

V.B.2 Advanced Hybrid Membranes for Next Generation PEMFC Automotive Applications

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- Nilesh Dale, Nissan Technical Center North America, Farmington Hills, MI
- Steven Hamrock, 3M Company, Fuel Cell Components Group, St. Paul, MN

Project Start Date: October 1, 2013
 Project End Date: September 30, 2016

- Increase HPA loading and organization for maximum proton conduction in two different perfluorinated polymer systems
- Begin the development of electrodes specifically for these membranes so that MEA testing can begin

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

The technical targets are shown in Table 1

TABLE 1. Progress towards Meeting Technical Targets for Membranes for Transportation Applications

Polymer System	DOE ASR Target 2017 $\Omega \text{ cm}^2$	ASR Result June 2015 $\Omega \text{ cm}^2$	Thickness μm	Conditions
System I TFVE-HPA	0.02	0.04	16	80°C 95%RH
System II FC-2178-HPA	0.02	0.01–0.02	10–20	>70°C 95% RH

ASR – area specific resistance; RH – relative humidity;
 TFVE – trifluorovinyl ether

Overall Objectives

- Fabricate a low cost, high performance polymer electrolyte membrane (PEM) that operates at the temperature of an automotive fuel cell stack and requires no system inlet humidification
- Optimize the membrane to meet durability, cross-over, and electrical resistance targets
- Incorporate the membrane into a 50 cm^2 membrane electrode assembly (MEA)

Fiscal Year (FY) 2015 Objectives

- Show that thin heteropoly acid (HPA) films can be fabricated and have a low area specific resistance at the temperature of an automotive fuel cell stack, whilst also functioning as an electrical resistor

FY 2015 Accomplishments

- Analyzed the reaction mechanism of the polymerization of trifluorovinyl ether (TFVE) and showed that the growing polymer chain must rotate; this analysis led to a solvent mediated improvement in the synthesis
- Redesigned the synthesis of the FC-2178-HPA material to increase efficiency and yield moving the polymer platform closer to the DOE cost target of <\$20 m^2
- Showed that the FC-2178-HPA material could be fabricated into films with thickness <20 μm , ASR of <0.02 $\Omega \text{ cm}^2$ and an electronic resistance of >1,000 $\Omega \text{ cm}^2$



INTRODUCTION

The objective of this project is to fabricate a low cost high performance hybrid inorganic/polymer membrane that has a proton ASR $<0.02 \text{ ohm cm}^2$ at the operating temperature of an automotive fuel cell stack (95–120°C) at water partial pressures from 40–80 kPa with good mechanical and chemical durability. Additionally the membrane will be optimized for low hydrogen and oxygen crossover with high electrical ASR at all temperatures and adequate proton ASR at lower temperatures. We also seek to gain valuable insights into rapid proton transport at the lower limit of proton hydration. Additional research will be performed to incorporate the membrane into a 50 cm^2 MEA.

The materials at the start of this project are at a technology readiness level (TRL) of 2, as we have shown that they have proton conductivity under high and dry conditions, but we have not yet consistently shown that they will function in an operational fuel cell. At the project's end the materials will be at a TRL of 4 and will be integrated into an MEA, demonstrating that they can function with electrodes as a single fuel cell. This work will enable hydrogen-powered fuel cells as it will negate the need for costly and bulky external humidification unit operations in the fuel cell system. Additionally excess water will not be an issue for freeze or fuel cell reactant supply. The project is addressing the 2017 DOE technical targets for membranes for transportation applications.

APPROACH

In past funding from the Department of Energy and National Science Foundation (NSF) we have developed completely new ionomer systems based on incorporation of inorganic super acids into polymer systems that have high proton conductivity under conditions of low humidity, higher temperature operation, high oxidative stability, and little swelling when wet. This project will perform the work to optimize the proton conductivity and mechanical properties in these materials to produce a robust thin film for polymer electrolyte membrane fuel cells (PEMFCs). The technical concept is to use functionalized inorganic super acids, which require little water to achieve high proton conductivity, as the protogenic group covalently attached to a polymer backbone optimized for all other functions of the membrane.

Many composite inorganic/polymer films have been fabricated, but unless the inorganic particles have dimensions on the nano-scale, there is no advantage as the improvement to film properties occurs at the particle polymer interface. The limit of this approach is to use molecules with high acidity as the highly activating functionalities, but to do this we must immobilize them, control the morphology of the proton conducting channel, and fabricate an amorphous material. The two moieties that have received the most attention and appear to greatly enhance proton transport are

HPAs and zirconyl phosphonates (ZrPs). In previous work, we demonstrated these materials as composite membranes [1-3], but the inorganic super acid in the membrane was not immobilized. Here, we continue our work to fabricate true hybrid materials where the inorganic super acid is incorporated as a functionalized monomer [4-6]. At the beginning of the project these materials were not yet fuel cell ready, as the syntheses were inefficient and there were no methods of processing the polymers into thin proton conductive films. In this project, we will overcome all of these disadvantages with an innovative approach to amorphous materials to produce high proton conductivity and all other properties desired of a PEM.

