V.G.3 Microstructural Design and Development of High Performance Polymer Electrolyte Membranes*

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- Case Western Reserve University, Cleveland, OH

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*Congressionally directed project

Objectives

- Develop novel polymer architectures capable of improved mechanical stability and conductivity at high operating temperatures (≥120°C) and low (≤50%) relative humidity (RH).
- Develop low-cost, effective membrane components (polymers and nano-particles).
- 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

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 ≤120°C and 50% RH operating conditions
- Cost: $20/m²
- Durability: 4,000 hours at temperatures above 80°C

Accomplishments

- Developed a process that allows for controlled sulfonation of a commercially available sulfonated polyphenylsulfone (S-PPSU) base polymer.
- Demonstrated improved mechanical (see Table 1) and dimensional stability over Nafion® membranes for the same thickness and test conditions.
- Successfully synthesized a chemically and thermally stable, compatible nano-particle (Sulfonated-octaphenyl polyhedral oligomeric silsesquioxane [S-POSS]) for use with the sulfonated base polymer.
- Achieved significant conductivity increases from a unique, multilayered membrane (using sulfonated [S-PPSU] and S-POSS) over Nafion® at 25% RH and 95°C.

TABLE 1. Dynamic Mechanical Analysis*

Membrane	Storage Modulus at 30°C (MPa)	Storage Modulus at 120°C (MPa)	Storage Modulus at 170°C (MPa)
Nafion® 117	600	23	3
Single-layer Sulfonated Radel (S-Radel)	1954	1750	884
Single-layer (20%S-POSS + 80% S-Radel)	1426	1120	23
Three-layer S-Radel/(20%S-POSS+80% S-Radel)/S-Radel	1348	1320	1202

* Performed by Michigan Molecular Institute

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 RH, 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 relative humidity, 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

S-PPSU was prepared using Radel® R 5000, Solvay Advanced Polymers 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 spectroscopy and size exclusion chromatography, respectively. The sulfonated Radel® R-5000 was solution cast in the laboratory into membranes 50 microns in thickness and characterized. The membranes were found to have excellent mechanical strength (see Table 1). Conductivity was still slightly less than that of Nafion® 212.

Two hydrophilic, conductive nano-additives were synthesized as shown in Figure 2. Each of the additives was approximately 1.5 nm in size. The

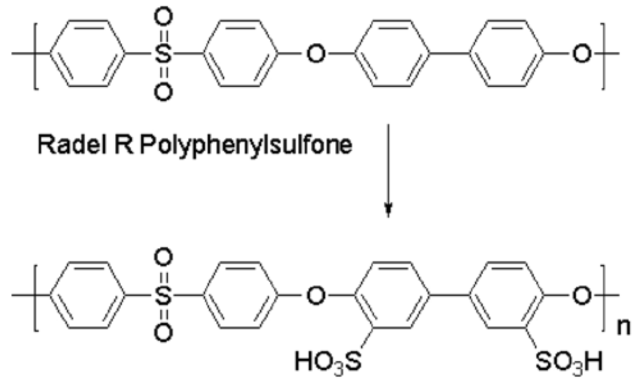

FIGURE 1. Structural Formulation of Radel R 5000 Polyphenylsulfone (Sulfonated)

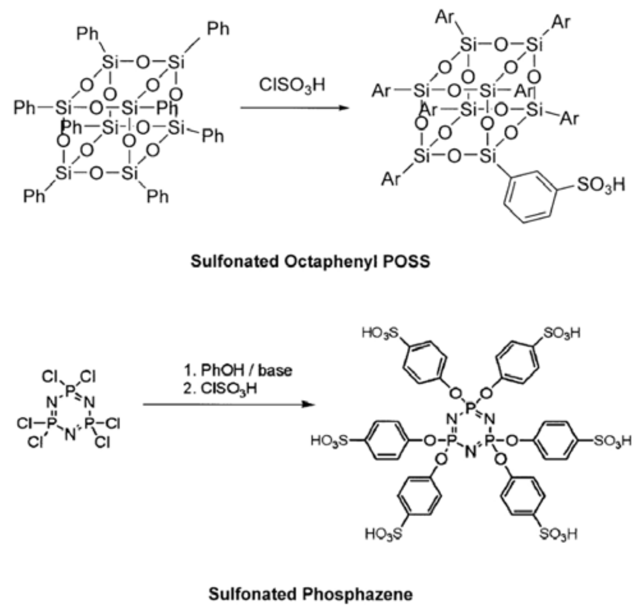

FIGURE 2. Structures of Synthesized Sulfonated POSS and Phosphazene

S-POSS and phosphazene additives were incorporated into the sulfonated Radel® R-5000 material in various concentrations. The best composite membranes of those tested were the ones that contained 20 wt% of additives on solids. However, it was found that incorporation of the nano-additives reduced the strength of the membranes. In order to improve the 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 S-POSS. Each layer was solution cast on top of the previous layer. Interlayer adhesion was evaluated and no delamination of individual layers was evident.

