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

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National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

MN019

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

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

Partners

- Argonne National Laboratory
  - Debbie Myers
- Colorado School of Mines
  - Svitlana Pylypenko
- Proton OnSite
  - Chris Capuano
- 3M Company
  - Mike Yandrasits
- Umicore
  - Sascha Toelle

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)

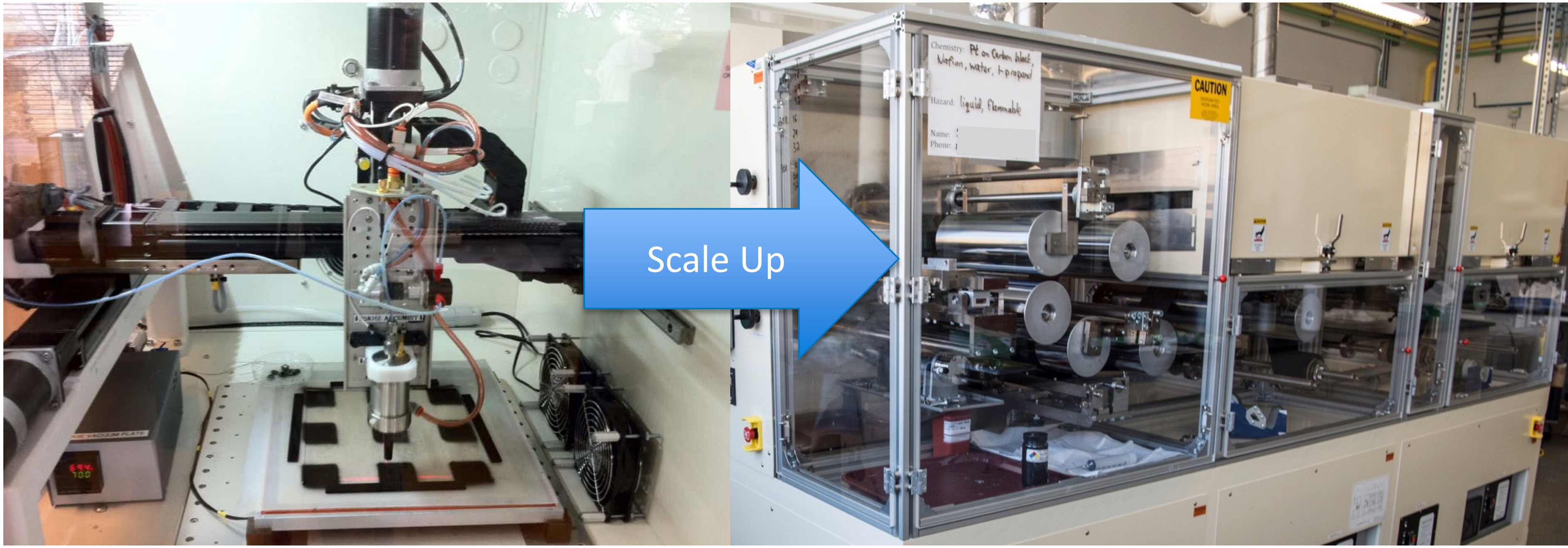
- Roll-to-roll (R2R) is the lowest cost/highest throughput method for production of FC/LTE materials
- R2R coating techniques require different ink formulation and have different physics than lab-scale processes
- Many researchers/producers do not have access to the infrastructure to understand how the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



