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

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National Renewable Energy Laboratory
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2020 Annual Merit Review and Peer Evaluation Meeting

TA008

Overview

Timeline and Budget

- Project start date: 10/1/16
- FY19 DOE funding: $300,000
- FY20 planned DOE funding: $ 300,000
  - NREL: $270,000
  - CSM: $30,000

Funded Partners

- Colorado School of Mines
  - Svitlana Pylypenko

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 expected to be the lowest cost/highest throughput method for MEA mass production, but it has yet to be proven that these methods can produce components meeting performance requirements
- 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
- Provides a knowledge and equipment platform for national lab and university materials development.

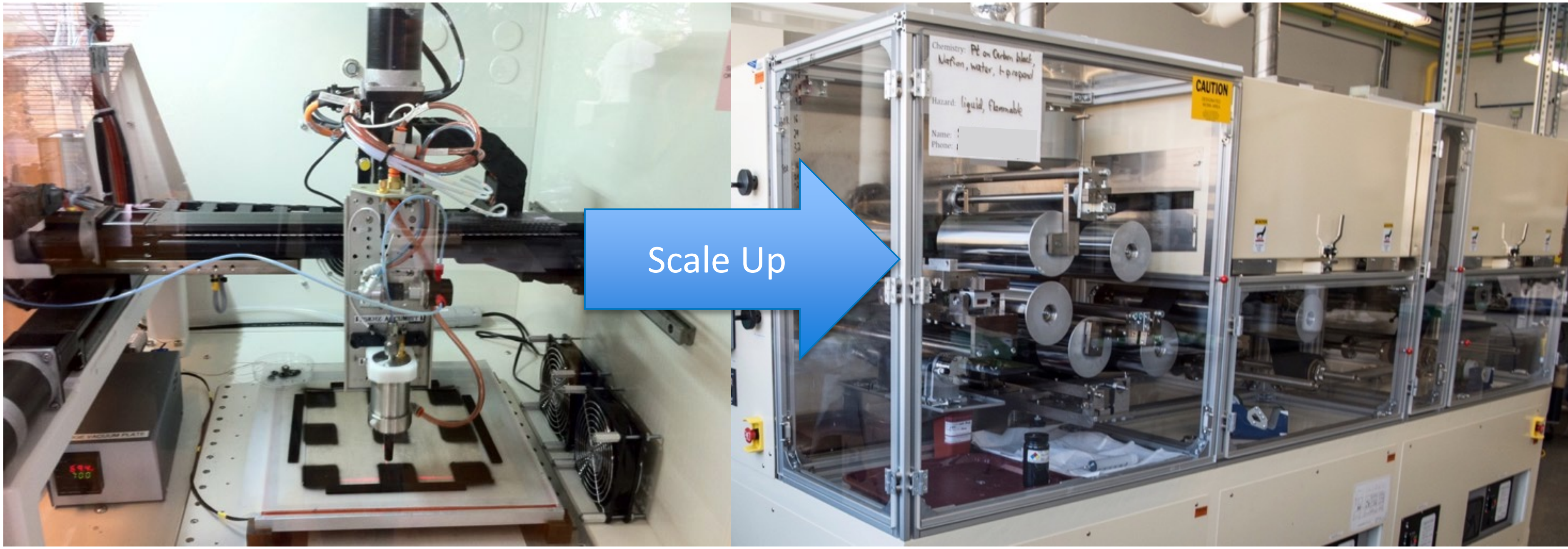
Relevance: Project Success Has Led to Additional DOE Projects

- **AMO Roll-to-Roll Consortium (TA007)**
  - Lead for Fuel Cell Core Lab Project
  - Lead for CRADA with Nel (joint funding from AMO and FCTO)
- **HydroGen (PD148)**
  - LTE/Hybrid Supernode (P148a)
  - Nel Hydrogen project (P155)
- **ElectroCat (FC160)**
- **HyET H2@Scale CRADA (H2006)**
  - "Membrane Electrode Assembly Manufacturing Automation Technology for the Electrochemical Compression of Hydrogen"
- **3M FY19 FOA Award (TA026)**
  - "Low-cost, High Performance Catalyst Coated Membranes for PEM Water Electrolyzers"
- **Nel Hydrogen FY19 FOA Award (TA036)**
  - "Advanced Electrode Manufacturing to Enable Low Cost PEM Electrolysis"
- **Lynntech TSA –** completed in 2019
- **Giner TSA –** upcoming

