

V.D.9 Improved, Low-Cost, Durable Fuel Cell Membranes

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Subcontractors:

- Johnson-Matthey Fuel Cells, Inc., Reading, Sonning Common, UK
- University of Hawaii, Honolulu, HI
- Virginia Polytechnic Institute and State University (Virginia Tech), Blacksburg, VA
- Oak Ridge National Laboratory, Oak Ridge, TN

Project Start Date: September 30, 2007
Project End Date: September 30, 2010

Objectives

- Develop a low-cost membrane capable of operating at 80°C and low relative humidity (RH) (<50%).
- Develop a low-cost membrane capable of operating at temperatures up to 120°C and ultra-low RH of inlet gases (<1.5 kPa).
- Elucidate ionomer and membrane failure and degradation mechanisms via ex situ and in situ accelerated testing.

Technical Barriers

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

- (B) Cost
- (A) Durability

Technical Targets

This project aims at developing low-cost, durable membranes and membrane electrode assemblies (MEAs) according to the 2010 DOE goals:

- Cost: \$20/m²
- Durability: 5,000 hr with cycling

Accomplishments

- Demonstrated and reproduced order-of-magnitude increase in conductivity for M70 lab-produced materials versus M43.
- Completed scale-up of novel monomer to multi-kilo scale for M70 polyelectrolyte (PE) synthesis.
- Identified (and eliminated) cause of PE leaching in initial batches of M70 membranes.
- Identified (and eliminated) cause of defects present in initial batches of M70 membranes.
- Completed successful M70 pilot blend production and membrane casting campaign.
- Demonstrated and optimized blending parameters to incorporate biPhenyl-based disulfonated polysulfone (BPSH)-type PEs into Kynar[®] poly(vinylidene fluoride) (PVDF) blend membranes.



Introduction

Proton exchange membrane (PEM) fuel cells rely on perfluorosulfonic acid containing perfluoropolymers (PFSA) for the construction of the membranes. The cost of these materials is high, largely due to the complexity and the number of steps involved in their synthesis. In addition, they suffer other shortcomings such as mediocre mechanical properties, poor gas barrier properties, and insufficient durability for automotive applications. To overcome these limitations, new membrane chemistries are needed, preferably based on readily available materials that will help keep the cost of commercial production of membranes low. The improvement of the proton conductivity of these materials under low RH conditions will allow for a wider range of operation of fuel cell stacks and reduce the complexity of the balance of plant, leading to lower overall cost and faster adoption of hydrogen fuel cells into automotive applications.

Approach

Arkema's approach comprises the preparation of blends of PVDF and highly sulfonated PEs, in which, the two polymers are very intimately mixed. The originality of this approach is to have a methodology to independently vary material properties that govern ion conductivity from other requirements. Kynar® PVDF provides an exceptional combination of properties that make it ideally suited as the non-sulfonated component in the polymer blend membranes. It exhibits outstanding chemical resistance in highly oxidative environments (such as hydrogen peroxide and bromine), as well as in extreme acidic environments (such as HF, HCl and H₂SO₄). As evidence of the exceptional electrochemical stability and mechanical toughness of Kynar® PVDF, it is widely used as binder material in lithium ion batteries. Also, these novel materials exhibit a design flexibility inherent to their production process and can offer a much lower cost than PFSA-type membranes (at equal production volume) because synthetic requirements and their preparation process is simpler.

Results

The new PE family (M70), is based on novel monomers, each bearing more than one sulfonate group as depicted in Figure 1. This material (PE alone) has an extremely low equivalent weight of ~150 g/molH⁺. When incorporated into a blend with a non-sulfonated polymer (Kynar® PVDF), we have found that an optimum equivalent weight of between 400 and 600 g/molH⁺ is best to produce membranes displaying adequate mechanical properties as well as high proton conductivity. The new materials are hydrolytically stable at 80°C under hydrated, acidic conditions and we have optimized the blending process with Kynar® PVDF and the membrane activation (protonation). The process conditions have been found to significantly influence membrane appearance, morphology, and conductivity.

