FUEL CELL PERFORMANCE AND DURABILITY

FC135: FC-PAD: Fuel Cell Performance and Durability Consortium

Presenters: Rod Borup, Adam Weber

Tuesday, April 30th 2019

Argonne NATIONAL LABORATORY
BERKELEY LAB
Los Alamos NATIONAL LABORATORY
NREL NATIONAL RENEWABLE ENERGY LABORATORY
OAK RIDGE National Laboratory

FC-PAD Presentation Outline

- FC-PAD Structure & Landscape
- Relevance, Overview & Objectives
- Approach: Revised Priorities, Milestones, Capabilities
- Durability:
  - Durability loading comparison (0.15 to 0.05 mg Pt/cm^2)
  - Voltage-Loss-Breakdown Modeling
  - Conditioning: Effect of Support & Alloys
- Performance and Catalyst Layer (CL) Analysis:
  - CL Agglomerate & Aggregate Ionomer Mapping: SAXS, AFM, STEM, Modeling
  - Mesoscale Transport & Water Management
    - Solvent and I/C effects, porous carbons
    - Cation migration, Ionomer thin films
    - Novel Catalyst Layer Structures: Array and nanowire
- Collaborations
- Future Work

FC-PAD: Consortium to Advance Fuel Cell Performance and Durability

Approach

Couple national lab capabilities with funding opportunity announcements (FOAs) for an influx of innovative ideas and research

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Objectives

- Improve component stability and durability
- Improve cell performance with optimized transport
- Develop new diagnostics, characterization tools, and models

Consortium fosters sustained capabilities and collaborations

Core Consortium Team*

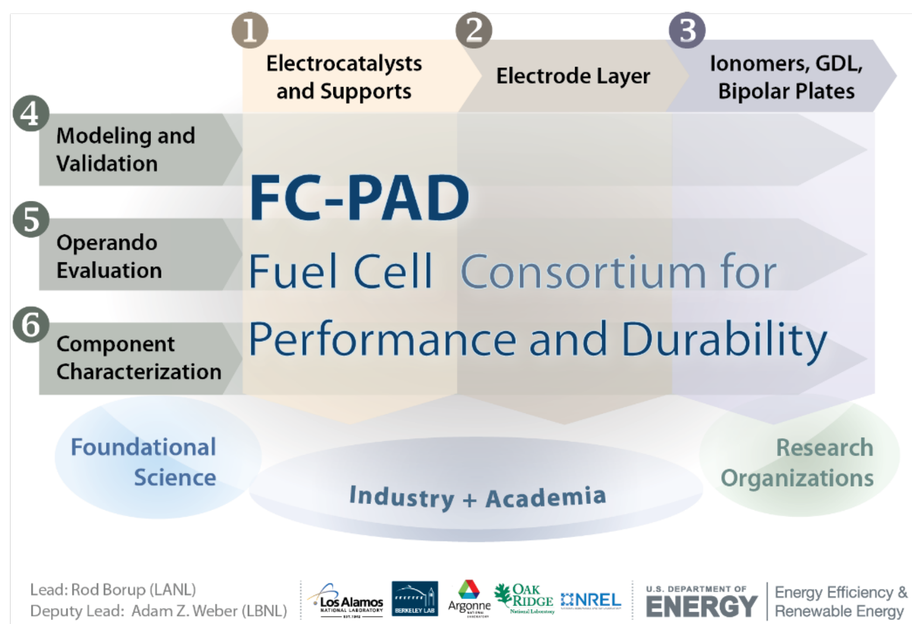
Argonne NATIONAL LABORATORY
Los Alamos NATIONAL LABORATORY
BERKELEY LAB
NREL NATIONAL RENEWABLE ENERGY LABORATORY
OAK RIDGE National Laboratory

Prime partners added in 2016 by DOE solicitation (DE-FOA-0001412)

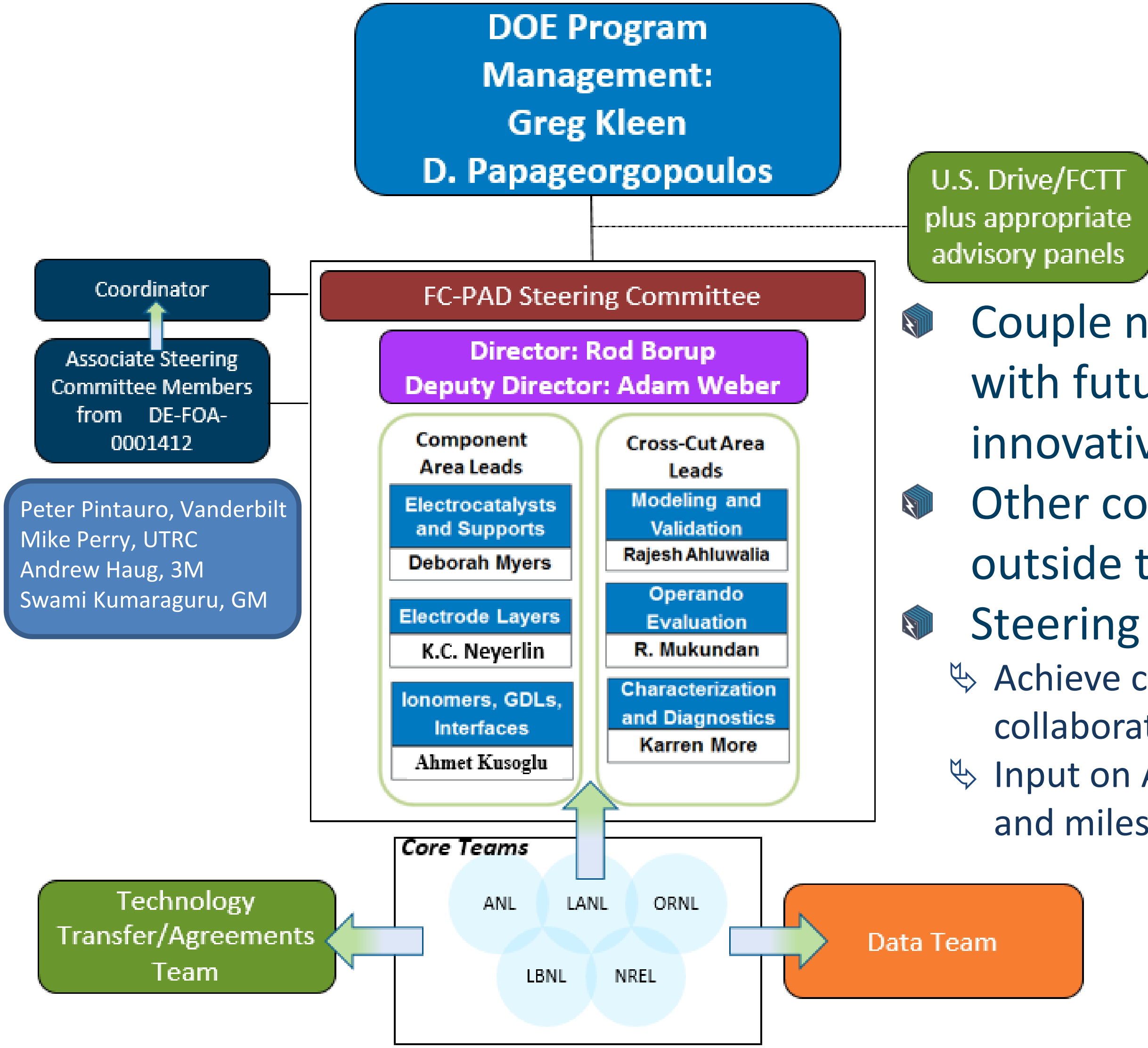
3M
GM
United Technologies Research Center
VANDERBILT

www.fcpad.org

Structured across six component and cross-cutting thrusts

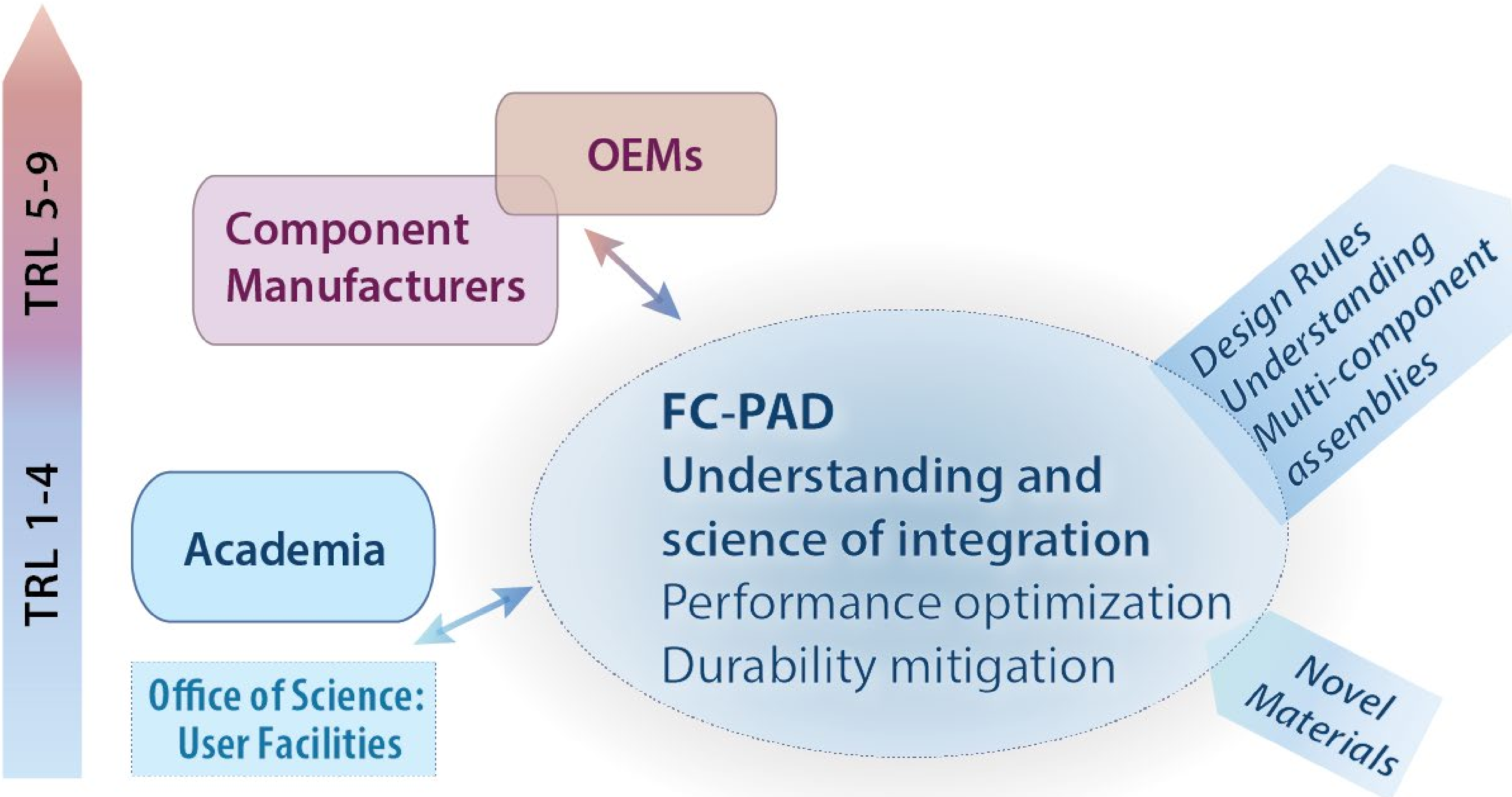


FC-PAD Organization



- Couple national lab capabilities with future FOAs to foster innovative ideas and new research
- Other collaborations continue outside the FOA process
- Steering committee input
  - Achieve consensus for no-cost, non-FOA collaborations within FC-PAD Core
  - Input on AOP (Annual Operating Plan) tasks and milestones

FC-PAD Landscape



- FC-PAD conducts research at pre-competitive development levels
- Primarily TRL 2, 3, 4
- FC-PAD directly interacts with OEMs, components suppliers and academia

FC-PAD Consortium - Overview & Relevance

Timeline

Project start date: 10/01/2015
Project end date: 09/30/2020

Budget

FY19 project funding: ~ $3,500,000
As proposed: 5-year consortium with quarterly, yearly milestones & Go/No-Go
Total Expected Funding: Dependent upon yearly budget allocation

Partners/Collaborations

(To Date Collaborations Only)

- Partners added by DOE DE-FOA-0001412 (GM, 3M, UTRC, Vanderbilt)
- No-cost collaborations listed at end of slides

Barriers (2025)

- Cost:
  - $35/kW system;
  - $17.5/kW$_{net}$ MEA
- Performance @ 0.8 V: 300 mA/cm^2 at < 0.1 mg PGM/cm^2
- Performance: 1,800 mW/cm^2
- Durability with cycling: 8,000 hours plus 5,000 SU/SD Cycles

- **Cost** targets not currently met; durability and performance being met at expense of cost; durability with system mitigation

- **Catalyst layer** is not fully understood and **is key for lowering costs** by meeting rated power
- Rated power@ low Pt loadings reveals unexpected losses

FUEL CELL PERFORMANCE AND DURABILITY

FC-PAD Consortium – Relevance & Objectives

Overall Objectives:

- Advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) and their *components* at a pre-competitive level
- Develop knowledge base for more durable and high-performance PEMFC materials & components
  - Understand science of component integration, e.g. ionomer interactions with carbon, interfaces between electrodes/GDL and/or electrodes/membranes
- Improve high-current density performance via:
  - Improved electrode structures
  - Reduced mass transport losses
- Improve component durability (e.g. membrane stabilization, self-healing, electrode-layer stabilization)
- *Provide support to DOE-funded FC-PAD projects from FOA-1412*

Approach: Highest Ranked Topics by FC-PAD/FCTT Steering Committee

Catalyst-layer Structure

- Correlate electrode microstructure and performance using characterization results and modeling to determine, for example, electrode transport properties
- Develop/measure key CCL parameters using multiple methodologies with consistent results
- Show where the ionomer is for different systems
- Effect of ink composition, processing, and fabrication method on electrode microstructure

Performance/Durability (Characterization, Experimental, Modeling)

- Understand/improve durability of alloy catalysts: effect of leaching on ionomer properties
- Understand/improve high current performance: R_{O2}, R_{H2}, different ionomers/carbons

New Capability and Modeling Development

- Develop novel methods, cells, and analysis techniques for in situ, ex situ and operando characterization of electrode layers and components
- Develop new high-resolution ionomer imaging and spectroscopy methods and develop and apply algorithms for structural reconstructions
- Develop novel methods, cells, and analysis techniques for in situ, ex situ and operando characterization of electrode and membrane layers and components
- Develop new diagnostic methods to understand transport processes
- Develop and apply Integrated predictive models of coupled performance and durability

FY2019 Q1 Milestone Status

QTR	Lab(s)	Progress Measures, Milestones, Deliverables	Comments
Q1	ANL	Demonstrate the electrode reconstruction method by analyzing the nano-CT data for an alloy catalyst and publish a paper on statistics for electrode and agglomerate structures	✓ Completed ✓ Data included in AMR ✓ Publication: Agglomerates in Polymer Electrolyte Fuel Cell Electrodes: Part I. Structural Characterization
Q1	LANL	Cation effect on thin layer ionomer structural changes with Ce and Co by NR	✓ Completed ✓ Data included in AMR
Q1	LBNL	Model developed and manuscript submitted for combined performance and membrane durability	✓ Completed ✓ Data included in AMR ✓ Publication Submitted
Q1	NREL	Quantify bulk electrode and local transport resistance as a function of either ink composition, processing or fabrication method	✓ Completed ✓ Data included in AMR
Q1	ORNL	Complete conditioning study with NREL and ANL and report/publish results	✓ Completed ✓ Data included in AMR

FY2019 Q2 Milestone Status

QTR	Lab(s)	Progress Measures, Milestones, Deliverables	Comments
Q2	ANL	**Direct numerical simulation demonstration:** Demonstrate the direct numerical simulation technique by determining oxygen and liquid transport in primary and secondary pores and across ionomer films in electrodes and agglomerates.	✓ Completed ✓ Data included in AMR ✓ Publication: Agglomerates in Polymer Electrolyte Fuel Cell Electrodes: Part I. Structural Characterization
Q2	LANL	**Direct imaging of catalyst layer cross-section:** Demonstrate electrochemical operation with direct imaging of catalyst layer cross-section (AFM) measuring ionomer layer thickness on carbon in dispersed catalyst layer structures.	✓ In progress ✓ Data included in AMR
Q2	LBNL	In-situ casting of ionomer demonstrated with two different solvent mixtures and two different ionomers EWs.	✓ In progress ✓ Q2 done for one EW. Waiting for next beam-time and also redesigning the casting stage.
Q2	NREL	Develop methodology for determining relative ionomer coverage on carbon and Pt. Demonstrate this capability as a function of either ink solvent ratio OR catalyst type (e.g. Pt/Vu vs Pt/HSC).	✓ In progress ✓ Data included in AMR
Q2	ORNL	Coordinate microstructural analysis of at least three new catalyst alloy MEAs before and after catalyst-cycling and C-corrosion ASTs (LANL, ANL, ORNL).	✓ In progress ✓ Data included in AMR

Joint National Lab FC-PAD Annual Milestone

Q4	9/30/2019	FC-PAD Overall Milestone	Understand effect of catalyst ink properties in terms of catalyst-ionomer-ink-solvent-composition (solvent, I/C, mixing and application methods, catalyst morphology (implementing 3 different catalyst systems comparing surface accessible Pt versus Pt in pores using various shaped-controlled catalysts)) on initial performance, O_2/H_2 limiting current, performance quantifying a 10% percentage improvement in initial performance in terms of high current density performance (current density at 0.675 V) reduction of limiting current and durability improvement (e.g. 30,000 cycles of the catalyst AST and/or DOE recommended drive cycle protocol).

In progress:

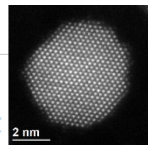
Ink solvent effects presented in AMR, I/C and application methods have been examined (on-going). Three catalyst systems have been examined with limiting currents. Catalyst AST examined for loading study. Conditioning/recovery protocols demonstrating improved performance. Demonstrated both increasing and decreasing the water content of the catalyst ink leads to 26% and 64% increases in non-Fickian transport resistance at 75% RH for water rich and nPA rich inks, respectively.

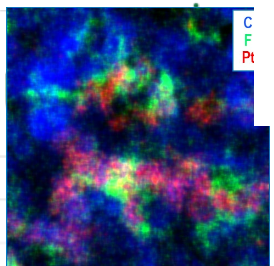
FC-PAD: Exploration of Critical Phenomena

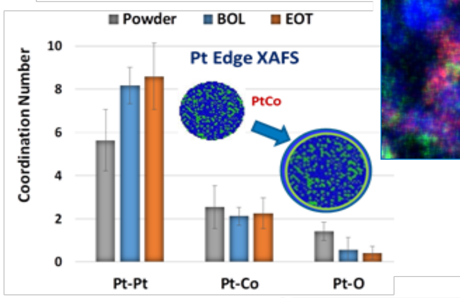
relavant phenomena & timescale	Reactions and Charge Transport	Mass Transport of Species	Kinetics and cell testing	Durability ASTs: RH, V,T cycling	Durability: Field Testing
	nsec - msec local nanostructure	sec - min component function	sec - hrs membrane-electrode	hrs - days fuel-cell	lifetime stack/system

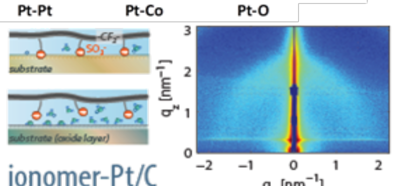
Characterization/Diagnostics

Catalyst



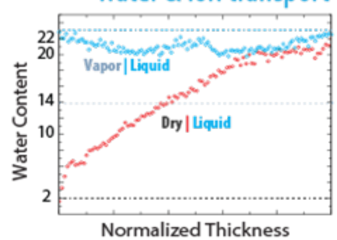


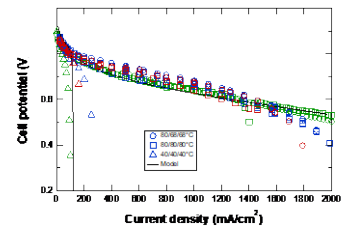


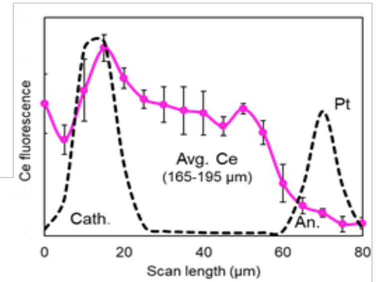


ionomer-Pt/C interactions

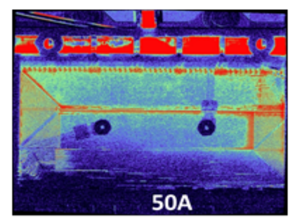
probing water & ion transport



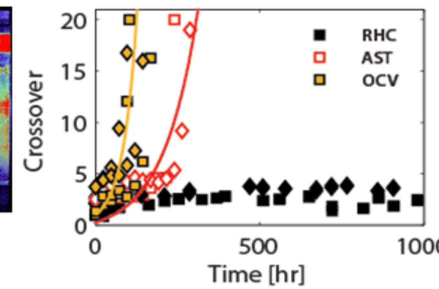




Monitoring, Measuring Degradation and Performance Decay



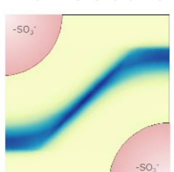
Operando Imaging



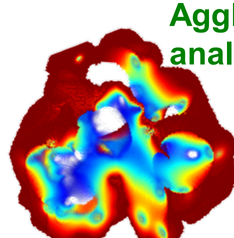
characterization of phenomena fundamental understanding ⟷ *performance-durability interplay: understanding and improvement*

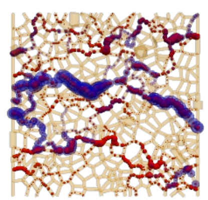
Modeling

Nanoscale

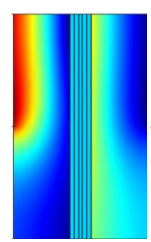


Agglomerate analysis

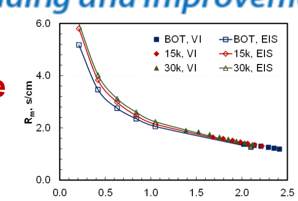




Component Transport



Cell-level performance and durability



Predicting life and decay

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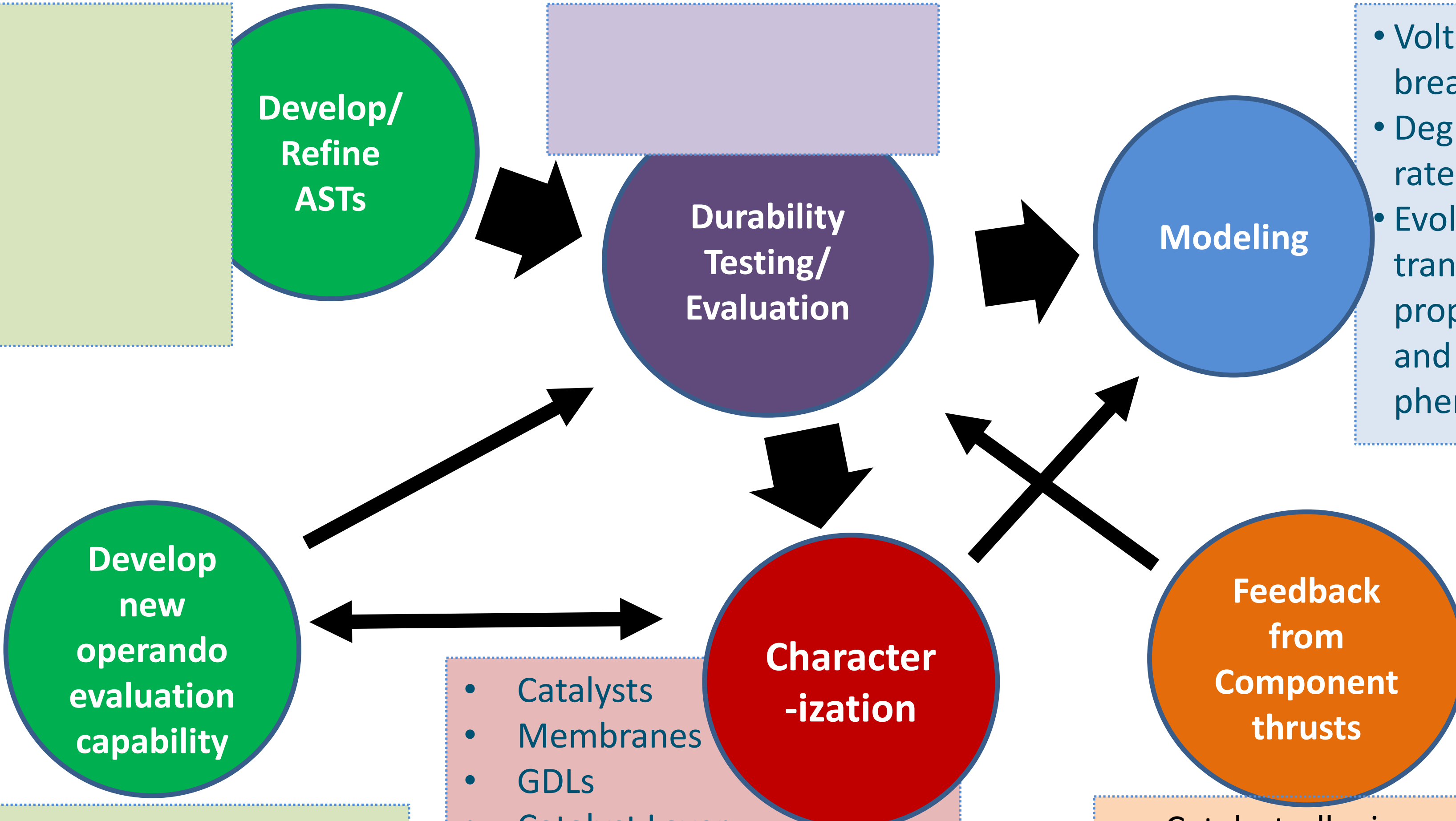
Durability Approach: Materials-based Solutions to Decrease Degradation



- Voltage-loss-breakdown
- Degradation rate
- Evolution of transport properties and phenomena

- Confocal XRF of cation migration
- Surface coverage by CO displacement

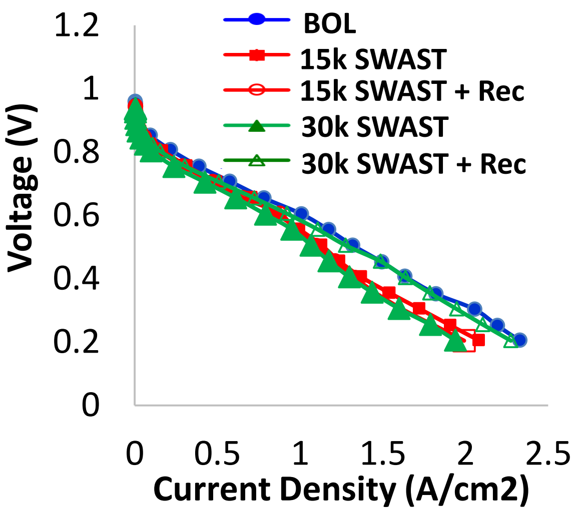
- Catalysts
- Membranes
- GDLs
- Catalyst Layer microstructure and stability
- Impact of microstructure on durability
- Identify degradation mechanisms & phenomena

