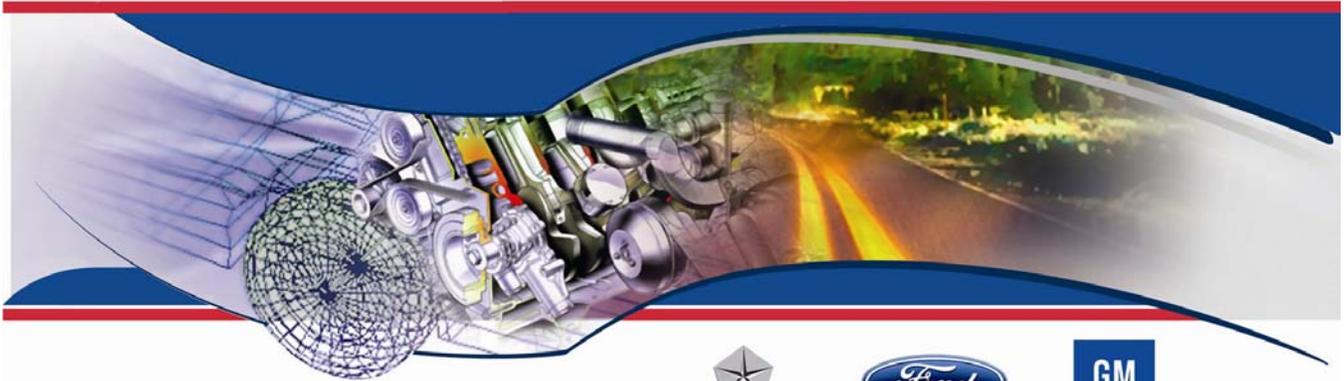


FreedomCAR & Fuel Partnership



U.S. DEPARTMENT OF
ENERGY

USCAR
UNITED STATES COUNCIL FOR AUTOMOTIVE RESEARCH LLC



ConocoPhillips

ExxonMobil



Shell Hydrogen

FreedomCAR and Fuel Partnership

2008

Highlights of Technical Accomplishments

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Preface

This report contains brief summaries of key technical accomplishments of the FreedomCAR and Fuel Partnership program for 2008. This program was initiated in 2002 as the FreedomCAR Partnership between the United States Department of Energy (DOE) and the United States Council for Automotive Research LLC (USCAR), the latter being a consortium comprised of Chrysler LLC, Ford Motor Company and General Motors Corporation. In 2003 the President's Hydrogen Fuel Initiative was unveiled. In response to this, the FreedomCAR Partnership was expanded in September 2003 to include five energy companies (BP America, Chevron Corporation, ConocoPhillips, ExxonMobil Corporation and Shell Hydrogen LLC (US)) and became the FreedomCAR and Fuel Partnership. In June 2008, to address the need to accelerate the research, development and deployment of Plug-In Hybrid Vehicles from the laboratory to the marketplace, DTE Energy and Southern California Edison were named as new members of the Partnership.

The accomplishments described in this report support the overall FreedomCAR and Fuel Partnership goals and the progress being made. These goals are the "Freedoms" originally embraced by the FreedomCAR Partnership:

- Freedom from dependence on imported oil
- Freedom from pollutant emissions
- Freedom for Americans to choose the kind of vehicle they want to drive, and to drive where they want, when they want and
- Freedom to obtain fuel affordably and conveniently.

Previous annual reports are available on the FreedomCAR and Fuel Partnership page on the USCAR website at www.uscar.org.

The material for the 2008 Highlights of Technical Accomplishments Report was selected from the many hundreds of projects now active and put into the form of single page accounts, arranged by subject matter corresponding to the various technical teams formed by the partnership. The Technical Teams are listed below:

Vehicle Technical Teams (Members from USCAR and DOE)

- Advanced Combustion & Emissions Control
- Electrical and Electronics
- Electrochemical Energy Storage
- Fuel Cells
- Materials
- Vehicle Systems Analysis

Joint Technical Teams (Members from USCAR, the energy partners and DOE)

- Codes and Standards
- Onboard Hydrogen Storage

Energy Technical Teams (Members from the energy partners and DOE)

- Hydrogen Production
- Hydrogen Delivery
- Fuel Pathway Integration

Each of the accomplishments summarized in this report was selected by the relevant technical team as representing a significant milestone reached, or breakthrough made, in 2008. It represents achievements in work that may well have begun in previous years but does not necessarily indicate that the final goals of a particular project have yet been met.

2008 FreedomCAR and Fuel Partnership Highlight

Hydrogen Engine Achieves 45% Efficiency

Ford Motor Company, Argonne National Laboratory
and Sandia National Laboratories

Hydrogen engines offer a path to sustainable high-efficiency transportation, while meeting Tier II Bin 5 emissions levels with near-zero CO₂ emissions. As a combustion fuel, hydrogen has many attractive properties. Ford Motor Company achieved 45% brake thermal efficiency with a research direct injection single-cylinder engine. This efficiency is a significant increase relative to current port-injected hydrogen engines that have peak efficiencies less than 40%. Fuel consumption maps projected from this work show that when hybridized, a hydrogen engine vehicle can offer fuel economy approaching fuel-cell powertrains. [Rousseau *et al.*, SAE 2008-01-2378]

The test engine used direct injection technology to create an efficient stratified fuel/air mixture during combustion. Stratification controls the fuel/air mixture for optimal combustion phasing, minimizes the wall heat transfer losses that reduce efficiency, and avoids pre-ignition at high loads. In-cylinder visualization techniques at Argonne and Sandia National Laboratories improved understanding of the effect of the injector design and the impact of H₂ injection on the in-cylinder flow field and were the keys to the engine optimization.

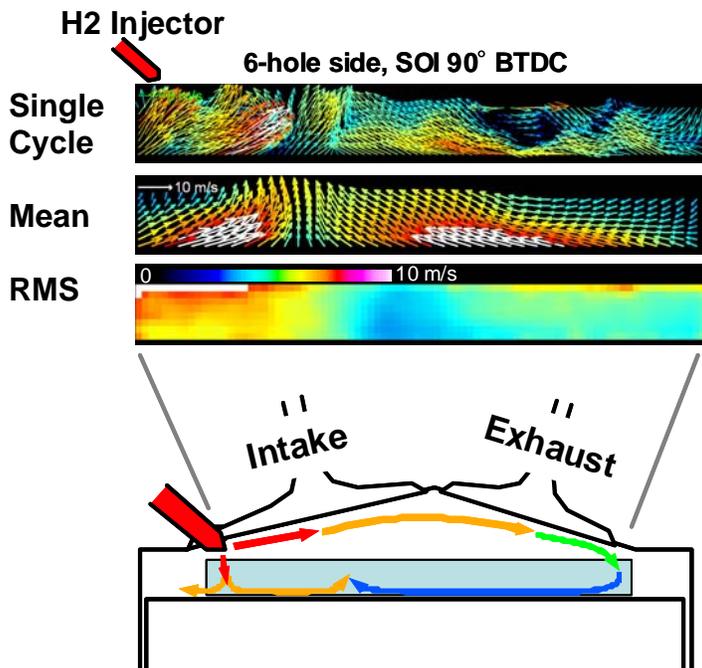


Figure 1: Sandia National Laboratories measured the velocity field (top 3 images) to show how the injection event influences the in-cylinder flow field, which in turn determines mixture preparation. Proper timing of the injection event enables stratification of the fuel and enables improved efficiency.

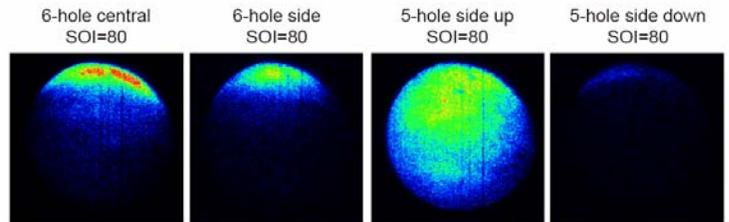


Figure 2: Argonne National Laboratory used an endoscopic technique to measure OH* intensities for various nozzle configurations in H₂-DI operation at the same injection timing (SOI). OH* intensities are indicators for air/fuel ratio and ultimately NO_x emissions. The injector nozzle design (number of holes and orientation) affects mixture and combustion stratification.

		
Date:		17-Jan-2008
Engine Speed:		3000 RPM
Injection Pressure:		98 bar
Net IMEP (720):		14.56 bar
FMEP:		0.70 bar
Resulting BMEP:		13.86 bar
Indicated Efficiency:		47.3%

Figure 3: Operating conditions for Ford's hydrogen combustion efficiency demonstration.

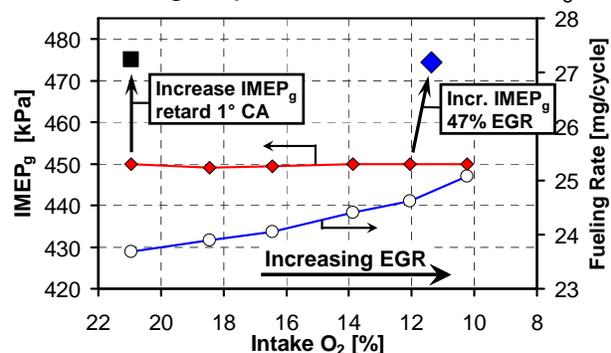
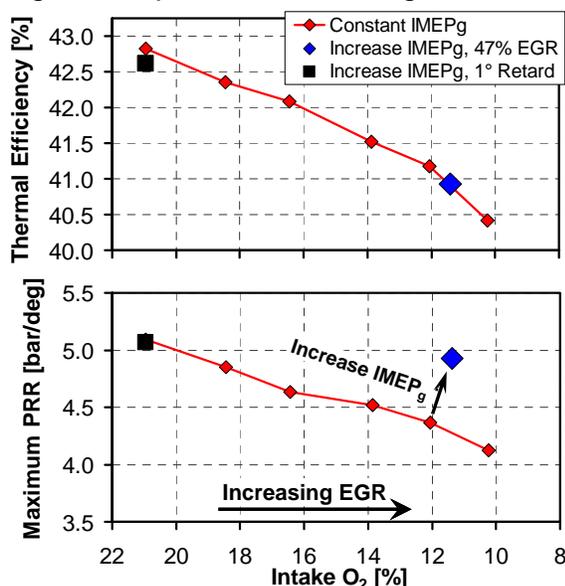
2008 FreedomCAR and Fuel Partnership Highlight

A Detailed Picture of Exhaust Gas Recirculation Effects on HCCI Operation Developed

Sandia National Laboratories

Gaining a better fundamental understanding of Homogeneous Charge Compression Ignition (HCCI) operation is critical to realizing its potential for increased engine efficiency. Exhaust gas recirculation (EGR) is widely used with HCCI operation for enhancing auto ignition and for rapidly controlling the in-cylinder temperature and thereby combustion timing. It is also often stated in the literature that EGR can help slow the HCCI combustion event, thereby reducing the maximum pressure-rise rate (PRR) to allow higher loads without knock. However, in previous research, the effect of EGR on PRR was convolved with its effect on combustion timing, making it difficult to determine specific cause-and-effect relationships as well as other potential negative effects of EGR. Well-controlled experiments isolating the effects of EGR on HCCI operation have been conducted to delineate these effects. This project provides a more comprehensive picture of EGR effects on HCCI operation and will help engine designers more effectively use EGR for controlling HCCI.

Results show that as EGR is increased over a wide range for fixed combustion timing, the thermal efficiency of the engine decreases for all conditions investigated (e.g., upper-left figure). Because of this drop in efficiency, the fueling must be increased to maintain constant power output, as measured by the gross indicated mean effective pressure (IMEP_g) (upper-right figure). Despite these drawbacks, EGR addition does decrease the maximum PRR, thus reducing the knocking propensity (lower-left figure). This allows the IMEP_g to be increased from 450 to 475 kPa without exceeding the maximum PRR observed without EGR addition (◆). However, the increase in IMEP_g allowed is very modest and can be easily achieved without EGR addition by retarding the combustion timing by only 1° crank angle (■), with almost no effect on the thermal efficiency or a 1.7% higher thermal efficiency (4% fuel savings) than the high-EGR case (left figures). In addition, contrary to intuition, another drawback of using EGR for well-mixed HCCI is that NO_x emissions increase if constant IMEP_g is maintained due to the higher temperatures resulting from the increased fueling required to maintain IMEP_g.



EGR effects for constant IMEP_g and combustion timing. Upper left: Efficiency. Right: IMEP_g and fueling rate. Lower left: Maximum PRR. The ◆ symbol shows the effects of increasing the IMEP_g with EGR. The ■ symbol shows the effect of a small 1° of combustion timing retard with no EGR.

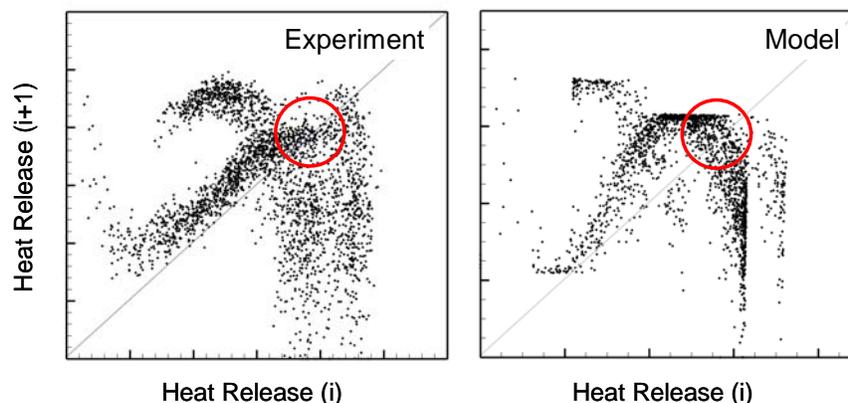
2008 FreedomCAR and Fuel Partnership Highlight

A Predictive Model Developed for Spark Assisted HCCI Combustion

Oak Ridge National Laboratory and Delphi Automotive Systems CRADA

Barriers to the successful implementation of homogeneous charge compression ignition (HCCI) combustion in production vehicles include a limited speed/load range due to high in-cylinder pressure rise rates and stability issues associated with the sensitivity of the combustion processes to in-cylinder conditions. An engine management approach is being developed which makes use of spark assist and a predictive model to expand the operational range of HCCI combustion through the stabilization of intermediate hybrid combustion modes. These combustion modes exhibit HCCI-like combustion with reduced pressure rise rates allowing for an expansion of the speed/load range. Oak Ridge National Laboratory (ORNL) model and controls experience in combination with Delphi component and subsystem experience is being used to develop and implement this approach on a multi-cylinder engine.

A low-order dynamic model was developed to predict the complex cycle-to-cycle interactions of spark assisted HCCI which have been observed in experiments. This model provides an improved understanding of the fundamental nature of HCCI combustion instabilities and forms the basis for a more simplified model which is in development for real-time control applications. Additionally, a new combustion metric based on high-speed in-cylinder pressure data was developed to provide rapid characterization of the spark assisted HCCI combustion event. The control concept makes use of the combustion metric from previous cycles in combination with the model to predict the next combustion event. A control action to fueling and/or spark timing is then made if deemed appropriate based on the prediction. This concept will be implemented on a multi-cylinder engine which makes use of advanced technologies from Delphi including a flexible valve system and a Cylinder Pressure Development Controller. This advanced hardware is key to high-speed characterization and control of a multi-cylinder engine. A patent for HCCI combustion control concepts was issued in October 2008 (US 7,431,011).



A low-order model was developed which is able to predict Spark Ignition, HCCI, and mixed-mode combustion as well as the cycle-to-cycle interaction of these modes. The region highlighted in red is the control target region and corresponds to conditions with the minimum variation in combustion.

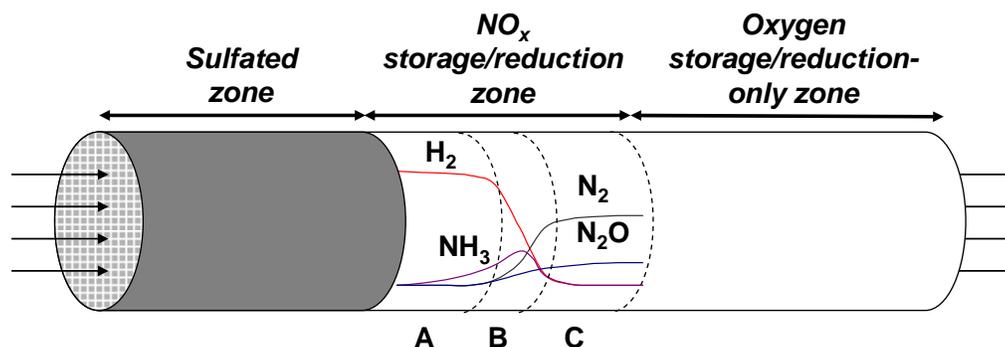
2008 FreedomCAR and Fuel Partnership Highlight

Understanding Lean NO_x Trap (LNT) Sulfur Tolerance

Oak Ridge National Laboratory and Sandia National Laboratories

An Oak Ridge National Laboratory (ORNL) team has applied a unique combination of experimental tools to resolve the detailed stages of sulfur (S) poisoning in lean NO_x trap (LNT) catalysts for lean gasoline direct-injected (GDI) engines. Using a commercial LNT catalyst, the team determined that LNT sulfur poisoning and desulfation (deS) are controlled by the interaction of two distinct solid-phase domains and four different chemical states of S in the catalyst. Adjusting operating strategies and catalyst formulations to maintain an optimal balance among these domains and S states is expected to be the key to reducing LNT cost as well as minimizing NO_x control fuel penalty for lean-burn engines.

In the past year, the ORNL team has focused its work on a commercial GDI LNT catalyst manufactured by Umicore. This catalyst has been identified as a benchmark standard by the technical focus groups working under the DOE-industry-academia collaboration known as CLEERS (Crosscut Lean Exhaust Emissions Reduction Simulation). Using highly specialized tools, the ORNL researchers measure spatial and temporal changes in catalyst structure and chemistry during sulfation and deS in a laboratory reactor that simulates conditions in an operating LNT. Recent results demonstrate that there are two distinct functional domains in the catalyst: 1) a largely deactivated zone at the leading edge of the catalyst that is poisoned by barium sulfate and 2) an essentially clean downstream zone that still retains significant capability for NO_x storage and reduction (NSR). As poisoning progresses, the deactivated zone grows at the expense of the NSR zone. Ammonia is generated at the upstream end of the NSR zone and begins to slip from the LNT exit as the NSR zone shortens. Even after many poisoning and deS cycles, significant NSR functionality can be maintained if the deS conditions are properly selected. The regeneration process is aided by the presence of non-barium sulfur storage sites in the catalyst, including alumina, magnesium-alumina, and ceria-zirconia. The ORNL team is implementing mathematical descriptions of this dynamic interplay as part of a joint LNT simulation model developed in collaboration with Sandia National Laboratories.



Specialized measurements have led to a new conceptual model of LNT poisoning depicted above. The most damaging (stable) S form concentrates at the upstream end, and NO_x removal shifts downstream with time. Ammonia slip begins to occur as the NO_x removal zone nears the catalyst exit. Non-barium storage sites for sulfur increase the effectiveness of desulfation.