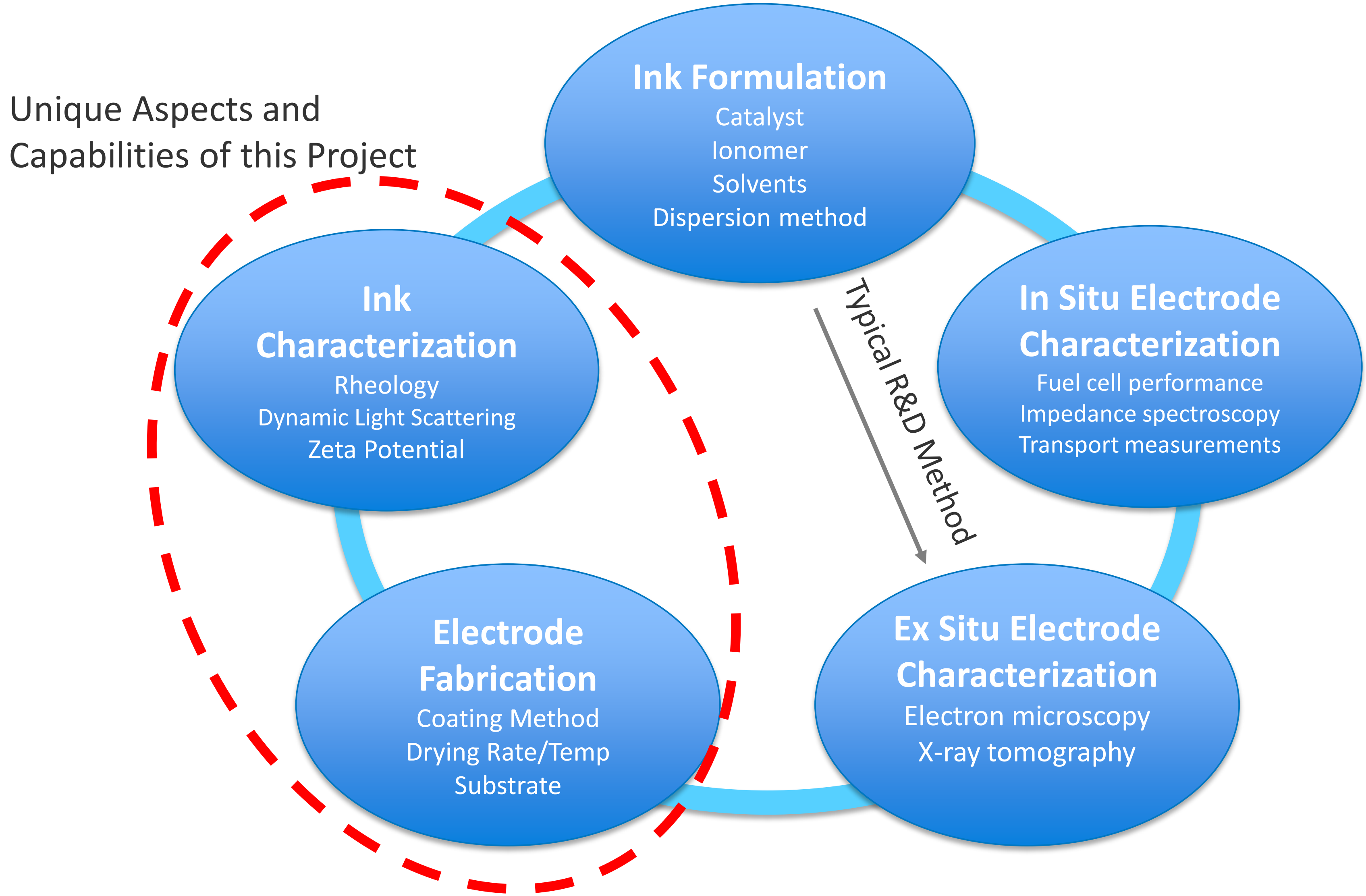
Used to demonstrate new materials and for fundamental studies

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



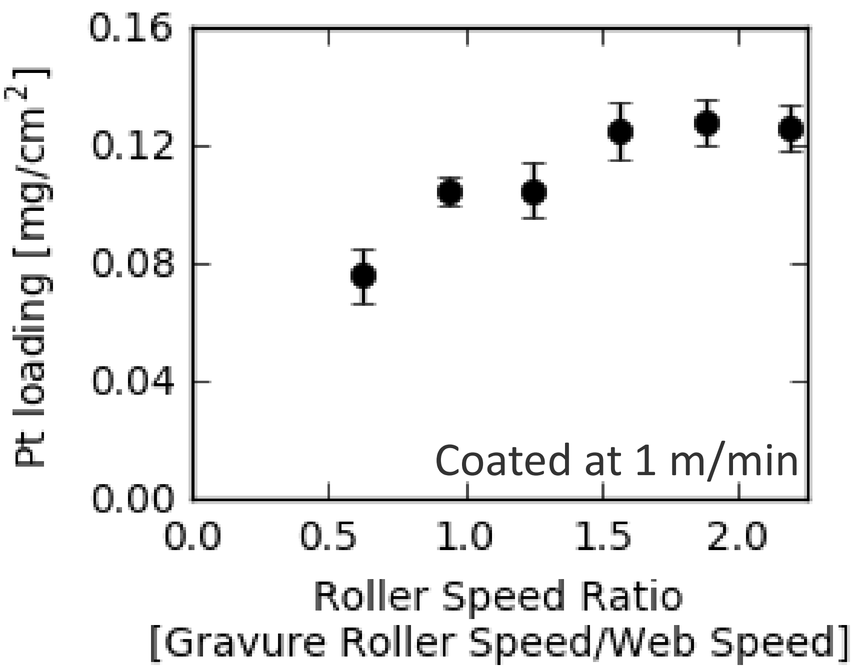
Approach: Project Schedule and Milestones

