IV.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

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

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

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 (>2000 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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- E. Distributed Generation Systems Durability
- O. Stack Material and Manufacturing Cost
- P. Component Durability

Approach

- Develop MEAs utilizing 3M proprietary perfluorinated sulfonic acid ionomer, which has demonstrated improved oxidative stability over baseline ionomers.
- Develop and validate individual component aging tests and characterization methods.
- Correlate single-cell test data and characterization data on virgin and aged components and MEAs, 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.

Accomplishments

- Improved oxidative stability of the gas diffusion layer (GDL). Increased GDL lifetime by >7x as measured in accelerated aging tests.

- Improved oxidative stability of membrane. Reduced fluoride ion emission in new end-group-modified ionomer by 4x over control.
- Developed accelerated test to measure catalyst stability.
- Implemented rotating ring disk electrode (RRDE) test based upon the work of Paulus et al.[1] to measure hydrogen peroxide generation on dispersed catalysts. (Peroxide is a known contributor to MEA decay.)
- Implemented reproducible techniques to characterize physical properties on virgin and aged GDLs and membranes.
- Completed studies on MEA sensitivity to cathode inlet gas pressure and anode and cathode gas inlet stoichiometry.
- Completed extended single-cell testing studying the effects of relative humidity (>1000 hrs), cell temperature (>1000 hrs), and current density (>2000 hrs) on MEA performance decay and fluoride ion release.

Future Directions

- Complete MEA component development and integration.
- Determine decay mechanisms and kinetic parameters from tested samples.
- Develop accelerated lifetime predictor tests and link to MEA lifetime.
- Initiate 3D modeling (University of Miami subcontract) and segmented cell work to probe MEA structures.
- Develop and implement strategies to mitigate decay mechanisms.
- 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. Applications for portable power, back-up power, motive power, and stationary power generation are being developed around the world. Estimates for the size of the fuel cell industry range as high as $50 billion by 2010. For this to be realized, however, considerable technical challenges still remain. The most significant of these challenges are those of cost and stationary system lifetime, where 40,000 hours of operation with less than 10% decay is desired.

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 will be used to predict MEA lifetime. All MEA development is based upon a new 3M proprietary perfluorinated sulfonic acid ionomer.

Results

Improvements to membrane oxidative stability that were achieved via end-group modification are illustrated in Figure 1. The accelerated test is conducted in 30% H_2O_2 at 70°C in the presence of Fe^{2+}. Fluoride ion release is measured periodically during the experiment to monitor membrane oxidative stability. The 3M end-group-modified membrane shows a significant increase in oxidative

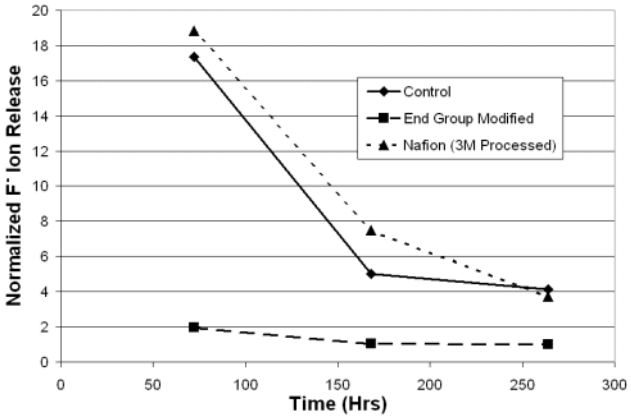

Figure 1. 3M Membrane End Group Oxidative Stability Comparison (Aging test conditions: 70°C, 30% H_2O_2, Fe^{2+}.)

stability over the non-modified control. For reference, a membrane made by 3M from Nafion® ionomer is also shown.

