Analysis of Durability of MEAs in Automotive PEMFC Applications

2011 DOE Hydrogen Program Fuel Cell AMR

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DuPont
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Project ID: FC089

Overview

Timeline

Start date: Sept 1, 2010

End of period 1: June 1, 2012

End of period 2: July 31, 2013

Currently 6% Complete

Budget

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

Barriers

Barriers addressed

- Fuel cell durability.

Technical Goals

- Cell durability model.
- Define Durability Tests
- MEA w/5000 hr lifetime & performance decline of <=7%

Partners

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

Objectives - Relevance

Durablity of the MEA is one of the major technical challenges to fuel cell commercialization.

This project addresses several areas that intend to fill gaps in the understanding of cell performance degradation. We intend to 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.)

The objectives of this project are:

- **Develop and/or confirm accelerated tests designed to separate individual degradation mechanisms.**
- **Develop an overall degradation model that correlates the stack operating conditions to degradation of the Membrane Electrode Assembly (MEA).**
- **Develop MEAs with a design lifetime target of 5,000 hours with ≤ 7% degradation and that show a clear path towards meeting the DOE 2015 technical targets.**

2010-2011 Objectives - Relevance

- Ensure that degradation mechanisms seen in MEA's tested in the project match experience from Nissan's previous stack tests.
- Determine most relevant testing methods to carry forward, based on relationship to historical degradation in automotive tests, degradation mechanisms observed, and testing efficiency.
- Determine if isolation of degradation effects has indeed been accomplished.
- Further determine if isolation of mechanisms is sufficient for materials development. That is, are there important interactions among degradation mechanisms that need to be addressed?

Overview – Approach

The project team will increase the understanding of MEA durability and improve durability of components. At a high level, the approach will consist of the following 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.
- Understand of the effect of realistic automotive cycling operation on the degradation of MEA components.
- Define the mechanisms and conditions that promote MEA degradation not only at a single cell level, but in the environment of an automotive fuel cell stack.
- Fabricate and deliver an MEA that has improved resistance to degradation for evaluation in a full-scale short stack.

Approach: Milestones & Go-No Go Decisions

Proposed	Actual	Milestone/Decision Points
9/25/2010	9/25/2010	Project Launch
5/31/2011		Decide on which accelerated tests to be used in addition to DoE specified tests. Tests will be selected based on results of post-mortem analysis.
10/31/2011		Selection of low-EW ionomer membrane. - Membrane design must meet accelerated durability targets. - Results verified in repeated lab testing
3/31/2012		Define MEA design for stack test - MEA based on durable materals as determined in the lab testing. - MEA must meet minimum performance and durability goals.
3/31/2012		**Go/No Go Decision 1 (Stack Testing)** 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. 1. Attain 5000 hr lifetime in durability with DoE cycling protocol. 2. Attain 1 kW/cm2 performance @ rated power at beginning-of-life in sub-scale testing. 3. 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).
3/31/2012		**Go/No Go Decision 2 (Completion of Model Development)** 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.
9/1/2012		Begin stack test. (GNG #1)
4/30/2013		Conclude stack test. Goal = 2,000 hours. (GNG #1)
9/30/2013		Model finalized and ready for publication. (GNG #2)

Approach – Define Accelerated Tests

Define & fabricate "standard" MEA builds for analysis of test methods.

Perform Durability Tests (replicates):

- DoE durability tests (Carbon, Electrocatalyst, Membrane Chemical & Mechanical Durability)
- Performance testing vs Relative Humidity (RH) & Temperature
- Proprietary start/stop testing (2 protocols) – mixed effects
- Oxygen open circuit testing (OCV) with Fluoride Emission Rate (FER) measurement – Primarily membrane
- Proprietary Load Cycling – Primarily electrode.

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

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

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

- Nissan to compare results to their historical life-cycle experience.

