Analysis of the Durability of PEM FC Membrane Electrode Assemblies in Automotive Applications Through the Fundamental Understanding of Membrane and MEA Degradation Pathways

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2010 DOE Hydrogen Program Fuel Cell Project Kick-Off

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Overview

Timeline (tentative)

Start date: Oct 1, 2010

End of period 1: June 1, 2012

End of period 2: Sept 30, 2013

Currently <5% Complete

Budget (tentative)

- $5.2 M ($2.5M/2.7M)
  - $4.1 MM
  - $1.1 MM
- FY10: $ 0.9 M
- FY11: $ 1.0 M Budgeted

Barriers

Barriers addressed

- Fuel cell component durability improved, to be competitive with current technologies.

Technical Goals

- Attain 5000 hr lifetime in durability with DoE cycling protocol.
- Attain 1 kW/cm2 performance at BOL in sub-scale testing with the extent of performance decline over lifetime of <=7%

Partners

- Nissan Technical Center North America
- Illinois Institute of Technology
- 3M
- Project lead: DuPont

Technical Program

1. Project Description
   1. Relevance & Objectives
   2. Approach
2. Work Plan (Detailed Approach)
   1. Work Plan Overview
   2. Accelerated Cell Aging Tests
   3. Develop Durable MEA's
   4. Analysis and Modeling
   5. Stack Testing
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3. Technical Background and Previous Results

Project Objectives

This project is under Topic 3A “Cell Degradation Studies”. The objective of Topic 3A is to improve the understanding of the degradation mechanisms of fuel cell materials and components.

The main objectives of this project are:

- To develop a fundamental understanding of PEM FC materials degradation mechanisms under automotive conditions that can lead to recommendations for mitigation.
- To develop membranes and MEA’s with a design lifetime target of 5,000 hours with <5% degradation and that show a clear path towards meeting the DOE 2015 technical targets.
- To understand the relationship between the stack operating conditions and MEA degradation.

Project Rationale

- **Establish the durability of next generation of materials capable of operating in a wider range of temperature and relative humidity – DOE’s 2015 technical targets**
- **Specifically, to better understand the durability at low relative humidity and during automotive cycling operation (including temperature, RH, load, start-up/shut-down, etc.)**
  - Degradation mechanisms specific to membranes capable of operating over wider ranges of operating conditions (temperature and relative humidity).
  - Degradation mechanisms specific to electrodes with low PGM loadings and other cell components while operating over wider ranges of operating conditions (temperature and relative humidity).

Approach

The project team will increase the understanding of MEA durability. At a high level, the approach will consist of the following steps:

- DuPont will provide state-of-the-art membranes, ionomers, and some catalyst materials for durability studies.
- 3M will provide NTSH catalyst and determine how to apply it effectively to DuPont membrane.
- Nissan will select GDL's and plates, and test and validate MEA materials.
- The team will work closely on the characterization and analysis of materials, before and after testing to identify with degradation mechanisms. IIT and DuPont will perform much of the characterization.
- Prof. Ramani's group at IIT will help in providing for basic understanding, analysis and model development.

Approach

In this project we plan to conduct the following main tasks:

