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
2019 Annual Merit Review and Peer Evaluation Meeting

TA008

Overview

Timeline and Budget

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

Partners

- Argonne National Laboratory
  – Debbie Myers
- Colorado School of Mines
  – Svitlana Pylypenko
- Proton OnSite
  – Chris Capuano
- Pajarito Powder
  – Alexey Serov and Barr Zulevi

Barriers

Barrier	Target
A. Lack of high-volume MEA processes	$20/kW (2020) at 500,000 stacks/yr
H. Low levels of quality control	

Relevance: Project Addresses MYRD&D Plan Milestones

Task 1: Membrane Electrode Assemblies	
1.2	Develop processes for direct coating of electrodes on membranes or gas diffusion media. (4Q, 2017)
1.3	Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste. (4Q, 2017)

Task 5: Quality Control and Modeling and Simulation	
5.5	Develop correlations between manufacturing parameters and manufacturing variability, and performance and durability of MEAs. (4Q, 2018)

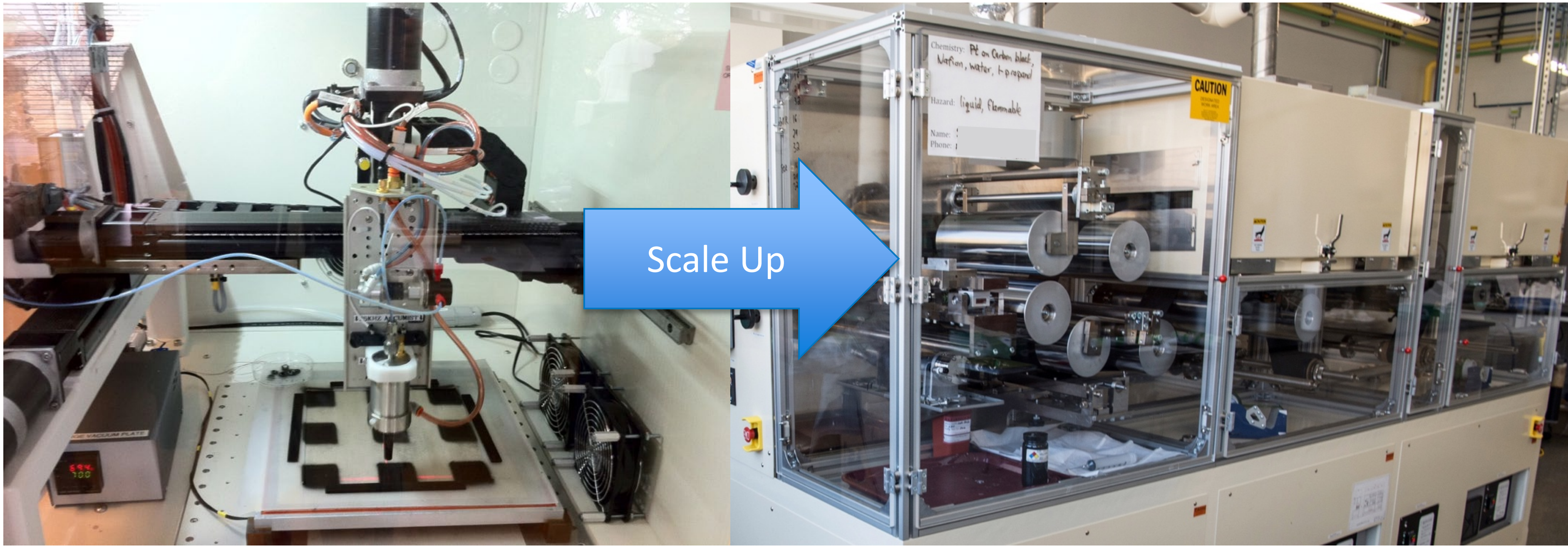
- Roll-to-roll (R2R) is the lowest cost/highest throughput method for production of FC/LTE materials
- R2R coating techniques require different ink formulation and have different physics than lab-scale processes
- Many researchers/producers do not have access to the infrastructure to understand how the 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 | **Large Scale – Roll-to-Roll (R2R)**