Analysis and Modeling (includes Materials Characterization & Analysis – Approach

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-Gas Diffusion Layer (GDL) contact resistance;
  - GDL permeability, porosity and hydrophobicity; GDL electrode contact resistance
  - Electrode utilization, active surface area, kinetic, ohmic & transport coefficients
  - Electrode-Polymer Electrolyte Membrane (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)

Develop Fundamental Understanding and Model of Degradation Mechanisms – Approach

Materials Characterization and Analysis of MEA's

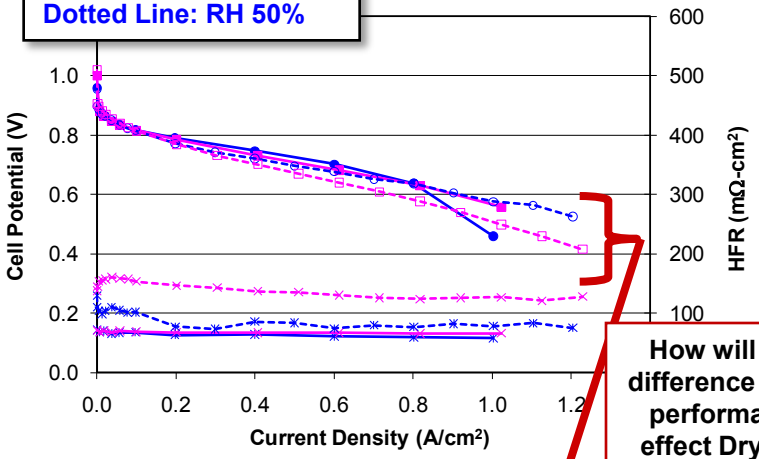
- Develop and determine tests that separate degradation mechanisms and allow for quantitative characterization of MEA failure modes.
- Materials used in various builds will be characterized so as to evaluate the effect of quantitative properties of one component on other components. E.g. Hydrophilicity 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.

- Infrared Spectroscopy (IR), Thermal Gravimetric Analysis (TGA), Nuclear Magnetic Resonance (NMR), Scanning and Transmission Electron Microscopy (SEM, TEM), X-Ray Photoelectron Microscopy (XPS), Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA),…

Flow-Field Effect – Approach

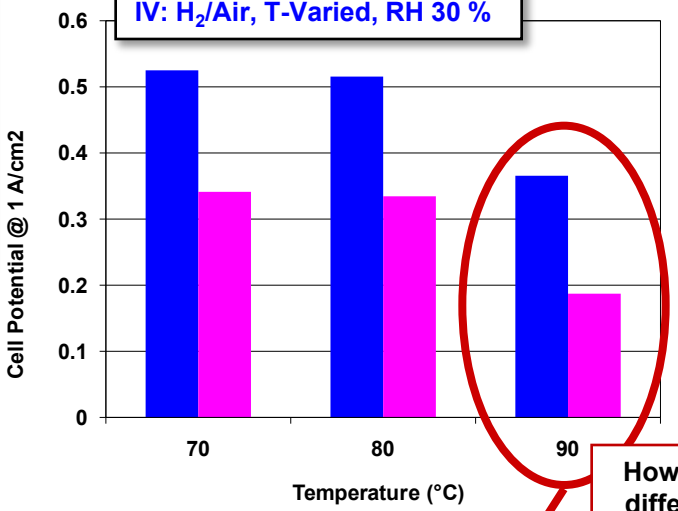
I-V: H_2/Air, 80°C
Solid Line: RH 100%
Dotted Line: RH 50%



