V.B.6 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: Reg 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

Contract Number: DE-FC36-03GO13098

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

Start Date: September 1, 2003
Projected End Date: June 30, 2007

Objectives

- Develop an understanding of membrane electrode assembly (MEA) failure mechanisms encountered under real world operating conditions and implement technologies to mitigate failure mechanisms.
- Develop an MEA with enhanced durability without negatively affecting fuel cell 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 (3.4.4.2) of the 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	2010 Target	Status
Durability	Hours	40,000	>12,000[a] >25,000[b]

[a] Demonstrated MEA lifetime to date
[b] Predicted MEA lifetime at 1% failure rate

Accomplishments

- Developed new test equipment to measure capillary pressure in gas diffusion layers (GDLs) as a means to characterize water transport in GDL pores.
- Completed investigation of reinforced membranes – determined reinforcement may not be necessary for membrane mechanical durability.
- Identified infant mortality membrane failure mode (failure at the membrane – catalyst interface) in MEA module testing and developed and implemented membrane edge protection solution to eliminate it.
- Utilized ionomer model compounds to identify likely 'points of attack' and provide insight into ionomer degradation mechanism. Concluded that membrane degradation is more than just carboxylic acid end group unzipping.
- Completed 121-channel segmented cell and investigated the effects of flow rate, load setting and GDL type. Determined high gas stoichiometry yields current uniformity.
- Utilized theoretical 3D fuel cell model to investigate effects of catalyst, membrane and GDL non-uniformity. Determined that electrode defects result in highly nonuniform current distribution and that a linear catalyst loading results in a nearly uniform current distribution.
- Initiated test in a field-ready system with a preliminary, durable MEA design. Verified there were no negative MEA–system interactions; test ongoing.
- Developed initial lifetime prediction model as a function of load cycle to estimate MEA lifetime relative to DOE's 2010 stationary system goals of 40,000 hours. At a 1% failure rate, baseline MEAs are predicted to last > 25,000 hours at 70°C and 100% relative humidity (RH) when operating under the modified load cycle profile. Demonstrated that load profile affects MEA durability. Load cycle without a near-open circuit voltage (OCV) setting

results in 13X lifetime improvement in comparison to load cycle with a near-OCV setting.

- Demonstrated statistically that the 3M PEM-based MEAs offer a 4X lifetime improvement over the baseline MEAs in accelerated durability tests with the near-OCV load profile.
- Developed correlations relating initial fluoride ion to lifetime under different operating conditions. Based upon this metric, the 3M PEM MEAs under the near-OCV load cycle at 70°C and 100% RH are estimated to last between 20,000 to 30,000 hours.

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, one of the most significant challenges to be met 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 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.

The project team consists of 3M, Plug Power, Case Western Reserve University, and the University of Miami. 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 University of Miami is primarily responsible for investigating MEA non-uniformities via modeling.

Results

Recognizing that present GDL characterization methods lack the ability to measure water transport because the measurement is routinely done in dry gas, a new instrument was designed to characterize capillary pressure in hydrophobic porous media. With this new instrument, changes in GDL water transport properties will be measured as a function of operating conditions and time as a means to determine failure mechanisms and develop strategies to mitigate them.

A primary MEA failure mode is membrane breach, which can occur as a result of mechanical stress, chemical stress or a combination of both. An internally developed model of mechanical stresses in an MEA indicated that the membrane is under high levels of stress under the lands in a flow field, which led to the hypothesis that if a reinforcing member is added to a membrane to carry the stress, the membrane mechanical failure rate should be reduced. In order to evaluate the hypothesis, 3M made several novel reinforced membranes from a variety of materials. The materials were tested for mechanical durability in an RH cycle test. The RH cycle test varies the RH from 0 to 150% while maintaining the cell temperature at 80°C. Only N_2 gas is supplied to the cell, thus eliminating any chemical degradation processes associated with H_2 and O_2. The membrane has failed when the gas crossover is greater than 10 sccm. Under the RH cycle test, neat membranes lasted longer than reinforced membranes. These observations are in agreement with Gittleman et al. [1] who concluded that there is no relationship between membrane mechanical properties and fuel cell durability.

Another means to strengthen a membrane mechanically is to add a barrier layer to the area outside of the MEA active area, i.e., the outer perimeter of the membrane, which can prevent tears in the membrane perimeter or at the membrane-catalyst interface. (A barrier layer cannot be added to the active area because the barrier layer blocks both proton and gas transport.) This approach was utilized to eliminate an MEA infant mortality, failure of the catalyst-membrane interface, in modules under this project.