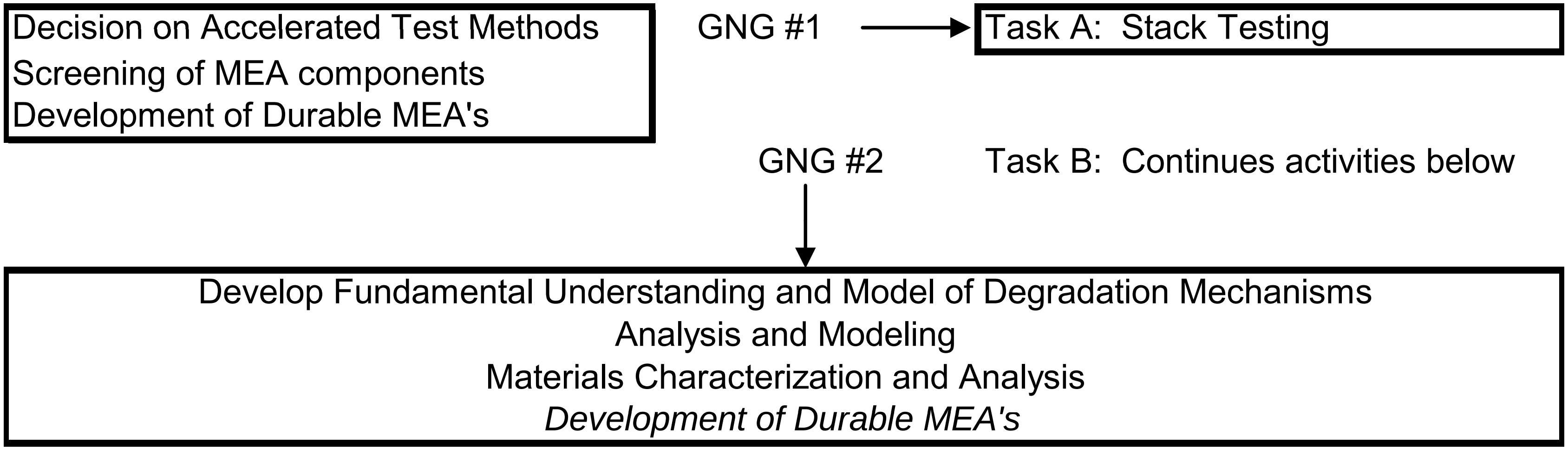
- Chemical degradation studies of the ionomers, not only in the membrane but also in the catalyst layer.
- Analysis of how chemical degradation impacts water management in the membrane and electrode layers.
- Understanding of the effect of realistic automotive cycling operation on the degradation of MEA components.
- Definition of mechanisms and conditions that promote MEA degradation not only at a single cell level, but in the environment of an automotive fuel cell stack.
- Fabrication and delivery of an MEA that has improved resistance to degradation for evaluation in a full-scale short stack.

Approach

The overall program is divided into two budget period, with two GNG decisions.

Period 1

Period 2



Decision on Accelerated Test Methods
Screening of MEA components
Development of Durable MEA's