Used to demonstrate new materials and for fundamental studies

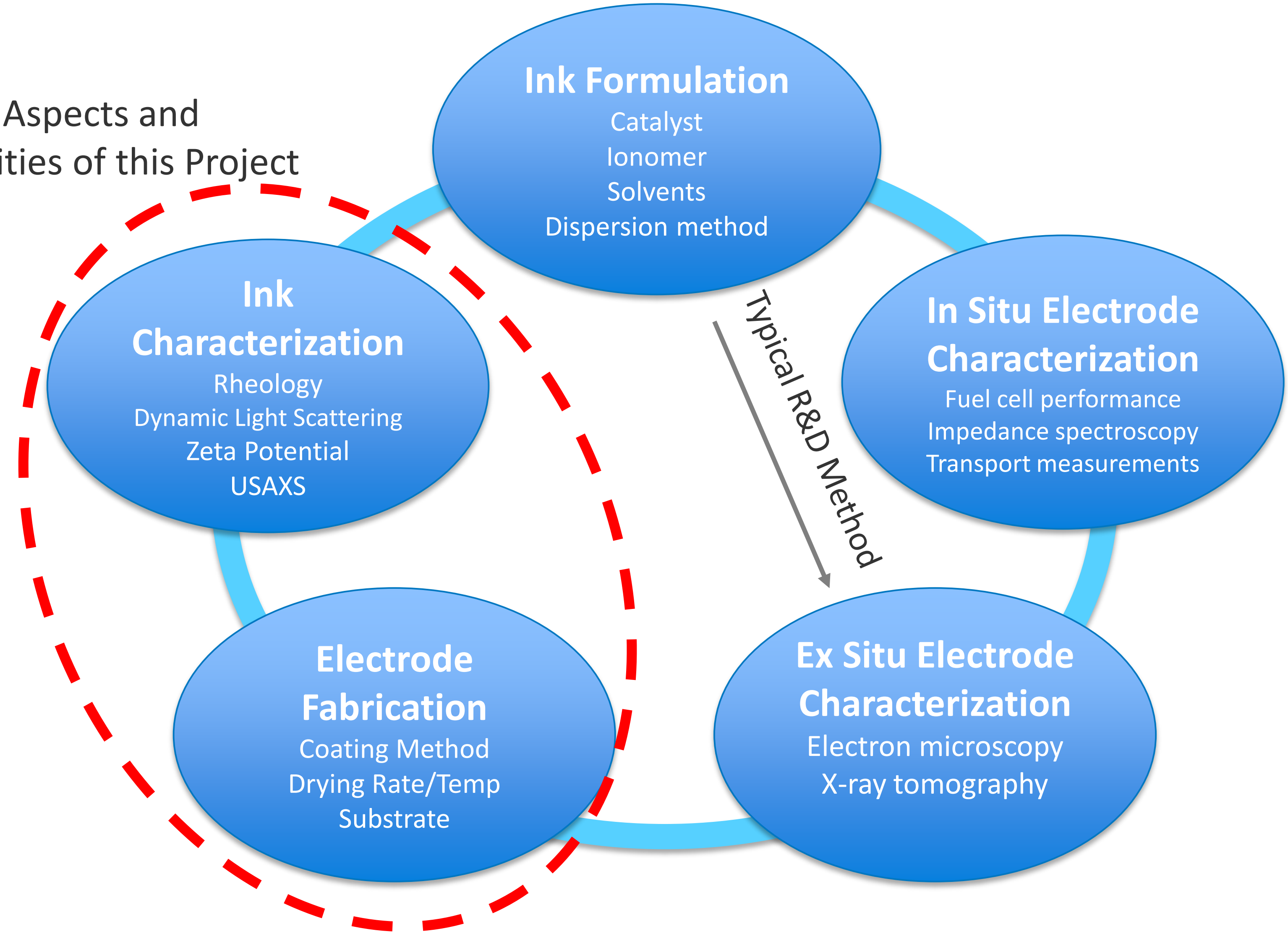
Conditions
- Dilute ink (~0.6 wt% solids)
- Ultrasonic mixing
- Sequential build up of layers
- Heated substrate
- Vacuum substrate

Needed to demonstrate scalability of materials and MEA/cell designs, and industrial relevance

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

Approach:
Integrated Approach for Processes Scale-Up

Unique Aspects and Capabilities of this Project

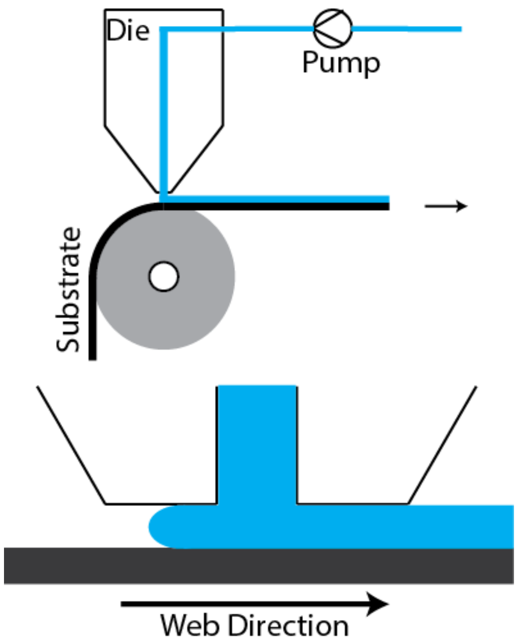


Approach: Project Schedule and Milestones

Qtr	Date	Milestone/Deliverable (as of 3/4/2019)	Type	Status
FY18 Q3	6/2018	Characterize impacts of coating flow types (slot – pressure driven vs. gravure – extensional) on catalyst layer performance.	QPM	MET after FY18 AMR
FY18 Q4	9/2018	Characterize influence of ink composition (solids content, solvent, support type, catalyst material) on catalyst ink rheology, particle size, stability, and coatability.	QPM	MET
FY19 Q1	12/2018	Perform ink development studies of unsupported LTE catalysts to understand influence of solvent and catalyst materials on ionomer-catalyst interactions.	QPM	MET
FY19 Q2	3/2019	Characterize influence of coating flow types on catalyst layer morphology.	QPM	MET
FY19 Q3	6/2019	Determine influence of solvent formulation on ionomer adsorption on catalyst/support.	QPM	On track
FY19 Q4	9/2019	Evaluate ink formulations, drying conditions, and substrates to reduce crack formation in fuel cell and electrolysis catalyst layers coated using scalable methods.	QPM	On track

Accomplishments and Progress: Characterized Influence of Coating Method on Performance

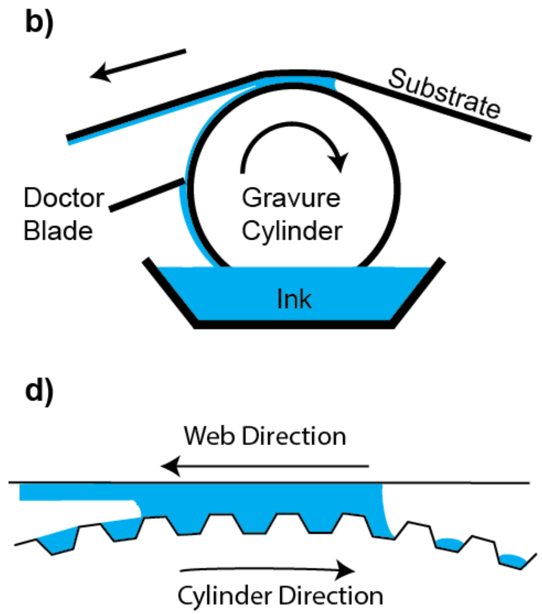
Slot Die Coating



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

Gravure Coating



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

Cons
- Smaller viscosity range
- Coating thickness less easily adjusted

- 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

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)

