VII.B.7 MEA and Stack Durability for PEM Fuel Cells

Michael T. Hicks
3M Company
3M Center, Building 0201-02-N-19
Saint Paul, MN 55144-1000
Phone: (651) 736-8433; Fax (651) 575-1187; E-mail: mike-hicks@mmm.com

DOE Technology Development Manager: Kathi Epping
Phone: (202) 586-7425; Fax: (202) 586-9811; E-mail: Kathi.Epping@ee.doe.gov

DOE Project Officer: Reginald Tyler
Phone: (303) 275-4929; Fax: (303) 275-4753; E-mail: Reginald.Tyler@go.doe.gov

ANL Technical Advisor: Thomas Benjamin
Phone: (630) 252-1632; Fax: (630) 252-4176; E-mail: Benjamin@cmt.anl.gov

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Subcontractors:
Case Western Reserve University, Cleveland, OH
Plug Power Inc., Latham, NY
University of Miami, Miami, FL

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Objectives

- Develop an understanding of membrane electrode assembly (MEA) failure mechanisms encountered under real world operating conditions.
- Develop an MEA with enhanced durability while maintaining performance.
- Determine optimum system operating conditions to extend MEA lifetime.
- Characterize life expectancy and performance degradation of the MEA in extended testing (> 2,000 hours) in a field ready fuel cell system using reformate fuel.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the 2005 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Durability

Technical Targets

Table 1. DOE Stationary Stack Systems Targets for Small (3 - 25 kW) Systems

Characteristic	Units	2005 Target	Status
Durability	Hours	16,000	>9,000[a] >16,000[b]

[a] Demonstrated MEA lifetime to date
[b] Predicted MEA lifetime

Approach

- Develop MEAs utilizing 3M proprietary perfluorinated sulfonic acid ionomer, which has demonstrated improved oxidative stability over PEMs made with Nafion® ionomer.
- Develop and validate individual component aging tests and characterization methods.
- Relate changes in MEA component physical properties to changes in MEA performance leading to a more focused materials development strategy.
- Optimize stack and/or MEA structure based upon modeling and experimentation.
- Selectively test MEA and stack designs for enhanced system durability and characterize life expectancy.
- Utilize lifetime statistical methodology to predict MEA lifetime under 'normal' conditions from 'accelerated' test data.

Accomplishments

- Completed initial round of ionomer model compound study to elucidate ionomer degradation pathway(s).
- Confirmed benefits of end group modified polymer. Increased lifetime by 89% under accelerated test conditions.
- Discovered new membrane additive that reduced membrane weight loss in accelerated tests by 27% over previous state-of-the-art.
- Implemented new measurement technique to measure gas diffusion layer (GDL) oxidative stability. New technique indicates latest GDL >1,500x more stable than baseline materials as measured in accelerated aging tests.
- Completed load setting studies that showed open circuit voltage (OCV) results in a 16x reduction in MEA lifetime compared to load cycle without OCV setting.
- Established relationship between fluoride ion release and MEA lifetime. Relationship is independent of MEA constructions studied.
- Utilized statistical lifetime methodologies to predict MEA lifetime under 'normal' conditions from 'accelerated' conditions. Baseline MEAs (no new components) predicted to last > 16,000 hours, which would meet DOE 2005 targets.
- Accelerated testing of multiple new MEA designs yielded a design with a 775% increase in lifetime over an MEA made from Nafion® 112.
- Completed extended single cell testing studying the effects of air bleed and CO level (>2,000 hrs) on MEA performance decay and fluoride ion release.
- Integrated new components into MEAs for module and stack testing. Module testing yielded a 1.5% voltage loss during the first 1,000 hours of testing.

Future Directions

- Complete MEA component development and integration.
- Utilize ^{19}F Nuclear Magnetic Resonance (NMR) to determine model compound degradation pathway.
- Develop and implement strategies to mitigate decay mechanisms.
- Determine Arrhenius constants for MEA lifetime-fluoride release relationship.
- Complete 3D modeling and segmented cell work investigating MEA structures.
- Develop model of peroxide formation, transport and consumption in an operating fuel cell. Incorporate peroxide model into overall MEA statistical lifetime prediction model.
- Design and fabricate stacks for system demonstration.