- Catalyst-alloying; particle growth, kinetics losses with leaching
- Catalyst-support corrosion
- Membrane stabilizers and cation migration

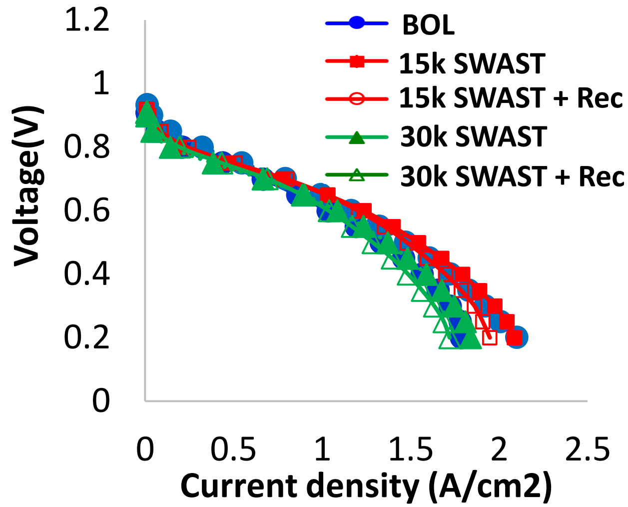
Durability Performance: Effect of Loading (0.15 to 0.05 mg_{Pt}/cm^2)

80 °C, 100% RH, 150KPa

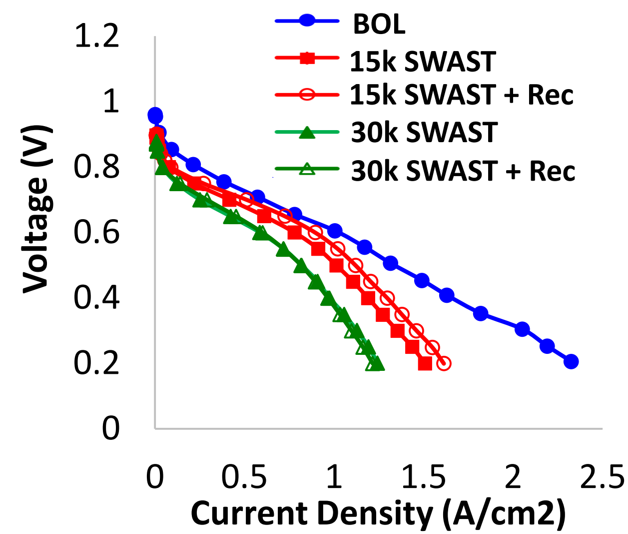
0.15 mg_{Pt}/cm^2



0.10 mg_{Pt}/cm^2



0.05 mg_{Pt}/cm^2

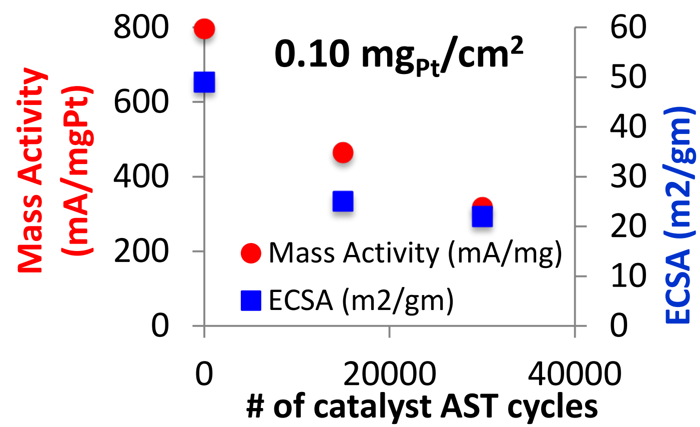


- After recovery @ 30,000 cycles, mainly kinetic losses observed

- ECSA and mass activity decrease
- Local transport still most significant loss at high current density

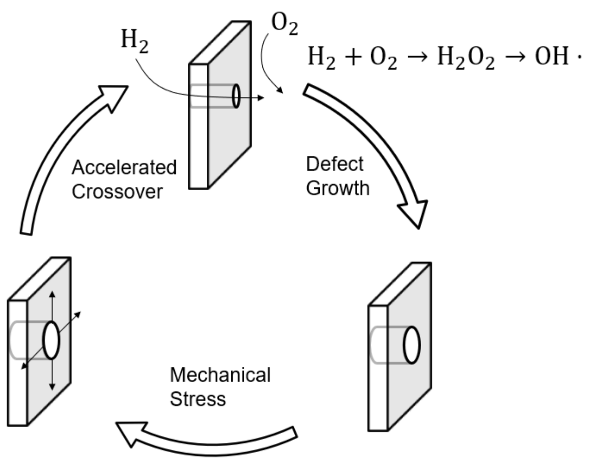
- ECSA loss due to particle size increase
- Mass activity loss due to Co leaching
- Durability losses (kinetic and transport) greatly exacerbated by lower loading

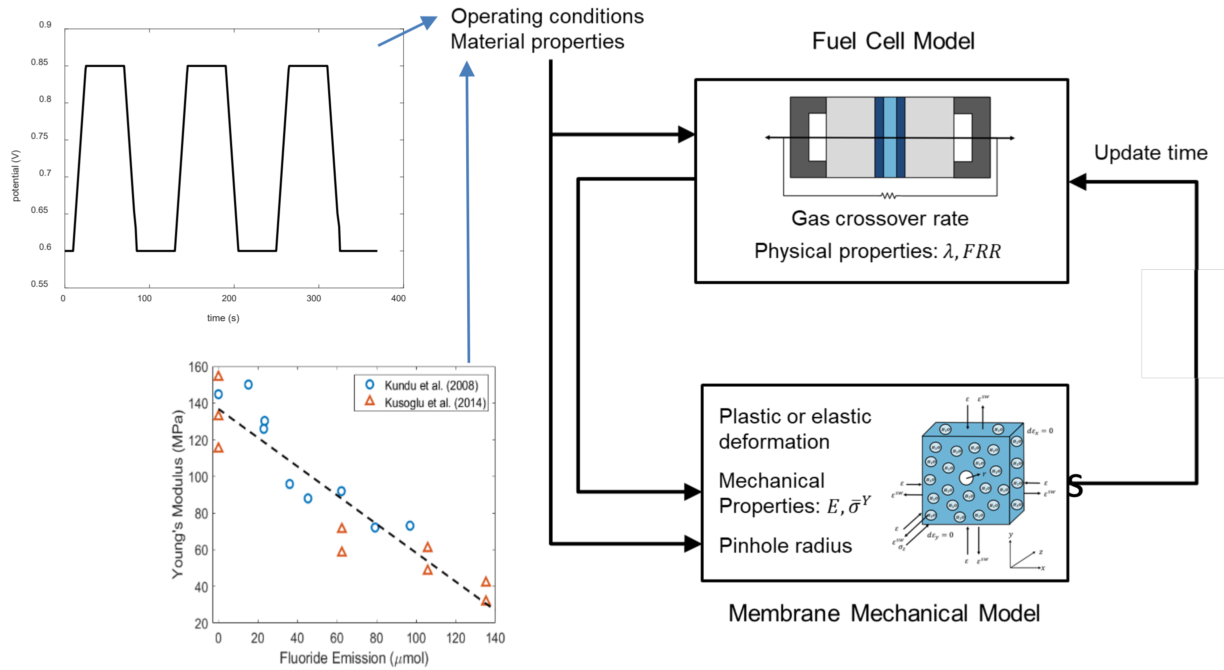
Square Wave Catalyst AST (0.6 – 0.95V)
80°C, 100% RH, 150kPa



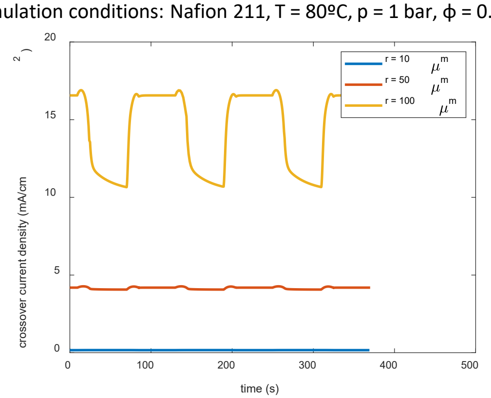
Coupled Durability and Performance Modeling

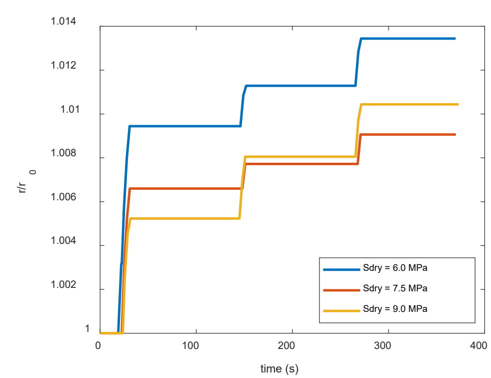
- Performance and mechanics interact synergistically
  - Evaluate membrane failure





Simulation conditions: Nafion 211, T = 80ºC, p = 1 bar, ϕ = 0.7 V, Feed stoichiometry = 1.2, Air Stoichiometry = 2





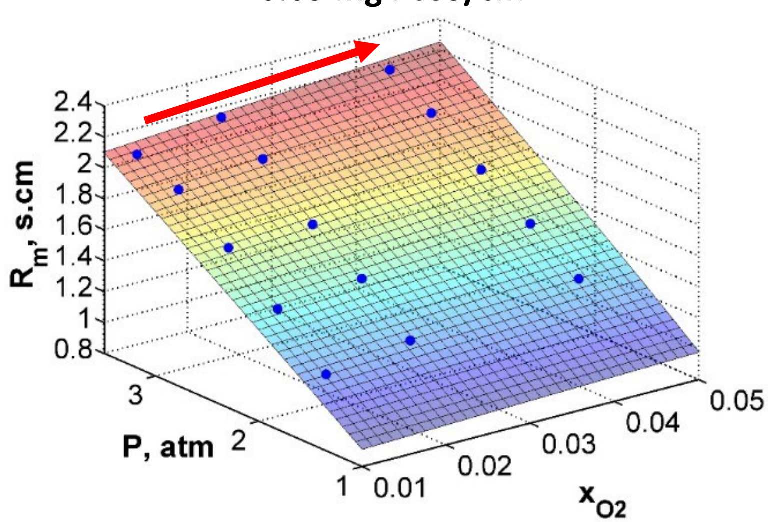
Observe pinhole growth due to induced hydration dynamics and crossover

Nonmonotonic effect of yield strength

S. Kundu, et al. *Polymer Degradation and Stability*, 93, 214 (2008); A. Kusoglu, et al. *ECS Electrochem. Lett.* 3, F33 (2014).

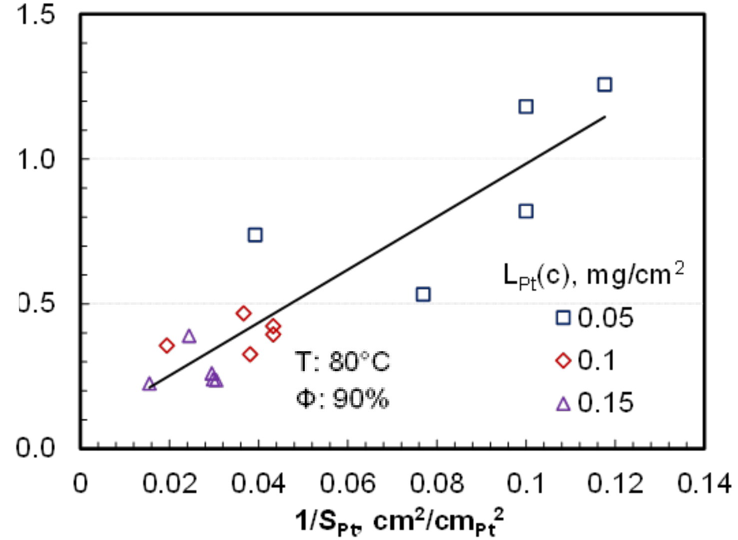
Modeling Voltage Loss During Catalyst AST Cycles

O_2 Transport Resistance at Limiting Current Density (i_L)



O_2 transport resistance (R_m) increases at higher O_2 mole fraction: $R_m = \frac{c_{O_2}}{i_L/4F}$

Knudsen Resistance and Ionomer Film Resistance



Decreasing catalyst loading and degradation during durability have similar effects on Ionomer film resistance

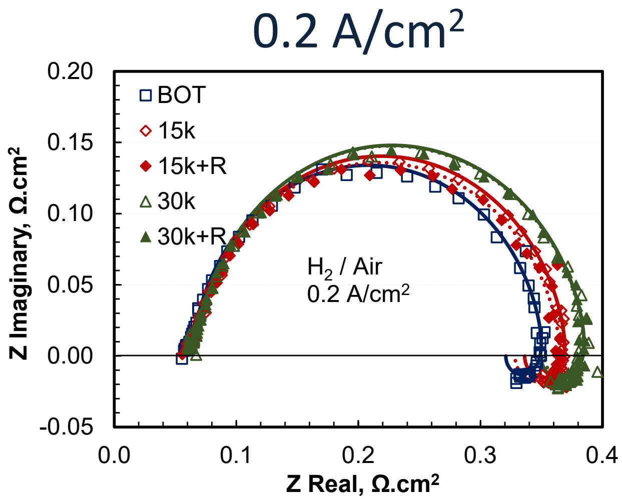
New Representation for R_m (Total Transport Resistance)

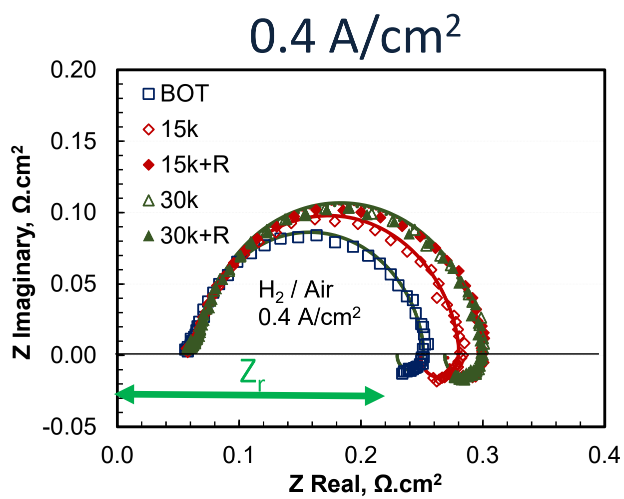
$$R_m = \left\{R_g \frac{P}{P_r} + R_d \frac{P}{P_r}\right\} + R_{Kn} + \left\{R_f + R_i \frac{i}{i_r}\right\}$$

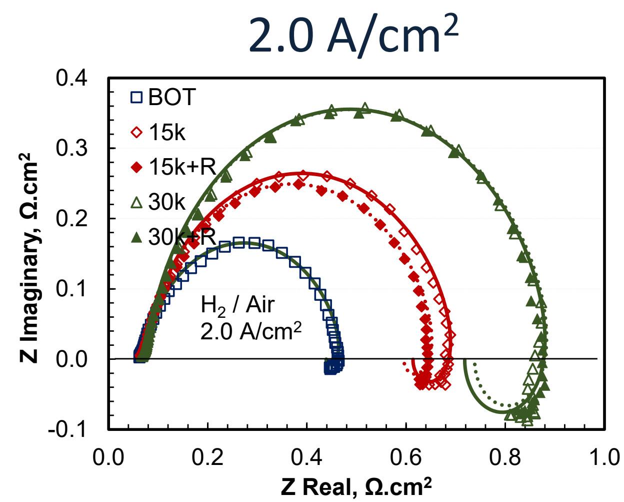
GC DM MPL/CCL CCL

Microstructural simulations indicate that flooding of primary pores in CCL explain R_m increasing at higher current density

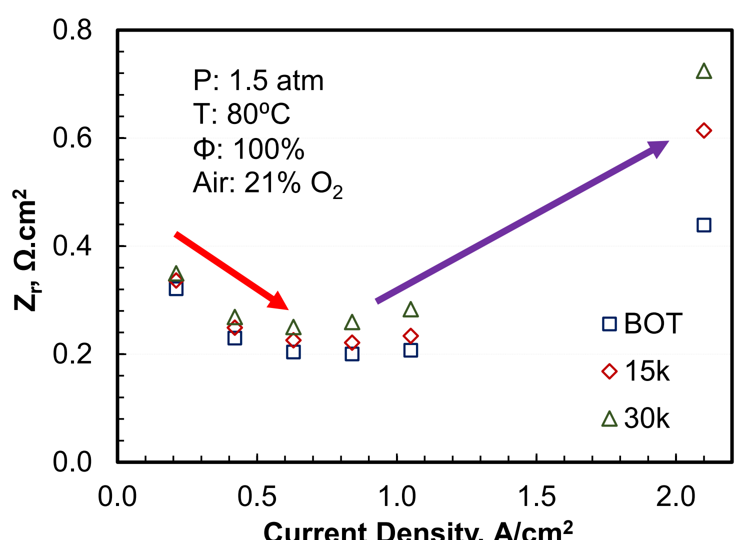
Modeling Impedance Data for DC Impedance







Fitting impedance data and low frequency inductive loop: DC Resistance (Z_r)

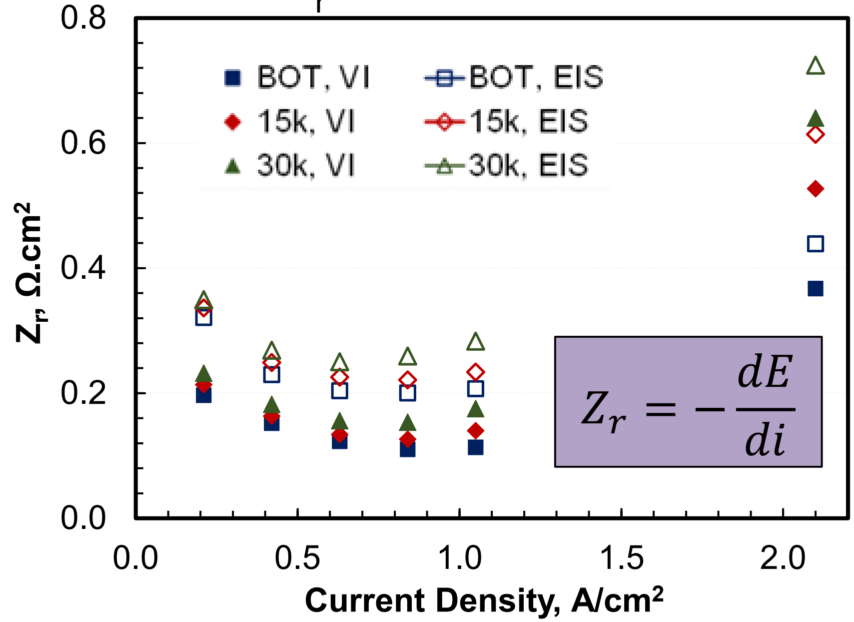


Dependence of DC impedance (Z_r) on current density:

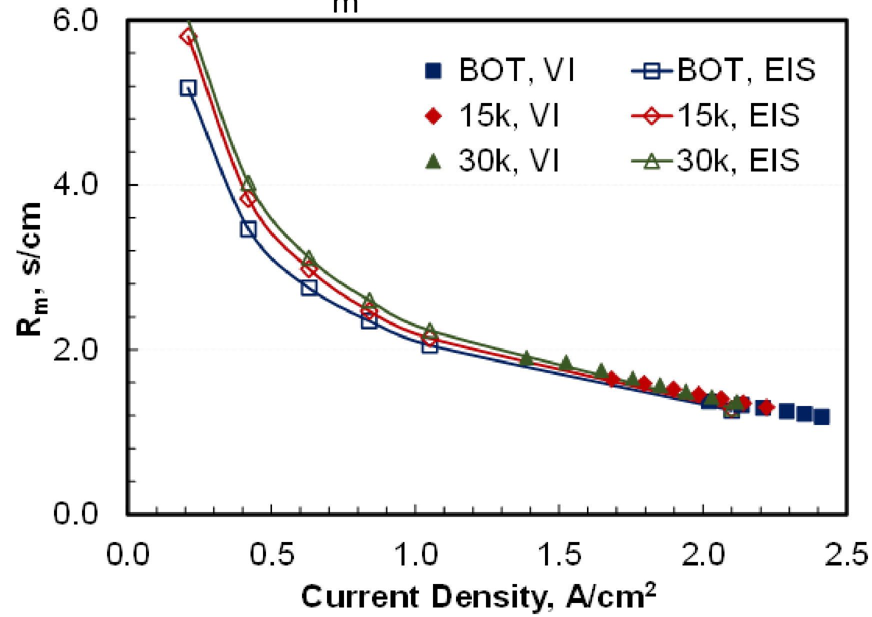
- Z_r decreases from 0.2 to 0.6 A/cm^2 because of decrease in kinetic resistance
- Z_r increases from 0.6 to 2.1 A/cm^2 because of mass transfer effects

O_2 Transport Resistance (R_m) from Impedance (EIS) and Polarization (VI) Data

Model developed to determine Oxygen Transport Resistance (R_m) from EIS and VI data



$$Z_r = -\frac{dE}{di}$$



Z_r(EIS) > Z_r(VI)
Trends are similar

- R_m decreases at higher i
- Small increase in R_m with AST
- Similar trends for R_m(EIS) and R_m(VI) at large i

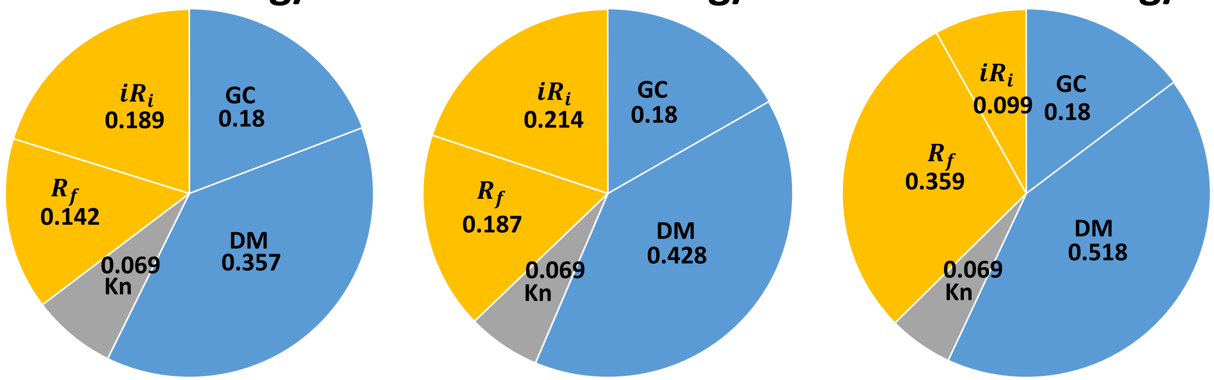
Model used to determine R_m as a function of current density and AST cycles

Catalyst Degradation Loss Breakdown

R_m at Limiting Current Density (i_L): 1.5 atm, 4% X(O_2), 80°C, 90% RH

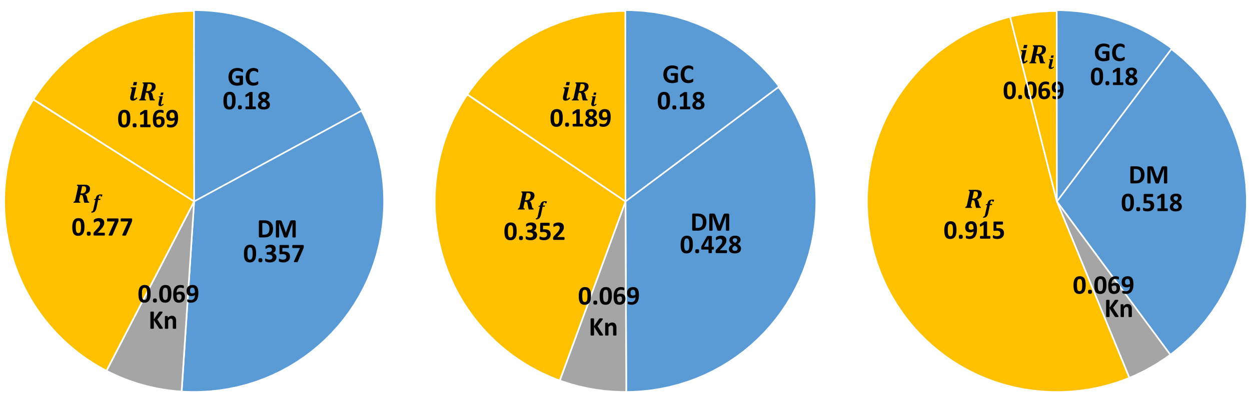
0.15 mg/cm² **0.1 mg/cm²** **0.05 mg/cm²**

BOL



i_L=615 mA/cm², R_m=0.937 s/cm | i_L=535 mA/cm², R_m=1.077 s/cm | i_L=471 mA/cm², R_m=1.224 s/cm

30k Cycles



i_L=548 mA/cm², R_m=1.052 s/cm | i_L=473 mA/cm², R_m=1.218 s/cm | i_L=329 mA/cm², R_m=1.751 s/cm

- At BOL, reducing Pt loading to 0.05 from 0.15 mg/cm² causes 30.6% increase in R_m
- After 30k cycles, R_m increased by 12.3% for 0.15 mg/cm² loading and by 43.1% for 0.05 mg/cm² loading, and is 66.4% higher in the lower loaded cell

Representation for R_m (Total Transport Resistance)

$$R_m = \left\{R_g \frac{P}{P_r} + R_d \frac{P}{P_r}\right\} + R_{Kn} + \left\{R_f + R_i \frac{i}{i_r}\right\}$$

GC DM MPL/CCL CCL

R_f = **Ionomer Film Resistance**

$$R_f = R_{O_2}/S_{Pt}$$

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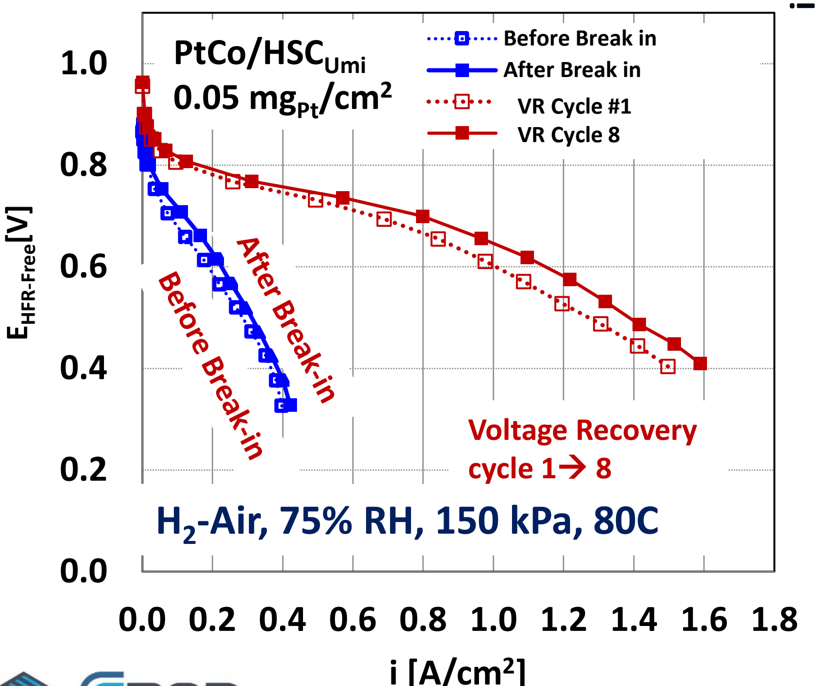
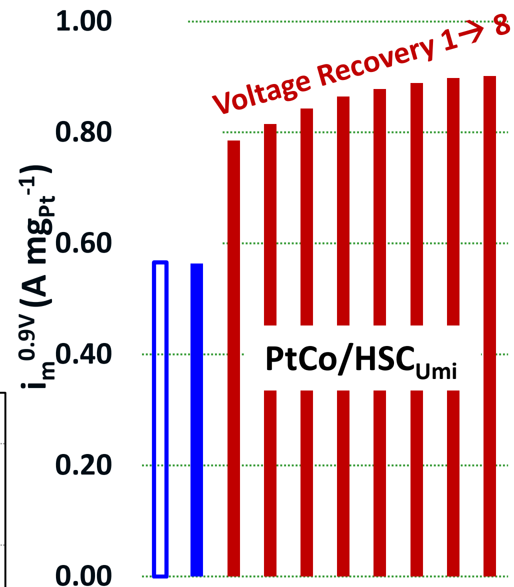
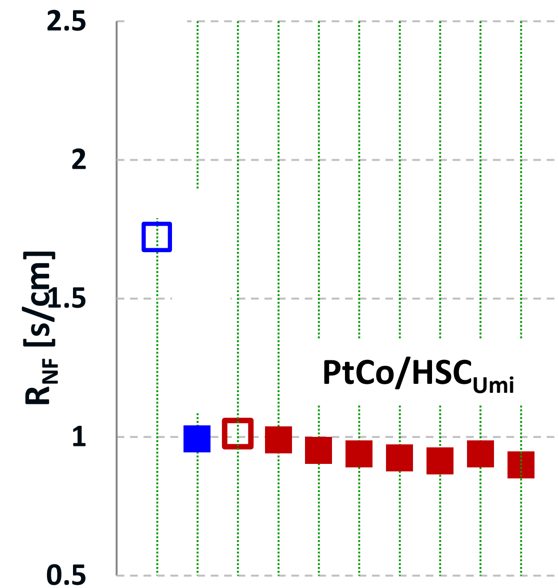
Transport Measurements Related to Conditioning

