

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

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Projected End Date: September 30, 2006

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

Technical Targets

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

- Cost: \$40/m²
- Durability at $\leq 80^{\circ}\text{C}$: 2,000 hr with cycling

Cyclic testing conditions were added subsequent to testing our first set of membrane candidates. We have achieved 2,000 hr durability under steady-state conditions and intend to incorporate cycling into all new membrane testing in the future. Cost projections for our polyvinylidene fluoride (PVDF) blends are consistent with the DOE target.

Approach

- Develop new material for membranes based on polyvinylidene fluoride/polyelectrolyte blends.
- Develop a process to make fuel cell membranes from these materials.
- Develop MEAs based on these novel membranes.

Accomplishments

Membranes

- Increased membrane conductivity from 100-130 mS/cm to 130-200 mS/cm (in water at 70°C).
- Improved conductivity at reduced relative humidities.
- Achieved good mechanical properties in the dry state.
- Process scaled up to the pilot plant.
- Developed high-throughput methodology for rapid screening.

Membrane Electrode Assemblies (MEAs)

- Initial performance comparable to commercial perfluorosulfonated acids (PFSA)-based MEA (Johnson Matthey).
- Demonstrated low relative humidity operation.
- MEA has excellent impermeability to hydrogen and oxygen.
- Achieved 2,100 hr endurance test. However, after 2,100 hr, the MEA was degraded (the failure mechanism was studied and is now understood; it is related to the polyelectrolyte chemistry).

Future Directions

- New families of polyelectrolytes (that cannot undergo the failure route observed in previous generations) will be synthesized.
- Prepare modified membranes using improved polyelectrolytes.
- Characterize membrane/MEA microstructure (Oak Ridge National Laboratory).
- Confirm improved MEA durability in a fuel cell.
- Begin MEA optimization based on new membranes (Johnson Matthey).
- Generate fuel cell data under UTC Fuel Cells protocol (University of Hawaii).

Introduction

Proton exchange membrane (PEM) fuel cells rely on perfluorosulfonated acids (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

The team lead by Arkema examines the feasibility of using materials based on PVDF/polyelectrolyte blends for the membrane. PVDF

exhibits an exceptional combination of properties, most notably mechanical, chemical and electrochemical properties. For example, Kynar[®] (Arkema's trade name for PVDF) is used in the chemical industry in very difficult environments such as hydrochloric (HCl) and hydrofluorhydric (HF) acids. It is also extensively used in lithium ion batteries, where PVDF "sees" a potential up to 4.2 V. These novel materials offer potentially a much lower cost than PFSA (at equal production volume) because their preparation process is simpler. However, because they are new and different from existing PFSA, each step must be revisited and optimized. This is particularly true for the composition of the MEA and its preparation process.

Indeed, nearly all MEAs used in prototypes today rely on PFSA and years of optimization that have gone into their fabrication.

Results

The first task is to prepare polyelectrolyte candidates of various architectures, compositions, molecular weights, polydispersity, etc. Many such polymers have been prepared and, after blending with Kynar[®], 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 screen is complete. The conductivity screen has been validated and the apparatus is now operational. 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 of the PVDF with the polyelectrolyte is now nearly optimized and is very reproducible on a laboratory scale. Several classical polymer film processes such as extrusion, water borne casting (from latex) and solvent casting have been studied. The process has been run several times at pilot plant scale and its excellent reproducibility demonstrated. Most of the pilot trials were carried out to produce membranes in the 17 to 50 μ range. Quality control demonstrated that the membrane quality is very consistently high. The activation step (acidification + rinsing) has been optimized at a lab scale. Specialized equipment will be needed for pilot scale-up. This equipment has been designed, and quotes have been obtained for its construction.

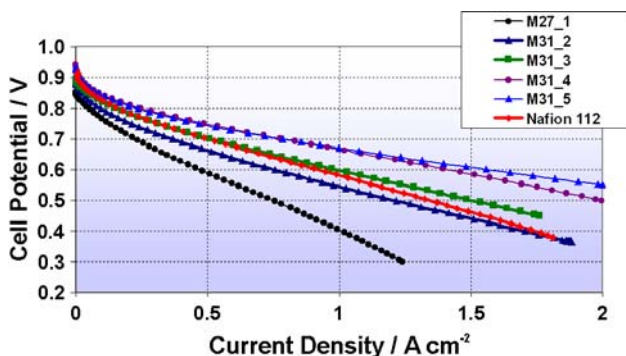


Figure 1. Performance Improvement in Successive MEA Generations Using the Same Membrane (M31)

We continued to improve the conductivity of the membrane, typically achieving 130-200 mS/cm at 70°C in water. We also improved conductivities at reduced relative humidities. However, the performance in these conditions remains inferior to that of PFSA.