Introduction

Proton exchange membrane fuel cells are poised to change the landscape of power generation over the next ten years. For this to be realized, however, considerable technical challenges must be overcome; one of the most significant challenges for stationary systems is lifetime, where 40,000 hours of operation with less than 10% decay is desired. This project is conducting fundamental studies on the durability of MEAs and fuel cell stack systems. Knowledge gained from this project will be applied toward the design and synthesis of MEAs and stack systems to meet DOE's 2005 and 2010 stationary fuel cell stack systems targets.

Approach

The approach for increasing stationary fuel cell system lifetime involves two interacting paths: optimization of MEAs and subcomponents for durability and optimization of system operating conditions to minimize performance decay. Ex-situ accelerated component aging tests are utilized to age components and determine failure modes. Aged components are then assembled into MEAs for performance testing in comparison to virgin MEAs. In this manner, the effect of component aging on MEA performance can be quantified and mitigation strategies can be implemented. In addition, 3D modeling and novel experimental approaches are used to probe the loci of degradation/failure within an MEA. A total system approach is used to study the interactions between stack design/operation and MEA performance/durability. With this approach, the system (stack and MEA) is optimized for durability. Finally, since 40,000 hours of testing is not obtainable during this 3-year project, test data generated from both accelerated and normal MEA operation are being used to predict MEA lifetime. All MEA development is based upon a new 3M proprietary perfluorinated sulfonic acid ionomer.

We have assembled a team consisting of 3M, Plug Power, Case Western Reserve University, and the University of Miami to carry out the approach. 3M is primarily responsible for component development, MEA integration and accelerated testing with statistical lifetime analysis; Plug Power is primarily responsible for investigating system variables, MEA testing in modules and stacks, and stack development; Case is primarily responsible for the development of diagnostic tools, physical property characterization, and formulating an ionomer degradation model; and the University of Miami is primarily responsible for investigating MEA non-uniformities via modeling.

Results

In order to elucidate decay mechanism(s) of perfluorinated sulfonic acid ionomers, a study of small molecule model compounds was initiated. The model compounds are selected such that they possess the same functional groups (COOH, SO_3H, CF_3, O, etc.) found in perfluorinated sulfonic acid ionomers. Degradation of the model compounds is conducted at 70°C in a solution of 100 mM model compound, 400 mM Fe^{2+} and 400 mM H_2O_2. Fluoride loss is used as the metric for model compound degradation, and ^{19}F NMR is being used to determine degradation pathways. The results of the experiments are summarized in Table 2. Analysis of the data indicates that SO_3H groups are stable, COOH groups and branched perfluoroethers in the presence of COOH are unstable, and branched side chains destabilize the ionomer.

Table 2. Model Compound Study - 24 hour test

Model Compound	F^- Release (% of total in MC)	Relative F^- Release
3M ionomer: $[(CF_2CF_2)(CF_2CF(R_1))]$	0.01 (0.1)	1.5 (14)
Nafion ionomer: $[(CF_2CF_2)(CF_2CF(R_2))]$	0.03 (0.26)	4.3 (37)
$CO_2HCF(CF_3)OC_3F_7$	0.08	11
$CO_2HCF(CF_3)OC_4F_8SO_3H$	0.28	40
$C_7F_{15}CO_2H$	0.02	2.8
$C_4F_9SO_3H$	0.008	1.1
$C_8F_{17}H$	0.007	1
$C_2F_5OC_3F_6SO_3H$	0.002	0.3
$C_2F_5OC_2F_3(CF_3)OC_2F_4SO_3H$	0.001	0.15

$R_1 = OC_4F_8SO_3H$
$R_2 = OCF_2CF(CF_3)OC_2F_4SO_3H$
Numbers in parenthesis based on side chain only

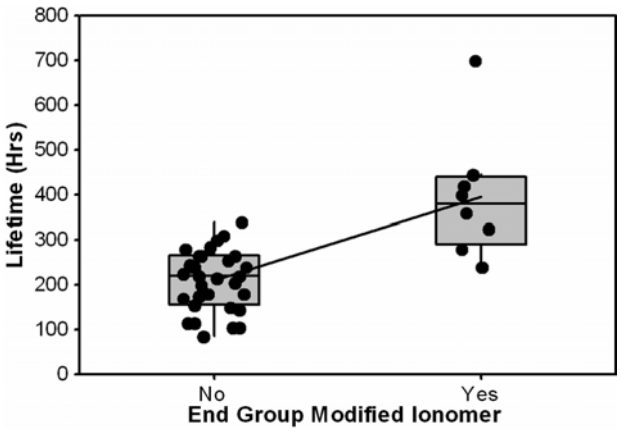

Figure 1. Effect of Ionomer End Group Modification on MEA Lifetime in Accelerated Testing

