

V.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 membranes that

meet or exceed a lifetime of 40,000 hours operation with <10% degradation in performance.

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

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
- (B) Cost

Technical Targets

This project involves conducting fundamental studies of the 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 to be achieved:

- Durability: 5,000 hrs with cycling (transportation); 40,000 hrs (stationary).

Accomplishments

- DuPont has developed an advanced membrane incorporating mechanical reinforcement and a chemically stabilized ionomer. Furthermore, we have also incorporated our advanced chemical stabilization into this advanced membrane that results in approximately 50 times lower fluoride emission rate (FER) under accelerated durability tests, and more than three times longer lifetimes with 14 times lower FER under automotive cycling conditions.
- Through model compounds, DuPont has established that reactive end groups and not the structure of the side chain make PFSA structures susceptible to attack by peroxy radicals.
- United Technologies Research Center (UTRC) has developed and optimized a peroxide mitigation (PM) strategy. Comparable cell performance was achieved with and without this PM, while keeping the durability benefits of peroxide mitigation.

- UTRC demonstrated 5,000 hrs durability on a 20 cell rainbow stack with 4,000 hrs accelerated cyclic durability and 1,000 hr accelerated constant load durability. This rainbow stack was composed of different MEA structures with and without the PM. All of the MEAs were based on DuPont's non-chemically stable (CS) reinforced membrane. Also, UTRC completed post-test analysis of the cells from this stack test and showed that neither leaks nor membrane thinning were observed in the cells with PM, while those without PM thinned by 50%.
- UTRC has developed and validated a physics-based multi-scale model of chemical degradation for PEMs. The model is capable of predicting the FER and location of membrane failure for neat Nafion[®] membranes.
- The University of Southern Mississippi (USM) has developed several analytical techniques to serve as diagnostic tools in the study of chemical degradation. The structure/property information generated by these techniques is correlated to elucidate degradation mechanisms. Scanning electron microscope (SEM) images show chemical degradation that produces bubbles that can become mechanical failure nuclei. Dielectric spectroscopy reveals changes in the molecular weight (MW) distribution as a result of chemical degradation.

Introduction

Achieving targets for operating life is a significant challenge in the commercialization of PEM fuel cell systems. Degradation of components under the demanding conditions present in fuel cells is responsible for many failures observed in system tests. Two modes of decay that predominate in PEMs are chemical attack by oxygen-based radicals and physical degradation as a result of mechanical stress [1,2]. There is also evidence of an interrelationship between these two modes. 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. The hydrogen peroxide can degrade into radicals that may attack weak spots in the PFSA polymer. After some degree of chemical degradation, the mechanical properties of the membrane 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

In order 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

DuPont has used PFSA model compounds to investigate the degradation mechanisms of PFSA polymers with hydrogen peroxide radicals. Some recently published studies [3] have suggested that the side chain of the Nafion[®] polymer, which contains a branched perfluoroether, might be more susceptible to degradation than linear PFSA side chain structures. In order to make a direct comparison of the degradation of PFSA structures containing linear and branched side chains, we synthesized the following two model compounds, which were reacted with Fenton's reagent (H₂O₂ and Fe²⁺):

Linear: HO₂C-CF(CF₃)-O-CF₂-CF₂-SO₃H

Branched: HO₂C-CF(CF₃)-O-CF₂-CF(CF₃)-O-CF₂-CF₂-SO₃H

The percent fluoride released from the linear and branched compounds, as measured by a fluoride ion selective electrode, were 0.655% and 0.391%, respectively. Further, analysis of the degraded Fenton test solutions by ¹⁹F nuclear magnetic resonance (NMR) indicated that while both model compounds showed evidence of degradation (fragments of the starting compound and fluoride), they both remained largely intact. Our results show that the linear and branched PFSA model compounds, which also include carboxylic acid groups, degraded to a similar extent when reacted with Fenton's reagent. This demonstrates that carboxylic acid groups, not branched perfluoroether groups render

PFSA structures susceptible to attack by hydrogen peroxide radicals.