GDL improvements are shown in Figure 2. In this test, GDLs are aged in 15% H_2O_2 at 82°C. After aging, an MEA is made with virgin GDL on the anode and an aged GDL on the cathode and then tested for initial performance to determine the effect of GDL aging on performance. Data for two different GDLs are presented; GDL 1 shows a significant loss in performance after 260 hours (Figure 2a), while GDL 4 shows little loss after 2000 hours. The loss of performance for GDL 1 is due to oxidation of the GDL, resulting in a more hydrophilic surface which causes MEA flooding. In comparison, GDL 4 does not oxidize, and its contact angle is constant during the aging test. GDLs have also been aged electrochemically by cycling the voltage from 0.3 V to 0.9 V vs. standard hydrogen electrode, which are voltages encountered during fuel cell operation. Electrochemical aging yields similar results to the peroxide aging experiments although the mechanism may be different. As in the peroxide aging experiment, GDL 4 is the most stable GDL under the electrochemical aging test.

Hydrogen peroxide is widely recognized as a root cause for MEA failure, as illustrated by its role in the membrane and GDL accelerated tests described previously. In order to understand hydrogen peroxide generation, an RRDE experiment was implemented to monitor peroxide generation of

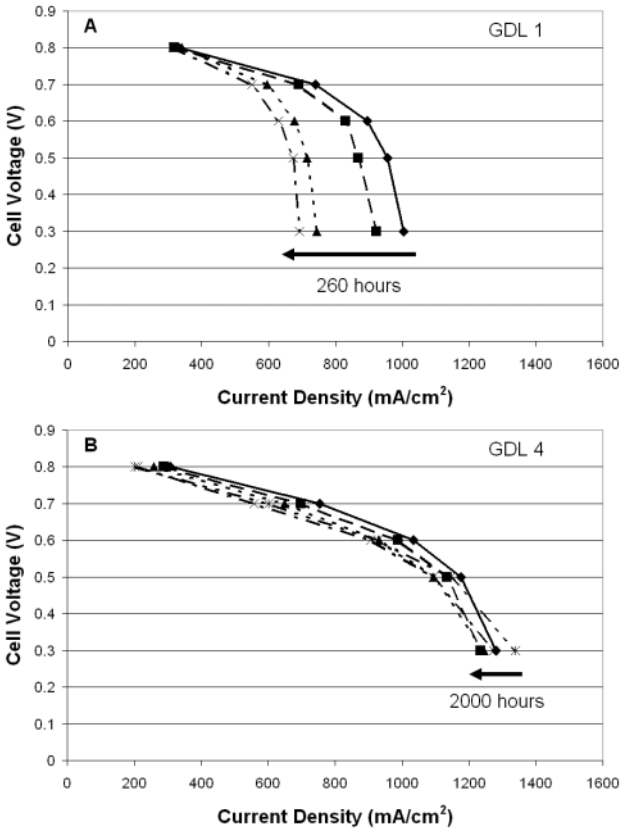

Figure 2. GDL Chemical Oxidative Stability (Aging test conditions: 82°C, 15% H_2O_2. Performance test conditions: 70°C cell at 100% RH, 800 sccm H_2 and 1800 sccm air.) Figure 2A – GDL 1; Figure 2B – GDL 4

several dispersed Pt/C catalysts from different vendors. Initial screening of catalysts yielded different peroxide generation rates for the different catalysts, and a more detailed design is underway to determine peroxide kinetics and mechanisms.

In order to screen catalysts for stability, an accelerated MEA test was developed for rapid screening. The test holds the cathode at 1.2 V relative to the anode with nitrogen flowing to the cathode and hydrogen to the anode. Periodically, the MEA catalyst samples are measured for surface area (via cyclic voltammetry) and performance under H_2/air. Results for one of the worst catalysts, A, and one of the better catalysts, J, are shown in Figure 3. Catalyst A loses ~80% of its surface area and >90% of its performance during the 50-hour test, while catalyst J is relatively unchanged during the test.

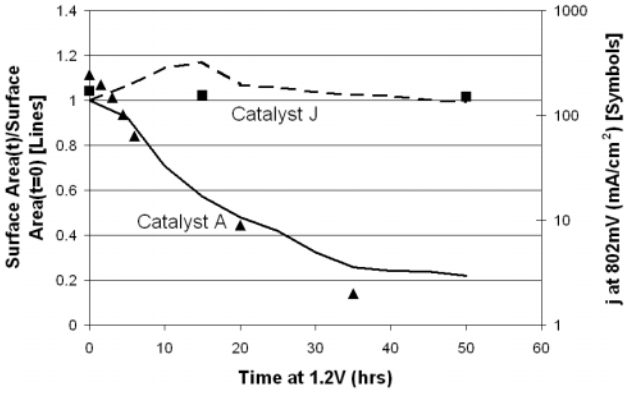

Figure 3. Cathode Catalyst Stability (Aging test conditions: 80°C at 100% RH, cathode 1.2 V relative to anode, N_2 on cathode, H_2 on anode. Performance test conditions: 70°C cell at 100% RH, 800 sccm H_2 and 1800 sccm air.)

