

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

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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.

FY 2017 Accomplishments

- Detailed processing study that resulted in reproducible 20 μm thin films that were of suitable mechanical robustness for MEA fabrication.
- Showed that in thicker films, 80 μm , that the DOE chemical or mechanical durability targets were easily met.
- Began work towards the fabrication of a 50 cm^2 MEA that meets all the DOE membrane targets simultaneously.



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, cross-over, and electrical resistance targets.
- Incorporate the membrane into a 50 cm^2 membrane electrode assembly (MEA).

Fiscal Year (FY) 2017 Objectives

- Achieve a membrane that meets all the DOE membrane targets simultaneously in the same film.
- Incorporate the material into a sub-scale MEA, 5–10 cm^2 , and test the materials using DOE and NTCNA protocols for chemical and mechanical durability, hydrogen or oxygen crossover, and performance.
- Fabricate a 50 cm^2 MEA for evaluation by the DOE or their designated third party.

INTRODUCTION

The objective of this project was to fabricate a low cost, high performance hybrid inorganic–polymer membrane that had a proton area specific resistance (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 was optimized for low hydrogen and oxygen crossover with high electrical ASR at all temperatures and adequate proton ASR at lower temperatures. We also gained valuable insights into rapid proton transport at the limit of proton hydration. Additional research was performed to incorporate the membrane into a 50 cm^2 MEA.

The materials at the start of this project were at a technology readiness level of 2, as we had shown that they had proton conductivity under high and dry conditions, but we had not yet consistently shown that they will function in an operational fuel cell. At the project's end the materials are at a technology readiness level of 4 and have been integrated into an MEA, demonstrating that they can function with

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

Characteristic/units	2020 Target	Status June 2017	Film Thickness μm	Measured Conditions
120°C and water partial pressures from 40–80 kPa/ $\Omega\text{ cm}^2$	0.02	0.015	10	110°C and 50% RH
80°C and water partial pressures from 25–45 kPa/ $\Omega\text{ cm}^2$	0.02	<0.01	20	80°C and 95% RH
30°C and water partial pressures up to 4 kPa/ $\Omega\text{ cm}^2$	0.03	0.01	20	30°C and 95% RH
H ₂ cross-over, mA/cm ²	2	2.7	20	
Chemical durability, h	<20% OCV loss 500 h	<4% 500+ h	80	90°C/30% RH/O ₂ More severe than DOE test
Mechanical durability 20,000 cycles	H ₂ Cross-over <15 mA/cm ²	H ₂ Cross-over <1 mA/cm ²	80	20,000 wet/dry 80°C

RH – relative humidity; OCV – open circuit voltage

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 addressed the 2020 DOE technical targets for membranes for transportation applications.

APPROACH

In past funding from the Department of Energy/National Science Foundation, we have developed completely new ionomer systems based on incorporation of inorganic super acids into polymer systems, which 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 proton exchange membrane fuel cells 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 heteropoly acids (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 have overcome all of these disadvantages with one down selected materials involving HPAs covalently attached to a commercial perfluorinated elastomer in an innovative approach to amorphous materials to produce high proton conductivity and all other properties desired of a proton exchange membrane.

RESULTS

At this stage in the project we have finished improving the chemical synthesis of the HPA material. At the beginning of the year, the material showed very promising ASR as a thin film but was not mechanically strong enough to meet the other DOE targets for fuel cell membranes. We achieved our first polarization curves by casting a thin film, 10 μm , on a gas diffusion electrode that was used as a support to obtain an MEA for testing. While this gas diffusion electrode supported MEA gave very encouraging results at 70% RH and 80°C, we were still required to produce a free standing film. We therefore cast 80 μm films for testing. The materials were fabricated into MEAs and was tested at the National Renewable Energy Laboratory in a mechanical durability test with 20,000 wet and dry cycles. The film easily met the end of test hydrogen cross-over target, with <1 mA of hydrogen cross-over current, Figure 1 (left), although the performance was not impressive at end of life as the membranes were too thick and the ASR was too high Figure 1 (right). These membranes were also sent to NTCNA for testing in the OCV chemical durability test under dry conditions at 90°C under oxygen. Usually, the incumbent perfluorosulfonic acid membranes, such as Nafion[®] without radical scavengers as additives, in these tests have poor chemical durability and