Small model compounds continue to be utilized to determine possible ionomer degradation pathways. A list of the model compounds evaluated is provided in Table 2. The model compounds are degraded via

Fenton's test (70°C, 100 mM model compound, 400 mM Fe^{2+} and 400 mM H_2O_2) or ultraviolet light (200-2400 nm @ 100 W). The metric for degradation is fluoride ion release, although all solutions are analyzed by ^{19}F nuclear magnetic resonance (NMR) to track changes in the model compound and determine degradation products. From the experiments, it is clear that COOH groups are easily degraded. However, there is also evidence of model compound hydrolysis. Isomers of Model Compound #3 have been evaluated. All Model Compound #3 isomers degrade at the same rate indicating that decarboxylation is the rate determining step. Model Compounds #1 and #2 degrade to the same final degradation products, indicating that they have similar reaction pathways.

TABLE 2. List of Model Compounds Evaluated

MC ID	Chemical Structure
1	$CO_2HCF(CF_3)OC_3F_7$
2	$CO_2HCF(CF_3)OC_4F_8SO_3H$
3	$CO_2HC_3F_6SO_3H$
4	$C_7F_{15}CO_2H$
7	$C_2F_5OC_3F_6SO_3H$
8	$C_2F_5OC_2F_3(CF_3)OC_2F_4SO_3H$

As a means to measure non-uniform current distribution and its effect on durability, a 121-channel segmented cell was constructed based upon printed circuit board technology. The cell contains a matrix of 11 columns by 11 rows in which the rows follow the quad serpentine flow field pattern. The approximate area of each segment is 0.41 cm^2 and only the cathode is segmented. A more uniform current distribution can be obtained by reducing the total current or by decreasing the air utilization (increasing the air flow) at a given current (Figure 1). The GDL backing also has an effect on the current distribution, although this effect appears to be secondary since it is dominated by air utilization.

3D modeling was also used to investigate current distribution as a function of operating conditions and MEA construction – specifically MEA constructions that are not easily manufactured such as variable catalyst loading, electrode thickness, GDL thickness, membrane thickness, and membrane conductivity. With a variable electrode loading following the flow channel, current uniformity is improved in comparison to a uniform catalyst loading. An opposite effect is observed for catalyst thickness. Surface defects in the catalyst thickness result in highly non-uniform current distributions.

By developing new durable components and MEAs separately from the system, there is the possibility that the selected 'best' MEA will not operate properly in the selected 'best' system. This possibility was recognized by the team and, in order to mitigate it, an intermediate durable MEA design was selected for system testing to evaluate possible negative MEA–system interactions. The first 500 hours of this test are shown in Figure 2. Analysis of the data indicates no negative MEA–system interactions which, in turn, validates the project's approach.

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% RH) 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 updated statistical analysis and MEA lifetime prediction are shown in Figure 3, and the load profiles used in the accelerated tests are shown in Figure 4. The MEAs used in these tests are made from baseline components. The data clearly indicate that MEA lifetime is dependent on load

