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

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Project ID: FC038

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Overview

Timeline
- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 77%

Barriers
- Barriers
  - Membrane performance (conductivity, mechanical properties, gas crossover)
  - Durability
  - Cost
- Targets
  - 0.10 S/cm proton conductivity at 120°C and 50% RH
  - 0.02 Ohm-cm² area specific resistance
  - 2 mA/cm² crossover for oxygen and hydrogen

Budget
- Total project funding
  - DOE $1,455,257
  - Contractor (CWRU and Vanderbilt) $481,465
- Funding received in FY09, $150,000
- Funding for FY10, $300,000

Interactions
3M Corporation
Nissan Technical Center
North America, Inc.
Relevance - NanoCapillary Network Membranes

The Concept: Use a “forced assembly” approach to fabricate a phase separated membrane composed of ionomeric nanofibers embedded in a uncharged/inert polymer matrix. Artificially create a nanomorphology similar to that for an ideal block copolymer.

1- Decouple mechanical and proton-conducting functions of the membrane materials
2 - 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

**Fiber composition:** Low EW perfluorosulfonic acid with sulfonated molecular silica

**Inert Matrix Polymer:** Norland Optical Adhesive (NOA) 63 (a UV-curable urethane-based pre-polymer)
Objectives

Project Objective:
To fabricate and characterize a new class of NanoCapillary Network proton conducting membranes for hydrogen/air fuel cells that operate under high temperature, low humidity conditions.
- High proton conductivity
- Low gas crossover
- Good mechanical properties

2009-2010 Project Goals:
Prepare NanoCapillary Network proton exchange membranes where high ion-exchange capacity (IEC) sulfonated polyphenylene (from Morton Litt’s group at Case Western Reserve University) replaces the sulfonated POSS and a commercially available polyphenylsulfone (uncharged) replaces NOA63.
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>March 2008</td>
<td>Milestone: Successfully electrospun sulfonated poly(arylene ether sulfone) (sPAES) and added varying amounts of sulfonated POSS (polyhedral oligomeric silsesquioxanes) to the ionomer nanofiber mats. Converted the mats into defect-free nanofiber network membranes.</td>
</tr>
<tr>
<td>April 2008</td>
<td>Milestone: Achieved a proton conductivity of 0.07 S/cm at 30°C and 80% RH, for a nanofiber network membrane (nanofibers composed of sPAES + sulfonated POSS, with Norland Optical Adhesive 63 as the inert matrix).</td>
</tr>
<tr>
<td>December 2008</td>
<td>Go/No-Go Decision: Achieved a proton conductivity of 0.107 mS/cm at 120°C and 50% RH for a nanofiber network membrane, where the fibers were composed of 825 EW PFSA polymer + SPOSS, with Norland Optical Adhesive 63 as the inert matrix.</td>
</tr>
<tr>
<td>March 2010</td>
<td>Milestone: Developed a new dual nanofiber electrospinning membrane fabrication scheme that eliminates the polymer impregnation step. NOA63 was replaced with polyphenylsulfone as the inert matrix polymer. Replaced sulfonated POSS with sulfonated polyphenylene.</td>
</tr>
</tbody>
</table>
Summary of Accomplishments for Year 2

1. Nanocapillary network membranes with sulfonated polysulfone (2.1 mmol/g IEC) + SPOSS.
   - Fiber mat compaction, interfiber welding and mat impregnation with Norland Optical Adhesive 63 (a UV photo-curable urethane-based pre-polymer)

2. Membranes achieved the DOE Year 2 proton conductivity target of 0.07 S/cm at 30°C and 80% RH

3. Membranes exhibited low gas permeability and good mechanical properties

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Tested sample</th>
<th>$O_2$ permeability (Barrer)</th>
<th>Young's Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogeneous film of sulfonated poly(arylene ether sulfone)</td>
<td>0.53</td>
<td>409</td>
</tr>
<tr>
<td>Nanofiber composite membrane</td>
<td>$0.18^{b}$</td>
<td>$528^{c}$</td>
</tr>
<tr>
<td>Nafion® 117</td>
<td>9.4</td>
<td>176</td>
</tr>
</tbody>
</table>
Technical Accomplishments for Year 3