Serpentine Channel: Blue Color

Straight Channel: Pink Color

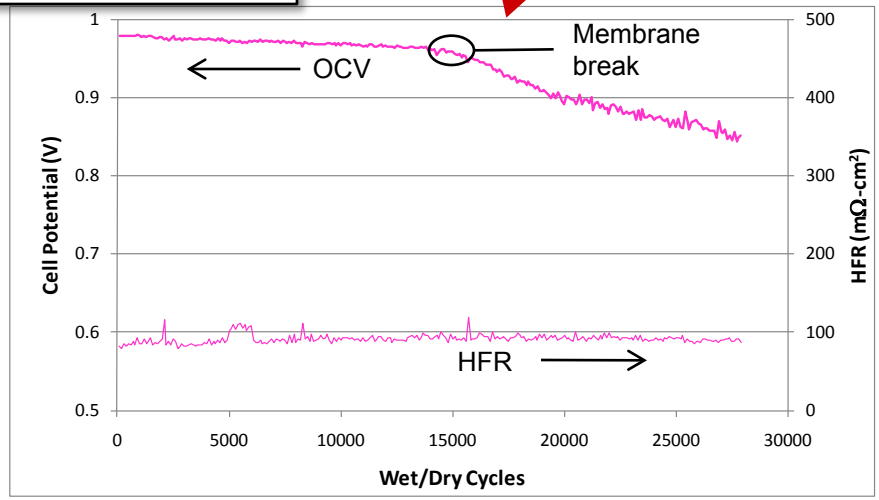
IV: H_2/Air, T-Varied, RH 30 %



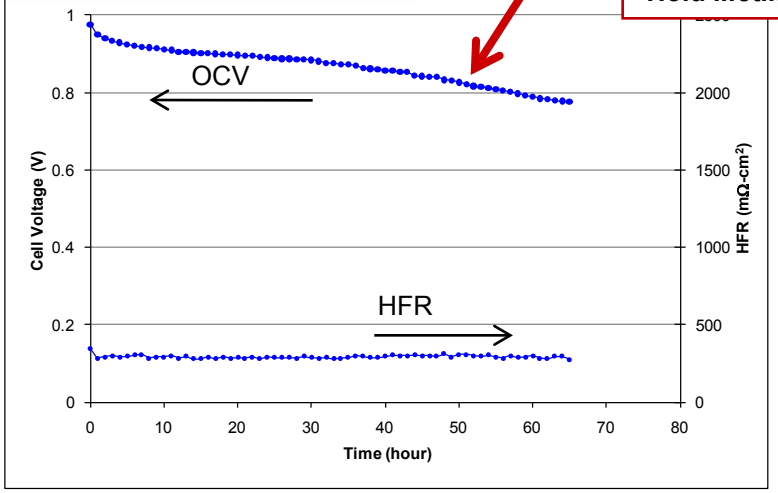
How will this difference in RH performance effect Dry/Wet Durability?

How will this difference in performance effect OCV Hold lifetime?

Dry/Wet Cycling (internal protocol)



OCV Hold: H_2/O_2, 90°C, 30%RH



NTCNA-FH
Fuel Cell Laboratory

Potential Interaction of Membrane Mechanical & Chemical Durability – Approach

Historical, internal data using proprietary lifecycle & Oxygen OCV test.

Membrane 1: Stabilized polymer, no reinforcement.

Membrane 2: Identical stabilized polymer, reinforced

- **Life-cycle test: Membrane 2 showed both significantly improved time to failure (>2.5X) and lower FER during test.**
- **Short-term oxygen OCV test showed similar results with respect to FER.**
- **Fenton's tests were within typical variation.**
- **Difference could not be accounted for by difference in polymer content in the reinforced area.**
- **Early mechanical damage allows increase in hydrogen crossover?**

Technical Progress - Overview

Primary progress has been in Task 1.0, Materials Synthesis and in preparatory work for Task 2.0, Durability Testing.

Task 1.0:

- Synthesis of short-side chain polymer with desired properties for standard testing..
- Fabrication of two standard membrane configurations using semi-commercial equipment.
- Identification and procurement of standard anode and cathode catalyst for initial analysis of durability protocols.
- Preparation and testing of inks and CCM's using the catalysts to ensure performance and suitability for semi-commercial coating.
- Coating of anode and cathode decals at desired Platinum loading.
- Initial testing of decals to ensure performance (in testing at writing)

Task 2.0

- Upgraded test equipment to handle specified DoE tests (ongoing at writing).

