

## V.D.12 Improved, Low-Cost, Durable Fuel Cell Membranes

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### Subcontractors:

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

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

### Technical Targets

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

- Cost: \$20/m<sup>2</sup>
- Durability: 5,000 hrs with cycling.

### Accomplishments

#### Membranes

- New M43 membrane developed with improved conductivity (vs. M41) at all RHs.
- Novel membrane (M70) developed based on di-sulfonated monomer-based polyelectrolyte.
- Block polysulfone ether polymers (BPSH)-based polyelectrolytes blended successfully with polyvinylidene fluoride (PVDF).
- The PVDF in the BPSH-based membranes significantly reduced the amount of swelling.

#### MEAs

- M43 passed > 20,000-cycle target in RH cycling test.
- M70 MEA outperformed M41- and M43-based MEAs.
- M70 MEA performance equivalent to NR-211 at high and moderate RH conditions.



### Objectives

- Develop a low-cost membrane capable of operating at 80°C at 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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Cost
- (B) Durability

### Introduction

Proton exchange membrane fuel cells rely on perfluorosulfonic acid (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 some applications.

### Approach

Arkema's approach consists of preparing blends of PVDF and a sulfonated polyelectrolyte. In these blends, the two polymers are intimately mixed. The originality of Arkema's approach is to decouple ion conductivity from the other requirements. Kynar<sup>®</sup> (Arkema's trade name for PVDF) provides an exceptional combination of properties that make it ideally suited for a membrane

matrix. 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 H<sub>2</sub>SO<sub>4</sub>). Due to the exceptional electrochemical stability and mechanical toughness of Kynar® PVDF, it is widely used as matrix material in lithium ion batteries. Also, these novel materials potentially offer a much lower cost than PFSA (at equal production volume) because their preparation process is simpler.

In our previous report, we have described Arkema’s M41 membrane and its properties including its excellent mechanical properties, low permeation to hydrogen, good proton conductivity, and good in situ performance (beginning of life, stability, etc.) at 80°C and 100% RH. The membrane was able to undergo short-term excursions at 120°C and open-circuit voltage hold testing at 90°C and 30% RH had shown improvement (3-4 times) over state-of-the-art PFSA membranes. However, limitations at low RH were shown and a new membrane, M43, has been developed with improved conductivity across the whole relative humidity range (Figure 1).

The process for fabricating this new membrane was validated, and hundreds of feet of high quality (defect-free) membranes were produced on a pilot line. The key relevant physical properties of the M43 membrane are equivalent to those of M41. The performance of the MEAs prepared from M43 is slightly lower than that of NR-211 at 80°C and high RH conditions (Figure 2). The M43 MEA resistance is higher than that of NR-211, as was expected from membrane conductivity data (Figure 1). Although the low RH performance of M43 MEA is improved over M41, it is still insufficient below 70% RH. However, M43-based MEA passed the criteria for RH cycling test (20,000+ cycles, Figure 3).

Considering the limitations described above, we have developed a new family of lower equivalent weight membrane (M70) that contains polyelectrolyte with

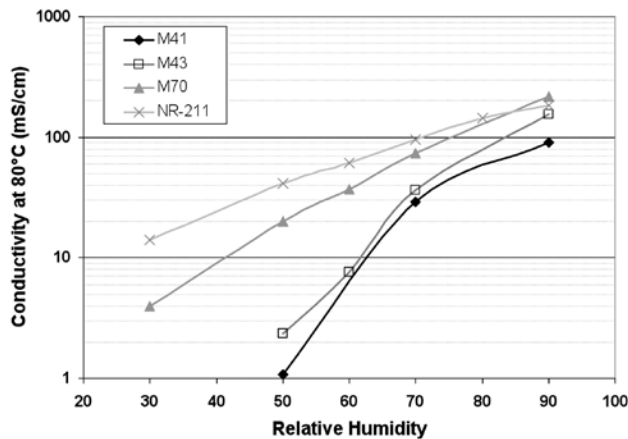


FIGURE 1. Ex situ proton conductivity of M41, 43, 70, and Nafion® NR-211 membranes as a function of RH at 80°C.

two sulfonic acid groups per monomer unit in order to improve both proton conductivity and water retention. The polyelectrolyte is hydrolytically stable at 80°C and we are optimizing the blending process with Kynar® PVDF and the membrane activation. The process conditions have a significant influence over appearance, morphology, and conductivity.

