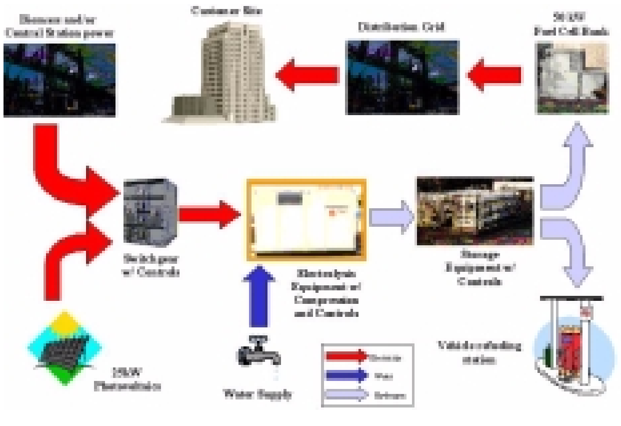

Figure 2. Hydrogen Power Park - Conceptual Drawing

The system components include: ~170 kW electrolyzer (effective for low volume on-site hydrogen requirements); compressed gas storage at +5,000 psi (proven, safe, relatively cost effective); 25 - 75 kW fuel cell bank (quiet, clean, efficient); refueling dispenser at up to 5,000 psi (state-of-the-art).

Results

Phase I (months 1 - 6) of the overall project plan has been completed with Phase II (months 7 - 18) in progress. Milestones achieved in Phase I included project team selection, establishment of optimal component/system technologies and sources, development of work plan and budget, establishment of codes and standards framework, and system site selection.

Key activities currently underway include system design & permitting - 20% complete, and equipment procurement - 75% complete. Future milestones include installation and commissioning of system (April 2004); development of an education and outreach program; operation, monitoring, and maintenance of the system; development of the project technical report; assessment of the economics and development of a business plan for distributed hydrogen energy systems, as appropriate; and documentation and publication of project results.

Conclusions

The project remains on-schedule with the original plan, despite a delay in reimbursement monies from FY03 to FY04 and a lack of fully developed subsystems that are representative of commercial units. Industry dynamics resulting from increased economic pressures and changing target markets have resulted in a lack of fuel cell power generation and hydrogen production subsystems that are ready for market. This presents increased risk of execution for system designers and integrators, as these subsystems must first be demonstrated and tested before being incorporated into complete systems and tested under real-world operating conditions.

In addition to these challenges, the current level of hydrogen codes and standards development has resulted in modifying system design and implementation plans to mitigate project execution risk.

The above challenges have, however, accelerated the development of component and hydrogen system applications knowledge within the company. This kind of rapid experience building is an important outcome of the technology validation program that increases the likelihood of successful development of technically and economically viable hydrogen energy systems.

FY 2003 Presentations

1. R. Regan, "DTE Energy Hydrogen Power Park" poster session, DOE Merit Review, Berkeley, CA (2003)

Power Parks System Simulation

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Objectives

- Develop a flexible system model to simulate distributed generation in power parks that use H_2 as an energy carrier.
- Analyze the dynamic performance of demonstration systems to examine the thermal efficiency and cost of both H_2 and power production.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- C. Hydrogen Refueling Infrastructure
- I. Hydrogen and Electricity Coproduction

Approach

- Develop a library of Simulink modules for the various components.
- Assemble the components into system models for the different power parks.
- Compare simulations to the operational data from demonstration sites.

Accomplishments

- The library of components includes reformers (steam methane reformers - SMR, autothermal reformers - ATR), a fuel cell stack, a multi-stage compressor, a high-pressure storage vessel, an electrolyzer, a photovoltaic (PV) collector, and a model for incident solar radiation.
- Simulation of the sub-components in the SunLine system compared favorably to the observed data. The model evaluates the thermal efficiencies of the PV and electrolyzer systems.

Future Directions

- Continue to develop additional modules in the Simulink library, including a wind turbine, a H_2-fueled internal combustion engine (ICE) generator, and a power conditioning system.
- Develop a layer of analysis to compute the cost of the power and H2 generated, including the initial capital costs of the components and the continuous operation costs during the life of the simulation.
- Compare the simulations of dynamic performance with data collected from demonstration sites at SunLine, Las Vegas, and Hawaii (HNEI).
- Implement a control strategy to direct the power within the park to meet the internal load while optimizing the energy efficiency and cost.

Introduction

The hydrogen program research plan [1] envisions the transition to widespread H_2 distribution will likely begin with distributed generation of H_2. This avoids, at least in the near term, the construction of H_2 pipelines, using existing distribution capabilities for fuels like natural gas. In addition, the cost of H_2 produced at small-scale facilities may be reduced by combining power generation by fuel cells or engines to supply local needs. Such distributed energy sites where power generation is co-located with businesses or industrial energy consumers are called power parks.

Proposed power parks use combinations of technologies. A local power source is often combined with a storage technology to adapt the dynamic nature of the source to the load. In some cases, the system operates completely separate from the utility grid. Alternatively, the power park may use the utility grid as a storage device, selling power to the utility when there is excess and drawing power when the local source cannot meet the load. The refueling facility at the City of Las Vegas is an example of this approach. The system is designed to operate the SMR in steady state, with the H_2 produced being split between a refueling station and a fuel cell stack selling power to the grid.

Often, power parks are sited in order to take advantage of a renewable energy source. Generation by photovoltaic collectors or wind turbines can be combined with energy storage technologies. Power parks provide an excellent opportunity for using hydrogen technologies. Electricity from the renewable source can be used to generate hydrogen by electrolysis, which is then stored for use in fuel cells or to refuel vehicles. The SunLine Transit Agency has been demonstrating the PV-electrolyzer-refueling system for a couple years, with the plan to bring some wind turbines on line in the next year.

The variety of technologies and their combinations that are being proposed for power parks suggests that each system will be novel, at least in some aspect of its design. Consequently, a flexible simulation tool will be very useful in evaluating the various systems and optimizing their performance with respect to efficiency and cost.

Approach

The deliverable of the project will be a flexible tool for simulation of the local power generation system, constructed in the language of Simulink software [2]. Simulink provides a graphical workspace for block diagram construction. The workspace provides the flexibility to quickly assemble components into a system, or to morph one system into another. Simulink performs dynamic simulation by integrating the system in time using a collection of ordinary differential equation solvers. After the simulation is completed, the solution can be examined by plotting variables at various states in the system. Simulink also contains modules for dynamic control and solution of iterative loops within the system.

The software design begins with development of a library of Simulink modules that represent components in the power system. The component models are based on fundamental physics to the extent practical. These models are generic, in that they are not customized to represent a specific brand or manufacturer's features for the component. However, the generic components from the library can be tied to a specific unit by relying on performance data. The library components can be quickly modified to represent new or specialized components, thereby expanding the library's collection.

Many of the basic modules that represent hydrogen and other gas mixtures use the Chemkin [3] software package to provide thermodynamic properties of the species and mixtures. For example, the SMR module uses equilibrium solutions for the chemical composition of both the catalytic reactor and the combustor sub-components.

Results

We have developed a library of Simulink modules for some of the various components being proposed for power parks. Existing components include reformers (SMR and ATR), a fuel cell stack, a multi-stage compressor, a high-pressure storage vessel, an electrolyzer, a PV collector, and a model for the incident solar radiation.

The reformer modules take an input flow rate of methane and compute the hydrogen output. The SMR module performs an internal balance to supply the energy required by the catalytic reactor by combusting the reformate stream. The ATR module includes some air in the process to balance the endothermic reforming with some partial oxidation of the fuel. In either type of reformer, the temperature at which the equilibrium reforming occurs depends on the energy balance and the mixture parameters (steam-to-carbon, oxygen-to-carbon). More detailed analysis of the reformer sub-systems is presented in references [4, 5], where the predictions of the models have been compared to data from small-scale reformers operated in our laboratories.

Combining electrolyzer and compressor modules provides a comparison to the electrolyzer operation data from the SunLine facility [6]. The electrolyzer module uses a simple energy balance, which is defined by a specified thermal efficiency. The compressor module represents an ideal multi-stage compression with uniform efficiency in each state. Figure 1 compares the steady-state model to SunLine's operation data for two electrolyzer units manufactured by Stuart Energy and Teledyne Energy Systems. The solid lines represent the thermal efficiency of the electrolyzers, while the dashed lines represent the combined efficiency that includes the power required to compress the H_2 from the output pressure of the electrolyzer to the storage pressure.

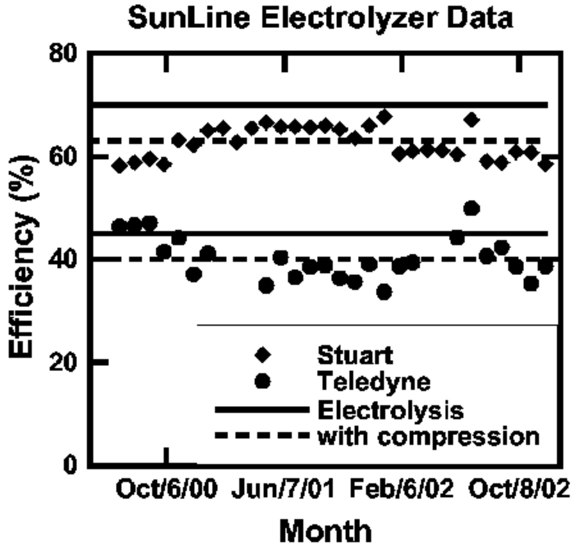

Figure 1. Comparison of the Simulated Thermal Efficiency for the Electrolyzers Operating at SunLine Transit Agency

The electrolyzer efficiency is adjusted so the combined efficiency matches the observed average. This analysis procedure backs out an estimate for the efficiency of the electrolysis step by using the computed compression power. The Stuart unit has a low-pressure output of 1 psig from the electrolysis, coupled to a 4-stage compressor that is estimated to be 50% efficient in each stage. From this input, the model matches the average data with an electrolysis efficiency of 70%. The Teledyne unit has a high-pressure output of 100 psig from the electrolysis, coupled to a 2-stage compressor that is estimated to be 20% efficient in each stage. For this comparison, the model suggests the average electrolysis efficiency is 55%.

The simulation of SunLine's data [6] for collection of electricity from the PV arrays is shown in Figure 2. The model uses an analytical formulation for the incident solar radiation [7] as a function of the location (longitude, latitude, and altitude) and time of year. The model for PV arrays is parameterized by the area, elevation angle, solar-to-electric conversion efficiency, and the tracking method. The solid curve in Figure 2 is the computed monthly solar energy collected for the PV arrays in Palm Springs through the year. The

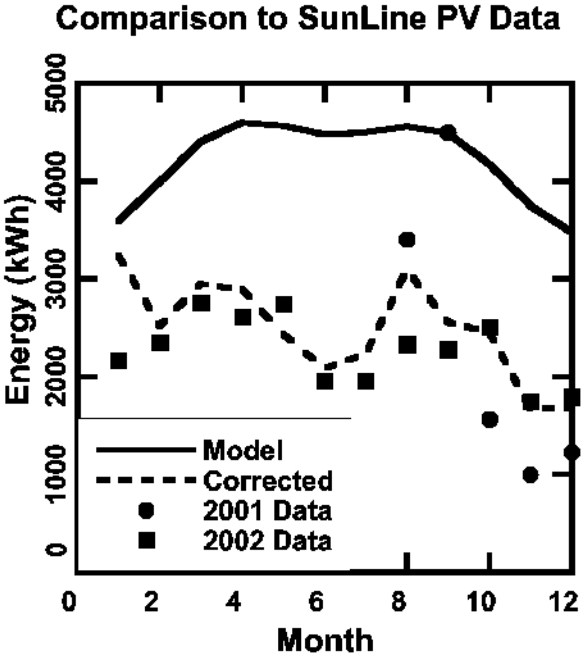

Figure 2. Comparison of the Simulated Electricity Collection for the PV Arrays Operated at SunLine Transit Agency

model integrates the daily solar collection, then sums over each month to compare to the SunLine data. The symbols show SunLine's data collected over the fall of 2001 (circles) and the entirety of 2002 (squares). There are two adjustments made in the simulation to match the observed data. First, the PV efficiency is 7%, which sets the overall power collected (solid curve); this represents the maximum solar energy collection for clear sky radiation. Secondly, SunLine's record for number of cloudy days per month is used to correct the clear-sky estimate on a monthly basis to produce the dashed curve in Figure 2. The corrected curve agrees quite well with data for SunLine's operation.

Conclusions

The power system simulations can be compared to operation data for demonstration power parks, like the facility at SunLine transit. Comparisons of the simulations to observed performance provide feedback on energy efficiency and real capability of the technologies. For example, without the simulation, SunLine personnel did not have a way to estimate that their PV system was operating at 7% solar-to-electric efficiency. Similarly, while they could infer the overall efficiency of the electrolyzer units, the model can provide estimates of the separate efficiencies of the compression and electrolysis stages of the operation.

Future efforts will apply the simulation tool to the entire system at SunLine, as well as demonstration sites at Las Vegas and Hawaii (HNEI). Model development will enhance the existing library modules and add new modules for wind turbines, ICE generators, and power conditioning. In preliminary development is a layer of analysis to compute the cost of the power and hydrogen generated. The cost analysis will accept input of the initial capital costs of the components, as well as the continuous operation costs during the life of the simulation, and add the costs using capital recovery factors. The simulation tool can be used in the planning and design of hydrogen technologies in distributed power systems.

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FY 2002 Publications/Presentations

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2. Lutz, A. E., Bradshaw, R. W., Bromberg, L., and Rabinovich, A., "Thermodynamic Analysis of Hydrogen Production by Partial Oxidation Reforming," *Int. J. of Hydrogen Engy*, accepted for publication.

Filling Up With Hydrogen 2000

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Objectives

- Design and build fuel appliances based on new low-cost electrolyser technology.
- Demonstrate hydrogen vehicle re-fueling using fuel appliance systems.
- Obtain '3rd party operating experience feedback' in refueling applications.
- Establish precedents for development of codes and standards.
- Determine cost effectiveness of fuel supply pathway.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Storage
- C. Hydrogen Refueling Infrastructure
- D. Maintenance and Training Facilities
- E. Codes and Standards
- H. Hydrogen from Renewable Sources

Approach

Prototype development involving building 8 different appliances: six Fleet Fuel Appliances and 2 Personal Fuel Appliances; each appliance project includes five phases:

- Design
- Build
- Test
- Customer evaluation
- Tear-down and post mortem

Accomplishments

- All six Fleet Fuel Appliance prototypes have been constructed, featuring different technical advances. All units have entered the customer evaluation phase. The Community Fuel Appliance (CFA) is now a commercial product offered at fixed scope and price.
- The Personal Fuel Appliance part of the program has been completed, and the final report for this part of the project has been submitted. The units continue to operate as demonstration prototypes.

Future Directions

- Complete installation of Mark I unit at SunLine Transit, 1000 Palms, California.
- Analyze performance of systems in the field; determine operating and manufacturing costs.
- Complete project by September 31, 2003. Report results and recommend improvements for next cycle of fuel appliance development.

Introduction

"Filling Up with Hydrogen 2000" is a prototyping development project intended to validate the Stuart Fuel Appliance Model for hydrogen vehicle fuel supply infrastructure. Stuart fuel appliances are purpose built on-site electrolytic hydrogen generators for refueling gaseous hydrogen vehicles. Using only electricity and water and having no emissions beyond oxygen, electrolytic fuel appliances can be readily deployed to create a highly distributed fuel supply network.

The objective of the Stuart/DOE project is to design, build and deploy a variety of fuel appliances. Two types of appliance are being built under this program: Fleet Fuel Appliances and Personal Fuel Appliances, both of which target the needs of nascent hydrogen vehicle commercialization. The Fleet Fuel Appliance targets buses, trucks and other centrally fueled fleet vehicles, where fuel production rates in excess of 400 SCFH are required. The Personal Fuel Appliance is geared towards consumer vehicles at the home or office and can be powered by the utilities found in the typical North American home. The production rate of these units is in the range of 50 SCFH. Both types of appliances are capable of delivering gaseous hydrogen at high pressure (up to 5000 psig) to the vehicle.

Approach

As presented in our Business Plan (Ref.1), the successful development and demonstration of fuel appliance technology will enable a cost effective pathway for building a hydrogen fuel supply infrastructure to support hydrogen vehicles in their early commercialization phase. The fuel appliance addresses the issue of fuel delivery by providing point-of-use fuel generation using existing energy utilities. Using the existing electricity grid, a full service infrastructure can be built up as a distributed network of small electricity-to-hydrogen fuel converters.

Key to meeting the market requirements is reducing the cost of electrolysis. Stuart's patented alkaline water electrolysis cell technology is designed to achieve the cost targets demanded by transportation fuels. The Compact Stuart Technology (CST) uses low-cost polymer and metal sheets, which are easily assembled in a stack. The CST electrolyser can be configured either as a single-stack or multi-stack electrolyser. The multi-stack electrolyser, having multiple cells in parallel, can run cell currents up to 30,000 amps and is suitable for large fueler applications. All the prototypes built under "Filling Up With Hydrogen 2000" use CST technology. The electrolyser packaged with the power system, compressor, purification and controls needed in a refueling application make up the fuel appliance.

"Filling Up With Hydrogen 2000" will provide an experience base with the cell stack technology for later commercialization and is a cost effective approach for equipment testing in that the user/ customer picks up operating costs for the benefit of the hydrogen produced. In addition to testing the cell technology, the prototype development plan provides public exposure to the fuel appliance concept, introducing customers to the idea of distributed on-site hydrogen production, and provides valuable precedents for the development of codes and standards and hydrogen project risk assessment. The operation of the bus fuel appliance (P3-1A) at SunLine Transit provides public access to the technology through SunLine. The low-pressure fueler (P3-1B LP) provides a demonstration of a system which can refuel metal hydride gas storage.

The high-pressure fueler (P3-1B HP) demonstrates the concept of a distributed "community fueler". The design of the bus fueler, P3-5, demonstrates the large format cell technology which could be used in large bus fleet fueling applications. The P4 prototypes are being used to test different configurations of the cell stack and integration with the compressor, including a pressurized stack configuration and integration with a wind turbine in a semi-stand-alone energy system. Testing of the personal fuel appliance (PFA P1 Model 25) by major automakers will provide the auto industry the opportunity to evaluate the concept of a small onsite hydrogen generator and a potential home-based fueling appliance.

Results

P3-1A: Bus Fuel Appliance, is now undergoing post-operation analysis. Over the three years at SunLine, it operated 3100 h and produced over 3.5 million SCF of hydrogen fuel. The appliance was used to fuel a variety of hydrogen and Hythane vehicles.

P3-1B (HP): Community Fuel Appliance, which produces up to 400 SCFH at 5000 psig, has operated for 5000 hours, producing 2 million SCF. The appliance has been used to test/certify hydrogen vehicle fuel tanks and fuel a fleet of Hythane vehicles. An identical version of this appliance has been delivered to the California Fuel Cell Partnership. (See Figure 1.)

P3-1B (LP): Community Fuel Appliance, which produces up to 400 SCFH at 200 psig, operated in-house for over 3000 h. It was refitted on a mobile deck and used for re-fueling a metal hydride - hydrogen fuel cell mining locomotive in a joint project with Fuel Cell Propulsion Institute (FCPI). (See Figure 2.)

P4-1A: Fuel appliance, capable of 400 SCFH at 6000 psig, incorporating higher-pressure stack, was tested in-house. Problems arose because of contamination on sensors used to control pressure in cell. Approach to CST cell pressurization has been abandoned with the company's acquisition of Vanderborre Hydrogen Systems and related cell stack technology.

P4-1B: Community Fuel Appliance, which can produce up to 900 SCFH, was used to test hydrogen motor generator set at Southwest Research Institute and is now being used to generate hydrogen from wind energy at a Palm Springs wind farm as part of a project with Southern California Air Quality Management District (SCAQMD). (See Figure 3.)

Mark 1: Commercial prototype of CFA-450 has been delivered to SunLine Transit 1000 Palms to replace P3-1A. This unit embodies all advancements learned from program. (See Figure 4.)

PFA Model 25: Personal fuel appliance has completed tour with Ford fuel cell vehicle. Final report has been issued.

Figure 1. P3-1B Fuel Appliance at Alameda County Transit, Richmond, CA

Figure 2. P3-1B Mobile Fuel Appliance for FCPI

Figure 3. P4-1B Fueler for SCAQMD Wind-Hydrogen Project

Conclusions

Fuel appliances can reliably meet the needs of hydrogen vehicle refueling, delivering gas up to 5000 psig. Prototyping has indicated further work is required to reduce equipment and installation costs and refine process automation.

Figure 4. Mark 1 Fueler for SunLine Transit

References

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Hydrogen Refueling Technology

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Subcontractor: SunLine Services, Thousand Palms, CA

Objectives

- Demonstrate hydrogen fueling station
- Develop and demonstrate on-site autothermal reforming (ATR) of natural gas
- Analyze hydrogen cost vs. target of $5/kg in 2003
- Evaluate fuel cell vehicle refueling under real-world conditions
- Support public education on hydrogen and fuel cells

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Hydrogen Production

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance
- E. Control and Safety

Technology Validation

- C. Hydrogen Refueling Infrastructure
- D. Maintenance and Training Facilities

Education

- B. Lack of Demonstrations or Examples of Real World Use

Approach

- Fabrication and testing of prototype (50 Nm^3/hr) natural gas reformer with pressure swing adsorption (PSA)
- Design and fabrication of demonstration (100 Nm^3/hr) natural gas reformer with PSA
- Installation and commissioning of demonstration unit
- Process design of compression, storage & dispensing (CS&D) system
- CS&D equipment design and selection
- CS&D installation and permitting

- Training of system operator
- Demonstration of integrated system
- Data acquisition, analysis and reporting
- Continuing public education on hydrogen and fuel cells at SunLine

Accomplishments

- Built and tested prototype reformer, including PSA system
- Completed design and began fabrication of demonstration reformer, including PSA system
- Designed, selected, and purchased CS&D equipment
- Obtained permitting required for demonstration at SunLine

Future Directions

- Complete fabrication of demonstration unit
- Deliver and install demonstration unit at SunLine
- Commission demonstration unit
- Install & commission CS&D equipment
- Demonstrate and evaluate integrated hydrogen refueling station

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Introduction

The objective of this project is to develop and demonstrate a hydrogen refueling station that combines HyRadix's on-site hydrogen generation technology with compression, storage and dispensing facilities designed by SunLine Services Group. The refueling station will be located at the SunLine facility in Thousand Palms, California, and will provide low cost hydrogen to fuel three fuel cell buses and several fuel cell cars and street sweepers. The refueling station will also provide hydrogen that will be blended with compressed natural gas (CNG) to form a hydrogen-compressed natural gas (HCNG) blend and used in SunLine's fleet of converted CNG buses.

HyRadix's hydrogen generation technology is based on ATR of natural gas combined with a PSA unit to purify the hydrogen. HyRadix's reformer will produce 100 Nm^3/hr of high purity (99.95%+) hydrogen. SunLine is drawing on their unique experience of being one of the few experienced operators of fuel cell vehicles to design and build a compression, storage and dispensing system to be integrated with the HyRadix reformer. The hydrogen will be compressed and stored at a pressure of 6250 psi to allow for dispensing at 5000 psi. The target refueling rates are 15 minutes per bus and 3-5 minutes per car. SunLine will also continue their directive to educate the public on hydrogen as an energy carrier and fuel cells.

Approach

The HyRadix hydrogen generation technology is based on autothermal reforming at a small scale, producing a reformate stream of 40-50% hydrogen. This gas stream is then purified to 99.95+% through a purpose-designed small-scale pressure swing adsorption unit. HyRadix built and tested a prototype 50-Nm^3/hr unit – half the output of the final demonstration unit – in order to incorporate improvements into the final design of the 100-Nm^3/hr demonstration unit. Autothermal reforming combines partial oxidation and steam reforming, making efficient use of heat, but does not require exotic metallurgy.

The SC&D system designed by SunLine will compress the hydrogen to 6250 psi, store it at that pressure and then dispense to the vehicles at a maximum of 5000 psi. The compression system comprises two-stage diaphragm compressors, which maximize energy efficiency, reduce manufacturing costs and increase flexibility while maintaining contamination-free hydrogen. The two-stage design permits startup under the high inlet pressure of the gas stream coming from the PSA. The storage component consists of high-pressure carbon fiber wrapped cylinders rated at a maximum pressure of 7250 psi. The dispenser system is a two-hose dispenser capable of dispensing at 3600 psi on one side and at 5000 psi on the other side for HCNG and fuel cell vehicles, respectively. The entire dispensing system will be rated for 7250 psi for safety reasons.

HyRadix will develop operations and maintenance manuals for the demonstration unit and provide on-site training to SunLine personnel. SunLine staff will be responsible for the operation of the unit during the demonstration phase.

Results

The most important result of the project to date has been the learning from the operation and testing of the prototype unit, which has resulted in improved design for the unit that will be placed in service at SunLine. Several burner designs and control schemes were tried. This helped give us a robust burner design. Operation of the prototype has also brought to attention the importance of reducing thermal mass for both the start-up time and for process efficiency. The unit was tested at several different flow rates. This is important to determine if any anomalies exist that may limit the range of performance. In addition, the unit was started and stopped many times. This provides confidence that the unit can be run safely and with repeatable results. Smooth start-up has been achieved in less time than is required for conventional steam reforming plants. In addition, extensive logic testing has taken place. These tests helped create the software that will run the 100-Nm^3/hr hydrogen unit.

The operation of the prototype (see Figure 1) has confirmed that it produces both reformate and high-purity hydrogen consistent with the project targets. Stream qualities were monitored, and these results helped prove that the unit removes the sulfur in the natural gas stream, has a stack-gas very low in NO_x and SO_x, and provides product hydrogen at target purity with almost undetectable levels of CO. The PSA unit was tuned to give optimum hydrogen purity. This tuning will help set the standard for all future units.

The 100-Nm^3/hr demonstration plant that will be installed at SunLine is in the final stages of fabrication, incorporating the learning from the prototype plant. (See Figure 2.) The unit is mechanically complete.

- All structural components are fabricated.
- All equipment is installed on the structure.
- All piping is installed between equipment.

Figure 1. Prototype Unit Operating at HyRadix

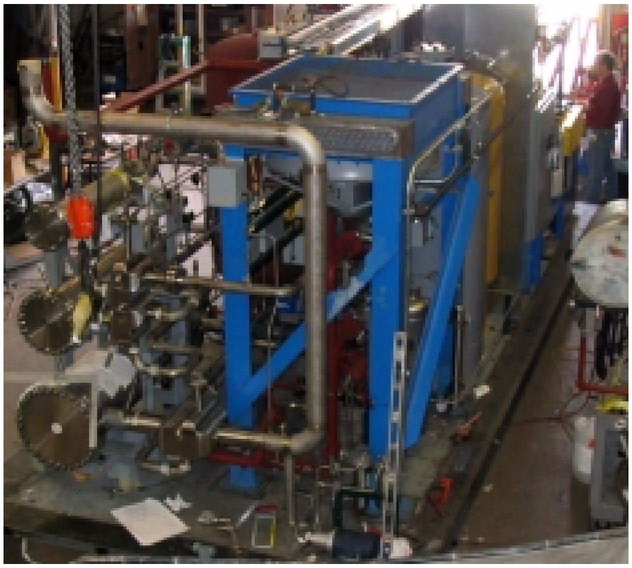

Figure 2. Demonstration Unit in Final Stages of Fabrication

- All tubing is installed between equipment.
- All tie-in connections are complete and ready for connection on site.
- All instrumentation is installed and wired.
- All power and control wiring is complete.

The enclosure is complete and painted.

- The enclosure protects the equipment from the elements.
- The enclosure is partially installed for shipping protection.
- The enclosure panels will be installed on site.

Testing is under way.

- All hydrostatic testing is complete.
- Leak testing is 50% complete.
- Instrument and electrical check-out is 35% complete.

Conclusions

- Operation and testing of the prototype unit has resulted in improved design for the demonstration unit.

- The prototype unit produces hydrogen consistent with targets and with very low emissions and CO.

FY 2003 Publications/Presentations

1. Davies, M., D. Cepla, and D. Sioui, "Small Scale On-site Hydrogen Generation for Refueling Applications from Multiple Feedstocks," National Hydrogen Association Conference, March 2003, Washington D.C

Fuel Cell Installation and Demonstration Project In Gallatin County, Montana

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Objectives

- Demonstrate operation of fuel cells and provide the hydrogen industry and the general public with a high-technology application of the units.
- Determine the degradation rate of the fuel cells and the point at which it becomes economically necessary to "restack" by essentially replacing the fuel cells themselves.
- Provide operational data to the Montana State University Electrochemical Engineering Research and Education Center to assist in the development of control equipment to optimize fuel cell performance when combined with other electrical sources.
- Maximize efficiency of the heat recovery (cogeneration) system.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Fuel Cells section

- E. Durability
- F. Heat Utilization

Technology Validation section

- I. Hydrogen and Electricity Coproduction

Education section

- B. Lack of Demonstrations or Examples of Real World Use

Approach

- Construct suitable stationary fuel cell installation site at a high-tech facility.
- Install redundant stationary fuel cells.
- Operate stationary fuel cells according to manufacturing and engineering specifications.
- Study/analyze performance and reliability of installed fuel cells based on operational data collection.
- Work in conjunction with Montana State University (MSU) to enhance complimentary fuel cell studies.

Accomplishments

- Completed construction and preparation of fuel cell installation site and related electrical/mechanical systems. (October, 2002)
- Purchased two (2) 250-KW stationary fuel cells from Pennsylvania Power and Light, engineered and manufactured by Fuel Cell Energy (FCE). (October, 2002)
- Facilitated physical installation and start-up of purchased fuel cells. (June, 2003)

Future Directions

- Finalize interconnection agreement with local energy supplier (Northwestern Energy) to allow for sale of surplus electricity.
- Capture and analyze data applicable to reliability and performance of fuel cells.
- Continue providing access to MSU for monitoring and analysis purposes.
- Investigate formation of local "micro-grid" to allow for expansion and distribution of demonstration site installation to neighboring facilities.

Introduction

In December 2001, a Design Team Conference was held at Zoot Enterprises, Inc. headquarters in Bozeman, Montana, to address basic design and operation issues relating to fuel cell installation and ownership. At this time, parties were designated to assist with architectural, engineering, construction, and installation tasks.

Two (2) 250-KW fuel cells were delivered and installed at the Zoot Enterprises facility in June 2003. Both units have completed the warm-up process and are currently being brought to full generation capacity.

Approach

Zoot Enterprises has taken an active role in the design, construction, and installation phases. It is expected that through this active involvement, we will be most successful in meeting the objectives of this project.

Monitoring systems and devices have been installed both by MSU and also as part of the fuel cell package supplied by FCE. Zoot Enterprises will collect supplemental operational data through maintenance records, billing records, and demonstration experiences.

Results

No results are available at this time, as the fuel cell operation phase has not begun. Installation is in progress.

Conclusions

As the operational phase of this project is due to begin in July 2003, no conclusions have been formulated from this project at the current time.

FY 2003 Publications/Presentations

1. Department of Energy - Technical Progress Report - October 2002
2. Department of Energy - Technical Progress Report - March 2003

Special Recognitions & Awards/Patents Issued

1. "Fuel Cells Delivered to Zoot Technologies" - June 18, 2003 article - Bozeman Daily Chronicle

Global Assessment of Hydrogen-Based Technologies

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Objectives

- Synthesize the state-of-practice for four potential hydrogen-based vehicle technologies.
- Compare performance, emissions, and fueling characteristics of the four technologies (instrumentation).
- Compare the four technologies in light of their potential role in a full-scale deployment.
- Assess hydrogen infrastructure needs to support deployment (at local, regional, and national levels).
- Offer education and training programs to increase the knowledge of the new technologies.
- Increase the awareness of the new technologies through various mechanisms such as promotional materials for public media, a web-site, college programs, and a Hydrogen Fair in the southeastern U.S. to demonstrate the various vehicle technologies, pumping stations, hydrogen storage, safety issues, etc.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Vehicles
- C. Hydrogen Refueling Infrastructure

Approach

- Evaluate candidate hydrogen-fueled vehicles for near and long-term use in the southeastern U.S. in terms of their efficiency, performance, and emissions. Four types of hydrogen-fueled vehicles are being assessed: hythane-fueled internal combustion engines (ICEs), hydrogen-fueled ICEs, hydrogen-fueled hybrid electric propulsion vehicles (HEV), and direct hydrogen fuel cells.
- Conduct rigorous performance and exhaust emissions testing of hydrogen technologies:
    1. ICE vehicles fueled with hydrogen-compressed natural gas (CNG) fuel mixtures (15-50% hydrogen, 50-85% CNG),
    2. ICE vehicles fueled with pure hydrogen, and
    3. Hydrogen-powered fuel cell vehicles.
- Estimate resource requirements and costs for the infrastructure needed to deliver new fuels to advanced technology vehicles. Argonne's Natural gas Infrastructure Component Cost (NICC) model will be applied to the southeastern U.S., specifically the Birmingham/Atlanta region, to develop cost

estimates and define additional hydrogen pathways. In addition, practical considerations in the design and development of fuel delivery facilities will be investigated.

- Evaluate the ability of the vehicle technologies described previously to contribute to improved air quality in the Southeast, with special attention given to the Atlanta metropolitan area. Argonne's Air Quality Credits (AIRCRED) and Greenhouse Gas Energy and Emissions in Transportation (GREET) models will be used to assess impacts of a large-scale deployment on pollution emissions.
- Determine the feasibility of using hydrogen fuel cell technologies for electric power generation. The potential to conduct an actual demonstration in the greater Birmingham, Alabama, area in such electric power applications as recreation parks, student housing facilities, or heavy industrial applications will be assessed to identify possible deployment locations and potential benefits. Measurements will be made to determine if the fuel cell technology will lead to pollution reduction and air quality enhancement, especially in an ozone non-attainment area such as Birmingham.
- Establish the Southeast Hydrogen Technology Consortium (SHTC) to examine ways to establish a hydrogen infrastructure in the Southeast and enhance the infrastructure and application of the technology. The members will be experts in the field and representatives of different areas and sectors with interest in hydrogen technologies for both power generation and transportation.

Accomplishments

- A Ford F-150 was tested at Argonne National Laboratory using the dynamometer facility in their Transportation Technology R&D Center during May, 2003. The Ford F-150 was run on a fuel mixture (hythane) of ~50% hydrogen and ~50% compressed natural gas. Emissions data were collected for carbon monoxide (CO), carbon dioxide (CO_2), total hydrocarbons (THC), nitrous oxides (NO_x), and particulate matter. The equivalent miles per gallon fuel consumption was also monitored. Results were obtained using cold starts, hot starts, standard vehicle testing, and highway testing. The University of Alabama at Birmingham (UAB) compared the results with typical (high and low) emissions performance for CO, THC, and NO_x, for light-duty and heavy-duty vehicles. The results indicated that using the 50% hythane fuel mixture, reductions in CO, THC, and NO_x exceeded 97%, 95%, and 94%, respectively, indicating that the emissions were reduced by more than an order of magnitude.
- The UAB study team has received training on use of the PSAT vehicle simulation model to compare the efficiency and emissions of hydrogen-fueled vehicles with conventional internal combustion vehicles.
- Data has been collected for inputs to the regional AirCred model.

Future Directions

- Evaluate additional test vehicles (hydrogen ICE and hydrogen fuel cell) for performance and emissions.
- Simulate and compare hydrogen-fueled vehicles to conventional ICEs.
- Use results of vehicle tests and simulations to evaluate potential impacts of a hydrogen vehicle deployment.
- Investigate infrastructure requirements for a hydrogen vehicle deployment, including potential hydrogen producers and transport mechanisms. Investigate codes and standards related to hydrogen fueling stations.

Introduction

Hydrogen-fueled vehicles hold the potential to reduce the emissions of pollutants and greenhouse gases currently associated with conventional gasoline- and diesel-fueled vehicles. Hydrogen-based vehicle technologies, however, are still in the very early stages of development, and their performance characteristics compared to conventional internal combustion engines (ICEs) are not well established. There are currently several promising hydrogen technologies available, but their potential for widespread deployment requires further evaluation. In the near term, hydrogen-fueled internal combustion engines (similar to conventional engines but modified to run on hydrogen or hydrogen-CNG blends) may prove to be the most immediately feasible technology. Another promising near-term technology are hydrogen-fueled hybrid electric vehicles, similar to the gasoline-powered hybrid electric vehicles already available, but with the gasoline motor replaced by a hydrogen-fueled motor. Hydrogen fuel cell vehicles may ultimately provide the lowest emissions of any hydrogen technology, but their development is also the most complex, and they are therefore generally considered a longer term option.

Any assessment of the potential for large-scale deployment of these hydrogen technologies must be based on measured vehicle performance characteristics, not simply estimates. Only with realistic emissions and vehicle performance measures can we develop reasonable estimates of what impacts a large-scale deployment would have on air quality and which vehicle technologies offer the most promising near-term and long-term benefits. Such an assessment will also need to consider the cost of the infrastructure required to fuel and maintain these vehicles. Large fleets of hydrogen vehicles will require hydrogen production plants, transport systems, and fueling stations that do not yet exist and whose costs are not yet known. The purpose of this study is to evaluate the performance characteristics of various hydrogen vehicle technologies, identify the most promising near- and long-term technologies, and fully understand the infrastructure that a large-scale deployment will require.

Approach

The research will follow two primary tracks: (1) an evaluation of the performance characteristics of four hydrogen-fueled vehicle technologies, and (2) an investigation of hydrogen infrastructure requirements. The study will examine four promising hydrogen vehicle technologies: hythane-fueled ICE vehicles, hydrogen-fueled ICE vehicles, hydrogen-fueled hybrid electric vehicles, and hydrogen fuel cell vehicles. The performance and emission characteristics of each type of vehicle will be measured at the Argonne National Laboratory test facility. The results of these tests will be incorporated into the PSAT vehicle simulation model and used to further compare the performance and emissions characteristics of each vehicle technology to conventional gasoline- and diesel-powered vehicles. The PSAT model outputs will then be input into the AirCred and GREET models to estimate the air quality impacts of a large-scale deployment of hydrogen vehicles in thes United States.

The second thrust of the research will be to investigate the infrastructure that such a large-scale vehicle deployment would require. Current hydrogen production and production capacity in the southeastern United States will be assessed, as will the production of fuels and resources required to produce hydrogen (CNG, coal, methane) and the

Figure 1. Ford F-150 Truck on Dynamometer at Argonne National Laboratory

transport systems (truck, rail, and pipeline) currently available to convey them. Based on the results from earlier portions of the study, estimates of the hydrogen demand for a large-scale vehicle deployment will be developed, and the cost of the additional infrastructure required to meet this demand will be assessed. The study will also examine the practical considerations involved in constructing and supplying hydrogen fueling stations in an urban environment.

Results

The study is currently getting underway. Results and conclusions will be provided as they become available.

FY 2003 Publications/Presentations

1. Presentation by Fouad H. Fouad to the Southern Research Institute at the Department of Energy Atlanta Regional Office on June 16, 2003.

Advanced Thermal Hydrogen Compression

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Objectives

- Develop a hydride thermal hydrogen compressor that operates in conjunction with advanced hydrogen production technologies and improves the efficiency and economics of the compression process.
- Construct and test a single-stage thermal compressor that employs miniature hydride heat exchangers and three purification technologies to determine threshold contamination levels (levels at which compressor performance is affected) for H_2O, O_2, CO, CO_2 and CH_4.
- Investigate compressor capabilities to perform the dual function of compression and purification for impurities that adversely affect fuel cell operation (CO and CH_4).
- Engineer and test hydride alloys suitable for long-term operation at high pressures over 5,000 psig.
- Validate the entire compressor process in a multi-stage, pilot-scale system.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Hydrogen Delivery

- B. High Costs of Hydrogen Compression

Hydrogen Storage

- S. Cost
- T. Efficiency

Approach

- Feasibility
  - Quantify H_2 quality anticipated from renewable production techniques.
  - Conduct preliminary design and safety analysis.
- Validate and Test
  - Determine hydride alloys' resistance to disproportionation.
  - Validate compressor operation to >5,000 psi.
  - Determine hydride alloys' tolerance to impurities while cycling.
  - Test effectiveness of three purification techniques (passive purification for H_2O & O_2, elevated temperature desorption for CO & CO_2, inert gas venting for N_2 & CH_4).

- Refine Product Design
  - Determine if compression with purification is a viable alternative for improving fuel cell performance.
  - Reduce capital cost via miniature hydride heat exchangers and rapid cycling.

Accomplishments

- Determined that hydride compression's low energy cost will substantially reduce the cost of high-pressure hydrogen.
- Demonstrated thermal compression to 8,000 psia with a clear path to 10,000 psia.
- Reduced hydrogen CO content from 300 ppm to less than 10 ppm to protect fuel cell catalyst.

Future Directions

- Determine upper limits and removal efficiencies for contaminants that might damage either fuel cells or advanced storage media.
- Refine product design.
- Demonstrate full-scale hydride thermal compression at a hydrogen refueling station.

Introduction

The hydride thermal compressor is an absorption-based system that uses the properties of reversible metal hydride alloys to silently and cleanly compress hydrogen; hydrogen is absorbed into an alloy bed at ambient temperature and, subsequently, is released at elevated pressure when the bed is heated. Compression energy can be supplied by hot water and, for the very high pressures being considered for on-board hydrogen storage, is a fraction of the energy cost of mechanical compression. The primary technical objective of this project is to determine whether hydride compressors can be used for non-pure hydrogen streams likely to result from advanced hydrogen production methods (i.e. from renewable resources), with the commercial objective of developing a viable hydride compressor that offers substantial benefits over mechanical compressors.

A pilot-scale hydride thermal compressor was built and is being tested to determine the extent to which a hydride compressor can both tolerate and remove impurities from the hydrogen stream. In particular, CO is present in hydrogen from many advanced production processes and must be removed to prevent damage to fuel cell electrode catalyst. Removing CO in the compression process can be more cost effective than other hydrogen purification schemes. A novel process has been developed that reduces carbon monoxide levels to less than 10 ppm. In addition, the compressor employs miniature hydride heat exchangers to reduce capital cost and has operated to pressures in excess of 8,000 psia.

Approach

Advanced Thermal Hydrogen Compression is a comprehensive project with three phases: feasibility, validation and test, and product refinement. A full-scale demonstration at a hydrogen refueling station is anticipated following the completion of the current project.

In the feasibility phase of the project, Ergenics, Inc. investigated the application of thermal hydrogen compression to hydrogen produced from renewable resources and developed a preliminary thermal compressor design for comparison with conventional mechanical compressors. A hazardous operation safety analysis of the thermal compressor system was completed. Thermal hydrogen compression was found to have distinct operational and economic advantages over mechanical compression for a majority of advanced hydrogen production processes.

