High Temperature Membrane with Humidification-Independent Cluster Structure

Ludwig Lipp
FuelCell Energy, Inc.
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Project ID # fc040

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Overview

Timeline
- Project start date: Jun 2006
- Project end date: Aug 2012
- Percent complete: 96%

Budget
- Total project funding
  - DOE share: $1500k
  - Cost share: $600k
- Funding received in FY11: $168k
- Planned Funding for FY12: $65k

Barriers
A. Durability: Membrane and MEA durability
C. Performance: High MEA performance at low RH & high T

Partners
- Univ. of Central Florida
  - Membrane characterization, MEA fabrication & evaluation
- Oak Ridge National Lab
  - Membrane and additive microstructural characterization
- Polymer Partner
  - Polymer & membrane fabrication & characterization
- Additive Partners
  - Additives synthesis & characterization
- Consultants
  - Polymer, additives
Relevance

Overall Objective:

Develop membranes that meet the DOE performance, life and cost targets, including improved conductivity and area specific resistance at up to 120°C and low relative humidity (25-50%).
Relevance

Development Objectives for Composite Membrane:

• Develop improved membrane polymer

• Develop membrane additives with high water retention (nano-zeolites)

• Develop membrane additives with high proton conductivity (superacids)

• Fabricate composite membranes (polymer + additives = mC²)

• Characterize polymer, additives and composite membranes

• Scale-up considerations for cost reduction strategy

• Fabricate MEAs using promising membranes and characterize
## Approach

<table>
<thead>
<tr>
<th>Target Parameter</th>
<th>DOE Target (2017)</th>
<th>Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area specific proton resistance at: 120°C and 40-80 kPa water partial pressure</td>
<td>0.02 Ω cm²</td>
<td>Multi-component composite structure, lower EW, additives with highly mobile protons</td>
</tr>
<tr>
<td>80°C and 25-45 kPa water partial pressure</td>
<td>0.02 Ω cm²</td>
<td>Higher number of functional groups</td>
</tr>
<tr>
<td>Hydrogen and oxygen cross-over at 1 atm</td>
<td>2 mA/cm²</td>
<td>Higher molecular weight polymer for stronger membrane structure</td>
</tr>
<tr>
<td>Minimum electrical resistance</td>
<td>1000 Ω cm²</td>
<td>Improved membrane thickness tolerance and additive dispersion</td>
</tr>
<tr>
<td>Cost</td>
<td>20 $/m²</td>
<td>Simplify polymer processing</td>
</tr>
<tr>
<td>Performance @ 0.8 V (¼ rated power)</td>
<td>300 mA/cm²</td>
<td>MEA with matching polymer in membrane and electrodes</td>
</tr>
<tr>
<td>Performance @ rated power</td>
<td>1,000 mW/cm²</td>
<td>Optimized ionomer content in electrodes</td>
</tr>
</tbody>
</table>
Approach: mC² Concept

Improvements Made:

- Lower EW (850 → 800-650)
- Higher Molecular Wt.
- Chemically stabilized polymer
- Smaller particle size (>80 → 30 nm)
- Increased proton density (1 → 2 mobile protons per molecule) and lower cost

Multi-Component Composite Membrane (mC²) with Functionalized Additives
Major Accomplishments

• High protonic conductivity – 0.113 S/cm* (DOE Target: >0.1 S/cm)

• Low cross-over – 0.3 mA/cm² * (DOE Target: <2 mA/cm²)

• Low electrical conductivity (high electrical resistance) – 2,860 Ωcm² * (DOE Target: >1000 Ωcm²)

• Transferred MEA Fabrication Technology to UCF
  - Easily fabricated into an MEA (in UCF’s Experience)

• Good CCM performance – 1247 mW/cm² at rated power* (DOE Target: >1000 mW/cm²)

• Good durability in UCF 11-day test protocol

* UCF Data
## Accomplishments: Risk Resolution

<table>
<thead>
<tr>
<th>Issues</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produce Stable Nanozeolites</td>
<td>Completed</td>
</tr>
<tr>
<td>Produce Nanozeolite Superacid Composites</td>
<td>Completed</td>
</tr>
<tr>
<td>Produce mC²/Polymer Composites</td>
<td>Completed</td>
</tr>
<tr>
<td>Increase Production Capacity of Nanozeolite</td>
<td>Completed</td>
</tr>
<tr>
<td>Decrease Cost of Superacids</td>
<td>Completed</td>
</tr>
<tr>
<td>Demonstrate Improved Conductivity</td>
<td>Completed</td>
</tr>
<tr>
<td>Demonstrate Reproducibility of Select Systems</td>
<td>Completed</td>
</tr>
<tr>
<td>Identify Best Slurry Compositions, Casting Substrates and Treatment Conditions that give Improved Conductivity</td>
<td>Completed</td>
</tr>
<tr>
<td>In-cell characterization and durability</td>
<td>In progress</td>
</tr>
</tbody>
</table>
Accomplishments: IP Discoveries

