VII.B.3 Enabling Commercial PEM Fuel Cells with Breakthrough Lifetime Improvements

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Objectives

- This project will result in lifetime improvements of low-temperature proton exchange membranes (PEMs) by seeking technologies that will prevent membrane failure.
- This will be accomplished by conducting research that elucidates failure mechanisms and lifetime extension technologies that yield membrane electrode assemblies (MEAs) that meet or exceed a lifetime of 40,000 hours operation with <10% degradation in performance under stationary operating conditions. In addition, the MEAs developed will meet or exceed requirements of automotive durability of 5000 hours lifetime with <10% performance degradation.

- We will identify and implement mitigation strategies to address the root causes of membrane failure.
- As the project progresses, the membranes with increased durability developed under this project will be validated through stack testing.

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
- B. Cost

Technical Targets

This project is conducting fundamental studies of durability of perfluorosulfonic acid (PFSA)-based membranes. Insights gained from these studies will be applied toward the design and synthesis of PEMs that will allow the following DOE 2010 targets:

- Durability: 5000 hrs (transportation); 40,000 hrs (stationary).

Approach

- DuPont and United Technologies Corporation (UTC) have worked together for over four years developing mechanisms of fuel cell membrane failure.
- As these mechanisms become understood, various mitigating strategies are identified, developed, and validated through a combination of modeling, *ex situ* peroxide studies, and fuel cell testing (both accelerated and non-accelerated). This project comprises the optimization and integration of each mitigation strategy.
- Advanced characterization techniques to do post-mortem analysis of samples tested under accelerated conditions will be used. Through these studies, we will be able to expand our understanding of the chemical and physical mechanisms of degradation and to evaluate the beneficial effects of various chemical and mechanical modifications of new fuel cell membranes. These understandings are incorporated into physics-based models for predictive capability.
- Stack testing will be used to validate the improved fuel cell components.

Accomplishments

- Significant progress has been made in producing membranes that incorporate both chemical and mechanical stabilization. These membranes are more resistant to chemical attack by peroxy radicals, exhibiting about 5x lower fluoride emission in the ex-situ peroxide (Fenton's) test. These membranes also show longer lifetimes than baseline materials under tests that include relative humidity (RH) cycles.
- Similar polymer fragments were identified in the product water from the open circuit voltage (OCV) durability test and the Fenton's test. This suggests that there is a similar mode of polymer degradation in these two tests. The results are consistent with a step-wise reaction originating from reactive polymer end-groups.
- UTC has developed a multi-scale PEM degradation model that predicts both the microscopic location and consumption of PEM material.
- UTC peroxide mitigation (Version 1) has been successfully integrated with DuPont's reinforced membrane technology. Over 500 hrs have been attained on a UTC short stack with integrated membrane electrode assembly (MEA) technology undergoing cyclic decay conditions.

Future Directions

- Further optimize membrane design and processing conditions to obtain higher isotropic mechanical strength and improved dimensional stability.

- Continue to investigate ionomer degradation through additional model compound studies.

- UTC will finalize development of Version 2 configuration of their peroxide mitigation strategy for improved beginning of life (BOL) performance, reduced performance decay, and reduced cost.

- UTC will continue their model development, including membrane degradation phenomena to provide predictions of membrane degradation location. An integrated chemical-mechanical model will be developed for comprehensive, multi-scale predictions of PEM degradation and failure. The model will be validated with rigorous post-test analysis of selected accelerated tests.

- UTC will execute a second short stack in late 2005 including the best, integrated MEA technology generated in this project.

- Continue development and optimization of analytical techniques at University of Southern Mississippi (USM) for post-mortem analyses of degraded membrane samples from sub-scale accelerated and fuel cell stack tests.

