Material-Process-Performance Relationships in PEM Catalyst Inks and Coated Layers

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Presenter: Scott Mauger
National Renewable Energy Laboratory
June 13, 2018

DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

MN019

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Overview

Timeline and Budget

• Project start date: 10/1/16
• FY17 DOE funding: $280,000
• FY18 planned DOE funding: $224,000
• Total DOE funds received to date: $280,000

Barriers

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Lack of high-volume MEA processes</td>
<td>$20/kW (2020) at 500,000 stacks/yr</td>
</tr>
<tr>
<td>H. Low levels of quality control</td>
<td></td>
</tr>
</tbody>
</table>

Partners

• Argonne National Laboratory
  – Debbie Myers
• Colorado School of Mines
  – Svitlana Pylypenko
• Proton OnSite
  – Chris Capuano
• 3M Company
  – Mike Yandrasits
• Umicore
  – Sascha Toelle
Task 1: Membrane Electrode Assemblies

<table>
<thead>
<tr>
<th>Task</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>Develop processes for direct coating of electrodes on membranes or gas diffusion media. (4Q, 2017)</td>
</tr>
<tr>
<td>1.3</td>
<td>Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste. (4Q, 2017)</td>
</tr>
</tbody>
</table>

Task 5: Quality Control and Modeling and Simulation

<table>
<thead>
<tr>
<th>Task</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>Develop correlations between manufacturing parameters and manufacturing variability, and performance and durability of MEAs. (4Q, 2018)</td>
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</tbody>
</table>

- Roll-to-roll (R2R) is the lowest cost/highest throughput method for production of FC/LTE materials
- R2R coating techniques require different ink formulation and have different physics than lab-scale processes
- Many researchers/producers do not have access to the infrastructure to understand how the conditions and processes of R2R will impact their materials
- Results directly relevant to researchers and producers
Relevance:
Project Success Has Led to Additional DOE Projects

- **AMO Roll-to-Roll Consortium (MN018, 6/14/18, 10:00)**
  - Lead for Fuel Cell Core Lab Projects
    - “Control of ionomer distribution in R2R coated electrodes”
    - “In situ X-ray scattering studies during dispersion of catalyst inks”
- **HydroGen (PD148, 6/13/18, 3:15 P.M.)**
  - Supporting four 2A projects
  - Supporting 2B Benchmarking project
- **ElectroCat (FC160, 6/13/18, 3:15 P.M.)**
  - “High-throughput fabrication of gradient electrodes for combinatorial testing”
  - Catalyst ink formulation and development research
- **HyET H2@Scale CRADA (H2006 6/14/18 6:30 P.M., poster)**
  - “Membrane Electrode Assembly Manufacturing Automation Technology for the Electrochemical Compression of Hydrogen”
- **Peroxygen Systems** – AMO-funded SBV
- **L’Innovator** – FCTO Pilot Incubator for MEA Production
  - Scale-up and R2R coating of licensed BNL/LANL IP
Approach:
Study Transition from Lab-Scale to Scalable Electrode Production

Lab Scale – Ultrasonic Spray
- Dilute ink (~0.6 wt% solids)
- Ultrasonic mixing
- Sequential build up of layers
- Heated substrate
- Vacuum substrate

Used to demonstrate new materials and for fundamental studies

Large Scale – Roll-to-Roll (R2R)
- Concentrated ink (~4.5-15 wt% solids)
- Shear mixing
- Single layer
- Room temp. substrate
- Convective drying

Needed to demonstrate scalability of materials and MEA/cell designs, and industrial relevance
Approach:
Integrated Approach for Processes Scale-Up