The S-PPSU membrane alone had excellent tensile strength and dimensional stability, however, conductivity was lower than desired. When the nano-additives were combined with the S-PPSU, the conductivity and water uptake increased 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. Dynamic mechanical analysis (see Table 1) was performed on the single-layer membranes of S-PPSU only and S-PPSU filled with 20% S-POSS as well as the three layer membrane as described above. Nafion®117 was used as the control. The data from Table 1 indicates excellent storage modulus for the three-layer membrane as compared to the single layer S-Radel® filled with the S-POSS nano-particle and Nafion®.

In order to test the performance of the three-layer membrane construction, a conductivity test was performed using 1) Nafion® 212 as the control, and 2) single layers of neat and S-POSS filled S-Radel®. Figure 3 clearly demonstrates the benefit of the hydrophilic nanoparticle incorporated into the sulfonated Radel® and the significant improvement in conductivity of the three layer membrane architecture at 90°C and 25% RH.

Pilot manufacturing trials were run using neat S-Radel® R-5000 (S-PPSU) material in a 20% solids solution in N-methylpyrrolidone. Defect-free, single-layer membranes ranging in thickness from 5 to 100 microns were produced using knife over roll and reverse gravure casting methods in a roll-to-roll format. In addition single layered, membranes of S-PPSU filled with S-POSS were also produced in this roll format. Three-layer membranes where the first and third layers were neat S-Radel® R 5000 and the middle layer S-Radel® R with 20% S-POSS were cast in individual layers of five to 25 microns in caliper using both knife over roll and reverse gravure.

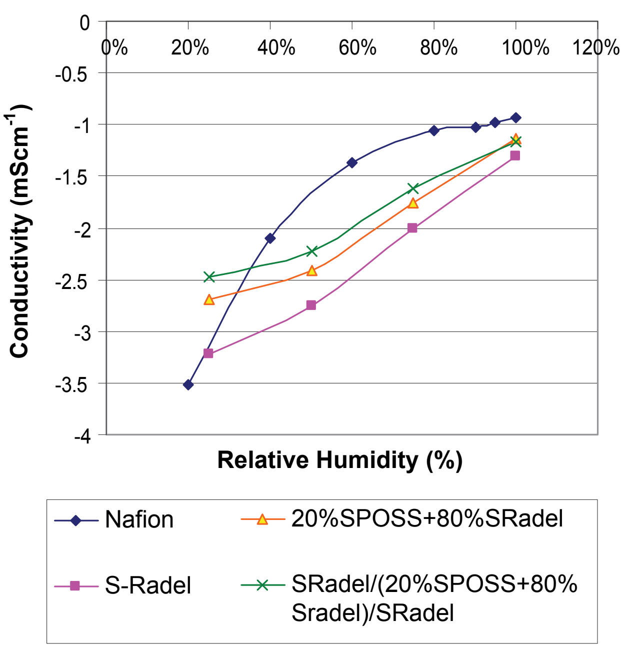

FIGURE 3. Conductivity of the Three-Layer Membrane at 90°C and Varying Humidity Levels

Conclusions and Future Directions

We have successfully demonstrated the ability to sulfonate a highly chemical resistant polyphenylsulfone polymer with ion exchange capacities ranging from 1.5-2.0 and having excellent storage modulus compared to Nafion®. 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 produced conductivities significantly higher than single layer S-Radel® membranes as well as Nafion® at 90°C and 25% RH. In addition dynamic mechanical analysis studies show excellent storage modulus for the multilayered membranes studied. Solution casting methods have been developed that will allow for production of defect-free, roll-to-roll thin (<25 microns) conductive membranes.

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

- Optimization of the synthesis of S-Radel® R 5000 and Sulfonated octaphenylPOSS.
- Optimization of the multiple layered membranes, including increased number of layers and/or concentration of nano-additives within the layers to aid in balance of mechanical properties and proton conductivity.
- Fuel cell testing of the multilayered membranes at temperatures from 90°C to 140°C and various relative humidity levels.
- Optimization of solution casting methodologies to produce high quality multi-layered membrane structures in a 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.

2. U.S. Provisional Patent Application No. 60/967,547. Multilayered Composite Proton Exchange Membrane and a Process for Manufacturing The Same, Pasco R Santurri, Joseph Mausar, James Duvall, Denise Katona. Filed: September 4, 2007.

FY 2008 Publications/Presentations

1. Proton-Conducting Polyhedral Oligosilsesquioxane (POSS) Nanoadditives for sulfonated polyphenylsulfone (S-PPSU) Hydrogen Fuel Cell Proton Exchange Membranes. Claire Thompson, Adrian Merrington, Peter Carver, Douglas Keeley, Joseph rousseau, Dennis Jucul, Steven Keinath, RM Nowak, Kenneth Bruza, Lowell Thomas, Denise Katona, Pasco Santurri, Journal of Applied Polymer Science.

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

3. *Center for Intelligent Fuel Cell Materials Design Phase 1, Poster Presentation at the 2008 Hydrogen Program Annual Merit Review, June 11, 2008.*