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

Presenters: Rod Borup, Karren More, Adam Weber

Thursday, June 14th 2018

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

Objectives

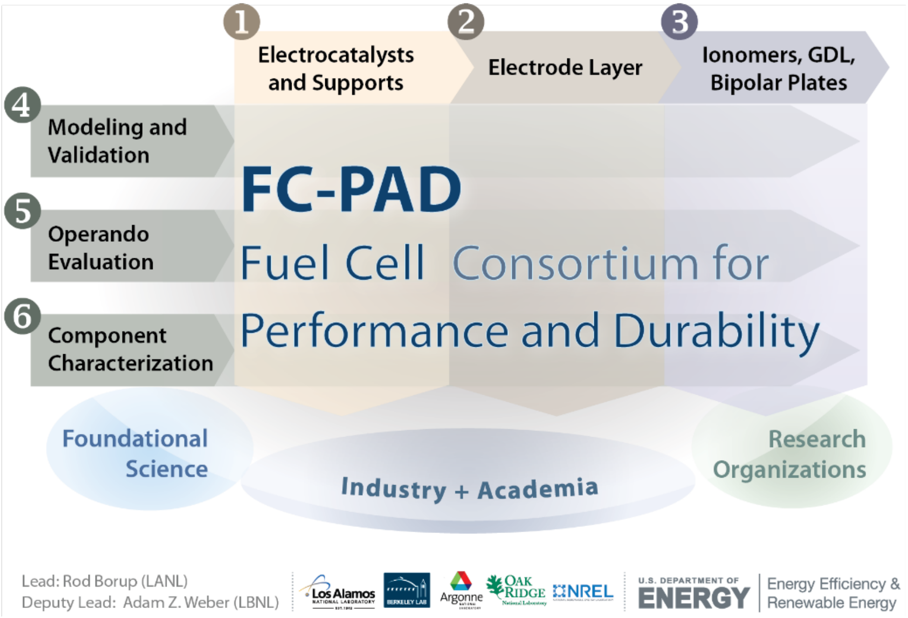
- Improve component stability and durability
- Improve cell performance with optimized transport
- Develop new diagnostics, characterization tools, and models

Consortium fosters sustained capabilities and collaborations

Core Consortium Team*

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

Structured across six component and cross-cutting thrusts



① Electrocatalysts and Supports

② Electrode Layer

③ Ionomers, GDL, Bipolar Plates

④ Modeling and Validation

⑤ Operando Evaluation

⑥ Component Characterization

FC-PAD

Fuel Cell Consortium for Performance and Durability

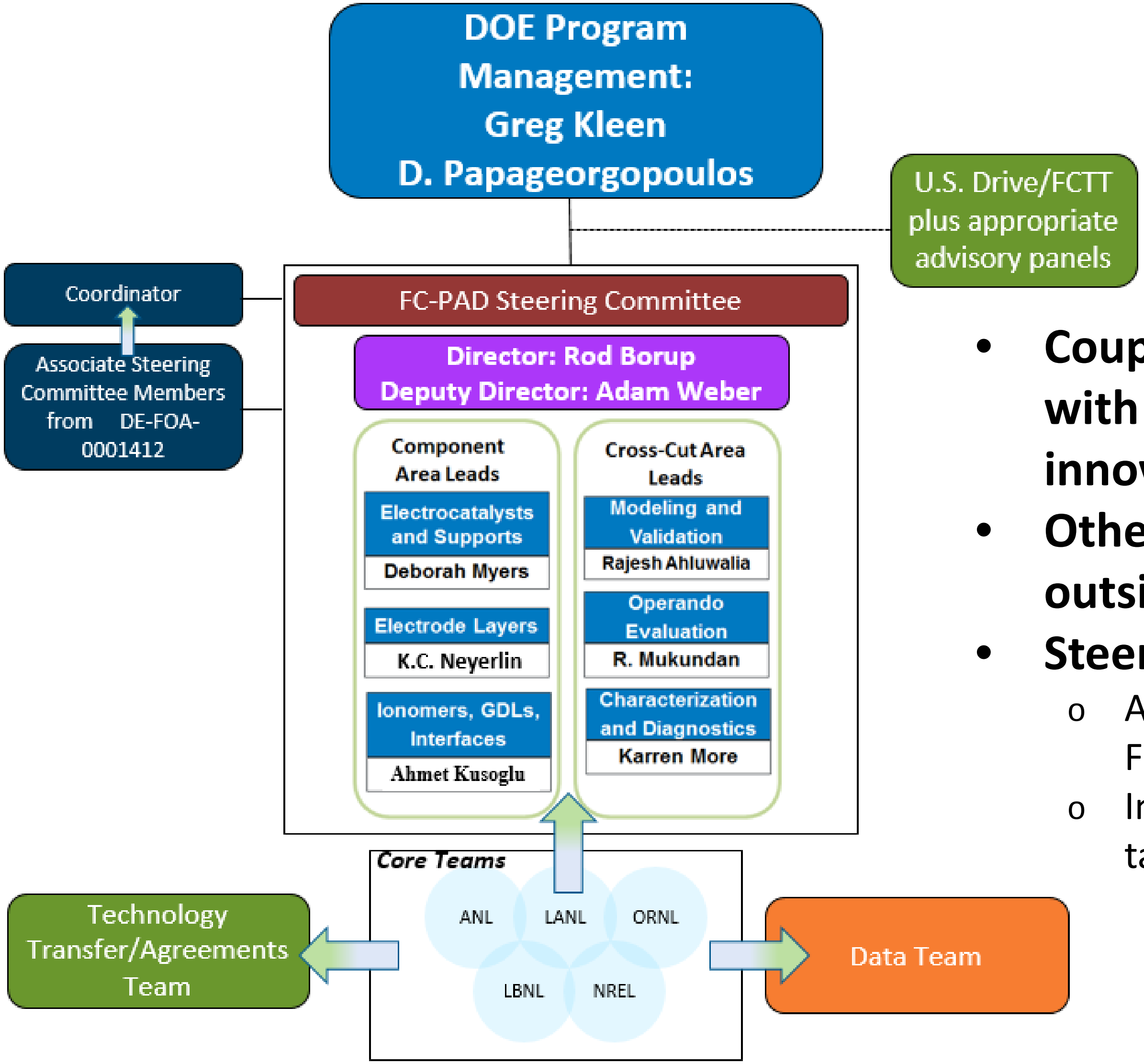
Foundational Science

Industry + Academia

Research Organizations

Lead: Rod Borup (LANL)
Deputy Lead: Adam Z. Weber (LBNL)

FC-PAD Organization

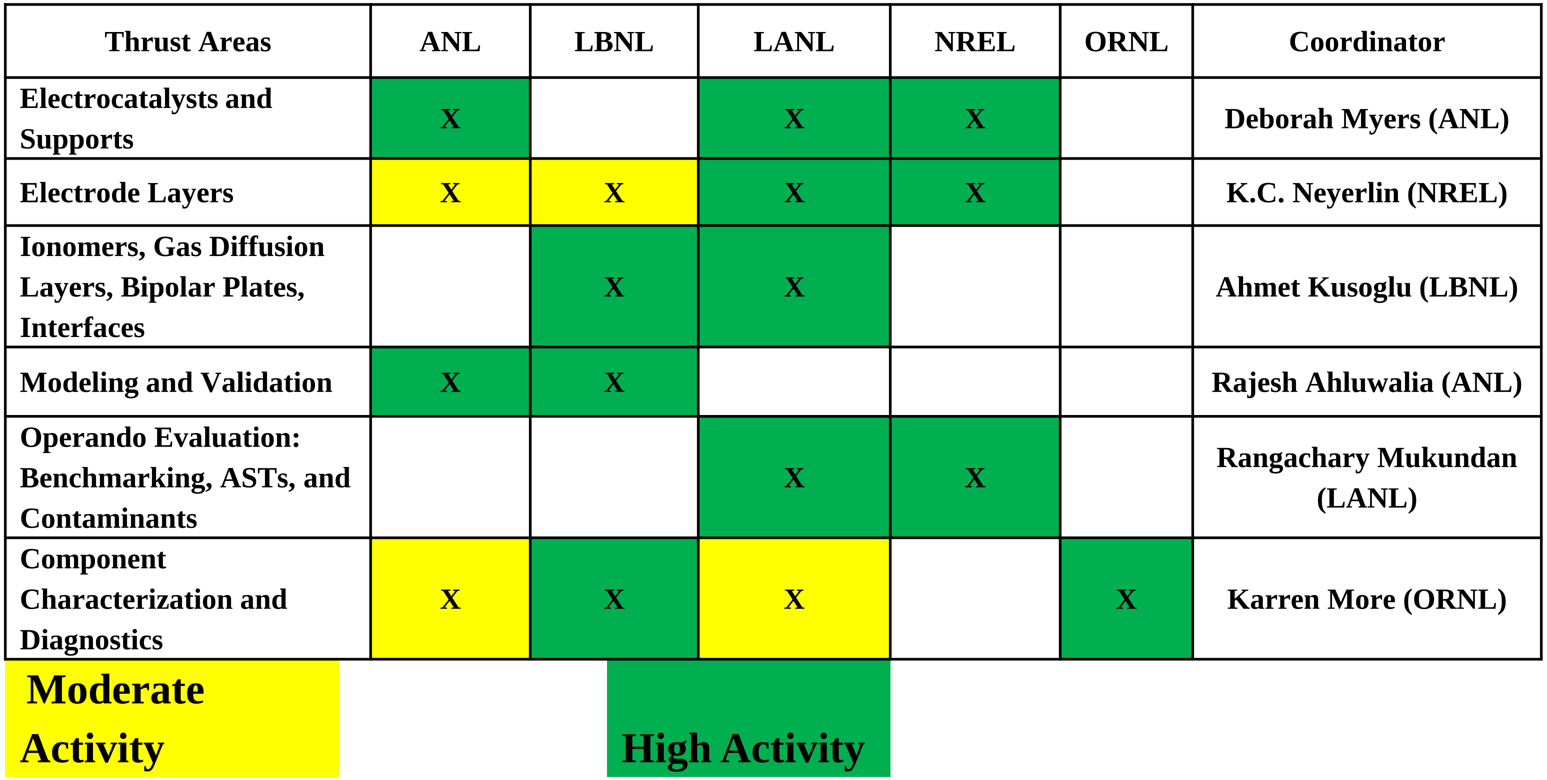


- **Couple national lab capabilities with future FOAs to foster innovative ideas and new research**
- **Other collaborations continue outside the FOA process**
- **Steering committee input**
    - Achieve consensus for no-cost, non-FOA collaborations from FC-PAD Core
    - Input on AOP (Annual Operating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

FC-PAD Thrusts, Coordinators, and NL Roles

DOE: **Dimitrios Papageorgopoulos**
Greg Kleen

Director: **Rod Borup**
Deputy Director: **Adam Weber**



Thrust Areas	ANL	LBNL	LANL	NREL	ORNL	Coordinator
Electrocatalysts and Supports	🟩 X		🟩 X	🟩 X		Deborah Myers (ANL)
Electrode Layers	🟨 X	🟨 X	🟩 X	🟩 X		K.C. Neyerlin (NREL)
Ionomers, Gas Diffusion Layers, Bipolar Plates, Interfaces		🟩 X	🟩 X			Ahmet Kusoglu (LBNL)
Modeling and Validation	🟩 X	🟩 X				Rajesh Ahluwalia (ANL)
Operando Evaluation: Benchmarking, ASTs, and Contaminants			🟩 X	🟩 X		Rangachary Mukundan (LANL)
Component Characterization and Diagnostics	🟨 X	🟩 X	🟨 X		🟩 X	Karren More (ORNL)

🟨 **Moderate Activity**

🟩 **High Activity**

- Coordination between thrusts
  - Thrusts do not stand alone; standardization of materials
  - Input from DOE, associate steering committee members, FCTT, AMR reviews
  - Support to FOA projects

FC-PAD Consortium - Overview & Relevance

Timeline

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

Budget

FY18 project funding: ~ \$4,000,000

As proposed: 5-year consortium with quarterly, yearly milestones & Go/No-Go

Total Expected Funding: Dependent upon budget allocation

Partners/Collaborations

(To Date Collaborations Only)

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

Barriers

- Cost: \$40/kW system;
  $\$14/\text{kW}_{\text{net}}$ MEA
- Performance @ 0.8 V: 300 mA / cm^2
- Performance @ rated power: 1,000 mW / cm^2 (150 kPa abs)
- Durability with cycling: 5,000 (2020) – 8,000 (ultimate) hours, plus 5,000 SU/SD Cycles

- **Mitigation** of Transport Losses
- **Durability** targets have not been met without system mitigation

- The **catalyst layer** is not fully understood and **is key in lowering costs** by meeting rated power.
- Rated power@ low Pt loadings reveals unexpected losses

FC-PAD Consortium – Relevance & Objectives

Overall Objectives:

- **Advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) at a pre-competitive level**
- **Develop knowledge base for more durable and high-performance PEMFC components**
    - Understand science of component integration
    - e.g. Ionomer interactions with carbon/interfaces between electrodes and GDL or membranes
- **Improve high current density performance**
    - 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: Overview

- **Develop knowledge base and optimize structures for more durable and high-performance PEMFC components**
- **Structured in 6 Thrust areas**
  - **Understand Electrode Layer Structures**
    - Advanced characterization techniques
    - Testing and diagnostics
    - Macroscale and Microstructure modeling
  - **Defining/Measuring Degradation Mechanisms**
    - Membrane: cation migration
    - Catalyst: Pt-alloy dissolution, carbon corrosion
  - **Novel Electrode Layer Design and Fabrication**
    - Ordered array electrode
    - Other concepts being investigated (not ready to report on)

Approach: Overview

FC-PAD Presentation: (One combined presentation)

- Overview, Framing, Objectives, Approach, Milestones
- Characterization of Commercial Components
- Durability: Membrane, Catalyst, Carbon Corrosion
- Performance – Novel MEA construction
- Thin film characterization
- Microstructural modeling

- **FOA-1412 Projects**
  - **FC155 (3M)**
  - **FC156 (GM)**
  - **FC157 (UTRC)**
  - **FC158 (Vanderbilt)**

FY2018 Q1, Q2 Milestone Status

QTR	Lab(s)	Progress Measures, Milestones, Deliverables	Comments
Q1	ANL, LBNL	Macroscale modeling converged for polarization behavior using scaled up properties from microstructural model. (LBNL, ANL) [From Q2 originally]	✓ Completed ✓ Data included in AMR
Q1	LANL	Carbon corrosion by direct CO_2 measurement comparison of 'identical' Pt/C and PtCo/C and comparison with thermal analysis stability	✓ Completed ✓ Data included in AMR
Q1	NREL, ORNL	Measurement of the effect of break-in processes on Pt/HSC, Pt/GrC and state-of-the-art PtCo/C activity, performance and resistance as well as catalyst layer morphology (NREL, ORNL, LANL, ANL)	✓ Completed ✓ Data included in AMR
Q2	ANL, LBNL, ORNL	Ionomer/solvent ink properties with 3M ionomer measured with three solvents of different dielectric constants and correlated to as-cast membrane film properties. Determine effects of three solvent compositions and sonication time of PtCo catalyst-ionomer inks on Co loss from catalyst, changes in catalyst atomic structure, and ink agglomerate structure. (ANL, LBNL, ORNL).	✓ Data included in AMR
Q2	LANL, NREL	Deliver/Deposit Pt by preferential CVD on at least three electrode templates (fabricated using electrospun nanofibers) to LANL from NREL. Characterize performance, access to active sites and local transport (NREL, LANL).	✓ Completed

FY2018 Q3, Q4 Milestone Status

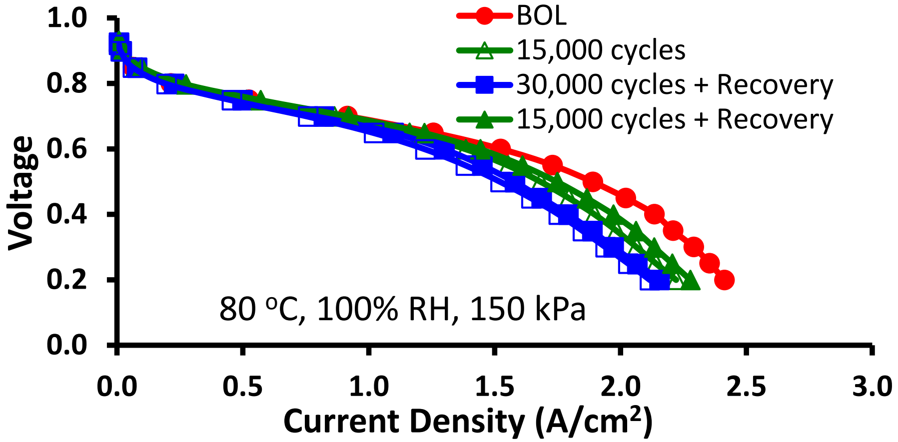
QTR	Lab(s)	Progress Measures, Milestones, Deliverables	Comments
Q3	ANL, LBNL, LANL, NREL, ORNL (All)	Establish correlation between in situ and ex situ examinations of cation effect on transport; quantify how applicable ex situ measurements are for in situ performance. Water uptake (ellipsometry), morphology (GISAXS and NR), and oxygen transport (microelectrode) measured for 2 different Nafion thin film thicknesses (between 10 and 150 nanometer) with 2 different Ce and Co doping levels determined by leaching rates and verified by microscopy. Measure O_2 and H_2 limiting current at 3 different RHs 25, 50, 100%. (LANL, ORNL, ANL, LBNL, NREL)	✓ In Progress/on track ✓ Data included in AMR
Q4	ANL, LBNL, LANL, NREL, ORNL (All)	Definition of the allowable cation contaminant level (e.g. Ce or Co) to limit performance degradation to 10% due to reduction of either proton conduction or oxygen transport from the cation/ionomer interactions. Provide a method to keep cation related performance reduction to 10%. (LANL, ORNL, ANL, LBNL, NREL)	✓ In Progress/on track ✓ Data included in AMR

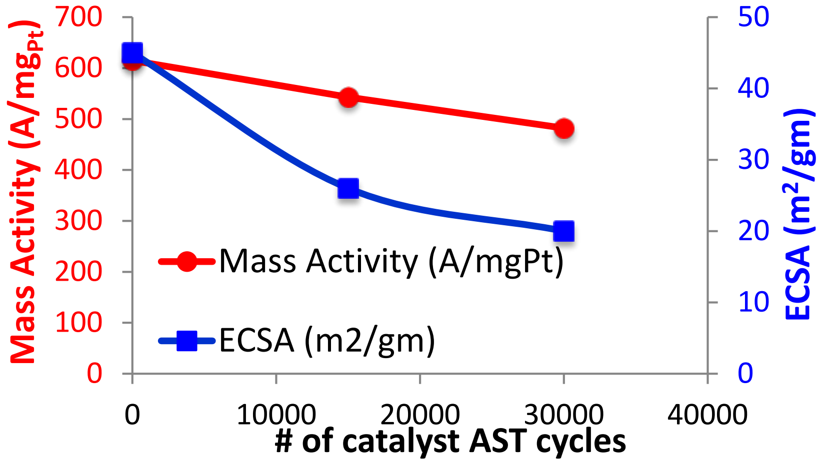
Approach: Durability

- **Results intended to guide component, cell, and stack development efforts to improve durability by identifying degradation mechanisms**
- **MEA durability is primary concern,**
  - Durability of other stack components, including bipolar plates……

- **Materials-based solutions to decrease degradation**
- **Component microstructure stability in three-phase region of reactant gas, electrolyte, and catalyst and impact of microstructure on durability**
- **Catalyst layer stability, including support stability, and methods to decrease support corrosion and compaction while maintaining appropriate pore structures**
- **Durability/aging and evolution of transport properties and phenomena**
- **Characterization of degradation phenomena in state-of-the-art membranes**
- **Identifying and characterizing degradation mechanisms associated with contaminants (e.g. Co leaching from alloy catalysts)**
  - Membrane/catalyst – cation migration (Co/Ce)
  - Catalyst – particle grown/alloying agent leaching/kinetic and transport losses
  - Catalyst support – alloying effect on carbon corrosion

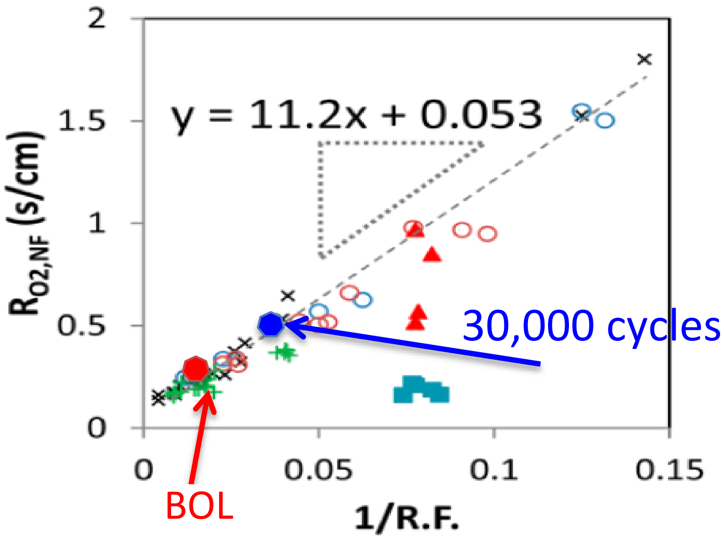
PtCo Alloy Catalyst Degradation



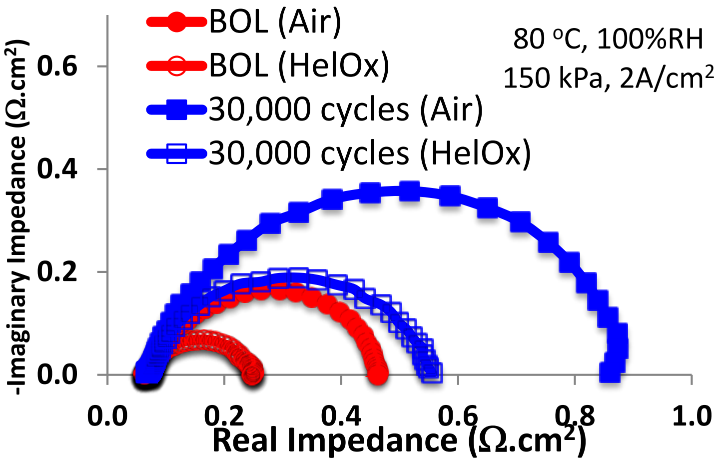


- **Small losses in low current region**
- **Larger losses in high current region**

- **ECSA loss due to particle size increase**
- **Mass activity loss due to Co leaching**