- The key factor to maintain nanoparticle zeolites indefinitely
- The adsorption of superacids on zeolite without affecting the zeolite structure
- The use of novel superacids in fuel cells
- The use of superacids adsorbed on zeolites in fuel cells
- The potential use of superacids adsorbed on zeolites as new H⁺ acid catalysts
- The key fact that casting solvents can reduce measured conductivities by an order of magnitude but can be removed by acid wash or time in high RH gas streams
Accomplishments: mC² Characterization

Relatively homogeneous dispersion of aggregated particles are observed in the membrane (#82) with a higher loading. The aggregated particles may have achieved a continuous 3-dimensional network.

Nano-zeolite structure remains intact after superacid deposition.

The microstructure is uniform across the ~60μm blank (#76) and ~20μm particle-incorporated (#82) membrane.

Achieved good distribution of additives in mC²
Conductivity Milestone at 120°C has been Independently Validated

Accomplishments: $mC^2$ Conductivity

1. Conductivity based on thickness measured at ambient temperature and RH
2. Through-plane resistance corrected for non-membrane ohmic resistance
Accomplishments: Area Specific Resistance

Through-Plane ASR of B10-FSEC-31

ASR almost meets the DOE target at 120°C and 50% RH
Accomplishments: Electrode Improvements

MEA performance as function of ionomer dry weight in the cathode electrode

120°C, 35% RH, H₂/Air

- Wt% ionomer in cathode: [32%, 29%, 25%, 15%]
- 630 mV at 1 A/cm²

95°C, 83% RH, H₂/Air

- Wt% ionomer in cathode: [32%, 29%, 25%, 15%]
- 700 mV at 2 A/cm²

* Corrected for Crossover H₂: Limiting current density in the Linear Sweep Voltammogram was deducted from the measured current densities in the polarization curves to isolate the effect of ionomer content in the cathode.

- **mC² Required Re-optimization of the MEA**
- **Achieved High Performance at High Temp. and High Current Density**
Accomplishments: mC² to MEA Development

Electrode Improvements Led to Higher Power
Accomplishments: 
**mC² Performance Stability**

Promising Stability at 95°C
## Accomplishments:
**MEA Comparison to DOE Targets**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>Target 2017</th>
<th>B2</th>
<th>B3</th>
<th>B5</th>
<th>B7</th>
<th>B9</th>
<th>B10</th>
<th>NRE 211</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area specific proton resistance at:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C and 40 - 80 kPa pH$_2$O</td>
<td>Ohm cm$^2$</td>
<td>≤ 0.02</td>
<td>0.08*</td>
<td>0.08*</td>
<td>0.064*</td>
<td>0.23*</td>
<td>0.110*</td>
<td>0.025*</td>
<td>0.15*</td>
</tr>
<tr>
<td>80°C and 25 - 45 kPa pH$_2$O</td>
<td>Ohm cm$^2$</td>
<td>≤ 0.02</td>
<td>0.02†</td>
<td>0.02†</td>
<td>0.016†</td>
<td>0.05†</td>
<td>0.045†</td>
<td>0.056†</td>
<td>0.02†</td>
</tr>
<tr>
<td>Maximum Hydrogen cross-over a</td>
<td>mA / cm$^2$</td>
<td>2</td>
<td>1</td>
<td>0.95</td>
<td>1.6</td>
<td>0.48</td>
<td>&lt;0.4</td>
<td>0.3</td>
<td>0.76</td>
</tr>
<tr>
<td>Minimum electrical resistance b</td>
<td>Ohm cm$^2$</td>
<td>1000</td>
<td>1200</td>
<td>800</td>
<td>417</td>
<td>500</td>
<td>2,860</td>
<td>1,836</td>
<td>2100</td>
</tr>
<tr>
<td>Performance @ 0.8V (¼ Power)</td>
<td>mA/cm$^2$</td>
<td>300</td>
<td>104</td>
<td>177</td>
<td>209</td>
<td>150</td>
<td>137</td>
<td>206</td>
<td>113</td>
</tr>
<tr>
<td>Performance @ rated power</td>
<td>mW/cm$^2$</td>
<td>1000</td>
<td>334</td>
<td>567</td>
<td>1239</td>
<td>482</td>
<td>577</td>
<td>1247</td>
<td>363</td>
</tr>
</tbody>
</table>

