Roll-to-roll Advanced Materials Manufacturing Lab Consortium

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Presenters: Claus Daniel and Scott Mauger
2018 Hydrogen and Fuel Cells Program
Annual Merit Review
June 14, 2018

MN018

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Overview

Timeline and Budget

- Project Start Date: 10/01/2016
- FY17 DOE/FCTO Funding: $1M (for CRADA work) leveraging $4M of AMO funding
- Anticipated recipient share: $1M
- FY17 spent: $0 of FCTO
- FY18 planned: $150K of FCTO for new CRADA with Proton OnSite

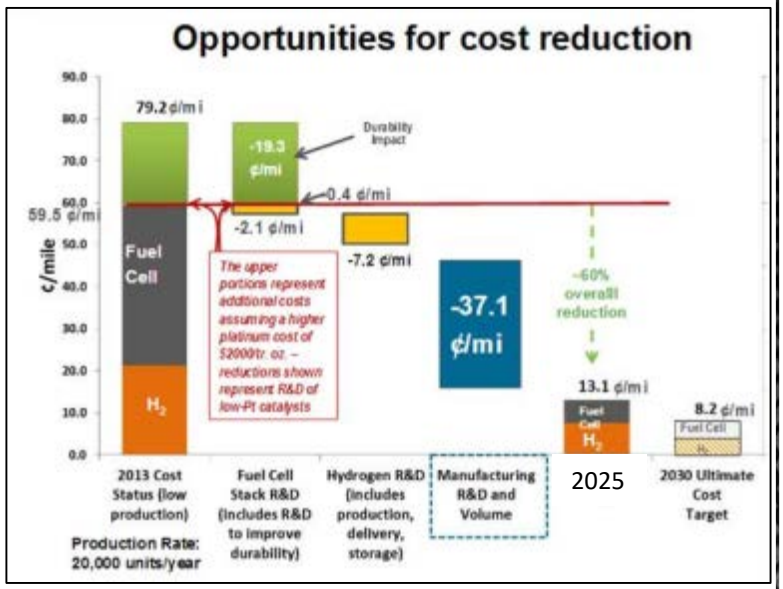
Technology Barrier

- Develop roll to roll manufacturing techniques to reduce the cost of automotive fuel cell stacks at high volume (500,000 units/year) from the 2008 value of $38/kW to $20/kW by 2025.

- Project partners:
  - ORNL, NREL, ANL, LBNL
  - Proton OnSite
  - Eastman Business Park

Relevance

- R2R is the only manufacturing process platform that will meet cost and volume targets for MEAs
- R2R enables conversion of multiple dissimilar materials into a multi-layer cell
- All DOE-sponsored cost analyses for high volume production of MEAs/cells assume R2R processing
- Cost reduction need: 60 cents/mile in 2013 to 13 cents/mile in 2025

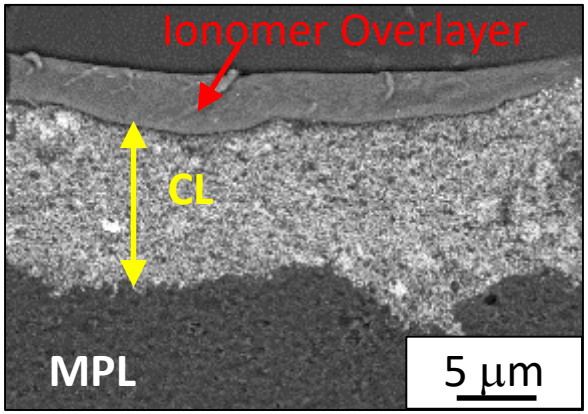


Approach: Consortium

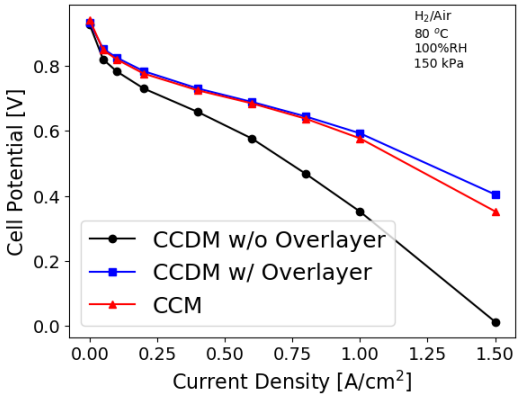
- Lab-industry consortium will enable the United States to capture a substantial portion of R2R opportunity on membranes and flexible devices
- Leverage unique capabilities across the four labs
- Goals depending on technology area:
  - Increase throughput by 5x and reduce production footprint
  - Reduce energy consumption by 2x
  - Increase production yield by 2x
  - Enable substantial shift of manufacturing to the United States by assisting in the development of a domestic supply chain

Approach: Fuel Cell Core Lab Project

- **The goal of this project is to explore, understand and optimize material and process parameters for single-process (no extra ionomer over-layer) R2R manufacturing of GDEs with comparable performance to CCMs**
- Current standard manufacturing practice for most PEM MEAs is by fabricating catalyst-coated membranes (CCM)
  - The electrodes are coated onto separate transfer liners and then hot-pressed onto the membrane, or
  - The electrodes are directly coated onto the membrane
- Limits to CCM production
  - The former method entails multiple additional steps and materials, due to the use of a transfer liner
  - The latter is very difficult due to swelling of the membrane during solvent- or aqueous-coating of the electrodes
- Gas diffusion electrodes (GDE) are recently becoming of more interest in the industry as a pathway for MEAs
  - The different structure of GDEs may provide improved performance and lifetime under some operating conditions
  - GDEs may also be easier to fabricate
    - Deposition onto the low-strength, highly liquid sensitive (hygroscopic) membrane is eliminated
    - Use of transfer liners is eliminated
- However, it appears that an over-layer of ionomer is required for GDEs to achieve performance comparable to CCMs



TEM of spray-coated GDE with ionomer over-layer (left); Performance comparison between lab-scale spray-coated CCM baseline and GDEs with and without over-layer (right)

