

V.M.14 High Temperature Membrane With Humidification-Independent Cluster Structure

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Technical Targets

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

- Membrane Conductivity at Inlet Water Vapor Partial Pressure of <1.5 kPa: At $\leq 120^{\circ}\text{C}$: 0.1 S/cm; at 20°C : 0.07 S/cm; at -20°C : 0.01 S/cm
- Cell Area Specific Resistance: 0.02 Ωcm^2

Accomplishments

- Multi-component composite membrane design identified for high temperature and low relative humidity (RH) operation.
- Improved baseline polymer was selected and characterized.
- Demonstrated membrane conductivity >2.5 times higher than Nafion[®] at 120°C and 25% RH, without loss in mechanical properties.
- Additives for water retention and protonic conductivity enhancement have been identified and fabricated. They show promise to further increase conductivity by three to five times to approach the DOE 2010 goal.
- An initial composite membrane was fabricated.



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°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, as identified in the updated Fuel Cells section (3.4.4) 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 (PEMs) that can operate at low RH and over a wide temperature range (-20 to 120°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 relative humidity at elevated temperatures up to 120°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 described in Table 1.

TABLE 1. Approach for the Composite Membrane

Target Parameter	DOE Target (2010)	Approach
Conductivity at: ≤120°C	0.1 S/cm	Lower equivalent weight
20°C	0.07 S/cm	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 ²	Stronger membrane structure; functionalized additives
Area specific resistance	0.02 Ωcm ²	Improve bonding capability for MEA
Cost	20 \$/m ²	Simplify 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 temperature	-40°C	Stabilized cluster structure design

Results

The main focus of the effort has been on increasing the proton conductivity at 120°C and 25% RH, without decreasing the mechanical properties. A multi-component composite membrane concept has been defined and named mC². It consists of four components:

- Co-polymer
- Support 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 (PFSA) with significantly higher conductivity than state-of-the-art polymers. The support polymer is designed to give a stable cluster structure and to enhance mechanical properties. 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 the high temperature as well as subfreezing conditions.

Moreover, the additives further reinforce the mechanical properties of the composite membrane.

To develop a thorough understanding of the underlying mechanisms and to guide the development of the additives and composite membrane structure, a simple model has been implemented [1]. It assumes that the proton conductivity of the composite membrane consists of three components:

$$\sigma_p = \sigma_{H^+}^{\Sigma} + \sigma_{H^+}^G + \sigma_{H^+}^E$$

These are surface conductivity, Grotthuss conductivity (proton hopping) and diffusion of protons. Each of the three components can be derived from the Nernst equation:

$$\sigma_{H^+}^{\alpha} = \frac{F^2}{RT} D_{H^+}^{\alpha} C_{H^+}^{\alpha}$$

Thus, the overall conductivity can be expressed through the Nernst-Planck equation:

$$\sigma_p = \frac{\varepsilon}{\tau} \left[\frac{F^2}{RT} \left\{ D_{H^+}^{\Sigma} C_{H^+}^{\Sigma} + \left(D_{H^+}^G + \frac{D_{H^+}^W}{1+\delta} \right) C_{H^+} \right\} \right]$$

The proton conductivity at the surface C_{H^+} and in the bulk $C_{H^+}^{\Sigma}$ is obtained from sorption thermodynamics. This also requires knowledge of the tortuosity τ , water content ε and respective diffusion coefficients D . The model has been employed to define the strategy to reach the overall conductivity goal, by estimating the contribution of each individual membrane component.

There are two main methods to determine the membrane conductivity as a function of temperature and RH, the in-plane and the through-plane conductivity method. There has been considerable debate on the benefits and challenges of each. DOE's High Temperature Membrane Working Group (HTMWG) has led the discussion and provided very useful insight [2-4]. An in-plane 4-electrode conductivity measurement is currently being developed by DOE with help from the Florida Solar Energy Center (FSEC) and BekkTech for evaluation of contractor's membrane samples to determine compliance with the conductivity milestone in Year 3 of the project. FCE participated in a conductivity measurement workshop organized by FSEC in February 2007 [5], which provided a first hands-on opportunity to measure the in-plane conductivity according to DOE's preliminary protocol and using FCE's membrane sample. FCE consequently purchased the recommended standardized hardware (from BekkTech, LLC and Fuel Cell Technologies, Inc.), and developed a setup, shown in Figure 1, which essentially reproduced BekkTech's results on both Nafion® and the improved membrane samples. This setup is now used to screen developmental membrane samples at 30, 80 and 120°C

