Nanofiber Composite
Proton Conducting Fuel Cell Membranes

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**H₂-Air Proton-Exchange Membrane (PEM) Fuel Cell**

The Ideal Membrane:
- Low sheet resistance (high conductivity and very thin) at high and low T and humidity
- Low areal dimensional changes during membrane hydration and dehydration
- Mechanically robust with moderate volumetric swelling
- Low fuel and oxygen crossover

High conductivity requires a high membrane ion-exchange capacity

But:  - Highly charged polymers swell excessively in water
- High water swelling lowers the effective (volumetric) concentration of membrane fixed charge sites and decreases the membrane’s mechanical properties

So:  - A membrane composed of a single homopolymer will not work!
- Consider blends, block copolymers, and composites

\[
2H_2 + O_2 \rightarrow 2H_2O
\]
Nanofiber Composite Membranes

1. Ionomer nanofibers surrounded by uncharged polymer.
2. Uncharged polymer nanofibers surrounded by (and reinforcing) an ionomer matrix.

(a) This “forced assembly” method allows for a wide choice of polymers for the ion conducting and uncharged phases (an alternative to blends and block copolymers)

(b) Intimate mixing of polymer components

(c) Decouple mechanical and ion-conducting functions of the membrane.

(d) Control independently both the size and the loading of the ion-conducting phase.

(e) Membranes can be made without a polymer impregnation step.
Nanofiber Composite Membranes – Processing a Dual Fiber Mat

Simultaneously electrospin a dual fiber mat

Interfiber voids are filled with ionomer

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

One fiber is a charged polymer (ionomer) like perfluorosulfonic acid (PFSA) and the second fiber is an uncharged/inert polymer (e.g., polyphenylsulfone)

Mat Processing

Method #1
“Melt” inert polymer around ionomer nanofibers

Interconnected 3-D network of ionomer nanofibers that provides mechanical strength

Interfiber voids are filled with ionomer

Method #2
“Melt” ionomer around inert polymer nanofibers

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

Interfiber voids are filled with ionomer
825 EW PFSA Nanofibers: Polymer Concentration Effect

10 wt% solution

1.21 mmol/g IEC PFSA from 3M Company

5 wt% solution

PFSA/PEO=90/10

PFSA/PEO=95/5

PFSA/PEO=99/1

No Fiber Formed.
Converting a Dual Nanofiber Mat into a Composite Membrane: Nafion + Polyphenylsulfone

1) Hot Press (Compact) @ 6,000 psi and 127°C for 40 sec.
2) Anneal (5 min. at 210°C in vacuum)
3) Boil 5 min. in 1M H₂SO₄ and 5 min. in water

Nafion softens/flows to fill inter-fiber voids

Dual Fiber Mat
Surface

1) Cold Press (Compact) @ 1500 psi and 25°C for 10 sec.
2) Expose to chloroform vapor for 3 min. at 50°C
3) Anneal (5 min at 210°C in vacuum)
4) Boil 5 min. in 1M H₂SO₄ and 5 min. in water

PPSU softens/flows to fill inter-fiber voids

Nafion with PPSU fibers

Cross-section

PPSU with Nafion fibers

Cross-section

Surface after PPSU Removal

\[
-(CF_2CF_2)_x-(CFCF_2)_y-(OCF_2CF)_z-OCF_2CF_2-SO_2H
\]

\[
\begin{array}{c}
\text{CF}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{PPSU} \\
\end{array}
\]
Conductivity and Volumetric Swelling: Nafion + Polyphenylsulfone

On-plane conductivity (measured in 25°C in water)

- Conductivity can be predicted by a volume fraction mixing rule (dashed line, above)
- Electrospun membranes have an exceptionally low percolation threshold (≤ 9 vol% Nafion)
- Volumetric swelling of nanofiber composite membranes in water also obeys a simple Nafion volume fraction mixing rule.

In-Plane volumetric swelling (measured at 100°C in water)

- Both membrane structures have the same volumetric swelling for a given Nafion volume fraction (swelling is lower than predicted by a mixing rule).
- PPSU-fiber/Nafion-matrix has lower in-plane swelling.
- Higher thickness swelling for Nafion fiber membrane (3-D PPSU connectivity creates isotropic swelling)
Mechanical Properties: Nafion + Polyphenylsulfone

PPSU improves mechanical properties of composite membranes

Nafion-fiber/PPSU-matrix has best mechanical properties (3-D PPSU connectivity)
Use thinner films in a membrane-electrode-assembly to compensate for the lower conductivity of a nanofiber composite membrane.