In the previous report, we showed that the combination of CS ionomer and mechanical reinforcement results in lower FER. We have been able to demonstrate further progress in durability by using a novel membrane that includes DuPont's advanced stabilization. This is a technology developed at DuPont in parallel to this project. Since our goal is to deliver the most durable membrane, based on our initial promising results (shown in Figure 1), we decided to incorporate this technology into the project. Figure 1 shows the FER in the open circuit voltage (OCV) test for the baseline 1 mil cast Nafion® membrane, 1 mil CS + reinforced membrane and a 1 mil reinforced membrane that includes our advanced stabilization. We conclude that the advanced stabilization provides a dramatic reduction of the FER, which is between 40 and 50 times lower than the baseline 1 mil cast Nafion® membrane.

DuPont has also conducted tests under automotive cycle conditions for a number of membrane prototypes. The results also show that the combination of CS ionomer and mechanical reinforcement results in lower FER. It is important to remark that FER is an important parameter for both durability and environmental concerns. Figure 2 shows that the CS + reinforced membrane has an FER between two and four times lower than the non-CS reinforced membrane. In addition, the membrane lifetime is also improved by including the CS ionomer, while the non-CS reinforced membrane failed after approximately 1,100 hrs of testing, while the CS reinforced membrane endured 2,500 hrs. Further improvements are achieved by introducing DuPont's advanced stabilization; we have achieved more

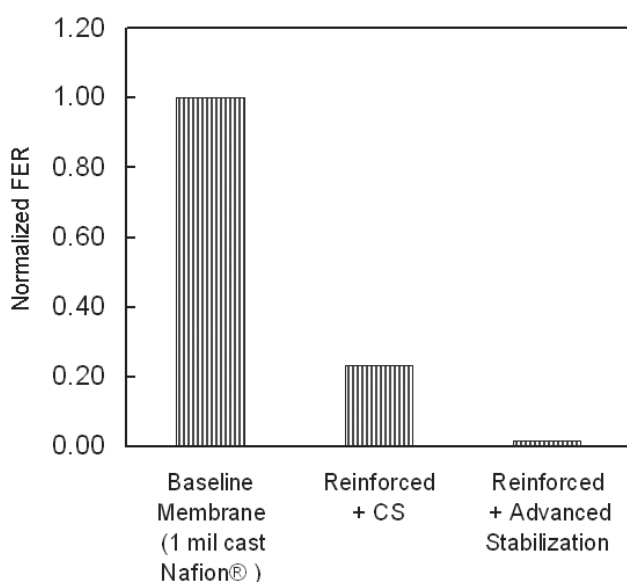


FIGURE 1. Performance under Accelerated OCV Conditions

than 3,000 hrs of testing with a FER that is four times lower than that of the CS + reinforced membrane. If this trend continues, we estimate that this membrane should achieve around 10,000 hrs in the cycle test before failure. The results shown in Figure 2 are noteworthy because they suggest that it is possible to meet the durability targets set by the DOE by combining DuPont's membrane reinforcement and advanced stabilization technologies.

UTRC has completed 5,000 hrs of testing on the 20-cell rainbow stack with integrated Version 1 PM with DuPont's non-CS reinforced membrane. The rainbow stack consisted of cells with varied MEAs, including seven cells with PM and UTRC electrodes, seven cells without PM and UTRC electrodes, and six cells without PM with DuPont electrodes. All these MEAs were made using DuPont non-CS reinforced membranes. The stack was subjected to accelerated conditions designed to emulate the load/thermal cycles involved in automotive power plants.

The variance in performance and reciprocal crossover in the cells with PM was minimal, while the variance in the cells without PM was large, as indicated by an early failure of cell 14 in Figure 3. The post-test analysis of the cells with and without PM has been completed. The cells with PM did not exhibit any leaks in stack and cell leak tests, while the cells without PM exhibited leaks in the active area and around edges. Additionally, no significant thinning of the membrane was observed in the cells with PM, while the cells without PM thinned by 50%. Based on the projection of the crossover data to failure and post-test analysis of the cells, a conservative estimate of an additional 4,000 hrs of cyclic durability is being projected on the cells with PM. These results represent the achievement of a significant milestone in meeting the durability targets of the DOE.