GNG #1

Task A: Stack Testing

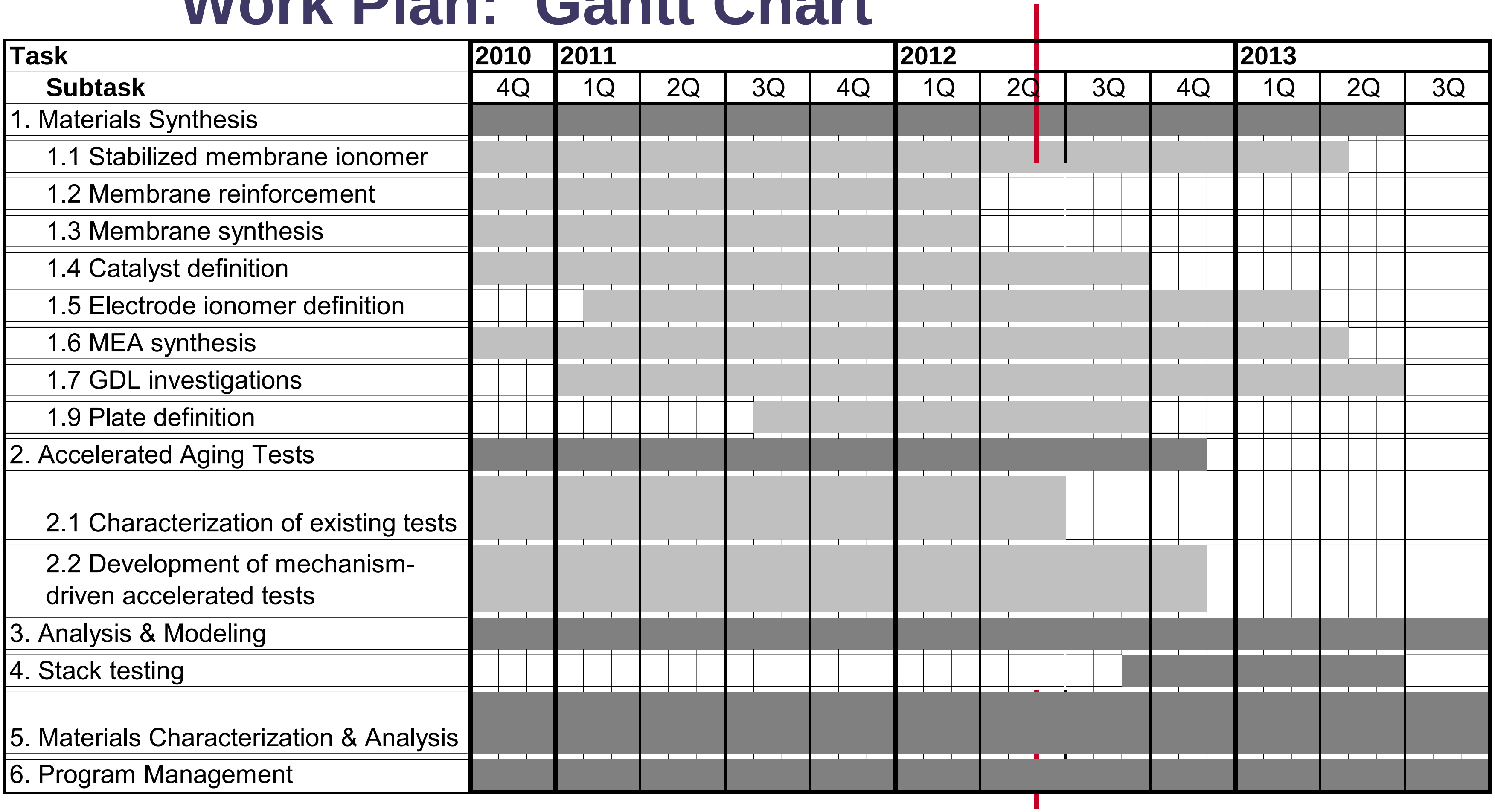
GNG #2

Task B: Continues activities below

Develop Fundamental Understanding and Model of Degradation Mechanisms
Analysis and Modeling
Materials Characterization and Analysis
Development of Durable MEA's

Go/No-Go #1 to determine whether to proceed to materials fabrication for stack testing.
Go/No-Go #2 to determine whether to continue with tasks related to Analysis & Modeling.

Work Plan: Gantt Chart



Task	2010	2011				2012				2013		
Subtask	4Q	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q	1Q	2Q	3Q
1. Materials Synthesis	■	■	■	■	■	■	■	■	■	■	■	
1.1 Stabilized membrane ionomer	■	■	■	■	■	■	■	■	■	■	■	
1.2 Membrane reinforcement	■	■	■	■	■	■						
1.3 Membrane synthesis	■	■	■	■	■	■						
1.4 Catalyst definition	■	■	■	■	■	■	■	■				
1.5 Electrode ionomer definition		■	■	■	■	■	■	■	■	■		
1.6 MEA synthesis	■	■	■	■	■	■	■	■	■	■	■	
1.7 GDL investigations		■	■	■	■	■	■	■	■	■	■	
1.9 Plate definition				■	■	■	■	■				
2. Accelerated Aging Tests	■	■	■	■	■	■	■	■	■			
2.1 Characterization of existing tests	■	■	■	■	■	■	■					
2.2 Development of mechanism-driven accelerated tests	■	■	■	■	■	■	■	■	■			
3. Analysis & Modeling	■	■	■	■	■	■	■	■	■	■	■	■
4. Stack testing								■	■	■	■	
5. Materials Characterization & Analysis	■	■	■	■	■	■	■	■	■	■	■	■
6. Program Management	■	■	■	■	■	■	■	■	■	■	■	■

Go/No-Go decisions

Work Plan: Overview

Three year program

Six Workstreams:

- Materials Synthesis – DuPont, 3M
- Accelerated Aging Tests – DuPont, Nissan TCNA, IIT
- Analysis and Modeling – IIT
- Stack testing – Nissan
- Materials Characterization and Analysis – DuPont, IIT, 3M, Nissan TCNA
- Program Management – DuPont

Go/No-Go decisions at ~20 months for:

- Materials Synthesis for Stack Testing
- Completion of Model Development

Work Plan: Milestones & GNG Criteria

Period 1 Milestones:

- Year 1, Quarter 3: Decision on which accelerated tests are to be carried on through detailed modeling work. The DoE-specified tests will be included in the analysis. Tests will be selected based on results of both in-situ data and postmortem analysis.
- Year 2, Quarter 3: Down selection of MEA components to be used for stack test. At end of Period 1, there are two go/no-go decisions.

Period 2 Milestones:

- Year 3, Quarter 3: Completion of testing of a full-scale short stack.
- Year 3, Quarter 3: Completion of additional testing and analyses to develop degradation model.
- Year 3, Quarter 4: Model finalized and in preparation for publication.

Work Plan: Milestones & GNG Criteria

Go/No-Go decision 1: MEA design must meet performance and accelerated durability targets with results verified in lab testing in order to proceed to fabrication and testing of a full-scale short stack.

