V.B.23 Characterization of PEMFC Membrane Durability: Changes in Physical Properties of Nafion® Membranes after Chemical Degradation*

Robert B. Moore (Primary Contact),
Kenneth A. Mauritz
University of Southern Mississippi
Department of Polymer Science
118 College Drive #10076
Hattiesburg, MS 39406-0001
Phone: (601) 266-4480; Fax: (601) 266-5635
E-mail: rbmoore@usm.edu

Gonzalo Escobedo
E.I. du Pont de Nemours and Company, Inc.
DuPont Fuel Cells
Chestnut Run Plaza, Building 701
Wilmington, DE 19805-0701
Phone: (302) 999-2762; Fax: (302) 999-2395
E-mail: Gonzalo.Escobedo@usa.dupont.com

DOE Technology Development Manager:
Amy Manheim
Phone: (202) 586-1507; Fax: (202) 586-9811
E-mail: Amy.Manheim@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

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

Contract Number: DE-FG36-06GO86065

Start Date: June 1, 2006
Projected End Date: November 30, 2007

*Congressionally directed project

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 hrs operation with <10% degradation in performance.
- We will identify characterization tools that are useful in defining changes in the chemical and physical properties of perfluorosulfonate ionomer (PFSI) membrane materials after accelerated chemical degradation 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 is conducting fundamental studies of the durability of 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 met:

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

Approach

Our approach has involved the use of advanced characterization techniques (listed here) to do post-mortem analysis of the physical and chemical properties of samples tested under accelerated degradation conditions.

- Morphology: environmental scanning electron microscopy (ESEM), transmission electron microscopy (TEM), Atomic force microscopy (AFM), small-angle x-ray scattering (SAXS), wide-angle x-ray diffraction (WAXD)
- Chemical composition/structure: fluorine 19 solid-state nuclear magnetic spectroscopy (^{19}F SSNMR), fourier transform infrared (FTIR) spectroscopy, energy dispersive x-ray (EDX)
- Mechanical/electrical properties: tensile testing, dynamic mechanical analysis (counterion effects), dielectric spectroscopy
- Transport properties: H+ conductivity, water diffusion by Pulsed field gradient spin echo nuclear magnetic resonance (PFGSE NMR) and solvent swelling, ionic mobility and gas transport

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. The structure/property information is correlated with control virgin characteristics to elucidate degradation mechanisms. This fundamental information will provide input to DuPont for the stimulation of membrane improvements.

Accomplishments

The fundamental relaxations of Nafion® were characterized using dynamic mechanical analysis (DMA) and correlated to morphological and chemical structure information from SAXS and nuclear magnetic resonance (NMR) studies as shown in Figure 1. 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°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°C and increases to ~135°C after being subjected to the Fenton's Reagent for 45 hours. A recent DMA study of Teflon® reinforced Nafion® versus extruded 112 shows an increase in the α relaxation temperature from 110°C to 120°C. Being able to increase the α relaxation temperature of Nafion® could be crucial in running PEMFCs at elevated temperatures due to a more stable, static network of ionic aggregates.

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 2). In general, bubble formation is somewhat less pronounced in the chemically-stabilized (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?

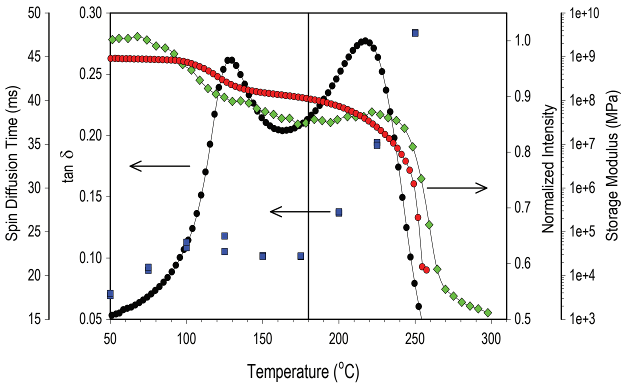

FIGURE 1. Correlation of DMA Relaxations with Variable Temperature SSNMR and SAXS Data

Dielectric spectroscopy (DS) is being developed as a diagnostic tool in the study of chemical degradation. As shown in Figure 3, degradation broadens the distribution of relaxation times - modes are less distinct and shift toward faster motions. The β relaxation is quite distinct with dielectric spectroscopy, and this relaxation (attributed to segmental motions) is strongly

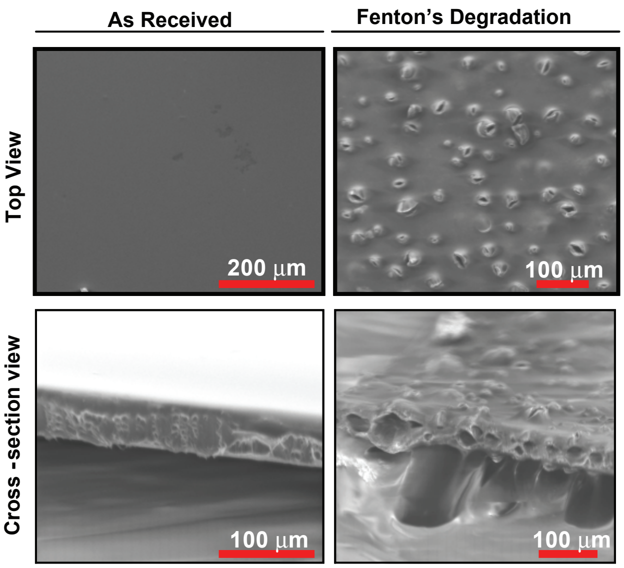

FIGURE 2. Bubble Formation in NRE 212 Membranes after 45 hr. Treatment with Fenton's Reagent at 80°C

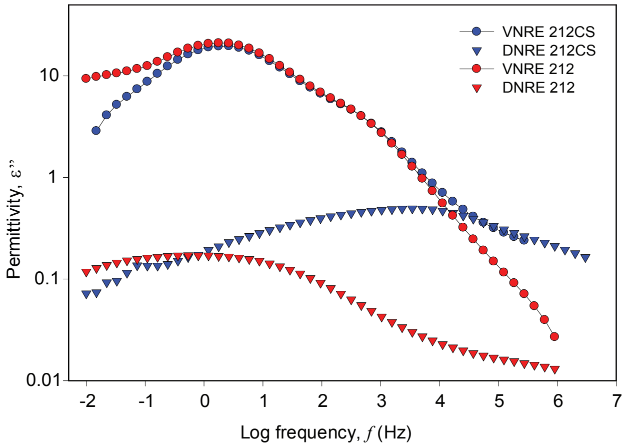

FIGURE 3. Dielectric Loss Permittivity versus Frequency Plots from Membranes Before and After Treatment with Fenton's Reagent

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 hrs 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 212 CS-Degraded membrane to higher frequencies suggests the formation of low molecular weight segments during chemical degradation.

Special Recognitions & Awards/Patents Issued

1. MRS Trophy Award at the 2005 Fall MRS Meeting for our work on the morphological and molecular origins of relaxations and transitions in Nafion®.

FY 2006 Publications/Presentations

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, 44, 2267.

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 Procesing Procedures," 2005 Fall ACS Meeting, Washington, D.C., September 1, 2005.