- Break-in
  - Reduction in Non-Fickian transport resistance (R_{nf})
    - Still figuring out the lack of polarization change
  - Removing majority of contaminants
- Voltage recovery (VR)
  - Improvements in mass activity
  - H_2/O_2-Air performance



Changes in R_{nF} and mass activity seem to occur independent of each other

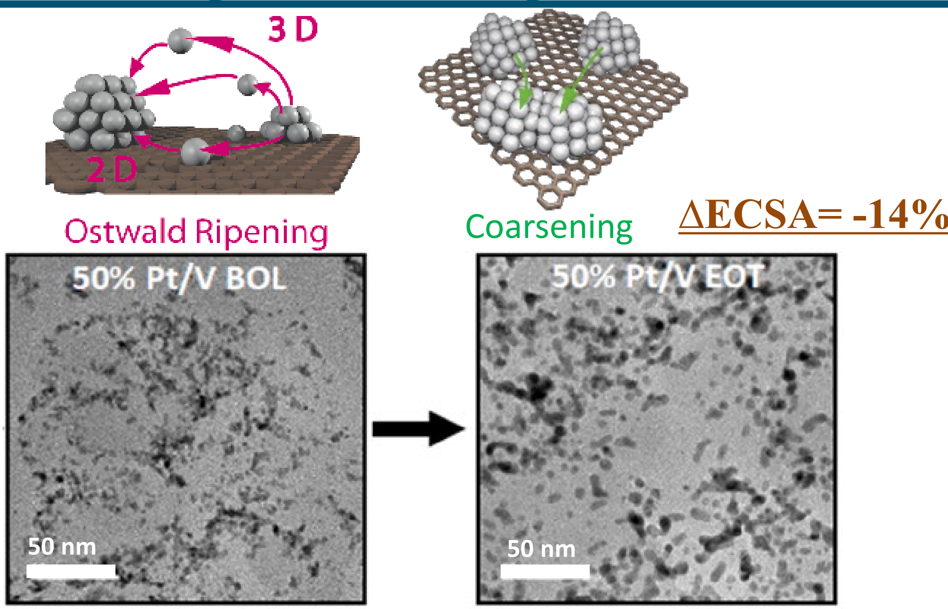


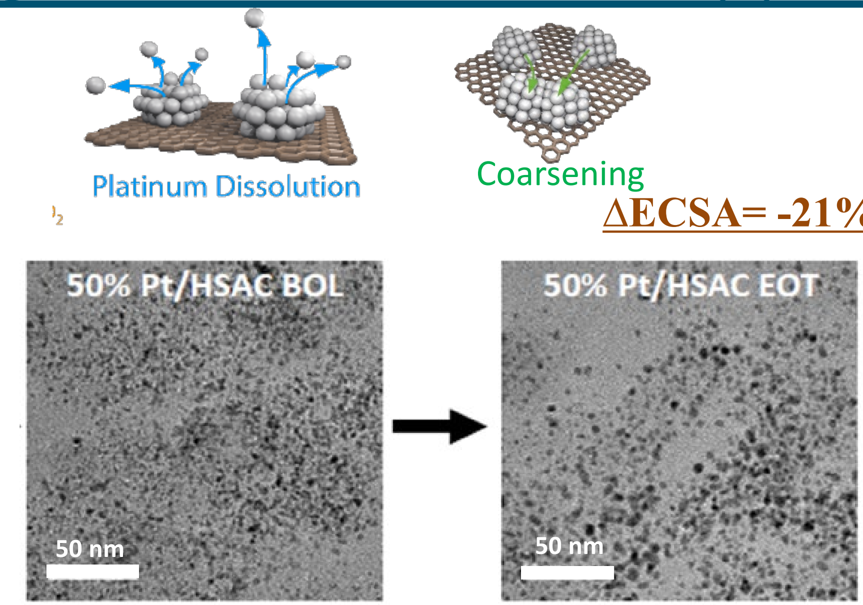


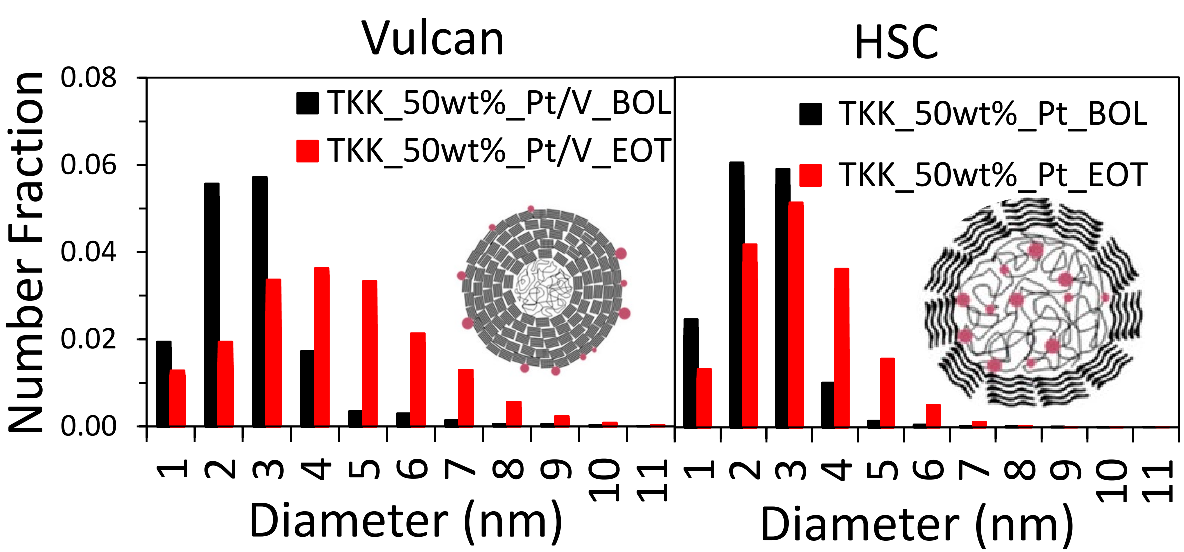
Suggests that break-in impacts local effects and voltage recovery more than macroscopic effects

First voltage recovery cycle is crucial for improved H_2/Air performance

Changes During Conditioning: Effect of Carbon Support







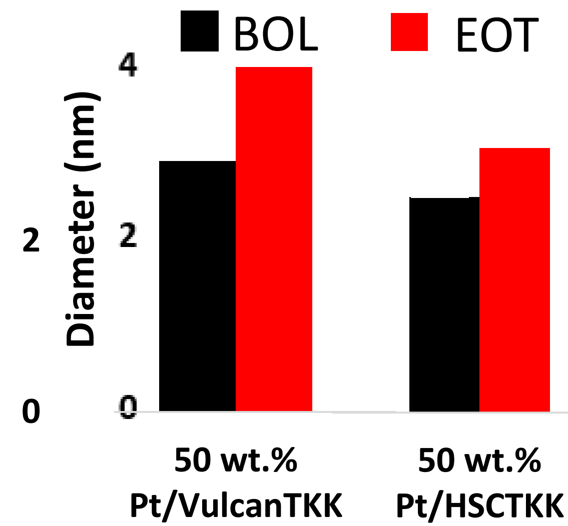
Pt/Vulcan$_{TKK}$ vs. Pt HSC$_{TKK}$

Differences in ECSA losses due to mechanisms contributing to particle growth (e.g. contributions due to particle coarsening, Pt-dissolution, and Ostwald Ripening)

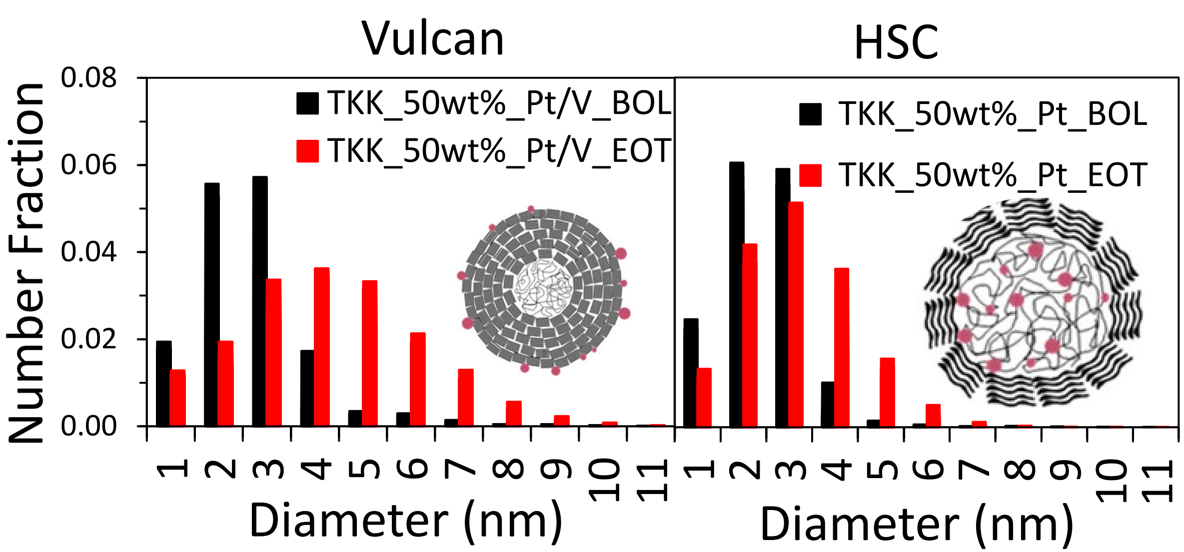
Conditioning Effect of Carbon Support Variation

50 wt% Pt TKK Catalyst

Catalyst	Loading [mg_{Pt}/cm^2]	ECSA [m^2/g_{Pt}]			δ [nm]		
		BOL	EOT	Δ	BOL	EOT	Δ
Pt/Vu_{TKK}	0.054	44.5	37.9	-14%	2.93	4.03	+37%
Pt/HSC_{TKK}	0.058	72.6	56.9	-21%	2.64	3.24	+22%



- Both Pt/V_{TKK} and Pt/HSC_{TKK} exhibit ECSA loss and particle growth
- Pt/V_{TKK} exhibited larger particle size growth compared to Pt/HSC_{TKK}



$Pt/Vulcan_{TKK}$

- Pt nanoparticles on surface have higher mobility, nucleation and growth

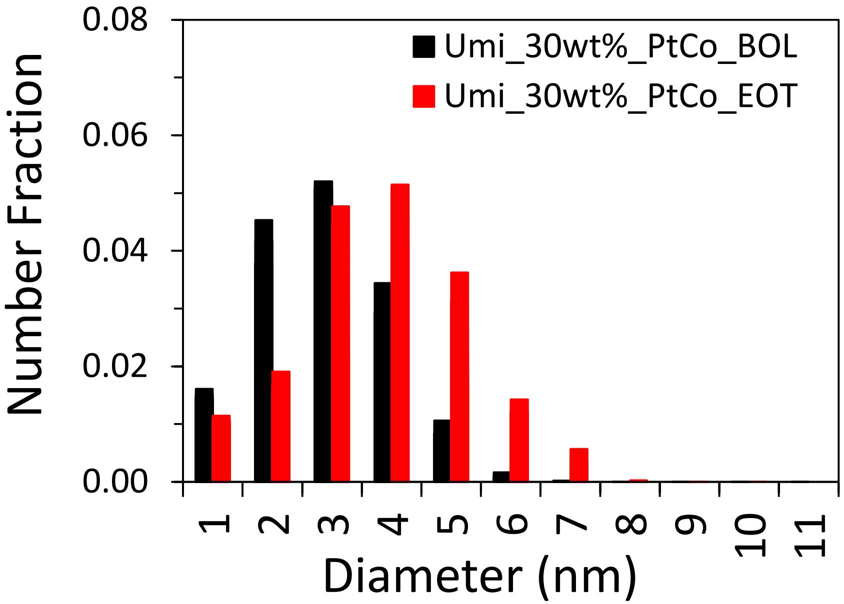
Pt/HSC_{TKK}

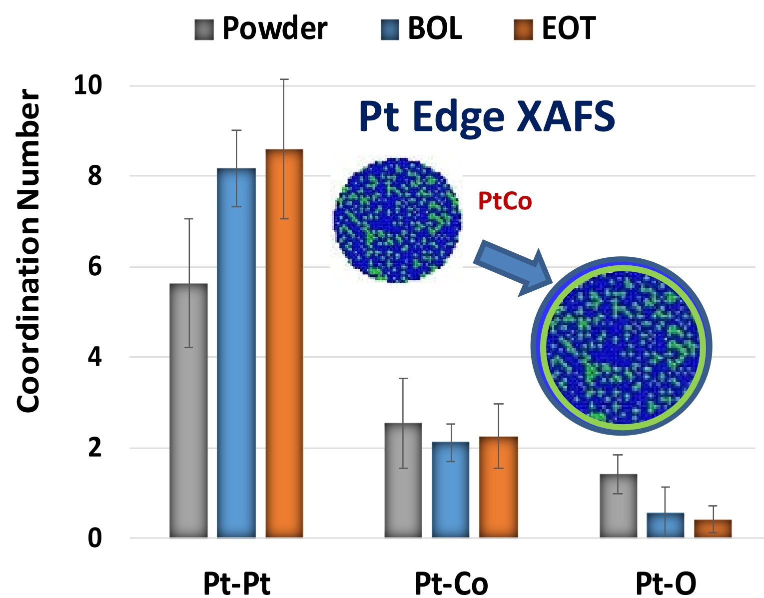
- Pt Nano particles within HSC micropores have preferential nucleation and limited mobility

Conditioning Effect on Catalyst Alloys: Pt vs. PtCo/HSC

30 wt% Umicore Catalyst

Catalyst	Loading [mg_{Pt}/cm^2]	ECSA [m^2/g_{Pt}]			δ [nm]		
		BOL	EOT	Δ	BOL	EOT	Δ
Pt/HSC_{Umi}	0.051	60.4	57.6	-4%	3.59	3.93	+9.5%
$PtCo/HSC_{Umi}$	0.048	56.3	56.5	0.3%	3.05	3.80	24%

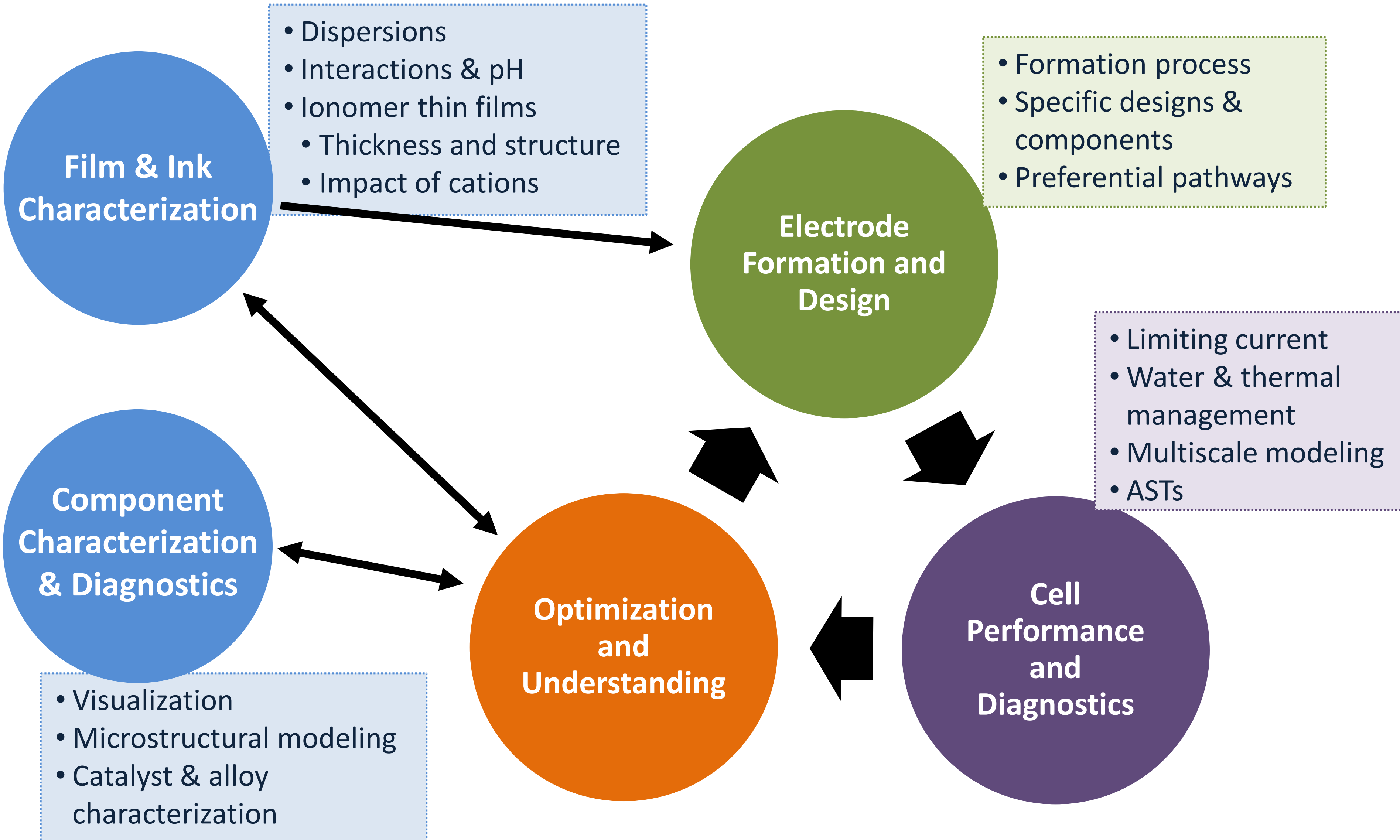




- Minimal reduction in ECSA during conditioning
- PtCo: wider particle size distribution than Pt
- Catalyst compositional changes occur during ink/MEA fabrication and conditioning

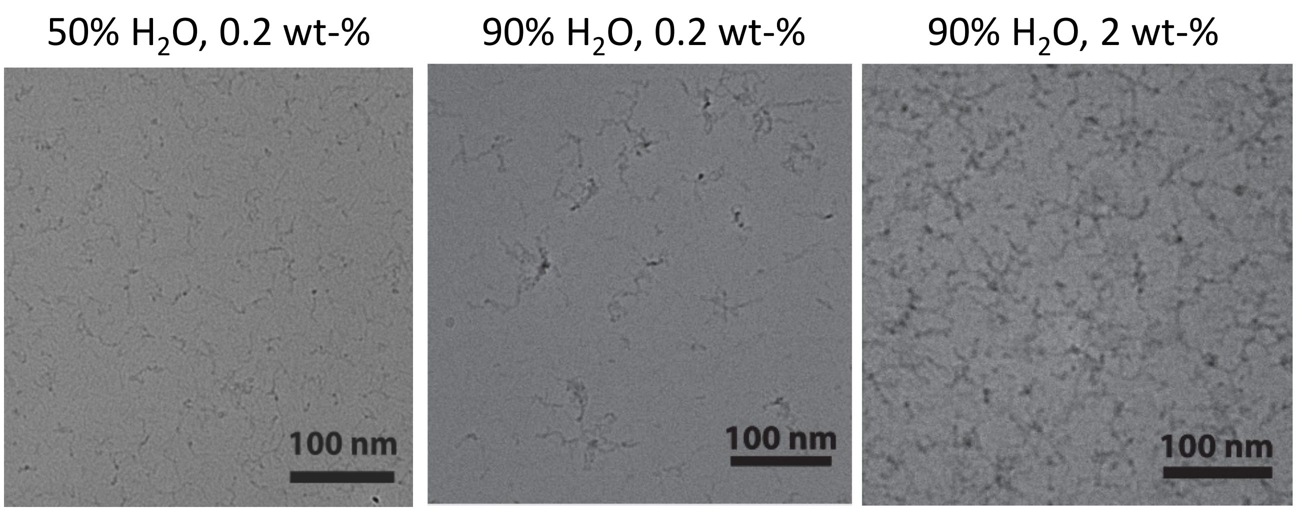
- Pt-Pt coordination number increase combined with less substantial increase of Pt-Co coordination indicates Pt particle growth and/or Pt enrichment due to Co dissolution

Approach: Electrode Layers and MEA Exploration



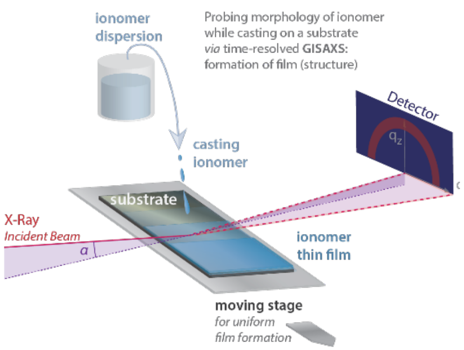
Agglomerates: Dispersions

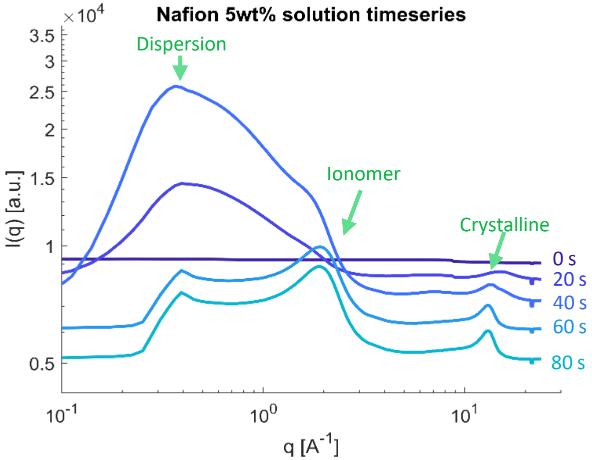
- Ionomer solutions: colloidal dispersions with multiple solvents and ionomer
  - Precursor to ionomer interactions



Aggregation from single strands to multi-strands with increasing water and solid amounts studied via cryo-SEM

Operando casting shows evolution of domain formation with crystallites then formation and growth of ionomer domains

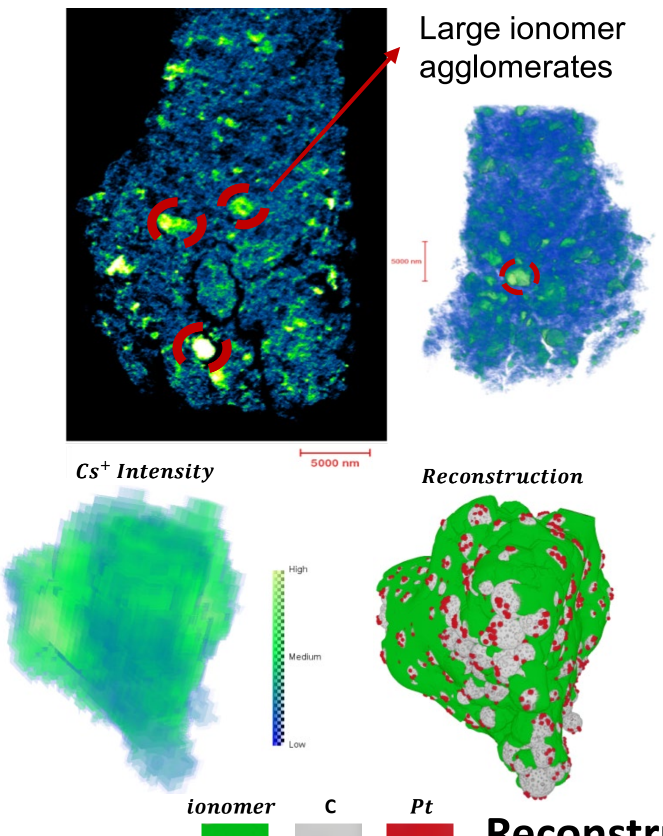




Characterization of Aggregates and Agglomerates

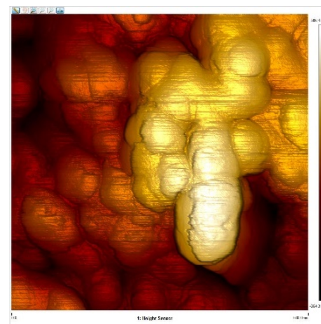
- Ionomer and Pt/C exhibit different aggregation behavior, resulting in various heterogeneities within electrode that can be detected with various methods
  - Multiple techniques used to measure ionomer and carbon aggregates and agglomerates
    - Ionomer thin films plus larger agglomerates (globules)
    - Carbon aggregates 50 to 200 nm; larger agglomerates

