V.G.16  Dimensionally Stable Membranes

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Subcontractor:
Research Foundation of the State University of New York (SUNY-ESF), Syracuse, NY

Project Start Date:  April 3, 2006
Project End Date:  April 1, 2011

Objectives

- Determine the effect of pore size and substrate thickness on conductivity and water uptake of dimensionally stable membranes (DSMs).
- Demonstrate polymerization conditions suitable for bulk polymerization of perfluorinated sulfonic acids (PFSAs).
- Demonstrate, by the 3rd Quarter 2007, membrane conductivity of 0.07 S/cm, at 80% relative humidity (RH), at room temperature, and using non-Nafion® materials. Samples will be prepared and delivered to the Topic 2 Awardee.
- Go/No-Go Decision: Demonstrate, by the 3rd Quarter, membrane conductivity >0.1 S/cm, at 25% RH at 120°C, using non-Nafion® materials. Samples will be prepared and delivered to the Topic 2 Awardee.

Technical Barriers

This project addresses the following technical barriers from the 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

Technical Targets

Progress has been made in achieving the DOE 2010 Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan technical targets. Table 1 lists the DOE’s technical targets and where our research stands to date. There are two other DOE targets for membranes relating to durability, which we have not yet addressed.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>2010 Target</th>
<th>GES Dimensionally Stable Membrane (DSM) Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Water Vapor Partial Pressure</td>
<td>kPa</td>
<td>1.5</td>
<td>20*</td>
</tr>
<tr>
<td>Oxygen Cross-Over</td>
<td>mA/cm²</td>
<td>2</td>
<td>1.5b</td>
</tr>
<tr>
<td>Hydrogen Cross-Over</td>
<td>mA/cm²</td>
<td>2</td>
<td>1.8b</td>
</tr>
<tr>
<td>Membrane Conductivity</td>
<td>S/cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating Temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20°C</td>
<td></td>
<td>0.10</td>
<td>0.093*</td>
</tr>
<tr>
<td>-20°C</td>
<td></td>
<td>0.07</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.01</td>
<td>Not tested</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>°C</td>
<td>≤120°C</td>
<td>95°C</td>
</tr>
<tr>
<td>Area Resistance</td>
<td>Ohm*cm²</td>
<td>0.02</td>
<td>0.03*</td>
</tr>
<tr>
<td>Cost</td>
<td>$/m²</td>
<td>20</td>
<td>~$100</td>
</tr>
<tr>
<td>Durability with Cycling</td>
<td>hours</td>
<td>5,000</td>
<td>Testing just initiated</td>
</tr>
<tr>
<td>&lt;80°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unassisted Start from Low Temperature</td>
<td>°C</td>
<td>-40</td>
<td>Untested</td>
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<tr>
<td>Thermal Cyclability in Presence of Condensed Water</td>
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<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

*95°C with H₂/Air at 20 psia balanced pressure; H₂/air stoich 1.1/2.0.
*bCross-over measured for 1 atm of pure H₂ and pure O₂ at 95°C and 50% RH.
*cFor 18 um DSM material operating at conditions listed above in (*)

Accomplishments

- Successfully demonstrated that DSMs based on laser drilling pores restrain x-y swelling (<5%) with a wide range of pore size and thickness.
- Polyimide and polysulfone both shown to be effective supports for the laser-drilled supports (limit in-plane swelling below 5%).
• Effective methods of generating new PFSA polymers have been generated. These have been generated via bulk polymerizations which will allow for the direct formation of the composite membrane.

• PFSA monomer homopolymerized. Generally a copolymerization of the acid-functionalized monomer with another perfluorinated ionomer is reported in the literature. This allows us to truly generate PFSA with any acid content we choose. Though patent literature covers the homopolymer, we believe that this is the first time that this has been achieved. This polymer has been incorporated in the DSM structure.

• Short-term (DOE 2008 High Temperature Membrane) conductivity targets have been met for room temperature conductivity. Promising results confirmed by independent lab (Bekktech) using a two-dimensional laser-drilled (2DSM) support material:
  - 0.0852 S/cm at 30°C and 80% RH vs. goal of 0.07.
  - 0.031 S/cm at 25% RH and 120°C is below DOE target, but getting closer.
  - 0.093 S/cm achieved at 120°C and 50% RH close to DOE upper target for RH.

• New PFSA material generated at SUNY-ESF and incorporated in three-dimensional (3DSM) support material:
  - Demonstrates 0.08 S/cm conductivity at 30% RH, approaching DOE target of 0.10 S/cm at 25% RH.
  - Demonstrated improved fuel cell performance at 95°C and 25% RH, 7 psig H₂/air (0.68 V at 500 mA/cm²).

### Results

GES has successfully imbedded high acid content PFSA materials in laser-drilled supports consisting of either polysulfone or polyimide (Kapton). Figure 1 shows the laser-drilled support, as well as the composite DSM. A matrix of support material, pore size, support thickness and equivalent weight (EW) of PFSA fill has been completed. When the supports are 10% of the total material and have no greater than 60% void space, they nearly eliminate swelling in the x-y direction. This is true regardless of hole size, acid content of the PFSA fill material, or whether polysulfone or polyimide was used as the support.

A sample composite material with low EW PFSA and 10% support material has demonstrated 2-3x the conductivity of Nafion®, the PFSA standard, over the entire range of RH as shown in Figure 2. This conductivity still falls short of the DOE target however, as seen in the figure. Previously it appeared that this approach would not be able to reach the DOE’s cost target, however in a separate DOE contract GES has demonstrated a successful method of micro-molding these substrates.

To further increase conductivity, PFSA materials with even higher acid content are being synthesized at SUNY-ESF under the direction of Israel Cabasso. A large number of materials have been synthesized, including the homopolymer of just the active monomer. Improvements in the synthesis of this polymer have led to a film-forming ionomer that can be readily incorporated in GES’s 3DSM structures. A cross-section of a 3DSM composite constructed with this new ionomer is shown in Figure 3. This material has demonstrated conductivity that is approximately twice that of the best 2DSM material to date and approximately five times that of Nafion® 112 over an entire range of RH as seen in Figure 2. Also seen in the figure is that this material comes very close to meeting the DOE target for conductivity. Though water soluble,
efforts are underway to cross-link the material in situ of the 3DSM support to prevent leaching.

Preliminary fuel cell testing has been carried out on a 2 mil DSM membrane consisting of a 1/3 mil polyimide support filled with 700 EW PFSA. In our first DSM membrane electrode assemblies (MEAs) the DSM MEA performed much better than Nafion® 112 at 95°C when fully humidified. However, the DSM and Nafion® 112 performances were not much different at 25% RH. This was unexpected; both the ex situ conductivity test, as well as an in situ impedance test, showed the DSM membrane to have much lower resistance. We attributed this to poor electrode design. With improved electrode structures the DSM performance is greatly improved, and far out-performs Nafion® 112 as also seen in Figure 4.