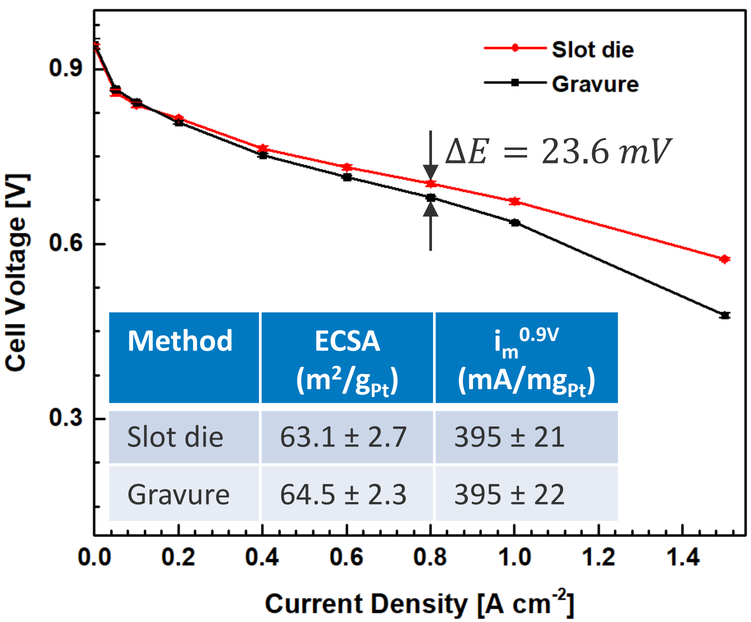
MEA Materials
- GDL: Freud. H23C8
- Memb.: Nafion NR-211 (25 µm)

Coating
- 1 m/min
- Oven: 80 ˚C

Accomplishments and Progress: Characterized Influence of Coating Method on Performance

Fuel Cell Performance

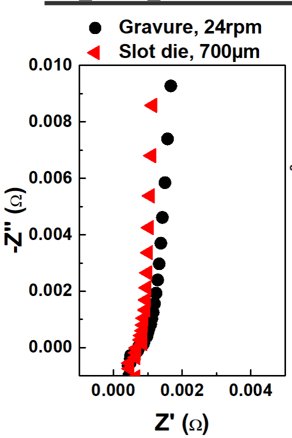
H_2/Air, 150kpa/150kpa, 80°C, 100%/100%RH, 50 cm^2

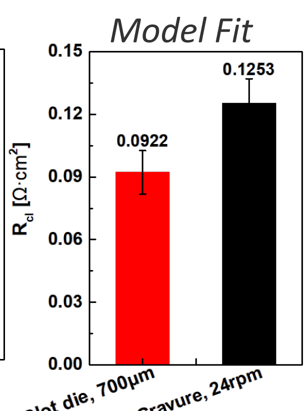


Method	ECSA (m^2/g_{Pt})	$i_m^{0.9V}$ (mA/mg_{Pt})
Slot die	63.1 ± 2.7	395 ± 21
Gravure	64.5 ± 2.3	395 ± 22

- ***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

H_2/N_2 Electrochemical Impedance Spectroscopy



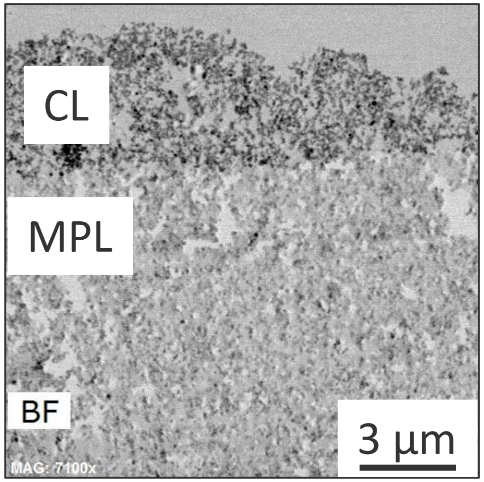


$$\Delta R_{CL} = 33.1\ m\Omega \cdot cm^2$$
$$\Delta E = i\Delta R_{CL}$$
$$\Delta E\left(0.8\frac{A}{cm^2}\right) = 26.5\ mV$$

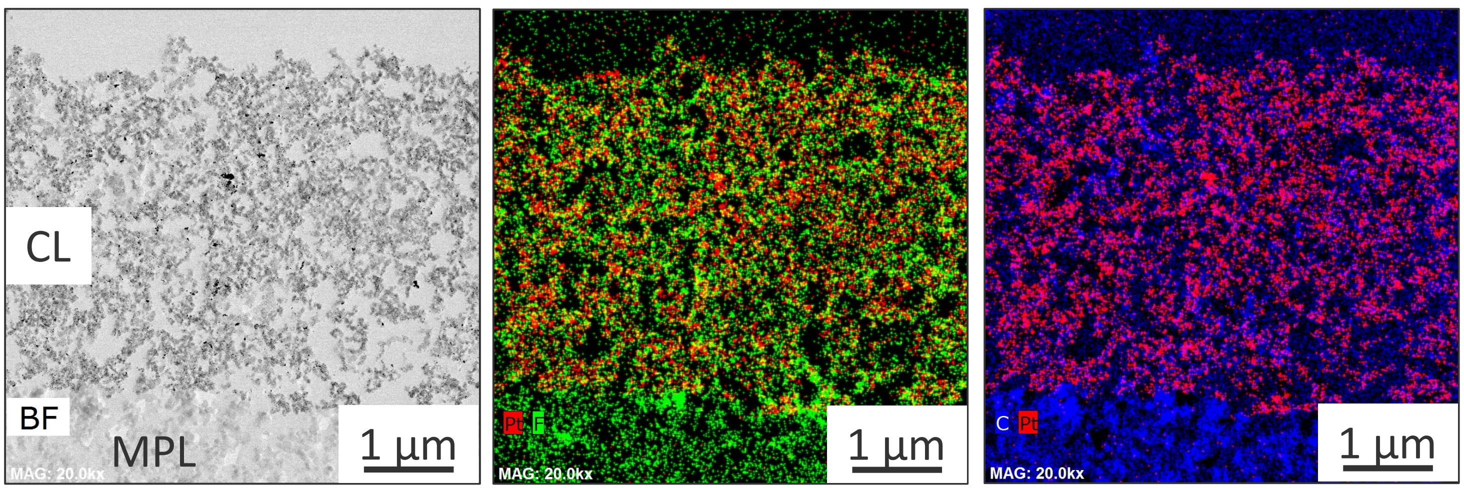
- EIS used to understand differences in proton conductivity
- ***Model fitting and analysis shows gravure results in higher effective catalyst layer resistance***