While the proton conductivity versus RH of M70 is below that of a PFSA-based membrane, particularly at low RH (Figure 2) we understand that ex situ conductivity measurements are only general trend indicators of in situ fuel cell performance. As such, we are moving forward with MEA fabrication and in situ testing of this material. In addition, we expect further improvement as work continues on the synthesis of



FIGURE 1. Depiction of M70 PVDF/PE Blend

this new PE, the blending process and membrane processing/activation.

The PE and the PVDF blend membrane produced using it are hydrolytically stable at 80°C, showing no chemical degradation in ex situ durability tests, but the blend membrane showed signs of sulfur loss due to leaching of the PE during aqueous processing/washing. The leaching was traced back to the synthesis of the PE. Specifically, one of the monomers used was not homogeneously distributed in the copolymer. A kinetic study of the polymerization revealed that this monomer is consumed at approximately twice the rate of that of the other species, and this problem was addressed by optimizing the monomer feed method during polymerization.

It was found that the M70 PE was not an exact 'drop-in' for the process previously used to produce M43 membranes. Therefore the blend formulation parameters were systematically explored to generate membranes with intimately-mixed PE and PVDF components (Figure 3). The new M70 membrane shows very impressive conductivity at 90% RH (>200 mS/cm), but has roughly half of the conductivity of NR-211 at 50% RH. MEA results of lab-produced membranes show that M70 has comparable beginning-of-life performance to PFSA membranes at high and moderate RH conditions at 80°C (Figure 4).

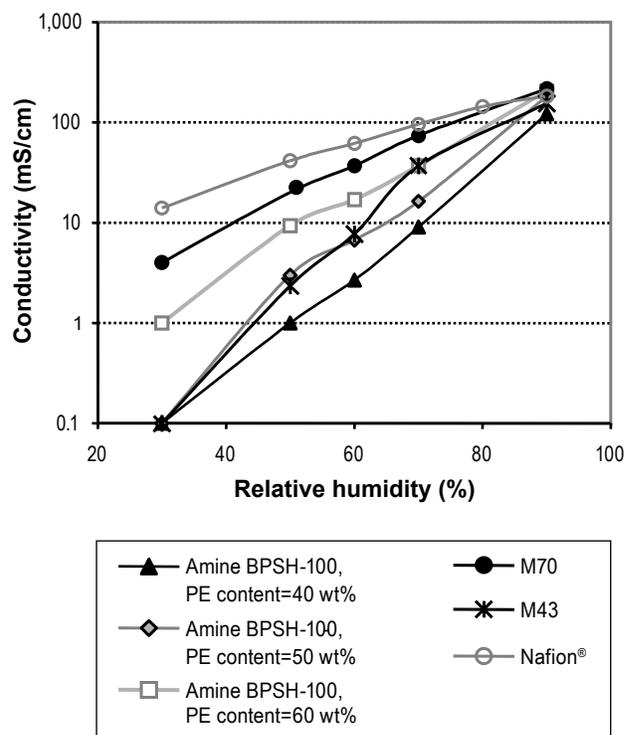


FIGURE 2. Comparison of proton conductivity vs. RH for various Kynar® PVDF/PE blend membranes.

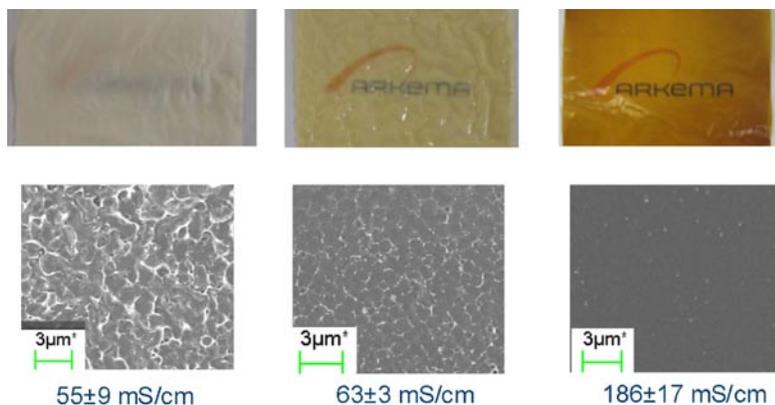


FIGURE 3. Depiction of blending process optimization. Left to right – improved polymer blending. Top row: optical micrographs of membrane samples showing increasing transparency. Bottom row: scanning electron microscopy images of membrane microstructure.