High Conductivity Nanofiber Composite Membranes

- 825 EW PFSA polymer (from 3M Corp.) was electrospun with sulfonated POSS + poly(acrylic acid)
- Nanofiber mats were welding and compacted
- Void volume was filled with Norland Optical Adhesive 63

PFSA fibers with 35 wt% sPOSS met the 2009 DOE proton conductivity target of 100 mS/cm at 120°C and 50% RH
Technical Accomplishments and Progress for Year 4

• Developed new nanofiber membrane fabrication methods; replaced Norland Optical Adhesive 63 with a commercially available polysulfone and eliminated a separate impregnation step.

• Characterized the new nanofiber membranes and tested them in a H₂/air fuel cell (investigated initial performance and durability).

• Began electrospinning mixtures of PFSA and sulfonated polyphenylene (as a replacement for sulfonated POSS).

• Electrospun and Nafion® hollow bore nanofibers (seeking better water retention and high conductivity at low humidity).

• Began to electrospin Pt/C-loaded nanofibers for fuel cell cell electrodes.
Nanofiber Network Membrane Fabrication Techniques – Original Method

Method was used during Years 1-3 of the project to fabricate membranes with sulfonated polysulfone and with perfluorosulfonic acid nanofibers.

Inert/uncharged polymer was Norland Optical Adhesive 63 (a UV-curable urethane-base pre-polymer) that was impregnated into the mat.

Prepare an ionomer nanofiber mat, then embed the mat with an uncharged/inert polymer

Nanofiber mat electrospinning

Mat compaction (to increase the volume density of fibers)

Creation of inter-fiber welds

Impregnation with an inert polymer

2.5 mmol/g IEC sulfonated polysulfone nanofiber mat

As-spun mat

Compacted mat

Compacted and welded mat
New Nanofiber Network Membrane Fabrication Technique – Methods #2 and #3 (Dual Fiber Electrospinning)

Simultaneously electrospin a dual nanofiber mat – one fiber is the ionomer and the second fiber is an uncharged/inert polymer (polyphenylsulfone or PVDF)

Mat Processing

Method #3
“Melt” inert polymer around ionomer nanofibers

Interfiber voids are filled with the inert polymer matrix that provides mechanical strength and controls swelling

Interconnected 3-D network of ionomer nanofibers

Method #2
“Melt” ionomer around inert polymer nanofibers

Inter-connected 3-D network of inert polymer nanofibers that provides mechanical strength

Inter-fiber voids are filled with ionomer
## Dual Fiber Electrospinning: Nafion® PFSA (0.91 mmol/g IEC) and Polyphenylsulfone

<table>
<thead>
<tr>
<th></th>
<th>Nafion®</th>
<th>Polyphenylsulfone (PPSU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Comp.</td>
<td>99:1 Nafion®:PEO (20 wt% total polymer)</td>
<td>20 wt%</td>
</tr>
<tr>
<td>Solvent</td>
<td>Isopropanol:Water in 2:1 vol. ratio</td>
<td>DMAc:Acetone in 8:2 vol. ratio</td>
</tr>
<tr>
<td>Voltage</td>
<td>4 kV</td>
<td>7.5 kV</td>
</tr>
<tr>
<td>SCD</td>
<td>6 cm</td>
<td>4 cm</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>0.21 mL/hr</td>
<td>0.09 mL/hr</td>
</tr>
</tbody>
</table>

PEO = Poly(ethylene oxide)
PPSU: Radel® R-5500NT polyphenylsulfone from Solvay Advanced Polymers LLC

SEM image of a mat containing Nafion®/PEO and PPSU nanofibers (where the two polymer were electrospun simultaneously)