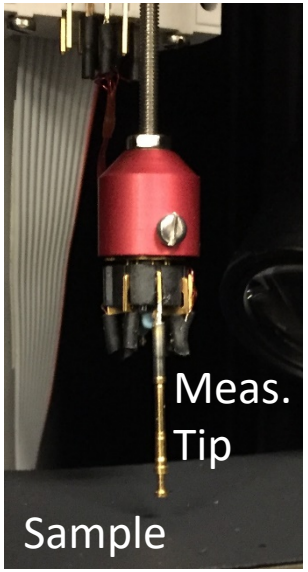


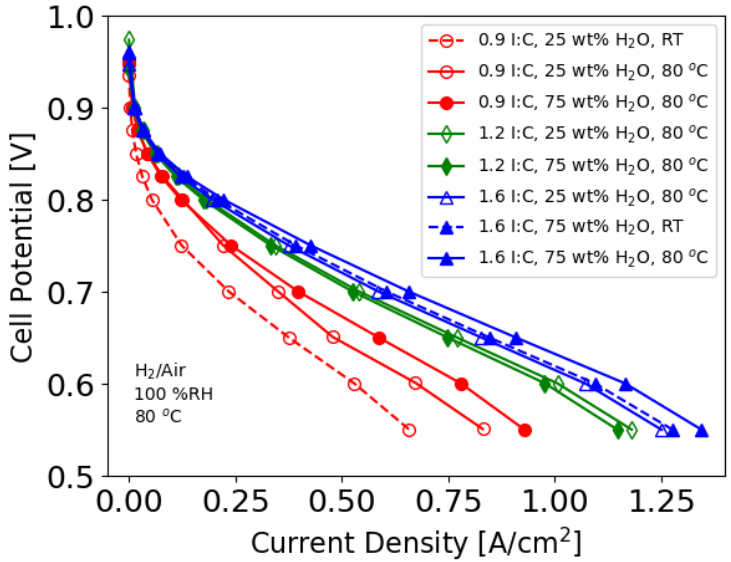
Collaborations: Lab Roles

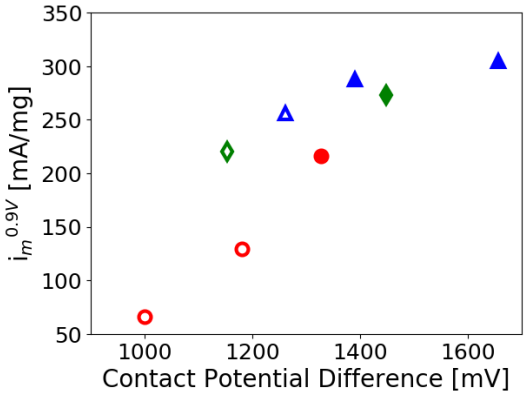
- Gas diffusion electrode studies
  - Gravure, slot die, and dual-slot coating (NREL, ORNL)
  - Coating consolidation modeling (LBNL)
  - XCT, Electron Microscopy, Kelvin Probe and XRF characterization (ANL, ORNL, NREL)
- Ink studies
  - Formulation, mixing and rheology (NREL, ORNL)
  - USAXS characterization (ANL)
  - Rheological modeling (LBNL)
- MEA component R2R lamination (ORNL)
- MEA fabrication and testing (NREL)
- QC development (NREL, ORNL)

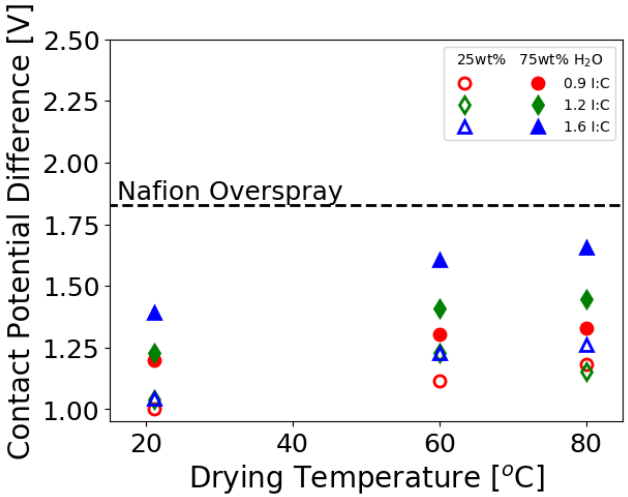
Accomplishments and Progress:

Developed New Kelvin Probe Method for Rapid Characterization of Surface Ionomer Content (NREL)









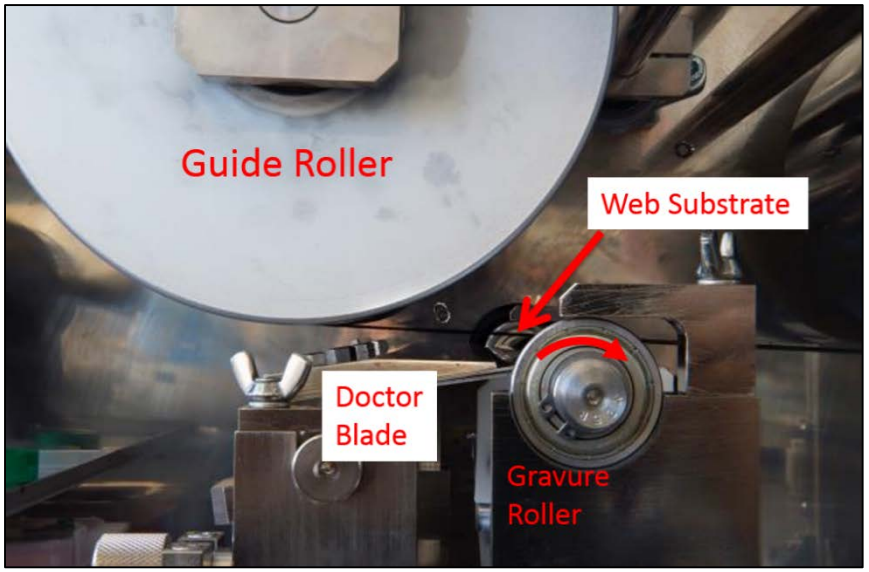
- Used Mayer-rod coating for screening of ink formulation and drying conditions
- Developed Kelvin probe method to provide a simple tool for measuring electrode surface ionomer content
- Observed strong correlation between ionomer content and MEA performance

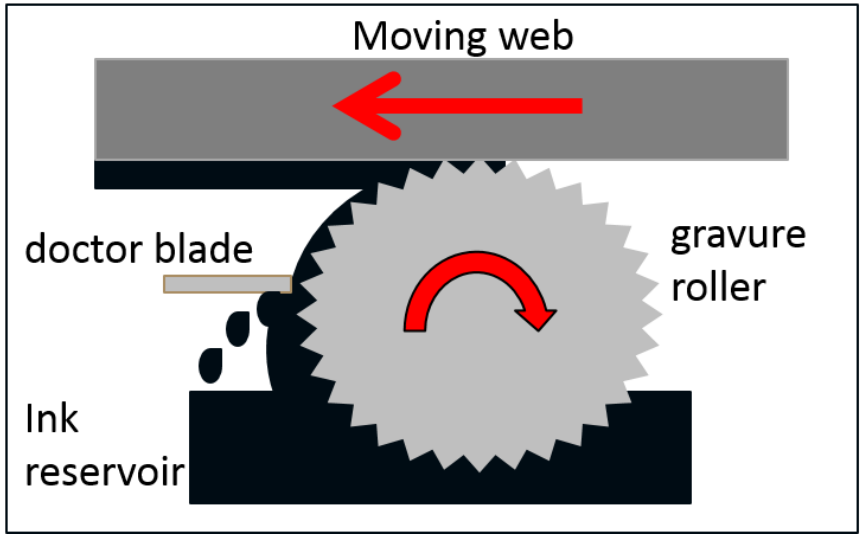
Accomplishments and Progress:

R2R Coating of Ionomer Gradient Electrodes (NREL)

Down-selection from rod-coating screening experiment to demonstrate successful R2R coating

