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

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Presenter - Scott Mauger
National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
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TA008

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Overview

Timeline and Budget

• Project start date: 10/1/16
• FY18 DOE funding: $224,000
• FY19 planned DOE funding: $0

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
• Pajarito Powder
  – Alexey Serov and Barr Zulevi
Relevance: Project Addresses MYRD&D Plan Milestones

<table>
<thead>
<tr>
<th>Task 1: Membrane Electrode Assemblies</th>
<th>Task 5: Quality Control and Modeling and Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 Develop processes for direct coating of electrodes on membranes or gas diffusion media. (4Q, 2017)</td>
<td>5.5 Develop correlations between manufacturing parameters and manufacturing variability, and performance and durability of MEAs. (4Q, 2018)</td>
</tr>
<tr>
<td>1.3 Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste. (4Q, 2017)</td>
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</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 (TA007, 5/1/19, 11:30 A.M.)**
  - Lead for Fuel Cell Core Lab Project
  - Lead for CRADA with Proton OnSite
- **HydroGen (PD148, 4/30/19, 8:30 A.M.)**
  - LTE/Hybrid Supernode
  - Supporting three 2A projects (Proton OnSite, Northeastern, ANL)
- **ElectroCat (FC160, 4/30/19, 8:30 A.M.)**
- **HyET H2@Scale CRADA (H2006, 4/30/19 6:30 P.M., poster)**
  - “Membrane Electrode Assembly Manufacturing Automation Technology for the Electrochemical Compression of Hydrogen”
- **3M FY19 FOA Award (TA026, 4/29/19, 6:30, poster)**
  - “Low-cost, High Performance Catalyst Coated Membranes for PEM Water Electrolyzers”
- **Peroxygen Systems** – AMO-funded SBV
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

Large Scale – Roll-to-Roll (R2R)

- Concentrated ink (~4.5-15 wt% solids)
- Shear mixing
- Single layer
- Room temp. substrate
- Convective drying

Used to demonstrate new materials and for fundamental studies

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
- USAXS

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

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

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

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

<table>
<thead>
<tr>
<th>Qtr</th>
<th>Date</th>
<th>Milestone/Deliverable (as of 3/4/2019)</th>
<th>Type</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>FY18</td>
<td>6/2018</td>
<td>Characterize impacts of coating flow types (slot – pressure driven vs. gravure – extensional) on catalyst layer performance.</td>
<td>QPM</td>
<td>MET after FY18 AMR</td>
</tr>
<tr>
<td>FY18</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>MET</td>
</tr>
<tr>
<td>FY19</td>
<td>12/2018</td>
<td>Perform ink development studies of unsupported LTE catalysts to understand influence of solvent and catalyst materials on ionomer-catalyst interactions.</td>
<td>QPM</td>
<td>MET</td>
</tr>
<tr>
<td>FY19</td>
<td>3/2019</td>
<td>Characterize influence of coating flow types on catalyst layer morphology.</td>
<td>QPM</td>
<td>MET</td>
</tr>
<tr>
<td>FY19</td>
<td>6/2019</td>
<td>Determine influence of solvent formulation on ionomer adsorption on catalyst/support.</td>
<td>QPM</td>
<td>On track</td>
</tr>
<tr>
<td>FY19</td>
<td>9/2019</td>
<td>Evaluate ink formulations, drying conditions, and substrates to reduce crack formation in fuel cell and electrolysis catalyst layers coated using scalable methods.</td>
<td>QPM</td>
<td>On track</td>
</tr>
</tbody>
</table>
Accomplishments and Progress: Characterized Influence of Coating Method on Performance

**Pros**
- High coating rates
- High uniformity (±5%)
- Closed system
- Wide range of viscosities
- Simple control of coating thickness

**Cons**
- Complex
- Rheology must be tuned for each process

**Ink Formulation**
- Pt/HSC (TKK TEC10E50E) – 3.2 wt%
- Nafion 1000EW (0.9 I/C)
- Water/1-propanol (70/30 or 25/75 v/v)

**MEA Materials**
- GDL: Freud. H23C8
- Memb.: Nafion NR-211 (25 µm)

**Coating**
- 1 m/min
- Oven: 80 °C

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**Slot Die Coating**
- Catalyst layers coated directly onto gas diffusion media
- 1 m/min at 10 cm wide
- Coatings used the same:
  - Ink formulation
  - Web speed
  - Drying temperature
  - Materials

**Gravure Coating**
- High coating rates
- Very high uniformity (±2%)
- Very thin liquid films
- Patterns
- Simpler operation

**Pros**
- High coating rates
- Very high uniformity (±2%)
- Very thin liquid films
- Patterns
- Simpler operation

**Cons**
- Smaller viscosity range
- Coating thickness less easily adjusted

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**Die**

**Pump**

**Substrate**

**Web Direction**

**Gravure Cylinder**

**Ink**

**Substrate**

**Web Direction**

**Cylinder Direction**
Accomplishments and Progress: Characterized Influence of Coating Method on Performance

**Fuel Cell Performance**

H$_2$/Air, 150kpa/150kpa, 80°C, 100%/100% RH, 50 cm$^2$

- **Slot die coating results in higher performance than gravure, regardless of ink formulation**
- Coating method does not impact kinetics or site accessibility
- Polarization curves suggest performance differences are due to differences in Ohmic losses between MEAs
- May also be differences in transport – needs further exploration