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



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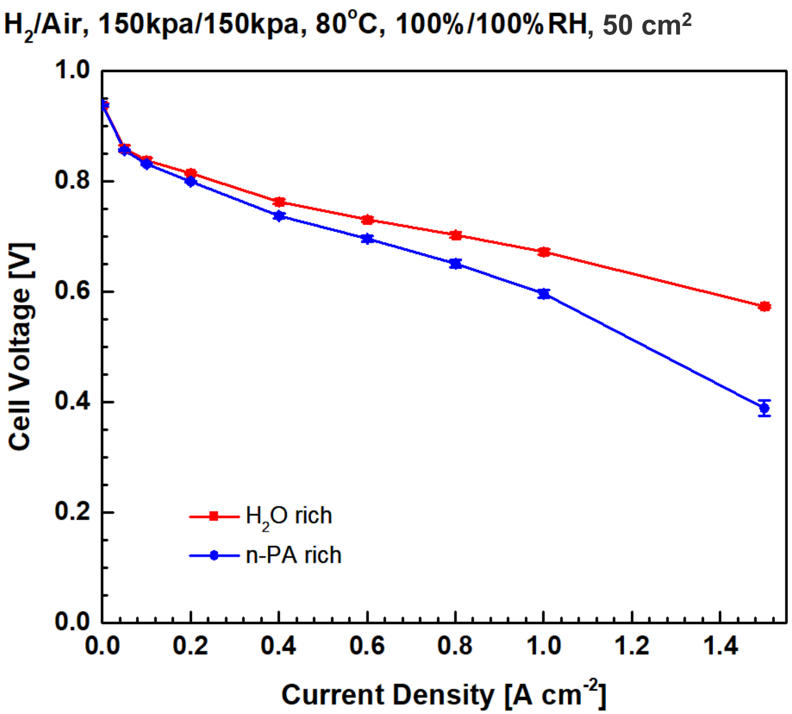
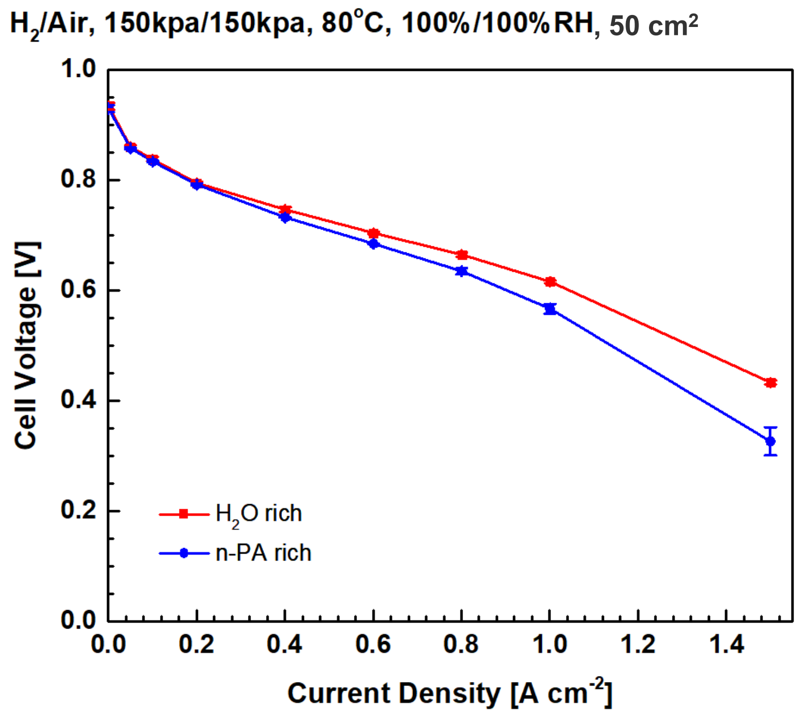
Accomplishments and Progress:
Determined Influence of Solvent Formulation on FC Performance

Slot Die



Gravure



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)

Cathodes: 0.12-0.13 mg_{Pt}/cm^2
Anodes: 0.1 mg_{Pt}/cm^2
GDL: Freudenberg H23C8
Membrane: Nafion NR211 (25 µm)

Cathodes directly coated on GDL using R2R coater and dried in 80 ˚C oven

- ***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)

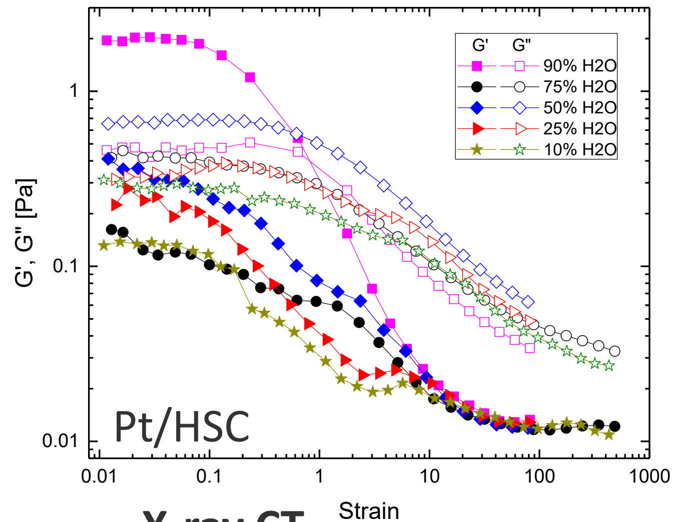
Accomplishments and Progress: Related Ink Formulation to Electrode Structure

