

V.G.7 Improved, Low-Cost, Durable Fuel Cell Membranes

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Subcontractors:

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

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

Objectives

- Develop a low-cost membrane capable of operating at 80°C at low relative humidity (<50%).
- Develop a low-cost membrane capable of operating at temperatures up to 120°C and ultra-low relative humidity 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) Durability
- (B) Cost

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

- Membranes
 - Down-selected M41 as initial technology platform.
 - M41 exhibits very good mechanical properties and far superior gas barrier properties than perfluorosulfonic acid (PFSA).
 - Fabrication scaled-up to pilot plant level.
- MEAs
 - Demonstrated beginning of life performance on a par with PFSA.
 - Demonstrated short-term 120°C excursions.
 - Achieved 1,000-hr durability test at 80°C, 100% relative humidity (RH) (JMFC).
 - Outperformed PFSA by a factor ~4 to 6 in open-circuit voltage (OCV) Hold Test.
 - Outperformed PFSA by a factor ~3 to 4 in Voltage Cycling Test.
 - Passed successfully 20,000 cycle Humidity Cycling Test.
 - Demonstrated acceptable performance as low as 65% RH.
 - Showed insufficient performance at low RH can be partially mitigated by using thinner membrane.



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 polyvinylidene fluoride (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® (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 extremely acidic environments (such as HF, HCl and H₂SO₄). 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

Under a previous contract, Arkema has developed a body of technology that led to the development of the M41 membrane. The key relevant physical properties of the M41 membrane are presented in Table 1. The mechanical properties are equal or better than those of PFSA 111.

TABLE 1. Physical Characteristics Comparison of PFSA 111 and Arkema M41 membrane.

Property	PFSA ¹ (25µm)	M41 (25µm)
Equivalent weight (g polymer/mole)	1100	800
Specific weight (g/cm ³)	1.8	1.5
Water uptake (%)	37	60
X,Y swell (%)	15	20
Thickness swell (%)	14	10-15
Tensile stress at break (%)	19	27
Elongation at break (%)	103	95
Tear strength (lb _f /in)	404	934
Tear propagation (lb _f)	0.0004	0.018
H ₂ permeation (mA/cm ²) at 80°C	1.5 (30µ)	0.5
Conductivity in water at 70°C (mS/cm)	160	130

¹ 25 µm unless otherwise noted

The scalability of the process was confirmed with M41. Several hundred feet of high quality (defect-free) membranes were produced on a pilot line.

The conductivity of M41 is only slightly inferior to that of PFSA. Thus, it is possible to prepare high

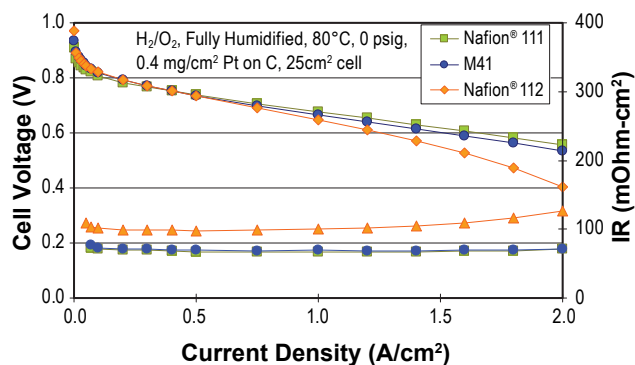


FIGURE 1. Beginning of Life Performance - M41 vs. Nafion® 111 and Nafion® 112

performance MEAs. Figure 1 shows a comparison between M41, Nafion® 111 and Nafion® 112-based MEAs. As expected from the ex situ conductivity measurements, M41 performance is very close to that of Nafion® 111 (25µ) and superior to that of Nafion® 112 (50µ). This experiment was conducted at 80°C under fully humidified conditions.

In an initial test, the capability of M41 to undergo temperature excursions to 120°C was assessed. An M41 MEA was subjected to three consecutive excursions: 2 hr, 3 hr and 3 hr at 120°C. Diagnostics were then run at 80°C. It was observed that the membrane was stable during the test. However, the MEA started to degrade after 5 hr at 120°C. This degradation was attributed to electrode degradation based on a higher oxygen gain and 20% loss of electrochemical area.

A 1,000-hr durability test at 80°C, under static conditions, was run by JMFC. There was no observed performance degradation during the duration of the test.

A series of accelerated durability tests per the DOE and/or U.S. Fuel Cell Council protocols were carried out. In the OCV durability test (illustrated in Figure 2), M41 outperforms PFSA benchmarks by a factor 4 to 6. It is noteworthy that no gas crossover was observed at failure unlike in the case of PFSA. Similarly in the Voltage Cycling Test, M41 exceeded the durability of the PFSA by a factor of approximately 4 (Figure 3). Further, M41 passed the 20,000 cycles RH test where M41 MEA is exposed at 80°C to alternate dry (0% RH) and fully humidified (“150%” RH) two minute cycles.