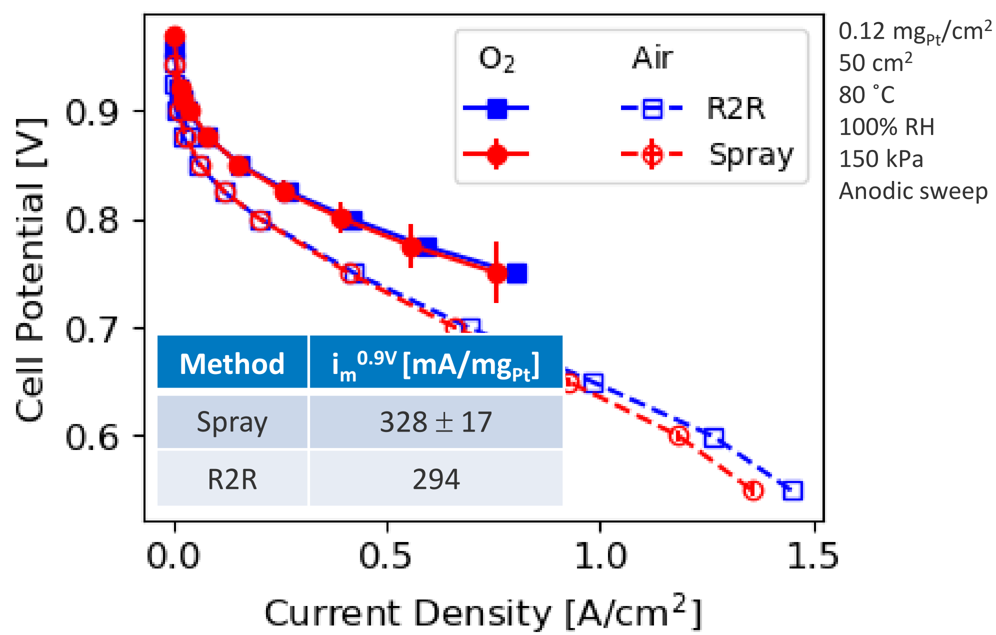
Qtr	Date	Milestone/Deliverable (as of 4/17/2018)	Type	Complete
FY17 Q3	6/2017	Fabricate and characterize baseline slot-die and micro-gravure roll coated electrodes on R2R coating station, at least one of which to meet the following criteria: 1. Achieving a target catalyst loading in the range of 0.05 to 0.2 mg Pt/cm^2 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, H_2/O_2, 150 kPa_{abs}	SMART	MET
FY17 Q4	9/2017	Fabricate and characterize baseline cast membranes on R2R coating station.	QPM	MET
FY18 Q2	3/2018	Perform initial ink development and coating of unsupported catalyst systems to support HydroGEN projects.	QPM	MET
FY18 Q3	6/2018	Characterize impacts of coating flow types (slot – pressure driven vs. gravure – extensional) on catalyst layer morphology and performance.	QPM	On track
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	On going

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/cm^2 ✓
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, H_2/O_2, 150 kPa$_{abs}$ ✓



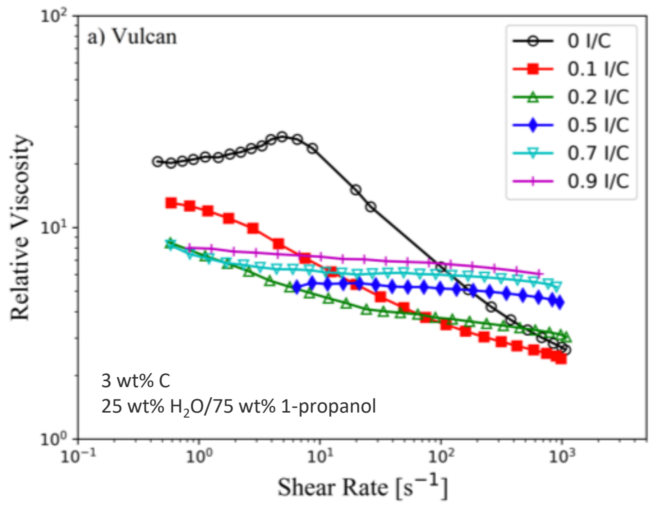


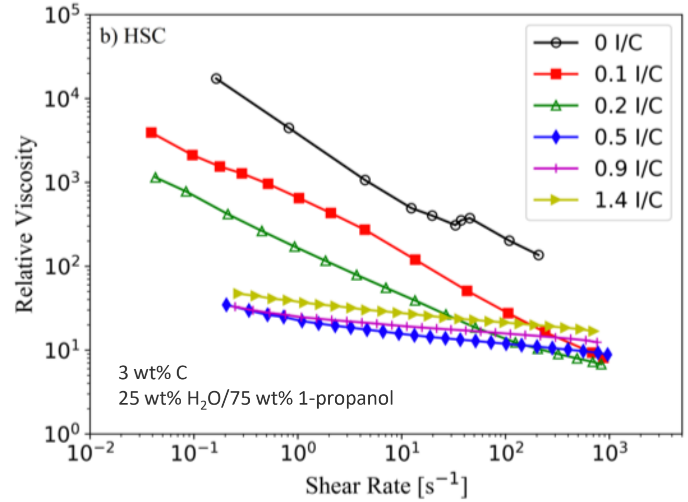
Method	$i_m^{0.9V}$ [mA/mg$_{Pt}$]
Spray	328 ± 17
R2R	294

R2R-Coated Electrodes Achieved 90% of Spray-Coated Electrodes Mass Activity

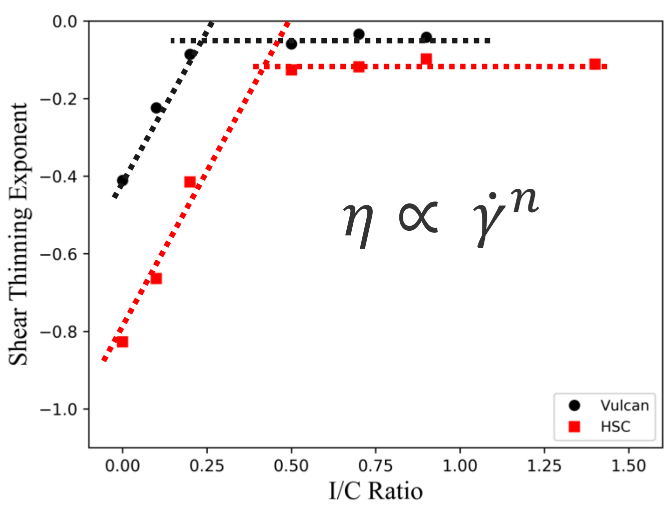
Accomplishments and Progress:
Rheology Correlated Carbon Support Properties with Optimized Electrode Properties