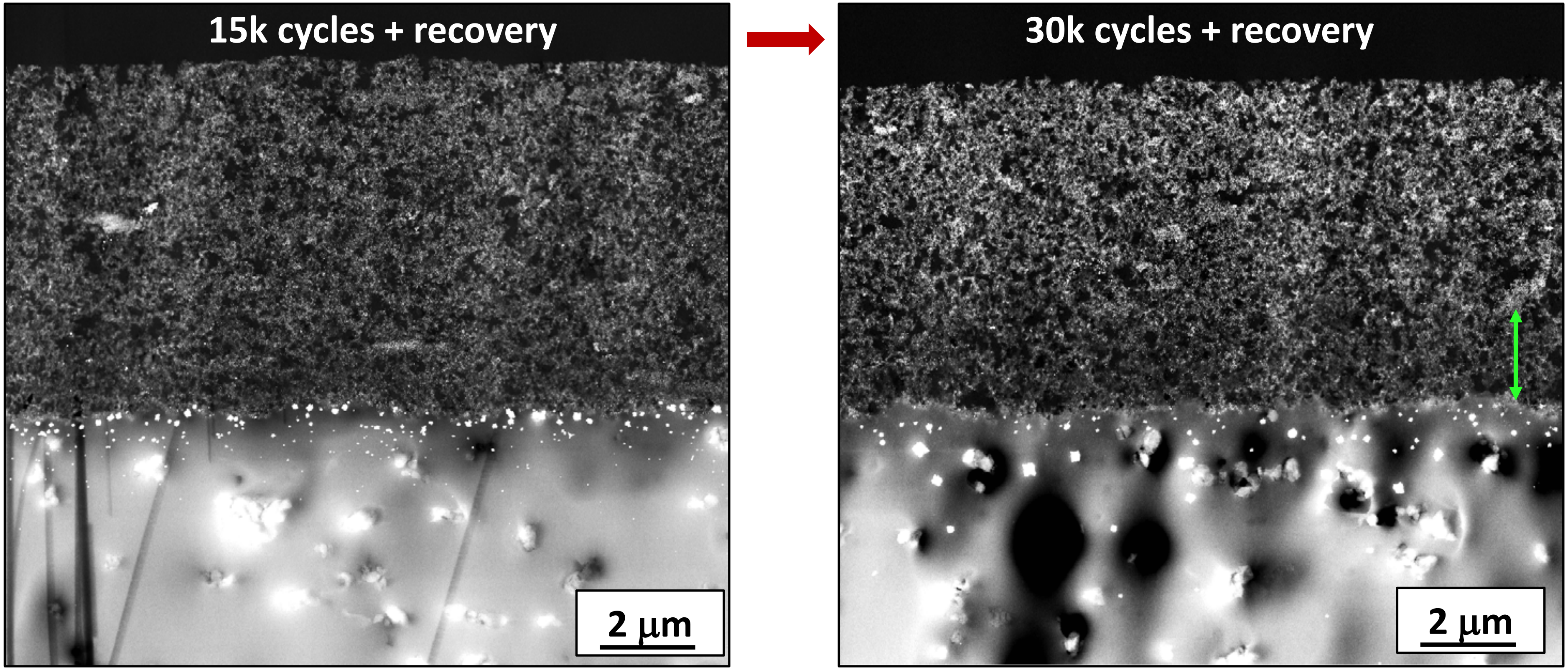


- **Local transport resistance increases**



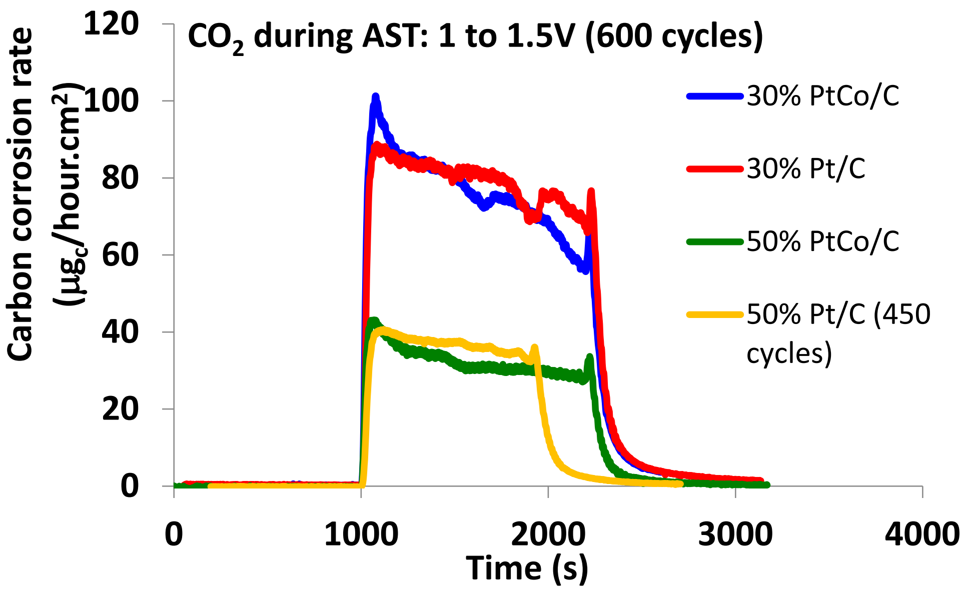
- **BOT : 75% MT losses recoverable in HelOx**
- **EOT : 40% MT losses recoverable in HelOx**

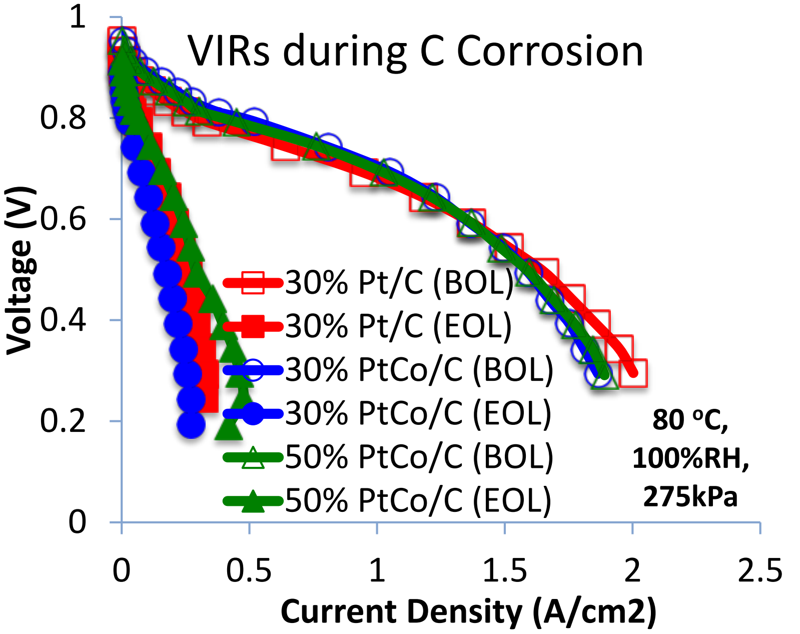
PtCo Alloy Catalyst Degradation



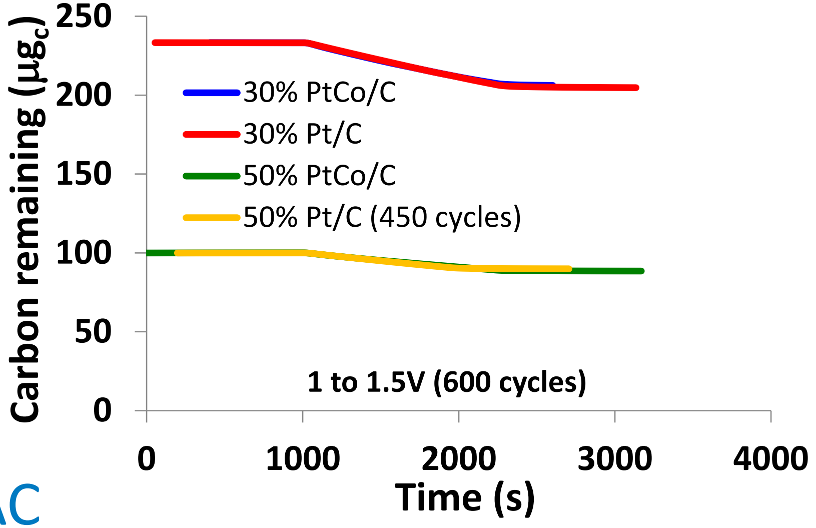
- Minimal CL *thickness* change
- Minimal CL *porosity* change
- Pt in membrane increases with cycles; ~2μm Pt-depleted zone after 30k cycles
- PtCo catalyst *size* (4.4nm vs. 5.5nm)
- Overall CL *composition* (Co:Pt 0.14 vs. 0.11)
- ***Mass activity loss due to Co leaching - partially recoverable***

Effect of Electrocatalyst Alloying on Carbon Corrosion



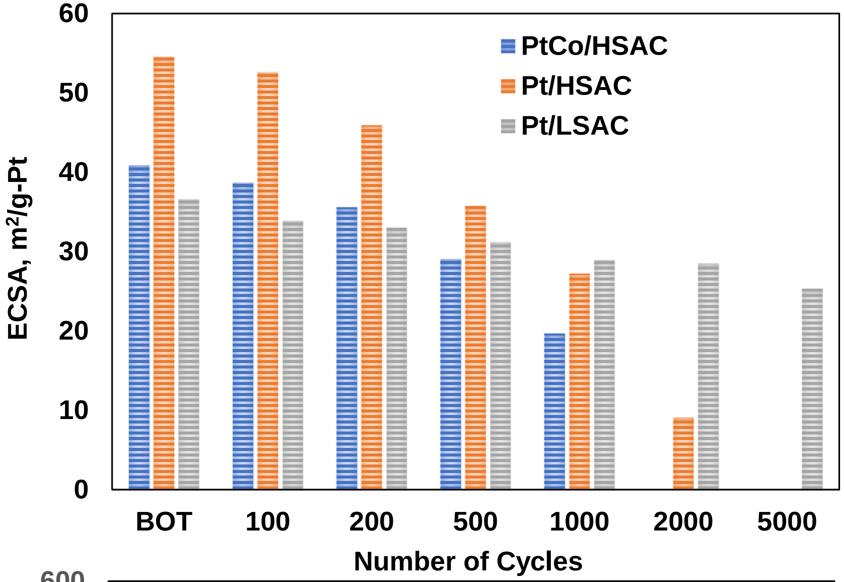


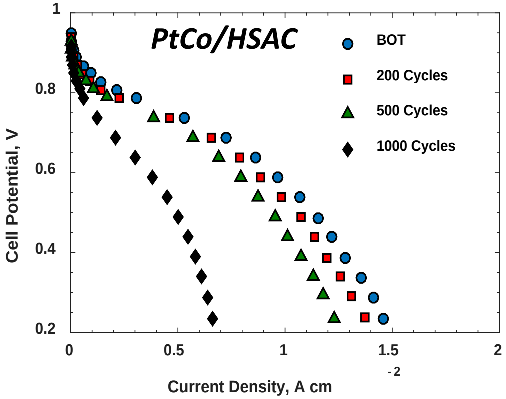
- Corrosion rate of Pt/C and PtCo/C are identical
- Corrosion rate of 50%Cat/C < 30%Cat/C
- Rate adjusted for total carbon is similar in 30% and 50%
- Alloy catalyst loses more performance than Pt catalyst even though corrosion rate is similar
- Mass transport limitations of alloy catalysts are worse than Pt catalysts at BOL
  - Exacerbated by C-corrosion

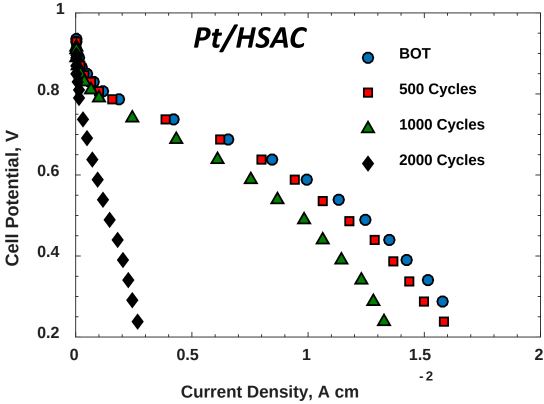


All carbons HSAC

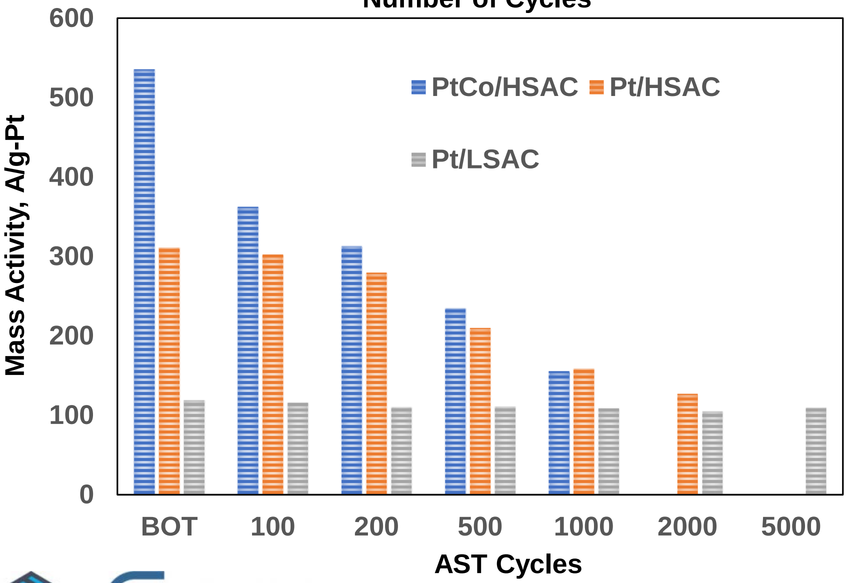
Catalyst Comparison during Carbon Corrosion







Pt/HSAC is more stable than PtCo/HSAC over 1000 cycles



Triangle Wave (1-1.5 V, 500 mV/s)

Distributed ORR oxide coverage kinetic model

- For Tafel kinetics, the ORR and CCL Ohmic overpotentials are separable

$$\eta_c = \eta_s^c + iR_\Omega^c\left(\frac{i\delta_c}{b\sigma_i}\right)$$

$$i = i_0 A_{Pt}(1-\theta)e^{-\frac{\omega\theta}{RT}}P_{O_2}^{\gamma}e^{\frac{\alpha nF}{RT}\eta_s^c}$$

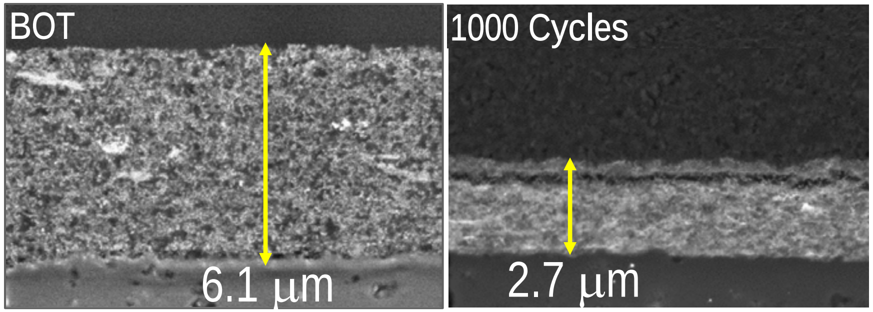
Losses after 1000 AST Cycles

Catalyst	ECSA (%)	MA (%)
PtCo/HSAC	52	71
Pt/HSAC	50	49
Pt/LSAC	21	8

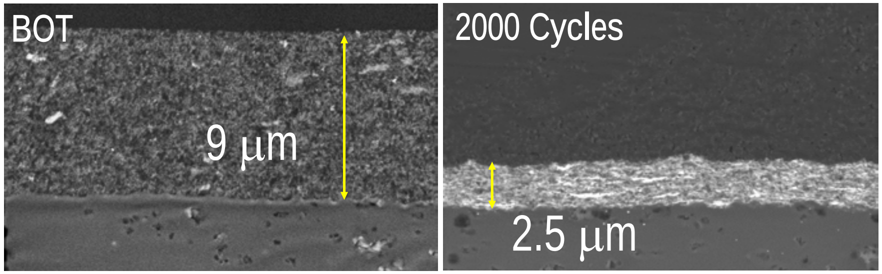
*Molar composition of Co in Catalyst: BOT / EOT

Changes in Electrode Microstructure

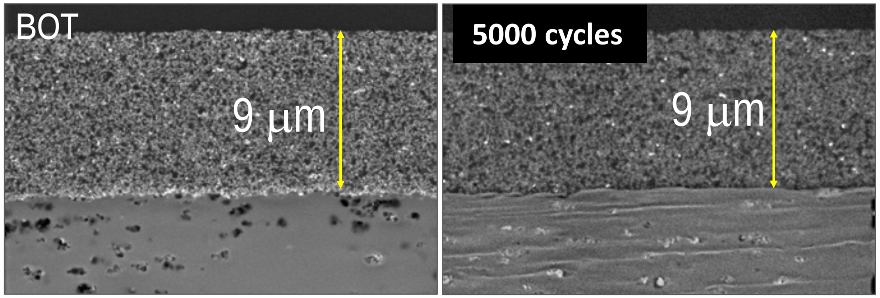
CCL Thickness



PtCo/HSAC

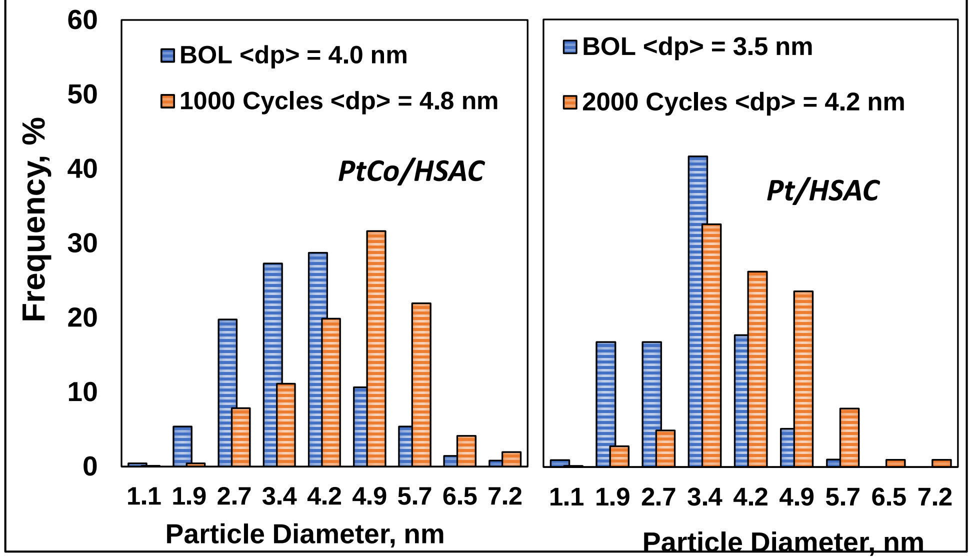


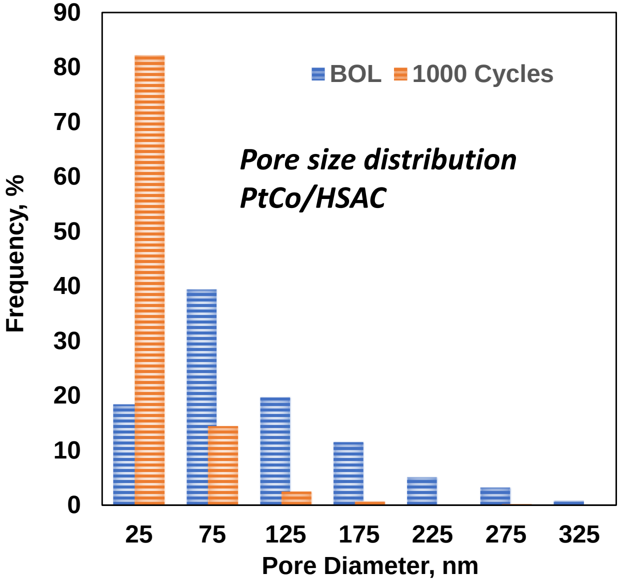
Pt/HSAC



Pt/LSAC

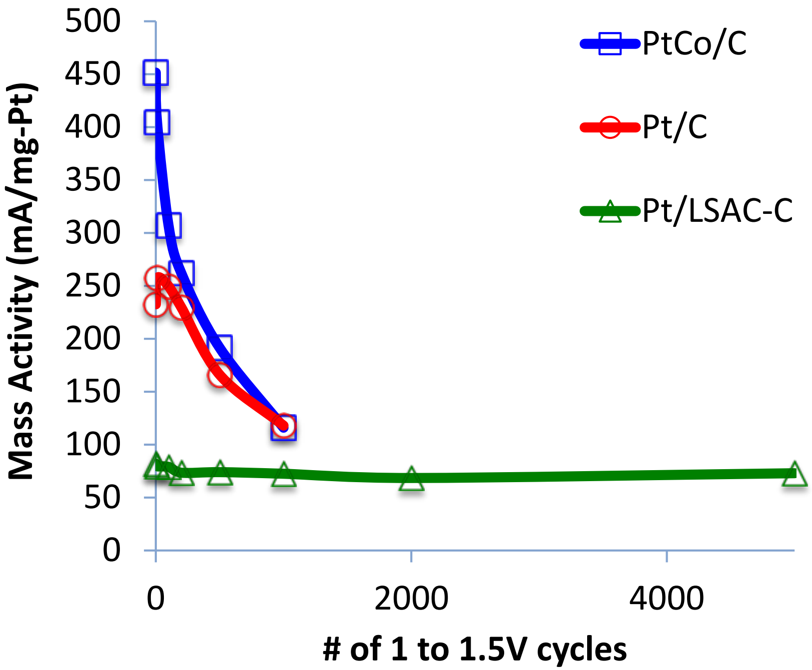
Particle Size Distribution

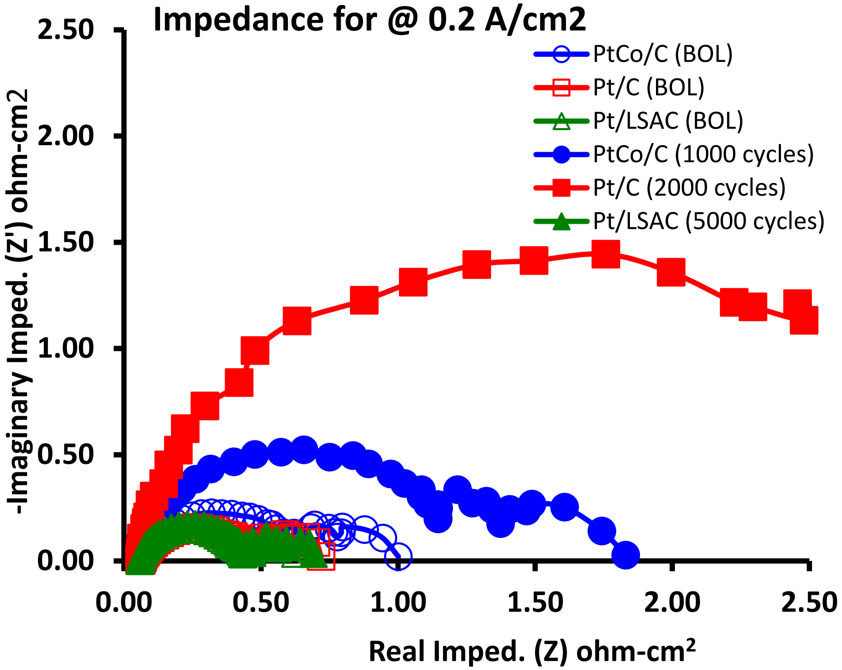




Moderate growth in catalyst particle size in HSAC electrode after 1000 cycles, but larger secondary pores have collapsed