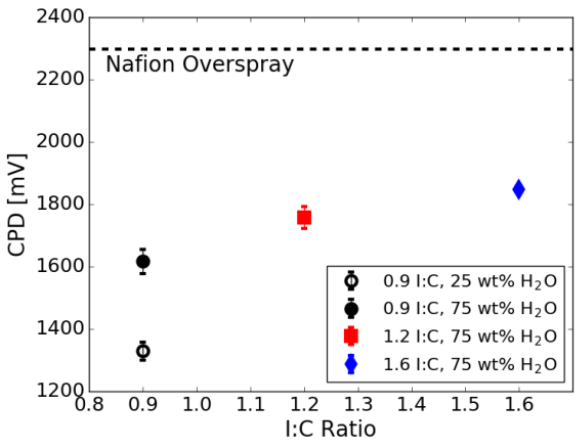
- Inks – Coated 2 m each
  - 0.9 I:C, 25 wt% H_2O
  - 0.9 I:C, 75 wt% H_2O
  - 1.2 I:C, 75 wt% H_2O
  - 1.6 I:C, 75 wt% H_2O
- Solvents: water and 1-propanol
- Catalyst: 50 wt% Pt/HSC
  - Loading: 0.1 ± 0.1 for all coatings
- Ionomer: Nafion 1000 EW
- Substrate: SGL 29BC
- Oven Temp: 80 ˚C
- Web Speed: 1 m/min

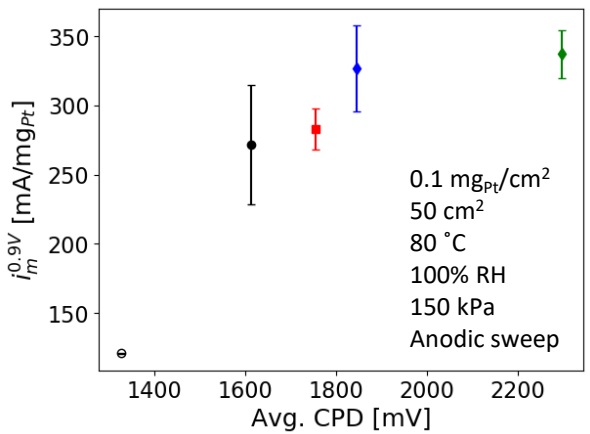


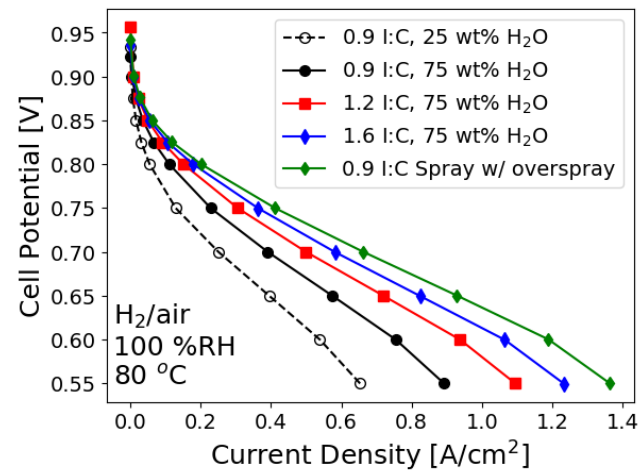


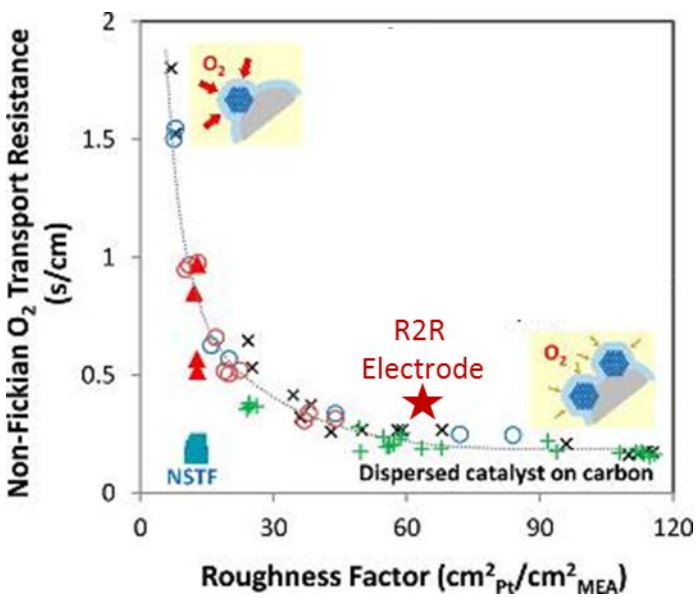
Accomplishments and Progress:

R2R Electrodes Achieved Equivalent Mass Activity to Spray-Coated Electrodes (NREL)









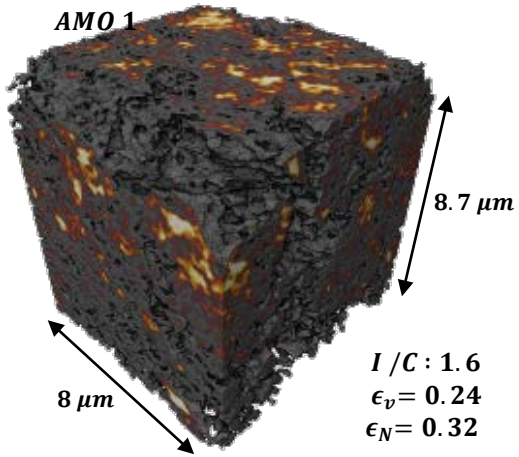
- Confirmed that R2R electrodes show the same trends as Mayer-rod electrodes
- Demonstrated R2R electrodes without ionomer overlayer produce equivalent mass activity to spray-coated electrodes with ionomer overlayer
- Utilized O_2 limiting current measurements to show oxygen mass transport can be further optimized

Published in: Anusorn Kongkanand; Mark F. Mathias; *J. Phys. Chem. Lett.* **2016,** 7, 1127-1137.