2008 FreedomCAR and Fuel Partnership Highlight

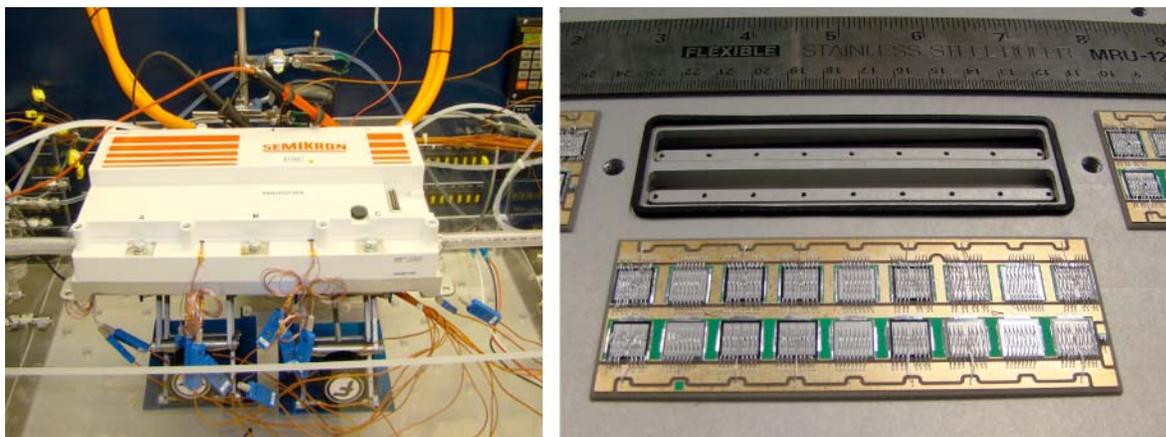
Direct Back-Side Cooling of Power Electronics

National Renewable Energy Laboratory

Power electronics are a critical subsystem used to condition the flow of electrical energy between the battery pack and electric motor in hybrid electric (HEV), plug-in hybrid electric (PHEV) and fuel cell (FCV) vehicles. Heat is generated as power flows through the electronic devices, which if not properly dissipated can degrade performance and cause failures due to thermally induced stress. In 2008, the National Renewable Energy Laboratory (NREL) completed testing of a novel prototype heat exchanger that combines jet impingement cooling with the elimination of materials that restrict the flow of heat. Testing at NREL showed a 37% reduction in thermal resistance when compared to a baseline pin-fin heat exchanger. The testing also demonstrated a more uniform temperature distribution across the devices. The tests were performed in conjunction with Semikron that provided the power electronics module and the baseline heat exchanger.

NREL researchers applied expertise in computational fluid dynamics, along with experimental results from single-jet experiments, and worked with engineers at Semikron to develop a practical and effective design. One key attribute of this prototype is that it eliminates the need for thermal grease by incorporating a seal that allows cooling directly on the backside of the direct-bonded copper layer. Thermal grease is a major bottleneck to the removal of heat and presents a number of manufacturing and reliability concerns. The design also reduces temperature variation between chips by directing impinging-jet coolant flow at a uniform temperature to all the devices simultaneously.

Effective thermal management is a key to achieving the FreedomCAR program targets for cost, weight, volume, and a 15-year life for power electronics. This technology will help eliminate the dedicated power electronics cooling loop by lowering the package thermal resistance and enabling the use of high temperature coolants.



Direct back-side jet impingement demonstrated in a Semikron inverter

2008 FreedomCAR and Fuel Partnership Highlight

High Temperature SOI Gate Driver

Oak Ridge National Laboratory

There is a strong need to reduce the cost and weight of power electronic systems in hybrid vehicles. One approach is through the elimination of secondary cooling loops. Significant savings result from removing the dedicated secondary loop used to cool the power electronics in hybrid electric vehicles (HEVs) and instead use the water/ethylene glycol directly out of the engine's radiator. In addition to reducing system costs, increased integration of electrical functions enable higher power density and reduced weight and volume. The use of this elevated temperature coolant to cool the high current carrying, heat producing power electronics will require new, high-temperature, electronic technologies to insure reliable operation over the life of the vehicles.

To address these issues Oak Ridge National Laboratory (ORNL) in conjunction with the University of Tennessee is working on a silicon on insulator (SOI) based, high temperature, high voltage, gate driver circuit for hybrid-electric-vehicle power-electronics that can work at an ambient temperature of 200°C.

A second generation, highly integrated, SOI chip has been designed and fabricated. Tests have shown the gate driver works reliably at temperatures of up to 225°C when driving a normally-off SiC MOSFET or a normally-on SiC JFET. Improved circuitry has been incorporated into the second generation which now includes a bootstrap capacitor and a voltage regulator.

Testing is complete on multiple samples of this second generation chip design with all functions integrated into the chip. The performance of these chips was both consistent and repeatable.

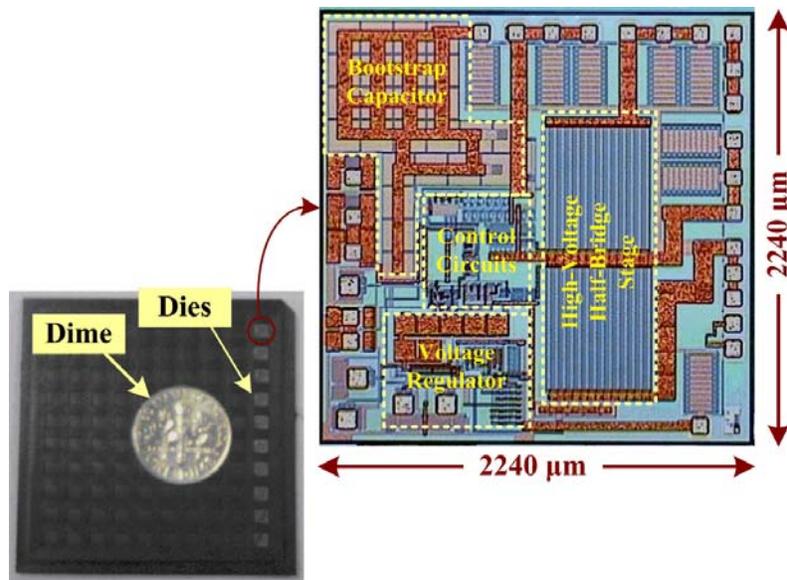


Figure 1: ORNL SOI Gate Drive Chip

2008 FreedomCAR and Fuel Partnership Highlight

Advanced DC to DC Converter

Oak Ridge National Laboratory

Direct current-to-direct current (DC to DC) converters play an important role in boosting battery voltage to the electric vehicle drive, providing an opportunity to reduce battery cost and size as well as improving the systems efficiency of some hybrid architectures. Oak Ridge National Laboratory in partnership with Michigan State University is developing an innovative DC to DC converter that employs the concept of modular multilevel voltage converters, producing a desired high voltage and/or high current output at extremely low distortion and with minimal magnetic components. The bidirectional converter proposed and investigated in this project delivers the desired output voltage and/or current waveform synthesized from the multiple voltage levels with less distortion, high-speed response, lower switching frequency, and higher efficiency. The topology makes it possible to employ available power semiconductor devices and capacitors as well as future silicon carbide (SiC) devices and high-temperature capacitors to provide the most efficient, least weight, and most compact power conversion system operable at underhood temperature limits of 200°C or higher.

A 30 kW continuous power DC to DC converter (shown in Fig. 1) has been assembled and tested this year. Efficiency results for the converter in the buck mode and boost mode are shown in Figs. 2 and 3, respectively. The efficiency has been in the 97 – 98% range. The transistors (IGBTs) chosen for this prototype have peak power less than the designed 55 kW, so a 2nd prototype is being developed with a different IGBT module which will achieve the targeted peak power rating. The weight of the first prototype converter was 6.5 kg and it occupied a volume of 3.1 liters, putting us on a path to meet our goals. Future SiC devices and high temperature capacitors likely could reduce the weight and volume by a factor of 2 to 3.

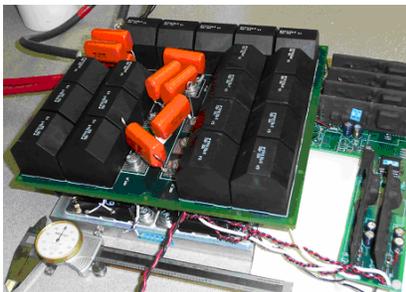
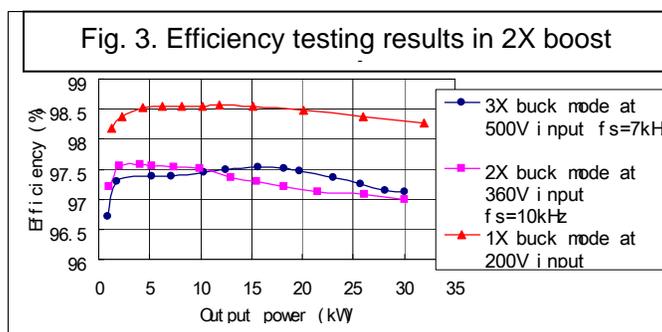
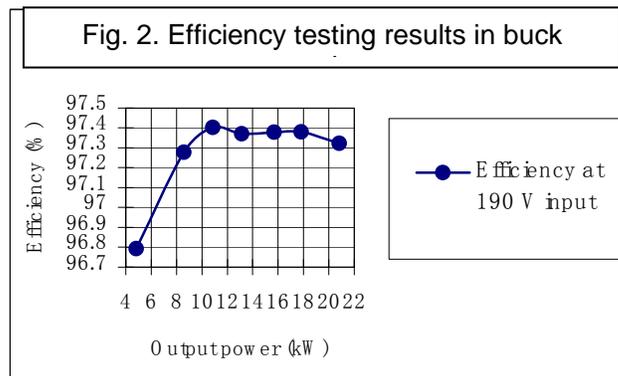


Fig. 1: Assembly of multilevel bidirectional DC to DC converter circuit and gate drive board.



2008 FreedomCAR and Fuel Partnership Highlight

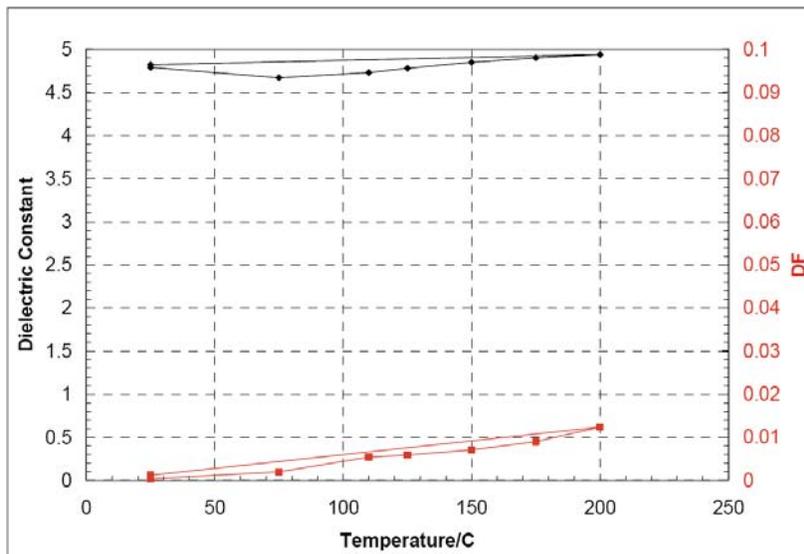
High Temperature Polymer DC Bus Capacitors

Sandia National Laboratories and Electronic Concepts, Inc.

One of the major challenges in meeting the aggressive FreedomCAR electric traction drive goals is high temperature operation. The traction drive inverter DC bus capacitor is currently one of the limiting factors to meeting the higher operating temperature targets, as well as reducing overall system volume, weight and cost.

A team of researchers at Sandia National Laboratories has designed and synthesized an inexpensive, novel polymer dielectric that has improved high temperature dielectric characteristics. The dielectrics have been cast into films as thin as 2 μm . These dielectric films have excellent performance up to temperatures of 175°C, almost double the temperature limit of current capacitors in traction drive inverters. The material properties of the newly developed polymer system meet or exceed the current 2015 FreedomCAR goals for high temperature capacitors.

The team is collaborating with industry (Electronic Concepts, Inc.) to produce thin films of the Sandia developed material as well as prototyping capacitors using this material for evaluation and testing.



Left Figure: Electrical characterization showing both the high dielectric constant and low dissipation factor (DF) of the Sandia developed high temperature polymer as a function of temperature. The low dissipation factor is indicative of low losses and the high dielectric constant is a measure of how well the dielectric material holds a charge.

Right Figure: Image showing the novel Sandia developed high temperature polymer dielectric.

2008 FreedomCAR and Fuel Partnership Highlight

NCA-Based Li-ion Battery Packs Delivered

Johnson Controls – SAFT HEV Program

Johnson Controls – Saft (JCS), headquartered in Milwaukee, is a joint venture between Johnson Controls (JCI) and Saft Inc. which combines Saft’s recognized lithium ion (Li-ion) cell technology with JCI’s automotive integration expertise.

A significant goal in the JCS FreedomCAR hybrid electric vehicle (HEV) program was to deliver complete battery systems that demonstrated the Saft NCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$)-based cell technology in combination with JCI automotive system technology. That goal was achieved in 2008 with the delivery of two HEV battery packs to Idaho National Laboratory (INL) and one to Argonne National Laboratory (ANL) for bench testing. Extensive cell-level testing was also conducted by JCS, INL, the National Renewable Energy Laboratory (NREL) and Sandia National Laboratories (SNL).

The two year program resulted in numerous cell, system and process level advancements which will enhance JCS’s ability to deliver a technically and commercially viable battery system for the HEV market. Cells were subjected to the full range of FreedomCAR protocol testing and met the program targets for cycle life (300,000 50Wh profile cycles) and calendar life (15 years). Innovations to the cell design also resulted in improved abuse tolerance, as independently confirmed by SNL. In addition to the technical accomplishments, JCS has developed a sophisticated battery system cost model and has defined process, logistics and infrastructure requirements for long-term recyclability of end-of-life batteries and systems.

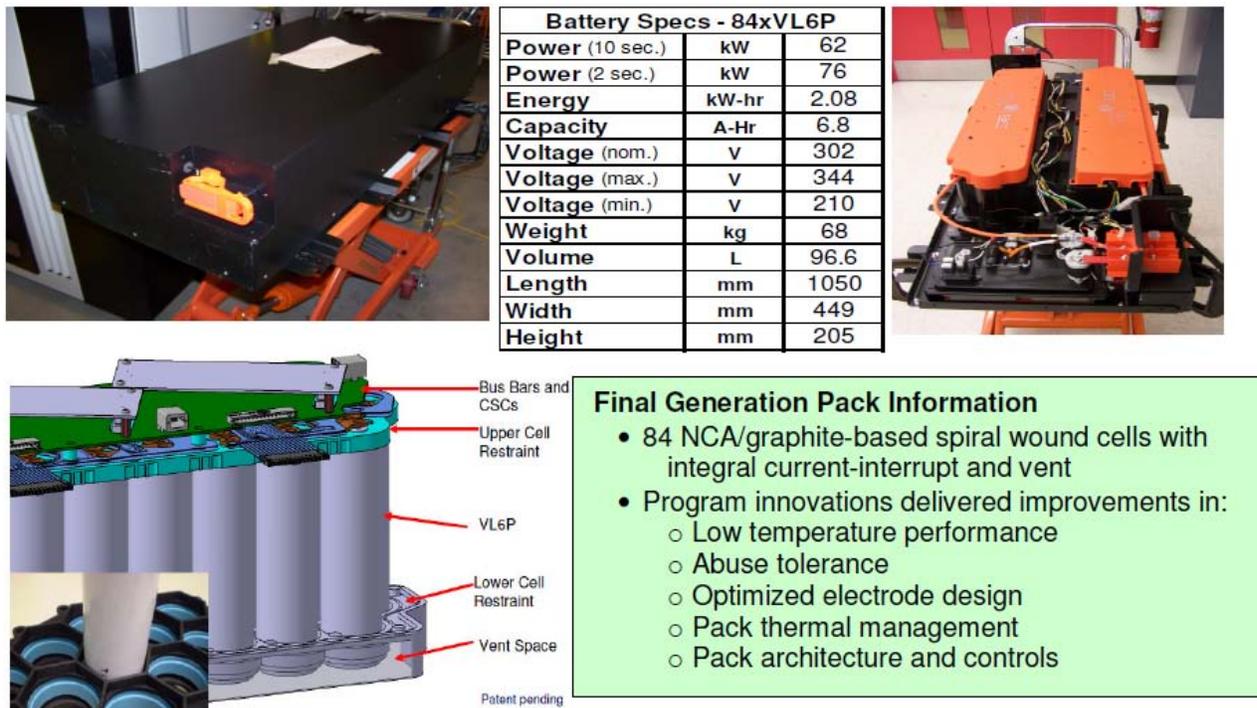


Figure 1: Johnson Controls – Saft FreedomCAR HEV Battery Pack Deliverable

2008 FreedomCAR and Fuel Partnership Highlight

Airless Spray Deposited Ceramic Separator

A123 Systems PHEV Program

A123 Systems has demonstrated a viable, low cost separator with improved strength at elevated temperatures. Improving cell abuse tolerance, without sacrificing performance or increasing cost, supports the integration of lithium ion (Li-ion) battery technology into vehicle level systems. This improved reliability is even more imperative when considering the higher energy cell and battery required for plug-in hybrid electric vehicle (PHEV) applications.

One function of the separator is to maintain a physical separation between the anode and cathode electrodes, to prevent electrical shorts. The separator material must both resist puncture and remain permeable enough for the electrolyte to maintain ionic conductivity. The A123 approach creates a separator by spraying a nano-composite separator (NCS) material (an optimum blend of inorganic/organic materials) onto the anode, cathode, or both electrodes, using an airless spray technique. Figure 1 shows that at both low and high temperatures, the NCS separator (at two inorganic/organic material ratios) has excellent puncture resistance relative to the current commercial polyethylene (Baseline PE) material separator used by A123. This characteristic is directly related to the abuse tolerance and safety of the cell. Additional test data has shown that cell performance is only marginally reduced by this type of separator. Additional development work is planned to improve coating consistency and increase the cost competitiveness.

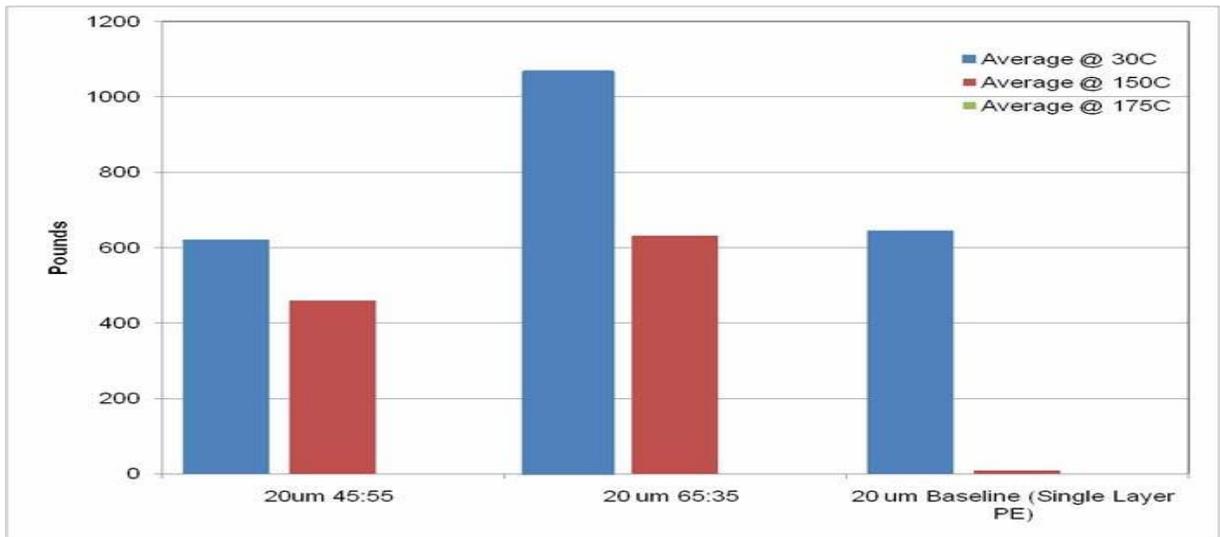


Figure 1: NCS film puncture performance at low and elevated temperatures vs. the Commercial Baseline PE product

2008 FreedomCAR and Fuel Partnership Highlight

Life and Safety Improvements of Li-ion Polymer Battery

Compact Power and LG Chem HEV Program

Compact Power (CPI)/LG Chem (LGC) designed and delivered a cell that utilizes a reduced cost-volatility cathode material based on spinel (manganese oxide) and which uses an advanced, mechanically-robust safety reinforced separator (SRS™) for improved abuse-tolerance.

