V.M.6 MEA and Stack Durability for PEM Fuel Cells

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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 and implement technologies to mitigate failure.
- 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 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	2011 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

- Used ionomer model compounds to identify likely 'points of attack' on perfluorosulfonic acid membranes (PFSA) and confirmed degradation pathways.
- Developed initial hydrogen peroxide model to study peroxide in operating fuel cells. Peroxide diffusion coefficients and decomposition rates were estimated.
- Demonstrated new test equipment to measure capillary pressure in gas diffusion layers (GDLs).
- Used 121-channel segmented cell to complete a series of durability experiments. Data from this study agreed with modeling predictions.
- Segmented cell fabricated to run in full stack.
- Developed film edge protection technology to minimize or prevent edge failures.
- Ongoing monitoring of membrane properties in accelerated tests.
- Developed initial lifetime prediction model to estimate MEA lifetime relative to DOE's 2011 stationary system goals.
- Predictive equation developed based on the relative humidity (RH) of inlet gases and initial fluoride release rates.
- Ongoing Saratoga system test with a preliminary durable MEA design. Stack has exceeded 7,700 hours and continues to run.
- Initiated 'Final' MEA and system test. Stack has exceeded the 2,000 hour demonstration requirement and continues to run.

Introduction

Proton exchange membrane fuel cells are expected 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 necessary. 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 manufacturing 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 used 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 4-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 the University of Miami is primarily responsible for investigating MEA non-uniformities via modeling.

Results

Model compound studies have been conducted throughout the course of this project as a means of identifying the likely pathways for the chemical degradation of the PFSA membranes. Table 2 lists the compounds that have been evaluated.

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	$C_2F_5OC_4F_6SO_3H$
8	$C_2F_5OC_2F_3(CF_3)OC_2F_4SO_3H$

It has been well established from previous work that the compounds that contain carboxylic acid groups (MC-1,2,3&4) degrade rapidly in the presence of peroxide. Model compounds 7 and 8 represent a model of the polymer side chains of the 3M ionomer and Nafion™ and do not contain the carboxylic acid groups. Liquid chromatography-mass spectroscopy (LC-MS) techniques were used to analyze the reaction products of these compounds after exposure to hydrogen peroxide solutions. It was determined that the reaction rate compared to the carboxylic acid compounds was significantly slower, however, the compounds did exhibit decomposition and preliminary decomposition products have been identified in both cases.

A series of full and half MEAs were made in order to measure the transport and reaction process for hydrogen peroxide. Assuming no decomposition reaction, a diffusivity (D) of 5.34e-7 cm^2/s was measured. In addition, the decomposition rate of peroxide in the catalyst layer was also measured. A value of 1.431e-10 mol/cm^3s was obtained in this case.

An instrument that was designed to characterize capillary pressure in hydrophobic porous media was used to measure transport properties in GDLs, microporous layers (MPLs) and catalyst layers. This information can be used to design GDLs that provide appropriate water management characteristics for a given catalyst layer.

The 121 channel segmented single cell was used in several durability tests. Both a constant current experiment and a constant voltage experiment were run. In the case of the constant current, post mortem analysis showed that the location where a pin hole forms might be related to localized low voltage. No clear relationship between localized current and hole location was observed for the case where a cell was run at constant voltage.

A segmented cell with 52 channels was designed to be used in a full-scale Plug Power GenSys stack. A schematic of this cell is depicted in Figure 1. The fabrication of this cell is nearing completion. This cell will allow cell uniformity to be measured for the first time in an operating stack. The cell can also be moved to various locations within the stack to give information