While many of the features of the M41 are very desirable, its performance at low relative humidity is insufficient. It becomes unacceptably low below 65% RH. The first task in this new project was to diagnose where the problem lies and whether the M41 technology can constitute a suitable starting platform for new membranes capable of operating at low relative humidities while maintaining the many desirable features of M41.

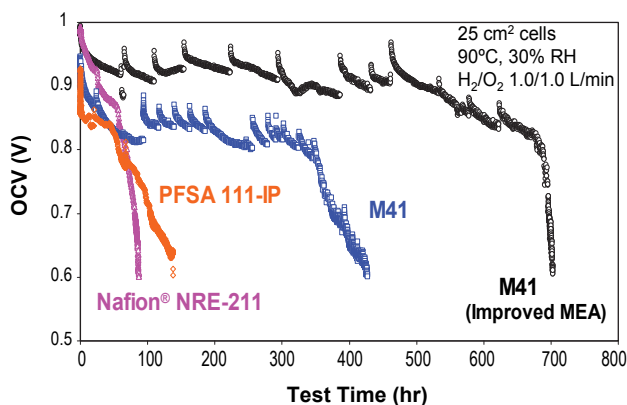


FIGURE 2. OCV Durability Test – M41 vs. Nafion® NRE 211 and PFSA 111 (Ion Power)

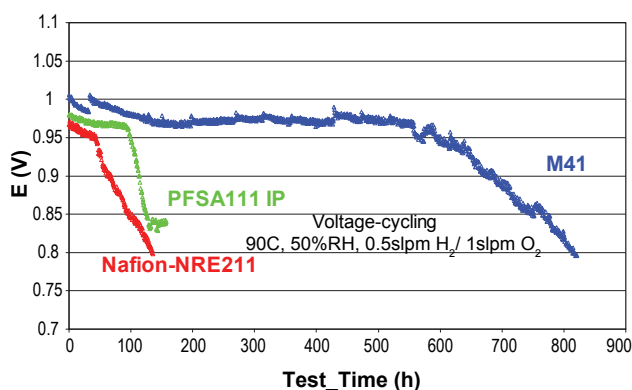


FIGURE 3. Voltage Cycling Durability Test – M41 vs. Nafion® NRE-211 and PFSA-111 (Ion Power)

We first demonstrated that if one electrode is fully humidified (anode or cathode), it is possible to operate with only 25% RH at the other electrode with minimal performance drop (See Figure 4).

Further, the low RH performance of M41 can be significantly improved by the use of thinner membranes (for example 18 μ vs. 25 μ). Incidentally, this improvement is only possible because M41 exhibits very good mechanical properties and outstanding gas barrier properties. It is believed that the back diffusion of the water formed at the cathode across a thinner membrane helps maintain a more hydrated anode. While the improvement is not sufficient to meet the DOE criteria of operability at low RH, we nevertheless concluded that the M41 technology was a good starting scaffold to develop high performance membranes.

Morphology control is one of the key parameters to achieve the goal at hand. By changing the membrane process, we were able to prepare a new membrane (M43) that exhibits significantly improved conductivity: 160 mS/cm (70°C in water). It was further shown that the ex situ conductivity at all RH was significantly