Technical Progress – Membrane Synthesis

Polymer synthesized for all standard polymer testing in project.

- **Standard polymer produced in semiworks scale equipment. Ion exchange capacity and molecular weight matches current developmental offerings.**
- **Processed using stabilized technology demonstrated in earlier DOE project.**
- **Partially converted to dispersion.**
- **Membranes produced using Polytetrafluoroethylene (PTFE) reinforcement and proprietary advanced stabilization system used in some commercial offerings of NAFION® membranes.**
- **Enough material available for extruded membrane and other cast membrane configurations detailed in the Approach section.**

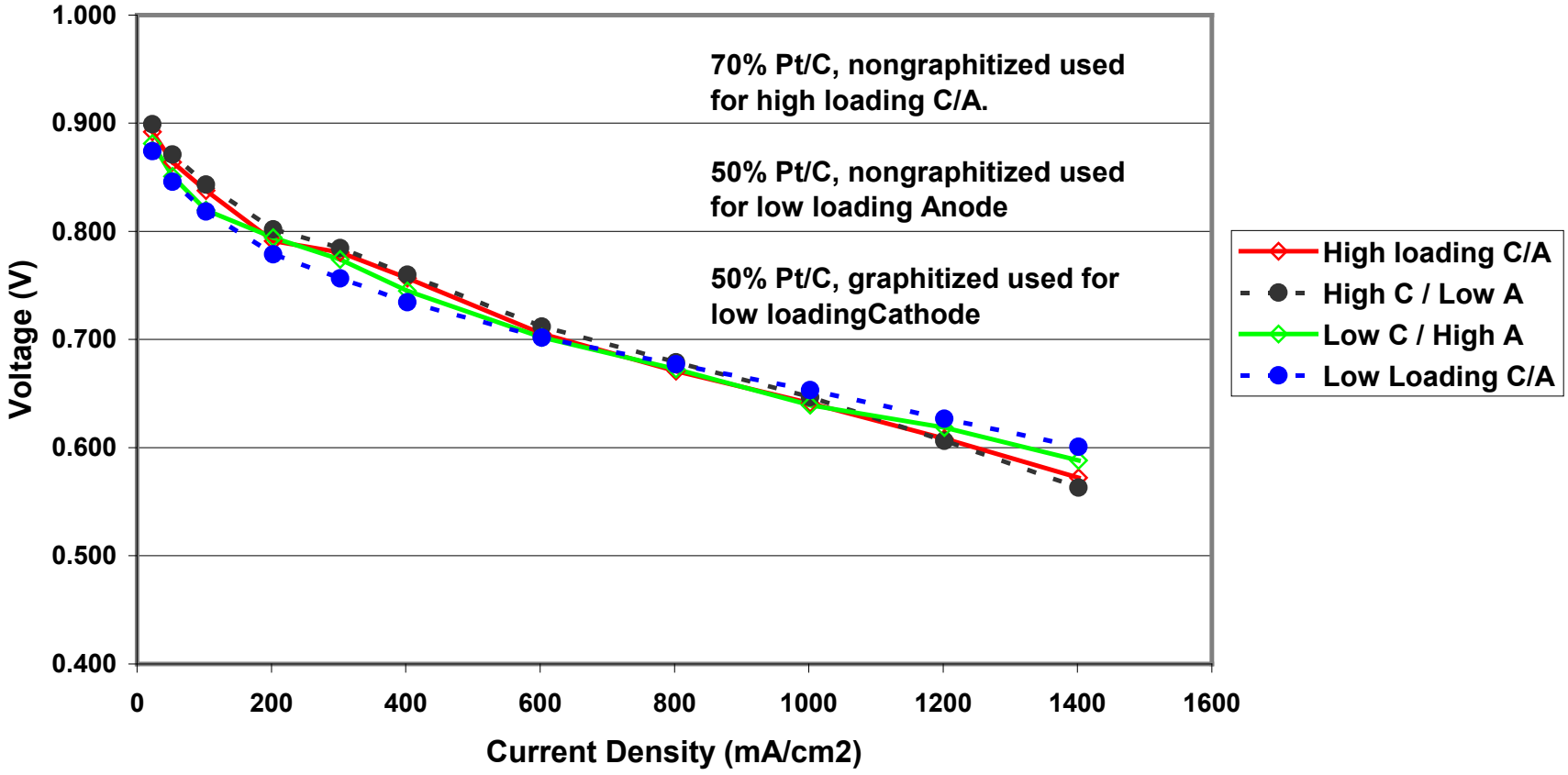
Technical Progress – CCM Synthesis

Catalyst, Ink and CCM's prepared for first Milestone work.

- **Anode catalyst: Purchased 50% Pt/C, nongraphitized.**
- **Cathode catalyst: Purchased 50% Pt/C, graphitized.**
- **Anode and cathode ink formulations confirmed and tested for performance and processing.**
- **Decals made on semicommercial scale equipment.**
- **CCM's made on standard membrane to test performance.**
- **Loadings used were based on desire to compare durability results for comparison to Nissan experience.**

Technical Progress – Decal Performance Check

Cross Comparison of Low-Loading Electrodes vs High Loading Electrodes Using NAFION® N211 Membrane
Test of Suitability of Catalyst, Ink Formulation and Printing
(65 C, 100% RH, 1.25 A - 1.67 C Stoich)

