

V.M.5 Development of a Low-Cost, Durable Membrane and Membrane Electrode Assembly for Stationary and Mobile Fuel Cell Application

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Subcontractors:

- Johnson Matthey Fuel Cells, Inc. - West Chester, PA
- UTC Fuel Cells – South Windsor, CT
- Georgia Institute of Technology - Atlanta, GA
- University of Hawaii (subcontractor to UTC Fuel Cells)
– Honolulu, HI

Start Date: October 1, 2003

Project End Date: June 30, 2007

Technical Targets

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

- Cost: Original \$40/m² now modified to \$20/m²
- Durability at ≤80°C: 5000 h with cycling

Accomplishments

Membranes

- Synthesized several families of polyelectrolytes.
- Demonstrated the universality of the poly(vinylidene fluoride) (PVDF)/polyelectrolyte blending process.
- Morphology characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM).
- Down-selected most stable polyelectrolyte based on ex-situ accelerated test (M40 Family).
- 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.
- Developed high-throughput methodology for rapid screening.
- Conductivity in the range of 130-150 mS/cm (in water at 70°C).

Membrane Electrode Assemblies

- Initial performance comparable to commercial perfluoropolymer (PFSA)-based MEA (Johnson Matthey).
- Excellent impermeability to hydrogen and oxygen.
- Achieved 1,000 h endurance test under static conditions at 80°C (Johnson Matthey).
- Demonstrated superior performance of new generation (M41) at 80°C vs. previous generation (M31).
- MEA operated with at 120°C for eight hours with no noticeable membrane degradation.
- MEA outperformed PFSA 111 MEA in the open circuit voltage (OCV) hold test.



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:

- (A) Durability
- (B) Cost

Introduction

Proton exchange membrane (PEM) fuel cells rely on perfluorosulfonic acid containing 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 required membrane properties 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 (Figure 1). 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® 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 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

We have previously reported the possibility of blending Kynar® PVDF – a very hydrophobic fluoropolymer – with proprietary sulfonated

(hydrophilic) polyelectrolytes. This process appears to be very general. The membranes prepared from such blends exhibit good mechanical properties, excellent proton conduction and low permeability to hydrogen and oxygen. They also offer potentially lower cost than PFSA materials.

The first generation membrane M31 exhibited such characteristics but its durability was limited (2,100 h at 60°). The degradation mechanisms were elucidated and a strategy was developed to prepare new families of polyelectrolytes that could not undergo these failure mechanisms. The best candidate was down-selected yielding to the M40s membranes (M40, M41, M42, M43 family). We will concentrate in this report on the M41 membrane.

The Arkema process yields very high quality, uniform, defect-free membranes. Their morphology can be controlled to a large extent by the processing parameters. In turn, it appears that the morphology directly affects conductivity as well as other physical characteristics. Figure 1 illustrates some of the morphology differences achievable as observed by TEM at Oak Ridge National Laboratory (ORNL).

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	130-150

¹ 25µm 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 performance MEAs. Figure 2 shows a comparison

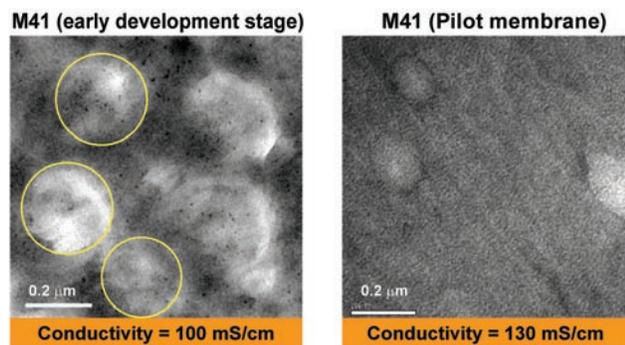


FIGURE 1. Influence on Morphology as Observed by TEM on Ex-Situ Proton Conductivity

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 h, 3 h and 3 h 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 h at 120°C. This degradation was attributed to electrode degradation based on a higher oxygen gain and 20% loss of electrochemical area (ECA).

