V.E.7 Analysis of Durability of MEAs in Automotive PEMFC Applications

Randal L. Perry
E.I. du Pont de Nemours and Company
Chestnut Run Plaza, 701/209
4417 Lancaster Pike
Wilmington, DE 19805
Phone: (302) 999-6545
Email: randal.l.perry @usa.dupont.com

DOE Managers
HQ: Kathi Epping Martin
Phone: (202) 586-7425
Email: Kathi.Epping@ee.doe.gov
GO: David Peterson
Phone: (720) 356-1747
Email: David.Peterson@go.doe.gov

Technical Advisor
Thomas Benjamin
Phone: (630) 252-1632
Email: Benjamin@anl.gov

Contract Number: DE-EE0003772

Subcontractors:
- Nissan Technical Center North America, Farmington Hills, MI
- Illinois Institute of Technology (IIT), Chicago, IL

Project Start Date: September 1, 2010
Project End Date: February 28, 2014

Fiscal Year (FY) 2012 Objectives

- Select and confirm accelerated stress tests (ASTs) designed to separate individual degradation mechanisms. The selected tests must ensure that degradation mechanisms seen in membrane electrode assemblies (MEAs) tested in the project match Nissan's automotive experience. The membrane portion of this work is focused on membranes made from short side-chain (SSC) perfluorsulfonic acid (PFSA) polymers.
- Modify selected tests to generate necessary data for developing an overall degradation model. This model will correlate stack operating conditions to degradation of the MEA.
- Define a material set based on initial tests to be used to develop the model and make it applicable to a range of MEA designs.
- Begin defining mitigation strategies for the mechanisms identified in the testing and modeling. These strategies will be used to 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. Actual MEA development is not part of the scope of the funded project. However, development is performed concurrently by DuPont, and some mitigation strategies from the project are included, and the developmental materials tested.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.5) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(C) Performance

The first is the primary focus, with the second being important to continue to stack testing.

Technical Targets

The technical targets are in terms of timelines and advancement of the modeling and mechanism studies. Performance targets are based on work done by DuPont outside the DOE project, but incorporating mitigation strategies developed in the project. Business changes at DuPont have changed the fuel cell focus from MEAs to membranes and dispersions. With the reduced resources in the MEA areas, we do not expect to meet durability or performance targets for MEAs, only for membranes. The primary project targets are:

- Select and confirm ASTs to be used for modeling work. Timing: 3/31/2012.

  Current Status: Complete 4/30/2012
- Select SSC PFSA membrane:
  - Membrane design must meet accelerated durability targets.
  - Results verified in repeated lab testing. Timing: 8/31/2012.

  Current Status: Mechanical Durability: 25,000 of 30,000 required cycles completed and still in progress using new reinforcement, vs <10,000 cycles with initial reinforcement.
- Chemical durability: Failure at ~400 of required 500 hrs.
- Define MEA design for stack test:
  - MEA based on durable materials as determined in the lab testing.

– MEA must meet minimum performance and durability goals. Timing: 9/30/2012.

Current Status: Catalysts limited to a class of commercially available materials. To date, catalysts attain about 80% of required life and 75% of performance.

- 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 5,000 hr lifetime in durability in automotive cycling protocol.
  2. Attain 1 kW/cm^2 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. Timing: 9/30/2012.

  Current Status: With the emphasis on membranes and dispersions rather than MEAs in DuPont, we do not expect to attain this target.

- Repeatability of AST data is verified to enable confidence in data for modeling work. Timing 9/30/2012.

  Current Status: Verified by ex situ testing. Not enough data have been developed for statistical confirmation.

- Stack test: Timing: 3/1/2013.

  Current Status: Not anticipated to be carried out.

- Model finalized and ready for publication. Timing: 3/31/2014.

  Current Status: Model framework complete, but still early in data acquisition stage.

FY 2012 Accomplishments

- Completed contractual agreements among DuPont, Nissan and IIT.
- Completed multiple repeats of ASTs and analyses for baseline materials.
- Evaluated results and selected ASTs to carry forward.
- Modified testing methods and equipment at Nissan and DuPont to generate more detailed modeling data from the ASTs.
- Illinois Institute of Technology completed project to automate analysis of polarization curves.
- Developed electrochemical impedance spectroscopy methodology to improve understanding of degradation properties.
- Increased mechanical durability of membranes from 8,000 to 16,000 cycles using membrane post-treatment methods.
- Further increased mechanical durability to greater than 25,000 cycles of the 30,000 cycle goal without loss of performance.

✧ ✧ ✧ ✧ ✧

Introduction

The components of an automotive fuel cell undergo significant stresses due to the variability of operating conditions: starting and stopping, idling, hill-climbing, cruising and so forth. This project involves the study of the effects of these stresses on the components of an automotive fuel cell stack operating under real-world driving conditions. In terms of the fuel cell stack, these driving conditions can be translated into conditions within the stack itself. For instance, at high temperature (>80°C) and low relative humidity (RH) conditions, the conductivity of many membranes become 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.