Rheology of Carbon Blacks





Shear thinning analysis

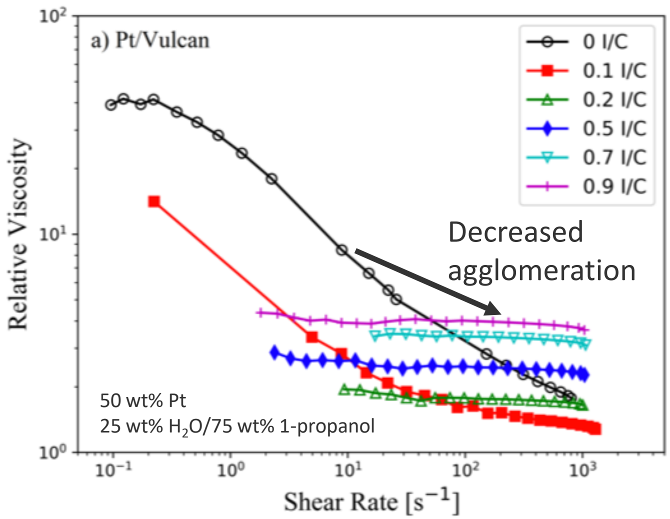


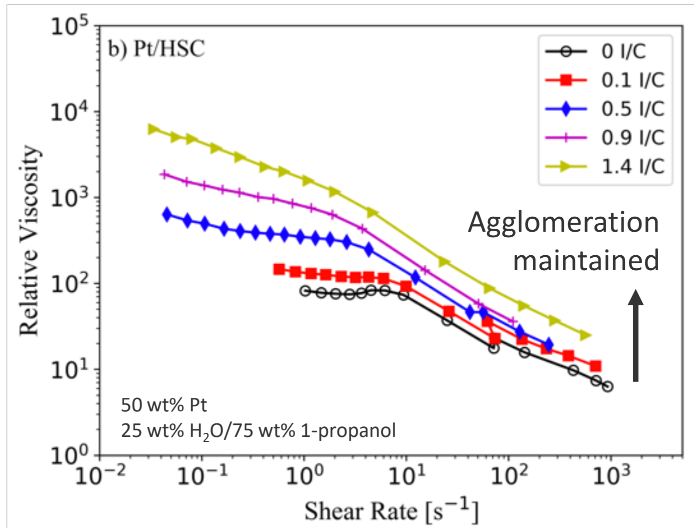
Carbon Black	Surface Area [m²/g]	Pore Volume (> 2 nm) [cm³/g]	I:C Onset of shear thinning plateau	"Optimized" Electrode I:C
Vulcan XC 72	237.1	0.52	0.25	0.5
High Surface Area	801.8	1.01	0.41	0.9

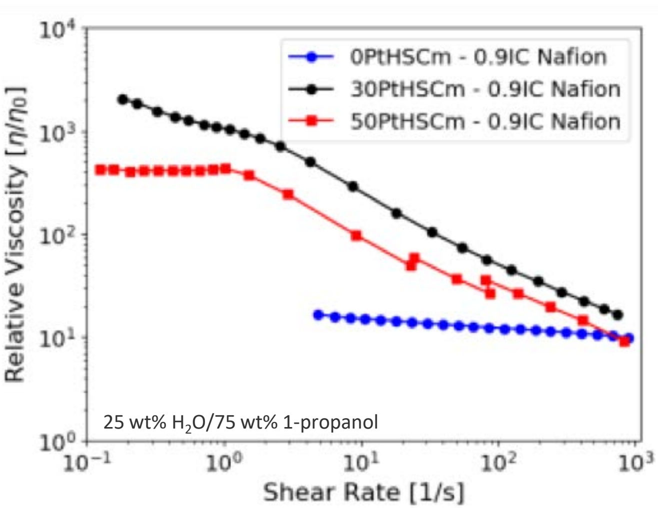
Observed linear correspondence between carbon-support pore structure, shear-thinning plateau, and optimized electrode I:C

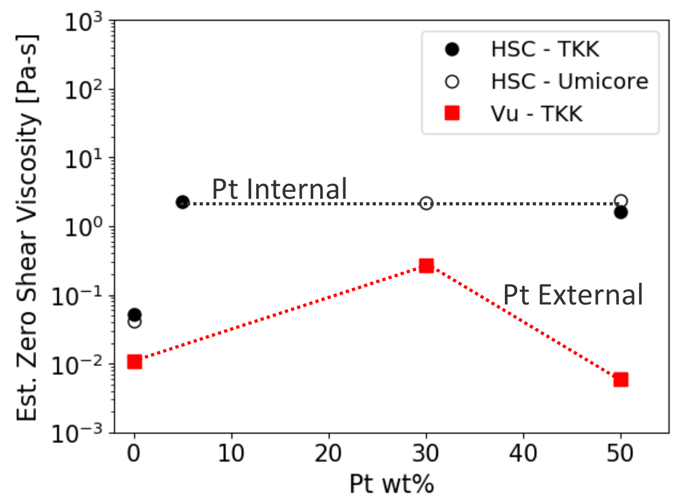
Accomplishments and Progress:

Demonstrated Differences in Rheological Influence of Pt catalyst



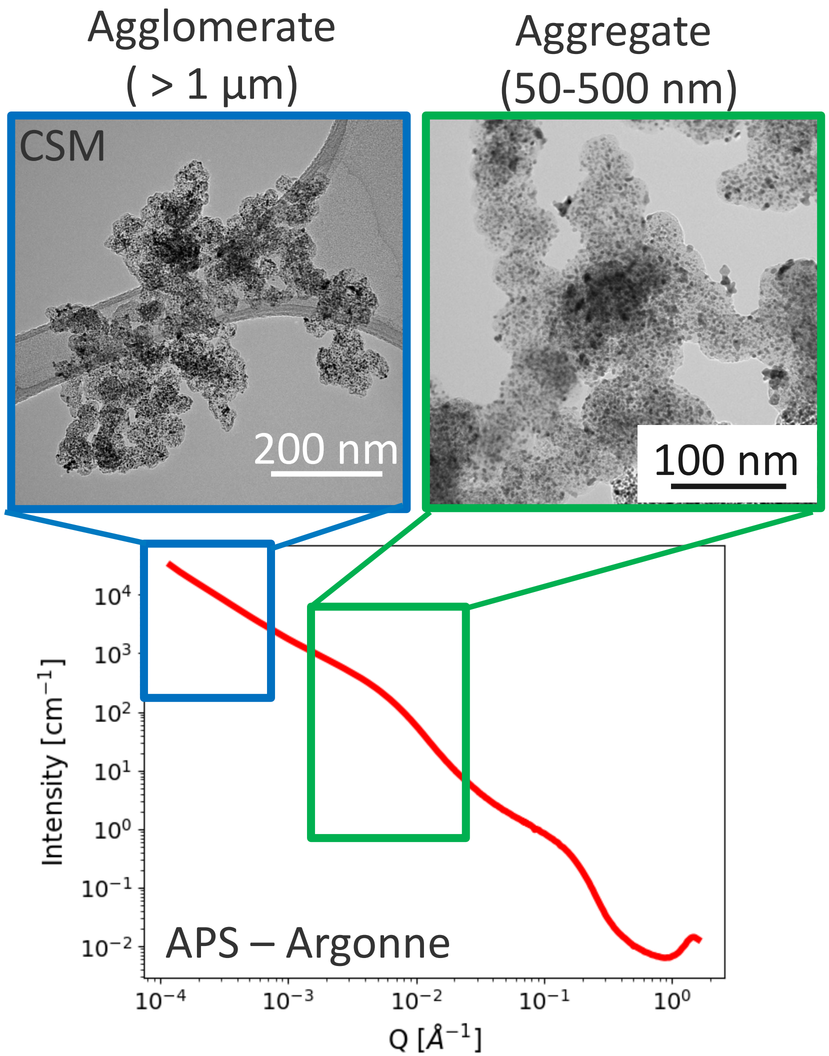


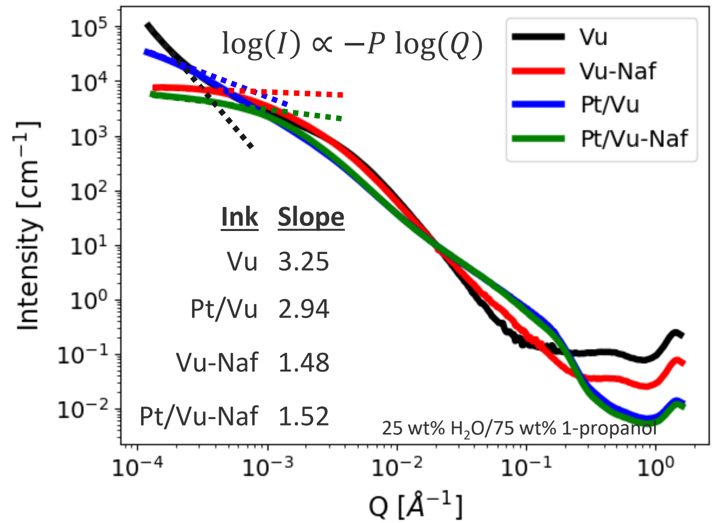


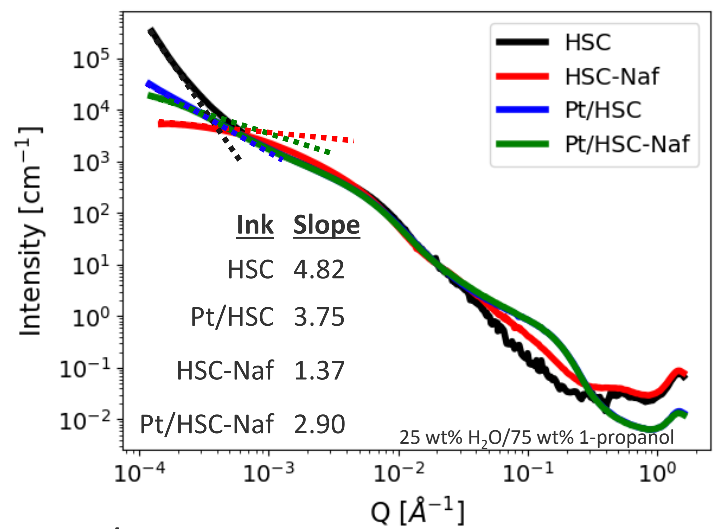


- Influence of Pt dependent on surface or internal location of Pt
- Determined that carbon chemistry influences interactions with Nafion