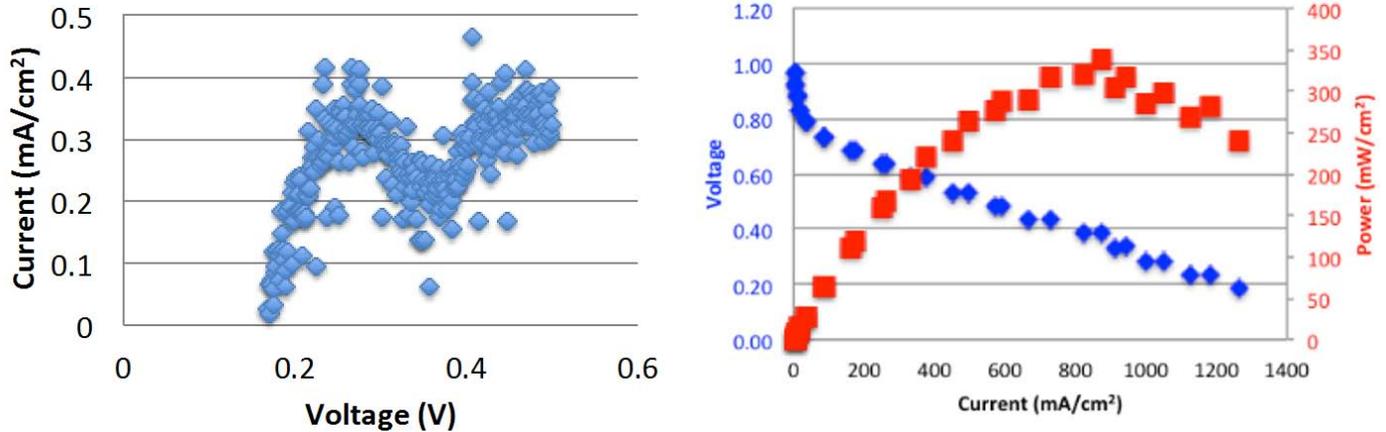


FIGURE 1. Hydrogen cross-over current (left) and polarization curve, 80°C, 100% RH, at end of test (right) for the 70 wt% HPA 80 μm film after the accelerated mechanical durability test, 20,000 wet/dry cycles

fail in the OCV hold evaluation. As shown in Figure 2, the benchmark perfluorosulfonic acid NR-211 membrane fails in the OCV hold test and lasts only 90 hours. In contrast, the CSM HPA 70 wt% 80 μm membrane clearly demonstrates a very strong chemical durability of >500 h without losing <5% of the initial voltage. This durability is remarkable and goes a long way in addressing one of the key challenges of fuel cell membranes. This exceptional durability behavior of the CSM membrane is partly due to its low gas cross-over and partly due to the hydrocarbon–inorganic nature of membrane materials. It is expected that a thinner CSM membrane will continue to exhibit such exceptional chemical durability.

We spent considerable time learning how to process the materials into thin films. The conductivity and ASR for a 20 μm and a 30 μm film at 80°C, 95% RH are shown in Figure 3 (left), and we were even able to fabricate a 10 μm film, Figure 3 (right). Unfortunately, the 10 μm film proved to not be suitable for MEA development and so a series

of 20 μm films were sent to NTCNA. Polarization curves with NTCNA MEAs are shown in Figure 4. The data in Figure 4 (left) using oxygen shows that the HPA membrane outperforms the incumbent perfluorosulfonic acid material. Unfortunately, the data in Figure 4 (right) using air shows that the MEA has severe mass transport limitations. This highlights that the next step in the development of these membranes for vehicular MEAs will need to focus on ionomer electrode development.