Dual fiber electrospinning of Nafion® and PVDF (Kynar® 760) was also performed successfully.
Generating Alternative Nanofiber Composite Membrane Structures form a Dual Fiber Mat

Electrospin Nafion® and PPSU

- Compress at 125°C
- Anneal, 150°C, 2 hr

- Anneal, 150°C, 2 hr

Methylene Chloride Vapor Exposure
18 hours, 25°C

Nafion® Matrix, PPSU Nanofibers
~70% Nafion® by Volume

Nafion® Nanofibers, PPSU Matrix
~60% Nafion® by Volume
Water Swelling and Mechanical Properties – Nafion® Surrounding PPSU Nanofibers

<table>
<thead>
<tr>
<th></th>
<th>In-Plane Swelling [%]</th>
<th>Volumetric Swelling [%]</th>
<th>Mass Swelling [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion® 212</td>
<td>37</td>
<td>75</td>
<td>36</td>
</tr>
<tr>
<td>Nanofiber Composite</td>
<td>5</td>
<td>35</td>
<td>22</td>
</tr>
</tbody>
</table>

(Swelling data taken after equilibrating in 100°C liquid water)

Dry Membrane (30°C, 30% R.H.)

Wet Membrane (Liquid H₂O)
Conductivity is consistently ~70% of Nafion® (volume fraction of Nafion® in the membrane is also ~70%)
H₂/Air Fuel Cell Performance - Nafion® Surrounding PPSU Nanofibers

- 80°C, 100% RH
- 0.4 mg/cm² Pt loading (anode and cathode)
- 30% Nafion® binder content
- decal method for MEA preparation

Nafion® 212 (51 μm)
Nanofiber composite (30 μm dry thickness)
Durability Cycling at 80°C

Limiting Current Test Conditions:
- Linear Sweep Voltammetry from 0-500 mV at 100% RH
- Hydrogen Flow Rate: 125mL/min
- Nitrogen Flow Rate: 500 mL/min

MEA Lifetime is Increased with the Composite Membrane

Durability Cycling Test Conditions:
- Nanofiber Composite (30 micron thick membrane): 2 minutes at 0% R.H. Hydrogen & Air, 2 minutes at 100% R.H. Hydrogen & Air
- Nafion® 212 (51 micron thick membrane): 15 minutes at 0% R.H. Air, 15 minutes at 150% R.H. Air (always 150% R.H. Hydrogen)
- 0.4 mg/cm² Pt Loading
- 125 mL/min Hydrogen Flow Rate and 500 mL/min Air Flow Rate
Proton Conductivity and Swelling – 3M 825 EW PFSA Surrounding PPSU Nanofibers

- Membrane was composed of ~80 wt% PFSA and 20 wt% PPSU
- PFSA was electrospun with 1 wt% PEO
- The nanofiber composite membrane has the same conductivity as Nafion® 212, but reduced in-plane swelling

### Preliminary Results

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity in Water at 23°C [S/cm]</th>
<th>In-Plane Water Swelling at 23°C [%]</th>
<th>Volumetric Water Swelling at 23°C [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanofiber Composite</td>
<td>0.095</td>
<td>5</td>
<td>43</td>
</tr>
<tr>
<td>(3M 825 EW:PPSU)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast 3M 825</td>
<td>0.115</td>
<td>25</td>
<td>85</td>
</tr>
<tr>
<td>Nafion® 212</td>
<td>0.095</td>
<td>19</td>
<td>35</td>
</tr>
</tbody>
</table>
Addition of Sulfonated Polyphenylenes to Nanofibers

The following polymers were synthesized by Morton Litt’s group at Case Western Reserve University and sent to Vanderbilt:

- **TPB5**
  - poly(4,4′-biphenyl-3,3′-disulfonic acid)-g-triphenylbenzene
  - (5% target, 1% actual grafts/crosslinks)