While the performance of the M70 is below that of PFSA-based membrane at low RH in terms of proton conductivity (Figure 1), we have initiated testing of laboratory-produced M70 membranes in MEAs, as we believe that ex situ proton conductivity is not the only factor contributing to MEA performance. M70-based MEA shows a polarization curve comparable to that

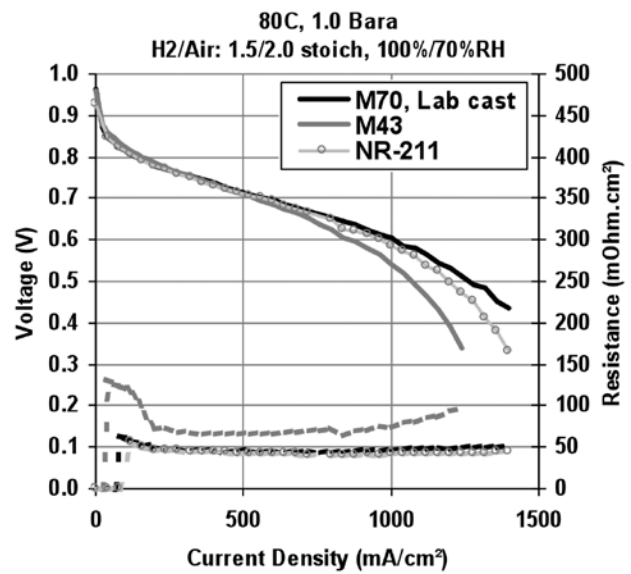


FIGURE 2. Polarization curve of M70, M43, and Nafion® NR-211 at 80°C and high (100/70%) RH.

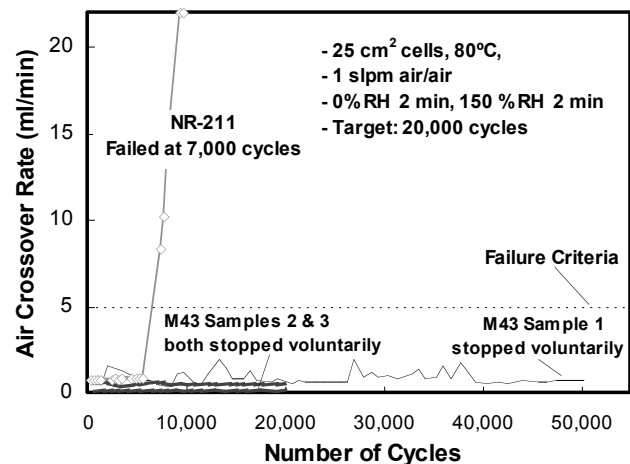
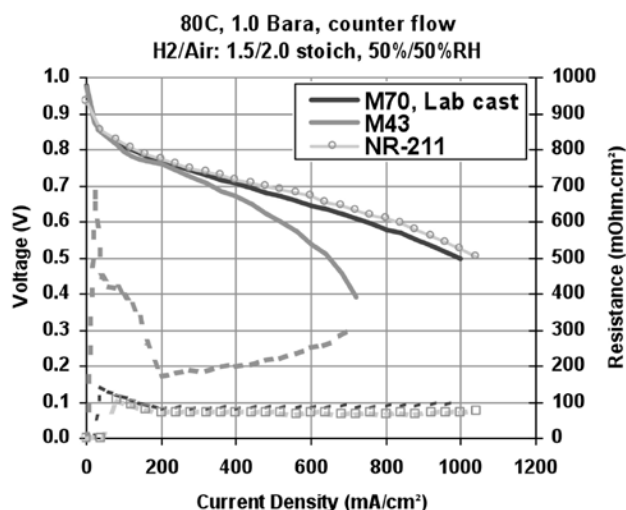


FIGURE 3. RH cycling test for M43 and Nafion® NR-211-based MEA at 80°C.