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

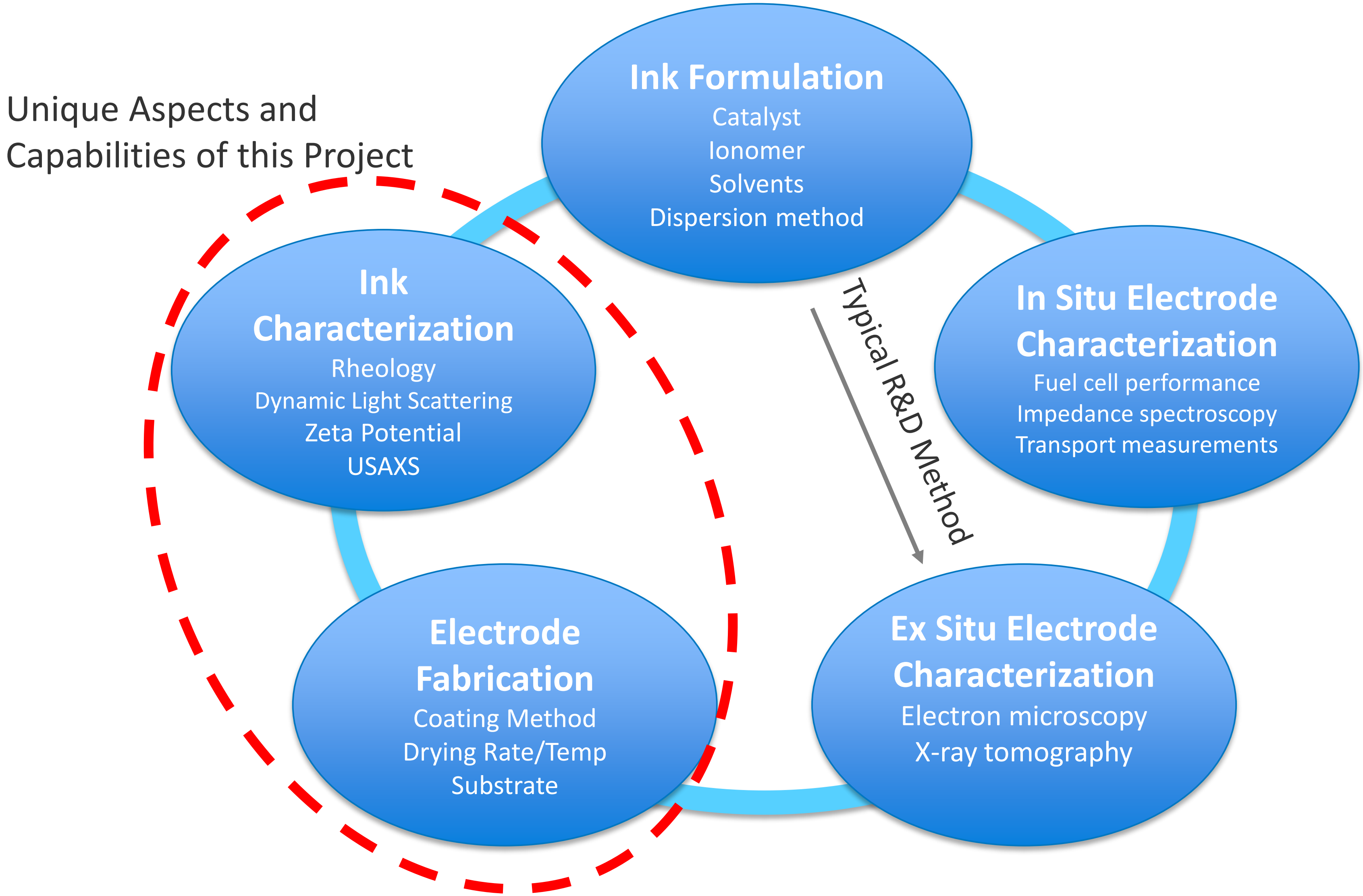
- Speed – cm^2/min
- Dilute ink (~0.6 wt% solids)
- Ultrasonic mixing
- Sequential build up of layers
- Heated substrate
- Vacuum substrate

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

Conditions

- Speed – 10s m^2/min
- 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

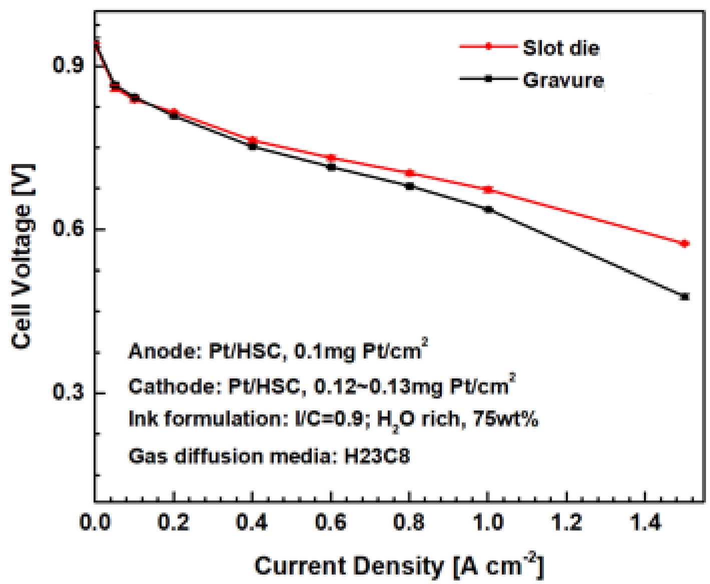
Qtr	Date	Milestone/Deliverable (as of 3/4/2019)	Type	Status
FY19 Q3	6/2019	Determine influence of solvent formulation on ionomer adsorption on catalyst/support.	QPM	MET
FY19 Q4	9/2019	Evaluate ink formulations, drying conditions, and substrates to reduce crack formation in fuel cell and electrolysis catalyst layers coated using scalable methods.	QPM	MET
FY20 Q1	12/2019	Prepare catalyst layers with PtCo/HSAC (or other current advanced alloy catalyst) coated using scalable lab methods (Mayer rod and/or doctor blade) and/or continuous roll-to-roll methods (slot-die and/or gravure) for comparison to non-alloy catalysts using standard initial performance testing. Catalyst layers will also be provided to FC-PAD for advanced characterization and durability testing.	QPM	MET
FY20 Q2	3/2020	Characterize the influence of ionomer chemistry on catalyst-ionomer interactions in catalyst ink dispersions.	QPM	MET
FY20 Q3	6/2020	Characterize the influence of catalyst ink solids concentration on catalyst layer microstructure and performance for electrodes coated using scalable coating methods using at least two different catalyst-types (e.g. Pt/C, LTE, PGM-free) and three concentrations.	AM	Delayed due to COVID
FY20 Q4	9/2020	Explore the effect of additives (e.g. binder materials) and/or catalyst ink modifications (e.g. sample preparation methodology) on catalyst layer crack formation.	QPM	Delayed due to COVID