- Attain 5000 hr lifetime in durability with DoE cycling protocol.
- Attain 1 kW/cm2 performance @ rated power at beginning-of-life in sub-scale testing.
- Attain extent of performance decline over lifetime (as in #1 above) of <=7%

Note: Criteria 1 and 3 above will be evaluated using projections based on accelerated testing results. (e.g., #1 will be extrapolated from 30,000 cycles).

Go/No-Go decision 2: Data generated at end of the first Budget Period can discriminate among the various cell components, to allow for continued efforts on modeling. The variability determined in the initial phase of accelerated tests must be small enough to make variations in measurements as a function of time and component statistically significant to an 80% confidence level.

Work Plan – Define Accelerated Tests

Define "standard" MEA builds

- DoE and several proprietary durability protocols
- Performance testing vs RH & Temperature
- Load Cycling – catalyst
- High Voltage Hold – catalyst support
- OCV with FER measurement – membrane
- Humidity Cycling – mechanical

Postmortem analyses at DuPont and IIT to define test which give best separation of degradation processes.

- Test multiples (≥5X)
- Modify tests if needed

Determine which tests methods to be used for remainder of program (Milestone 1)

Work Plan: Develop Fundamental Understanding and Model of Degradation Mechanisms

Materials Characterization and Analysis of MEA's

- Develop and determine tests that separate degradation mechanisms and allow for quantitative characterization of MEA failure modes.
- Materials used in various builds will be characterized so as to evaluate the effect of quantitative properties of one component on other components. E.g. Hydrophilicity of GDL vs. catalyst degradation.
- Accelerated tests will be coupled with ex-situ tests to aid in evaluation of components and interfaces. The appendix provides descriptions of a number of planned tests.
- Accelerated testing will be performed on multiple samples taken off-line at different times to develop time dependence of degradation mechanisms

A wide variety of ex-situ tests and characterization methods are available.

- IR, TGA, NMR, SEM, TEM, EMPA, XPS, TGA, DSC, DMA,…

Work Plan: Fabricate Durable MEA's

Screening experiments simultaneous with initial test development:

- Limit testing; designed screening experiment
- Examples of screening variables:
  - Membrane EW; extruded vs cast reinforced
  - GDL type
  - Graphitized carbon catalysts; Pt alloys; NTSF catalyst
  - Effect of electrode ionomer type
- Reduce variables to 6-12 builds for detailed testing

Detailed designed experiment using suite of accelerated and performance tests on reduced number of build combinations

- Develop mitigating strategies based on observed degradation mechanisms.
- Improve build as understanding increases.
- Define material for stack test.

Work Plan: Stack Testing

Full-scale, short-stack testing will be performed on one or two “best” MEA designs.

- Go/No-Go criteria must be met in sub-scale testing.
- Testing planned for minimum 2,000 hrs.
- Performance & postmortem analyses used to verify sub-scale results.
- Operating conditions defined by the testing contractor, based on their criteria.
- Baseline MEA’s will be included as controls.

MEA fabrication

- Membrane from DuPont
- CCM fabrication at DuPont or contractor, depending on catalyst type.
- MEA5/7 fabrication at contractor.

Work Plan: Analysis and Modeling (includes Materials Characterization & Analysis

IIT will lead development of models of the degradation process within the MEA. DuPont will lead development of models for chemical degradation of the polymer.

- Kinetic and materials models of the degradation process at the component level
- Cell and ex-situ testing will establish the rate-of-change of
  - Electron conductivity of bipolar plate; Plate contact angle
  - Plate-GDL contact resistance;
  - GDL permeability, porosity and hydrophobicity; GDL electrode contact resistance
  - Electrode utilization, active surface area, kinetic, ohmic & transport coefficients
  - Electrode-PEM contact resistance
  - PEM conductivity, gas permeability and ROS generation rates.
- These data will be used with other available data, including stack test results, to formulate component degradation models.

Integration of the component models into a cell model.

- Integrate degradation model into literature models for cell performance. (e.g. Williams)

Technical Background

DOE durability program (2003-2007)

- **DuPont Fuel Cells team developed degradation mechanisms and several mitigation strategies for low temperature PEMs.**
- **The DuPont Fuel Cells team developed durable PEMs by mitigating the elementary steps in the overall failure process.**
- **The overall degradation mechanism, starts with chemical attack of the polymer membrane that leads to degradation of the membrane material properties. Under the unique local physical stress of the seal edge, cracks and fissures form and ultimately the membrane fails to separate the reactants, leading to the catastrophic failure of the fuel cell system..**
- **Mitigation strategies for each of these failure modes were identified and validated by modeling, *ex-situ* peroxide studies, and fuel cell testing. Optimizing and combining each of the various mitigation strategies was the strategy applied to that project.**

Chemical and Mechanical Stability of PFSA PEMs.

