Center for Intelligent Fuel Cell Materials Design:
Microstructural Design and Development of High Performance Polymer Electrolyte Membranes

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Project ID #
FCP-12

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Overview

Timeline
- Project start: 6/1/06
- Project end: 5/28/08
- Percent complete: 95%

Budget
- Total project funding
  - DOE $1,485,000
  - Contractor $624,144
- Funding received in FY07
  - $798,310
- Funding for FY08
  - $107,360

Barriers
- O - Stack Material Cost
- P - Durability
- R - Thermal / Water mgmt.

Partners
- Chemsultants International
- Michigan Molecular Institute
- Case Western Reserve University
Objectives

• Develop novel polymer / nanoparticle multiple-layer membrane with
  - improved mechanical stability
  - improved conductivity
  - $\geq 120^\circ$C / $\leq 50\%$ RH operational capability

• Identify a solution casting methodology suitable for roll-to-roll, multiple-layer membrane fabrication

Requirements

High proton / Low electron conductivity
Low permeability to fuel
Low electro-osmotic drag coefficient
Good chemical stability
Ease of membrane fabrication
Objectives - Technical Approach

- **Base Polymer Synthesis/Modification**
- **Nanoparticle/Additive Synthesis**

**Optimize Polymer to Balance Properties**

**Incorporation of Nanoparticles/Additives**

**Optimization via Loadings/Layers**

**Pilot Manufacturing Trials**

**Membrane Characterization**
- Water Uptake
- Mechanical Strength
- Conductivity
- Fuel Cell Testing

**Deliverables**
- Higher Mechanical Strength/Durability
- Improved Water Management
- Increased Conductivity @ ≥ 120°C/≤ 50% RH
- Cost Effective
- Roll-to-Roll Manufacturable

Deliverables

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- Improved Water Management
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- Roll-to-Roll Manufacturable
## Milestones

<table>
<thead>
<tr>
<th>Year</th>
<th>Milestone</th>
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</table>
| 2007 | • Development of a procedure for the synthesis and characterization of Sulfonated Radel R-5000 with a target balance of physical, chemical and electrical properties.  
• Development of a procedure for the synthesis of a multi-sulfonated, Octa-Phenyl POSS nanoparticle |
| 2008 | • Development of a multilayer Proton Exchange Membrane with a balance of physical, chemical and electrical properties that combines the best fuel cell attributes of sulfonated Radel R-5000 and Sulfonated POSS  
• Development of a composite membrane with the optimal Sulfonated POSS loading and dispersion for high T / low RH conditions  
• Development of a solution casting application to produce thin, multilayer proton exchange membranes in a roll to roll form. |
Approach

Systematic design - from theory to experiments

\[ \sigma = F^2 \sum Z_i^2 \mu_i C_i \]  \hspace{1cm} (1)

\[ D_i = \mu_i RT \]  \hspace{1cm} (2)

\[ \sigma = \frac{D_i Z_i^2 C_i}{kT} \]  \hspace{1cm} (3)

\( \sigma \): Conductivity
\( F \): Faraday constant
\( Z_i \): charge
\( \mu \): mobility
\( C_i \): proton density
\( D_i \): diffusion coefficient

\( C_i = f \) (proton density, acidity)

Parameter 1
Parameter 2

\( D_i = f \) (local friction, tortuosity)

Parameter 3
Parameter 4
Parameter control for experiments

1. Proton density:
   SPOSS has an IEC of 3.5 mmol/g, higher than Nafion at 0.92 mmol/g

2. Acidity:
   Proton acidity from SPOSS is slightly lower than proton acidity from Nafion, but the synthesis is simplified.