Life (*cycle and calendar*), abuse-tolerance and cost are major challenges for most lithium ion (Li-ion) based hybrid electric vehicle (HEV) batteries. One method to improve cell durability is to improve the cell separator toughness and puncture strength. Improved separator toughness allows for more reliable batteries that also resist short circuits and punctures.

A highlight of the work in 2008 was the fabrication and delivery to USABC of cells and modules using the new SRS separator. The SRS membrane uses a proprietary ceramic coating that has provided a 6x increase in separator toughness. The efficacy of this high puncture strength separator with respect to abuse-tolerance and performance was demonstrated both in cells and modules.

Safety Reinforced Separator (SRS)

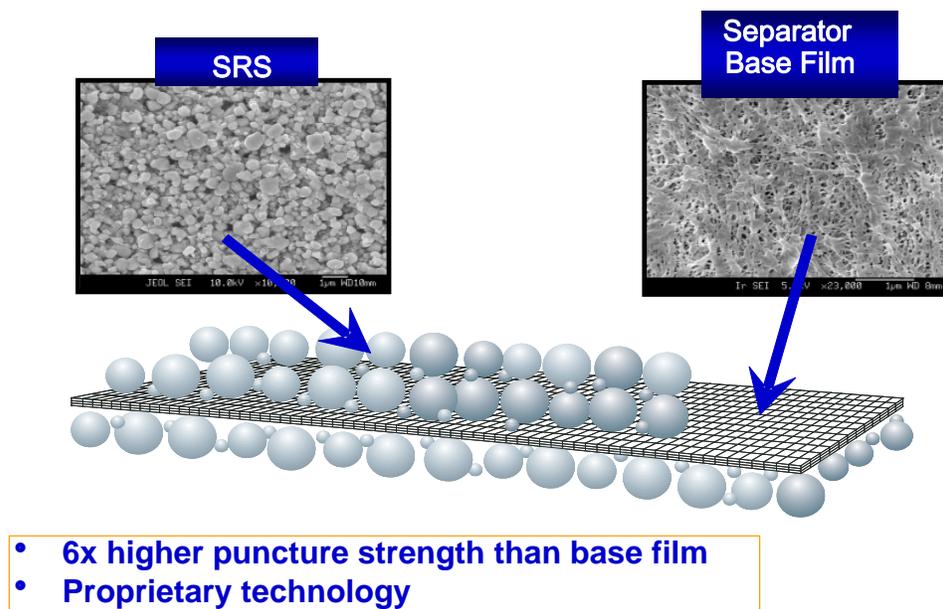


Figure 1: Structure of the new separator, SRS.

2008 FreedomCAR and Fuel Partnership Highlight

A Li-ion Battery Using Stable Nano-Lithium Iron-Phosphate Cathode

A123 Systems - HEV Program

Under the United States Advanced Battery Consortium (USABC) development program, a new cylindrical cell based on the iron phosphate chemistry was designed and developed for the high power hybrid electric vehicle (HEV) application. A123 Systems developed a proprietary doped nano-lithium iron-phosphate cathode, which dramatically improved safety characteristics when compared with cobalt, nickel, and manganese oxides found in commonly used lithium ion (Li-ion) batteries. USABC uses an abuse severity rating system that ranks batteries on a scale from 1-7 (one being the safest). Automotive standards require batteries to fall into a range of 1-4. None of the cobalt, nickel and manganese oxide battery systems can achieve such ratings in all abuse tests.

These cells were independently tested for various abusive conditions at Sandia National Laboratories. Severity level of the reactions was classified as shown in the table below. Severity level 2 refers to loss of electrolyte, and severity levels 3 and 4 indicate venting of the cells (under and over ½ the weight of the electrolyte respectively).

Cell ID	Test Performed	Severity Level
284	4amp OC	3
387	12amp OC	3
211	1mohm short	2
278	10mohm short	2
410	Thermal Ramp 100%SOC	4
450	Thermal Ramp 50%SOC	4
505	Separator Stability 147 °C	4
543	Separator Stability 157 °C	4



Venting at Designed Vent Port



A123 abuse severity test utilizing European Council for Automotive R&D (EUCAR) hazard level ranking standards

2008 FreedomCAR and Fuel Partnership Highlight

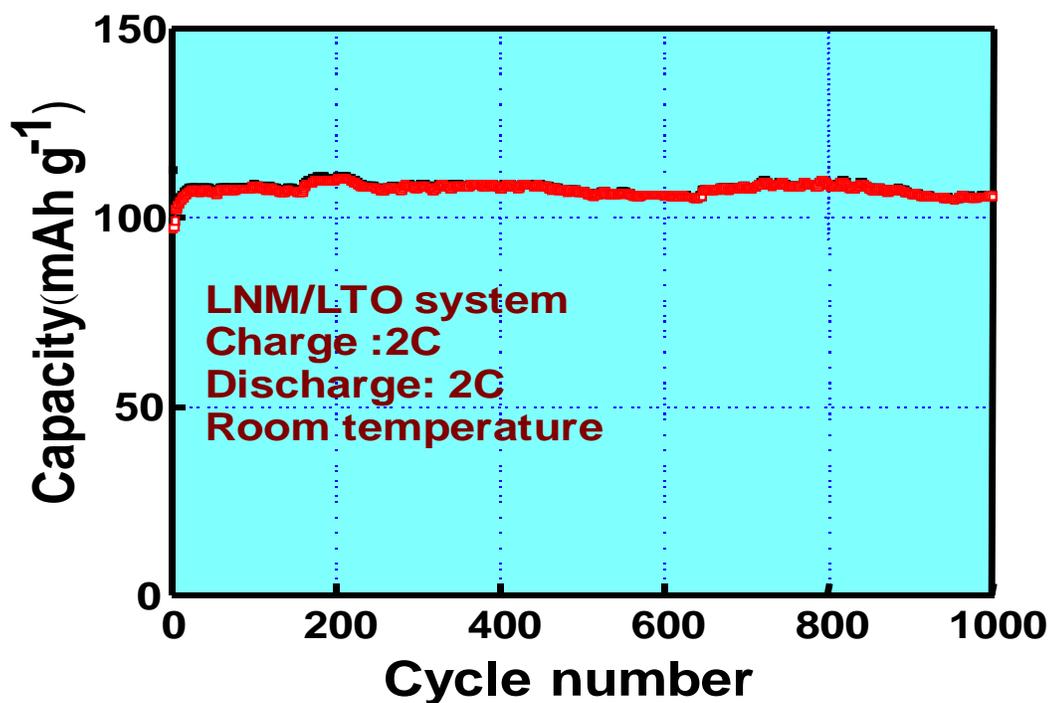
Development of a Li-ion Battery for Plug-In Hybrids with Life and Safety Improvements

EnerDel PHEV Program

The new $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNM)/LTO battery developed by EnerDel in this program is capable of meeting the 10-mile plug-in hybrid electric vehicle (PHEV) requirements. Argonne National Laboratory (ANL) has recently developed a high voltage positive electrode for use with Lithium Titanate Oxide (LTO) negatives in lithium ion (Li-ion) batteries. Current Lithium Titanate negatives with carbon based positives are limited to ~2.5V operation, thus preclude building a battery suitable for plug-in hybrid systems. The LNM material from ANL coupled with LTO negatives produces a 3.2V cell.

Furthermore, LTO's ability to prevent formation of lithium dendrites that could damage cells is key to extended life and safety. Compared to current carbon-based negatives, LTO requires a much larger over potential of 1.5V vs. (0.08V for graphite) to form lithium dendrites. Additionally, the promise of long life relates to Lithium Titanate's "zero strain" characteristic; it can avoid large volume changes during operation, unlike graphite which undergoes phase transformations and staging during usage. Relatively abundant raw materials allow LTO to be a low-cost alternative to current negatives.

The production scale-up of this material (LNM), is one of the major tasks of this program. The figure below shows that the capacity (which relates to vehicle range) remains stable for 1000 charge/discharge cycles so far in small lab-scale batteries. Next steps include addressing the stability of the liquid electrolyte solution.



2008 FreedomCAR and Fuel Partnership Highlight

New Ionomer Achieves Low Temperature Conductivity Target

3M

3M has achieved the DOE/FreedomCAR room temperature (RT) proton conductivity target (70 mS/cm at 25°C, 80% relative humidity (RH)) with a low equivalent weight (EW) membrane based on its PFSA ionomer (Compound 1A). Use of novel chemical groups on the ionomer have the potential to lower EW without compromising mechanical properties. Membranes with low EWs have very good conductivity under hot, dry conditions. Figure 1 shows the conductivity of two membranes prepared by 3M, tested at RT. The 640 EW membrane has a conductivity of 80 mS/cm at 25°C, 80% RH, exceeding the DOE target for RT conductivity.

3M has begun characterization of these new materials. The 3M team prepared a series of polymers changing the chemical group interacting with the protons to look at the effects of acidity on conductivity. One such alteration uses a new aromatic imide (compound 1B at right), that allows unique proton interaction. In addition these polymers can be cross-linked to enhance mechanical properties. The conductivity of compound 1B versus the standard ionomer, 1A, shown in Figure 2. 3M is attempting to understand why the aromatic imide exhibits lower conductivity at low RH; possibilities include lower acidity and different ionomer morphology.

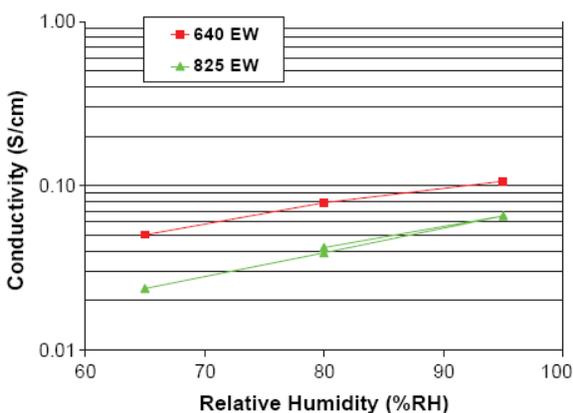
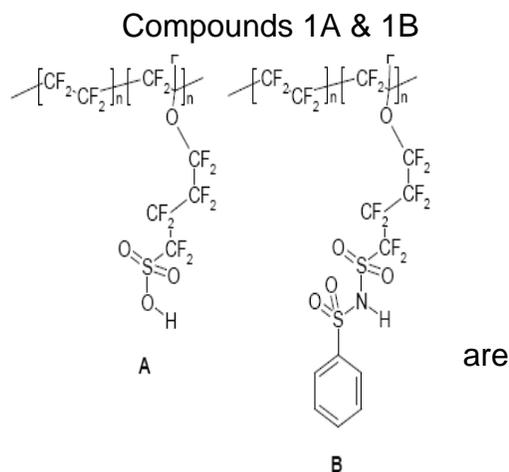


Figure 1: Lower EW PFSA membranes gave higher conductivity at all %RH at 25°C

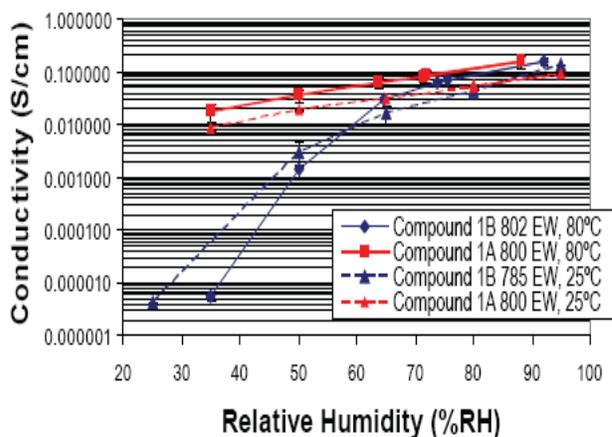


Figure 2: 1A still has higher conductivity than 1B at lower RH

2008 FreedomCAR and Fuel Partnership Highlight

Exceeded 7,300 Hours Durability With MEA Under Load Cycling

3M

Cost and durability are the main barriers to hydrogen fuel cells. 3M is exploring ternary catalysts to reduce the amount of platinum in its catalyst film, thereby reducing cost. 3M also is conducting multiple accelerated durability tests. Figure 1 shows the results of tests using seven dispersed catalyst Membrane-Electrode-Assemblies (MEAs), four nanostructured thin film (NSTF) MEAs without stabilization, and two NSTF MEAs with a membrane stabilized dimensionally by incorporating the 3M ionomer into an expanded Teflon matrix (courtesy of W. L. Gore and Associates), followed by acid washing. The seven dispersed catalyst MEAs failed within 600 hours; the four NSTF MEAs without stabilization had an average lifetime of 3500 hours, and the durability of the stabilized NSTF MEA more than doubled to 7300 hours under load cycling. This result exceeds the 5000 hour FreedomCAR durability target, although it was only a single cell test.

In addition, 3M improved performance with reduced Pt loading by improving the catalyst/membrane interface and lowering both the cathode and anode loading. Initially, 3M's catalyst coated membrane consisted of a NSTF Pt-Co-Mn ternary at a loading of 0.2 mg-Pt/cm^2 on both the anode and cathode sides of a 3M Polymer Electrolyte Membrane (~ 35 microns, 850 equivalent weight). In 2008, 3M reduced the size of the microstructure features of the NSTF support, which improved mass transport to the catalyst at high current densities, and reduced loading on the anode and cathode to 0.1 mg/cm^2 and 0.15 mg/cm^2 , respectively. These improvements enable better water transport through the anode, reducing high frequency resistance and iR-loss at high current densities without kinetic losses. The resulting total Pt content of 0.27 g/kW at 0.61 V is between the 2010 and 2015 targets.

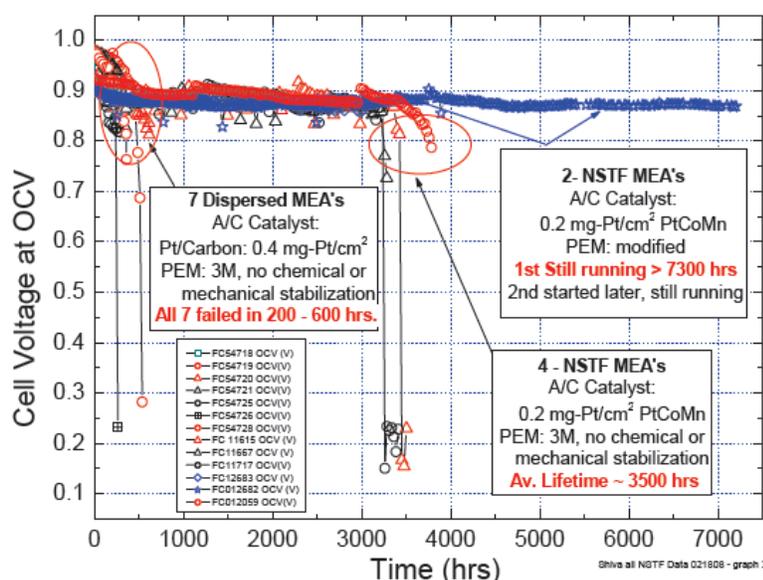
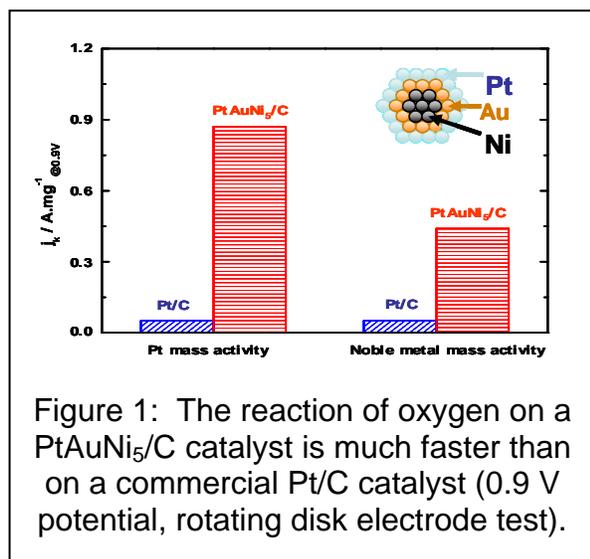


Figure 1: Durability of 3M MEAs under load cycling

2008 FreedomCAR and Fuel Partnership Highlight

Improved Fuel Cell Cathode Electrocatalysis: Pt Monolayer on Core-shell Nanoparticle

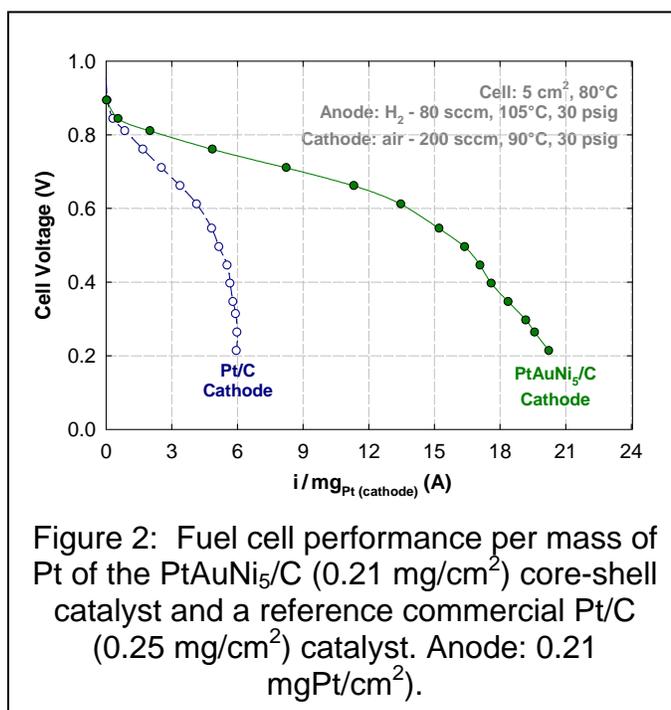
Brookhaven National Laboratory and Los Alamos National Laboratory



class of electrocatalysts consisting of a non-precious metal core and precious metal shell, with a Pt monolayer on the shell surface (a PtAuNi₅/C catalyst is depicted in the inset in Figure 1). As demonstrated using rotating disk electrode (RDE) testing of the PtAuNi₅/C catalyst, the core-shell approach resulted in up to 20-times higher mass activity of Pt and up to 5-times higher mass activity of all noble metals than a reference commercial Pt/C catalyst (Figure 1). The electrochemical and X-ray absorption data suggest that the enhanced catalyst activity is due to a decrease in PtOH coverage, likely caused by the interaction of Pt and Au layers.

Improved mass activity of Pt translates into substantially better fuel cell performance (Figure 2). Without much optimization, the PtAuNi₅/C catalyst has shown a 3.3-fold performance advantage per Pt atom over a reference Pt/C catalyst in the entire range of fuel cell voltage. Current efforts focus on improving the stability of alloy nanoparticles and scaling-up synthesis of this type of catalyst.

Thanks to high energy-conversion efficiency, the polymer electrolyte fuel cell (PEFC) is expected to play an important role in automotive transportation. However, large-scale commercialization is contingent upon a substantial reduction in the amount of platinum needed for the oxygen reduction reaction (ORR) at the fuel cell cathode. While platinum (Pt) is a catalyst of choice for both PEFC electrodes, much larger quantities of metal are required for the cathode because the reaction rate is significantly slower for oxygen than for hydrogen. To lower the Pt content in ORR catalysts, Brookhaven National Laboratory (BNL) scientists have developed a new



2008 FreedomCAR and Fuel Partnership Highlight

Demonstrated High Conductivity at Low RH with Two Polymer Systems Using Rigid Rod Architecture

Case Western Reserve University

Polymer electrolyte membranes that can operate at high temperature and low relative humidity (RH) would reduce costs by eliminating the need for gas humidification and allowing the use of standard automotive radiators. Case Western Reserve University has developed polymers based on rigid rods of sulfonated aromatic polymers with a few bulky or angled chemical units which force the polymer chains apart over their whole length. This creates an architecture with permanent pores lined with sulfonic acid groups. These permanent pores allow the material to hold water very strongly, leading to high conductivity even at very low relative humidities. As illustrated in the figure below, conductivities exceeding that of Nafion have been demonstrated for two rigid rod structures, poly(biphenylene disulfonic acid) (PBPDSA) and polyphenylene disulfonic acid (PPDSA). Conductivities greater than 0.1S/cm have been demonstrated for polyphenylene disulfonic acid (PPDSA) at relative humidities below 50%. While the polymers developed to date are not stable at high RH, the decreased dependence of their conductivity on RH suggest this strategy may be successful for developing high temperature, low RH membranes. Future work is focused on stabilizing these materials at high RH by increasing molecular weight, cross-linking, and other methods.