*Measured at 120°C and 70 kPa water partial pressure
†Measured at 80°C and 38 kPa water partial pressure
a. Measure in humidified H$_2$/N$_2$ at 25°C
b. Measure in humidified H$_2$/N$_2$ using LSV curve from 0.4 to 0.6 V at 80°C
c. Determined by subtracting contact resistances from cell current interrupt values

Most targets met, good progress towards remaining targets
Collaborations

Prime

• FuelCell Energy, Inc. (Industry):
  – Leading fuel cell developer for over 40 years

Partners

• University of Central Florida (University):
  – Membrane characterization, MEA fabrication & evaluation

• Scribner Associates, Inc. and BekkTech LLC (Industry):
  – Membrane through-plane and in-plane conductivity

• Oak Ridge National Lab (Federal Laboratory):
  – Membrane and additive microstructural and chemical characterization

• Polymer Company (Industry):
  – Polymer and membrane fabrication, initial characterization

• Additive Partners (Industry/University):
  – Additives synthesis, functionalization and characterization

• LGC Consultant LLC (Industry):
  – Additive synthesis and integration into mC²
Collaborations: Team Efforts

- Polymer: Synthesized >20 batches of polymer and ionomer dispersion
- Water-retaining Additive: Synthesized and purified >30 batches of nano-zeolite
- Protonic Conductivity Enhancer: Synthesized >5 batches of 1 and 2-proton molecules
- Functionalized Additive: Fabricated 3 batches of Protonic Conductivity Enhancer deposited on Water-retaining Additive
- Membrane and mC² Fabrication: >15 batches of polymer membrane film and >30 batches of mC² membrane film
- Microstructural Characterization: ORNL characterized >10 membrane samples and >10 additive samples
- MEA: UCF fabricated 13 MEAs
- Cell Testing: >30 cells tested, including 12 cells at UCF
Proposed Future Work

• Durability: Characterization of mC$^2$ mechanical and chemical stability per DOE protocols (UCF – funding permitting)

• Complete invention disclosure

• Complete final report
Progress Summary

• Developed technology to synthesize mC² components and to integrate them

• Membrane exceeds DOE 120°C conductivity target at 50% RH and approaches ASR target

• Developed MEA fabrication process with UCF that is compatible with mC²

• Preliminary optimization of ionomer content in cathode led to good 120°C MEA performance of 510 mV at 1 A/cm², 35% RH (UCF)

• At near-term target of 95°C: 585 mV at 2 A/cm², 83% RH (UCF)

• Cell data exceeds DOE power density target (UCF)
## Project Summary Table

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<tr>
<th>Characteristic</th>
<th>Units</th>
<th>DOE 2017 Target</th>
<th>FY11-12 Result</th>
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<td>mA / cm(^2)</td>
<td>2</td>
<td>0.3 (\checkmark)</td>
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*Values are at 80°C unless otherwise noted*

\(^a\) Measure in humidified H\(_2\)/N\(_2\) at 25°C

\(^b\) Measure in humidified H\(_2\)/N\(_2\) using LSV curve from 0.4 to 0.6 V at 80°C

\(^c\) Determined by subtracting contact resistances from cell current interrupt values
Acknowledgements

• DOE: Donna Ho, Greg Kleen, Tom Benjamin, Kathi Martin, Jason Marcinkoski, Amy Manheim, Reg Tyler and John Kopasz

• UCF: Jim Fenton, Darlene Slattery, Marianne Rodgers, Paul Brooker, Nahid Mohajeri, Len Bonville, Russ Kunz (Testing protocols, membrane and MEA evaluation)

• Scribner Associates, Inc.: Kevin Cooper (Conductivity measurements)

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

• ORNL: Kelly Perry, Karren More (Microstructural characterization)

• FCE Team: Pinakin Patel, Ray Kopp, Jonathan Malwitz, Chao-Yi Yuh, Nikhil Jalani, Adam Franco, Al Tealdi