High Temperature Membrane with Humidification-Independent Cluster Structure

Ludwig Lipp
FuelCell Energy, Inc.
June 11th, 2008

Project ID #
FC23

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
• Start: July 2006
• End: May 2011
• 38% complete

Budget
• Total project funding
  – DOE share: $1500k
  – Contractor share: $600k
• DOE share spent to date: $400k
• Funding for FY08: $225k to date

Barriers
• Low Proton Conductivity at 25-50% Inlet Relative Humidity and 120°C

Partners
• Polymer Partner
  – Polymer & membrane fab. and characterization
• UConn
  – Membrane conductivity and gas crossover
• Consultants
  – Polymer, additives
Acknowledgements

- DOE: Jason Marcinkoski, Amy Manheim, Reg Tyler, Tom Benjamin and John Kopasz

- UCF: Jim Fenton & Team (Testing protocols, membrane conductivity)

- BekkTech LLC: Tim Bekkedahl (In-plane conductivity measurement)

- FCE Team: Pinakin Patel, Ray Kopp, Jonathan Malwitz, Nikhil Jalani
FCE Overview

• Leading fuel cell developer for over 30 years
  – MCFC, SOFC, PAFC and PEM (up to 2 MW size products)
  – Over 200 million kWh of clean power produced world-wide (>60 installations)
  – Renewable fuels: over two dozen sites with ADG fuel
  – Ultra-clean technology: CARB-2007 certified: Blanket permit in California

• Highly innovative approach to fuel cell development
  – Internal reforming technology (45-50% electrical efficiency)
  – Fuel cell-turbine hybrid system (55-65% electrical eff.)
  – Enabling technologies for hydrogen infrastructure
    • Co-production of renewable $\text{H}_2$ and $\text{e}^-$ (60-70% eff. w/o CHP)
    • Solid state hydrogen separation and compression

• High temp. membrane: leverage existing experience in composite membranes for other fuel cell systems (PAFC, MCFC, SOFC)
# Approach for the Composite Membrane

<table>
<thead>
<tr>
<th>Target Parameter</th>
<th>DOE Target (2010)</th>
<th>Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity at: 120°C</td>
<td>100 mS/cm</td>
<td>Multi-component composite structure, lower EW</td>
</tr>
<tr>
<td>: Room temp.</td>
<td><strong>70 mS/cm</strong></td>
<td>Higher number of functional groups</td>
</tr>
<tr>
<td>: -20°C</td>
<td>10 mS/cm</td>
<td>Stabilized nano-additives</td>
</tr>
<tr>
<td>Inlet water vapor partial pressure</td>
<td>1.5 kPa</td>
<td>Immobilized cluster structure</td>
</tr>
<tr>
<td>Hydrogen and oxygen cross-over at 1 atm</td>
<td>2 mA/cm²</td>
<td>Stronger membrane structure; functionalized additives</td>
</tr>
<tr>
<td>Area specific resistance</td>
<td>0.02 Ωcm²</td>
<td>Improve bonding capability for MEA</td>
</tr>
<tr>
<td>Cost</td>
<td>&lt;40 $/m²</td>
<td>Simplify polymer processing</td>
</tr>
<tr>
<td>Durability:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- with cycling at &gt;80°C</td>
<td>&gt;2000 hours</td>
<td>Thermo-mechanically compliant bonds, higher glass transition temperature</td>
</tr>
<tr>
<td>- with cycling at ≤80°C</td>
<td>&gt;5000 hours</td>
<td></td>
</tr>
<tr>
<td>Survivability</td>
<td>-40°C</td>
<td>Stabilized cluster structure design</td>
</tr>
</tbody>
</table>
Technical Accomplishments

• Performed 3 iterations of advanced Polymer Membrane; comprehensive characterization

• Multi-Component Composite (mC²) membrane: synthesized >20 batches

• Three different additives for water retention and protonic conductivity enhancement have been fabricated and tested

• Conductivity measurements: >20 samples analyzed, incl. 9 samples verified by BekkTech. Results are encouraging

• Conductivity is used as a “progress marker”; cell test provides a more realistic picture
Technical Milestone Status

• Baseline membrane material and processing technique selected (6 month milestone met)

• Screened promising additives for baseline composite membrane (12 month milestone met)

• Baseline membrane fully characterized (18 month milestone met)

• Advanced Membrane material/composition/processing defined (18 month milestone met)

• 0.07 S/cm at 80% RH at R.T. (21 month milestone met)
Composite Membrane Concept

Multi-Component System with Functionalized Additives
Development Steps to Conductivity Goal

Membrane Conductivity Improvements Progressed as Planned
Proton Transport in Composite Membrane

Surface (requires chemically bound water)

Grotthuss (requires free water)

\[ \sigma_p = \sigma_{H^+}^\Sigma + \sigma_{H^+}^G + \sigma_{H^+}^E + \sigma_{H^+}^A \]

