V.B.4 Development of a Low-Cost, Durable Membrane and Membrane Electrode Assembly for Stationary and Mobile Fuel Cell Application

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Subcontractors:

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Objectives

- Develop a low cost, durable membrane.
- Develop a low cost, durable membrane electrode assembly (MEA)
- Validate the MEA performance in single cells and in stacks.

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:

(B) Cost
(A) Durability

Technical Targets

This project aims at developing low cost, durable membranes and MEAs according to the 2010 DOE goals:

- Cost at $40/m^2$.
- Durability at $\leq 80°C$: 5,000 hr. with cycling.

Accomplishments

Membranes

- Synthesized several families of polyelectrolytes.
- Demonstrated the universality of the poly(vinylidenefluoride) (PVDF)/Polyelectrolyte blending process.
- Morphology characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).
- Polyelectrolyte scaled-up to pilot plant level.
- Blending process scale-up to pilot level.
- Membrane fabrication process scaled-up to pilot plant level.
- Good mechanical properties.
- Elucidated failure mechanism of first generation membranes (M31).
- Designed new polyelectrolyte structures that could not undergo the identified degradation mechanism.
- Preparation of new polyelectrolyte and membrane (M40) scale-up to pilot plant level.
- Developed high-throughput methodology for rapid screening.
- Conductivity in the range of 110-140 mS/cm (in water at 70°C).

Membrane Electrode Assemblies (MEAs)

- Confirmed low cost manufacturing potential.
- Initial performance comparable to commercial perfluorosulfonated acid (PFSA)-based MEA (Johnson Matthey).
- Demonstrated low relative humidity operation.
- Excellent impermeability to hydrogen and oxygen.

- Achieved 2,100 hr. endurance test.
- Demonstrated superior performance of new generation (M40) at 80ºC vs. previous generation (M31).
- MEA operated with minimal loss at 120ºC for one hour.

Introduction

Proton exchange membrane (PEM) fuel cells rely on 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 and insufficient durability for some applications.

Approach

In the traditional approach to ionomers for PEMs, all the features required are "packaged" in one macromolecule. They include: proton conductivity, mechanical properties, long-term endurance, water management, etc. This is the case, for example, for PFSA-containing membranes.

Arkema's approach consists in preparing blends of PVDF and a sulfonated polyelectrolyte. In these blends, the two polymers are very intimately mixed. The originality of Arkema's approach is to decouple ion conductivity from the other requirements. Kynar® 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_2SO_4). 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.

Results

The first task is to prepare polyelectrolyte candidates of various architecture, composition, molecular weight, polydispersity, etc. Many such polymers have been prepared and, after blending with Kynar® PVDF, were processed to make membranes.

At Georgia Tech, we are developing high throughput techniques for rapid screening. While the membrane preparation tool is still being developed, the mechanical

and the conductivity screens are complete. Finally, we are also working on a water-vapor sorption high throughput screen. This will allow us to assess water solubility and diffusivity in membranes.

The blending process is key in mixing two highly dissimilar polymers: PVDF for mechanical properties and the polyelectrolyte for proton conduction. Through the use of the Arkema blending process, the nature of these two polymers can vary widely while maintaining compatibility. The process is simple and provides a lower cost route to membrane material design.