Mass activity and Performance Losses





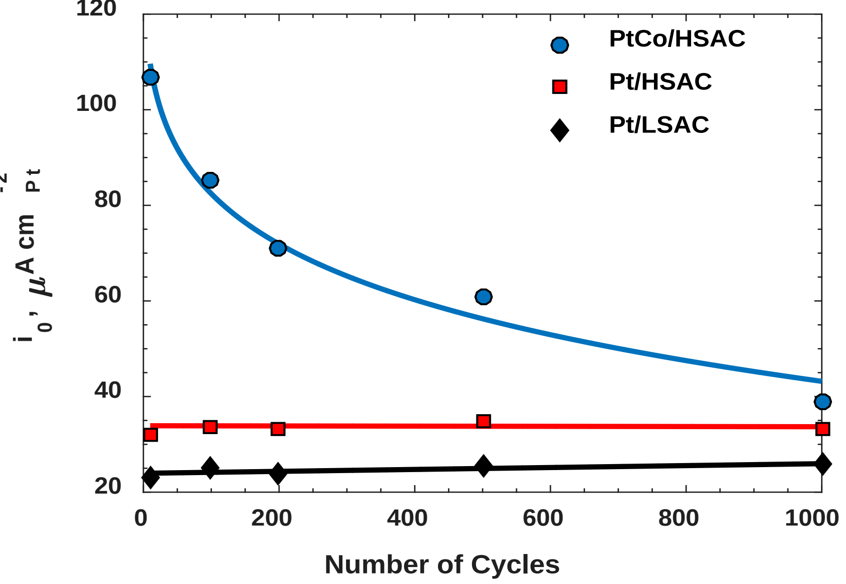
- ECSA loss tracks tracks particle size increase for Pt/C (3.5 to 4.2nm) and PtCo/C (4 to 4.8nm)
- Mass activity loss of PtCo is a lot higher due to Co leaching (Pt:Co changes from 76:24 to 84:16)

- Kinetic Resistance @ BOL : Pt/LSAC > Pt/C > PtCo/C (Open symbols)
- Kinetic resistance @ EOL: Pt/C (2000 cycles) > PtCo/C (1000 cycles) > Pt/LSAC (5000 cycles)
- Mass transport @ BOL PtCo/C > Pt/C > Pt/LSAC

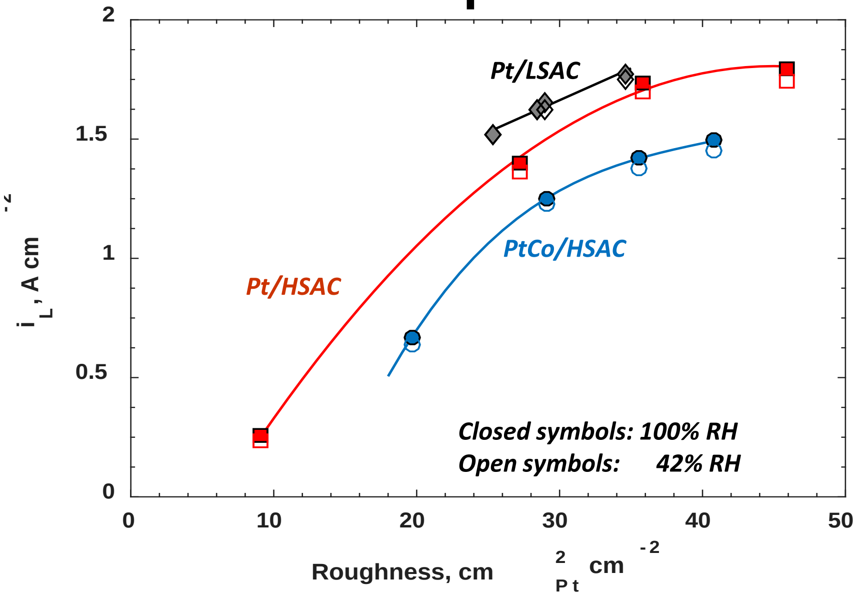
- Kinetic region: PtCo/C has much higher resistance after corrosion experiment
- Mass transport region: Similar result but even at BOL Pt/C is better than PtCo/C

Breakdown of Electrode Losses

Kinetic Losses

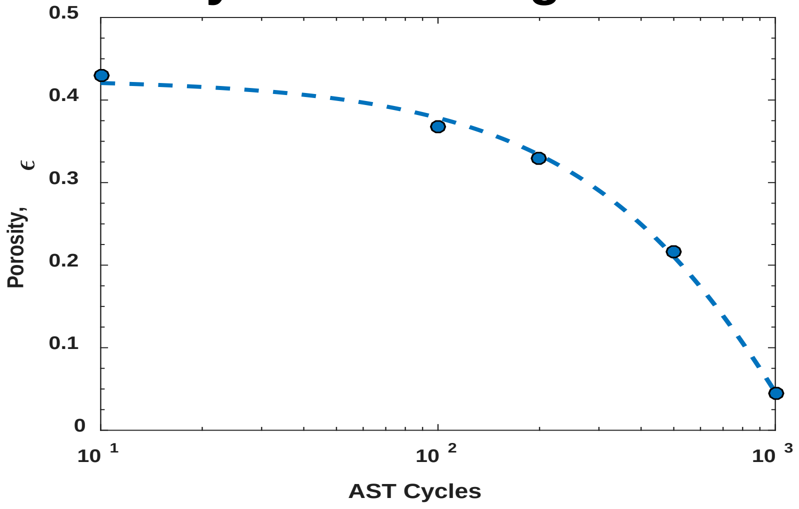


Mass-Transport Losses

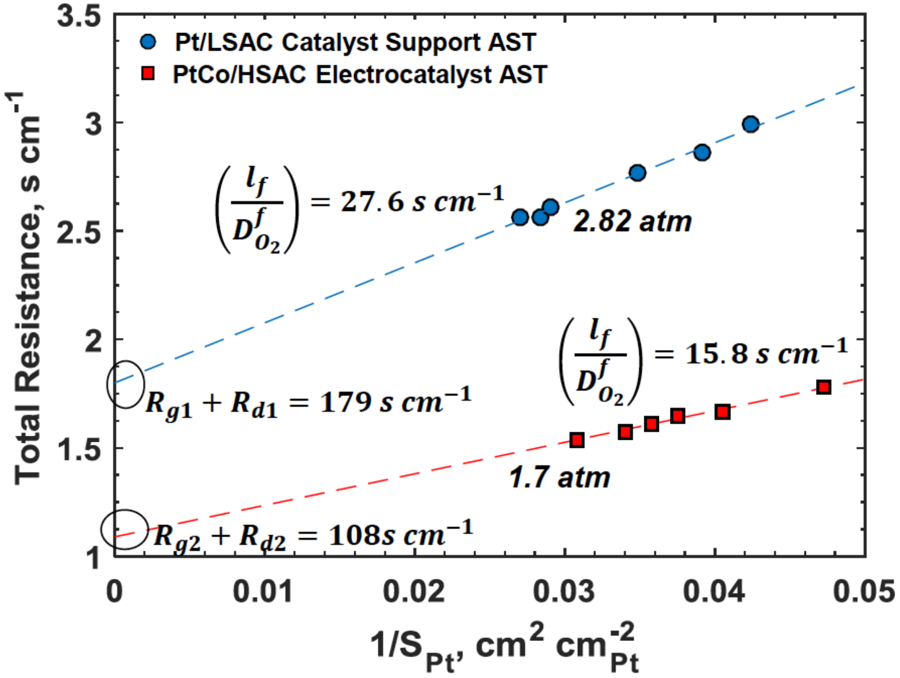


- Kinetic losses during carbon corrosion due to Co leaching from active catalyst
- Increased local transport resistance due to loss in surface area (ECSA)
    - Pt and PtCo HSAC show additional transport losses
- Porosity as function of AST cycle estimated assuming constant carbon corrosion rate and knowing initial and final CCL thickness/porosity

Porosity Loss During Corrosion



Modeling of Ionomer Film Resistance (R_f)



Assume small changes in CCL thickness in catalyst AST and support AST for Pt/LSAC

- ☐ Film resistance controls O_2 transport in CCL:

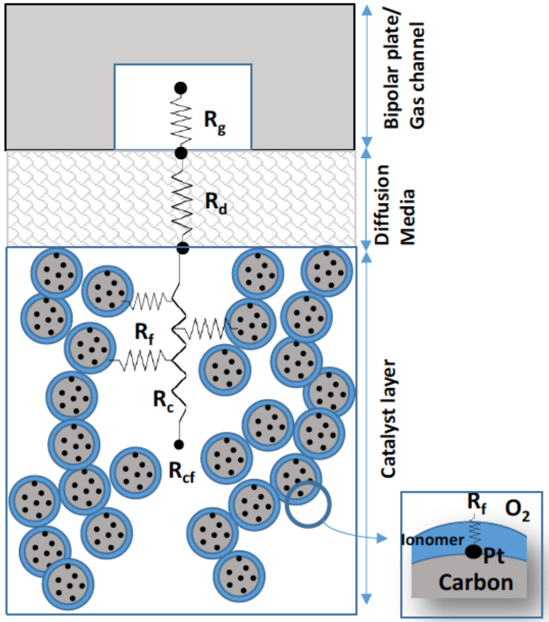
$$R_f \gg R_c$$

$$R_m = \frac{4FC_{O_2}}{i_L} = R_g + R_d + R_f$$

$R_f = 27.6\ s\ cm^{-1}$ Pt/LSAC; $15.8\ s\ cm^{-1}$ PtCo/HSAC

- ☐ GDL has remained stable

$$\frac{R_{g1} + R_{d1}}{P_1} = \frac{R_{g2} + R_{d2}}{P_2} = 63.5\ s\ cm^{-1} atm^{-1}$$



Electrode resistance from 1D macro-homogenous model for O_2 transport in CCL

$$R_{cf} = \left(\frac{R_c}{\beta}\right) \coth\beta\ ;\ R_c = \left(\frac{l_c}{D^c_{O_2}}\right); R_f = \left(\frac{l_f}{D^f_{O_2} S_{Pt}}\right)$$

$$\beta = \sqrt{\frac{R_c}{R_f}}$$

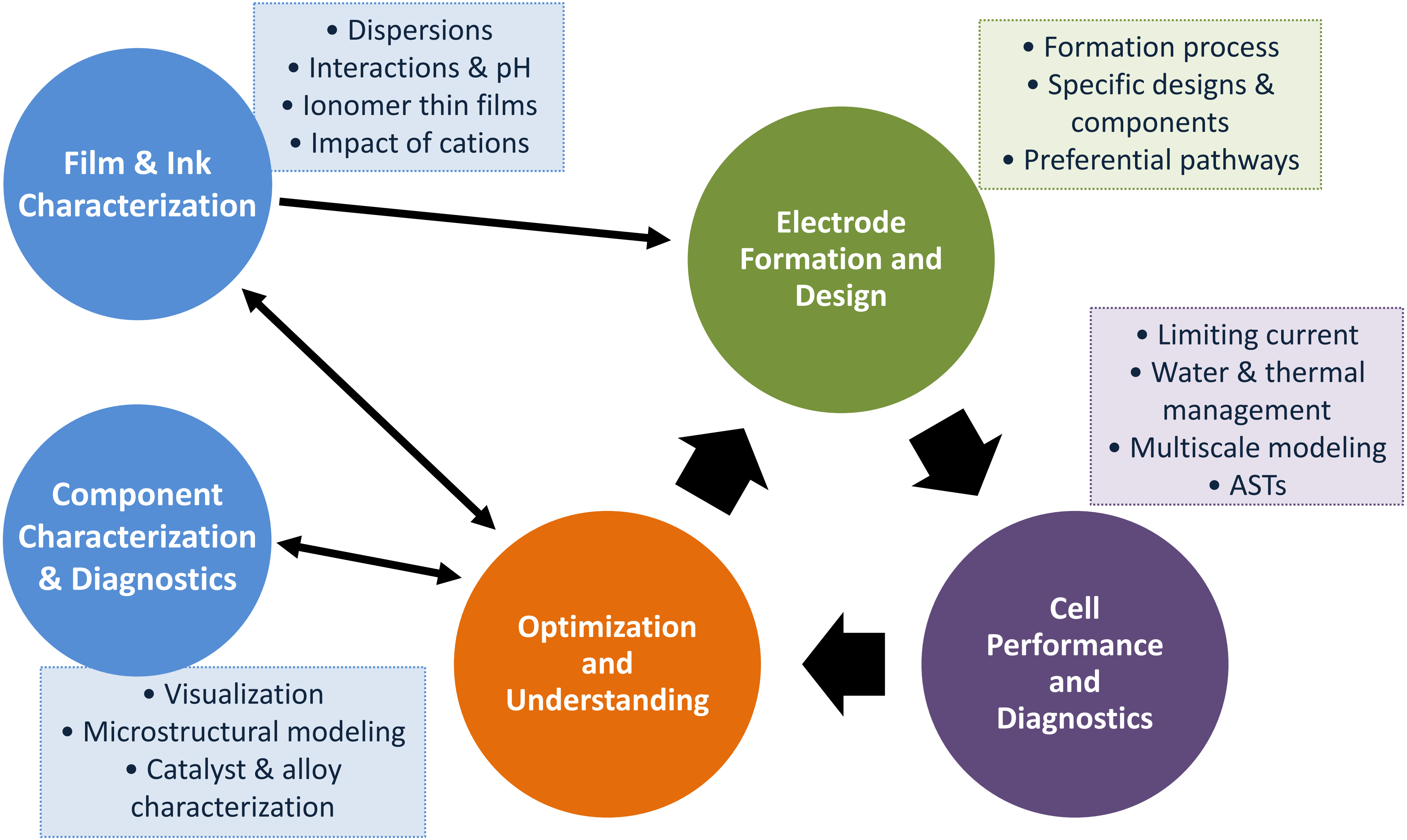
R_c = Pore resistance

R_f = Film resistance [s cm^{-1}]

$l_{c/f}$ = Catalyst/film thickness [cm]

D_{O2} = Pore/film diffusivity [cm^2 s^{-1}]

Approach: Electrode Layers and Optimization



- Dispersions
- Interactions & pH
- Ionomer thin films
- Impact of cations

Film & Ink Characterization

Electrode Formation and Design

- Formation process
- Specific designs & components
- Preferential pathways

Component Characterization & Diagnostics

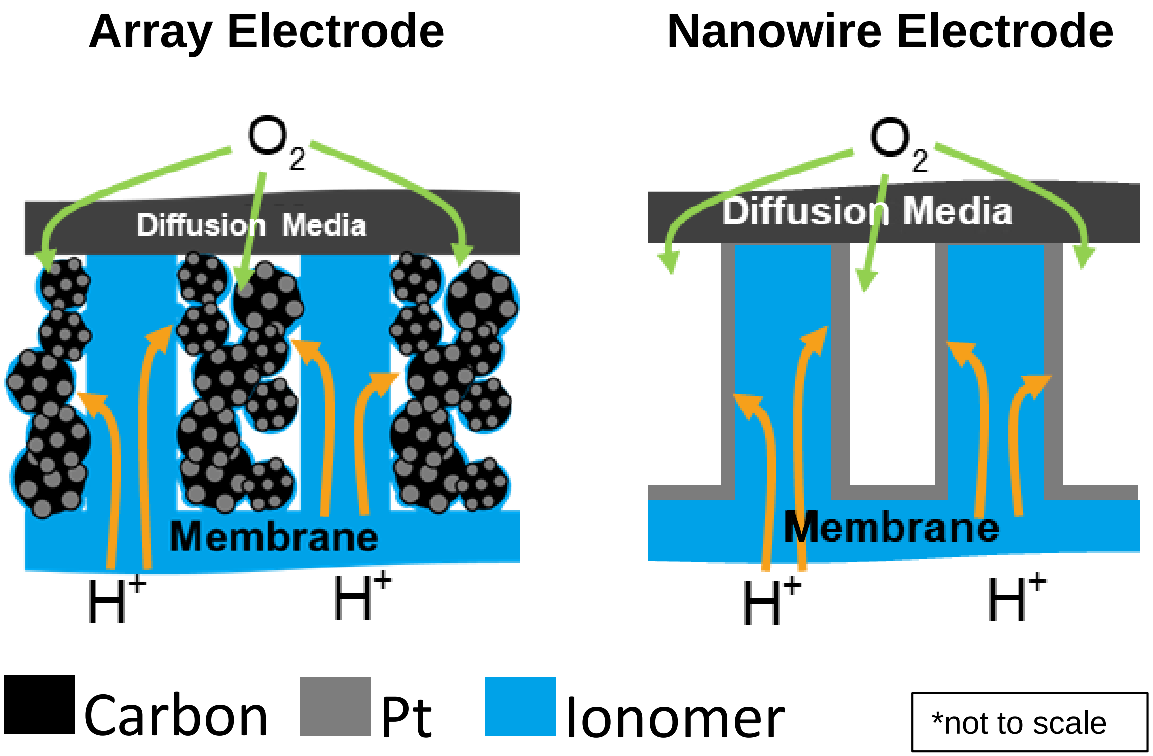
- Visualization
- Microstructural modeling
- Catalyst & alloy characterization

Optimization and Understanding

Cell Performance and Diagnostics

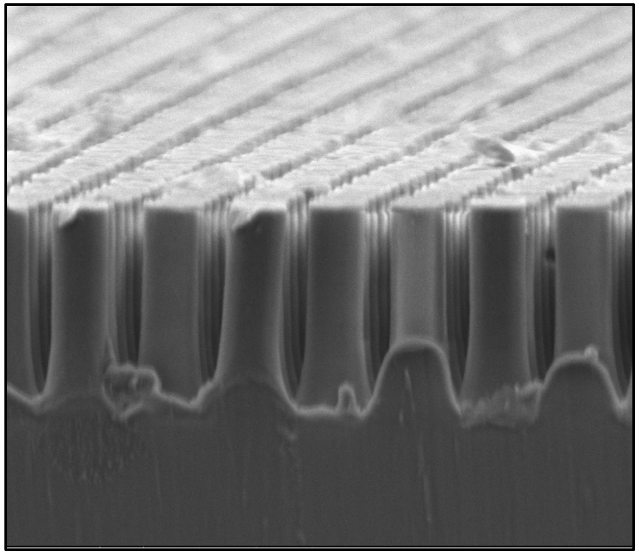
- Limiting current
- Water & thermal management
- Multiscale modeling
- ASTs

Ordered Array Electrode

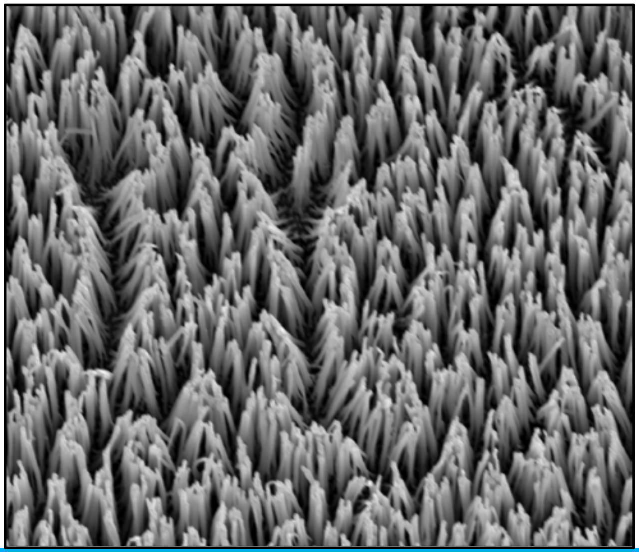


*not to scale

Array Electrode



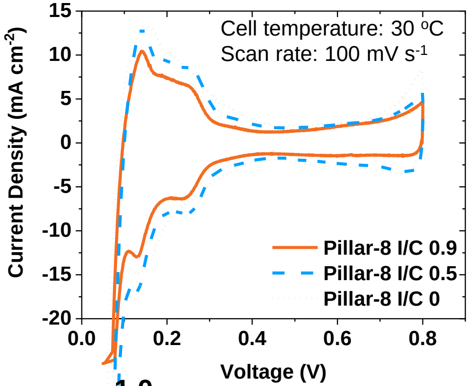
Nanowire Electrode

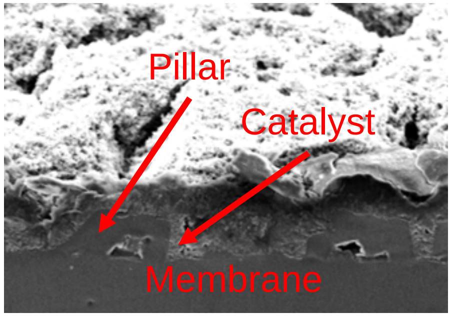


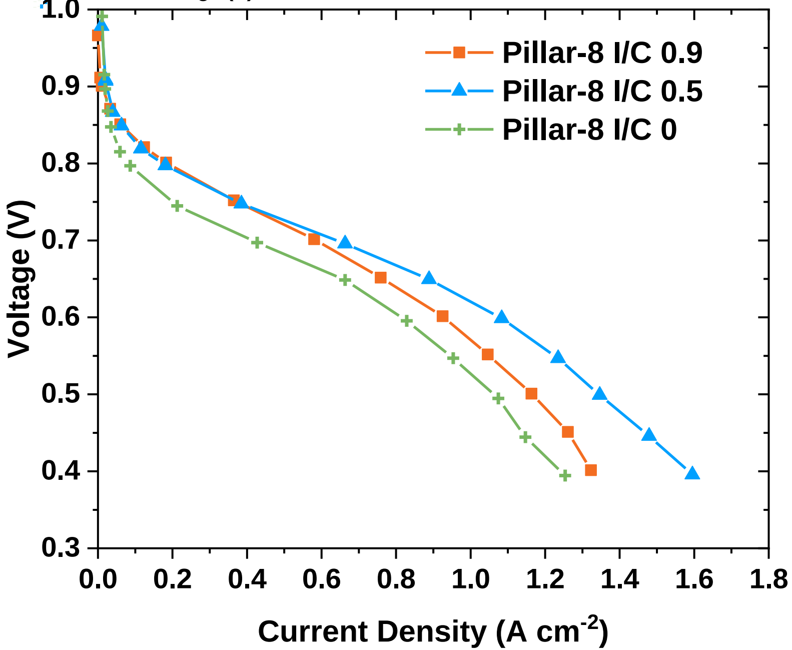
- Meso-structured electrode relies on vertically aligned ionomer channels for long-distance H+ transport
- Catalyzed elements can have reduced ionomer content