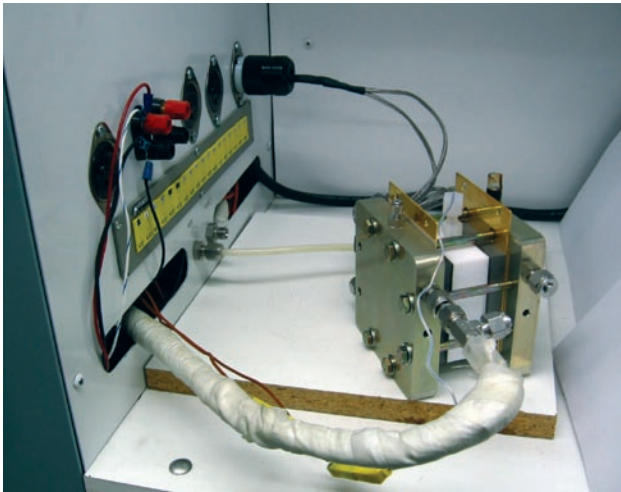


FIGURE 1. In-Plane Membrane Conductivity Measurement at FCE

and RH in the range of 20 to 100%. Promising samples are then sent to BekkTech for verification.

Conductivity data from one such sample is shown in Figure 2 and compared to a Nafion® membrane of equal thickness. At 25% RH, FCE's improved baseline membrane (which consists of co-polymer only) has a conductivity of 15 mS/cm, compared to 6 mS/cm for Nafion®. This is a 2.5x improvement. As Figure 2 shows, the improved conductivity was observed throughout the RH range measured. It reduced the gap to the DOE goal from a needed 17x improvement for Nafion® to 7x. The 25% RH point was chosen based on input from DOE's HTMWG [6]. It is believed that 25% RH inside a stack operating at 120°C can be achieved by recycling product water from the cathode to the inlet air, which is fed at a water vapor partial pressure of <1.5 kPa [7].

Additive development was focused on identifying and screening suitable additives for improved water retention and protonic conductivity. It builds on other similar efforts at FCE. Desired properties include proton conductivity less dependent on RH, and higher conductivity at subfreezing temperatures. Also lower cost additives can contribute to reduced membrane cost, and provide opportunity to improve the mechanical properties of the composite membrane. Potential issues are solubility of the additives in water, electrochemical stability at fuel cell operating or open circuit voltage (OCV) condition and non-uniform dispersion. Reduction in volume fraction of the co-polymer is an additional concern.

Based on these criteria, initial water retaining and proton conducting additives were selected, their physical and chemical properties characterized, and integrated into the co-polymer. In-plane conductivity measurements are shown in Figure 3, compared to a

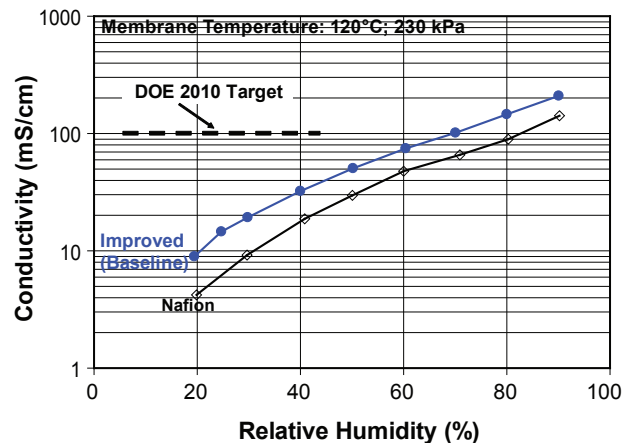


FIGURE 2. Improved Baseline Membrane Offers 2.5x Better Conductivity over Nafion®