This project is aimed at a better understanding of the degradation mechanisms in the fuel cell stack, and to develop a model to quantify the rate of degradation. Further, the project intends to use the knowledge gained from these and other degradation studies to determine mitigation methods for those mechanisms. Although this project does not include materials development, it is expected that a parallel program, unfunded by the DOE, will develop improved materials based on these mitigation strategies, especially for the membrane and electrode ionomers. These materials will be tested for durability as part of the project.

Approach

The general approach involves testing various components in several ASTs and using both in situ and ex situ methods to analyze the degradation and postulate the degradation mechanisms. These proposed mechanisms are tested by making modifications to the MEAs and further testing in the ASTs. The actual implementation is performed in an iterative fashion.

These studies on materials both before and after the accelerated tests are 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 are then extended to a wider range of components, so that a quantitative model of stack degradation is developed. Next, the results of degradation mechanism work are used to develop methods to mitigate some of these mechanisms in order to increase the durability of the membrane electrode assemblies. These mitigation methods are incorporated into the next phase of testing, and the process continues.

Results

While the contractual agreements were being negotiated, the work focused on testing baseline materials of SSC PFSA membranes with commercially available catalysts and gas diffusion layers (GDLs). Numerous samples were tested using AST protocols from Nissan and the Fuel Cell Tech Team (FCTT). The protocols used are designed to separate four well-known MEA degradation mechanisms:

- Dissolution and re-deposition of the platinum catalyst
- Corrosion of the carbon catalyst support by oxidation
- Chemical degradation of the membrane
- Mechanical failure of the membrane due to mechanical stresses.

Nissan performed tests using their own protocols. DuPont ran the US Fuel Cell Council AST and rebuilt test stations to run the FCTT ASTs. These AST protocols are summarized and compared in Table 1.

From an efficiency perspective, there was a bias toward the Nissan protocols for the catalyst layer due to their significantly shorter test time. After multiple tests were run using all the ASTs, the results of both in situ and ex situ testing were compared. The in situ testing included polarization curves, electrochemically active surface area, hydrogen crossover, and shorting resistance. The ex situ tests included scanning electrode microscope and transmission electron microscope studies, chemical analysis for membrane composition, and fluoride in the cell effluent. Table 2 summarizes the comparison of the methods.

The detailed data were reviewed internally and with the Fuel Cell Tech Team. The conclusions of the project team are that:

- Baseline material set and test protocols show reasonable consistency and behave (in most ways) as expected.
- Nissan ASTs for catalyst degradation appear to demonstrate the same degradation mechanisms as the FCTT ASTs. The FCTT ASTs cause more degradation over the duration of the test, as expected.
- Nissan catalyst ASTs are advantageous for data generation due to much shorter test duration. Supplemental FCTT catalyst ASTs will be run to generate data more representative of end-of-life.
- Nissan and FCTT ASTs results for chemical durability were surprising due to the small differences. Nissan AST was expected to be harsher due to the use of oxygen over air. The differences between the US Fuel Cell Council AST and the others agree with data previously released by General Motors.
- Differences in the post mortem results of the FCTT and Nissan membrane durability tests were surprising. We will continue some of both tests until the reasons for the differences are understood.

TABLE 1. Comparison of AST Protocols used for Baseline Samples

Test Protocol	Voltage Profile	Test Time	Temp/ RH	Notes
Carbon Corrosion (Nissan Start-Stop B)	Triangle sweep. 1.0-1.5 V 2 s/cycle	1,000 cycles <1 hr	80°C 100%	Significantly faster
Carbon Corrosion (FCTT AST)	Hold at 1.2 V	400 hr	80°C 100%	
Test Protocol	**Voltage Profile**	**Test Time**	**RH**	**Notes**
Pt Dissolution (Nissan Load Cycle)	3 s @ 0.95 V 3 s @ 0.6 V	10,000 cycles 17 hr	80°C 100%	Significantly faster
Pt Dissolution (FCTT AST)	Triangle sweep. 0.6-1.0 V 16 s/cycle	30,000 cycles 134 hr	80°C 100%	
Test Protocol	**Voltage Profile**	**Test Time**	**RH**	**Notes**
Chemical Stability (Nissan OCV hold)	Open Circuit	500 hr	90°C 30%	Oxygen on cathode
Chemical Stability (FCTT AST)	Open Circuit	500 hr	90°C 30%	Air on cathode
Chemical Stability (US Fuel Cell Council AST)	Open Circuit	72 hr	90°C 30%	Oxygen on cathode
Test Protocol	**Voltage Profile**	**Test Time**	**RH**	**Notes**
Mechanical Durability (Nissan)	(varies)	30,000 cycles ~1,500 hr	0% to >100%	at 80°C
Mechanical Durability (FCTT AST)	N/A	20,000 cycles 1334 hr	0% to >100%	at 80°C

Going forward, Nissan ASTs will be used as the primary protocols for catalyst degradation, and the FCTT ASTs will be the primary protocols for membrane degradation.

The data generated during the baseline testing was evaluated for use in model development. A number of shortcomings were discovered, and the protocols were refined to provide better data and analysis tools.