- **KOct**
  - poly(1,4-phenylene-2,5-disulfonic acid)-g-octylbenzene
  - (10% grafts)

- **DPE5**
  - poly(1,4-phenylene-2,5-disulfonic acid)-g-diphenylether
  - (5% target, 1% actual grafts/crosslinks)
Results with Sulfonated Polyphenylene - Conductivity of Homogeneous Membranes

Solution Cast 825 EW PFSA + KOct (35 wt% KOct)

- From an extrapolated Arrhenius plot of conductivity vs 1/T: The conductivity of a homogeneous membrane at 120°C and 50%RH will be 0.125 S/cm.
- For a nanofiber mat with 0.70 volume fraction of proton conducting nanofibers, the expected proton conductivity will be 0.94 S/cm.
Electrospinning PFSA (825 EW) with Sulfonated Polyphenylene (TPB5)

Electrospinning Conditions
- 17 wt% Polymer (3M (825 EW):TPB5:PEO, 74:25:1)*; solvent was 1-propanol/water (2/1 vol/vol)
- 7.5 kV, 6cm SCD, 0.6 mL/hr

*Some TPB5 precipitated out of solution and was not incorporated into the nanofibers

Average Fiber Diameter = 825 nm

We have not yet made dual fiber mats with PFSA and sulfonated polyphenylene.
Electrospinning Nafion® Nanofibers with a Hollow Bore

Use a coaxial spinneret

Electrospinning Conditions:

<table>
<thead>
<tr>
<th></th>
<th>Sheath</th>
<th>Core</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>25 wt% 99:1 Nafion®:PEO (10^6 MW)</td>
<td>Heavy Mineral Oil (Aldrich)</td>
</tr>
<tr>
<td>Solvent</td>
<td>Isopropanol: Water in 2:1 ratio</td>
<td>None</td>
</tr>
<tr>
<td>Voltage</td>
<td></td>
<td>7.5kV</td>
</tr>
<tr>
<td>SCD</td>
<td></td>
<td>5 cm</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>0.6 mL/hr</td>
<td>0.05 mL/hr</td>
</tr>
</tbody>
</table>

Post electrospinning procedure:

1) Anneal as-spun mat for 0.5 hours at 150°C.
2) Immerse the mat in octane overnight to extract mineral oil in the bore.
Electrospinning Nafion® Nanofibers with a Hollow Bore: SEMs of Fiber Mats

SEM image of hollow fibers electrospun from: 25 wt% 85:15 Nafion®:PEO (300K MW)

- Bore diameter: 1.4 µm
- Wall thickness: 1 µm
- Total fiber diameter: 3.4 µm

SEM image of hollow fibers electrospun from: 25 wt% 99:1 Nafion®:PEO (10^6 MW)

- Bore diameter: 0.71 µm
- Wall thickness: 1 µm
- Total fiber diameter: 2.7 µm

From SEMs: >95% of the fibers contained a hollow bore
A Fuel Cell Cathode Composed of Electrospun Nanofibers

Electrode Electrospinning Conditions:

<table>
<thead>
<tr>
<th>Composition</th>
<th>7.76 wt% catalyst/polymer in solvent, with 64:10:26 Pt(20%)/C:Nafion®:450K poly(acrylic acid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Isopropanol/Water in 2:1 ratio</td>
</tr>
<tr>
<td>Voltage</td>
<td>3.5kV</td>
</tr>
<tr>
<td>SCD</td>
<td>6 cm</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>0.3 mL/hr</td>
</tr>
</tbody>
</table>

Post electrospinning treatment and testing:

1. Anneal as-spun mat at 200°C in vacuum for 2 hr. (volume fraction of fibers is ~ 0.20)
2. Prepare MEA by hot pressing anode and cathode onto Nafion® 212 (use normal decal electrode/method to make anode)
3. Boil MEA in H₂SO₄ and then boil in water, one hour each; no evidence of poly(acrylic acid) (PAA) removal.
4. Put MEA (5 cm²) into fuel cell test fixture; run break-in and V-i performance experiments
SEM surface image of 64:10:26 (Pt/C: PFSA: PAA) Fibers
Fibers were annealed at 200°C
Average fiber diameter = 420 nm