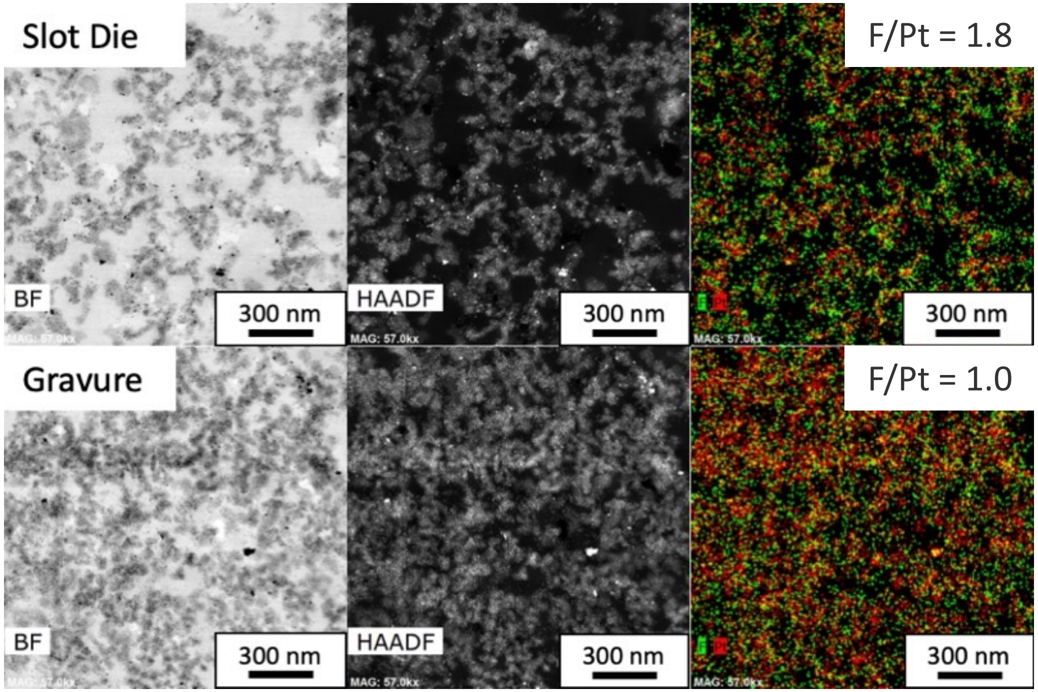
This project is part of NREL's Manufacturing R&D Project (TA001)

Accomplishments and Progress: Utilizing Microscopy to Understand Influence of Coating Methods