CONCLUSIONS AND UPCOMING ACTIVITIES

- 80 μm films of the HPA materials demonstrated that the mechanical and chemical durability tests were easily passed, with the material showing exceptional durability in an OCV test under hot and dry conditions.
- 20 μm films were produced and demonstrated excellent performance in fuel cell testing under humid conditions.
- To achieve materials that will fully function under hot and dry conditions, further innovations will be needed in film processing.
- The full potential of these films will not be realized in fuel cell applications until a comprehensive study of ionomer formulation and electrode design is initiated and completed. The team is now looking for further sponsorship of these efforts.

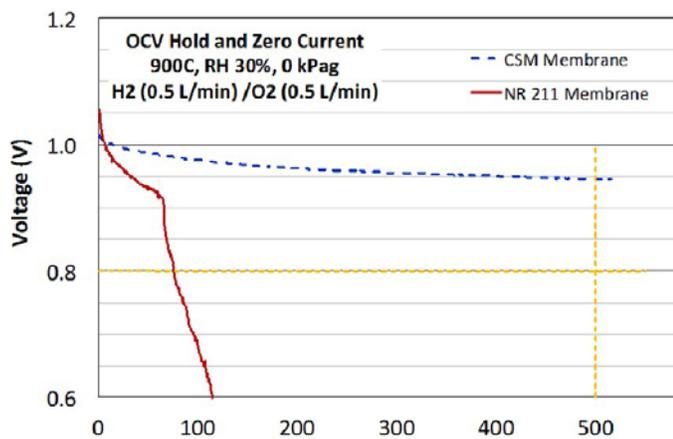


FIGURE 2. Accelerated chemical durability test for the 70 wt% HPA 80 μm film

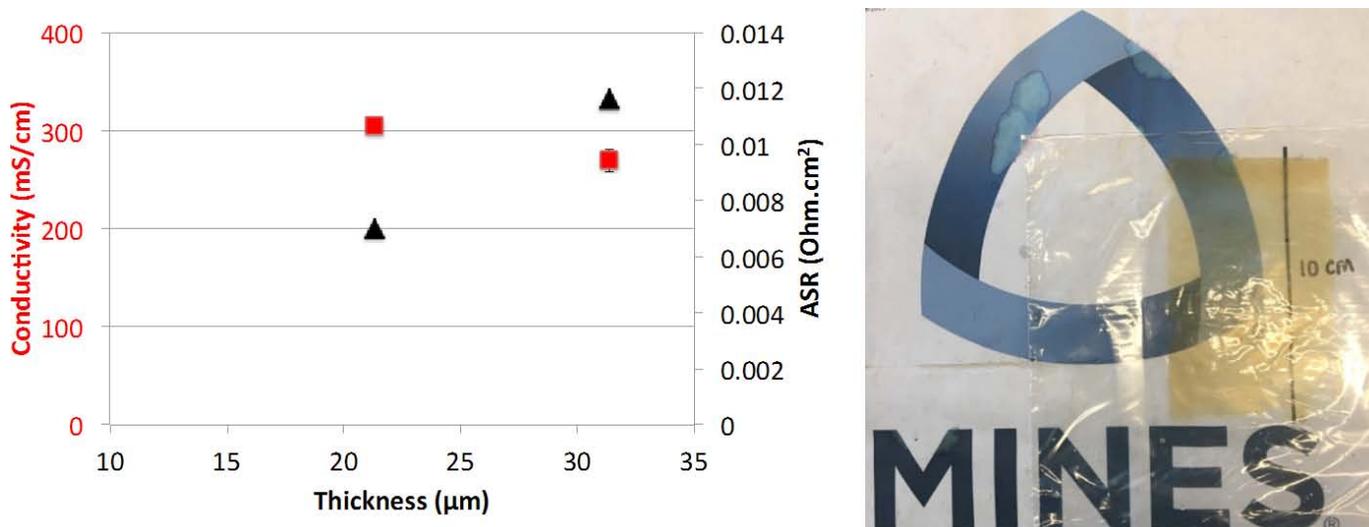


FIGURE 3. Conductivity (red) and ASR (blue) for 70 wt% HPA thin films at 80°C, 95% RH (left) and a large area 10 µm film (right)

