NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

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Project ID #FC20

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Overview

Timeline
• Start date 4/15/2006
• End date 4/15/2011
• Percent complete 40%

Barriers
• High proton conductivity membranes at high T and low RH.
• Chemically stable membranes with good mechanical properties.
• Membranes with low gas permeability.

Budget
• Total project funding
  – DOE $1,455,257
  – Contractor (CWRU) $481,465
• Funding received in FY07, $300,000
• Funding for FY08, $350,000

Interactions
Eric Fossum
Dept. of Chemistry
Wright State University,
Dayton, OH
Project Objective

To fabricate and characterize a new class of NanoCapillary Network (NCN) proton conducting membranes for hydrogen/air fuel cells that operate under high temperature, low humidity conditions.

2007-08 Project Goals

Fabricate membranes with the following properties:
1. 0.07 S/cm proton conductivity at 30°C and 80% relative humidity.
2. Good mechanical properties.
3. Low gas permeability.

Identify a roadmap to achieve high conductivities at lower humidity and higher temperatures (Year 3 milestone of 0.1 S/cm at 50% RH and 120°C).
## Milestones

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
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</thead>
<tbody>
<tr>
<td>Nov-07</td>
<td>Milestone: Fabricated a series of nanofiber network cation-exchange membranes with different volume fractions of interconnected fibers (from sulfonated poly(arylene ether sulfone)) in an inert matrix. Measure proton conductivity in water and water swelling (at 25°C), tensile strength, and gas (oxygen) permeability.</td>
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<tr>
<td>March-08</td>
<td>Milestone: Added varying amounts of sulfonated POSS (polyhedral oligomeric silsesquioxanes) to sulfonated poly(arylene ether sulfone) and electrospun nanofiber mats. Converted the mats into defect-free nanofiber network membranes. Measured proton conductivity at 30°C and 80% RH.</td>
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<tr>
<td>April-08</td>
<td>Go/No-Go Decision: Achieved a proton conductivity of 0.7 S/cm at 30°C and 80% RH, for a nanofiber network membrane containing proton conducting fibers (sPAES with sulfonated POSS) and Norland Optical Adhesive as the inert matrix.</td>
</tr>
</tbody>
</table>
Approach - Nanofiber Network Membranes

The Concept: Fabricate a phase separated membrane composed of ionomeric nanofibers embedded in a uncharged and inert polymer matrix. Artificially create the nanomorphology desired in a copolymer.

1- Decouple mechanical and proton-conducting functions of the membrane

2- Remove percolative problems of classical blended and composite systems

3- Control independently both the size and the loading of the proton-conducting phase

4- Use nano-fibers/capillaries and inorganic particles to exploit interfacial effects, capillary condensation and other nano-phenomena
Plan and Approach - Tasks

Red (done) – Green (ongoing) – Blue (upcoming)

> **Task 1  Sulfonated Polymer Synthesis**
  - Different polymer IECs
  - Polymer crosslinking studies
  - Polymer characterizations

> **Task 2  Electrospinning Process Development**
  - Creation of a fiber mat (with and without sulfonated POSS)
  - Fiber Compaction and Welding Studies

> **Task 3 Matrix Polymer Identification and Membrane Fabrication**
  - Identify an inert (uncharged) polymer
  - Develop method for adding polymer to the fiber mat

> **Task 4 Membrane Characterization**
  - Equilibrium water swelling as a function of T and RH
  - Preliminary through-plane and in-plane conductivity at different T and RH
  - Thermomechanical analysis
  - Mechanical properties
  - Oxygen permeability
  - SEM and TEM micrographs of membrane cross sections
  - Thermal analysis (DSC and TGA) of the sulfonated and non-sulfonated polymers

> **Tasks 5 Membrane Composition/Structure Optimization**
Membrane Fabrication Steps

1. Synthesize sulfonated poly(arylene ether sulfone) (sPAES) with a high ion-exchange capacity (2.1-2.6 mmol/g) and high molecular weight.

