

# V.G.15 High Temperature Membrane with Humidification-Independent Cluster Structure

Ludwig Lipp (Primary Contact), Pinakin Patel,  
Ray Kopp  
FuelCell Energy (FCE), Inc.  
3 Great Pasture Road  
Danbury, CT 06813  
Phone: (203) 205-2492; Fax: (203) 825-6273  
E-mail: llipp@fce.com

DOE Technology Development Manager:  
Terry Payne  
Phone: (202) 586-9585; Fax: (202) 586-9811  
E-mail: Terry.Payne@hq.doe.gov

DOE Project Officer: Reg Tyler  
Phone: (303) 275-4929; Fax: (303) 275-4753  
E-mail: Reginald.Tyler@go.doe.gov

Technical Advisor: Thomas Benjamin  
Phone: (630) 252-1632; Fax: (630) 252-4176  
E-mail: benjamin@anl.gov

Contract Number: 36-06GO16033

Start Date: June 1, 2006  
Projected End Date: May 31, 2011

## Technical Targets

This project is developing a composite membrane to meet the following DOE 2010 technical targets for membranes:

- Membrane Conductivity: At  $\leq 120^{\circ}\text{C}$ : 0.1 S/cm; at room temperature: 0.07 S/cm; at  $-20^{\circ}\text{C}$ : 0.01 S/cm
- Cell Area Specific Resistance:  $0.02 \Omega\text{cm}^2$

## Accomplishments

- Performed three iterations of advanced polymer membrane, followed by comprehensive ex situ and in situ characterization.
- Synthesized over 20 batches of multi-component composite ( $\text{mC}^2$ ) membrane.
- Fabricated and tested three different additives for water retention and protonic conductivity enhancement.
- Measured conductivity of more than 20 membrane samples, including nine samples verified by BekkTech.
- Met the DOE room temperature conductivity goal of 0.07 S/cm at 80% relative humidity (RH).
- Demonstrated a 2x improved power density at high temperature and low relative humidity in a  $25 \text{ cm}^2$  fuel cell membrane electrode assembly (MEA) fabricated with  $\text{mC}^2$  containing the functionalized additives.



## Objectives

- Develop humidity-independent, thermally stable, low equivalent weight composite membranes with controlled ion-cluster morphology, to provide high proton-conductivity at up to  $120^{\circ}\text{C}$  (overall goal: meet DOE 2010 targets).
- Improve mechanical properties to significantly increase the durability and reduce the gas cross-over.
- Expand the operating range to sub-freezing temperatures.

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

## Introduction

This project is focused on the development of composite proton exchange membranes that can operate at low RH and over a wide temperature range ( $-20$  to  $120^{\circ}\text{C}$ ). The goal is to develop a structure in which ion-conducting clusters remain intact at low RH. A major challenge is that current proton conducting polymers cannot sufficiently hold on to water under these conditions. Since the conduction mechanism relies on movement of hydrated species, the conducting path is compromised, resulting in low performance. Membranes that can operate at lower RH at elevated temperatures up to  $120^{\circ}\text{C}$  will reduce the fuel cell system complexity and cost. This project is developing a composite membrane, in which both the ionic conductivity and mechanical properties are enhanced to meet DOE's ambitious goals for transportation fuel cells.

## Approach

The approach to address each of the DOE target parameters is summarized in Table 1. The room temperature conductivity target is the major Fiscal Year 2008 milestone and is therefore highlighted in the table.

**TABLE 1.** Approach for the Composite Membrane

Target Parameter	DOE Target (2010)	Approach
Conductivity at : ≤120°C	0.1 S/cm	Multi-component composite structure, lower equivalent weight
: Room Temp.	<b>0.07 S/cm</b>	Higher number of functional groups
: -20°C	0.01 S/cm	Stabilized nano-additives
Inlet water vapor partial pressure	1.5 kPa	Immobilized cluster structure
Hydrogen and oxygen cross-over at 1 atm	2 mA/cm <sup>2</sup>	Stronger membrane structure; functionalized additives
Area specific resistance	0.02 Ωcm <sup>2</sup>	Improved bonding capability for MEA
Cost	\$20/m <sup>2</sup>	Simplified polymer processing
Durability: - with cycling at >80°C - with cycling at <80°C	2,000 hours 5,000 hours	Thermo-mechanically compliant bonds, higher glass transition temperature
Unassisted start from low temp.	-40°C	Stabilized cluster structure design

