Polymer Blend Proton Exchange Membranes

R. A. Weiss and M. T. Shaw
University of Connecticut
May 25, 2004

This presentation does not contain any proprietary or confidential information.
Objective

Develop new membranes based on polymer blends for operation at temperatures of 120°C or higher
Budget

DOE Funding FY04 = $ 95,000
Technical Barriers and Targets

DOE Technical Barriers For Fuel Cell Components

O. Stack Material and Manufacturing Costs
P. Durability
R. Thermal and Water

DOE Technical Targets for Membranes (Automotive) for 2005

- Membrane conductivity (operating temperature) \( \sim 0.1 \, \text{S/cm} \)
- Operating temperature \( \geq 120^\circ\text{C} \)
- Membrane cost \( \sim $50/\text{kW} \)
- Membrane durability \( > 4000 \, \text{h} \)
- Hydrogen/oxygen cross-over (MEA) \( \sim 5 \, \text{mA/cm}^2 \)
- Survivability \( \sim -20^\circ\text{C} \)
**Approach**

Develop high temperature PEMs with controlled morphology using acid-base polymer blends

1. **Thermodynamics:** develop a percolated ionic pathway at the interface of a spinodal morphology of a polymer blend comprising a sulfonated polyketone and a polyimide or similar second component

2. **Electro-dynamics:** Orient a dispersed phase of the conductive sulfo-polyketone in a polyimide matrix by applying an electric field during membrane casting
Handling and disposing of SO$_3$: normal handling procedures for strong acids; disposal by neutralization

Handling of hydrogen: normal handling procedures of high-pressure gas; high-flow-rate ventilation

Handling and disposing of solvents: normal OSHA/EPA procedures used
**Project Timeline**

<table>
<thead>
<tr>
<th>Phase I</th>
<th>Phase II</th>
<th>Phase III</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/02 - 10/03</td>
<td>10/03 - 10/04</td>
<td>10/04 - 12/06</td>
</tr>
<tr>
<td>Phase I</td>
<td>Phase II</td>
<td>Phase III</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Phase I: Feasibility**
  1. Optimize preparation of sulfonated PEKK (SPEKK) ionomers
  2. Prepare/Evaluate SPEKK/polyether imide (PEI) blend membranes

- **Phase II: Morphology Development**
  3. Develop spinodal structure for SPEKK/PEI membranes and characterize membrane performance
  4. Develop procedure for orienting SPEKK/PEI membranes and characterize membrane performance
  5. MEA production and testing

- **Phase III: System Optimization**
  6. Optimize membrane composition and morphology for high temperature SPEKK/PEI PEM
  7. Design and evaluate other blend PEMs
Technical Accomplishments/Progress

Developed Membranes Based on Poly(ether ketone ketone)

- High temperature stability ($T_g \sim 155^\circ C; T_m \sim 360^\circ C$)
- Excellent mechanical properties (engineering thermoplastic)
- Excellent chemical and solvent resistance
- Excellent oxidative stability
- Adequate resistance to desulfonation
Optimized procedure for preparing sulfonated PEKK (SPEKK)

\[
\text{[O-} \begin{array}{c} \text{C} \\ \text{C} \end{array} \text{O-} \begin{array}{c} \text{C} \\ \text{C} \end{array} \text{n} + n\text{SO}_3/H_2\text{SO}_4 \xrightarrow{k_S} \text{[O-} \begin{array}{c} \text{C} \\ \text{C} \end{array} \text{O-} \begin{array}{c} \text{C} \\ \text{C} \end{array} \text{SO}_3\text{H} \text{n} + n\text{H}_2\text{O} \xrightarrow{k_D}
\]

\[
\text{IEC} = IEC_\infty \left[1 - \exp\left(-t/\tau\right)\right]
\]

![Graph showing IEC vs Time with different temperatures and symbols]

open symbols → PEKK T/I = 8/2
closed symbols → PEKK T/I = 6/4
**Proton Conductivity of SPEKK**