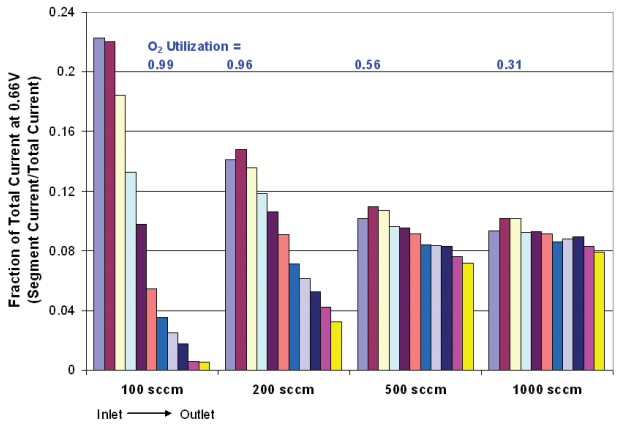

FIGURE 1. Effect of Flow Rate on Current Distribution

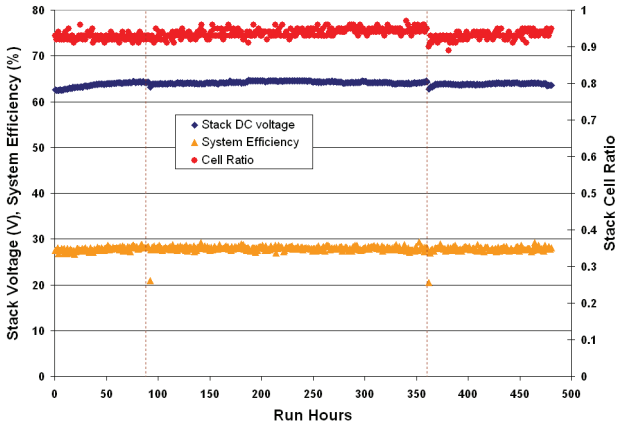

FIGURE 2. MEA system Test – First Durable MEA Testing in Field-Ready System

profile. There is a 13X improvement in MEA lifetime when switching from the near-OCV load cycle profile to the modified load cycle profile. Unlike lifetime averages, which only offer a single metric for lifetime, statistical analysis offers the probability that an MEA will fail at any point in time. As a result, statistics allow the system lifetime at a 1% MEA failure rate to be estimated; an important point because most systems consist of 100 MEAs and, if any one fails, then the system has failed. Using Figure 3, the 1% failure rate for baseline MEAs is approximately 2,000 to 26,000 hours depending on the load profile. Figure 5 statistically compares accelerated test results from baseline MEAs to new 3M PEM-based MEAs operating under the near-OCV load profile. Under these test conditions, the 3M PEM MEAs last 4X longer than the baseline MEAs.

Figure 6 illustrates the importance of monitoring fuel cell fluoride ion emissions as a means to predict lifetime. It was found that initial fluoride ion release strongly correlates with accelerated lifetime resulting in R^2 values ranging from 0.77 to 0.89 depending on operating conditions. The practical significance of the data is two-fold: (1) the data indicate that MEA lifetime can be estimated during the initial start-up, and (2) MEAs do not have to be tested to failure in order to estimate lifetime, i.e., sample throughput can be dramatically increased. Additionally, Figure 6 contains initial fluoride ion data for 3M PEM MEAs. Using fluoride ion release as the prediction method, the 3M PEM MEAs are predicted to last between 20,000 to 30,000 hours under the harsh, near-OCV load profile.

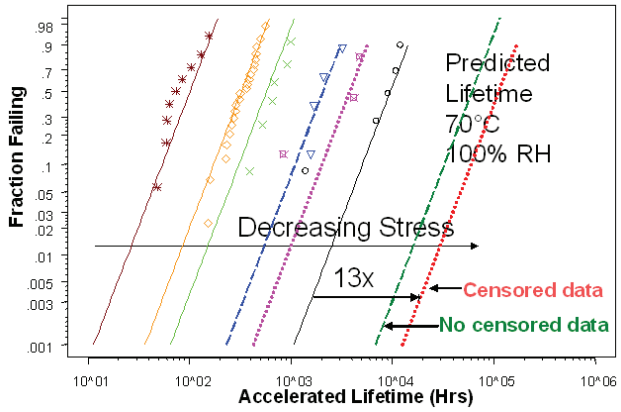

FIGURE 3. Statistical Lifetime Predictions From Accelerated Test Data (Symbols – data points; lines – model fits; censored data – test is ongoing; no censored data – no experimental data, prediction only.) Data and predictions for baseline components MEAs.