Unique Aspects and Capabilities of this Project

**Ink Formulation**
- Catalyst
- Ionomer
- Solvents
- Dispersion method

**Ink Characterization**
- Rheology
- Dynamic Light Scattering
- Zeta Potential

**Electrode Fabrication**
- Coating Method
- Drying Rate/Temp
- Substrate

**Ex Situ Electrode Characterization**
- Electron microscopy
- X-ray tomography

**In Situ Electrode Characterization**
- Fuel cell performance
- Impedance spectroscopy
- Transport measurements

**Typical R&D Method**
## Approach: Project Schedule and Milestones

<table>
<thead>
<tr>
<th>Qtr</th>
<th>Date</th>
<th>Milestone/Deliverable (as of 4/17/2018)</th>
<th>Type</th>
<th>Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>FY17 Q3</td>
<td>6/2017</td>
<td>Fabricate and characterize baseline slot-die and micro-gravure roll coated electrodes on R2R coating station, at least one of which to meet the following criteria:  &lt;br&gt; 1. Achieving a target catalyst loading in the range of 0.05 to 0.2 mg Pt/cm²  &lt;br&gt; 2. Achieving the target loading at a line speed of at least 1 m/min  &lt;br&gt; 3. For an MEA with R2R-coated CCDM, achieving at least 70% of the average mass activity (900 mV-IR-free) of MEAs containing spray-coated CCDMs, under testing conditions of 80 °C, 100% RH, H₂/O₂, 150 kPa&lt;sub&gt;abs&lt;/sub&gt;</td>
<td>SMART</td>
<td>MET</td>
</tr>
<tr>
<td>FY17 Q4</td>
<td>9/2017</td>
<td>Fabricate and characterize baseline cast membranes on R2R coating station.</td>
<td>QPM</td>
<td>MET</td>
</tr>
<tr>
<td>FY18 Q2</td>
<td>3/2018</td>
<td>Perform initial ink development and coating of unsupported catalyst systems to support HydroGEN projects.</td>
<td>QPM</td>
<td>MET</td>
</tr>
<tr>
<td>FY18 Q3</td>
<td>6/2018</td>
<td>Characterize impacts of coating flow types (slot – pressure driven vs. gravure – extensional) on catalyst layer morphology and performance.</td>
<td>QPM</td>
<td>On track</td>
</tr>
<tr>
<td>FY18 Q4</td>
<td>9/2018</td>
<td>Characterize influence of ink composition (solids content, solvent, support type, catalyst material) on catalyst ink rheology, particle size, stability, and coatability.</td>
<td>QPM</td>
<td>On going</td>
</tr>
</tbody>
</table>
Accomplishments and Progress: Achieved FY17 SMART Milestone

Fabricate and characterize baseline slot-die and micro-gravure roll coated electrodes on R2R coating station, at least one of which to meet the following criteria:

1. Achieving a target catalyst loading in the range of 0.05 to 0.2 mg Pt/cm²
2. Achieving the target loading at a line speed of at least 1 m/min
3. For an MEA with R2R-coated CCDM, achieving at least 70% of the average mass activity (900 mV-IR-free) of MEAs containing spray-coated CCDMs, under testing conditions of 80 °C, 100% RH, H₂/O₂, 150 kPaₐₚₛ

Coated at 1 m/min

% of MASS ACTIVITY

<table>
<thead>
<tr>
<th>Method</th>
<th>$i_{m, 0.9V}$ [mA/mgPt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray</td>
<td>328 ± 17</td>
</tr>
<tr>
<td>R2R</td>
<td>294</td>
</tr>
</tbody>
</table>

0.12 mgPt/cm²
50 cm²
80 °C
100% RH
150 kPa
Anodic sweep

R2R-Coated Electrodes Achieved 90% of Spray-Coated Electrodes Mass Activity
Accomplishments and Progress:
Rheology Correlated Carbon Support Properties with Optimized Electrode Properties

Rheology of Carbon Blacks

Shear thinning analysis

<table>
<thead>
<tr>
<th>Carbon Black</th>
<th>Surface Area [m²/g]</th>
<th>Pore Volume (&gt; 2 nm) [cm³/g]</th>
<th>I:C Onset of shear thinning plateau</th>
<th>“Optimized” Electrode I:C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan XC 72</td>
<td>237.1</td>
<td>0.52</td>
<td>0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>High Surface Area</td>
<td>801.8</td>
<td>1.01</td>
<td>0.41</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Observed linear correspondence between carbon-support pore structure, shear-thinning plateau, and optimized electrode I:C
Accomplishments and Progress:
Demonstrated Differences in Rheological Influence of Pt catalyst

- Influence of Pt dependent on surface or internal location of Pt
- Determined that carbon chemistry influences interactions with Nafion
Accomplishments and Understanding: X-Ray Scattering Correlated Ink Microstructure to Rheology

- Utilized power-law slope analysis to characterize agglomeration
- Determined that ionomer breaks up Vulcan agglomerates but does not for HSC
Accomplishments and Progress: Determined Solvent Influence on Ionomer-Carbon Interaction

- Demonstrated that high water-content solvent causes stronger ionomer-carbon interaction
- Stronger interaction leads to stabilization of the ink and smaller agglomerates
- It is expected that this will lead to better electrode performance - fuel cell testing planned to confirm hypothesis
Accomplishments and Progress:
Inks Formulation of Unsupported Catalysts to Support LTE

- Demonstrated that unsupported catalysts display similar agglomeration behavior as Pt/Vu
- Rheology and zeta potential measurements showed similar stabilization against agglomeration by Nafion
- Interacting frequently with Proton OnSite to ensure relevance
- Future studies to include new materials: Pt black, high-surface area IrOx
Accomplishments and Progress:
Coating of Unsupported Catalyst Inks to Support LTE

- Demonstrated a wide range of loading possible using scalable coating method
- Achieved loadings are consistent with state-of-the-art and future targets
- Our previous experience suggests these inks will be coatable with R2R methods: gravure and slot-die

<table>
<thead>
<tr>
<th>Ink Concentration (wt% IrO\textsubscript{x})</th>
<th>Ir Loading (mg/cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.29 – 0.65</td>
</tr>
<tr>
<td>25</td>
<td>1 – 1.7</td>
</tr>
</tbody>
</table>