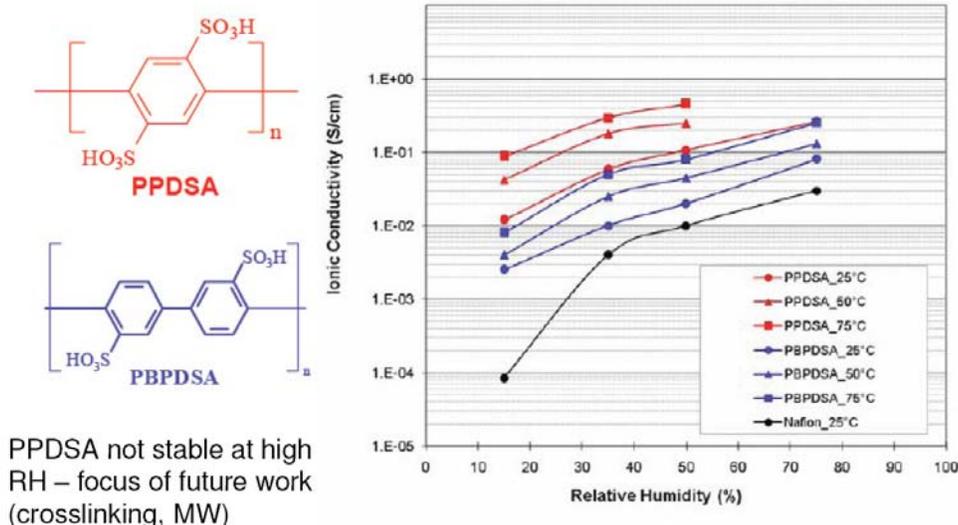


Figure 1: Conductivity of two rigid-rod type polymers which demonstrate conductivity >0.1S/cm at less than 50% RH.

2008 FreedomCAR and Fuel Partnership Highlight

A Membrane with Over Twice the Conductivity of Nafion and Reduced In-Plane Swelling

Giner Electrochemical Systems

Membrane swelling and shrinking due to changes in relative humidity (RH) during automotive cycles has been shown to lead to membrane degradation and failure. Giner is developing dimensionally stabilized membranes (DSMTM), shown in Figure 1, using two-dimensional (2D) and three-dimensional (3D) supports. These DSMs provide mechanical stability and allow the use of lower equivalent weight (EW) ionomers known to have better conductivity under low relative humidity (RH). A sample composite 2DSM membrane with low EW perfluorinated sulfonic acid ionomer and 10% support material has demonstrated 2-3 times the conductivity of the standard Nafion® 112 over the entire range of RH, as shown in Figure 2. This 2DSM membrane is based on pores drilled by lasers in an inert support and limits in-plane swelling below 5%.

Though more conductive than Nafion® 112, this 2DSM membrane is still short of the DOE's conductivity targets. In order to improve conductivity further, a lower equivalent weight homopolymer, was incorporated in the 3DSM. This membrane has come very close to meeting the DOE targets; however, the homopolymer is water soluble and eventually leaches out of the 3DSM support. Efforts have begun to cross-link this polymer to make it insoluble. Finally, RH cycling of the 2DSM and 3DSM materials has been initiated to demonstrate the superior mechanical attributes of these materials.

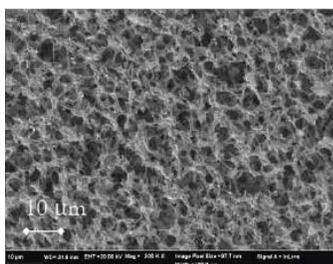
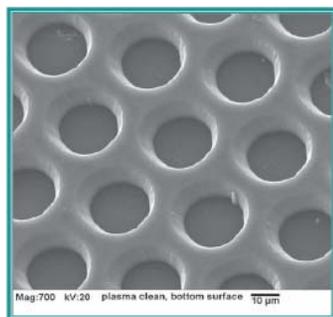


Figure 1: 2D (top) and 3D (bottom) DSMTM

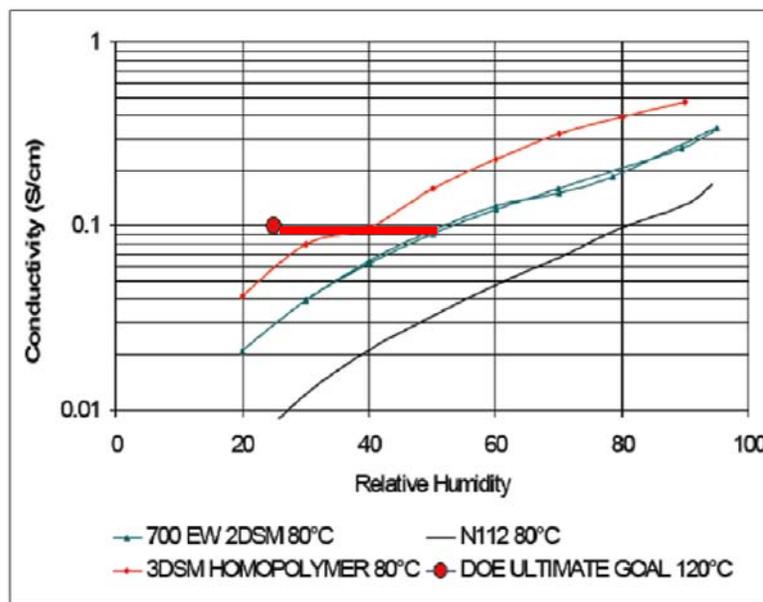


Figure 2: Conductivity of a 2DSM consisting of 700E\ PFSA in a polyimide support as well as that of the 3DSM with the SUNY-ESF homopolymer at 80°C

2008 FreedomCAR and Fuel Partnership Highlight

Impurity Migration in Fuel Cells

Los Alamos National Laboratory

Los Alamos National Laboratory (LANL) made significant progress in 2008 toward understanding impurity migration in fuel cells. Impurities in hydrogen and air can negatively impact the performance of fuel cells. Understanding how impurities migrate in fuel cells and the exact mechanisms of performance inhibition allows development of more robust fuel-cell technology. Some impurities, such as common sulfur compounds, have been shown to adsorb strongly to the electrode surfaces blocking surface sites for catalytic splitting of diatomic hydrogen on the anode and diatomic oxygen on the cathode. LANL successfully measured the hydrogen sulfide crossover rate at differing relative humidity and membrane thicknesses.

LANL's previous work demonstrated that very small amounts of hydrogen sulfide can affect the kinetically slower oxygen reduction reaction on Pt surfaces. The possibility of hydrogen sulfide (H_2S) from the hydrogen fuel poisoning the catalyst on the oxygen side of the fuel cell cannot be neglected. H_2S is a polar molecule with a very high solubility in water, and since the fuel cell membrane is highly permeable to water, hydrogen sulfide permeation is a possibility. Three types of transport mechanisms may occur; dry membrane permeation, co-permeation with water, and electro-osmotic drag where the movement of protons in the operation of the cell drag impurities along. The permeation rate across wet membranes was many times greater than for dry membranes as illustrated in Figure 1. The rate was significantly faster for thinner, higher performance membranes. The crossover of sulfur-containing molecules from the anode to the cathode means that impurity adsorption onto the cathode must also be considered even if the fuel cells are operating on highly filtered air. The permeation data is vital to the theoretical modeling of long-term fuel cell operation on less than pure fuels.

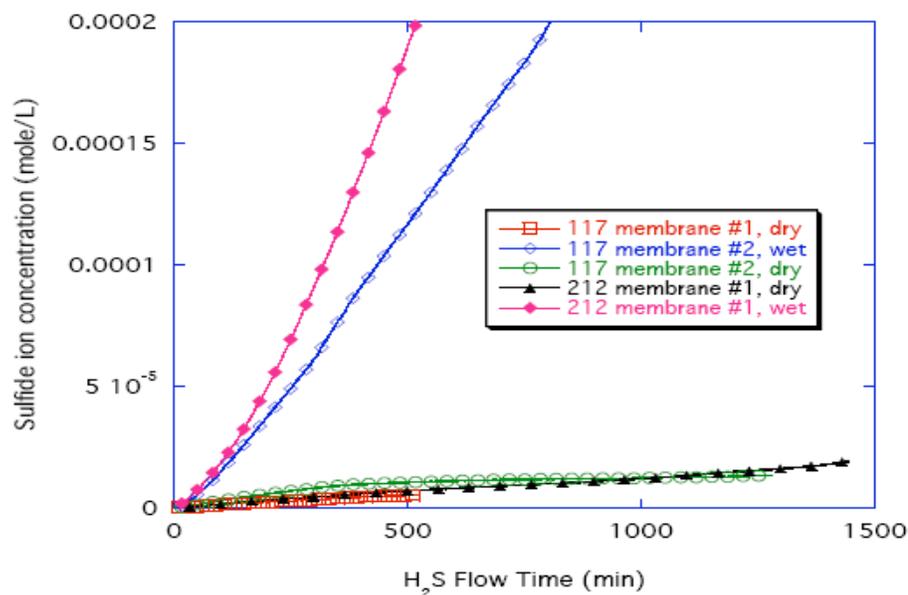


Figure 1: Sulfur crossover versus time for two thicknesses of membranes N117-175 μm and N212-51 μm and zero or 100% relative humidity

2008 FreedomCAR and Fuel Partnership Highlight

Improved Methods for Imaging Water in Operating Fuel Cells

National Institute for Standards and Technology

The National Institute for Standards and Technology (NIST) has dramatically improved the ability to visualize water in fuel cells. Managing the flow of water and gases inside a fuel cell is critical for maintaining power and efficiency. If the water created when hydrogen and oxygen react is not effectively removed, droplets may accumulate to the extent that they block the flow of gas to reaction sites and thereby slowing reaction and reducing power. However, removing too much water may dry out the polymer electrolyte membrane and decrease the conduction of protons, also reducing power. Fuel cells must also endure and operate in temperatures that will freeze water. When starting up in sub-freezing conditions, gas flow must be set to remove water before it freezes, while also allowing the fuel cell to heat up to operating temperature. The variation in the humidity, pressure and temperature of the air used by the fuel cell system further complicates water management.

NIST has developed the only non-intrusive technique for visualizing and quantifying water inside an operating fuel cell. During the past year, spatial resolution of images has been refined down to 25 microns. This allows gradients of liquid water to be observed in thin MEA component layers. Numerous experiments have been performed to validate phenomena predicted in mathematical modeling, and to demonstrate the importance of micron scale thermal gradients. These experiments have led to improved performance through invention and implementation of water-proofing methods that mitigate water leakage as confirmed through neutron imaging, shown in Figure 1. Newly added freeze/thaw capability to -40°C has enabled the development of shutdown purging mechanisms critical to fuel cell durability. Finally, further resolution improvement to only 10 microns has been shown to be feasible in a detector that is less sensitive to naturally occurring gamma background noise.

No microporous layer or water-proofing



Figure 1: Experimental data identifying water leakage (orange) and effective mitigation (blue).

2008 FreedomCAR and Fuel Partnership Highlight

Microstructural Characterization of PEM Fuel Cell Membrane-Electrode Assemblies

Oak Ridge National Laboratory

There are two, related, Membrane-Electrode-Assembly (MEA) visualization needs: provide details about the types of catalyst-layer microstructures that deliver optimum fuel cell performance and durability, and show how MEA fabrication techniques affect the microstructure of catalyst layers. During the past year, there has been an accelerated effort to implement the HAADF-STEM (high-angle annular dark field - scanning transmission electron microscopy) also known as the Z-contrast technique to characterize the unique structures of cathode catalyst nanoparticles at an extremely high resolutions of <0.1 nm. This technique is particularly useful for imaging various types of catalyst because of contrast variations between catalyst particles and supports. The elements in alloy catalysts such as Pt-Co, Pt-Pd and Pt-Cr, and in carbon supports have atomic number differences large enough to be distinguished in images created with this high-precision instrument. To achieve precision and accuracy when viewing phenomena at the atomic level, great care is taken to isolate microscopy instruments from the external environment. But it is highly important to observe chemical phenomena that occur in fuel cells in the environment to which they will be exposed while in actual use. This past year, Oak Ridge National Laboratory (ORNL) has observed catalyst particles exposed to a very relevant operating condition, temperature, by developing a tiny heater that fits inside the column of the electron microscope. The changes that occur when individual catalyst particles are heated can be seen in a sequence of images over time, while special measures are taken to protect the sensitive instrument.

One of ORNL's experiments characterizes a mechanism by which catalytic surface area is reduced, resulting in the degradation of fuel cell performance over time (shown in figure 1). Whole Pt particles actually move across the carbon support surface (rather than moving one atom at a time) toward a nearby Pt particle. Once in contact, the Pt particles coalesced, and rather than forming a polycrystalline "agglomerate" of nanoparticles (as might be expected when two small particles touch), the Pt particles formed a larger, single-crystal particle with relatively less area for electrochemical reactions. By characterizing performance degradation mechanisms, effective mitigation strategies can be developed.

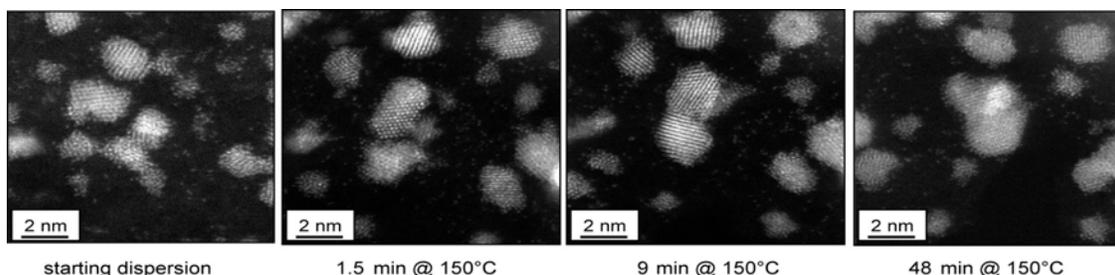


Figure 1: Sequence of HAADF-STEM images of Pt/C showing Pt nanoparticle coalescence during heating for 48 minutes at 150°C

2008 FreedomCAR and Fuel Partnership Highlight

Systems Analysis of Hydrogen Storage Options

Argonne National Laboratory

The DOE applied hydrogen storage program is investigating a wide-range of materials with the potential to store sufficient hydrogen to enable a driving range greater than 300 miles. On-board reversible and off-board regenerable (e.g. chemical hydrides or chemical hydrogen storage) materials are part of the portfolio. The FreedomCAR and Fuel Partnership hydrogen storage performance targets are based upon a system. Systems analysis such as that conducted by Argonne National Laboratory (ANL) is critical to rank the material approaches on an equivalent basis by projecting system performance using the material's operating properties.

Examples of ANL's work in assessing materials' properties are found in analysis of chemical hydrides. For chemical hydrides, the recovered spent fuel from the vehicle must be efficiently recycled and regenerated to its starting composition in order for the carrier to be an acceptable storage media. A viable fuel system would satisfy not only system targets for weight, volume, cost, and minimum full flow rate of hydrogen but also the DOE's goal of greater than 60% well-to-tank energy efficiency.

For each storage option, ANL collaborated with the material developers to develop a flowsheet for off-board regeneration (Figure 1). ANL determined the energy consumption for each step in the flowsheet and computed the overall fuel cycle efficiency. ANL compared the calculated well-to-tank (WTT) efficiencies for chemical hydrides with the efficiencies for physical storage methods (compressed and liquid hydrogen). ANL calculated WTT efficiencies between 12 to 23% for the electrolysis routes and the direct reduction methods for regenerating sodium borohydride from its spent fuel. Depending on the availability of low-grade waste heat, ANL estimated a WTT efficiency of 40-55% for regenerating alane by an organometallic route. ANL calculated a WTT efficiency of ~60% or higher for rehydrogenation of an organic liquid carrier in multi-stage, catalytic trickle-bed reactors with regenerative intercooling (Figure 2).

These analyses provide important information on the regeneration of chemical hydrogen carriers currently under study. They also identified the most energy intensive processes in the regeneration scheme that need to be modified or optimized in order to improve the overall energy efficiency.

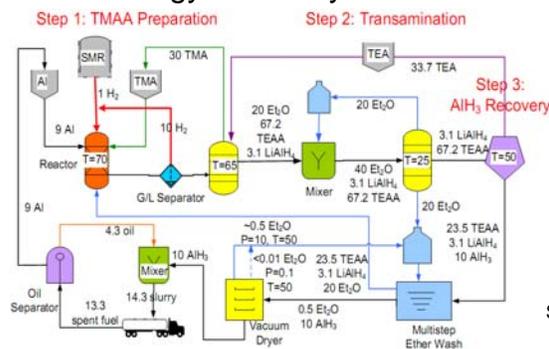


Figure 1: Flowsheet for regeneration of AlH₃ by organometallic route

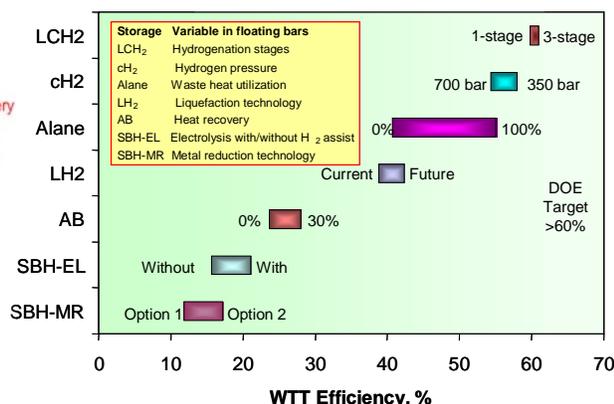


Figure 2: Preliminary results for WTT efficiency of different storage options

2008 FreedomCAR and Fuel Partnership Highlight

Identifying Areas for Storage System Cost Reduction

TIAX LLC

Hydrogen storage system costs are less well known than fuel cell system costs, because of its earlier stage of development. There has been significant open literature and proprietary work conducted to understand the key cost drivers of fuel cell systems; less work has been conducted on storage systems. Work by TIAX helps fill this gap of understanding the issues that most directly impact on-board storage system cost. TIAX has conducted techno-economic assessments for hydrogen storage technologies. The overall project objective is to provide an independent analysis to help guide the DOE and developers toward promising R&D and commercialization pathways by evaluating them on a consistent basis. Hydrogen technologies evaluated to date represent the major storage methods and include:

- Physical - 350 and 700 bar compressed H₂, liquid H₂, cryo-compressed
- Reversible on-board - sodium alanate
- Regenerable off-board - sodium borohydride hydrolysis, N-ethylcarbazole
- Cryogenic sorbents - activated carbon

TIAX utilizes product-based (e.g. activity-based) cost models to project high-volume (i.e., 500,000 units/yr) manufactured cost for the on-board storage system, and H₂A-based discounted cash flow models to project hydrogen selling prices based on the required off-board (i.e., refueling) hydrogen infrastructure. Subsequently, these results are vetted by developers, key stakeholders, and/or industry experts and refined based on their feedback. This is an on-going and iterative process so that the DOE can increasingly focus their efforts on the most promising technology options. TIAX also works with the relevant organizations to evaluate the well-to-wheel or lifecycle cost, primary energy use, and environmental impact of each storage system.

The figure below shows a sample comparison plot of the on-board storage system manufactured cost for various technologies assuming high-volume production. These plots compare the cost of major sub-systems as well as total system cost relative to DOE targets. For example, the carbon fiber tanks account for over 75% of the compressed H₂ storage systems' cost, while balance of plant components make up a significant portion of the cryogenic storage systems' cost. These on-board cost results are combined with hydrogen selling price projections to generate ownership cost results. Also shown in the figure below are the results of a single-variable sensitivity analysis performed on the cryo-compressed storage system. Sensitivity analyses enable DOE to capture and track the uncertainty in the cost models for critical cost parameters.