Strict control of the resulting blend morphology is required to obtain the high proton conductivity necessary for fuel cell applications. Blending hydrophilic and hydrophobic polymers typically yields gross phase separation of the two polymers as shown on the SEM micrograph in Figure 1a. However, the Arkema process allows for Kynar® PVDF and sulfonated polyelectrolytes to be compatibilized, producing a much finer morphology and yielding excellent proton conductivities as shown in Figure 1b. More detailed TEM analysis of a compatibilized membrane was conducted at Oak Ridge National Laboratory (ORNL). It shows that phase separation still occurs but on a nanometer scale as seen in Figure 2.
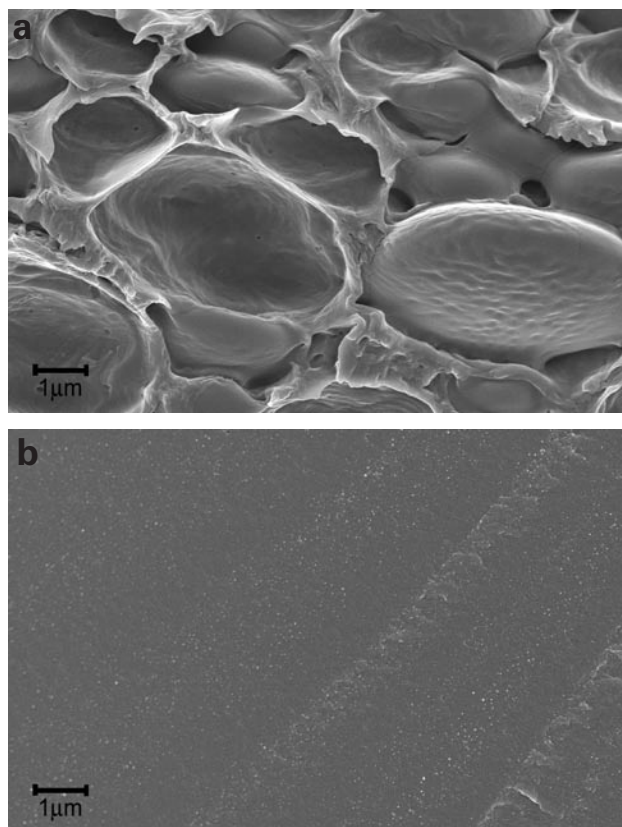

FIGURE 1. 10k Magnification SEM images of (a) Uncompatibilized and (b) Compatibilized Membranes
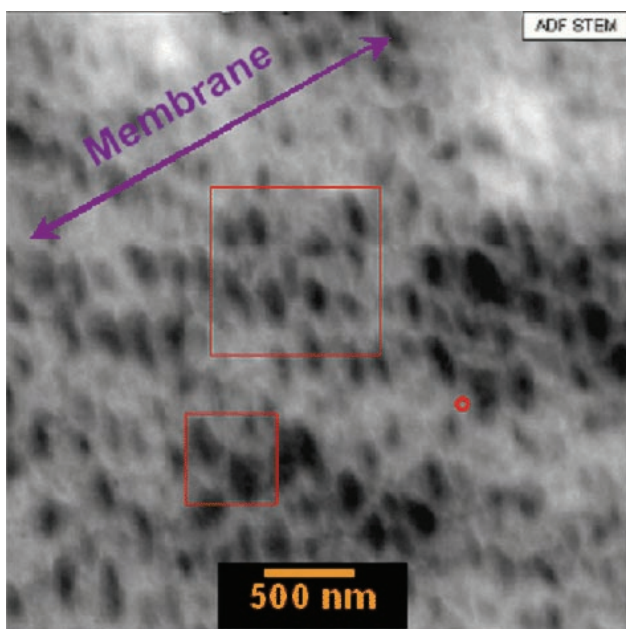
FIGURE 2. High Magnification TEM Image of an M31 Membrane (dark regions are polyelectrolyte domains)

TABLE 1. Physical Characteristics Comparison of PFSA and Arkema M31 Membrane.

Property	PFSA[1]	M31 (25μm)
Conductivity (mS/cm at 70°C, fully hydrated)	180-200	120-150
Areal Resistance ($\Omega \cdot cm^2$ at 25°C)	0.05-0.06	0.02
Tensile Strength (MPa)	36	45
Tear Resistance (gf/mm)	1,100	6,700
Hydrogen Cross-over (mA/cm^2)	1.6 (30 μm)	1.0
Oxygen Cross-over (mA/cm^2)	1.5 (30 μm)	0.8
Water Uptake (%)	37	68
Hot Water Stability (%) (weight loss, 2000 hr., 80°C)	1.8	1.5-3.0
Dimensional Stability (%) (swelling in water x-y)	15	27
Endurance in Fuel Cell (hr) (lab scale)	5,000	2,000 @ 60°C (test stopped)

[1] 50 μm unless otherwise noted

The Arkema process yields very-high quality, uniform, defect-free membranes. The key relevant physical properties of our first generation membrane are presented in Table 1. Mechanical properties are significantly superior to those of Nafion® 112, enabling the use of thinner (25 μm) membranes for MEA fabrication. The M31 membrane yields conductivity values slightly lower than that of PFSA membranes. However, since the optimum thickness for the Arkema membrane is around 25 μm, its areal resistance is lower than that of Nafion® 112 (50 μm). Thus, it is possible to achieve comparable beginning-of-life MEA performance. In addition, the Kynar® PVDF matrix imparts lower oxygen and hydrogen gas crossover compared to PFSA membranes.