UTRC has also showed progress in their physics-based model for predicting the location of membrane

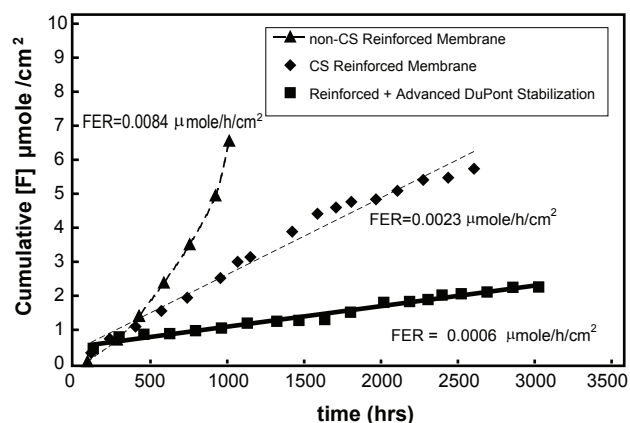


FIGURE 2. Performance under Automotive Cycling Conditions

attack and FER, under constant potential hold. The fundamental understanding from in-situ and ex-situ tests, coupled with a hypothesis verified through atomistic calculations, forms the basis for this model. The results from the simulations are shown in Figures 4 and 5. Figure 4 shows that the model is capable of predicting the location of the attack, which coincides with the maximum radical concentration in the membrane. Figure 5 compares the predictions obtained with the model with the experimental FER data obtained for neat, i.e., non-reinforced membranes. The model is able to give a good quantitative prediction of the FER as a function of membrane thickness.

USM has characterized the fundamental relaxations of Nafion® using dynamic mechanical analysis (DMA) and correlated this to morphological and chemical structure information from small angle x-ray scattering

(SAXS) and NMR studies as shown in Figure 6. The high temperature α relaxation is now assigned to motions associated with the onset of a dynamic electrostatic network, while the low temperature β relaxation is assigned as true glass transition (T_g of H^+ -form Nafion® is observed ca. $-20^\circ C$). After conducting a series of chemical degradation tests (using the standard Fenton's reagent) to prepare degraded membranes, the DMA studies revealed that with degradation, the α relaxation shifts to higher temperatures. The α relaxation for the virgin Nafion® films is approximately $110^\circ C$ and increases to $\sim 135^\circ C$ after being subjected to the Fenton's reagent for 45 hours. A recent DMA study of reinforced versus extruded (Nafion® N112) membrane shows an increase in the α relaxation temperature from $110^\circ C$ to $120^\circ C$. Being able to increase the α relaxation temperature of Nafion® could be crucial in running PEM fuel cells at elevated temperatures due to a more stable, static network of ionic aggregates.

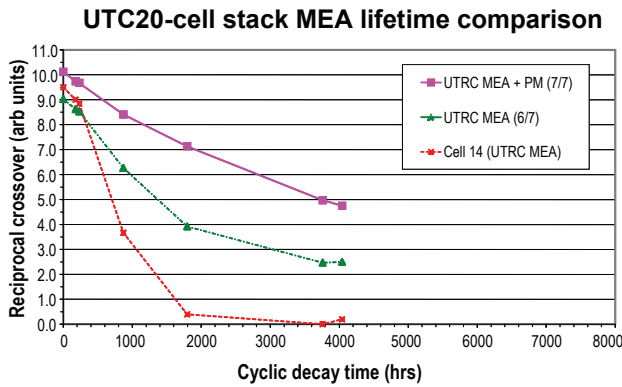


FIGURE 3. Results of reciprocal crossover measurements for MEAs that include and exclude the UTRC PM technology. The solid data points are average measurements of a UTRC short stack undergoing high temperature load and high voltage thermal cycling.

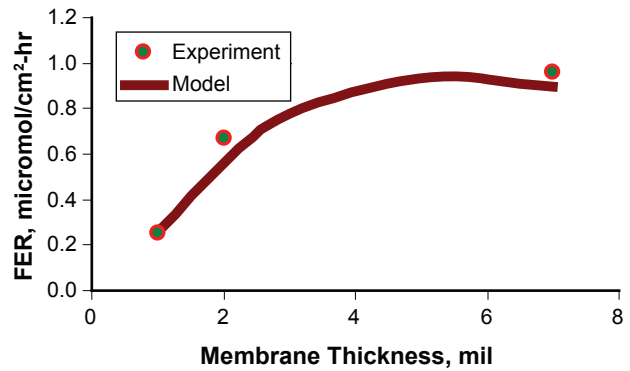


FIGURE 5. Comparison of experimental data and model predictions is shown. The experimental data used for the model validation are from V. Mittal et al., ECS 2005 fall meeting.