2019 Fuel Cell Performance

H_2/Air, 150kpa/150kpa, 80°C, 100%/100%RH, 50 cm²

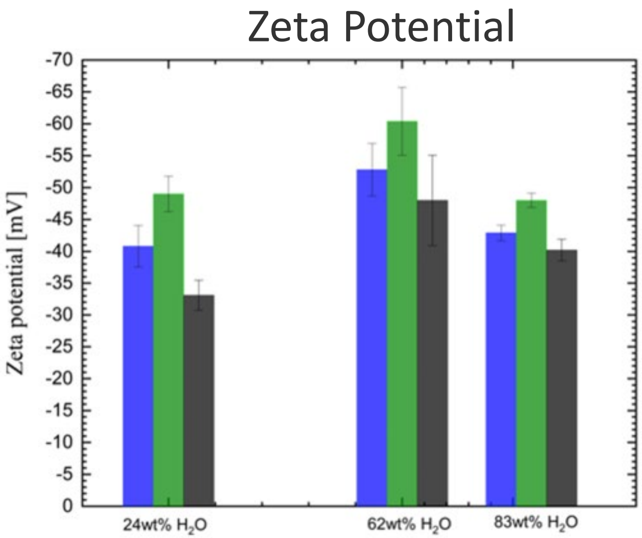


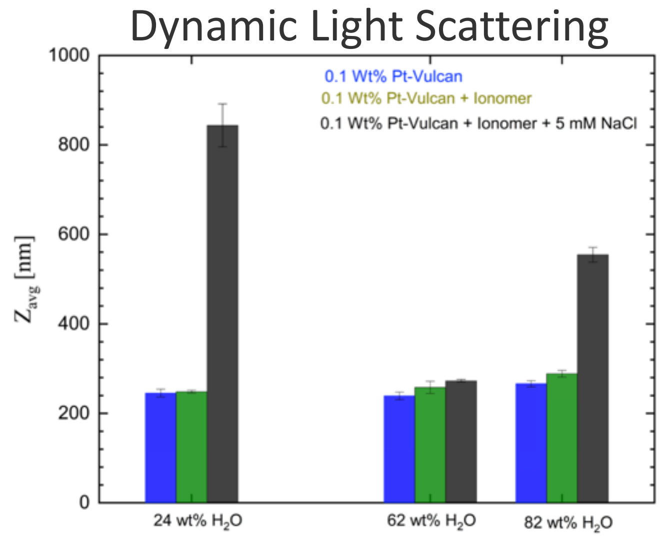


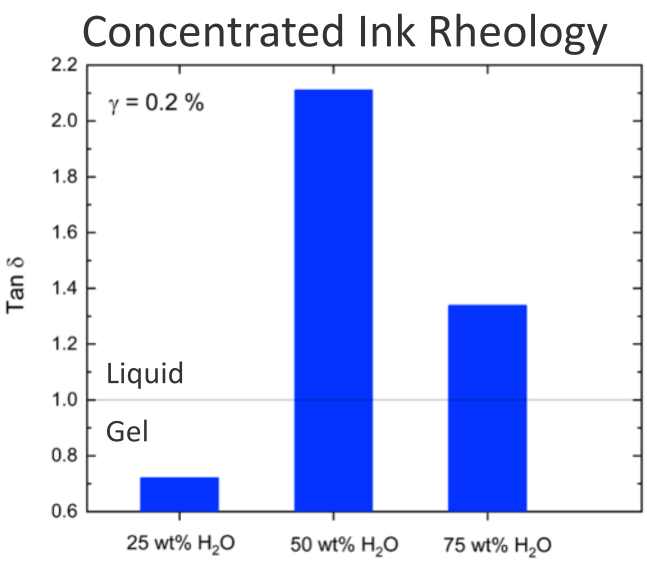
- Slot die coating results in higher performance than gravure
- H_2/N_2 EIS showed performance difference due to differences in catalyst layer resistance
- *TEM demonstrates coating method influences catalyst layer morphology*
- Slot die catalyst layer more porous likely due to lower shear rates during coating
- Gravure leads to less ionomer in catalyst layer, high shear rates may be forcing ionomer into MPL
- Lower ionomer in gravure coated CL consistent with EIS results.

MINES

Accomplishments and Progress:
Determined Influence of Solvent Formulation on Ionomer Structure on Catalysts





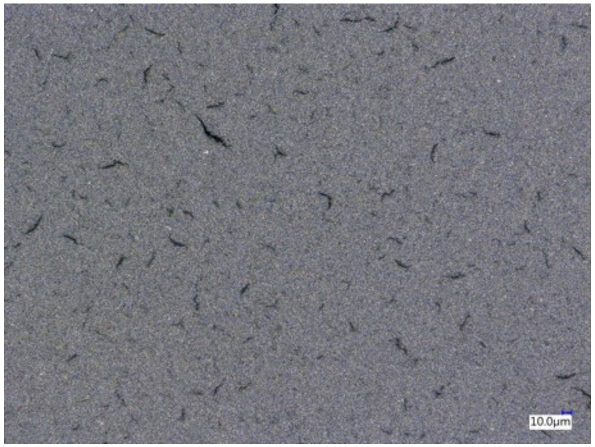


- Addition of salt screens electrostatic repulsion due to SO_3^- groups
- No change in particle size for 62 wt% H_2O indicates strong steric stabilization – adsorbed ionomer is less compacted
- Concentrated ink with moderate water content has liquid-like rheology – well dispersed – consistent with DLS of dilute inks
- *Catalyst ink structure consistent with catalyst layer transport properties and electrochemical performance*

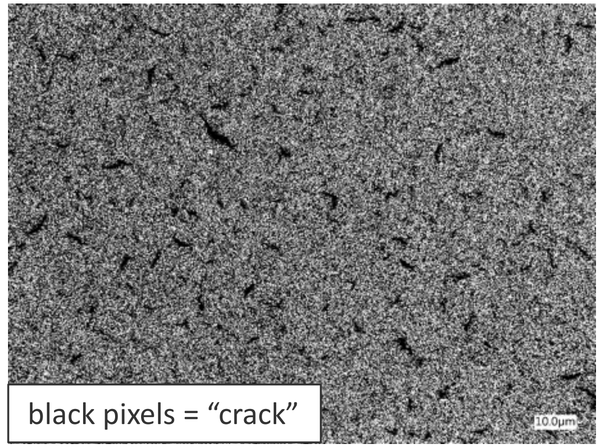
Work done in collaboration with K.C. Neyerlin and FC-PAD

Accomplishments and Progress:
Development of Accurate Crack Measurement Algorithm

Original Image

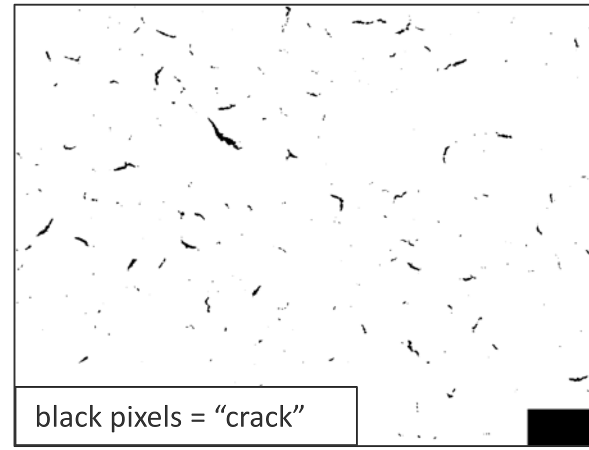


Otsu's Method[1]