In the validation and test phase of the project, a pilot-scale compressor and test stand were built and are being operated to determine the extent to which a hydride compressor can both tolerate and remove impurities from the hydrogen stream. While testing is on-going, excellent results have been achieved and are reported below.

Product refinement has included the demonstration of hydride compression to 8,000 psia with a clear path to 10,000 psia. In addition, complexity and cost of the compression process have been reduced through the identification of disproportionation resistant hydride alloys [1]. A competitive analysis of compressor efficiency and fuel costs for operation at 5,000 and 10,000 psia indicates that hydride compression has eight times lower energy cost than mechanical compression, which will be necessary to meet the hydrogen delivery cost goals of \$3.00 per gallon of gasoline equivalent by 2004 and \$1.50 per gallon of gasoline equivalent by 2010.

Results

Effect of CO on Alloy Capacity. Ergenics developed and demonstrated a novel CO elimination process that allows the hydride compressor to tolerate and remove CO from the hydrogen stream. Figures 1 and 2 show the effect of CO on alloy capacity with cycling. Figure 1 shows that hydride alloy capacity undergoes a gradual reduction with cycling when hydrogen with CO is fed to the compressor without the CO elimination feature. If left alone, compressor performance would rapidly degrade. The positive impact of the novel CO elimination process is shown in Figure 2, where alloy capacity remains stable as the alloy is cycled.

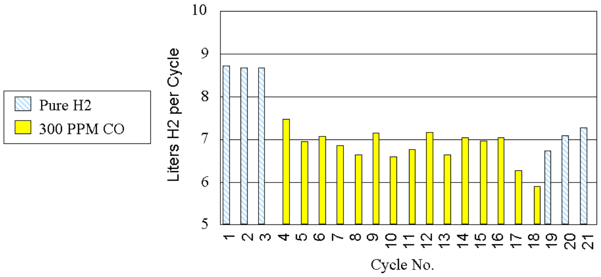


Figure 1. When 300 ppm CO Is Added to Feed Hydrogen, Alloy Capacity Gradually

During testing with CO, the compressor alloy behavior was periodically checked for changes by pressure-composition-temperature (PCT) isotherm tests. Figure 3 shows that the CO elimination feature allows the compressor alloy to maintain its performance over repeated cycles. In order to verify that the PCT performance was not being affected by potential test stand leakage, two additional absorption tests, numbers 3 and 4, were done after 10 cycles. The results conform to the isotherm of “Abs. 2” and have been omitted from Figure 3 for clarity. The slight differences in plateau pressure are a result of ambient temperature differences on the days the tests were performed.

CO Elimination. The composition of the compressor discharge with the CO elimination feature is depicted in Figure 4. The CO elimination process results in a reduction of CO from 300 ppm at

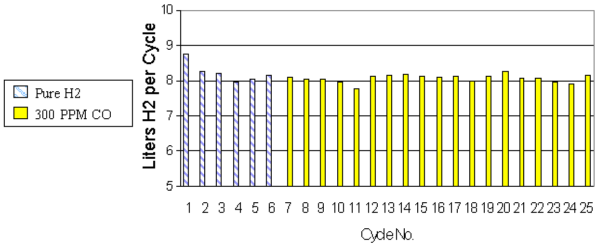


Figure 2. The CO Elimination Feature Maintains Alloy Capacity at a Constant Level

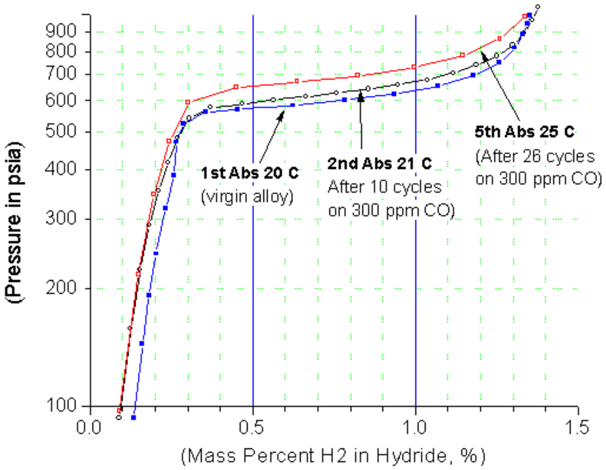


Figure 3. PCT Tests Indicate the Hydride Alloy Is Not Damaged During Testing with CO

the compressor inlet to the 10 ppm level necessary to protect fuel cell catalyst. Figure 4 illustrates that most of the CO is converted into methane (CH_4) and the methane is released in large spikes (>1,000 ppm) at the beginning of each cycle. This suggests that methane can be removed from the hydrogen stream via inert gas venting using an economically small amount of hydrogen. A momentary opening of the vent valve will sweep the methane away. Ultimately, the vent gas will be routed to the hot water heater for recapture of its heating value.

Very High Pressure. The compression capability of the advanced hydride compressor is presented in Figure 5, which plots inlet and outlet hydrogen pressure and inlet water temperature vs time for one compression cycle. Compressed hydrogen is vented via a back-pressure regulator. For this test, the regulator was set at 8,200 psia (56 MPa). The slight fluctuation in water temperature is associated with the natural gas heater cycling on and off and, interestingly, causes a slight, but detectable, fluctuation in hydrogen pressure.

The test stand uses an ethylene glycol-water mixture for the heat transfer fluid, which has an upper temperature limit of 175°C to prevent boiling. Substituting the ethylene glycol-water mixture with a silicone-based heat transfer fluid will permit operation to 200°C with pressures over 10,000 psia.

Energy Cost and its Effect on the Delivered Cost of Hydrogen. The hydride thermal compressor is a form of "heat engine" based on the Carnot thermodynamic cycle [2]. Its energy efficiency is based on the temperature difference between a hot energy source and a cold heat sink (i.e. hot water and cooling water), with efficiency increasing with a larger difference in temperature.

By using a traditional form of heat energy, such as natural gas, cycle economics benefit from an increase in hot water temperature. Using a heat transfer fluid from a gas-fired heater at 130°C and 30°C cooling water, hydride compressor efficiency is approximately 15 percent. While 15 percent is about 1/2 that for an electric-motor-driven mechanical compressor operating around 3,000 psia, electricity is about 6 times costlier than natural gas, so the hydride compressor will enjoy a 67% lower energy cost.

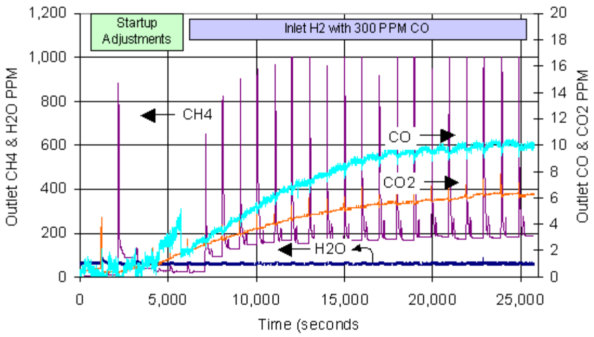


Figure 4. The CO Elimination Feature Reduces Outlet CO Concentration from 300 to 10 ppm

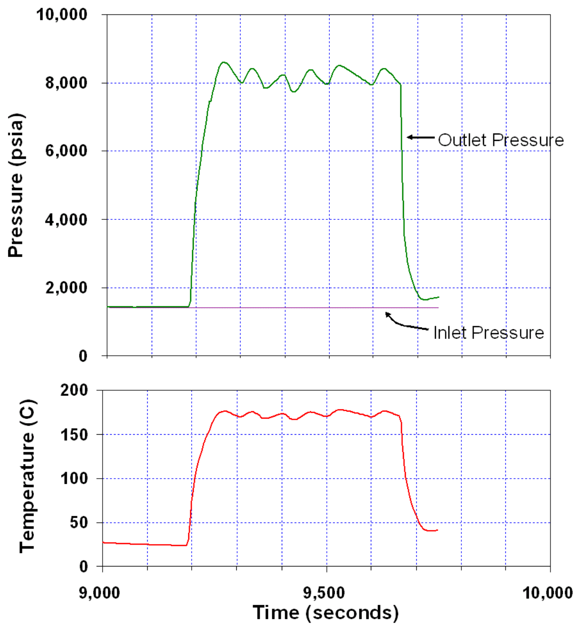
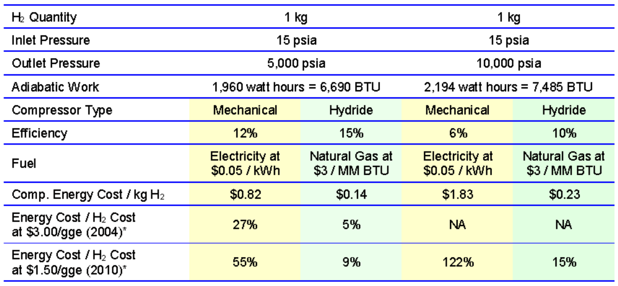


Figure 5. Testing to 8,000 psia



H_2 Quantity	1 kg		1 kg	
Inlet Pressure	15 psia		15 psia	
Outlet Pressure	5,000 psia		10,000 psia	
Adiabatic Work	1,960 watt hours = 6,690 BTU		2,194 watt hours = 7,485 BTU	
Compressor Type	Mechanical	Hydride	Mechanical	Hydride
Efficiency	12%	15%	6%	10%
Fuel	Electricity at $0.05 / kWh	Natural Gas at $3 / MM BTU	Electricity at $0.05 / kWh	Natural Gas at $3 / MM BTU
Comp. Energy Cost / kg H_2	$0.82	$0.14	$1.83	$0.23
Energy Cost / H_2 Cost at $3.00/gge (2004)*	27%	5%	NA	NA
Energy Cost / H_2 Cost at $1.50/gge (2010)*	55%	9%	122%	15%

Figure 6. Hydride Thermal Compression's Low Energy Cost Will Substantially Reduce the Cost of Hydrogen

The energy cost savings are magnified at the high pressures being looked at for the first generation of hydrogen vehicles. Mechanical compressor efficiencies decline to a range of 8% to 12% at 5,000 psia and only 4% to 6% at 10,000 psia. Hydride compression efficiencies remain in the 15% and 10% range, respectively. A table relating compression energy cost as a function of the DOE hydrogen cost targets is presented in Figure 6. Hydride compression reduces energy cost from 5 to 8 times.

Conclusions

The hydride thermal hydrogen compressor demonstrated high compression, tolerance to impurities, and the ability to both compress and purify hydrogen. An energy cost analysis shows hydride compression substantially reduces the delivered price of high-pressure hydrogen.

Advanced thermal hydrogen compression directly supports the technical targets established in the Department of Energy's Multi-Year Research, Development and Demonstration Plan as follows:

- **H_2 Cost:** Reduce compression energy costs by up to an order of magnitude to meet the H_2 cost goals of:
  - Long Term: $1.50/gallon of gasoline equivalent (2010)
  - Near Term: $3.00/gallon of gasoline equivalent (2004)
- **Energy Density:** Demonstrate pressures of 5,000 and 10,000 psi to support high pressure tank development.
- **H_2 Purity:** Increase H_2 quality to protect both fuel cell catalyst and advanced hydrogen storage materials (<10 ppm CO).
- **Complex/Carbon Materials:** Knowledge of impurity effects on compressor hydrides will establish a baseline for understanding impurity impact on advanced storage materials (alanates & carbon nanomaterials).

References

1. D. DaCosta, M. Golben. "Disproportionation Resistant Alloy Development for Hydride Hydrogen Compression", Proceedings 2002 U.S. Department of Energy Hydrogen Program Annual Review Meeting, Golden, May 6-8, 2002, NREL/CP-610-32405.

2. D. DaCosta, M. Golben, D.C. Tragna. "Metal Hydride Thermal Hydrogen Compression", Proceedings 14th World Hydrogen Energy Conference, Montreal, June 9-13, 2002.

FY 2003 Publications/Presentations

1. D. DaCosta, M. Golben. "Thermal Hydrogen Compression with Purification", International Energy Agency Hydrogen Implementing Agreement, Task 17 - Solid and Liquid State Hydrogen Storage Materials Workshop, Geneva, Switzerland, September 9-11, 2002.

Uninterrupted Power Source

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Objectives

To supply a fuel cell/battery power plant system which can supply immediate power (from l to 5 kW) to the grid in case of power failure

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- D. Fuel Cell Power System Benchmarking

Approach

- Design a 1- to 5-kW fuel cell/battery power plant system
- Test at in-house and in outside laboratories
- Analyze the results of the tests and finalize the design

Accomplishments

- Since the inception of this project, testing of a 300-watt Apollo alkaline fuel cell coupled with a lead cobalt battery has been carried out.
- In December, 2002, a 2.2-kW alkaline fuel cell and lead-acid battery were tested at Hydrolec Incorporated of Jacksonville, Florida, one of Apollo's customers.
- From January to June, 2002, a 2.5-kW alkaline fuel cell was tested by Apollo at a fuel cell manufacturing plant in Cologne, Germany.
- Preparations are being made in September, 2003, to test a 2-kW alkaline fuel cell and lead cobalt battery at the Florida Atlantic University.
- An ammonia cracker was developed and tested at the Technical University of Graz in Austria under the direction of Dr. Karl Kordesch. This provides an excellent method of delivering hydrogen to the fuel cell.
- The ammonia cracker has been in continuous operation at Apollo's laboratory in Fort Lauderdale, Florida.
- A larger and more advanced version of the ammonia cracker was developed and tested at the Apollo Fuel Cell Laboratory in Austria and has been sent to Fort Lauderdale, Florida, for further testing and evaluation. Plans are to test it at the Florida Atlantic University.

- Production of a special battery for the Apollo Power Plant system has been subcontracted to Millennium Battery Company, a manufacturer of batteries in Miami, Florida.
- A study of power plant-to-grid switches has been made.
- A study of hydrogen sensors has been made.

Future Directions

- A 2-kW Apollo Power Plant has been built and will be installed at the Florida Atlantic University in Boca Raton, Florida, for demonstration to interested parties.
- A 5-kW Apollo Power Plant will be built, using experience gained from the 2-kW unit, to be delivered to DOE.

Introduction

Many companies are developing fuel cells which can be used to supply instant power to the grid in case of grid failure. In the low temperature fuel cell field (70-80°C), development has proceeded on two types of fuel cells: the alkaline fuel cell (AFC), which has been used by the National Aeronautics & Space Administration (NASA) since the Apollo Moon Mission of the 1960s, and the proton exchange membrane (PEM) fuel cell. The AFC has the highest cell voltage and efficiency of any fuel cell but was considered too expensive for commercial applications. However, it has been shown that the AFC can be produced at a much lower cost than its competitor for earth applications, and it has been demonstrated that the AFC is less complicated, not requiring humidification and air compressors. Also, it has been shown that the AFC can be advantageously shut down during periods when its energy is not needed, while the PEM fuel cell can never be routinely shut down. To take advantage of this shut-down feature, Apollo Energy Systems has developed a system wherein a battery can be paralleled with the AFC and can do most of the work while the AFC is dormant. This prolongs the life of the AFC and results in lower overall cost since the fuel cell (which operates only intermittently) is more expensive than the battery (which is in continuous operation). It has also been found that the AFC can operate on far less noble metal catalyst than the PEM fuel cell, resulting in a lower manufacturing cost.

Therefore, Apollo Energy Systems has embarked on a program of AFC development coupled with battery development and plans to produce Apollo Power Plants for residential, commercial and industrial applications and Apollo Electric Propulsion Systems for application in land, water and air vehicles.

Approach

Several prototype Apollo Power Plants of different electrical sizes will be tested and evaluated so as to create a performance base for sizing the final prototype fuel cell and battery combination (see Figure 1). Tests will be carried out at Apollo's laboratory in Fort Lauderdale, Florida, at the laboratory of one of Apollo's customers, at a fuel cell facility in Germany, at a local university (Florida Atlantic University of Boca Raton, Florida), and finally at Apollo's pilot plant in Florida which is planned to be constructed in the last quarter of 2003.

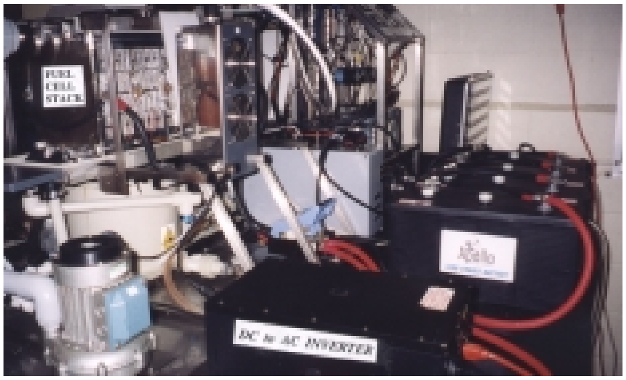

Figure 1. 2 kW Apollo Power Plant with Alkaline Fuel Cell stack, Lead Cobalt Battery and DC to AC Inverter

Results

- A 300-watt Apollo Power Plant has been built and is under constant test in Apollo's laboratory in Ft. Lauderdale, Florida. Results to date are positive.
- A 2-kW Apollo Power Plant has been built and will be installed at the Florida Atlantic University in Boca Raton, Florida.

Conclusions

- The basic concept of combining an AFC with a lead cobalt battery has been shown to be technically viable.
- As a result of this work, Apollo believes that Apollo Power Plants for stationary use and Apollo Electric Propulsion Systems for use in vehicles, boats and aircraft can be produced and effectively utilized, at reasonable prices.

FY 2003 Publications/Presentations

Six papers published in the Handbook of Fuel Cells - Fundamentals, Technology and Applications (ISBN: 0-471-49926-9), by John Wiley & Sons, Ltd., Chichester, UK, 2003:

1. Hydrogen/Oxygen (Air) Fuel Cells with Alkaline Electrolytes, M. Cifrain and K. Kordesch, Volume 2, Part 4, pp 267-280
2. Stack Materials and Design, K. Kordesch and V. Hacker, Volume 4, Part 4, pp 765-773
3. Ammonia Crackers, V. Hacker and K. Kordesch, Volume 3, Part 2, pp 121-127
4. A Comparison Between the Alkaline Fuel Cell (AFC) and the Polymer Electrolyte Membrane (PEM) Fuel Cell, K. Kordesch and M. Cifrain, Volume 4, Part 4, pp 789-793
5. Alkaline Methanol/Air Power Devices, G. A. Koscher and K. Kordesch, Volume 4, Part 9, pp 1125-1129
6. Automotive Development, V. Hacker and K. Kordesch, Volume 4, Part 11, pp l217-1223

Abstracts of four papers to be presented at Fuel Cell Conferences in 2003

1. Electronic Abstract, Ammonia as Hydrogen Source for an Alkaline Fuel Cell-Battery Hybrid System, K. Kordesch, V. Hacker, G. Faleschini, G., Koscher, M. Cifrain, *Fuel Cell Seminar, Miami Beach, Florida, November 3-6, 2003*
2. Flowing Electrolyte Direct Methanol Fuel Cells, D. James, X. Deng, K. Kordesch, *Fuel Cell Seminar, Miami Beach, Florida, November 3-6, 2003*
3. Alkaline Fuel Cells (An Overview) - Tutorial on Fuel Cells, K. Kordesch and M. Cifrain, *204th Meeting of the Electrochemical Society, Orlando, Florida, October 12-17, 2003*
4. Can Refillable Alkaline Methanol-Air Systems Replace Metal-Air Cells?, K. Kordesch and G. Koscher, *23rd Power Sources Symposium, September 22-24, Amsterdam, Holland*

Special Recognitions & Awards/Patents Issued

1. 2 Patent Applications have been filed on Alkaline Fuel Cells, Karl Kordesch, M. Cifrain
2. 1 Patent Application has been filed on an Ammonia Cracker, Gottfried Faleschini, Viktor Hacker, Karl Kordesch
3. 3 Patent Applications have been filed on Tri-Polar Lead-Cobalt Batteries, Robert Aronsson

Development of a Hydrogen Fuel Based Power Park (New FY 2004 Project)

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Subcontractors:
Collier Technologies - Reno, Nevada
Arizona Public Service - Phoenix, Arizona

Objectives

- Develop the process requirements for a hydrogen fuel based power park utilizing photovoltaic and electric grid energy inputs and providing hydrogen energy storage for electricity generation, hydrogen for vehicle fueling, potable water, and chilled water cooling.
- Demonstrate each component required to support the power park concept.
- Analyze the economic viability of the power park based on component costs and performance, and estimates of power park construction cost.
- Develop safe design practices for hydrogen handling.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- D. Maintenance and Training Facilities
- H. Hydrogen from Renewable Resources
- I. Hydrogen and Electricity Coproduction

Approach

The focus of this project is to evaluate the technical and economic feasibility of a hydrogen fuel based power park. The project will develop the process requirements for a hydrogen fuel based power park designed to provide a maximum electrical power of 100 kW, daily electric energy output of 200 kWh and daily hydrogen motor fuel output of 18 kg. The viability of the process will be demonstrated by development and testing of prototype equipment for each component of the power park process. Based on the results of this testing, performance and cost data will be projected for full size process components. The economic feasibility of the power park will then be evaluated based on alternative resources for electricity generation, hydrogen motor fuel production, production of potable water and chilled water for cooling.

Energy inputs to the power park will include photovoltaic and electric utility grid. A 6-kW photovoltaic array will be used to demonstrate the photovoltaic component of the power park process. Energy storage will be in the form of gaseous hydrogen produced from either electrolysis of water or a proton exchange membrane (PEM) fuel cell. The hydrogen will be compressed and stored at high pressure (as much as 700 bar). A hydrogen compression and storage system with 172 kg of high pressure hydrogen storage will be used to demonstrate the storage component of the power park concept.

During periods of peak electrical demand, power park electrical output will be supplemented by generation resources fueled with stored hydrogen. A 100-kW hydrogen fueled engine generator will be used to demonstrate the generation component of the power park process. A fuel cell will be incorporated in the power park generation component if found to be economically feasible based on published performance data and prices.

In addition to electrical energy output, the power park will provide hydrogen motor fuel. The Arizona Public Service hydrogen fueled internal combustion engine powered fleet will be used to demonstrate the vehicle fueling component of the power park. The vehicle fleet consists of thirteen vehicles utilizing hydrogen and hydrogen blends with compressed natural gas.

As a byproduct of the electric generation using hydrogen fuel, the power park will provide potable water and cooling. The cooling component of the power park process will be demonstrated using exhaust heat from the 100-kW hydrogen fueled engine generator to produce up to 20 tons of cooling in absorptive cooling units. The potable water component of the power park process will be demonstrated by collecting and processing water from the exhaust of the 100-kW hydrogen fueled engine generator.

With both cost and performance results available from the power park concept component testing, the overall power park performance and economics will be modeled and compared with alternative sources of energy production, storage and delivery. Additionally, power park system safety issues will be evaluated, including design, regulatory, standards and building code issues.

Research and Development of a Proton Exchange Membrane Fuel Cell, Hydrogen Reformer, and Vehicle Refueling Facility

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Subcontractor: Plug Power Inc., Latham, NY

Objectives

- Design, develop, and demonstrate small on-site H_2 production system for stationary fuel cells and H_2 fuel stations.
- Design, construct, and operate a multipurpose refueling station to dispense H_2/CNG blends and pure H_2.
- Design, construct, install and operate a H_2-fueled stationary 50-kW fuel cell.
- Maintain safety as a top priority in the design and operation of the fueling station and fuel cell.
- Evaluate operability, reliability, and economic feasibility of integrated power generation and vehicle fueling system.
- Obtain adequate operational data on fuel station to provide basis of future commercial fueling station designs. Develop appropriate "standard" designs for commercial applications.

A related goal, beyond the scope of the current project, is to expand the current "Energy Station" facility to serve as the first commercial facility when sufficient hydrogen demand develops. A vision is to have this facility ultimately serve as a link in an emerging regional/national H_2 corridor.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- C. Hydrogen Refueling Infrastructure
- E. Codes and Standards
- I. Hydrogen and Electricity Coproduction

Approach

- Several small-scale natural gas based fuel processing technologies under development by others were tested in the laboratory and field environments prior to and during the period of the current project. These included partial oxidation (POX), autothermal reforming (ATR), and steam methane reforming (SMR) technologies.
- POX technology was eliminated from further consideration prior to the start of the current project.
- The ATR and SMR fuel processors were integrated with small-scale pressure swing adsorption (PSA) systems and tested extensively.

- Based on the experience from the testing and on the results of an economic analysis, the final technology selection was made.
- The 50-kW fuel cell stack design was based on existing 7.5-kW reformate-based stack modules developed for residential power generation. Modifications were made to allow operation on pure hydrogen.
- Fuel station design was based on previous experience gained from over 15 H_2 and H_2/CNG fuel stations. The ability to dispense various blends of H_2 and CNG is provided for in the design.
- Extended duration operation of the fully integrated hydrogen generation, fuel cell, fuel station system will be conducted to address robustness, performance, and economic feasibility of this "Energy Station" concept.

Accomplishments

- Based on extensive test results and an economic analysis, SMR technology was selected for the fuel processor.
- An SMR fuel processor from Harvest Energy Technologies integrated with a PSA system from QuestAir Technologies was installed and started up at the Las Vegas site in August 2002. The unit operated well and achieved H_2 product purity in excess of 99.95%.
- The multipurpose fuel station was commissioned in July 2002 (started up with delivered liquid hydrogen). CNG/H_2 and H_2 fuel dispensing have been successfully performed on a fueling test rig, CNG/H_2 internal combustion engine (ICE) vehicles and H_2 fuel cell vehicles.
- The 50-kW stationary fuel cell was started up in August 2002 on hydrogen supplied by the SMR unit.

Future Directions

- Begin extended unattended operation of the stationary fuel cell.
- Achieve extended integrated operation of the reformer, fuel cell and fuel station.
- Collect site performance data to assess overall operation of the system.
- Build up vehicle fleet to include 6 H_2/CNG buses and several light duty vehicles. This is dependent on a separately funded effort.

Introduction

Small-scale on-site hydrogen production technology that can operate on readily available fuels such as natural gas will be required to provide hydrogen fuel stations in certain locations where delivered hydrogen is not readily available. However, small-scale natural gas based hydrogen reformers are not fully developed and will suffer from poor economics due to their small scale and due to poor utilization rates in the early years of hydrogen vehicle development. One approach to achieving high utilization rates of the reformer is to baseload it with a stationary fuel cell that produces electric power while the intermittent vehicle-fueling load is handled by diverting a portion of the hydrogen from the fuel cell to the fuel station as and when needed. This co-production of hydrogen fuel and electric power is referred to as an "Energy Station". The objective of this project is to demonstrate the technology and validate the commercial viability of an alternative fuel station for dispensing blends of hydrogen and compressed natural gas (CNG) and pure hydrogen to vehicles, and the co-production of electricity from a stationary fuel cell. A team of three organizations-Air Products and Chemicals Inc., Plug Power Inc., and the City of Las Vegas-come together to develop, design, procure, install, and operate this "Energy Station" in Las Vegas, Nevada. This refueling station includes onsite hydrogen generation equipment supplied by Air Products and a stationary fuel cell powered electric generator supplied by Plug Power under a subcontract. The City of Las Vegas (CLV) is providing the site location and the operating and maintenance staffing for the refueling station. The DOE cooperative agreement covers a five-year nominal period (1999-2004) for development, design, installation, startup, and operation of the refueling station.

Figure 1 is a block diagram of the proposed refueling facility. In addition to the on-site hydrogen generation, a standard merchant liquid hydrogen supply system (liquid hydrogen storage tank and vaporizers) was installed to satisfy initial demand for hydrogen at the refueling station and to provide back-up supply for additional system reliability. The hydrogen compression, storage, blending and dispensing systems are capable of supplying pre-determined blends of H_2 and CNG to be dispensed to trucks and buses with ICEs converted to run on H_2/CNG mixtures. The station will also be able to dispense pure hydrogen to vehicles. Currently there are one light duty vehicle (LDV) and one para-transit bus fueled with the CNG/H_2 blend. The fuel cell operates on pure hydrogen to generate electric power, which is put back on the local power grid. The fuel cell will be operated to balance the hydrogen demand on the hydrogen generator for vehicle refueling.

Upon successful testing/operation of the first CNG/H_2 fueled para-transit bus, CLV will proceed to convert six new CNG fueled buses to CNG/H_2 blended fuel operation. They expect to have all six buses converted over a six-month period, nominally one bus per month through December 2003. H_2 demand growth is expected to continue as additional buses and light duty vehicles are converted to the alternative fuels over the remaining two years of the demonstration project. It is also proposed that a natural gas-based onsite hydrogen generator will be installed and operated at the refueling station.

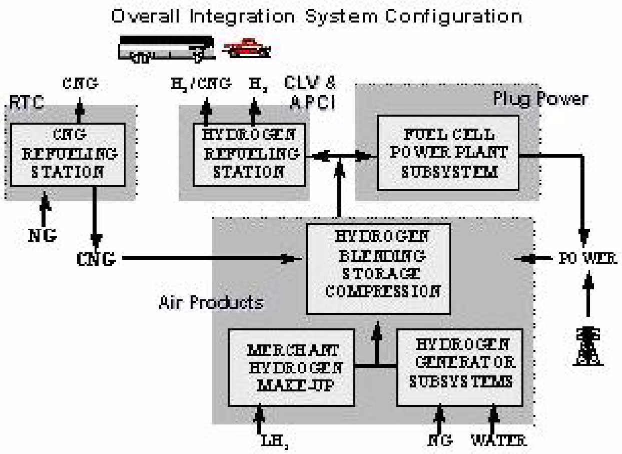

Figure 1. Overall Integration System Configuration

Should the alternative vehicle refueling demonstration station prove to be successful, it is anticipated that vehicle fleets would continue to grow.

Approach

Air Products evaluated various small-scale developmental natural gas reformation technologies via extensive laboratory and field testing. These technologies included partial oxidation, autothermal reforming and steam methane reforming. These test results were the basis for technology selection for the fuel processor. The fuel processor was integrated with a PSA system supplied by QuestAir to develop the on-site system capable of generating pure hydrogen from natural gas.

The 50-kW fuel cell was built by assembling eight 7.5-kW residential fuel cell stacks developed by Plug Power for the residential power market. The residential system was designed to operate on reformate; thus, modifications were required for the pure hydrogen service in this project. Extensive testing of the fully-assembled module at Plug Power's Latham, New York, facility was conducted to qualify individual systems and the final system configuration.

Results

Hydrogen Generator. The hydrogen generator (see Figure 2) was installed, commissioned and placed into

Figure 2. View of the Hydrogen Generator (Left) and Fuel Cell (Right)

operation in the summer of 2002. On-spec hydrogen production, with purity in excess of 99.95%, was established in August 2002. Successful process operation of the hydrogen generator was achieved without process modification to the system after ex-works delivery of the unit to the site for operation.

Since the initial establishment of hydrogen production, the unit has achieved an aggregate run-time of over 2200 hours. The integrated hydrogen generator system controls have been demonstrated to achieve the full range of expected operability control. The hydrogen generator is capable of one-button start, with automated start-up ramping and subsequent load following capability. The hydrogen generator can be, and is, operated remotely, including remote start-up where the appropriate control permission exists based on the automated system's diagnosis of the unit status. In other words, the system is engineered to recognize the potential of conditions from a shutdown mode that necessitate a physical check prior to restart. Consequently, the system can also recognize the safe condition from which a remote start can be initiated via telemetry with the appropriate control program interface. Consistent with this, remote operation and monitoring of the hydrogen generator has been demonstrated during this period.

Produced hydrogen has been utilized for electrical power production by the fuel cell power plant, as well as for fueling of ICE vehicles with H_2/CNG blends and fuel cell vehicles with hydrogen when required.

The fuel cell continues to establish the majority of demand for the on-site generated hydrogen during fuel cell availability. The availability of the fuel cell, however, has not been highly reliable. As expected, vehicle-fueling demand is insufficient for utilization of the full hydrogen generator production capacity. The fuel cell has been able to present a demand for the produced hydrogen during the anticipated fleet build-up period.

Fueling Station. Operation of the fueling station was established in July 2002. The fueling station segment of the Energy Station consists of liquid hydrogen storage, gaseous hydrogen storage, product compression, CNG/H_2 fuel blending, and CNG/H_2 and hydrogen fuel dispensing (see Figure 3).

The CNG/H_2 fuel dispensing was tied into the City of Las Vegas's fuel consumption accounting system for seamless accounting with their existing fleet of CNG vehicle operations.

Since operation of the fueling station was established, satisfactory vehicle fueling functionality has been demonstrated. Fueling operations have been performed for both hydrogen fuel cell vehicles as well as blend CNG/H_2 internal combustion engine vehicles.

Fully integrated control functionality of the Energy Station has been demonstrated.

Stationary Proton Exchange Membrane (PEM) Fuel Cell . The 50-kW PEM fuel cell was initially started up in August 2002, and a continuous run time of 160 hours was logged. The unit successfully ran for three days before it was tripped by the reformer. It was restarted successfully and ran another three days before it was tripped due to single cell failure.

Several operational issues were identified and fixes implemented:

- Scanning of individual cell voltage was unreliable and was traced to a design issue with the cell scanner approach in multiple-stack configurations. The scanner cards were redesigned, successfully installed, and operational in April 2003.
- There was inadequate draining of water from multiple stacks with a common drain. The water

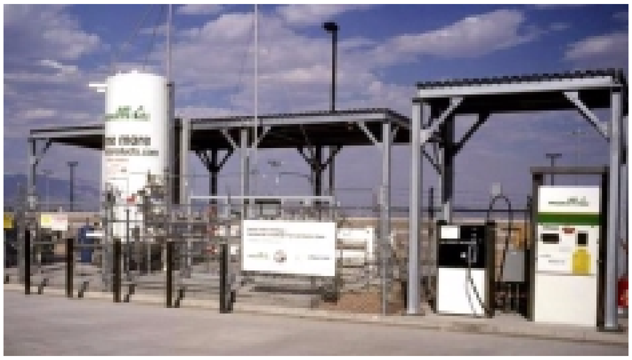

Figure 3. View of the Fuel Station

drain valve was successfully modified in April 2003.

Following these fixes, the unit continued to have operational issues with cell voltage falloff that made continuous operation an issue. This issue appears to fault the concept of multiple stacks with no provision to accommodate the need of each stack with respect to voltage output, over stoichiometric flows to both anode and cathode, humidity of both anode and cathode, and temperature of each stack. The fuel cell stack will be replaced during the week of July 16, 2003, and will be restarted.

A possible issue with timing of electric load shedding on shutdown has been identified. The timing will be analyzed and software and/or hardware modifications made to eliminate potential ground looping, which may be contributing to stack failures.

Conclusion

- The Energy Station is a viable operational concept. The fuel cell has provided a demand for hydrogen during the initial stages of fleet build-up with low levels of vehicle fueling demand.
- Integrated control functionality is critical to system-wide reliability and operability.
- Vehicle fleet build-up continues to be a primary challenge to satisfactory utilization of hydrogen fueling infrastructure efforts.
- The fuel cell design approach of multiple stacks with no ability to independently manage gas flows, temperature, humidity and power is in question.
- An excellent list of lessons learned has been compiled. Additional lessons learned from Plug Power single-stack 5-kW systems will be combined in future designs.
- Current operating performance predicts we will meet the 2-3 months operation with minor tweaks.

FY 2003 Publications/Presentations

Presentations on the "Energy Station" concept and the Las Vegas project have been given to various audiences separately or in conjunction with a discussion of developing hydrogen infrastructure, including:

1. Hydrogen Expo 2002, Hamburg, Germany, October 10-12, 2002 - "Pathways to Building Infrastructure to Support the Hydrogen Economy"

2. U.S. - Australian Climate Action Partnership Opportunities Roundtable, Washington, DC, November 4, 2002 - "Role of Hydrogen as an Energy Resource for the United States"

3. Hydrogen Energy Systems Society of Japan Symposium, Tokyo Institute of Technology, Tokyo, Japan, December 11, 2002 - "Hydrogen Economy Strategies- a U.S. Perspective"

4. SAE Telephone/Webcast, April 3, 2003 - The Path to the Emission-Free Vehicle through the Use of Hydrogen as a Fuel - "Hydrogen Fuel Infrastructure - Creating the Future"

Special Recognitions & Awards/Patents Issued

1. Special Member award from the National Hydrogen Association for " … development of the Las Vegas Refueling Station, the world's first energy station featuring the co-production of hydrogen and electricity …"

Fuel Choice for Fuel Cell Vehicles: Stakeholder Risk Analysis

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Objectives

- Assess opportunities and risks of various fuel cell vehicle (FCV) and fuel pathways, with specific focus on a transtion to a hydrogen infrastructure options.
- Assess impact on the various stakeholders (e.g. car manufacturers, energy companies, government, etc.) and how risks could be shared and minimized.
- Determine what range of factors might trigger the introduction of FCVs (e.g. oil price increase, carbon taxes, FCV cost reduction).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Hydrogen Production

- AD.Market and Delivery

Hydrogen Delivery

- A. Lack of Hydrogen/Carrier and Infrastructure Options Analysis

Hydrogen Storage

- V. Life Cycle and Efficiency Analysis

Approach

- Develop a net present worth (NPW) analysis of both the fuel and vehicle aspects, but with the focus on the transitional risks of a hydrogen fuel infrastructure.
- Generate a "straw-person" scenario of the hydrogen infrastructure introduction based on results from previous work, literature sources, and additional analysis.
- Present the straw-person scenario assumptions and NPW results to a quorum of FCV developers, fuel distributors, and fuel producers.
- Refine the analysis and rank the fuel pathways with respect to a set of performance criteria, in particular to overall financial risk.

Accomplishments

- Constructed a NPW analysis for hydrogen.
- Generated a straw-person scenario focusing on two hydrogen fuel chains: forecourt (i.e. on-site, distributed) natural gas-based production and central natural gas-based production with liquid hydrogen delivery.

- Presented the straw-person results to a limited number of stakeholders.
- Updated the NPW analysis assumptions based on stakeholder input to date.

Future Directions

- Define "lowest-cost" and "most likely" hydrogen infrastructure scenarios and present NPW results to a larger stakeholder audience.
- Define a straw-person FCV scenario and present NPW results to a limited number of stakeholders.
- Evaluate feedback and update model as appropriate based on stakeholder input.
- Evaluate the technology risk, financial exposure, and safety and regulatory risks associated with the various fueling options for each respective stakeholder.
- Generate final report for DOE vetted by key stakeholders.

Introduction

In the previous phase of work, TIAX assessed the well-to-wheel energy use, greenhouse gas emissions and ownership costs of various fuel choices for fuel cell vehicles (FCVs) at a future point in time assuming high capacity factors and high manufacturing production volumes for equipment (Lasher, et al 2001). However, alternative fuels, especially hydrogen, will require significant up-front investment during a transition period, representing a risk to both vehicle manufacturer and fuel provider. The financial risks involved in each of the fuel options vary, and the risk may shift from one player in the value chain to another. Dealing with this risk represents a formidable barrier to the use of alternative fuels, especially hydrogen, for FCVs. In the current phase of work, the DOE has commissioned TIAX to assess the relative risks of various fuel pathways for use in FCVs.

Approach

In order to evaluate financial risks and the effect that potential triggers may have on the various stakeholders, we will develop a net present worth (NPW) analysis. The NPW analysis will take into account the time value of money so that early investments are weighted more heavily than future profits. We will start with an assumed number of FCVs on the road and estimate how the alternative fuel infrastructure (i.e. hydrogen) will be introduced over time. Other inputs will include capital costs as a function of production volume, operating costs, fuel prices (e.g. gasoline, hydrogen), and fuel savings. The NPW analysis will include both the fuel and vehicle aspects, but with the focus on the transitional risks of a new fuel infrastructure.

We will generate a "straw-person" scenario of the hydrogen infrastructure introduction based on results from previous work, literature sources, and additional analysis. We will present the straw-person scenario assumptions and results to a quorum of FCV developers, fuel distributors, and fuel producers, to verify and refine the assumptions and the analysis and discuss the risk aspects for each stakeholder. Based on the feedback from these presentations, we will refine our analysis and rank the fuel chains with respect to a set of performance criteria, in particular to overall financial risk.

Results

We have developed a straw-person scenario with preliminary input assumptions. The assumed hydrogen FCV introduction is based on the conservative scenario results from DOE's Vision Model. Hydrogen infrastructure introduction is assumed to be built up regionally with 10% regional coverage achieved in the 3rd year (10% coverage means one in ten existing fueling stations would have hydrogen capacity). Hydrogen infrastructure proceeds from region to region so that local coverage can be achieved while maintaining reasonable capacity factors. In a single region, hydrogen fueling stations are carefully constructed to coincide with appropriate FCV introduction over a 15-year period. A single region is assumed to be similar in size and make-up to the South Coast Air Quality Management

District (SCAQMD). The 50-year infrastructure introduction for the whole U.S. is presented in Figure 1. Note that we have assumed installations will favor smaller stations (30 FCV/day capacity) with their higher capacity factors in the early years (0-20 years) compared to larger stations. However, larger stations (300 FCV/day capacity) are favored overall when demand increases due to their lower capital costs per unit hydrogen capacity. Capital costs for the fueling station equipment are reduced using progress ratios as production volumes (i.e. number of fueling stations) increase.

A NPW model was constructed for forecourt and central plant hydrogen generation for use in direct hydrogen FCVs. The model can be used to track the NPW results for various input assumptions, such as FCV and hydrogen infrastructure introduction scenarios, central plant size, hydrogen selling price, fueling station capital and energy costs, and many others. Figure 2 is an example of the sensitivity of the hydrogen infrastructure NPW to various input parameters. The straw-person baseline scenario assumes hydrogen is sold for $2.80/kg (excluding tax), which would result in cost parity with a conventional vehicle on a $/mi basis assuming 30 mpg and $1.07/gal for a conventional vehicle and 80 mpeg for a hydrogen FCV. The model is also set up to track cash flow and capital investment over time for the various stakeholders. Figure 3 is an example of the cash flow and capital investment of the entire hydrogen infrastructure.