**FIGURE 4.** Polarization curve of M70, M43, and Nafion® NR-211 at 80°C and moderate (50/50%) RH.

of PFSA-based MEA (NR-211) at high (100/70%) and moderate (50/50%) RH, as illustrated in Figures 2 and 4.

In another area of research, we have successfully prepared membranes by incorporating BPSH60 polyelectrolytes, prepared by our partner at Virginia Tech, in our Kynar® matrix. The swelling in water is significantly reduced in these membranes, but still high enough to compromise the membrane conductivity. We also observed substantial polyelectrolyte leaching and morphology rearrangement. Copolymers with high ion exchange capacity have been shown to have good proton conductivity at low RH but poor mechanical stability and high swelling/leaching. The introduction of the crosslinkable groups into the polymer should address these problems.

## Conclusions and Future Directions

Improved ex situ proton conductivity of new M43 membranes at high RH has led to improved MEA performance over our previous generation (M41). However, the performance below 70% is still insufficient, even though the M43-based membrane passes 20,000+ cycles in RH cycling test.

A new membrane generation, M70, was developed with improved ex situ proton conductivity across the RH spectrum. Laboratory prepared MEAs from M70 membranes showed equivalent performance to PFSA-based MEAs at high (100/70%) and moderate (50/50%)

RH. In parallel, we have successfully incorporated BPSH-based polyelectrolytes in our Kynar® matrix and have shown significant reduction in swelling. However, the effect still needs to be minimized in order for these membranes to have acceptable proton conductivity at low RH.

Based on these results, we will continue to optimize the M70 membrane and activation processes in order to maximize conductivity and MEA performance (especially at low RH). We will also optimize the synthesis of our M70 polyelectrolyte monomer for the purpose of scaling up and preparing pilot line-based membranes for further testing and sampling to Johnson-Matthey. With continued promising results, larger MEAs will be supplied to the University of Hawaii for further testing.

To limit swelling and potential leaching of the BPSH polyelectrolyte, Virginia Tech is developing BPSH-based materials with higher ion exchange capacities containing amine or tetraepoxide functional groups that are suitable for crosslinking. We will incorporate these new materials in our process and evaluate the resulting membrane properties in MEAs as they become available.

We will also study M70 and BPSH-based membrane morphology at Oak Ridge National Laboratory and determine structure/property relationships. New families of polyelectrolytes will be prepared and tested if the performance of M70 and BPSH-based MEAs are deemed insufficient.

## FY 2009 Publications/Presentations

1. “Improved, Low-Cost, Durable Kynar® Fuel Cell Membranes” presentation to the DOE Team – Golden, CO 1/27/2009. M. Foure, J. Goldbach, W. He.
2. “PVDF/Phosphonated Polyelectrolyte Blend Membranes”. Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2009 – Pacific Grove, CA 2/16/2009.
3. “Improved, Durable, Low-Cost Fuel Cell Membranes” presentation to Freedom CAR Tech Team – Detroit, MI 10/07/2008 – J. Goldbach, W. He.
4. “Improved, Low-Cost, Durable Kynar® Fuel Cell Membranes” 2008 Fuel Cell Seminar & Exposition, Phoenix, AZ. Oct. 29, 2008. D. Mountz (Poster).
5. “State-of-the-Art and Challenges in Polymer Electrolyte Fuel Cell Membranes. NIST NSMC joint meeting – Gaithersburg, MD 11/06/2008 – J. Goldbach.