We have also continued to improve the quality of our MEAs. As the membranes are chemically and physically different from PFSA membranes, we found that they require specific optimization. Figure 1 illustrates the progress achieved (with the same membrane) on successive generations of MEAs. Key parameters include assembly parameters (such as temperature, pressure, contact time) and the composition of the gas diffusion layer. For this work, electrodes have been sourced from Johnson Matthey and E-TEK (see Figure 2).

However, while the short-term durability of the Kynar[®]-based MEAs appears to be comparable to that of the PFSA-based MEAs in oxygen or air, long-term durability is not. A 2,100 hr endurance test was carried out (60°C, oxygen, 100% relative humidity, 550 mA/cm²), but the decay rate was 45 μ V/h. A very detailed post mortem analysis was performed. The analysis showed that the membrane had lost large amounts (30-50%) of sulfur – that is equivalent to the sulfonic acid loss.

A very large effort was devoted to elucidate the failure mechanism. It was unambiguously established that the sulfur loss mechanism was due to migration of polyelectrolyte oligomers and to hydrolytic cleavage of a particular bond yielding to the loss of the sulfonic acid moiety. It is also

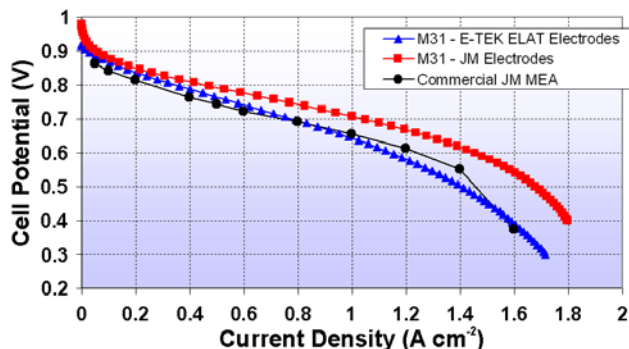


Figure 2. Polarization Curve of M31-Based MEA Using Johnson Matthey and E-TEK Electrodes vs. a Commercial MEA from Johnson Matthey

noteworthy that a cooperative effort with Oak Ridge National Laboratory has started to help characterize degradation and morphology changes in the Arkema membrane/MEA associated with process parameters and long-term testing.

As measured at Johnson Matthey, we found out that hydrogen permeability of the Arkema MEA is about one-third that of PFSA. Similarly, oxygen permeability is about one-half that of PFSA.

Armed with this information, we designed accelerated tests to rapidly pre-screen polyelectrolyte candidates. We also designed several strategies to prepare membranes that should not undergo the decay mechanism described above. This is now the focus of our effort for the coming year.

Conclusions

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 hydrogen and oxygen or air at 60°C and 100% relative humidity. We showed that the durability is greatly impacted by the quality of the MEA. However, at this early stage, the decay rate is still one order of magnitude too high: 45 μ V/h over a period of 2,100 hr.

Considerable effort has been 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. In addition, rapid screening techniques were developed to prepare membranes and measure conductivities, mechanical properties and water sorption.

Future work will focus on the synthesis and scale-up of new, stable polyelectrolyte families. Improved membranes and MEAs will be prepared and evaluated. The electrode and electrode catalyst optimization work will continue. The preparation of the promising candidates with respect to improved proton conductivity and durability will be scaled up. We will also continue to work on the membrane manufacturing and scale up the activation process. Johnson Matthey will address the MEA composition and manufacturing process, as both needs to be optimized for the membrane. UTC Fuel Cells will become more involved in the validation when suitable MEAs become available.

FY 2005 Publications/Presentations

1. Presentation at the 2004 Fuel Cell Seminar - November 3, 2004, San Antonio, TX.
2. Quarterly Review Meeting - January 6, 2005, Washington, D.C.
3. Presentation for the Argonne National Laboratory Tech Support Meeting - January 10, 2005.
4. Presentation at the 2005 DOE Hydrogen Program Review - May 24, 2005, Washington, D.C.