

V.M.10 Microstructural Design and Development of High Performance Polymer Electrolyte Membranes*

Denise Katona (Primary Contact), Michael Blumena, Joseph Mausar and Pasco Santurri
Chemsultants International Inc.
9079 Tyler Road
Mentor, OH 44060
Phone: (440) 974-3080; Fax: (440) 974-3081
E-mail: dkatona@chemsultants.com

DOE Technology Development Manager:
Pete Devlin
Phone: (202) 586-4905; Fax: (202) 856-9811
E-mail: Peter.Devlin@ee.doe.gov

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

Contract Number: DE-FG36-06GO86043

Subcontractors:

- Michigan Molecular Institute, Midland, MI
- Case Western Reserve University, Cleveland, OH

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

* Congressionally directed project

Technical Targets

The goal of this project is to design, characterize and solution cast new polymer electrolyte membranes that will exhibit improved performance at high temperature and low RH conditions. These membranes will be designed to meet the DOE 2010 targets for fuel cell membranes for transportation applications, specifically:

- Good proton conductivity (0.1 S/cm) at $\leq 120^{\circ}\text{C}$ and 50% RH operating conditions
- Cost: $\$20/\text{m}^2$
- Durability: 2,000 hours at temperatures above 80°C

Accomplishments

- Developed a process that allows for controlled sulfonation of a commercially available polyphenylsulfone (PPSU) base polymer.
- Demonstrated improved mechanical and dimensional stability over Nafion[®] membranes for the same thickness and test conditions.
- Successfully synthesized two nano-additives for use with the sulfonated base polymer.
- Achieved a membrane conductivity of >0.1 S/cm at 80°C and 100% RH for a composite nanoparticle/polyphenylsulfone system.

Objectives

- Develop novel polymer architectures capable of improved mechanical stability and conductivity at high operating temperatures ($\geq 120^{\circ}\text{C}$) and low ($\leq 50\%$) relative humidity (RH).
- Develop innovative polymer solution casting processes, methodologies and new membrane structures, including multi-layer membranes, suitable for commercial scale roll-to-roll production.

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
- (D) Water Transport within the Stack



Introduction

Perfluorosulfonic acid (PFSA), i.e. Nafion[®], is the standard material for use as the polymer electrolyte in fuel cells. Existing polymer electrolyte type fuel cells must operate near ambient conditions and with humidified gas streams to ensure high enough conductivity (0.1 S/cm). At temperatures above 80°C and low relative humidity, dehydration of Nafion[®] (and other PFSA-type materials) occurs, resulting in deactivation of the membrane due to loss of proton conductivity. In addition, Nafion[®] exhibits a drastic loss of mechanical strength under those conditions. Consequently, there is a great need for less costly alternative membrane materials that perform well in elevated temperatures and low RH, both of which are encountered in automotive and stationary applications.

Approach

Our approach to achieving membranes with the above described properties is to choose a commercially

available base polymer that has high mechanical strength and thermal/chemical stability and modify it, via sulfonation of the backbone, to render it conductive. The modified polymers being developed in this project may not achieve high enough proton conductivity alone to meet the DOE targets. Therefore, hydrophilic, conductive nano-additives will also be developed to aid in water management and improve overall conductivity. The proton conductive nano-additives will be incorporated in the modified polymer and solution cast into various membrane systems. Solution casting methods are currently being developed and utilized to strategically cast uniform, defect-free mono and multi-layered composite membranes.

Results

Sulfonated polyphenylsulfone, PPSU, (Radel[®] R-5000, Solvay Advanced Polymers) was prepared via a unique method using chlorosulfonic acid with acetic anhydride as an activating agent. Figure 1 shows the structural formula of Radel[®] R-5000 polyphenylsulfone with two $-SO_3H$ groups on the biphenyl unit. Degree of sulfonation and molecular weight were determined by 1H nuclear magnetic resonance (NMR) spectroscopy and SEC (size exclusion chromatography), respectively. The sulfonated Radel[®] R-5000 was solution cast into membranes 50 microns in thickness and characterized. The membranes were found to have excellent mechanical strength and dimensional stability. Conductivity was equal to or slightly less than that of Nafion[®] 212, depending on the degree of sulfonation.