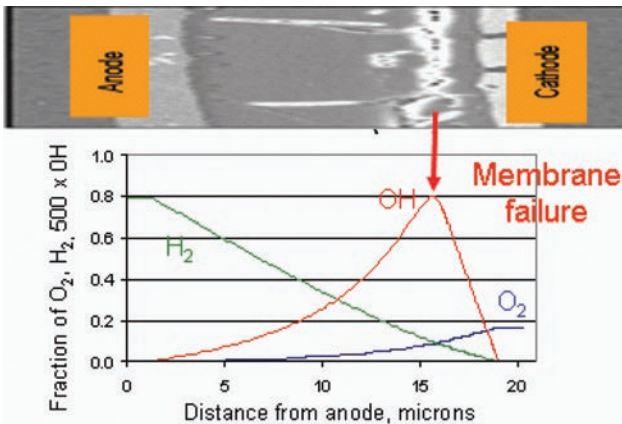


FIGURE 4. Post test of a degraded membrane showing the location of failure in the cell (upper micrograph). Comparison of the location of the attack coincides with the maximum radical concentration in the membrane.

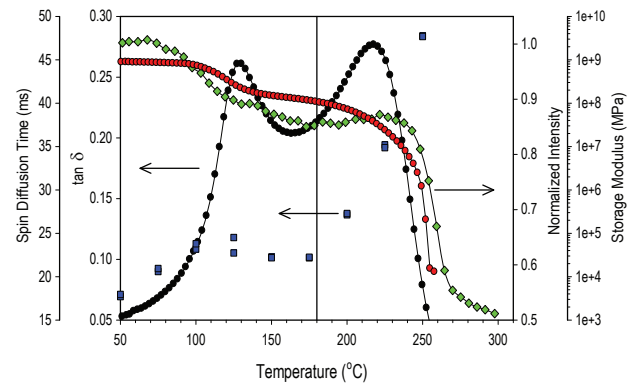


FIGURE 6. Correlation of DMA Relaxations with Variable Temperature Solid State NMR and SAXS Data

After 45 hours in the Fenton's reagent, large bubbles are formed throughout the membrane. At the membrane surface, the bubbles rupture to yield surface cracks. In the cross-section, interior lateral cracks are formed as the bubbles coalesce (see Figure 7). In general, bubble formation is somewhat less pronounced in the CS membranes, relative to the non-CS membranes. However, chemical stabilization does not completely prevent bubble formation. Non-uniform bubble formation in the CS membranes during the accelerated chemical attack may suggest chemical and/or physical heterogeneity. A key question from these studies concerns the factors that lead to bubble nucleation. Are these artificially created defects linked to crack and pinhole formation observed following long-time fuel cell operations?

USM has also developed dielectric spectroscopy (DS) as a diagnostic tool in the study of chemical degradation. Figure 8 shows the DS results for virgin and degraded, CS (212 CS) and non-CS (212) 2 mil cast (non-reinforced) Nafion[®] membranes. As shown in Figure 8, degradation broadens the distribution of relaxation times - modes are less distinct and shift toward faster motions. The β -relaxation is quite distinct with DS and this relaxation (attributed to segmental motions) is strongly affected by chemical degradation. As expected, chemical stabilization of Nafion[®] yields little, if any change in the characteristic dielectric relaxation profile of the membrane in the undegraded (virgin) state. Chemical degradation (after 45 hours in Fenton's reagent) causes a distinct broadening. Based on previous studies of other degradable polymers, this broadening of the distribution of relaxation times

associated with the β -relaxation is consistent with a broadening in the molecular weight distribution. The shift of the broadened β -relaxation in the CS-degraded membrane to higher frequencies suggests the formation of low molecular weight segments during chemical degradation.

Conclusions and Future Directions

- Our studies indicate that carboxylic acid groups, not branched side-chains make PFSA compounds susceptible to attack by peroxy radicals.
- DuPont membrane with advanced stabilization has enabled a 50-time reduction in fluoride emission in the OCV test. This membrane also shows other significant improvements: 14 times lower FER and more than three times longer life times under automotive cycling conditions.
- UTRC has demonstrated 4,000 hours in stack test under accelerated cyclic conditions. The DOE 2010 Technical target is 5,000 hours durability with cycling at $<80^{\circ}\text{C}$.
- UTRC has made significant progress in their modeling effort. The physics-based chemical degradation model has been developed and validated. The model is able to predict FER for non-reinforced membranes and is able to predict the membrane failure location.
- USM has developed analytical techniques to investigate the effects of degradation on the morphology of the membrane. SEM shows chemical degradation, which produces bubbles that can become mechanical failure nuclei, and dielectric spectroscopy reveals changes in the MW distribution as a result of chemical degradation.