Ordered Array Electrode

Array Electrode

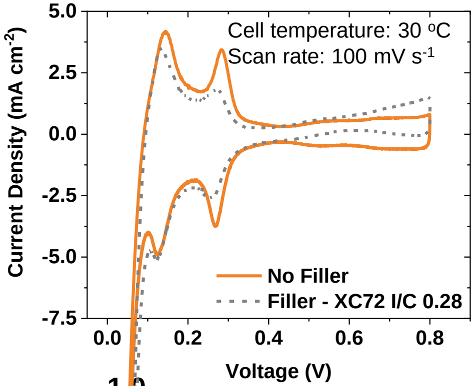


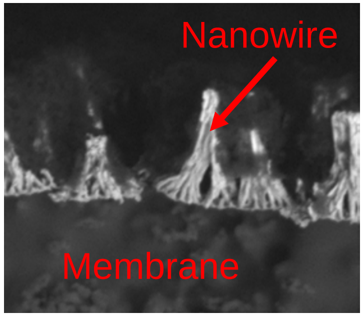


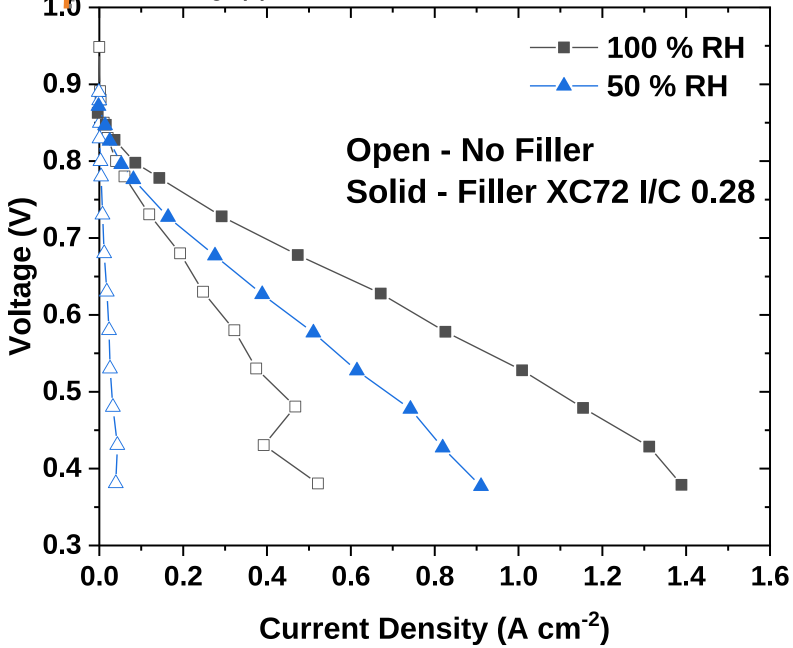


Loading (A/C) = 0.08/0.1 mg cm^{-2}, Catalyst: TEC10E50E, Temperature: 80 ºC, Pressure:150 kPa abs

Nanowire Electrode







Loading (A/C) = 0.1/0.15 mg cm^{-2}, Catalyst: TEC10E50E, Temperature: 80 ºC, Pressure:150 kPa abs

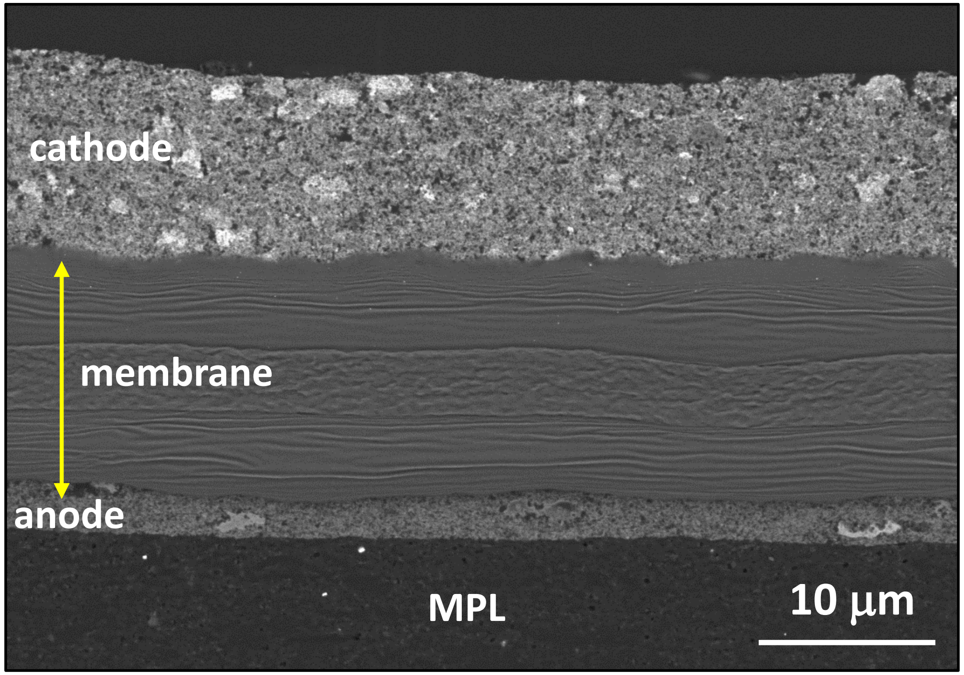
Approach: Establish SOA Commercial Components

Toyota Mirai Components Provided by USCAR

Analysis - inform current SOA material set in terms of composition, structure, performance, and durability. Set current benchmark that new materials can be compared with and may provide information about materials not previously explored in open literature.

- **Cell sections provided by USCAR**
  - 300 hr operation (not “fresh”)
  - 3000 hr operation (“real-world” drive)

- **Task 1: Materials Analysis**
  - Task 1a: Catalyst and support
  - Task 1b: Electrode layer
  - Task 1c: Membrane and Ionomer
  - Task 1d: GDL/MPL
  - Task 1e: Metal Bipolar Plate
- **Task 2: Performance Analysis**
  - Task 2a: Water management in flowfield
  - Task 2b: Material durability performance

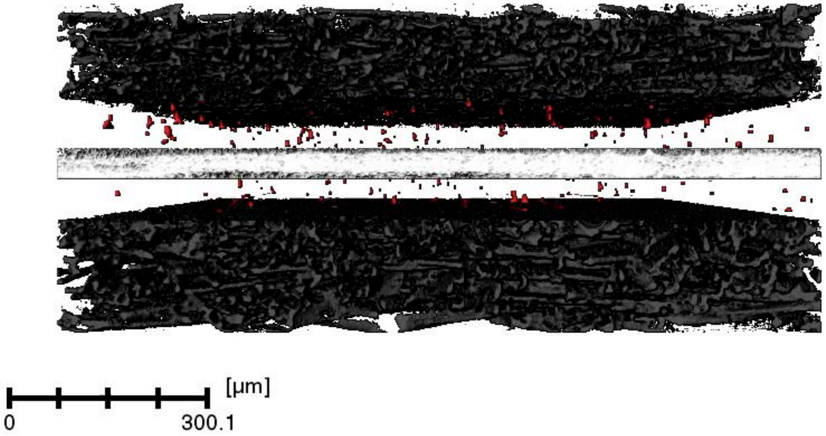


Mirai: A case study in FC-PAD Characterization Capabilities

Techniques	Component	Material Data/Information
SEM/EDAX	MEA	MEA dimensions, composition, structure
TEM-cross-sections	MEA	MEA dimensions, composition, structure, ionomer mapping
TEM-Particle size distributions	MEA	Catalyst particle distribution, size
XRF	MEA	Elemental quantitation
XRF Mapping	MEA	Elemental mapping
XCT	MEA	MEA structure
TGA-MS	Catalyst Layer	catalyst wt %/ I/C ratio
SAXS	Catalyst	catalyst particle distribution
EXAFS	Catalyst	Pt-Pt, Pt-Co bonding distances
XRD	Catalyst	catalyst particle distribution
FTIR	Membrane	Membrane composition
NMR	Membrane/Ionomer	Membrane composition/eq. wt
Titration	Membrane	Membrane equivalent weight
Testing - O2/Air Polarization	MEA	Catalyst layer performance
Testing - Catalyst AST	Catalyst	Catalyst durability
Testing - Carbon Corrosion AST	Catalyst Support	Catalyst support durability
NDIR- Carbon Corrosion	Catalyst Support	Carbon corrosion measurements
MIP	GDL/MEA	Component porosity
BET	GDL/MEA	Component surface area/pore-size distribution
Contact Angle - Sessile Drop	GDL/Bipolar Plate	Component Hydrophobicity
Contact Resistance	Bipolar Plate	Contact Resistance
XPS	Bipolar Plate	Bipolar plate elemental analysis
XPS - Depth profiling	Bipolar Plate	Bipolar plate coating structure

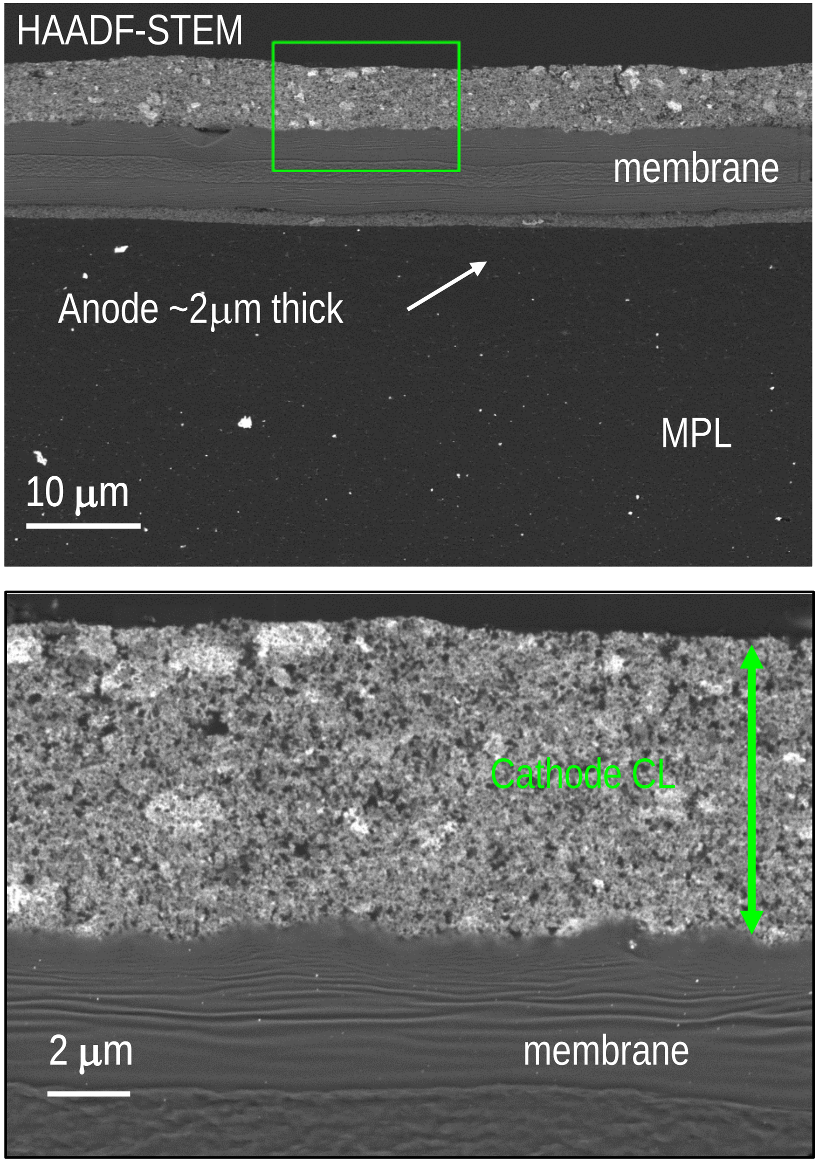
Mirai: MEA Component Summary

- **Cathode**
  - PtCo/C: Pt = 87mole%, 0.315 mg_{Pt}/cm^2
  - Cathode layer ~ 10μm
  - GDL separates from catalyst layer
- **Anode**
  - Anode layer ~ 2.3 μm; 0.050 mg_{Pt}/cm^2
  - GDL does not separate from catalyst layer
- **GDLs**
  - Anode: ~ 150 μm total with ~ 60 μm MPL
  - Cathode: ~ 160 μm total with ~ 40 μm MPL
  - High concentration of CeO_x particles in MPLs; ~ 60 $\mu g/cm^2$ on cathode; ~ 120 $\mu g/cm^2$ on anode



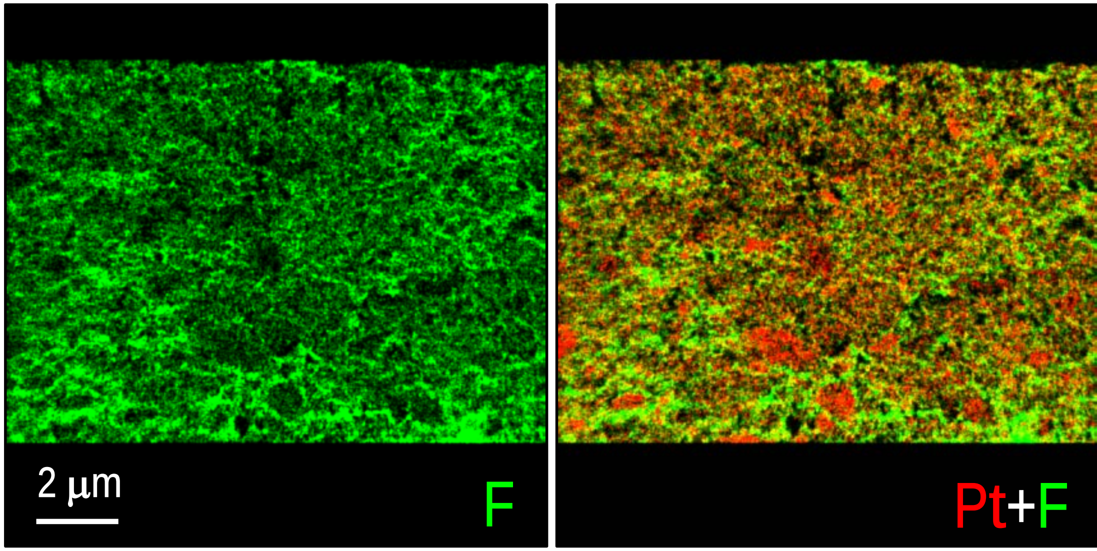
- **Membrane**
  - ~ 10 – 10.5 μm reinforced with ePTFE; Nafion side chain
  - EW of the membrane ionomer ~ 901 ± 1 g/meq by acid-base titration
- **Bipolar Plate**
  - Cathode Ti foil with Ti porous mesh; ~ 80 nm carbon coating by XPS depth profile
  - Anode serpentine; ~ 80 nm carbon coating by XPS depth profile

Mirai: MEA Component Summary - CCL

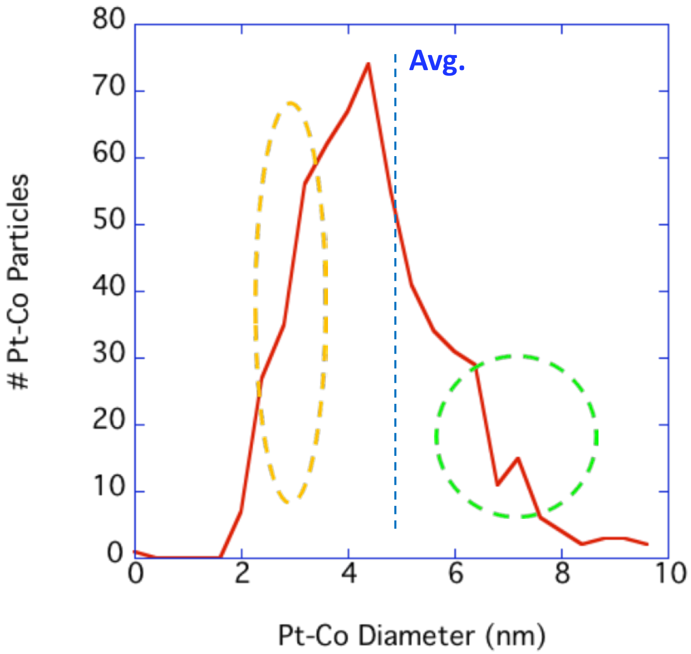


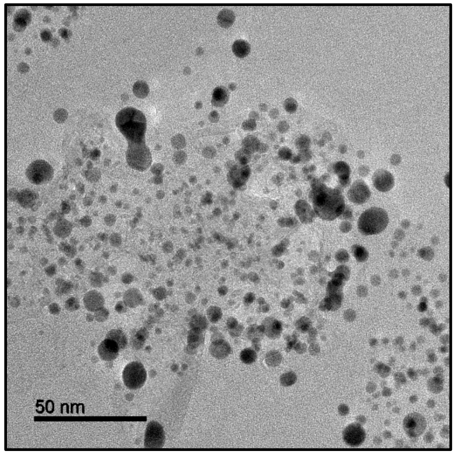
CCL observations after 300hr:

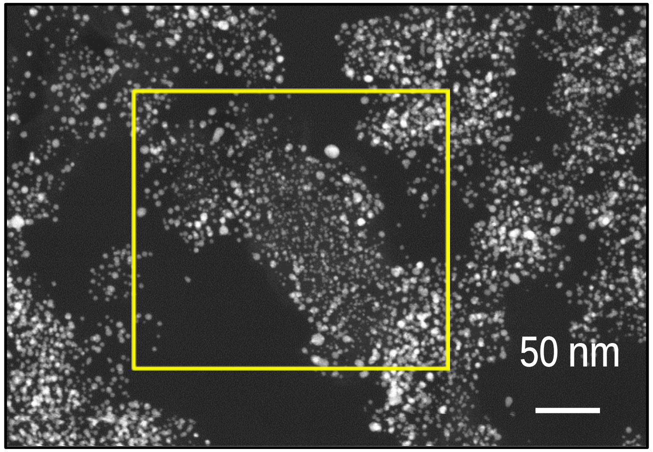
- Cathode CL ~ 9-10 μm thick and relatively dense
- Ionomer distribution non-uniform within CL
- Localized regions of highly agglomerated PtCo/C
- Agglomerated PtCo/C not well infiltrated by ionomer
- Rough CL/membrane interface



Mirai: MEA Component Summary - Electrocatalyst



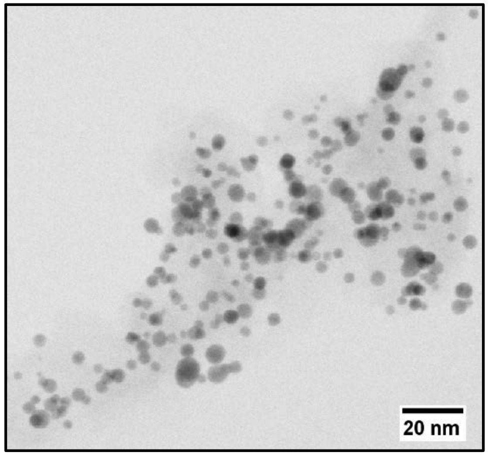


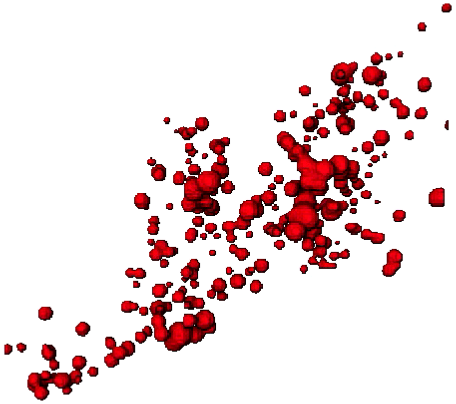


- Carbon support is acetylene black (AB)

- Smaller Pt-Co particles on “inside” of AB
  - typically ~2-3 nm

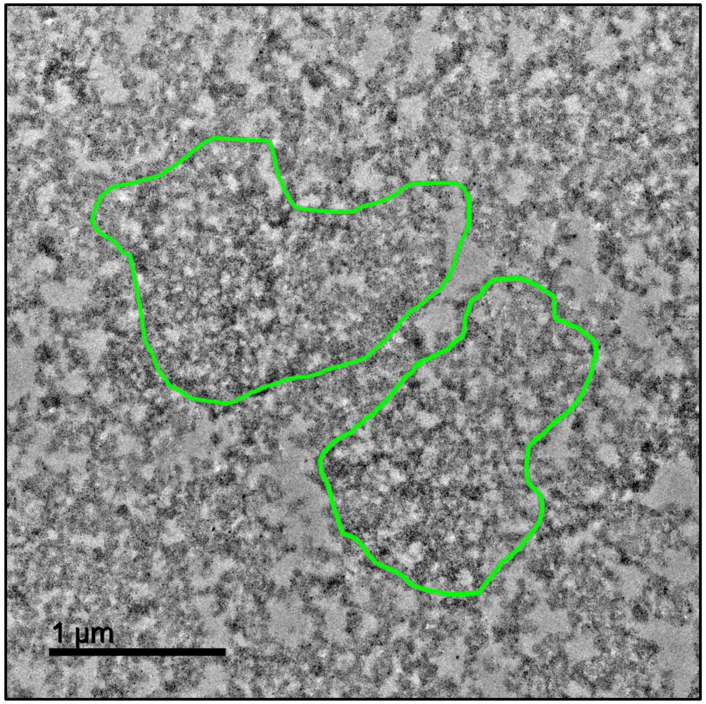
- Larger Pt-Co particles on “surface” of AB
  - particles range in size from 5-10 nm
  - large particles decorate surfaces of secondary pores

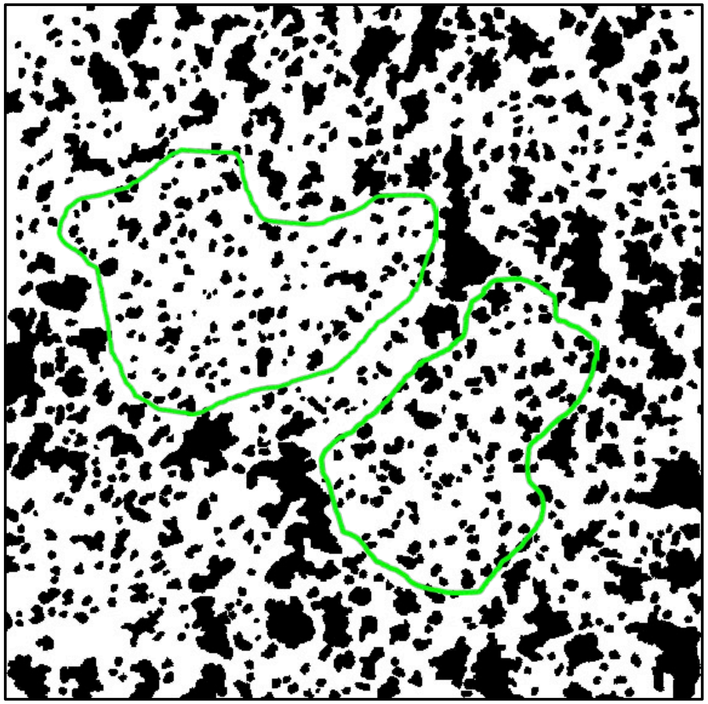




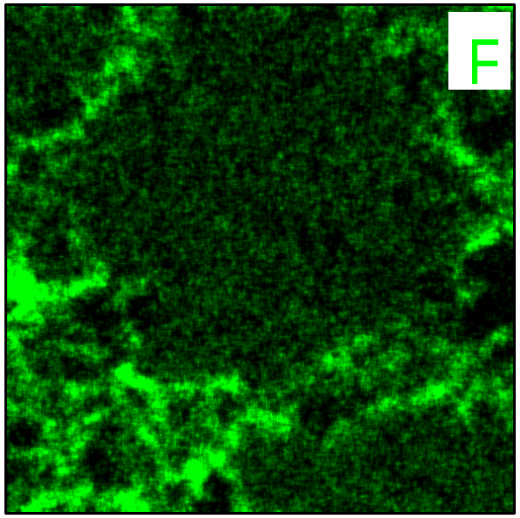
Average Pt-Co nanoparticle diameter = 4.7nm