Two hydrophilic, conductive nano-additives were synthesized as shown in Figure 2. Each of the additives was approximately 1.5 nm in size. The sulfonated polyhedral oligomeric silsesquioxane (POSS) and phosphazene additives were incorporated into the sulfonated Radel[®] R-5000 material in various concentrations and evaluated. The best composite membranes of those tested were the ones that contained

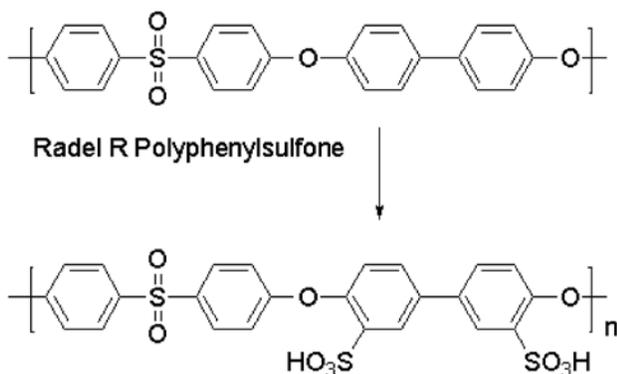


FIGURE 1. Structural Formula of Radel[®] R-5000 Polyphenylsulfone before and after Sulfonation

20 weight percent of additives on solids. However, it was found that incorporation of the nano-additives reduced the tensile strength of the membranes and those containing the sulfonated POSS had a slightly rough surface. In order to improve the tensile strength and keep a good balance between all the desired properties, a three-layered membrane was made. The three-layered membrane consisted of two outer layers comprised of the virgin sulfonated Radel[®] R-5000 polymer and a center layer with 20 weight percent sulfonated POSS. Each layer was solution cast on top of the previous layer. Interlayer adhesion was evaluated and no delamination of individual layers was evident. Tensile strength, water uptake, dimensional stability and conductivity tests were performed.

Table 1 shows the test data for the sulfonated Radel[®] R-5000 PPSU membranes and nano-additive

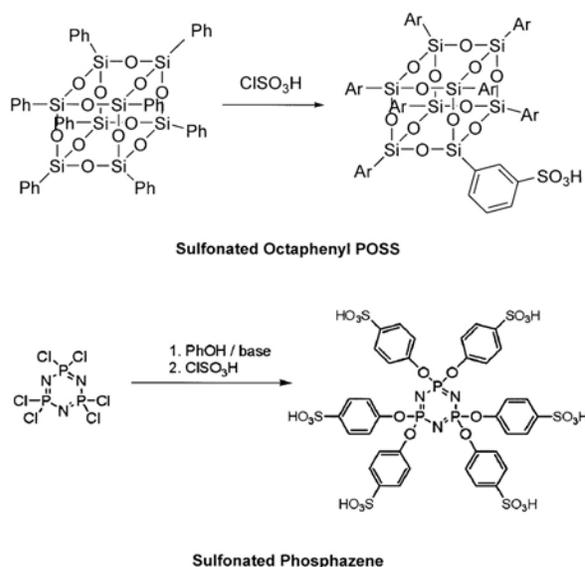


FIGURE 2. Structures of Synthesized Nano-Additives: Sulfonated POSS and Sulfonated Phosphazene

TABLE 1. Physical Characteristics of Sulfonated PPSU and Composite Membranes as Compared to Nafion[®] 212 at 50 μm Total Thickness

| Sample Membrane | Tensile Strength ^a (N/mm ²) | Water Uptake (%) | Conductivity ^a (S/cm) | Conductivity ^b (S/cm) | Dimensional Stability Lc (%) |
|------------------------------|--|------------------|----------------------------------|----------------------------------|------------------------------|
| S-PPSU | 33 | 53 | 0.049 | 0.080 | 0 |
| S-PPSU + 20% S-POSS | 23 | 83 | 0.054 | 0.073 | +1.4 |
| 3 Layer S-PPSU/S-POSS | 33 | 64 | 0.046 | 0.073 | +1.3 |
| S-PPSU + 20% S-Phosphazene | 23 | 68 | 0.082 | 0.101 | pending |
| 3 Layer S-PPSU/S-Phosphazene | 26 | 53 | 0.066 | 0.098 | pending |
| Nafion [®] 212 | 25 | 50 | 0.099 | 0.100 | +10.4 |