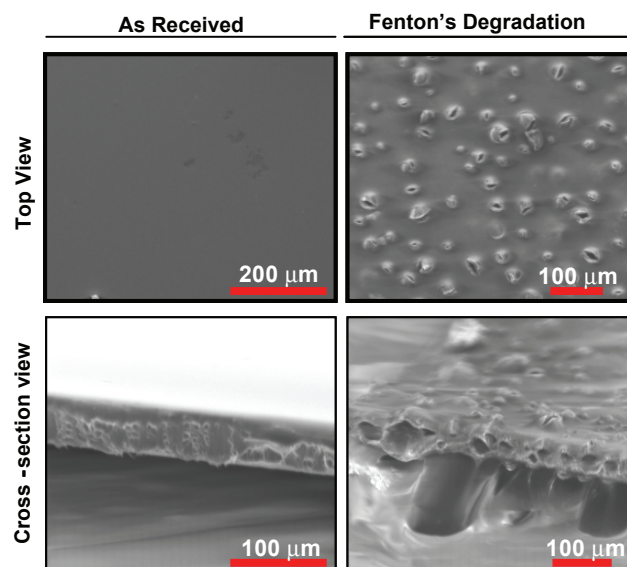


FIGURE 7. Bubble Formation in NRE 212 Membranes after 45 hr. Treatment with Fenton's Reagent at 80°C

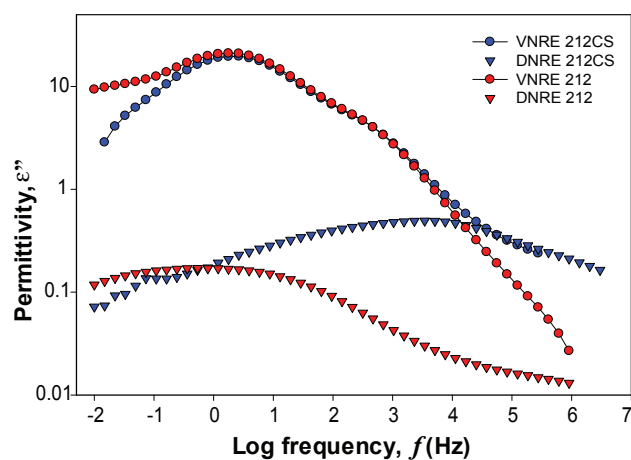


FIGURE 8. Dielectric loss permittivity versus frequency plots from 2 mil cast Nafion[®] membranes before (cleaned) and after (degraded) treatment with Fenton's reagent.

Future Directions

DuPont

- Conclude accelerated and cyclic testing of reinforced membranes with advanced stabilization.
- Characterize samples from accelerated durability tests.
- Finalize cost analysis for improved membrane.

UTRC

- Finalize version 2 MEA configuration that provides improved beginning-of-life performance, reduced performance decay, >5,000 hrs cyclic durability and reduced cost.
- Verify manufacturability of advanced peroxide mitigation strategy (version 2) in sub-scale and full-size cell tests.
- Execute a second short stack in late 2006 that includes the best, integrated MEA technology available, including version 2 peroxide mitigation, DuPont chemically stabilized and reinforced membrane.

USM

- Having established the moisture effect on β -relaxation peaks resolution, samples will be routinely analyzed in this fashion so that the degradation of different samples can be compared in a quantifiable fashion. More detailed future analyses include the extraction of relaxation times (τ) and their distributions. This information directly relates to the molecular weight distribution that has evolved at a given stage of degradation because it is a general principle that τ for the T_g – related relaxation decreases (β -relaxation) with decreasing MW.
- Characterize degraded samples from accelerated tests at DuPont.

Special Recognitions & Awards/Patents Issued

1. Prof. Moore from USM was awarded the MRS Trophy Award at the 2005 Fall MRS Meeting for his work on the morphological and molecular origins of relaxations and transitions in Nafion®.

