

## V.C.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 and Michael Yandrasits, 3M Fuel Cell Components Group, St. Paul, MN

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Project End Date: July 31, 2017

### Overall Objectives

- Fabricate a low-cost, high-performance proton exchange membrane to operate at the temperature of an automotive fuel cell stack, with excursions to 120°C and requiring no system inlet humidification.
- Optimize the membrane to meet durability, crossover, and electrical resistance targets.
- Incorporate the membrane into a 50-cm<sup>2</sup> membrane electrode assembly (MEA).

### Fiscal Year (FY) 2016 Objectives

- Show that heteropoly acid (HPA)-containing films can be fabricated thin and have a low area specific resistance (ASR) at the temperature of an automotive fuel cell stack and at higher temperatures likely to be operational transients whilst also functioning as an electrical resistor.

- Increase HPA loading and organization for maximum proton conduction in a functionalized commercial fluoroelastomer manufactured by 3M.
- 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

DOE 2020 Target Conditions	2020 ASR Target $\Omega \text{ cm}^2$	ASR Result June 2016 $\Omega \text{ cm}^2$	Film Thickness $\mu\text{m}$	Measured Conditions
120°C and water partial pressures from 40–80 kPa	0.02	0.015	40	110°C and 95% RH
80°C and water partial pressures from 25–45 kPa	0.02	<0.01	10	80°C and 95% RH
	0.02	0.018	40	80°C and 50% RH
30°C and water partial pressures up to 4 kPa	0.03	<0.005	10	30°C and 95% RH

RH – relative humidity

### FY 2016 Accomplishments

- Continued to redesign 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<sup>2</sup>.
- Showed that the FC-2178-HPA material could be fabricated into films with thickness <20  $\mu\text{m}$  and ASR of <0.02  $\Omega \text{ cm}^2$  at a range of temperatures from 30°C to 110°C and RH from 50% to 95%.

- Began work on making large-area reinforced membranes for incorporation into MEAs and fuel cell testing.



## INTRODUCTION

The objective of this project is to fabricate a low-cost, high-performance hybrid inorganic/polymer membrane that has a proton ASR of  $<0.02 \text{ ohm cm}^2$  at the operating temperature of an automotive fuel cell stack (95–120°C) at water partial pressures from 40 kPa to 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 limit of proton hydration. Additional research will be performed to incorporate the membrane into a 50-cm<sup>2</sup> MEA.

The materials at the start of this project are at a technology readiness level 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 technology readiness level 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 2020 DOE technical targets for membranes for transportation applications.

## APPROACH

With past funding from DOE and the National Science Foundation (NSF), we have developed completely new ionomer systems based on incorporation of inorganic super acids into polymer systems. These ionomer systems demonstrate high proton conductivity under low-humidity conditions, as well as 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 proton exchange membrane fuel cells (PEMFCs) in automotive applications. The technical concept is to use functionalized inorganic super acids that utilize little water for high proton conductivity as the protogenic group covalently attached to a polymer backbone optimized for all other functions of the membrane.

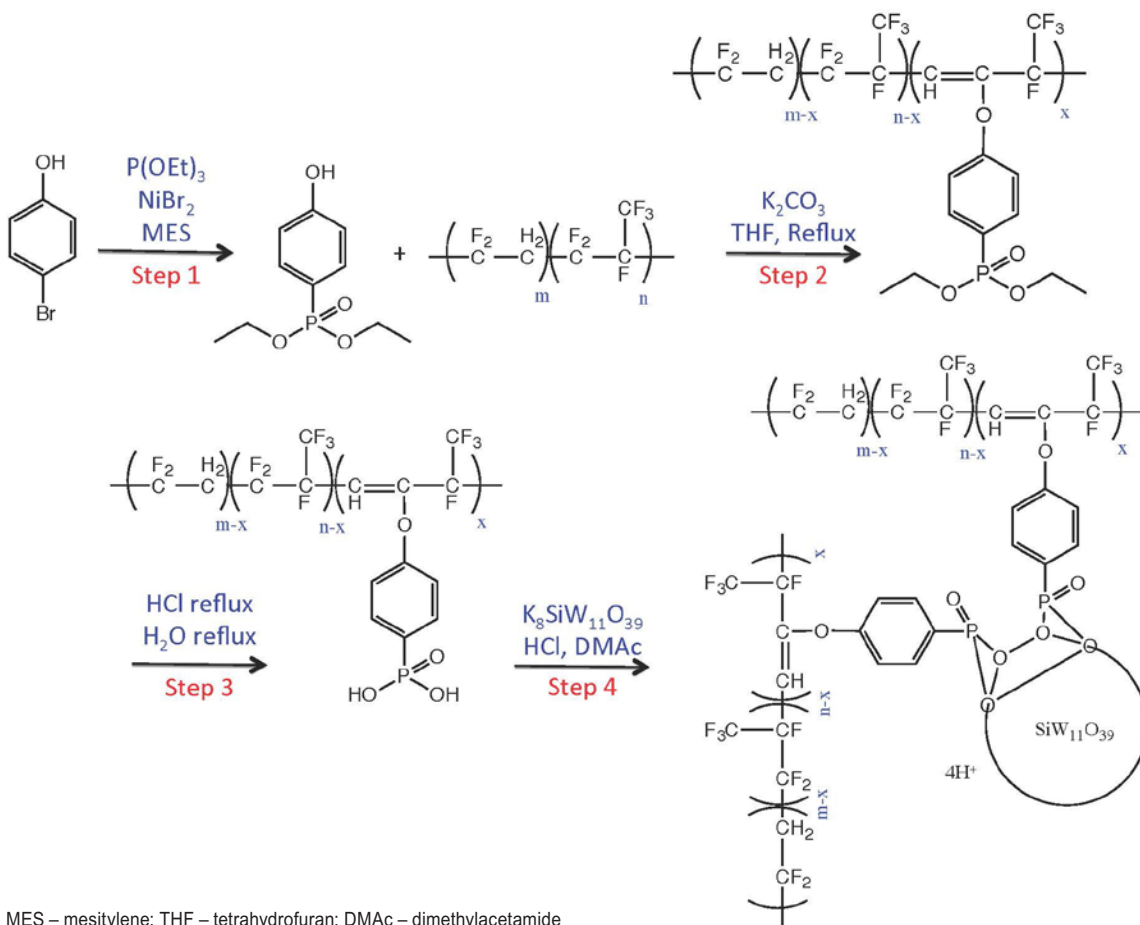
Many composite inorganic/polymer films have been fabricated, but unless the particles have dimensions on the nano-scale, there is no advantage, as the improvement to