a - membranes conditioned in acid/water at 25°C

b - membranes conditioned in acid/water at 80°C

composites. As evident from the data, the sulfonated PPSU membrane alone had excellent tensile strength and dimensional stability. However, conductivity was lower than desired. When the nano-additives were combined with the sulfonated PPSU, the conductivity and water uptake increased, especially for the sulfonated phosphazene material; but a loss of tensile strength was seen. In an effort to balance all the properties, a three-layered membrane incorporating the nano-additives in the center was prepared and results show increase in tensile strength while maintaining conductivity and dimensional stability. The ultimate goal is to retain moisture in the center of the membrane at high temperature and lower humidity operating conditions in the fuel cell. In order to test the performance of the three-layered membrane, a fuel cell test was performed. Figure 3 is the current density plot at 100% RH and 50% RH at the anode. The results show that the sulfonated PPSU membrane alone failed at lower (50%) RH, but the three-layer composite membrane performance is reduced only slightly. This result indicates the nano-additive helped retain moisture in the membrane under low humidity conditions.

Pilot manufacturing trials were run using the Radel[®] R-5000 PPSU material in a 20% solids solution in N-methylpyrrolidone (NMP). Defect-free membranes ranging in thickness from 35 to 100 microns were produced using knife-over-roll and reverse-gravure casting methods. Casting trials will continue with emphasis on creating uniform, multiple layered composite membranes with varying layer thicknesses and compositions.

Conclusions and Future Directions

During the past year of work, we have successfully demonstrated ability to sulfonate a highly chemical resistant polyphenylsulfone polymer, rendering it conductive. In addition, two nano-additives were synthesized that have been shown to contribute to the overall properties of the membrane, especially water uptake and conductivity. The multi-layered membrane approach has been shown to be effective in the fuel cell operation at lower RH. Solution casting methods continue to be developed that will allow for production of defect-free, roll-to-roll thin conductive membranes.

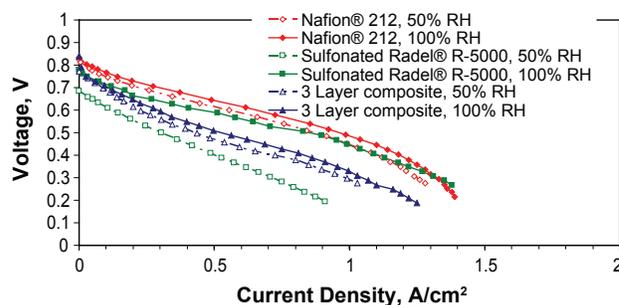


FIGURE 3. Hydrogen fuel cell performance at 80°C and 100%, 50% RH at the anode. Electrode area: 5 cm² with catalyst loading 0.4 mg/cm², 40% Pt/C and Nafion[®] ionomer.

Future work will focus on designing the multilayered composite membrane system to meet or exceed the 2010 DOE requirements for fuel cell operation at high temperature and low RH conditions. Specifically:

- Synthesis of two additional nano-additives to further enhance water management and conductivity at 120°C and 50% RH.
- Design of multiple layers, including increased number of layers and/or concentration of nano-additives within the layers to aid in balance of mechanical properties and proton conductivity.
- Continue to solution cast the desired materials into a multi-layered structure using the manufacturing casting equipment to produce a high quality roll-to-roll membrane prototype.

Special Recognitions & Awards/Patents Issued

1. U.S. Patent Filing: US 60/923,297. Improved Fuel Cell Proton Exchange Membranes, Bob Nowak, Claire Hartmann-Thompson, Lowell Thomas, Dale Meier and Ken Bruza. Filed: April 13, 2007.

FY 2007 Publications/Presentations

1. *Center for Intelligent Fuel Cell Materials Design Phase I*, presented at the 2007 DOE Hydrogen Program Annual Merit Review, May 16, 2007, Arlington, VA.