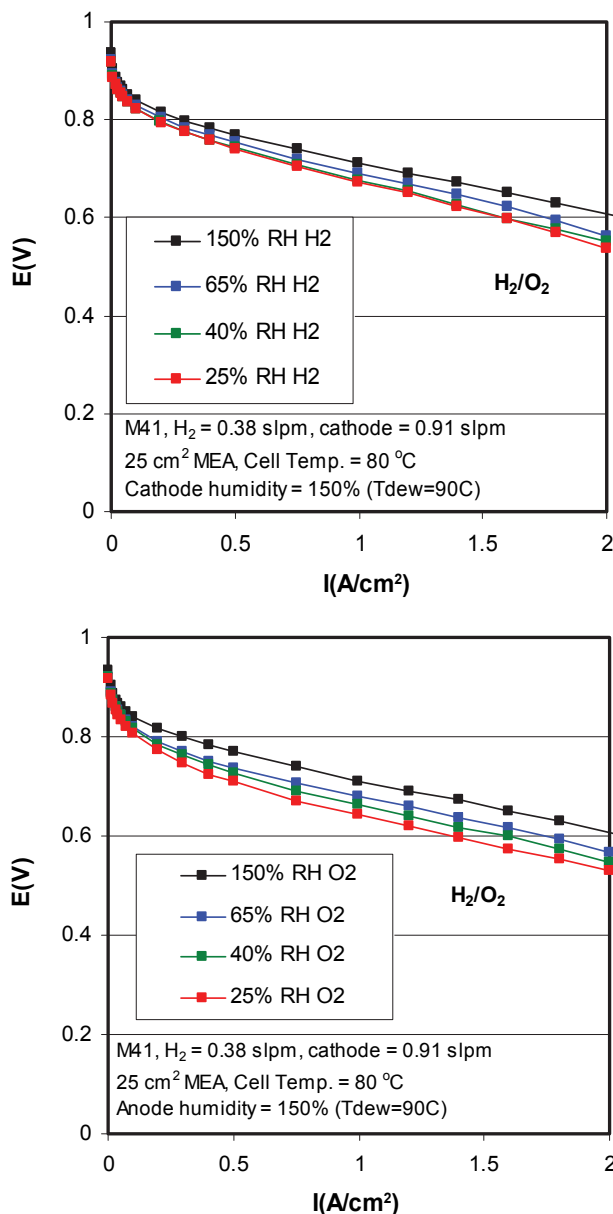


FIGURE 4. Effect of RH on M41 MEA Performance Top: Cathode is Fully Humidified and Anode Inlet RH is Varied, Bottom: Anode is Fully Humidified and Cathode Inlet RH is Varied

improved over M41. Tests are in progress to assess MEA performance.

Another critical parameter is the composition and architecture of the polyelectrolyte. By analogy to phosphoric acid fuel cells which can operate at high temperatures and 0% RH, we incorporated various amounts of phosphonic moieties in the polyelectrolyte. Several candidates were prepared with various ratios of sulfonic acids/phosphonic acids. The polyelectrolytes thus obtained were subsequently blended with PVDF using the Arkema process and the corresponding membranes (M51, M52 and M53) were prepared.

Unfortunately all of these membranes underperformed the M41 benchmark at 80°C as well as 120°C at all relative humidities. This approach has thus been abandoned.

Conclusions and Future Directions

Arkema has developed a novel approach to membrane based on Kynar® PVDF and proprietary polyelectrolyte blends. The overall process is readily scaleable. It should offer lower cost vs. PFSA (at equal volume). The M41 generation features excellent mechanical properties and impermeability to hydrogen as well as good proton conductivity. Good beginning of life performance has been observed at 80°C and 100% RH. The membrane was stable during 1,000 hr at 80°C and 100% RH. It appears to be able to undergo short-term excursions at 120°C. OCV Hold testing at 90°C and 30% RH has shown a 4-6 times improvement versus state-of-the-art PSFA membranes. In the Voltage Cycling Test at 90°C and 50%, the M41 has also a 3-4 times higher durability than PFSA membranes. M41 also passed the 20,000 cycles in the RH Cycling Test.

The limitation of the M41 membrane resides in its inability to function well at low RH. This can be partially mitigated by using thinner membranes. Another key for advanced membranes is the morphology control. Using this approach, a new membrane (M43) featuring improved conductivities across the whole relative humidity range has been developed. In the

next step, we will determine whether the actual M43 MEA performance correlates with the ex situ data. Morphology will be studied at Oak Ridge National Laboratory. An attempt to modify the polyelectrolyte composition by incorporating phosphonic acid functionalities did not provide the expected improvements in conductivity at low RH. Other families of polyelectrolytes are being prepared and will be tested in the next period.

Special Recognitions & Awards/Patents Issued

1. US Patent 7,396,880 – Blend of Ionic (co) Polymer Resins and Matrix (co) Polymers. J. Goldbach, S. Gaboury, R. Umpleby, J. Parvole and D. Mountz.

FY 2008 Publications/Presentations

1. Durable, Low-cost, Improved Fuel Cell Membranes. 2007 Fuel Cell Seminar & Exposition, San Antonio, TX. Oct. 16, 2007. J. Yi, S. Gaboury, J. Goldbach, D. Mountz, T. Zhang, M. Foure (Poster).
2. Low-cost, Durable Kynar® Based Fuel Cell Membranes – J. Goldbach, D. Mountz, J. Yi, T. Zhang, S. Gaboury, M. Foure. 2007 Fuel Cells Durability & Performance Conference – Miami, FL. November 15, 2007.
3. Improved, Low-Cost, Durable Fuel Cell Membranes. J. Goldbach, D. Mountz, T. Zhang, W. He, J. Yi, S. Gaboury and M. Foure. 2008 DOE Hydrogen Program Review Presentations. Washington, D.C., June 10, 2008.