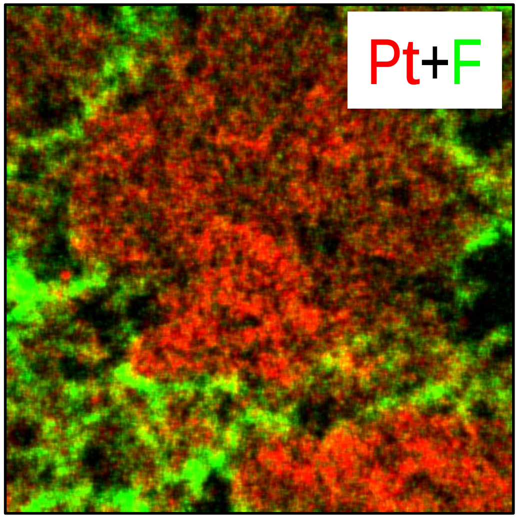
Mirai: MEA Component Summary - Porosity



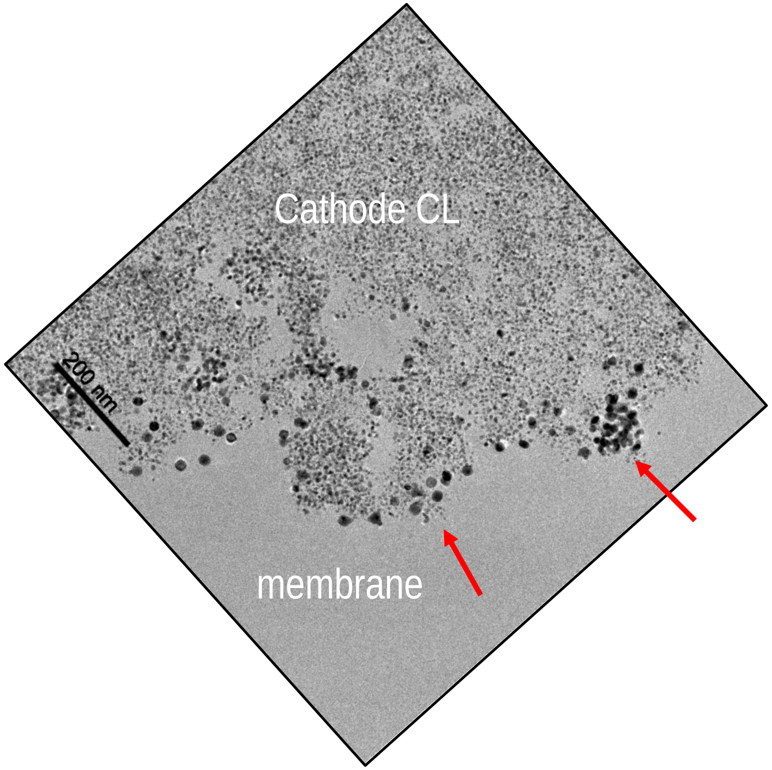


- Avg. equivalent secondary pore diameter = 75 nm
- Green outlined regions show two “dense” Pt-Co/AB agglomerates that exhibit smaller pore sizes
- Larger secondary pores are between agglomerates (with most of ionomer)

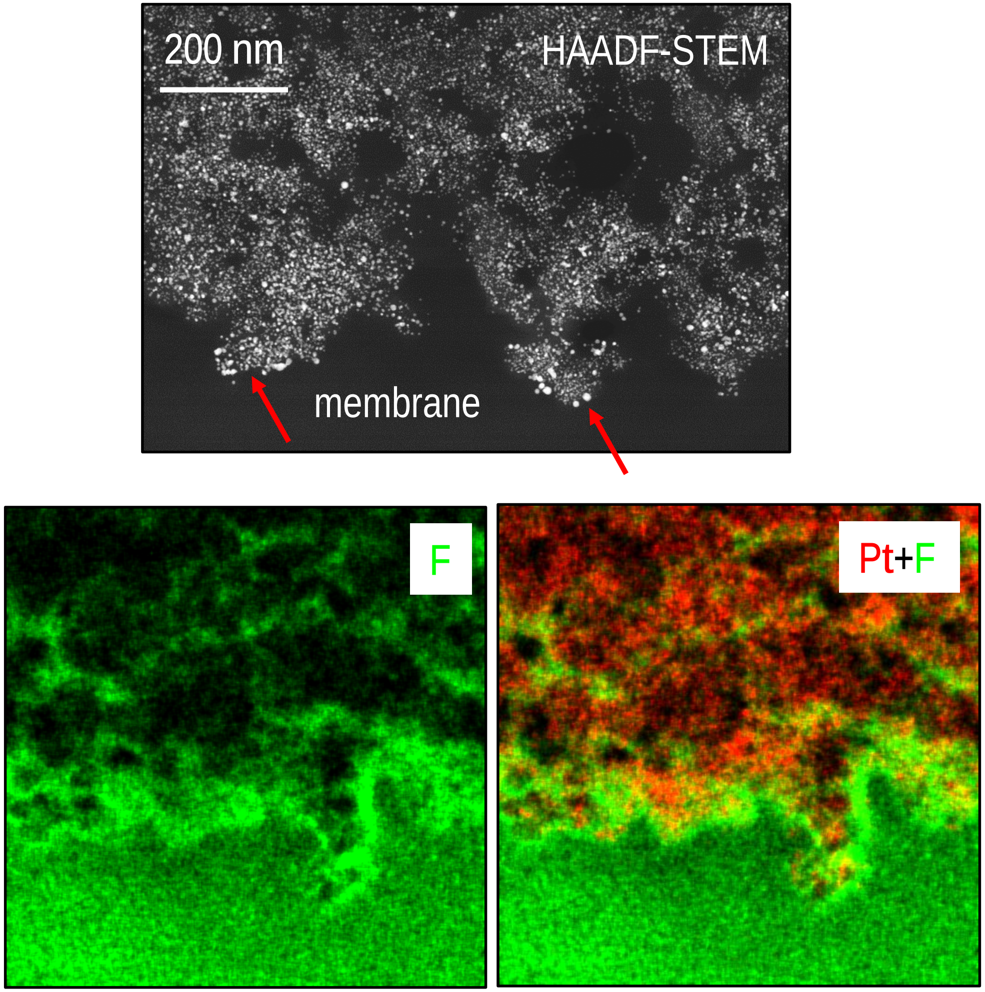




Mirai: MEA Component Summary – Interface

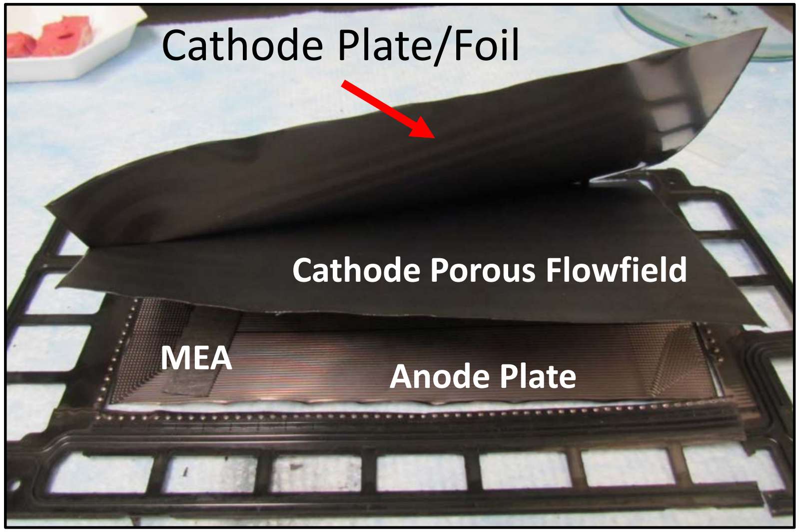


- Rough CL/membrane interface (~1 µm)
- Pt-Co/AB agglomerate protrusions extend into membrane
- Very large ~20 nm dia. “Pt-only nanoparticles” present at interface but do not form a continuous layer

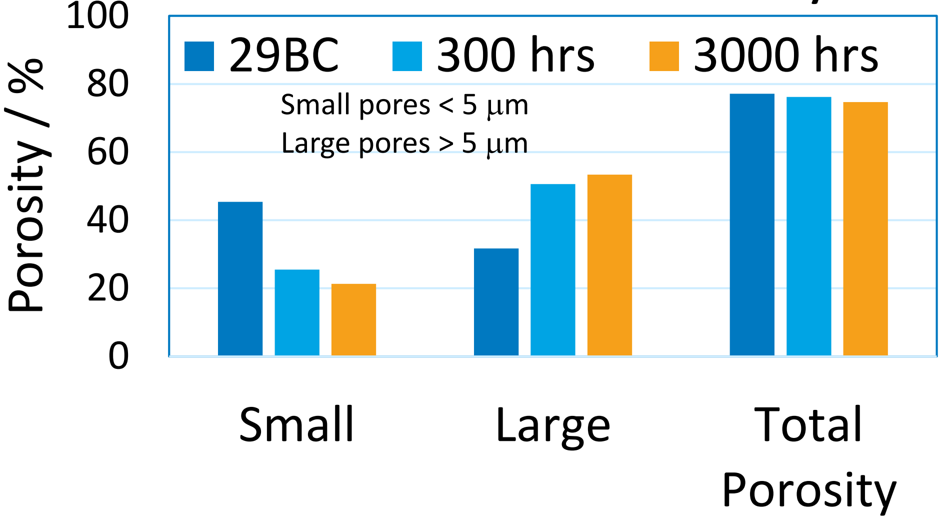


Uniform, continuous enrichment of F
at CL/membrane interface ~100nm thick

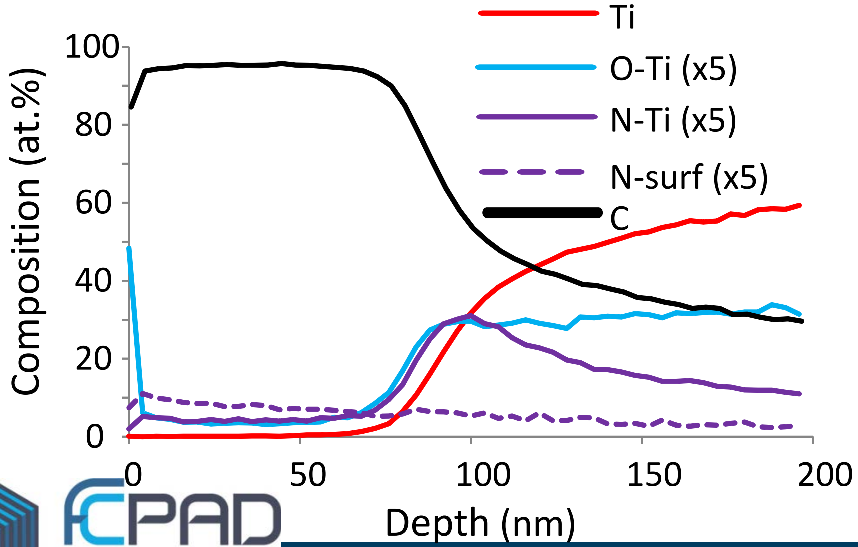
Mirai Component Summary: Bipolar Plate/GDL



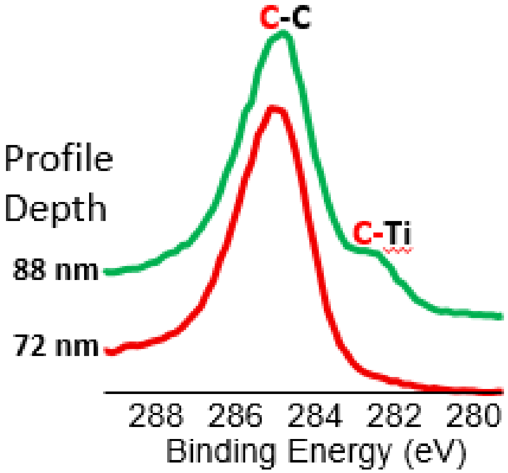
Cathode GDL Porosity



Depth Profile of Bipolar Plate



C 1s XPS



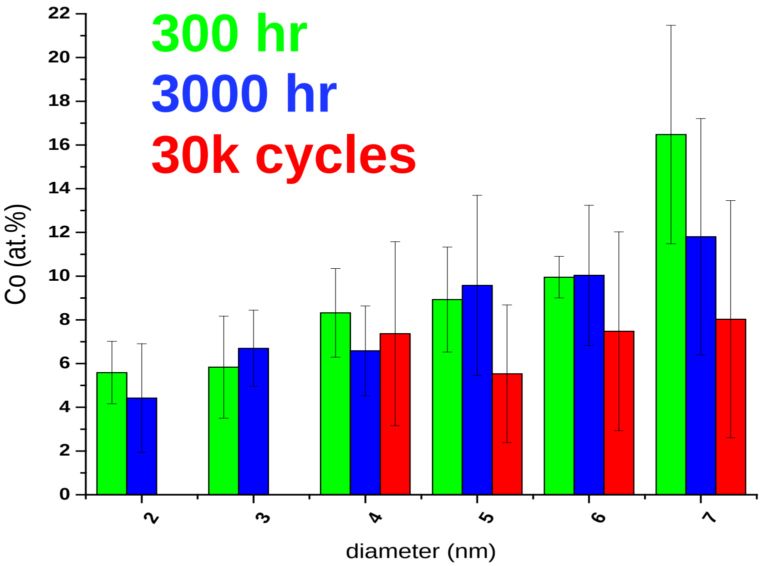
Mirai: Catalyst/Catalyst-Support ASTs

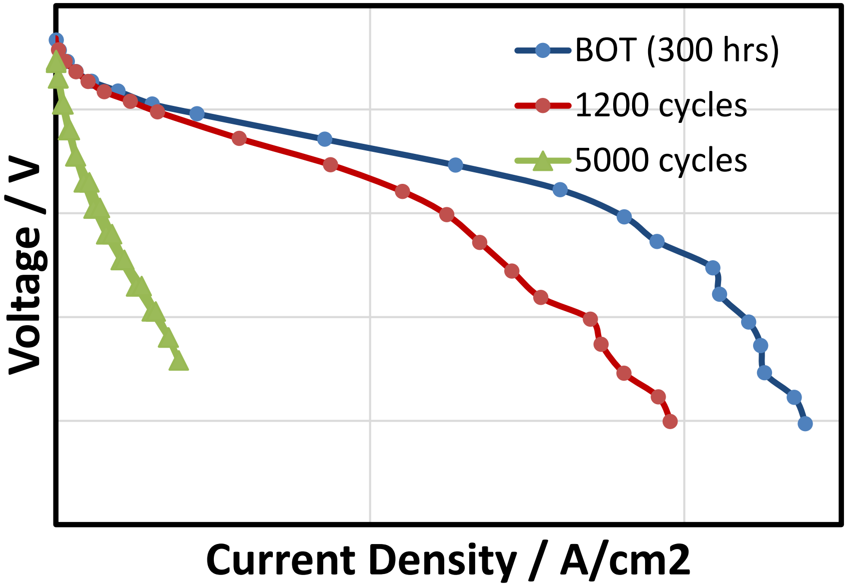
No changes to structure or chemistry observed (catalyst, support, ionomer, membrane) observed after 3000 hr "real-world driving"

Mitigation strategies implemented were successful

DOE FCTT–recommended durability protocols applied to assess stability under more aggressive conditions:

- **Catalyst AST (0.6 – 0.95V square wave)**
  - Loss of ~ 25% of ECSA; CL thinning to 6μm
  - VIR performance loss of ~ 25 mV at 1.0 A/cm^2
  - XRD/TEM show particle growth and loss of Co
  - Particle growth from 4.7 to 6.7 nm
- **Catalyst Support AST (1.0 – 1.5V cycle)**
  - ~ 50 mV loss at 1200 cycles (HSAC shows large performance loss at this point)
  - Little performance remaining after 5000 cycles
  - ECSA 60% loss at 5000 cycles; particle growth from 4.7nm to 5.3nm
  - CL thinning from ~ 10 to 3μm

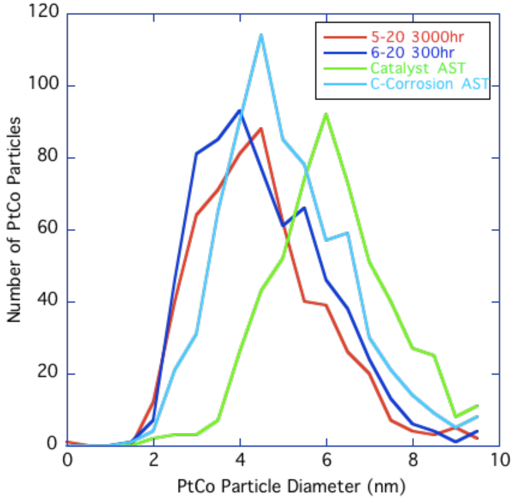


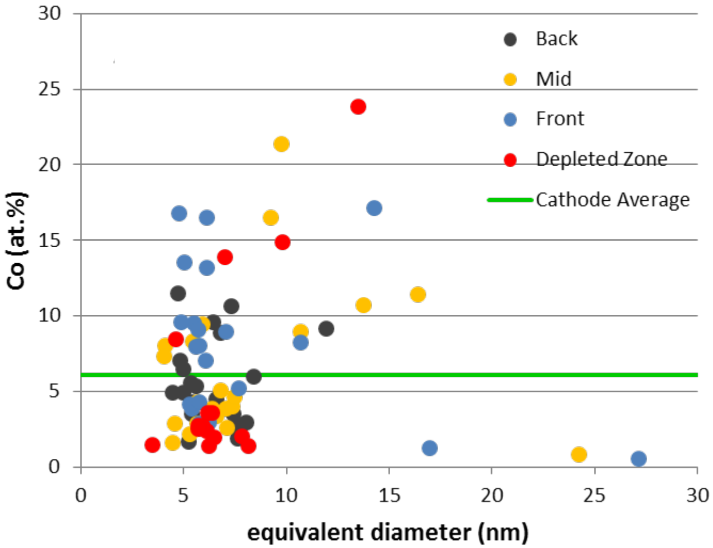


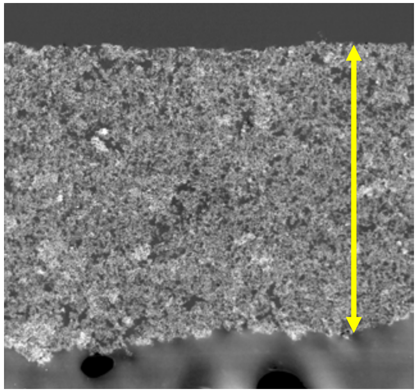
Mirai: Catalyst/Catalyst-Support ASTs

No changes to structure or chemistry observed (catalyst, support, ionomer, membrane) observed after 3000 hr “real-world driving”

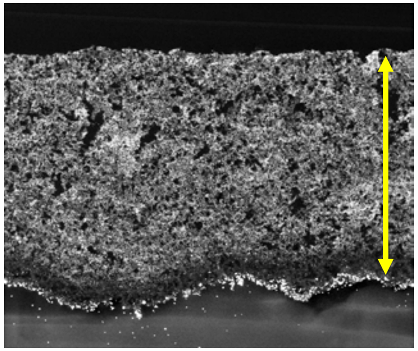
Materials are not stable during DOE FCTT–recommended durability protocol ASTs



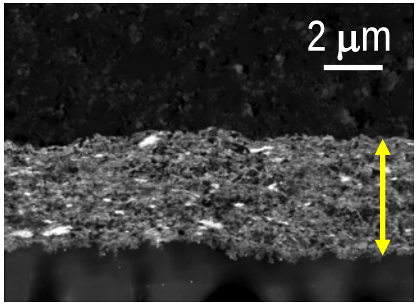




300 hr

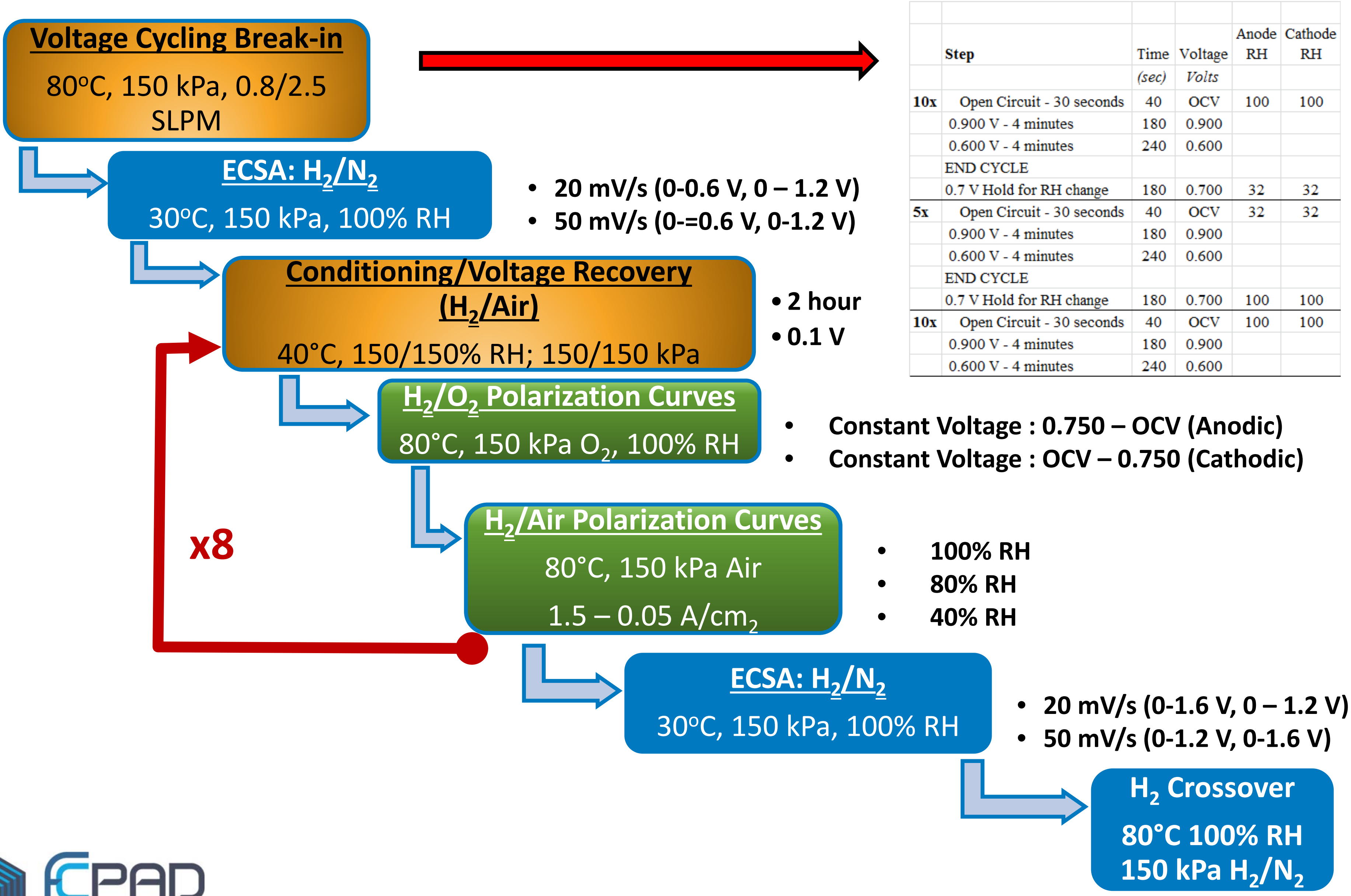


Catalyst AST



Catalyst-support AST

Conditioning: Testing Protocol



Voltage Cycling Break-in

80°C, 150 kPa, 0.8/2.5 SLPM

	Step	Time (sec)	Voltage Volts	Anode RH	Cathode RH
10x	Open Circuit - 30 seconds	40	OCV	100	100
	0.900 V - 4 minutes	180	0.900		
	0.600 V - 4 minutes	240	0.600		
	END CYCLE				
	0.7 V Hold for RH change	180	0.700	32	32
5x	Open Circuit - 30 seconds	40	OCV	32	32
	0.900 V - 4 minutes	180	0.900		
	0.600 V - 4 minutes	240	0.600		
	END CYCLE				
	0.7 V Hold for RH change	180	0.700	100	100
10x	Open Circuit - 30 seconds	40	OCV	100	100
	0.900 V - 4 minutes	180	0.900		
	0.600 V - 4 minutes	240	0.600		

