V.E.3 Analysis of Durability of MEAs in Automotive PEMFC Applications

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Subcontractors:
- Nissan Technical Center North America, Farmington Hills, MI
- Illinois Institute of Technology, Chicago, Illinois
- 3M, St. Paul, MN

Project Start Date: September 1, 2010
Project End Date: August 31, 2013

Objectives

- Develop and/or confirm accelerated tests designed to separate individual degradation mechanisms. The final tests must ensure that degradation mechanisms seen in membrane electrode assemblies (MEAs) tested in the project match experience from Nissan's previous stack tests.
- Develop an overall degradation model that correlates the stack operating conditions to degradation of the MEA. Data generated using the accelerated tests defined above will be used in the model.
- 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.

Technical Barriers

This project addresses technical barriers from Section 3.4 – Fuel Cells, of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan. The primary technical barrier addressed is:

(A) Durability

There are also some basic requirements in

(C) Performance

but this is a secondary concern, aimed primarily at having performance acceptable to Nissan in order to run the stack test, and to ensure that the durability model is relevant to current materials.

Technical Targets

In order to meet the objectives, a series of milestones were developed that act as technical targets. The last two milestones have Go/No-Go criteria to be met before they are completed. None of the milestones have yet been completed.

- Decide which accelerated tests will be used in addition to DOE specified tests. Tests will be selected based on results of post-mortem analysis. Target date: 5/31/2011.
- Select specific low-equivalent weight membrane for use in stack test. The membrane design must meet accelerated durability targets with results verified in repeated lab testing. Target date: 10/31/2011.
- Define MEA design for stack test. The MEA will be based on durable materials as determined in the lab testing, and must meet minimum performance and durability goals. Target date: 3/31/2012.
- If data generated from the accelerated tests can be shown to discriminate among the various cell components, complete development of durability model. Target date: 8/31/2013.
- If MEA design meets targets, begin stack test to verify lab performance and durability model. Target completion date: 4/20/2013.

Fiscal Year (FY) 2011 Accomplishments

The project was divided into five tasks plus project management, which are more parallel than sequential. The accomplishments are organized by task. Only Task 1 and 2 have been worked on to date. Tasks 3 through 5 are listed for completeness, but no work has begun on these tasks

Task 1.0 Materials Synthesis

- Synthesize short-side chain polymer with desired properties for standard testing.
- Fabricate two standard membrane configurations using semi-commercial equipment.
- Apply semi-commercial coating of anode and cathode decals at desired platinum loading.

- Fabricate catalyst-coated membranes (CCMs) for initial durability tests at DuPont and Nissan.

Task 2.0 Accelerated Aging Tests

- Upgraded test equipment to handle specified DOE tests.
- Began initial accelerated tests at DuPont and Nissan.
- Testing currently in progress includes DOE, Nissan and US Fuel Cell Council accelerated tests.

Task 3.0 Analysis and Modeling

Task 4.0 Stack Testing

Task 5.0 Materials Characterization and Analysis

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Introduction

This project deals with the study of the stresses and forces expected in an automotive fuel cell stack operating under real-world driving conditions. For the fuel cell stack, these driving conditions include a wide variety of conditions that stress various components that make up the fuel cell stack. For instance, at high temperature (>80°C) and low relative humidity (RH) conditions, the conductivity of many membranes becomes low, resulting in the failure of fuel cell operation [1]. Moreover, membrane mechanical properties also deteriorate under prolonged humidity cycling, leading to membrane failure [2]. The DOE considers the durability of fuel cell components to be among the major technical barriers for successful implementation of fuel cell systems. The minimum required life expectancy for automotive fuel cell stacks is 5,000 hours.

Incremental improvements will not suffice to bridge the gap between today's technology and the market requirement. This project is focused on both improving the understanding of the mechanisms of component failure, and rapidly incorporating this understanding into component design and thus accelerate the delivery of proton exchange membrane fuel cells (PEMFCs) into the marketplace.

