

V.D.10 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 $\leq 120^{\circ}\text{C}$: 0.1 S/cm; at room temperature: 0.07 S/cm; at -20°C : 0.01 S/cm.
- Cell Area Specific Resistance: 0.02 Ωcm^2 .

Accomplishments

- Prepared three batches of improved co-polymer, with successively lower equivalent weight.
- Fabricated and characterized six additive batches for water retention and protonic conductivity enhancement.
- Developed a new solvent system for improved additive dispersion and casting.
- Synthesized over ten batches of multi-component composite (mC^2) membrane.
- Measured conductivity of more than 25 membrane samples, including 12 samples verified by BekkTech.
- Met the DOE 120°C conductivity goal of 0.1 S/cm at 50% relative humidity (RH).
- Demonstrated $>2\text{x}$ improved conductivity at 120°C over 2008 ($\sim 3\text{x}$ higher than NRE-212[®]).
- Met all program milestones for the year.



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 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°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°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 120°C conductivity target is the Fiscal Year 2009 Go/No-Go milestone and is therefore highlighted in the table.

TABLE 1. Approach for the Composite Membrane

| Target Parameter | DOE Target (2010) | Approach |
|---|----------------------------|--|
| Conductivity at: $\leq 120^{\circ}\text{C}$ | 0.1 S/cm | Multi-component composite structure, lower equivalent weight |
| : Room Temp. | 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 | Improved bonding capability for membrane electrode assembly |
| Cost | \$20/m ² | Simplified polymer processing |
| Durability: - with cycling at $>80^{\circ}\text{C}$ - with cycling at $<80^{\circ}\text{C}$ | 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 the Go/No-Go milestone conditions of 120°C and 50% RH. In-plane conductivity measurements at 120°C as a function of RH were carried out on the composite membranes. The results, shown in Figure 1, clearly demonstrate that the DOE target of 100 mS/cm at 50% RH has been met. The data show an improvement in conductivity over that of the improved polymer of ~50% when water retaining additive is added, and >130% when both additives are incorporated. The result is a conductivity of mC² of ~3x that of state-of-the-art Nafion® membrane (NRE-212®).

FCE's concept for the multi-component composite membrane, named mC², has been used in our design of more conductive membranes. The efforts were centered on improving each of the following mC² components:

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

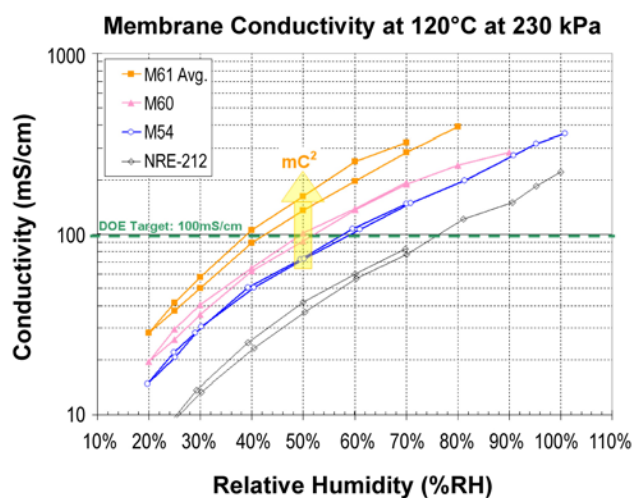


FIGURE 1. Conductivity of improved polymer (M54) is significantly enhanced by incorporating water retaining additive (M60) and water retaining additive with protonic conductivity enhancer (M61).

The co-polymer provides the basic building block for the membrane. It is an advanced perfluorinated sulfonic acid with significantly higher conductivity than state-of-the-art polymers. The conductivity of the co-polymer was increased compared to FY 2008 by increasing the number of functional groups and by improving the polymer formulation. This resulted in a 50% increase in conductivity (measured at 120°C and 50% RH).

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 [1]. This path is designed to efficiently transport protons at high temperature as well as subfreezing conditions. Additive development was focused on particle size reduction and improvements in the dispersion and uniformity of the composite membrane.

Development of a new synthesis process led to reproducible additive particle size <100 nm, as shown in Figure 2. The nature and morphology of the particles was studied by X-ray diffraction measurements, chemical analysis by inductively coupled plasma, surface area analysis and transmission electron microscopy [2]. Process modifications were developed to stabilize particle size during the processing of the additives into a composite membrane. Moreover, the interaction between the water retaining additive and the protonic conductivity enhancer was studied. The additives were modified to allow for immobilization of the protonic conductivity enhancer on the water retaining additive particles. This interaction strengthens the synergy between the additives and ensures stability during mC² fabrication and in the fuel cell environment.

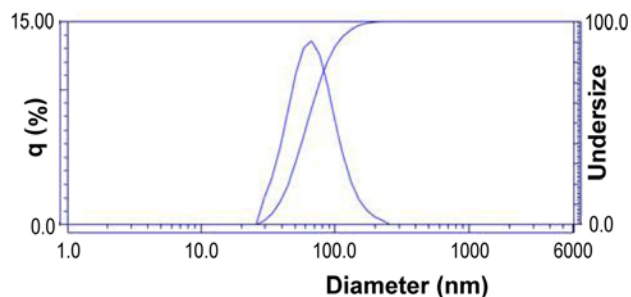


FIGURE 2. Water retaining additive average particle size < 100 nm was achieved with a new synthesis process, as confirmed by dynamic light scattering.

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. A three times higher conductivity at 120°C compared to state-of-the-art Nafion® membrane has been demonstrated. In the next year we will continue the composite membrane development, with an emphasis on the following activities:

- Continue to develop advanced polymer dispersions.
- Optimize and further simplify integration of the additives.
- Measure progress towards DOE's conductivity and area specific resistance targets.
- Perform cell testing at 95°C and 120°C.
- Initiate membrane durability testing.
- Expand membrane characterization to track progress towards DOE 2015 targets.

FY 2009 Publications/Presentations

1. Presentation to the FreedomCAR Tech Team on March 18, 2009.
2. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2009 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Arlington, VA, May 18-22, 2009.

References

1. 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.
2. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2009 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Arlington, VA, May 18-22, 2009.