Introduction

The objective of this project is to improve the operational lifetime of low-temperature PEMs by developing technologies that will prevent membrane failure. It is understood that under some conditions in the fuel cell environment, hydrogen and oxygen can combine to form hydrogen peroxide. This peroxide can degrade into radicals that may attack weak spots in the PFSA polymer. After some degree of chemical degradation, the membrane mechanical properties become negatively affected, and the membrane may eventually rupture as it experiences mechanical stresses during fuel cell operation. This project seeks to enhance membrane durability by addressing each step of this degradation scheme.

Approach

To mitigate the negative effects of peroxide attack, we are developing novel PFSA polymers that demonstrate increased resistance to chemical attack. We are also developing strategies that allow peroxide to decompose benignly before any chemical attack can occur in the membrane. These two strategies will be optimized and combined with novel composite membrane structures designed to increase mechanical strength. In parallel, improved edge seal designs are being developed to prevent mechanical stresses from damaging the membrane under or around the edge seal. This project seeks to optimize each of these mitigation strategies and incorporate

them all together into more durable fuel cell components. The various mitigation strategies will be validated through a combination of modeling, *ex situ* testing, and fuel cell testing (both accelerated and non-accelerated) – including tests in stacks. In addition, modeling and post-mortem characterizations are being used to expand our understanding of the chemical and physical mechanisms of degradation, and also to evaluate the beneficial effects of the mitigation strategies.

Results

We have made significant improvements in membrane properties. An intermediate prototype, known as Gen A membrane, was selected for stack testing in December, 2004. Figure 1 compares the mechanical properties of Gen A membrane vs. 1 mil cast Nafion®. Despite the fact that Gen A does not include the chemically stabilized ionomer, its performance in various accelerated tests was remarkably good (Figures 3 and 4). We believe that a key membrane failure mode is fatigue caused by stresses imposed by humidity and thermal cycling. This is particularly relevant in automotive applications, where the system undergoes start/stop cycles. Figure 2 compares the OCV decay rate measured under accelerated conditions (95°C, 50% RH) for several membranes showing different % swelling. The data suggest a relationship between the dimensional stability of the membrane and the OCV decay rate. These results provide a basis to the
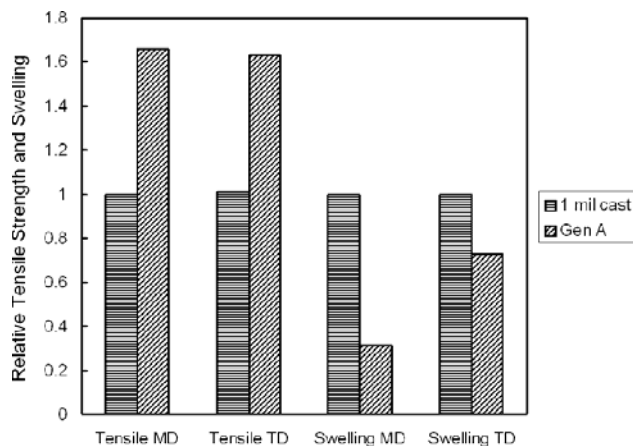
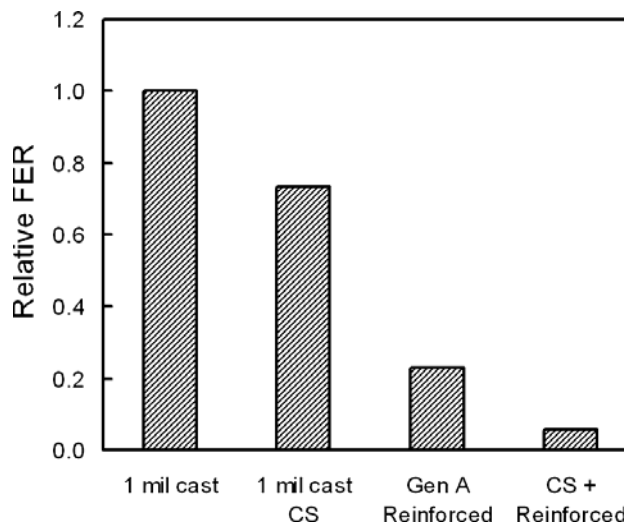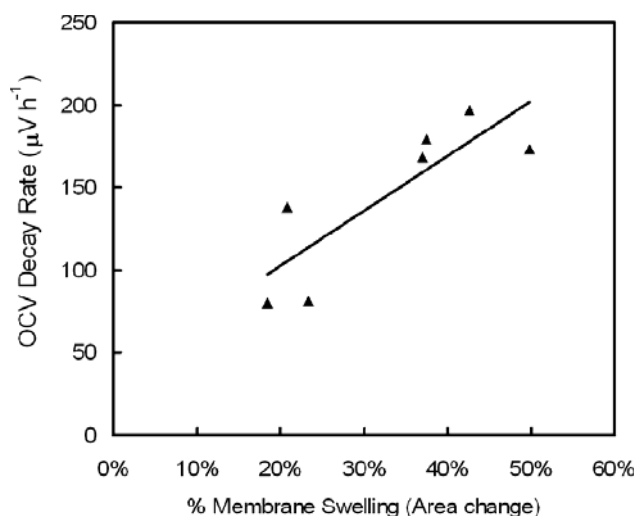**Figure 1.** Properties of Gen A Membrane Relative to 1 mil cast Nafion®