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. 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 proton exchange membrane.

## RESULTS

We have now down-selected the materials under consideration to HPA functionalized fluoroelastomers. In Figure 1 we show the current synthesis that has been optimized to increase yield and purity in each step, minimize the total number of steps, and decrease the use of solvents. This not only allows more rapid synthesis of the materials but also facilitates scale-up and should allow the DOE cost targets for the material to be achieved. The key to the synthesis is to first do the functionalization on a small molecule. In step 1, *para*-bromophenol is converted to the *para*-phenol phosphonic diethyl ester. The diethylphosphonic acid is then reacted with the fluoroelastomer under basic conditions where the polymer dehydrofluorinates and is functionalized by the small molecule. This step is a major improvement on the older procedure where the polymer was dehydrofluorinated in a separate step, which led to lack of control of where the phosphonic acid would attach to the polymer. In the third step, the ester is hydrolyzed to the phosphonic acid. Finally, the lacunary HPA ( $\text{SiW}_{11}\text{O}_{39}^{8-}$ ) is added to form cross-linking bonds to the polymer. These last two steps can be performed in one pot. We experienced some difficulties in attachment of the lacunary HPA as we were drying the phosphonic acid functionalized membrane in a vacuum oven, which led to the formation of the unreactive phosphonic anhydride. Fortunately, the anhydride was easily unzipped back to the phosphonic acid by simply boiling the polymer. The resultant film is a transparent brown film of 10–40  $\mu\text{m}$ .

The proton conductivities of these materials at 95% RH and temperatures from ambient to 95°C remain some of the highest observed for polymer electrolytes; recently, values approaching  $1 \text{ S cm}^{-1}$  have been achieved under these



