High Temperature Membrane with Humidification-Independent Cluster Structure

Ludwig Lipp
FuelCell Energy, Inc.
May 19th, 2009

Project ID #
fc_10_lipp

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

Timeline
• Start: June 2006
• End: May 2011
• 60% complete

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

Budget
• Total project funding
  – DOE share: $1500k
  – Contractor share: $600k
• Funding received in FY08: $346k
• Funding for FY09: $300k

Partners
• Polymer Partner
  – Polymer & membrane fab. and characterization
• Additive Partners
  – Additives synthesis and characterization
• Consultants
  – Polymer, additives, visualization
Acknowledgements

- **DOE**: Donna Ho, Terry Payne, Jason Marcinkoski, Amy Manheim, Greg Kleen, 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 275 million kWh of clean power produced world-wide (>50 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 H₂ and 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)
Relevance

Objectives:

• Develop polymer membranes with improved conductivity at up to 120°C

• Develop membrane additives with high water retention and proton conductivity

• Fabricate composite membranes

• Characterize polymer and composite membranes (in-plane conductivity)
Relevance

Impact of HTM:

• Higher conductivity membranes increase power density and efficiency of the fuel cell stack

• Operation at low relative humidity (RH) eliminates need for external humidification → simplifies the fuel cell system

• Operation at elevated temperatures simplifies thermal management (smaller radiator)

• Simpler system increases overall efficiency of fuel cell power plant → contributes to DOE cost goal ≤ $45/kWₑ

• Reduced weight of automotive fuel cell system leads to higher fuel efficiency
## 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>70 mS/cm</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>20 $/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>
Composite Membrane Concept

Co-polymer

Support Polymer

Water Retention Additive

Protonic Conductivity Enhancer

Integration Design Process

Immobilized Clusters

$mC^2$

Multi-Component System with Functionalized Additives
## Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>FY08 Goal</th>
<th>FY09 Goal</th>
<th>Current Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characterize Baseline Membrane</td>
<td>complete</td>
<td>-</td>
<td>complete ✓</td>
</tr>
<tr>
<td>Define Advanced Membrane</td>
<td>complete</td>
<td>-</td>
<td>complete ✓</td>
</tr>
<tr>
<td>Room Temperature Conductivity 70 mS/cm at 80% RH</td>
<td>-</td>
<td>74 mS/cm ✓</td>
<td></td>
</tr>
<tr>
<td>Select Preferred Design for mC²</td>
<td>complete</td>
<td>-</td>
<td>complete ✓</td>
</tr>
<tr>
<td>Screen Nano-additive Incorporation Options</td>
<td>-</td>
<td>complete</td>
<td>complete ✓</td>
</tr>
<tr>
<td>Characterize Advanced Membrane</td>
<td>-</td>
<td>complete</td>
<td>complete ✓</td>
</tr>
<tr>
<td>120°C Conductivity: <strong>Go/No-Go</strong></td>
<td>-</td>
<td>100 mS/cm at 50% RH</td>
<td>86-148 mS/cm ✓</td>
</tr>
</tbody>
</table>

**All FY08 and FY09 Milestones Met**
Technical Accomplishments

Major Achievements:

• Met Room Temperature Conductivity Milestone
  • 74 mS/cm confirmed by BekkTech

• Met High Temperature (120°C) Conductivity Milestone
  • 86-148 mS/cm for mC²

• Incorporation of Additives into mC² at the Nano-scale

• All Program Milestones Met
Technical Accomplishments

Design of Experiments Leading to Accomplishments since last Review:

- Three preparations of improved co-polymer, with successively lower equivalent weight (EW)
- Development of new solvent system for improved additive dispersion and casting
- Fabrication and characterization of six additive batches (water retaining and proton conducting)
- Synthesis of over 10 batches of mC², >15 samples
- >25 membrane conductivity tests, including 12 samples verified by BekkTech
Membrane Conductivity at R.T.