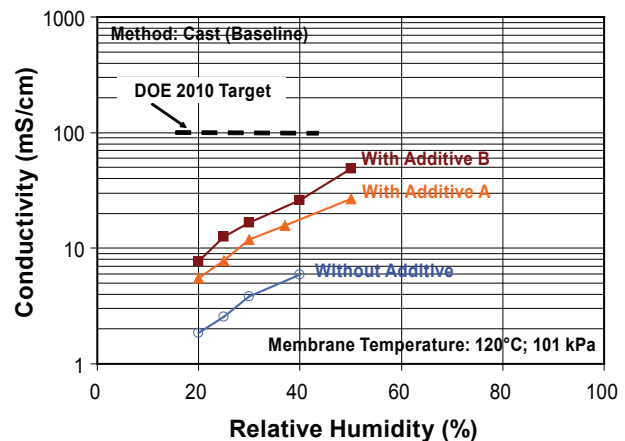


FIGURE 3. Additives Provide Conductivity Improvement in the Range of 3 to 5x (Preliminary Data)

membrane prepared in an identical process, but without additives. It can be seen that the water retaining additive A provided a 3x improvement in conductivity at 120°C and 25% RH, while the protonic conductivity enhancing additive B imparted a 5x improvement. While these results are very encouraging, opportunities for further improvement have been identified. As the scanning electron micrograph in Figure 4 shows, significant agglomeration of the nano-size additive occurred. Changes in the fabrication process are underway to improve the dispersion of additives and the membrane morphology.

Room temperature conductivity measurements of the improved baseline membrane showed 50 mS/cm at 80% RH. Therefore, 70% of the milestone for 2008 has been reached. Mechanical properties of the improved baseline membrane and a comparable Nafion® membrane of equal thickness have been determined.

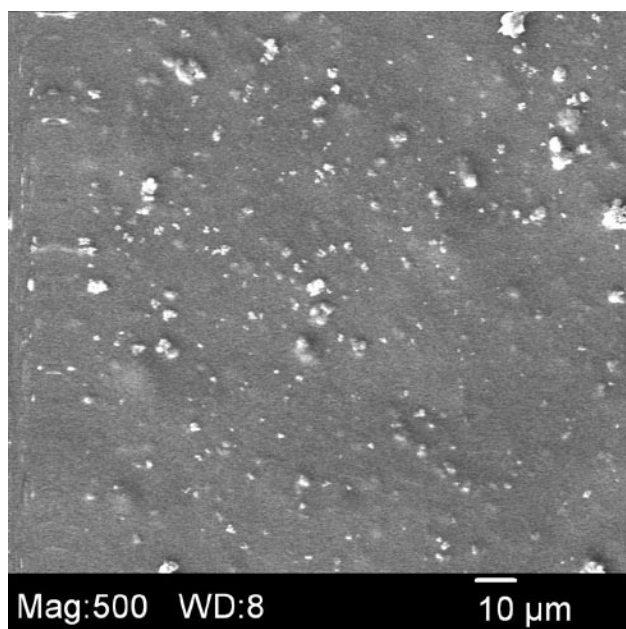


FIGURE 4. Additive Agglomeration Provides Opportunity for Further Improvement

They include tensile modulus, tensile strength and elongation at break, measured at room temperature and 50% RH. The results are within $\pm 16\%$ of Nafion[®], and equivalent on average. Therefore, the 2.5x improvement in conductivity was achieved without loss in mechanical properties.

Conclusions and Future Direction

A multi-component composite membrane design for high temperature and low relative humidity operation has been identified. A 2.5x higher conductivity compared to Nafion[®] has been demonstrated, without loss in mechanical strength. Functionalized additives show promise to further increase the conductivity by 3 to 5x. In the next year we intend to continue the composite membrane development, focusing on the following areas:

- Improvement of the functionality of the individual components of the composite membrane. These include co-polymer, support and additives. Each will be characterized in terms of physical properties, chemical compatibility and processability, as well as conductivity.

- Fabrication and characterization of improved baseline membrane.
- Improvement of the dispersion of the additives.
- Evaluation of additive loading.
- Study of effect of combination of multiple additives.
- Support of DOE's comprehensive membrane classification effort [8].
- Continue to measure progress towards DOE's conductivity targets.

FY 2007 Publications/Presentations

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7. J. Fenton, personal communication.
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