Ionomer Dispersion Impact on PEM Fuel Cell and Electrolyzer Durability

Hui Xu (PI)
Giner Inc.
Newton, MA

June 8, 2015

This presentation does not contain any proprietary or confidential information
Technical Targets

- Validate the scalability and processibility of MEAs
- Integrate Giner dimension-stabilized membrane (DSM) with LANL ionomer dispersion to create MEAs mechanically and chemically stable

Timeline

- Project Start Date: 6/9/2014
- Project End Date: 3/8/2015

Budget

- Total Project Value: $149,949
- Total Funding Spent: $149,949

Barriers Addressed

- PEM fuel cell and electrolyzer durability

Partners

- LANL: Dr. Yu-Seung Kim
Relevance: LANL Non-aqueous Ionomer Dispersion Technology Transfer and Commercialization

DOE Fuel Cell Catalyst Technical Targets

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>2020 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum group metal (PGM) total content (both electrodes)</td>
<td>g/kW</td>
<td>&lt;0.125</td>
</tr>
<tr>
<td>PGM total loading (both electrodes)</td>
<td>mg/cm²</td>
<td>&lt;0.125</td>
</tr>
<tr>
<td>Loss in catalytic (mass) activity ²,³</td>
<td>% loss</td>
<td>&lt;40</td>
</tr>
<tr>
<td>Loss in performance at 0.8 A/cm² ²</td>
<td>mV</td>
<td>30</td>
</tr>
<tr>
<td>Loss in performance at 1.5 A/cm² ²</td>
<td>mV</td>
<td>30</td>
</tr>
<tr>
<td>Mass activity @ 900 mV_R-free ³</td>
<td>A/mg_PGM</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Nafion® from Water/2-Propanol

Nafion® from NMP

Nafion® from Glycerol

Premature electrode & electrode-membrane interface failure

Performance decrease due to Pt nano-catalyst agglomeration

Performance decrease was compensated with time dependent structural change

In water/2-propanol

In glycerol

In NMP
Combining Giner’s DSM technology with LANL’s ionomer dispersion technology may deliver lower-cost MEAs that are mechanically and chemically stable.
Particle morphology in dispersion is critical for membrane and electrode properties. LANL performed SANS and dynamic light scattering to investigate the particle morphology. Recently we found that the particle morphology of NMP dispersion is different from what we know.

\[
I(Q) \propto \Delta \rho \left<P(Q)S(Q)\right>
\]

\[
I(Q) = I_g(0) \exp\left[-Q^2\xi^2/2\right] + I_k(0)/(1 + Q^2\xi^2) + B
\]

Particle size from DLS: RH = 8.7 nm

Current morphology is more consistent with electrode porosity and fuel cell mass transfer behavior

Hybrid membranes obtained using Giner’s high throughput DSM platform.
• Conductivity of the DSMs was measured in liquid water at various temperatures and compared to Nafion®212 (N212).
• Conductivity was as expected for the lower equivalent weight DSM, and higher than expected for the N1100 based DSM.
DSMs show higher stiffness than unsupported N212

- Low EW DSM (865-17-1) shows some loss of stiffness under high RH conditions, but is still higher than N212 at all temperatures
Accomplishment: MEA Stability via Voltage Cycling

Ionomer: Nafion® in DMAc; T=80 °C; RH=100%; ambient pressure; 50 cm² MEA; Voltage cycling from 0.6 to 1.0 V; H₂ flow: 1 L/min; O₂ flow rate 2 L/min

| Cycle: Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V. Single cell 25 cm² |
| Number: 30,000 cycles |
| Cycle time: 16 seconds |
| Temperature: 80°C |
| Relative humidity: Anode/cathode 100%/100% |
| Fuel/oxidant: Hydrogen/N₂ (H₂ at 100 sccm and N₂ at 50 sccm for a 25 cm² cell) |
| Pressure: Atmospheric pressure |