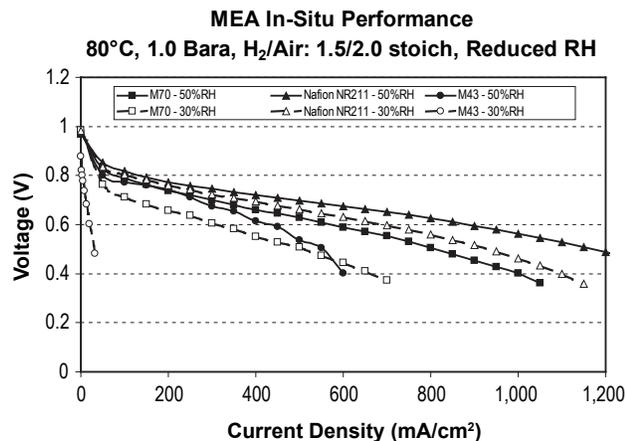


FIGURE 4. MEA performance of Nafion® NR211, M70 and M43 membranes at varying inlet RH.

Based on these promising results, a pilot-scale campaign of M70 was run to perform more detailed studies of its properties, including beginning of life performance, open circuit voltage durability, and RH cycling. Early in the fourth quarter of 2009 we produced kg-scale quantities of M70 PE, which unfortunately produced severe defects in the lab-cast membrane made to qualify the material. After a careful analysis of the materials tested, we traced the problem back to two parameters associated with the polymerization. These parameters were adjusted to make a second kg-scale batch that has not produced any substantial amount of defects. A pilot production run of this material was conducted in May 2010 and is currently under evaluation.

As an alternative to the PE materials generated in-house, polyether-sulfone copolyelectrolytes

(bisphenolsulfone [BPS]-type) have remained interesting due to their extreme thermal stability. BPS materials containing higher sulfonic acid contents (BPS-100) with and without crosslinkable endgroup functionality have been investigated in PVDF-blend membranes for conductivity under varying RH conditions. As these materials have vastly different chemical structures from those used in M43 and M70, reoptimization of blending parameters has been necessary. It was found that intimately-mixed blends of PVDF and BPS-100 without crosslinkable endgroups could be produced under the proper conditions. However, these materials showed a significant amount of PE leaching during processing and operation due to the lack of crosslinking in the BPS-100 materials.

To address the polyelectrolyte leaching, Prof. McGrath's group at Virginia Tech has provided BPS-100 materials bearing amine or alkyne end-group functionality to crosslink the BPS. We have investigated the blending of these materials as well as the concurrent crosslinking during membrane production on the laboratory-scale. We have seen success in reducing the amount of leaching observed using these materials but the conductivities of the membranes are not as high as M70 (Figure 2).

Conclusions and Future Directions

- Evaluated and addressed blending and defect problems in M70 materials.
- Completed successful pilot casting campaign of M70 membrane.
- Confirmed order-of-magnitude increase in conductivity of M70 versus M43.
- Confirmed improved in situ MEA performance under low RH conditions of M70 vs. M43.
- Evaluated and successfully blended BPS-100 materials.
 - Continuing testing of pilot-produced M70 membranes.
 - Continuing process development toward commercialization of M70 membranes.

Special Recognitions & Awards/Patents Issued

1. U.S. Patent 7,629,426 B2 – “Blend of Ionic (Co) Polymer Resins and Matrix (Co) Polymers” – 12/08/09, J. Goldbach.

FY 2010 Publications/Presentations

1. “Improved, Durable, Low-Cost Fuel Cell Membranes” presentation to Freedom CAR Tech Team – Detroit, MI, November 2009 – C. Roger, D. Mountz.
2. “Low-Cost, Durable, Improved Kynar® Fuel Cell Membranes”, 2009 Fuel Cell Seminar & Exposition, Palm Springs, CA, November 2009 –W. He.
3. “PVDF-based Fuel Cells” Fuel Cells: Materials, Challenges, and Break-through – University of Pennsylvania, Philadelphia, PA, September 2009 – D. Mountz.
4. “Improved, Durable, Low-Cost Fuel Cell Membranes” DOE Annual Merit Review – Washington, D.C., June 2010 – J. Goldbach.