Based upon the model compound studies, one would expect a polymer without COOH end groups would last longer than a polymer with COOH end groups. The improvements to MEA lifetime resulting from polymer end group modification (no COOH groups) are shown in Figure 1. The accelerated test is conducted at 90°C cell temperature with 70°C anode and cathode dew points, operating under H_2/air with a 7 psig anode overpressure and load profile A (Figure 2). Under these test conditions, MEAs made with the end group modified 3M polymer last 89% longer than MEAs made from non-end group modified 3M polymer (contains COOH end groups).

Another means to improve membrane durability is through additives designed to mitigate membrane degradation via hydrogen peroxide. This project has built upon additive work previously developed under DOE Cooperative Agreement No. DE-FC36-02AL67621. Under this project, new additives have been discovered that reduce membrane weight loss when exposed to 1 M H_2O_2 at 90°C for five days by 27% over the previous state-of-the-art developed under DE-FC36-02AL67621 or by 61% over the control (no additives).

GDL stability was characterized in terms of a corrosion test as the time for 50 coulombs to pass at a given voltage. Fifty coulombs was chosen because the baseline GDL surface changed from hydrophobic to hydrophilic at this point. This test indicates that the downselected GDL for this project is > 1,500x more stable than baseline materials.

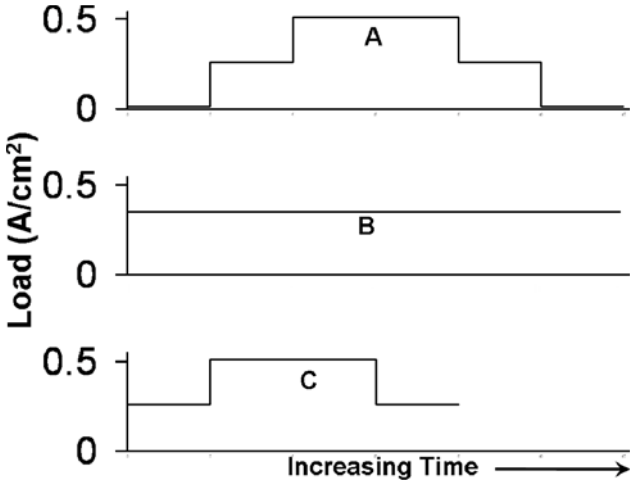

Figure 2. Load Profiles Used in Accelerated Tests

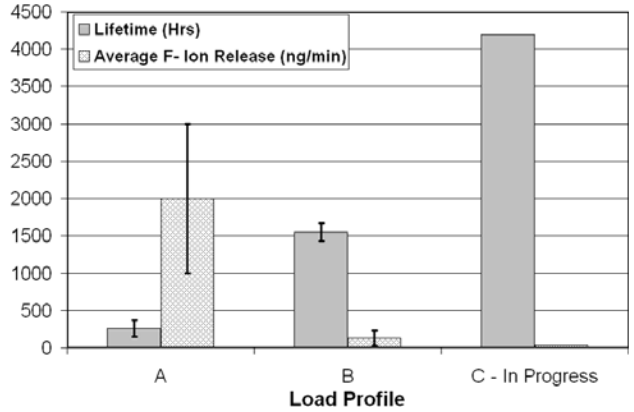

Figure 3. Effect of Load Profile on MEA Lifetime in Accelerated Tests

The effect of load profile on MEA lifetime is shown in Figure 3 and the load profiles are described in Figure 2. The accelerated tests are conducted at 90°C cell temperature with 70°C anode and cathode dew points, operating under H_2/air with a 7 psig anode overpressure. The results clearly indicate that OCV setting results in a significant (16x) reduction in MEA lifetime and that load cycling without OCV setting is better than a constant load setting. Interestingly, the MEAs with the longest lifetime also have the lowest fluoride ion release. With additional analysis of other MEAs for the lifetime-fluoride ion release relationship, a correlation between lifetime and fluoride ion release was developed (Figure 4). The relationship is valid for both initial and average fluoride release indicating that the decay mechanism is constant over the lifetime of the test.