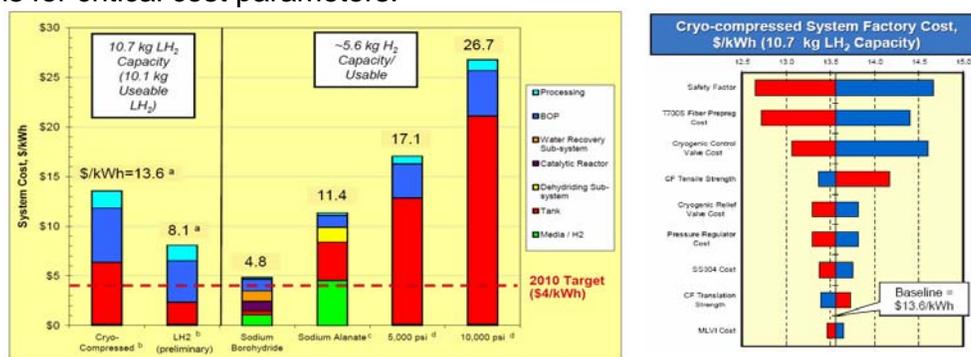


Figure: Sample On-board System Cost Comparison Plot and Sensitivity Analysis Results Tornado Chart

2008 FreedomCAR and Fuel Partnership Highlight

MB₁₂H₁₂ Effects on Borohydride Reversibility

NASA JPL, Caltech and GE

Metal borohydrides have high theoretical hydrogen contents (e.g., 18 and 15 percent by weight for LiBH₄ and Mg(BH₄)₂, respectively). Borohydrides are generally very difficult to recharge, making on-board refueling slow and difficult. Catalysts and other approaches have been applied to this problem, with only limited reversibility improvements achieved. The team has shown the reversibility difficulty relates to the formation of MB₁₂H₁₂ intermediates.

Achieving practical reversibility requires an understanding of the reaction barriers that may be present in partially or fully dehydrogenated metal borohydrides. Boron (B) intermediate species are difficult to identify by conventional x-ray or neutron diffraction techniques because they are often amorphous. The use of nuclear magnetic resonance (NMR) spectroscopy has been able to circumvent this experimental dilemma. NMR measures characteristic resonance spectra of atoms between a strong magnetic field and an applied radio frequency (RF) field. Using the isotope ¹¹B and solution NMR spectroscopy techniques, the intermediate decomposition phases of Li- and Mg-borohydride have been definitively shown to contain the [B₁₂H₁₂]⁻² anionic species (see Figures 1 and 2). Thus the stable intermediate phases Li₂B₁₂H₁₂ and MgB₁₂H₁₂ apparently form during decomposition and likely constitute major reaction barriers inhibiting reversibility in decomposed LiBH₄ and Mg(BH₄)₂, respectively.

The formation of MB₁₂H₁₂ intermediate phases is likely a general phenomenon with borohydrides. The key R&D challenge is to now learn how to prevent the formation of that phase in order to enhance general borohydride reversibility.

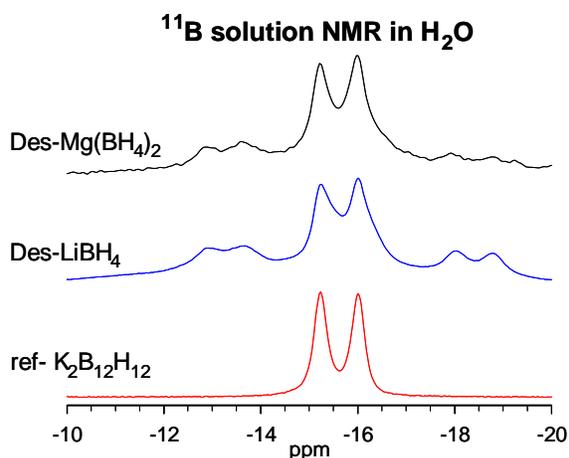


Figure 1: Two NMR spectra (referenced to standard K₂B₁₂H₁₂) conclusively shows the stable [B₁₂H₁₂]⁻² anion unit (shown in Figure 2) is present in dissolved LiBH₄ and Mg(BH₄)₂ decomposition products.

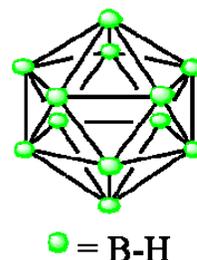


Figure 2: The [B₁₂H₁₂]⁻² anion unit.

2008 FreedomCAR and Fuel Partnership Highlight

Chemical Hydrogen Storage Materials Down Select

Partners of the Chemical Hydrogen Storage Center of Excellence

In order to maximize utility and focus limited resources on the most promising materials, DOE established a down selection milestone in its Multi-Year RD&D Plan for chemical hydrides in FY2008. The Chemical Hydrogen Storage Center of Excellence (CHSCoE) developed criteria for the decision based on the potential to meet key DOE 2010 technical targets. By applying these criteria to all materials explored by the Center, the remaining portfolio was prioritized and moved forward to Phase 2 R&D activities.

Decision criteria (see Table 1) included gravimetric capacities, regenerability, phase change during dehydrogenation, kinetics of hydrogen release, and material stability. From these criteria, a decision tree (see Figure 1) was developed, and applied to each material or class of materials. The CHSCoE partners have studied more than 62 materials or classes. Several approaches to hydrogen release have also been explored by the Center, including thermolysis, catalysis, and hydrolysis. Other concepts such as hydrogen release from coupled endothermic – exothermic systems and hydrogen storage in nanoparticle materials were also examined.

As a result of the down select, approximately 50% of the materials were deselected due to low capacity, slow release rate or high release temperature. Materials that were discontinued included endothermic organic hydrides, nanoparticles, and magnesium alkoxides, among others. Another 30% were conditionally down selected with short-term issues that need to be resolved for continued research. Among those were carbenes, certain metal amidoboranes, and methylamine borane. Only 20% of the materials were selected to continue as priority R&D within the Center. Among those were ammonia borane, some metal amidoboranes, and certain alkylamine boranes.

The report in its entirety was posted on the DOE website at:

http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/chs_coe_down_select.pdf

Table 1

Criterion	Description	Metric
Gravimetric Capacity	Maximum calculated hydrogen weight fraction	> 7 wt. % H ₂
Potential to Regenerate On-Board	Potential to rehydrogenate spent fuel directly	yes/no/maybe
Regenerable	Ability to chemically reprocess spent fuel off board	yes/no/maybe
Acceptable Phase Change	Problematic liquid to solid phase change, or volatile byproducts	yes/no/maybe
Acceptable Release Rate	Maximum rate of hydrogen release, T < 125 °C	> .02g H ₂ /s/kg material
Material Stability	Stable in fuel tank < 50 °C	yes/no/maybe
Endothermic Release	Hydrogen release occurs endothermically	yes/no/maybe
Low Temperature	For endothermic reactions, temperature of release < 200 °C (with potential for lower T, i.e., 80 °C, release)	Temperature

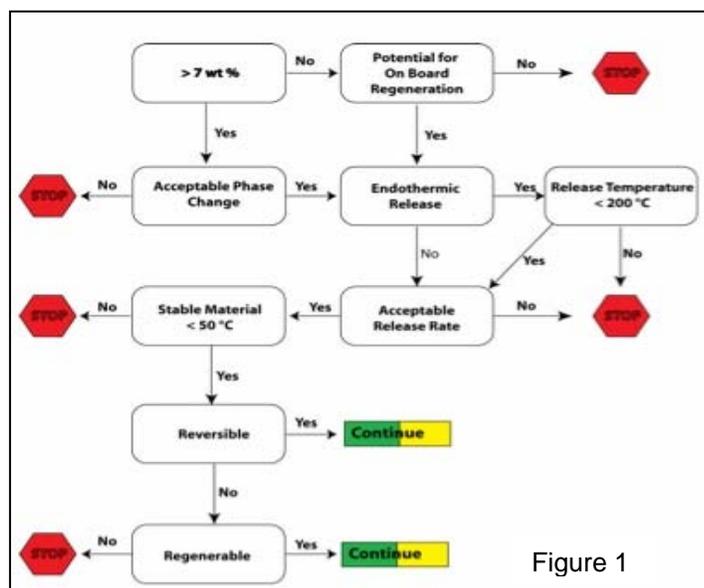


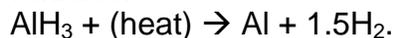
Figure 1

2008 FreedomCAR and Fuel Partnership Highlight

Alane Regeneration Via Adduct

Brookhaven National Laboratory

Alane (AlH_3) is a metastable hydride that can be decomposed to supply H_2 for a fuel cell or internal combustion engine vehicles:



This simple reaction has favorable properties for vehicular H_2 storage: theoretical volumetric capacity 150 g H_2/L , gravimetric capacity 10 wt% H_2 , release temperature less than 100°C , kinetic desorption rates at $\sim 100^\circ\text{C}$ nearly fast enough to supply a fuel cell vehicle and low desorption heat requirement ($\Delta H_{\text{des}} \approx 10 \text{ kJ/mol H}_2$). While the low ΔH_{des} has a distinct engineering advantage for desorption, the drawback is that H_2 -depleted alane (Al metal or AlH_x) requires very high H_2 pressures for hydrogenation back to alane (AlH_3). As shown in Figure 1, 7 kbar (700 MPa) H_2 pressure would be theoretically required for direct Al rehydrogenation/hydriding at room temperature (298K). Such high pressures are impractical for on-board refueling and likely too expensive for off-board regeneration.

A promising route to reduce the severity of regeneration conditions has been discovered at Brookhaven National Laboratory (BNL). BNL has found Ti-doped aluminum (Al) can be recharged to AlH_3 at modest pressure in certain solutions of a group known as Lewis acids. The stabilizer solution can be an amine (triethylenediamine, TEDA), with alkali hydride (LiH), in a solvent (tetrahydrofuran, THF), among others. This strategy suggests possible multistep processes, all under mild chemical conditions, for forming AlH_3 -adducts followed by harvesting and adduct removal steps. BNL has synthesized the adduct alane-TEDA and has attempted to harvest neat alane by evaporating the adduct, as shown in Figure 2. Although the alane-adduct formation step requires $<100^\circ\text{C}$ and a few bar H_2 pressure, the energy and temperature required to free the TEDA and recover pure AlH_3 proved to be too high.

Thus the remaining challenge is to find the best adduct that allows mild Al hydrogenation conditions but minimum energy to recover the pure alane. There are many possibilities being explored from both theoretical and experimental directions. AlH_3 -pyridine and AlH_3 -pyrazine based adducts show promise for the future.

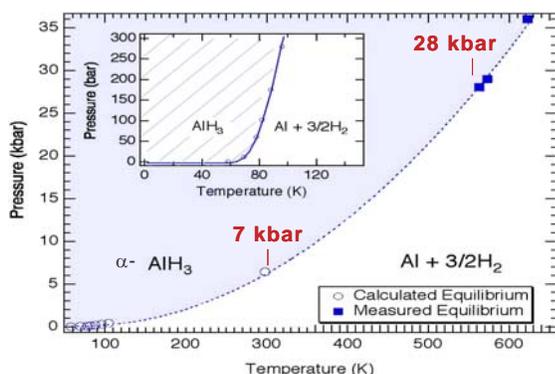


Figure 1: Pressure-temperature phase diagram for $\alpha\text{-AlH}_3$. Direct hydriding of Al has been accomplished only at $P > 25$ kbar and $T = 550\text{-}600\text{K}$.

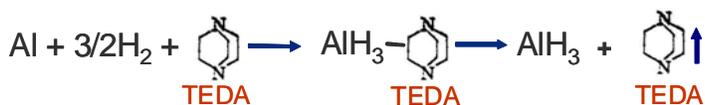


Figure 2. Two-step reaction to hydride Al to the AlH_3 -TEDA adduct, followed by separation of the TEDA from the desired AlH_3 . Only the first step has been demonstrated. The AlH_3 -TEDA bonds are too strong to break without H_2 loss. Weaker amine adducts are being sought.

2008 FreedomCAR and Fuel Partnership Highlight

Metal Hydrides Materials Down Selected

Metal Hydride Center of Excellence

In order to ensure focus of limited resources on the most promising materials, the DOE conducted a down selection decision for metal hydrides in FY2008. The Metal Hydride Center of Excellence (MHCoe) developed criteria for the down selection based on potential to meet key DOE 2010 technical targets. By applying these criteria to all materials explored by the Center, down selected materials were prioritized and moved forward for further study in the Center's Phase 2 R&D activities.

While a variety of requirements must be met for a commercially viable hydrogen storage system, the MHCoe focused on five primary performance metrics on which Go/No-Go materials decisions were based: 1) the material's hydrogen storage gravimetric density should be ~5 weight percent with a clear potential for significantly higher, 2) the material should be at least 50% reversible, 3) the material should release its hydrogen at temperatures below 350°C, 4) the material's non-hydrogen volatilization products should not exceed 1000 ppm for a single thermal cycle and 5) the material should release hydrogen and reabsorb hydrogen in less than 24 hours. These criteria were used as guidelines in determining if specific material systems had sufficiently promising characteristics to warrant further work. They were not applied with absolute rigidity, nor do they substitute for the full DOE system targets for on-board hydrogen storage.

Of the 51 materials investigated in the MHCoe, 27 have satisfied the five performance metrics listed above (i.e. show promise as a viable hydrogen storage material) and are being studied further.

Among the materials being considered further, the incorporation of LiBH₄/MgH₂ into highly porous aerogels remains of interest due to the potential to improve the kinetic and thermodynamic properties of this material by nanoconfinement. Borohydride materials (Ca(BH₄)₂, Mg(BH₄)₂, etc.) remain of great current interest because these materials have a high hydrogen gravimetric storage density. Amide/Imide materials, the Li₃AlH₆/3LiNH₂ and LiMgN systems, are being pursued because they have reasonable theoretical hydrogen gravimetric capacities (~ 7 – 8 wt. %) and are reversible at temperatures between 250°C and 300°C. Aluminum hydride (AlH₃) continues to be of interest due to its high hydrogen capacity (10 wt. %) and favorable hydrogen release kinetics at low (100°C) temperatures. Three research groups in the MHCoe will continue to investigate methods to rehydrogenate Al metal under moderate conditions.

The complete report is posted on the DOE website at:
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/mhcoe_materials_downselect_report_fy07.pdf.

Examples of Approaches Discontinued:

- MgH₂/Si : **not reversible X**
- 2LiNH₂ + MgH₂ : **wt. % limited X**
- Li₂Zn(BH₄)₄ : **high diborane X**

Examples of Approaches Continued:

- LiBH₄/MgH₂ in aerogels ✓
- LiMgN, Li₃AlH₆/3LiNH₂ ✓
- A_xMn(BH₄)_y [A=Li, Na, K] ✓
- AlH₃, and 22 other systems ✓

2008 FreedomCAR and Fuel Partnership Highlight

Improved Ammonia Borane Regeneration Efficiency and Yields

Chemical Hydrogen Storage Center of Excellence

Systems based upon chemical hydrogen storage materials require sufficient H₂ content by volume and weight as well as energy efficient H₂ release and low-cost methods to recharge the material back to its original state. Ammonia borane (AB), NH₃BH₃, is one of the unique materials that can potentially meet the storage system requirements due to its high hydrogen content (potential of ~19 wt% on a material basis), and favorable operating temperatures. However, it is not possible to directly rehydrogenate the spent fuel, thus off board chemical processing is required. Efficient AB regeneration is key to the application of AB as on-board hydrogen storage material.

The Chemical Hydrogen Storage Center of Excellence has demonstrated three routes to chemical reprocessing of spent fuel based upon novel approaches of digestion with superacids, thiols, and alcohols. These routes share a general approach of first digesting the spent fuel of approximate stoichiometry of BNH_x, to avoid formation of thermodynamically limiting intermediates. Digesting the spent fuel converts the material to a form that is more readily returned to ammonia borane with a chemical reducing agent such as a metal hydride. This general approach is shown in Figure 1.

Working closely with theorists within the Center has allowed a rapid screening of a wide variety of digestion and reducing agents. Matching the thermodynamics of digestion with reduction has resulted in improvements in efficiency of these three routes as is shown in Figure 2. Significant progress has been made on the thiol route and the thermodynamic regeneration efficiencies have improved significantly from 60 to 80%. This AB regeneration route has been demonstrated in lab scale in greater than 70% yield. The Center has also demonstrated the conversion of digestate to AB at greater than 95% yield. As each regeneration scheme is developed, the Center is finding synergy between the approaches, leading to 'hybrid' schemes with overall improvements in energy efficiency of regeneration of spent fuel.

These advances come as a result of the Center's closely integrated team of experimentalists and theorists, working in concert with engineers who are charged with developing an overall assessment of process efficiency. This multidisciplinary approach to problem solving continues to make improvements in hydrogen release and regeneration of chemical hydrogen storage systems.

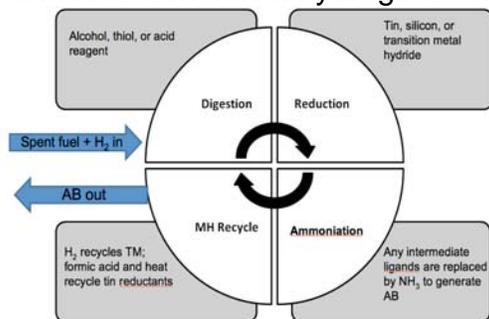


Figure 1

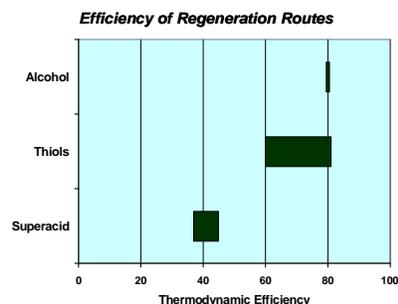


Figure 2

2008 FreedomCAR and Fuel Partnership Highlight

Higher Hydrogen Binding Energy on Adsorbents

UC-Berkeley, UC-Santa Barbara and Texas A&M

Storing hydrogen using adsorbent materials is attractive because the uptake and release kinetics of hydrogen is fast, and the energy required to release hydrogen is relatively low. These advantages have been offset by the low amount of hydrogen stored on a volumetric basis and the need for cryogenic temperatures (e.g. 77K, the temperature for liquid nitrogen at 1 atm) and moderate pressure to maintain high capacity. The main goal for automotive storage applications is to develop materials that will store hydrogen closer to ambient temperatures and moderate pressures. The goal is to increase heats of adsorption from physisorption (e.g. via van der Waals forces) levels of 4-6 kJ/mol to stronger binding of 15-25 kJ/mol that is intermediate between physisorption and chemisorption. Three teams have made progress in different ways.

Several strategies have been put forward by the research community to raise the operating temperature of sorbent materials from cryogenic to near-ambient temperatures without compromising capacity. These include synthesis of coordinatively unsaturated metal sites that could bind one or more dihydrogen (H_2) molecules, design of pore aspect ratio and size/diameter, and use of charged frameworks to increase van der Waals-type forces. Overarching is the need to increase the number and strength of hydrogen binding sites (e.g. through surface area) to increase overall capacity.

Three recent approaches have been successfully demonstrated which address the above challenges toward enhanced hydrogen binding in sorbents. 1) Researchers at UC-Berkeley have synthesized nanoporous coordination solids that have improved performance at cryogenic temperature and moderate pressure (total of 11.5wt% and 77g/L at 77K and 170 bar for air-free $Zn_4O(BDC)_3$, surface area of 3800 m^2/g). They have since developed methods to attach transition metals such as Cr, Mo to the benzene linkers to provide additional higher energy binding sites for dihydrogen molecules (Figure 1). They have generated $Zn_4O[(BDC)Cr(CO)_2(H_2)]_3$ that is stable at 298K. 2) Researchers at UC-Santa Barbara are looking at three classes of materials using hybrid materials with fluorinated organic linkers and materials with open metal sites that could bind more than one dihydrogen. They have found that use of fluorine was shown to increase H_2 binding energy by ~50% (Figure 2). 3) Researchers at Texas A&M have developed MOF materials with open-metal sites designated PCN-12 with initial H_2 binding enthalpies of 12 kJ/mol. These binding energies may potentially increase the low-pressure H-capacity by up to 75% over adsorbents with typical physisorption binding (Figure 3). These tailored materials have volumetric hydrogen densities which range from 24-45 g/L (on the basis of best-case material-only crystal densities).