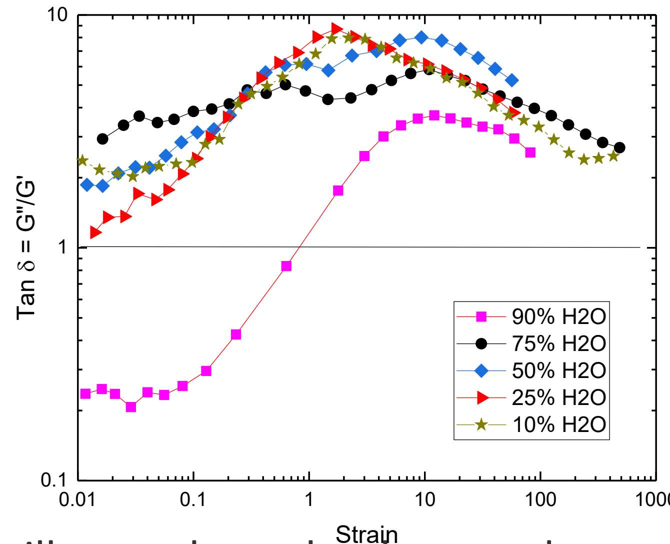
Dynamic Oscillatory Shear Rheology

$G = G' + iG''$

■? - elastic modulus (G')

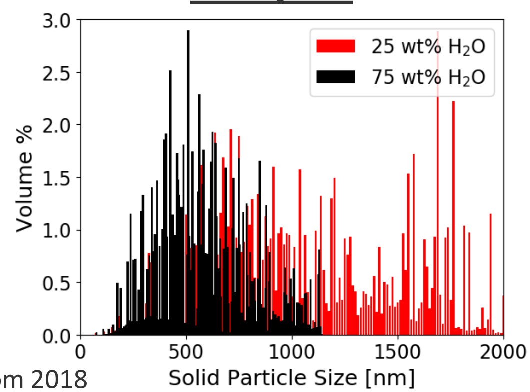
□? - viscous modulus (G'')





Increasing Elasticity = More Aggregation

X-ray CT



From 2018 AMR – MN018

- 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***

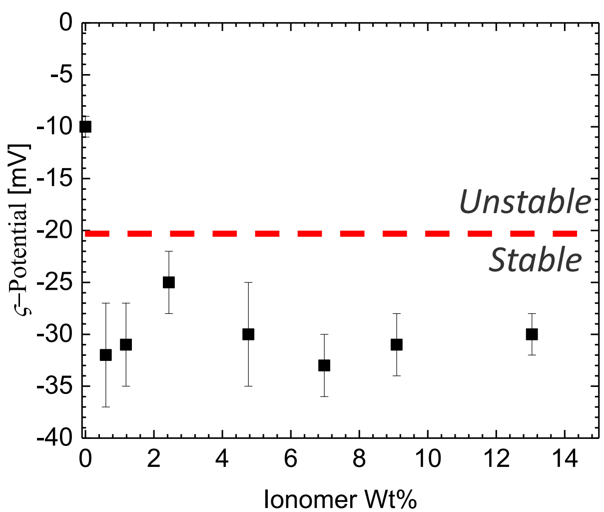
Accomplishments and Progress:

Determined Electrosteric Stabilization Effects of Nafion on IrO_2 Catalyst Ink

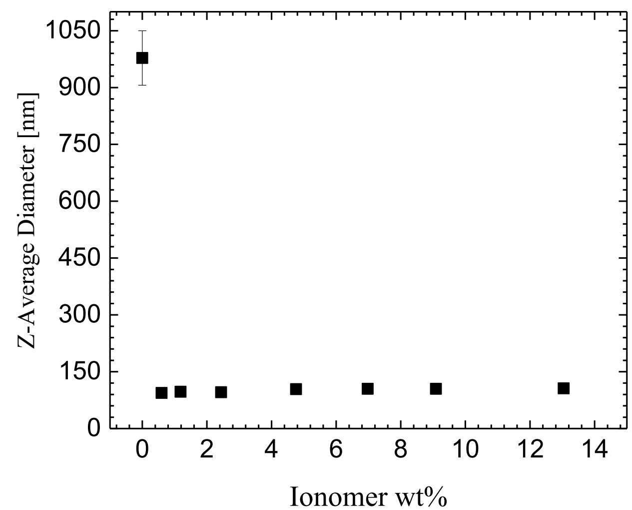
Procedure to remove free ionomer

This procedure is required to limit study to catalyst particles

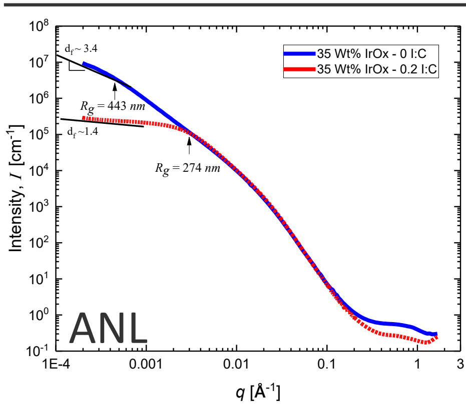
Zeta Potential



Dynamic Light Scattering



USAXS of Concentrated Ink



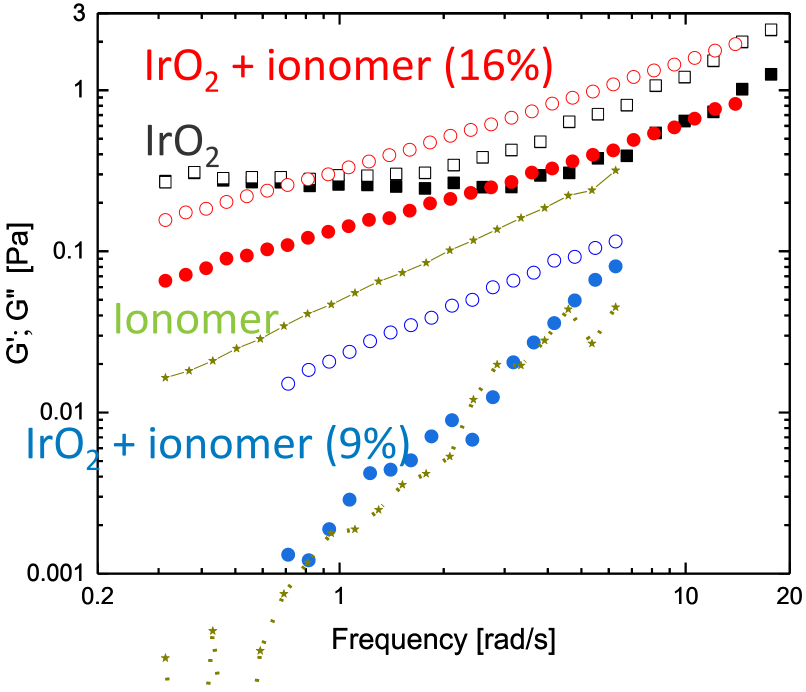
- ***Zeta potential measurements show Nafion is adsorbing on catalyst particle surface and providing electrostatic stabilization***
- Stabilization of IrO_2 leads to significant decrease in effective catalyst particle size
- USAXS measurements of concentrated inks verify DLS and zeta potential measurements of dilute inks

Accomplishments and Progress: Characterized Interactions in IrO_2-Nafion Ink

Small Amplitude Oscillatory Shear Rheology

■? - elastic modulus (*G'*)

□? - viscous modulus (*G"*)

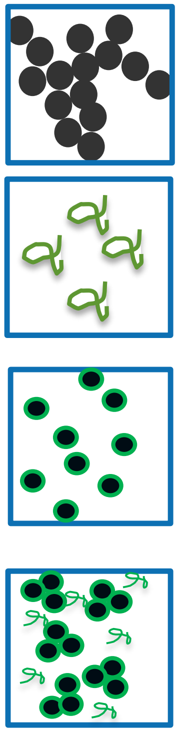


G', G" ~ ω^0 – Gel

G' ~ω^2 G" ~ ω^1 – Liquid like

G' ~ω^2 G" ~ ω^1 – Liquid like

G', G" ~ $\omega^{0.6}$ – Gel-like



- 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

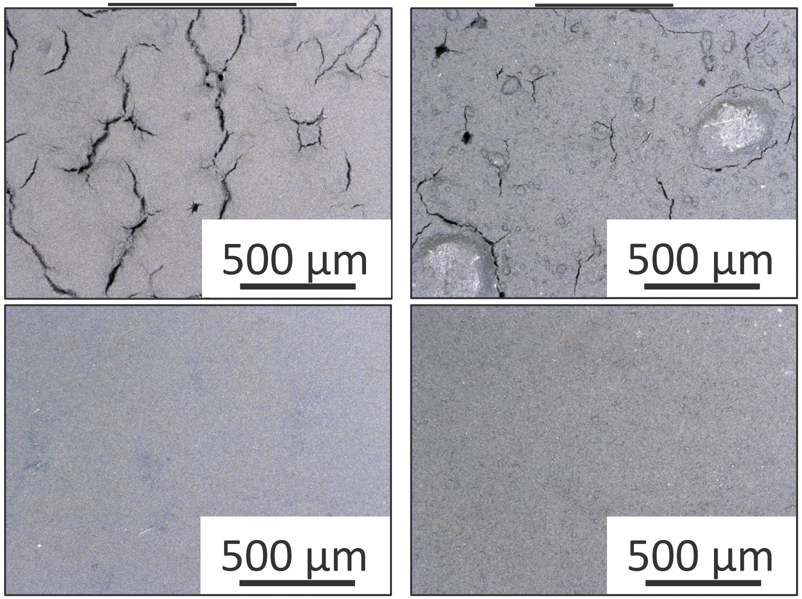
Accomplishments and Progress: Initiated Research on Electrode Crack Mitigation

Influence of Substrate – MPL Roughness

Uncoated | Coated

SGL 29BC

Freud. H23C8



Catalyst Layer Details

50 wt% Pt/HSC, 1000 EW Nafion, 0.9 I:C

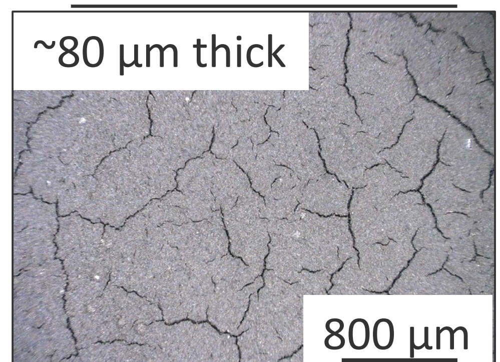
Catalyst loading: 0.12 mg_{Pt}/cm^2

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

PGM-free electrode



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

Collaborations

Institution	Role
National Renewable Energy Laboratory - Prime Mike Ulsh, Scott Mauger, Sunilkumar Khandavalli, Jason Pfeilsticker, Min Wang, Radhika Iyer, K.C. Neyerlin	Ink formulation studies, electrode production and coating, rheology, MEA performance testing, advanced diagnostics
Argonne National Laboratory Debbie Myers, Jae Hyung Park, Nancy Kariuki	Small angle x-ray scattering of catalyst inks – critical for understanding rheology measurements and catalyst ink microstructure
Colorado School of Mines Svitlana Pylypenko, Samantha Medina	Electron microscopy of catalyst materials and electrodes
Proton OnSite Chris Capuano	LTE catalysts and materials
Pajarito Powders Alexey Serov and Barr Zulevi	PGM-free catalyst powders
Oak Ridge National Laboratory Karren More, Dave Cullen	Assisting with electron microscopy