Figure 2. Relationship Between OCV Decay Ratio and Membrane Swelling

hypothesis that durability is enhanced through improvements in dimensional stability, presumably due to a reduction of the impact of the shrinkage stresses. This was also verified through *ex-situ* tests.

We continue making progress with our chemically stabilized ionomer, validating the results reported for FY 2004. Several new multi-kilogram-size batches of chemically stabilized polymer were evaluated and found to be comparable to previous small-scale batches in both the degree of end-group reduction and peroxide radical stability. Using [19]Fluorine Nuclear Magnetic Resonance (^{19}FNMR) analysis, we identified similar polymer fragments in the product water from the OCV durability test and

Figure 3. Performance in OCV Degradation Test

the Fenton's test, suggesting that there is a similar mode of polymer degradation in these two tests. The results are consistent with a step-wise reaction originating from reactive polymer end-groups. We have also tested the chemically stable ionomer under accelerated conditions. A 25-μm, chemically stabilized (CS) cast membrane survived 10x longer and had 5x lower OCV decay rate than a standard 25-μm cast membrane in an accelerated fuel cell test run at 95°C and 50% RH.

Significant progress has also been made in producing membranes that incorporate both chemical and mechanical stabilization. These membranes are more resistant to peroxy radicals, exhibiting about 5x lower fluoride emission in the Fenton's test. The OCV durability testing of these membranes has also shown similar or lower fluoride emission rates (Figure 3).

Our partners at UTC have integrated their peroxide mitigation (Version 1) with DuPont's Gen A membrane. Version 1 has been shown already to reduce substantially the fluoride emission rate (FER) under hot, dry accelerated tests, and under both constant and cyclic load profiles. UTC is currently working on Version 2 to maintain these membrane durability benefits while providing improved BOL performance and reduced performance decay under accelerated tests (automotive conditions). Version 2 is also projected to have reduced costs compared to Version 1.
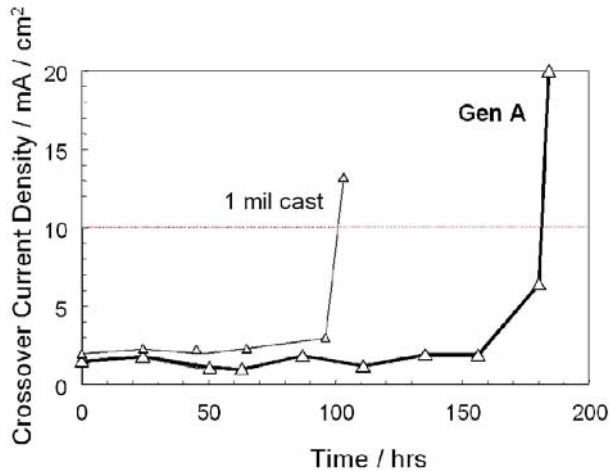
Figure 4. Comparative Lifetimes of MEAs Using DuPont's Gen A versus 1-mil cast Nafion® Membrane in the RHLC Test Protocol