The chemical degradation of the PFSA polymer consists of these steps:

- Crossover oxygen reacts with hydrogen from the anode side to produce H_2O_2.
- The H_2O_2 decomposes in presence of Fenton's cations to produce •OH or •OOH radicals.
- These radicals preferentially attack reactive endgroups of the polymer to initiate scission reactions:

$$Rf - CF_2COOH + \bullet OH \rightarrow Rf - CF_2\bullet + CO_2 + H_2O \quad (1)$$

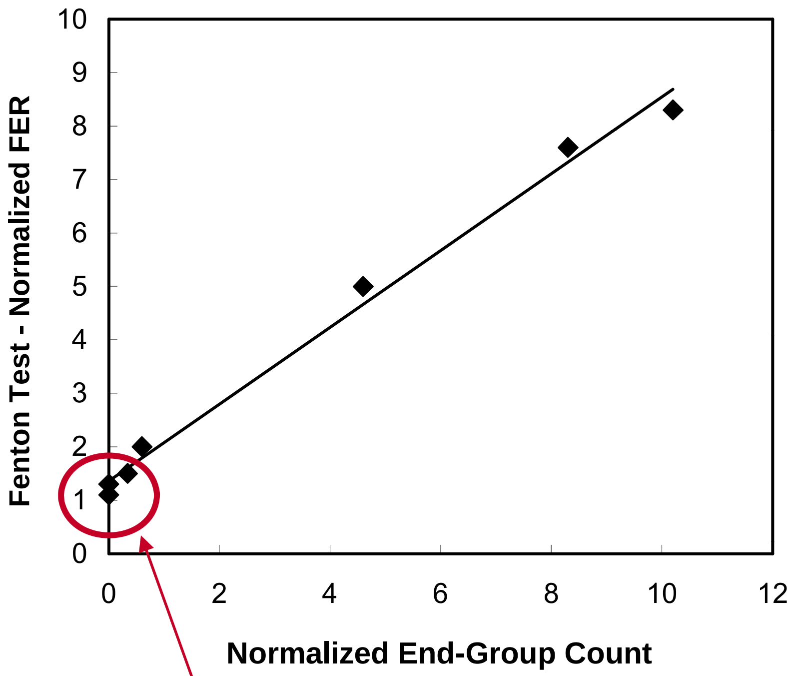
$$Rf - CF_2\bullet + \bullet OH \rightarrow Rf - CF_2OH \rightarrow Rf - COF + HF \quad (2)$$

$$Rf - COF + H_2O \rightarrow Rf - COOH + HF \quad (3)$$

Analysis led to technologies to reduce the reactive centers within the polymer in order to minimize the effect of the polymer degradation mechanisms. An 8X reduction in fluoride emissions in Fenton's was achieved, along with a comparable reduction in OCV testing.

Chemical and Mechanical Stability of PFSA PEMs.

- There is a residual fluoride emission detected in Nafion® ionomers with virtually zero concentration of reactive endgroups.
- One of the objectives of this proposal is to understand other degradation mechanisms that contribute towards this residual degradation.



Relative Fluoride Emission vs. Normalized End-group Count for Nafion® Ionomers. Fenton's test conditions: 85C, 3 cycles with fresh reagent, 30% H_2O_2, 20 ppm Fe^{2+}.

Residual fluoride emissions

Chemical and Mechanical Stability of PFSA PEMs.

- **Another key membrane failure mode that was analyzed is fatigue, caused by stresses imposed by humidity and thermal cycling.**