The extreme versatility and robustness of the blending process was demonstrated by successfully blending very dissimilar polyelectrolytes with PVDF. With minimal optimization, a large group of polyelectrolytes with significantly different compositions can be blended with Kynar® PVDF. In particular, several commercially available sulfonated polymers were successfully blended with PVDF including poly(2-acrylamido-2-methylpropane sulfonic acid), poly(styrenesulfonic acid), and poly(acrylic acid).

The scalability of the Arkema process was also demonstrated during the development of M31. Over the past few years, ten pilot trials have been conducted yielding thousands of square feet of high quality (defect free) membranes. Membranes in the 15 μm to 50 μm thickness range were produced on a routine basis.

Early in the development process, it was observed that the Arkema membrane is not a drop-in replacement for PFSA materials such as Nafion®. Specific MEA optimization was needed for best performance. After optimization, it was possible to obtain excellent beginning-of-life in-cell performance, comparable to, or greater than that of PFSA as illustrated in Figure 3.

However, while the beginning of life performance of this first generation membrane (M31) was comparable to that of commercial PFSA, the long-term durability was not. A 2,100 hr endurance test was carried out (60°C, oxygen, 550 mA/cm^2), but the decay rate was 45 µV/h. The post mortem analysis showed that the membrane had lost large amounts of sulfur. After thorough investigation, the degradation mechanisms of these membranes are fully elucidated and understood.
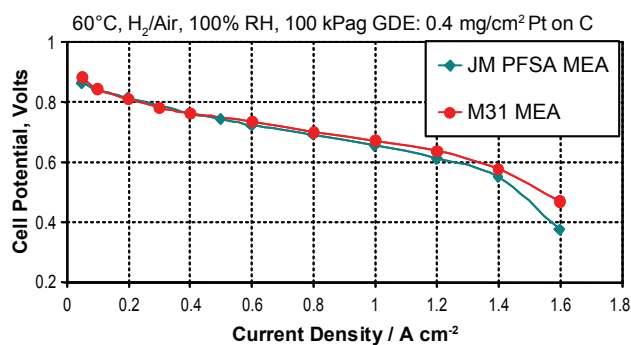

FIGURE 3. Validation of Beginning-of-Life M31 MEA Performance at JMFC

It was shown that the rate and mechanism of degradation are dependent upon the polyelectrolyte architecture and composition. The work done at ORNL was particularly helpful.

A very large effort was devoted to the synthesis of new, proprietary families of polyelectrolytes that could not undergo the same degradation pathways. In parallel, accelerated *ex-situ* tests have been developed to rapidly screen new candidates and identify families with enhanced stability. As shown in Figure 4, polyelectrolytes C and D show much lower rates of degradation. The most promising of these candidates is polyelectrolyte D which, shows no statistically significant increase in degradation products over 2500 hours of testing. The membranes produced with polyelectrolyte D are hereby referred to as M40. M40 has been successfully fabricated on a lab-scale for several months and its measured properties show good reproducibility in *ex-situ* testing.

An MEA based on an M40 membrane has been developed and tested to determine the effect of temperature on the performance as shown in Figure 5.
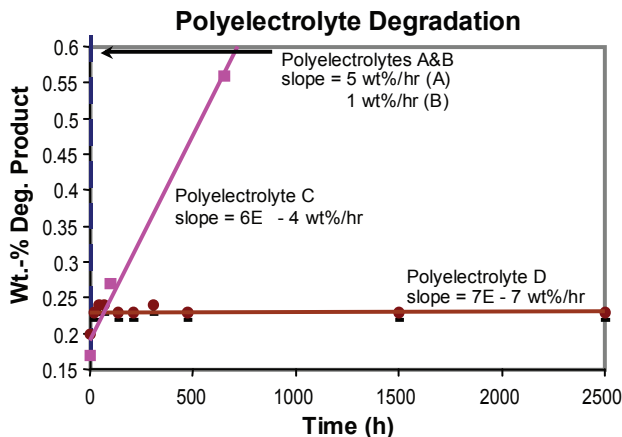