Nano X-ray tomography

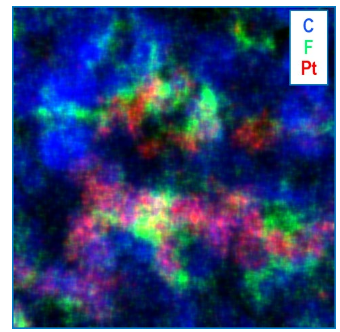


Reconstruction

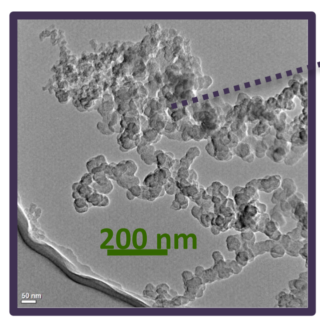
AFM

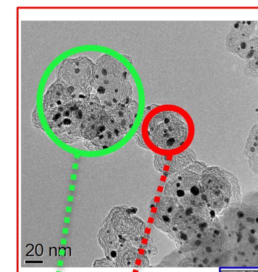


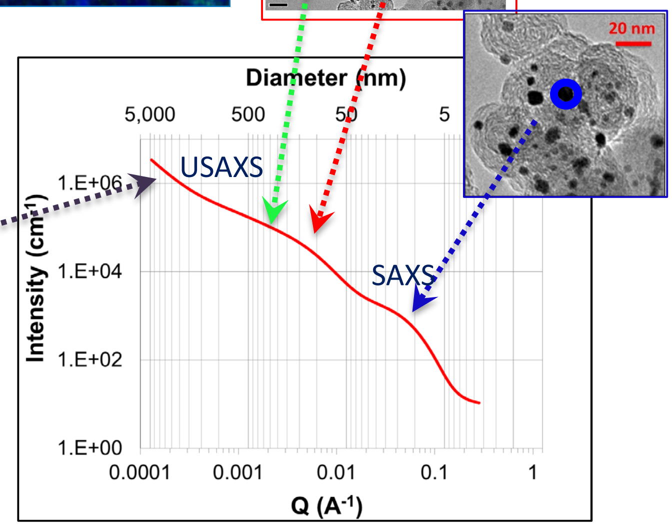
STEM



X-ray Scattering

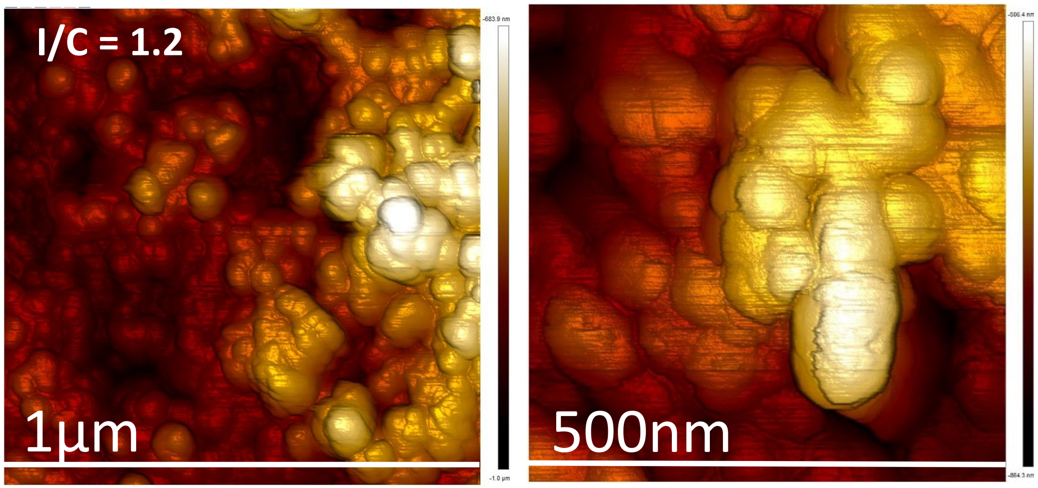






Ionomer and Agglomerate Imaging of Catalyst Layers

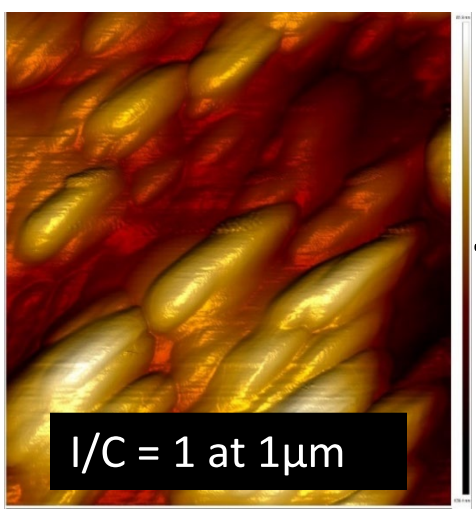
AFM Height Imaging



- Higher resolution shows individual particles in aggregates
- Differences in aggregates measured with spray coated vs painted
- Particle diameter ranges fit previous data from TEM/SAXS
- Large variability in particle diameter & ionomer thickness

To measure ionomer thickness:

Height



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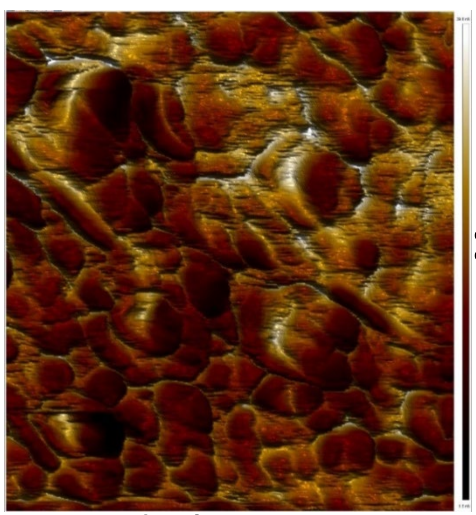
Adhesion



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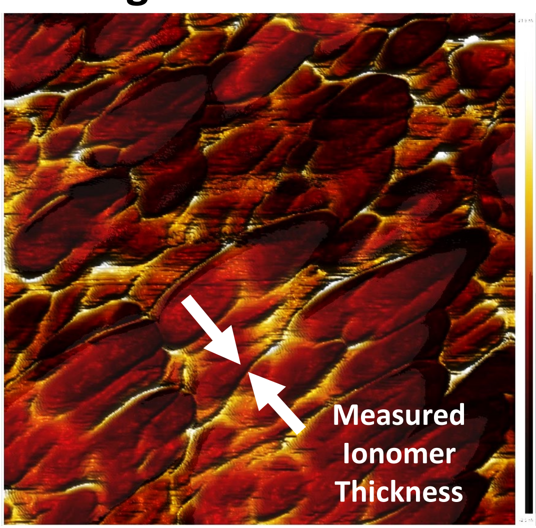
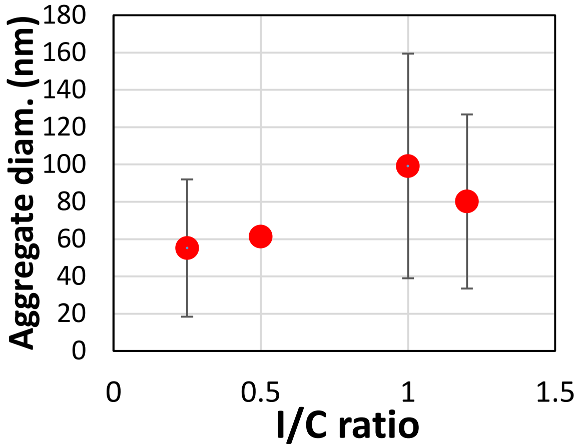
Height with adhesion



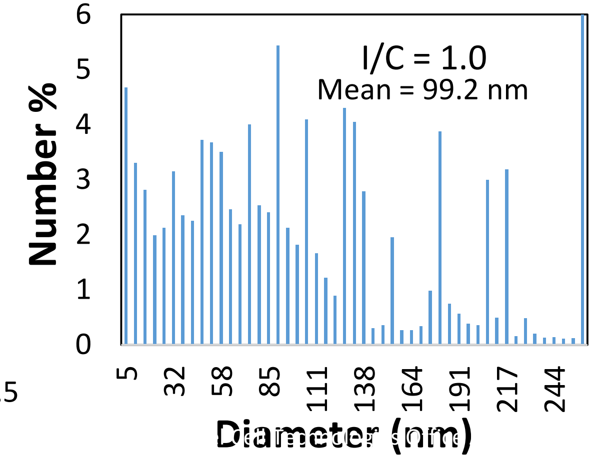
MEAs made by Spraying

Measurements of Pt/C Aggregate Measurements (AFM & SAXS) and Ionomer Layer Thickness (AFM)

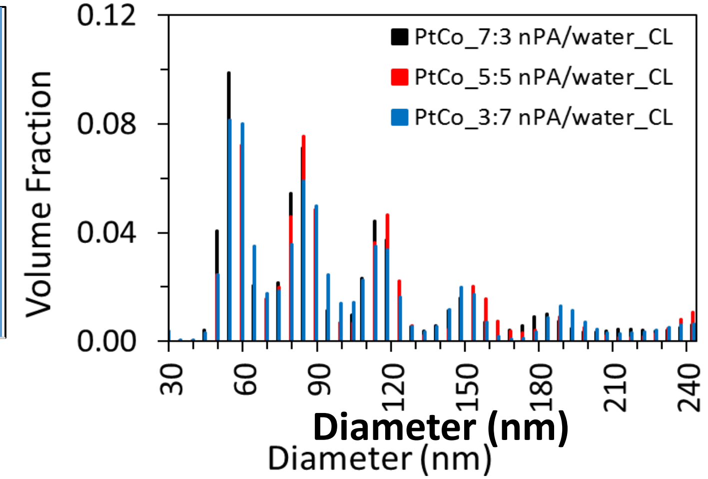
Mean Pt/C Aggregate Diameter



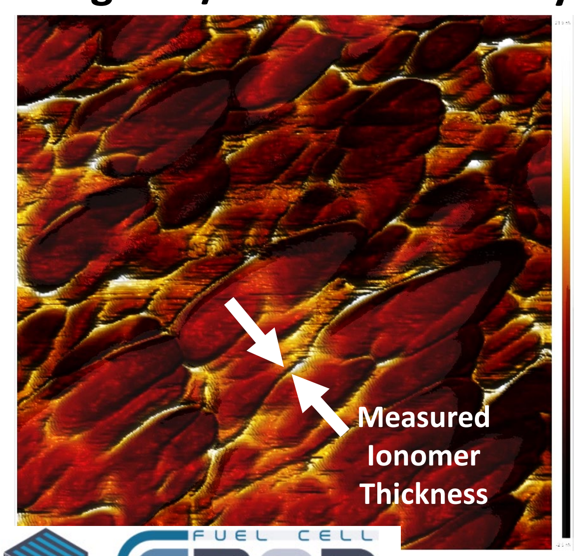
Particle size Distribution



PSD by SAXS: Carbon aggregates 0.02 > q > 0.001)



Height w/ adhesion overlay



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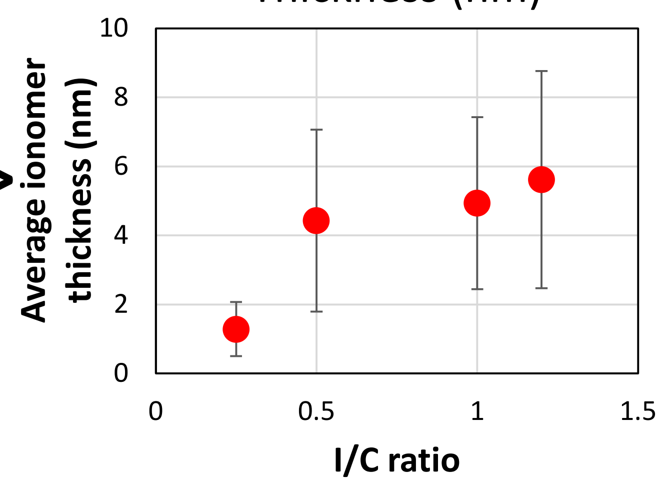
Average Ionomer Thickness (nm)



- Large variability in particle diameter and ionomer thickness
- Positive correlation between I/C ratio and ionomer thickness

MEAs made by hand painting

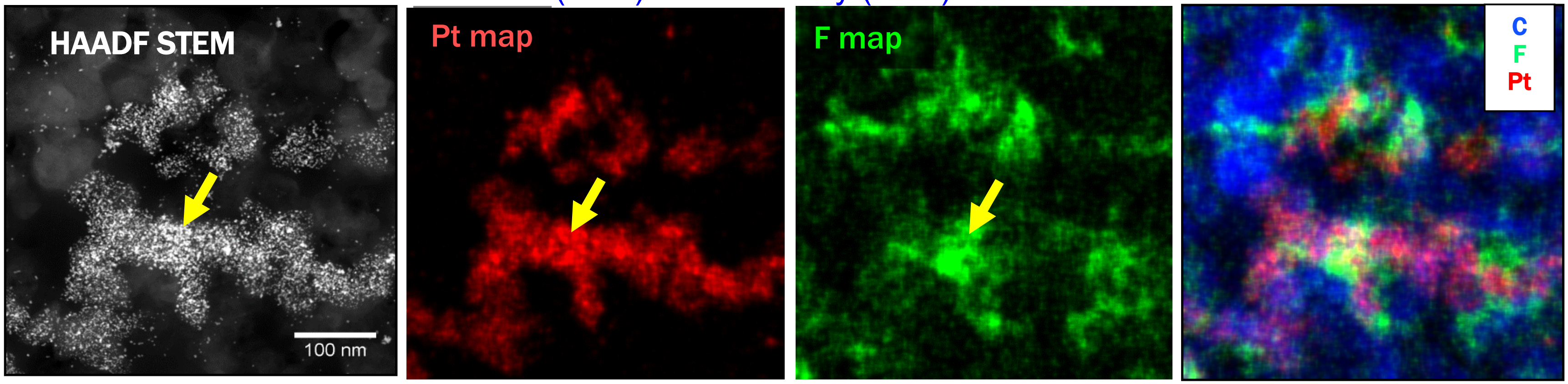
Ionomer Dispersion within Catalyst Layers

Comparing Ionomer+C and Ionomer+Pt/C

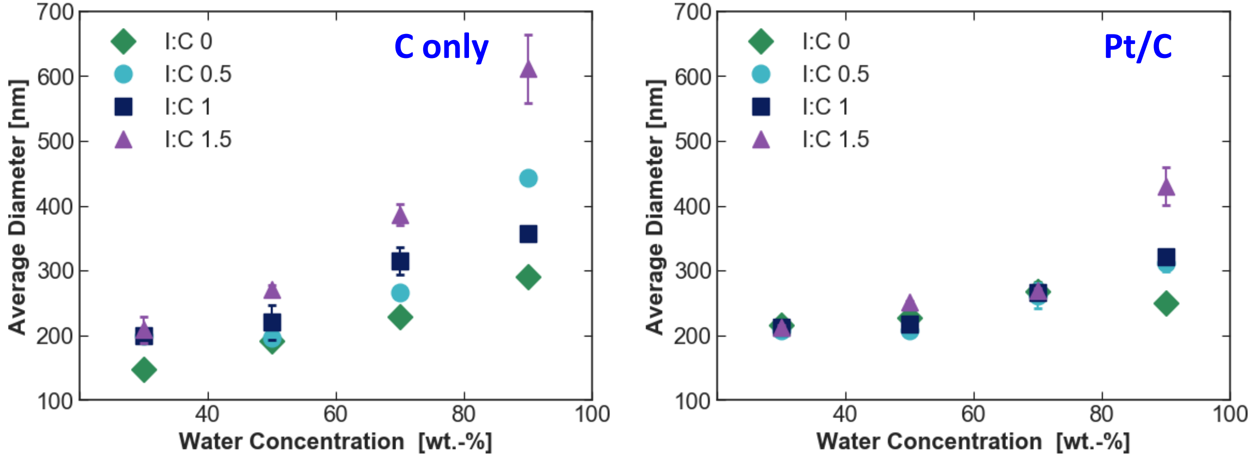
- Increased interactions between ionomer + Pt/C compared to Ionomer + carbon
- Evidence that ionomer is predominantly associated with Pt/C regions
  - ➢ Pt/ionomer interactions dominate aggregation in inks (by dynamic light scattering)

Pt/HSAC (50%) + HSAC-only (50%) in CL

CL



Ink

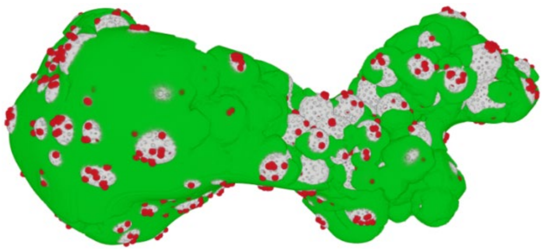


Higher agglomeration without Pt

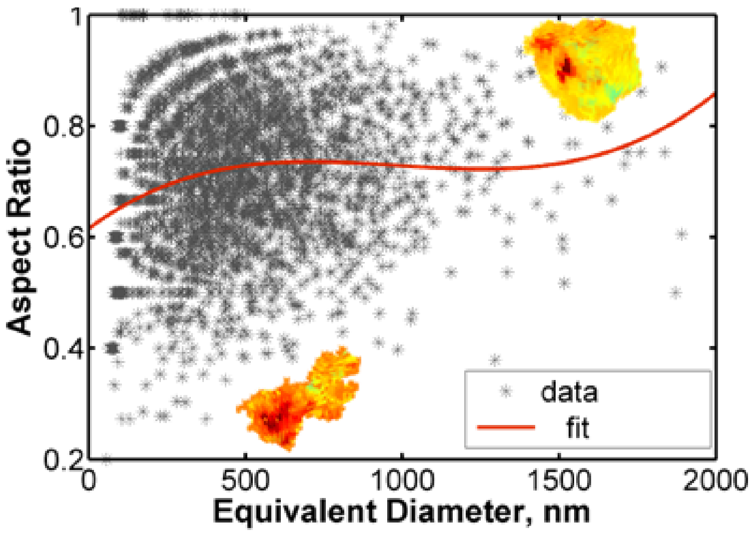
Modeling of Microscale Transport-Catalyst Layer Agglomerates

- Explore agglomerate structures and understand mechanisms limiting of transport

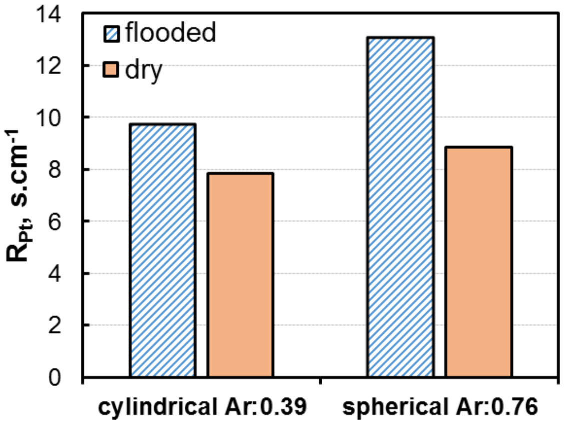
Agglomerates identified by applying binary separation algorithm to segmented phase contrast images

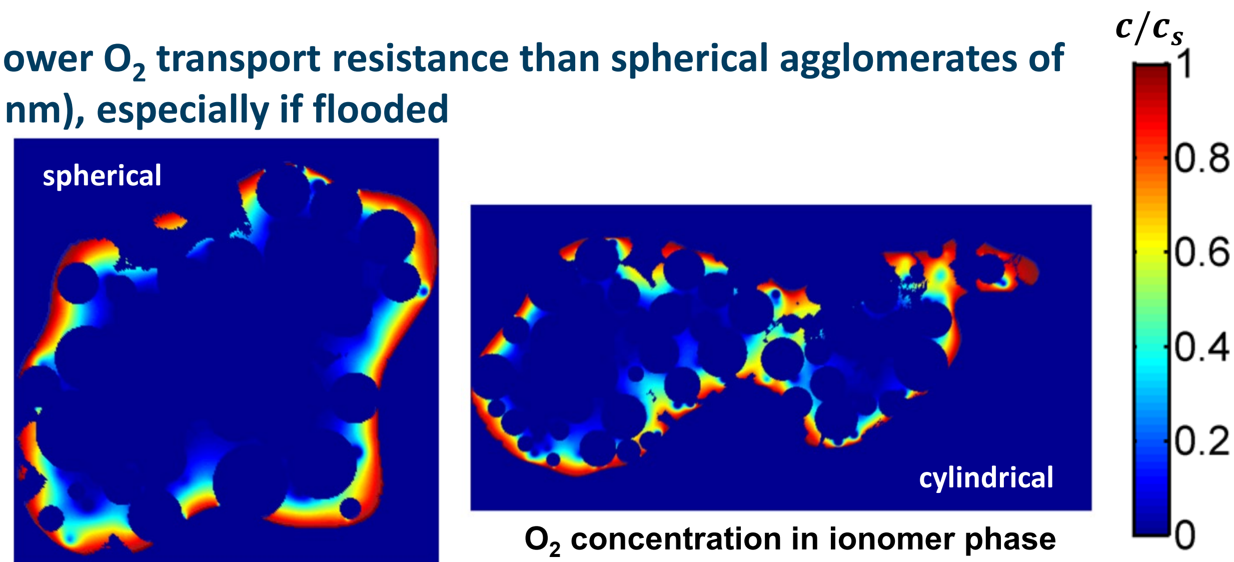


Reconstructed agglomerate includes porous C, Pt, and ionomer distributions from absorption contrast images



Cylindrical agglomerates show lower O_2 transport resistance than spherical agglomerates of same equivalent diameter (500 nm), especially if flooded

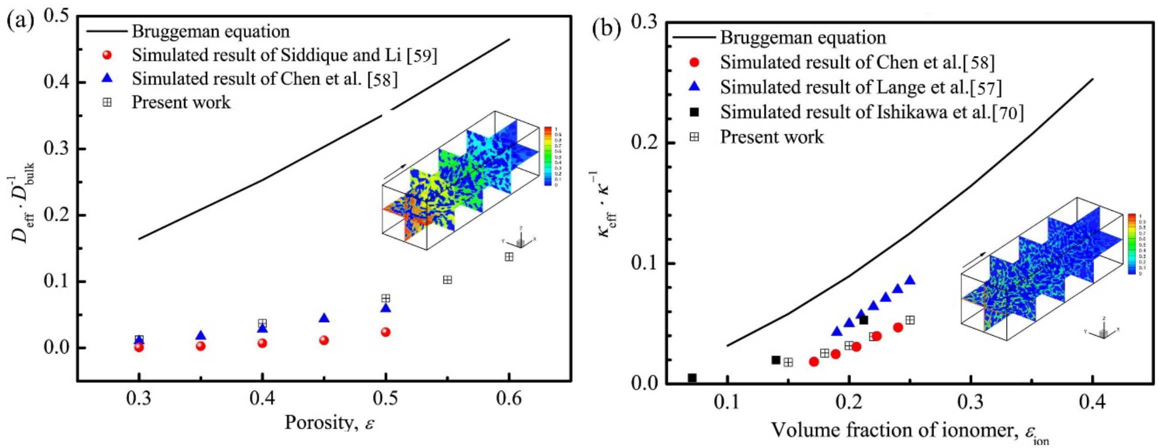




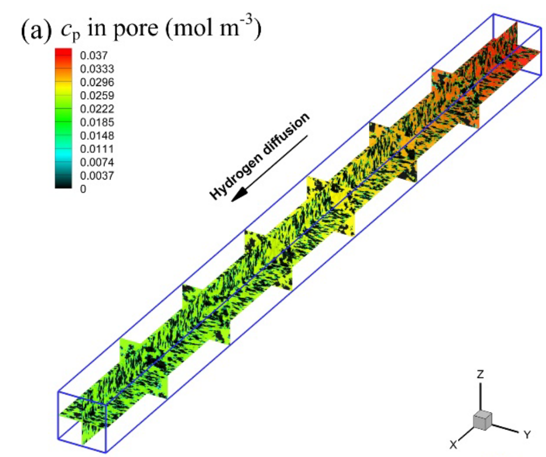
O_2 concentration in ionomer phase (flooded agglomerates)

Mesoscale Transport

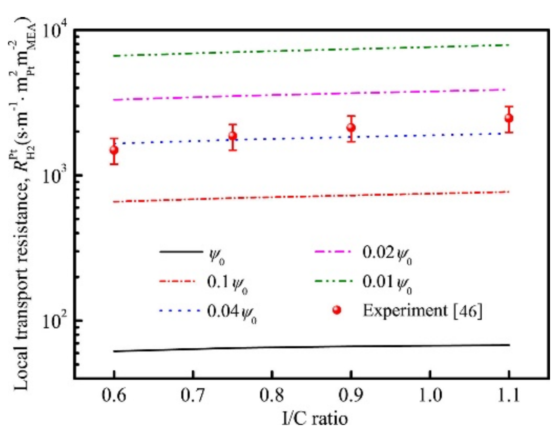
- Catalyst layer modeling at microscale is critical to resolve accurate trends
  - Tortuosity has different dependence than expected

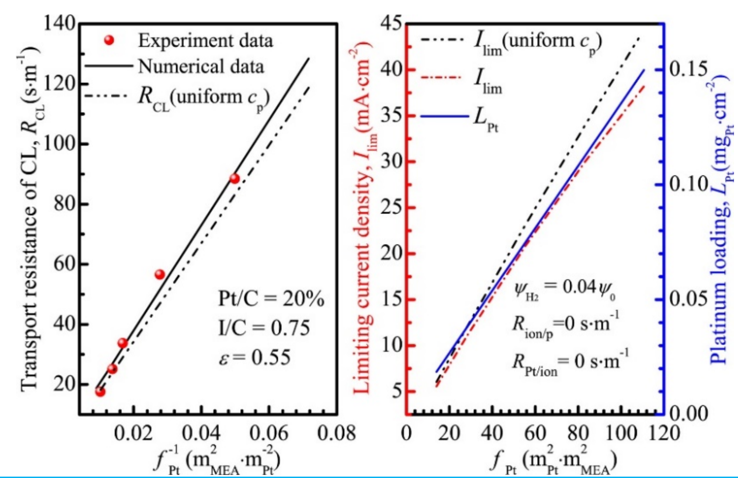


Lattice Boltzmann simulation on constructed CL with local transport effects



  - Ionomer thin film must be about 4% of bulk ionomer properties to agree with limiting-current data
    - Simulations show good agreement with data
    - Local transport resistance is limiting but some effects of ion adsorption as well

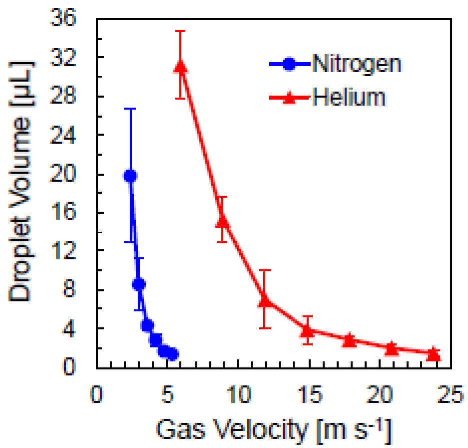


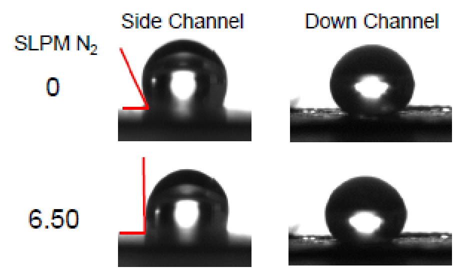


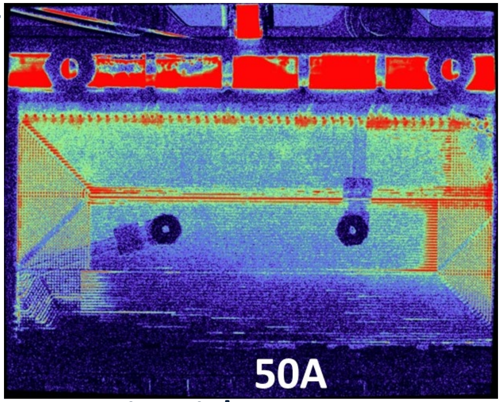
Water Management

Accomplishments

- Anode can flood since harder to remove water due to H_2/droplet interactions
  - Experiments show more He than N_2 needed to remove droplet