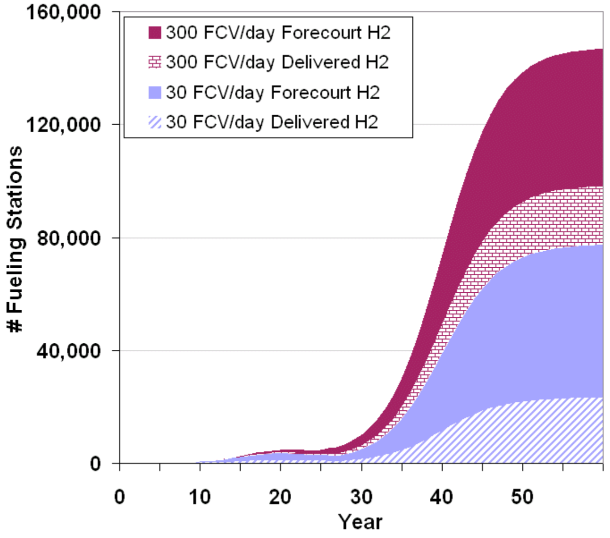

Figure 1. National Hydrogen Stations Buildup - Straw-person Scenario

It should be noted that the straw-person assumptions are based on projections of the future cost of a high efficiency hydrogen infrastructure. We did not use DOE targets, and there is on-going work at DOE and various industries to improve costs and performance beyond those projected here. In addition to refining the straw-person analysis, incorporating the potential improvements from the following could improve the straw-person NPW and cash flow results:

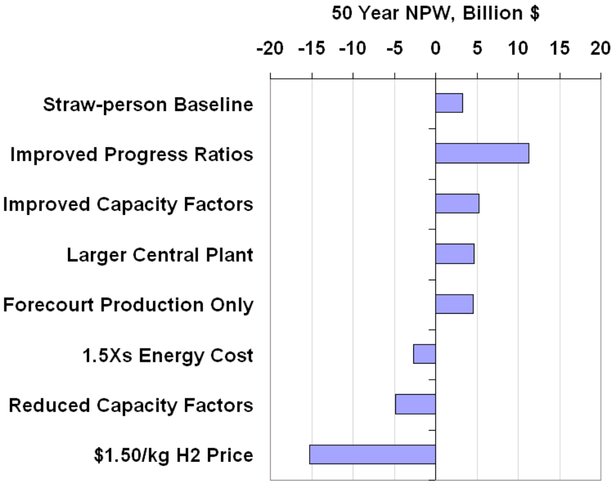

Figure 2. Hydrogen Infrastructure 50-Year NPW Sensitivity - Straw-person Scenario

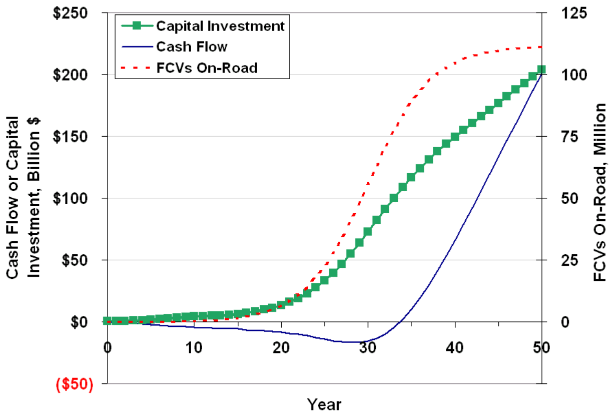

Figure 3. Cash Flow and Capital Investment for Hydrogen Infrastructure - Straw-person Scenario

- Utilize existing excess hydrogen capacity (e.g. methanol and ammonia plants)
- FCV demonstrations and fleets (e.g. buses, government vehicles, etc.)
- Hydrogen internal combustion engine vehicles
- Energy stations (i.e. hydrogen forvehicle fueling and stationary power)

Conclusion

Using the straw-person scenario for hydrogen infrastructure introduction, a few general conclusions can be drawn:

- Hydrogen production costs could ultimately be low (<\$2/kg), but initial costs are high due to high capital cost and low capacity factors in the early years (see Figure 4).

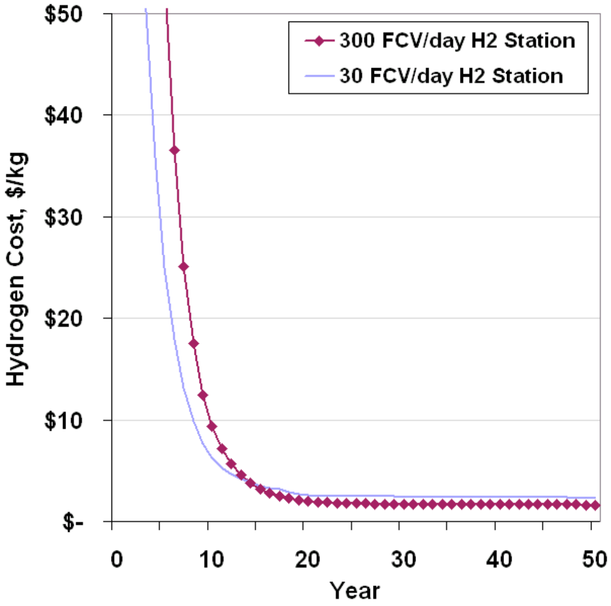

Figure 4. Projected Hydrogen Costs from Forecourt Stations - Straw-person Scenario

- If hydrogen were priced to provide cost-parity with conventional vehicles, the hydrogen infrastructure stakeholders could turn a profit in the long-run, but break-even would not be achieved for many years.
- Near-term pathways are needed to improve capacity factors and reduce capital cost of the hydrogen infrastructure.

References

1. Lasher, S., J. Thijssen, S. Unnasch, "Guidance for Transportation Technologies: Fuel Choice for Fuel Cell Vehicles", 2001 Annual Progress Report - Fuels for Advanced CIDI Engines and Fuel Cells, EERE OTT, November 2001

FY 2003 Publications/Presentations

1. Lasher, S., "Guidance for Transportation Technologies: Fuel Choice for Fuel Cell Vehicles", presented at 2002 American Chemical Society Meeting, Boston MA, August 18-22, 2002

2 Thijssen, J., "Fuel Choice for Fuel Cell Vehicles: Near-Term and Long-Term Perspectives", poster at 2002 Fuel Cell Seminar, Palm Springs CA, November 18-21, 2002

Hydrogen Commercialization: Transportation Fuel for the 21^{st} Century

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Objectives

- Relocate and reassemble the Clean Air Now Project and the Schatz Energy Research Center Project (SERC).
- Produce, compress, store, and dispense hydrogen using grid, solar, and wind electricity and determine cost.
- Move fuel cell vehicles to SunLine from the City of Palm Desert for continued testing.
- Produce hydrogen from a natural gas autothermal reformer.

Approach

- Hire a construction manager to implement the detailed construction plans developed in the earlier phase of the project and adapt them to the SunLine site.
- Prepare the site.
- Construct the following:
- SERC Hydrogen Production Building
- The Palm Desert Vehicle Building
- The Zweig Community and Outreach Building (contribution by SunLine Transit Agency)
- Pad and distribution system for the Solar Flat Plate Arrays
- Pad and distribution system for the Solar Photovoltaic Tracking Arrays
- Pad and utilities for the Stuart Energy electrolyzer
- Pad for the 4,000 psi ground storage tanks
- Pad for the 3,130 psi hydrogen tube trailer
- Pad, utilities and wall for small vehicle refueling area
- Hydrogen underground distribution system
- Pad for hydrogen dispenser at the SunLine public fueling island

Accomplishments

- Installed the following:
    - 0.1-kg Teledyne Energy Systems electrolyzer
    - PDC hydrogen compressor and fueling area for small vehicles
    - 3-kg Stuart Energy electrolyzer

  - 218 Solar Flat Plate Arrays
  - 144 Solar Photovoltaic Tracking Arrays
  - 4,000 psi ground storage tanks
  - 3,130 psi hydrogen tube trailer
  - Dispensing system for small vehicles
  - Dispensing system for buses and automobiles
  - Hydrogen Burner Technologies natural gas partial oxidation reformer
  - 5000 psi ground storage
  - 5000 psi compressors
  - 5000 psi dispenser
  - Controls and valving
- Tested three fuel cell golf carts.
- Tested one street legal neighborhood electric vehicle.
- Tested one EXCELLSiS (formerly-now Ballard) 40-foot fuel cell bus for 13 months.
- Tested one 30-foot ISE Research, Thor Industries, El Dorado, UTC Fuel Cells fuel cell bus for 6 months in fixed route transit service.
- Tested two older model L-10 Cummins internal combustion engine (ICE) buses operating on blended hydrogen and compressed natural gas (CNG) buses.
- Upgraded and modified two new Cummins-Westport 5.9 l B+ internal combustion engines to operate on blended hydrogen and CNG (HCNG).
- Developed the first hydrogen technician training manual, "Hydrogen Fuel Cell Engines and Related Technologies," which is posted on the National Renewable Energy Laboratory's (NREL's) website, and from October 2002 to August 14, 2003, there were 508,321 "hits".
- Demonstrated the production of hydrogen using the Stuart Energy P-3 electrolyzer to support the operation of the XCELLSiS fuel cell (FC) bus and the ThunderPower hybrid electric FC bus (see Figure 1).
- Demonstrated the production of hydrogen from solar energy using the Teledyne Energy Systems Altus 20 electrolyzer (see Figure 2).

Stuart P3 Hydrogen Production

Year	Scf H_2	KWh
2000	833,500	108,100
2001	1,754,737	209,524
2002	832,536	107,933

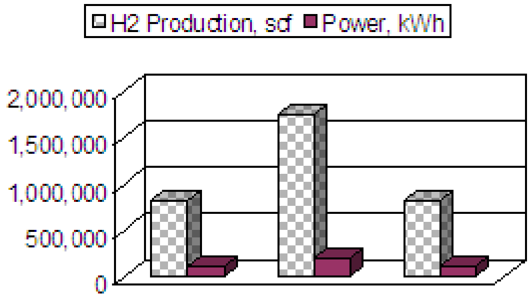

Figure 1. Hydrogen Production Data for the Stuart Energy Electrolyzer

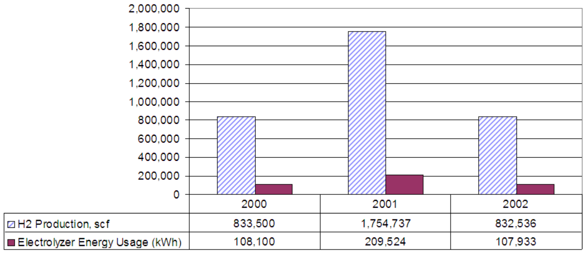

Figure 2. Hydrogen Production Data for the Teledyne Electrolyzer

- Demonstrated the production of hydrogen from solar energy using the Teledyne electrolyzer (see Figure 3).
- Demonstrated the production of hydrogen from the Hydrogen Burner Technology (HbT) natural gas reformer.

Future Directions

- Collect data on the operation of two blended HCNG ICE buses in fixed route service and two Cummins Engine CNG 5.9 l B+ buses in fixed route service, and compare the results.
- In cooperation with Alameda County (AC) Transit, who is purchasing 3 Van Hool 40-foot fuel cell hybrid electric buses, purchase through a Federal Transit Administration (FTA) grant a Van Hool 40-foot fuel cell hybrid electric bus for fixed route service for SunLine Transit Agency.
- Purchase, using SunLine's replacement bus program, a 40-foot New Flyer hydrogen ICE bus for fixed route service.
- Investigate the emissions reduction effects of adding an oxidation catalyst to the ICE HCNG and CNG buses in testing.
- Install and operate a HyRadix natural gas auto-thermal reformer.
- Collect data and investigate the parameters affecting the production of hydrogen from the natural gas reformer.

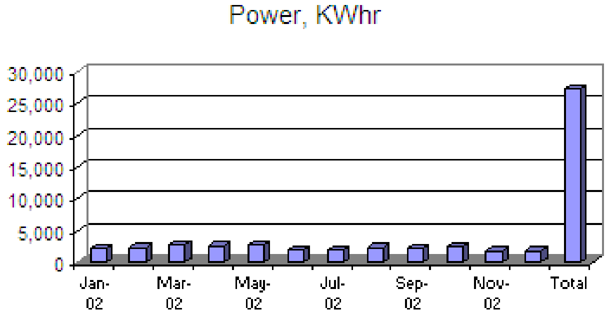

Figure 3. Siemens Solar Panels and Eco-Energies Photovoltaic Tracking Arrays

[illegible]

Period	Energy (kWh)
Jan-02	2,166
Feb-02	2,349
Mar-02	2,757
Apr-02	2,612
May-02	2,774
Jun-02	1,961
Jul-02	1,962
Aug-02	2,330
Sep-02	2,275
Oct-02	2,502
Nov-02	1,746
Dec-02	1,791
Total	**27,225**

Introduction

The President's call to reverse America's growing dependence on foreign oil harkens to the decision SunLine Transit Agency's board of directors made in 1994. That was the year SunLine accomplished the unthinkable by becoming the first transit agency in the world to park all of its diesel buses and switch overnight to a fleet powered 100% by clean-burning compressed natural gas (CNG). That was only the beginning.

Since 1999, SunLine Transit Agency has worked with the U.S. Department of Energy (DOE), U.S. Department of Defense (DOD), and the U.S. Department of Transportation (DOT) to develop and test hydrogen infrastructure, fuel cell buses, a heavy-duty fuel cell truck, a fuel cell neighborhood electric vehicle, fuel cell golf carts and internal combustion engine buses operating on a mixture of hydrogen and compressed natural gas (CNG).

SunLine has cultivated a rich history of testing and demonstrating equipment for leading industry manufacturers in a pre-commercial environment. Visitors to SunLine's "Clean Fuels Mall" from around the world have included government delegations and agencies, international journalists and media, industry leaders and experts and environmental and educational groups.

This is the final report of a three-year success story, which began with the DOE's decision to establish a hydrogen infrastructure in Southern California at SunLine Transit Agency in Thousand Palms, California. SunLine was tasked with taking two then-current DOE projects and moving them to SunLine to create an infrastructure that produced, compressed, stored and dispensed hydrogen to fuel cell vehicles using grid, solar and wind power.

The investment made by the DOE has yielded significant benefits. Not only was the project constructed as scheduled, but it has surpassed the original goals under SunLine's Best Test Center for Alternate Energy Technologies to become part of SunLine's daily operations and maintenance activities. In other words - our "rolling laboratory" has taken the technology out of the science lab and into the real world.

Approach

The basic approach to the development of the hydrogen infrastructure and the testing of fuel cell vehicles was to treat all of the equipment as if it were commercialized. With this philosophy, all of the problems and issues would be brought forward in terms of operability, maintainability, supportability, reliability, and durability. This type of field testing is valuable to manufacturers and developers because it gives them the areas that need solutions before the product is declared commercialized. It educates the early adopters of technology in the requirements to employ the technology in service. The downside is that early adopters are placed on the "bleeding edge" of cash flow unless the new expensive technology is subsidized by government or private investment.

Results

One of the project's significant objectives was to educate the public on the safety and reliability of fuel cell vehicles. By demonstrating fuel cell bus service using compressed hydrogen in a normal transit operation, officials and riders alike got to experience for themselves the pollution-free transportation technology of the future. Another objective was to show the potential to other transit operators for using a liquid fuel reformed to hydrogen in fuel cell buses.

To further enhance the public education component of the project, SunLine developed several additional strategies. Thirteen two-minute "Energy Matters" videos were distributed to PBS stations in major California media markets. The videos covered such topics as alternative fuels, electricity and the grid, fuel cells, micro-turbines, and new car technologies. The videos were also made available to teachers and administrators for classroom use.

SunLine worked with College of the Desert and other partners to develop the first training manual for hydrogen fuel cells and related technologies. The curriculum, funded in part by the Federal Transit Administration and the Department of Defense, is set to be delivered to students at College of the Desert and other community colleges throughout the state through the California Community Colleges' EdNet initiative.

The Hydrogen Fuel Cell Engines and Related Technologies training manual has also been posted on the NREL website. From its introduction in October 2002 to August 14, 2003, the manual received 508,321 hits. According to NREL, this is the largest number of hits they have ever recorded in that short of a time span. From April 28, 2000, to the current date, over 6,000 visitors from 31 countries have visited SunLine Transit Agency to see and hear the story of the development of the Clean Fuels Mall.

Conclusions

Other than cost, SunLine's track record of experience has identified several challenges to hydrogen commercialization:

- The need to improve fuel cell reliability
- The need to engage the insurance industry in overcoming liability issues
- The establishment of reasonable codes and standards
- The implementation of comprehensive hydrogen education and outreach programs to elevate public awareness to mainstream levels

SunLine has effectively demonstrated the need for a path of continuous improvement. Investments in fuel cell technology should be made on a measured basis of how they contribute to the global body of knowledge. While it is important to test and demonstrate the technology, it is also important to invest wisely. Finite resources should be devoted to those organizations and programs that have demonstrated a passion to make things work, the policies and political will to further hydrogen and fuel cell development and the capability to perform technology transfer to future organizations.

Selective investment is a must.

References

1. Final Report to the Department of Energy, February 2003, "Hydrogen Commercialization: Transportation Fuel for the 21st Century", Contract Number: DE FC36-96GO10139

Development of a Turnkey Commercial Hydrogen Fueling Station

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Subcontractors:
H2Gen Innovations, Inc. - Alexandria, VA
Pennsylvania State University - University Park, PA
QuestAir Technologies Inc. - Burnaby, BC, Canada

Objectives

To demonstrate the potential for an economically viable stand-alone, fully integrated hydrogen fueling station based upon the reforming of natural gas by striving to:

- Develop a cost-effective solution to the reforming of natural gas to produce a reformate stream;
- Develop an efficient, cost-effective means to purify the hydrogen-rich reformate to pure hydrogen employing pressure swing adsorption (PSA);
- Develop a commercially acceptable system to compress, store, meter, and dispense hydrogen into vehicles;
- Efficiently integrate the process steps mentioned above into a safe, user-friendly, cost-effective fueling station;
- Demonstrate the operation of the fueling station at Penn State University;
- Maintain safety as the top priority in the fueling station design and operation; and
- Obtain adequate operational data to provide the basis for future commercial fueling stations.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance (O&M)
- E. Control and Safety

Approach

This nine-quarter project is being managed in three phases, with Stage Gate reviews between each phase.

- In Phase 1, conceptual designs and preliminary cost evaluations for each major sub-system in the fueling station will be completed. Options will be developed and compared for the reformer system, PSA system, compression, storage, and dispenser.
- In Phase 2, sub-system R&D will be performed to test the concepts put forth in Phase 1. Technical viability and fueling station costs will be validated.

- Phase 3 will include fabrication, installation, and testing of the full-scale hydrogen generator and dispenser at Penn State. This fueling station will be designed to deliver 50 nm^3/hr of hydrogen.

Accomplishments

- Completed Phase 1 study. Held Stage-Gate meeting between U.S. DOE and Air Products management. Decision made to proceed with the project.
- Initiated Phase 2 development work, as outlined below.

Future Directions

- Complete Phase 2 - Subsystem Development. In this phase, the most promising subsystem designs assessed in Phase 1 will be further developed. Lab testing of certain components will be carried out. Recommendations for the optimal fueling station components will be made. Phase 2 is currently underway.
- Execute Phase 3 - System Deployment. Scale-up and detailed engineering design of all equipment will be completed. Fabrication of all equipment and installation at Penn State will follow. Finally, the fueling station will be started up and put into operation at Penn State University. This will include 6 months of operation and testing.

The expected schedule for all three Phases is outlined in the table below:

Task	Date
Phase 1 Pre-Contract Technical Development	Oct 2001 - March 2002
Cooperative Agreement Award	29 March 2002
Phase 1 Conceptual Design and Economic Evaluation	April 2002 - June 2002
Phase 2 Subsystem Development	July 2002 - July 2003
Phase 3 System Deployment	August 2003 - June 2004
Phase 3 System Deployment - Operation & Testing	July 2004 - December 2004

Introduction

The transition to hydrogen as a fuel source presents several challenges - one of the major hurdles is the cost-effective production of hydrogen in small quantities. In the early demonstration phase, hydrogen can be provided by bulk distribution of liquid or compressed gas from central production plants; however, the next phase to fostering the hydrogen economy will likely require onsite hydrogen generation to institute a pervasive infrastructure. Providing inexpensive hydrogen at a fleet operator's garage or local fueling station is a key enabling technology for direct hydrogen fuel cell vehicles (FCVs). The objective of this project is to develop a comprehensive, turnkey, stand-alone hydrogen fueling station for FCVs with state-of-the-art technology that can be cost-competitive with current hydrocarbon fuels. Such a station will help to promote the advent of the hydrogen economy for buses, fleet vehicles, and ultimately personal vehicles.

Approach

The development efforts are expected to build on preliminary work accomplished by the major partners. Air Products, as the overall project manager, is responsible for the total system integration and final development of the installed equipment. As the system integrator, Air Products will ensure that the system is fully optimized and that all of the individual components are compatible to deliver the lowest cost hydrogen fuel. This nine-quarter project is being managed in three phases, with Stage Gate reviews between each phase.

During Phase 1 of the project, subsystem conceptual designs were formulated and costed. Options were developed and compared for the reformer system, PSA system, compression, storage, and dispenser. Air Products has worked with H2Gen and other reformer suppliers to develop and to evaluate the applicability of auto-thermal reforming (ATR), partial oxidation (POX), and steam methane reformer (SMR)-based reforming systems. At the end of Phase 1, Air Products confirmed the team's ability to reach the cost targets via a confirmed definition of scope and execution costs and identified the partners for further development of components in Phase 2.

In Phase 2, currently underway, the most promising subsystem designs assessed and selected in Phase 1 will be further developed. Lab testing of certain components will be carried out. Recommendations for the optimal fueling station components will be made. Air Products engineers, working with the selected reforming partner, will optimize the design of the reformer and build and test components of this reactor in a laboratory. Air Products will be directly responsible for the design of the dispenser, which will be tested in a shop prior to installation on site. Because of the partners' relationships with the automotive manufacturers, we will solicit their assistance for inclusion of commercial features such as vehicle communication. Finally, Air Products will act as the system integrator to pull together the various pieces into a comprehensive turnkey unit and to minimize the total cost of delivered hydrogen.

During Phase 3, scale-up and detailed engineering design of all equipment will be completed. The engineered system will be analyzed for DFMA (Design for Manufacture and Assembly), and the assembled system will include instrumentation for data collection and provisions for remote monitoring of operation. Fabrication of all equipment and installation at Penn State will follow. Then, the fueling station will be started up and put into operation at Penn State University. This will include 6 months of operation and testing. Finally, we will validate the cost of hydrogen delivered from the installed fueling station, and we will estimate the impact of mass-producing components.

Results

General:

Phase 1 work completed. Presentation made to DOE headquarters representatives on August 7, 2002. Major conclusions of Phase 1 report:

- Project schedule validated – on target.
- Project budget validated – on target.
  - Completed general process specifications for all major equipment.
  - Obtained quotes and updated cost estimates.
  - Re-validated development costs with principal investigators for each area of the fueling station.
- Cost-effective route to production and delivery of hydrogen from a commercial fueling station identified.
  - Cost of hydrogen from stations improves with mass production and with scaling to larger station sizes.
  - \$1.50/gallon gasoline equivalent is a stretch goal, but attainable.
  - Stand-alone hydrogen station is technically and economically feasible.

Phase 2 kicked-off. Of critical importance to the success of this project is the availability of vehicles (or other hydrogen demand) at the Penn State site to validate the performance of the installed fueling station. Penn State (PSU) and Air Products recognized that fuel cell hydrogen buses will not be available by January 2003, the targeted commissioning date for the hydrogen fueling station. A team was established to develop a plan for the station and for making vehicles available. The team met in January, February, and March 2003 and consisted of representatives from Air Products, PSU Hydrogen Institute, DOE (Philadelphia Regional Office), State of Pennsylvania Department of Environmental Protection (DEP), Center Area Transport Authority (CATA), PSU Pennsylvania Transportation Institute, and PSU Office of Physical

Plant (OPP). The team's recommended plan is for the PSU Hydrogen Institute to take the lead in a project to:

1. convert several CATA compressed natural gas (CNG) buses to run on a H_2/CNG blend,
2. convert several PSU OPP utility vans from CNG to H_2/CNG blend,
3. purchase for PSU OPP one hydrogen internal combustion engine utility van,
4. upgrade the CATA and PSU facilities for operation with a H_2/CNG blend,
5. provide required training, and
6. run and maintain the fueling station for a period of 3 years.

This proposal has met with the approval of PSU and Air Products, and it is being reviewed by Pennsylvania DEP for a funding decision. In order to match station and vehicle availability, the Phase 2 end-date was extended from March 2003 to July 2003, and system startup will be rescheduled from January 2004 to July 2004.

Currently, Phase 2 work is ongoing. Progress towards Phase 2 goals is outlined below:

Reformer:

- Air Products completed a Phase 1 engineering study to update the comparison of ATR, POX, and SMR technologies to determine the optimum route to small-scale H_2 production. The major conclusions were:
  - Advanced Technology SMR's are more cost competitive than the other evaluated technologies for small-scale reforming applications used in hydrogen fueling stations.
  - Of the reformers evaluated, H2Gen's heat exchange reformer and Harvest's regenerative reformer offer the lowest cost of hydrogen. Of the two, H2Gen's system has the greatest potential to provide the low-cost option, but H2Gen's system is also the higher risk option, both technically and economically.
- H2Gen development work continued into the Fall of 2002. Then, a meeting was held between DOE headquarters and Air Products project personnel to determine the best technical path forward on Phase 2 with respect to the reformer development. Conclusions: While H2Gen continued to make progress, they were behind scheduled milestones. A decision was reached to switch to another reformer vendor as the reformer supplier for the remainder of this project.
- Process engineering development work continues on optimization of reformer system, including desulfurization, shift, steam generation, heat exchange, and valving.
- A preliminary process flow diagram (PFD) has been developed.

Hydrogen PSA Purifier:

- Air Products' adsorbent development continued. Novel structured adsorbents and advanced beaded adsorbents show significant improvement in bed size and hydrogen recovery. PSA cycle development work concluded – it was used to fully utilize the advanced adsorbents' capabilities. Laboratory experiments have been completed.
- The lab to test the new PSA rotary valve was completed, and testing has commenced. Thus far, the valve has over 800,000 cycles and is leak-tight. An outside supplier for the valve has been identified and has made the first valve for testing.
- Air Products concluded the successful testing of its "alpha" prototype hydrogen PSA unit at an Air Products hydrogen production facility. The data collected on this PSA unit served to verify several of the significant technical "step-outs" being taken in the new PSA design being developed by the Air Products team. The system ran continuously since July 2002, successfully producing hydrogen at <2 ppm CO with high hydrogen recovery. The system met all engineering targets for hydrogen production, hydrogen recovery, and purity.
- Air Products fabricated a "beta" hydrogen PSA test unit. The unit has been placed next to the "alpha" test unit mentioned above. The "beta"

PSA unit is now in operation, and data is being collected.

- QuestAir completed their Phase 1 work to improve their HyQuestor hydrogen purifier. Preliminary design and cost summaries are done and are included in QuestAir's Phase 1 report to Air Products. QuestAir initiated Phase 2 work.
- QuestAir continued their Phase 2 development work. They have optimized the design of their system and have built their laboratory test rig. QuestAir tested their PSA system and is preparing their Phase 2 summary report.

Hydrogen Compression, Storage, and Dispensing:

- Air Products has completed the preliminary engineering work to determine the optimum configuration and selection of components for the hydrogen dispenser.
- Laboratory equipment to test hydrogen flow meters for use in the dispenser has been purchased, and the lab unit is being fabricated. The test plan is prepared –initiation of testing is anticipated in late Summer 2003.

Conclusions

Work progresses on Phase 2 of this aggressive project to determine the viability of a commercial turnkey hydrogen fueling station. Over the past year, the team completed Phase 1 and derived the following conclusions from its Phase 1 study:

- A cost-effective route to production and delivery of hydrogen from a commercial fueling station was identified.

- The cost of hydrogen from stations improves with mass production and with scaling to larger station sizes.

- The $1.50/gallon gasoline equivalent cost is a stretch goal, but attainable.

- Stand-alone hydrogen stations are technically and economically feasible.

FY 2003 Publications/Presentations

1. Quarterly and Annual Reports to U.S. DOE, as required per the Cooperative Agreement, were submitted by Air Products.

2. Annual Program Merit Review presentation was made by David Guro of Air Products at the DOE meeting held in Berkeley, CA, in May 2003.

Development of a Natural Gas to Hydrogen Fuel Station

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Subcontractor: FuelMaker Corporation

Objectives

- The overall objective is to develop cost-competitive technology suitable for distributed production of high-pressure hydrogen from natural gas to fuel hydrogen-powered vehicles.
- Design and test a fast-fill natural gas to hydrogen fueling system with 40-60 kg/day delivery capacity.
- Produce high-pressure hydrogen at $2.50/kg or less to meet intermediate cost targets.
- Demonstrate innovative, compact natural gas steam reforming system and appliance-quality hydrogen compressor technologies.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- E. Control and Safety
- Z. Catalysts
- AB. Hydrogen Separation and Purification

Approach

- Undertake system design and analysis to identify pathways for meeting cost and performance targets.
- Conduct subsystem development and laboratory testing to confirm unit operation and suitability for complete system application.
- Combine subsystems into an overall integrated system that incorporates system controls and safety features.
- Conduct lab and field experiment testing to validate the complete system for performance, operability, and reliability.

Accomplishments

- Comprehensive subsystem and system design report completed.
- Laboratory prototype fuel processor (alpha unit) subsystem built and tested under a wide range of operating conditions, including start-up, steady-state, turndown, and dynamic response rates.

- Full-scale high-pressure hydrogen cascade and environmental chamber constructed.
- First-principle hydrogen cylinder filling model developed (CHARGE H_2).
- Comprehensive set of hydrogen fast-fill tests conducted on two different types of cylinders, including tests beginning at cold and hot ambient temperatures.
- Documented and reported on degree of in-cylinder temperature rise and spatial variability during fast-filling process.
- Paper presented at National Hydrogen Association (NHA) meeting on fast filling of hydrogen cylinders.
- Advanced hydrogen filling dispenser algorithm developed (H_2 AccuFill).
- All-new, oil-free primary hydrogen compressor designed and built for compressing reformed gases (80% hydrogen/20% carbon dioxide) up to 100 psig.
- Pressure swing adsorption (PSA) test facility constructed.
- PSA tests initiated to evaluate multi-component fuel treatment and removal strategies.
- Comprehensive model developed for analyzing hydrogen-fueling station costs, including capital, operating, and maintenance cost elements. Program includes Monte Carlo techniques to account for uncertainty and variability in cost drivers.
- Paper on hydrogen fueling system economics prepared and presented to World Hydrogen Energy Conference.
- Engaged in various technology transfer and communications efforts, including: display of system design at event for President Bush, presentation at SAE TOPTEC, presentation for SAE Industry-Government meeting, International Energy Agency Forum, and one-on-one meetings with various North American, European, and Asian organizations and companies.

Future Directions

- Complete subsystem testing and evaluation of fuel processor, primary compressor, PSA fuel purification, secondary compressors, and dispenser filling algorithm.
- Continue building of the first-generation integrated natural gas to hydrogen fueling system, beginning with system "front end" that includes fuel processor, water treatment and recovery, and primary compression, followed by the system "back end" including PSA subsystem, secondary compression, storage, and dispenser hardware.
- Work with various parties interested in technology transfer, licensing, and/or testing of core subsystems and overall integrated fueling station.

Introduction

A key impediment to expanded fuel cell vehicle use is fueling infrastructure. The use of distributed hydrogen fueling systems is seen as an intermediate pathway to permit infrastructure development (with future development of a hydrogen pipeline delivery infrastructure). This project aims to leverage the substantial natural gas delivery infrastructure by developing a distributed natural gas to hydrogen fueling system.

Several key technologies are being developed in this project. This includes a highly compact, cost-effective steam methane reformer and fuel-processing technology originally developed by GTI for stationary proton exchange membrane (PEM) fuel cells. This unit has been adapted to serve as a hydrogen generator for fueling stations. Experience with compressed natural gas vehicles is being leveraged through modification and development of intermediate and high-pressure hydrogen compressors with FuelMaker Corporation. An additional core effort is development of a hydrogen dispenser with an advanced filling algorithm that will permit accurate and complete filling of compressed hydrogen vehicles under a range of conditions. These advanced subsystems - reforming, fuel cleanup, compression, storage, and dispensing - will be incorporated into an integrated and cost-competitive small natural gas to hydrogen fueling station that will support hydrogen fueling infrastructure development and expansion.

The specific goals for this project are a fast-fill natural gas to hydrogen fueling system with 40-60 kg/day delivery capacity. DOE goals include providing hydrogen at costs of $2.50/kg or less, as part of an intermediate path to $1.50/kg.

Approach

The project approach is to develop and test key subsystems (fuel processor, compression, fuel purification, storage, and dispensing) and then integrate these subsystems with controls into an overall cost-effective hydrogen fueling solution. The project approach includes three phases: 1) Design, 2) Development and Lab Testing, and 3) Field Testing. Through these progressive phases, GTI anticipates building a proven small natural gas to hydrogen fueling system that can support the development and expansion of a distributed hydrogen-fueling infrastructure.

This project is leveraging developments in the stationary PEM fuel cell and compressed gas vehicle market sectors. GTI has developed a high-efficiency, compact steam methane reformer and fuel processor for stationary fuel cells. Modification of this fuel processor comprises a core element of this project. GTI is working with FuelMaker Corp. to develop intermediate-pressure (100 psig and less) and high-pressure hydrogen compressors based on experience with their oil-free designs, as well as fuel purification solutions. An advanced filling algorithm is being developed and tested to allow for complete and accurate filling of vehicles.

Results

The project began in February 2002 with a focus on subsystem and system design. A comprehensive design and analysis report was submitted in September 2002. This covered all of the key subsystems as well as a first-generation integrated system design. Figure 1 shows a detailed description of the key subsystems. The footprint for the system (excluding hydrogen storage) is approximately 8' by 14'. This could be made more compact in the future, but the current emphasis is on system functionality over form.

Work has been conducted using the GTI compact fuel processing system. Normally, this unit contains a steam methane reformer, shift conversion system to maximize hydrogen yield, and methanation reactor for CO control. Testing of the complete system indicates the ability to reliably obtain high hydrogen concentrations of 80% with CO levels reliably below 10 ppm.

An additional set of tests was conducted with the methanation reactor removed from the fuel processing system. This testing was to determine CO levels under different conditions so that sizing of the PSA system could be considered for CO control. In this way, there was an effort to look at the capital and operating cost trade-offs between methanation and additional PSA subsystem material used for CO removal. Figure 2 shows one set of results when testing the fuel processor without the methanation step in a repeat test mode. These data are being incorporated into the PSA system design and testing.

GTI completed a comprehensive set of tests on fast-filling of high-pressure hydrogen cylinders under a range of starting ambient temperature conditions, starting pressure levels, varying time of fill, and other key parameters. Figure 3 shows representative test results, with thermocouples placed on the exterior of a Type 4 cylinder and at various

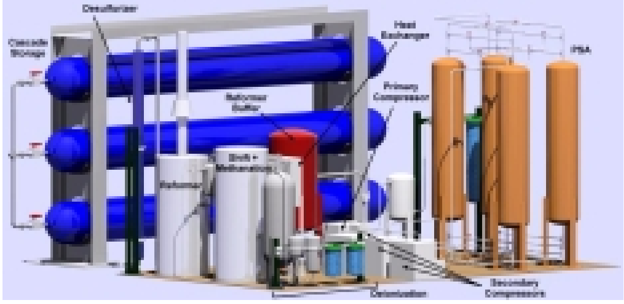

Figure 1. Hydrogen Fueling System Details

points along the internal central axis of the cylinder. The degree of temperature rise in this example is over 140°F. Depending on the point of measurement and time of measurement, there can be substantial differences in temperature within the cylinder. Additional tests were also run on a Type 3 cylinder.

Figure 4 shows a summary of the testing results to date. As a first order, the degree of temperature rise is proportional to the change in pressure from the beginning to the end of the fill process. Secondary factors come into play to result in variations in the degree of temperature rise (e.g., cylinder type, time of fill, etc.).

Testing on hydrogen cylinder filling was conducted at low, moderate, and high ambient temperature conditions using the GTI full-scale environmental chamber equipped with a hydrogen storage cascade (Figure 5). This facility is fully instrumented with data acquisition equipment

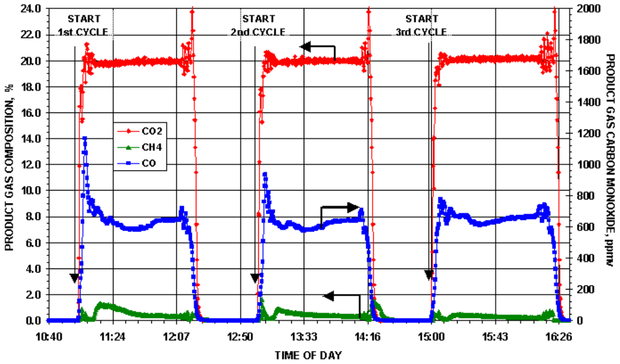

Figure 2. Compact Fuel Processor Testing Without Methanation for CO Control

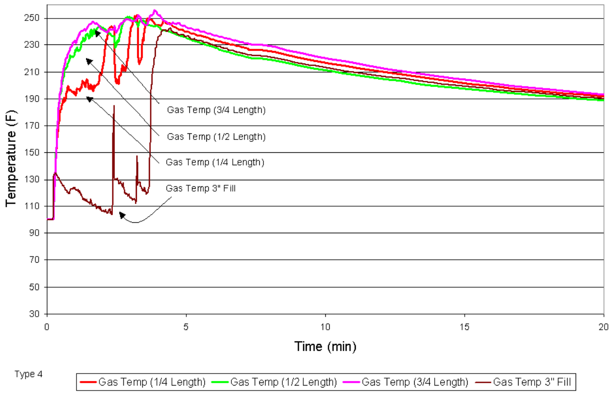

Figure 3. Temperature Measurements During Hydrogen Cylinder Filling

GTI has developed a first-principle thermodynamic model of the hydrogen cylinder filling process (a program called CHARGE H2). We are now using this model and empirical data from the testing program to develop a dispenser control algorithm that will enable proper hydrogen cylinder filling. This algorithm is called H2 AccuFill and leverages a GTI patented approach.

A brand new compressor, referred to as a primary compressor, has been designed and built by FuelMaker during the past year. This unit is designed to take reformate gas (H_2/CO_2) from low

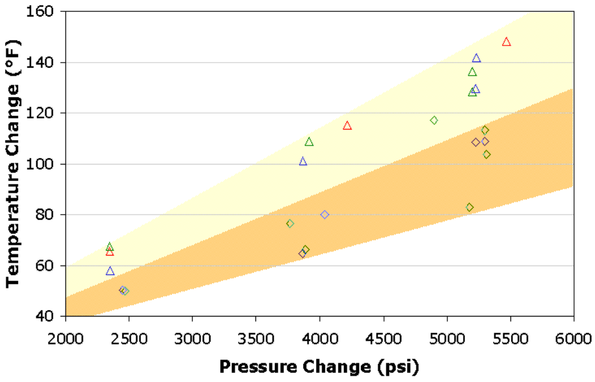

Figure 4. Summary of Hydrogen Fill Tests

Figure 5. GTI Hydrogen Environmental Chamber

pressure to levels of 60-100 psig. The output of the primary compressor is then fed to a PSA system for removal of CO_2 and other trace gases. Figure 6 shows a computer-aided design (CAD) drawing of the primary compressor.

Work is underway in building the first-generation completely integrated natural gas to hydrogen fueling system. An 8' by 14' steel skid has been constructed, and the front end of the system (fuel processor, water treatment and recovery, and primary compressor) is being installed and readied for testing. The back end of the system will be installed during the second half of CY 2003.

Conclusion

1. There are challenges with meeting the system cost targets in the near term; a substantial element of the cost target rests on the price of natural gas.
2. The application of a natural gas fuel processing system originally developed for stationary PEM system application has proven successful.
3. Fuel processor start-up time and dynamic response rates are acceptable for fast-fill stations that incorporate high-pressure cascade storage systems.

Figure 6. FuelMaker Primary Compressor Design

4. Fuel processor efficiencies up to 83% are anticipated based on testing and evaluation efforts to date.
5. Preliminary data indicates an optimum cost trade-off for CO control using a combination of shift conversion and PSA system operation.
6. Significant thermal effects are seen with fast filling of high-pressure hydrogen cylinders.
7. Meaningful spatial variations in hydrogen gas temperature occur with a hydrogen cylinder during fast filling.
8. Preliminary results indicate that a dispenser-based filling algorithm should be suitable for achieving a complete cylinder filling under most conditions.

FY 2003 Publications/Presentations

1. Richards, M. and Liss, W., "Reformer-Based Hydrogen Fueling Station Economics," World Hydrogen Energy Conference, June 2002.
2. Liss, W., "Development of Hydrogen Fueling Systems," Presentation to Japan Gas Association, June 2002.
3. Richards, M. and Liss, W., "Natural Gas Reformer-Based Hydrogen Fueling Station Modeling," NGV International Conference 2002, Oct. 2002.
4. Richards, M., Liss, W., and Kountz, K., "Natural Gas Reformer-Based Hydrogen Fueling Station Modeling," GTI Natural Gas Technologies Conference, Oct. 2002.
5. Liss, W., "Distributed Hydrogen Fueling System & Infrastructure Development," Presentation to International Energy Agency Annex XV, Nov. 2002.
6. Richards, M., Liss, W., and Kountz, K., "Modeling and Testing of Fast-Fill Control Algorithms for Hydrogen Fueling," NHA Annual Meeting, March 2003.
7. Liss, W., "Developing a Retail Hydrogen Market," SAE Fuel Cell TOPTEC, April 2003.

Fuel Cell-Powered Front-End Loader Mining Vehicle

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Natural Resources Canada, Ottawa, Ontario, Canada
Newmont Mining, Elko, Nevada
Nuvera Fuel Cells, Cambridge, Massachusetts
Placer Dome Technical Services, Vancouver, British Columbia, Canada
Southwest Research Institute, San Antonio, Texas
Stuart Energy Systems, Mississauga, Ontario, Canada
University of Nevada, Reno, Nevada

Objectives

- Develop a mine loader powered by a fuel cell
- Develop associated metal-hydride storage and refueling
- Demonstrate the loader in an underground mine in Nevada

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Vehicles
- B. Storage

Approach

- Perform a cost/benefit analysis of fuel cell mine vehicles including cost of producing hydrogen, method of hydrogen transfer, vehicle manufacturer costs, mine recurring costs, and ventilation savings
- Develop an electrolysis refueling station and demonstrate refueling concepts in Nevada
- Determine power requirements (duty cycle), drive system, hybridization options, and onboard energy storage for a Caterpillar-Elphinstone R1300, 165 hp (123 kW), 3.5 cubic yard mine loader
- Perform a detailed engineering design of powerplant, metal-hydride storage, drive system, and control system
- Fabricate powerplant and metal-hydride storage and bench test
- Integrate powerplant, metal-hydride storage, and system components into base vehicle
- Complete risk assessment and certify for underground demonstration
- Test entire vehicle and demonstrate in an underground mine in Nevada

Accomplishments

- Completed manufacturing of electrolyzer and demonstrated refueling concepts in Nevada with a fuel cell-powered locomotive
- Completed final reports for cost/benefit analysis including "Best Methods of Hydrogen Transfer", "Operating Costs of Hydrogen Production", and "Ventilation Benefit Analysis"
- Completed preliminary design identifying duty cycle, single electric drive motor, battery hybrid configuration, and amount of metal hydride storage
- Received diesel-powered R1300 from manufacturer for verification of detailed component layout
- Ordered 100 kW fuel cell stacks from manufacturer

Future Directions

- Complete detailed engineering design for powerplant, metal-hydride storage, drive system, hydraulics, and operating controls
- Fabricate and test powerplant, metal-hydride storage, drive system components, hydraulic components, operating controls, and cooling components
- Integrate associated fuel cell powertrain components into R1300 base vehicle
- Test fuel cell system and compare to baseline diesel-powered performance parameters
- Complete risk assessment and underground certification with the Mine Safety and Health Administration (MSHA)
- Evaluate performance and durability in an underground mine in Nevada

Introduction

Underground mining is the most promising application in which fuel cell vehicles can compete strictly on economic merit (1). The mining industry, one of the most regulated, faces economic losses resulting from the health and safety deficiencies of conventional underground traction power. Conventional power technologies - tethered (including trolley), diesel, and battery - are not simultaneously clean, safe, and productive. Solution of this problem by fuel cells would provide powerful cost offsets to their current high capital cost. Lower recurring costs, reduced ventilation costs, and higher vehicle productivity could make the fuel cell vehicle cost-competitive several years before surface applications. The diesel-powered version of the test loader is shown in Figure 1.