<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic mass activity*</td>
<td>At beginning and end of test minimum</td>
<td>≤40% loss of initial catalytic activity</td>
</tr>
<tr>
<td>Polarization curve from 0 to ≥1.5 A/cm²</td>
<td>After 0, 5k, 10k, 20k, and 30k cycles</td>
<td>≤30 mV loss at 0.8 A/cm²</td>
</tr>
<tr>
<td>ECSA/cyclic voltammetry**</td>
<td>After 0, 5k, 10k, 20k, and 30k cycles</td>
<td>≤40% loss of initial area</td>
</tr>
</tbody>
</table>

No MEA voltage loss after voltage cycling
ECSA of MEA Upon Voltage Cycling

- Cyclic voltammogram (CV) profile is very stable upon voltage cycling;
- Negligible ECSA change after 30,000 cycles

Original Calculated ECSA 82 m²/g
MEA Stability upon RH Cycling

Ionomer: Nafion® in DMAc; T=80 °C; ambient pressure; 50 cm² MEA; RH cycling from dry to 100%; H₂ flow: 1 L/min; O₂ flow rate 2 L/min

<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crossover</td>
<td>Every 24 hours</td>
<td>≤2 mA/cm²</td>
</tr>
<tr>
<td>Shorting resistance</td>
<td>Every 24 hours</td>
<td>&gt;1,000 ohm cm²</td>
</tr>
</tbody>
</table>

MEA performance is well retained after 12,000 cycles
• Stable CV and no ECSA change upon RH cycling
• Extremely low H₂ crossover: 0.4 mA/cm², no electrical shorting
Giner Protocol: 1.4 V to 1.8 V voltage cycling; 30 seconds for each voltage

Two Categories of Anode Catalysts
- Baseline: 2 mg/cm² Ir black
- 0.4 mg/cm² Ir/WₓTi₁₋ₓO₂, demonstrating comparable performance to baseline

LANL Ionomer Dispersion
- 5 wt% Nafion in NMP
Electrolyzer MEA Stability Test

- 2 mg/cm² Ir Black
- 0.4 mg/cm² Ir/WₓTi₁₋ₓO₂

- Good compatibility between catalyst and ionomer
- Excellent MEA durability demonstrated
## Performance Schedule

<table>
<thead>
<tr>
<th>Task</th>
<th>% Time</th>
<th>Month</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Prepare ionomer dispersions</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>2. Make DSM using dispersed ionomer</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>3. Characterize membrane properties</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>4. Make fuel cell and electrolyzer MEAs</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>5. Validate PEM fuel cell durability</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>6. Evaluate PEM electrolyzer durability</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Report</td>
<td>5</td>
<td>X</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Milestone #</th>
<th>Description</th>
<th>Scheduled Time</th>
<th>Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Obtain DSMs using LANL ionomer dispersions and Giner porous support</td>
<td>Month 3</td>
<td>100%</td>
</tr>
<tr>
<td>2</td>
<td>Achieve fuel cell MEA &lt; 20 mV drop after 30,000 cycles 0.6 to 1.0 V.</td>
<td>Month 7</td>
<td>100%</td>
</tr>
<tr>
<td>3</td>
<td>Achieve electrolyzer MEA &lt; 20 mV drop after 10,000 cycles 1.4 to 1.8 V.</td>
<td>Month 9</td>
<td>100%</td>
</tr>
</tbody>
</table>
Proposed Future Work

- Scale-up of non-aqueous ionomer dispersion
- Scale-up of DSM-based MEA fabrication
  - Based on Giner’s roll-to-roll DSM technology
- More applications in PEM electrolyzers
- Licensing and commercialization
Acknowledgments and Collaborations

- Financial support from DOE SBIR/STTR Program
- Subcontractor
  - Dr. Yu-Seung Kim and David Langlois at LANL
- Giner Personnel
  - Jason Willey
  - Tom McCallum
  - Brian Rasimick
  - Zach Green
  - Corky Mittelsteadt
Summary

• LANL non-aqueous ionomer dispersion technology has been further validated at Giner in more scalable and processible conditions via accelerated stress tests;

• Hybrid membranes using Giner’s DSM supports and LANL ionomer show good conductivity and improved mechanical properties;

• The combination of hybrid membrane and non-aqueous ionomer-based electrodes produces chemically and mechanically stable MEAs

• The non-aqueous ionomer also demonstrates good compatibility with OER catalysts in electrolyzer, leading to excellent stability upon voltage cycling