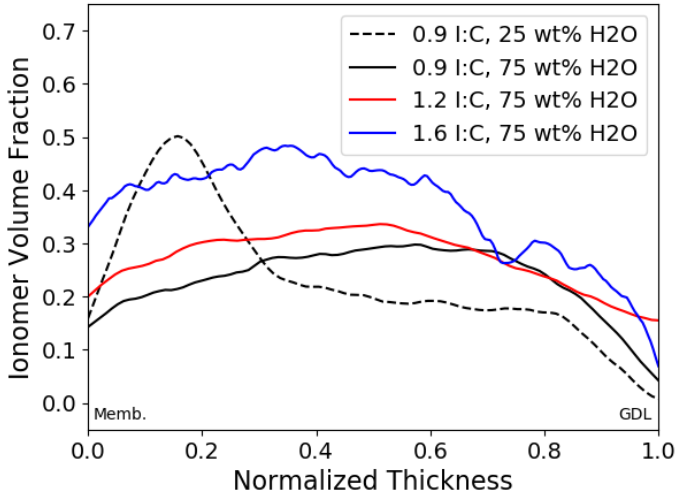
Accomplishments and Progress:

Completed X-ray Computed Tomography of GDEs (ANL)

3D Visualization

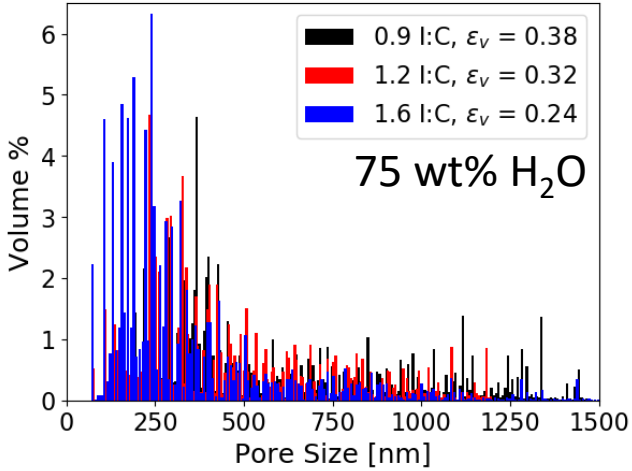


Ionomer Distribution

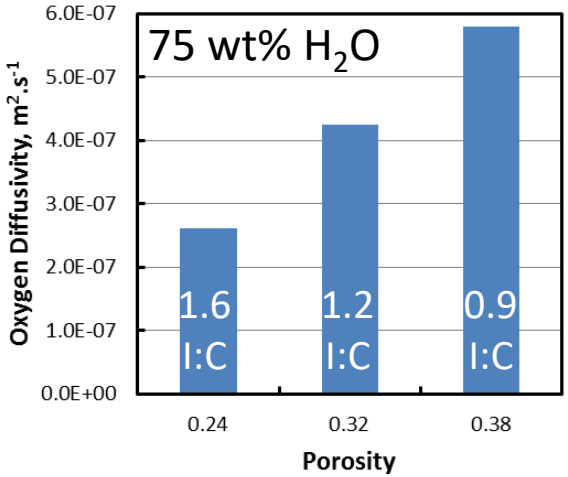


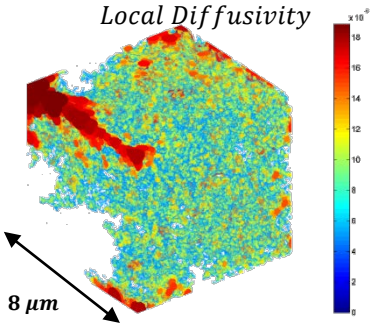
- Verified ionomer gradient structure
- Confirmed that solvent influences ionomer gradient
- Correlated pore size distribution and transport modeling to oxygen resistance measurements

Pore Size Distribution



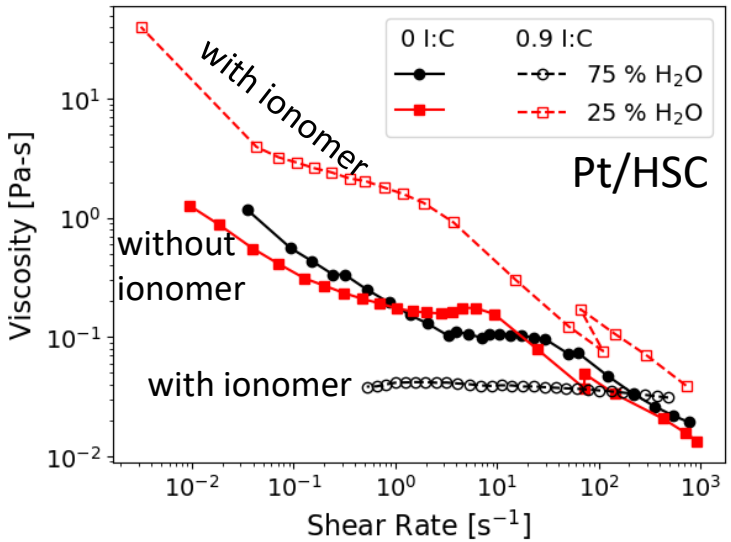
Oxygen Transport Modeling

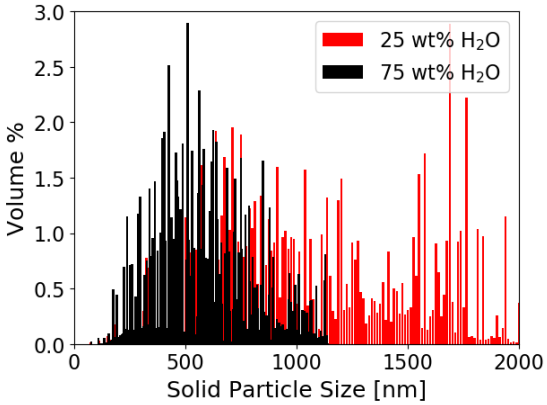


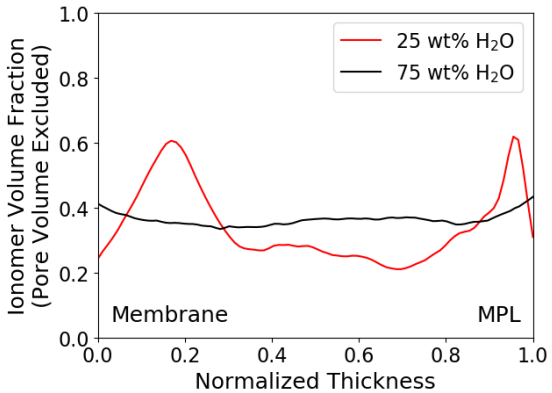


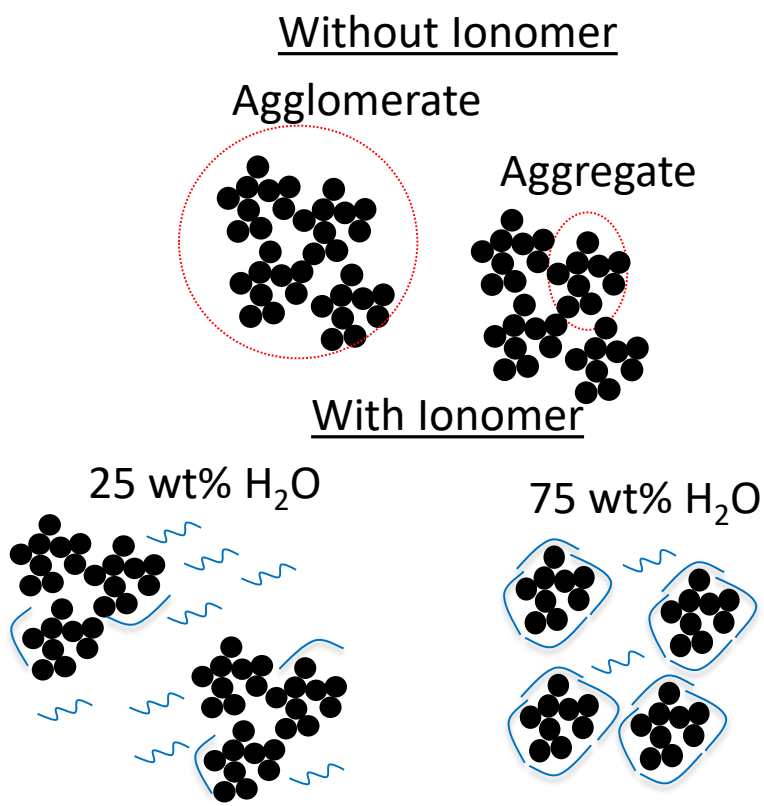
Accomplishments and Progress:

Elucidated Solvent Influence on Ionomer Adsorption to Catalyst (NREL)







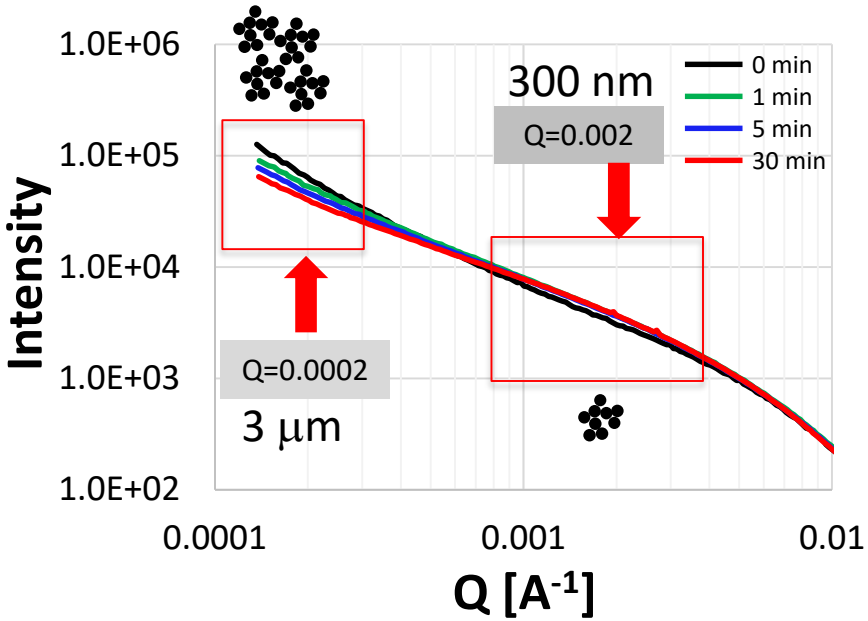


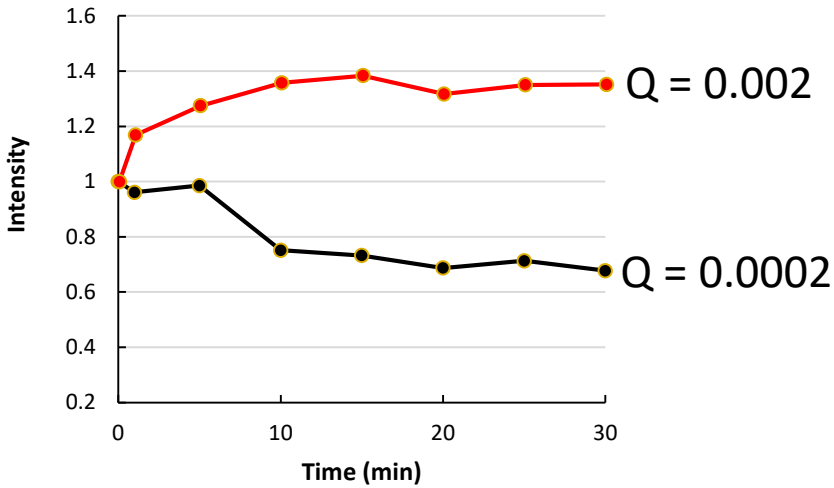
- Identified solvent influence on catalyst aggregation and electrode microstructure
- Future effort will focus on tuning ionomer association with catalyst and drying to optimize ionomer gradient

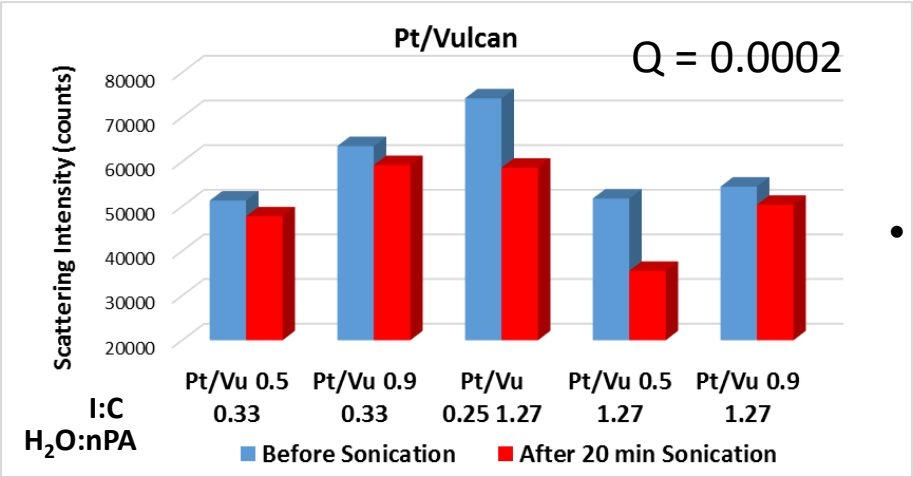
Accomplishments and Progress:

Studied Influence of Ink Dispersion Process and Formulation on Ink Microstructure (ANL)

In Situ USAXS Measurements







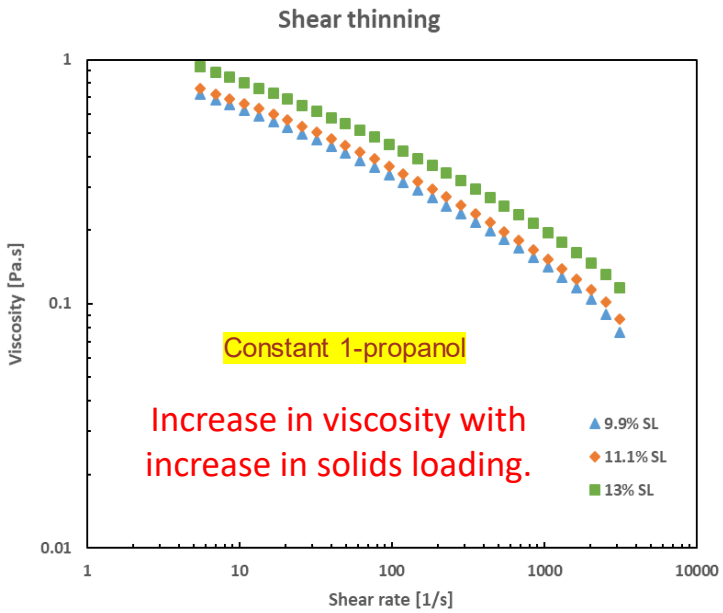
- Studied multiple dispersion methods
  - Ultrasonication
  - Wet Milling
  - High-Shear Mixing
- Correlated USAXS measurements to rheology and XCT results
  - Higher water content leads to less agglomeration