Approach

A joint venture between the Fuelcell Propulsion Institute (a nonprofit consortium of industry participants) and Vehicle Projects LLC (project management) provided the basis for this three-phase project, a key production element of underground mining. To ensure the design meets industry needs, various mining industry participants will evaluate and provide input regarding performance, productivity, and operator ergonomics.

Figure 1. Diesel-Powered Mine Loader.

The first phase of the project will perform a cost/benefit analysis comparing diesel and fuel cell vehicle recurring costs, fuel costs, energy efficiency, and ventilation costs that will determine the feasibility of commercialization. Different refueling concepts will be verified by manufacturing an electrolyzer and using Vehicle Projects' fuel cell-powered locomotive. To understand all of the power requirements, a duty cycle based on real operating conditions, will be established. This will assist in determining the type of drive motor, onboard energy storage, and whether a standalone fuel cell or hybrid powerplant will be used. Software modeling will be used to understand the energy requirements needed to satisfy the duty cycle over an entire operating shift.

In Phase 2, detailed engineering design, project partners will design the powerplant, metal-hydride storage, hydraulic interface, cooling system, system controls, and layout. Engineering drawings and the bill of materials will be the deliverables.

The final phase involves fabricating the powerplant, metal-hydride storage, and all subsystems; integrating them into the base vehicle; testing all systems; completing the risk assessment and certifying the vehicle for underground evaluation; and testing in a production mine in Nevada.

Results

The cost/benefit analysis indicates substantial savings in ventilation costs of anywhere from 24% to 53%, depending on the type of mine operation. This can result in up to $1.5 million a year in savings in primary ventilation system costs if the existing diesel-powered loader fleet were replaced with fuel cell power. This is a substantial cost savings that could offset higher fuel cell-power capital costs. In addition, the cost of producing hydrogen via electrolysis is under $5.00 per kg based on $0.06 per kW for electricity. With the fuel cell powerplant being almost twice as efficient as a diesel engine, the cost of hydrogen approaches the cost of diesel.

Two methods of refueling the metal-hydride storage, recharging directly onboard and swapping of storage modules, were successfully demonstrated with the use of Vehicle Projects' fuel cell-powered locomotive in Nevada. Recharging of 3 kg of hydrogen can be accomplished in under one hour.

Ongoing detailed design, based on the established duty cycle shown in Figure 2, has identified a hybrid powerplant design. In conjunction with using 100 kW (continuous) proton exchange membrane fuel cell stacks, an additional 70 kW, stored in lead-acid batteries, will be available to provide enough power to handle the peak-power requirements. Regenerative braking will not be used in this design due to the complexity and reliability.

Conclusions

The problems of vehicle emissions and noise have negative economic consequences for underground vehicle applications. Fuel cells coupled with reversible metal-hydride storage, by solving these problems, offer cost offsets - higher productivity and lower operating costs - that can make underground fuel cell vehicles cost-competitive sooner than surface applications. Our fuel cell-powered, electric drive loader with metal-hydride storage will exhibit greater torque characteristics than the diesel equivalent and is anticipated to be more productive, while emitting zero emissions and lower noise. Because of the stringent regulations for underground mines, metal-hydride storage is an ideal technology that has been proven with Vehicle Projects' fuel cell-powered locomotive.

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A. R. Miller, Tunneling and Mining Applications of Fuel Cell Vehicles. *Fuel Cells Bulletin*, July 2000, pp. 5-9.

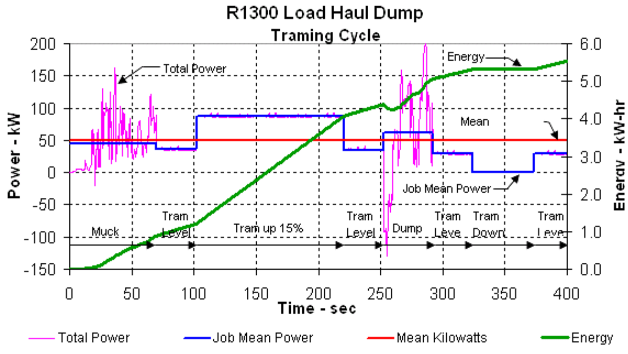

Figure 2. Duty Cycle for the Fuel Cell-Powered Loader

Presentations

1. R. Sage, "Fuelcell Mine Loader and Prototype Locomotive", Canadian Institute of Mining Annual Conference & Exhibition, Vancouver, British Columbia (2002)
2. A.R. Miller, "The Fuelcell Mining Vehicles Development Program: An Update", Canadian Institute of Mining Annual Conference & Exhibition, Montreal, Quebec (2003)

Advanced Underground Vehicle Power and Control Fuel Cell Mine Locomotive

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Kappes, Cassiday & Associates, Reno, Nevada
Placer Dome Technical Services, Vancouver, British Columbia, Canada
Sandia National Laboratory, Livermore, California
University of Nevada, Reno, Nevada

Objectives

- Develop a zero-emissions, fuel cell powered metal-mining locomotive
- Evaluate its safety and performance, primarily in surface tests
- Evaluate its productivity in an underground mine in Canada

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Vehicles
- B. Storage

Approach

- Design 14 kW fuel cell powerplant
- Design metal-hydride storage
- Integrate powerplant and hydride storage onto locomotive base vehicle
- Conduct preliminary tests and evaluate
- Refine final design
- Perform safety and risk analysis and complete documentation to meet regulatory approval
- Evaluate productivity performance in an underground metal mine

Accomplishments

- Designed 17 kW fuel cell powerplant and metal-hydride storage
- Integrated powerplant and metal-hydride storage onto locomotive base vehicle
- Performed preliminary testing and evaluation in Nevada
- Completed safety and risk assessment

- Completed documentation for regulatory approval
- Tested and evaluated productivity performance in an underground metal mine

Future Directions

- Project successfully completed and closed out January 2003

Introduction

Underground mining is the most promising application in which fuel cell vehicles can compete strictly on economic merit (1). The mining industry, one of the most regulated, faces economic losses resulting from the health and safety deficiencies of conventional underground traction power. Conventional power technologies - tethered (including trolley), diesel, and battery - are not simultaneously clean, safe, and productive. Solution of this problem by fuel cells would provide powerful cost offsets to their current high capital cost. Lower recurring costs, reduced ventilation costs, and higher vehicle productivity could make the fuel cell vehicle cost-competitive several years before surface applications. The fuel cell locomotive is shown in Figure 1.

Figure 1. Fuel Cell Mine Locomotive

Approach

A joint venture between the Fuelcell Propulsion Institute (a nonprofit consortium of industry participants) and Vehicle Projects LLC (project management) provided the basis for the 2-phase project. In Phase 1, Sandia National Laboratories was tasked with the design of the fuel cell powerplant and the metal-hydride storage, as well as system integration. Phase 2 included system evaluation, safety and risk assessment, and underground testing in a production environment.

To ensure the locomotive was designed with industry in mind, various industry participants were involved to assess the design for risk and functionality. When the locomotive was tested underground, all regulatory requirements were met.

Results

The locomotive's fuel cell power system uses proton exchange membrane (PEM) fuel cells. No traction battery is employed, and the vehicle is thus a pure fuel cell vehicle. Two stacks in electrical series provide 126 V and 135 A at the continuous rated power of 17 kW gross. Parasitic losses are less than 10%, a very good performance result. Waste heat from the stacks provides the heat to desorb hydrogen from the metal-hydride bed. A heat exchanger links the two isolated thermal systems: (a) the hydride-bed heating/cooling loop and (b) the stack cooling loop. Figure 2 depicts the schematic layout of the powerplant and metal-hydride storage. Specifications of the fuel cell and battery versions of the locomotive are compared in Table 1.

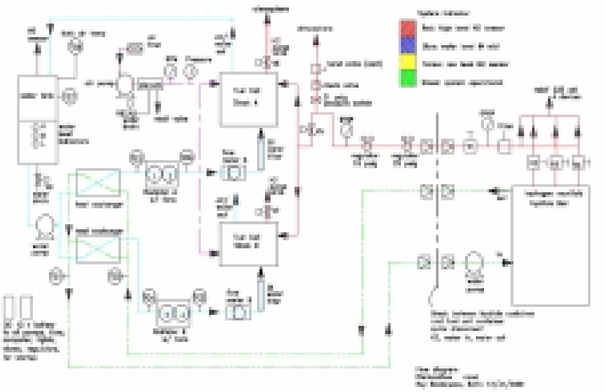

Figure 2. Schematic Layout of the Fuel Cell Powerpla and Metal-Hydride Storage

Table 1. Battery and Fuelcell Specifications

Comparison of Battery and Fuelcell Locomotives		
Parameter	**Battery**	**Fuelcell**
Power, rated continuous	7.1 kW (gross)	17 kW (gross)
Current, rated continuous	76 A	135 A
Voltage at continuous rating	94 V (estimated)	126 V
Energy capacity, electrical	43 kWh	53 kWh
Operating time	6 h (available)	7.5 h
Recharge time	8 h (min)	1 h (max)
Vehicle weight	3,600 kg	2,500 (without ballast)

The hydride storage system stores 3 kg of hydrogen, sufficient for eight hours of locomotive operation at the predicted 6 kW average power of its duty cycle. Hydride subsystem design allows for rapid change-out (swapping) of a discharged bed with a freshly charged unit. Recharging will utilize gaseous hydrogen and has been measured at approximately one hour.

The Mine Safety and Health Administration (MSHA) focused on possible hazards of hydrogen underground, including detailed review of process piping and electrical routing. The assessment indicated a few changes required to meet existing standards and helped to establish new standards for hydrogen-fueled underground mine vehicles.

MSHA measured noise levels (Table 2) of the locomotive under a number of operating conditions, including acceleration (2). Unlike some fuel cell vehicles, our locomotive is very quiet under all conditions. It emanates a pleasant, low frequency purring, and normal conversation can easily be carried out while standing beside the operating powerplant. Consequently the steel-wheel-to-steel-track generated noise will be the most prevalent.

The locomotive was successfully tested and evaluated in two underground mines, one an experimental mine, the other a gold production mine (27 level, 4,000 feet underground). Pulling upwards of 20 tons, the locomotive performed flawlessly logging over 60 hours of runtime. Prior to underground testing a complete documentation package was approved including an extensive risk assessment and site-specific safety evaluations. A large portion of this regulatory approval will set the basis for future fuel cell-powered underground mining vehicle specifications.

Table 2. Average Recorded Sound Levels

Average Sound Levels for the Locomotive		
Location / Condition	**dBA***	**Linear****
Operator Position/Traveling Forward, Run #1 (Full Throttle)	75.3	80.1
Operator Position/Traveling Forward, Run #2	76.6	85.1
Operator Position/Traveling in Reverse, Run #1 (Full Throttle)	76.6	85.2
Operator Position/Traveling in Reverse, Run #2	76.2	82.2
Operator Position/Idle	74.4	81.2
6 Inches from Blower on Right Side/Idle	78.9	85.3
6 Inches from Top Vent on Right Side/Idle	80.8	84.3
6 Inches from Control Panel on Left Side/Idle	79.5	84.0
1 Foot in Front of Locomotive/Idle	75.3	81.9
Background Near Area of Tests	73.4	78.3

* Sound Level using an "A-weighted" network
** Sound Level using an unweighted network (flat response)

Conclusions

The problems of vehicle emissions and noise have negative economic consequences for underground vehicle applications. Fuel cells coupled with reversible metal-hydride storage, by solving these problems, offer cost offsets - higher productivity and lower operating costs - that can make underground fuel cell-vehicles cost-competitive sooner than surface applications. Our hydride-fuel cell locomotive, like the battery version, is a zero-emissions vehicle. However, the fuel cell locomotive has greater net power, greater energy storage, higher gravimetric energy and power density, higher volumetric power density, and substantially faster recharging. Because weight is not an issue, safe and compact metal-hydride storage is an ideal storage technology for underground locomotive applications.

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1. A. R. Miller, Tunneling and Mining Applications of Fuel Cell Vehicles. *Fuel Cells Bulletin*, July 2000, pp. 5-9.

2. Special Acoustical Field Investigation, Hydrogen Fuel Cell Powered Locomotive. *Investigative Report PP-025-02O*, Mine Safety and Health Administration, Pittsburgh, PA, 17 May 2002.

Presentations

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2. A. Miller, “Fuelcell Locomotives”, European Fuel Cell Forum, Lucerne, Switzerland (2002)

UNIGEN® Regenerative Fuel Cell For Uninterruptible Power Supply

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Objectives

Demonstrate hydrogen fuel cell based uninterruptible power supply with

- Economic viability
- Real world applications
- Regulatory code compliance

Achieve performance goals:

- Power output 3^+kW
- Run time of <240 hours per year typical
- Storage capacity of 50 hours
- Instantaneous operation upon grid failure
- Maintain digital equipment with continuous electrical supply

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Technology Validation

- I. Hydrogen and Electricity Coproduction

Education

- B. Lack of Demonstrations or Examples of Real World Use

Hydrogen Codes and Standards

- O. Insurance Companies Recognize Current Standards

Approach

- Fabricate UNIGEN® Regenerative Fuel Cell (RFC) Uninterruptible Power Supply (UPS) using modular components allowing flexibility in power output, run time, and recharge time
- Demonstrate technology performing useful work in a high visibility location with access to decision makers that are key to realizing the common usage of hydrogen based systems
- Obtain permits for siting and operation of the UNIGEN® RFC UPS unit through co-authoring of new code with local authority

Accomplishments

- Completed development tests and preliminary design of UNIGEN® RFC UPS
- Established the Mohegan Energy, Environmental, Economics Education Center as the demonstration site
- Established working agreement with local authorities at Mohegan Sun to co-author codes for siting and operation at their facility

Future Directions

- Complete final design of 3-kW RFC UPS and fabricate
- Co-author a code to be adopted by the Mohegan Tribe for UNIGEN® RFC UPS
- Perform full system validation test at Proton
- Install UNIGEN® RFC UPS at Mohegan Energy, Environmental, Economics Education Center

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Introduction

The UNIGEN® Regenerative Fuel Cell (RFC) for Uninterruptible Power Supply (UPS) project was initiated in October of 2002 as part of the U.S. Department of Energy State Energy Program (DOE/SEP). The objective of the project is to demonstrate a fuel cell based UPS with economic viability. The UPS is required to provide 1-kW to 5-kW of high quality electrical power to digital equipment without interruption in case of a power outage in a real world application. The UNIGEN® RFC UPS being fabricated by Proton Energy Systems as part of the project provides 3 kW of electrical power without interruption during a loss of grid power using a proton exchange membrane (PEM) fuel cell that utilizes pure hydrogen for power generation and a PEM electrolyzer for refilling the hydrogen storage system after the grid has returned to normal.

A significant aspect of the demonstration phase is the permitting process for siting the unit. As there is no one inclusive regulation that applies to an RFC UPS, one needs to be developed as part of the project. The generation of the regulation is a collaborative effort between Proton Energy Systems and the Public Safety Office of the Mohegan Tribe. Once completed, the Mohegan Tribe will adopt the regulation just as existing National Fire Protection Association (NFPA) regulations for mature technologies are recognized today.

Approach

The project has three separate goals, each requiring its own approach. The goals and the approach taken to meet each of them are given in the following paragraphs.

Economic Viability. There are three main attributes to the regenerative fuel cell power system as it is used in a back-up power scenario. These are power output, run time, and recharge rate. The power output is determined by the size of the fuel cell. The runtime is determined by the capacity of the hydrogen storage portion of the system. The recharge rate is determined by the output rate of the electrolyzer used to generate the hydrogen. The approach of the Proton UNIGEN® system is to separate these attributes into modular components. The modular system components allow flexibility in meeting the particular needs of future end users by easily accommodating different output powers, back-up times, and recharge times. Modular component systems are fitted to the customer's need in a building block approach, enabling a "buy as you need" scenario. Modular components also allow capability for future expansion with maximum reuse of hardware, avoiding the need for total system reconfiguration. Modular components greatly simplify maintenance, as field repairs become a simple module swap.

Real World Application. One of the significant challenges facing the common use of hydrogen-based technology is the general reluctance to adopt new technologies based on a lack of understanding and negative safety perception of hydrogen. Demonstrations outside the laboratories where the technologies are performing useful work in approachable atmospheres are key to breaking down these barriers. The approach to this aspect of the project is to site the RFC UPS where the potential for educational impact is greatest. The Mohegan Energy, Environmental, Economics Education Center provides a unique opportunity for showcasing the technology in a real world application. The Center receives about 1,000 visitors annually, with the majority being professionals, government representatives, and academics involved in the use, research, and industrial deployment of alternative energy technologies. Educating these decision makers is the first step in realizing the hydrogen economy future.

Regulatory Code Compliance. As with any new technology, one of the significant challenges is the acceptance by local officials who are chartered with ensuring safety of the general public. This is also the case with the UNIGEN® Regenerative Fuel Cell UPS. Local safety and fire officials are familiar with the regulations outlined in documents published by the NFPA. They use these guidelines when assessing the installation and operation of equipment at their facilities. Since hydrogen technology based equipment is relatively new, the current regulations do not provide the required guidance in all areas. The approach used in this project is to co-author a regulation with the local safety and fire officials, pulling applicable pieces from established regulations as they apply to the UNIGEN® RFC UPS. Having the demonstration at the Mohegan Sun facility offers a unique opportunity to accomplish this. The Mohegan Tribe is a recognized sovereign nation with its own governing body. As such, there is the ability to generate a new regulation that will be applicable to their facilities. The number of agencies and cognizant parties is small, so the authoring and adoption process has a shorter cycle time versus regulations covering the state or national levels.

Results

The UNIGEN® Regenerative Fuel Cell for Uninterruptible Power Supply demonstration project is making groundbreaking progress in all three of the key areas identified. The design and development of the modular components, establishment of a real world application for demonstration, and regulatory code generation are on a clear path leading to success of the project.

The modular system design has progressed through the preliminary phase by meeting the goal of a truly configurable system that will serve the needs of a variety of end users. The design of the system complies with the regulatory codes as they apply to each aspect of the technology. Development testing in the area of power transfer has resulted in a seamless transition from grid to fuel cell generated electrical power suitable for digital equipment.

The real world application in a high visibility location has been established. Agreement has been reached with the Mohegan Energy, Environmental, Economics Education Center Administrator that the UNIGEN® RFC UPS will provide needed back-up power to the Center's twin 200-kW PC25 fuel cells' monitoring and safety systems. Without these systems, the PC25s are required to shut down during a power outage. The UNIGEN® RFC UPS gets its power to recharge the hydrogen storage system from the PC25s as well. The notion of a fuel cell based UPS keeping a fuel cell based power plant online during conventional grid failures is one that will create a lasting impact on visitors to the Center.

The regulatory codes, as they apply to all types of hydrogen based equipment and codes pertaining to the design and installation of industrial equipment, have been reviewed for applicability to the UNIGEN® RFC UPS. A subset of these codes has been identified in draft form, and a preliminary siting plan has been developed. The Mohegan Sun Public Safety Official and the Fire Marshall have affirmed their support of the project and the generation of the new regulation. Once the regulation is complete and accepted by the Mohegan Tribal Government, it can be used as an example for other national associations in generation of standards for similar equipment.

Conclusions

The UNIGEN® Regenerative Fuel Cell for Uninterruptible Power Supply project is well on its way towards successful completion in September of 2004. Progress towards each of the three objectives has been positive, with results building upon one another. Development testing has yielded a design that will meet the performance objectives of the project. The modular component concept will enable economic viability in the future and has been designed for fuel cell based UPS system with power output in the 1 kW to 5 kW range. The barriers commonly associated with the public perception of hydrogen technology safety have been broken down through mutual cooperation and understanding of both the technology and the responsibility of the local authorities in keeping the public safe.

Codes and Standards Analysis

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Objectives

- Quantify ignitability of hydrogen-air mixtures in motion.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Hydrogen Safety

- C. Validation of Historical Data

Hydrogen Codes and Standards

- B. Competition between ICC and NFPA

Approach

- Design: generate apparatus to produce repeatable hydrogen leaks into the interior of a 5000 square-foot warehouse. Produce experimentally verified computer model of hydrogen cloud formed by leak apparatus.
- Test: locate the boundaries of ignitable cloud formed by hydrogen leak with electrical spark.
- Analyze: compare boundaries of experimentally determined combustible cloud to boundaries of clouds defined by upper propagating lean limit of combustion (4.0% concentration hydrogen) and downward propagating lean limit of combustion (10.0% concentration hydrogen). Determine explanation for observed behavior.
- Design: generate apparatus to produce homogeneous hydrogen-air mixture flows in exhaust ducts.
- Test: test the ignitability of lean homogeneous hydrogen-air mixtures in exhaust ducts.
- Analyze: determine the ignitability of homogeneous hydrogen-air mixtures in exhaust ducts as a function of Reynolds number.

Accomplishments

- Modeling: completed experimentally verified computer model of 20 SCFM hydrogen leak. Leak was directed horizontally and 4 feet above the floor (see Figure 1).
- Design: completed design of sonic throttle experimental apparatus to accurately leak 20 SCFM hydrogen through 0.372 inch diameter orifice in center of 8 foot by 8 foot wall (Figures 2 and 3).
- Examination: examined ignition characteristics of hydrogen cloud formed by 20 SCFM leak (Figure 4).

Future Directions

- Evaluate data taken to date and compare with published data.
- Analyze published data to determine applicability to this research effort.
- Conduct more ignitability tests with hydrogen leaks and flows of hydrogen-air mixtures in ducts.

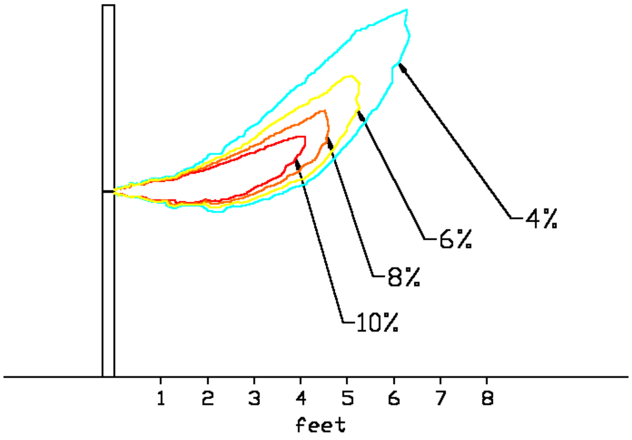

Figure 1. Model Results for 20 SCFM Hydrogen Leak

Figure 3. Leak Test Apparatus

Figure 2. Test Wall for Leaks

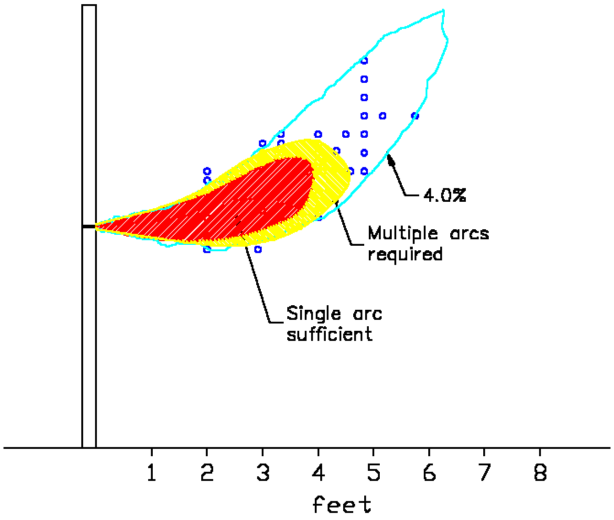

Figure 4. Ignitability of 20 SCFM Hydrogen Cloud

Introduction

Four percent (4.0%) is a commonly quoted value for the lean limit of combustion (references 1-3). This value is then used as an indicator of ignitability in the determination of separation distances and electrical environment classification. Four percent concentration represents the upward propagating lean limit of hydrogen in a quiescent environment. Ten percent concentration represents the downward propagating lean limit of hydrogen in a quiescent environment. The values of lean limit that apply for a moving gas mixture (hydrogen leaks, flow in exhaust ducts) is somewhere between 4.0% and 10%. This work intends to determine what concentrations of hydrogen in air are ignitable under these conditions.

Approach

The approach is to produce a variety of hydrogen leaks and flows of hydrogen-air mixtures in ducts and test their ignitability. Parameters can then be developed to determine how close an ignition source can be to a hydrogen leak and what concentration of hydrogen is ignitable in an exhaust duct.

Results

The first set of test results are depicted in Figure 4. The experimentally verified computer model of a 20 SCFM hydrogen leak shows 4.0% concentration at a distance of 76 inches horizontally from the leak source in the wall. Using the commonly quoted value for the lean limit of combustion, this location should be ignitable. In actuality, the cloud could not be ignited unless the ignition source was 55 inches from the wall. This was true even though the ignition source was 110 millijoules (minimum ignition energy is three millijoules). The ignition source was required to be 47 inches from the wall to ignite the cloud with a single arc. At 55 inches, hundreds of arcs were required to produce ignition.

Conclusions

The separation distance defined by 4.0% hydrogen concentration is 38% greater than the separation distance defined by the actual ignitability of a 20 SCFM hydrogen leak.

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2. Lewis, B., and von Elbe, G., 1987, Combustion, Flames and Explosions of Gases, Academic Press Inc., Orlando, Florida

3. Glassman, I., 1987, Combustion, Academic Press Inc., Orlando, Florida

Hydrogen Codes and Standards

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Clean Vehicle Education Foundation, Washington, DC
CSA America, Inc., Cleveland, OH
LCC, Ltd., Clementon, NJ
National Hydrogen Association, Washington, DC
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Objectives

- Facilitate creation and adoption of model building codes and equipment standards for hydrogen systems in commercial, residential, and transportation applications.
- Provide technical resources to harmonize development of international standards among the International Organization for Standardization (ISO), International Electrotechnical Commission (IEC), and Working Party on Pollution and Energy (GRPE).

Technical Barriers

This project addresses the following technical barriers from the Codes and Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Limited Government Influence on Model Codes
- B. Competition between ICC and NFPA
- C. Limited State Funds for New Codes
- D. Large Number of Local Government Jurisdictions (approximately 44,000)
- E. Officials Training Differences
- F. Limited DOE Role in the Development of ISO Standards
- G. Inadequate Representation by Government and Industry at International Forums.
- H. International Competitiveness
- I. Strategic Conflicts between Domestic and International Standards Objectives
- J. Consensus National Agenda on Codes and Standards
- K. Lack of Domestic Industry Support at International Technical Committees
- L. Competitiveness in Copyright of Published Standards
- M. MNFPA 55 has not yet been completed, but is currently in progress
- N. Lack of Technical Data to Revise NFPA 55 Standard (for underground and aboveground storage)
- P. Current Large Footprint Requirements for Hydrogen Fueling Stations

Approach

- Support and facilitate the timely and efficient incorporation of hydrogen safety issues into existing and proposed codes and/or standards promulgated by organizations such as the International Code Council (ICC), National Fire Protection Association (NFPA), Society of Automotive Engineers (SAE), and ISO.
- Support and encourage technical and operational consistency among and across the codes and standards developed by different organizations.
- Disseminate and share information on development of codes and standards.
- Identify critical gaps and deficiencies in codes and standards and formulate recommendations for addressing them.
- Familiarize building code officials, fire safety officials, local/state/federal policymakers, and other strategic stakeholders (e.g., homebuilders, architects, transportation regulators) with hydrogen technologies and the related codes and standards.
- Create "national template" to harmonize standards, codes, and regulations.
- Develop generic licensing agreement for web-based access to standards.
- Develop training modules and conduct workshops with ICC and NFPA.
- Develop unified national agenda and support consistent representation of technical experts from industry and government at key global venues.
- Develop comprehensive R&D plan and program for validation of codes and standards.
- Actively seek opportunities to work collaboratively with other DOE programs and non-federal organizations involved in hydrogen-related codes and standards efforts to streamline codes and standards development and minimize duplication of efforts.

Accomplishments

- Hydrogen safety incorporated in 2003 edition of ICC model codes.
- Developed draft template for national standards, codes, and regulations for hydrogen vehicles, fueling/service/parking facilities, vehicle/facility interface, and on-site hydrogen generation, and for stationary and portable fuel cells.
- Testing underway to establish technical basis for separation distances for safe bulk storage of hydrogen.
- Draft performance-based regulations for compressed and liquid hydrogen storage for vehicles completed by United Nations-European Economic Council Working Party on Pollution and Energy (UN-ECE/GRPE) informal group on Hydrogen/Fuel Cells.
- Standards under development and on-going coordination with American Society of Mechanical Engineers (ASME) Hydrogen Steering Committee; Underwriters Laboratory (UL) Standards Technical Panel 2264 Hydrogen Generators; NFPA Hydrogen Coordination Committee; CSA America Technical Advisory Group for on-board gaseous hydrogen container standard; International Hydrogen Infrastructure Group Codes and Standards Working Group; California Fuel Cell Partnership Codes and Standards Working Group; and Working Group for Emergency Response Guide for Fuel Cell Buses, U.S. Fuel Cell Council Codes and Standards Working Group.
- Organization agreements among U.S., Canada, and Japan in place for Partnership for Advancing the Transition to Hydrogen (PATH).

Future Directions

- Refine overall codes and standards coordination program.
- Create centralized, publicly accessible web-based data center.

- Negotiate DOE license from primary standard and code development organizations.
- Create one-stop technical assistance for hydrogen projects including directory of primary contacts for information and technical assistance.
- Convene annual safety, codes, and standards summit meeting.
- Initiate comprehensive R&D plan for validation of standards.
- Develop hydrogen safety training packages for local code officials with NFPA and ICC.
- Identify and fund appropriate experts to fully participate in development of Global Technical Regulations for on-board storage and other hydrogen-related regulations under development.
- Develop Global Technical Regulations for hydrogen fuel cell vehicles that include harmonized regulations for on-board hydrogen storage and are harmonized with U.S. Federal Motor Vehicle Safety Standards.
- Develop harmonized standards for fuel cell power plants.

Introduction

The development and promulgation of codes and standards are essential if hydrogen is to become a significant energy carrier and fuel. Codes and standards are critical to establishing a market-receptive environment for commercializing hydrogen-based products and systems. With the help of key stakeholders, the Hydrogen, Fuel Cells & Infrastructure Technologies Program of the U.S. Department of Energy (DOE) and the National Renewable Energy Laboratory (NREL) are coordinating a collaborative national effort by government and industry to prepare, review, and promulgate hydrogen codes and standards needed to expedite hydrogen infrastructure development.

DOE has sponsored work in codes and standards as a key part of its efforts since 1995. The initial efforts included support for the National Hydrogen Association (NHA) to conduct national codes and standards workshops at least annually to bring together experts to address key issues and needs. These and other efforts sponsored by DOE have encouraged organizations such as the International Code Council (ICC), the National Fire Protection Association (NFPA), the Society of Automotive Engineers (SAE), Underwriters Laboratory (UL), and the Compressed Gas Association (CGA) to conduct national activities in hydrogen codes and standards. Federal agencies such as the Department of Transportation (DOT), the National Aeronautics and Space Administration (NASA), and the National Institute of Standards and Technology (NIST) also have regulatory or mission-related interests in hydrogen regulations, codes, and standards. Under this project, DOE has assumed leadership in accelerating the creation and adoption of a harmonized set of national and international standards, codes, and regulations that are essential for the safe use of hydrogen by consumers in the U.S. and worldwide.

Approach

The federal government has an indirect and relatively limited role in the voluntary consensus process through which codes and standards are developed in the U.S. Because of the importance of establishing a harmonized set of standards upon which model codes and regulations can be based, DOE, primarily through NREL, has devoted considerable effort to facilitate and coordinate this consensus process. Much of this effort is carried forth through the DOE Hydrogen Codes and Standards Coordinating Committee (HCSCC). In addition to serving as the database repository, clearinghouse, and gatekeeper for the codes and standards activities being conducted within DOE, the HCSCC also collaborates with other national and international organizations involved in codes and standards activities. The HCSCC conducts monthly conference calls to update participants on current activities and to discuss key issues and convenes quarterly meetings to:

- Coordinate codes and standards development efforts and prevent duplication of efforts,
- Identify critical deficiencies and gaps in hydrogen codes and standards development efforts that

could adversely impact market acceptance and penetration,

- Collaboratively determine a strategy and action plan to address critical gaps and deficiencies, and
- Identify specific opportunities for organizations to work collaboratively in developing codes and standards.

Once developed, standards are usually incorporated into model codes that, in turn, must be adopted by state and local jurisdictions to have the force of law. In 2001, the model codes of the ICC did not include hydrogen as an energy source or fuel cells as either power-generating devices or appliances. To address this limitation, the ICC established an Ad Hoc Committee (AHC) on hydrogen technologies, at the request of DOE, to reduce the time needed to have the model codes amended to include hydrogen technologies. As part of a collaborative process, DOE sponsored the participation of experts to the AHC to help ensure a balanced membership of hydrogen users, producers, and regulator interests. This process was successful, and the 2003 edition of the ICC model codes contain provisions for hydrogen use in and around buildings and consumer facilities.

In addition to sponsoring activities related to ISO TC197 and other international standards development organizations (SDOs), DOE is helping to organize the Partnership for Advancing the Transition to Hydrogen (PATH) to link and unify hydrogen interests of the U.S., Canada, Japan, Argentina, and other countries in the Pacific Rim and the Americas. The goals of PATH are to identify and build on a community of interest among members by addressing common issues and to increase knowledge and activities concerning hydrogen, particularly safety and codes and standards. PATH will also help interested hydrogen parties in non-member countries to organize hydrogen activities and contribute to the strengthening of the international hydrogen community.

Results

The key results of the domestic codes and standards effort were the inclusion of hydrogen applications in the 2003 edition of the ICC model codes and the creation of "national templates" through which DOE, NREL, and the major SDOs and model code organizations will coordinate the preparation of critical standards and codes for hydrogen technologies and applications. Provisions for the safe use of hydrogen are now incorporated in the ICC's International Building, Residential, Fire, Mechanical, and Fuel Gas Codes. Additional work to reduce the footprint of hydrogen fueling stations will be considered under the ICC's 2003-04 code cycle that, if successful, will be incorporated in the 2006 edition of the ICC model codes.

The draft template for hydrogen applications on vehicles and in fueling, service, and parking facilities is shown in Figure 1. The draft template for on-site hydrogen generation and for stationary and portable fuel cells is shown in Figure 2. The templates designate lead and supporting organizations for the standards and codes to be developed and were prepared in workshops by consensus of the organizations shown. This consensus overcomes the historic competitiveness among the organizations to develop and sell standards and model codes and is a

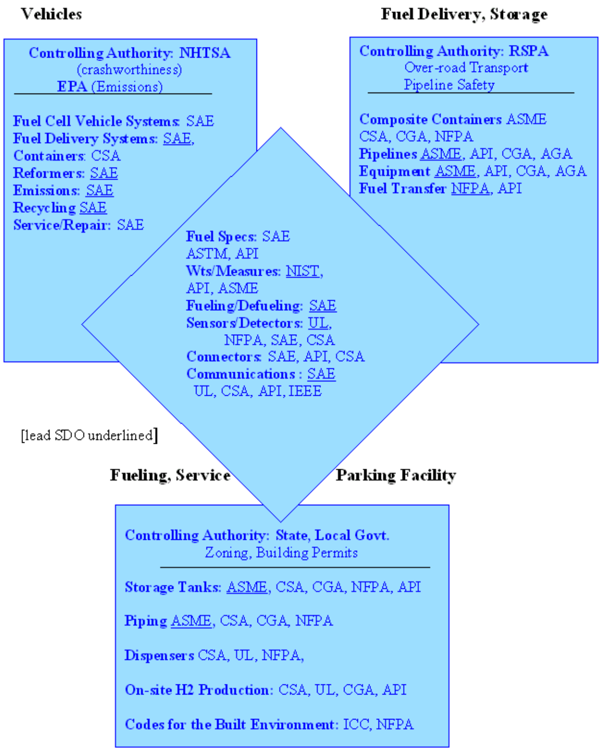

Figure 1. Draft Template for Vehicle Systems and Refueling Facilities

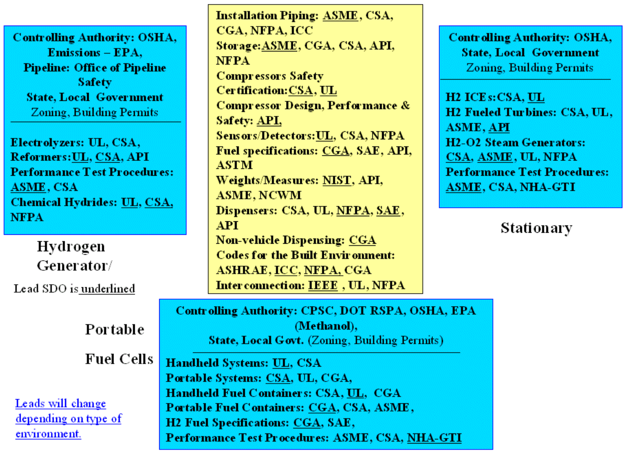

Figure 2. Draft Template for On-Site Hydrogen Generation and Fuel Cells

critical step in creating a collaborative and cooperative national agenda for hydrogen codes and standards.

The key results in international codes and standards were the launching of PATH and the strengthening of the collaboration among DOE, DOT, and the Environmental Protection Agency (EPA) in representing the interests of the U.S. government and industry at the GRPE. The DOE is now a full participant at international forums at which discussion and negotiations on global technical regulations affecting hydrogen take place. Internationally accepted hydrogen standards can facilitate trade among nations and lower regulatory trade barriers. If hydrogen is to become a major energy carrier, the hydrogen interests of key countries must be coordinated, and countries new to hydrogen must be introduced to its benefits and safe use.

Conclusions

DOE has supported a growing and increasingly important effort to coordinate the development and promulgation of hydrogen codes and standards. In addition to supporting specific projects to develop codes, such as that of the ICC/AHC, and standards, such as that of ISO TC197, the DOE is supporting the coordination of many other efforts so that codes and standards can be developed and adopted as efficiently as possible and so that the lack of codes and standards will not be a barrier to the commercialization of hydrogen technologies. Support of codes and standards efforts will remain an important part of the Program for many years to come.

FY 2003 Publications/Presentations

1. Domestic Codes and Standards: DOE Status Report, Fuel Cell Summit VII, College Park, MD, May 2003.
2. Codes and Standards: The International Scene, Fuel Cell Summit VII, College Park, MD, May 2003.
3. Hydrogen Codes and Standards, Hydrogen, Fuel Cells and Infrastructure Technologies Program, 2003 Merit Review and Peer Evaluation Meeting, Berkeley, CA, May 2003.
4. Domestic Codes and Standards: DOE Status Report, International Hydrogen Infrastructure Working Group, The Woodlands, TX, May 2003.
5. Hydrogen Codes and Standards, National Hydrogen Association, Codes and Standards Workshop, Ft. Worth, TX, October, 2002.

Special Recognitions & Awards/Patents Issued

1. National Hydrogen Association Meritorious Service Award to Guy Tomberlin, Chair, ICC Hydrogen Ad Hoc Committee, March 6, 2003

Carbon Monoxide Sensors For Reformate Powered Fuel Cells

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Objectives

Hydrogen reformate gas powered fuel cell systems require sensors for carbon monoxide level monitoring and feedback control.

- Develop a low temperature sensor for measuring 10-100 ppm range concentrations for stack poisoning control.
- Develop a high temperature sensor for the measurement of 0.1 to 2% carbon monoxide in the reformate gas for fuel processor control.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors

Approach

Two electrochemical sensor types are being investigated for high and low temperature carbon monoxide sensing:

- An oxide solid electrolyte device based on the kinetics of the electrode reactions is being developed for both the high and low temperature applications.
  - Yttria-doped zirconia and gadolinia-doped ceria oxygen ion conductors and strontium yttrium zirconium oxide proton conductor are being investigated as the solid electrolyte.
  - Several metals, including Pt, Pd, Au, Ru and Ni, are being evaluated as the sensing and reference electrodes.
- A low temperature amperometric device based on the carbon monoxide inhibition of hydrogen oxidation kinetics at the electrodes of a polymer electrolyte membrane (PEM) fuel cell is being developed for the low temperature application.
  - Sensors based on perfluorosulfonic acid polymer electrolytes are being evaluated.
  - Different catalyst loadings of carbon supported and un-supported Pt, Ru and Pt/Ru alloys are being evaluated as electrodes.

Accomplishments

- Ceramic electrolyte based sensors that operate at 150-300°C have been developed. These sensors respond well to 10-100 ppm carbon monoxide in a simulated reformate stream.

- Amperometric low temperature carbon monoxide sensors based on a polymer electrolyte have been developed and tested under a variety of conditions. These devices respond well at ambient temperature to 10-100 ppm carbon monoxide in hydrogen streams.
- Polymer electrolyte based sensors have been optimized to operate at 70^{o}C and respond to 100-1000 ppm of CO in a simulated reformate stream.

Future Directions

- Analyze the response time of the oxide and polymer electrolyte based sensors.
- Evaluate the performance of the polymer and oxide electrolyte based systems under practical fuel reformate conditions.
- Evaluate the stability of the response of the oxide electrolyte based sensors.
- Modify the electrodes of the oxide electrolyte based sensor to enable it to detect higher concentrations of CO (0.1-2%) at $T > 250^{o}$C.
- Demonstrate a prototype oxide based sensor with a patterned heater incorporated on the sensor electrolyte body.