FY 2006 Publications/Presentations**Presentations by DuPont Team Members**

1. “Strategies for Mitigation of Perfluorosulfonic Acid Degradation in PEM Fuel Cells”, K. Schwiebert, K. Raiford, G. Escobedo, F. Principe, and G. Nagarajan, 208th meeting of the Electrochemical Society, Oct. 16-21, 2005, Los Angeles, CA.
2. “Strategies to Improve the Durability of Perfluorosulfonic Acid Membranes for PEM Fuel Cells”, G. Escobedo, KFTCA International Symposium, December 8-9 2005, Washington, D.C.

Two extended abstracts have also been submitted for publication to the above conferences during the reporting period.

Presentations by UTRC Team Members

1. Determination of Hydrogen Peroxide Generation/Decomposition Kinetics Using RRDE on Vulcan, 10, 20, and 50% Vulcan-Supported Pt Electrodes, by Hadi Yehia, David A. Condit, Vadim V. Atrazhev, Nikolai S. Erikhman, Sergei F. Burlatsky, Ned E. Cipollini. Submitted to Journal of Electrochemical Society.
2. Membrane Degradation in PEMFC's, 208th meeting of the Electrochemical Society, Oct. 16-21, 2005, Los Angeles, CA.
3. Attack of the Killer Radicals, MRS 2005 Fall Meeting, Nov. 27-Dec. 1, Boston, MA. Received best paper award.

Presentations by R.B. Moore (USM)

1. Phillips, A.K.; Moore, R.B. “Mechanical and Transport Property Modifications of Perfluorosulfonate Ionomer Membranes Prepared with Mixed Organic and Inorganic Counterions,” *J. Polym. Sci., Part B: Polym. Phys.* 2006, in press.
2. Page, K.A.; Cable K.M.; Moore, R.B. “SAXS Analysis of the Thermal Relaxation of Anisotropic Morphologies in Oriented Nafion® Membranes,” *Macromolecules* 2006, 39, 3939.
3. Page, K.A.; Cable K.M.; Moore, R.B. “Molecular Origins of the Thermal Transitions and Dynamic Mechanical Relaxations in Perfluorosulfonate Ionomers,” *Macromolecules* 2005, 38, 6472.
4. Page, K.A.; Moore, R.B. “Influence of Electrostatic Interactions on Chain Dynamics and Morphological Development in Perfluorosulfonate Ionomer Membranes,” *Mater. Res. Soc. Symp. Proc.* 2005, 856E, BB6.4.1. **Trophy Award**

5. Phillips, A.K.; Moore, R.B. "Morphological Manipulation and Plasticization of the Electrostatic Network in Perfluorosulfonate Ionomers," *Mater. Res. Soc. Symp. Proc.* 2005, 856E, BB8.11.1.
6. Osborn, S.J.; Moore, R.B. "Effects of Humidity and Partial Neutralization on the Mechanical Properties of Perfluorosulfonate Ionomer Membranes," *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2005, 46(2), 597.
7. "Probing the Molecular and Morphological Origins of Dynamic Behavior in Nanostructured Membrane Systems," Department of Chemistry, Virginia Tech, Blacksburg, VA, March 23, 2006.
8. "Probing the Glass Transition of Perfluorosulfonate Ionomers," Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, February 17, 2006.
9. "Molecular and Morphological Origins of the Mechanical Behavior of Nanostructured Perfluorosulfonate Ionomers," DuPont Fuel Cells, Wilmington, DE, September 27, 2005.
10. "Correlations between Spectroscopic, Morphological, and Dynamic Mechanical Information to Determine the Molecular Origins of Thermal Relaxations in Perfluorosulfonate Ionomer Membranes," Department of Chemistry, University of North Carolina, Chapel Hill, NC, September 21, 2005.
11. Alteration of membrane properties of Perfluorosulfonate Ionomers using Solution and Melt Processing Procedures," 2005 Fall ACS Meeting, Washington, DC, September 1, 2005.

References

1. D. Curtin et al., *J. Power Sources*, **131**, 41 (2004).
2. A. B. LaConti et al., in *Handbook of Fuel Cells*, W. Vielstich, A. Lamm, H. Gasteiger, Editors, p. 647, John Wiley and Sons Ltd., Chichester, England (2003).
3. M. Debe, Proceedings of the 2005 DOE Hydrogen Program Merit Review, U.S. Department of Energy, Hydrogen Program, Arlington, VA (2005).

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