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

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

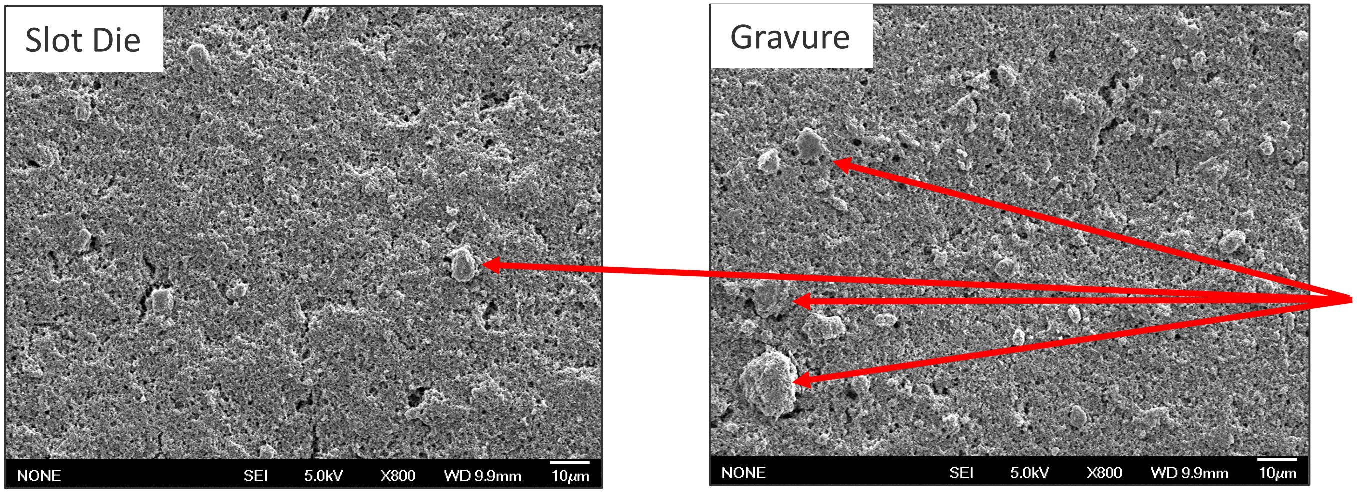
Accomplishments:

- 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

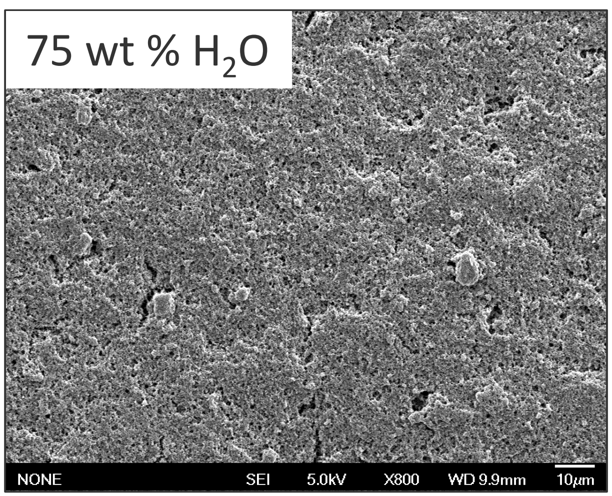
Accomplishments and Progress:
Utilized Electron Microscopy to Evaluate R2R-Coated Electrodes