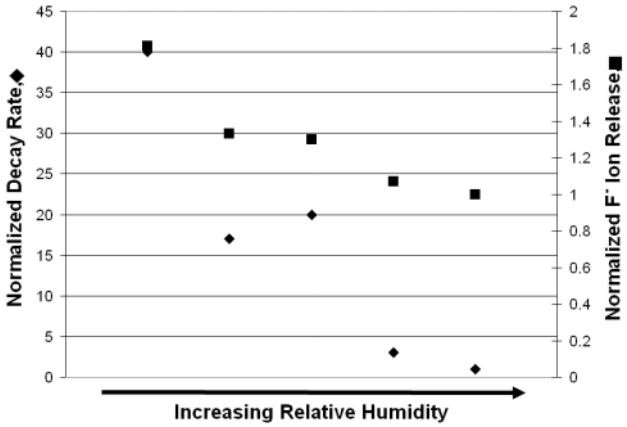

Figure 4. Relative Humidity MEA Latitude Testing for >1000 Hours

A significant amount of testing has been completed to determine the optimal system operating conditions in order to minimize performance decay. Experiments have investigated the effect of relative humidity (RH) (Figure 4), current density (Figure 5) and cell temperature on decay rate and fluoride ion release rate. Both decay and fluoride ion release rates decrease with increasing RH. Fluoride ion release rate decreases, then levels off with increasing current density, while the decay rate exhibits a maximum value. Cell temperature does not significantly affect either the decay or fluoride ion release rate. Diagnostic studies have also been completed investigating the effect of cathode inlet pressure and anode and cathode inlet stoichiometry on MEA performance and durability. From the

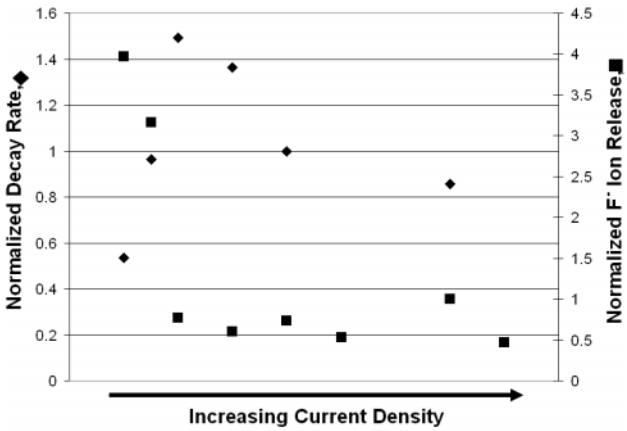

Figure 5. Current Density MEA Latitude Testing for >2000 Hours

cathode pressure studies, it was determined that performance is limited by oxygen reduction reaction kinetics and mass transport in the catalyst layer. The stoichiometry studies defined a minimum cathode stoichiometry that was dependent on current density and a minimum anode stoichiometry that was independent of current density in order to obtain good performance. In addition, a 1000-hour endurance test is ongoing to determine the effect of stoichiometry on MEA decay rate.

Conclusions

In conjunction with accelerated MEA component testing, new, more durable MEA components have been developed. The new components in combination with a better understanding of the effect of operating conditions on durability should bring stationary fuel cell systems closer to the 40,000-hour lifetime goal.

"Nafion" is a registered trademark of DuPont.

References

1. U.A. Paulus et al, *J. Electrochemical Society*, 495 (2001) 134-145.

FY 2004 Publications/Presentations

1. M. T. Hicks, “MEA and Stack Durability for PEM Fuel Cells”, 2004 Hydrogen, Fuel Cells and Infrastructure Technologies Program Review, Philadelphia, PA (2004).