A 1,000 h durability test at 80°C, under static conditions, was run by Johnson Matthey Fuel cells. As shown in Figure 3, there was no observed performance degradation during the duration of the test.

We have begun to run accelerated durability tests per the DOE and/or US Fuel Cell Council protocols. We have completed the OCV Hold test. M41 was compared to PFSA 111 (from Ion Power). For this

accelerated test, the cell temperature was maintained at 90°C with hydrogen flow with 30% relative humidity (RH). Over the course of the test, the hydrogen crossover rate and the magnitude of electrical shorting though the membranes were measured by the electrochemical crossover test method. Failure in the OCV test is considered to be the time at which the OCV drops below 0.6 V. For the three M41 replicates, times to failure (in hours) were 429, 318, and 430 compared to 62, 138, and 49 for PFSA 111, consistent with literature values for this material. On average, the M41 lasted over 4 times longer than PFSA 111. Both MEA types exhibited a decrease in shorting resistance at the end of the testing, however, the M41 MEAs showed no significant increase in the hydrogen crossover rate at the end of the durability test, while the failed PFSA 111 MEAs all exhibited significant hydrogen crossover. Typical test results are illustrated in Figure 4. Post mortem analysis on PFSA 111 revealed local pinholes likely due to chemical degradation. On the other hand, M41 exhibited no sign of thinning or pinholes at the end of the test, suggesting a different failure mechanism exists for M41 membranes.

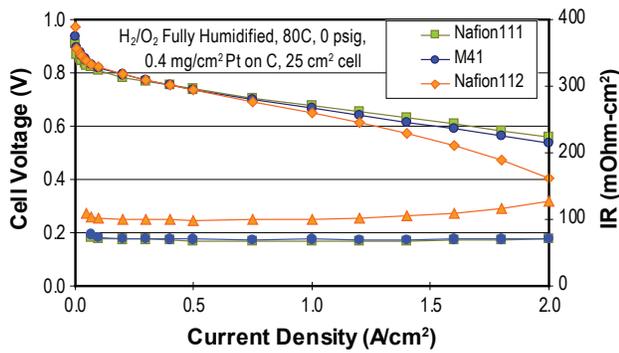


FIGURE 2. Beginning of Life Performance: M41 vs. Nafion[®] 111 and Nafion[®] 112

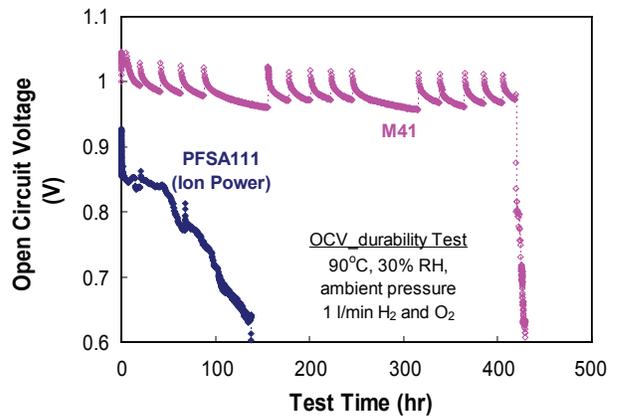
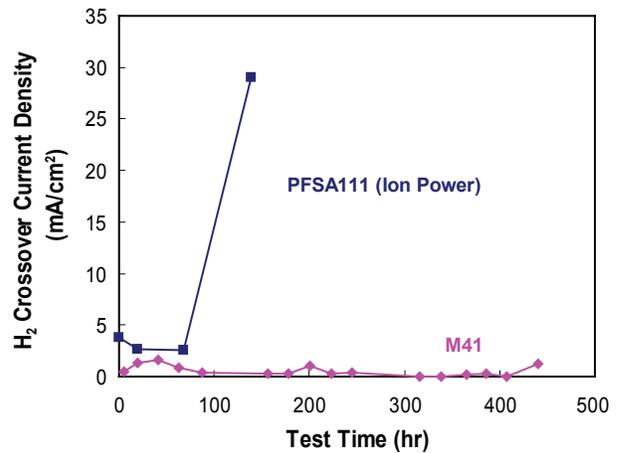