Accomplishments and Understanding:
X-Ray Scattering Correlated Ink Microstructure to Rheology

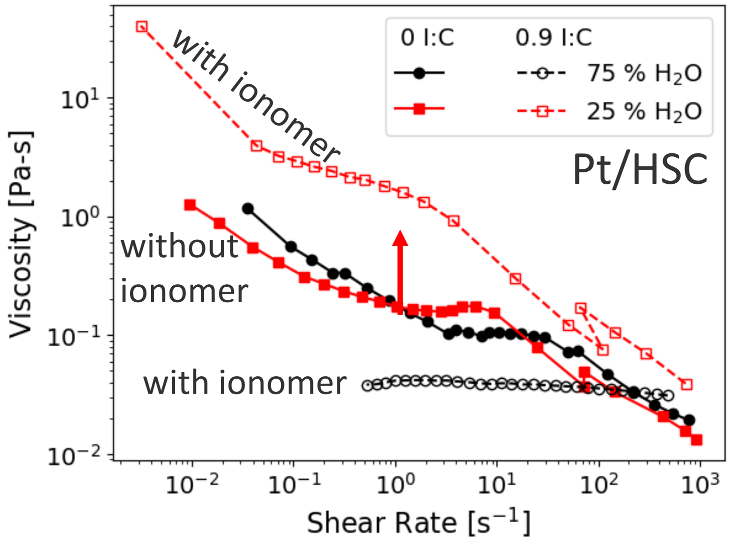




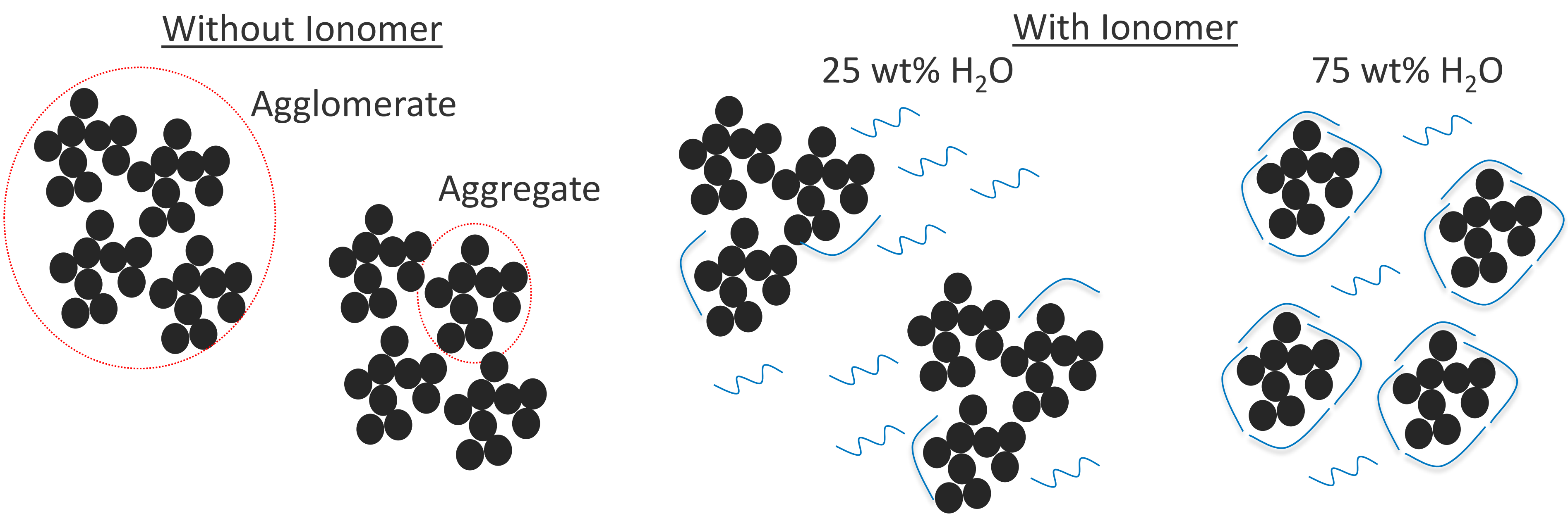


- Utilized power-law slope analysis to characterize agglomeration
- Determined that ionomer breaks up Vulcan agglomerates but does not for HSC