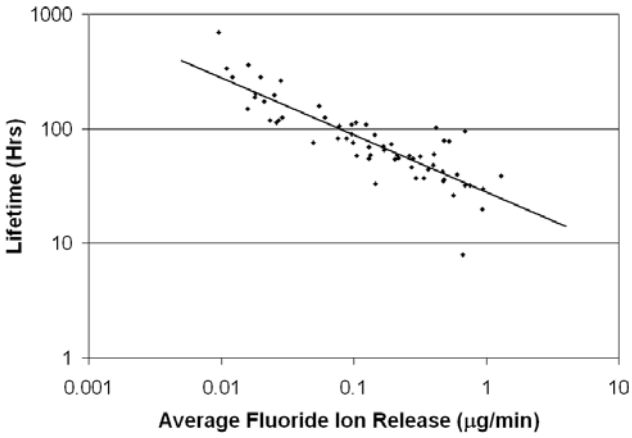

Figure 4. Relationship Between MEA Lifetime and Fluoride Ion Release in Accelerated Tests (A portion of the data are from DOE Cooperative Agreement No. DE-FC36-02AL67621.)

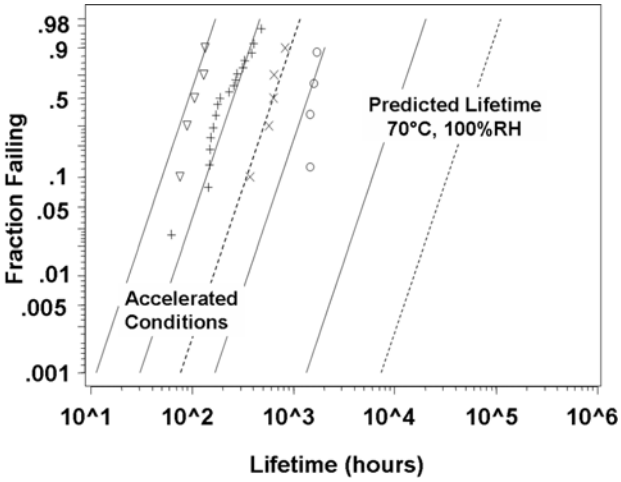

Figure 5. Example of Statistical Analysis of Accelerated Test Data with MEA Lifetime Prediction (Symbols - data points; lines - model fits; solid lines - load profile A; dashed lines - load profile B.)

In addition to improving the durability of the MEA and its components, efforts are also underway to optimize system operating conditions to minimize performance decay. Two such variables under evaluation are CO and air bleed level. Air bleed is routinely applied to the anode in order to alleviate the anode overpotential loss due to CO poisoning. However, air bleed also contributes to membrane and ionomer degradation because it aids in the generation of hydrogen peroxide. Extensive single cell testing (>2,000 hours) has clearly shown that both performance and fluoride release increase with air bleed levels. Since MEA lifetime is inversely proportional to fluoride release, it is important to select CO and air bleed levels based upon both fuel cell performance and durability metrics. As a continuing effort to understand system parameters, a 1,000-hour module test was completed with an intermediate MEA design consisting of new MEA components.

Statistical methods for accelerated test planning and analysis have been utilized extensively as a means to predict MEA lifetime under 'normal' (70°C cell and 100% relative humidity) conditions from 'accelerated' test conditions. This approach is needed because there is not enough time under this contract to determine if an MEA meets DOE's 2010 40,000-hour lifetime requirement for stationary fuel cell systems. An example of the statistical analysis and MEA lifetime prediction is shown in Figure 5. The lifetime data are for MEAs made entirely from base materials, that is, no improved components are used in the fabrication of these MEAs. One percent of the MEAs (1 MEA in a stack of 100 cells) are expected to fail at 3,000 to 18,000 hours depending on the load profile. In order to determine the accuracy of these predictions, MEAs are currently under test at the 'normal' test conditions; as the samples fail, they will be used to validate the predictions and/or refine the analysis. To date, these MEAs have accumulated over 9,000 hours of test data at the 'normal' conditions.