Crack Area = 56.5%

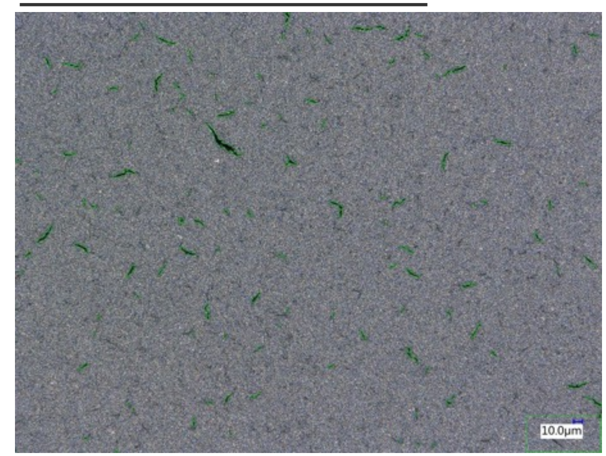
NREL Method



Crack Area = 0.839%

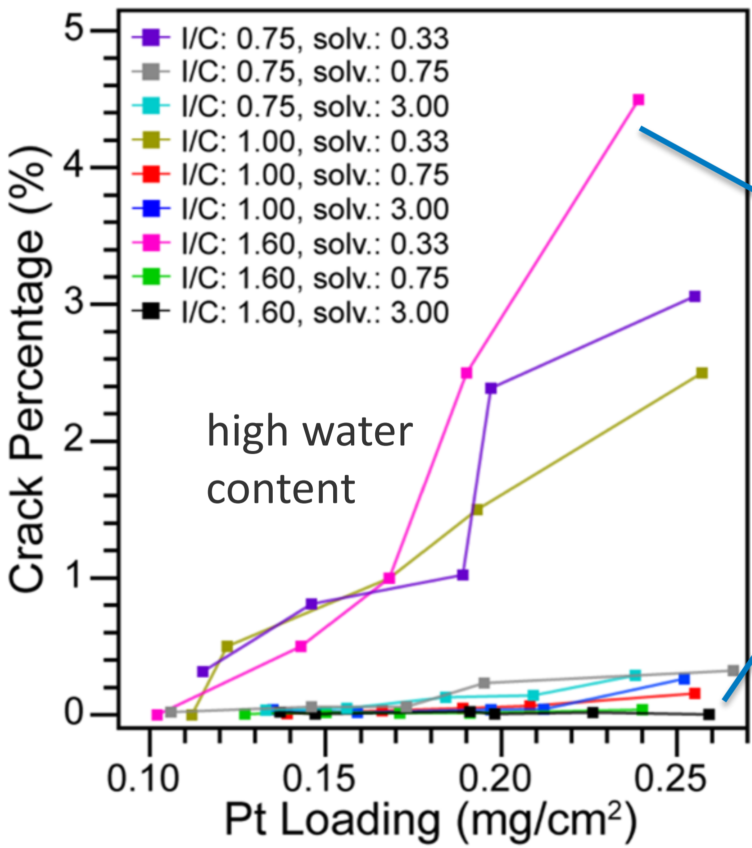
- Currently available methods/software (Otsu's method, ImageJ, etc.) do not accurately detect cracks in catalyst layers due to heterogeneity of catalyst layer surface images
- *NREL-developed algorithm reduces noise, thresholds, and filters image to accurately determine crack area*
- Algorithm validated using control images with known crack areas and contrast
- Algorithm code is open-source (developed in Python)

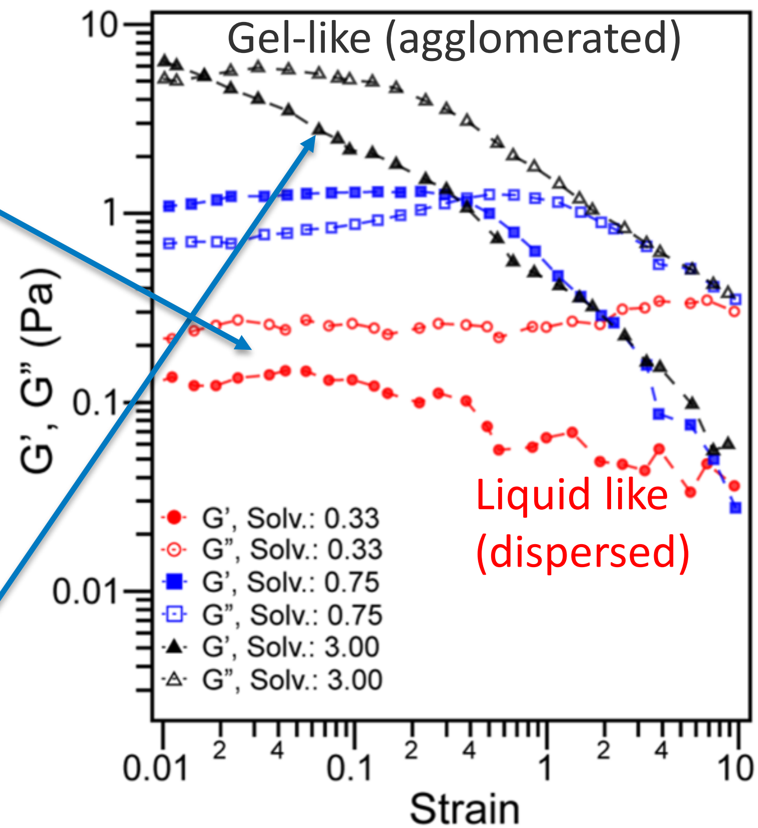
Original Image Overlaid with NREL-Method Cracks



1) Otsu, *IEEE Trans. Syst., Man, Cybern.* **1979**, 9(1), 62-66.