Approach

Degradation mechanisms for all stack components are being studied at varying levels of detail. At a high level, the determination of degradation mechanisms consists 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.
- Understanding of the effect of realistic automotive cycling operation on the degradation of MEA components.
- Definition of 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.
- Fabrication and delivery of an MEA that has improved resistance to degradation for evaluation in a full-scale short stack.

These studies on materials both before and after running the accelerated tests will be used first to compare with Nissan stack results and define the best set of accelerated tests to use in this project. The testing and analyses will then be extended to a range of components, so that a quantitative model of stack degradation can be developed.

Next, the results of degradation mechanism work will be used to develop methods to mitigate some of these mechanisms in order to increase the durability of the membrane electrode assemblies. The improved MEAs will be used in a stack test at Nissan to verify both the model and the improvements in durability.

Results

The start of the testing program has been delayed while confidentiality agreements and subcontracts were being worked out among the parties. The confidential disclosure agreements were signed in June 2011, and materials were then shared so testing could begin. The completion of these agreements also allows the legal work on the actual contracts to begin.

While the agreements were being negotiated, the work focused on defining, fabricating and purchasing the base materials. Because the project is defined for a certain class of short side-chain polymers, the first task in the project involved preparation of materials to be used in the evaluation of the accelerated tests. A short side-chain polymer with the desired range of properties was synthesized in semiworks-scale equipment. Some of this material was converted to dispersion, and several small lots of reinforced membranes were produced on semi-works scale equipment. The team agreed on the importance of testing repeatable materials from processes that could produce semi-commercial quantities of material and be scaled up easily. These membranes use an expanded polytetrafluoroethylene reinforcement, and DuPont's proprietary advanced stabilization system, and were made in nominal thicknesses of 16 and 27 microns. All membranes for the initial phase of the project use the same polymer composition.

The team agreed on using a specific commercially available cathode catalyst. The catalyst consists of 50% Pt on an acetylene carbon black support. A supply of cathode decals based on this ink formulation was produced on the semi-commercial coating line. Both 0.15 and 0.35 mg Pt/cm^2 loadings were produced. This decal supply will be used for the remainder of the accelerated test evaluation work. It is not optimized for either performance or durability, but is in the right performance and property range for evaluation of testing methods.

The semi-commercial decals were then transferred to N211 and tested under our standard conditioning test to ensure the material quality. These results were compared to CCMs using previous generation materials. These results led us to the conclusion that the electrodes are suitable for the next phase of the work. Once the suitability of the materials was confirmed CCMs were prepared for initial durability tests at DuPont and Nissan.

Test equipment at DuPont was upgraded to handle specified DOE tests, which differed considerably from DuPont's internal testing. Both Nissan and DuPont have begun the accelerated tests of the base materials, but significant test results are not yet available.

Conclusions and Future Directions

Short-Term

- Complete contractual arrangements for all subcontractors and participants.
- Complete automation of DOE Durability Test Protocols.
- Complete analysis of baseline materials.
- Complete first set of accelerated tests and begin post-mortem analyses.
- Make decision on acceleration tests to use in the model development. We anticipate a overall delay of six months due to the timing of the confidentiality agreement and formal contracts.

2011-2012

- Fabricate alternative membranes and CCMs and complete designed experiment to better define effects of material properties on degradation.
- Fabricate durable materials for stack test.

FY 2011 Publications/Presentations

1. 2011 AMR presentation, May 13, 2011.

References

1. A.V. Anantaraman, C.L. Gardner, "Studies on ion-exchange membranes. Part 1. Effect of humidity on the conductivity of Nafion®", *Journal of Electroanalalytical Chemistry*, **1996**, *414*, 115-120.

2. F. Bauer, S. Denneler, M. Willert-Porada, "Influence of temperature and humidity on the mechanical properties of Nafion® 117 polymer electrolyte membrane" *Journal of Polymer Science: Part B*, **2005**, *43*, 786-795.