UTC and DuPont have developed subscale, accelerated tests for screening prototype MEAs. Included are an OCV hold test under hot, dry conditions for MEA chemical stability, and a relative humidity/load cycle (RHLC) test for combined chemical/mechanical stability. Figure 4 shows that DuPont's new reinforced membrane (Gen A) provides ~2x improvement in lifetime over the 1-mil cast membrane baseline. Such results will translate into substantial durability improvements in automotive drive cycle environments, where temporal and platform gradients in load and relative humidity exist.

UTC has also made significant progress in their modeling effort. Quantum mechanical modeling has been performed at the atomistic scale to indicate which reactions should be considered for the formation/consumption of hydrogen peroxide and radicals. These results have been incorporated into a working MEA-scale model that predicts the rate/location of net peroxide generation and radical formation. Figure 5 shows a screenshot of the working model and two different peroxide concentration profiles for different accelerated test conditions. The model was validated experimentally using numerous rotating-ring disk and sub-scale fuel cell test results.

The initial results of accelerated single-cell tests of integrated Version 1 peroxide mitigation with DuPont's Gen A membrane at UTC indicated
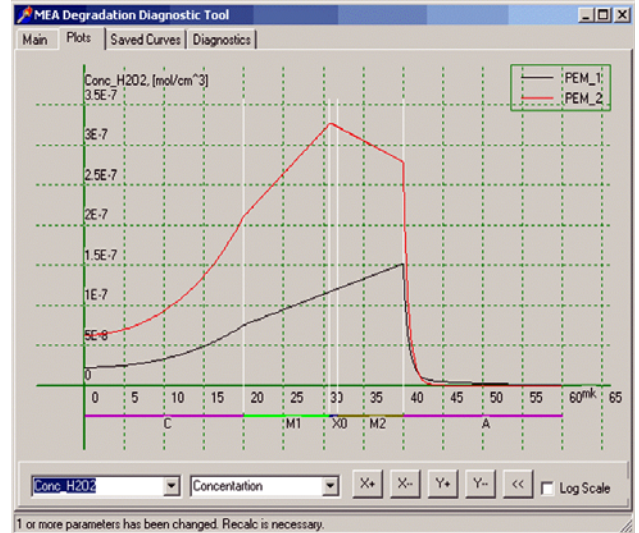

Figure 5. Peroxide Concentration Profiles from UTC Multi-Scale Model Under Two Different Accelerated Test Conditions
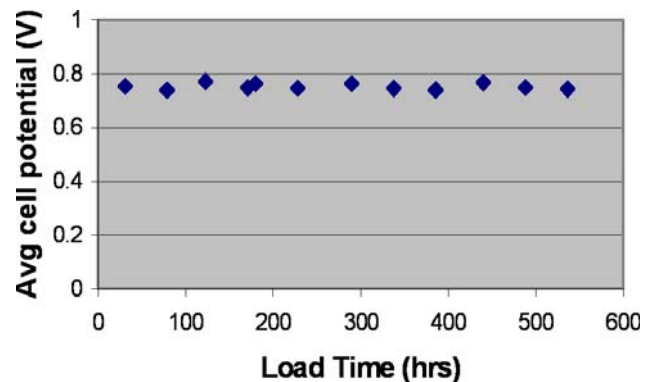

Figure 6. Average Cell Voltage at 500 mA/cm^2 During Hydrogen-Air Load Calibrations of a UTC Short Stack Undergoing Load and Thermal Cycling

problematic seal materials and cell designs that accelerated membrane failure. These problems have been addressed in a new stack hardware, which is being utilized in short-stack testing of the integrated MEA. Figure 6 shows the average cell voltage (at 500 mA/cm^2) versus load time in a UTC Fuel Cells short stack (20 full-size cells) measured during the load cycle. The stack is undergoing accelerated conditions designed to emulate the load/thermal cycles involved in automotive power plants. Over 500 hrs have been attained on this stack, which exhibits low degrees of performance losses thus far.