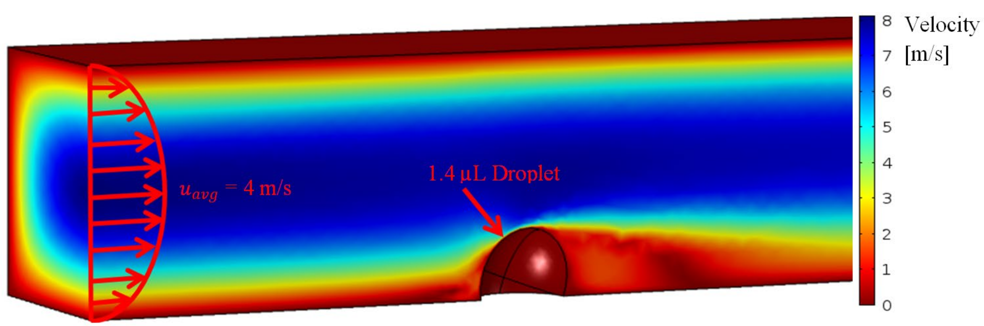




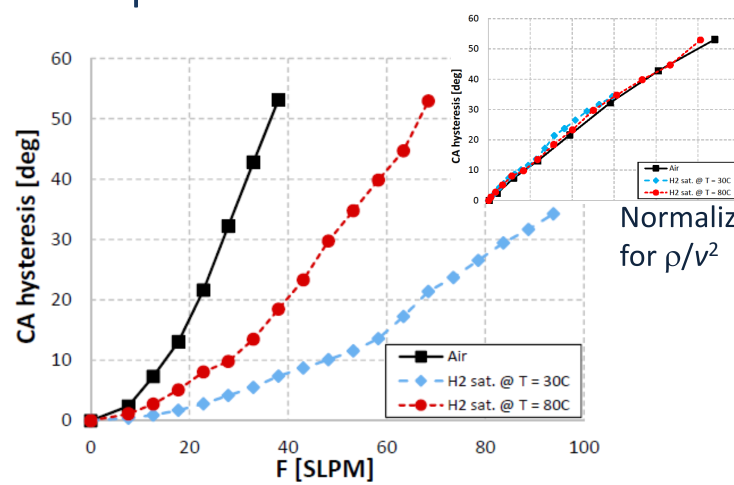


Liquid water on anode in Mirai

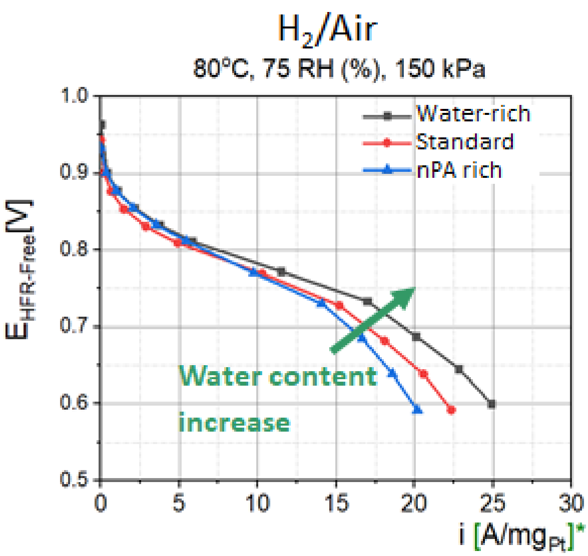
  - Simulations agree that gas density plays critical role for droplet detachment

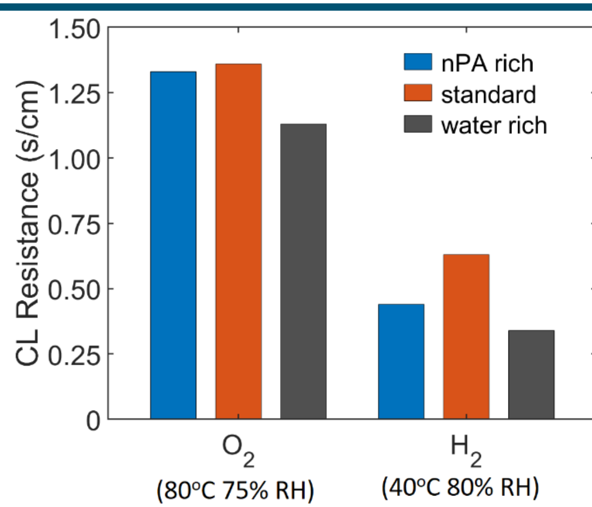


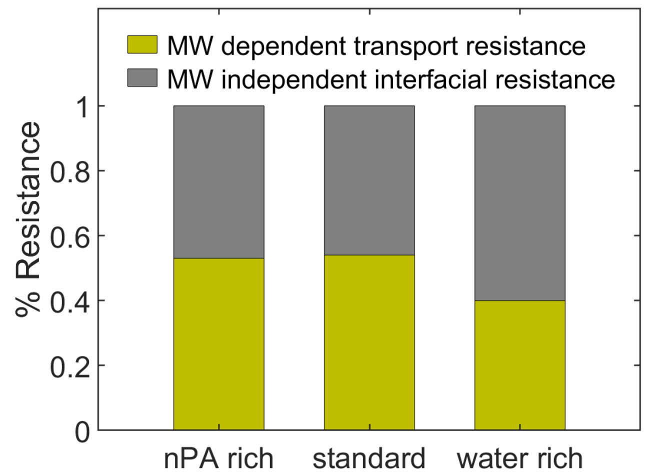
Coupled flow and deformation model

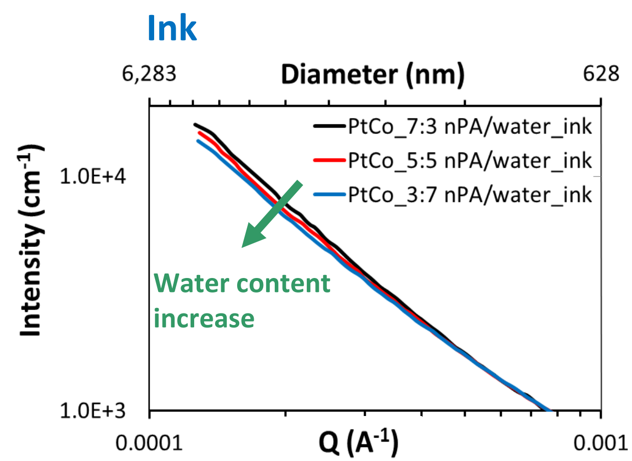


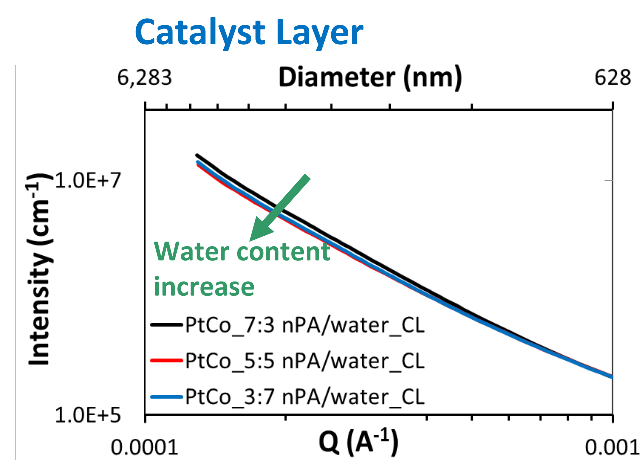
Case Study: Ink Solvents











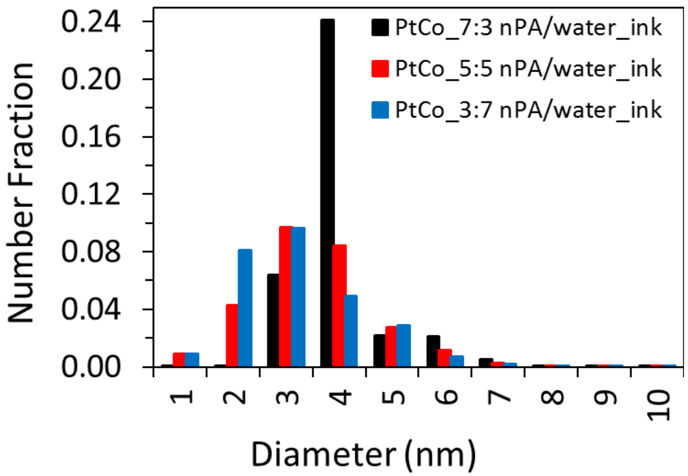
- Performance improvement with water-rich ink
  - Reduction in non-Fickian and MW dependent transport percentage of resistance
  - Decrease in agglomerate size both ink and CL

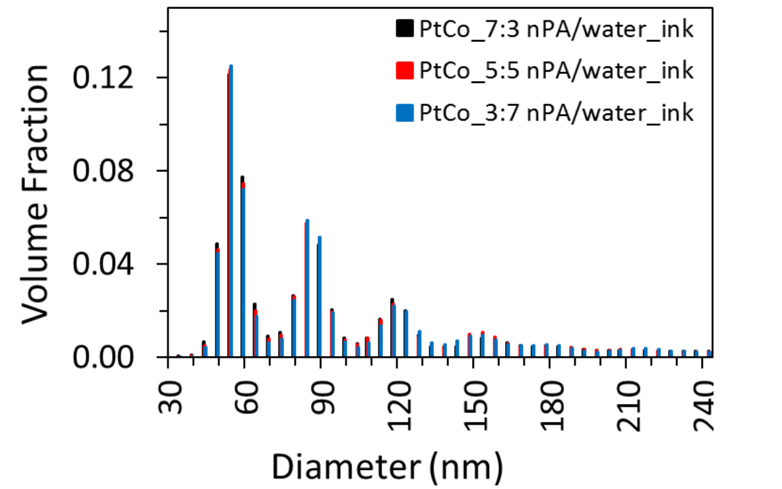
Case Study: Ink Solvent

PSD: Catalyst particles (1.5-10 nm) q > 0.026

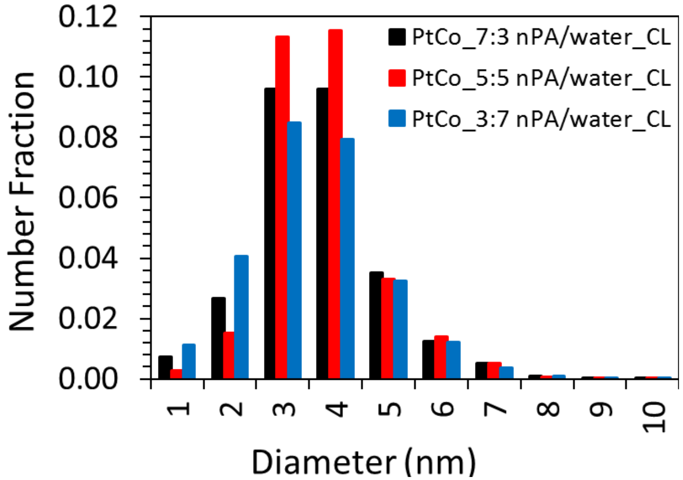
PSD: Carbon aggregates (10-250 nm) 0.02 > q > 0.001)

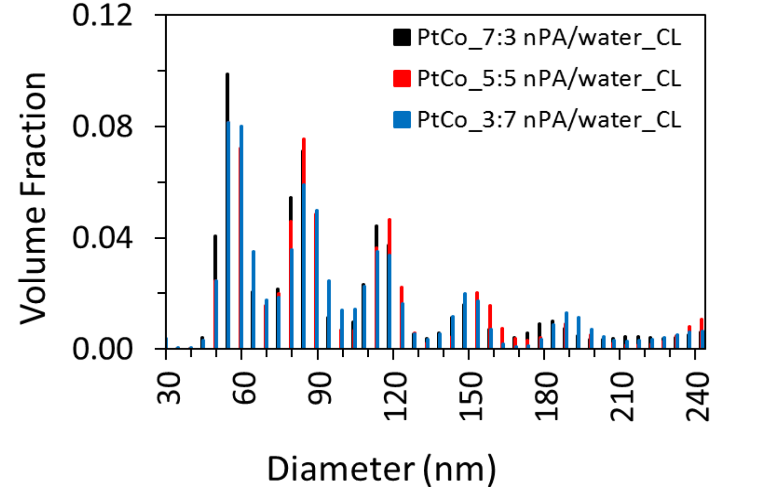
PtCo inks





PtCo CLs

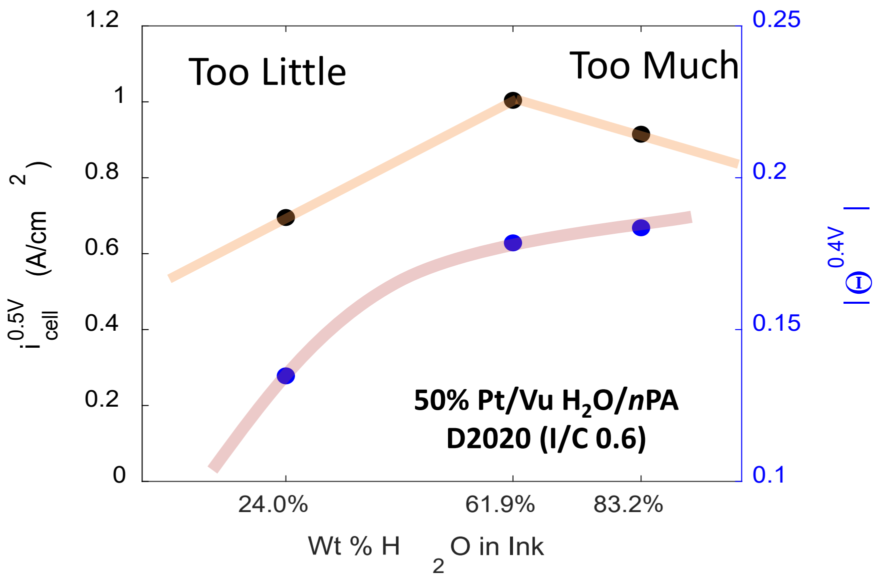


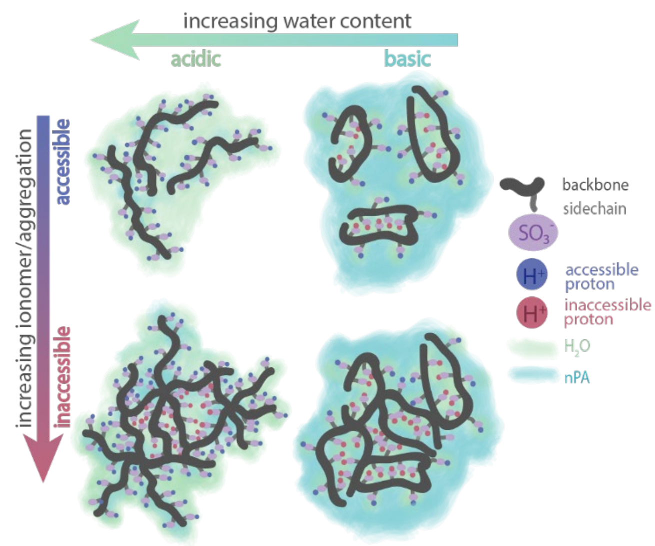


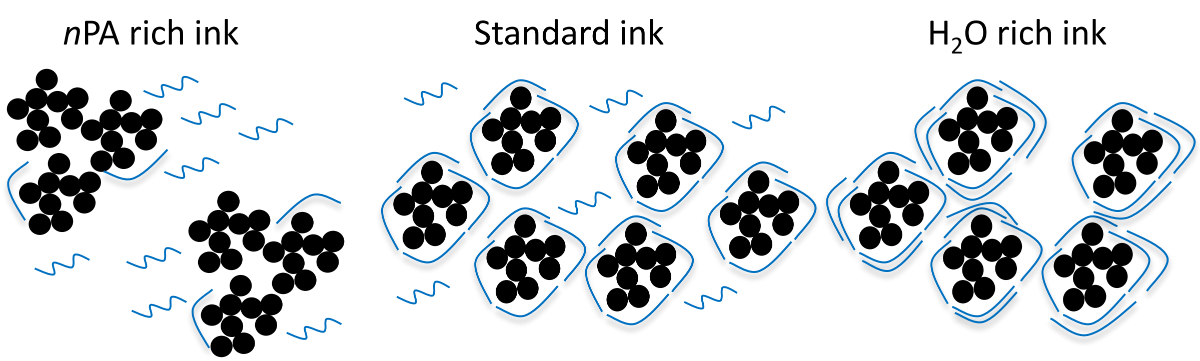
- For both inks and CLs, carbon aggregates show similar PSDs for all solvent ratios
- For both inks and CLs, water-rich solvent results in smaller agglomerates

Case Study: Ink Solvent

- Higher Θ with increased ink water content
  - Aggregates grow due to increased ionomer/particle interactions
- Slightly water-rich ink exhibits best performance due to trade-off between coverage and structure
  - High water contents - aggregation of side-chains and looser structure, whereas with
  - High propanol contents - clustering and reverse-micelle structure



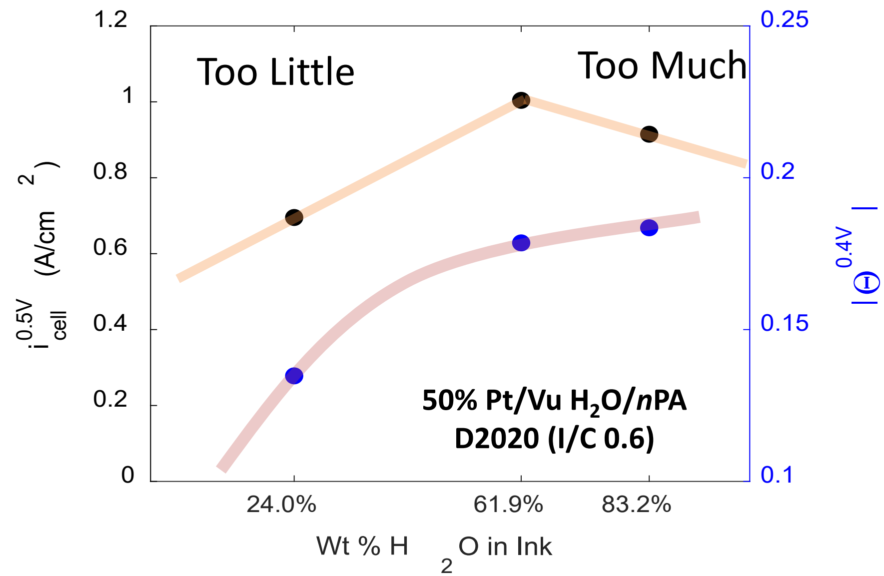


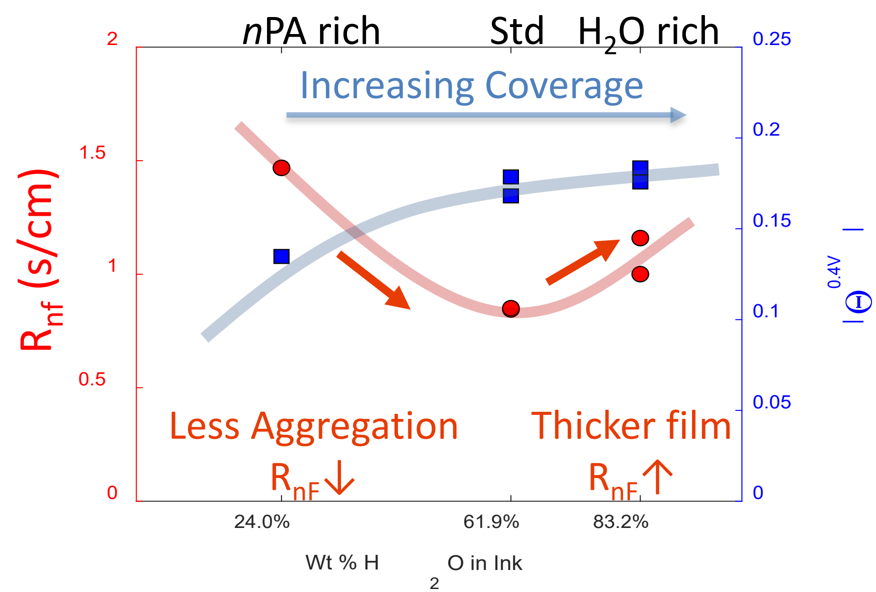


Berlinger et. al, : J. Phys. Chem. B 2018, 122, 7790–7796

Case Study: Ink Solvent

- Higher Θ with increased ink water content
  - Aggregates grow due to increased ionomer/particle interactions
- Slightly water-rich ink exhibits best performance due to trade-off between coverage and structure
  - High water contents - aggregation of side-chains and looser structure
  - High propanol contents - clustering and reverse-micelle structure
- Larger solvent effects in O_2 transfer-limited region
  - Better aggregate break-up in water rich inks
  - Additional ionomer leads to thicker films on or near Pt
  - Similar to that observed for non-limiting case

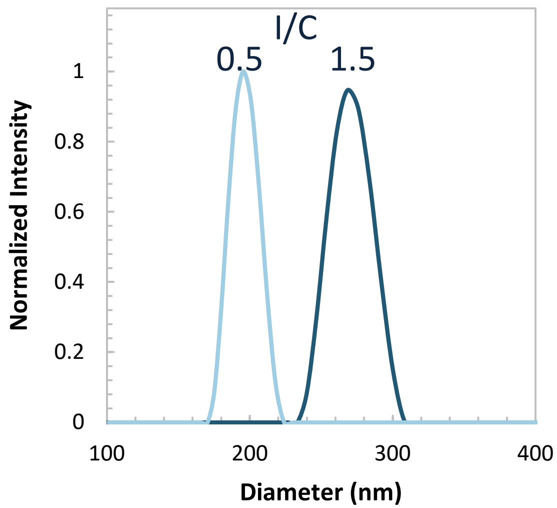




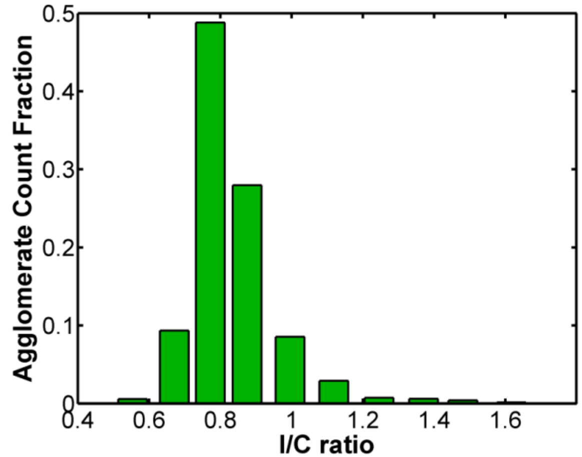
I:C Study

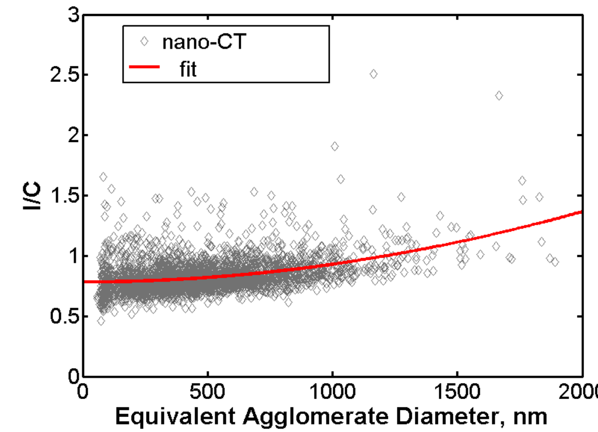
- With increasing I:C, more carbon agglomeration and larger agglomerates
  - Observed in both ink (*ex situ*) and catalyst layer (*in situ*)

Ink (Dynamic light scattering)



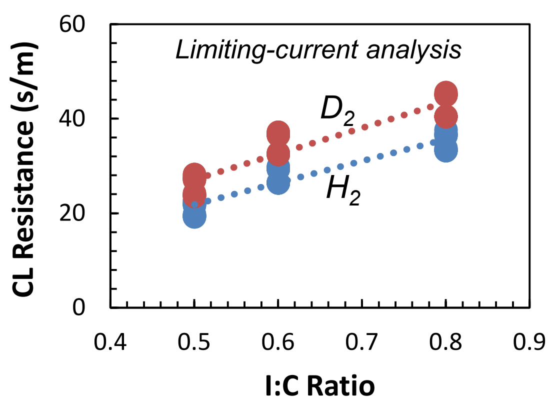
Catalyst Layer (X-ray computed tomography)





I/C ratio statistics based on Cs^+ intensity

- Results in more resistance
  - Higher interfacial and lower transport for lower EW
    - Impacted more by side-chain spacing and density than side-chain length
  - Agrees with *ex situ* film results

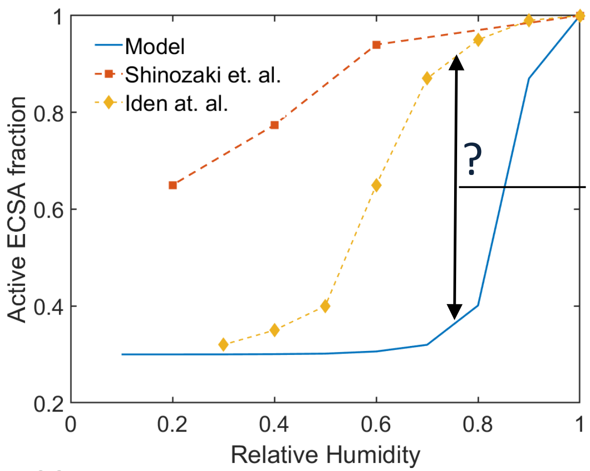


Ionomer	Interfacial (s/m)	Transport (s/m)
Nafion 1100	$\sim 0 \pm 1.3$	46.2 ± 2.0
3M 1000	0.2 ± 1.3	37.3 ± 2.2
3M 825	8.7 ± 1.0	24.6 ± 2.1

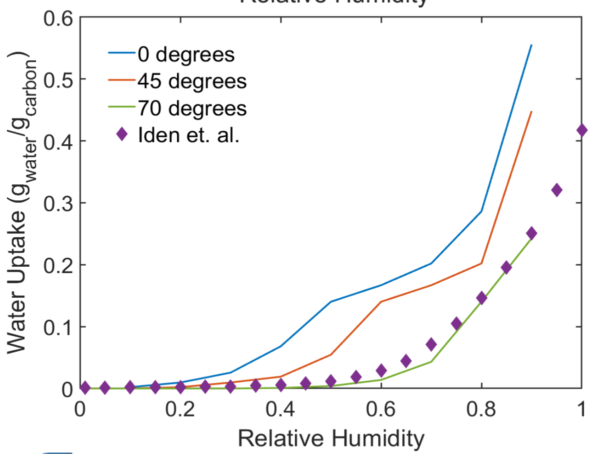
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

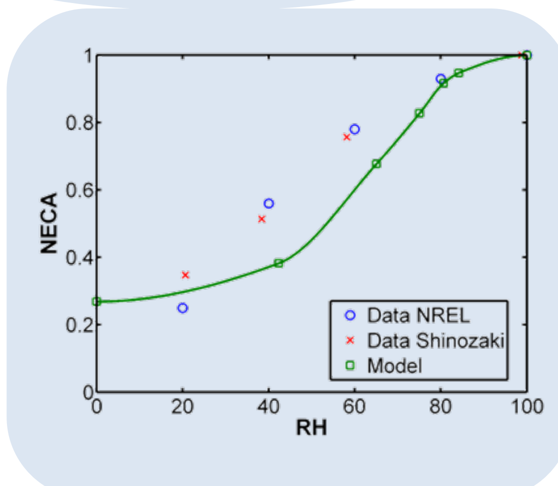
Increased Complexity: Porous Carbons

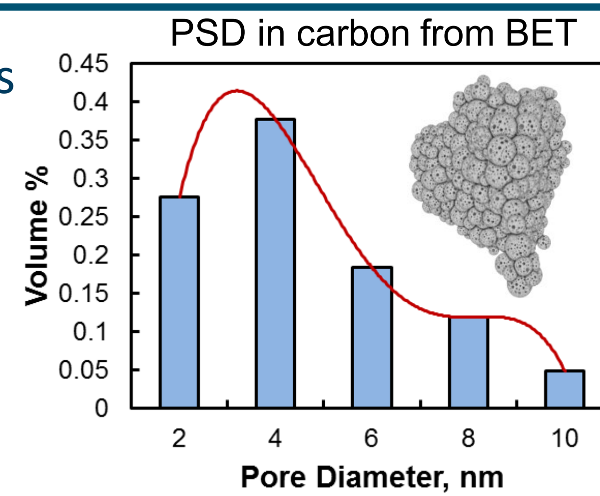
- Multi-mechanisms - water filling of porous carbons
  - Increasing RH results in higher ECSA
  - Adsorption and capillary condensation must occur