<table>
<thead>
<tr>
<th>Method</th>
<th>ECSA (m$^2$/gPt)</th>
<th>$i_m^{0.9V}$ (mA/mgPt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slot die</td>
<td>63.1 ± 2.7</td>
<td>395 ± 21</td>
</tr>
<tr>
<td>Gravure</td>
<td>64.5 ± 2.3</td>
<td>395 ± 22</td>
</tr>
</tbody>
</table>

\[ \Delta E = 23.6 \text{ mV} \]

\[ \Delta R_{CL} = 33.1 \text{ mΩ} \cdot \text{cm}^2 \]

\[ \Delta E = i\Delta R_{CL} \]

\[ \Delta E \left(0.8 \frac{A}{cm^2}\right) = 26.5 \text{ mV} \]

**H$_2$/N$_2$ Electrochemical Impedance Spectroscopy**

- EIS used to understand differences in proton conductivity
- **Model fitting and analysis shows gravure results in higher effective catalyst layer resistance**
Accomplishments and Progress: Utilizing Electron Microscopy to Evaluate R2R Coated Electrodes

Slot-die Coated Electrode

- **TEM analysis shows slot-die coating produces favorable electrode morphology**
  - Electrode shows good porosity
  - Pt and F (Nafion) are well distributed throughout the electrode
- Do not observe penetration of catalyst layer into MPL
- Further imaging and analysis on-going to establish links between catalyst layer morphology and performance
Accomplishments and Progress: Determined Influence of Solvent Formulation on FC Performance

**Slot Die**

$H_2/\text{Air}, 150\text{kpa}/150\text{kpa}, 80^\circ\text{C}, 100%/100\%\text{RH}, 50\ \text{cm}^2$

![Graph 1](#)

- **Ink Formulations**
  - Pt/HSC (TKK TEC10E50E) – 3.2 wt%
  - Nafion 1000EW (0.9 I/C)
  - Water/1-propanol (70/30 or 25/75 v/v)

- **Components**
  - Cathodes: 0.12-0.13 mg$_{\text{Pt}}$/cm$^2$
  - Anodes: 0.1 mg$_{\text{Pt}}$/cm$^2$
  - GDL: Freudenberg H23C8
  - Membrane: Nafion NR211 (25 µm)

- **Preparation**
  - Cathodes directly coated on GDL using R2R coater and dried in 80 °C oven

- **Observations**
  - Water-rich inks are superior, regardless of coating method, or electrode type (GDE vs CCM), carbon-support type, or concentration
  - Collaborating with K.C. Neyerlin/FC-PAD to further understand electrochemical mechanisms for performance differences and relate results to ink characteristics (FC135)
Accomplishments and Progress: Related Ink Formulation to Electrode Structure

Dynamic Oscillatory Shear Rheology

\[ G = G' + iG'' \]
- elastic modulus (\( G' \))
- viscous modulus (\( G'' \))

- Utilized oscillatory shear rheology to characterize influence of solvent composition on microstructure
- Modifying the solvent composition changes the amount of aggregation
- Determined link between ink microstructure to electrode microstructure
  - More aggregated ink (more gel-like) leads to larger solid particles sizes in electrode
Accomplishments and Progress:
Determined Electrosteric Stabilization Effects of Nafion on IrO₂ Catalyst Ink

Procedure to remove free ionomer

![Diagram showing the process of removing free ionomer](image)

This procedure is required to limit study to catalyst particles

Zeta Potential

![Graph showing zeta potential](image)

Dynamic Light Scattering

![Graph showing dynamic light scattering](image)

USAXS of Concentrated Ink

![Graph showing USAXS of concentrated ink](image)

- Zeta potential measurements show Nafion is adsorbing on catalyst particle surface and providing electrostatic stabilization
- Stabilization of IrO₂ leads to significant decrease in effective catalyst particle size
- USAXS measurements of concentrated inks verify DLS and zeta potential measurements of dilute inks
Accomplishments and Progress: Characterized Interactions in IrO$_2$-Nafion Ink

Small Amplitude Oscillatory Shear Rheology

- **F** - elastic modulus ($G'$)
- **□** - viscous modulus ($G''$)

<table>
<thead>
<tr>
<th>Frequency [rad/s]</th>
<th>$G'$</th>
<th>$G''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

- Rheology shows addition of low-level of ionomer stabilizes IrO$_2$ particles, consistent with other measurements
- **Higher levels of ionomer addition lead to more gel-like behavior indicating more interparticle interactions, suggestive of aggregation**
- Aggregation may be due to depletion flocculation, indicating there is free, dispersed ionomer – more analysis needed to confirm
Accomplishments and Progress: Initiated Research on Electrode Crack Mitigation

