Ionomer Dispersion Impact on PEM Fuel Cell and Electrolyzer Performance and Durability

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Giner, Inc.
Newton, MA

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Project Overview

Timeline
• Project Start Date: 7/28/2015
• Project End Date: 5/27/2018

Budget
• Total Project Value
  - $1.15 million
  - $1.14 million

Barriers Addressed
• PEM fuel cell and electrolyzer performance and durability

Technical Targets
• Elucidate how ionomer dispersions impact electrode structures and performance
• Create fuel cell MEAs that are mechanically and chemically stable (DOE 5000 hrs. target)
• Develop processable and scalable MEAs fabrication platforms using LANL ionomer dispersion and Giner DSMs

Project Nature
• First DOE Technology Transfer Opportunity Project (SBIR-TTO)

Partners
• LANL: Dr. Yu-Seung Kim
• UConn: Dr. Jasna Jankovic
• ORNL: Dr. Karren More
# Relevance

## DOE Fuel Cell Catalyst Technical Targets

<table>
<thead>
<tr>
<th>Parameter</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 ¹,²</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 ilk-free ³</td>
<td>A/mol</td>
<td>0.44</td>
</tr>
</tbody>
</table>

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### From Water/2-Propanol
- Premature electrode & electrode-membrane interface failure

### From NMP
- Performance decrease due to Pt nano-catalyst agglomeration

### From Glycerol
- Performance decrease was compensated with time dependent structural change
Technical Approaches

Proposed Phase IIB work

**Processibility**
- Roll-to-roll production of DSM
- Ultra spraying or roll coater to make MEAs

**Scalability**
- From LANL 5cm² to 50-100cm² full MEAs

**Durability**
- Chemical Stability: Voltage Cycling
- Mechanical Stability: RH Cycling

**Profitability**
- Fuel Cell MEAs for external customers
- Electrolyzer MEAs for Giner MW stacks
Pt/C Electrodes Fabrication

Catalyst: Tanaka Pt (47 w.t. %)/C  Membrane: Nafion 212

- Magnetic Stirring - 2 days
- Mayer Bar Coating

- Ionomer in the electrode and membrane are both in acid form so re-protonation is not required
- Both ink mixing and coating processes are easily scalable

- Drying at 60°C for 30 min, then vacuum oven overnight @150°C
- Pt loading was verified by XRF
- Decal transfer is successful for all the electrode studied.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Boiling Point (°C)</th>
<th>Viscosity @ 25°C (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPA</td>
<td>82.6</td>
<td>1.96</td>
</tr>
<tr>
<td>NPA</td>
<td>97</td>
<td>1.96</td>
</tr>
<tr>
<td>EG</td>
<td>197.3</td>
<td>16.9</td>
</tr>
<tr>
<td>BUT</td>
<td>235</td>
<td>89.24 @ 20°C</td>
</tr>
<tr>
<td>PEN</td>
<td>242</td>
<td>114.6</td>
</tr>
</tbody>
</table>
Accomplishment: More Non-Aqueous Ionomer Dispersions (Giner)

<table>
<thead>
<tr>
<th>Sample Abbreviation</th>
<th>Description</th>
<th>I/C</th>
<th>Pt Loading (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPA</td>
<td>Nafion in 2-propanol/water</td>
<td>0.6</td>
<td>0.19</td>
</tr>
<tr>
<td>NPA</td>
<td>Nafion in 1-propanol/water</td>
<td>0.6</td>
<td>0.175</td>
</tr>
<tr>
<td>EG</td>
<td>Nafion in ethylene glycol</td>
<td>0.6</td>
<td>0.21</td>
</tr>
<tr>
<td>BUT</td>
<td>Nafion in butanediol</td>
<td>0.6</td>
<td>0.19</td>
</tr>
<tr>
<td>PEN</td>
<td>Nafion in pentanediol</td>
<td>0.6</td>
<td>0.18</td>
</tr>
<tr>
<td>PEN-3M</td>
<td>3M 825 EW in pentanediol</td>
<td>0.6</td>
<td>0.17</td>
</tr>
</tbody>
</table>
The solvent has significant impact on ink particle size and distribution. Other than IPA/H₂O based ink, the ink with Pentanediol-3M ionomer also exhibits large agglomerates, and its electrode contains many pinholes.
TEM of Fresh Electrodes