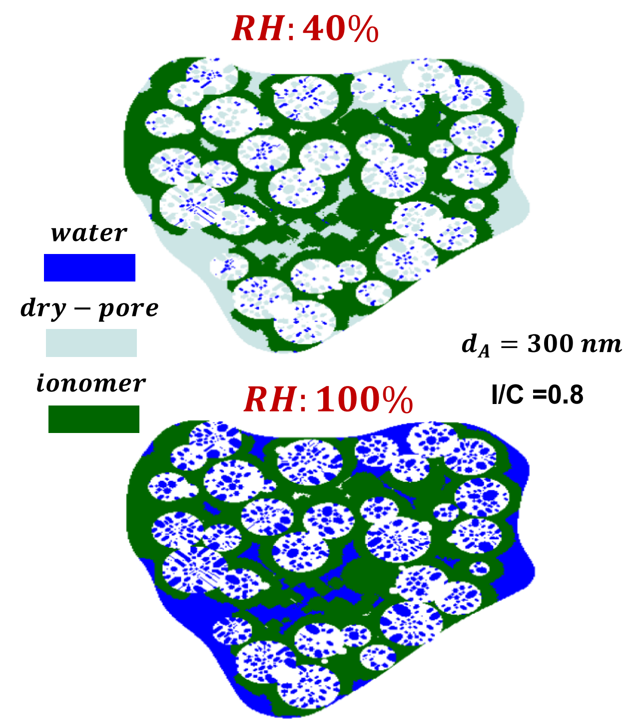


Water adsorption
Irregular shaped pores
Preferential Pt location



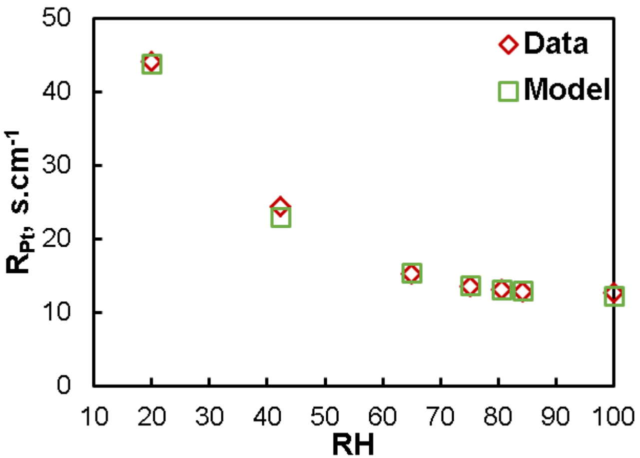


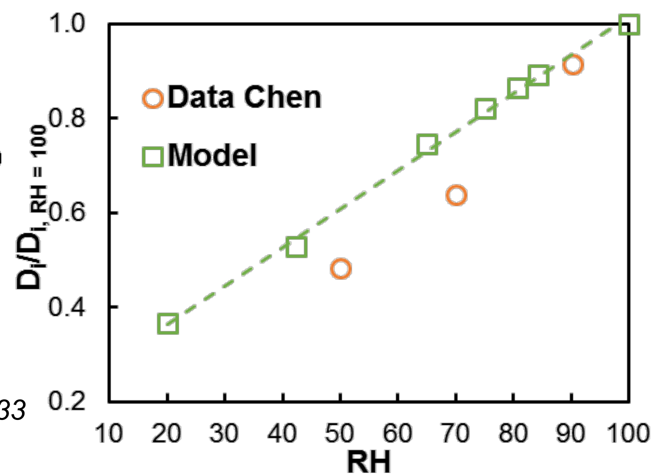


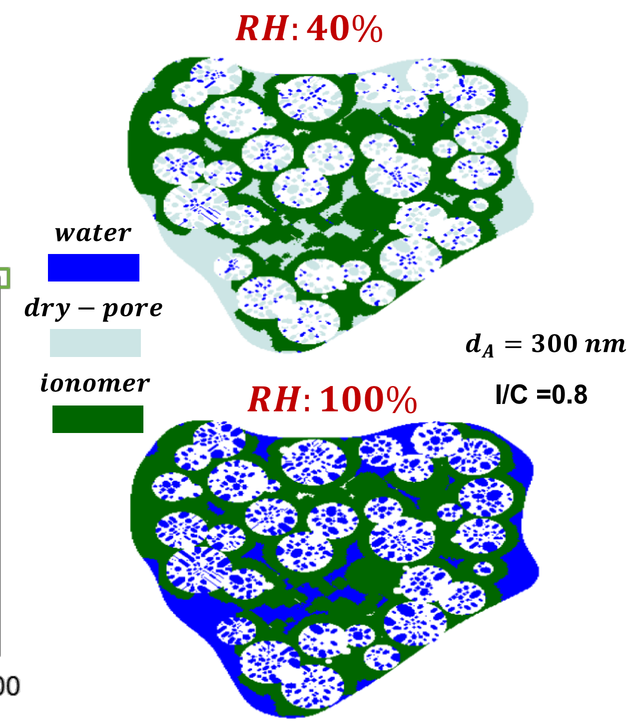


Increased Complexity: Porous Carbons

- Multi-mechanism - water filling of porous carbons
  - Adsorption and capillary condensation
  - Particles inside carbon pores result in 2 - 3 s/cm higher local resistance compared to solid carbon
    - Low ECSA manly responsible for high resistance at low RH
      - Reduction in local resistance, R_{Pt}, with higher RH slows down after 65% RH due to flooding
    - Decreased diffusivity due to longer path-length to reach active Pt site





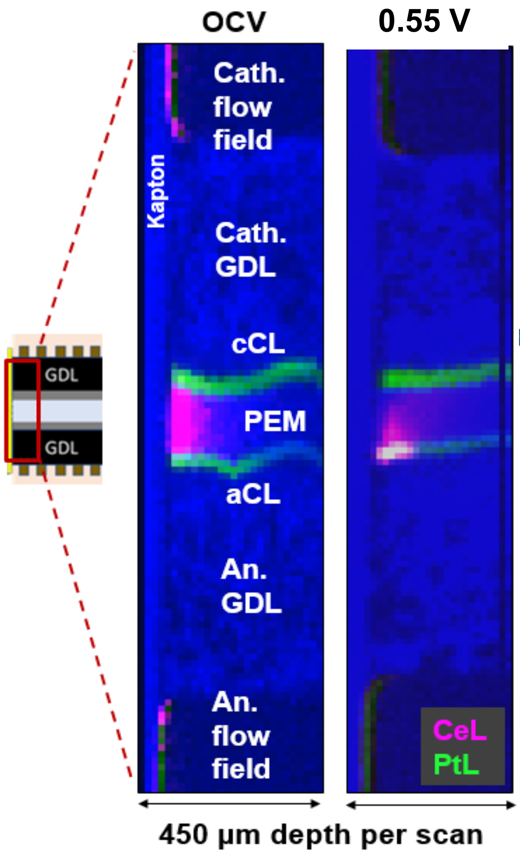


D. Chen, *J. Electrochem. Soc. 2019 166(2): F24-F33*

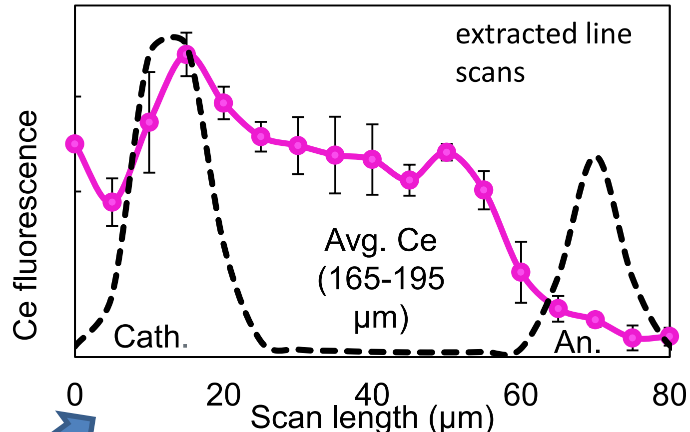
Ce Migration: Experiments

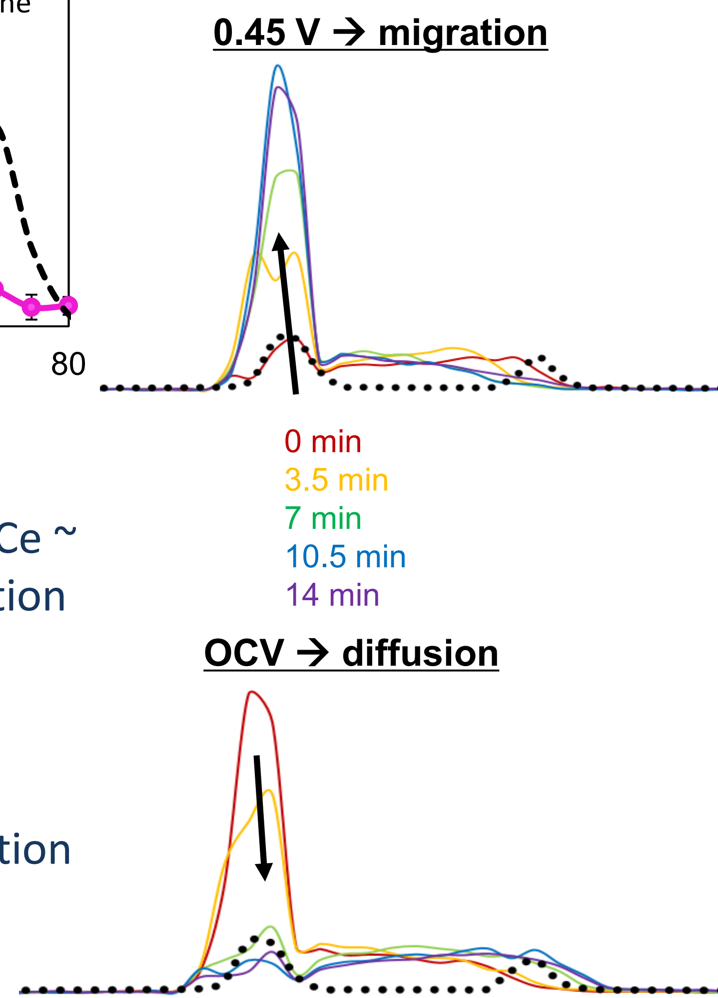
Observing Ce migration during and after applied potential

80˚C/50% RH H_2/air



NR-212 w/ 13% Ce(III); 0.05/0.1 mg/cm² 10% Pt/V

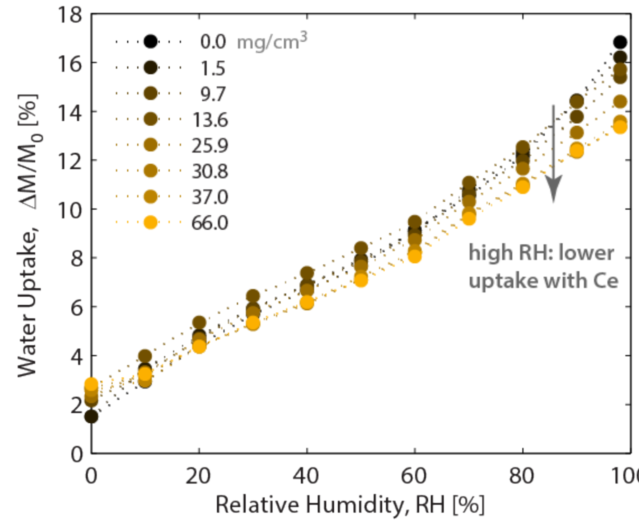


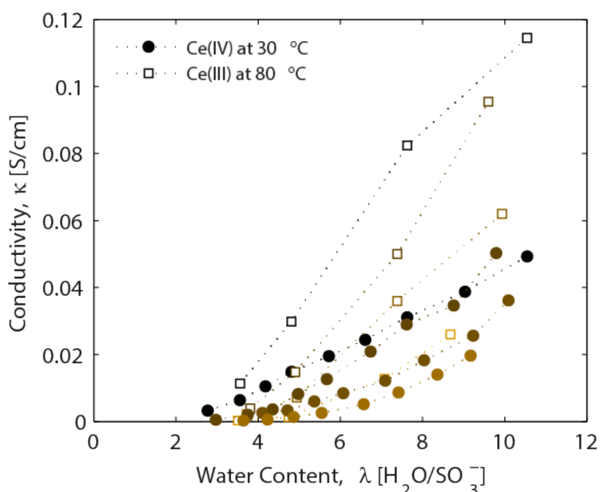


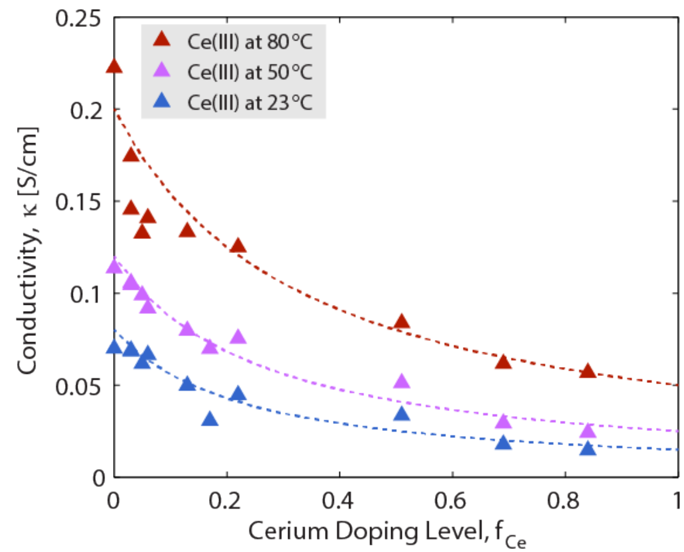
- Removing load redistributes Ce ~ 5 minutes; half that of migration
- Ce moves towards cathode during operation - balance between diffusion and migration

Ce Migration: Membrane Properties

- Ce impacts membrane water uptake properties but only at higher RHs
  - Decreased water uptake
    - Opposite of that in thin films
- Dramatic decrease in conductivity in liquid water with Ce doping
  - Increased activation energy with loading
  - No master curve, suggesting conductive network differences

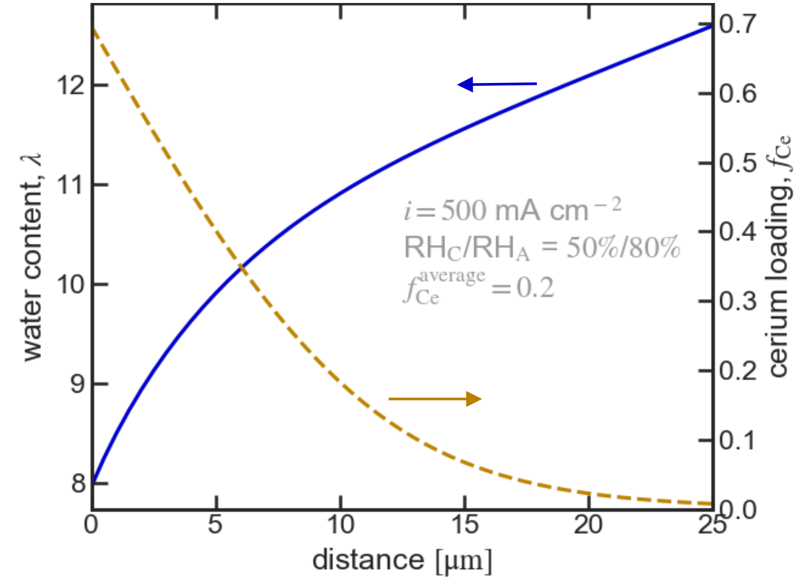


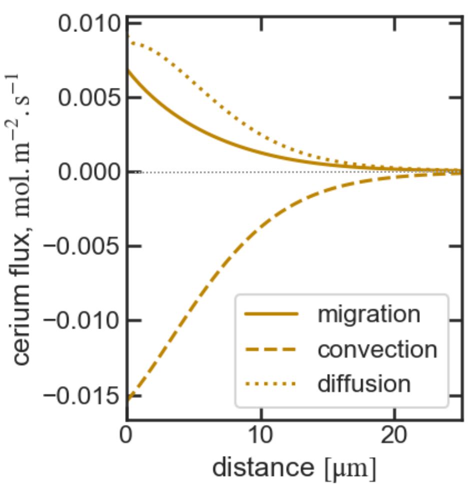


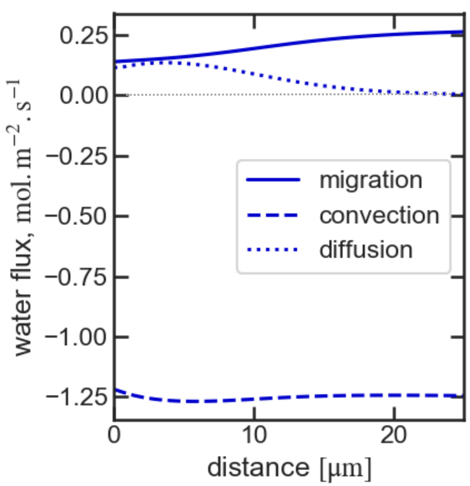


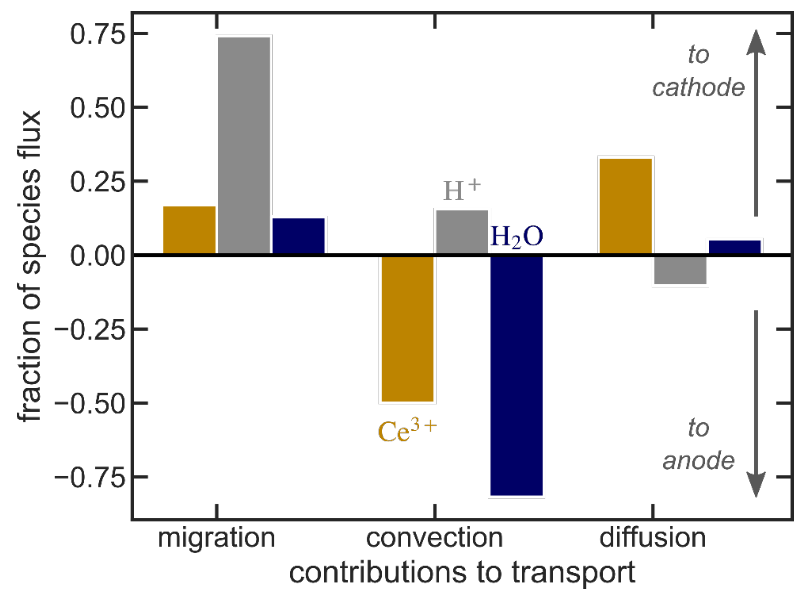
Ce Migration: Modeling

- Utilize interactions for Ce transport and examine transport at multiple scales
  - Concentrated solution theory model shows balance between migration and diffusion that push Ce to the cathode and water convection that pushes Ce to the anode
  - Heterogeneous ion distributions also change proton and water transport





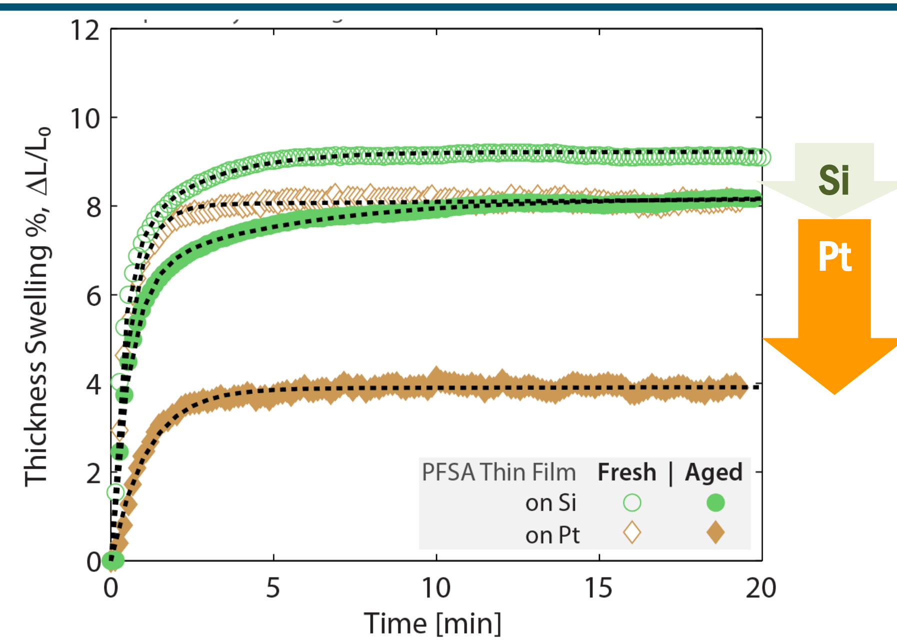


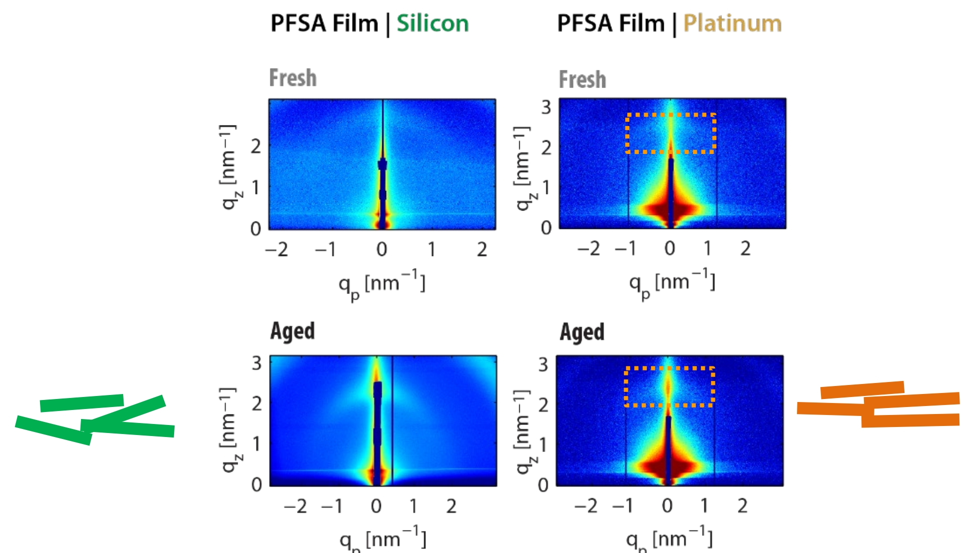


Ionomer Thin Films: Impact of Ageing

- Hygrothermal ageing of ionomer films
  - Films are held at 70C, 85% RH for 2 and 4 days

	Fresh film	Aged Film
Swelling	Si > Pt	Si >> Pt ↓
Swelling Kinetics	Si > Pt	Si >> Pt ↓
Domain Orientation	Si < Pt	Si << Pt ↑

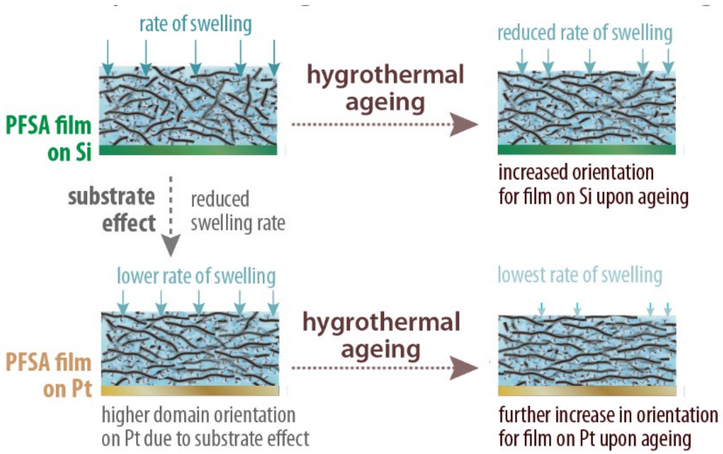




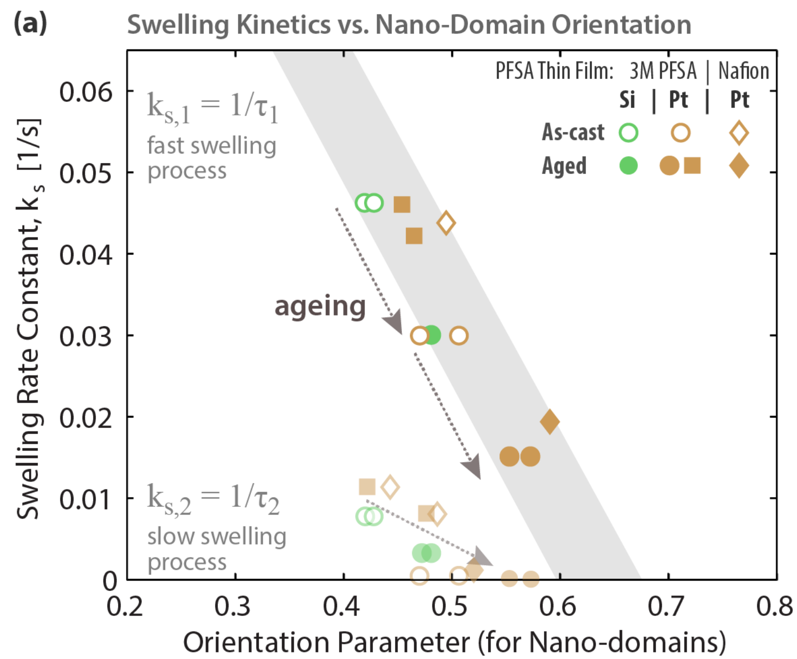
M Tesfaye, D. Kushner, A. Kusoglu, ***ACS Applied Polymer Materials*** (Accepted Manuscript)

Ionomer Thin Films: Impact of Ageing

- Reduced rate of swelling is inversely proportional to nanodomain orientation



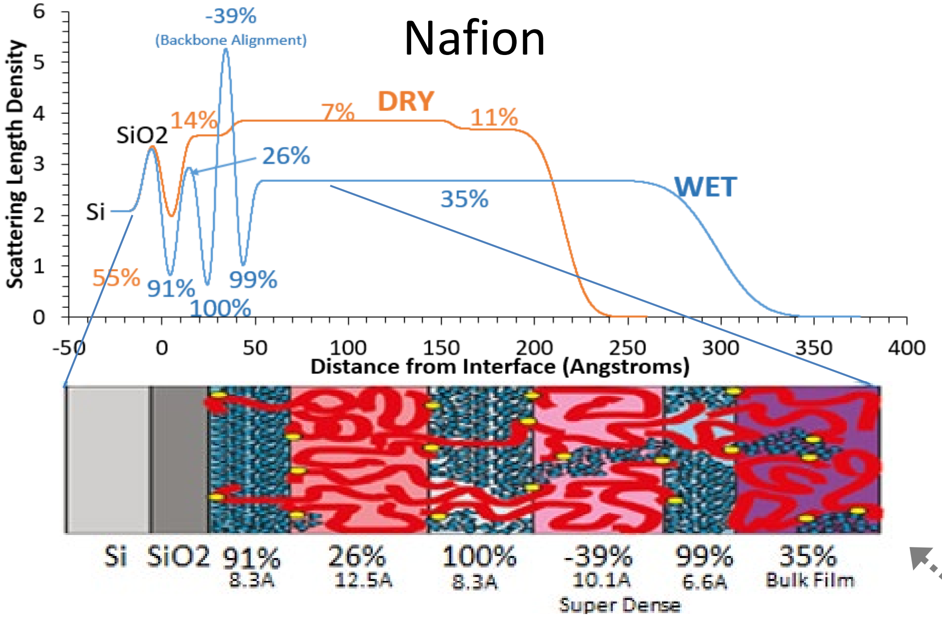
- Time constant ~ Orientation
  - Thickness swelling slows down when domains are preferentially aligned