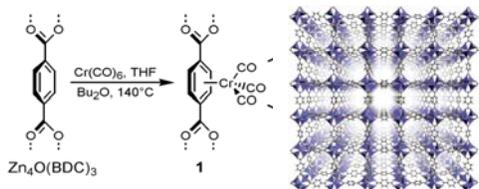


Figure 1: Metal atom exposure to Enhance binding energy

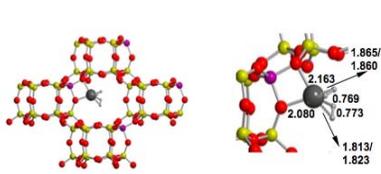


Figure 2: Fluorine used to increase metal atom binding to H_2

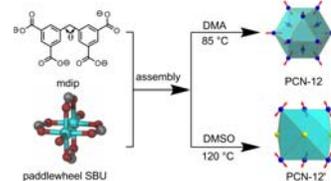


Figure 3: PCN material with 12kJ/mole binding energy

2008 FreedomCAR and Fuel Partnership Highlight

Improved Hydride Kinetics via Carbon Aerogel Scaffolds

HRL Laboratories, LLC and Lawrence Livermore National Laboratory

Metal borohydrides can have a very high hydrogen storage content. For example, Lithium Borohydride (LiBH_4) can be thermally decomposed according to the reaction $\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 1.5\text{H}_2$, theoretically yielding nearly 14 weight percent hydrogen. While these high capacities present a very attractive option for on-board supply of H_2 fuel, the decomposition kinetics of LiBH_4 are too slow and thermodynamic constraints dictate impractically high temperatures for hydrogen desorption. Collaborative work during 2008 by HRL Laboratories, LLC (HRL) and Lawrence Livermore National Laboratory (LLNL) has shown that kinetics, and possibly thermodynamics, can be improved by nesting the LiBH_4 in porous carbon aerogels (“scaffolds”).

Nanoporous carbon scaffolds improve kinetics of metal hydrides by limiting hydride particle size and reducing diffusion distances. In addition, very small particle sizes and subtle chemical reactions with the carbon substrate may improve the thermodynamics, thus leading to reduced desorption temperatures. Using LiBH_4 as a model system, HRL and LLNL have worked together to optimize the pore volume and size of aerogel carbon scaffolds to reduce the weight penalty and increase the desorption kinetics of the LiBH_4 itself. As shown in Figure 1 (left), dynamic desorption temperatures can be reduced by nearly 100°C by incorporating the hydride in C-aerogels. Pore volume and size is critical to the process; a high pore volume, 25 nm pore size C-aerogel made by LLNL gave the best overall results ($> 7 \text{ wt}\% \text{ H}_2$ desorbed below 450°C). As shown in Figure 1 (right), the use of aerogel scaffolding increased the 300°C isothermal decomposition kinetics of LiBH_4 by a factor of 60 relative to a graphite-mixed control sample.

While these initial results are promising, several challenges remain. Continuing efforts aim to apply this concept to destabilized hydride mixtures, e.g., $\text{LiBH}_4 + \text{MgH}_2$. Future work will attempt to further improve kinetics, reduce desorption temperatures, increase gravimetric capacity (by minimizing scaffold mass), identify optimal scaffolds, and establish stability with respect to H_2 absorption/desorption cycling.

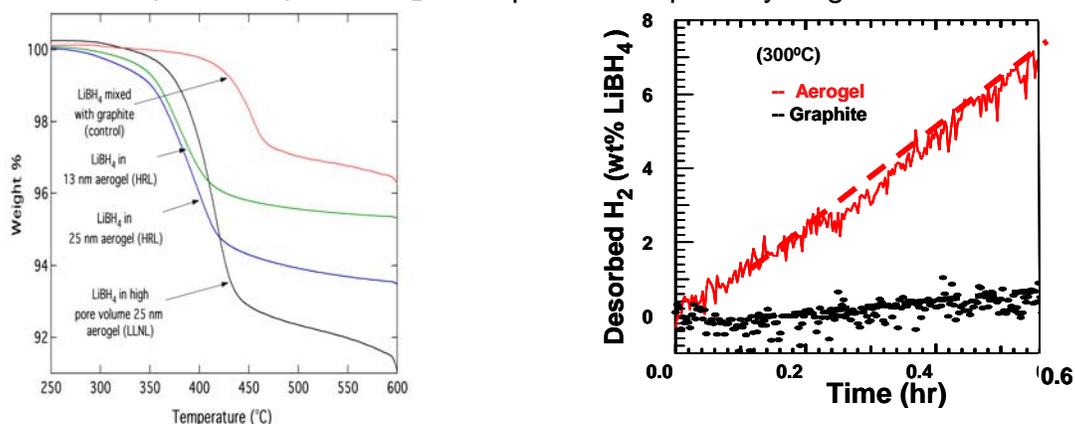


Figure 1: Desorption curves for various C-aerogel-scaffolded LiBH_4 samples compared to a graphite-mixed control sample. Left: Temperature-programmed desorption (TPD); Right: 300°C isothermal desorption (backpressure $< 0.05 \text{ bar}$)

2008 FreedomCAR and Fuel Partnership Highlight

Development of Textile Based Carbon Fiber Precursor

Oak Ridge National Laboratory

Oak Ridge National Laboratory (ORNL) and FISIFE S.A. (Lisbon, Portugal) have developed a lower cost carbon fiber precursor based on textile grade, polyacrylonitrile (PAN) fiber containing vinyl acetate co-monomers. Carbon fibers offer significant weight saving potential because of their high strength, high modulus, and low density. The use of carbon fibers is currently restricted by its high cost, which is \$8 to \$15 per pound, of which fifty percent is attributable to the cost of the precursor. The new precursor material is similar to a slightly modified version of knitting yarn. A small chemical modification to the polymer composition was developed followed by a low cost, in-plant chemical pretreatment of the textile grade material while the fiber was still in the un-collapsed state. This was accomplished by the determination of the best concentration-temperature-exposure profiles in a proprietary chemical bath to render the fiber rapidly oxidizable and subsequently carbonizable by conventional processes. This was done using readily available and inexpensively implementable manufacturing techniques that currently exist in textile PAN plants. Finally, precursor-to-carbon fiber time-temperature-tension processing conditions were determined for converting the precursor into finished carbon fiber.

This lower cost precursor is targeted to produce a new grade of carbon fiber for high volume industries including automotive body and chassis applications. Automotive program requirements target finished carbon fibers that have tensile strengths in excess of 250 KSI and moduli of at least 25 MSI, but cost between \$5.00 - \$7.00 per pound. That cost goal would allow the introduction of carbon fiber based composites into a greater number of applications for future vehicles, windmills, bridge reinforcement, pressure vessels and other high volume industries. Currently strengths in excess of 363 KSI GPA and moduli in excess of 31 MSI have been achieved using the textile grade precursor without optimization of the fiber tensioning during oxidation, stabilization and carbonization. Next steps include developing high volume finished product forms and development of sizing and surface treatment that make this carbon fiber and other carbon fibers compatible with automotive resin systems.



Figure 1: Typical Carbon Fiber Precursor (Front –Bottom)
Chemically Pre-Treated Textile Based Carbon Fiber Precursor (Back – Top)

2008 FreedomCAR and Fuel Partnership Highlight

Lightweight (Rear) Chassis Structures

Auto Steel Partnership

Chassis components make up a substantial portion of a passenger vehicle's weight. Today's steel chassis structures make use of architectures and materials that have been in use for many years. Unlike body structures, little work has been undertaken to reduce the mass of steel chassis structures through the use of Advance High Strength Steel (AHSS), and new design and manufacturing concepts.

In keeping with the FreedomCAR's goal of affordably reducing the mass of passenger vehicles, the goals of this project are to: 1.) develop design solutions for steel chassis structures that result in a 25% mass reduction at no more than a 9% cost premium, and 2.) communicate the solutions to chassis engineers. Specific issues addressed include the application of AHSS, new design architecture, manufacturability, cost, fatigue and corrosion resistance.

Manufacture and test of Phase I design, substituting readily available AHSS materials for conventional steels, demonstrated successful use of AHSS in the rear chassis structure. It demonstrated the ability to achieve a 15% mass savings, and to address fatigue and corrosion concerns associated with reduced thickness of the advanced steels. A virtual testing methodology was developed for evaluating the durability of chassis structures, which will minimize the need to build and physically test parts in the future.

Simulation of the Phase II "clean sheet" redesigned assembly indicates a 27% mass reduction using advanced optimization techniques and DP590, DP780 and TRIP780 AHSS.

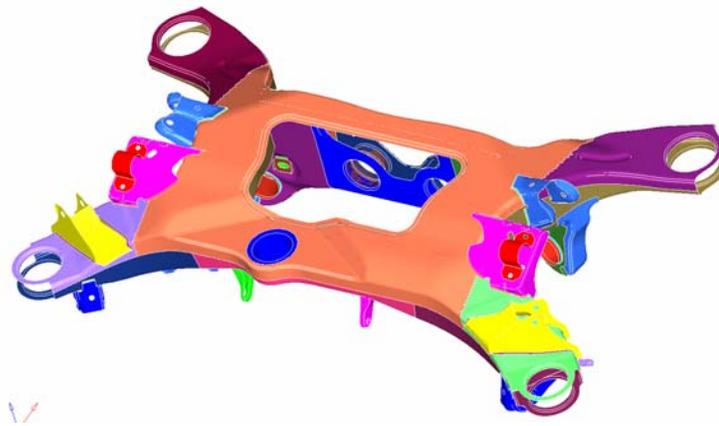


Figure 1: Rear Cradle Phase II Proposal -
Achieved 27% mass save with no loss of stiffness.

The team is completing forming simulations and corrosion test analyses of components of the structure and completing the cost analysis for the Phase II final design. Completion of the final report and transfer of the knowledge gained will follow.

2008 FreedomCAR and Fuel Partnership Highlight

Magnesium Front End Design and Development

USAMP Automotive Metals Division

The overall target for the Automotive Lightweighting Materials in FreedomCAR is a 50% weight reduction compared to baseline, predominantly-steel, vehicle structures. Magnesium alloys, the lightest of the structural engineering metals, can be effective in approaching this goal, if used extensively. Most current North American vehicles are front-heavy with a front-to-rear mass ratio above 55/45. Reducing front end mass for a near 50/50 mass ratio can enhance driving and handling performance as well as improve vehicle fuel economy.

The Magnesium Front End Design and Development (MFEDD) project of the Automotive Metals Division of USAMP specifically addresses mass reduction and weight distribution by the formulation of designs for magnesium-intensive, structural “front end” assemblies for unibody (car) and Body on Frame (truck) front end structures. The goal of the MFEDD project is to develop engineering design/analysis and technical cost modeling for magnesium front end structures for selected unibody and body-on-frame vehicle architectures that will accomplish 50% mass reduction compared to the steel baselines with equivalent performance and acceptable costs.

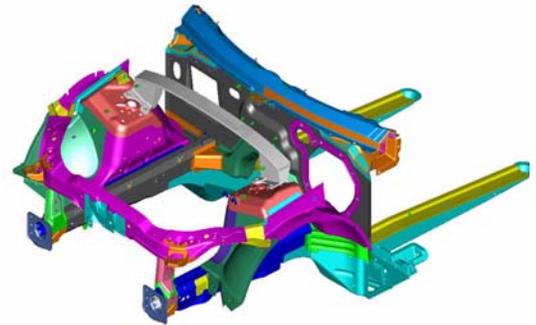


Figure 1: Baseline steel “unibody” front structure

This is a companion project to the Magnesium Front End Research and Development (MFERD) project, which is an international cooperative effort to develop the enabling manufacturing and materials technologies that could eventually permit the deployment of such structures in a mass-manufacturing environment.

Project Accomplishments

- Initial design iteration indicates 45 to 47 % mass reduction

	Unibody (Car)		Body on Frame (truck)	
	No. of Parts	Mass (Kg)	No. of Parts	Mass (Kg)
Steel Baseline	79	84.3	16	70.7
MFEDD Magnesium Design	35	46.1	3	37.5
Reduction	44 (55%)	38.2 (45%)	13 (81%)	32.2 (47%)

- Completed Technical cost modeling for the unibody steel front end baseline

Future Work

- Future design iterations are ongoing to increase mass saving (approaching 50%) and improve simulations in crashworthiness and durability using magnesium properties developed in the MFERD project, as are technical cost modeling efforts to generate understanding in cost structure using magnesium components.

2008 FreedomCAR and Fuel Partnership Highlight

Engineering Property Tools for Tailored Polymer Composite Structures

Pacific Northwest National Laboratory

Injection-molded long-fiber thermoplastics (LFTs) offer good mechanical performance and thus can be used for structural applications to reduce vehicle weight. However, the lack of modeling tools limits the use of LFTs for automotive structural applications. The objective of this research project is therefore to develop predictive engineering tools to enable the design of LFT automotive components.

One of the key issues for the prediction of mechanical properties of LFTs is the knowledge of fiber orientation in the as-formed composite. Pacific Northwest National Laboratory (PNNL) has worked with the University of Illinois at Urbana-Champaign to develop a new fiber orientation model for LFTs. This Anisotropic Rotary Diffusion model, implemented in the Moldflow code, allowed accurate fiber orientation predictions in LFT samples.

In parallel, constitutive models for LFTs have also been developed and validated to predict some relevant behaviors that an LFT part can exhibit in practice. These behaviors are related to thermoelastic properties, elastic-plastic response, creep, and damage. The constitutive models account for key microstructural features such as fiber length, orientation, curvature, and volume fraction distributions, as well as micro-defects and nonlinearities such as matrix damage and plasticity, and fiber/matrix debonding.

A code named “EMTA” was developed to compute the thermoelastic properties of LFTs. In addition, the developed elastic-plastic, creep, and damage models were implemented in the ABAQUS finite element code and were used for structural analyses. Oak Ridge National Laboratory has performed experimental tests that have validated molded LFT characteristics and resulting composite properties.

Future work will include model developments to address fiber length attrition, fatigue and impact damage of LFTs.

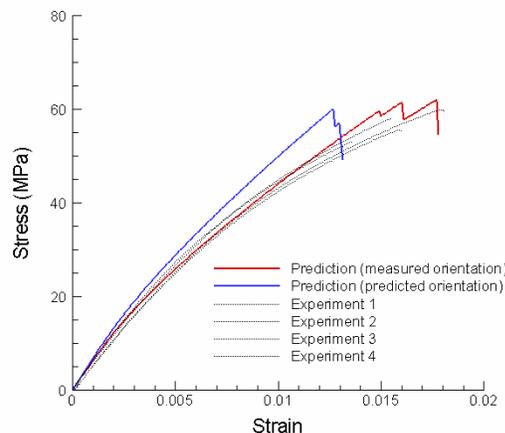


Figure 1: Red line shows very good correlation of (EMTA – ABAQUS) constitutive model predicted results obtained based on measured fiber orientation. Blue line shows reasonably good correlation based on predicted fiber orientation.

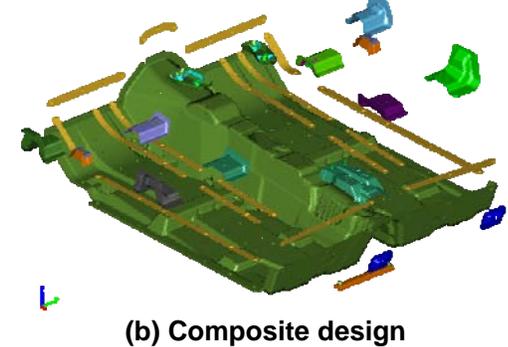
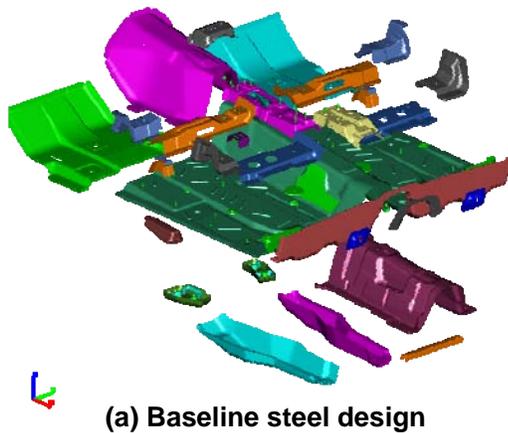
2008 FreedomCAR and Fuel Partnership Highlight

Development of a Structural Composites Underbody

Automotive Composites Consortium

The goal of the Development of a Structural Composites Underbody project, is to develop an underbody that will carry crash loads, and be part of the primary vehicle structure, while demonstrating the mass savings and parts consolidation advantages of composites. Composite underbodies in production vehicles, such as the Chevrolet Corvette, do not currently take the loads in a crash event. The primary research objectives of this project are: 1) A 2 ½ minute cycle time (100k vehicles per year, 2 shift operation), 2) Developing methods of joining and assembly of the underbody to the vehicle, and 3) Processes for fabricating oriented reinforcement within the time window.

A preliminary composite underbody design integrating 16 stamped steel components into a single molded floor, was developed to replace the steel assembly from a production donor vehicle (see figures). Vehicle level stiffness had equivalent or better performance to the donor vehicle while crash performance met applicable government and industry requirements. Design methodologies were developed to achieve acceptable performance for Full Frontal, Frontal Offset Deformable Barrier, Side, and Rear Offset Impact. Computer Aided Engineering stiffness, crash performance, and mass assessments achieved potential mass savings of 14.9 kg, a 31% decrease over the donor vehicle.



The materials and processes system selected for the underbody was a glass fabric sheet molding compound (SMC) with a high elongation core (HEC). Based on manufacturing considerations and the technical cost model, the use of carbon fiber composite could have saved an additional 3 kg, but at a cost of \$75 per kg saved. The glass fabric SMC has been demonstrated in several molding trials, and material properties measured.

A methodology was developed to join the composite underbody to the steel vehicle frame using weld bonding. The spot welds provide peel-stoppers for the adhesive bond, and serve as the fixture for the uncured adhesive that is cured in an electro-coat bath. A US patent application was submitted.

The full design of the underbody includes a component manufacturing plan, a joining and assembly to the vehicle structure plan, and validation of materials, processes, and analysis assumptions. This phase is now underway, with a rear tub surrogate tool selected to fabricate samples and evaluate the validity of material, processing, and analytical assumptions. Future work includes fabrication and testing of the underbody.

2008 FreedomCAR and Fuel Partnership Highlight

Fuel Efficiency Improvements for Hydrogen Internal Combustion Engine-Powered Vehicles

Argonne National Laboratory

Fuel cell vehicles are the subject of extensive research and development because of their potential for high efficiency, zero mobile emissions and petroleum consumption reduction. Because fuel cell vehicles are not yet viable, the demand for hydrogen is limited, and very few fueling stations are being built. To accelerate the development of a hydrogen economy, some OEMs in the automotive industry have been working on the hydrogen-fueled internal combustion engine (H₂-ICE) as an intermediate step. Also, several Department of Energy (DOE) projects are currently focusing on using a direct-injection hydrogen engine as a means to reach the 45% peak efficiency goal set by the FreedomCAR and Fuel partnership. This study confirms DOE's position that hydrogen internal combustion engine vehicles could act as a bridging technology towards a widespread hydrogen infrastructure. See related 2008 ACEC accomplishment on page # 1.

Argonne's PSAT modeling and simulation tool was used to evaluate the potential fuel efficiency benefits of fuel cells and hydrogen engines across different powertrain configurations, in comparison with a conventional gasoline vehicle as baseline:

Fuel Cell Systems:

- Current status:
500 W/kg,
55% peak efficiency
- FreedomCAR goal:
650 W/kg,
60% peak efficiency

Hydrogen Engine:

- Current technology characteristics from experimental data from Argonne on 2.3L engine with supercharged, intercooled, H₂ port injection (37% peak efficiency)
- Future technology for a direct injection (DI) H₂-engine extrapolated from single cylinder data (45% peak efficiency).