Introduction

The detection and measurement of carbon monoxide in high temperature reformate streams is of vital importance to the successful implementation of fuel cells for transportation. Much research is being performed to optimize low cost fuel reformer systems that convert liquid hydrocarbon fuels to hydrogen gas containing fuel streams. This hydrogen gas typically feeds a polymer electrolyte membrane (PEM) fuel cell utilizing a platinum based anode. It is well known that low concentrations (10-100 ppm) of carbon monoxide impurities in hydrogen can severely degrade the performance of PEM fuel cell anodes.[1] This performance degradation is due to strong adsorption of carbon monoxide on the electro-active platinum surface sites where hydrogen is normally oxidized to protons.[1]

Therefore, the proper design of combined fuel cell stack and reformer systems must pay careful attention to the minimization of carbon monoxide before the processed fuel stream enters the stack. Many reformer systems use a secondary preferential oxidation (PrOx) reactor that selectively oxidizes the carbon monoxide present in the reformate stream. The efficiency of this PrOx reactor will depend on the accurate and rapid measurement of the inlet (or outlet) CO concentration at the reactor. Moreover, current fuel cells use air-bleeding methods to reduce the carbon monoxide poisoning of the Pt anode. Since this method involves the mixing of 2-6% air with the fuel stream, it results in a decrease in the energy efficiency of the fuel cell system and can greatly benefit from the accurate determination of the CO content of the fuel stream entering the stack. Hence, CO sensors that measure the CO content of the fuel stream before and after the PrOx reactor can be used for feedback control, thus allowing these integrated fuel cell systems to operate at maximum energy efficiency. We are designing and developing solid-state electrochemical sensors meeting these criteria, leading to the demonstration of prototype sensors.

Approach

High temperature carbon monoxide sensors. Los Alamos National Laboratory (LANL) is developing high temperature zirconia- and ceria-based electrochemical sensors to measure CO in hydrogen streams. These sensors would operate at 150-400^{o}C and can be used for feedback control either before or after the PrOx reactor. We have successfully developed novel mixed-potential sensors that are capable of measuring ppm levels of CO in air. The unique design of these sensors makes them robust, stable and reproducible.[2,3] In this project, we are working on modifying the electrodes of these devices to enable them to work in a hydrogen atmosphere.

We are also exploring the possibility of using proton-conducting electrolytes and using these sensors in an amperometric mode.

Low temperature carbon monoxide sensors. Low temperature carbon monoxide sensors based on the reversible carbon monoxide adsorptive poisoning of precious metal electrodes are also being developed at LANL. The addition of metals such as ruthenium to the platinum anode catalyst is known to greatly improve the hydrogen-oxidation kinetics in the presence of CO. An amperometric sensor that senses the differential CO inhibition of the hydrogen oxidation reaction at 2 electrodes can be fabricated from a platinum electrode, a proton conductor and a platinum ruthenium alloy electrode. While the current density of the platinum electrode will be influenced by the surface coverage of carbon monoxide, the current density at the Pt/Ru alloy electrode should be relatively unaffected. This difference in the electrode current density in the presence of CO can be used to fabricate a low temperature CO sensor. In this project, we are optimizing the electrode composition, precious metal loading and operating temperature of these ampereometric sensors in order to develop a CO sensor that will sense 1-100 ppm CO in the inlet fuel stream of a fuel cell stack.

Results

Oxide electrolyte based sensors were prepared by sputtering or brush-painting various metal electrodes on to oxygen-ion conducting electrolytes. The sensor configuration is shown in Figure 1, where the electrolyte used was either $Zr_{0.85}Y_{0.15}O_{1.95}$ (YSZ) or $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO), and the electrodes used were selected from Pt, Ru, Pd, Au or Ni. The substrate was 0.5 mm thick, and the electrodes were 0.5-100 μm thick. When a CGO electrolyte with 1 μm thick Pt and Ni sputtered electrodes was exposed to CO, an electromagnetic field (EMF) that was proportional to the CO concentration developed across the Pt and Ni electrodes. The response of this sensor to 100-500 ppm CO in a base gas of $68\%H_2/29\%CO_2/3\%H_2O$ at an operating temperature of 250°C is shown in Figure 2 (circles). The Pt electrode was positive with respect to the Ni electrode, indicating that CO poisoning lowers the EMF (less negative) of the Pt electrode. However, the response to CO decayed over time, probably due to some irreversible poisoning of the Ni electrode. When the sensor was operated at a negative bias of 1 μamp, the stability of the sensor was found to improve. This improvement in the stability of the sensor, shown in Figure 2 (squares), can be

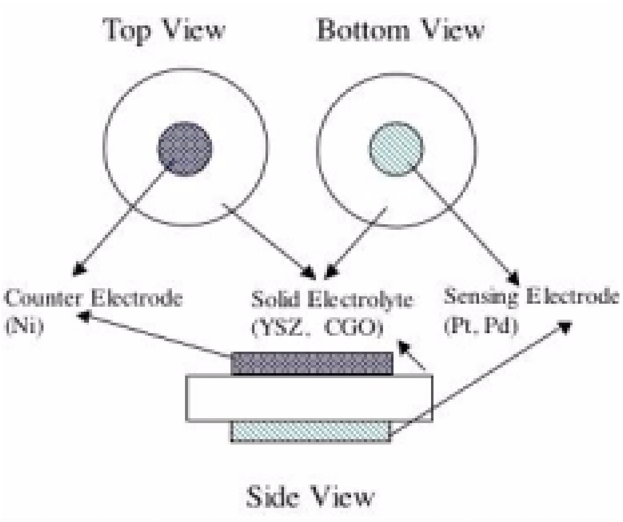

Figure 1. Schematic of Sensor Configuration

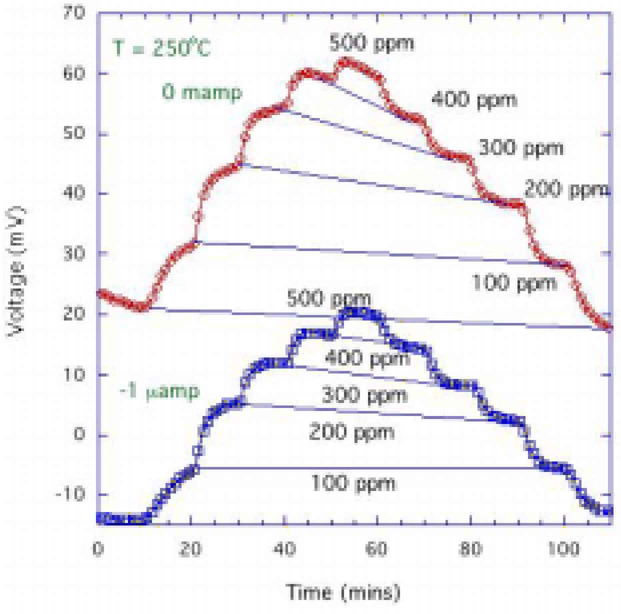

Figure 2. Response of a Pt/CGO/Ni sensor to 100-500 ppm CO in a Base Gas of $68\%H_2/29\%CO_2/3\%H_2O$ at an Operating Temperature of 250°C [Bias = 0 µamp (circles); Bias = –1 µamp (squares).]

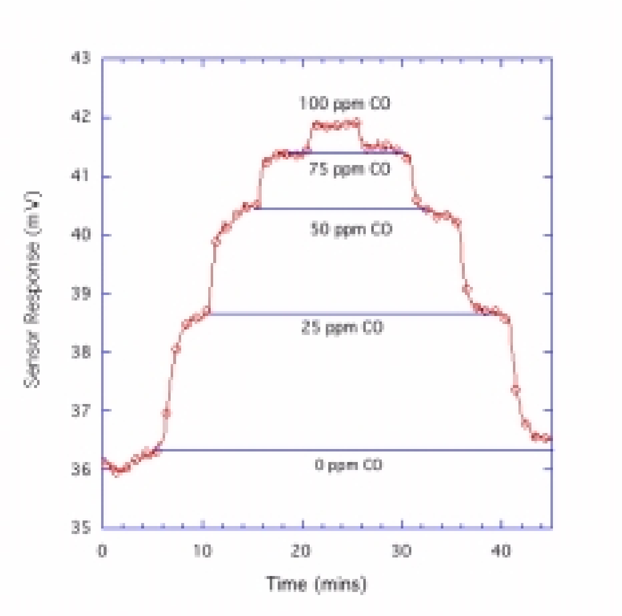

Figure 3. Response of a Pt/CGO/Ni Sensor to 25-100 ppm CO in a Base Gas of 68%H_2/29%CO_2/3%H_2O at an Operating Temperature of 240°C

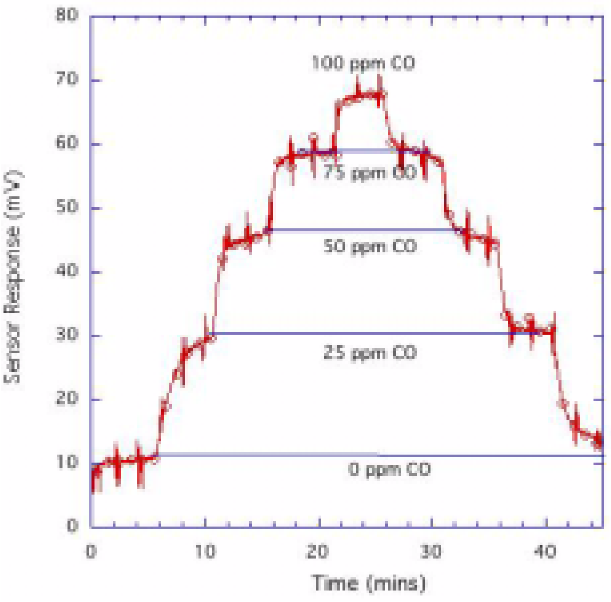

Figure 4. Response of a Pd/YSZ/Ni Sensor to 25-100 ppm CO in a Base Gas of 68%H_2/29%CO_2/3%H_2O at an Operating Temperature of 185°C

attributed to the cleaning of the CO from the surface of the Ni electrode.

The stability of the CGO-electrolyte based sensors was found to improve with a decrease in the operating temperature and the total exposure to CO of the sensor electrodes. This is demonstrated by the sensor response to 25-100 ppm CO at 240°C (Figure 3). A stable sensor response of 6 mV was obtained for 100 ppm of CO in a 68%H_2/29%CO_2/3%H_2O fuel stream. Moreover, this response was found to be largely independent of the H_2 and H_2O content of the fuel stream. However, this sensor did show some decay in the response when exposed to 100 ppm CO for greater than 1 hour.

The sensor response to CO was optimized by studying various electrode and electrolyte combinations, and maximum response was obtained for a sensor using a YSZ electrolyte with a sputtered Ni electrode and a brush-painted Pd electrode. This sensor had a response of 60 mV to 100 ppm CO in a base gas of 68%H_2/29%CO_2/3%H_2O at an operating temperature of 185°C, as shown in Figure 4. Although this is a 10 fold improvement in the sensor sensitivity as compared to the CGO based sensors, these sensors showed a similar decay in the sensor response when exposed to low concentrations of CO for long periods of time or high concentrations of CO for short periods. The response time of this sensor was less than 1 minute and was limited by the flow rates of the gases used in our experiment. This sensor also possessed the required sensitivity to detect 1-100 ppm of CO in the fuel inlet stream of the fuel cell stack and has the potential to be used to as a CO sensor for stack control.

Conclusions

- Developed polymer electrolyte based sensors for the monitoring of 10-100 ppm carbon monoxide at room temperature and 100-1000 ppm carbon monoxide at 70°C.
- Successfully developed oxide electrolyte based sensors for the detection of 10-100 ppm CO in the fuel inlet of a fuel cell stack. These sensors operate and $T \geq 150$°C and have a response time less than 1 minute.
- Future work includes the optimization of the sensor response time and stability. The electrodes of this oxide sensor will be modified

to try and develop a CO sensor for reformer control that can measure 0.1 to 2% CO. A patterned heater will be incorporated in these sensors, and prototypes that work in a reformate stream will be demonstrated.

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2. R. Mukundan, E. L. Brosha, and F. H. Garzon, "A low temperature sensor for the detection of carbon monoxide in hydrogen". Presented at the SSI-14 Conference, California, June 24 (2003).

3. R. Mukundan, E. L. Brosha, and F. H. Garzon, "A low temperature sensor for the detection of carbon monoxide in hydrogen". Submitted to the special issue of the Journal of Solid State Ionics, May (2003).

Electrochemical Sensors for Proton Exchange Membrane Fuel Cell Vehicles

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Objectives

- Develop a hydrogen safety sensor operating below 500°C with 1 second response time and low sensitivity to humidity and hydrocarbons
- Develop a hydrogen fuel sensor for reformate fuel monitoring for hydrogen concentrations ranging between 10 to 100%
- Develop a CO sensor for reformate fuel monitoring (future)

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors

Approach

Safety sensor

- Utilize proven solid state electrochemical technology comparable to automotive exhaust gas oxygen sensors based on oxygen conducting ceramic electrolytes
- Apply novel nanocrystalline electrode materials with high electronic conductivity to reduce response time and operating temperature
- Design and build micro-sensor configuration to minimize heater power requirements

Fuel sensor

- Develop and characterize an amperometric sensor using a known proton conducting oxide electrolyte
- Correlate 'pumping' current with hydrogen concentration in simulated reformate gas
- Reduce operating temperature by applying novel electrode/electrolyte materials to enhance conductivity and surface exchange
- Ensure electrolyte stability in reformate environment by performing appropriate thermal characterization and electrochemical testing

Accomplishments

Safety sensor

- Operating temperature has been reduced to 430 - 460^{o}C
- An integrated, planar heater/sensor design has been established (heated substrates supplied by Ford)

- Preliminary testing indicates no baseline drifting over several hundred hours
- External collaborators interested in testing/commercialization are being explored (Ford is currently testing)

Fuel sensor

- A candidate electrolyte with high stability versus CO_2 has been selected
- Preliminary laboratory prototypes have been fabricated and are being tested

Future Directions

Safety sensor

- Finalize sensor design
- Locate external collaborator interested in testing/commercialization (Ford has agreed to test sensor)

Fuel Sensor

- Evaluate various materials, processing techniques, and designs
- Fabricate first prototype
- Seek industrial collaboration
- Develop integrated fuel sensor

Introduction

Proton exchange membrane fuel cells (PEMFCs) are among the most promising clean power system technologies being developed for transportation applications. However, the use of hydrogen and other combustible gases for automotive applications requires new on-board safety sensors and controls to prevent fire and explosion hazards. In addition, if hydrogen fuel is supplied by an on-board reformer, additional control and monitoring devices are needed in order to protect and to efficiently operate the PEMFCs.

The purpose of this project is to design, fabricate, and demonstrate solid state electrochemical sensors for various H_2 monitoring applications on PEMFC vehicles. The first phase of the project has focused on the development of a hydrogen safety sensor intended to be deployed at critical locations on the vehicle to detect potentially dangerous hydrogen leakage. Currently, that portion of the project is being completed, and development of a hydrogen fuel sensor is being initiated. The fuel sensor is intended to monitor the fuel quality (i.e. percent hydrogen) in the gas stream supplied from an on-board hydrogen reformer (reformate gas). Reformate gas is typically a severe environment containing a variable mixture of H_2, H_2O, N_2, CO, CO_2, and residual hydrocarbons. Both of these sensors are being developed by applying novel materials to established electrochemical sensor technologies.

Approach

Our approach to the hydrogen safety sensor is based on established solid-state electrochemical sensor technology. The proposed sensor consists of two electrodes on an oxygen conducting electrolyte. One electrode serves as a reference and the other as a sensing electrode. The electrode materials are selected so that they have different catalytic activities toward the oxidation of hydrogen gas. This causes the electrodes to reach some kinetically limited potential determined by the concentration of hydrogen in a hydrogen/air mixture. The sensor operates by measuring the difference between these electrode potentials, and the hydrogen concentration can be correlated with the magnitude of this potential difference. Similar sensors have been proposed in the past [1]; however, sensitivity and response speed were insufficient for the proposed safety sensor application. We have proposed that by using a higher conductivity electrode material, response time can be reduced to the point where the sensor becomes suitable for the safety application. For that reason, the current safety sensor uses a metal oxide (indium oxide) doped to promote electronic conductivity. The resultant fast response, along with the sensitivity of the sensor, will be shown below.

The hydrogen fuel sensor operates on a very different principle whereby the hydrogen is electrochemically dissociated and pumped through a proton conducting ceramic membrane at high temperature. The pumping current (at constant applied voltage) can be correlated to the hydrogen concentration in the test gas. The approach to realizing this sensor will proceed in two parts. The first will be to demonstrate the sensing technology using a known proton conductor with established stability in the reformate environment. However, since these materials tend to be comparatively poor proton conductors, the operating temperature will be required to be fairly high (~600°C). The second part of the developmental effort will be to explore novel proton conductors to identify the best candidate providing the optimum combination of conductivity and stability for the proposed application. Once identified, this ‘optimum’ electrolyte will be implemented in the sensor technique demonstrated in the first part of the project. Progress towards these goals will be discussed below.

Accomplishments

Safety sensor. During the prior efforts, a safety sensor was demonstrated which had good sensitivity and response time, but relatively high operating temperature (500°C). That sensor consisted of electrodes on an unheated substrate, and testing required that the sensor be heated using a laboratory tube furnace. During FY 2003, the principal goals were to modify the sensor to reduce the operating temperature below 500°C, and to demonstrate an integrated, self-heated design. Figure 1 shows that integrated design, where the yttria-stabilized zirconia (YSZ) electrolyte is attached to the surface of an alumina substrate containing an integrated Pt resistive heater [2]. The one-inch scale bar in the figure shows the sensor size. Also shown in the figure are the electrode size and location. It is worth noting that the electrodes are misaligned from the heating element, causing the power consumption (~5.4 W at 440°C) of this sensor to be ~20% elevated for a given temperature. This misalignment is being corrected in the next generation design.

Figure 2 shows the sensor response, at 440°C, to 3300 ppm (0.33%) H_2 in air containing 10% and 100% relative humidity. The data show the sensor baseline near 0 mV in the absence of H_2, and a reproducible response of ~225 or 250 mV (10 and

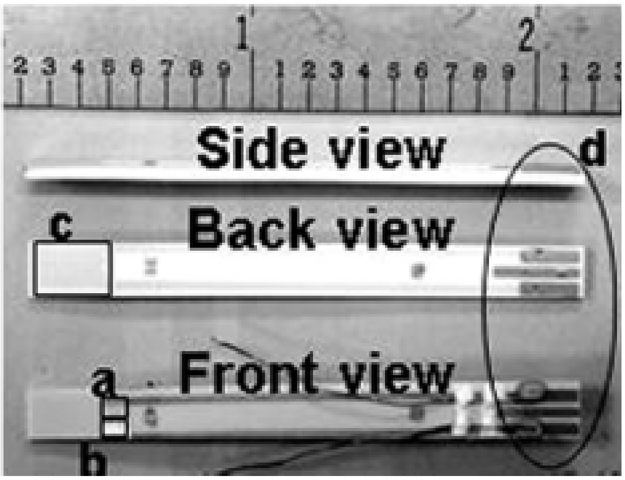

Figure 1. H_2 Safety Sensor Prototype Showing a) Sensing Electrode, b) Reference Electrodes, c) Resistive Heater, and d) Electrical Connections; the Scale Bar at the Top Is in Inches

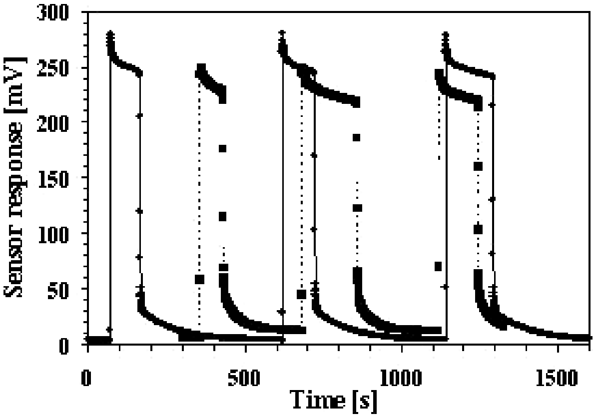

Figure 2. Response of the Hydrogen Safety Sensor, Operated at 440°C, to 3300 ppm H_2 in Air Containing 10% (squares) and 100% (crosses) Relative Humidity

100% relative humidity, respectively). It is clear that the sensor responds within approximately one second (which is the DOE technical target) to the addition of the H_2. The slight overshoot is a consequence of the low operating temperature, and it may be possible to reduce this effect by modifying the reference electrode to reduce the interfering response there. Long term testing indicates that the sensor baseline is stable and that the sensor response is reproducible over a period of several hundred hours.

Figure 3 shows the response of the sensor, again at 440°C and in 10% and 100% relative humidity, to varying H_2 and CH_4 concentrations in air. The data show a slight (~10%) reduction in sensitivity in the presence of high relative humidity. This slight cross-sensitivity is considered to be acceptable since discussions with commercial end-users indicate generally severe degradation in performance with humidity for the commercially available sensors. The data also show that the sensor has a very high sensitivity at low H_2 concentration. This sensitivity is an attractive feature for early leak detection. Finally, the selectivity versus CH_4 is shown to be approximately five to one.

Fuel sensor. Development of the H_2 fuel sensor has been initiated, and a preliminary prototype sensor has been fabricated from a Sr-zirconate electrolyte with known stability in H_2O and CO_2 gas. Figure 4 shows the pumping current (i.e. the response) of that sensor operated at 600°C as a function of H_2 concentration. The test gas was composed of the indicated concentration of H_2 with 20% H_2O and a balance of N_2. These data clearly demonstrate that the device is sensitive to the concentration of H_2 in the test gas. Further testing is underway to evaluate the cross-sensitivity to CO_2 and H_2O. By incorporation of a diffusion-limiting porous barrier over one of the electrodes, it should be feasible to force the response of the sensor to be linear versus the H_2 concentration.

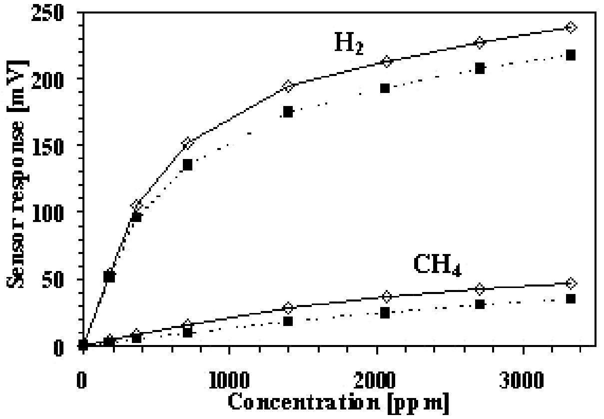

Figure 3. Response of the Sensor, Operated at 440°C, to H_2 and CH_4 in Air Containing 10% Relative Humidity (diamonds) and 100% Relative Humidity (squares)

Conclusions and Future Work

A H_2 safety sensor has been demonstrated with an integrated, self-heated design operating at 430 - 460°C. Preliminary testing indicates no baseline drifting over several hundred hours. External collaborators interested in testing/commercialization are being explored. A candidate electrolyte has been identified for the H_2 fuel sensor with high stability versus CO_2. Preliminary laboratory prototypes have been fabricated and are being tested. Ongoing developmental efforts for the fuel sensor include evaluation of various materials, processing techniques, and designs. In addition, an industrial collaboration will be sought to facilitate the eventual commercialization of an integrated fuel sensor.

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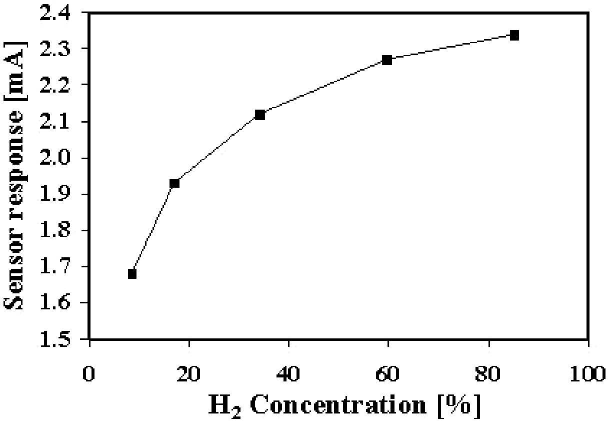

Figure 4. Fuel Sensor Response versus H_2 Concentration at 600°C, 20% H_2O, Balance N_2; Applied Bias Is 250 mV

zirconia and a metal oxide electrode," Sensors and Act., B35-36, (1996) 130-135.

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1. L. P. Martin and R. S. Glass, "Electrochemical Sensors for PEMFC Vehicles," presented at the DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review, (Berkeley, CA, May 19-22, 2003).
2. L. P. Martin, Q. Pham, and R. S. Glass, "Electrochemical Hydrogen Sensor for Safety Monitoring," poster presented at The 14th International Meeting on Solid State Ionics, (Monterey, CA, June 22-27, 2003).
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Interfacial Stability of Thin Film Sensors

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Objectives

The goal of this project is to develop safe, low cost, lightweight, reliable hydrogen safety sensors that can be used wherever hydrogen is used, stored, or transported. Safety sensors need to satisfy the following requirements established by DOE:

- Measurement range: 0.1–10% H_2 in air
- Operating temperature: -30°C – +80°C
- Response time: <1 s
- Accuracy: 5%
- Gas environment: ambient air, 10–98% relative humidity (RH) range
- Lifetime: 5 years
- Selectivity from interference gases, such as hydrocarbons, is needed.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Hydrogen Safety

- A. Limited Historical Database for Components
- C. Validation of Historical Data
- D. Technical and Scientific Understanding of Systems Limits the Value of Protocols
- F. Liability Issues
- L. Expense of Data Collection and Maintenance
- M. Quality of Data

Hydrogen Delivery

- D. High Capital Cost of Pipelines

Fuel Cells

- B. Sensors

Technology Validation

- C. Hydrogen Refueling Infrastructure

Hydrogen Production

- E. Control and Safety

Approach

- Investigate the stability of thin films that undergo optical changes in the presence of hydrogen.
- Construct test articles of thin films and subject them to environmental stresses.
- Measure response of hydrogen sensing to environmental stresses and aging.
- Develop improved protective strategies.

Accomplishments

- Designed optical sensor configurations that meet most DOE criteria for safety sensors.
- Demonstrated sensor lifetimes in excess of 1 year.
- Measured response of test articles to thermal stresses (-20°C to +80°C) and relative humidity (0% to 100%).
- Analyzed subtle compositional differences in protective coatings that result in dramatic changes in performance.
- Supported NREL's photobiological hydrogen production project by constructing large area sensor plates for semi-quantitative evaluation of hydrogen-producing algae.

Future Directions

- Investigate the fundamental behavior of the protective coatings in order to optimize performance.
- Analyze the response of optical sensors coated with protective polymeric chemical vapor deposition (CVD) films when exposed to low temperature and high humidity environments.
- Design a control package for probing the status of the thin film optical sensors.
- Fabricate prototypes for testing.

Introduction

Public perception of the hazards of hydrogen fuel use, its production, and storage, as well as governmental regulation will require extensive safety precautions and codes to be in place before hydrogen can be incorporated into the energy infrastructure in a meaningful way. Currently, commercial hydrogen detectors are not useful for widespread use, particularly in transportation, because they are too bulky, expensive, and dangerous. Work sponsored by DOE has developed promising technologies for satisfying the future demands. Specific performance targets for safety sensors have been proposed:

- Measurement range: 0.1%–10% H_2 in air
- Operating temperature: -30°C – +80°C
- Response time: <1 s
- Accuracy: 5%
- Gas environment: ambient air, 10%–98% RH range
- Lifetime: 5 years
- Selectivity from interference gases, such as hydrocarbons, is needed.

Sensors that exhibit physical changes when exposed to hydrogen have been fabricated and tested, and they have the potential to provide inexpensive hydrogen detection. For example, there are thick film and thin film metallic sensors that exhibit conductivity changes when hydrogen adsorbs on the surface and is incorporated into the lattice. There are thin film sensors that are deposited as a part of a field-effect transistor, where accumulation of atomic hydrogen at the metal/insulator interface results in a change of response from the circuit. Finally, there are chemochromic sensors, where reaction of thin films with hydrogen gas results in an optical change that can be sensed by a probe beam of light. All four of these configurations have the potential for degradation in their performance over time due either to mechanisms that are inherent in their construction, effects of their cyclic interaction with hydrogen, or contamination from impurities in the environments in which they will be used. Prior research to study these issues has ranked their importance to the various sensor concepts and has suggested the relevant mechanisms. This work has led, in turn, to methods of mitigating these factors. The research reported here addresses these issues and is directed toward substantially extending the lifetime and utility of these sensors, especially in the configuration that is based upon the optical response of the sensor materials. This concept appears to offer the greatest safety by design, and it would appear to meet cost goals.

Approach

All of the thin film safety sensor designs currently use a Pt group metal (usually Pd or an alloy) as the hydrogen dissociation catalyst. Atomic hydrogen is the species that causes a physical change in the sensing material, thereby providing a means to detect the presence of hydrogen. In the case of multiple layers of thin films forming the detection ensemble, the interfaces between layers, including the surface of the dissociation catalyst, control the response of the sensor. Changes in the interfaces most often result in degradation in the performance of the device. Consequently, our research and development activities deal mainly with the stability of the interfaces and the approach to the performance goals listed in the objectives.

Work this year concentrated upon understanding the performance of a protective coating, which in prior years had shown extraordinary promise to prolong the life of the Pd catalyst. The approach was to study the influence that various parameters (e.g., precursor purity, the details of the synthesis, and deposition techniques) played in the performance of the film. The objective was to optimize the performance of the coating and extend the lifetime of the sensors past the one-year mark that had been accomplished in FY 2002.

A secondary effort was to characterize the performance of the sensors over an expanded range of temperatures and relative humidities. Specifically, the temperature range for characterization was extended to -30°C to +80°C, and the relative humidity range was extended to 0% to 100%. The sensors were tested in the full target range of the DOE goals for safety sensors.

Results

The results of the studies on the synthesis and preparation of the protective coating for the sensor films were mixed. Replication of early results proved elusive, although it was shown that the performances of the protective coatings are sensitive to almost every aspect of the preparation. A great deal of analytical work has suggested why the results of this study were mixed and has pointed to the fact that additional fundamental work is needed to fully understand the functioning of these films and their sensitivity to the details of their preparation.

The performance of typical tungsten oxide sensor elements at various temperatures is illustrated in Figures 1 and 2. The data indicate that the tungsten oxide sensors operate reasonably well in a temperature range from 0°C to +80°C. However, excursions to the upper temperature apparently result in irreversible changes in the WO_3 film that affect performance (Figure 1, 19°C after heating). This irreversible change does not constitute a fatal flaw in the design of these sensors, since the performance is

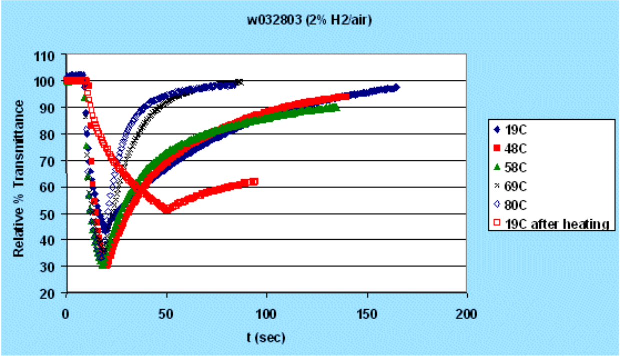

Figure 1. Optical Sensor Response to 2% Hydrogen in Synthetic Air at Temperatures from 19°C to 80°C

likely adequate (rather than optimum) after the material changes. At temperatures below 0°C, the performance of the sensors degrades rapidly (Figure 2). We think that it is likely that the formation of ice on the catalyst surface progressively covers the hydrogen dissociation sites. This inhibits both the response to hydrogen and recovery after exposure. At temperatures below –10°C, the response of the sensor may be degraded to the point where response is deemed unacceptable. There are two approaches to mitigate the problem of condensation and ice formation at these temperatures. One is to use a physical barrier to inhibit the diffusion of water through the coating, while allowing hydrogen to diffuse at a relatively high rate. The other is to periodically pulse the light source to such an intensity as to evaporate a substantial amount of the ice that fouls the Pd surface. Studies of these methods had to be deferred to another year.

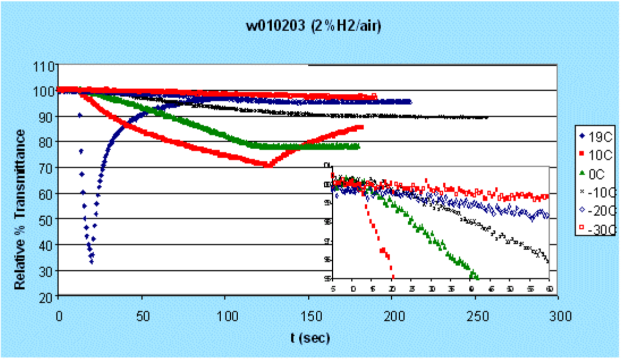

Figure 2. Optical Sensor Response to 2% Hydrogen in Synthetic Air at Temperatures Ranging from –30°C to 19°C

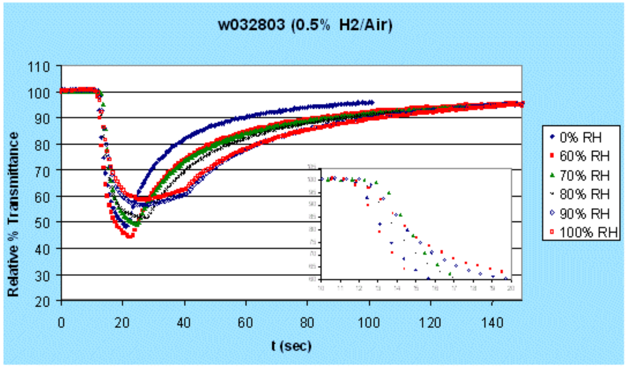

Figure 3. Response of a WO_3 Sensor to 0.5% Hydrogen in Air at Room Temperature and Various Relative Humidities

The response of a typical WO_3 based sensor to 0.5% hydrogen in air is shown in Figure 3. Increasing relative humidity slows the response of the sensors, which is observed by the change in slope of the curves in the inset. The inset is a magnification of the “knee” region of the curve showing more detail of the sensor response upon admission of hydrogen into the gas stream. Another observation is that increasing relative humidity decreases the depth of coloration at saturation. However, neither of these effects represents a fatal flaw in the operation of the devices as safety sensors. We believe that we can improve the performance of these sensors in high humidity by the application of polymeric thin films with surface properties designed to minimize the interaction with water vapor. Preliminary experiments with such films give a good indication that they will inhibit the ingress of water to the catalyst surface.

Conclusions

The performance of optical thin film sensors are represented in tabular form as follows:

- Measurement range: 0.02% – 10% H_2 in air
- Operating temperature: -20°C – +80°C
- Response time: <1 s
- Accuracy: needs to be determined
- Gas environment: ambient air, 0% – 100% RH range
- Lifetime: 1 year
- Interference resistant (e.g., all other gases)

Significant progress was made this year in understanding the sensitivity of our best protective coating to variations in the synthesis techniques. Furthermore, measurements of the response of the sensor under extremes of temperature and relative humidity have produced encouraging results. It appears that the major remaining criteria to meet, and the focus of future work in the area, is the durability of the sensor elements in realistic atmospheres.

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2. E. Ozkan, P. Liu, S.-H. Lee, C. E. Tracy, J. R. Pitts, and S. K. Deb, "Preparing Mesoporous Tungsten Oxide Thin Films Using Non-Ionic Surfactants as the Templates by Sol-Gel Deposition Process," Solid State Ionics (submitted).
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5. P. Liu, S.-H. Lee, C. E. Tracy, J. A. Turner, J. R. Pitts, and S. K. Deb, "Electrochromic and Chemochromic Performance of Mesoporous Thin-Film Vanadium Oxide," Solid State Ionics (submitted).
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Development of Sensors for Automotive Fuel Cell Systems

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Objectives

Develop technology and a commercial supplier base capable of supplying physical and chemical sensors required to optimize the operation of proton exchange membrane (PEM) fuel cell power plants in automotive applications.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors
- E. Durability

Approach

The team assembled for this project will perform the following tasks:

1. Obtain representative samples of physical parameter sensors currently available to meet the targets specified in the fuel cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program (HFCIT) Multi-Year R,D&D Plan (MYP).
2. Design and construct a facility for testing physical and chemical sensors under simulated reformer exit conditions.
3. Determine the suitability of state-of-the-art physical parameter sensors for the extreme environment of a PEM fuel cell power plant by testing them in a combination of laboratory and simulated fuel cell flow stream environments.
4. Assist the sensor manufacturers, where necessary, to modify their sensors to achieve the requisite performance and durability goals.
5. Modify baseline chemical sensing technologies to create sensors capable of measuring the gas concentrations listed in the HFCIT Multi-Year R,D&D Plan while operating in a PEM fuel cell environment.
6. Validate and document the performance and durability of the developed sensors by exposing them to a combination of laboratory and simulated fuel cell flow stream environments.
7. Install the developed sensors on a PEM fuel cell at UTC Fuel Cells (UTCFC) for final testing.

Accomplishments

- Designed and constructed physical and chemical sensor test facility for simulated reformer test gas stream.
- Developed software for continuous monitoring and operation of the test facility.
- Developed α-prototype H_2 safety sensor and began testing.
- Completed physical sensor survey and have obtained candidate sensors for evaluation.

Future Directions

- Evaluate physical sensors in United Technologies Research Center (UTRC) facility followed by tests at UTCFC on the S300 gasoline-fired reformer breadboard facility.
- Obtain electrochemical and micro electromechanical system (MEMS) chemical sensors and evaluate in UTRC and Illinois Institute of Technology (IIT) test facilities.
- Optimize sensor performance and reliability.
- Deliver sensor suite for testing at UTCFC gasoline-fueled reformer PEM cell facility.

Introduction

The present state-of-the-art in fuel cell power plant sensor technology is embodied in the UTC FC PAFC PC 25 and PEM S200 power plants. Sensors measuring all of the parameters defined in the HFCIT Multi-Year R,D&D Plan are utilized in designing and setting up these power plants. However, none of the chemical sensors and only a very few of the physical sensors are "on-board" the power plant, and only temperature and stack differential pressure, in the S200, are measured continuously for control purposes. Production automotive fuel cell power plants require all of these sensors to be on-board the power plant, and to provide data signals on a continuous basis to optimize fuel cell operation and protect the cell stack from damage.

Approach

UTCFC is, or will be, evaluating the sensors described above in the appropriate test facilities by supplying a synthesized gas stream of known inlet gas composition and determining the response accuracy of each sensor at the required operating temperature. By controlling the inlet gas composition and mass flow, a fixed reference will be established to which the sensor response will be compared as a function of time. This effort is being conducted in UTRC, IIT and UTCFC facilities. Baseline sensor technology taken from a combination of production PC25, S200 and fuel cell development laboratory applications is being subjected to a series of performance, durability and cost reduction studies. Concurrent with this portion of the task, a detailed review of alternate sensors is being conducted. New advanced solid state electrochemical and MEMS sensors are being developed at NexTech, Inc. and Advanced Technical Materials Incorporated (ATMI), which include new transduction principle development, new sensing materials and fabrication development, and sensor prototyping. Appropriate sensors will be ranked according to the probability of successful test outcome. Initial qualification tests will be conducted by IIT in the PEM Fuel Cell Benchmark Facility. These tests will consist of installation and exposure of baseline sensors to precisely controlled temperature, humidity, pressure, and gas mixture conditions. Sensor response versus these parameters will be logged.

Second level testing will be conducted at UTRC. During these tests, the sensors will be installed in a chamber through which gases simulating an autothermal reformer (ATR) exhaust stream (created by mixing gases, heating and humidifying as necessary, to obtain the desired composition) will flow. The sensors will be evaluated for accuracy, speed of response, cross sensitivity to non-target parameters and test gas parameters. The tests will operate continuously, during which time a computer utilizing National Instruments LabView software will control and log all test parameters, including gas composition, sensor output, and control safety systems.

It is assumed that repetition of the above testing cycle will be required due to non-performance of some sensors. If baseline sensors cannot demonstrate performance meeting the targets in the HFCIT Multi-Year R,D&D Plan, alternates will be selected.

Results

A team has been assembled to address the development and evaluation of physical and chemical sensors meeting the requirements listed above. Table 1 shows the breakdown of responsibilities for each of the team members.

UTRC has constructed a physical and chemical sensor test facility capable of subjecting candidate sensors to gas compositions simulating operation in a gasoline/natural gas-fueled reformer-based fuel cell system. IIT will be evaluating all sensors developed during execution of this project in their PEM fuel cell test facility. The facility design is shown in Figure 1; Figure 2 is a photograph of the flow controllers, steam generator, and condenser.

UTRC has begun evaluation tests on a hydrogen sensor manufactured by H2Scan, Inc. in both dry and moisturized gas streams consisting of H_2 and N_2, with CO_2 and trace concentrations of methane added. Results of these tests are shown in Figures 3a and 3b.

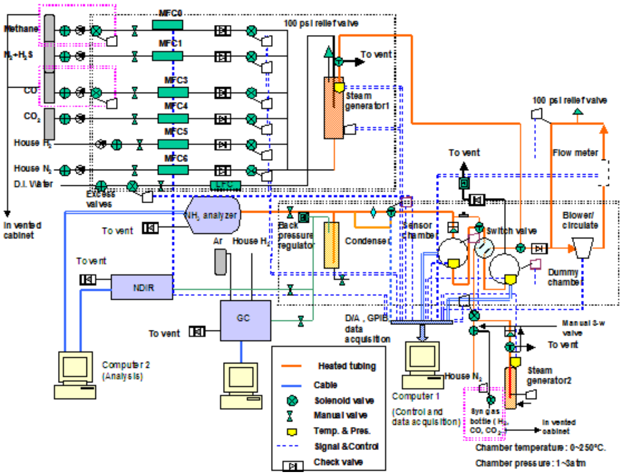

Figure 1. UTRC PEM Fuel Cell Gas Stream Simulator and Sensor Testing Rig

Conclusions

The tests show the H_2 sensor has a linear response to the concentration of H_2 present in the gas stream. The sensor indicates no cross-sensitivity to methane under the conditions investigated. The sensor shows excellent repeatability among the tests conducted so far. The sensor response time (t_{90}) in dry gas environment is about 30 seconds and the response time is extended to 100 to 140 seconds in a moisturized gas stream. The sluggish response as a result of operation in a humid environment may impact the cost-effectiveness of deploying the sensor in PEM fuel cells. This aspect of the overall sensor performance needs to be improved significantly.

