# V.M.1 Improved, Low-Cost, Durable Fuel Cell Membranes

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#### Subcontractors:

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

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## **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/m<sup>2</sup>
- Durability: 5,000 h with cycling



# **Approach and Background**

In the traditional approach to ionomers for proton exchange membranes (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 perfluorosulfonic acids (PFSA) containing membranes.

Arkema's approach consists in preparing blends of poly(vinylidenefluoride) (PVDF) and a sulfonated polyelectrolyte (Figure 1). In these blends, the two polymers are very intimately mixed. The originality of



FIGURE 1. Arkema's Blended Membrane Approach

Arkema's approach is to decouple ion conductivity from the other requirements. Kynar<sup>®</sup> 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<sup>®</sup> 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.

A first generation Kynar<sup>®</sup>-based membrane (referred to as M31) was previously developed and tested at Arkema. During this development process, significant insight into, and optimization of the blending process was achieved. In addition, optimization of MEA structures was accomplished, showing that Kynar<sup>®</sup>-based membranes can have beginning-of-life performance equivalent to Nafion<sup>®</sup>. Upon extended testing of these first-generation materials, however, an unacceptable decline in fuel cell performance was observed (Figure 2) and traced unequivocally to a particular chemical structure within the polyelectrolyte. Building on knowledge acquired during M31 development, the production and testing of new generations of blended membranes incorporating polyelectrolytes devoid of the problem structure was rapidly accomplished. The most promising of these generations is referred to as M41, which also exhibited the excellent beginning-oflife performance but with dramatically improved ex-situ and *in situ* stability, as illustrated in Figures 2 and 3, respectively.

#### **Project Plan**

While M41 exhibits excellent beginning-of-life performance at higher relative humidities (>50%) and excellent accelerated durability, performance at lower relative humidities (<50%) is not sufficient to meet the 2010 DOE performance targets. Thus, this project



FIGURE 2. M31, M41 and Nafion® Ex-Situ Chemical Stability



FIGURE 3. OCV hold Performance to Measure M41 and PFSA *In Situ* Accelerated Chemical Stability

is aimed at developing a modified membrane with enhanced performance at lower relative humidities and higher temperatures. The basic project concept builds on the PVDF/polyelectrolyte blending technology described in previous sections. Figure 4 explains the proposed project workflow for the development of improved fuel cell membranes.

The first three steps in the project workflow shown above call out the major challenges of this project:

- The polyelectrolytes developed will have to be compatibilized into a PVDF matrix. Polyelectrolytes designed for the highest temperature/lowest humidity conditions will incorporate protogenic groups capable of operation in ultra-low to zero humidity conditions (i.e., non-sulfonic acid). These groups will also be bound to the polyelectrolyte to avoid leaching observed in other high temperature membranes.
- The membranes developed with these new polyelectrolytes will need to exhibit high proton conductivity and excellent durability. The morphology formed during membrane preparation will need to be understood and controlled to achieve the necessary conductivity. Accelerated durability methods will be required to rapidly screen materials and identify potential degradation mechanisms.
- MEA development will focus on the challenges of the entire system durability under low humidity and high temperature conditions. Degradation

Polyelectrolyte - Membrane Development Development	MEA Development	In-cell Durability Testing	◆ MEA Post-Mortem Analysis
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FIGURE 4. Project Workflow for Polymer Electrolyte Membrane Development

mechanisms associated with catalysts, supports, and gas diffusion layer components will need to be measured by accelerated cyclic testing and separated from potential degradation issues associated with the membrane.

The project team has been assembled to ensure the core competencies needed to meet these challenges are present.

# FY 2007 Publications/Presentations

1. "Improved, Low-Cost, Durable Fuel Cell Membranes" M. Foure. Fuel Cell Project Kick-off Meeting, Washington, D.C., February 13, 2007.

2. "Improved, Low-Cost, Durable Fuel Cell Membranes",

S. Gaboury, J. Goldbach, D. Mountz, J. Yi, M. Foure, K. More, J. McGrath (S. Gaboury), Poster at the 2007

Annual Merit Review & Peer Evaluation. Washington, D.C., May 17, 2007.