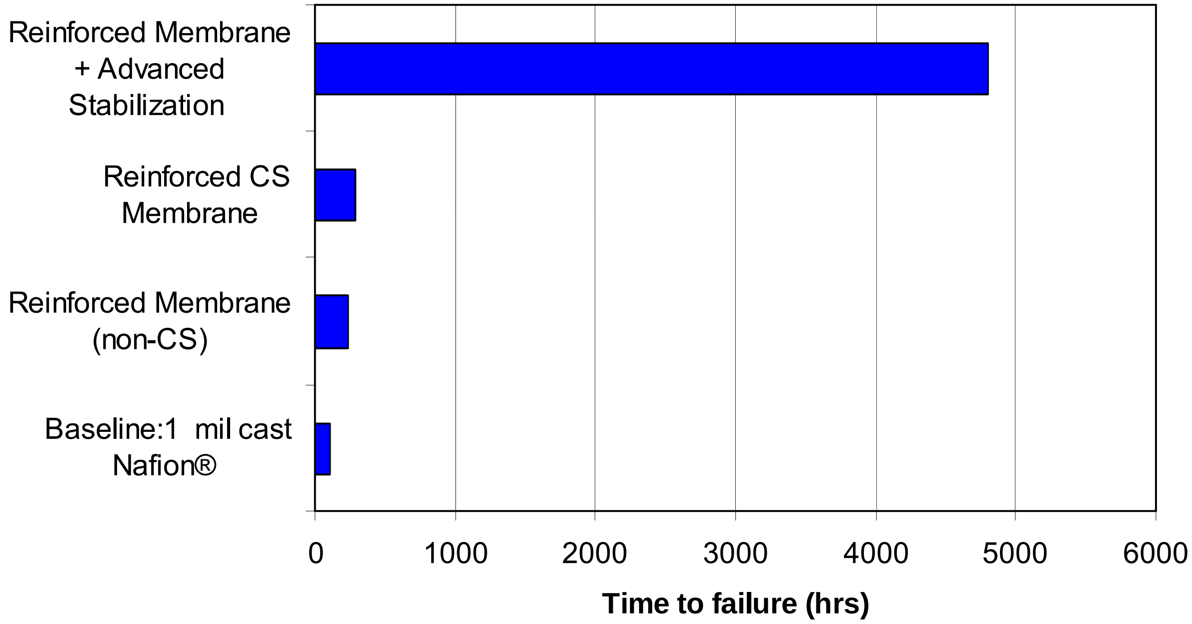
  The PEM develops weak points that develop eventually lead to tears and cracks, and ultimately, to the catastrophic failure of the membrane. This is a particularly serious issue in automotive applications, where the membrane is subject not only to load, but also to start-stop and freeze-thaw cycles.

  DuPont developed proprietary membrane reinforcement strategies that were deployed to extend membrane life by reinforcing the membrane to reduce the magnitude and effect of the stresses developed during cyclic operation conditions.

DuPont has pursued further work to limit the effects of degradation by developing a proprietary advanced stabilization technology, which has showed outstanding improvements in PEM lifetime under accelerated durability tests.

Chemical and Mechanical Stability of PFSA PEMs.

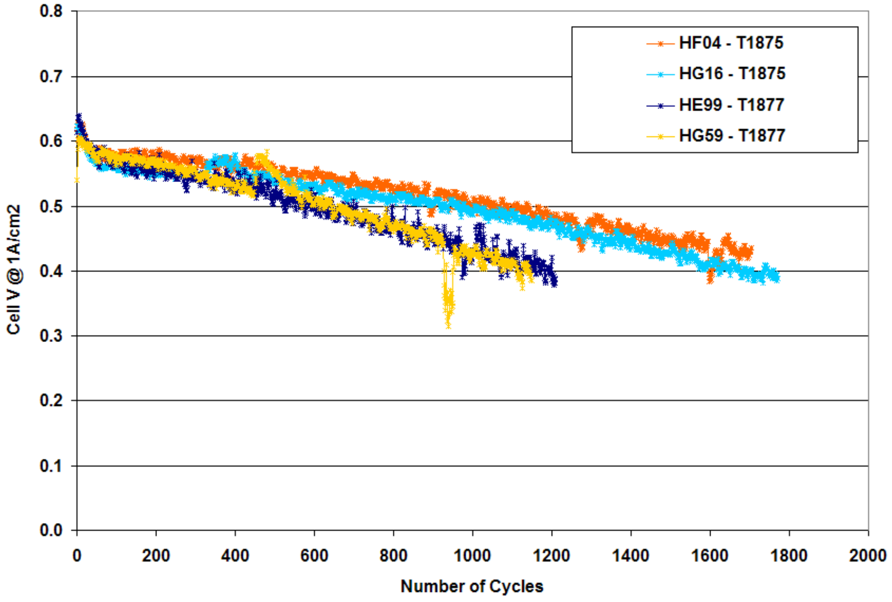
The Figure below shows the time to failure in a demanding fuel cell accelerated test that combines chemical and mechanical degradation through load (20-800 mA/cm2, H2-O2) and relative humidity cycles (0-100% RH, N2), respectively.