Table 1. Sensor Development Team Responsibilities

Team Member	T	ΔP	RH	flow	O_2	CO	H_2	SO_2	H_2S	NH_3	Technological Expertise / Responsibility
UTC FC	X	X	X	X	X	X	X	X	X	X	Testing on S300 Breadboard
UTRC	X	X	X	X	X	X	X	X	X	X	Testing in reformate simulator
ATMI							X	X	X	X	Develop Using MEMS Silicon Microhotplate
IIT	X		X		X	X	X	X	X	X	Testing in Benchmark Facility
NexTech						X		X	X	X	Develop Using Solid State Electrochemical

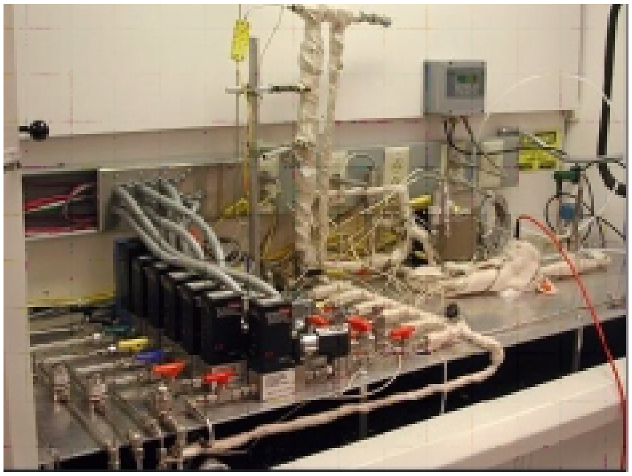

Figure 2. UTRC PEM Fuel Cell Gas Stream Simulator: Gas Flow Control System, Steam Generator, and Test Chamber

The candidate sensor selected for hydrogen detection has demonstrated excellent sensitivity and selectivity for H_2. The durability of the sensor is being tested in the simulated reformate stream.

Results of the physical sensor survey are summarized in Table 2.

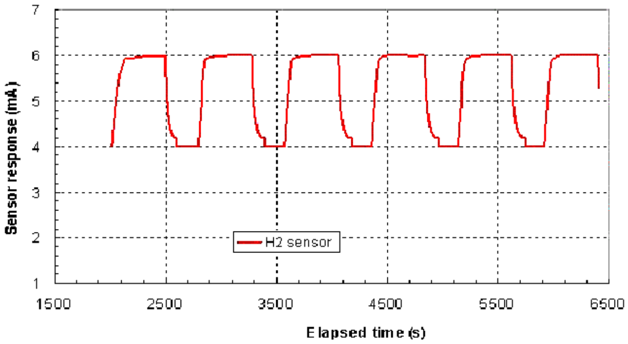

Figure 3a. Response of H_2 Sensor to Hydrogen in Dry Gas Stream

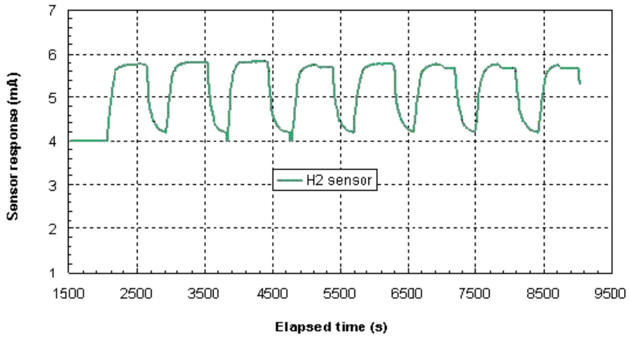

Figure 3b. Response of H_2 Sensor to Hydrogen in Simulated Reformate Gas Stream

Table 2. Results of Physical Sensor Survey

Sensor	***Meet DOE/FC tech. specs***	***Further effort***	***Technical gap/stretch***
Humidity	*Yes/Yes*	*Validate new technologies (MEMS sensor) to improve the recovery time*	*Medium*
Flow rate	*Yes/No*	*Collaborate with vendors to improve stability*	*High*
Differential pressure	*Yes/Yes*	*Collaborate with vendors for size and cost reduction*	*Medium*
Temperature	*Yes/Yes*	*Identify inexpensive thermistors for high temperature*	*Low*

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1. DOE Workshop: "Sensor Needs and Requirements for Fuel Cells and CIDI/SIDI Engines," Robert S. Glass, Ed., published by Lawrence Livermore National Laboratory, April, 2000

2. Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, June 3, 2003

3. "Solicitation for Financial Assistance Applications No. DE-RP04-01AL67057 Research and Development and Analysis for Energy Efficient Technologies in Transportation and Buildings Applications"; DOE Albuquerque Operations Office, November 21, 2000

FY 2003 Publications/Presentations

1. DOE Sensor Program 4th Quarter Review, submitted March 5, 2003.

2. DOE Hydrogen & Fuel Cells Annual Program Review, May 19-22, 2003

Micro-Machined Thin Film H_2 Gas Sensors

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Objectives

- Optimize process conditions, focusing on improving yield and uniformity.
- Investigate the physics and chemistry of the sensing materials and sensing mechanisms.
- Develop improved sensor packaging and electronics system integration.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors

Approach

- Introduce new process steps to improve device yield.
- Analyze chemical, electrical, and mechanical aspects of sensor characteristics.
- Survey device packaging possibilities; down-select most appropriate option.
- Develop real-time signal conditioning and processing algorithms and platforms.
- Implement industry-standard control practices and knowledge-based management (KBM).

Accomplishments

- Improved the post-packaging fabrication yield to greater than 80%.
- Created novel surface treatment methodology for surface micro-machined structures.
- Identified novel piezo-resistive transduction mechanisms.
- Designed a microprocessor-based evaluation kit equipped with on-board signal conditioning and processing.

Future Directions

- Evaluate characteristics of sensors fabricated with new processing steps.
- Explore new piezo-resistive device structures.
- Tailor sensors for specific applications.
- Deploy evaluation kits to test sites.

Introduction

There is a common need in all hydrogen applications to detect and quantify the amount of hydrogen present. Not only is hydrogen detection necessary for life safety reasons, but effective hydrogen monitoring is also required for optimal process control of hydrogen-based energy systems. These needs call for a sensor technology that can accommodate many diverse requirements. For industrial applications, sensors must be hydrogen-selective and immune to impurity gases commonly present in hydrogen feedstock. A fast speed of response is a critical requirement for life safety monitoring and a necessary feature for real-time control of processes that run on rapid duty cycles. We have developed and characterized novel Micro-Electro-Mechanical System (MEMS)-based hydrogen sensors to meet this growing need.

The novel hydrogen sensors developed at ATMI are based on a MEMS device platform. The MEMS platform, known as a micro-hotplate, is a suspended thermal isolation structure with an embedded heater element (Semancik, *et al.*, 2001). The new sensors employ rare earth metal thin films as the active sensing layer and use reversible metal hydrogenation as the sensing mechanism. The extent of hydrogenation depends on the gas-phase hydrogen concentration, and hydrogenation can increase the electrical resistance by several orders of magnitude, making it a very sensitive transduction mechanism.

Approach

Our approach has been to design, fabricate, and characterize MEMS-based gas sensors of different layouts and film chemistries. The understanding gained during characterization is subsequently used as feedback to the next design cycle. A schematic of the layered structure that makes up the sensor is shown in Figure 1. The micro-hotplate layout was designed in-house and fabricated by a foundry service. A rare earth metal thin film with a palladium-based capping layer was subsequently deposited onto the micro-hotplate platform and serves as the active sensing layer. Substantial effort has been devoted to mapping the fabrication process flow, which involves 11 steps and over 110 variables. Knowledge-based management (Schmidt, et al., 1999) and other data-driven quality control protocols have been applied to identify the issues affecting sensor yield and uniformity.

While the sensor construction is relatively straightforward, the sensor characteristics can be quite complex due to strong coupling of chemical reactions, electrical probing, and mechanical movement. For example, hydrogen must first adsorb, dissociate, and diffuse through the cap layer. Upon reaching the sensing layer, it reacts with the sensing material to form hydride of relevant phases. When the hotplate temperature is raised above ambient to expedite these chemical reactions, it also modifies the hydrogen content and electrical resistance of the hydride film and causes the micro-hotplate platform to deflect. The deflection in turn modifies the stress state of the sensor stack, changing the film properties. We have used a wide variety of microscopy techniques as well as electrical characterization to study and model sensor behaviors.

Results

Using KBM techniques such as resistance as a function of H_2 concentration, temperature, and voltage, we identified the contact interface between the Al interconnect and the sensing layer as a primary candidate for improvement in order to improve yields and uniformity. It was further determined that the interface layer was affected by both non-planar surface topography and the formation of native oxide on the surface of the Al interconnect prior to deposition of the sensing layer. Process steps were

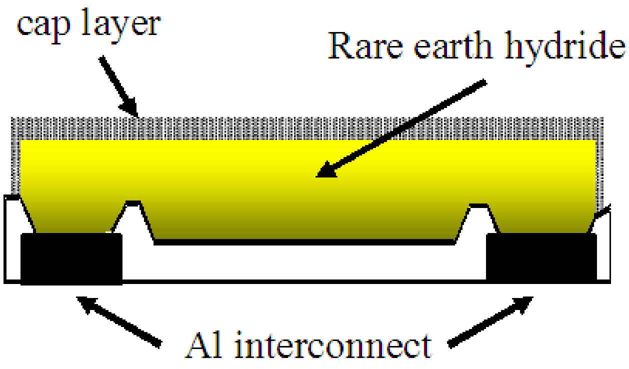

Figure 1. Schematic of Functional Layer Stack on a Micro-Hotplate Platform

added to planarize the structure and clean the contact area *in situ*. A representative result comparing the surface topography of a sensor structure, measured by stylus profilometry, before and after the planarization step is shown in Figure 2. The new processing steps help ensure that the sensing layer deposited is uniform across the platform surface, and that there is good electrical contact to the underlying Al interconnects. Addition of these steps to the fabrication process improved the pre-packaging yield to greater than 80% and reduced intra-die variation, as shown in Figure 3.

In addition to improving the fabrication yield, we have made appreciable progress towards understanding the chemical, electrical, and mechanical aspects of the sensing mechanism. The mechanical aspect had been less apparent in the past, but its effects are magnified now that additional processing steps have improved the electrical contact. Additionally, new microscopy techniques have enabled the visualization of the mechanical behavior for the first time. In particular, bending of micro-hotplate platform has been observed via a confocal microscope, as shown in Figure 4. Moreover, as the hydride film absorbs hydrogen, its volume expands, and the extent of deflection changes. The heater element embedded on the micro-hotplate platform, made of a piezo-resistive element, changes its electrical resistance when the deflection modifies the stress states of the platform. It was recognized that this phenomenon can serve as the basis for a separate, piezo-resistive mechanism in addition to the original chemi-resistive mechanism for signal transduction. Chemi- and piezo-resistive responses of a representative sensor are shown in Figure 5. The two mechanisms together, with no modification to sensor construction, provide a unique sensor package that has high sensitivity around lower explosion level (LEL - 4% H_2 in air) and a large dynamic range beyond LEL.

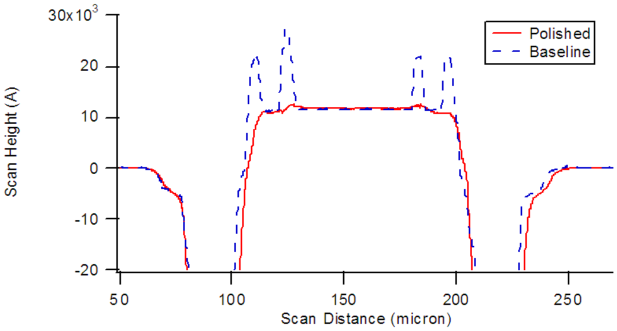

Figure 2. Representative Result of Surface Planarization

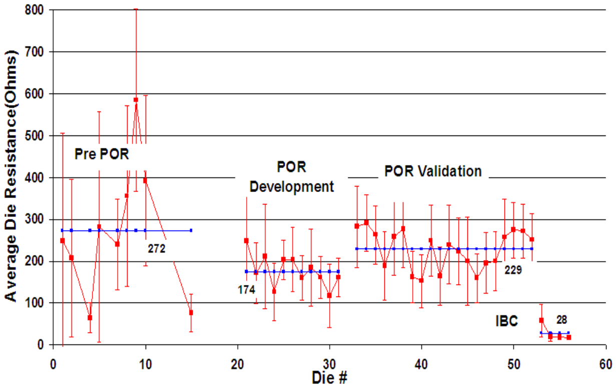

Figure 3. Yield Improvements as Function of Process Improvements vs. Process of Record (POR)

An electronic signal conditioning and processing system was developed to provide a simple device for collaborators to interface with their detection system. The system includes signal conditioning circuitry for proper power sourcing and resistance measurement, as well as real-time signal processing software running on a microprocessor embedded on the circuitry. When coupled with a data-logging device such as a personal digital assistant, as illustrated in

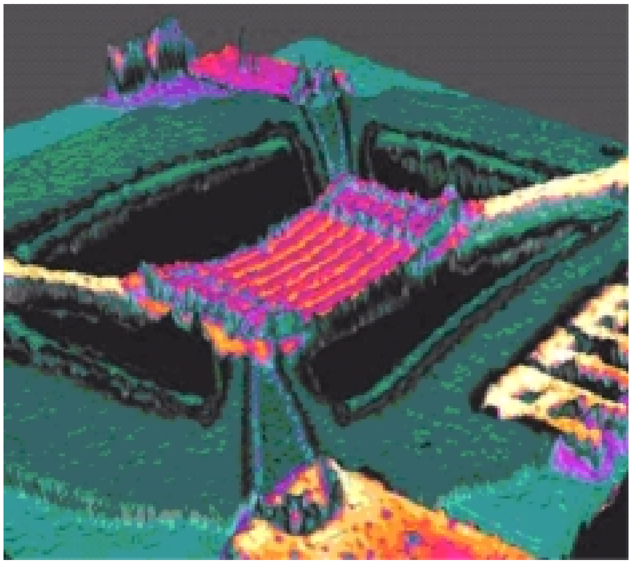

Figure 4. Representative Confocal Microscopy Image of a Sensor

Figure 6, the system becomes a stand-alone unit that can be easily transferred to test sites to verify sensor performance in real-life settings. Systems have been deployed at several locations in the U.S. and Europe.

Conclusions

- Improved fabrication yield and device uniformity have been demonstrated.
- The interdependency of chemical, electrical, and mechanical properties of the sensor operation has been characterized and studied.
- An innovative piezo-resistive transduction mechanism was discovered.
- Signal conditioning/processing of sensor response was implemented for system integration.

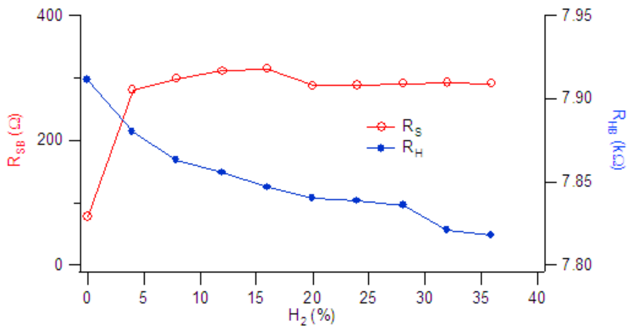

Figure 5. Representative Sensor Responses up to 40% H_2

Figure 6. Photo of an Evaluation Kit with Signal Conditioning/Processing Capability

- KBM techniques have been applied with encouraging feedback for the continuing improvement of sensor fabrication.

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2. S.R. Schmidt, M.J. Kiemele, and R.J. Berdine, *Knowledge Based Management*, Air Academy Press & Associates, CO, 1999.

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1. "MEMS based hydrogen gas sensors," submitted to *Journal of Electrochemical Society.*
2. "MEMS based hydrogen sensors for emerging applications," presented at *Connecticut Microelectronics and Optoelectronics Consortium Symposium*, Storrs, Connecticut (2003).

Special Recognitions & Awards/Patents Issued

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2. F. DiMeo and G. Bhandari, "Micro-machined thin film hydrogen gas sensor, and method of making and using the same," U.S. Patent 6,265,222 (2001)
3. F. DiMeo and T.H. Baum, "Micro-machined thin film sensor arrays for the detection of H_2, NH_3, and sulfur containing gases, and method of making and using the same," U.S. patent application 2002/0017126, allowed
4. F. DiMeo and P. Chen, "Rare earth metal sensor," U.S. patent pending
5. I.-S. Chen and F. DiMeo, "Chemical sensor responsive to change in volume of material exposed to target particle," U.S. patent pending

Sensor Development for Proton Exchange Membrane Fuel Cell Systems

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Micro Substrates Corporation, Tempe, AZ

Objectives

- Establish the requirements for each physical sensor.
- Develop packaging strategies for the sensors to minimize sensor cost.
- Design and fabricate prototype sensors.
- Test sensors in third party fuel cells.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors

Approach

- Task 1. Sensor Requirements: establishes the requirements for each physical sensor and develops common packaging strategies.
- Task 2. Sensor Development: development of sensor concepts from Task 1 that culminates in sensor design engineering of prototype sensors.
- Task 3. Prototype Build & Test: fabrication and testing of the developed sensors culminating in demonstrations of the prototype sensors.
- Task 4. Field Testing: testing of prototype sensors at fuel cell and fuel processor companies.

Accomplishments

- Interviewed 10 fuel cell development companies.
- Developed customer images diagram.
- Extracted customer requirements from interviews.
- Deployed survey to 60 recipients.

Future Directions

- Finalize sensor requirements and review with DOE.
- Brainstorm the requirements for the top 2-3 solutions for each sensor.
- Prioritize solutions.
- Create Engineering Development Specification (EDS) for top priority concept for each physical sensor.
- Obtain DOE review and approval of EDS.
- Begin sensor development.

Introduction

The technical approach for this project is to look at the fuel cell system and establish the requirements for each physical sensor, then develop packaging strategies for the sensors to minimize sensor cost. Prototype sensors will be designed and fabricated at Honeywell and then the sensors will be tested in third party fuel cell systems at fuel processor companies.

Approach

In the initial phase of the project, the requirements provided by DOE in the solicitation for the individual physical sensors were investigated thoroughly and refined as needed. Honeywell interviewed fuel cell and fuel processor companies, listed in Figure 1, to attain the requirements of each customer.

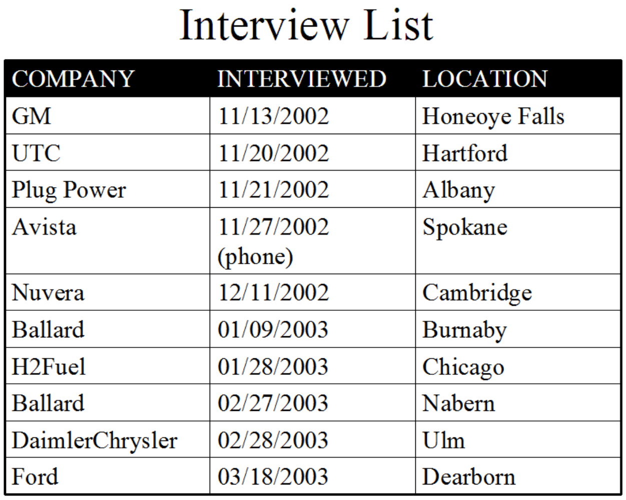
A fact-based methodology, Language Analysis, that is part of a product definition process, Market Driven Product Definition (MDPD®), will be employed to glean fact-based information from the customer interviews. A final step in the MDPD® process is surveying the market with the requirements created from the interviews. A Kano Survey provides requirement validation from the broad market again through a fact-based methodology. During this development, it is Honeywell's objective to continuously re-evaluate the sensor requirements in light of new developments in the field, contracting agency inputs, and our own development status. Our goal is a continuous improvement in the sensor requirements during the initial prototype design and testing phase, leading to realistic, achievable requirements by the time final prototypes are to be developed and tested. Industry inputs will be employed to help define packaging requirements and associated common packaging methodologies across all the sensor developments.

Results

Several customers were interviewed during the MDPD® process; the customer group is presented in Figure 1. The verbatim transcripts of the interviews were scrubbed to find customer images and requirements. Metrics were also pulled from the interview data during the scrubbing.

The customer images were reduced onto the customer image map shown in Figure 2. These images describe the emotion in the customer's voice. It shows that they have a problem that needs to be solved.

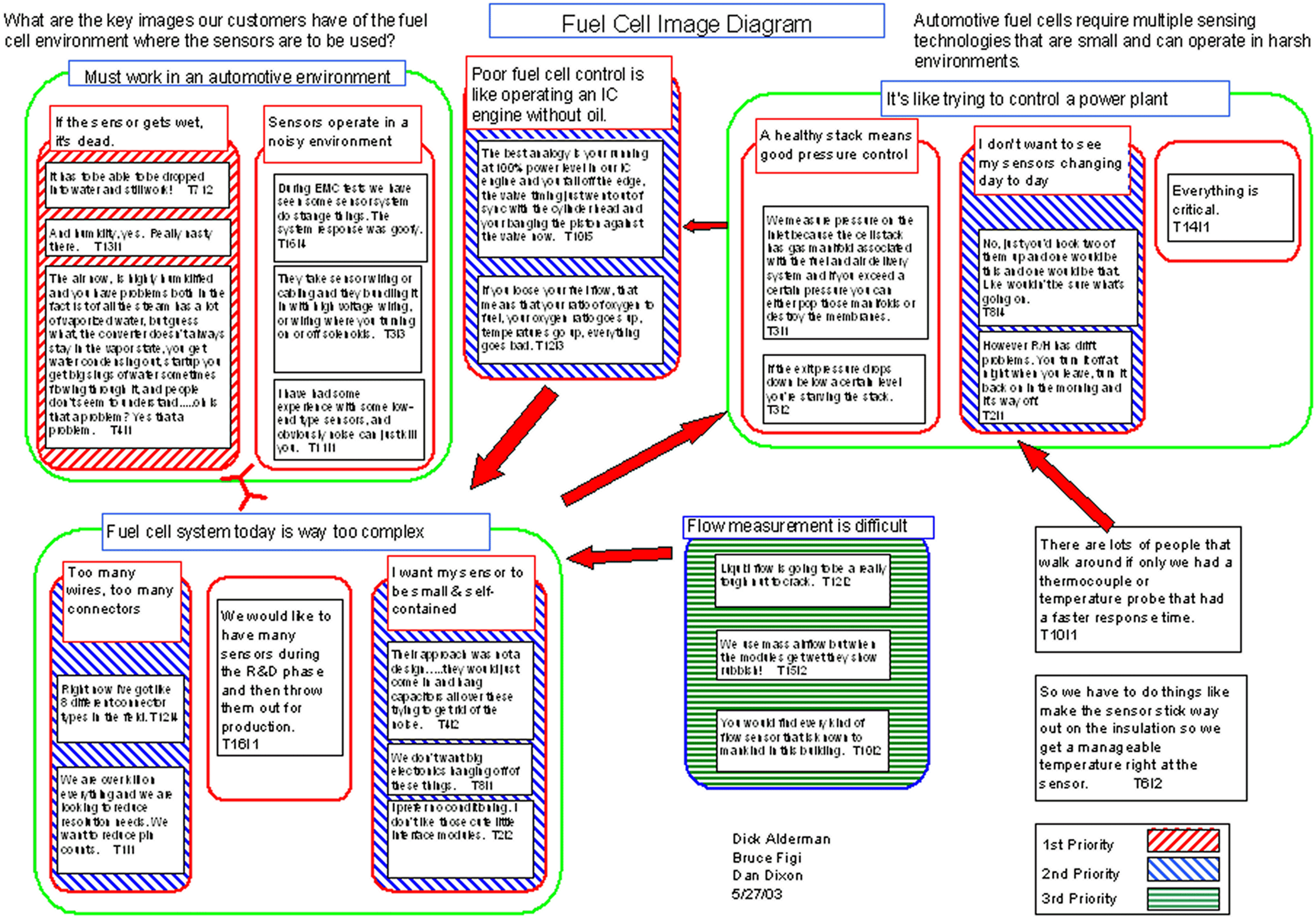
The customer requirements were also reduced onto a customer requirements map as shown in Figure 3. Solutions for these requirements will be



Interview List

COMPANY	INTERVIEWED	LOCATION
GM	11/13/2002	Honeoye Falls
UTC	11/20/2002	Hartford
Plug Power	11/21/2002	Albany
Avista	11/27/2002 (phone)	Spokane
Nuvera	12/11/2002	Cambridge
Ballard	01/09/2003	Burnaby
H2Fuel	01/28/2003	Chicago
Ballard	02/27/2003	Nabern
DaimlerChrysler	02/28/2003	Ulm
Ford	03/18/2003	Dearborn

Figure 1. Interview List



Fuel Cell Image Diagram

What are the key images our customers have of the fuel cell environment where the sensors are to be used?

Automotive fuel cells require multiple sensing technologies that are small and can operate in harsh environments.

Must work in an automotive environment

If the sensor gets wet, it's dead.

It has to be able to be dropped into water and still work! T7I2

And humidity, yes. Really nasty there. T13I1

The air now, is highly humidified and you have problems both in the fact is tof all the steam has a lot of vaporized water, but guess what, the converter doesn't always stay in the vapor state, you get water condensing out, startup you get big slugs of water sometimes flowing through it, and people don't seem to understand.....oh is that a problem? Yes that a problem. T4I1

Sensors operate in a noisy environment

During EMC tests we have seen some sensor system do strange things. The system response was goofy. T16I4

They take sensor wiring or cabling and they bundling it in with high voltage wiring, or wiring where you turning on or off solenoids. T3I3

I have had some experience with some low-end type sensors, and obviously noise can just kill you. T1I11

Poor fuel cell control is like operating an IC engine without oil.

The best analogy is your running at 100% power level in our IC engine and you fall off the edge, the valve timing just went out of sync with the cylinder head and your banging the piston against the valve now. T10I5

If you loose your fuel flow, that means that your ratio of oxygen to fuel, your oxygen ratio goes up, temperatures go up, everything goes bad. T12I3

It's like trying to control a power plant

A healthy stack means good pressure control

We measure pressure on the inlet because the cell stack has gas manifold associated with the fuel and air delivery system and if you exceed a certain pressure you can either pop those manifolds or destroy the membranes. T3I1

If the exit pressure drops down below a certain level you're starving the stack. T3I2

I don't want to see my sensors changing day to day

No, just you'd look two of them up and one would be this and one would be that. Like wouldn't be sure what's going on. T8I4

However R/H has drift problems. You turn it off at night when you leave, turn it back on in the morning and its way off T2I1

Everything is critical. T14I1

There are lots of people that walk around if only we had a thermocouple or temperature probe that had a faster response time. T10I1

So we have to do things like make the sensor stick way out on the insulation so we get a manageable temperature right at the sensor. T6I2

Fuel cell system today is way too complex

Too many wires, too many connectors

Right now we got like 8 different connector types in the field. T12I4

We are overkill on everything and we are looking to reduce resolution needs. We want to reduce pin counts. T1I1

We would like to have many sensors during the R&D phase and then throw them out for production. T16I1

I want my sensor to be small & self-contained

Their approach was not a design.....they would just come in and hang capacitors all over these trying to get rid of the noise. T4I2

We don't want big electronics hanging off of these things. T8I1

I prefer no conditioning. I don't like those cute little interface modules. T2I2

Flow measurement is difficult

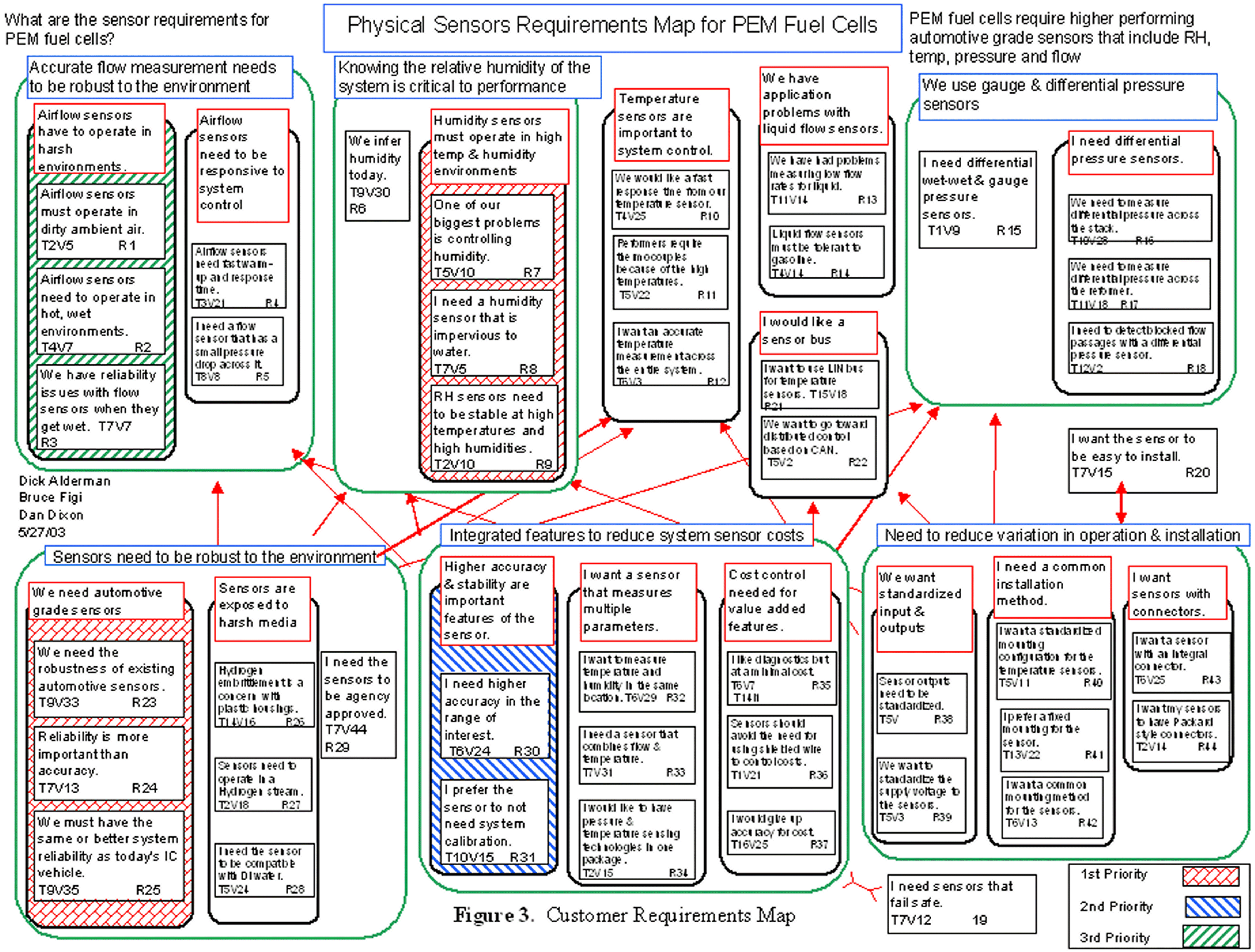
Liquid flow is going to be a really tough nut to crack. T12I2

We use mass airflow between the modules get wet they show rubbish! T15I2

You would find every kind of flow sensor that is known to mankind in this building. T10I2

Dick Alderman
Bruce Figi
Dan Dixon
5/27/03

Figure 2. Customer Image Map



What are the sensor requirements for PEM fuel cells?

Physical Sensors Requirements Map for PEM Fuel Cells

PEM fuel cells require higher performing automotive grade sensors that include RH, temp, pressure and flow

Accurate flow measurement needs to be robust to the environment

Airflow sensors have to operate in harsh environments.

Airflow sensors must operate in dirty ambient air. T2V5 R1

Airflow sensors need to operate in hot, wet environments. T4V7 R2

We have reliability issues with flow sensors when they get wet. T7V7 R3

Airflow sensors need to be responsive to system control

Airflow sensors need fast warm-up and response time. T3V21 R4

I need a flow sensor that has a small pressure drop across it. T8V8 R5

Knowing the relative humidity of the system is critical to performance

We infer humidity today. T9V30 R6

Humidity sensors must operate in high temp & humidity environments

One of our biggest problems is controlling humidity. T5V10 R7

I need a humidity sensor that is impervious to water. T7V5 R8

RH sensors need to be stable at high temperatures and high humidities. T2V10 R9

Temperature sensors are important to system control.

We would like a fast response time from our temperature sensor. T4V25 R10

Reformers require thermocouples because of the high temperatures. T5V22 R11

I want an accurate temperature measurement across the entire system. T5V3 R12

We have application problems with liquid flow sensors.

We have had problems measuring low flow rates for liquid. T11V14 R13

Liquid flow sensors must be tolerant to gasoline. T4V14 R14

I would like a sensor bus

I want to use LIN bus for temperature sensors. T15V18 R21

We want to go toward distributed control based on CAN. T5V2 R22

We use gauge & differential pressure sensors

I need differential wet-wet & gauge pressure sensors. T1V9 R15

I need differential pressure sensors.

We need to measure differential pressure across the stack. T10V28 R16

We need to measure differential pressure across the reformer. T11V18 R17

I need to detect blocked flow passages with a differential pressure sensor. T12V2 R18

I want the sensor to be easy to install. T7V15 R20

Dick Alderman
Bruce Figi
Dan Dixon
5/27/03

Sensors need to be robust to the environment

We need automotive grade sensors

We need the robustness of existing automotive sensors. T9V33 R23

Reliability is more important than accuracy. T7V13 R24

We must have the same or better system reliability as today's IC vehicle. T9V35 R25

Sensors are exposed to harsh media

Hydrogen embrittlement is a concern with plastic housings. T14V16 R26

Sensors need to operate in a Hydrogen stream. T2V18 R27

I need the sensor to be compatible with DI water. T5V24 R28

I need the sensors to be agency approved. T7V44 R29

Integrated features to reduce system sensor costs

Higher accuracy & stability are important features of the sensor.

I need higher accuracy in the range of interest. T6V24 R30

I prefer the sensor to not need system calibration. T10V15 R31

I want a sensor that measures multiple parameters.

I want to measure temperature and humidity in the same location. T6V29 R32

I need a sensor that combines flow & temperature. T7V31 R33

I would like to have pressure & temperature sensing technologies in one package. T2V15 R34

Cost control needed for value added features.

I like diagnostics but at a minimal cost. T6V7 T14II R35

Sensors should avoid the need for using shielded wire to control costs. T1V21 R36

I would give up accuracy for cost. T16V25 R37

Need to reduce variation in operation & installation

We want standardized input & outputs

Sensor outputs need to be standardized. T5V R38

We want to standardize the supply voltage to the sensors. T5V3 R39

I need a common installation method.

I want a standardized mounting configuration for the temperature sensors. T5V11 R40

I prefer a fixed mounting for the sensor. T13V22 R41

I want a common mounting method for the sensors. T6V13 R42

I want sensors with connectors.

I want a sensor with an integral connector. T6V25 R43

I want my sensors to have Packard style connectors. T2V14 R44

I need sensors that fails afe. T7V12 19

1st Priority ▨
2nd Priority ▨
3rd Priority ▨

Figure 3. Customer Requirements Map

brainstormed by a cross functional team. The solutions will be prioritized, and engineering teams will work the concepts.

Metrics were also scrubbed from the transcripts, and those metrics were used in the customer survey to help define the bounds on the functional and environmental conditions for each physical sensor. The customer list for the survey is shown in Figure 4.

Conclusions

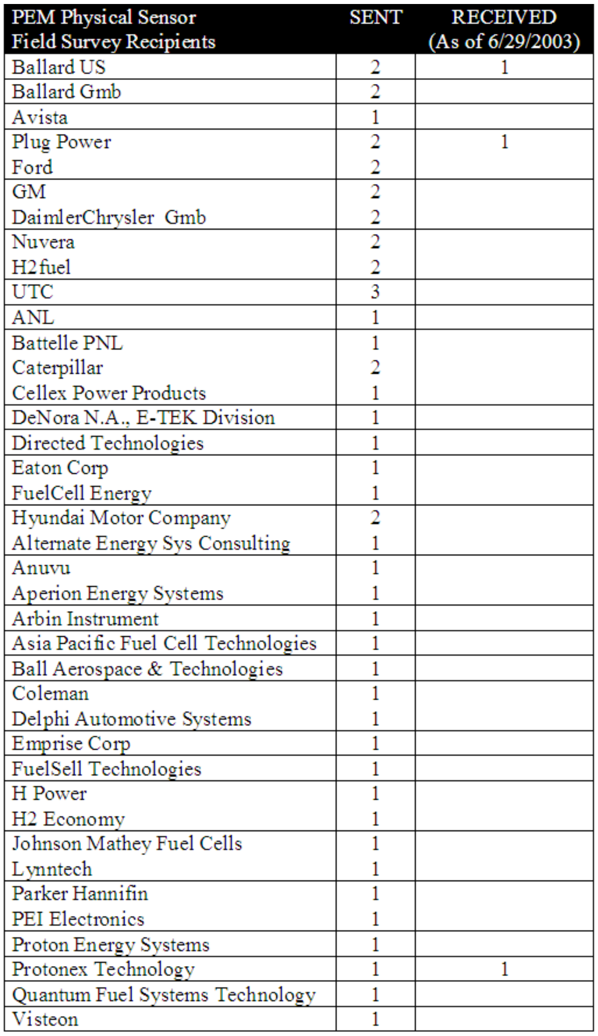
Many of the Task 1 conclusions will come from the survey feedback. Many of the preliminary DOE requirements for physical sensors line up with the metrics from the customer interviews.

Technical hurdles that have been identified are as follows:

- General
  - Meeting cost targets.
- Relative Humidity Sensing
  - Stability over application life.
  - Ability to provide feedback in two-phase flow.
- Flow Sensing
  - Providing a stable, accurate output in non-condensing and condensing environments.

FY 2003 Publications/Presentations

1. 2003 Merit Review - Sensor Development for PEMFC Systems, Bruce Figi, Honeywell Sensing & Controls



PEM Physical Sensor Field Survey Recipients	SENT	RECEIVED (As of 6/29/2003)
Ballard US	2	1
Ballard Gmb	2	
Avista	1	
Plug Power	2	1
Ford	2	
GM	2	
DaimlerChrysler Gmb	2	
Nuvera	2	
H2fuel	2	
UTC	3	
ANL	1	
Battelle PNL	1	
Caterpillar	2	
Cellex Power Products	1	
DeNora N.A., E-TEK Division	1	
Directed Technologies	1	
Eaton Corp	1	
FuelCell Energy	1	
Hyundai Motor Company	2	
Alternate Energy Sys Consulting	1	
Anuvu	1	
Aperion Energy Systems	1	
Arbin Instrument	1	
Asia Pacific Fuel Cell Technologies	1	
Ball Aerospace & Technologies	1	
Coleman	1	
Delphi Automotive Systems	1	
Emprise Corp	1	
FuelSell Technologies	1	
H Power	1	
H2 Economy	1	
Johnson Mathey Fuel Cells	1	
Lynntech	1	
Parker Hannifin	1	
PEI Electronics	1	
Proton Energy Systems	1	
Protonex Technology	1	1
Quantum Fuel Systems Technology	1	
Visteon	1	

Figure 4. Survey Customer List

Gallium Nitride Integrated Gas/Temperature Sensors for Fuel Cell Systems

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Objectives

- Fabricate gallium nitride (GaN) field effect transistor (FET) sensors to resolve and detect carbon monoxide in a background of varying hydrogen concentration and high water content at T>250°C
- Develop method for resolving CO at 10 ppm from H_2 interference
- Validate sensors and analysis in operational reformers

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors
- K. Emissions and Environmental Issues
- L. Hydrogen Purification/Carbon Monoxide Cleanup

Approach

- GaN and silicon carbide (SiC) are semiconductors with large band gaps and are an attractive option for high temperature electronic applications including gas monitoring
- Catalytic metals such as platinum, rhodium and palladium are good candidates for the gate metal in GaN FET sensors for CO detection
- The same metals are well known catalysts in the preferential oxidation (PROX) process for oxidizing trace amounts of CO by reaction with oxygen in excess H_2
- Test GaN FET sensors in mixtures of H_2 and CO for array analysis of CO
- Develop a simple analysis method for extracting CO concentration from background H_2 effects

Accomplishments

- Completed main effect testing of CO (0-80 ppm) and H_2 (30-70%)
- Developed quantitative method for reliably detecting CO at 10 ppm in 30-70% H_2

Future Directions

- Determine consistency or reproducibility of calibration results in CO and H_2
- Confirm higher fabrication yield by improved gate metal adhesion
- Complete testing of Rh and Zr gate metals

- Field test working hydrogen reforming processes to validate process control and analysis statistics
- Test in wet and dry hydrogen sources (ca H_2O ~ 25%vol)
- PdAg abandoned in favor of Zr due to potential surface segregation of Ag and alloys in general leading to sensor drift

Introduction

A low-cost sensor capable of resolving CO (1-100 ppm) in hydrogen (30-75%) and water vapor (25%) is needed but technically difficult to achieve. Platinum based sensors have been used for CO detection, but the cross-sensitivity of CO and hydrogen precludes their selective measurement of CO. Similar cross-sensitivity is expected for any single metal with a catalytic response to CO. A method is needed to resolve the CO in a background of varying hydrogen concentration. Arrays of inexpensive sensors have been proposed as a solution for when selectivity of an individual sensor is insufficient to reliably detect and measure the gas of interest. This project demonstrates how an array can be used for resolving the CO and hydrogen concentrations using two GaN FET sensors with a Pt and Rh gate metal and a two-component calibration matrix of 25 pairs of CO and hydrogen concentrations. The measurements of gate voltage at each of the 25 calibration points are used to compute a three-dimensional response surface. The intersection of the response surfaces for the different gate compositions is used to resolve and measure the concentrations of CO and hydrogen.

Approach

Recent work on SiC FET sensors using catalytic metal gates has been reviewed (1) and suggests SiC FETs with metal gates are attractive candidates for high temperature gas monitoring. GaN based devices and circuits are also an attractive option for high temperature applications including gas monitoring. The effect of gas on GaN FETs with metal gates has been studied and reported (2). Catalytic metals such as platinum, rhodium and palladium are good candidates for the gate metal in GaN devices because they have been shown to form good Schottky barriers on n-GaN. These metals are also suggested for this application because each has shown catalytic activity in the preferential oxidation (PROX) process for oxidizing trace amounts of CO by reaction with oxygen in excess hydrogen.