TABLE 2. Summary of Comparison of Test Results from ASTs Used in the Project

Test Protocol	Test Time	ECA Loss	IV Loss	Comments
Carbon Corrosion (Nissan Start-Stop B)	8 hrs	29-35%	30-35%	Cathode thinned ~15%
Carbon Corrosion (FCTT AST)	>400 hrs	>35%	30-35%	Cathode thinning ~25%
Test Protocol	**Test Time**	**ECA Loss**	**IV Loss**	**Comments**
Pt Dissolution (Nissan Load Cycle)	<24 hrs	35-45%	4-10%	Pt growth 5-10 nm; Pt migration (including large crystals)
Pt Dissolution (FCTT AST)	>135 hrs	>40%	14-25%	Similar to Nissan. Some larger Pt in cathode.
Test Protocol	**Test Time**	**Time to fail**	**FER**	**Comments**
Chemical Stability (Nissan OCV hold)	500 hrs	450-500 hrs	3-4	1 - OCV fail, 1 - no fail. Different microscopy results than FCTT AST
Chemical Stability (FCTT AST)	500 hrs	400 hrs	0.4-0.7	Hydrogen crossover fail
Chemical Stability (US Fuel Cell Council AST)	72 hrs	N/A (72 hr)	0.05	FER is 60% of Nafion® XL; But, FER >> Nafion® XL in long-term test.
Test Protocol	**Test Time**	**Time to fail**	**Cycles**	**Comments**
Mechanical Durability (Nissan)	~1,500 hrs	100 hrs	12k cycles	OCV Failure
Mechanical Durability (DOE - DuPont)	>1,350 hrs	400 hrs	8,000 cycles	Shorting Resistance Failure

OCV – open circuit voltage; FER – fluoride emission rate

- The polarization curves were extended so that they include at least five points each over four decades of current.
- Polarization curves are performed for four different cathode gasses: air, oxygen, 21% oxygen in helium, and 4% oxygen in nitrogen.
- Due to the time required to measure four extended polarization curves, the frequency of testing was reduced. At least four sets of curves are measured on each sample in the carbon corrosion and platinum dissolution ASTs. These are beginning of life (BOL), end of life, and at least two intermediate measurements. In all, this allows discrimination of various kinetic and mass-transfer effects at several stages of electrode degradation.
- IIT developed a computer program developed for rapid data organization and analysis.
- Additional membranes and catalysts were defined for the next set of tests.

Modifications to the test stations at Nissan and DuPont were required to perform these tests. These modifications are complete, and testing is underway.

The poor mechanical performance of the baseline membranes led to several variations of the membrane, and some additional needs in testing. First, the baseline membrane, which is reinforced with expanded polytetrafluoroethylene (ePTFE) was treated after manufacture to improve the integrity of the PFSA phase. By varying the conditions of the treatment, the membrane was able to achieve about 16,000 cycles in duplicate tests, compared to 8,000 before the treatment. There was little change in BOL performance, though there was some loss in chemical durability. The cause of this loss is under study.

In order to more fully understand this mechanism, a set of materials is being tested that use different reinforcements and both SSC and long side-chain polymers. Use of a mechanically weaker reinforcement (in terms of tensile modulus and tear) that reduces swell has been shown to significantly increase lifetime in the mechanical durability test, currently achieving 25,000 cycles and still under test as of this writing. The results are preliminary, but we expect to see significant effects of polymer type and reinforcement type on the membrane durability, and are beginning to explore chemical mechanisms.

Conclusions and Future Directions

- Despite differences in the electrical potential used in the tests, and the additional acceleration factor involved, the Nissan and FCTT catalyst durability tests exhibit similar degradation mechanisms.
- The testing strategy going forward appears to be a reasonable balance of gathering important data and improving sample throughput.
- Further interactions between mechanical and chemical durability were noted, though not understood.

In the next quarter (until the Go/No-Go decisions):

- Complete extended data acquisition and multiple gas testing for modeling of catalyst layer with three different catalysts.

- Continue generating data for modeling, using variants of baseline MEA and GDL.
- Test a matrix of SSC and long side-chain PFSA polymers and mechanically different reinforcements (ePTFE and others) to continue analysis of mechanical/chemical durability interaction.
- Include new ionomers and alternative reinforcements in durability testing.
- Complete ex situ analysis of new test samples.
- Analyze in situ and ex situ data to ensure that results have statistical significance to model building.
- Revise preliminary model as need.

FY 2013

- Continue above items in the iterative method described in the approach.
- Develop mitigation strategies based on analysis of new membrane material sets.
- Test proposed model against data from modified material sets in lab cells.

FY 2012 Publications/Presentations

1. 2012 AMR presentation, May 16, 2012.

2. Poster at Spring 2012 ECS meeting, based in part on work in this project. **Investigating the effect of accelerated catalyst durability tests on PEM fuel cell performance using electrochemical impedance spectroscopy.** Gregory DiLeo, Ramesh Yadav, Nilesh Dale, Kev Adjemian (Nissan)

3. 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.

4. 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.