All the vehicles were sized with the same algorithm, taking into account the vehicle and component assumptions, the constraints for performance. The power electronics and charge sustaining energy storage systems were also sized to ensure all the regenerative energy above 2mph is captured in the battery on a UDDS cycle. Findings of this project were:

- Conventional H₂-ICE suffers from lower power density
- H₂-ICE has more efficiency potential than initially thought when hybridized
- Power split configuration (3rd bar in Figure 1) offers the best fuel consumption when using H₂-ICE due to added inefficiencies in the series configuration
- Drive-cycle efficiency of H₂-FC remains higher than H₂-ICE

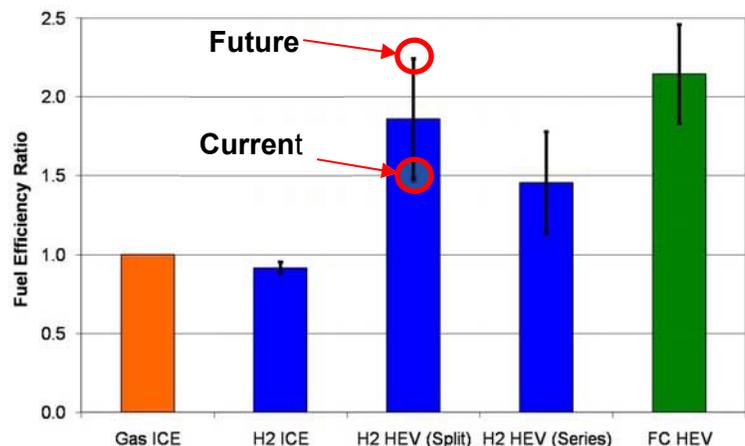


Figure 1: Fuel efficiency of H₂-ICE and H₂-FC HEV powertrains versus gasoline reference

2008 FreedomCAR and Fuel Partnership Highlight

Renewable Fuel Vehicle Modeling and Analysis

National Renewable Energy Laboratory

Renewable fuels and advanced technology vehicles offer some of the most promising pathways to reduce our dependence on foreign oil. Renewable fuels directly displace petroleum while advanced technology vehicles improve the efficiency to reduce the amount of fuel needed. The combination of the two has the potential to create petroleum reduction pathways with greater benefits than either would provide individually. Each conventional flex-fuel vehicle using E85 can reduce petroleum consumption 60% to 80% by directly displacing gasoline, as seen in Figure 1.

Achieving the large reductions in gasoline use across the fleet from flex-fuel conventional vehicles requires more E85 than is currently produced in the U.S. today or is planned for production under the Renewable Fuel Standard (RFS). In 2007, the U.S. produced 6.5 billion gallons of ethanol. By 2022, the RFS mandates 36 billion gallons per year. A US fleet of only conventional flex-fuel vehicles could use over 100 billion gallons per year. Therefore, the RFS would supply renewable fuels for 1/3rd of the vehicles. Advanced vehicles could stretch the renewable fuel supply to more vehicles. If the entire fleet were HEVs, the RFS could supply the necessary E85 for half of the fleet. Not only do flex-fuel HEVs require less ethanol, but with above \$4.00/gallon gasoline, they are more marketable than other options. Although more expensive, the entire fleet could be supplied by the RFS if it is composed of Plug-in Hybrid Electric Vehicles (PHEVs) with 40 miles of 'all electric range' (AER), reducing gasoline use by over 90%.

Renewable fuels and advanced vehicle combinations have great potential to reduce transportation petroleum use. If enough ethanol is produced, flex-fuel conventional vehicles could displace 60% to 80% of light duty vehicle petroleum consumption. Flex-fuel HEVs can reduce petroleum consumption further and at less cost. AER PHEV40s could reduce petroleum consumption by over 90%, but at a greater cost.

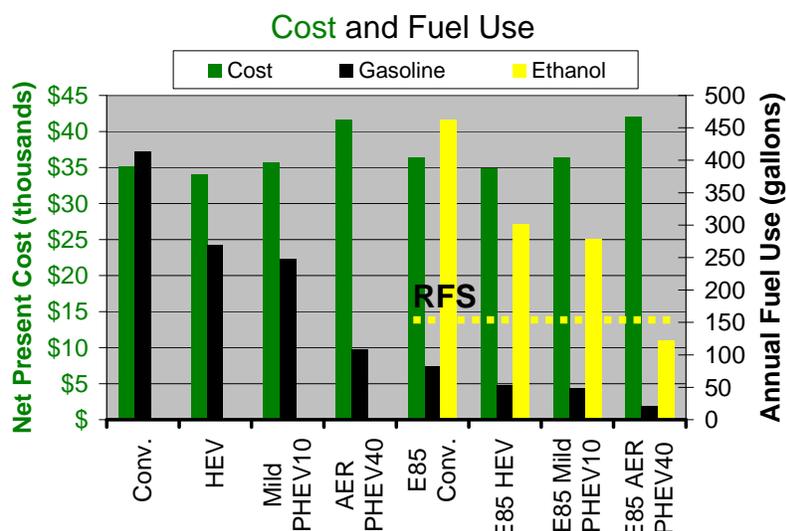


Figure 1: Cost and fuel use

2008 FreedomCAR and Fuel Partnership Highlight

Cold Temperature Performance of a PHEV Battery

Argonne National Laboratory

The performance of a Plug-in Hybrid Electric Vehicle (PHEV) battery decreases at cold temperatures, and is predicted to have a significant impact on vehicle efficiency. An experiment was performed at Argonne National Laboratory (ANL) to quantify the impact of cold battery temperature on the 'All Electric Range' (AER) of a plug-in vehicle, using the Battery Hardware in the Loop (HIL) approach.

The ANL HIL approach involves connecting the battery to the real-time simulation model of a vehicle + controller, with the virtual vehicle programmed to follow standard dynamometer cycles. The vehicle controller uses the feedback provided by the battery management system, as a part of its energy management strategy.

1. The Johnson Controls Saft VL41M Li-ion battery was cooled down to low starting temperatures of -7 and 0 degrees C, at a SOC of ~ 90%.
2. For each starting temperature, the virtual vehicle was subjected to consecutive EPA Urban Dynamometer Drive Schedule cycles, until the SOC dropped to ~ 30% (60% delta SOC).
3. During the test, the battery temperature was allowed to rise due to heat loss. (During the test, the battery was not force cooled to remain at the initial temperature). This emulates a real life scenario, where battery temperature would rise with internal resistance losses.
4. The same test was conducted at 20 degrees C, as a baseline.

Table 1(a) quantifies the impact of low temperature on vehicle AER. The reason for reduced AER can be attributed to a decrease in energy provided by the battery to the vehicle. This energy, in turn, was split into three categories: (1) Energy lost due to increase in internal impedance, (2) Energy lost due to battery power restrictions, and (3) Other energy losses inherent to the battery as detailed in Table 1 (b).

Initial Battery Temp	AER (miles)	Percent Drop in AER
20 °C	17.4	0%
0 °C	15.7	9%
-7 °C	15.0	13%

Table 1(a): Impact of low initial temperature on vehicle AER

Initial temp of the test	ΔWh compared to Wh delivered at 20°C	$\Delta I^2 R t$ as % of ΔWh (1)	$\Delta Regen$ as % of ΔWh (2)	$\Delta Other$ losses as % of ΔWh (3)
0°C	530	8%	34%	58%
-7°C	730	12%	34%	54%

Table 1(b): Contribution of various battery factors

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Infrastructure Materials Availability Analysis

Fuel Pathways Integration Technical Team

The team has initiated an analysis of the early infrastructure needs for hydrogen deployment in light-duty transportation. Infrastructure elements were discussed for various hydrogen production pathways with an initial focus on distributed production (Steam Methane Reformer (SMR) and electrolysis). Assuming an aggressive fuel cell vehicle penetration scenario (10 M vehicles on-the-road in 2025 with 8,000 fueling facilities) potential national, regional, and local impacts were explored. Comparison of resource needs and timing with current and/or projected future industry production offers a way to assess whether infrastructure issues could constrain the hydrogen system build-out. On a national scale, the team explored steel and dispenser needs for forecourt hydrogen refueling stations and carbon fiber needs for both cascade (high pressure) storage vessels at forecourt stations and in hydrogen tanks on-board vehicles.

Steel needs for low pressure hydrogen storage tanks at forecourt stations are estimated to be approximately 1% of current (2006) U.S. steel production. Therefore, it is not anticipated that steel needs for hydrogen stations would have a significant impact on the industry. Similarly, production of hydrogen dispensers is not expected to have significant impact. For the vehicle penetration scenario examined, a maximum of 12,000 new hydrogen dispensers would be required per year. While this is a significant number in comparison to gasoline dispenser demand, it is assumed that hydrogen dispensers would generally be substituted for gasoline dispensers by 2025 resulting in very little net change in demand. Carbon fiber needs for forecourt cascade storage vessels are estimated to be approximately 3% of projected worldwide carbon fiber demand in 2025 and carbon fiber demand for vehicle storage tanks is estimated to be approximately 48% of projected worldwide demand. In total, hydrogen storage tanks in 2025 are estimated to require approximately 50% of total projected worldwide carbon fiber production (Figure 1), suggesting that DOE may wish to further investigate the ability of the carbon fiber industry to accommodate this incremental growth.

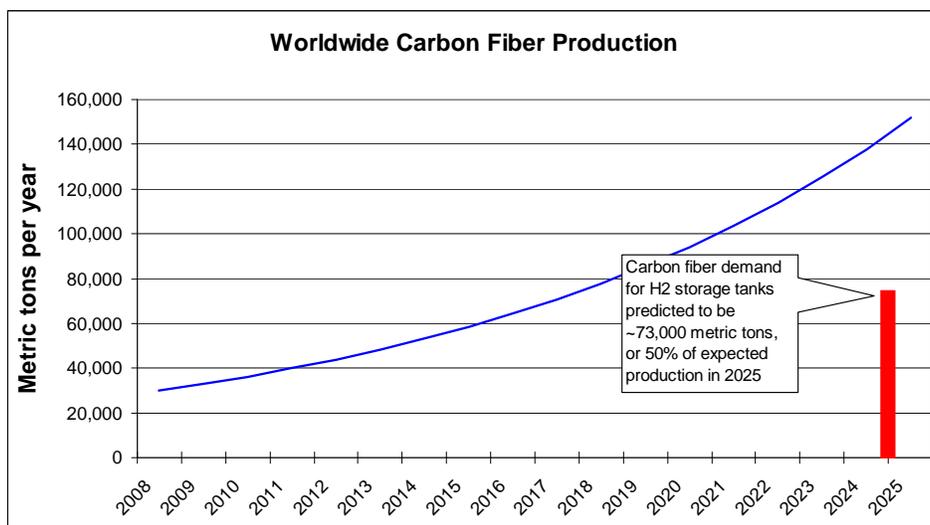


Figure 1: Worldwide Carbon Fiber Production

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Resource Availability Analysis

Fuel Pathways Integration Technical Team

The team has developed estimates, on a well-to-wheels (WTW) basis, of resources needed for various hydrogen and alternative fuel pathways. Resources such as water, electricity, and platinum constitute potential limitations to implementation of hydrogen technologies and facilities. By analyzing the resource needs for each element of various hydrogen pathways, the team is able to identify which hydrogen production pathways are most likely to face resource limitations, as well as which resources represent the greatest barrier to development of hydrogen infrastructure. As evidenced by Figure 1, the electrical usage of the Distributed Electrolysis hydrogen production pathway is the highest of the hydrogen pathways followed by central production pathways with liquefaction and liquid delivery. The hydrogen production pathway with the lowest electrical use is the central coal with pipeline delivery because the gasification process produces power which is used internally in the production system.

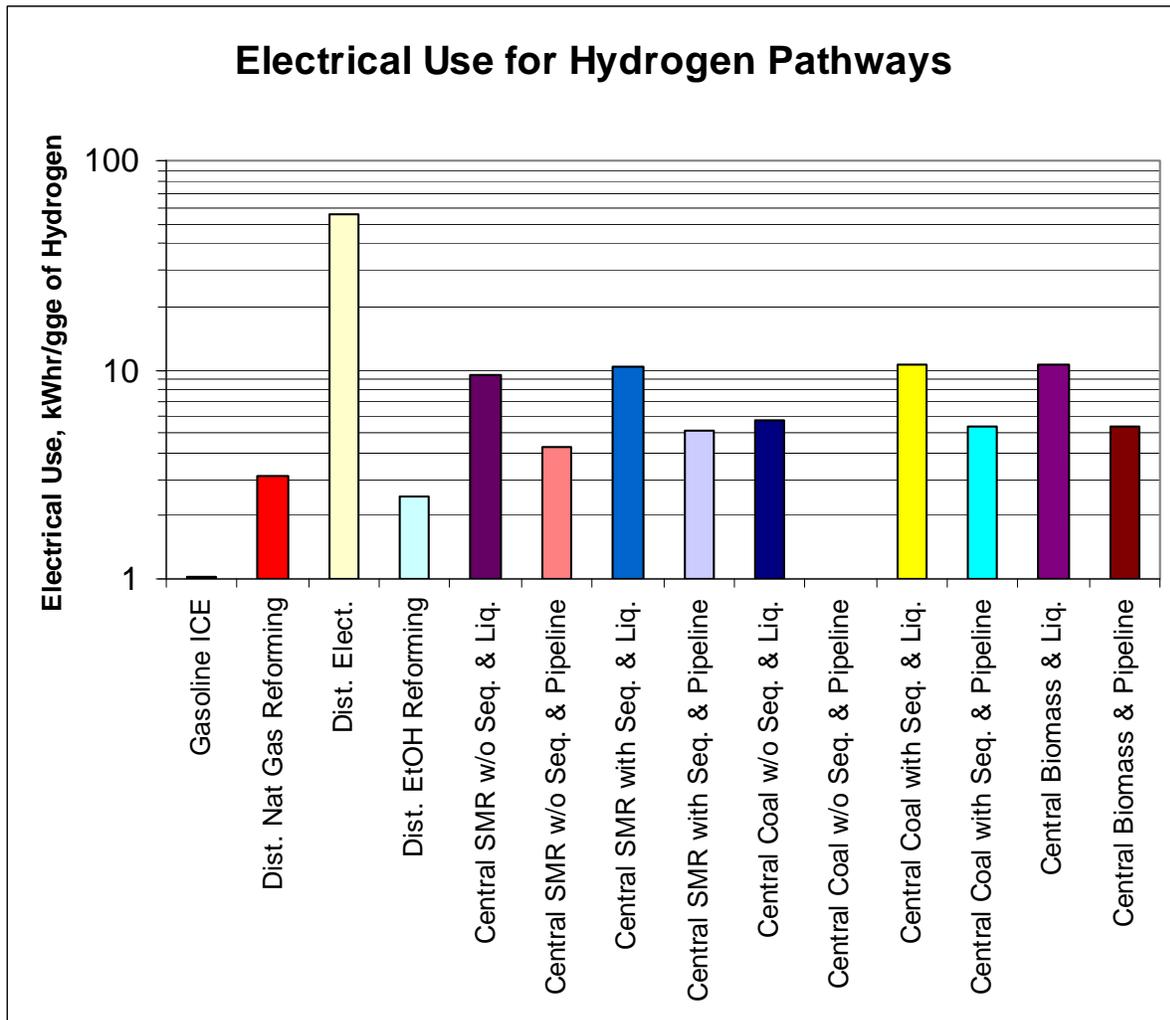


Figure 1: Electrical use for various hydrogen production pathways

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Well-to-Wheels Analysis Refinement

Fuel Pathways Integration Technical Team

Well-to-wheels (WTW) analysis is used to estimate the energy use and emissions for complete hydrogen pathways, from feedstock production to vehicle fuel use. The Fuel Pathways Integration Technical Team (FPITT) has been reviewing the Department of Energy's WTW analysis process and the assumptions and data used to conduct such analysis with the goal of identifying issues and gaps based on the energy industry's experience. During 2008, the production of hydrogen via biomass gasification in central facilities and delivery of liquid hydrogen via truck and trailer was reviewed. Several gaps and opportunities in the modeling and analysis have been identified:

1. The current H2A designs involve woody biomass exclusively. A herbaceous biomass model should be developed.
2. Understanding of the GHG emissions related to biomass production needs to be improved and, because the amount of carbon dioxide sequestered by the soil changes from year to year, a standard method of quantifying and explaining those emissions needs to be developed.
3. The cost of liquefaction (economic, energy requirement, and associated emissions) is large, as can be seen in the figure. Much of the economic cost is due to the capital expense of the liquefaction system. For liquefaction to become an important component in a hydrogen infrastructure, its costs will need to be reduced.

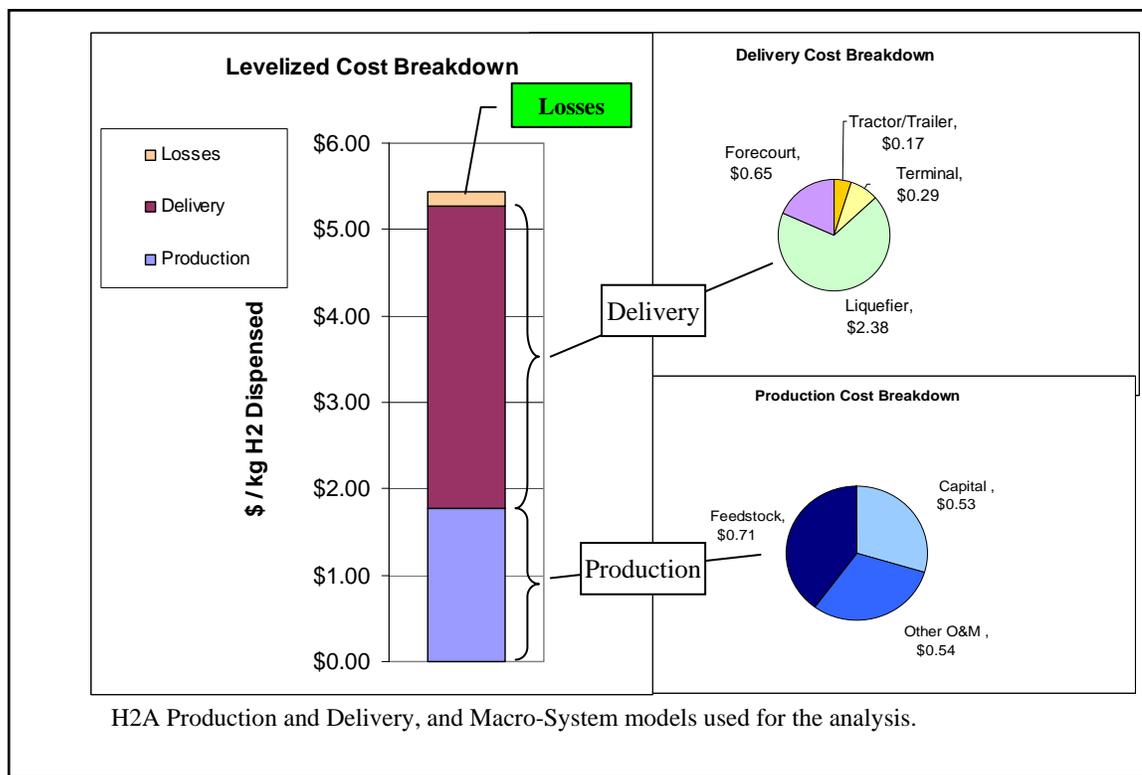


Figure 1: Levelized Cost Breakdown of the Biomass / Liquid Delivery Pathway

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Inexpensive Delivery of Cold Hydrogen in Glass Fiber Composite Pressure Vessels

Lawrence Livermore National Laboratory

Delivering hydrogen in today's low capacity compressed hydrogen tube trailers is expensive. The DOE Hydrogen Program has the goal of delivering hydrogen for \$1/kg. Substantial cost reductions appear possible with development of advanced pressure vessels. Lawrence Livermore National Laboratory (LLNL) demonstrated 40% strengthening of glass fiber (GF) when operated at low temperature (Figure 1a). This provides two potential advantages: 1) reduced tank costs at similar pressures as conventional tank materials, resulting in lower potential capital cost per delivery trailer, and 2) increased capacity resulting in lower labor cost. LLNL identified these synergies, which promise to considerably reduce the cost of hydrogen delivery and dispensing to a vehicle:

1. *Optimization of operating pressure and temperature:* Today's hydrogen delivery technologies (compressed and liquid) are restricted to single points at extremes of the hydrogen phase diagram. LLNL explored the entire phase diagram searching for pressures and temperatures that result in high storage density without the thermodynamic penalty of hydrogen liquefaction. Cold high-pressure hydrogen (~200 K and up to 700 bar) appears most promising.
2. *Use of inexpensive glass fiber:* GF is an inexpensive high-performance alternative to carbon fiber at low temperature. GF is synergistic with low temperature operation; strengthening ~40% as it cools from 300 K to 80 K. Cold GF delivers unequalled performance per unit of cost. GF expands weight-limited trailer capacity and reduces capital expense, resulting in low delivery cost (Figure 1b).