Results

Device characterization, architecture, control electronics, the calibration system and chemical analysis of the metal gate GaN FET sensors used in this study are described in the DOE reports in Reference 2. The time history of responses of the Pt sensor is shown in Figure 1. Figures 2 and 3 show the response surfaces for a Pt and Rh gate GaN MODFET sensor. The contours of constant gate voltage were mapped using MathCAD from measurements at 25 ppm CO and hydrogen concentration pairs in the range required for the application above. The plots are a two-dimensional representation of a three-dimensional surface. A single measurement of gate voltage for either of the different sensors could indicate any combination of CO and hydrogen along a constant voltage contour. CO and hydrogen are resolved by the combined measurement using sensors with sufficiently different response surfaces. For an unknown blend of CO and hydrogen, the gases are resolved and concentrations determined from where the contours

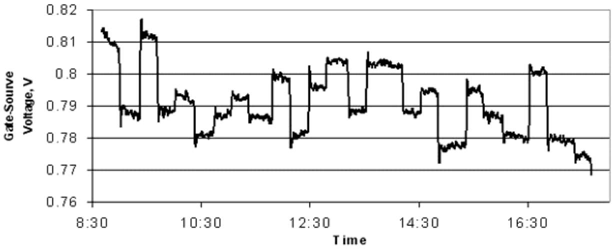

Figure 1. Typical Calibration Run (Twenty-five calibration pairs of CO and H_2 are delivered to the sensor in random order pair presentation to minimize systematic error. There are three source gases: CO in H_2 (1000 ppm), H_2 and N_2, with a total flow = 1356 cm^3/min at T = 250ºC and P = 1 atm. The system limited response time = 15 sec to 90% of full scale.)

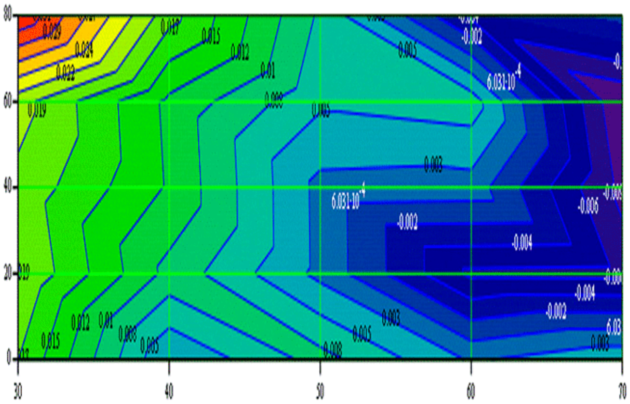

Figure 2. Pt Response Surface at 250ºC (Mapping is a fit to the calibration data. Calibration pairs are at grid intersections. Contour spacing is 1 standard deviation.)

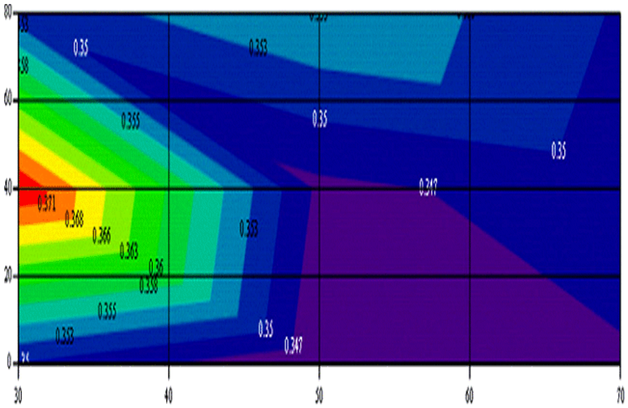

Figure 3. Rh Response Surface at 250ºC (Closer spacings improve precision. 90º crossing angles for contours from different sensors improve accuracy. Straighter contours improve accuracy. Single crossings increase confidence.)

computed for the Pt and Rh sensors intersect. These data suggest the detection of CO at 10 ppm is possible over most of the range.

Conclusions

Laboratory results confirm arrays of GaN FET sensors can be used to detect the contamination of as little as 10 ppm CO in H_2 fuels used in proton exchange membrane fuel cells. These sensor arrays can operate in temperatures exceeding 250°C, thus eliminating the need for water separation before analysis.

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2. Y. Kokubun, T. Seto and S. Nakagomi, Jpn. J. Appl. Phys., 40, L663-L665 (2001). J. Schalwig, G. Muller, M. Eickhoff, O. Ambacher and M. Stutzman, Sensors and Actuators B-Chemical, 87, 425-430 (2002). B.P. Luther, S.D. Wolter and S.E. Mohney, Sensors and Actuators B, 56,164 (1999). S.C. Pyke and L. Sadwick, DOE Report, http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/32405b16.pdf, 2002. S.C. Pyke and L. Sadwick, DOE Report, http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/30535ay.pdf, 2001. And S.C. Pyke, J-H. Chern, J. Hwu and L. Sadwick, DOE Report, http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/28890ii.pdf, 2000.

Special Recognitions & Awards/Patents Issued

1. Invited paper to be presented at "High Band Gap Material FET Chemical Sensors", IEEE Sensors 2003, Toronto, October 21-24, 2003.

Fiber Optic Temperature Sensors for PEM Fuel Cells

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Micro-Materials, Inc., Tampa, FL

Objectives

The objective of this research is to develop a low-cost, durable and fast-responding temperature sensor for proton exchange membrane (PEM) fuel cells. Temperature and temperature gradients within the fuel cell membrane electrode assembly (MEA) are a key indicator of the operational condition of the cell and its ability to respond to a required load. The thermal state of a fuel cell stack directly affects its ability to deliver energy on start-up or under adverse environmental conditions. Furthermore, localized hot spots within the MEA can lead to greatly reduced operational life and even catastrophic failure. Hence, realtime feedback of the thermal condition of a cell or stack can be utilized to control the stack, optimize performance, and monitor the condition of critical components and sub-components.

Currently, thermocouplers and thermistors are being used to monitor the thermal condition at a few locations in operating fuel cell stacks. After a few months effort and a review of our technology with fuel cell developers, the ability to measure temperature at many more locations, with a small, low-cost and electrical non-conductive sensor was considered of great interest. Additionally, the fiber optic sensors provide a safe way of making temperature measurements within the stack without the possibility of electrically shorting the stack to ground as may be the case with a conductive sensor like a thermocouple or thermistor. Finally, the ability to make many cost effective temperature measurements with a technology that is fast, durable and electrically insulating is of great interest to fuel cell developers.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors
- C. Thermal Management

Approach

- Identify and characterize the optimum fluorescent medium (materials and possible binders and or matrices) for fast-responding, accurate and robust temperature measurement;
- Demonstrate material compatibility of the sensor with the fuel cell;
- Explore the most appropriate temperature measurement zones and arrays within the membrane and stack configuration;

- Explore alternate wave guide approaches to optimize sensor robustness, expand the range or density of measurements, and minimize cost of implementation;
- Develop and test probe concepts for cost effective implementation, functionality, durability, and performance;
- Develop a low-cost electronics package that readily integrates with fuel cell systems; and
- Study alternate probe configurations that may lead to sensing other critical parameters (e.g. humidity or flow measurements).

Accomplishments

- Appropriate fluorescent transducer materials have been identified and characterized that will provide fast-responding (milliseconds) and accurate (<1% of range) temperature information from a fuel cell membrane electrode assembly;
- Low-cost probe designs have been tested in the lab that will provide temperature data from operating fuel cells;
- Initial field tests show that accurate and reliable temperature information can be gathered from operating fuel cells;
- New intellectual property (2 patent disclosures) has been developed in the areas of embedded wave guide sensors and spatially resolved temperature sensors that may lead to system designs that were previously unattainable; and
- Collaborative relationships are developing with several fuel cell designers and end users to gain perspective on designs and facilitate testing and implementation.

Future Directions

- Probe designs will be evaluated in the lab and prepared for field tests;
- Measurement system design issues will be addressed (signal processing, packaging, etc.);
- Alternate probe concepts will be evaluated that could lead to previously unattainable functionality, performance, and cost targets;
- Field tests will be planned to evaluate system compatibility, durability and performance under real conditions; and
- Emerging possibilities to sense other important parameters or leverage to other related applications will be explored (e.g. humidity and flow, leverage to other fuel cell types, etc.).

Introduction

The need for an accurate, reliable and fast-responding temperature sensor has been identified as a critical need for advanced fuel cell designs. Temperature, thermal gradients, and thermal history play a key role in determining the health of a fuel cell and its ability to respond to instantaneous power demands. Furthermore, real-time thermal diagnostic sensors will allow designers to increase stack power density by reducing operating margins and quickly identifying the development of hot spots that could cause catastrophic failure.

This project is focused on the development of an optical fiber based temperature measurement probe that utilizes the unique fluorescence properties of certain materials to detect temperature. The persistence of light emitted (fluorescence) by these materials (thermographic phosphors) is proportional to their absolute temperature. Thus, one can measure the fluorescence lifetime as a means of accurately inferring the temperature of a material. The fluorescence lifetime, as a rule, gets shorter as temperature increases. Other related emission characteristics, such as the fluorescence amplitude or phase of a modulated fluorescence signal, can also be used to infer temperature. The technique can be applied over a wide range of temperatures (-270°C to >1700°C) and is potentially very accurate and durable.

In practice, one attaches, grows or dopes a length of fiber optic cable with the phosphor material included to the end of another fiber optic cable that is used to transmit the light signal to and from the measurement electronics. This impregnated length of fiber is inserted into the temperature measurement zone of interest. The impregnated fiber is excited by a light emitting diode (LED) or laser source, and the fluorescence signal is collected with a photodiode. The fluorescence signal is then analyzed, and a temperature is determined. Temperatures have been determined to better than 0.01°C accuracy in the laboratory.

Thus far, two similar materials (chromium doped yttrium aluminum garnet and ruby) have been identified that exhibit the appropriate characteristics for a fast, accurate and reliable temperature measurement over the range of -40°C to 150°C, the operating range for automotive fuel cells. Being developed now is the fiber optic probe to implement the measurement technique in operating fuel cells. The fiber optic probe can be very small in profile, low mass, low cost and rugged for real world applications. It is also electrically insulating, thus avoiding the possibility of shorting the fuel cell to ground. The measurement electronics can also be implemented in a very low-cost and robust manner, creating a temperature measurement system that is very attractive for commercial system diagnostics and control.

Approach

The development process for this technology was initiated by an in-depth study of fuel cell designs and operating conditions. Once a clear picture of the measurement need and operating environment was gathered, exploratory research was performed to identify and characterize candidate fluorescent materials for the measurement. These candidate materials were studied in the laboratory, and optimum materials were selected. These optimum materials are now being implemented into various probe designs for further laboratory study. Favorable probe designs will then be installed in actual fuel cells to gather information about system compatibility, performance and durability.

Parallel to the exploratory work described above, alternate probe design and implementation strategies are being conducted with the goal of optimizing system performance, reliability and cost. During this process, two novel discoveries have been made in response to the challenge of creating a measurement technique that would be very low cost, reliable and yet scalable to many measurements distributed throughout the fuel cell. One concept involves the development of embedded wave guide sensors within the fuel cell, thus minimizing the need for intrusive probes inserted into the fuel cell. The other concept involves the development of a single fiber optic sensor that has the ability to measure temperature at a local region anywhere along the length of the fuel cell. This technique may facilitate many temperature measurements through a fuel cell stack with only a single measurement probe.

Considerable progress has been made on the development of initial prototype probes for field testing. Also, novel technologies have emerged that will potentially lead to highly useful and economically viable sensor technologies. Furthermore, our discoveries portend the possibility of other sensor modalities (humidity and flow) that would provide additional needed information about the internal performance and condition of operating and developmental fuel cells.

Results

Several fluorescing materials were successfully tested which exhibited all the characteristics required and sufficient for an inexpensive temperature measurement system. These characteristics are:

1. Temperature dependence in the desired range;
2. The ability to be excited to emit using a light emitting diode or other low-cost source;
3. Sufficient excitation efficiency to be detected with an inexpensive photodiode or other low-cost detector; and

4. Adequate brightness for use with small diameter optical fiber.

Both powder (phosphor) and crystalline materials were tested. Figure 1 shows how the fluorescence decay time decreases as temperature is increased for one of the materials tested. At present, ruby spheres, items that are inexpensive and commercially available, appear to be the most appropriate as fluorescent transducers. YAG:Cr and Gd_2O_2S:Eu are potential alternatives.

Figure 2 shows a portion of the calibration curve for the ruby sphere in comparison with a competing material, YAG:Cr phosphor. Useable emission is expected up to at least 700°C, making it a candidate for current PEM fuel cells as well as future designs that potentially operate at higher temperatures. Figure 3 illustrates a small diameter fiber (50 micron core, 110 micron cladding) inserted into a demonstrator fuel cell. Shown with the fuel cell is a water electrolyzer that generates hydrogen and oxygen to power the fuel cell. The cell was operated at 200 mW power output, and its performance was monitored before and after the temperature sensor was inserted. The temperature measurement was performed as follows: 1) disassemble the cell and place a small spot of phosphor on the polymer membrane, 2) position the fiber adjacent to the phosphor spot, 3) reassemble the cell and operate, 4) transmit light into the cell via the fiber and collect the fluorescence signal back through the same fiber, and 5) process the fluorescence signal to determine temperature.

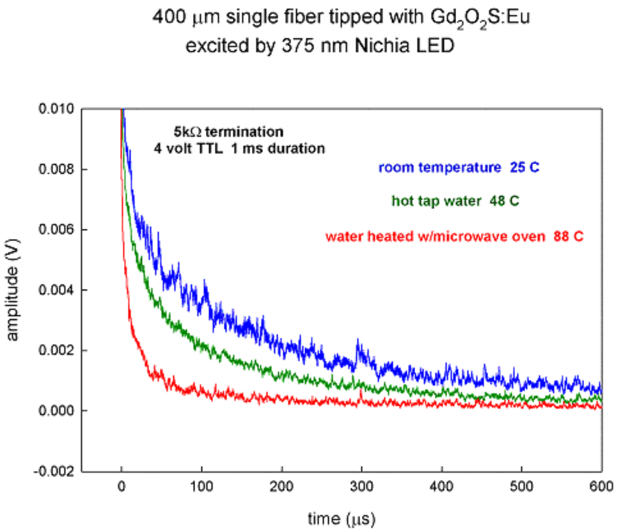

Figure 1. Example of How Temperature Affects Decay Time of a Phosphor (TTL = transistor-transistor logic)

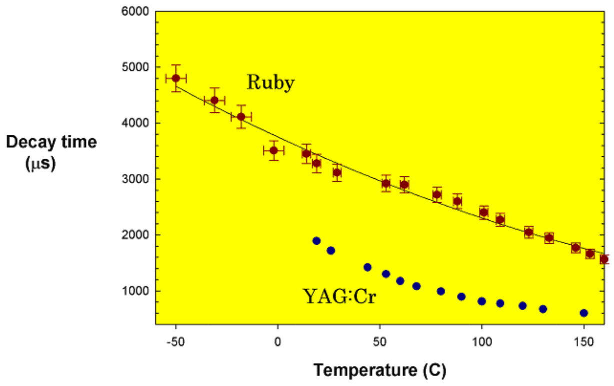

Figure 2. First Calibration Run for Ruby and YAG:Cr Phosphor

Temperature measurements were acquired without any noticeable change to the operation of the fuel cell. Viable fluorescence signal levels have also been achieved with an optical fiber pair with core diameters of 50 microns.

Figure 4 depicts various probe configurations that are under consideration. Laboratory tests are being conducted to optimize the signal-to-noise ratio of these probe designs.

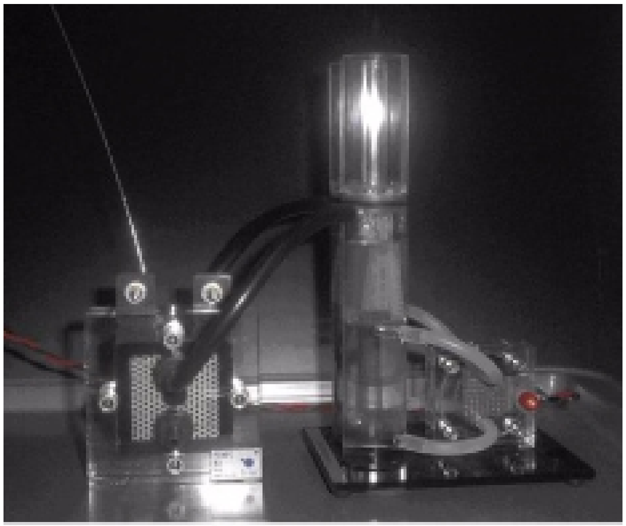

Figure 3. Example of Low Profile Fiber Temperature Sensor Inserted into Demonstrator Fuel Cell

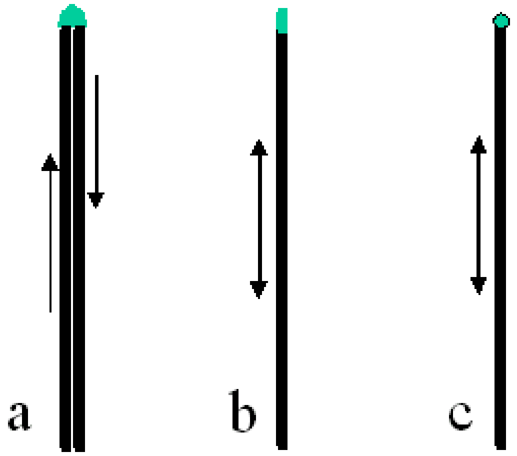

Figure 3. Three Probe Designs under Consideration: (a) Dual Fiber Probe with Phosphor Impregnated Matrix (glass or polymer) Tip; (b) Single Fiber Probe with Doped Fiber Sensing Element Grown to Tip; and (c) Single Fiber Probe with Doped Sphere Attached (cemented or epoxied) to Tip

Conclusions

- Appropriate fluorescent transducer materials have been identified and characterized that will provide fast-responding and accurate temperature information from a fuel cell membrane electrode assembly.
- Low-cost probe designs have been studied in the lab that will provide temperature data from operating fuel cells.
- Initial field tests show that accurate and reliable temperature information can be gathered from operating fuel cells.
- Long term field testing is needed to verify material compatibility between the fuel cell and the sensor probes and to characterize probe durability.

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FY 2003 Publications/Presentations

1. A poster on fluorescence thermometry was presented at the U.S. Department of Energy Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting in Berkeley, CA, May 2003.
2. A description of progress is planned for the 2003 Fuel Cell Seminar to be held in Miami Beach, November 3-7, 2003.
3. A paper on spatially resolved temperature measurement and embedded wave guide sensors is being prepared for submission to Review of Scientific Instruments.

Special Recognitions & Awards/Patents Issued

1. A patent disclosure has been filed on embedded wave guide sensors and their fabrication in polymer thin films.
2. A patent disclosure has been filed on spatially resolved fiber optic temperature measurement.

Hydrogen Composite Tank Project

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Objectives

Develop a palladium nanowire-based hydrogen sensor that has fast response, is resistant to reactive gases, operates at room temperature, and it intrinsically safe.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors

Approach

We propose to develop a hydrogen gas (H_2) sensor based on palladium nanowire arrays (PNAs) as shown in Figure 1. We discovered these sensors in 2001 (Favier et al., 293 *Science* 2227) and demonstrated that PNAs exhibit a variety of desirable attributes for the detection of hydrogen gas, including:

- Fast response (<25 ms baseline to 90% signal for 5% H_2 in N_2),
- Room temperature operation,
- Efficient power utilization (10^{-7} - 10^{-8} watts), and
- Resistance to poisoning by reactive gases including O_2 and CO.

Beginning in 2004, we will embark on a three-year project to improve PNA H_2 sensors for use in real-world hydrogen sensing applications. The goals of this project can be summarized as follows:

First, the performance of PNA H_2 sensors will be optimized over a range of environmental parameters including humidity and temperature (from –40°C to 200°C) while in the presence of contaminating gases such as CO, O_2, and H_2S. Sensor parameters to be optimized will include the nanowire diameter and length and the identity and thickness of the polymer support. Second, we shall seek to improve the performance of PNA H_2 sensors at high temperatures (where preliminary experiments show the limit-of-detection for H_2 is much higher than at ambient temperature – e.g. >5% at 80°C). Of particular interest is the use of palladium alloys with both nickel and silver since such alloys exhibit higher hydrogen solubility at elevated temperatures. Third, we will investigate the feasibility of several new types of H_2 sensors based on the PNA design. One idea to be explored involves the use of coaxially layered bimetallic nanowires in which an ultra-thin copper cladding is electrochemically applied to core nanowires composed of pure palladium. Because the chemisorption of many interfering species (e.g., CO, hydrocarbons) is weaker on copper than on

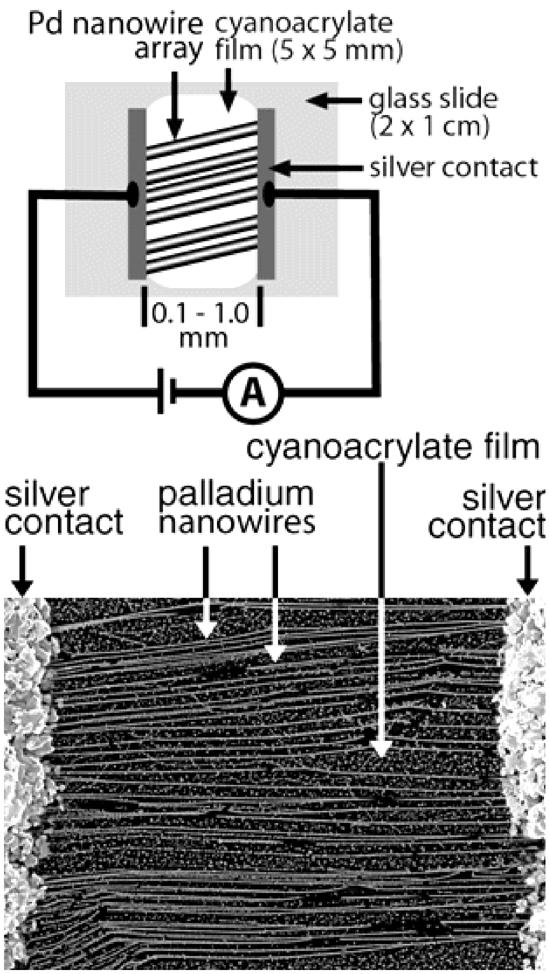

Figure 1. (top) Schematic Diagram of PNA H_2 Sensor, (bottom) Scanning Electron Microscopy (SEM) Image of a PNA H_2 Sensor (The total width of this SEM image is approximately 300 µm.)

palladium, this copper outer layer will filter out these contaminants while permitting dihydrogen to dissociate and penetrate to the palladium core. A second direction will be the development of a sensor architecture that can be prepared directly on silicon surfaces using conventional silicon microfabrication technology. Our first efforts in this direction have culminated in a recent publication (*Analytical Chemistry* **75** (2003) 4756). These early results already suggest that an exciting new generation of microfabricated hydrogen sensors, exploiting a sensing mechanism closely related to that responsible for the operation of the PNA H_2 sensors, are possible.

Education Program Element Planning and Multi-Year R,D&D Plan Development

DOE Technology Development Manager: Christy Cooper
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Contractor: SENTECH, Inc., Bethesda, MD

Objectives

- Prioritize activities to reach the target audiences critical to realizing the hydrogen economy
- Identify key education actions that DOE should support
- Secure stakeholder involvement in DOE's newly established Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Education Program Element
- Begin a serious dialogue with stakeholders on the content of and issues related to an Education Program Element about hydrogen and fuel cells
- Develop an education chapter for the HFCIT Multi-Year R,D&D Plan

Technical Barriers

This project addresses the following technical barriers from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Lack of Awareness
- B. Lack of Demonstrations or Examples of Real World Use
- C. Institutional Barriers and Access to Audiences
- D. Regional Differences

Approach

- Draft a detailed education plan outline
- Conduct a workshop to obtain stakeholder input to and feedback on draft plan outline
- Publish education workshop proceedings to initiate additional stakeholder feedback
- Develop section 3.8 of the HFCIT Multi-Year R,D&D Plan, incorporating the draft education plan elements and iterative stakeholder input

Accomplishments

- Held successful workshop for stakeholder input to the education plan
- Published draft education workshop proceedings for comment
- Published finalized education workshop proceedings with stakeholder input incorporated
- Completed a draft education section of the HFCIT R,D&D Plan for stakeholder comment
- Completed a revised education section for the R,D&D Plan, with stakeholder input incorporated

Future Directions

- Finalize the education section of the R,D&D Plan in accordance with recommendations from the National Academy of Sciences and stakeholder comments
- Conduct education program activities during FY 2004 consistent with the goals, objectives, tasks, and milestones identified in the R,D&D Plan

Introduction

The *National Energy Policy* and the *National Hydrogen Energy Roadmap ("Roadmap")*, two guiding documents for DOE hydrogen activities, pay special attention to education. The *National Energy Policy* recommends that the Secretary of Energy develop an education campaign to communicate the benefits of alternative energy technologies, including hydrogen. The *Roadmap*, which lays the foundation for a national move toward the use of hydrogen energy, also establishes a priority for education activities and suggests that education is an appropriate activity for the federal government.

Following the *National Energy Policy* and *Roadmap* recommendations, the HFCIT Program established the Education Program Element to accomplish the overall objective of educating target audiences about the long-term benefits and near-term realities of hydrogen, fuel cell systems and related infrastructure. The Education Program Element will help audiences to do the following:

- Understand the concept and value of a hydrogen economy
- Recognize the near-term realities and opportunities of hydrogen and fuel cell technologies
- Develop an accurate picture of hydrogen safety issues
- Understand, where appropriate, their part in facilitating the transition to a hydrogen economy

Approach

In order to begin a serious dialogue with specialists on the content of, and issues related to, an educational program about hydrogen and fuel cells, a workshop was convened in Washington, DC, on December 4 and 5, 2002. More than 60 individuals participated in the meeting representing industry, government, non-governmental organizations, national laboratories and universities. Specific objectives of the meeting were to solicit inputs regarding the following:

- Goals and objectives for DOE's hydrogen and fuel cell-related education activities
- Identification of factors driving the need for educational activities
- Identification and prioritization of audiences
- Creative thinking on educational projects and activities that DOE could support
- Prioritization of activities to reach the target audiences.

Following the meeting, a proceedings record was drafted and circulated among the participants and other interested parties for feedback. The comments were incorporated into a finalized proceedings record that was made publicly available on the HFCIT website.

Subsequent to the workshop, the Education Program Element worked with other components of the HFCIT Program to develop a Multi-Year R,D&D Plan for the period FY 2004 - FY 2010. The outputs of the education workshop were considered during the development of the education segment of this draft plan. The incorporation of stakeholder consultations and inputs into the R,D&D Plan development process was crucial to establishing a dialogue on hydrogen and fuel cell education activities, and to securing stakeholder support for HFCIT Education Program Element activities.

Results

The results of these planning and program development activities include the following:

- Development of a comprehensive plan for hydrogen and fuel cell education activities for FY 2004 through FY 2010 that identifies key education activities for DOE involvement and prioritizes activities for near-term implementation
- Publication of section 3.8 of the HFCIT R,D&D Plan, on Education
- Development of a database of more than 60 hydrogen and fuel cell education groups and major stakeholders
- Establishment of a dialogue between and among the HFCIT Program, through the Education Program Element, and the hydrogen and fuel cell community on educational needs and activities

Conclusions

- The Education Program Element will focus initially on target audiences that can facilitate hydrogen and fuel cell demonstration and commercialization:
  - State and local governments
  - Large-scale end-users
  - Safety and code officials
  - Teachers and students
  - Interested public
- Educational activities will be coordinated with other HFCIT program element activities, particularly those for Technology Validation, Safety, and Codes and Standards, as well as with other DOE programs to extend the reach of educational activities.
- The educational potential of hydrogen and fuel cell demonstrations will be realized by leveraging existing information/education conduits to maximize visibility among the general public, state and local decision makers, and other target audiences and stakeholders.
- The Education Program Element will focus initial efforts to do the following:
  - Develop basic "groundwork" materials that provide program background and general information about hydrogen and fuel cells, and establish a formal distribution mechanism for these materials
  - Enhance the presence of hydrogen and fuel cells in K-12 and university education
  - Facilitate educational activities for state and local governments and large-scale end-users
  - Facilitate information exchange and partnerships among emerging local, state, regional, and national hydrogen, fuel cell, and clean energy efforts

FY 2003 Publications/Presentations

Presentations on the Education Program Element and the R,D&D Plan development process were made at the following events:

- Hydrogen, Fuel Cells, and Infrastructure Technologies Program Forum, October 2002
- HFCIT Education Plan Workshop, December 2002
- National Hydrogen Association Annual Meeting, March 2003
- National Clean Cities Conference, May 2003

Section 3.8 of the HFCIT R,D&D Plan, on Education, was published for comment in draft form in June 2003.

Baseline Knowledge Assessment

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Objectives

- Conduct a literature search to identify previous surveys that measure knowledge of hydrogen technologies
- Identify non-survey metrics for assessing the current public visibility of hydrogen technologies
- Develop and implement a plan for conducting national surveys of targeted audiences to determine each population's awareness of, knowledge about, and opinions concerning hydrogen and related technologies
- Design a survey that assesses the general public's knowledge of hydrogen and related technologies

Technical Barriers

This project addresses the following technical barriers from the Education section of the Hydrogen, Fuel Cells, and Infrastructure Technologies (HFCIT) Program Multi-Year R,D&D Plan:

- A. Lack of Awareness
- C. Institutional Barriers and Access to Audiences
- D. Regional Differences

Approach

- Conduct a literature search for previously conducted surveys that are related to the hydrogen economy, hydrogen technologies, and fuel cells
- Establish liaison with Office of Management and Budget (OMB) and prepare paperwork for obtaining OMB approval for conducting surveys
- Identify specific educational content for the target audiences (general public, students and educators, state and local agencies, and large-scale users) to consider when developing survey instruments
- Develop survey instrument for public survey and initiate development of other survey questionnaires

Accomplishments

- Completed draft literature search and documented results
- Began dialogue with appropriate contacts to obtain OMB approval of surveys
- Submitted draft Federal Register Notice about the information collection to the DOE office of the Chief Information Officer
- Completed planning for and design of general public survey, initiated work on surveys for other populations, and initiated collection of non-survey metrics
- Initiated survey analysis plan

Future Directions

- Conduct and analyze surveys of the general public, students and educators, state and local government agencies, and large-scale users
- Determine and document the baseline knowledge of hydrogen and fuel cells for the four populations involved in the surveys
- Identify subject areas where hydrogen knowledge is lacking
- Identify institutional barriers that prevent target audiences from receiving instruction or becoming informed about hydrogen technologies and applications
- Use the survey results to identify differences, where appropriate, among audiences, regions, genders, and age groups
- Determine the appropriate mechanism for conveying information about hydrogen and hydrogen technologies to each of the audiences
- Continue collection and analysis of non-survey metrics
- Document survey and non-survey metrics findings in a report

Introduction

The HFCIT Program needs to determine the baseline knowledge of hydrogen and fuel cells in the United States in order to design an appropriate educational program and, in the future, to assess the effectiveness of education activities. Baseline knowledge of hydrogen and fuel cells will be determined through surveys of four distinct population groups - the general public, students and educators, state and local governments, and potential large-scale users and/or agencies that impact large-scale users. Each of these populations is very different and requires a different approach for assessing knowledge. While recognizing that knowledge-assessment surveys cannot pinpoint causality of changes in knowledge and opinions, subsequent surveys identical in methodology to the baseline surveys can measure changes from baseline knowledge levels. The effect of the educational program will be measured in terms of program activities designed to impact baseline knowledge levels.

Approach

This task was initiated during FY 2003 through planning sessions, a literature search, and pilot questionnaires to ensure that the surveys were well-defined and that the objectives for both current and future surveys would be accomplished. A matrix was prepared that mapped each survey audience against the primary categories of educational information to ensure that the survey questions would address the appropriate content.

Results

Because this is a new task, there are no results to report at this time.

Conclusions

Although surveys have been conducted by several organizations concerning alternative fuels, and some surveys have been conducted on hydrogen and/or fuel cell applications, there has been no statistically designed, random survey of the U.S. population to determine the baseline knowledge of hydrogen and fuel cells. Nor has there been a systematic collection and assessment of non-survey materials related to the hydrogen economy. This type of hard evidence is needed in order to prepare the appropriate educational materials for the very wide-ranging audiences targeted for the HFCIT Program.

FY 2003 Publications/Presentations

1. Truett, et al. *Literature Review for the Baseline Knowledge Assessment of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program,* Draft Final Report, June 2003

Database of Existing Hydrogen and Fuel Cell-related Courses and Research Activities at Universities

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Objectives

- Develop a comprehensive online catalog of college and university programs teaching and conducting research in the areas of hydrogen and fuel cell technologies
- Categorize institutions by accreditation status; collect and organize information on institutions: location, unit offering program, research and course descriptions; gather data on faculty and their research interests
- Verify and maintain the database
- Launch the catalog on the web

Technical Barriers

This project addresses the following technical barriers from the Education section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Lack of Awareness
- C. Institutional Barriers and Access to Audiences

Approach

- Search web and review literature to determine if information is already accessible
- Determine accreditation level of programs to be included
- Identify conference and seminar participants as well as authors of specialized books and magazines affiliated with schools
- Gather information on faculty and institutions with an interest in hydrogen and fuel cell technology
- Verify credibility and accuracy (via web and personal interviews) of data yielded by research
- Organize information by institution and create a searchable online database of over 70 institutions within the scope of this phase
- Develop methods of collecting and verifying upcoming data

Accomplishments

- Documented current availability of educational opportunities related to hydrogen economy and fuel cell technologies

- Described programs and courses
- Collect data on faculty and research members

Future Directions

- Designed searchable online catalog for use by educators, students, advisors, and government agencies
- Confirm accuracy of data by creating a validation website for ongoing updates
- Launch the catalog on the web
- Increase number of tables linked to the main database, creating connections to individuals and research projects to help users refine searches
- Include statistics on Ph.D. graduates from institutions (e.g., number of dissertations on hydrogen and fuel cell topics, etc.)
- Include statistics of patent applications from affiliated institutions related to hydrogen and fuel cell technologies
- Increase and maintain information in the catalog

Introduction

The purpose of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Education Program is to develop and conduct an education and training campaign that communicates the long-term benefits and near-term realities of hydrogen fuel cell systems and related infrastructure. A necessary element of this goal is to achieve a level of awareness of hydrogen's benefits among educators, other key target audiences, and eventually the public, while supporting the creation of the skilled and informed workforce required for a hydrogen future. As the R,D&D Plan for Education notes, initial education efforts will focus on teachers and students, state and local governments, safety and code officials, and large-scale end-users, all of whom are critical to sustained education efforts. The catalog resulting from this study documents the current availability of educational opportunities related to the hydrogen economy and fuel cell technologies as an aid to these targeted audiences.

Approach

This research considered only institutions of higher education with engineering programs accredited by the Accreditation Board for Engineering and Technology (ABET). U.S. accreditation is a voluntary, non-governmental process of peer review used to assure quality in educational institutions and programs. Most of the information included in the catalog has been gathered by searching university, library, and interest group web sites. The study has also identified people participating in conferences, seminars, or workshops covering hydrogen and fuel cell technology topics. Additionally, data has been accumulated by searching library databases and reviewing literature in the form of books, textbooks, conference proceedings, handbooks, industry and research-related overviews, government reports, and others. Information has also been obtained by phone and email contact with researchers and teaching faculty as well as authors of books related to hydrogen and fuel cells technologies.

The study includes over 70 institutions, describing them on specific levels of detail. However, the accuracy of some data is questionable since school webmasters and professors often do not update their pages frequently. Therefore, in order to deliver precise and exact information, the database will be validated and will be maintained on an ongoing basis by means of a validation web site. This kind of interactive web site would give the directors of the research programs and faculty members the opportunity to express their willingness to be included in the catalog as well as to view and modify the data presented.

Results

A catalog has been developed in the form of a searchable database that categorizes detailed information about institutions offering research programs or courses related to hydrogen or fuel cell technologies. The catalog includes the following information: institution's name, location, organizational units offering related programs (academic department, center, and laboratory), types and names of courses covering hydrogen economy and fuel cell technology topics, descriptions of the research programs and courses, and names of faculty and research members affiliated with the program. This database will be linked to a database containing records of over 300 faculty and research members as well as their research interests, and full contact information like mailing address; email; homepage links; affiliated school; and academic department, center, or laboratory links.

The catalog should be useful to many audiences, including educators (teaching faculty, counselors and advisors) who are looking for new career opportunities in research and teaching, students (undergraduate and graduate, current and prospective students) searching for educational and research programs that fit their interests, and business entrepreneurs seeking new technologies in research centers. Stakeholders such as state and local governments needing objective and accurate information in order to make informed decisions about sponsoring certain programs will also find the catalog useful.

Conclusions

The catalog promises to become an essential instrument in the search for hydrogen- and fuel-cell-related educational opportunities for a broad spectrum of users. It may also be a useful tool for measuring the current status of hydrogen and fuel cell education and may provide a baseline for planning to expand hydrogen and fuel cell education programs. Government agencies such as DOE could use the catalog as a reference point in measuring the effectiveness of upcoming efforts to raise awareness and public support.

As hydrogen research and education expands, new information about programs, courses, and educators involved in activities related to hydrogen and fuel cells will be added to the catalog. Additional tables will be made available through links, making the database more comprehensive for educators, students, government agencies, and perhaps the general public.

Reduced Turbine Emissions Using Hydrogen-Enriched Fuels

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Objectives

- Quantify effect of hydrogen addition on gas turbine combustion and emissions.
- Establish a scientific and technological database for lean combustion of hydrogen-enriched fuels in gas turbines.
- Establish numerical simulation capabilities that will facilitate design optimization of hydrogen and hydrogen-enriched lean gas turbine combustors.
- Develop criteria for use of hydrogen addition as a control knob to eliminate instabilities related to varying product gas composition.

Technical Barriers

- The addition of hydrogen to hydrocarbon fuels affects flame stability, combustor acoustics, pollutant emissions and combustor efficiency. Few of these issues are clearly understood.
- Designing a system that can operate over a wide range of fuels while controlling emissions is a challenging task.

Approach

- Design and fabricate a lean premixed swirl burner that simulates the basic features of gas turbine combustors.
- Apply advanced experimental diagnostics to understand fluid dynamics, combustion chemistry, and pollutant formation.
- Develop a computational model for combustor performance in parallel with the experimental program based on next generation Large Eddy Simulation (LES) technique. Use experimental database for model validation.
- Identify problem areas in practical gas turbine combustors where hydrogen enrichment of hydrocarbon fuels could be beneficial.

Accomplishments

- Characterized operation of lean premixed swirl burner over a range of conditions.
- Quantified effect of H_2 addition on lean flame stability and characterized flame structure. Selected target flame conditions for detailed experimental study and model validation.
- Fabricated atmospheric- and high-pressure versions of a lean premixed swirl burner in collaboration with National Energy Technology Laboratory (NETL).
- Selected General Electric Aircraft Engines (GEAE) swirlcup injector to evaluate the advantages of H_2-addition in a production fuel injector. Completed hardware for installation of swirlcup injector in test stand.

- Formed new collaboration with Pratt and Whitney to evaluate a production fuel injector for use with H_2-blended fuels.
- Continued international effort through International Energy Agency (IEA) to address H_2-enriched hydrocarbon fuels for low emission, high efficiency gas turbine combustion. Defined program elements and identified modeling and experimental task areas.

Future Directions

- Complete detailed mapping of velocity field for model validation in the nonreacting swirl burner. Obtain detailed measurements of the velocity, temperature, species concentration fields and exhaust emissions under reacting conditions. Quantify effects of H_2 addition.
- Establish a representation of flow characteristics in the swirl burner using the LES model approach.
- Establish a framework for modeling hydrogen-enriched lean premixed combustion in the presence of acoustically-active flame processes.
- Complete development of test matrix for GEAE swirlcup fuel injector and perform testing. Identify areas where hydrogen enrichment could be beneficial.
- Continue the formation of a broad consortium of industrial partners.
- Continue development of international collaborations through the IEA.

Introduction

The development of advanced combustion capabilities for gaseous hydrogen and hydrogen-blended hydrocarbon fuels in gas turbine applications is an area of much current interest. Driving this interest are several current needs. One need is the cost-effective utilization of alternative fuels with a wide range of heating values. For example, fuels containing significant amounts of hydrogen are often produced as a by-product in coal gasification combined cycle installations. These product gases could provide a significant source of cost-effective fuel for gas turbines. A second need is related to the recognition that ultra-lean premixed combustion is an effective approach to NO_x emission reduction from gas turbine engines. Hydrogen blended with traditional hydrocarbon fuels significantly improves flame stability during lean combustion and allows stable combustion at the low temperatures needed to minimize NO_x production.

A longer-term need is the desire to eliminate unburned hydrocarbon (UHC) and CO_2 emissions. Gas turbines account for 15% of U.S. CO_2 emissions, which is a significant fraction of the total current CO_2 emissions. This number will increase to nearly 30% as natural gas turbines replace older coal-fired steam generation plants. The use of hydrogen-blended hydrocarbon fuels thus provides both a solution to the immediate need for NO_x reduction and also a transition strategy to a carbon-free energy system in the future.

Approach

The addition of hydrogen to hydrocarbon fuels affects both the chemical and physical processes occurring in flames. These changes affect flame stability, combustor acoustics, pollutant emissions and combustor efficiency. Few of these issues are clearly understood. This project will investigate issues surrounding the use of hydrogen and hydrogen-enriched hydrocarbon fuels in gas turbines. Both experimental and modeling approaches are being utilized. The experimental data will be obtained using an array of advanced laser diagnostic techniques that provide information on flame structure, fluid dynamics, combustion gas species concentrations and temperature. These measurements, in addition to providing direct insights into the effects of hydrogen enrichment on combustion and pollutant emissions, will provide the technological database needed for the parallel development of a numerical code, based on the LES technique, to simulate lean premixed combustion of hydrogen and hydrogen-enriched fuels. Close collaborations have been developed with industrial partners to provide a mechanism for the transfer of this technology to practical applications in stationary and aircraft gas turbines. These collaborations will facilitate the identification of problematic areas related to practical gas turbine design and hardware. Areas where hydrogen addition could prove beneficial will be identified, and the potential merits of hydrogen-enriched hydrocarbon fuels will be demonstrated.

Results

The lean premixed swirl burner shown in Figure 1 is representative of land-based industrial applications. This burner will be used to study combustion of hydrogen and hydrogen-blended hydrocarbon fuels. The design emphasizes well-characterized flow and boundary conditions to facilitate the development of a database for LES model validation. Emphasis with regard to LES has been placed on providing support calculations for design purposes and establishing an initial baseline-modeling framework for treatment of hydrogen-enriched, premixed methane flames. The burner design is operationally relevant to industrial devices and is optimally tuned for flow and diagnostic capabilities at the Sandia Combustion Research Facility.