Accomplishments and Progress:

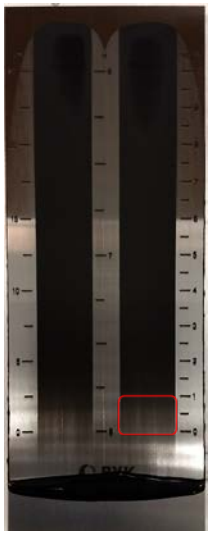
Optimization of High Solids Loadings Inks and Rheology Characterization with Constant 1-Propanol Concentration (ORNL)

Solid Loading	Mixing Speed (rpm)	Mixing Time (min)
9.9 wt%	4000	60
11.1 wt%	4000	60
13.0 wt%	4000	60

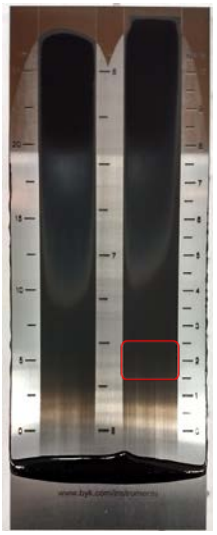
Component	9.9 wt% (g)	11.1 wt% (g)	13.0 wt% (g)
Carbon Black	3.99	4.48	5.28
Nafion D2020	3.59	4.04	4.75
Water	57.96	57.22	55.98
1-propanol	10.93	10.94	10.94



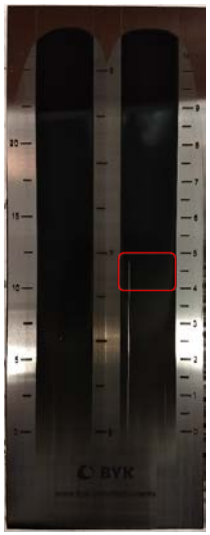
Hegman Gauge Measurement of Particle Size