2. Electrospun nanofiber mats (using DMAc and 2-butoxyethanol as the solvent). Use a rotating and oscillating drum as the fiber collector (to produce a large mat of uniform thickness and fiber volume fraction). Typical fiber density of the mats was 0.20.

3. Densify the fiber mats to increase fiber volume fraction. Use 3 minute compaction (with no heat). Pressure vs. fiber volume fraction relationship was determined. Fiber volume fraction can be controlled from 24-80%.

4. Weld intersecting fibers to make a 3-D fiber network. Expose densified mat to organic solvent in a sealed chamber (DMF or 2-butoxyethanol).

5. Fill the voids between fibers with NOA63 and UV cure.
Nanofiber Composite Membranes – Fabricated Structures

2.5 mmol/g IEC sPAES fibers

Electrospin
14 kV, 8 cm SCD, 1600 rpm, 0.04 ml/h. Fiber density = 0.20

Compact
fiber density = 0.30 at 700 psi;
fiber density = 0.64 at 13,000 psi for 3 min

Create interfiber welds
expose mat to DMF vapor 7 - 18 minutes at 25°C

Impregnate the densified and welded mat with a solvent-less, inert, and uncharged polymer (Norland Optical Adhesive, NOA63, photopolymerizable thiol-ene based resin)
Nanofiber Composite Membranes – The Final Membrane

Embed the welded fibers in Norland Optical Adhesive (NOA63) – a solvent-less polyurethane photopolymer – and then UV cure.

![Image](image1.png)

![Image](image2.png)

![Image](image3.png)

![Graph](graph.png)

- Proton conductivity (S/cm)
- Water uptake (g H₂O / g dry memb.)

Fiber Volume Fraction

Homogeneous NOA film

Homogeneous sPAES film
# Nanofiber Network Membranes

## Gas Permeation and Mechanical Property Data

<table>
<thead>
<tr>
<th>Tested sample</th>
<th>$O_2$ permeability (Barrer)</th>
<th>Young's Modulu’s&lt;sup&gt;a&lt;/sup&gt; (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogeneous solution cast film of sulfonated poly(arylene ether sulfone) - 2.5 mmol/g</td>
<td>0.53</td>
<td>409</td>
</tr>
<tr>
<td>UV cured NOA63 film</td>
<td>0.038</td>
<td>960</td>
</tr>
<tr>
<td>Nanofiber composite membrane of sulfonated poly(arylene ether sulfone) fibers impregnated with NOA63</td>
<td>0.18&lt;sup&gt;b&lt;/sup&gt;</td>
<td>528&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Nafion ® 117</td>
<td>9.4</td>
<td>176</td>
</tr>
</tbody>
</table>

<sup>a</sup> determined from Instron tests at room temperature. All samples were dried in air for 48 hrs

<sup>b</sup> 60% fiber volume fraction

<sup>c</sup> 80% fiber volume fraction
High Conductivity Nanofiber Composite Membranes

Blends of sulfonated poly(arylene ether sulfone) and sulfonated POSS (polyhedral oligomeric silsesquioxanes) were electrospun

Sulfonated Octaphenyl Polyhedral Oligomeric Silsesquioxanes (SPOSS)

Cage Structure & Hydrophilic Acid Groups

Increase Water Retention and increase in the number of acid groups

High conductivity at low humidity
SEM of sPAES/sPOSS Electrospun Mats

40 wt% SPOSS+SPAES52

SPAES52

300-500 nm fiber diameter.
Proton Conductivity of sPAES/sPOSS Nanofiber Composite Membranes – Our Results

70-75% fiber volume fraction; 50-70 μm membrane thickness, 2.1 mmol/g IEC

In-plane conductivity measured in a Bekktech cell in a controlled humidity/temperature oven (30°C and 80% relative humidity)