- Solvent has significant impact on electrode microstructures
  - Better Ionomer and Pt distribution with EG and BUT
  - Smaller secondary pores with EG and BUT

Images taken by Oak Ridge National Laboratory
Performance Comparison by Solvents

Cell temp: 80 °C, anode: 80 °C, cathode: 75 °C, ambient Pressure

- Performance ranking: nPA > Ethylene glycol ≈ Butanediol ≈ Pentanediol ≈ Pentanediol (3M) > IPA
Electrode Durability

Durability test: voltage cycling between 0.6 and 1.0V. @80°C, 100%RH, 0.2 SLPM H₂ / 0.075 SLPM N₂

- NPA 80°C, 100%RH, H₂-Air
  - ΔV @ 1A/cm² = 65~80 mV
  - ΔV @ 1A/cm² = ~36 mV

- IPA 80°C, 100%RH, H₂-Air
  - ΔV @ 1A/cm² = 65~79 mV
  - ΔV @ 1A/cm² = ~30 mV

- BUT 80°C, 100%RH, H₂-Air
  - ΔV @ 1A/cm² = ~65~80 mV

- EG 80°C, 100%RH, H₂-Air
  - ΔV @ 1A/cm² = ~30 mV

EG and BUT MEAs demonstrated significantly lower degradation than nPA and IPA baselines.
### TEM-EDS maps - quantification:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt loading-XRF, mg/cm²</th>
<th>Pt loading-EDS, mg/cm²</th>
<th>Thickness (TEM), um</th>
<th>Porosity (total), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>nPA BOL decal</td>
<td>0.175</td>
<td>0.18</td>
<td>4.09</td>
<td>68</td>
</tr>
<tr>
<td>nPA EOT CCM</td>
<td>0.175</td>
<td>0.12</td>
<td>4.21</td>
<td>71</td>
</tr>
<tr>
<td>IPA BOL decal</td>
<td>0.19</td>
<td>0.19</td>
<td>4.38</td>
<td>68</td>
</tr>
<tr>
<td>IPA EOT CCM</td>
<td>0.19</td>
<td>0.17</td>
<td>5.13</td>
<td>73</td>
</tr>
<tr>
<td>BUT BOL decal</td>
<td>0.19</td>
<td>0.20</td>
<td>4.03</td>
<td>65</td>
</tr>
<tr>
<td>BUT EOT CCM</td>
<td>0.19</td>
<td>0.14</td>
<td>5.42</td>
<td>73</td>
</tr>
<tr>
<td>EG BOL decal</td>
<td>0.21</td>
<td>0.20</td>
<td>4.08</td>
<td>62</td>
</tr>
<tr>
<td>EG EOT CCM</td>
<td>0.21</td>
<td>0.16</td>
<td>5.11</td>
<td>71</td>
</tr>
</tbody>
</table>

- Consistent Pt loading by XRF and EDS
- Uniform ionomer and Pt distribution for nPA and BUT samples
- IPA sample had very non-uniform ionomer and Pt distribution, with a lot of agglomeration of both components
- EG sample had slightly non-uniform ionomer distribution
- All BOL decals had a thin ionomer layer on the cathode-decal interface
- All EOL cathodes show increase in total porosity between 4-14%, with BUT and EG showing the largest change

Images taken by UCONN
Pt PSD - quantification

- High magnification (180k) TEM images taken for Pt particle size analysis (PSD)
- EG and BUT: smaller particle size increase (200 particles were measured for PSD for each sample)
All cathodes experienced increase in thickness after testing (BUT and EG highest; nPA the lowest increase)

All EOL cathodes show increase in total porosity between 4-14% (BUT and EG highest)

All EOL samples experienced Pt loss from the cathode (10-32%) to membrane
EOT HR TEM-EDS-Pt Distribution