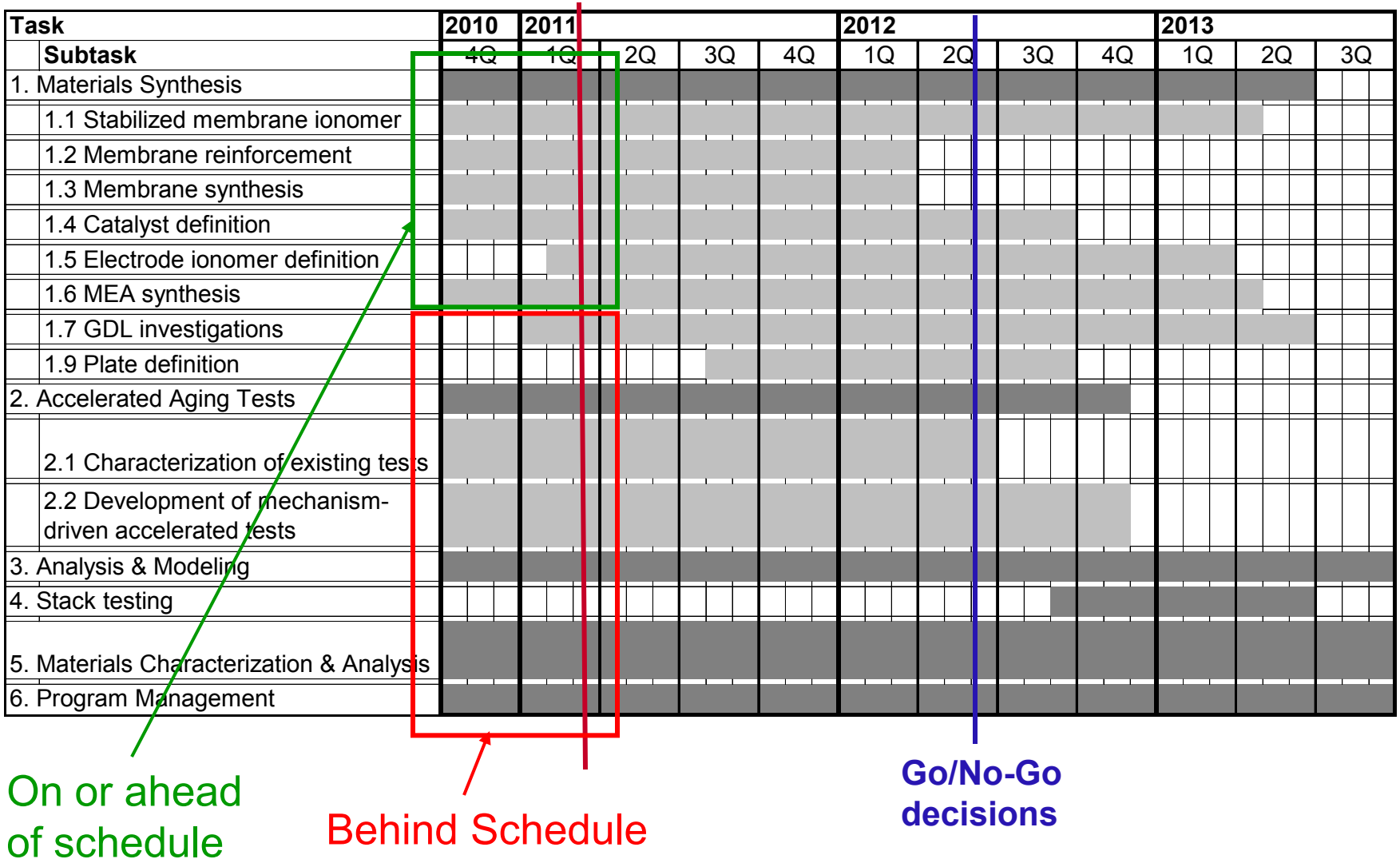


Technical Progress – Durability Testing

Tests Defined; Equipment Upgrade in Progress

- **Current DoE durability tests will be used at least in Milestone 1, where tests are defined for ongoing work.**
- **Existing equipment checked to define needed upgrades, e.g.:**
  - New load sources for updated Electrocatalyst Durability Test (voltage cycle)
  - Additional gas feeds to increase number of test stations that can run intermediate diagnostics.
  - Additional controls and feeds to run multiple stations for Membrane Mechanical Durability Test (RH cycling).
  - Ready for manual operation of all tests, automatic operation of others. Upgrades to automatic operation of all tests in progress.
  - DuPont OCV and Nissan OCV, Nissan Proprietary Start/Stop Cycles, and Load Cycling Tests in place.

Technical Progress: Gantt Chart



Collaborations

DuPont NAFION® (prime)

Program management
Membranes, ionomers, & MEA's
Materials characterization & analysis. Durability testing using internal and DoE accelerated tests.

Illinois Institute of Technology—Vijay Ramani (sub)

Post mortem characterization of component materials
Fundamental understanding guidance for testing necessary to complete model development
Develop model of degradation mechanisms (lead).

Nissan Technical Center North America (sub)

Accelerated durability testing
Stack testing
Materials characterization & analysis
Model development

3M (sub)

MEA's combining NTSH catalyst and DuPont membranes.
Understanding of the methodology for MEA fabrication on durability.
Characterization and analysis of 3M materials.

Future Work

Short term:

- Complete contractual arrangements for all subcontractors and participants.
- Complete automation of DOE Durability Test Protocols.
- Milestone 1 Complete (anticipate 3 month delay)

2011-2012

- Complete Milestones 2&3 and Go/No-Go Decision Process
- Fabricate alternative membranes & Catalyst Coated Membranes (CCM's) and complete designed experiment to better define effects of material properties on degradation.
- Fabricate durable materials for stack test.

Summary

Materials prepared and quality confirmed.

All materials made in at least semiworks scale in equipment proven to scale to manufacturing scale.

Testing methods in place for initial durability testing.

Business changes slowed initial startup of program

Approach well-defined and materials and equipment in place for start when all legal arrangements are complete.

Spendout very low, but expected to be on track with completion of milestones.

Technical Back-up Slides

Fabricate Durable MEA's – Approach

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.

Where feasible, use semiworks-scale equipment for fabrication

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 atomic force 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.

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

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

PEM

- To establish a better understanding between the macroscopic rate of PEM chemical degradation estimated during in-situ accelerated testing to factors contributing 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.