RESULTS

Work was performed on two polymer systems that have both shown promising proton conductivities under automotive fuel cell operating conditions. We stopped work on the zirconyl phosphonate system described in last year's report, as we were unable to make the material stable to boiling water despite its high proton conductivity. Progress towards making fuel cell ready membranes for the two remaining systems is described below.

The thermal polymerization of TFVE-derived HPA monomers proved to be very challenging. Many different approaches were investigated, including replicating the heating steps of the base polymerization. To further investigate this system a computational study was initiated. The results from this study are shown in Figure 1, which shows the minimum energy pathway. The mechanism necessitates that the growing polymer chain rotate 180° . Clearly to achieve this the viscosity of the polymerizing system must be reduced. We, therefore, started using a solvent, ethylene glycol, and rigorously excluded oxygen from the reaction vessel. The ^{19}F nuclear magnetic resonance (NMR) is shown in Figure 2. The large central peak is attributed to the desired perfluorocyclobutane moiety that is the result of the polymerization of the TFVE groups. Clearly very few end groups remain and an analysis of the spectrum

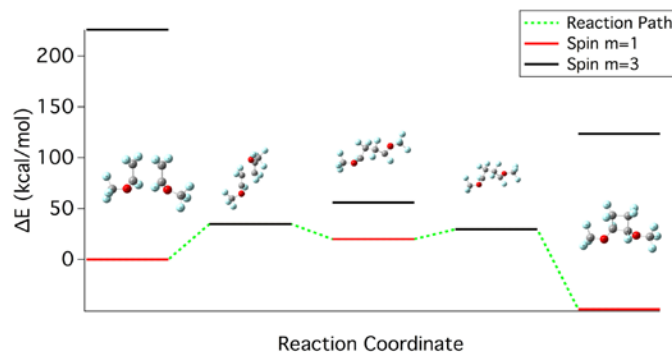


FIGURE 1. Computational study of TFVE monomer polymerization

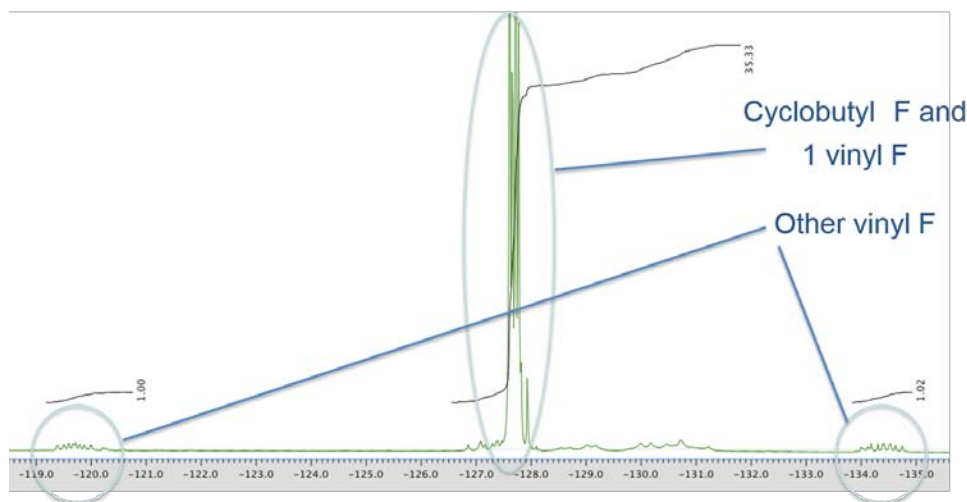


FIGURE 2. ^{19}F NMR of the high MW TFVE-HPA polymer

gives a molecular weight (MW) of $21,500 \text{ g mol}^{-1}$. While this result was very encouraging, we have, to date, been unable to make films from this material. We do feel that due to its very high proton conductivity, it will have utility as an ionomer in the electrode catalysts layer.

The original synthesis of the FC-2178-HPA polymer involved too many manipulations and isolations of the polymer that resulted in poor yields and a very inefficient time-consuming synthesis. In order to fix these issues a convergent synthesis was developed in which more of the key steps were performed on a small molecule precursor. The steps were all standardized and improved to maximize yield and purity. A new method was developed to control the ion exchange capacity, and methods were developed to improve the cross-linking in the membrane. All these improvements have allowed the scale up and synthesis of large area materials for testing by our partners. The materials now have consistently high proton conductivities. Freestanding thick films can be readily made with $\sigma > 0.1 \text{ S cm}^{-1}$ at temperatures above 60°C and 95% RH. Data for one such film with a thickness of $176 \mu\text{m}$ is shown in Figure 3. It has been challenging so far to make this material free standing and so it must be supported. The ASR data of another sample as a $12 \mu\text{m}$ thin film supported on Kapton[®] is shown in Figure 4. The ASR can clearly be seen to be $< 0.02 \Omega \text{ cm}^2$ above 70°C at 95% RH.