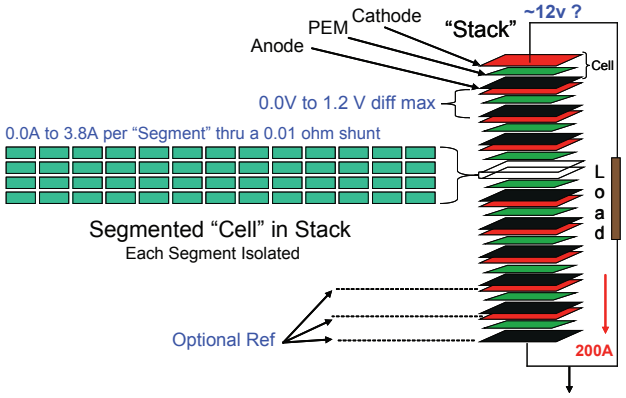

FIGURE 1. Segmented Cell Design for Full-Sized Stack

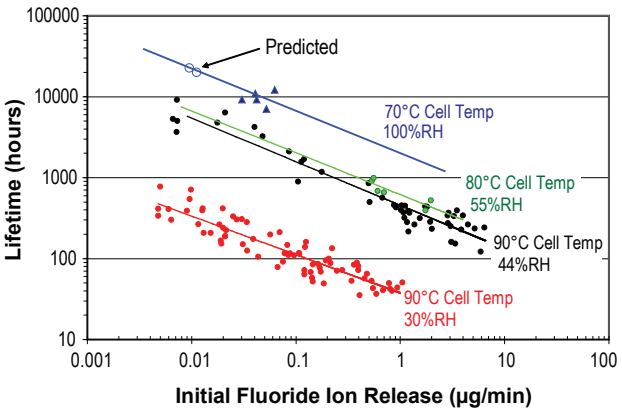

FIGURE 2. Accelerated Lifetime vs. Initial Fluoride Release Rate

about the cell operation relative to the cell location (for example the middle of the stack vs. near the end plates).

Edge protection has been identified as a need for MEAs expected to last a significant amount of time. Previous efforts to protect the edge were focused on a method of coating a protective layer directly to the membrane prior to assembly of the MEA. Recently, a protective film has been developed using a proprietary pressure sensitive adhesive. MEAs fabricated with this film have been started in single cell and short stack durability testing.

An extensive statistical model has been developed in order to predict the likely durability of an MEA design. This effort is necessary in order to design an MEA that could meet the DOE targets of 40,000 hours of continuous operation (4½ years). Over 300 single cell durability tests have been run throughout the course of this project under several conditions designed to accelerate failure. The harshest conditions were low humidity with a load cycle that included some time at open circuit voltage (OCV). Figure 2 shows the correlation between initial fluoride release rate and lifetime for several conditions. The fluoride release from this graph was combined with a factor accounting for the different relative humidities and the following predictive equation was developed.

$$Lifetime = \frac{A}{T+273} + H * Ln\left(\frac{RH}{100-RH}\right) + F * Ln(FRR) + I$$

Where:

- A = Arrhenius Constant
- H = Humidity Constant
- RH = Relative Humidity
- F = Fluoride Release Constant
- FRR = Fluoride Release Rate
- I = Intercept

Note: Load Cycle differences not included yet

This equation provides accurate predictions of lifetime for the operating conditions covered by the dataset used to develop the model. However, the model does not provide accurate predictions of lifetimes for conditions outside of those covered by the dataset. An illustration of this point is shown in Table 3. The conditions in Table 3 are the cell temperature (CT), anode dew point (AD) and cathode dew point (CD), CT/AD/CD. The first three sets of conditions (90/60/60, 90/70/70, and 70/70/70) were the conditions for the experiments used to derive the model. For these conditions the agreement between the predicted and actual lifetimes is very good. However, for the 90/90/90 condition, which is not covered by the dataset used to develop the model, the predicted lifetime is clearly incorrect.

TABLE 3. Predicted vs. Actual Lifetimes

Conditions (CT/AD/CD)	Fluoride Release µg/min	Equation Prediction Lifetime (hrs)	95% Lower Confidence Interval (hrs)	95% Upper Confidence Interval (hrs)	Actual Lifetime (hrs)
90/60/60	0.457	63	56	70	56
90/70/70	1.11	329	291	372	347
70/70/70	0.042	9,272	11,314	13,817	10,984
90/90/90	0.5	5,633,891	1,079,697	29,410,394	Not Run

Operation of the stack based on an intermediate MEA design has continued without incident with the stack accumulating over 7,720 hours of operation (Figure 3). The MEAs used in this design had the stabilized 3M ionomer membrane that included developments made during this project. The rate of voltage performance loss of this stack is still approximately 7-8 microVolt/cell/hour. The stack is still extremely stable and appears to be the strongest stack at its life used in the fleet based on its performance at this stage of runtime. Little or no maintenance has been

