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

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Overview

Timeline
- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 20%

Barriers
- High proton conductivity membranes at high T and low RH.
- 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 FY06, $280,000
- Funding for FY07, $296,620

Interactions
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Dept. of Chemistry
Wright State University,
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Objectives

• 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.
  – Electrospun nm-size fibers of high ion-exchange capacity polymer that are vapor welded and imbedded in an uncharged polymer matrix
  – Addition of molecular silica to further enhance water retention
  – Employ the concept of capillary condensation for membrane water retention.
Plan and Approach – Proposed Membrane Morphology

Structure for NanoCapillary Network (NCN) membranes:

The electrospun sulfonated polymer fibers with/without molecular silica are interconnected by vapor welding and the inter-fiber spaces are filled by a nonconducting, gas impermeable polymer
Plan and Approach

> **Task 1 Sulfonated Polymer Synthesis**
  - Different polymer IECs
  - With and without molecular-level silica
  - Polymer crosslinking studies
  - Polymer characterizations

> **Task 2 Electrospinning Process Development**
  - Creation of a fiber mat
  - Fiber 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**
  - Bubble point test
  - 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**
Year 1 Tasks

**Prepared Sulfonated Polymers**
- Sulfonated poly (ether ether ketone)
- Sulfonated poly (arylene ether sulfone)
- Prepare polymers of different ion-exchange capacity (IEC)

**Electrospinning Process Development**
- Fabricated fiber mats with a different average fiber diameter
- Increase the density of fibers in a mat
- Develop fiber welding strategies

**Mat Characterization Studies**
- Proton conductivity of the mat before inert polymer impregnation
- Thermal analysis of the mat (TGA and DMA)

**Initial Impregnation Experiments**
- Use of a solvent-less UV curable thermoset
Poly(ether ether ketone) was sulfonated at room temperature to a range of different ion-exchange capacities (IECs) using concentrated sulfuric acid.

Electrospinning used 1.6 mmol/g IEC sPEEK (room temperature water-equilibrated membrane conductivity of 0.06 S/cm)
Electrospinning of sulfonated Poly(ether ether ketone) (sPEEK)

Drum rotation speed: from 0 to 1800 rpm

Lateral reciprocation:
Travel is +/- 4cm from the center position of the drum.

Electrospun Mat - 16 cm long, 8 cm wide and 50 μm thick after electrospinning for 10 hours; sPEEK (IEC 1.65) solution in DMAc.

Result: Large area mats with uniform fiber density were produced
Electrospun Fiber Diameter

sPEEK (IEC 1.65) fibers electrospun on the rotating drum at 445 cm/s, 2kV/cm, 8cm spinneret-to-collector distance

(a) 25 wt% sPEEK in DMAc and 12% mat density

(b) 30 wt% sPEEK in DMAc and 13% mat density

Result: Fiber diameter can be control by solution concentration
Enhancement of Fiber Density in a Mat (heat treatment)

Optical microscope images in reflection

DMA study of the macroscopic orientation of electrospun fibers: Macroscopic orientation does not influence the shrinkage of the mat.

Result: Thermal treatment near 200°C allows for significant mat shrinkage.
More on Enhancement of Fiber Density in a Mat

Use of oven

Mat suspended in oven

Mats were hung to avoid friction on the surface acting in opposite direction to shrinkage.

Use of laminator

A stack of the mat (in a Teflon frame) with two Teflon covers was passed through the laminator with controlled heating.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Electrospun Mat (sPEEK IEC=1.65 mmol/g)</th>
<th>Densified Mat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mat Density [%]</td>
<td>Heat Treatment</td>
</tr>
<tr>
<td>A</td>
<td>13.6</td>
<td>In oven at 200°C</td>
</tr>
<tr>
<td>B</td>
<td>12.6</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>12.8</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>15.0</td>
<td>In laminator at 200°C</td>
</tr>
<tr>
<td>E</td>
<td>14.7</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>14.4</td>
<td></td>
</tr>
</tbody>
</table>

Result: Thermal treatment increases the mat density by a factor of 3
Results:
- Thermal treatment increases fiber diameter (conservation of fiber volume results in an increase in fiber diameter when there is a shrinkage in mat length)
- For a similar mat density, the laminator method for mat compaction results in smaller fiber diameters, as compared to an oven treatment
Vapor Welding of Fibers

- Densified fiber mats (~42% fiber content) were equilibrated with ethanol vapor at room temperature for a given period of time.
- The vapor-exposed mat was then dried under vacuum.

<table>
<thead>
<tr>
<th>Density of the mats</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unwelded (t = 0 min)</td>
<td>42%</td>
</tr>
<tr>
<td>Welded (t = 3 min)</td>
<td>74%</td>
</tr>
<tr>
<td>Over-welded (t = 5 min)</td>
<td>****</td>
</tr>
</tbody>
</table>

**Results:**
(1) There is an increase in mat density with fiber welding and (2) The proton conductivity of a compacted/welded mat is consistent with the mat density and the conductivity of sPEEK.
Preliminary Results for Embedding Mats Using a UV-curable Thermoset

Results: NOA 63 (UV curable thermoset) is suitable to embed a sPEEK electrospun mat
Synthesis and Characterization of sPAES Polymers

![Chemical structures]

**Results:** We have synthesized a high conductivity polymer, which will be electrospun into mats.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Actual mol % of SDCDPS</th>
<th>Film Conductivity (S/cm)</th>
<th>Solubility in DI water</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPAES50/BP</td>
<td>67,400</td>
<td>109,300</td>
<td>42</td>
<td>0.07</td>
<td>Insoluble</td>
</tr>
<tr>
<td>sPAES60/BP</td>
<td>70,500</td>
<td>131,400</td>
<td>52</td>
<td>0.121</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

*TGA results of sPAES/BP polymers measured in air*

*Samples were pre-dried at 150 °C for 30 min under N₂ atmosphere*
Relevance: Membranes that conduct protons at high temperature and low relative humidity are needed for hydrogen/air PEM fuel cells.

Approach: Use an electrospun NanoCapillary Network (NCN) membrane micromorphology where an interconnected mat of proton conducting polymer nanofibers are imbedded in an inert polymer matrix.

Technical Accomplishments and Progress: Electrospun fiber mats have been fabricated from sulfonated poly(ether ether ketone). The mats have been compacted and the fibers welded. The proton conductivity of densified/welded mats has been measured.

Proposed Future Research: Increase the proton conductivity of fiber mats and impregnate the mats with inert polymer.

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**Future Work 2007-08**

**Increase the proton conductivity of electrospun mats**
- Refine methods for increasing the density of fibers in a mat by: (i) Changing the electro-spinning conditions (e.g., spinneret potential, flow rate, spinneret to collector distance) and (ii) Varying the mat compaction and welding methods.
- Use a higher IEC polymer to create the fibers (sPEEK and/or sulfonated polysulfone) with a homogeneous (fully dense) polymer conductivity of at least 0.12 S/cm.
- Investigate electrospinning with high IEC polymers in different counterion forms.

**Impregnate compacted and welded fiber mats with an inert polymer**
- Look at different impregnation polymers, different mat densities, and nanofiber mats of different IEC.

**Continue to investigate and characterize the properties of electrospun mats of an ion-exchange polymer**
- Determine the mechanical properties of the mats as a function of ion-exchange capacity and mat density.
- Determine the effect of a water boiling pretreatment step on the proton conductivity of electrospun mats.