ECSA: H_2/N_2

30°C, 150 kPa, 100% RH

- **20 mV/s (0-0.6 V, 0 – 1.2 V)**
- **50 mV/s (0-=0.6 V, 0-1.2 V)**

Conditioning/Voltage Recovery (H_2/Air)

40°C, 150/150% RH; 150/150 kPa

- **2 hour**
- **0.1 V**

H_2/O_2 Polarization Curves

80°C, 150 kPa O_2, 100% RH

- **Constant Voltage : 0.750 – OCV (Anodic)**
- **Constant Voltage : OCV – 0.750 (Cathodic)**

x8

H_2/Air Polarization Curves

80°C, 150 kPa Air

1.5 – 0.05 A/cm_2

- **100% RH**
- **80% RH**
- **40% RH**

ECSA: H_2/N_2

30°C, 150 kPa, 100% RH

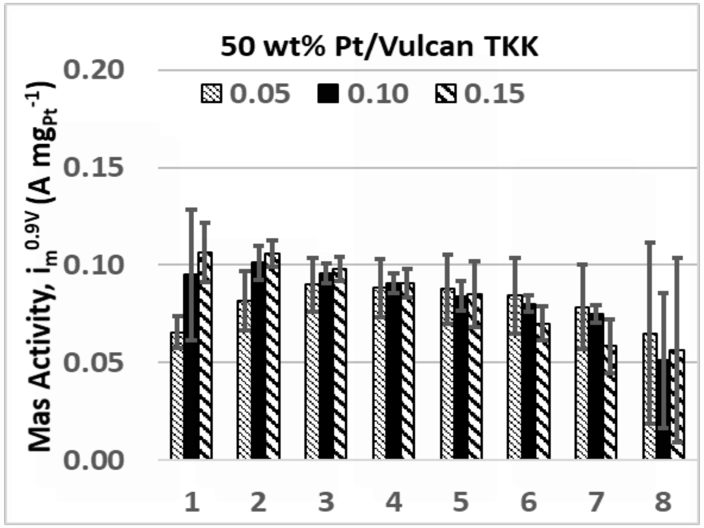
- **20 mV/s (0-1.6 V, 0 – 1.2 V)**
- **50 mV/s (0-1.2 V, 0-1.6 V)**

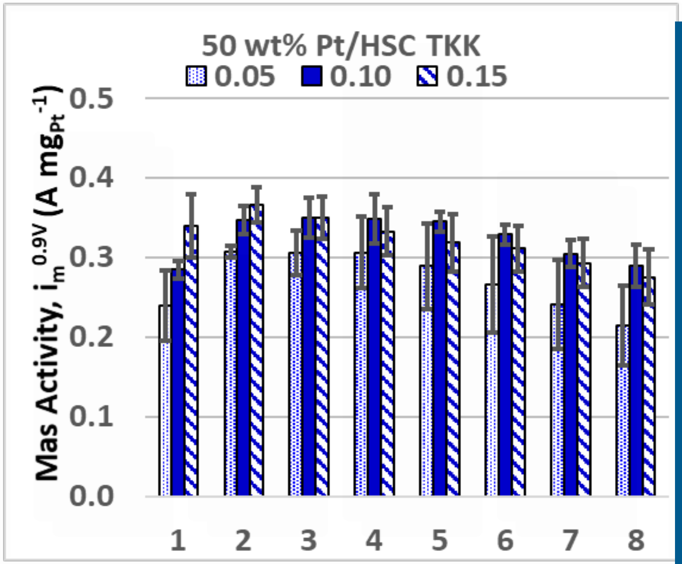
H_2 Crossover

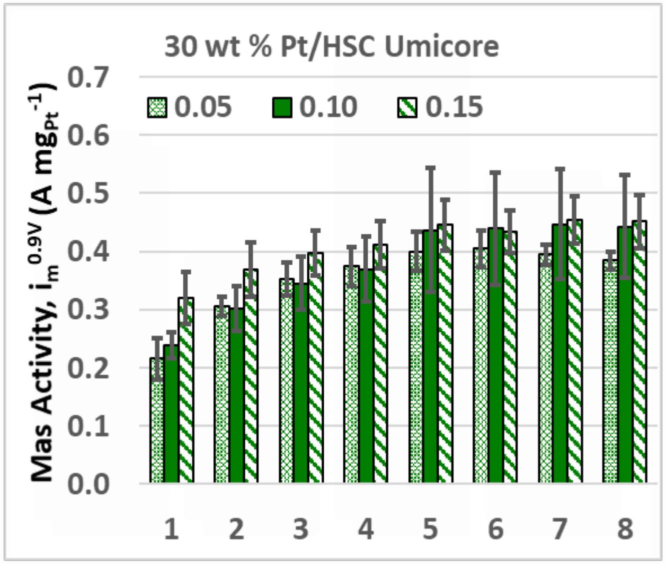
80°C 100% RH

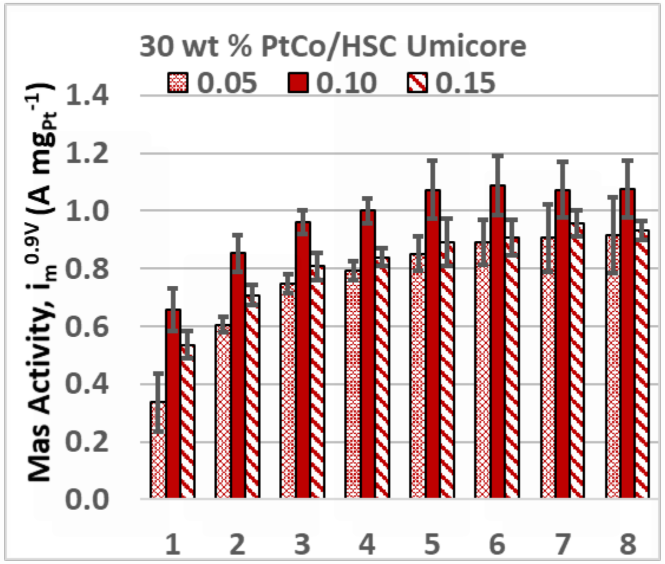
150 kPa H_2/N_2

Conditioning: Cathodic Mass Activities


50 wt% Pt/Vulcan TKK


50 wt% Pt/HSC TKK


30 wt % Pt/HSC Umicore


30 wt % PtCo/HSC Umicore

General Conclusions:

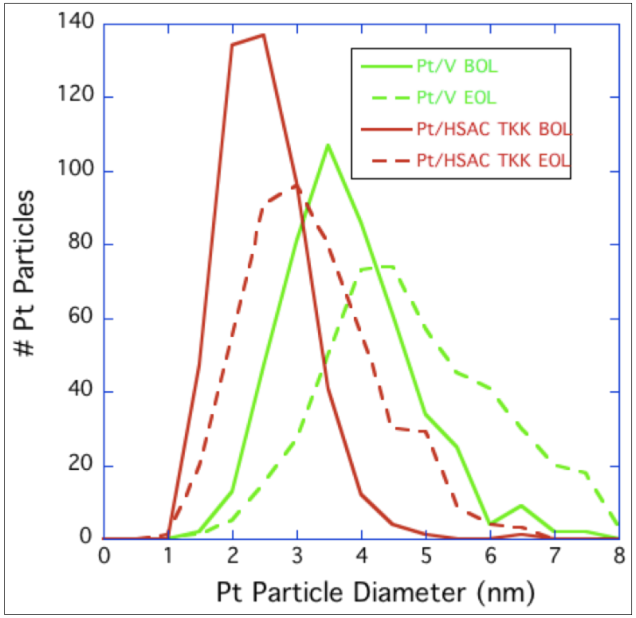
Rigorousness of conditioning required to reach maximum performance does not appear to depend exclusively on generic nature of carbon support or presence of an alloy

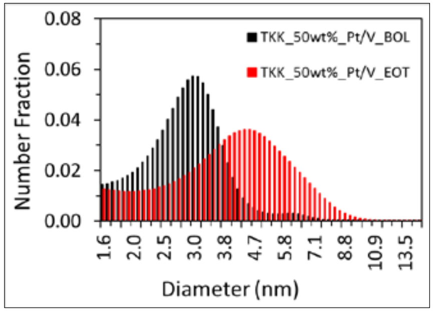
Superficial observation would be that variables during the catalyst synthesis process may play a role

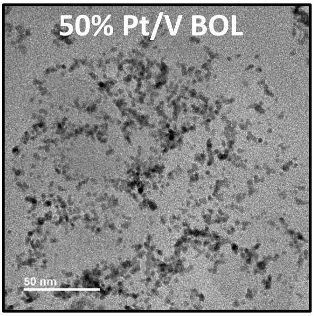
When compared to higher loadings, lower loadings exhibit their largest disparity in performance in first conditioning cycle

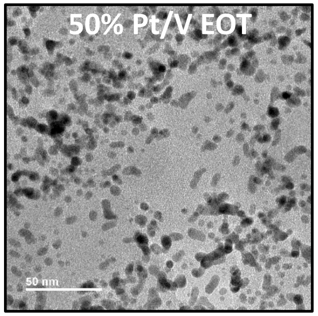
Up to 2-3x variation between “initial” and peak $i_m^{0.9V}$

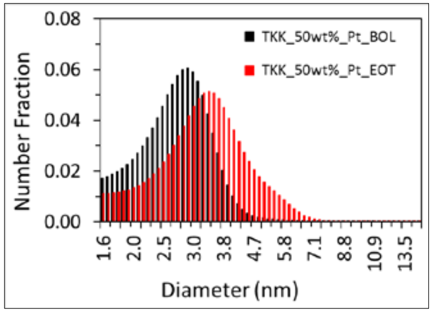
Conditioning: Effect of Carbon Support

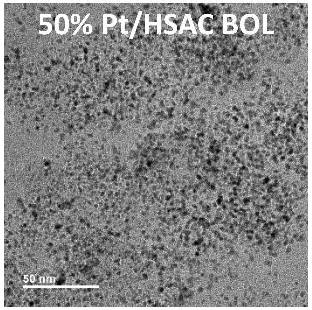


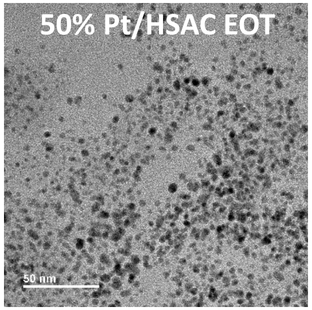










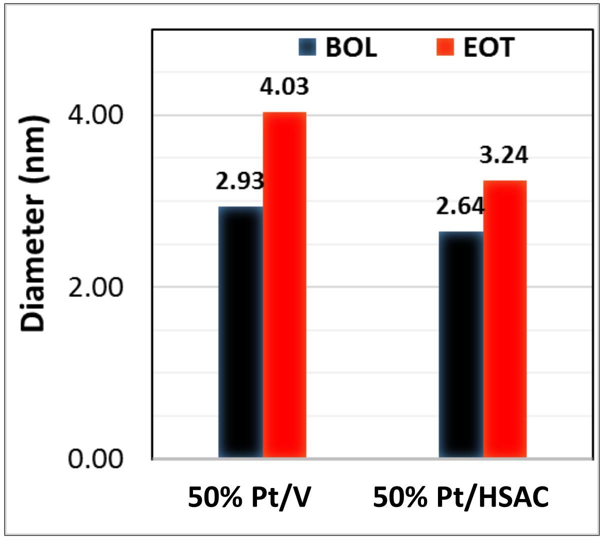


Particle size change greater for Pt/V during conditioning:

>30% change in Pt particle size on Vulcan during conditioning

vs.

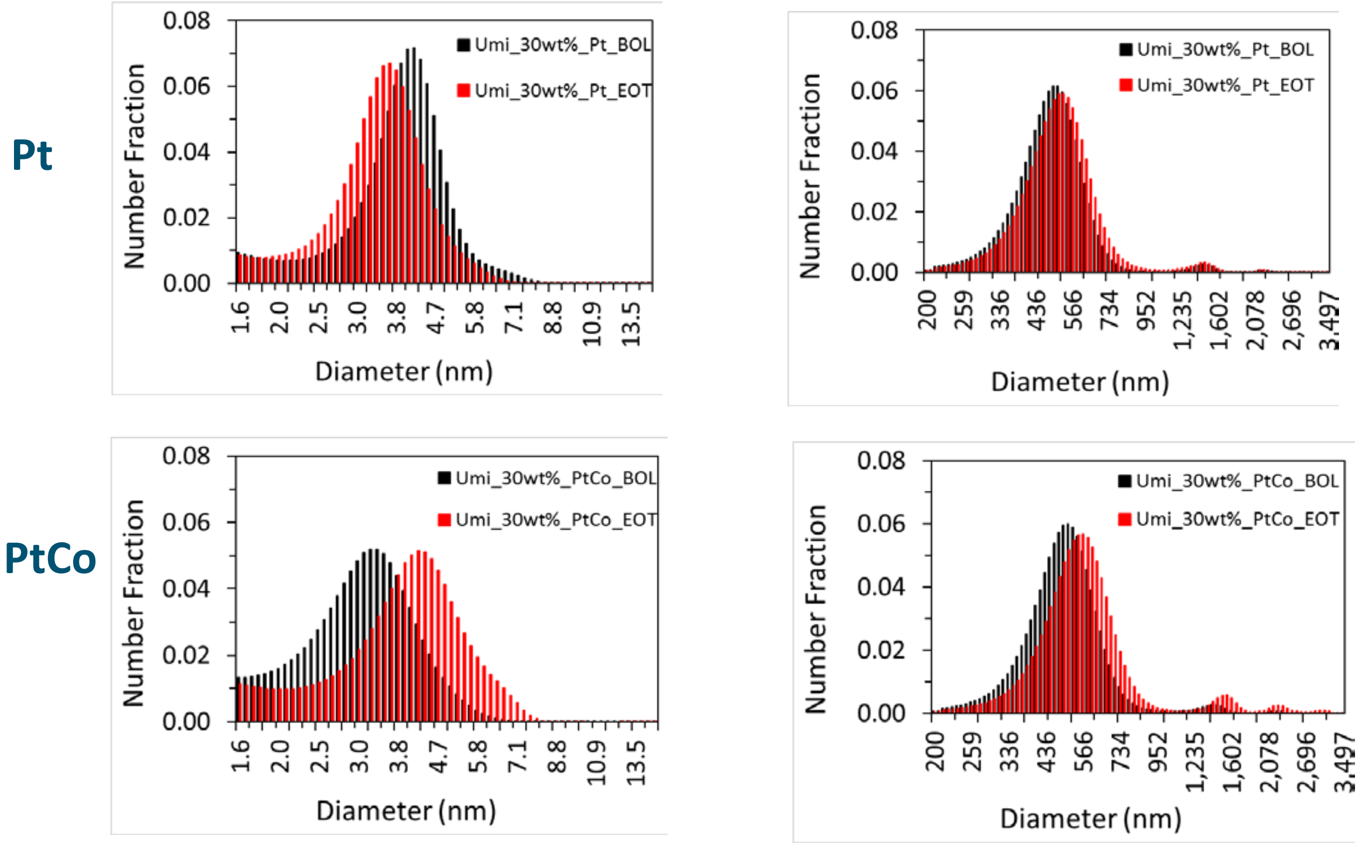
~20% change in Pt particle size on HSAC



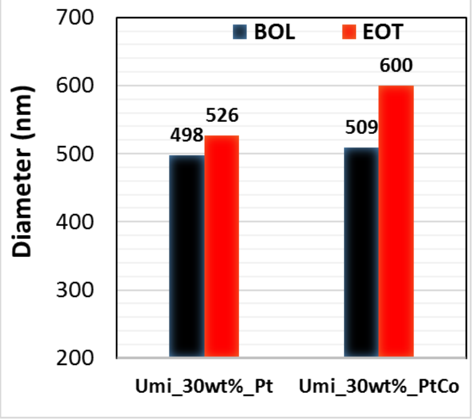
Conditioning: Effect of Catalyst Alloying

Catalyst Particles

Carbon Agglomerates

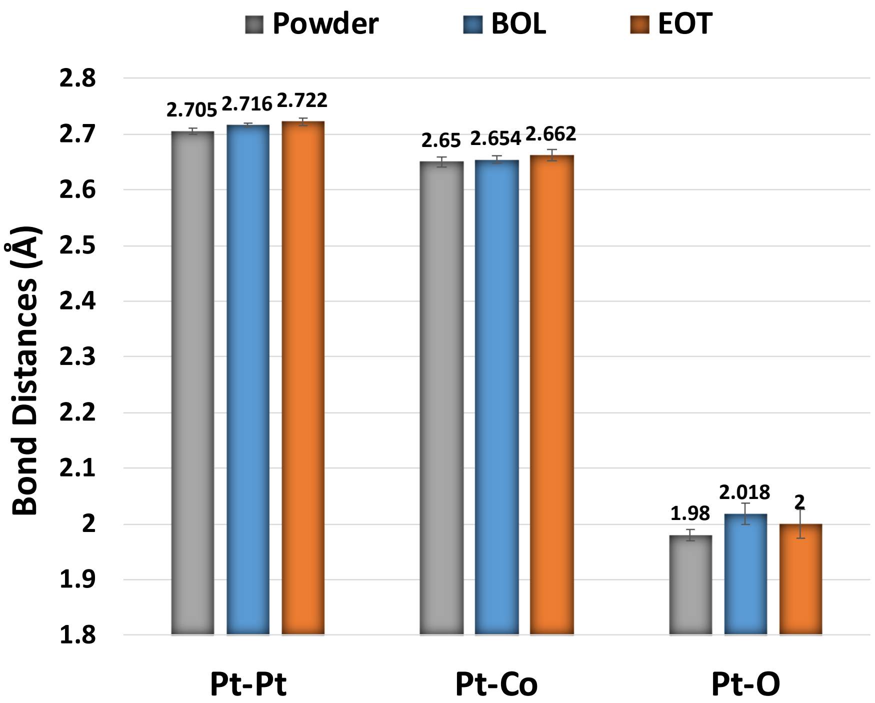


Carbon Agglomerate Diameter

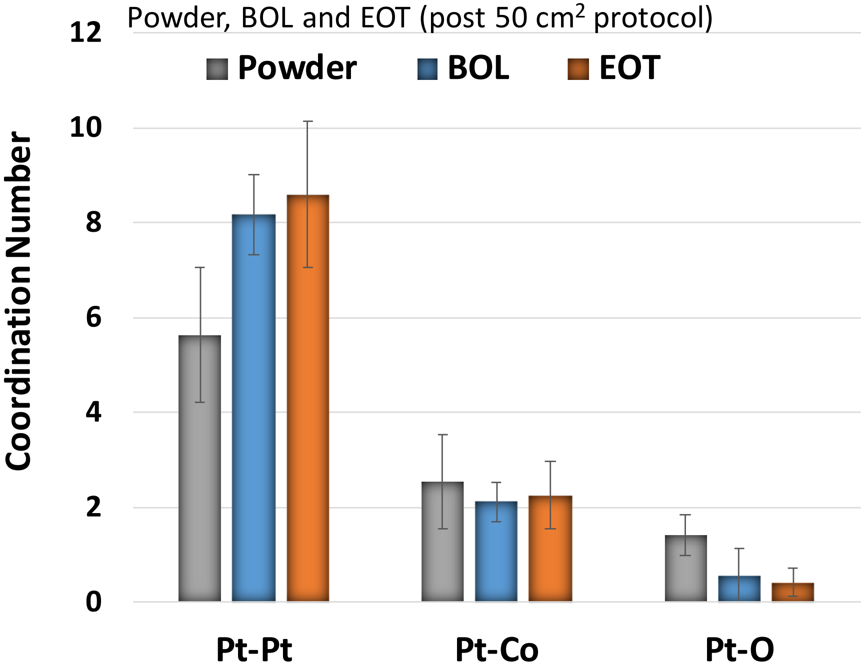


- PtCo catalyst particle size increases after conditioning (EOT)
- Carbon agglomerates are larger after conditioning: negligible for Pt but notable for PtCo

XAFS - Co Leaching During Conditioning



30 wt% PtCo/HSC Umicore; ~0.05 mg-Pt/cm²; Powder, BOL and EOT (post 50 cm² protocol)



- % Compression of Pt-Pt bond in Pt-Co wrt Pt-only catalyst: Powder: 1.9%; BOL: 1.5%; EOT: 1.3%
- 30 wt.% Pt/HSAC Umicore Pt-Pt bond length:

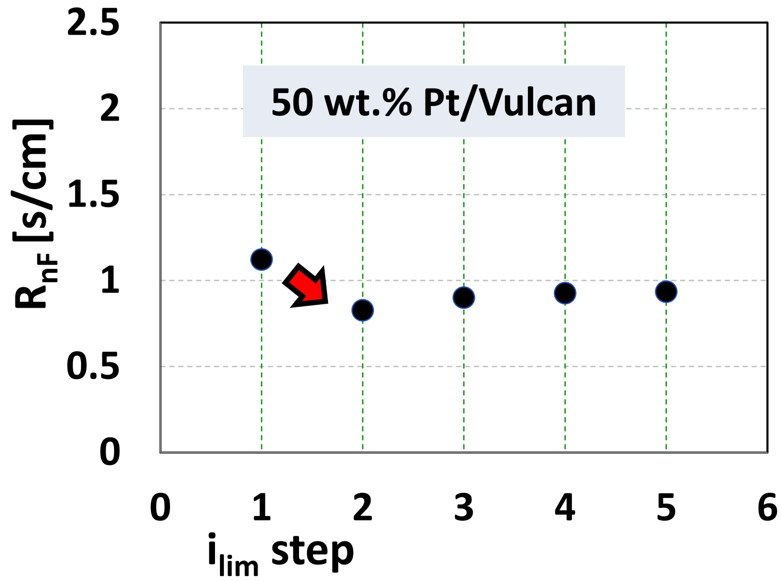
  BOL MEA: 2.758 Å

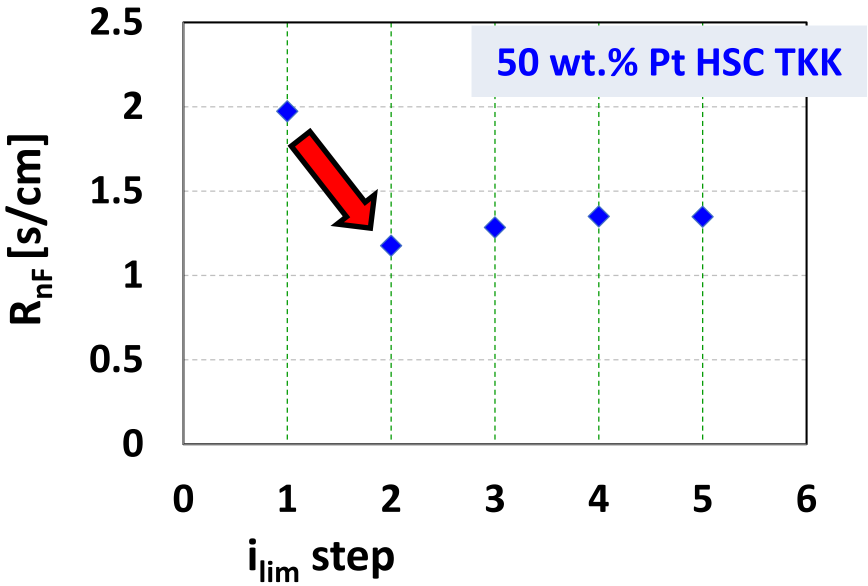
  EOT MEA: 2.760 Å

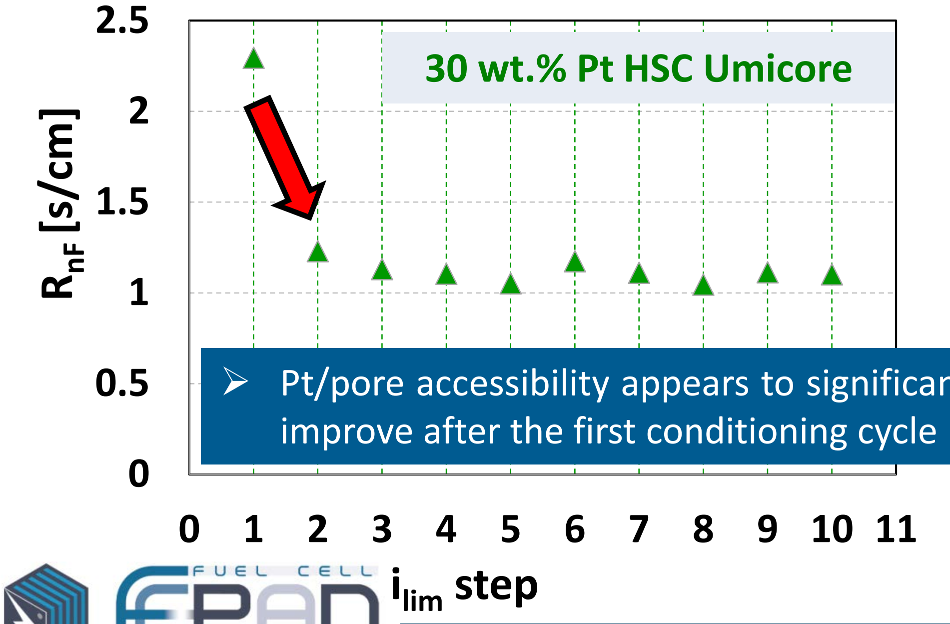
Pt-Pt coordination number increase, combined with less substantial decrease of Pt-Co coordination indicates Pt particle growth and/or Pt shell formation.

- ➢ For PtCo/HSAC Umicore Pt-Pt bond distance becoming more “Pt-like” while $i_m^{0.9V}$ increases
- ➢ For PtCo/HSAC Umicore Pt-Pt bond distance relatively unchanged while $i_m^{0.9V}$ increases

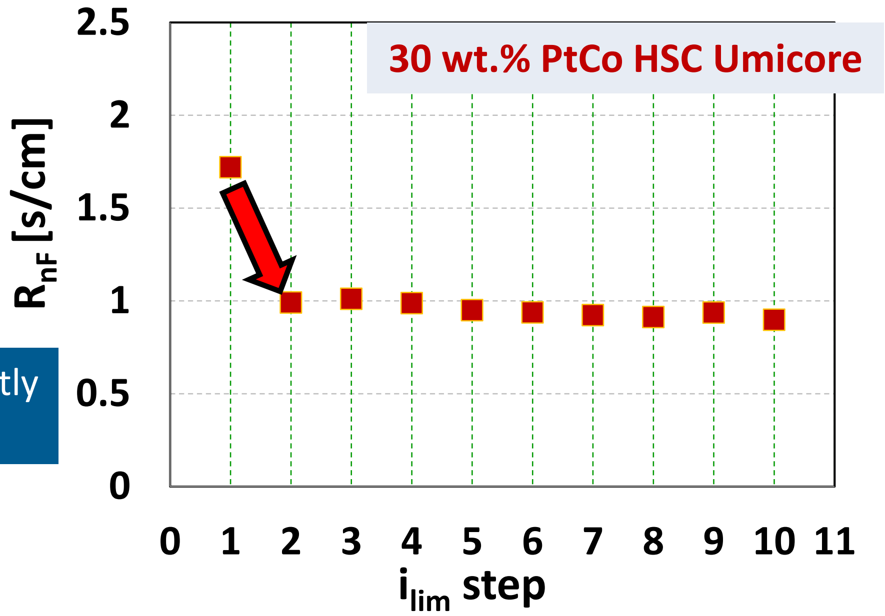
R_{nF} *f*(conditioning) 80°C, 75% RH







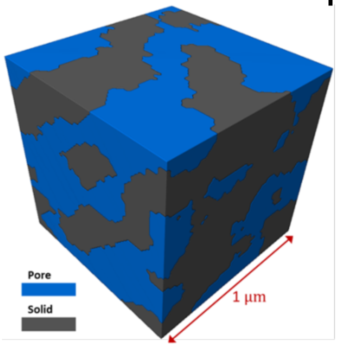
- Pt/pore accessibility appears to significantly improve after the first conditioning cycle

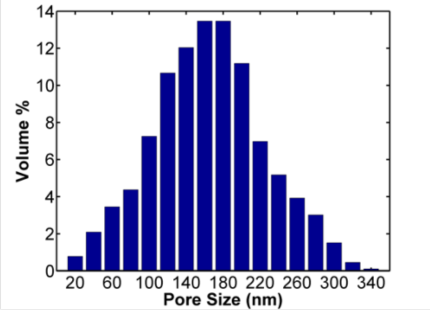


Input for Electrode Microstructure Reconstruction

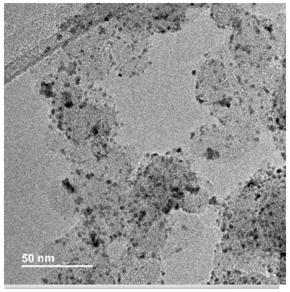
Method to reconstruct electrode microstructure from multiple datasets

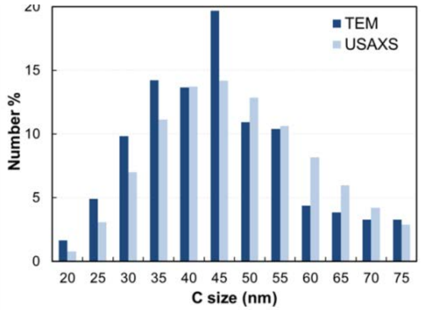
Nano-CT data for morphology of the secondary pores



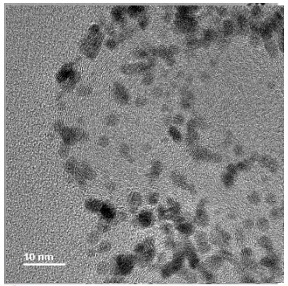


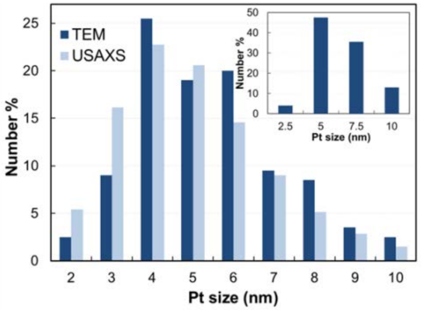
TEM and USAXS data for C particle size distribution



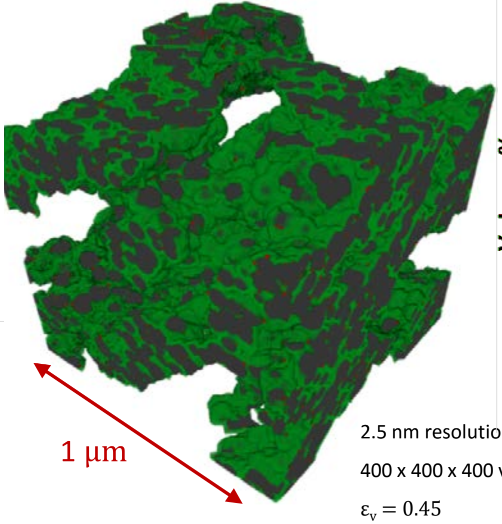


TEM and USAXS data for Pt particle size distribution





Resulting Microstructure

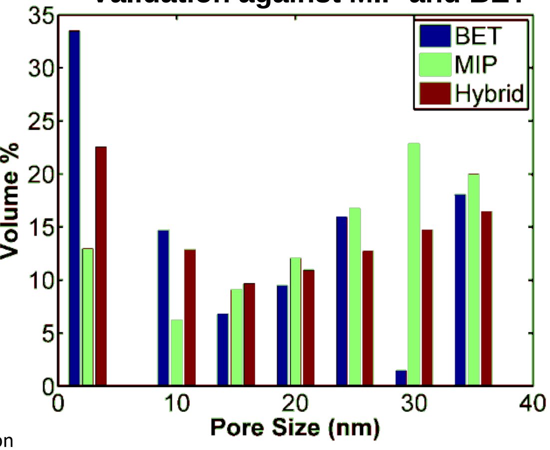


2.5 nm resolution

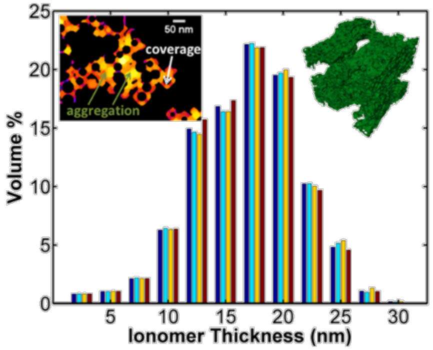
400 x 400 x 400 voxels

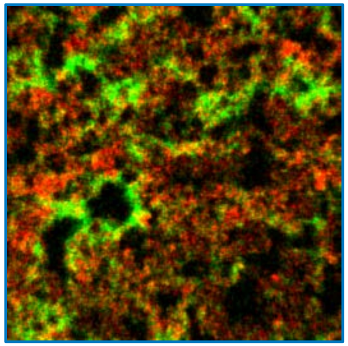
$\varepsilon_v = 0.45$

Validation against MIP and BET



Calculated ionomer size distribution is independent of random C and Pt placement – does not directly correspond to ionomer film coverage

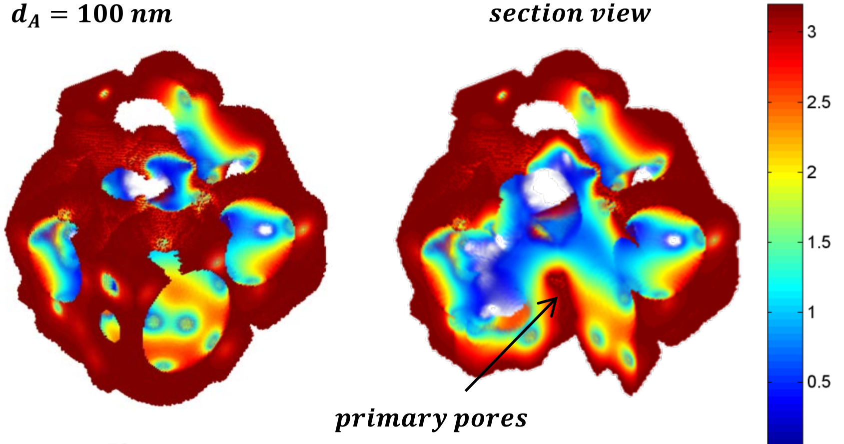


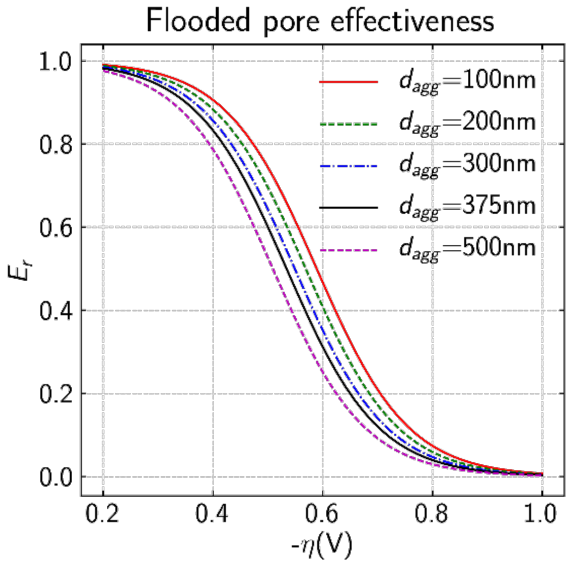


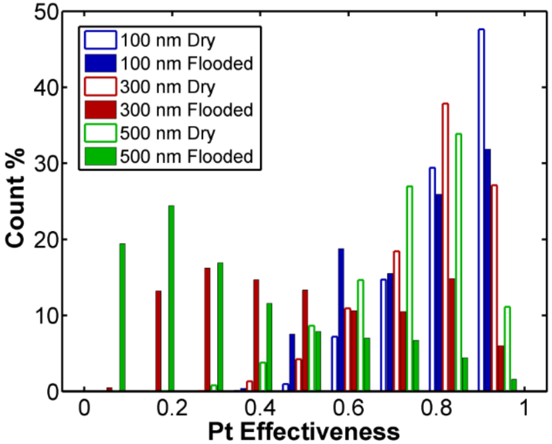
Microstructural Modeling

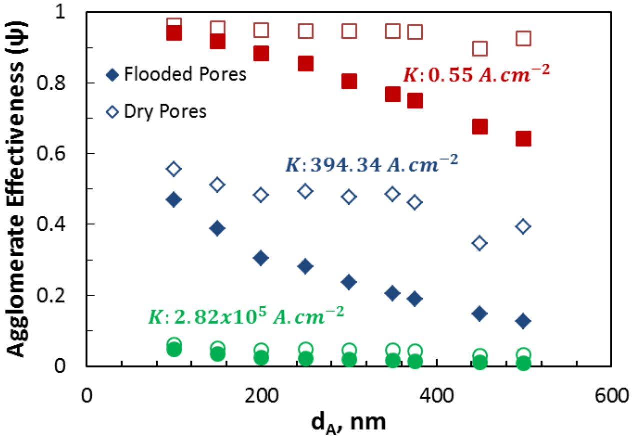
$$Effectiveness\ Factor, Er = \frac{Actual\ reaction\ rate}{Rate\ if\ not\ slowed\ by\ diffusion}$$

Direct numerical simulation of O_2 transport in multi-phase agglomerate









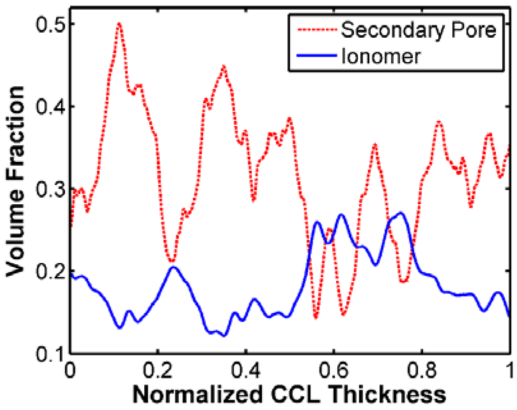
$$c^r_{O_2} = 34.1\ mol.m^{-3}$$

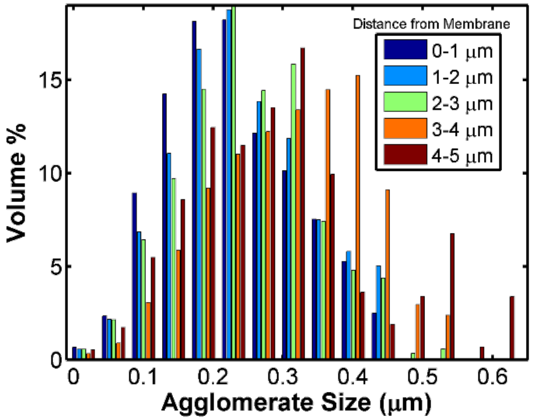
$$i = K\left(\frac{c_{O_2}}{c^r_{O_2}}\right)$$

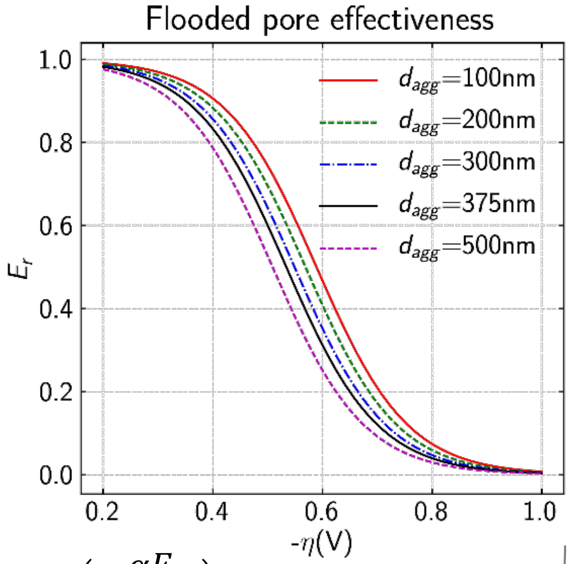
- Catalyst effectiveness is generally smaller if particles are closer to agglomerate center, at higher current density, and if pores are flooded

Multiscale Modeling

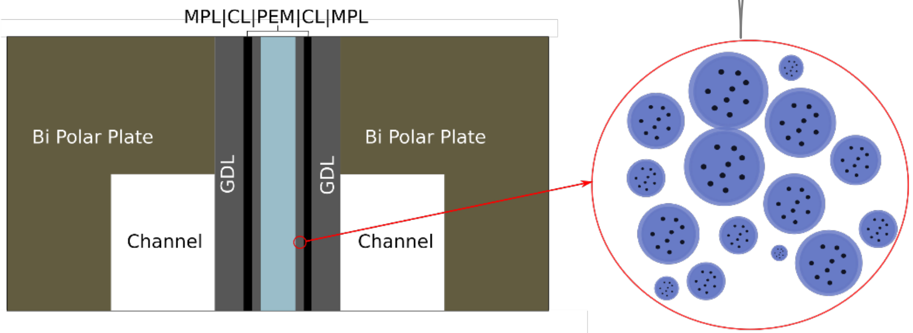
$$\textbf{\textit{Effectiveness Factor, Er}} = \frac{\textbf{\textit{Actual reaction rate}}}{\textbf{\textit{Rate if not slowed by diffusion}}}$$







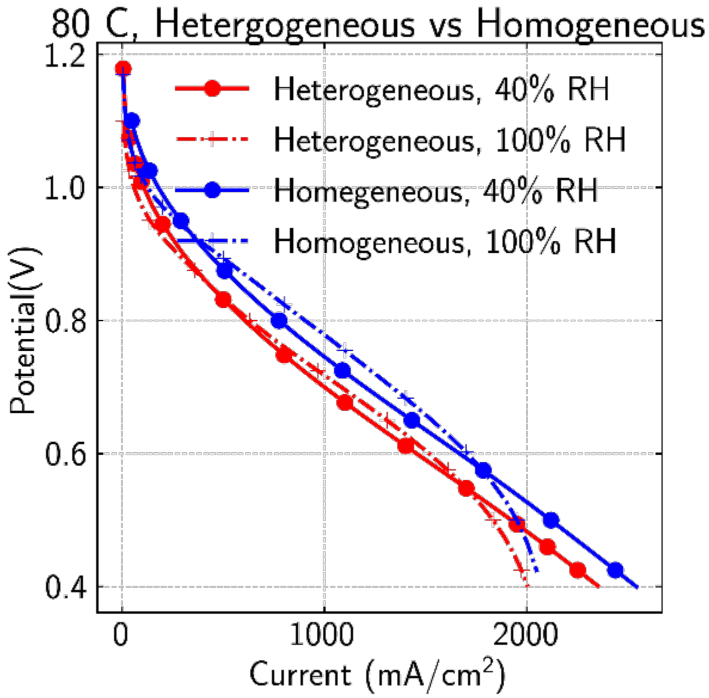
Average current: $$i(x) = \sum_r \phi\{r(x)\}E_r\{r(x)\}A_v\{r(x)\}i_0\left(\frac{c_{O_2}}{c_{O_2}^{ref}}\right)\exp\left(-\frac{\alpha F}{RT}\eta\right)[1-\epsilon_v(x)]$$

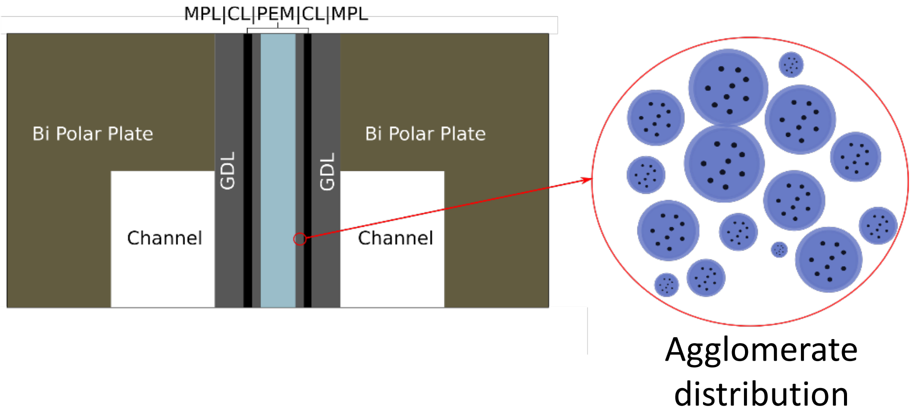


Agglomerate distribution

- Incorporated microscale modeling and features in macroscale model
- CL structure is highly heterogeneous