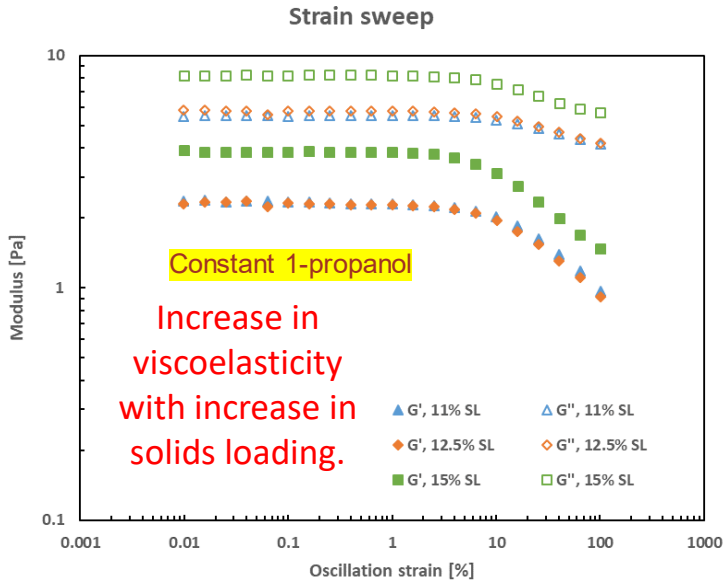
9.9% Solid loading
1 micron



11.1% Solid loading
2 micron

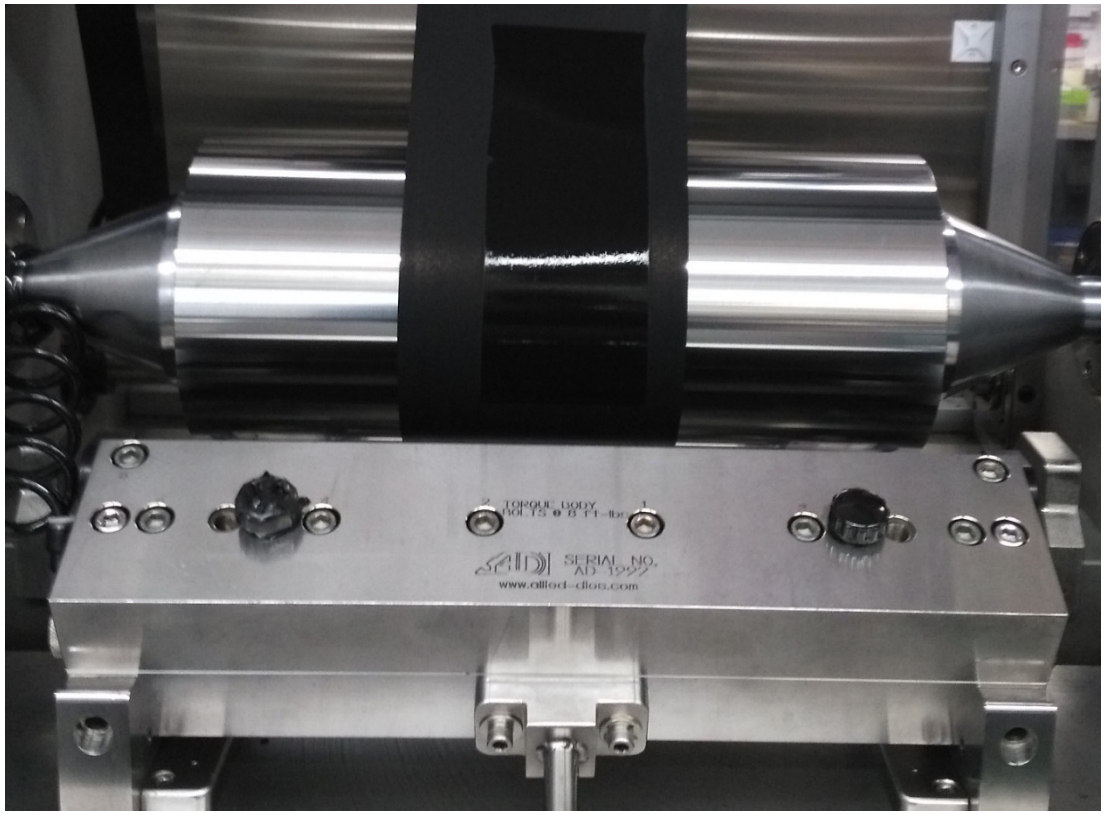


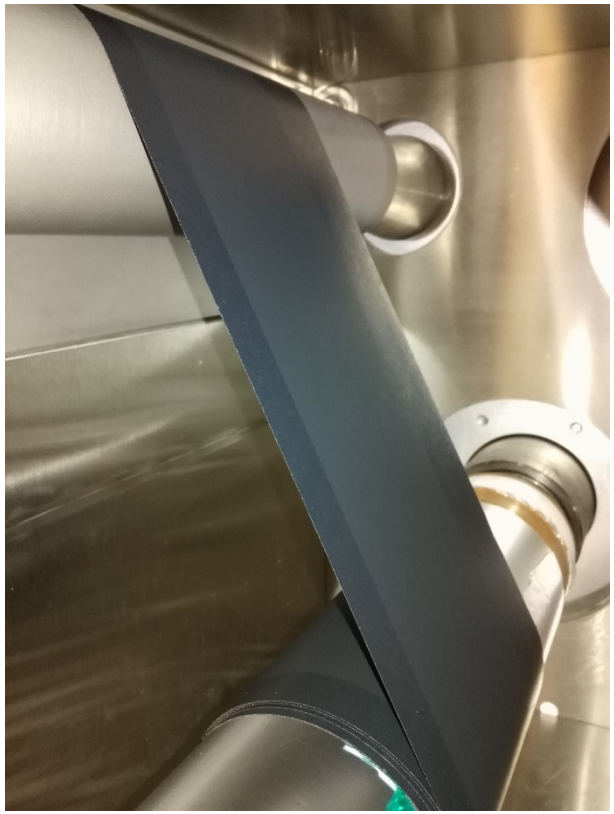
13% Solid loading
4-5 micron



Accomplishments and Progress:

Successful Slot-Die Coating of Ink Formulation with Vulcan XC-72R and Nafion D2020 Dispersion (No Pt) on SGL 29BC GDL Substrate (ORNL)



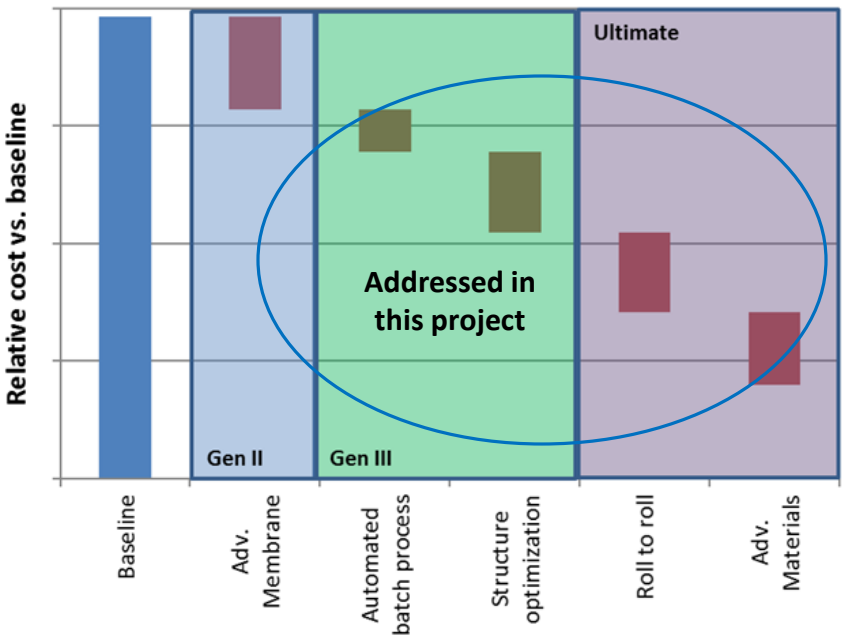


- Wet (left) and dry (right) Pt-less GDE coating on SGL GDL 29BC substrate (4” wide coating with ~12% dispersion solids loading).

Tech Transfer Activities

CRADA Project with Proton OnSite: "Roll to Roll Manufacturing of Electrolysis Electrodes for Low Cost Hydrogen Production"

- Project funding:
  - $300K in-kind cost share from Proton
  - $300K funding from DOE (50:50 FCTO, AMO)
- Proton collaborators: Prasanna Mani, Chris Capuano, Kathy Ayers
- Lab collaborators: NREL, ORNL, ANL
- Task areas:
  - Fundamental studies of ink formulation, rheology, and stability
  - Demonstration of R2R direct coating of electrode onto membrane
  - Advanced characterization of coated electrodes
  - In situ testing to verify performance targets
  - Development of in-line electrode inspection



Proton OnSite

Future Work

FY18

- Rheology
- Multi-spectral imaging
- Coatings
- Characterization at the advanced photon source
- Electron microscopy

FY19

- Initial phase field modeling of ionomer-rich-surface coating consolidation (LBNL)
- Performance testing to understand process effects

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

Summary

Relevance:

- R2R is the only manufacturing process platform that will meet cost and volume targets for PEM MEAs
- Cost reduction need: 60 cents/mile in 2013 to 13 cents/mile in 2025

Approach:

- Leverage unique capabilities, facilities, expertise across the four labs
- Focus on MEA structure of industrial interest (GDEs)
- Achieve reduction in process steps and energy consumption

Collaborations:

- ORNL, ANL, LBNL, NREL, Eastman Business Park, industry

Accomplishments:

- Demonstrated single-process GDEs with performance approaching target
- Utilized XCT to determine influence of solvent and ionomer content on electrode morphology
- Characterized catalyst ink microstructure with USAXS

Future Work:

- Additional inks and coating studies, including dual-slot
- Initiate rheology modeling

Response to Reviewer Comments

- This project was not reviewed last year.