- 80°C, 100% RH
- Anode and Cathode: 0.4 mg/cm² Pt loading with 30% Nafion binder content

- Nafion 212 (51 µm)
- Nanofiber composite (30 µm dry thickness; Nafion with a PPSU nanofiber reinforcement mat; (~60 vol% Nafion)
**H₂/Air Fuel Cell Durability Test (at Open Circuit Voltage)**

- 25 cm² MEA
- 80°C, 100% RH
- Anode and Cathode: 0.4 mg/cm² Pt loading with 30% Nafion binder content

- Cycling: 2 minutes 100% RH H₂/Air, 2 minutes 0% RH H₂/Air. 25 cm² cell, 125 mL/min H₂, 500 mL/min air flow rates,

- Nafion 212 failed after 546 hours
- The Nanofiber Composite Membrane failed after 842 hour (a 54% increase in lifetime)
Composite Membrane Fabrication with 660EW PFSA

<table>
<thead>
<tr>
<th>Membrane Processing (PPSU-fiber/660EW-matrix)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Dual-fiber Electrospinning 3M660/PEO and PPSU</td>
</tr>
<tr>
<td>2) Compress to 6000 psi at 127°C</td>
</tr>
<tr>
<td>3) Anneal 2 hours at 150°C in vacuum</td>
</tr>
<tr>
<td>4) Soak in 1M H₂SO₄ for 16 hours at 23°C</td>
</tr>
<tr>
<td>5) Soak in water for 6 hours at 23°C (replacing with fresh water periodically)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3M 660 EW</th>
<th>Polyphenylsulfone (PPSU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Comp.</td>
<td>99.7:0.3, 660EW:PEO (30 wt% total polymer)</td>
</tr>
<tr>
<td>Solvent</td>
<td>n-propanol:water in 2:1 wt. ratio</td>
</tr>
<tr>
<td>Voltage</td>
<td>7.0 kV</td>
</tr>
<tr>
<td>SCD</td>
<td>5.5 cm</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>0.40 mL/hr</td>
</tr>
</tbody>
</table>

Surface of Dual-fiber Electrospun Mat

Cross-section of Dense Membrane (3M660 reinforced by PPSU fibers)
In-Plane Proton Conductivity and Swelling

• 3M660/PPSU: 70 vol% 3M660 and 30 vol% PPSU fibers (54 µm thick)

• Nafion 212 is a commercial film from DuPont (51 µm thick)

Swelling Data
(Swelling in 23°C liquid water)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Mass Swelling [%]</th>
<th>Volumetric Swelling [%]</th>
<th>In-Plane Swelling [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3M660EW/PPSU Composite</td>
<td>53</td>
<td>87</td>
<td>5</td>
</tr>
<tr>
<td>Cast 660 EW film</td>
<td>71</td>
<td>137</td>
<td>84</td>
</tr>
<tr>
<td>Nafion 212</td>
<td>16</td>
<td>35</td>
<td>25</td>
</tr>
</tbody>
</table>

• Lower in-plane swelling than Nafion 212, but over twice the conductivity

• 3M660 and the 3M660/PPSU composite have higher water uptake than Nafion (due to higher IEC), but have the same number of waters per sulfonic acid group.
Initial fuel cell study:
- Composite membrane composition: 58 vol% 3M660 and 42 vol% PPSU
- Conductivity is 72 mS/cm at 80°C, 60%RH (vs. 46 mS/cm for Nafion)
- Nanofiber composite MEAs prepared at 3M Company

Fuel cell conditions:
- 125 ml/min H₂ and 500 ml/min air, no back pressure
- N211: Nafion 211 membranes with 0.4 mgPt/cm² GDE w/ Nafion binder
- 3M660/PPSU: 3M660/PPSU composite (43 µm thick). 0.25 mgPt/cm² with 3M825 EW binder
Conclusions

• An entirely new membrane fabrication scheme has been developed.
• A dual fiber electrospinning method requires no polymer impregnation steps for membrane fabrication.
  • PFSA nanofibers surrounded by inert polymer (polyphenylsulfone)
  • Inert polymer (polyphenylsulfone) nanofibers surrounded by PFSA
• A nanofiber composite membrane (Nafion polymer with reinforcing polyphenylsulfone nanofibers; 30 µm in thickness) was processed into a hydrogen/air fuel cell MEA.
  • Power densities at 80°C and full humidification matched those of commercial Nafion 212
  • Nanofiber composite membrane exhibited superior durability during RH cycling (~50% improvement over Nafion 212)
• 660 EW PFSA from 3M Company was successfully electrospun and a dual fiber mat (with electrospun nanofibers of polyphenylsulfone) was converted into a functional proton conducting membrane.
  • In-plane water swelling was very low (5% in RT water) and the conductivity was high (0.093 S/cm at 120°C and 50% RH)
  • The membrane was fabricated into a fuel cell MEA (at 3M Co.) and H₂/air fuel cell tests at low RH were performed. The membrane performed significantly better than Nafion 212 for 25%<RH<93% and T=100°C and 120°C.
Acknowledgements

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  • Dr. Ryszard Wycisk (Research Associate Professor)
  • Dr. Jon Choi (former Ph.D. student)

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