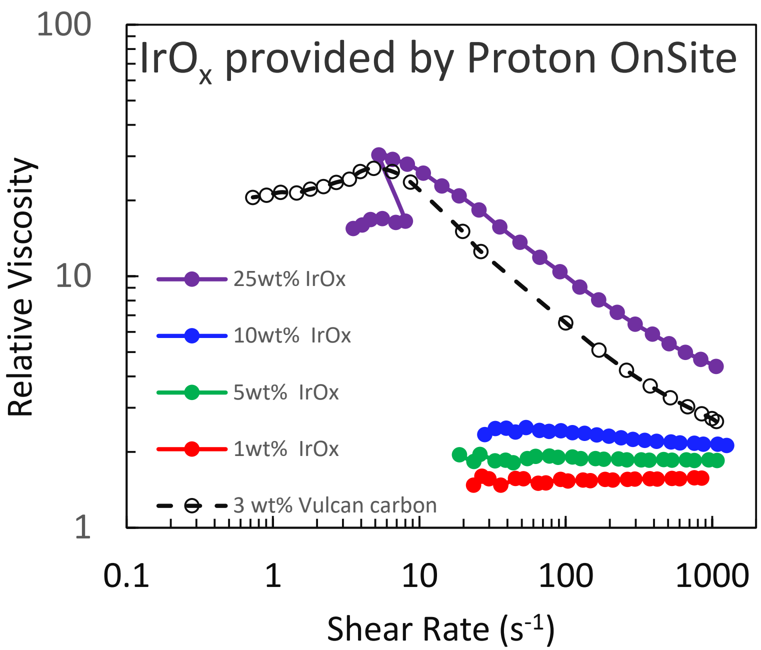
Accomplishments and Progress:
Determined Solvent Influence on Ionomer-Carbon Interaction

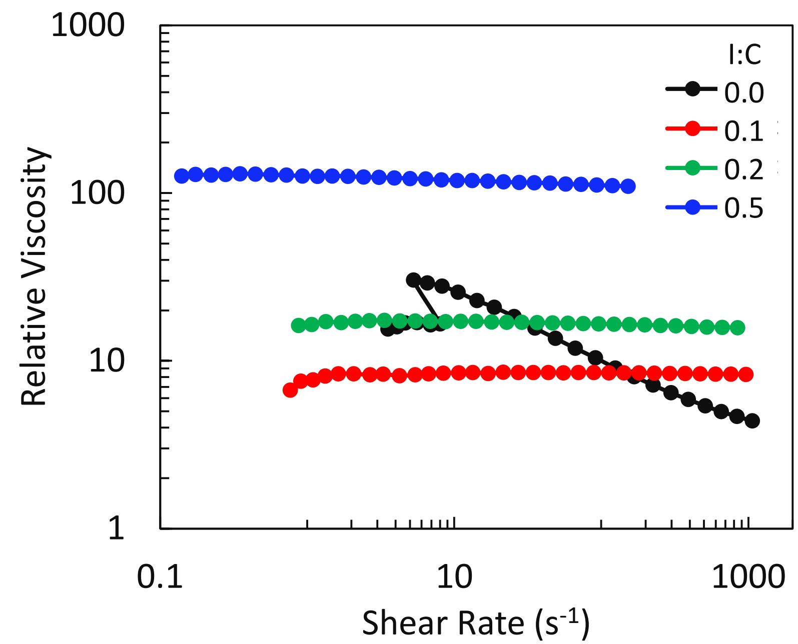


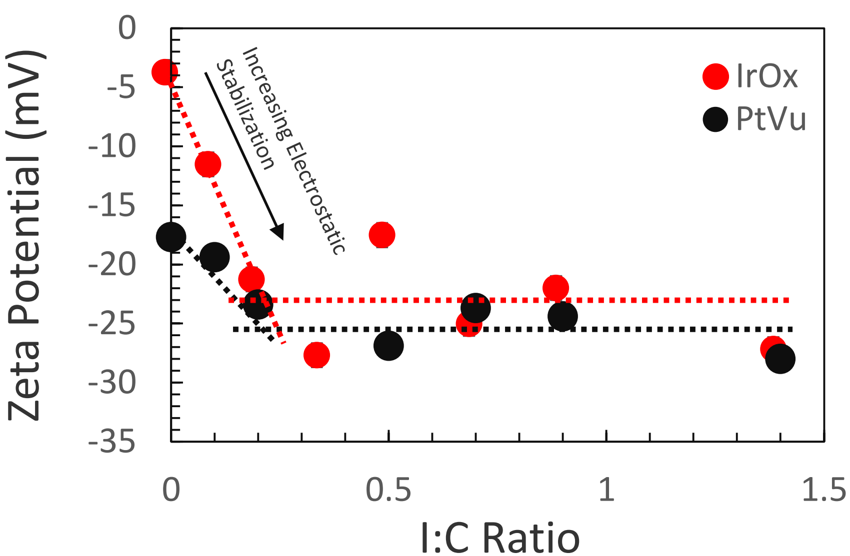
- Demonstrated that high water-content solvent causes stronger ionomer-carbon interaction
- Stronger interaction leads to stabilization of the ink and smaller agglomerates
- It is expected that this will lead to better electrode performance - fuel cell testing planned to confirm hypothesis