Accomplishments and Progress:
Determined that Decreased Agglomeration Leads to More Cracks



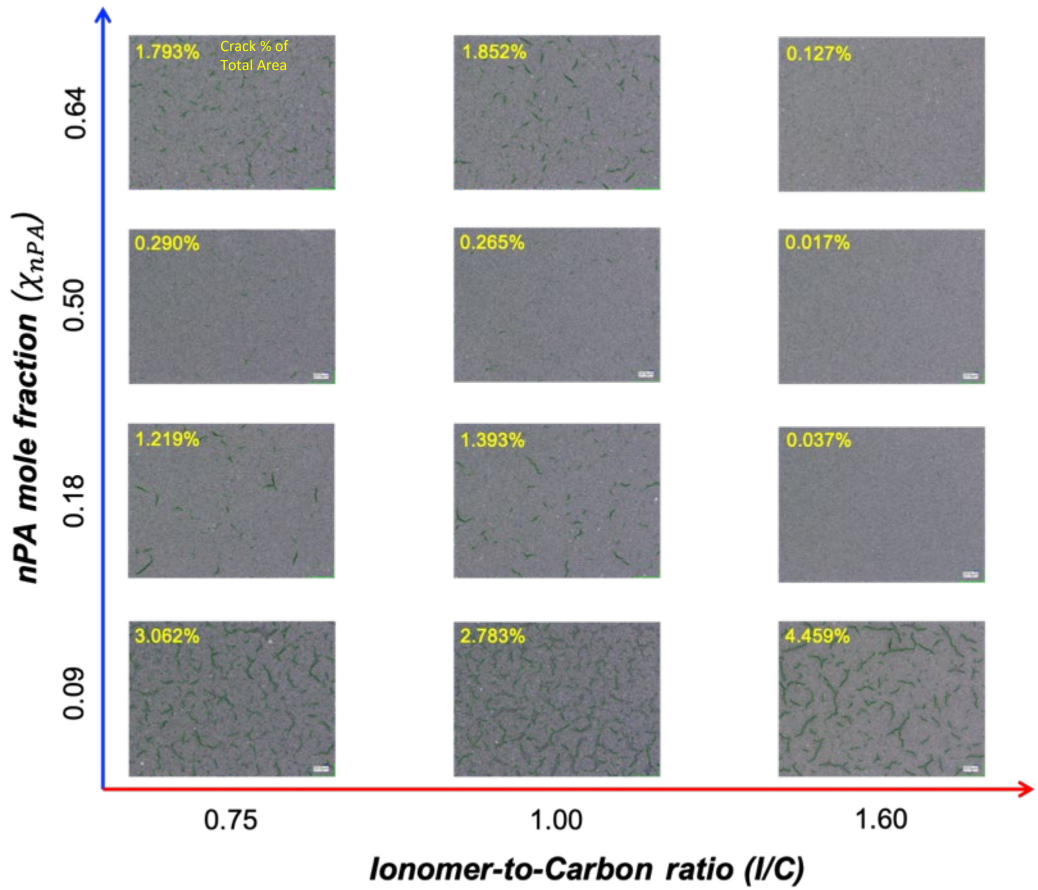


- Studied loadings relevant to light-duty and heavy-duty fuel cells and low-temperature electrolysis
- *Increased agglomeration leads to decrease in cracks, due to decreased packing density, capillary pressure during drying, and increased particle size*
- Results consistent with stress-limited drying physics:

$$h_{max} = 0.64 \left[\frac{GM\phi_{rcp}R^3}{2\gamma}\right]^{1/2} \left[\frac{2\gamma}{(-P_{max})R}\right]^{3/2}$$

Singh et al., *Langmuir* **2009**, 25(8), 4284-4287

Accomplishments and Progress: Completed ANOVA Analysis of Factors Influencing Cracking



ANOVA Analysis	F-Value	Prob > F
I/C	1.33	0.29312
nPA	39.06	6.98 x 10^{-7}
Rod Size	5.21	0.00699
I/C*nPA	3.47	0.03185
I/C*Rod Size	0.37	0.92123
nPA*Rod Size	1.98	0.11670
R^2: 89%		

- *ANOVA statistical analysis shows 1-propanol content has highest F-value indicating strongest impact on cracking*
- Inks that result in least cracked catalyst layers also lead to lower initial electrochemical performance, though a causal relationship has not been established
- Need to further explore the relationships between ink formulation, cracking and performance, especially as a function of loading/thickness