SEM surface image of 64:10:26 (Pt/C: PFSA: PAA) fibers
after 24 hrs of operation in cell (carbon paper removed)

Fuel Cell Performance of an Electrospun Fiber Cathode

Future Work:

- Remove or eliminate PAA
- Decrease fiber size
- Increase fiber porosity
- Optimize catalyst/ionomer weight ratio
- Continue fuel cell tests (short and long term)

Regular Decal method: 86 wt% Pt/C and 14 wt% Nafion®

Polarization curves at 80°C, 100% RH H₂/air; Nafion® 212 membrane; 100 ml/min H₂, 500 ml/min air, 0.40 mg/cm² anode and cathode Pt loading.
Collaborations

Partners

- **3M Corporation (Industry):** Provides samples of short side-chain low EW PFSA polymer (in solution) for electrospinning studies and membrane development; provides background information on casting membranes from solutions of low EW PFSA (e.g., polymer annealing conditions)

- **Nissan Technical Center North America, Inc. (Industry):** Collaborations with Nissan Technical Center NA involve sharing of MEA testing protocols.
1. Prepare and test nanofiber composite membranes with PFSA + sulfonated polyphenylene + polyphenylsulfone (use the dual fiber electrospinning approach).
   - Determine the effect of sulfonated polyphenylene loading on membrane conductivity, swelling, and mechanical properties. Study 825 and lower EW PFSA ionomers.
   - Compare properties of composite membranes where ionomer nanofibers are surrounded by uncharged polymer and uncharged polymer nanofibers are surrounded by ionomer.
   - Investigate a sulfone bridge crosslinking scheme, with the addition of diphenylether or triphenylbenzene (for low EW PFSA with sulfonated polyphenylene).

2. Examine different inert/uncharged polymers
   - Compare polysulfone, PVDF, and other uncharged polymers (e.g., polybenzimidazole) in nanofiber composite membranes; focus on water swelling and membrane mechanical properties. Identify the best uncharged polymer.

3. Further characterize electrospun hollow bore Nafion® fibers
   - Convert the hollow bore fiber mats into membranes by compaction, welding and impregnation. Characterize the resulting films in terms of proton conductivity, water uptake/retention, and mechanical properties.

4. Prepare and test MEAs with nanofiber network composite membranes

5. Continue to investigate and improve on the performance of electrospun nanofiber fuel cell electrodes (focus on the cathode).
   - Decrease the electrode fiber diameter and/or create fiber porosity
   - Optimize the ink (and fiber) catalyst/polymer composition
   - Perform electrochemical characterization tests

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**Proposed Future Work**
Summary of 2009-10 Work

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

Approach: Fabricate nanofiber network composite membranes from high IEC ionomers with highly charged particles (either sulfonated POSS or sulfonated polyphenylene).

Technical Accomplishments and Progress: Norland Optical Adhesive was replaced by polyphenylsulfone as the inert/uncharged component in nanofiber composite membranes. Sulfonated POSS was replaced by sulfonated polyphenylene. New methods for membrane preparation were developed (dual polymer fiber electrospinning followed by mat processing with the elimination of a polymer impregnation step).

Technology Transfer/Collaborations: Continued collaborations with 3M Corporation and Nissan Technical Center North America. Gave numerous presentations, wrote papers, and submitted a patent application.

Proposed Future Research: Prepare high conductivity fuel cell membranes using low EW PFSA with/without sulfonated polyphenylene. Investigate different uncharged polymer supports, including polyphenylsulfone, PVDF, and PBI. Investigate polymer crosslinking schemes. Test the new membranes in a H₂/air fuel cell. Continue to develop methods for electrospinning nanofiber electrode structures.

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