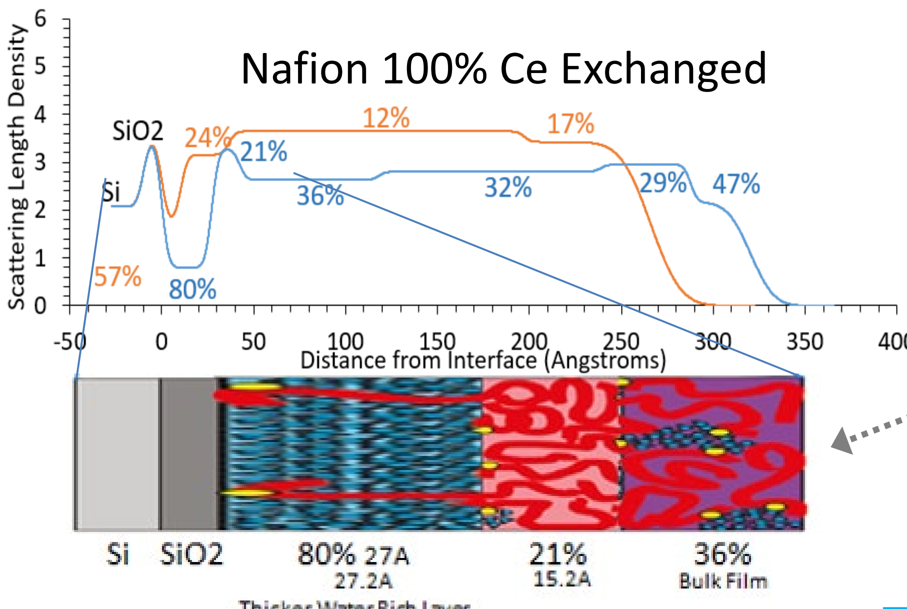


- Hold at RH/T intensifies ionic interactions impacting orientation
- Critical for cell operation and performance decay
- Implications for conditioning

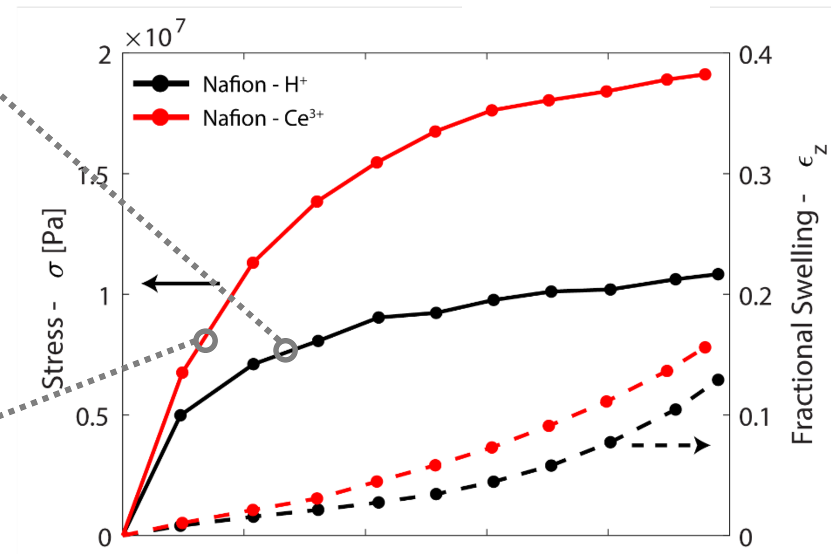
M Tesfaye, D. Kushner, A. Kusoglu, ***ACS Applied Polymer Materials*** (Accepted Manuscript)

Ionomer Thin films: Cerium Doping





- Connection between structure and thermodynamic/mechanical properties is altered by cation exchange
  - Similar structures in the dry state - manifests in similar mechanical response and swelling at low RH
  - At high water content, more interspersed water results in higher stress and modulus for Ce-exchanged film
  - Nafion thin films on Pt also demonstrate complicated water/surface structure which Ce modifies
- Swelling response agrees with more water in Ce-exchanged film

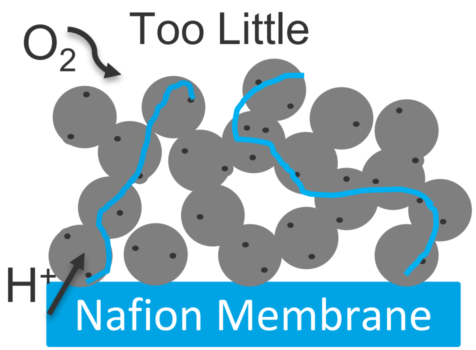


G_H = 304 Mpa

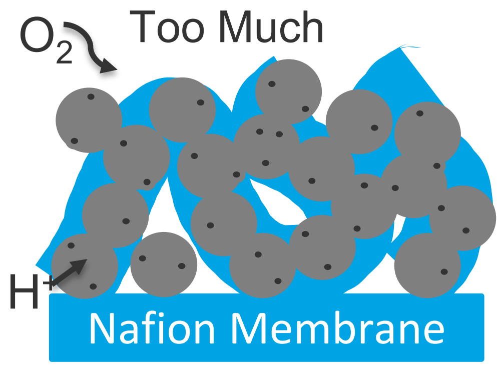
G_{Ce} = 323 MPa

Optimizing CL Structure (Ionomer Distribution)

Control ionomer content & distribution

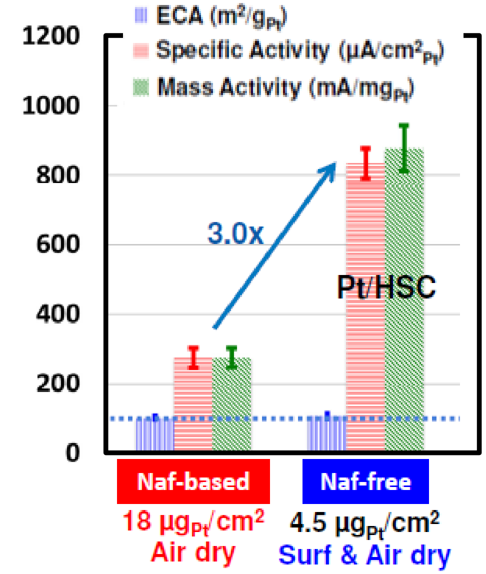


- Poor H^+ Transport
- Lower Pt utilization



- Decreased O_2 transport
- Site and Pore Blockage

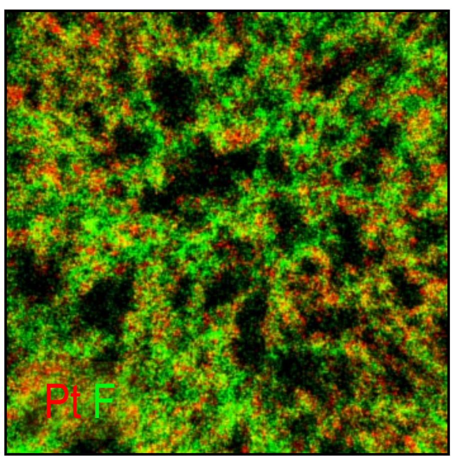
Ionomer Inhibits ORR

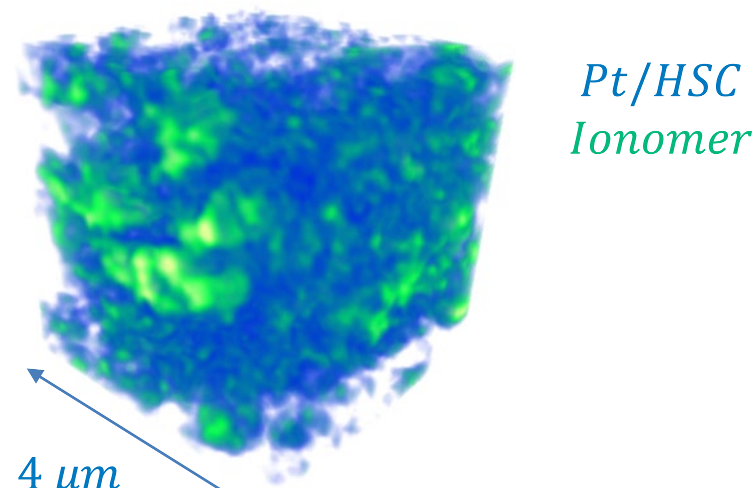


Challenge: Difficult to control and characterize

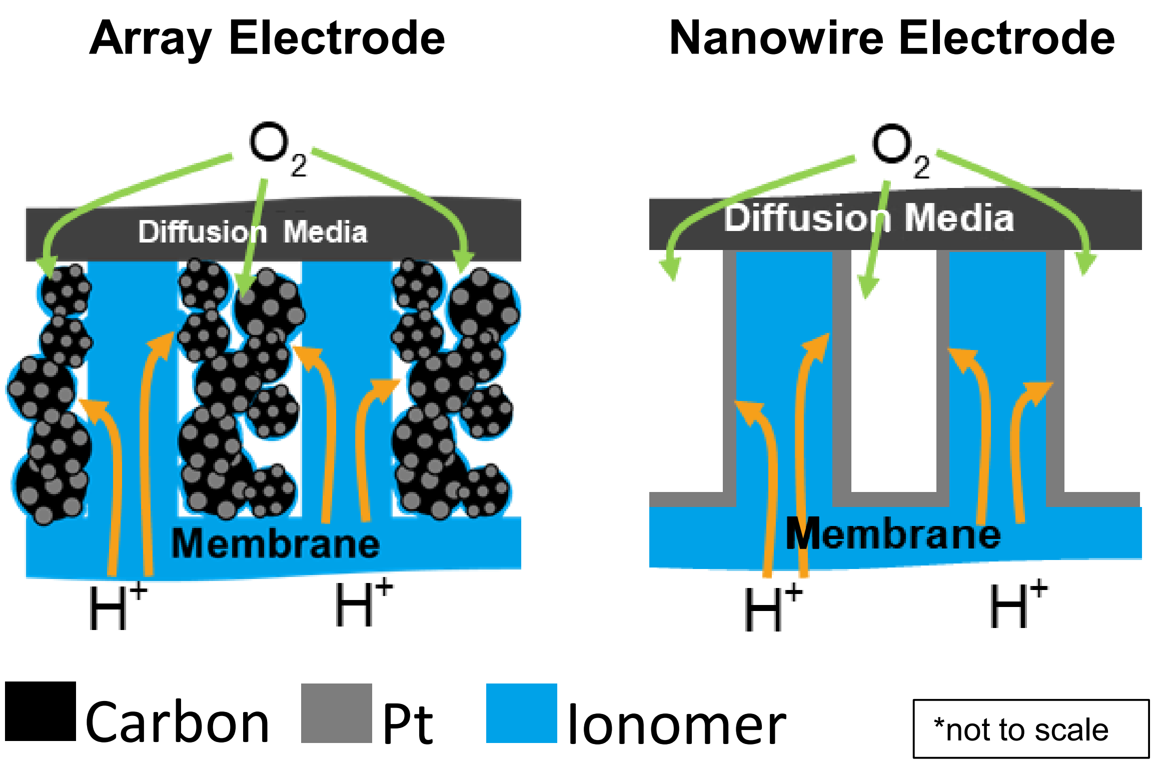
SEM elemental map

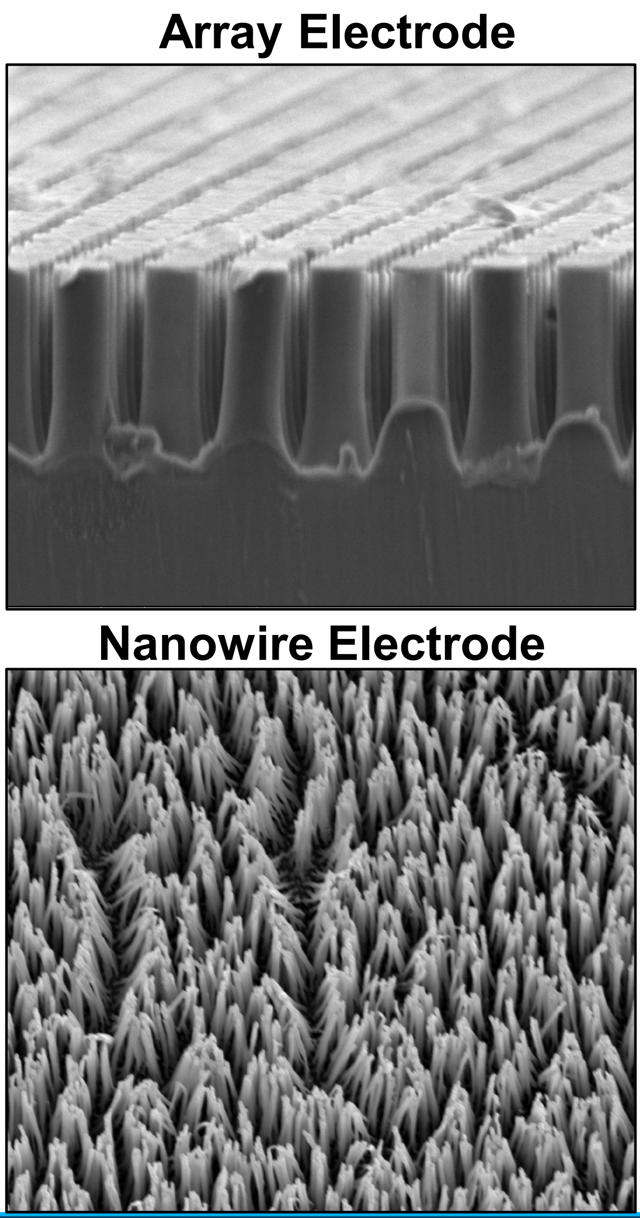
Umicore 0.1 mg PtCo/HSC - Bulk I:C 0.9





Ordered Array Electrode

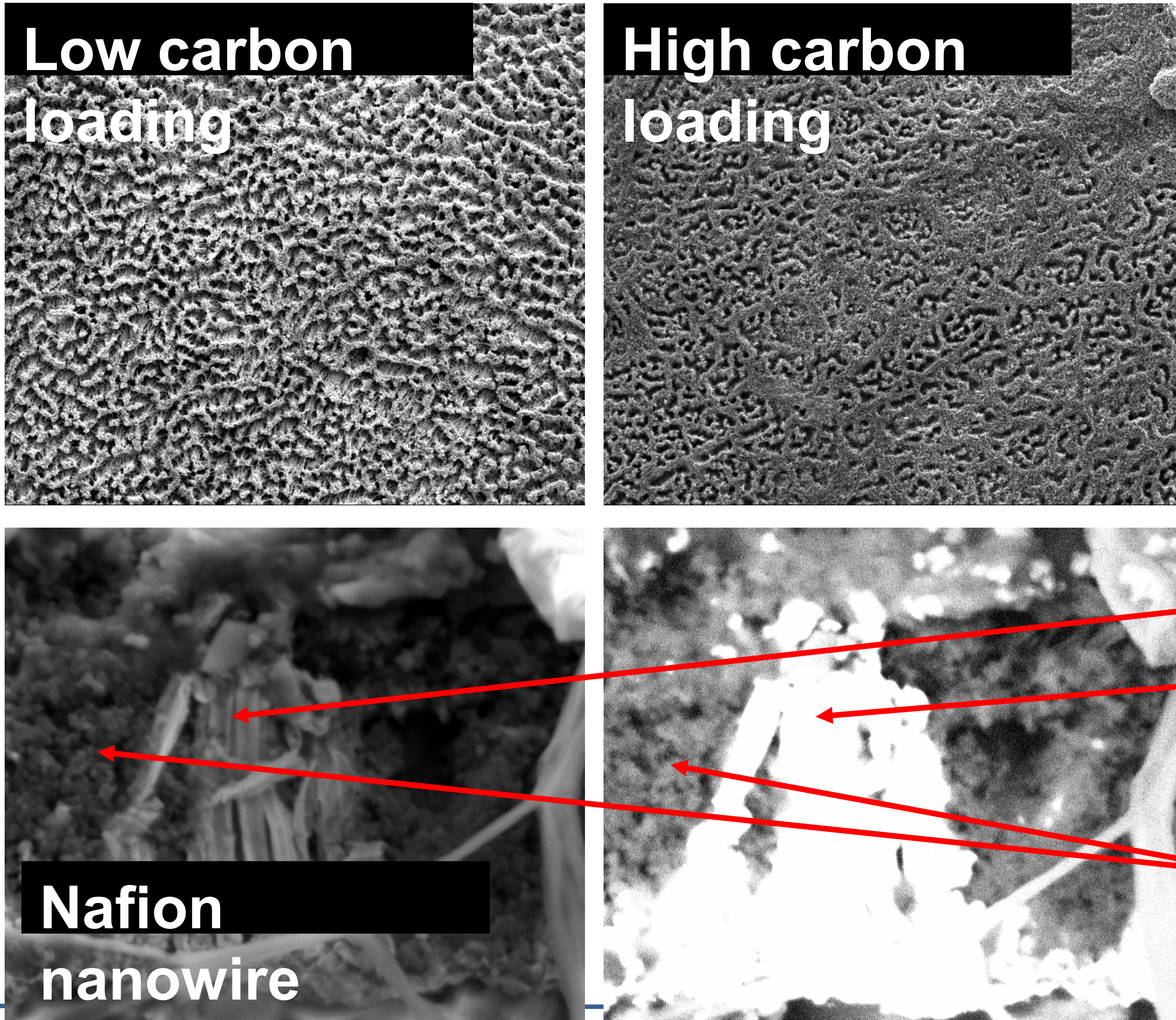




- Meso-structured electrode relies on vertically aligned ionomer channels for long-distance H+ transport
- Catalyzed elements can have reduced ionomer content

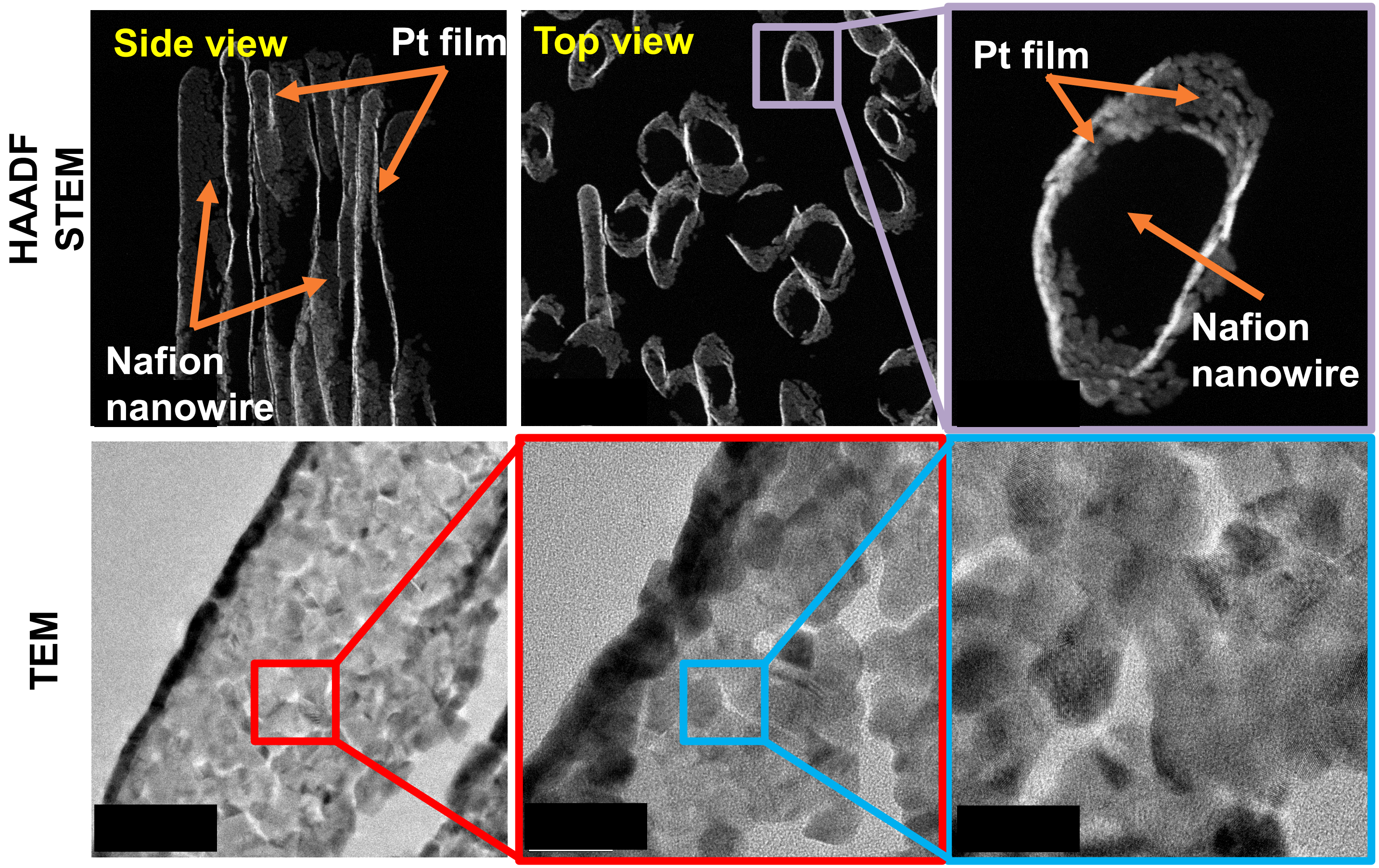
Nanowire Electrode: Carbon Filler in Void Space

Carbon filler - Vulcan (XC-72)



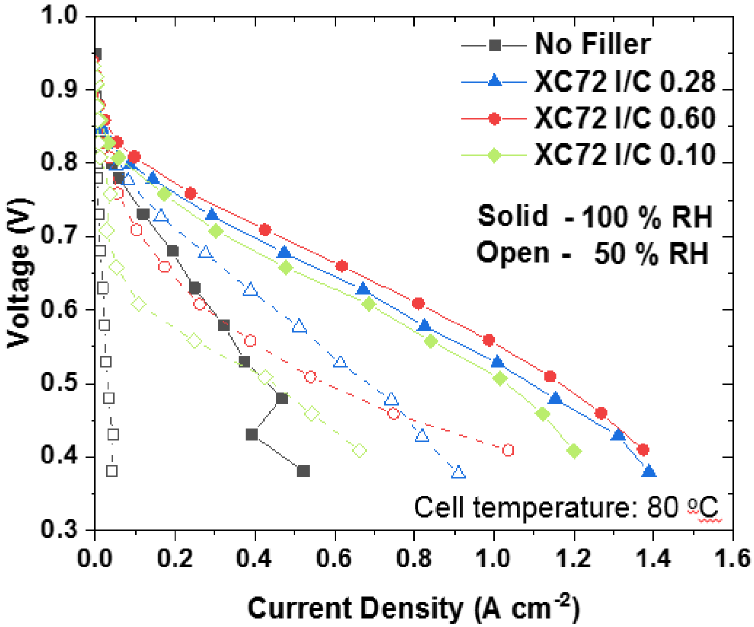
- Carbon filler used to fill void space and provide mechanical support
- Cross-sections reveal that filler helps prevent nanowire collapse during cell compression

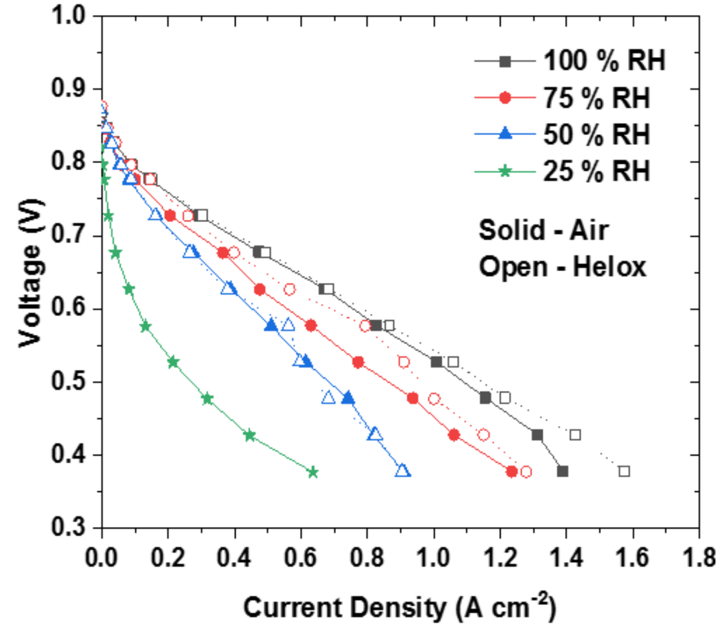
Pt Film on Nafion Nanowire



- STEM and TEM images reveal thin conformal coating of Pt surrounding Nafion nanowires
- Pt forms separate crystallites during deposition; crystallites merge as loading increases

Filler Carbon Stabilizes Structure – Transport not limiting





- Cathode loading: 0.15 mg_{Pt} cm^{-2}
- Vulcan (XC-72) with I/C = 0.28

Electrode	ECSA ($m_{Pt}^2 g_{Pt}^{-1}$)	Roughness ($cm_{Pt}^2 cm_{geo}^{-2}$)
No Filler	15.1±0.07	25.6±0.12
Vulcan Filler (0.28)	15.0±0.16	22.4±0.24
Vulcan Filler (0.60)	13.5±0.05	25.9±0.01
Vulcan Filler (0.10)	10.7±0.21	21.0±0.42

- Carbon filler enables improved performance
- Further development of electrode structure to prevent nanowire bundling is needed

Collaborations (FOA-1412 Partners)

- Core FC-PAD team consists of five national labs
  - Argonne, Lawrence Berkeley, Los Alamos, Oak Ridge and NREL
  - Materials, data and students frequently travel between labs

Interactions with DOE-awarded FC-PAD Projects (FOA-1412)
POC assigned for each project to coordinate activities with PI
FC-PAD work related to those presented in those AMRs

FC155: 3M - PI: Andrew Haug – FC-PAD POC: Adam Weber
FC156: GM - PI: Swami Kumaraguru – FC-PAD POC: K.C. Neyerlin
FC157: UTRC - PI: Mike Perry – FC-PAD POC: Rod Borup
FC158: Vanderbilt - PI: Peter Pintauro – FC-PAD POC: Rangachary Mukundan

- 30% of National Lab budget supports FOA projects
  - Equal support to each project
- Two in-person FC-PAD meetings held annually - include FOA members with individual sessions held to discuss interactions and progress

Collaborations (Non-FOA activities)

Institutions	Role
Umicore	Supply SOA catalysts, MEAs
UC Irvine	GDL imaging
University Carlos III of Madrid	Microscale simulations
TKK	Supply SOA catalysts
Johnson Matthey	Catalysts and CCMs
CEA (and ID-FAST EU Consortium)	Membrane studies
Ion Power	Supply CCMs
Xi'an Jiaotong University	CL mesoscale modeling
NIST – National Institute of Standards and Tech.	Neutron imaging
Simon Fraser University	Ionomer
University of Alberta	GDL and flowfield modeling; ink studies
US Drive	Mirai analysis
Xi'an Jiaotong University	CL mesoscale modeling
LEMTA, CNRS/Université de Lorraine	Shut-down/Start-up testing