Additive Contribution

\[ \sigma_{H^+}^\alpha = \frac{F^2}{RT} D_{H^+}^\alpha C_{H^+}^\alpha \]

\[ \sigma_p = \epsilon \left[ \frac{F^2}{RT} \left\{ D_{H^+}^\Sigma C_{H^+}^\Sigma + \left( D_{H^+}^G + \frac{D_{H^+W}}{1+\delta} \right) C_{H^+} \right\} \right] + \frac{\epsilon_A}{\tau_A} \left[ \frac{F^2}{RT} D_{H^+}^A C_{H^+}^A \right] \]

\[ C_{H^+}^\Sigma \text{ and } C_{H^+} \text{ obtained from sorption thermodynamics} \]

Maintaining High Proton Concentration and High Mobility are Focused
## Mechanical Properties: Nafion vs. Baseline and Improved

**ASTM D638, 23°C, 50% RH**

<table>
<thead>
<tr>
<th>Membrane (Dry state)</th>
<th>N112</th>
<th>Baseline M15</th>
<th>Improved M39</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test direction</td>
<td>MD</td>
<td>TD</td>
<td>MD</td>
</tr>
<tr>
<td>Tensile Modulus, MPa</td>
<td>232</td>
<td>208</td>
<td>182</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>38</td>
<td>23</td>
<td>34</td>
</tr>
<tr>
<td>Elongation at Break, %</td>
<td>117</td>
<td>228</td>
<td>162</td>
</tr>
</tbody>
</table>

**Mechanical Strength is Maintained**
Membrane Conductivity at R.T.: FCE Data

DOE Goal 70 mS/cm

In-plane 4-electrode conductivity at 30°C

DOE Room Temperature Conductivity Target Met
Membrane Conductivity at R.T.: Validation

Rationalizing Differences in Measurement Results
(Variability in Water Content during Measurement)
Membrane Water Uptake

~50% Increase in Water Uptake Compared to N112
In-Plane Conductivity at 120°C 25% RH

Almost 3x Improved Membrane Conductivity vs. N112
Cell Performance at 120°C and 25% RH

High Cell Performance Achieved
Area Specific Resistance

- Low Area Specific Resistance (ASR) Achieved
- Improved Membrane has Lower ASR than Baseline, as Expected
Membrane Additive Development

Benefits:
- Conductivity less dependent on RH
- Conductivity at subfreezing temp.
- Potentially lower cost
- Design for mechanical strength

Anticipated Issues:
- Water solubility
- Electrochemical stability
- Compete for “real estate”
- Additive particle size
- Non-uniform dispersion
Membrane Additive Development

Strategy for retaining water and increasing conductivity at low RH

High RH

Low RH

Unsupported Proton Conductor

Functionalized Additive

Smaller Particles

(Higher Surface Area)
Composite Membrane Processing: Casting

Critical steps in membrane casting:
• Evaporation *(Time, Temp.)*
• Sintering *(Time, Temp.)*

Preliminary results of parametric analysis:
• Resistance to dissolution increases with time & T
• Membrane resistance increases with time and temp.
• Hydrogen permeability largely unaffected
Cast Membrane Mechanical Properties

- Cast Membrane Modulus Comparable to Extruded
- Longer Sintering Time Improves Modulus
Composite Membr. Conductivity at R.T.

BekkTech Test Data

Significant Progress is Being Made in the mC² Process
Composite Membrane Cell Testing: 100% RH

Performance is Comparable at 100% RH

75°C, 22 psig, fixed gas flows; air 1300 sccm, H₂ 650 sccm, 25 cm² active area
Composite Membrane Cell Testing: 20% RH

mC² Shows ~50% Improvement Compared to Blank
Composite Membrane Performance as $f(T)$

Additives Effective in Maintaining Good Cell Performance at High Temperature and Low RH

35% RH, 1 A/cm$^2$, 22 psig, stoich: fuel 3.5, air 2.8, 25 cm$^2$ cell
Future Work

• Improve additive dispersion
• Optimize composite membrane processing conditions for additives
• Study effect of additive loading
• Gas permeation and conductivity measurements
• Durability Testing:
  – RH Cycling
  – OCV Testing
  – Single cell testing
• Pursuing collaboration with OEM
Future Work

• Upcoming Key Milestones:
  – Select preferred design for the composite membrane (8/08)
  – Meet conductivity target of 100 mS/cm at 50% RH at 120°C (5/09 Go/No-Go)
  – Conductivity testing by DOE (annually)
Project Summary

• Fabricated 3 polymer iterations, 3 types of additives and >20 composite membr. batches

• Demonstrated 20% improved conductivity over 2007 and ~3x higher than Nafion 112®, without loss in mechanical properties

• Composite membrane shows significantly better cell performance at low RH than expected from conductivity tests

• Achieved low cell resistance
## Project Summary Table

### DOE 2010 Technical Targets for Membranes for Transportation Applications

<table>
<thead>
<tr>
<th>Performance Parameter</th>
<th>Units</th>
<th>2010 Target</th>
<th>Standard Membrane (Nafion® 112)</th>
<th>FY07-08 Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity at 30°C and 80% RH</td>
<td>mS/cm</td>
<td>70</td>
<td>38</td>
<td>56-78</td>
</tr>
<tr>
<td>Conductivity at 120°C and 25% RH</td>
<td>mS/cm</td>
<td>100</td>
<td>6.7</td>
<td>17.7</td>
</tr>
</tbody>
</table>