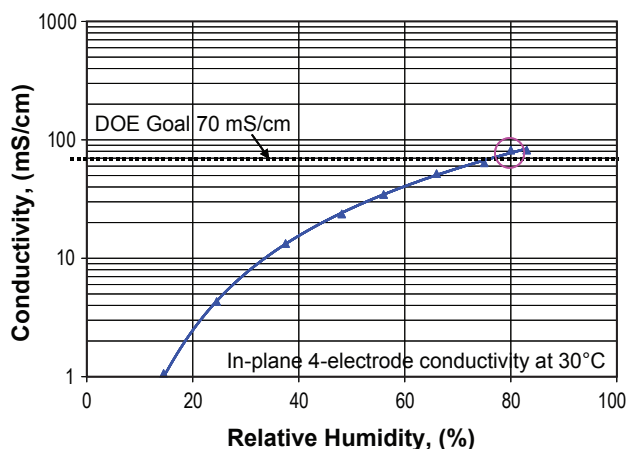
## Results

The main focus of this year's effort has been on increasing the proton conductivity at room temperature and 80% RH, as well as at 120°C and low RH, without decreasing the mechanical properties. In-plane conductivity measurements at room temperature as a function of relative humidity were carried out on the improved polymer membrane. The results, shown in Figure 1, clearly demonstrate that the DOE target of 70 mS/cm at 80% RH has been met.

FCE's concept for the multi-component composite membrane, named mC<sup>2</sup>, has been used in our design of more conductive membranes. The efforts were centered on improving each of the following mC<sup>2</sup> components:

- Co-polymer
- Water retention additive
- Protonic conductivity enhancer

The co-polymer provides the basic building block for the membrane. It is an advanced perfluoro sulfonic acid with significantly higher conductivity than state-of-the-art polymers. The conductivity of the co-polymer was increased compared to FY 2007 by increasing the



**FIGURE 1.** Improved Membrane has met DOE Room Temperature Conductivity Goal

number of functional groups and by improving the polymer formulation. This resulted in a 20% increase in conductivity (measured at 120°C and 25% RH). Tensile tests performed in accordance with ASTM D638 at room temperature and 50% RH have shown that the improved co-polymer has equivalent mechanical properties (such as tensile modulus, tensile strength and elongation at break) to the FY 2007 co-polymer. Thus, the conductivity improvements were achieved while maintaining mechanical strength, which is a key factor in membrane durability.

The functionalized additives are designed to retain water at the low RH conditions and to enhance the composite membrane's proton conductivity by providing an alternate proton conduction path. This path is designed to efficiently transport protons at high temperature as well as sub-freezing conditions. To develop a more in-depth understanding of the underlying mechanisms and to guide the development of the additives and composite membrane structure, the model developed previously [1] has been refined. It was expanded to include a separate term for the additive contribution (highlighted in yellow):

$$\sigma_p = \frac{\epsilon}{\tau} \left[ \frac{F^2}{RT} \left\{ D_{H^+}^S C_{H^+}^S + \left( D_{H^+}^G + \frac{D_{H^+W}}{1+\delta} \right) C_{H^+} \right\} \right] + \frac{\epsilon_A}{\tau_A} \left[ \frac{F^2}{RT} D_{H^+}^A C_{H^+}^A \right]$$

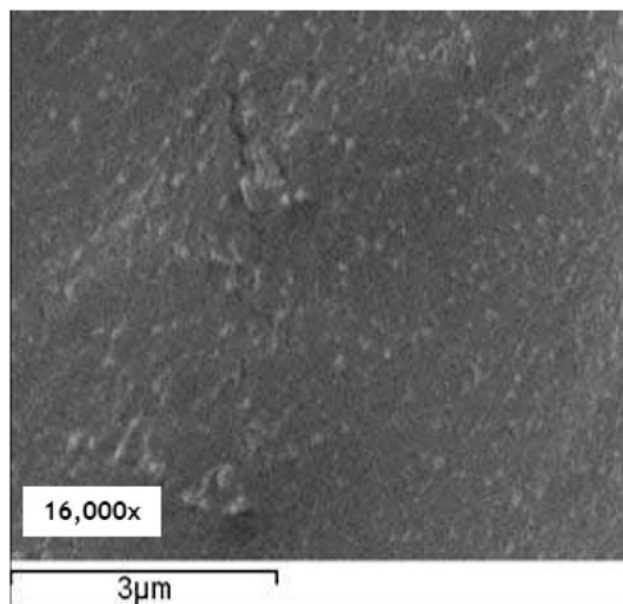
The model allows predicting the conductivity of the composite membrane, in which a certain volume percent of ionomer has been replaced by additive particles. It shows that it is critical for the additives to possess higher proton concentration  $C_{H^+}$  and proton mobility (expressed through the diffusion coefficient  $D_{H^+}$ ) than the ionomer.