Influence of Substrate – MPL Roughness

<table>
<thead>
<tr>
<th>SGL 29BC</th>
<th>Uncoated</th>
<th>Coated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="uncoated.png" alt="" /></td>
<td>![coated.png]</td>
</tr>
<tr>
<td>Freud. H23C8</td>
<td>![uncoated.png]</td>
<td>![coated.png]</td>
</tr>
</tbody>
</table>

Catalyst Layer Details
- 50 wt% Pt/HSC, 1000 EW Nafion, 0.9 I:C
- Catalyst loading: 0.12 mg\textsubscript{Pt}/cm\textsuperscript{2}
- Catalyst Layer Thickness: 3-4 µm
- Drying time: < 1 min in 80°C convection oven

Substrate surface influences catalyst layer cracking
- Cracks in MPL can propagate into direct-coated catalyst layer
- Crack-free catalyst layers can be coated on uncracked MPL

Future Work
- Continue work on Pt/C
- Explore other systems: PGM-Free, LTE
- Understand critical thickness limits
- Research ink formulation strategies to mitigate cracking
Accomplishments and Progress: Responses to Previous Year Reviewers’ Comments

• This project was not reviewed last year
<table>
<thead>
<tr>
<th>Institution</th>
<th>Role</th>
</tr>
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<tbody>
<tr>
<td>National Renewable Energy Laboratory - Prime</td>
<td>Ink formulation studies, electrode production and coating, rheology, MEA performance testing, advanced diagnostics</td>
</tr>
<tr>
<td>Mike Ulsh, Scott Mauger, Sunilkumar Khandavalli, Jason Pfeilsticker, Min Wang, Radhika Iyer, K.C. Neyerlin</td>
<td></td>
</tr>
<tr>
<td>Argonne National Laboratory</td>
<td>Small angle x-ray scattering of catalyst inks – critical for understanding rheology measurements and catalyst ink microstructure</td>
</tr>
<tr>
<td>Debbie Myers, Jae Hyung Park, Nancy Kariuki</td>
<td></td>
</tr>
<tr>
<td>Colorado School of Mines</td>
<td>Electron microscopy of catalyst materials and electrodes</td>
</tr>
<tr>
<td>Svitlana Pylypenko, Samantha Medina</td>
<td></td>
</tr>
<tr>
<td>Proton OnSite</td>
<td>LTE catalysts and materials</td>
</tr>
<tr>
<td>Chris Capuano</td>
<td></td>
</tr>
<tr>
<td>Pajarito Powders</td>
<td>PGM-free catalyst powders</td>
</tr>
<tr>
<td>Alexey Serov and Barr Zulevi</td>
<td></td>
</tr>
<tr>
<td>Oak Ridge National Laboratory</td>
<td>Assisting with electron microscopy</td>
</tr>
<tr>
<td>Karren More, Dave Cullen</td>
<td></td>
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</tbody>
</table>
Challenges and Barriers

• Improve understanding of correlations between ink formulation, coating methods, and electrode properties and performance
• Extend learnings from Pt/C to LTE and other materials systems
• Expand capabilities to study new catalyst/material systems
• Perform studies to demonstrate the scalability of new MEA materials
Proposed Future Work

• Continue research to understand influence of coating methodology on performance and morphology
• Continue development of techniques and understanding of ionomer-catalyst interactions in inks
• Evaluate ink formulations, drying conditions, and substrates to reduce crack formation in fuel cell and electrolysis catalyst layers coated using scalable methods (FY19 Q4 QPM)
• 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
**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:**
- Determined that slot-die coating results in higher performance MEAs than gravure coating
- Related catalyst ink microstructure to electrode microstructure
- Improved methods for dynamic light scattering and zeta potential to better understand catalyst – ionomer interactions
- Initiated work on electrode cracking – showed that MPL cracks can induce catalyst layer cracks
Technical Back-Up Slides
Accomplishments and Progress: Utilized Electron Microscopy to Evaluate R2R-Coated Electrodes

Comparison of Coating Method

Slot Die

Gravure

Fewer aggregates in slot die coated electrodes

Comparison of Ink Formulation

75 wt % H₂O

25 wt % H₂O

Fewer aggregates with water-rich ink formulation

Colorado School of Mines
Accomplishments and Progress:
Utilized Electron Microscopy to Evaluate R2R-Coated Electrodes

- TEM analysis shows slot-die coating produces favorable electrode morphology
  - Electrode shows good porosity
  - Catalyst and ionomer are well distributed throughout the electrode
Does susceptibility of Pt-alloy catalysts to leaching in acids impact shelf-life stability of catalyst inks?

**Steady Shear Rheology**

- Same inks measured over a period of 8 weeks
- Pt/HSC shows no change in rheology, indicating no change in aggregation – **stable**
- **PtCo/HSC shows increase in viscoelasticity, indicating increased aggregation – unstable**
  - Co ions could screen surface charges and reduce electrostatic stabilization

**Oscillatory Shear Rheology**