Further advantages come from delivery of cold hydrogen: delivering 200 K hydrogen avoids overheating and over pressurizing, increasing the fill speed and potentially reducing the cost of vehicular storage. Vessel designs can be simplified if their operating pressure and temperature never exceed the nominal rating, and the safety of operations is improved without a filling pressure transient above rated pressure.

Experiments to date show promise for achieving the Hydrogen Program's delivery goals. Future plans focus on proving the concept in small-scale GF pressure vessels.

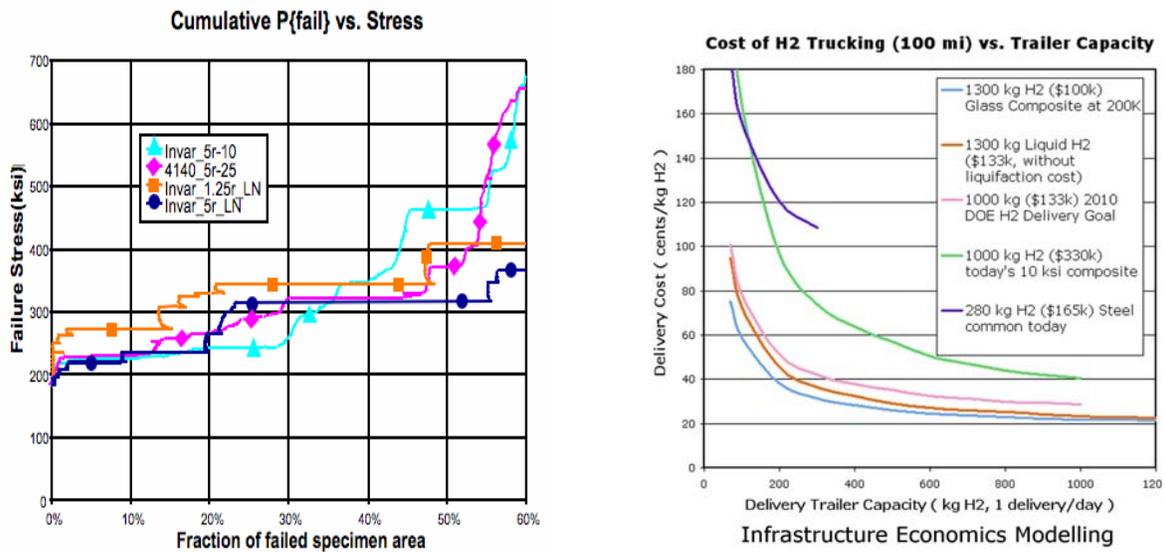


Figure 1: (a) 40% strength increase (80 K); (b) Cost of delivering cold H₂ from production

2008 FreedomCAR and Fuel Partnership Highlight

Fiber-Reinforced Polymer Materials for Hydrogen Pipelines

Oak Ridge National Laboratory and Savannah River National Laboratory

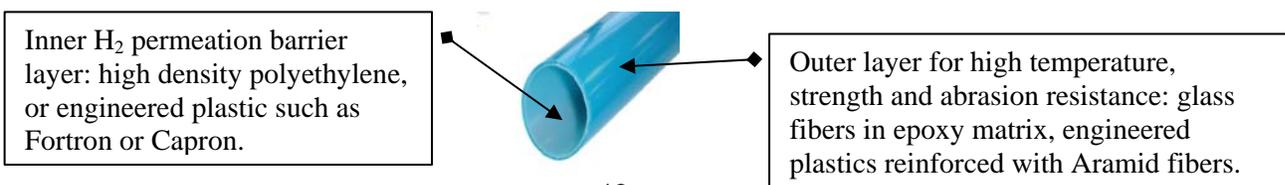
Oak Ridge National Laboratory and Savannah River National Laboratory established a test protocol to evaluate fiber-reinforced polymer pipelines (FRPP) and long-term compatibility materials in high-pressure hydrogen. Low cost and energy efficient delivery of hydrogen from centralized production facilities to dispensers for transportation will require a new network of pipelines to handle significant hydrogen transmission. Extensive cost analysis confirms that pipelines are the most economical method for transmitting substantial quantities of hydrogen over large distances. However, the existing carbon steel pipeline network is old/degraded and operating near 100% capacity handling fuels (e.g., natural gas). The capital cost associated with new steel pipelines is prohibitively high with regard to current cost targets for delivered hydrogen, and steels suffer from potential embrittlement resulting from exposure to high pressure hydrogen under certain loading conditions. Thus, less expensive alternatives to traditional pipeline steels are under consideration.

FRPP have the potential to significantly reduce capital cost and provide safe and reliable hydrogen delivery. Existing FRPP technology is used extensively in oil and natural gas operations, and can be extended to hydrogen service. Up to one mile of FRPP, depending on diameter, can be spooled, transported, and then installed as a seamless monolith, dramatically reducing labor costs associated with joint preparation and welding as well as minimizing inspection requirements. FRPP will require little, if any, of the external corrosion protection required for steel pipelines in buried service. The purpose of the present effort is to assess the suitability of FRPP materials for hydrogen service by:



- Determining permeation or leak rates that can be expected for high-pressure hydrogen.
- Evaluating compatibility of FRPP and their constituent materials for long-term service.

Tests include soaking materials in high pressure hydrogen under accelerated aging conditions for up to eight months followed by a battery of evaluations that include: 4-point bending, burst tests, parallel plate compression, and standard mechanical properties (tensile and yield strength, elongation). The FRPP specimens all have “passed” or exceeded the material ratings for equivalent pressure air service and revealed no hydrogen induced degradation. Blow-down tests of pipeline specimens reveal no adverse interactions. Hydrogen leakage measurements in pipeline specimens pressurized with hydrogen reveal acceptable rates comparable to those observed for steels. The permeation rates were found to be even lower than expected. Taken together, these results suggest significant opportunity to develop FRPP material for hydrogen applications. DOE expects technology demonstrations (field exposures) to be incorporated into future evaluations.



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Hydrogen Production from Sunlight Powered Biological Water Splitting

J. Craig Venter Institute and the National Renewable Energy Laboratory

Scientists are finding ways to harness natural biological processes that convert and store the energy of sunlight as renewable hydrogen. Optimizing biological hydrogen production requires understanding the enzymatic pathways through which hydrogen is formed at the molecular level. Increasing hydrogen production duration and rate in photobiological water splitting are two challenges that need to be overcome to make this pathway viable. Advances toward overcoming these challenges were made by the J. Craig Venter Institute and the National Renewable Energy Laboratory (NREL), as detailed below.

The J. Craig Venter Institute cloned a novel hydrogenase using environmental DNA samples and expressed a functional hydrogenase in an organism (see Figure 1). This is the first report of conversion of a piece of environmental DNA (rather than DNA from a specific organism) into a function NiFe-hydrogenase – providing a completely new approach for screening novel hydrogenases from environmental microbes. This accomplishment provides the capability to greatly expand the library of potential hydrogen producing enzymes in order to develop the necessary attributes for efficient and effective water splitting. The overall project objective is to develop an O₂-tolerant cyanobacterial system for sustained and continuous light-driven hydrogen production from water.

NREL developed a bio-degradable matrix (see Figure 2) for immobilizing cells that increases light-conversion efficiency and protects the hydrogen producing system from oxygen inactivation for up to 6 days. The light conversion efficiencies are still low, but significant. This represents the first report of a light conversion efficiency of over 1% for a wild-type green alga and brings this renewable technology a step closer to an O₂-tolerant algal system for sustained, efficient, and cost effective light-driven hydrogen production from water.

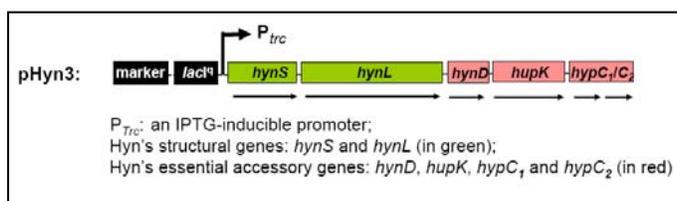


Figure 1: J. Craig Venter Institute's vector system to transfer genes of O₂-tolerant hydrogenase.

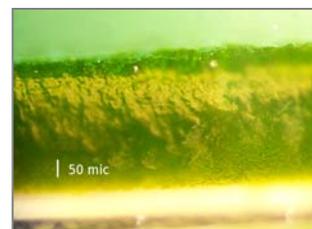


Figure 2: NREL's bio-degradable matrix for immobilizing cells that increases light-conversion efficiency and protects the hydrogen producing system from oxygen inactivation.

2008 FreedomCAR and Fuel Partnership Highlight

Hydrogen Production from Water Electrolysis

Giner Electrochemical Systems, Inc.

Reduction of capital cost and increases in system efficiency are needed to help hydrogen production from water electrolysis become more economically attractive. Advances in water electrolysis technology have been realized through significant improvements in electrolyzer performance.

- Giner Electrochemical Systems, Inc. (GES) developed an electrolyzer that produces hydrogen at 1,200 psig (reducing the need for after-production compression) with a stack efficiency of 67% (making better use of the electricity input). The company developed lower cost fabrication methods for key cell components, including an advanced high efficiency membrane. (Figure 1).
- GES reduced their projected hydrogen cost to \$4.76/gge (see http://www.hydrogen.energy.gov/pdfs/review08/pd_10_hamden.pdf) using standard H2A assumptions (see http://www.hydrogen.energy.gov/h2a_analysis.html#assumptions) and they have developed a pathway with the potential to achieve the 2012 DOE target of \$3.70/gge.
- GES also demonstrated 74% efficiency (LHV) using an advanced membrane in a single electrolysis cell (Figure 2). They are currently integrating the membrane into a stack. The increased efficiency will bring the capital cost and electricity requirements for this technology down to help the technology become more economically attractive.



Figure 1: Giner Electrochemical Systems' 1,200 psig Electrolyzer

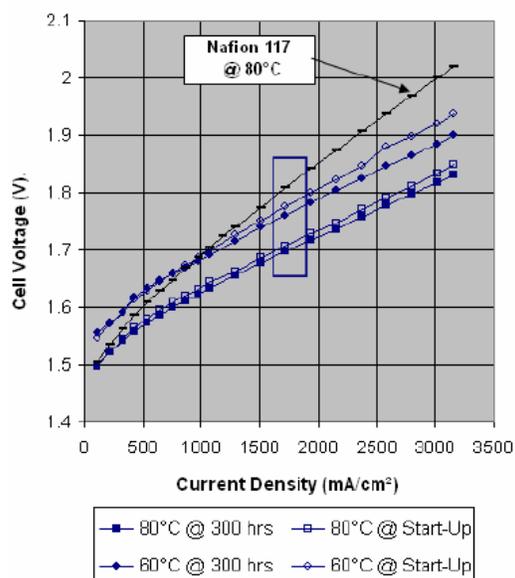


Figure 2: Giner Advanced Membrane achieving 74% efficiency (LHV) at 1,700 mA/cm²

2008 FreedomCAR and Fuel Partnership Highlight

Hydrogen Fuel Station Permitting Compendium National Renewable Energy Laboratory

Facilitating the permitting of hydrogen fueling stations (HFS) is a high priority for both the Partnership and the Department of Energy's Hydrogen Technical Advisory Committee. The National Renewable Energy Laboratory (NREL) conducted national and regional workshops with HFS developers and code officials and implemented a web-based information compendium to meet the needs and recommendations of developers and authorities having jurisdiction (AHJ). In FY08 these workshops were aimed at working with code officials directly involved in reviewing and permitting hydrogen installations. The compendium identifies the applicable codes and standards to permit a HFS and in FY08 a database containing the specific citations from those codes and standards applicable to HFS was added. The compendium also contains fact sheets on hydrogen technologies and key HFS equipment, a network chart of code officials who have permitted HFS, and best practices for application of codes and standards for hydrogen utilizing technologies. The compendium provides a one-stop information source that has facilitated the permitting of HFS by educating code officials thus making the permitting process faster. A sample page from the compendium is shown in Figure 1.



Figure 1: Sample page from the Hydrogen Fuel Station Permitting Compendium

2008 FreedomCAR and Fuel Partnership Highlight

Hydrogen Component Standards

DOE National Laboratories

Hydrogen codes and standards are required to allow authorities having jurisdiction (AHJ) to permit hydrogen facilities such as hydrogen fueling stations and to allow for the use of hydrogen fuel cell vehicles. Hydrogen safety requirements have been successfully integrated into building and fire codes and the hydrogen fueling and gas storage and handling codes. These codes in turn reference a complete set of hydrogen component standards. The DOE has made a major effort to assist in the development of these component standards and much of the codes and standards research conducted at the DOE National Laboratories is done to support the development of these standards. In FY 2008 the following significant accomplishments were achieved in hydrogen component standards development.

ORGANIZATION	DOCUMENT	FY 2008 ACCOMPLISHMENT
Society of Automotive Engineers (SAE)	J2719 Information Report on the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles	Document issued April 18, 2008
Society of Automotive Engineers (SAE)	J2579 Technical Information Report for Fuel Systems in Fuel Cell and other Hydrogen Vehicles	Document issued January 4, 2008
Society of Automotive Engineers (SAE)	J2617 Recommended Practice for Testing Performance of PEM Fuel Cells Stack Sub-system for Automotive Applications	Document issued November 11, 2007
CSA America	HGV 4.1 Compressed Hydrogen Dispensers	Draft document being balloted
CSA America	HGV 4.2 Hoses and Hose Assemblies	Draft document being balloted
CSA America	HGV 4.4 Breakaway Devices for Hoses	Draft document being balloted
Compressed Gas Association (CGA)	H-5 Installation Standard for Bulk Hydrogen Systems	Document Issued March 12, 2008

2008 FreedomCAR and Fuel Partnership Highlight

Fuel Quality Round-Robin Testing

Los Alamos National Laboratory

In support of the multi-lab effort to measure, report, analyze, and model the effects of fuel quality on fuel cell performance, a round-robin test sequence was conducted. In addition to ensuring that the testing laboratories were sufficiently proficient in applying their testing equipment and the testing protocols, the effort was geared towards increasing confidence in the generated data that are to be used to model the effects of impurities on fuel cell performance and to establish national (SAE) and international (ISO) standards for hydrogen fuel quality. The participating laboratories were the University of Hawaii/Hawaii Natural Energy Institute, Clemson University/Savannah River National Laboratory, University of Connecticut, University of South Carolina, and the National Institute of Standards and Technology.

A test cell was prepared for the round-robin test (Figure 1). Los Alamos National Laboratory (LANL) tested the cell using the DOE/LANL/USFCC testing protocols to generate polarization curves. Each participating fuel cell testing laboratory received the cell, performed the prescribed tests, reported the results, and sent the test article to the next testing lab.

Initial and post round-robin testing at LANL confirmed that no degradation in cell performance occurred during the round-robin test. As indicated in the figure below, there was good agreement among the sites. Differences in the low-current-density/high-voltage region are likely due to different humidification schemes, which are being addressed through discussions among the testing labs.

This is a significant accomplishment because it establishes a foundation for consistent and reproducible measurements of the effect of contaminants in the hydrogen fuel stream on the performance of PEM fuel cells for road vehicles. Validation of consensus test protocols is critical for the development of an ISO international standard for hydrogen fuel quality by 2011.

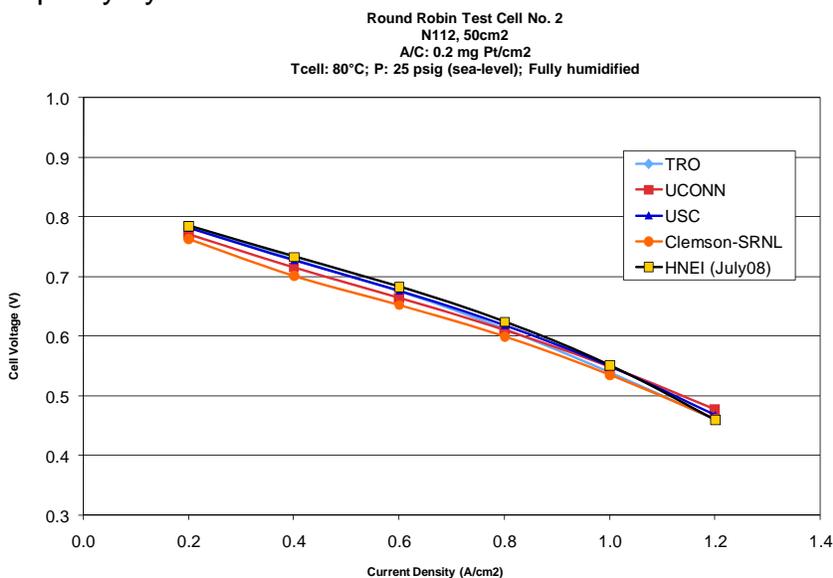


Figure 1: Round-Robin Test Cell No. 2

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Technical Basis Established for NFPA 55 Separation Distances

Sandia National Laboratories

The existing separation distances in National Fire Protection Association (NFPA) 55 for bulk storage of hydrogen have been challenging from both an enforcement and a compliance perspective because the basis for the values was undocumented, making alternative compliance strategies difficult. To address this issue, a joint task group with members from both NFPA 2 and NFPA 55 and the research community was formed to validate or revise the existing separation distances. Quantitative risk assessment techniques were used to incorporate applied research on unintended releases into a risk-informed decision-making process for the code committee. By using the risk-informed approach combined with direct researcher participation in the task group, code developers do not need to be experts in fluid dynamics, combustion, material science, or quantitative risk assessment. Rather, they can focus on the overall work product of the task group to digest the technical information and produce relevant code change proposals. This process was completed for NFPA 55 and a new approach to specifying separation distances was accepted by the Technical Committee and is currently on schedule to be issued in the 2009 edition of NFPA 55.

The task group (TG) followed the following general sequence in the risk-informed code development process: 1) develop models of hydrogen release (Sandia National Laboratories (SNL)), 2) validate the models with physical testing (SNL), 3) develop risk acceptance criteria (TG members), 4) use models to perform parametric studies (pressure, leak size, etc...) (TG members), 5) define typical gaseous hydrogen (GH2) installation process and instrument diagrams from which a quantitative risk analysis (QRA) can be performed (TG Members), 6) perform QRA (TG Members), 7) use QRA results as guidance in finalizing the input assumptions for the model's, risk informed decision making – (TG Members), and 8) develop separation distances (TG Members).

Comparison of Select Separation Distances: NFPA 55-2005 –v- 2009 Edition		
Exposure*	NFPA 2005 Separation Distance	NFPA 2009 Separation Distance
Lot Lines	5ft	10 ft
Air intakes	50 ft	10 ft

* Any generalized “before and after” comparisons of separation distances are of limited value because the NFPA 55-2005 separation distances were based on volume of H2 stored and the NFPA 55-2009 separation distances are based on storage pressure and piping system internal diameter.