Future Work: Heavy-Duty Applications

Heavy-Duty Deviations from Light-Duty (Durability & Efficiency)

- Much longer lifetimes (1,000,000 miles; 25,000-30,000 hrs)
- Different drive cycles compared with light-duty
  - Long-haul and delivery also have substantially differing drive cycles
- Focus on improved efficiency - higher operating temperatures (better kinetics), higher emphasis on lower stack power density (higher voltage)
- Cost targets are less stringent depending upon efficiency and durability payback

Initial FC-PAD Workscope

- Understand the heavy-duty fuel cell operating space and prioritize research directions
  - Examples include: more idle time, fewer start/stops (long haul), more time at high voltage, minimizing voltage clipping, understand efficiency hit due to gas crossover through membrane for extended idle, low-power operation with high-power extended spikes. Understand the effect of membrane additives, membrane thickness, catalyst particle size and catalyst alloying under heavy duty operating modes.
- Refine applicable models, characterization, and diagnostics to heavy-duty operating conditions & materials
- Develop refined ASTs for extended life-time prediction with appropriate heavy-duty materials and operating conditions

Planned activities on understanding of component properties, structures and transport phenomena is applicable to both light- and heavy-duty

Future Work: Component and Cell Understanding

Material and characterization studies

- Catalyst alloy studies including dissolution and high-potential kinetics
- Directly measure ionomer film properties and morphology on operating electrodes
  - TEM (EELS, EDS and tomography (4D STEM), GiSAXS, NR

Catalyst layer studies

- Continue exploration of different catalyst layer structures; low and moderate Pt loadings
  - Microstructural reconstruction and modeling for catalyst layers including multiphase flow
  - Understanding the size and impact of Pt/C aggregates and agglomerates
- Translational studies from ink to catalyst-layer structure
- Low-voltage cryo-STEM, AFM

Durability

- Evaluate external system component contaminants (e.g. Fe++) and mechanism for transport to MEA
- Characterize electrode microstructural changes as a result of ageing
- Local resistance analysis (e.g. O_2 and H_2 limiting current) related to impact of metal alloy catalyst leaching on ionomer transport resistance
- Evaluate catalyst loading comparison between light-duty and heavy-duty on MEA durability

Water and thermal management

- Modeling of water droplet detachment and GDL/channel interface
- Water visualization in operating cell components
- Integrate and evaluate various components to elucidate emergent phenomena
- Translational modeling going from ex-situ property data to operando performance

Summary

- **Relevance/Objective:**
  - Optimize performance and durability of fuel-cell components and assemblies
- **Approach:**
  - Use synergistic combination of modeling and experiments to explore and optimize component properties, behavior, and phenomena
- **Technical Accomplishments:**
  - Measurements and modeling effect of loading with durability potential cycling
  - Transport measurements during MEA conditioning evaluating carbon support effect
  - Evaluation of aggregate and agglomerates in catalyst layer by multiple complimentary techniques and their impact by microscale transport modeling
  - Evaluation of catalyst-ink solvent effect on catalyst layer structure and performance
  - Measured thin film ionomer structural changes in ionomer/water structure with cations
  - Operando measurements and modeling of Ce and Co profiles with applied potential
  - Developed catalyst-layer architectures with better transport and structural stability
- **Future Work:**
  - Greater focus on heavy duty applications, with greater emphasis on efficiency and durability
  - Continue to develop the knowledge base to improve catalyst layer structures and component integration for fuel cell performance, efficiency, and durability

What (Who) is FC-PAD? National Lab Contributors

Argonne National Laboratory

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Greg Kleen

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- Fuel Cells Program Manager & Technology Manager:
  - Dimitrios Papageorgopoulos
  - Greg Kleen

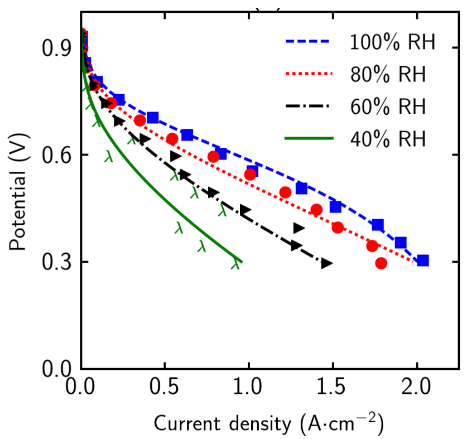
- Organizations we have collaborated with to date

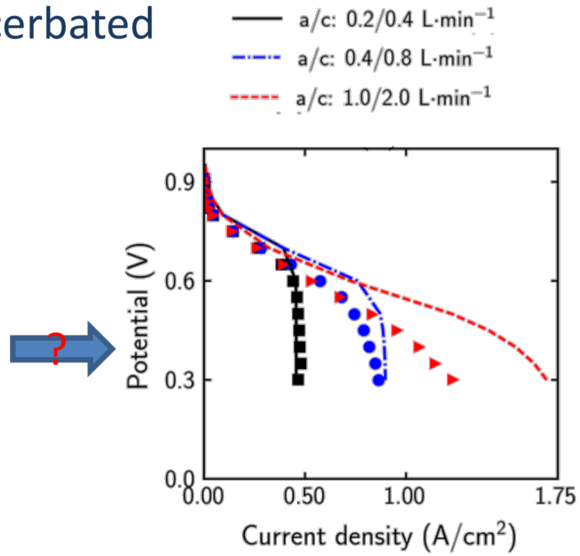
- User Facilities
  - DOE Office of Science: SLAC, LBNL-Advanced Light Source, ANL-Advanced Photon Source, LBNL-Molecular Foundry, ORNL-Center for Nanophase Materials Sciences, ANL-Center for Nanostructured Materials
  - NIST: BT-2

Technical Back-Up Slides

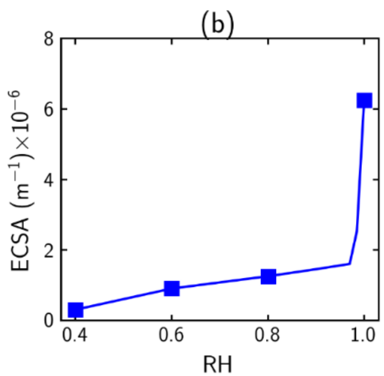
Macroscale Transport

- Models can be used to obtain critical parameters
  - Comparison of integral vs differential demonstrates that gas flow is important in integral and humidity changes are exacerbated

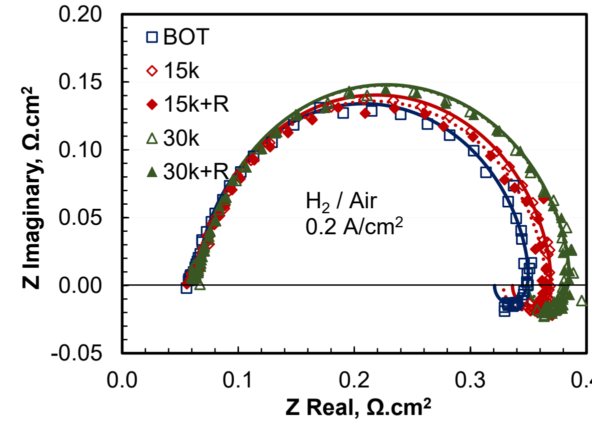


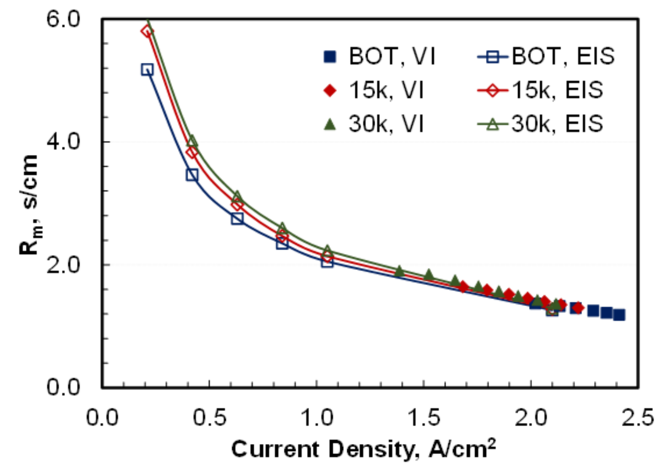


Functional form of surface area as a function of RH is elucidated



  - Impedance analysis allows for determination of local resistance
    - Only small growth after catalyst AST

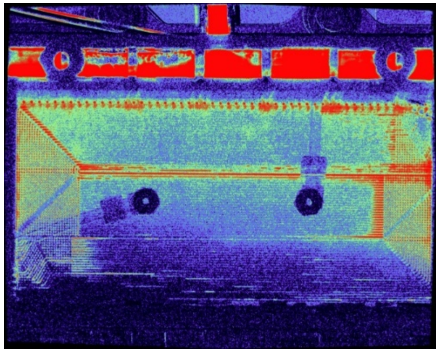




FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Water Imaging of Operating Short Stack (Mirai)
USCAR Matrix of Operating Conditions

50A



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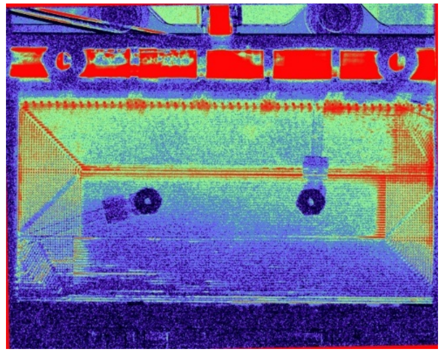

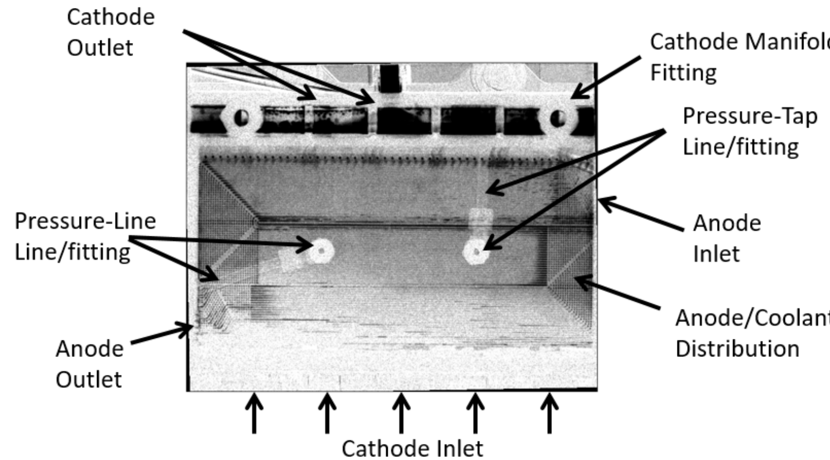

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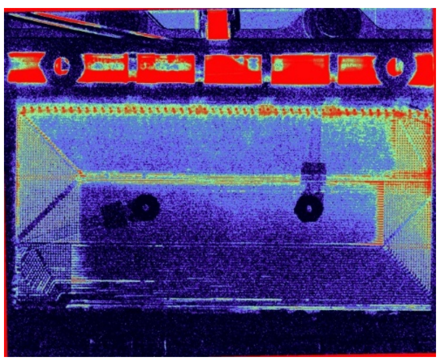

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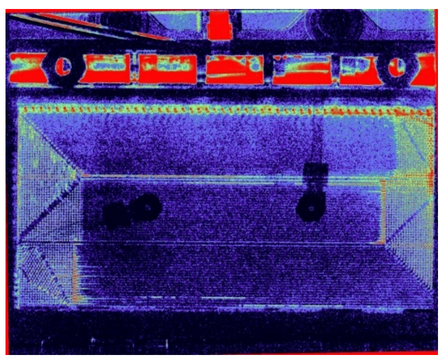
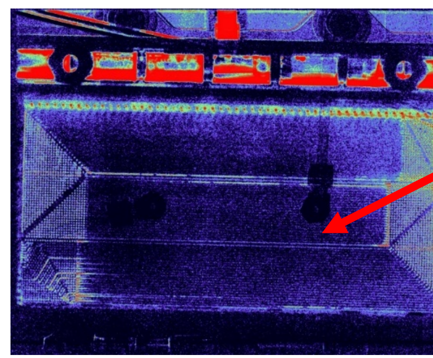


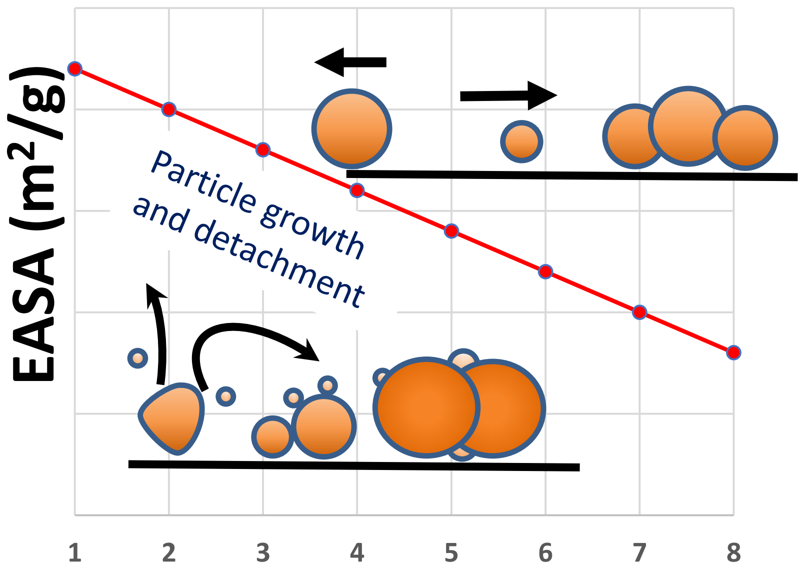
312A



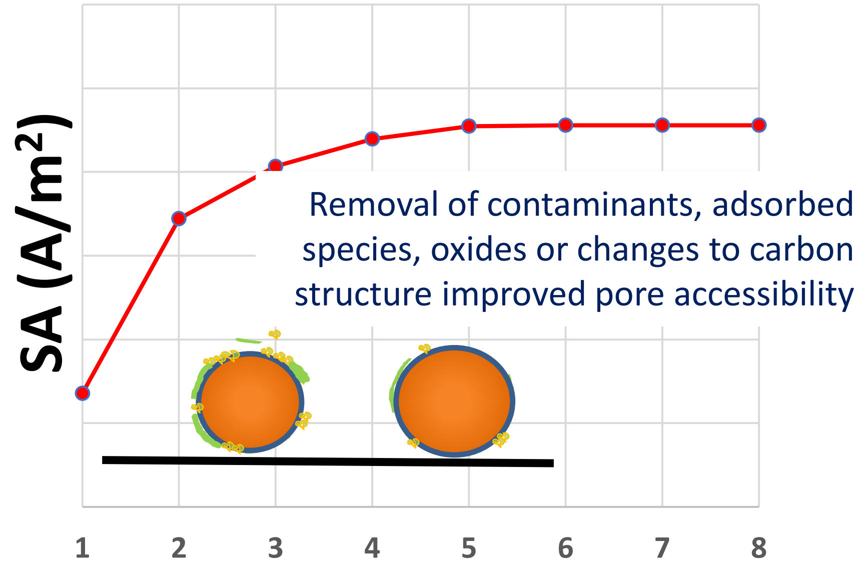
High Current & Flowrates show much less liquid water than low current/flowrates

- Liquid water primarily on Anode side; Stack water is primarily sensitive to anode flowrate
- All conditions show some water; especially at 2/3 serpentine interface and cathode outlet weld area
- Anode Inlet/outlet (and Cooling serpentine returns) show water build-up.

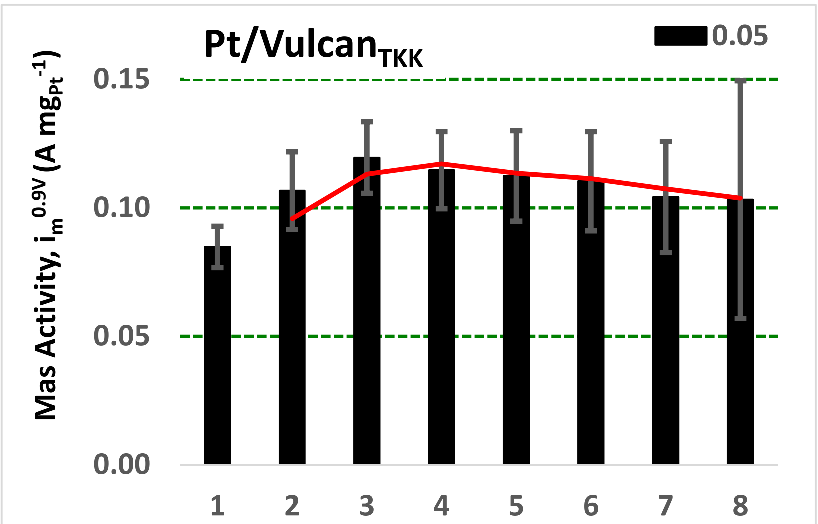
Effect of ECSA, Δδpt & Specific Activity on $i_m^{0.9V}$

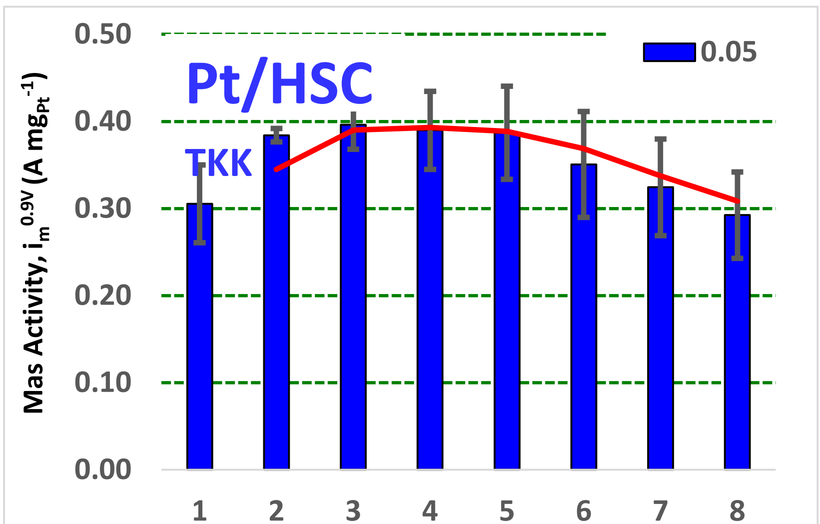


X



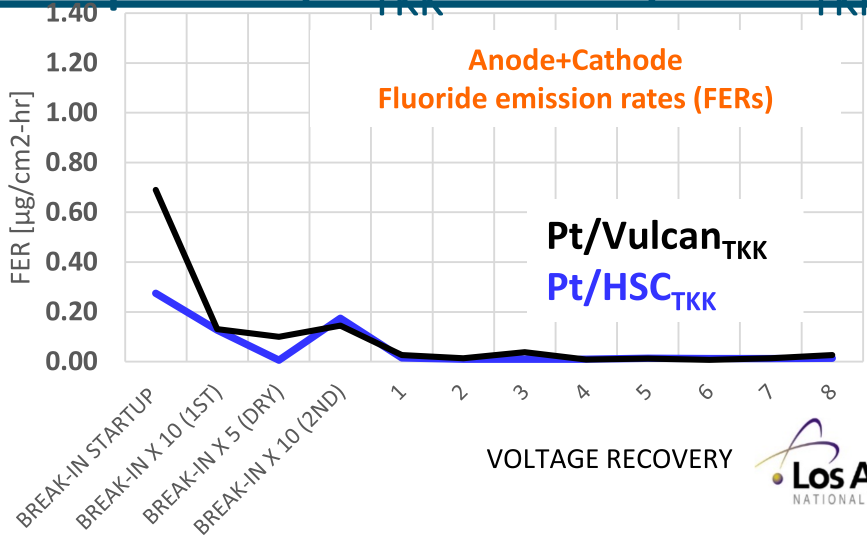
- Highest Mass Activity (m²/g) : optimal no. of active sites and activity per site

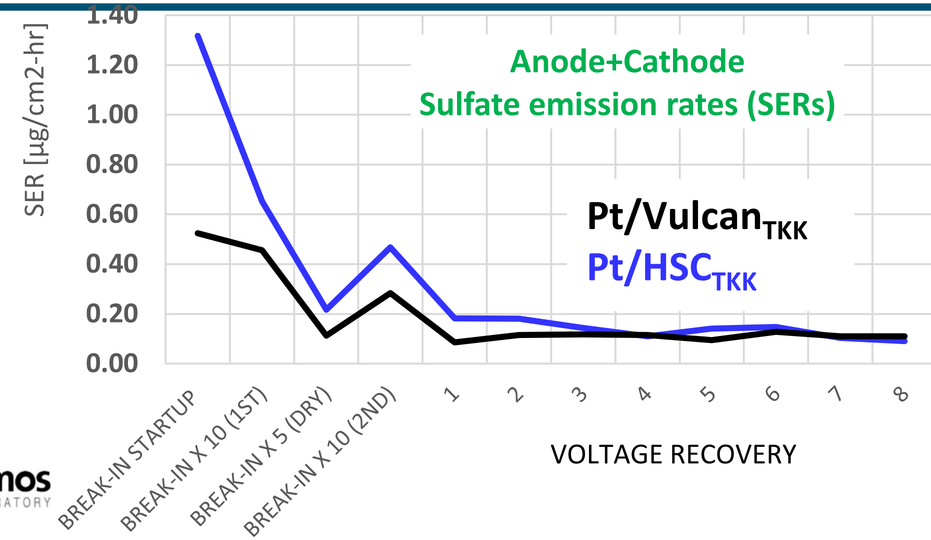




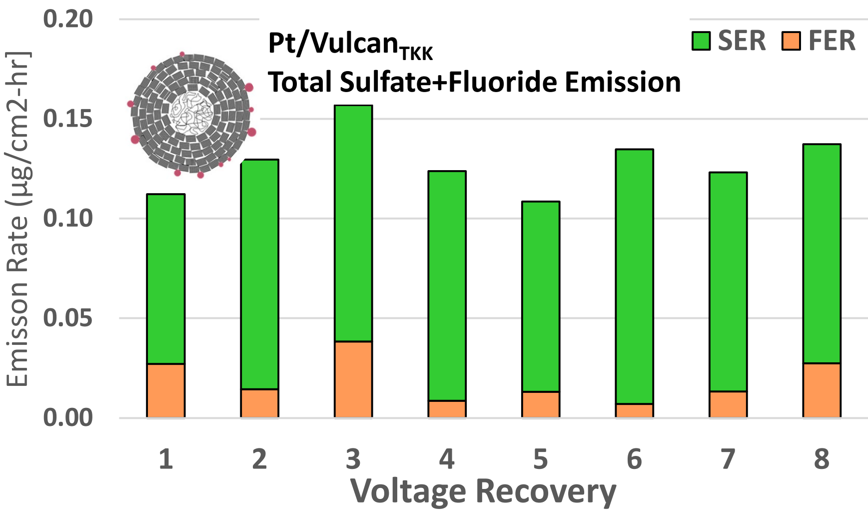
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

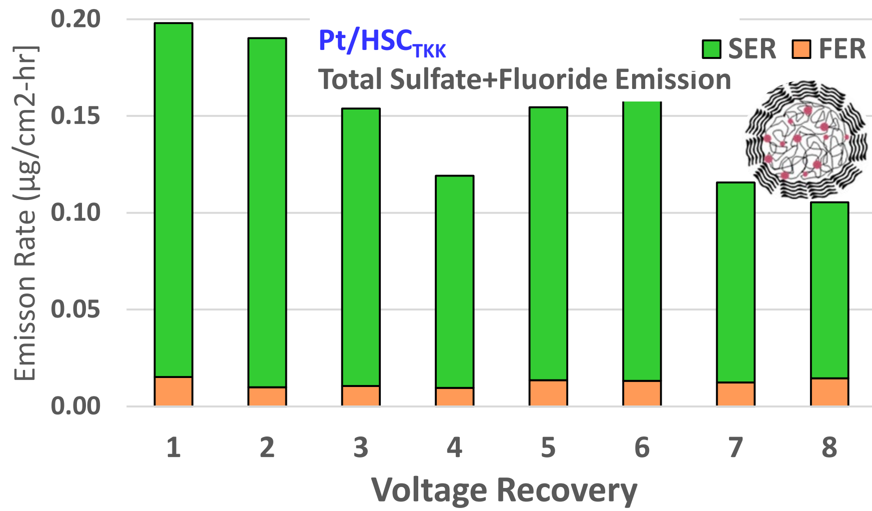
Effluent Emission Rates During Conditioning and Recovery Steps – Pt/V$_{TKK}$ and Pt/HSC $_{TKK}$





- ➢ **Majority of the sulfate and fluoride contaminants are released during the break-in**





- ➢ **Continual removal of total contaminants with consecutive VR cycles can have a positive impact on Specific activity --> lead to potential improvements in mass activity of the catalysts**

Ce Modeling Details Backup Slide

- Driving forces: cerium, solvent (subscript 0) gradient and migration

$$\boldsymbol{N}_{\mathrm{Ce}} = -\alpha_{\mathrm{CeCe}}\nabla\mu_{\mathrm{Ce,H}} - \alpha_{\mathrm{Ce0}}\nabla\mu_0 + \frac{t_{\mathrm{Ce}}}{z_{\mathrm{Ce}}}\frac{\mathbf{i}}{F}$$

$$\boldsymbol{N}_{\mathrm{H}} = -\alpha_{\mathrm{CeH}}\nabla\mu_{\mathrm{Ce,H}} - \alpha_{\mathrm{H0}}\nabla\mu_0 + \frac{t_{\mathrm{H}}}{z_{\mathrm{H}}}\frac{\mathbf{i}}{F}$$

$$\boldsymbol{N}_0 = -\alpha_{\mathrm{Ce0}}\nabla\mu_{\mathrm{Ce,H}} - \alpha_{00}\nabla\mu_0 + \xi\frac{\mathbf{i}}{F}$$

- Transport coefficients derived from Stefan-Maxwell treatment with bulk solution diffusion coefficients and hydrodynamic theory of flow in pores.
- Chemical potentials (ideal cerium and proton thermodynamics)

$$\mu_0 - \mu_0^{\mathrm{ref}} = RT\ln RH$$

$$\mu_{\mathrm{Ce,H}} - \mu_{\mathrm{Ce,H}}^{ref} = \mu_{\mathrm{Ce}} - \mu_{Ce}^{ref} - \frac{z_{\mathrm{Ce}}}{z_{\mathrm{H}}}\left(\mu_H - \mu_H^{ref}\right)$$

$$= RT\ln\frac{\frac{f_{Ce}}{z_{Ce}}}{\lambda} - \frac{z_{\mathrm{Ce}}}{z_{\mathrm{H}}}RT\ln\frac{1-f_{\mathrm{Ce}}}{\lambda}$$

- Relative humidity boundary condition on water
- Zero flux of cerium
- Applied potential

	Variable		Variable
$\boldsymbol{N_i}$	Species molar flux	z_i	Valance
α_{ij}	Transport coefficient	F	Faradays constant
μ_i	Chemical potential	ξ	Electroosmotic coefficient
$\mathbf{i}$	Current density	ref	reference
t_i	Transferenc e number	λ	Water content
f_{Ce}	Fraction cerium loading		