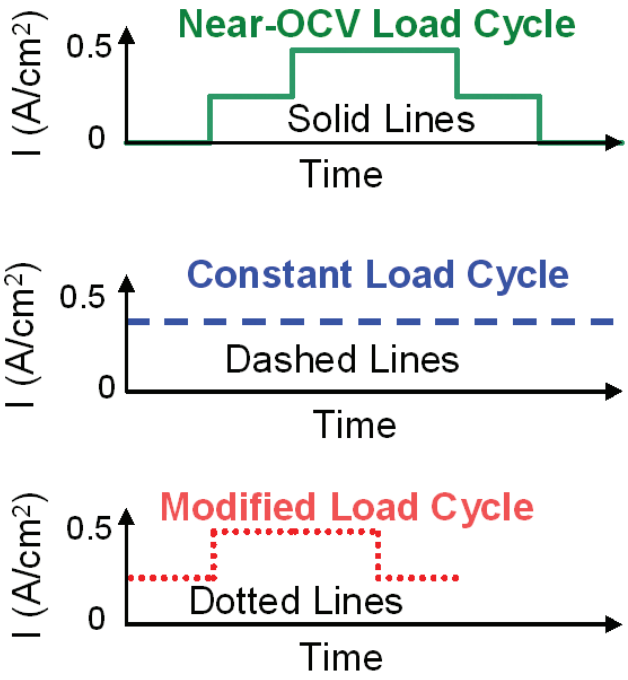

FIGURE 4. Load Profiles used in Accelerated Tests

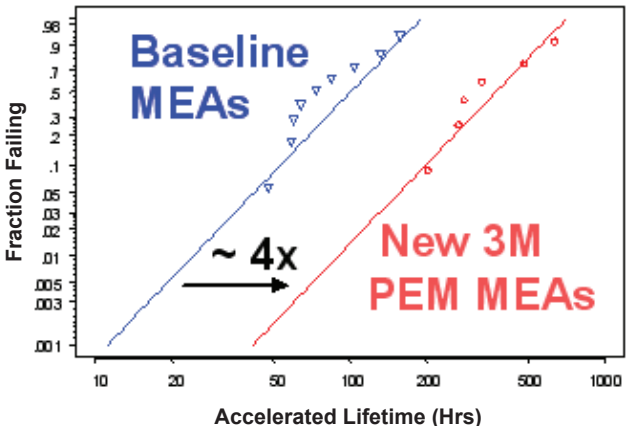

FIGURE 5. Statistical Comparison of MEA Designs in Accelerated Testing

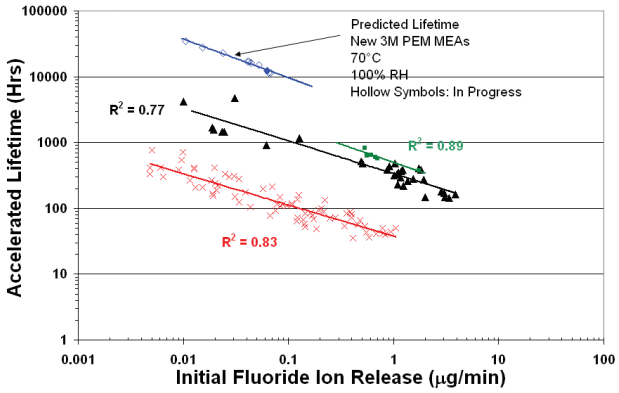

FIGURE 6. Fluoride Ion Mapping of Accelerated Test Data

Conclusions and Future Directions

- Developed new MEAs and utilized statistical lifetime analysis and accelerated test methodology to demonstrate projected MEA lifetime of >25,000 hours.
- Continue to utilize model compound studies to understand membrane decay mechanisms.
- Investigate the effects of operating conditions on durability via segmented cell, 3D modeling and module testing in field ready systems.
- Continue to refine lifetime prediction model and incorporate fluoride ion release into the model.
- Need to select 'final' MEA and system design and conduct 2,000 hour demonstration test.

FY 2006 Publications/Presentations

1. D. Stevens, M. Hicks, G. Haugen, J. Dahn, "Ex situ and in situ stability studies of PEMFC catalysts: Effect of carbon type and humidification on degradation of the carbon," *J. Electrochem. Soc*., 152 (12), A2309 (2005).

2. D. Schiraldi and C. Zhou, "Chemical durability studies of PFSA polymers and model compounds under mimic fuel cell membrane conditions," 230th ACS Meeting, Washington, D.C., August 2005.

3. M. Hicks, D. Pierpont, P. Turner, T. Watschke, M. Yandrasits, "Component Accelerated Testing and MEA Lifetime Modeling," 2005 Fuel Cell Testing Workshop, Vancouver, BC, September 2005.

4. J. Dahn, D. Stevens, A. Bonakdarpour, E. Easton, M. Hicks, G. Haugen, R. Atanasoski, M. Debe, "Development of Durable and High-Performance Electrocatalysts and Electrocatalyst Support Material," 208th Meeting of The Electrochemical Society, Los Angeles, CA, October 2005.

5. D. Pierpont, M. Hicks, P. Turner, T. Watschke, "Accelerated Testing and Lifetime Modeling for the Development of Durable Fuel Cell MEAs," 208th Meeting of The Electrochemical Society, Los Angeles, CA, October 2005; *ECS Transactions*, Vol 1, 2006.

6. M. Hicks, K. Kropp, A. Schmoeckel, R. Atanasoski, "Current Distribution Along a Quad-Serpentine Flow Field: GDL Evaluation," 208th Meeting of The Electrochemical Society, Los Angeles, CA, October 2005; *ECS Transactions*, Vol 1, 2006.

7. G. Haugen, D. Stevens, M. Hicks, J. Dahn, "Ex-situ and In-situ Stability Studies of PEM Fuel Cell Catalysts: the effect of carbon type and humidification on the degradation of carbon supported catalysts," 2005 Fuel Cell Seminar, Palm Springs, CA, November 2005.

8. D. Pierpont, M. Hicks, P. Turner, T. Watschke, "New Accelerated Testing and Lifetime Modeling Methods Promise Development of more Durable MEAs," 2005 Fuel Cell Seminar, Palm Springs, CA, November 2005.

9. M. Hicks, R. Atanasoski, "3M MEA Durability under Accelerated Testing," 2005 Fuel Cell Durability, Washington, D.C., December 2005.

10. Z. Qi, Q. Guo, B. Du, H. Tang, M. Ramani, C. Smith, Z. Zhou, E. Jerabek, B. Pomeroy, J. Elter, "Fuel Cell Durability for Stationary Applications - From Single Cells to Systems," 2005 Fuel Cell Durability, Washington, D.C., December 2005.

References

1. Gittleman et al., Fall AIChE Meeting, October 2005.