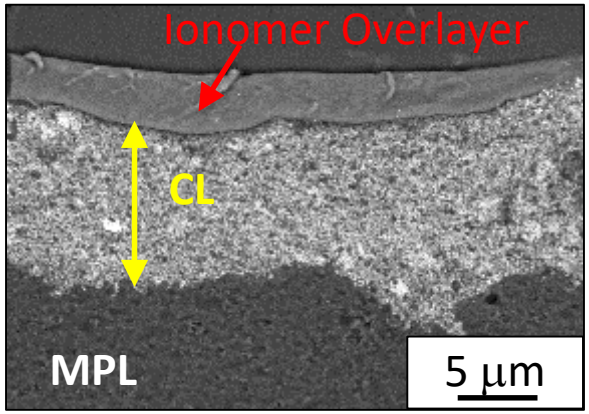
Acknowledgement

Thanks to all collaborating researchers at ORNL, NREL, ANL, and LBNL

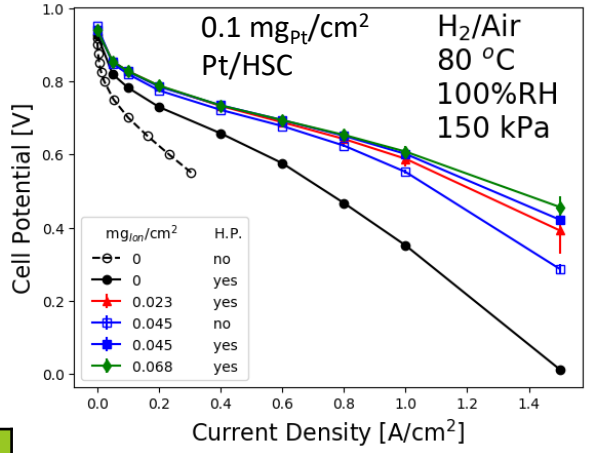
Funding from DOE-EERE-AMO and FCTO

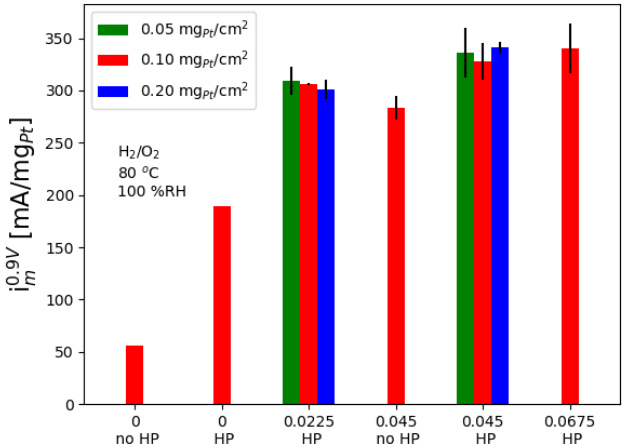
Technical Backup Slides

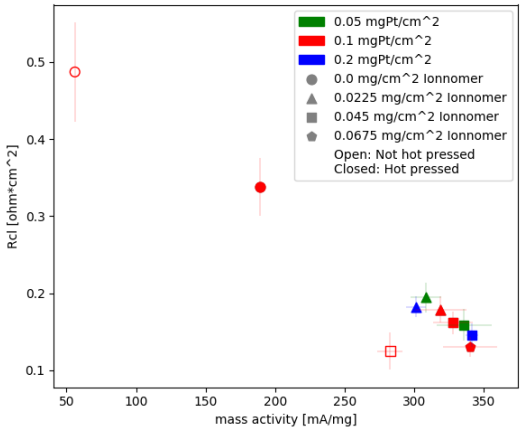
Accomplishments and Progress: Determined the Function of the Ionomer Overlayer

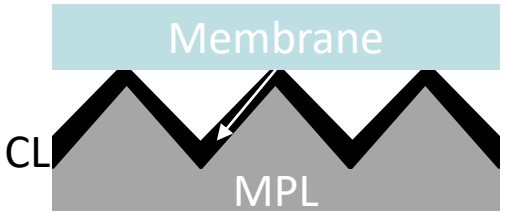


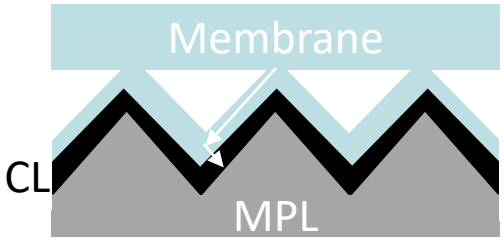
Overlayer [mg/cm²]	RMS Roughness	
	Stylus Profilometer [µm]	AFM [nm]
0	15.8	133
0.0225	12.4	107
0.045	16.6	10.6











Technical Accomplishments

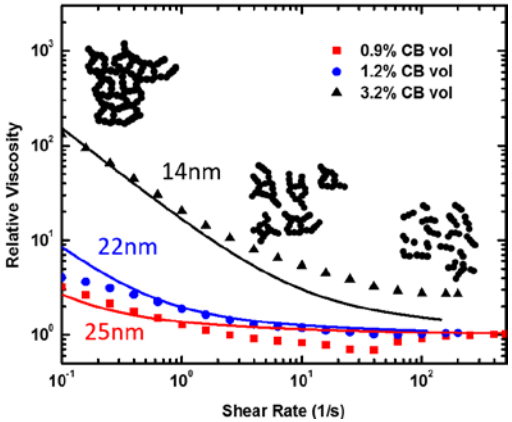
Completed small-scale coating studies with Mayer rod and bar (NREL)

- Diffusion Media: SGL 29BC
- Loading: 0.15-0.2 mg/cm^2
- Catalyst: 50 wt% Pt/HSC
- Concentration: 3 wt% Pt/HSC
- Ionomer-to-Carbon: varied
- Solvents: water and 1-propanol
- Drying: convection oven or fume hood
- Sample Area: 10 cm x 12 cm

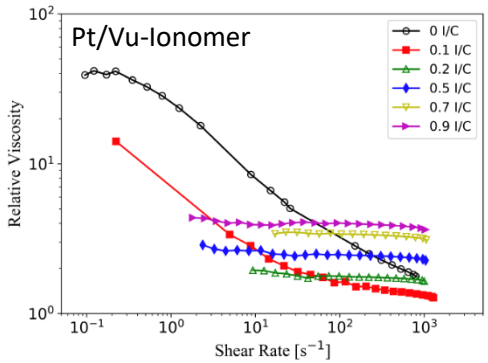
Future Work:

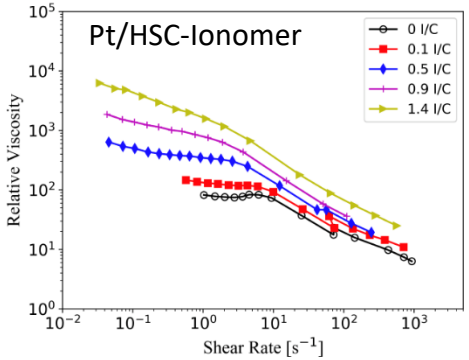
Adaptation of battery electrode ink rheological model to fuel cell CL layer ink (LBNL)

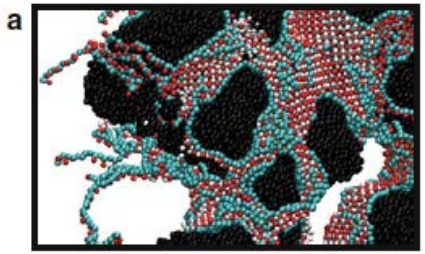
Battery Electrode Ink Modeling

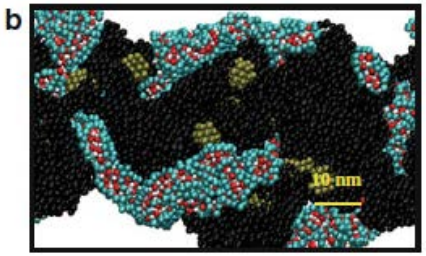


Fuel Cell Electrode Ink Rheology









Malek, et al., Electrocatalysis, 2011, 2: 141-157

Inks for battery electrodes and fuel cell catalyst layers have similarities – porous carbon, polymer binder – but fuel cell catalyst inks are more complex due to catalyst and ionomer (charged copolymer). A new model may need to be developed to account for these additional complexities.

Details and next steps

- NREL and LBNL met on 12/22/17 to plan for model adaptation
- NREL has provided experimental data to LBNL

CRADA solicitation selection process

- FedBizOps solicitation
- Pre-negotiated CRADA with no negotiation with industry
- short response time from industry
  - Selection criteria
    - MRL level and potential change in MRL due to proposed barrier being removed
    - Technology alignment with EERE and consortium
    - Application of primary metrics of success: Throughput, energy, yield
- Recommendation for funding provided to DOE for final selection
- 10-18 month execution on CRADAs