New MEA designs, incorporating more durable MEA component technologies, have been fabricated and tested under accelerated test conditions. The results are summarized in Figure 6. The accelerated test conditions are 90°C cell temperature with 60°C anode and cathode dew points, operating under H_2/air with a 7 psig anode overpressure and load profile A (Figure 2). For comparison, an MEA made with Nafion® 112 membrane is included. MEA design B shows a significant lifetime improvement over the MEA made with Nafion® 112.

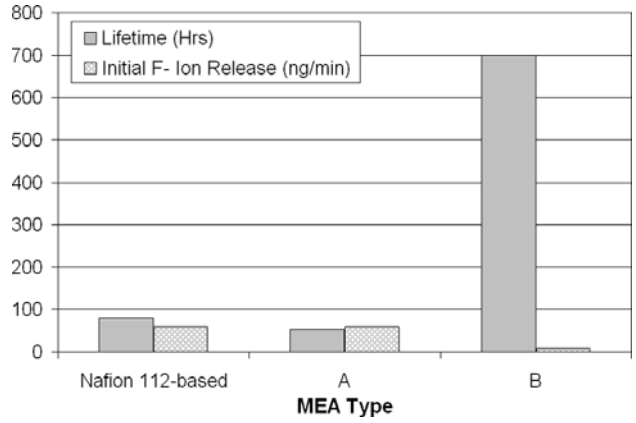

Figure 6. Accelerated Test Data of New MEAs

Conclusions

New, more durable MEAs have been developed and tested under accelerated conditions during this project that show a significant improvement in MEA lifetime over baseline MEAs. Utilizing statistical lifetime methodology, these MEAs are predicted to last longer than the required DOE 2005 targets. Incorporating these MEAs into systems with 'benign' operating conditions (avoiding conditions that are known to shorten MEA lifetime such as OCV setting and high air bleed) should bring the 40,000-hour lifetime goal closer to reality.

Nafion® is a registered trademark of DuPont.

FY 2005 Publications/Presentations

1. C. Zhou, T. Zawodzinski, Jr., D. Schiraldi, "Chemical Changes in Nafion® Membranes Under Simulated Fuel Cell Conditions," 228th ACS Meeting, Philadelphia, PA, August 2004.
2. M.T. Hicks, "Accelerated Testing – Application to Fuel Cells," 2004 Fuel Cell Testing Workshop, Vancouver BC, Canada, September 2004.
3. Agarwal, U. Landau and T. Zawodzinski, Jr., "Hydrogen Peroxide Formation During Oxygen Reduction On High Surface Area Pt/C Catalysts," 206th ECS Meeting, Honolulu, HI, October 2004. (Presentation and Paper)
4. C. Zhou, T. Zawodzinski, Jr., D. Schiraldi, "Chemical Changes in Nafion® Membranes Under Simulated Fuel Cell Conditions," 206th ECS Meeting, Honolulu, HI, October 2004.
5. M. Pelsozy, J. Wainright and T. Zawodzinski Jr., "Peroxide Production and Detection in Polymer Films," 206th ECS Meeting, Honolulu, HI, October 2004. (Presentation and Paper)
6. J. Frisk, W. Boand, M. Hicks, M. Kurkowski, A. Schmoeckel, and R. Atanasoski, "How 3M Developed a New GDL Construction for Improved Oxidative Stability," 2004 Fuel Cell Seminar, San Antonio, TX, November 2004.
7. D. Schiraldi, "Chemical Durability Studies of Model Compounds and Nafion® under Mimic Fuel Cell Conditions," Advances in Materials for Proton Exchange Membrane Fuel Cells, Pacific Grove, CA, February 2005.
8. S. Hamrock, "New Membranes for PEM Fuel Cells," Advances in Materials for Proton Exchange Membrane Fuel Cells, Pacific Grove, CA, February 2005
9. C. Zhou, T. Zawodzinski, Jr., D. Schiraldi, "Chemical Durability Studies of Model Compounds and Nafion® under Mimic Fuel Cell Conditions," 229th ACS Meeting, San Diego, CA, March 2005.
10. D. Schiraldi and C. Zhou, "Model Compound Studies of Fuel Cell Degradation," High Temperature Membrane Working Group, 2005 Hydrogen Fuel Cells Infrastructure and Technology Review, Washington, D.C., May 2005.
11. M. Yandrasits, "Mechanical Property Measurements of PFSA Membranes at Elevated Temperatures and Humidities," 2nd International Conference on Polymer Batteries and Fuel Cells, Las Vegas, NV, June 2005.