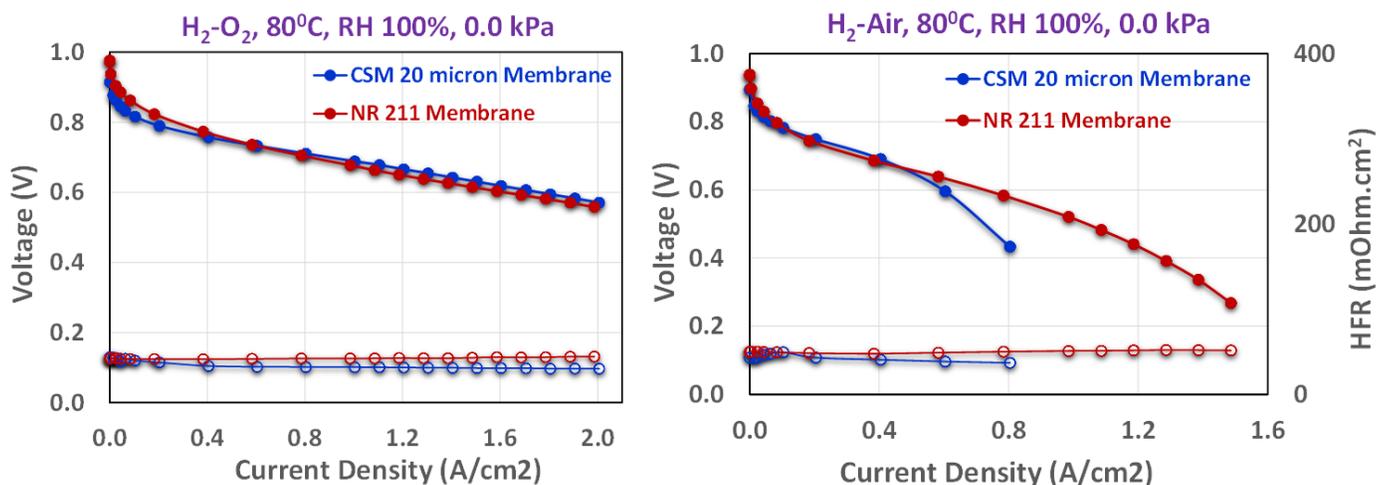


FIGURE 4. Polarization curves for 70 wt% HPA 20 µm film at 80°C, 100% RH, using oxygen (right) and air (left)

FY 2017 PUBLICATIONS/PRESENTATIONS

1. “Developing New Polymer Electrolyte Membranes to Enable Electrochemical Energy Conversion.” A.M. Herring, invited oral presentation presented at Columbia University, New York, NY, April 2017.
2. “Developing New Polymer Electrolyte Membranes to Enable Electrochemical Energy Conversion.” A.M. Herring, invited oral presentation presented at University of New Mexico, Albuquerque, NM, May 2017.
3. “Developing New Polymer Electrolyte Membranes to Enable Electrochemical Energy Conversion.” A.M. Herring, invited oral presentation presented at Sandia National Laboratory, Albuquerque, NM, May 2017.

4. “Using Heteropoly Acids As a Proton Conductor in High Temperature Proton Exchange Membrane Fuel Cells.” A.M. Herring, A. Motz, and M.-C. Kuo, invited oral presentation presented at the 231st meeting of the Electrochemical Society, New Orleans, LA, May 2017.
5. “Advanced Hybrid Membranes for Next Generation PEMFC Automotive Applications.” A.M. Herring, invited oral presentation presented at the Annual Merit Review and Peer Evaluation Meeting (AMR) for the Hydrogen and Fuel Cells Program, Washington, D.C., June 2017.
6. “Membranes for Hotter and Drier Proton Exchange Membrane Fuel Cell Operation Based on the Heteropoly Acids.” A.M. Herring, Andrew R. Motz, Tara P. Pandey, and Mei-Chen Kuo, oral presentation, presented at Solid State Ionics – 21, Padova, Italy, June 2017.

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