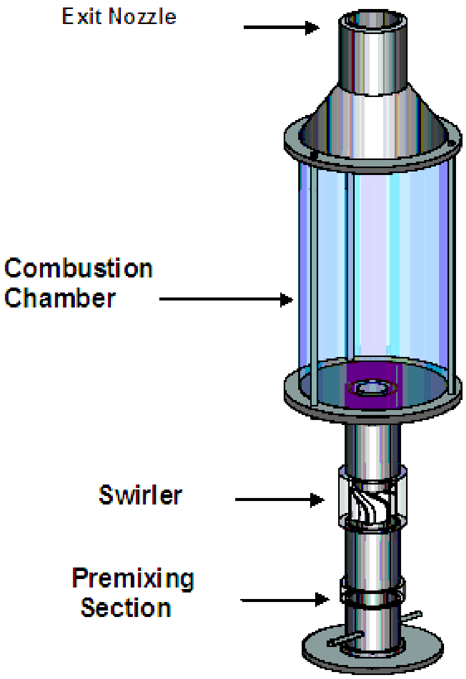

Figure 1. Lean Premixed Swirl Burner Designed to Study Combustion of Hydrogen and Hydrogen-Blended Hydrocarbon Fuels

The stability and burning characteristics of fuel-lean hydrogen/methane/air flames were characterized over a range of operating conditions in the swirl burner. Figure 2 shows the effect of hydrogen addition on flame stability, where the variable n_{H2} is the fraction of hydrogen in the fuel (n_{H2}=0 corresponds to pure methane and n_{H2}=1 is pure hydrogen). The equivalence ratio, f, is a measure of the fuel/air ratio. These measurements were obtained by igniting the flame and then decreasing the fuel/air ratio until the flame completely extinguished, or blew out. The flame typically becomes unstable as the blowout condition is approached. Increasing the hydrogen content from 0% to 20% results in a significant shift in flame blowout conditions to leaner fuel/air ratios. Since operation at leaner fuel/air ratios results in a lower flame temperature and reduced NO_x emissions, hydrogen addition will allow stable operation at the lean conditions needed to limit NO_x emissions.

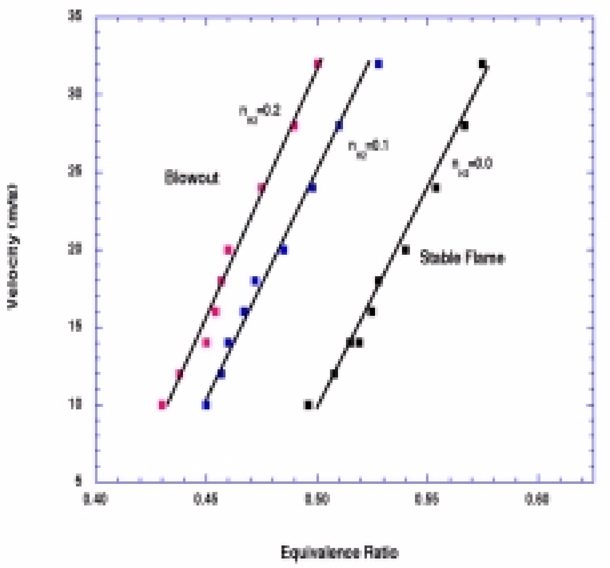

Figure 2. Effect of Hydrogen Addition on Flame Stability in Lean Swirl Burner

A previous study analyzed the potential of controlling NO_x emissions with the addition of hydrogen [1]. It was found that up to 20% hydrogen addition is a competitive alternative to traditional NO_x control technologies, providing NO_x levels of about 3 ppm. This study was extended to include the potential benefits of reduced CO_2 emissions by hydrogen addition as well as NO_x reduction. Figure 3 compares the cost of NO_x removal using H_2 addition with the costs of conventional selective catalytic reduction of NO_x ($SCONO_x$) and chemical absorption for CO_2 removal. While 60-100% hydrogen addition is not competitive with $SCONO_x$ alone, up to 75% hydrogen addition is cost competitive when the cost of CO_2 removal is included.

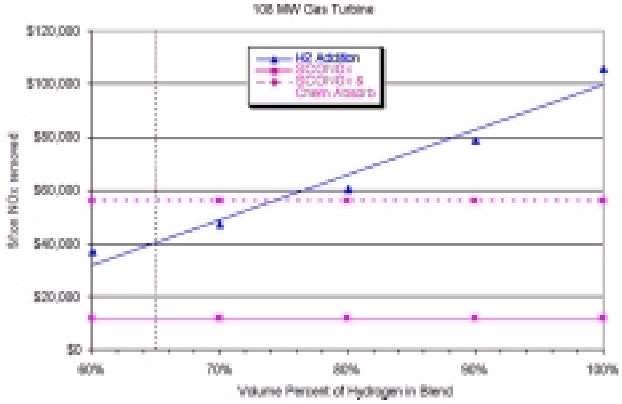

Figure 3. Cost sensitivity to percent hydrogen in natural gas. Estimated NO_x emissions are 1 ppm with high percentage CO_2 reduction.

Conclusions

- Hydrogen addition significantly improves flame stability and allows stable burner operation at the lean fuel/air ratios needed for reduced NO_x emissions.
- Up to 65% hydrogen addition for NO_x reduction to the 1 ppm level is cost competitive with current control technologies when both NO_x emissions and the cost of CO_2 removal are considered.

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3. Vagelopoulos, C. M., Oefelein, J. C. and Schefer, R. W., "Response of Lean Premixed Methane Flames to Hydrogen Enrichment", Proceedings of the Third Joint Meeting of the U.S. Sections of the Combustion Institute, March 17-19, Chicago, IL (2003).

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Premixed Methane Flames", 14th Annual U.S. Hydrogen Conference and Hydrogen Expo USA, March 4-6, Washington, D.C. (2003).

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Developing a Thermodynamic Fuel Cell

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Objectives

Demonstrate a combustion-based approach to electrical generation, maximizing the thermodynamic cycle and thus achieving high efficiency and near-zero emissions, while facilitating a path to hydrogen and hydrogen-rich fuels utilization.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell Transportation Systems section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- D. Fuel Cell Power System Benchmarking

Approach

- Analyze significant components of the thermodynamic fuel cell, including homogeneous charge compression ignition (HCCI) combustion, linear electrical generation and two-stroke cycle charging, employing experimental and computational means.
- Design major sub-systems based on achieving maximum electrical conversion efficiency and minimal operating emissions.
- Integrate components into a full-scale prototype with a rated power output of 30 kW.
- Demonstrate the device's operating performance and fuel versatility.

Accomplishments

- Experimentally established the potential of HCCI combustion using a free piston configuration (30-kW, 2-kW sizes) to realize significant improvements in thermal efficiency and NO_x emissions.
- Computationally analyzed, designed and constructed a full scale linear alternator. Collaborated with Magnequench, Int. to design and manufacture a similar, but significantly different linear alternator at no cost to Sandia.
- Reconfigured a 4-cylinder Caterpillar engine to test the performance of the two linear alternator designs at full power output.
- Computationally developed an optimized gas transfer system with respect to the thermodynamic fuel cell's operating characteristics and two-stroke cycle dynamics.
- Investigated the performance of a hybrid thermodynamic fuel cell/turbine system.
- Completed preliminary designs for a 4-kW free piston gas compressor (Sandia funded).

Future Directions

- Measure and evaluate linear alternator performance. Modify/adjust configurations based on dynamic testing.
- Investigate additional scavenging designs incorporating late, port fuel injection for short-circuited emissions control. Verify computational results using a free piston, single-stroke scavenging experiment.
- Develop control schemes to facilitate nominal operation.
- Integrate components into a full-scale demonstration prototype.
- Form industrial consortium for commercial application.

Introduction

High efficiency, low emissions electrical generators will lead to a path for renewable hydrogen-based fuel utilization. Electrochemical fuel cells are generally considered to be ideal devices for these applications, where hydrogen or methane is used as the fuel. However, the extensive development of the internal combustion engine, and the existence of repair and maintenance industries associated with piston engines, provide strong incentives to remain with this technology until electrochemical fuel cells are proven reliable and cost competitive.

The thermodynamic fuel cell is based on utilizing homogeneous charge compression ignition (HCCI) combustion of very lean ($\phi \sim 0.3$) fuel-air mixtures to approach ideal Otto cycle performance (the most thermodynamically efficient option for piston engines). HCCI is extremely rapid (nearly constant-volume), with numerous ignition points occurring throughout the charge; chemical kinetics dominate while there are no flame propagation or fuel diffusion requirements [1]. In addition, virtually any fuel-air mixture can be used, with NO_x emissions controlled through sufficient charge dilution and rapid expansion of the combustion gases [2]. Sandia's concept, illustrated in Figure 1, employs a free piston/linear alternator combination to facilitate direct electrical generation, thus enabling electronic control of the HCCI process and therefore the performance of the fuel cell. Structural integrity (for high peak pressures), design simplicity and cost issues are addressed with this unique design.

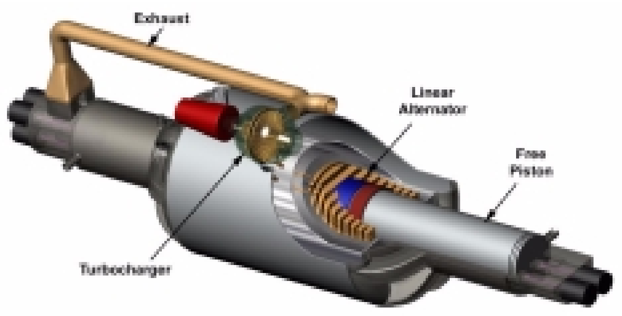

Figure 1. Thermodynamic Fuel Cell

Approach

This research project aims to investigate and resolve critical issues involved in developing the thermodynamic fuel cell. The end goal is to construct a full-scale prototype that can demonstrate the device's efficiency and emissions potential, as well as its fuel versatility. Major processes of HCCI combustion, linear electrical generation and two-stroke cycle charge delivery have been investigated in previous years using both experimental and computational means. The objective has been to verify the capabilities of the critical components while determining the factors that will affect the performance of the integrated configuration.

During fiscal year 2003, efforts were made to continue to design, build and test various components, and to further develop industrial partnerships; commercial relationships are expected to facilitate the rapid transfer of this technology to the marketplace after concept demonstration. Work this year focused on aspects of the linear alternator and the scavenging system, as well as additional studies investigating the benefits of a combined thermodynamic fuel cell / turbine hybrid system.

Results

The alternator test rig, illustrated in Figure 2, became operational this year, with issues regarding the piston's integrity seemingly resolved. A test procedure has been developed and preliminary data acquired using the Magnequench constructed alternator, without the inclusion of the permanent magnets. The magnets will be attached to the piston next and tests run under both load and no-load conditions. A switching mechanism will need to be developed to achieve the rated output for this design (as explained in previous FY reports); however, comparison with Magsoft FLUX2D software's performance predictions and an evaluation of its accuracy should be possible in the coming months.

Multi-dimensional modeling of the scavenging system was employed to analyze and design an optimal arrangement; this configuration will be fabricated and tested using a single-cycle experiment. Figure 3 illustrates an arrangement expected to give very good performance (charge replacement greater than 90%, with fuel trapping capabilities near 100%). In this "stratified-scavenging" design, an initial charge of fresh air (yellow) flushes the combustion products from the cylinder (orange), while a rich fuel-air mixture (blue) is introduced late in the gas transfer process. A late, port fuel-injected configuration to be investigated in FY 2004 represents a natural progression in this component's development and should improve short-circuiting controllability.

Full cycle thermodynamic modeling utilizing zero-dimensional representations of the in-cylinder processes, the free piston dynamics, and assumed efficiencies for a turbocharger/compressor combination, was used to conduct a feasibility study analyzing a thermodynamic fuel cell/turbine combination [3]. Simulations were conducted over a range of possible boost pressures, from 1.2 bar through 3.0 bar. The results indicated that the emissions performance is unchanged for these variations; however, the free piston dynamics can be significantly altered by an increase in cylinder pressure. For the highest boost case, the frequency increased 45%. In addition, the combustion pressures were also calculated to be sensitive to any boost, with the peak pressure increasing to 445 bar (from 230 bar) for the 3.0 bar boost case.

The performance improvements for the hybrid system are presented in Figure 4. The changes in generating efficiency (↑7% at 2.5 bar) and power density (↑38% at 3.0 bar) with increasing boost pressure are plotted. It can be seen that there is a maximum efficiency that can be reached in this hybrid arrangement due to the performance limit of current turbocharger and compressor technologies. The power density, on the other hand, did not seem to have a limit for the conditions investigated.

Figure 2. Alternator Test Rig

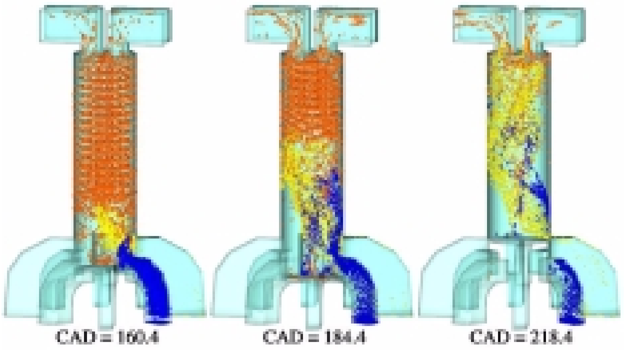

Figure 3. Calculated Stratified-Scavenging Flows

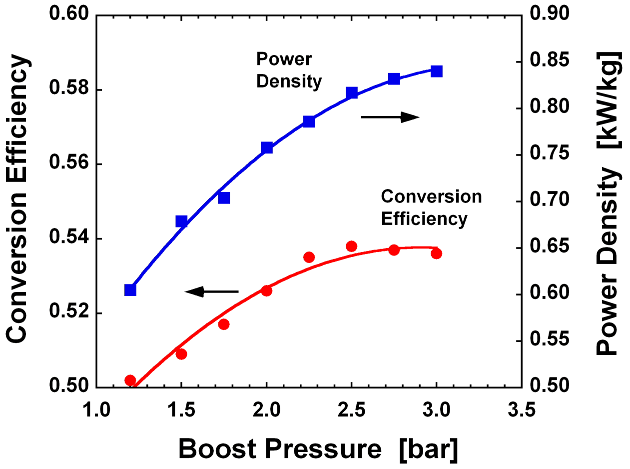

Figure 4. Fuel-to-Electricity Conversion Efficiency and Power Density vs. Boost Pressure

Conclusions

- The thermodynamic fuel cell represents a near term (2010) option for achieving the DOE's Hydrogen, Fuel Cells and Infrastructure Technologies Program goals of significantly advancing the operating efficiency and emissions performance of electrical generating devices, while creating a path for renewable hydrogen-based fuel utilization.
- A prototype design is moving forward, with the performance of each major sub-system being quantified.
- To date, no unsolvable barriers have materialized.

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Special Recognitions & Awards/Patents Issued

1. Van Blarigan, P., "Free-Piston Engine," US Patent # 6,199,519 B1

2. Harry L. Horning Memorial Award, Society of Automotive Engineers, 1998

HCNG Heavy Duty Vehicle Prime Mover

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Objectives

- Develop a low-emissions heavy-duty vehicle engine repowering package that seamlessly replaces existing natural gas and diesel engines in today's buses and trucks.
- Exceed DOE's goal of reducing emissions by 75% compared to 1998 emission standards by achieving a 99.5% reduction. Corresponding emission levels of carbon monoxide (CO) will be <1 ppm; non-methane hydrocarbon (NMHC) emissions will be <0.05 g/hp-hr; and oxides of nitrogen (NO_x) will be <0.15 g/hp-hr.
- Maintain or enhance current vehicle driveability by effective selection, matching, and configuring of off-the-shelf components.
- Meet DOE's requirement to maintain thermal efficiency by obtaining an overall thermal efficiency of greater than 35%.
- Prove and enhance the engine design through in-service testing.
- Develop a public/private partnership to implement a commercialization plan that will bring new business and economic opportunities to Nevada.

Technical Barriers

This project addresses the following technical barrier from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Vehicles

Approach

- Use hydrogen added to natural gas (HCNG) to achieve high charge dilution ratios to create near-zero NO_x emissions.
- Incorporate an alternative engine design from that of current heavy-duty engines. Engine design features include:
  - Nickel silicon carbide cylinder bores
  - Quiescent combustion
  - Higher rpm operation
  - Larger displacement
  - Mass air flow engine control

Accomplishments

- Demonstrated 0.14 g/hp-hr simulated driving cycle NO_x emissions.
- Produced equivalent power and torque to natural gas engine.
- Demonstrated 38% engine efficiency.
- Bus is currently operating in Las Vegas.

Future Directions

- Expand the work to convert five additional City of Las Vegas buses to HCNG.
- Market HCNG hydrogen technology to other transit districts.

Introduction

The use of hydrogen as a fuel additive to extend the lean burn limit of conventional fuels has been repeatedly demonstrated to be a viable approach to achieving near-zero exhaust emissions from internal combustion engines. This technology is intended to be a near-term application for hydrogen and to accelerate hydrogen infrastructure development given the current economic climate. Hydrogen fuel-related problems such as high fuel cost, high prime mover costs (fuel cells) and low energy density are largely overcome by supplementing an existing, higher energy storage density, lower-cost fuel, such as natural gas, and implementing a low-cost prime mover such as internal combustion engines.

Demonstrating that this low-cost hydrogen technology can improve emissions of oxides of nitrogen by a factor of thirty over current generation natural gas engines can create the incentive by which a hydrogen infrastructure can be developed that will be necessary for the successful implementation of fuel cells.

Approach

Collier Technologies, LLC is using charge dilution as the mechanism for controlling harmful exhaust emissions. The basic technique employed is to combine exhaust gas recirculation (EGR) and lean burn. Cooled and dried EGR is used to control NO_x emissions and lean burn to control CO and NMHC emissions. It is anticipated that lean burn will achieve approximately 2 to 4% oxygen in the exhaust. This will allow an off-the-shelf oxidizing catalyst to achieve very high conversion rates for both CO and NMHC emissions. Because the exhaust gas temperatures will be comparatively very low (<1000°F), catalyst lifetime should be extremely high (>100,000 miles).

To achieve near-zero NO_x emissions (10 to 20 ppm) using charge dilution, the engine must operate with an overall lambda (air-fuel ratio divided by the stoichiometric air-fuel ratio, including EGR) of between 1.8 and 2.0. To achieve this value, at least 30%, by volume, of the fuel must be hydrogen. Any less than that will not support sufficiently consistent combustion from cylinder to cylinder or from cycle to cycle. Any attempts to achieve this through mechanical means (high turbulence combustion chambers, etc.) will result in loss of engine efficiency through increased combustion chamber heat transfer rates and increased NO_x emissions compared to "quiescent" or open combustion chambers and hydrogen addition to the fuel. The result is that mechanical enhancement (swirl, tumble, etc.) for lean burn will require higher values of lambda to achieve equivalent NO_x emissions to that achieved by hydrogen as a fuel enhancement.

Results

A 30-ft transit bus was purchased by DOE and shipped to Collier Technologies (then called NRG Tech) for conversion to HCNG operation. This bus came equipped with a Cummins 8.3L natural gas engine. The project called for characterizing the exhaust emissions from the current configuration so that the benefits of HCNG can be quantitatively assessed. Baseline exhaust emissions were taken from the engine using a steady state emissions test protocol that is designed to simulate the heavy-duty driving test procedure. This protocol is as follows:

Engine rpm at maximum torque value

Test Point 1100% loadEmissions are 15% of final value

Test Point 275% loadEmissions are 15% of final value

Test Point 350% loadEmissions are 15% of final value

Test Point 410% loadEmissions are 10% of final value

Engine rpm at maximum power value

Test Point 5100% powerEmissions are 10% of final value

Test Point 675% powerEmissions are 10% of final value

Test Point 750% powerEmissions are 10% of final value

Test Point 8IdleEmissions are 15% of final value

The results of testing the Cummins engine that was installed in this bus using the protocol listed above are shown in Table 1.

Emissions results for the 8.8L Collier Technologies engine using the same testing protocol and using a 30/70 mixture of hydrogen and natural gas are shown in Table 2.

Table 1. 8-Mode Steady State Emissions Summary
Cummins 8.3L Natural Gas Engine (as received)

Individual Modes		NO_x g/hp-hr	THC g/hp-hr	NMHC (g/hp-hr)	CO g/hp-hr	Weighting Factor
1400 rpm	- 100% Load	7.42	5.21	0.16	0.19	0.15
	- 75% Load	4.70	2.57	0.08	0.22	0.15
	- 50% Load	5.67	3.37	0.10	0.25	0.15
	- 10% Load	5.77	7.70	0.23	0.59	0.10
2400 rpm	- 100% Load	1.18	2.82	0.08	0.28	0.10
	- 75% Load	0.80	4.26	0.13	0.32	0.10
	- 50% Load	0.44	5.56	0.17	0.37	0.10
800 rpm	- Idle	6.96	107.74	3.23	12.98	0.15
Weighted 8 Mode (g/hp-hr)		4.60	19.87	0.58	2.20	
Weighted 8 Mode (g/kw-hr)		6.16	26.63	0.78	2.95	

Table 2. 8-Mode Steady State Emissions Summary
HCNG Bus Engine

Individual Modes		NO_x g/hp-hr	THC g/hp-hr	NMHC (g/hp-hr)	CO g/hp-hr	Weighting Factor
1800 rpm	- 100% Load	0.15	3.70	0.11	0.00	0.15
	- 75% Load	0.12	3.86	0.12	0.00	0.15
	- 50% Load	0.09	4.86	0.15	0.00	0.15
	- 10% Load	0.13	8.82	0.26	0.00	0.10
2800 rpm	- 100% Load	0.21	3.31	0.10	0.00	0.10
	- 75% Load	0.15	3.77	0.11	0.00	0.10
	- 50% Load	0.10	5.75	0.17	0.00	0.10
800 rpm	- Idle	0.22	7.21	0.22	0.00	0.15
Weighted 8 Mode (g/hp-hr)		0.15	5.11	0.15	0.00	
Weighted 8 Mode (g/kw-hr)		0.20	6.85	0.21	0.00	

Conclusions

Emissions, power, torque, and efficiency goals have been met with our project methodology. NO_x emissions have been reduced by a factor of 30 when compared to the existing engine without a loss of power, torque characteristics or fuel efficiency. Major milestones for the remainder of the project will be to demonstrate drivability in an operating bus and verify exhaust emissions in a driving test.

Acronyms and Abbreviations

Δspec	Absorbance-difference kinetic spectrophotometry
Å	Angstrom (one hundred-millionth of a centimeter)
A/C	Air Conditioner
ABET	Accreditation Board for Engineering and Technology
AC	Alternating Current
ACR	Autothermal Cyclic Reforming
AER	Absorption-Enhanced Reforming
AFC	Alkaline Fuel Cell
Ag	Silver
AGB	Anode Gas Burner
AHC	Ad Hoc Committee
AirCred	Air Quality Credits
Al	Aluminum
Al_2O_2	Aluminum Oxide
$AlCl_3$	Aluminum Chloride
ANL	Argonne National Laboratory
ANT	Albany NanoTech
APU	Auxiliary Power Unit
a-Si	Amorphous Silicon
ASME	American Society of Mechanical Engineers
ASR	Area Specific Resistance
ASU	Air Separation Unit
atm	atmosphere
ATMI	Advanced Technical Materials Incorporated
ATP	Adenosine Triphosphate
ATR	Autothermal Reformer/Reforming/Reactor
Au	Gold
B	Boron
barg	Bar Gauge
bdt	Bone Dry Ton
BNL	Brookhaven National Laboratory
BOP	Balance of Plant
BP	British Petroleum
BPSH	Biphenyl sulfones
Br	Bromine
BSE	Back Scattered Electron
BTU	British Thermal Unit
C	Carbon
^oC	Degrees Centigrade
C_2H_4	Ethylene
Ca	Calcium
$CaBr_2$	Calcium Bromide
CAD	Computer Aided Design
CAE	Computer Aided Engineering
CaO	Calcium Oxide
CARB	California Air Resources Board
CATA	Center Area Transport Authority
CBS	Specific Strain of Rubrivivax Gelatinosus
CCH	Complex Compound Hydride
CCHS	Complex Compound Hydrogen Storage System
CCM	Catalyst Coated Membrane
Ce	Cerium
CE	European Conformity
CEC	California Energy Commission
CEM	Compressor Expander Motor/Continuous Emissions Monitoring
CERMET	Ceramic and Metal
CESI	Catalytic Energy Systems Inc
CF	Capacity Factor
CFA	Community Fuel Appliance
CFD	Computational Fluid Dynamics
CFR	Code of Federal Regulations
CGA	Compressed Gas Association
CGO	Cerium-Gadolinium Oxide ($Ce_{0.8}Gd_{0.2}O_{1.9}$)
CH_2	Compressed Hydrogen Gas
CH2-ISS	Compressed Hydrogen Gas Integrated Storage System
CH_4	Methane
Chl	Chlorophyll
CIGS	Copper-Indium-Gallium-Diselenide
CL&P	Connecticut Light and Power
CLV	City of Las Vegas
cm^2	Centimeters Squared
CMS	Crash Management System
CMWG	Carbon Materials Working Group
CNG	Compressed Natural Gas
CNR	Center for Neutron Research
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COE	Cost of Electricity
COGEN	Combined Building Heat and Power
COS	Carbonyl Sulfide
CPO	Catalytic Partial Oxidation
CPS	Chemical Process Simulation
cpsi	cells per square inch

CPSS	Combinatorial Powder Synthesis System
Cr	Chromium
CS	Constant Stoichiometry
CS&D	Compression, Storage and Dispensing
CSMP	Cabot Superior Micropowders
CST	Compact Stuart Technology
Cu	Copper
Cu_2O	Cuprous Oxide
CVD	Chemical Vapor Deposition
CVI	Chemical Vapor Infiltration
CWRU	Case Western Reserve University
CY	Calendar Year
DBEDT	Department of Business, Economic Development and Tourism (Hawaii)
DC	Direct Current
DCF	Discounted Cash Flow
DCM	Dichloromethane
DEP	Department of Environmental Protection
DER	Distributed Energy Resources
DFMA	Design for Manufacture and Assembly
DG	Distributed Generator
DME	Dimethylether
DMFC	Direct Methanol Fuel Cell
DNA	Deoxyribonucleic Acid
DNS	Direct Numerical Simulation
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
DP	Differential Pressure
DRIFTS	Diffuse Reflectance mid-Infrared Fourier Transform Spectroscopy
DSC	Differential Scanning Calorimetry
DTI	Directed Technologies Inc.
EB/GDL	Electrode Backing/Gas Diffusion Layer
EdNet	Educational Network
EDS	Engineering Development Specification
EERE	Energy Efficiency and Renewable Energy
EIHP	European Integrated Hydrogen Project
ELAT®	Registered Trademark of De Nora North America, Inc., covers GDLs and GDEs
EMF	Electromagnetic Field
EMI	Electromagnetic Interference
EMPA	Electron Microprobe Analysis
EPA	U.S. Environmental Protection Agency
EPR	Electron Paramagnetic Resonance
EPRI	Electric Power Research Institute
ERD	Energy Recovery Device
ESA	Electrochemical Surface Area
ESR	Electron Spin Resonance
ESS	Energy Storage System
ETS	Engelhard Titanosilicate (commercial membrane material name)
EXAFS	Extended X-ray Absorption Fine Structure
F	Force
FASTER	Feasibility of Acceptable Start Time Experimental Reactor
FC	Fuel Cell
FCCP	carbonyl cyanide *m*-chlorophenylhydrazone
FCE	Fuel Cell Energy
FCEV	Fuel Cell Electric Vehicle
FCPI	Fuel Cell Propulsion Institute
FCPS	Fuel Cell Power System
FCS	Fuel Cell System
FCTF	Fuel Cell Test Facility (Hawaii)
FCV	Fuel Cell Vehicle
Fd	Ferredoxin
Fe	Iron
Fe_2O_3	Ferric Oxide
Fe_3O_4	Magnetic Iron Oxide
$FeCl_3$	Ferric Chloride
$FePO_x$	Iron Phosphate
FET	Field Effect Transistor
FID	Flame Ionization Detector
FIT	Florida Institute of Technology
FMEA	Failure Mode and Effect Analysis
FP1	Fuel Processor One
FPD	Flame Photometric Detector
FPES	Fluorinated Polyether Sulfone
FPS	Fuel Processing System
FRACAS	Failure Reporting, Analysis and Corrective Action System
FreedomCAR	U.S. Department of Energy Automotive Research Partnership
FS-PEEK	Fluorinated Sulfonated Polyetheretherketone
FTA	Federal Transportation Administration

FTE	Full Time Equivalent
FUDS	Federal Urban Driving Schedule
g	Gram
GA	General Atomics Corporation
gal	Gallon
GaN	Gallium Nitride
GC	Gas Chromatograph/Gas Chromatography
GCtool	Power system analysis software developed by ANL
Gd_2O_2S:Eu	Gadolinium Oxy-Sulfide doped with Europium
GDATP	General Dynamics Armament & Technical Products
GDE	Gas Diffusion Electrode
GDL	Gas Diffusion Layer
GDS	Galvanodynamic Scan
Ge	Germanium
GEAE	General Electric Aircraft Engines
GGA	Generalized Gradient Approximation
gge	Gasoline Gallon Equivalent
GHG	Green House Gas
GHSV	Gas Hourly Space Velocity
GJ	Gigajoule (10^9 joules)
GREET	Greenhouse Gas Energy and Emissions in Transportation
GRPE	Working Party on Pollution and Energy
GTI	Gas Technology Institute
ΔH^o	Heat of Formation
H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen Sulfide
HAZOP	Hazardous Operations
HBr	Hydrobromic acid
HBT	Hydrogen Burner Technology
HC	Hydrocarbon
HCCI	Homogeneous Charge Compression Ignition
HCl	Hydrochloric Acid
HCN	Hydrogen Cyanide
HCNG	Hydrogen Compressed Natural Gas
HCSCC	Hydrogen Codes and Standards Coordinating Committee
HDPE	High Density Polyethylene
HECO	Hawaiian Electric Company
HELCO	Hawaii Electric Light Company
HEV	Hybrid Electric Vehicle
HF	Hydrogen Fluoride
HFCIT	Hydrogen, Fuel Cells, and Infrastructure Technologies
HHV	Higher Heating Value
HI	Hydroiodic Acid
HiQ	High-Efficiency, Quick Start Fuel Processor
HNEI	Hawaii Natural Energy Institute
HPA	Heteropolyacid
HPE	Hybrid Photoelectrode
H-PEDOT	Poly-3,4-ethylenedioxythiphene and ethylene glycol
HTE	High Temperature Electrolysis
HTGR	High Temperature Gas-cooled Reactor
HTM	Hydrogen Transport Membrane/ High Temperature Membrane
HTS	High Temperature Shift
HWCVD	Hot Wire Chemical Vapor Deposition
HX	Heat Exchanger
HydA1	Algal Hydrogenases
HYSYS	Aspen Technologies' CPS
I	Electrical Current
ICC	International Code Council
ICE	Internal Combustion Engine
ICEV	Internal Combustion Engine Vehicle
ICR	Interfacial Contact Resistance
IEA	International Energy Agency
IEC	International Electrotechnical Commission
IFS™	Interactive Future Simulations
IIT	Illinois Institute of Technology
INEEL	Idaho National Engineering and Environmental Laboratory
INS	Inelastic Neutron Scattering
IOS	Intelligent Optical Systems, Inc.
IPA	International Platinum
Ir	Iridium
IR	Infrared
ISO	International Organization for Standardization
ISS	Integrated Storage System
ISURF	Iowa State University Research Foundation
ITM	Ion Transport Membrane
ITO	Indium Tin Oxide
JHU/APL	Johns Hopkins University Applied Physics Laboratory
JPL	Jet Propulsion Laboratory
K/^{o}K	Degrees Kelvin

K_2O	Potassium Oxide
KBM	Knowledge Based Management
KC_x	Potassium Carbon when used with Intercalated Graphites
kg	Kilogram
KTH	Swedish Royal Institute
kW	Kilowatt
kW_e	Kilowatt electric
kWh	Kilowatt hour
kW_{th}	Kilowatt Thermal
La	Lanthanum
La-Ni-Al	Lanthanum-Nickel-Aluminum alloy
LANL	Los Alamos National Laboratory
lb	Pound
LC	Lumped Capacitance
LCHPP	Low Cost Hydrogen Production Platform
LDA	Local Density Approximation
LDRD	Laboratory Directed Research and Development
LDV	Light Duty Vehicle
LED	Light Emitting Diode
LEL	Lower Explosion Level
LES	Large Eddy Simulation
LH_2	Liquid Hydrogen
LHC	Light Harvesting Complex
LHV	Lower Heating Value
$LiAlH_4$	Lithium Aluminum Hydride
LiF	Lithium Fluoride
LLNL	Lawrence Livermore National Laboratory
LME	London Metals Exchange
LOX	Liquid Oxygen
LP	Linear Polarization
LTS	Low Temperature Shift
LV	Level Indicator
mA	MilliAmps
MC	Multicomponent
MDPD®	Market Driven Product Definition
MEA	Membrane Electrode Assembly
MEMS	Micro Electromechanical System
mg	Milligrams
Mg	Magnesium
MgH_2	Magnesium Hydride
MgO	Magnesium Oxide
MMBtu	Million British Thermal Units
MMD	Mass Median Diameters
Mn	Manganese
Mo	Molybdenum
MOFS	Multiplexed, Optical Fiber Sensor

mole/(m^2Pa•s):	Mole per Meter Squared Pascal Second
MPa	Mega Pascals
mpeg	Miles per Equivalent Gallon
mpg	Miles Per Gallon
MRI	Magnetic Resonance Imaging
MSE	Mercury/mercurous Sulfate reference Electrode
MSHA	Mine Safety and Health Administration
MSU	Montana State University
MSW	Municipal Solid Waste
mV	MilliVolts
mW	Megawatt
mWh	Megawatt hour
MWNT	Multi-Wall Nanotubes
N_2	Nitrogen
Na	Sodium
$NaAlH_4$	Sodium Aluminum Hydride
$NaBH_4$	Sodium Borohydride
NAFION®	Registered Trademark of E.I. DuPont de Nemours
NASA	National Aeronautics and Space Administration
Nb	Niobium
$NbPO_x$	Niobium phosphate
NEBS	Network Equipment Building Standards
NELHA	Natural Energy Laboratory Hawaii Authority
NERI	Nuclear Energy Research Initiative
NETL	National Energy Technology Laboratory
NFC	Near Frictionless Carbon
NFPA	National Fire Protection Association
NG	Natural Gas
NGASE	Natural Gas Assisted Steam Electrolyzer
NH_3	Ammonia
NHA	National Hydrogen Association
NHE	Normal Hydrogen Electrode
Ni	Nickel
NICC	Natural Gas Infrastructure Component Cost
NIF	Neutron Imaging Facility
NiO	Nickel Oxide
NIST	National Institute of Standards and Technology
nm	Nanometer
Nm^3	Normal Cubic Meter

NMHC	Non-Methane Hydrocarbon
NMOG	Non-Methane Organic Gases
NMR	Nuclear Magnetic Resonance
NO_x	Nitric Oxides
NPW	Net Present Worth
NREL	National Renewable Energy Laboratory
NRL	Naval Research Laboratory
NSLS	National Synchrotron Light Source
Ωcm^2	Ohm-Centimeter-Squared
O	Oxygen
O&M	Operation and Maintenance
O/C	Oxygen to Carbon ratio
O_2	Oxygen
OCP	Open Circuit Potential
OEM	Original Equipment Manufacturer
OH	Hydroxal Radical
Ohm-cm^2	Ohm-centemeter-squared
OMB	Office of Management and Budget
OPP	Office of Physical Plant
ORNL	Oak Ridge National Laboratory
ORR	Oxygen Reduction Reaction
OTM	Oxygen Transport Membrane
OTT	Office of Transportation Technologies
P	Pressure
PADT	Phoenix Analysis and Design Technologies
PAFC	Phosphoric Acid Fuel Cell
PAMPAS	Poly 2-acrylamino-2-methyl-1-propanesulfonic acid-co-styrene
PATH	Partnership for Advancing the Transition to Hydrogen
PBI	Polybenzimidazole
PCR	Polymerase Chain Reaction
PCT	Pressure Composition Temperature
Pd	Palladium
PDPA	Phase Doppler Particle Analyzer
PDU	Process Development Unit
PEC	Photoelectrochemical
PEDOT	Poly-3,4-ethylenedioxythiphene
PEEK	Polyetheretherketone
PEFC	Polymer Electrolyte Membrane Fuel Cell
PEM	Proton Exchange Membrane/ Polymer Electrolyte Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
PEN	Positive Electrolyte Negative
PFA	Personal Fuel Appliance
PFCT	Porvair Fuel Cell Technology, Inc
PFD	Process Flow Diagram
PFSA	Perfluorinated Sulfonic Acid
PGM	Platinum Group Metal
pH	Power of the Hydrogen Radical
PHA	Preliminary Hazard Analysis
PI	Principal Investigator
PM	Particulate Matter/ Particulate Membrane/ Precious Metal
PNA	Palladium Nanowire Arrays
PNNL	Pacific Northwest National Laboratory
POTW	Publicly Owned Treatment Works
PO_X	Partial Oxidation
PP	Polypropylene
PP1R	Power Plant One Reformate
ppb	Parts Per Billion
ppbv	Parts Per Billion by volume
ppm	Parts Per Million
ppmv	Parts Per Million by Volume
ppmw	Parts Per Million by Weight
PR	Progress Ratio
PROX/PrOx	Preferential Oxidation
PS	Photosystem
PSA	Pressure Swing Adsorption
psi	Pounds Per Square Inch
PSI	Paul Scherrer Institute
psia	Pounds Per Square Inch Absolute
psig	Pounds Per Square Inch Gauge
PSII	Photosystem II
PSU	Pennsylvania State University
Pt	Platinum
Pt-WO_3	Platinum-Tungsten Oxide
PV	Photovoltaic
R&D	Research and Development
RAM	Reliability and Maintenance
RD&D/R,D&D	Research, Development & Demonstration
RDE	Rotating Disk Electrode
Re	Rhenium
REI	Reaction Engineering International
RFC	Regenerative Fuel Cell
RFG	Reformulated Gasoline
RH	Relative Humidity
Rh	Rhodium
RHE	Real Hydrogen Electrode/ Reversible Hydrogen Electrode
RI	Receding Interface
ROI	Record of Invention
RPI	Rensselaer Polytechnic Institute

rpm	Revolutions per Minute
RRDE	Rotating Ring-disk Electrode
RTI	Research Triangle Institute
Ru	Ruthenium
Rz	Roughness (vertical)
S	Sulfur
S/C	Steam to Carbon ratio
S/cm	Siemens per Centimeter
S300	Series 300 Fuel Processing and PEM Cell System
S-A	Sulfur-Ammonia
SAE	Society of Automotive Engineers
SC	Single Component
SCAQD	South Coast Air Quality District
Sccm	Standard Cubic Centimeters per Minute
SCFD	Standard Cubic Feet per Day
SCFH	Standard Cubic Feet per Hour
SCFM	Standard Cubic Feet per Minute
SCONO$_x$	Selective Catalytic Reduction of NO$_x$
SCW	Supercritical Water
SCWO	Supercritical Water Oxidation
SDS-PAGE	Sodium-Dodecyl-Sulfate Polyacrylamide Gel Electrophoresis
SDSU	San Diego State University
Se	Selenium
SEM	Scanning Electron Microscope
SEP	Subscale Engineering Prototype
SERC	Schatz Energy Research Center
SF$_6$	Sulfur Hexafluoride
SGS	Subgrid Scale
SHE	Standard Hydrogen Electrode
SHTC	Southeast Hydrogen Technology Consortium
S-I	Sulfur-Iodine
SiC	Silicon Carbide
SLPM	Standard Liters Per Minute
SMP	Superior MicroPowders
SMR	Steam Methane Reformer
SN	Tin
SNG	Synthetic Natural Gas
SNL	Sandia National Laboratory
SNLL	Sandia National Laboratory Livermore
SnO$_x$	Tin Oxide
SO$_2$	Sulfur Dioxide
SOA	State-Of-the-Art
SOEC	Solid Oxide Electrolysis Cell
SOFC	Solid Oxide Fuel Cell
SPC	Statistical Process Control
SR	Steam Reforming/Reformer
Sr	Strontium
SRTC	Savannah River Technology Center
STAR	Substrate-based Transportation Autothermal Reformer
STEM	Scanning Transmission Electron Microscope
STH	Solar To Hydrogen
SULEV	Super Ultra Low Emissions Vehicle
SUNY	State University of New York
SUV	Sport Utility Vehicle
SV	Space Velocity
SVT	Single Vane Test
SWNT	Single Wall Nanotubes
SWPO	Supercritical Water Partial Oxidation
SwRI	Southwest Research Institute
T	Temperature
Ta	Tantalum
TCD	Thermal Conductivity Detector
TCD	Thermocatalytic Decomposition
TCWSC	Thermochemical Water-Splitting Cycle
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl Orthosilicate
TEX	Texas Energy System, LLC
TGA	Thermal Gravimetric Analysis
THC	Total Hydrocarbons
Ti	Titanium
TiCl$_3$	Titanium Trichloride
TiCl$_4$	Titanium Tetrachloride
TiO$_2$	Titanium Dioxide
TIVM	Torroidal Intersecting Vane Machine
tla	Truncated Light-Harvesting Chlorophyll Antenna
TMI	Technology Management, Inc.
TMY	Typical Meteorological Year
tpd	English tons per day
T-RFLP	Terminal Restriction Fragment Length Polymorphism
TRU	Truck Refrigeration Unit
TVA	Thermovolumetric analyzer
UAB	University of Alabama at Birmingham
UC	University of California
UGA	University of Georgia
UGCM	Unitary Gas Control Module
UH	University of Hawaii
UHC	Unburned Hydrocarbons

UHM	University of Hawaii at Manoa
UHV	Ultrahigh Vacuum
UK	University of Kentucky
UL	Underwriters Laboratory
UNIGEN®	A Registered Trademark of Proton Energy Systems, Inc.
UOP	Universal Oil Products
UPS	Uninterruptible Power Supply
US DOE	United States Department of Energy
USC	University of South Carolina
UT-3	University of Tokyo-3
UTC	United Technologies Corporation
UTCFC	United Technologies Corporation Fuel Cells Division
UTRC	United Technologies Research Center
UV	Ultraviolet
V	Volt
V	Vanadium
VASP	Vienna Ab Initio Simulation Package
VC	Vulcan Carbon
VNT®	Variable Nozzle Turbine
V_{oc}	open circuit potential
Vol.%/Vol%	Percent by volume
w	Width
W	Tungsten
W_e	Watts electric, typically refers to the output from a PEM fuel cell
WGS	Water Gas Shift
WO_3	Tungsten Trioxide
wt	Weight
Wt	Watts thermal, typically refers to heat transfer duty
wt.%/wt%	Weight percent
XRD	X-ray diffraction
Y	Yttrium
YAg:Cr	Yttrium Aluminum Garnet doped with Chromium
yr	Year
YSZ	Yttria Stabilized Zirconia ($Zr_{0.85}Y_{0.15}O_{1.95}$)
Z-60	0 to 60 mph Acceleration
ZEV	Zero Emission Vehicle
Zn	Zinc
Zr	Zirconium
ZSM	Zeolite Type Membranes

Index of Primary Contacts