3. Local friction:
   Water may form tight bonding to –SO₃H from SPOSS or SRadel at lower RH.

4. Proton transfer path (Tortuosity)
   Polymer matrix and nanoparticles need to be compatible. A suitable casting solution solvent helps the particles disperse well inside the polymer matrix.
Material concept

Polymer as binder
Nanoparticles as additives
Materials selection

IEC = 3.5 mmol/g

IEC = ~1.5 mmol/g
POSS nanoparticles successfully sulfonated.
Accomplishments

Material characterization

$^1$H NMR

Radel R-5000 polymer successfully sulfonated.
Accomplishments

Optimal SPOSS loading

<table>
<thead>
<tr>
<th>SPOSS loading (%)</th>
<th>Conductivity (mS/cm⁻¹) Room temperature, immersed in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>53</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>20</td>
<td>71</td>
</tr>
<tr>
<td>30</td>
<td>56</td>
</tr>
<tr>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

20% SPOSS is the optimum loading for maximum in-plane conductivity
Accomplishments

Nanoscale particle dispersion

TEM image of a close-up of a cross section of 20% SPOSS / 80% sulfonated Radel R-5000 film cast from DMSO solvent, scale bar 1 micron, domain size in the 100 to 500 nm range.

Nanometer scale SPOSS was successfully dispersed inside the polymer matrix
Accomplishments

Improved conductivity at 25%RH and 90°C

Membrane with 20% SPOSS has improved conductivity vs. Nafion at 25%RH, 90°C.
Accomplishments

Water uptake at 25%RH and 90°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Water uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 112</td>
<td>3.0</td>
</tr>
<tr>
<td>SRadel</td>
<td>4.4</td>
</tr>
<tr>
<td>20% SPOSS + 80% SRadel</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Composite membrane provides better water uptake and leads to better conductivity. ASTM D1042 testing indicates membrane swelling is reduced by adding SPOSS particles.
Accomplishments

Increasing mechanical strength by using a multiple layer structure

The 1st and 3rd unfilled polymer layers provide flexibility and mechanical strength.
### Accomplishments

Increasing mechanical strength by using a multiple layer structure

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Storage Modulus at 30°C (MPa)</th>
<th>Storage Modulus at 120°C (MPa)</th>
<th>Storage Modulus at 170°C (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 117</td>
<td>600</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Single-layer Sulfonated Radel (SRadel)</td>
<td>1954</td>
<td>1750</td>
<td>884</td>
</tr>
<tr>
<td>Single-layer (20% SPOSS + 80% SRadel)</td>
<td>1426</td>
<td>1120</td>
<td>23</td>
</tr>
<tr>
<td>3-layer SRadel / (20% SPOSS + 80% SRadel / SRadel)</td>
<td>1348</td>
<td>1320</td>
<td><strong>1202</strong></td>
</tr>
</tbody>
</table>

**3 layer membrane maintains a high storage modulus at 170°C.**
Accomplishments

Conductivity improvement at 25% RH and 90°C

Multiple-layer structure improves proton conductivity at 25% RH and 90°C.
Accomplishments

Benefit of Multiple layer membrane

Voids may exist inside the single-layer membrane, especially near the particles.

When the $3^{rd}$ layer is coated on the “semi-wet” $2^{nd}$ layer, the polymer solution settles down to the $2^{nd}$ layer and fills the voids.

Multiple-layer structure increases mechanical strength and fills potential voids formed in composite layer.
Accomplishments

Fuel cell testing at 50%RH, 80°C

Multiple-layer composite membrane has similar performance to Nafion at 50%RH and 80°C.
Accomplishments
Solution casting multiple-layer membranes

Knife over roll process

3-layer membrane

5-layer membrane
Future Work

• Optimize the caliper (thickness) of individual membrane layers and of the total multiple-layer membrane

• Expand membrane pilot casting trials for optimum multiple-layer formation development

• Complete additional fuel cell testing of multiple-layer membranes at 25% RH and 120°C.
Future work – optimize layer & membrane thickness

Caliper “x” needs to be thin enough to prevent membrane drying, but conversely it must also be thick enough to provide sufficient mechanical strength.
Summary

• A method to prepare high proton conducting SPOSS particles was developed. The ion exchange capacity achieves 3.5 mmol/g.

• Membranes produced with 20% sulfonated POSS particles and 80% sulfonated Radel R-5000 polymer have conductivity close to $10^{-2}$ Sc m$^{-1}$ at 25% RH and 90°C.

• Pilot scale casting carried out using a commercial scale process produces uniform and pin-hole free multiple-layer membrane structures.