MEA Degradation Studies

- **The degradation studies at DuPont have been centered on the membrane. Nevertheless, the durability of the MEA as a whole has also been addressed.**
- **Nissan and DuPont developed a join effort to understand the mechanisms and conditions that lead to the degradation of the electrode layer.**

- Carbon corrosion is a major contributor to MEA degradation under start-stop cycle operation.
- The rate of this reaction is highly dependent on the amount of water present in the electrode, and slightly dependent on the oxidative stability of the carbon in the catalyst layer.
- DuPont demonstrated an improvement in start-stop testing by Improving optimizing water management in the electrode.



Performance in start-stop cycle test of MEAs with different water management design.

MEA Degradation Studies

Degradation of the ionomer in the electrode layers was also studied.

- The DuPont team developed a technique to determine if the ionomer in the electrode degrades under certain aggressive testing conditions (e.g., Start/Stop testing).
- Solid state NMR was the technique of choice for analyzing the ionomer, due to its unique capability to handle the presence of carbon and Pt in the test samples.
- The added promise from Solid State NMR was that it potentially enabled to sample from different sections of the same CCM due to its tolerance for the catalyst and since no further preparation was required for analysis.
- Differences in ionomer degradation were able to be distinguished from different cell test protocols and Fenton's test.
- The Fenton's test showed the highest degradation.

Collaborations

DuPont NAFION® (prime)

- Industrial supplier of membranes & diuspersions
- Will provide program management, membranes, electrode ionomers and some MEA's based on available catalysts.
- Provide materials characterization & analysis, incorporation of mitigation strategies into new products,
- Durability testing using internal and DoE accelerated tests.

Nissan Technical Center North America (sub)

- Subsidiary of Nissan Motor Company, OEM
- Provide accelerated durability testing, stack testing, some materials characterization & analysis

Collaborations

3M (sub)

- Industrial supplier of ionomer, MEA's and fabrication technology to the fuel cell industry.
- Provide MEA's combining NTSH catalyst and DuPont membranes.
- Develop understanding of the methodology for MEA fabrication on durability.
- Provide characterization and analysis of 3M materials.

Illinois Institute of Technology—Vijay Ramani (sub)

- Provide post mortem characterization of component materials
- Provide fundamental understanding guidance for testing necessary to complete model development
- Develop model of degradation mechanisms.

Collaborations

DOE plays a critical role in the proposed program in fostering effective collaborations among key industry members and university partners representing a diverse set of perspectives. The diverse team assembled will ensure robust solutions that could not be achieved independently by any of the proposed.

Further, other interactions and guidance fostered by the DoE outside the specific project are vital for developing the knowledge base necessary for accomplishing the technical objectives in the fuel cells programs.

Supplemental Slides

Specific Research Motivation

The proposed program deals with the study of:

- **The stresses and forces expected in an automotive fuel cell stack operating under real-world driving cycles. These cycles typically include excursions to high temperature (>80 C) and low relative humidity (RH) conditions.**
- **Commercial Nafion® membranes are known to have low conductivity at high T and low RH, resulting in the shutting down of fuel cell operation. Moreover, membrane mechanical properties also deteriorate under prolonged humidity cycling, leading to membrane failure.**
- **From our past experience in fuel cells, we recognize that the operational limitations and limited durability of fuel cell MEA's membranes are among the major technical barriers for successful implementation of fuel cell systems. The team's focus on durability is intended to rapidly resolve this issue to accelerate the delivery of PEM fuel cells into the marketplace.**
- **Carbon corrosion on the catalyst supports, Pt sintering and dissolution, and changes in water management due to degradation of GDL's are also known to severely impact cell durability.**

Analysis and Modeling: Details

Plate-GDL.

- Ex-situ accelerated degradation tests on the bipolar plate, GDL and the corresponding interface will be estimated in this task.
- The wettability of the plate material will be monitored through contact angle measurements using standard apparatus and its surface morphology will be followed by microscopy (AFM).
- Plate resistivity will be measured using DC methods.
- The GDL will be diagnosed by monitoring carbon surface area (measured by cyclic voltammetry), gas permeability (Gurley number, estimated by pressure drop measurements for a given flow rate), ratio of hydrophobic to hydrophilic pores (estimated by measuring mass uptake in selected solvents with well-defined wetting properties) and porosity/pore size distribution (mercury porosimetry or BET) as a function of time on stream during the accelerated test.
- The interface between the plate and GDL will be monitored by preparing stacks of plate material-GDL interfaces with different numbers of repeating units and monitoring the change in contact resistance (obtained by extrapolating the plot of stack resistance vs. stack thickness down to zero thickness) as a function of time on stream of the accelerated test.