Finally, the team at USM has been working on developing methods to accurately monitor changes in

membrane structure (molecular and morphological) that occur during fuel cell operation. Baseline characteristics of virgin membranes are currently being evaluated using a wide array of physical and chemical methods of characterization, including small angle x-ray scattering, wide angle x-ray diffraction (WAXD), nuclear magnetic resonance, attenuated total reflectance Fourier transform infrared spectroscopy, mechanical testing and microscopy (environmental scanning electron microscopy, atomic force microscopy, and transmission electron microscopy). The construction of a database of chemical, morphological, and physical property characteristics is underway. Preliminary WAXD analysis of the degraded material indicates slight changes in the crystalline composition relative to the virgin material. Procedures for microscopic analysis of the membrane surfaces are being optimized for detailed surface comparisons and correlations with the Fourier transform infrared results. A thorough analysis of the molecular origins of thermal transitions and mechanical relaxations in Nafion[®] has been completed, and a manuscript describing the results of this study has been accepted for publication in the journal *Macromolecules*. We expect that through the results obtained from these analyses, we will be able to gain a deeper understanding of the chemical and physical mechanisms of degradation.

Conclusions

- We have made significant improvements in membrane durability by incorporating our mechanical and chemical stability strategies.
- The analytical and modeling work developed as part of this project will allow us to better understand the mechanisms and effects of membrane degradation. This knowledge will allow us to propose new degradation mechanisms and will guide the development of our mitigation strategies.

- Our results indicate that it is now possible to consider that the goal of a fuel cell membrane with 5000 hours durability under automotive conditions and 40,000 hours durability under stationary conditions can be realized once each of these additive improvements is optimized and incorporated into fuel cell components.

FY 2005 Publications/Presentations

1. "Durability of Perfluorosulfonic Acid Membranes", K. Raiford at the 2004 Gordon Research Conference – Fuel Cells, July 27th 2004, Roger William University, Bristol RI.

2. "Summary of PEM Fuel Cell Durability at the United Technologies Research Center", T. Madden at the 2004 Gordon Research Conference – Fuel Cells, July 28, 2004, Roger William University, Bristol RI.

3. "Determination of Hydrogen Peroxide Generation/Decomposition Kinetics Using RRDE on Vulcan, 10, 20, and 50% Vulcan-Supported Pt Electrodes", H. Yehia, S. Burlatsky, D. Condit, and T. Madden at the 2004 Joint Electrochemical Society International Meeting, October 3-8, 2004, Honolulu, HI.

4. "Enabling Commercial PEM Fuel Cells with Breakthrough Lifetime Improvements", S. Kumar and T. Madden, Quarterly Program Review, December 8, 2004, DOE Headquarters, Washington, DC.

5. "Durability of Perfluorosulfonic Acid Membranes", K. Raiford at the Meeting of the American Chemical Society Polymer Section entitled "Advances in Materials for Proton Exchange Fuel Cells" - February 20-23, 2005, Asilomar Conference Grounds, Pacific Grove, CA.

6. "Enabling Commercial PEM Fuel Cells with Breakthrough Lifetime Improvements", G. Escobedo at the 2005 DOE Hydrogen Program Review, May 24, 2005, Arlington, VA.

7. "Molecular Origins of the Thermal Transitions and Dynamic Mechanical Relaxations in Perfluorosulfonate Ionomers", K. Page, K. Cable, and R. Moore – accepted for publication in *Macromolecules*.