BekkTech Data, 30°C, 80%RH

DOE Conductivity Goal: 70mS/cm

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N112</td>
<td>30</td>
</tr>
<tr>
<td>M47</td>
<td>50</td>
</tr>
<tr>
<td>M55</td>
<td>60</td>
</tr>
<tr>
<td>M54</td>
<td>72</td>
</tr>
<tr>
<td>M65</td>
<td>74</td>
</tr>
</tbody>
</table>

Room Temperature Conductivity Goal Met

2008  2009
Membrane Conductivity at R.T.

Conductivity Meets DOE Target; >2x Nafion®
Membrane Conductivity at 120°C

Conductivity Approaching DOE Target; >2x Nafion®
Additive Development

Additive TEM

Additive Particle size <100 nm

Confirmed Structure and Particle Size
Additive Interaction

Protonic Conductivity Enhancer “docks” onto Water Retaining Additive Pores

Interaction Strengthens Synergy between Water Retention and Proton Conduction
Membrane Conductivity Measurements

- Conductivity Measurements and Non-Reproducibility
  - Samples are Non-Reproducible
    - Thickness Variation
    - Porosity Variation
    - Skin Effect
    - Non-Uniform Distribution of Additives
  - Measurement Method
    - Equipment
      - Compression Non-Uniformity
      - Contact Surfaces
      - In-Plane vs. Thru-Plane
    - Process Condition
      - RH During Cell Assembly
      - RH: Timing of Saturation
      - Pressure Control
      - Temp. Control and Sample Temp.
      - Hysteresis
    - Analysis
      - High-Frequency Resistance
      - Scanning DC Method (-0.1 to 0.1 V)

Improved Sample Reproducibility
Increased Measurement Reproducibility
Conductivity Reproducibility

Membrane Conductivity at 120°C at 230 kPa

All Three Samples Tested Exceed DOE Target

148 mS/cm

DOE Target: 100 mS/cm

FuelCell Energy
Effect of Additives on Conductivity

Membrane Conductivity at 120°C at 230 kPa

Additives Increase Conductivity → \( mC^2 \) Concept Validated
Membrane Conductivity at 120°C

Exceeded 100 mS/cm Goal
>3x Improved Membrane Conductivity vs. NRE-212

FuelCell Energy
Collaborations

Comprehensive Team Integrates Specialized Expertise

Polymer Company
- Advanced Polymer Dispersion Development
- Characterization

Fluoropolymer Consultant
- Evaluate Advanced Polymer Options

Nano-Materials Consultant
- Additive Design & Sourcing

Nano-Materials Co.
- Water Retaining Additive Synthesis

University
- Protonic Conductivity Enhancer Synthesis
- Environmental Chamber
- Characterization Hardware & Testing

Graphic Art Studio
- Visualization & Animation
- Guidance, Review Meetings
- HT & LRH WG Meetings

- Membrane Validation
- In-plane Conductivity

MO3223

FuelCell Energy
Proposed Future Work

• Continue to develop advanced polymer dispersions

• Optimize and further simplify integration of additives

• Expand membrane characterization to track progress towards DOE 2015 targets

• Cell testing at 95 and 120°C

• Durability Testing
Proposed Future Work

Upcoming Key Milestones:

• Go/No-Go decision for composite membrane (46 month milestone)

• Select low-cost, long life membrane design (50 month milestone)

• Readiness to meet DOE targets (1000 hr stability test – 52 month milestone)

• Membrane/MEA evaluation by DOE (annually)
Project Summary

• Fabricated 3 polymer iterations, 6 nano-additive batches and >10 composite membrane batches

• Improved mC² uniformity and conductivity with concurrent process simplification

• Integrated additive functionalization and composite membrane fabrication

• Demonstrated >2x improved conductivity at 120°C over 2008 (>3x higher than NRE-212®)
## 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® NRE-212</th>
<th>FY08-09 Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity at 30°C and 80% RH</td>
<td>mS/cm</td>
<td>70</td>
<td>33</td>
<td>74</td>
</tr>
<tr>
<td>Conductivity at 120°C and 50% RH</td>
<td>mS/cm</td>
<td>100</td>
<td>39</td>
<td>86-148</td>
</tr>
</tbody>
</table>