Analysis and Modeling: Details

GDL-electrode.

- The interface between the GDL and the electrode in the unitized MEA will be monitored as a function of time on stream (using multiple identical test samples run for different times) through high resolution electron microscopy.
- The fractional loss of contact or delamination (if any) will be monitored as a function of time.
- Independently, stacks of GDLs coated with electrodes identical to those used in MEAs will be prepared with various thicknesses. The change contact resistance will be monitored ex-situ as a function of time as described in the previous task.
- The contact resistance due to the GDL-electrode interface will be discriminated from that due to the GDL-GDL interface in the stack by comparing against stacks of uncoated GDLs.

Analysis and Modeling: Details

Ionomer/support/catalyst interface within electrode.

- MEA electrode layers (with the appropriate ionomer loading) will be prepared containing non-catalyzed and catalyzed carbon. The interface between ionomer and carbon will be monitored in-situ using cyclic voltammetry by estimating the surface area of carbon as a function of time on stream.
- The interface between ionomer and catalyst will also be probed using this technique by estimating and monitoring the catalyst utilization as a function of time. In addition the kinetic, ohmic and transport losses within the electrode (for catalyzed samples) will be quantified by analysis of polarization data and using electrochemical impedance spectroscopy as a diagnostic.
- Data obtained with oxygen, air, 4% oxygen (balance N2) and helox as oxidants will be analyzed to extract meaningful kinetic, ohmic and transport parameters.
- The membrane ohmic and all contact resistances will be estimated through the current interrupt and HFR methods.
- The 4% oxygen data will be used to get an estimate of the true limiting current, which in turn will provide estimates of effective diffusivity through the GDL and electrode.
- Data obtained using oxygen as the oxidant at low current densities will be corrected for parasitic reactions and for ohmic and transport losses and used to extract key kinetic parameters (principally the Tafel slope, and specific activity at a fixed overpotential of 300 mV).

Analysis and Modeling: Details

Electrode-PEM interface.

- The electrode-PEM interface will be probed ex-situ using contact resistance as the primary metric.
- Successive layers of PEM and electrodes will be hot-pressed together to yield a “stack” (no GDL or bipolar plates).
- Stacks with different thickness (no. of layers) will be subjected to the accelerated test cycles and the contact resistance will be monitored as a function of time using electrochemical impedance spectroscopy (HFR measurements).
- Cross-sections of the “stacks” will also be examined using high resolution electron microscopy to identify the extent of delamination at the interface.

Analysis and Modeling: Details

PEM

- To establish a better understanding between the macroscopic rate of PEM chemical degradation estimated during in-situ accelerated testingto factors contributin g to degradation, in-situ probes will be used by IIT to study the rate of generation and/or concentration of reactive oxygen species (ROS; e.g. hydrogen peroxide, hydroxyl radical, and hydroperoxyl radical) within the PEM of an operating fuel cell.
- Two approaches will be used for this purpose. The first approach will involve embedding platinum wire microelectrodes at specified locations within the PEM. These microelectrodes will be used as an electrochemical probe to obtain local hydrogen peroxide concentrations within the PEM at different stages of each accelerated testing protocol. The local hydrogen peroxide concentrations will be correlated to the FER, which will be concomitantly monitored during testing.
- The second approach will involve the use of in-situ fluorescence spectroscopy to monitor the rate of generation of hydrogen peroxide as well as free radicals within the PEM of an operating PEFC during the accelerated test protocols. A thin fiber-optic probe will be introduced into the PEM, which in turn will contain a dye that will react (selectively) with either hydrogen peroxide or a given free radical. As these ROS are generated during the accelerated test, they will interact with the fluorescent dye to introduce a change in the observed fluorescence. The rate of change of fluorescence will be monitored as a function of time on stream of accelerated test and through this measure, the rate of generation of each ROS will be correlated to the macroscopic estimates of PEM degradation such as the FER.
- Accelerating factors will be estimated by taking a ratio of the rate of ROS generation as compared to a defined baseline test. In addition to estimating H2O2 content, the probes can also be used to estimate the hydrogen and oxygen permeability through the PEM as a function of time. The former will be estimated by a simple linear sweep voltammetry experiment, while the latter will be estimated using chronopotentiometry (using a separate dynamic hydrogen reference electrode). These properties, as well as PEM conductivity (AC impedance) will be monitored as a function of time on stream for each accelerated test. The influence of ionomer EW on the rate and mechanism of degradation of the PEM will be studied in detail.