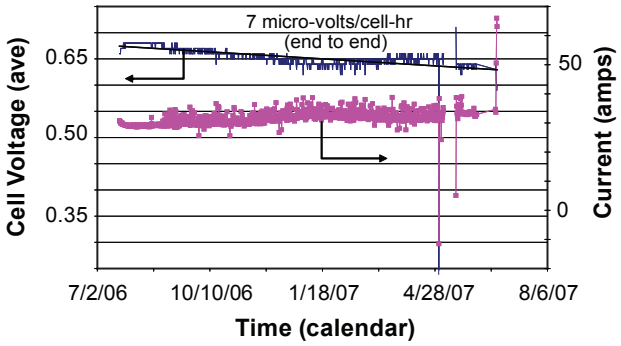

FIGURE 3. Stack Durability Results for Intermediate MEA and System Test

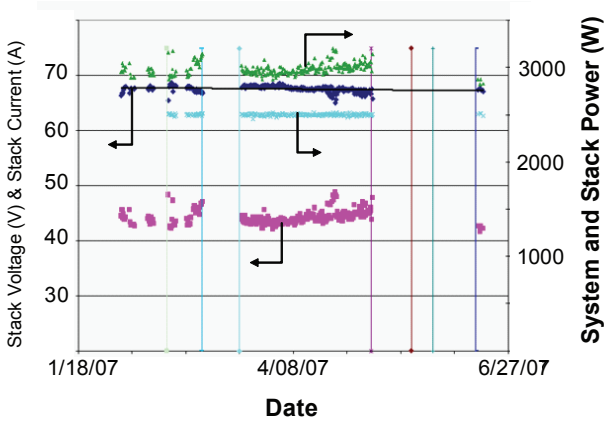

FIGURE 4. Stack Durability Results for Final MEA and System Test

required for this system post installation of the stack and the stack is still performing at a minimum cell ratio (lowest to average cell voltage ratio) of 0.978 at 7,720 hrs. Currently, maintenance data is being recorded on this system to get additional information.

The final MEA design has been chosen based on membrane, catalyst, and GDL developments over the course of this project. The MEAs and system have been assembled and are currently operating in the Plug fleet. This system has accumulated 2,080 hours at a steady power of 2.5 kW and exceeded the 2,000 hour demonstration requirement for this project. The stack degradation is extremely low at 3.5 microvolts/cell-hr (end to end method) and is meeting its efficiency requirements. Figure 4 shows the durability plot for this stack. It is expected that the stack will continue to run past the end of this project.

Conclusions and Future Directions

- Model compound studies have shown two degradation pathways for PFSA-based membranes; carboxylic acid end groups and ether containing side chains.
- A method of detecting hydrogen peroxide transport and decomposition rates was developed and used to assign diffusion and rate constants for these processes.
- Experiments using a 121 channel segmented cell validated results predicted from theorectical 3D modeling.
- A full-scale segmented cell has been fabricated for use in an operating Plug Power stack. Data will be generated from this stack in the next few months.
- The statistical model developed has been used to successfully predict lifetimes based on fluoride ion release rates and relative humidity.
- A Plug Power stack with an intermediate MEA and system design has run for over 7,700 hours.
- The final MEA design has been chosen. The development efforts used to select materials and system operating conditions appear to have been effective. The stack has met the project demonstration target of 2,000 hours.

FY 2007 Publications/Presentations

1. M. Yandrasits and S. Hamrock, "3M Membrane Technology" Fluoropolymers 2006, October 17th 2006, Charleston, SC.

2. R. Subbaraman, T. Zawodzinski, M. Pelsozy, R. Sidik, A. Agarwal, U. Landau, C. Zhou, D. Schiraldi, B. Edwards, "The Origin and Fate of Peroxide in PEM Fuel Cells" 210th Meeting of the Electrochemical Society, October 30-November 1, 2006, Cancun, Mexico.

3. Z. Qi, "Fundamental Issues of PEM Fuel Cell Durability and Performance", Fuel Cells Durability & Performance 2006, December 6-8, 2006, Miami Beach, FL.

4. M. Hicks, "Application of Accelerated Testing and Statistical Lifetime Modeling to MEA Development", Advances in Materials for Proton Exchange Membrane Fuel Cell Systems, February 19, 2007, Asilomar, CA.