FIGURE 4. Open Circuit Voltage Testing at 90°C, 30% RH
Top: Hydrogen Crossover as a Function of Time; Bottom: OCV as a Function of Time

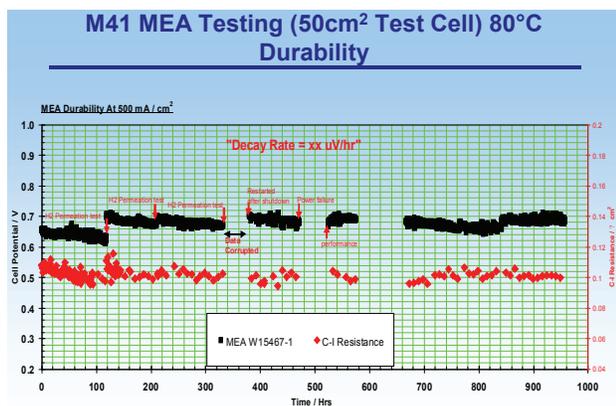


FIGURE 3. Long-Term Durability Testing Under Steady Conditions at 80°C (Johnson Matthey Fuel Cells data)

RH cycling and voltage cycling durability tests are currently in progress.

Other Accomplishments

- Georgia Tech developed novel high-throughput equipment to prepare libraries of Kynar[®] PVDF and polyelectrolyte blends under various conditions and component ratios. Screening technologies were developed to measure water sorption, conductivity and mechanical properties.
- Johnson Matthey Fuel Cells prepared 400 cm² M31 MEAs for large-scale single cell testing at the University of Hawaii using UTC Fuel Cells hardware. While the initial results were inferior to the Johnson Matthey commercial MEA, the capability of making large MEAs was demonstrated.
- Johnson Matthey Fuel Cells developed improved electrodes (HISPEC 9100) to work with the Arkema M41 membrane. With such electrodes, oxygen performance is nearly identical to that of their PFSA commercial MEA. Improved electrodes gave increased performance using air as oxidant, however, slightly lower than the JMFC commercial MEA.

Conclusions and Future Directions

Arkema has developed a novel approach to membranes based on Kynar[®] PVDF and proprietary polyelectrolyte blends. The overall process is readily scaleable. It should offer lower cost vs. PFSA and lower cost vs. PFSA (at equal volume). The latest generation (M41) 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 h at 80°C and 100% RH. It appears to be able to undergo short terms excursions at 120°C. OCV hold testing at 90°C and 30% RH has shown a 3-4 times improvement versus state-of-the-art PSFA membranes.

Future work will focus on completing RH cycling and voltage cycling tests as well as preparing 400 cm² M41 MEAs (Johnson Matthey) for single cell testing in the UTC Fuel Cells hardware at the University of Hawaii.

A limitation of the M41 membrane family is its ability to function well at low RH. This is a major objective of a new award (Pending Award Number: DE-FG36-07GO17008) to work in this area.

Patents Issued

1. European Patent No 1,455,408. “Method for Preparing Membrane Electrode Assemblies” L. Hedhli, K. Adjemian, T. Culp, G. Silverman.

FY 2007 Publications/Presentations

1. “Combination toolkit for PEM development”, AIChE National Meeting, San Francisco, CA, November 2006, Poster presentation. Meredith, J.C.; Reed, Keith; Zapata, Pedro; Basak, Pratyay.
2. “Development of a Low Cost, Durable Membrane and Membrane Electrode Assembly for Fuel Cell Applications”, 2006 Fuel Cell Seminar, Hawaii, November 2006, Oral presentation. S. Gaboury, M. Foure, J. Goldbach, D. Mountz, J. Yi, S. Mullapudi, J. Reinkingh, J. Smith (S. Gaboury).
3. “Development of Low –Cost, Durable Membrane and MEA for Stationary and Mobile Fuel Cell Applications”, J. Yi, D. Mountz, J. Goldbach, T. Zhang, S. Gaboury and M. Foure. (J. Yi) 2007 Annual Merit Review & Peer Evaluation. Washington, D.C., May 16, 2007.