FIGURE 4. Sulfur Loss Data for Different Polyelectrolytes at 80°C
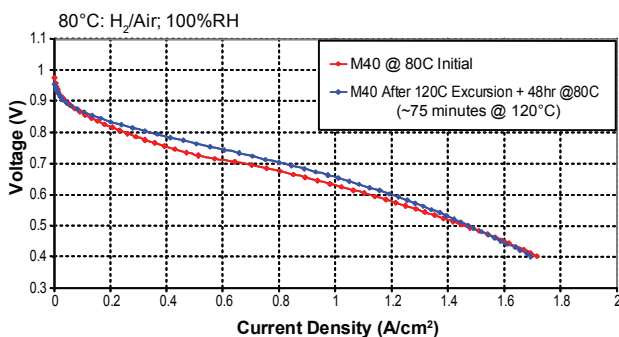

FIGURE 5. Comparison of M40 Performance After 120°C Temperature Excursion for 75 Minutes

No degradation was observed during a 48-hour, 80°C experiment, even after a planned 120°C excursion for 75 minutes. Performance is consistent with the *ex-situ* hydrolysis results shown above. In fact, a slight improvement in performance can be observed, which may be attributed to improved conditioning during the high temperature testing.

Conclusions and Future Directions

Arkema is developing a new membrane. It is based on novel PVDF/sulfonated polyelectrolyte blends. Procedures have been developed for each step of the fabrication process. Due to the low cost of the starting materials and the simplicity of the manufacturing process, the Arkema membrane should be less expensive than commercially available PFSA based membranes. The membrane features excellent mechanical properties and impermeability to hydrogen as well as good proton conductivity. Provided that the composition and manufacturing process of the MEA is adapted for the PVDF-based membrane, good polarization curves were obtained under oxygen or air at 60°C and 100% relative humidity. We showed that the durability is greatly impacted by the quality of the MEA using otherwise the same membrane.

However, the durability of the first generation membrane (M31) was limited (2,000 hr). A great deal of effort was expended to elucidate the failure mechanism in long term testing. It was shown to be linked to migration of polyelectrolyte oligomers as well as cleavage of certain bonds in the polyelectrolyte. A strategy has been developed to prepare new families of polyelectrolytes that should not undergo either failure mechanism.

A considerable effort was devoted to the preparation and testing of such new families of polyelectrolytes. One of them (Polyelectrolyte D) showed particularly promising results in accelerated tests. The membrane constructed with this polyelectrolyte (M40) shows equally encouraging results. In addition, rapid screening techniques were developed to prepare membranes, measure conductivities, mechanical properties and water sorption (Georgia Tech).

Future work will focus on the scale-up of all the steps (monomer synthesis, polymerization, blending, membrane fabrication). Also, the MEA composition and fabrication parameters will be optimized in conjunction with Johnson Matthey Fuel Cells. Accelerated testing (OCV hold, voltage cycling and humidity cycling) will be carried out at Arkema, Johnson Matthey Fuel Cell and/or the Hawaii Natural Energy Institute, depending on the type of test size and configuration of the MEA and cell.

Patents Filed

1. U.S. Patent Filing US 11/409,648. Blend of Ionic (Co) Polymer Resins and Matrix (Co) Polymers. James Goldbach, David Mountz, Robert Umpleby, Julien Parvole, Scott Gaboury. Filed: April 24, 2006.

FY 2005 Publications/Presentations

1. Presentation to the FreedomCAR Tech Team – Detroit, August 10, 2005.

2. Presentation at the 2005 Fuel Cell Seminar – Palm Springs, November 16, 2005.

3. Presentation to the DOE – Washington, D.C., March 2, 2006.

4. J.T. Goldbach, K.L. More, S.R. Gaboury, M. Foure, D.A. Mountz, A.L. Manheim; "Nano-Scale Investigation of Morphologies in Polymer Electrolyte/PVDF Blend Membranes"; Proceedings of the 2006 AICHE Spring Meeting, Presented April 27, 2006, Orlando, FL.

5. Presentation at the 2006 DOE Hydrogen Program Review, Arlington, May 17, 2006.