Additive development was focused on particle size reduction and improvements in the dispersion and uniformity of the composite membrane. A combination of mechanical particle size reduction and classification

resulted in a reduction in average particle size by one order of magnitude. It also resulted in a narrower particle size distribution. This led to much more homogeneous composite membranes, as shown in the scanning electron micrograph in Figure 2. It is evident that the additive particles are well below 1  $\mu\text{m}$ , and are relatively uniformly dispersed.

A study of the casting process used for composite membrane fabrication resulted in the selection of a new solvent system. This system was found to be more compatible with the surface properties of the water retaining and proton conducting additives, thereby enhancing stability of the dispersion. It also allows for more controlled solvent evaporation and membrane sintering steps. A parametric analysis of these two steps was used to carry out a preliminary optimization of the composite membrane casting process. This resulted in cast membranes with a tensile modulus equivalent or better than that of extruded membranes of the same thickness and fabricated from the same co-polymer material [2]. A study of the effect of additive loading on membrane conductivity, mechanical properties and cell performance is underway.

Two composite membranes identified as promising in the ex situ screening tests were subsequently tested in situ. MEAs were fabricated from electrodes containing the same co-polymer as the membranes. They were assembled into 25  $\text{cm}^2$  single cells and their performance compared to an MEA prepared with identical electrodes and a blank membrane. The latter was prepared using the same processing technique, but without additives.



**FIGURE 2.** Scanning Electron Micrograph of Composite Membrane Cross-Section Shows Submicron Particle Size and Uniform Additive Distribution have been Achieved

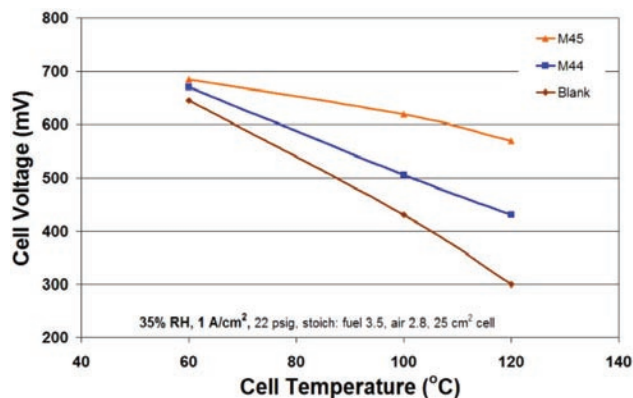
The first composite membrane, M44, contained FCE's water retaining additive. The second composite membrane, M45, contained both the water retaining additive and the proton conductivity enhancing additive. The total quantity of additive per quantity of ionomer was comparable in both mC<sup>2</sup> samples (~1% wt).

Figure 3 shows the cell voltage as a function of temperature at a current density of 1  $\text{A}/\text{cm}^2$ , measured at low relative humidity (35% RH). Significant performance improvement of the composite membranes at low temperature (60-80°C) was observed. This improvement is enhanced at high temperature (120°C). The composite membrane with both water retaining and proton conducting additives (M45) achieved twice the voltage and therefore twice the power density (0.57  $\text{W}/\text{cm}^2$ ) of the blank membrane (without additives). This confirms the effectiveness of the additives in retaining water at high temperature, and the added benefit of providing highly proton conducting pathways dispersed throughout the membrane.

## Conclusions and Future Direction

A multi-component composite membrane design for high temperature and low RH operation has been successfully implemented to fabricate membranes with enhanced conductivity and cell performance. A three times higher conductivity at 120°C compared to Nafion<sup>®</sup> has been demonstrated, without loss in mechanical strength. Composite membranes incorporating functionalized additives have shown significantly improved cell performance. At 120°C and low RH, twice the power density was observed, compared to a membrane without the additives. In the next year we will continue the composite membrane development, with an emphasis on the following activities:

- Improve the functionality of the individual components of the composite membrane. This



**FIGURE 3.** Composite Membrane Performance as a Function of Temperature: Additives are effective at maintaining good cell performance at high temperature and low relative humidity.

activity will focus on the co-polymer and functionalized nano-additives. Each will be characterized in terms of physical properties, chemical compatibility and processability, as well as conductivity.

- Optimize composite membrane processing conditions for uniform dispersion of the additives.
- Evaluate additive loading, including its effect on membrane conductivity and mechanical properties.
- Initiate membrane durability testing.
- Continue to measure progress towards DOE's conductivity targets.

## References

1. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2007 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting, Washington, D.C., May 16, 2007.
2. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2008 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting, Washington, D.C., June 11, 2008.