A sample of the polymer with a 15 wt% loading of HPA was sent to Nissan USA for baseline testing. From previous work with our Generation I materials we know that $> 50 \text{ wt}\%$ of HPA is necessary to achieve a phase-separated film with adequate proton conductivity. Nevertheless, Nissan USA was able to demonstrate that an MEA could be constructed and tested in fuel cell hardware. Both hydrogen and oxygen crossover were shown to be very low in this film; however, this result could be due to low loading of HPA. It is still a

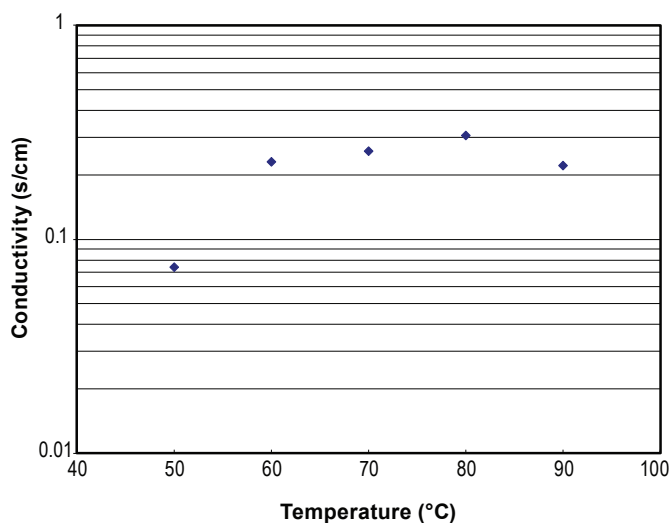


FIGURE 3. Proton conductivity as a function of temperature for a $176 \mu\text{m}$ FC-2173-HPA polymer at 95% RH

very encouraging result that indicates some of the advantages of this system that hopefully will be propagated into the films with practical proton conductivities.

CONCLUSIONS AND FUTURE DIRECTIONS

- Understood how to polymerize TFVE-HPA polymers and demonstrated that high MW materials could be achieved
- Improved the synthesis of the FC-2178-HPA system and showed that films could be produced with high proton conductivity and thin films with low ASR
- Continue to improve the fabrication of thin TFVE-HPA polymers or FC-2178-HPA materials with higher HPA

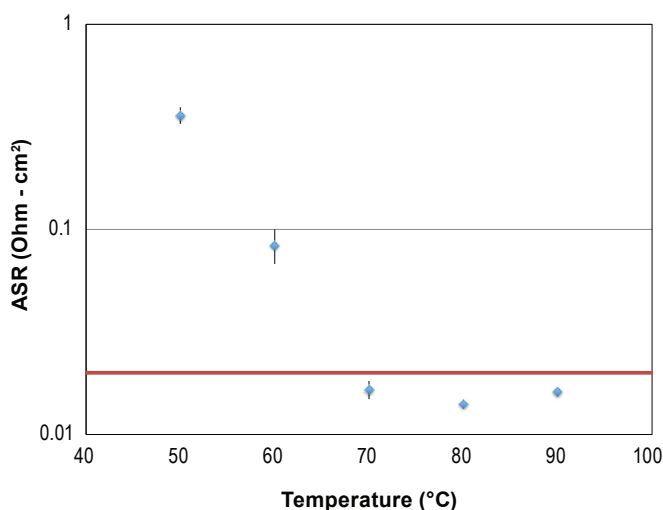


FIGURE 4. ASR of a 12 μm FC-2173-HPA polymer at 95% RH

loadings and incorporate into MEAs for testing and optimization with our partners

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. “Acidic Ion Exchange Membrane And Method For Making And Using The Same.” Gregory J. Schlichting, and Andrew M. Herring, US patent application 13/052,968, March 21, 2011.
US patent 8,906,270 issued December 9, 2014

FY 2015 PUBLICATIONS/PRESENTATIONS

1. “Advanced Hybrid Membranes for Next Generation PEMFC Automotive Applications.”
2. A.M. Herring, J.L. Horan, M.-C. Kuo, and A.R. Motz, oral presentation, presented at CARISMA 2014, Cape Town, South Africa, December 2014.
3. “Synthesis and characterization of water stable, silicotungstic acid functionalized perfluorocyclobutyl polymer electrolyte.” A.M. Herring, J.L. Horan, M.-C. Kuo, and A.R. Motz, poster presentation, presented at 249th ACS Meeting, Denver, CO, March 2015.
4. “Synthesis and Characterization of Water Stable, Silicotungstic Acid Functionalized Perfluorocyclobutyl Polymer Electrolyte,” Andrew R. Motz, Mei-Chen Kuo and Andrew M. Herring, poster presentation, 20th International Conference on Solid State Ionics, Keystone, CO, June 2015.

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