**FIGURE 1.** Improved synthetic route to produce the HPA hybrid materials

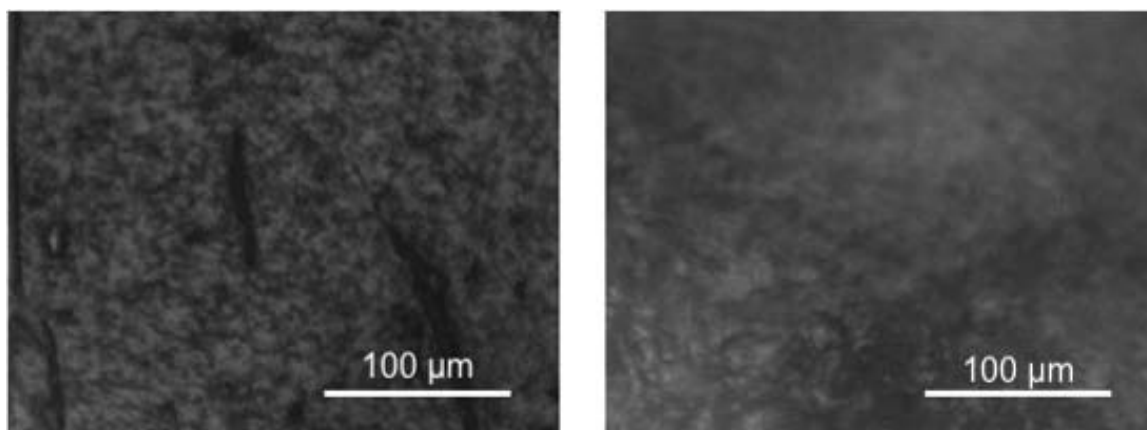
conditions at 95°C. The materials easily meet the DOE ASR targets at 30°C and 80°C, with ASRs at 95% RH < 0.01 Ω cm<sup>2</sup> throughout this temperature range. The objective of this project is low ASRs at higher temperatures and low RHs enabling fuel cell operation at lower partial pressures of water than can currently be achieved. Our initial approach to meet these objectives was to simply increase the HPA loadings from 70 wt% to 80 wt%. At 70 wt% loading, we approached an ASR of 0.1 Ω cm<sup>2</sup> at 110°C and 50% RH; increasing the loading to 80 wt% achieved an ASR at best of 0.03 Ω cm<sup>2</sup>, which was just shy of the DOE target at 120°C and low partial pressure of water. Our emphasis had been on casting 10-μm films; microscopic examination of the films at 10 μm revealed a series of cracks, which could be eliminated by casting 40-μm films (Figure 2). This had a dramatic effect on the ASR. The 10-μm films at 110°C and 50% RH typically had values from 0.03 Ω cm<sup>2</sup> to 0.1 Ω cm<sup>2</sup>, but the 40-μm films all had ASRs lower than 0.02 Ω cm<sup>2</sup> (Figure 3), which satisfied the project's year two go/no-go decision point.

To improve film properties, we have initiated a film processing study. Moderate heat treatment of the material leads to a film that swells only *ca.* 40 wt%, whereas the

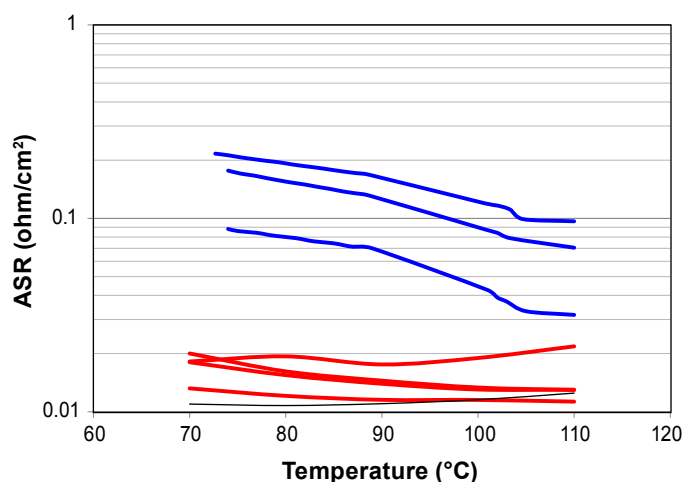
unprocessed films typically swell *ca.* 100 wt%. We believe that the improvements to the film are due to the formation of additional crosslinks in the material as more of the lacunary HPA are bound in a bifunctional manner. Boiling films with 70 wt% loadings of HPA still lose 10 wt% of their mass. Our working hypothesis is that dually bound HPA should be stable to boiling water, so it is obvious from these studies that we still have not perfected the crosslinking process. Nevertheless, boiled films of this chemistry still have exceedingly high ionic conductivities. The final optimized films are expected to be brittle, so we have begun studies to support the material in 10-μm expanded polytetrafluoroethylene. Initial attempts have produced transparent, strong films.

## CONCLUSIONS AND FUTURE DIRECTIONS

- A completely overhauled synthetic scheme has been implemented and now allows the HPA-containing material to be synthesized in scaled-up batches quickly and efficiently.



**FIGURE 2.** Scanning electron microscope images of 80 wt% HPA films: (left) 10  $\mu\text{m}$  and (right) 40  $\mu\text{m}$



**FIGURE 3.** ASRs for 80 wt% HPA films: 10  $\mu\text{m}$  (blue) and 40  $\mu\text{m}$  (red)

- Materials can be boiled with minimal HPA loss, and they give ASRs  $<0.02 \Omega \text{ cm}^2$  under a variety of conditions.
- Further improvements in film processing should yield fully cross-linked and water-stable materials with low ASRs that will meet DOE targets under all conditions.
- In the final year of this project, the material will be integrated into MEAs for testing, and all remaining barriers for membranes for automotive applications will be overcome.

## FY 2016 PUBLICATIONS/PRESENTATIONS

**1.** “Water Uptake in Novel, Water-Stable, Heteropoly Acid Films.” A.R. Motz, J.L. Horan, M.C. Kuo, and A.M. Herring, oral presentation, presented at the 228th ECS Meeting, Phoenix, AZ, October 2015.

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