Images taken by UCONN

mild Pt agglomeration

BUT

Fluorine
Platinum
Carbon

nPA

IPA

EG
EOT HR TEM-EDS-Ionomer Distribution

Images taken by UCONN

nPA

IPA

BUT

mild Pt agglomeration

EG

F Fluorine
Pt Platinum
C Carbon
## Comparison of MEAs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>nPA</td>
<td>• Uniform ionomer and Pt distribution</td>
<td>• Significant Pt agglomeration and particle size growth at EOT</td>
</tr>
<tr>
<td></td>
<td>• Decent coating quality and ease of drying</td>
<td>• Large degradation upon voltage cycling</td>
</tr>
<tr>
<td></td>
<td>• Best BOL performance</td>
<td></td>
</tr>
<tr>
<td>IPA</td>
<td>• Common solvent in MEA fabrication</td>
<td>• Large cracks</td>
</tr>
<tr>
<td></td>
<td>• Fast drying</td>
<td>• Non-uniform ionomer and Pt distribution</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Significant Pt agglomeration and particle size growth at EOT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Large degradation upon voltage cycling</td>
</tr>
<tr>
<td>BUT</td>
<td>• Uniform ionomer and Pt distribution</td>
<td>• Dries slowly</td>
</tr>
<tr>
<td></td>
<td>• Decent coating quality when mixing long</td>
<td>• May need long time low energy mixing</td>
</tr>
<tr>
<td></td>
<td>• Smallest Pt particle size growth</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Greatly improved durability upon voltage cycling</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Comparable BOL performance</td>
<td></td>
</tr>
<tr>
<td>EG</td>
<td>• Decent coating quality when mixing long</td>
<td>• Slightly non-uniform ionomer distribution</td>
</tr>
<tr>
<td></td>
<td>• Smaller Pt particle size growth than baseline</td>
<td>• May need long time low energy mixing</td>
</tr>
<tr>
<td></td>
<td>• Greatly improved durability upon voltage cycling</td>
<td>• Dries slowly</td>
</tr>
<tr>
<td></td>
<td>• Comparable BOL performance</td>
<td></td>
</tr>
</tbody>
</table>
EG-based Electrode Durability

**EG, 80°C, 100%RH, H2-Air**

- ΔV @ 1A/cm² = ~36 mV

**EG-boiled, 80°C, 100%RH, H2-Air**

- ΔV @ 1A/cm² = ~51 mV

- EG-MEA after boiled in DI H2O for 1 hour

**nPA with 20%EG, 80°C, 100%RH, H2-Air**

- ΔV @ 1A/cm² = ~44 mV

- nPA baseline with 20%EG

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**EG-MEA after boiled in DI H2O for 1 hour**

- After boiling, EG-MEA exhibits slightly lower OCV, and higher voltage degradation.
- With nPA baseline, adding 20%EG helps to lower the degradation to be similar as EG sample

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<table>
<thead>
<tr>
<th>cycles</th>
<th>ECSA (m²/g)</th>
<th>Cdl (mF/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EG</td>
<td>EG-boiled</td>
</tr>
<tr>
<td>0</td>
<td>50</td>
<td>44</td>
</tr>
<tr>
<td>1000</td>
<td>41</td>
<td>40</td>
</tr>
<tr>
<td>10000</td>
<td>32</td>
<td>27</td>
</tr>
<tr>
<td>30000</td>
<td>26</td>
<td>24</td>
</tr>
</tbody>
</table>
Summary

- Ionomer dispersions in a variety of solvents have been investigated; solvent affects ionomer morphology and re-conformation.
- Ionomer dispersions impact the electrode structures in the BOL and EOT, including ionomer distribution, catalyst distribution, porosity and thickness etc.
- Ionomer dispersions influence fuel cell electrode performance and durability. Samples with high boiling point solvent-dispersed Nafion ionomer demonstrate greatly improved durability and comparable performance as baseline.
- The good durability in EG and BUT samples may be related to the trace amount of high boiling point solvents in the electrode, which help to protect the Pt from growing fast during voltage cycling.
- Electrode restructuring upon voltage cycling (thicker and more porous electrode @EOT) may provide more resiliency to mitigate electrode deformation and transport loss.
Future Work

- Perform TEM of fresh MEAs compared to decals and decayed MEAs
- Further test the non-aqueous ionomer based electrode under more realistic accelerated stress testing (AST) conditions
- Explore state-of-the-art components integrated with non-aqueous ionomer to make low Pt and high power MEAs (Phase IIB)
  - High-performance Pt and its alloys
  - Thin membranes (DSM)
- Electrode scale-up (Phase IIB)
Acknowledgments

- Financial support from DOE SBIR/STTR Program
- Program Manager
  - Ms. Donna Ho
- Dr. Yu-Seung Kim at LANL (Subcontractor)
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- Dr. Jasna Jankovic at UCONN (TEM/STEM-EDS analysis)
- Giner Personnel