Accomplishments and Progress: Demonstrated Performance Trends in R2R PtCo GDEs

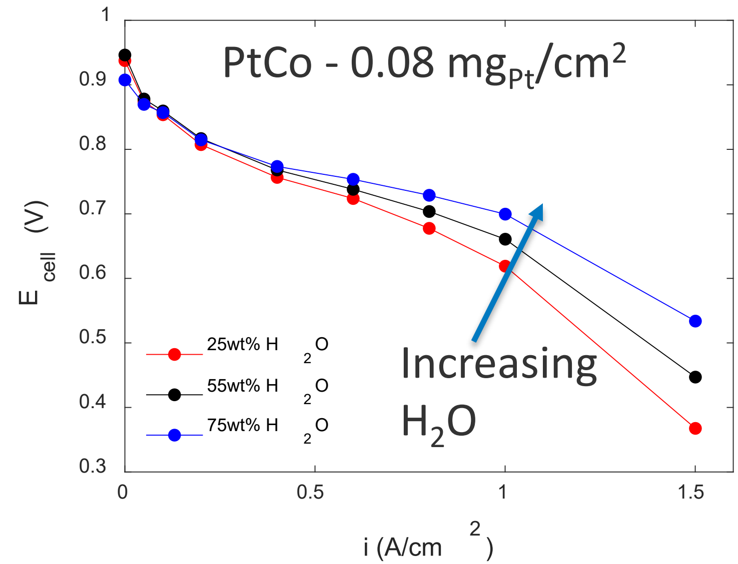
Materials

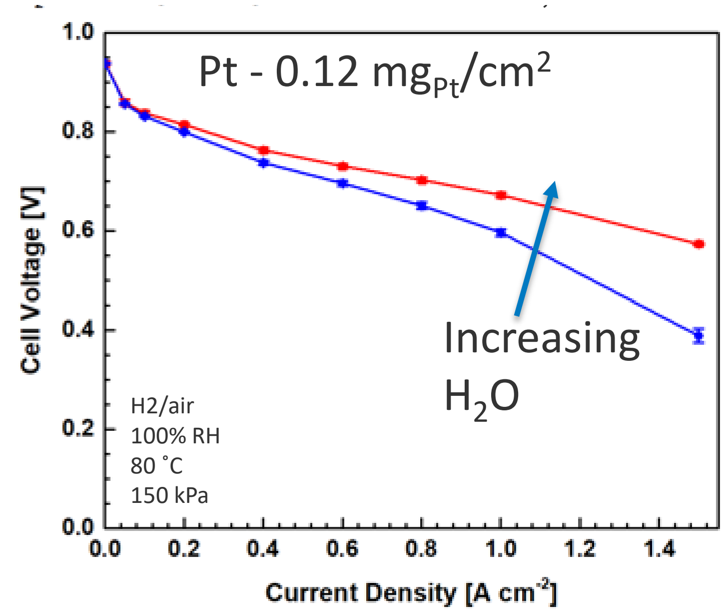
- Catalysts: Umicore PtCo/HSC
- Ionomer: Nafion 1000 EW
- Cathode Loading: 0.08 and 0.15 mg_{Pt}/cm^2
- Membrane: 25 µm Nafion
- GDL: Freudenberg H23C8

Coating

Speed: 1 m/min
Ink: 7 wt% solids
Water/1-propanol Ratios:
75/25, 55/45, 25/75 w/w

- Collaboration with FC-PAD – R2R-coated materials provided to FC-PAD for advanced characterization and durability testing
- *PtCo GDEs show same performance trend as Pt GDEs – increasing H_2O increases performance*
- Performance trends are the same in wide RH range (40-100 %RH)

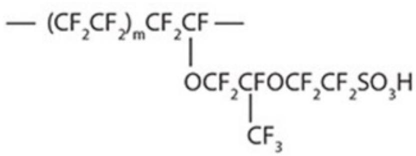




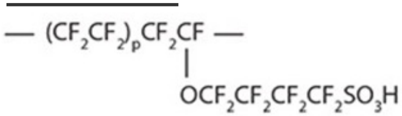
Accomplishments and Progress:
Demonstrated Influence of Ionomer Equivalent Weight on Catalyst Inks

Studying effects of ionomer side chain length and spacing with three different ionomers

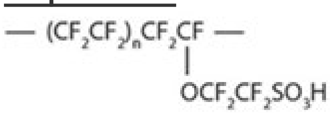
Nafion



3M PFSA

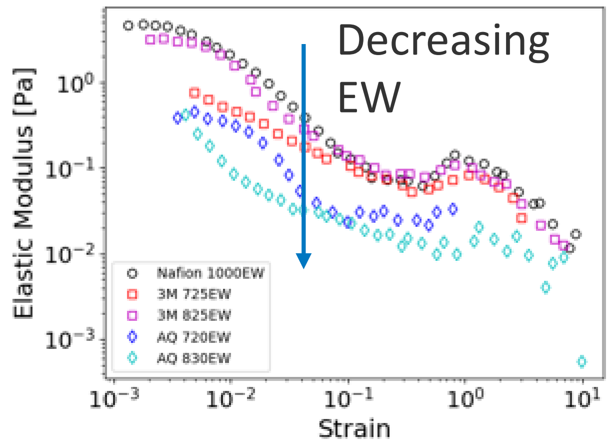


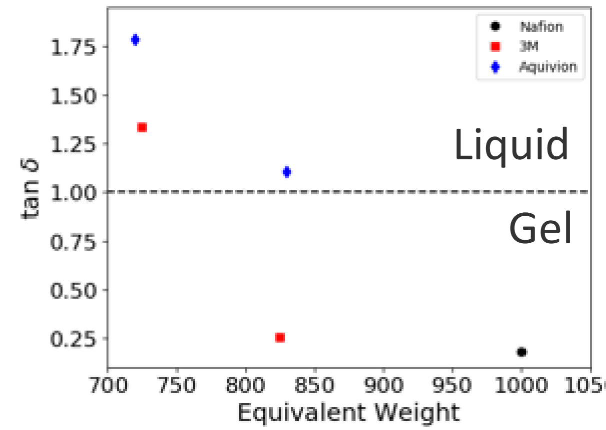
Aquivion



https://www.sigmaaldrich.com/technical-documents/articles/materials-science/perfluorosulfonic-acid-membranes.html

Rheology of Catalyst Inks with Ionomer of Different EW





$$\tan\delta = \frac{G''}{G'}$$

G' – elastic modulus
G'' - viscous modulus

Ionomer	Carbons in Side Chain	EW	Side Chain Spacing
Nafion	5	1000	5.7
3M PFSA	4	825	4.5
		725	3.5
Aquivion	3	830	5.5
		720	4.4

- *Decreasing EW leads to decrease in elastic modulus indicating an increase in dispersion of catalyst particles*
- Low EW ionomers show liquid-like rheology ($\tan\delta > 1$)
- Rheology shows greatest dependence on sidechain length
- And less dependence on side chain spacing