IrO\textsubscript{x} provided by Proton OnSite
Accomplishments and Progress: Demonstrated R2R Membrane Casting

- Demonstrated a range of thicknesses possible by adjusting dispersion flow rate and/or web speed
- High cross-web and down web uniformity at ~meter lengths

<table>
<thead>
<tr>
<th>Flow Rate [mL/min]</th>
<th>Web Speed [m/min]</th>
<th>Average Thickness [µm]</th>
<th>Std. Dev. Cross Web [µm]</th>
<th>Std. Dev Down Web [µm]</th>
<th>Down web length measured [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>10.5</td>
<td>0.4</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>14.1</td>
<td>0</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>15</td>
<td>0.7</td>
<td>21.5</td>
<td>1.6</td>
<td>1.5</td>
<td>0.6</td>
</tr>
</tbody>
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**Uniform Nafion Membranes Cast at Relevant Thicknesses**
Accomplishments and Progress: Responses to Previous Year Reviewers’ Comments

• This project was not reviewed last year
## Collaborations

<table>
<thead>
<tr>
<th>Institution</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>National Renewable Energy Laboratory - Prime</strong>&lt;br&gt;Mike Ulsh, Scott Mauger, Sunilkumar Khandavalli, K.C. Neyerlin, Jason Pfeilsticker, Katherine Hurst, Jonathan Stickel&lt;br&gt;</td>
<td>Ink formulation studies, electrode production and coating, rheology, membrane casting, MEA performance testing, advanced diagnostics, catalyst porosity/surface area analysis</td>
</tr>
<tr>
<td><strong>Argonne National Laboratory</strong>&lt;br&gt;Debbie Myers, Jae Hyung Park, Nancy Kariuki&lt;br&gt;</td>
<td>Small angle x-ray scattering of catalyst inks – critical for understanding rheology measurements and catalyst ink microstructure</td>
</tr>
<tr>
<td><strong>Colorado School of Mines</strong>&lt;br&gt;Svitlana Pylypenko, Samantha Medina, Caleb Stetson&lt;br&gt;</td>
<td>Electron microscopy of catalyst materials and electrodes</td>
</tr>
<tr>
<td><strong>Technical Univ. of Munich</strong>&lt;br&gt;Hubert Gasteiger, Jan Schwämmlein&lt;br&gt;</td>
<td>Stack testing – starting April 2018</td>
</tr>
<tr>
<td><strong>Proton OnSite</strong>&lt;br&gt;Chris Capuano&lt;br&gt;</td>
<td>LTE catalysts and materials</td>
</tr>
<tr>
<td><strong>3M Company</strong>&lt;br&gt;Mike Yandrasits&lt;br&gt;</td>
<td>Ionomer powders</td>
</tr>
<tr>
<td><strong>Umicore</strong>&lt;br&gt;Sascha Toelle&lt;br&gt;</td>
<td>Catalysts</td>
</tr>
</tbody>
</table>
Challenges and Barriers

- Improve understanding of correlations between ink formulation/properties, electrode properties, and electrode performance
- Determine relationships between coating parameters, electrode morphology, and performance
- Establishing capabilities to study new catalyst/material systems
- Perform studies to demonstrate the scalability of new MEA materials
Proposed Future Work

• Explore influence of coating flow type on catalyst layer morphology, properties, and performance (FY18 Q3 QPM)
  – Gravure vs. slot die
  – Influence of shear rates

• Continue Inks Characterization Research (FY18 Q4 QPM)
  – Multiple support types, ionomer equivalent weights, etc.
  – Expand range of solvents beyond water and 1-propanol
  – Develop correlations between ink properties (rheology, particle size, etc.) and electrode properties/performance

• Perform early-stage fundamental R&D for PGM-free, AEM-FC, and LTE catalyst systems

Any proposed future work is subject to change based on funding levels
Summary

**Objective:** Study material-process-performance relationships for R2R PEMFC/EC cell materials to understand relationships between process science and material properties and performance

**Relevance:** Addressing MYRD&D milestones. This project is enabling for other DOE-funded research

**Approach:** Understand impacts of ink formulation, coating and drying physics on ink microstructure, coatability, film morphology, electrochemistry, proton conduction and mass transport

**Accomplishments:**

- R2R-coated electrodes achieved 90% of the mass activity of spray coated electrodes and equivalent high-current density performance
- Discovered differences in rheological properties of supported catalyst inks suggesting differences in polymer-particle and/or particle-particle interactions - function of support and solvent.
- Used USAXS to determine mechanism for rheological results
- Performed inks formulation and coatings of unsupported catalyst
- Cast uniform membranes at range relevant thicknesses
Thank You

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Technical Back-Up Slides

(Include this “divider” slide if you are including back-up technical slides [maximum of five]. These back-up technical slides will be available for your presentation and will be included in Web PDF files released to the public.)