

## V.B.11 Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications

Jimmy W. Mays

University of Tennessee  
Department of Chemistry  
552 Buehler Hall  
Knoxville, TN 37996  
Phone: (865) 974-0747; Fax: (865) 974-9304  
E-mail: jimnymays@utk.edu

DOE Technology Development Manager:

Kathi Epping

Phone: (202) 586-7425; Fax: (202) 586-9811  
E-mail: Kathi.Epping@ee.doe.gov

DOE Project Officer: Reg Tyler

Phone: (303) 275-4929; Fax: (303) 275-4753  
E-mail: Reginald.Tyler@go.doe.gov

Technical Advisor: Walt Podolski

Phone: (630) 252-7558; Fax: (630) 972-4430  
E-mail: podolski@cmt.anl.gov

Contract Number: DE-FG36-06GO16037

Subcontractor:

University of Southern Mississippi (USM)  
Hattiesburg, MS

Start Date: April 1, 2006

Projected End Date: March 31, 2011

### Objectives

- Design, synthesize and characterize new non-Nafion<sup>®</sup> proton exchange membrane (PEM) materials that conduct protons at low (25-50%) relative humidity (RH) and at temperatures ranging from room temperature to 120°C.
- To achieve these objectives, a range of homopolymer and copolymer materials incorporating poly(cyclohexadiene) (PCHD) will be synthesized, derivatized, and characterized.

### 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 targeted toward the development and characterization of PEMs that can meet conductivity requirements specified by DOE (conductivity >0.1 S/cm at 50% RH at 120°C), as well as achieving lower cost and meeting other 2010 performance criteria:

- Cost: \$40/m<sup>2</sup>
- Durability: 2,000 h at operating temperature >80°C
- Survivability: -40°C
- Thermal cyclability in the presence of condensed water
- Area specific resistance: 0.02 Ohm-cm<sup>2</sup>
- Hydrogen crossover: 2 mA/cm<sup>2</sup>
- Oxygen crossover: 2 mA/cm<sup>2</sup>
- Inlet water vapor partial pressure: 1.5 KPa
- Operating temperature: ≤120°C

### Approach

1,3-Cyclohexadiene is a potentially inexpensive monomer that can be polymerized to yield a range of novel polymers and copolymers incorporating an unsaturated 6-membered ring into the polymer backbone. The ring structure imparts superior mechanical and thermal properties. Furthermore, PCHD can be aromatized, sulfonated, or fluorinated, allowing for tuning of key properties such as conductivity, hydrophilicity, permeability, morphology, thermal stability, crystallinity, and cost. We are synthesizing a range of homopolymer and copolymer materials incorporating PCHD.

For samples synthesized by Mays, Mauritz (USM) is developing a strategy of extracting both proton conductivity ( $\sigma$ ) and polymer relaxation data from dielectric loss ( $\epsilon''$  vs. frequency =  $f$ ) spectra of membranes using the powerful technique of broadband dielectric spectroscopy (DS) using a Novocontrol Concept 40 system. A working hypothesis is that relaxations, i.e., long- and short-range polymer motions, interact with water cluster dynamics and thereby affect proton hopping along hydrogen-bonded water molecules.

In addition, the mechanical and thermal characteristics of the new membranes will be elucidated, and strategies for growing nanoscale metal oxide nanoparticles within the membranes (to improve proton

conductivity and thermal properties) will be developed by Mauritz.

Typically,  $\sigma$  is determined in an experiment using a 4-point probe and polymer relaxations are investigated separately using dynamic mechanical analysis (DMA). We obtain both measurements in a single experiment to identify coupling between the two processes. One advantage of DS over DMA is that experiments are conducted over a considerably broader frequency range. As depicted in Figure 1, using data for Nafion<sup>®</sup> with a small amount of water, the phenomena that are detected in order of increasing frequency are membrane/electrode interfacial polarization  $\rightarrow$  DC conduction (straight line with slope  $\sim 1.0$ )  $\rightarrow$  membrane structural relaxation (molecular motions). Conductivity is determined by the equation  $\sigma = \epsilon_0 \epsilon'' \omega$  ( $\omega = 2\pi f$ ,  $\epsilon_0 =$  vacuum permittivity) using any corresponding  $\epsilon''$  and frequency values along the linear segment.