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- "…but the need is less clear. The original equipment manufacturers and electrode manufacturers have excellent electrode knowledge; it is not clear that the national laboratories should be trying to develop this knowledge."
  - Some fuel cell OEMs may know how to make electrodes, but not all do, and this information is not publicly available. Small-medium businesses do not have R2R process capabilities. Less understanding exists in the LTE space. The project also provides a knowledge and equipment platform supporting other national lab and university materials development.
- "It would be great to see the isotherm work on the catalyst inks as a function of ionomer loading and how that varies with the solvent system."
  - We continue to work on this. This was part of our Q3 QPM for FY19.
- "The project team should add more industry interactions."
  - This is being addressed through the AMO- and FCTO-funded R2R Collaboration (TA007), with the collaboration of two U.S. fuel cell and two U.S. electrolyzer manufacturers

Tech Transfer Activities: Leveraging Expertise in Projects with Industry

- Completed one Strategic Partnership Project and currently setting up another
- Lynntech (completed)
  - Optimized ink formulation for R2R coating using materials supplied by Lynntech
  - Conducted roll-to-roll catalyst layer coatings
  - Provided coated materials to NREL colleagues for QC analysis (TA001)
  - Coated materials provided to Lynntech

- Giner (upcoming)
  - Conduct rheological measurements of FC and LTE catalyst inks
  - Optimize coating and drying conditions to achieve R2R-coated catalyst layers with target loading
  - Coated materials will be supplied to Giner

Collaborations

Institution	Role
National Renewable Energy Laboratory - Prime Michael Ulsh, Scott Mauger, Sunilkumar Khandavalli, Jason Pfeilsticker, Min Wang, Radhika Iyer, K.C. Neyerlin, Tim Van Cleve, Carlos Baez-Cotto	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
3M Andrew Haug, Mike Yandrasits	Ionomer powders and dispersions

Remaining Challenges and Barriers

- Improve understanding of effects of ionomer chemistry and processing on interactions with catalysts
- Extend cracking studies to LTE materials
- Cracking tends to be more prevalent in ink formulations that result in higher electrochemical performance. Need to understand if (and how) these are related.
- Develop understanding of how catalyst ink concentration influences processability, performance, and cracking behavior

Proposed Future Work

- Extend cracking studies to IrO_2 catalysts
- Explore strategies (additives, processing) to mitigate cracking in catalyst layers
- Perform in situ testing studies to better understand relationships between cracking and electrochemical performance
- Continue studies on influence of ionomer chemistry on catalyst ionomer interactions
- Study influence of catalyst concentration on processability, microstructure, and electrochemical performance of fuel cell and LTE catalyst layers

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, ionomer EW, and catalyst type on ink microstructure, electrochemistry, cracking behavior, and catalyst – ionomer interactions

Accomplishments:

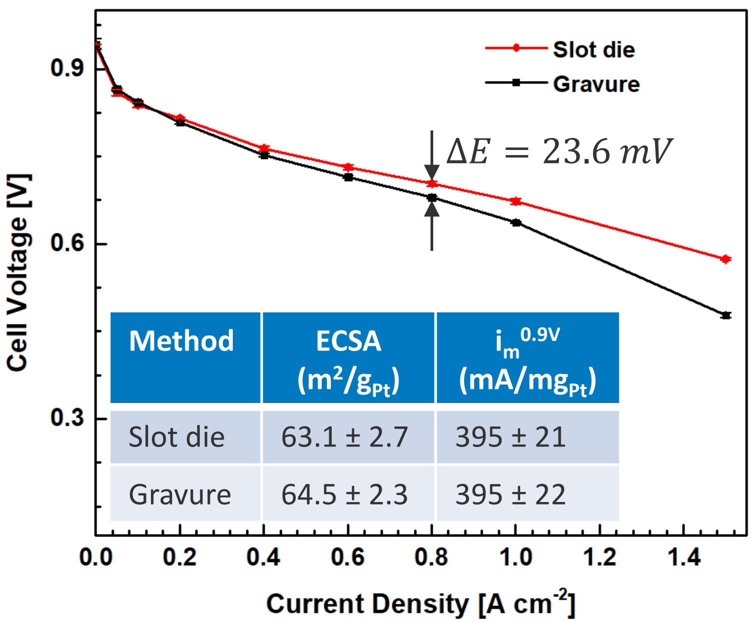
- Determined that slot-die coating results in more porous catalyst layer structure than gravure coating
- Developed open-source script for analyzing catalyst layer cracking
- Determined that higher nPA content in catalyst ink lowers crack percentage
- Initiated work effects of ionomer EW in inks – lower EW leads to better dispersion of Pt/C particles

Technical Back-Up Slides

Accomplishments and Progress (2019): Characterized Influence of Coating Method on Performance

Fuel Cell Performance

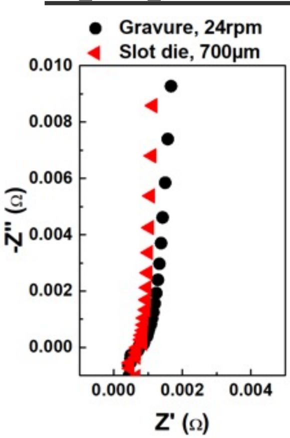
H_2/Air, 150kpa/150kpa, 80°C, 100%/100%RH, 50 cm^2

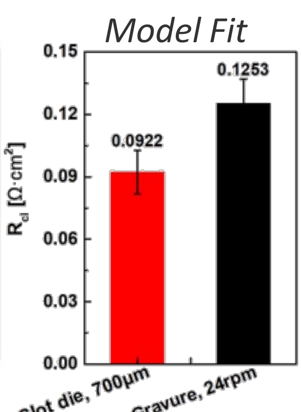


Method	ECSA (m^2/g_{Pt})	$i_m^{0.9V}$ (mA/mg_{Pt})
Slot die	63.1 ± 2.7	395 ± 21
Gravure	64.5 ± 2.3	395 ± 22

- ***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***