Accomplishments and Progress:
Inks Formulation of Unsupported Catalysts to Support LTE







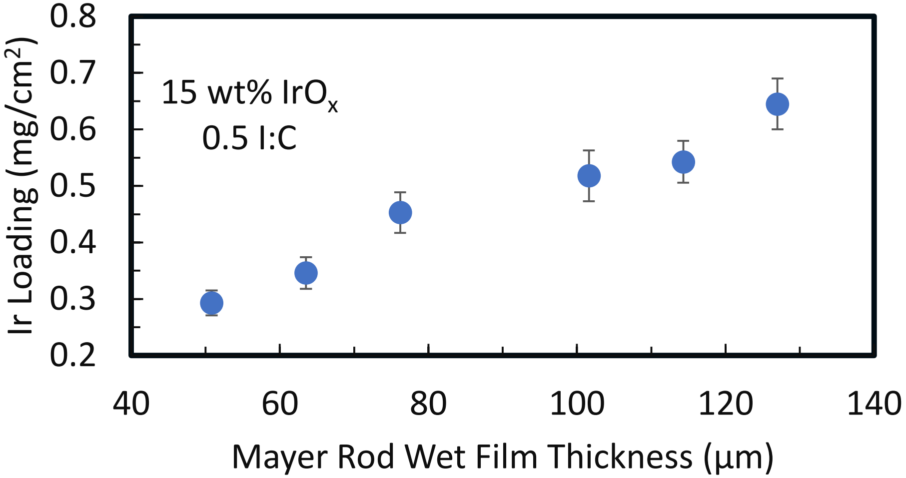
- Demonstrated that unsupported catalysts display similar agglomeration behavior as Pt/Vu
- Rheology and zeta potential measurements showed similar stabilization against agglomeration by Nafion
- Interacting frequently with Proton OnSite to ensure relevance
- Future studies to include new materials: Pt black, high-surface area IrO_x

Accomplishments and Progress:
Coating of Unsupported Catalyst Inks to Support LTE

Mayer Rod Coating

Ink Concentration ($wt\%\ IrO_x$)	Ir Loading (mg/cm^2)
15	0.29 – 0.65
25	1 – 1.7

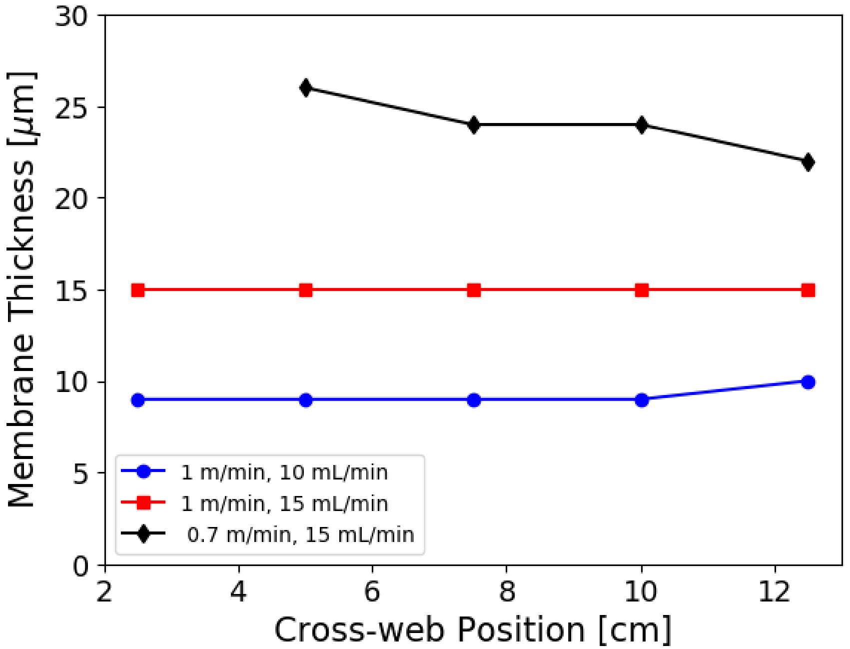
IrO_x provided by Proton OnSite



- 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

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



Flow Rate [mL/min]	Web Speed [m/min]	Average Thickness [μm]	Std. Dev. Cross Web [μm]	Std. Dev Down Web [μm]	Down web length measured [m]
10	1	10.5	0.4	1.0	1.2
15	1	14.1	0	0.5	0.6
15	0.7	21.5	1.6	1.5	0.6

Uniform Nafion Membranes Cast at Relevant Thicknesses

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, K.C. Neyerlin, Jason Pfeilsticker, Katherine Hurst, Jonathan Stickel	Ink formulation studies, electrode production and coating, rheology, membrane casting, MEA performance testing, advanced diagnostics, catalyst porosity/surface area analysis
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, Caleb Stetson	Electron microscopy of catalyst materials and electrodes
Technical Univ. of Munich Hubert Gasteiger, Jan Schwämmlein	Stack testing – starting April 2018
Proton OnSite Chris Capuano	LTE catalysts and materials
3M Company Mike Yandrasits	Ionomer powders
Umicore Sascha Toelle	Catalysts

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 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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Publication Number

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.)