**SPEKKs:**
- For IEC ~ 1.8 - 2.1 meq/g, conductivity ~ 10^{-1} S/cm
- Water insoluble when IEC < 2.3 meq/g
- 20-150 μm membranes can be cast from NMP or DMAc

**Graph:**
- **AC 2pt**
- **DC 4pt**
- **AC 4pt**

**Immersed in H₂O**
- **98% RH**

**Data Points:**
- Nafion™ 112 (immersed): 0.09 S/cm
- Nafion™ 112 (98% R.H.): 0.06 S/cm
### Methanol Crossover for SPEKK in MEA

<table>
<thead>
<tr>
<th></th>
<th>Resistance (ohm cm²)</th>
<th>Methanol Crossover (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(H₂/O₂, 80 °C)</td>
<td>(1M MeOH, 80 °C)</td>
</tr>
<tr>
<td>SPEKK (1.8 meq/g)</td>
<td>0.07</td>
<td>0.22</td>
</tr>
<tr>
<td>Nafion™</td>
<td>0.05</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**SPEKK membranes:**
- Good proton conductivity (~ 0.1 S/cm)
- Improved methanol permeability resistance vs. Nafion™
MEA Performance of SPEKK PEMs

Reasonably good MEA performance

IEC

2.0 meq/g

1.2 meq/g

80°C / 75% R.H. (H₂/O₂)
Blends of SPEKK with Poly(ether imide) (PEI)

- Strong H-bonding interactions are expected
- Ionomer provides acid groups for proton conductivity
- Relatively hydrophobic PEI provides mechanical integrity
Hypotheses:

- Ion-rich interphase provides pathway for proton conductivity
- Percolated conductive path present before water is added
- Amount of water required for conductivity will be less than for conventional ionomer membrane
**Effect of PEI content on conductivity (RT)**

Increasing PEI concentration:

- Lowers conductivity (but still > 0.01 S/cm for $c_{PEI} < 30\%$
- Reduces water concentration
- Improves mechanical properties of wet membrane
Controlling the Blend Morphology: Film Casting T

- Dispersed phase size decreases with casting temperature
- Dispersed phase size increases with increasing PEI
Controlling the Blend Morphology: Electric Field Alignment

SPEKK dispersed phase can be oriented by applying an AC electric field across the membrane during processing (solution or melt).
Controlling the Blend Morphology: Electric Field Alignment

- **Technical Accomplishments/Progress**
- **30/70 SPEKK/PEI**
- Oriented at 200°C; \( E = 10 \text{ kV/cm}; \ f = 20 \text{ Hz} \)

Electric field alignment of SPEKK phase significantly increases the membrane conductivity.
## Interactions and Collaborations

**Oxford Performance Materials (OPM): SPEKK development and blend membrane development; MEA fabrication and testing**

### Leveraging Resources:

<table>
<thead>
<tr>
<th>Agency</th>
<th>Dates</th>
<th>Award</th>
<th>Outputs/Objectives</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Inventions &amp; Innovations (OPM)</td>
<td>2003-05</td>
<td>$250K</td>
<td>Ongoing: sPEKK and sPEKK blend based MEAs. (subcontract to UConn)</td>
</tr>
<tr>
<td>DOE (UConn)</td>
<td>2003-05</td>
<td>$191K</td>
<td>Ongoing: Development of methods for controlling domain structure of polymer blends for PEM applications using thermodynamics and electric fields</td>
</tr>
<tr>
<td>Connecticut Global Fuel Cell Center (UConn)</td>
<td>2003-04</td>
<td>$75K</td>
<td>Development of equipment for electric field orientation of polymer films during film preparation</td>
</tr>
<tr>
<td>NSF (UConn)</td>
<td>1994-02</td>
<td>$1.1M</td>
<td>Fundamental studies of the thermodynamics of ionomer blends</td>
</tr>
</tbody>
</table>
Future Plans

Remainder of FY 2004:

- Develop ternary phase diagrams for SPEKK/PEI/solvent, using different solvents
- Produce membranes with spinodal structure
- Optimize equipment and procedures for electric field orientation of membranes
- Fabricate MEAs with controlled morphology blend membranes