<table>
<thead>
<tr>
<th>Sample</th>
<th>σ (S/cm)</th>
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</thead>
<tbody>
<tr>
<td>40% SPOSS + SPAES52 from 2-butoxyethanol</td>
<td>0.094</td>
</tr>
<tr>
<td>35% SPOSS + SPAES52 from 2-butoxyethanol</td>
<td>0.084</td>
</tr>
<tr>
<td>25% SPOSS + SPAES60 from 2-butoxyethanol</td>
<td>0.069</td>
</tr>
<tr>
<td>SPAES52 from 2-butoxyethanol (2.1 mmol/g IEC)</td>
<td>0.022</td>
</tr>
<tr>
<td>SPAES60 from 2-butoxyethanol (2.6 mmol/g IEC)</td>
<td>0.030</td>
</tr>
<tr>
<td>Nafion 212</td>
<td>0.038</td>
</tr>
</tbody>
</table>
Proton Conductivity of sPAES/sPOSS Nanofiber Composite Membranes – Bekktech Results

4 Electrode Conductivity

Conductivity (mS/cm) vs. Relative Humidity (%RH)

- Case 52S35N (4-10-08) 120C
- Case 52S35N (4-9-08) 80C
- Case 52S35N (4-9-08) 30C

Conductivity Calculated based on dry dimensions and no swelling.
Summary of 2007-08 Work

Relevance: Seeking novel high performance membrane materials for high temperature and low relative humidity PEM fuel cell operation.

Approach: Nanofiber network membranes were fabricated from sulfonated poly(arylene ether sulfone) with/without sulfonated POSS. The inert matrix polymer for embedding the fibers was NOA63.

Technical Accomplishments and Progress: Demonstrated 0.07 S/cm proton conductivity at 30°C and 80% RH. Nanofiber network membranes exhibited good mechanical properties with low oxygen permeability.

Technology Transfer/Collaborations: Actively seeking an industrial collaborator. Presentations, publications, and a university invention disclosure.

Proposed Future Research: Increase membrane conductivity at low humidity and high temperature, without the loss of mechanical properties.

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<table>
<thead>
<tr>
<th>Date</th>
<th>Membrane Material</th>
<th>Proton Conductivity</th>
</tr>
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<tbody>
<tr>
<td>2006-07</td>
<td>Sulfonated poly(ether ether ketone) and NOA63 – 1.6 mmol/g IEC, fiber vol. fraction = 0.80</td>
<td>0.037 (in water at 25°C)</td>
</tr>
<tr>
<td>Nov. 2007</td>
<td>Sulfonated poly(arylene ether sulfone) and NOA63 – 2.5 mmol/g IEC, fiber vol. fraction = 0.77</td>
<td>0.11 (in water at 25°C)</td>
</tr>
<tr>
<td>March 2008</td>
<td>Sulfonated poly(arylene ether sulfone) with sPOSS and NOA63 – 2.1 mmol/g IEC, 40 wt% sPOSS, fiber vol. fraction = 0.70-0.75</td>
<td>0.07 (30°C and 80% RH) 0.17 (80°C and 80% RH) 0.062 (80°C and 60% RH)</td>
</tr>
</tbody>
</table>

DOE Year 2 milestone target (0.07 S/cm at 30°C and 80% RH) was met
Future Work 2008-09

• Increase the proton conductivity of electrospun mats at low RH
  • Use a higher IEC polysulfone polymer to create the nanofibers
  • Increase the sPOSS loading in the nanofibers (> 40 wt%)
  • Use POSS with phosphonic acid functionalities
  • Investigate the addition of poly(phenylene disulfonic acid) to the nanofibers – from M.Litt’s project
  • Add zirconium phosphate sulfophenyl phosphonate (high IEC) to the nanofibers for low RH/high T (> 100°C) conductivity

• Stabilize the nanofiber morphology
  • Crosslinking of high IEC sPAES (creation of sulfone or biphenyl/disulfone bridges)
  • Covalent-bond stabilization of sPOSS

• Replace NOA63 for better chemical/thermal stability and better strength at high T
  • Acid-resistant epoxy (thermally cured EP42-2LV from Master Bond Inc.)
  • Polymer melt impregnation

• Upcoming Milestone: 0.1 S/cm at 120°C and 50% RH