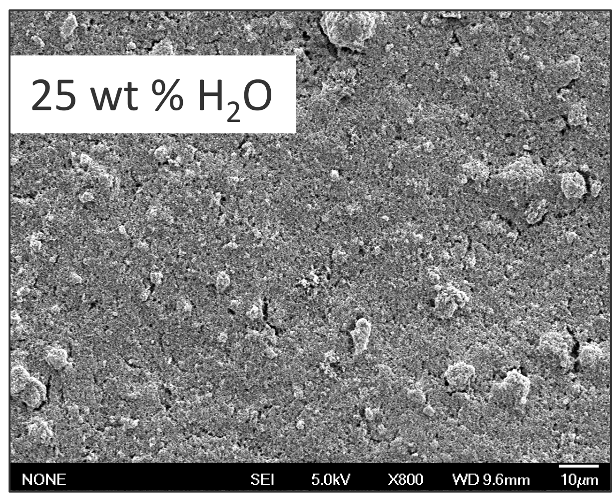
Comparison of Coating Method



Fewer aggregates in slot die coated electrodes

Comparison of Ink Formulation





Fewer aggregates with water-rich ink formulation

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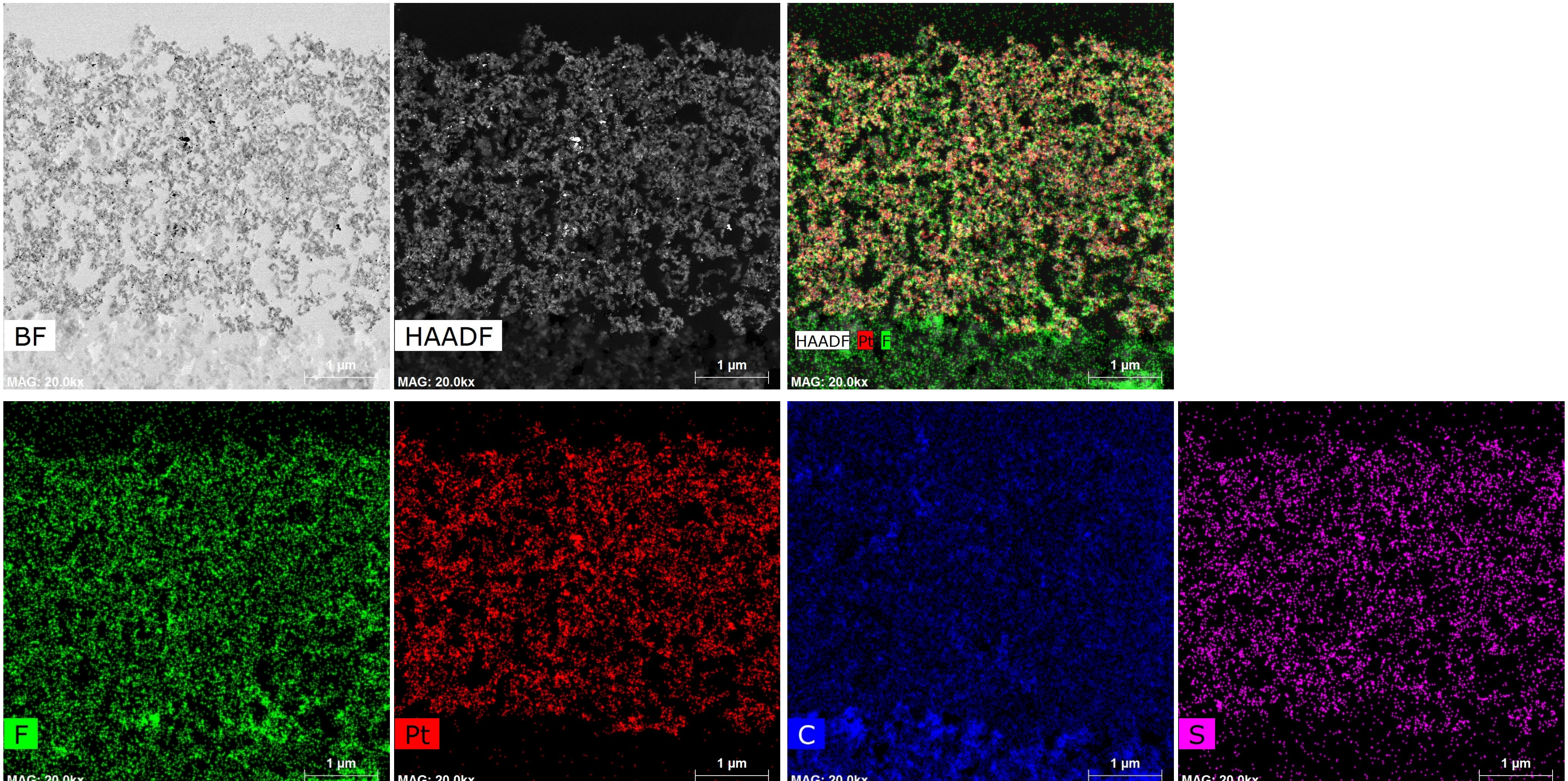
Accomplishments and Progress:
Utilized Electron Microscopy to Evaluate R2R-Coated Electrodes



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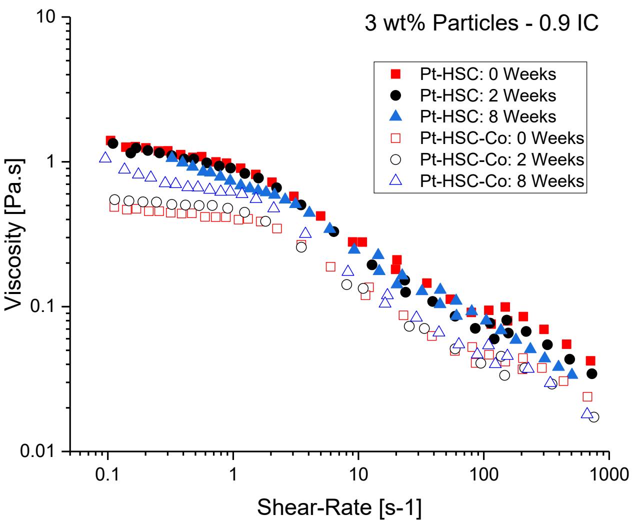
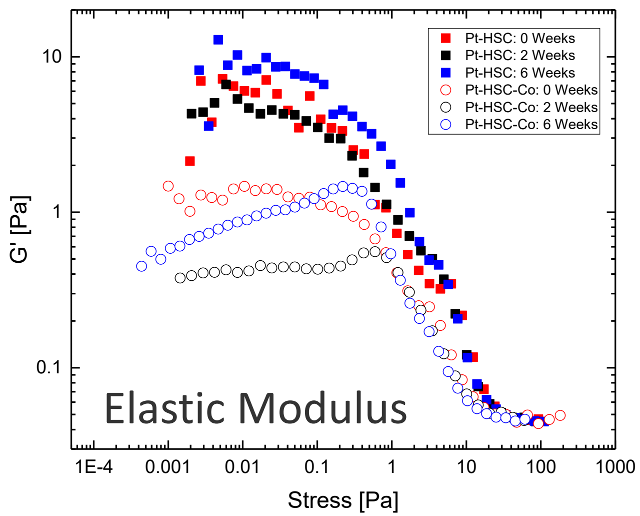
- ***TEM analysis shows slot-die coating produces favorable electrode morphology***
  - Electrode shows good porosity
  - Catalyst and ionomer are well distributed throughout the electrode

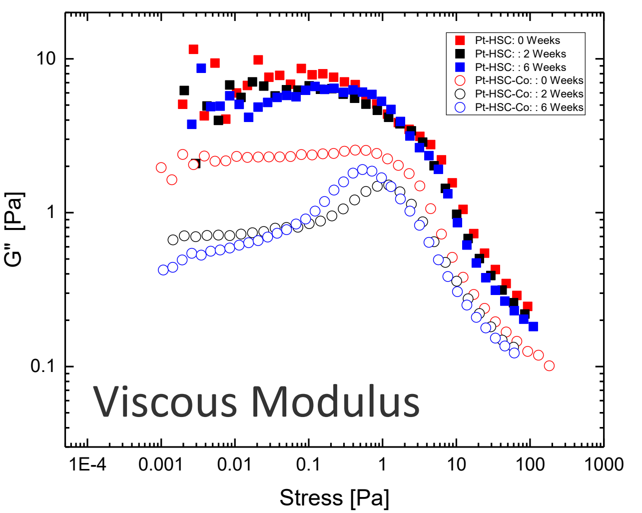
Accomplishments and Progress:
Characterized Shelf-Life Stability of Catalyst Inks: Pt vs PtCo

Does susceptibility of Pt-alloy catalysts to leaching in acids impact shelf-life stability of catalyst inks?

Steady Shear Rheology **Oscillatory 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