The 4-point probe method can be criticized in that it measures conductivity in the film in-plane direction rather than perpendicular to the plane. Also, the lines of the non-uniform electric field are more concentrated near the surface where the membrane water concentration is higher than in the middle. In the DS method, the uniform field is perpendicular to the plane. The direct current conductivity can then be obtained

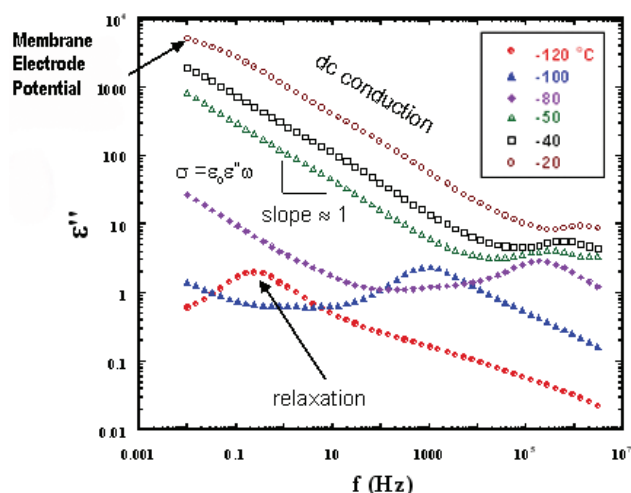


FIGURE 1. Dielectric Loss Spectra of Nafion<sup>®</sup>

by subtracting the contribution of membrane/electrode polarization at the lowest frequencies.

After the direct current contribution is subtracted from the total spectra, polymer relaxations can be isolated and analyzed using the Havriliak-Negami equation, and distributions of relaxation time can be extracted. We are cultivating this analysis also with regard to membrane durability, particularly with regard to peroxide degradation. Shifts in the distribution of relaxation times are related to shifts in polymer membrane molecular weight distribution.

Efforts are underway to carefully control the amount of water ( $\#H_2O$  molecules/ $SO_3H$  group) into the membranes so that conductivity and relaxation behaviors can be related to hydration microstructure.

## Accomplishments

Crosslinked and sulfonated PCHD films have been synthesized and characterized, and work has begun on measuring their thermal properties and proton conductivity. A membrane of crosslinked, aromatized (90 mol %) and sulfonated (13 mol %) PCHD was tested. Water uptake was 5.3 wt%. Proton conductivity was measured for this membrane using a 4-point fixture immersed in water (J. Sayre, Battelle):  $1.2 \text{ E-}02 \text{ S/cm}$  at room temperature and  $2.8 \text{ E-}02 \text{ S/cm}$  at  $80^\circ\text{C}$ .

A membrane of crosslinked, non-aromatized, and sulfonated (47 mol %) PCHD was also tested. Water uptake was 4 wt%. Proton conductivity:  $1.6 \text{ E-}02 \text{ S/cm}$  at room temperature and  $3.6 \text{ E-}02 \text{ S/cm}$  at  $80^\circ\text{C}$ .

## FY 2006 Publications and Presentations

1. "Poly(cyclohexadiene) – Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. W. Mays, T. Huang, H. Zhou, and K. Mauritz, poster presentation at the 2006 DOE Hydrogen Program Review, Washington, DC, May 16–19, 2006.
2. "Poly(cyclohexadiene) – Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. W. Mays, T. Huang, H. Zhou, and K. Mauritz, oral presentation at the High Temperature Membranes Working Group, DOE Hydrogen Program Review, Washington, DC, May 16–19, 2006.