Multiscale Modeling



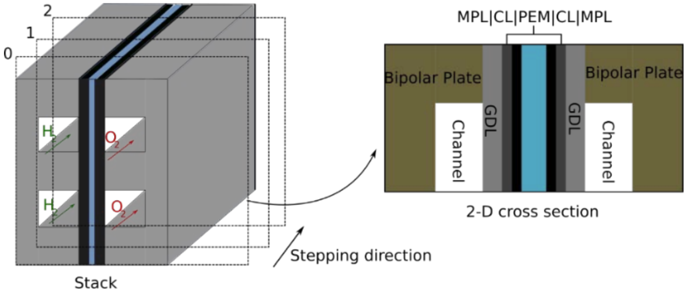


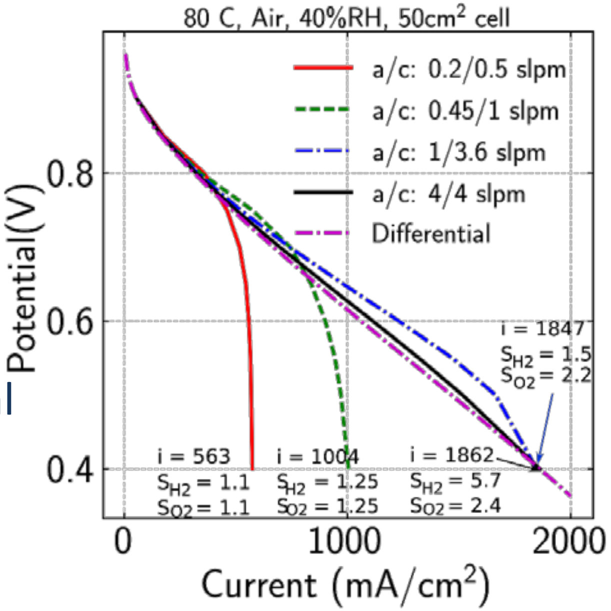
Agglomerate distribution

- Incorporated microscale modeling and features in macroscale model
- Local reductions in porosity results in transport bottleneck and under-utilization of CL
  - Most of current is produced by smaller agglomerates
- Accounting for heterogeneities can be critical for computing performance accurately
  - No well-defined representative elementary volume (REV)
  - Conventional agglomerate models can underpredict/overpredict depending on estimated ionomer thickness

Differential to Integral Cell

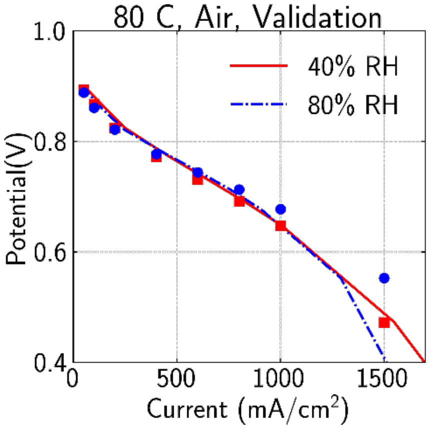
- Develop 1+2D model to examine going from differential to integral cells
  - 2D model trained on differential cell data

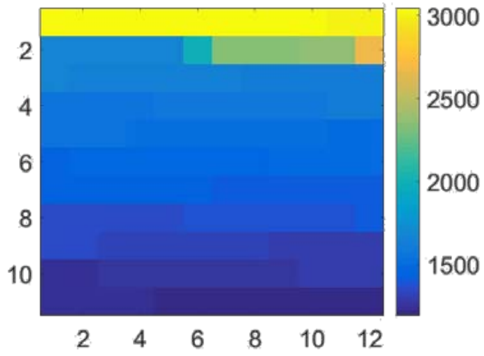




  - Once above 3 stoich. start approaching differential cell conditions
    - Similar predictions at low current densities
    - Intermediate currents, integral model shows slightly higher performance due to better membrane hydration

- Predictions for integral cell model
  - Accurate predictions at 40% RH
  - Discrepancy at 80% RH and high current
    - Model predicts sooner flooding



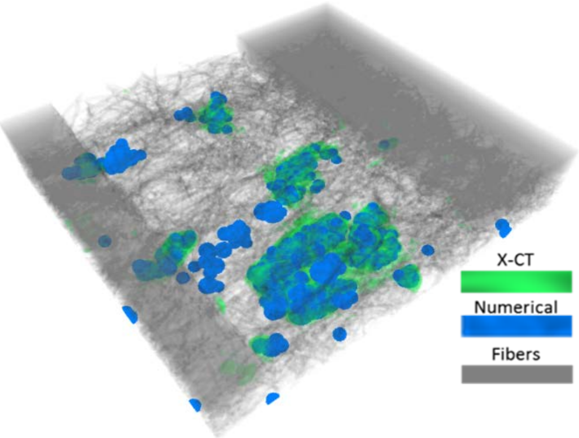


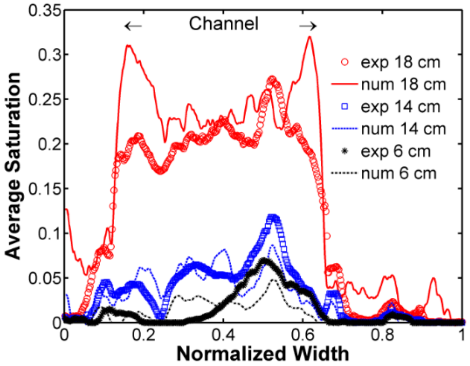
Segment current density at 0.32 V

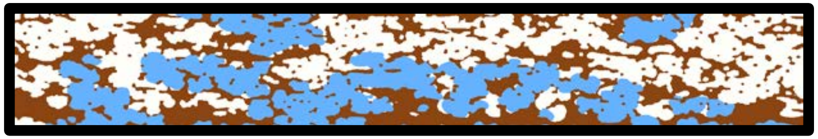
Pore-scale Modeling

- Model water in GDLs using direct simulation or lattice Boltzmann

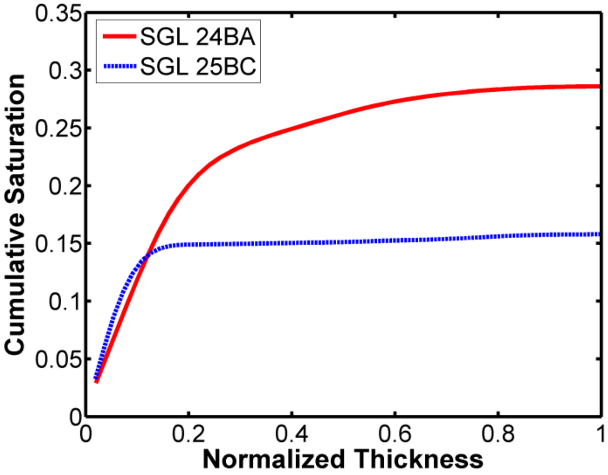
Water invasion in SGL compared with micro-XCT data*



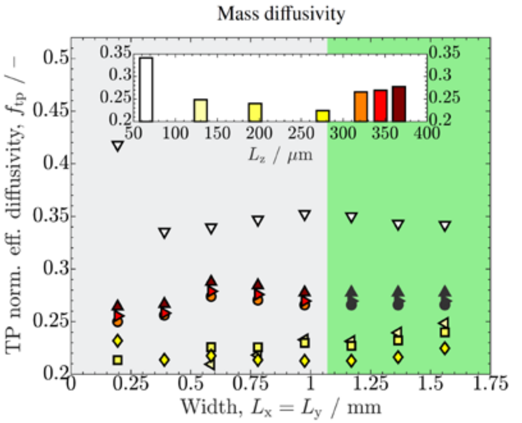




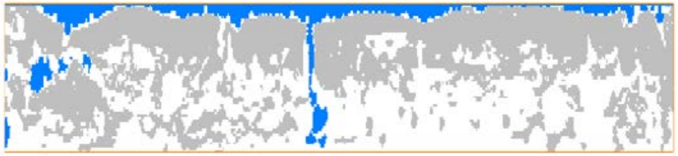
At 2 A/cm^2, water is transported through cracks in MPL leading to 50% lower saturation



Cannot define a through-plane REV



SGL 25BC

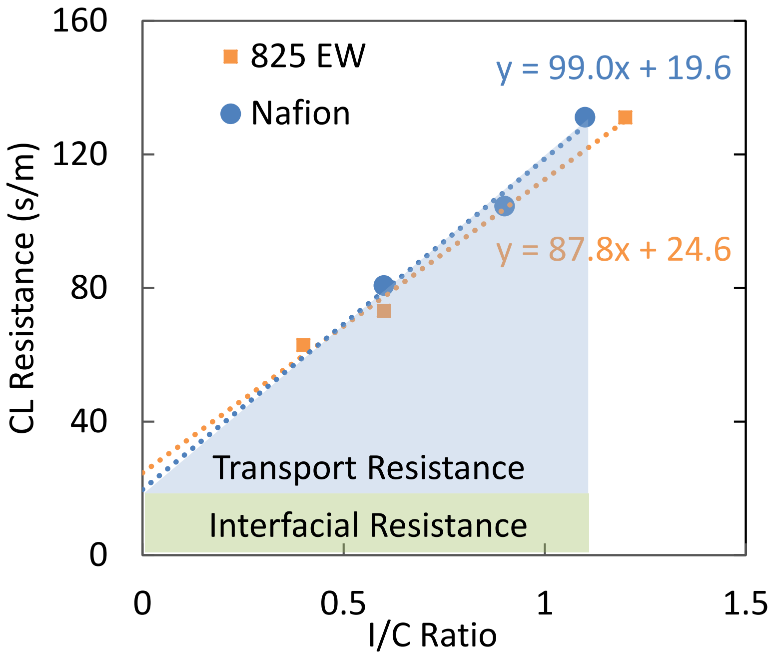


SGL 24BA

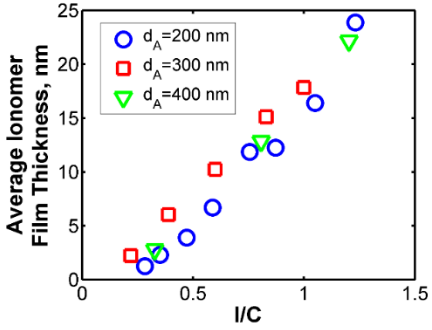
*Zenyuk, Parkinson, Hwang, and Weber, Electrochemistry Communications 53 (2015) 24-28

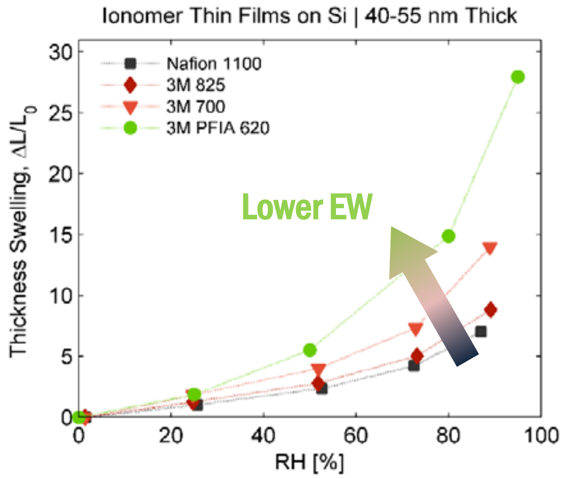
Impact of Ionomer EW on Local Resistance

- Examine local resistance with H_2 limiting current and varying I/C
  - At I/C 0.6:
    - 30% interfacial for 825 EW
    - 25% interfacial for 1100 EW
  - Activation energy suggests transport through water or ionomer is limiting
  - Phenomena agrees with thin-film analysis

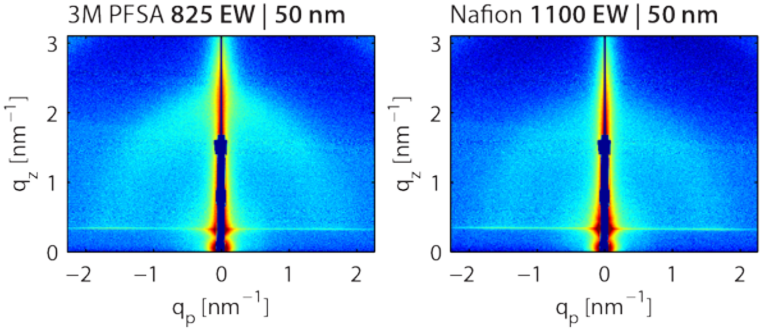


I/C from reconstruction correlates to thicker ionomer film

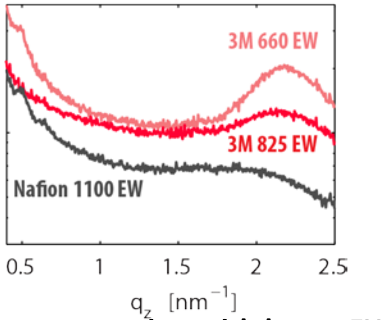




Higher swelling with low EW

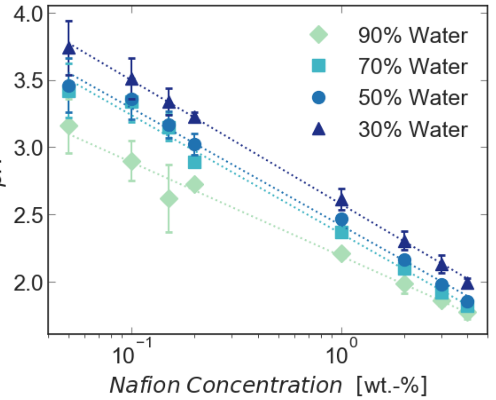


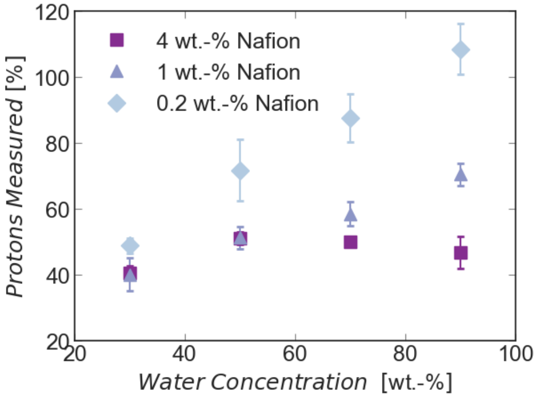
More alignment near the substrate



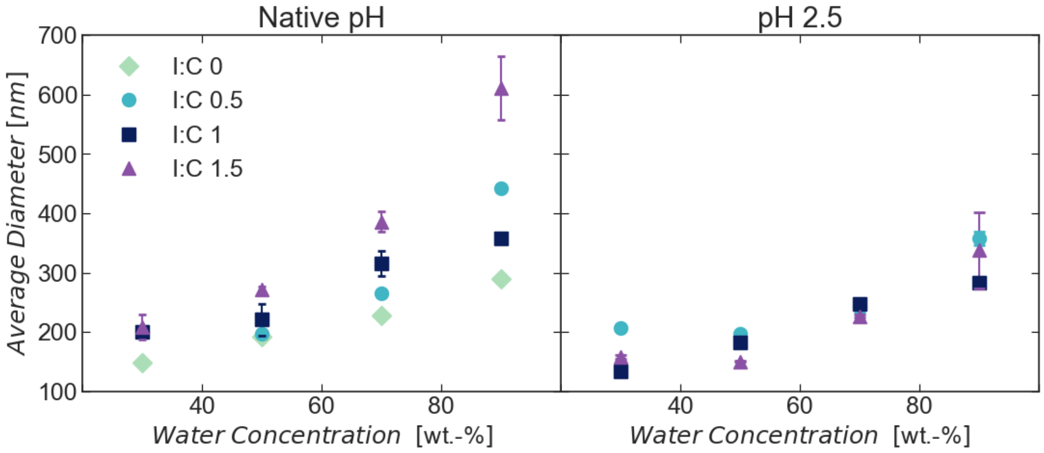
Better phase separation with lower EW

Effect of Ink Solvent and Dispersion Nature

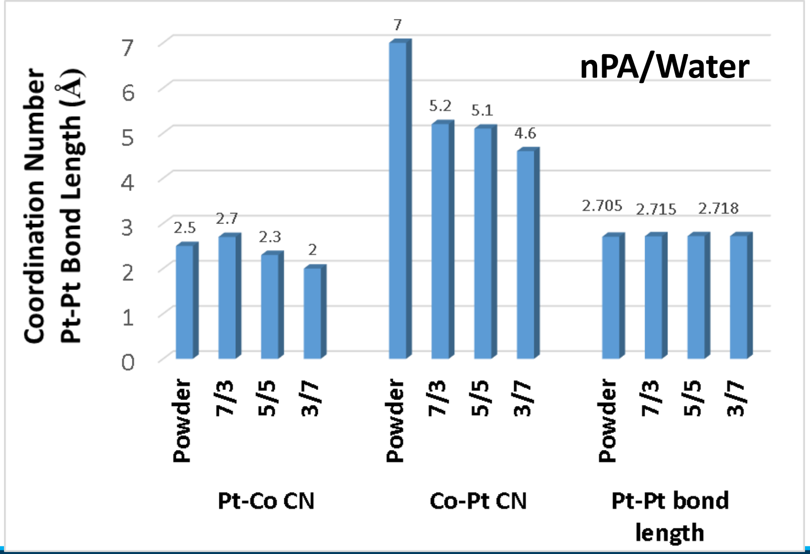




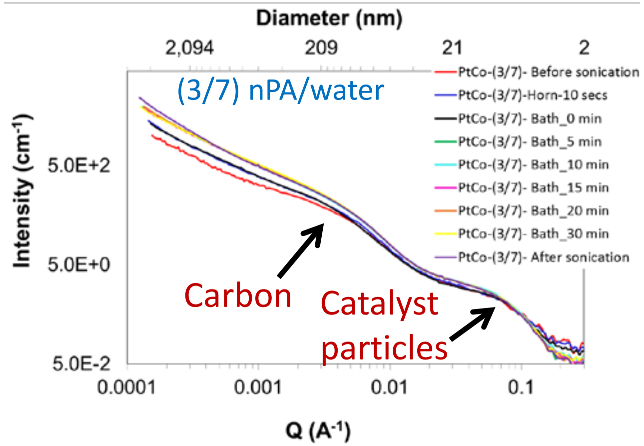
- Nafion dispersions have an inherent pH
  - Higher nafion loadings lead to higher aggregation and less accessible protons
- pH affects electrostatic interactions controlling ink aggregation, which can be removed by removing inherent pH
- Pt-Co, Co-Pt coordination numbers decrease with increasing water content and Co leaches into ionomer/solvent
  - Co leaching increases with water content

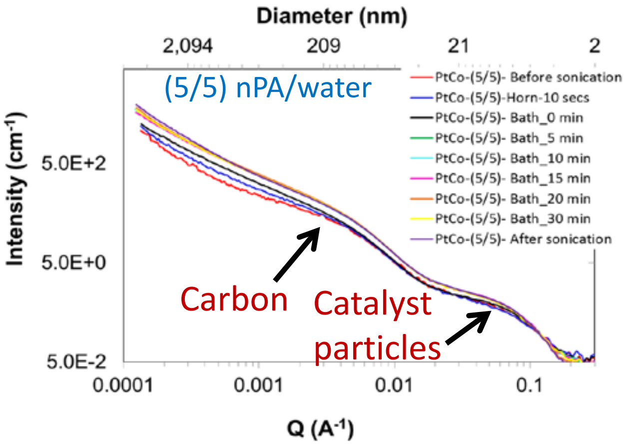


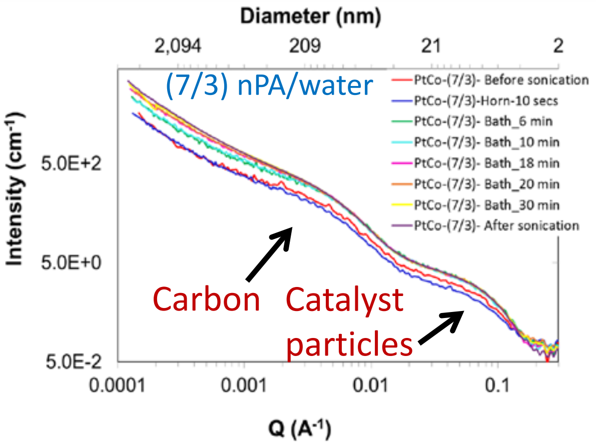
Umicore PtCo (27.5 wt% Pt, 3 wt% Co/HSAC
3M 825 EW ionomer (I/C=0.7). Solid content: 0.33 wt%

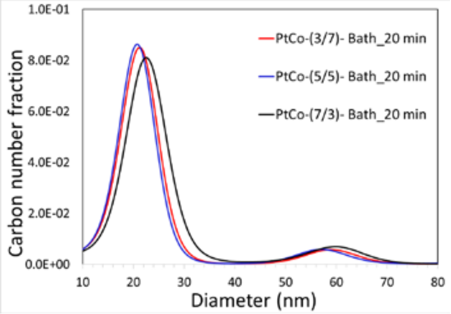


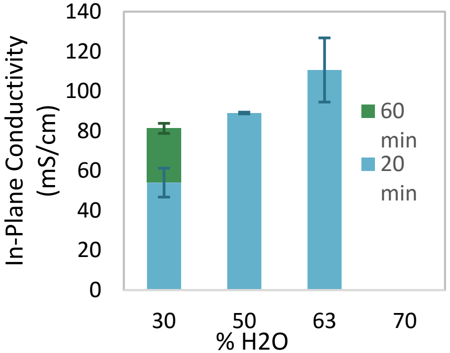
Solvent Effects on PtCo/Ionomer Ink Dispersion







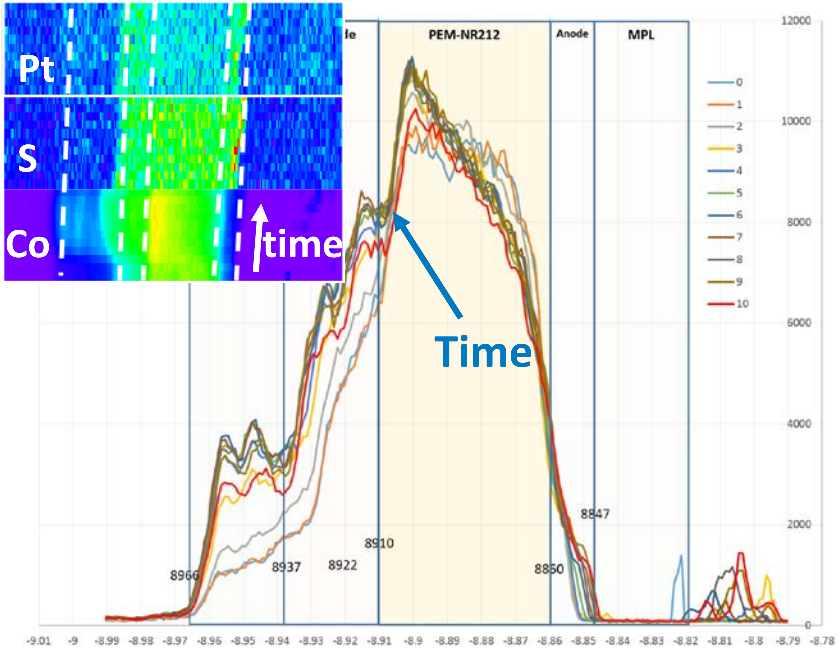




- Scattering intensity at q<0.01 Å-1 increases with sonication time - break-up of agglomerates >2 µm
  - Agglomerate break-up reaches steady-state after 20 min of sonication
  - Agglomerate break up is faster and yields smaller particle sizes with higher water content inks (5/5 and 3/7, nPA/Water)
- In-plane conductivity of ionomer films cast from ionomer dispersions increases with increasing water content and sonication time
  - Connectivity of ionomer strands increases with water content

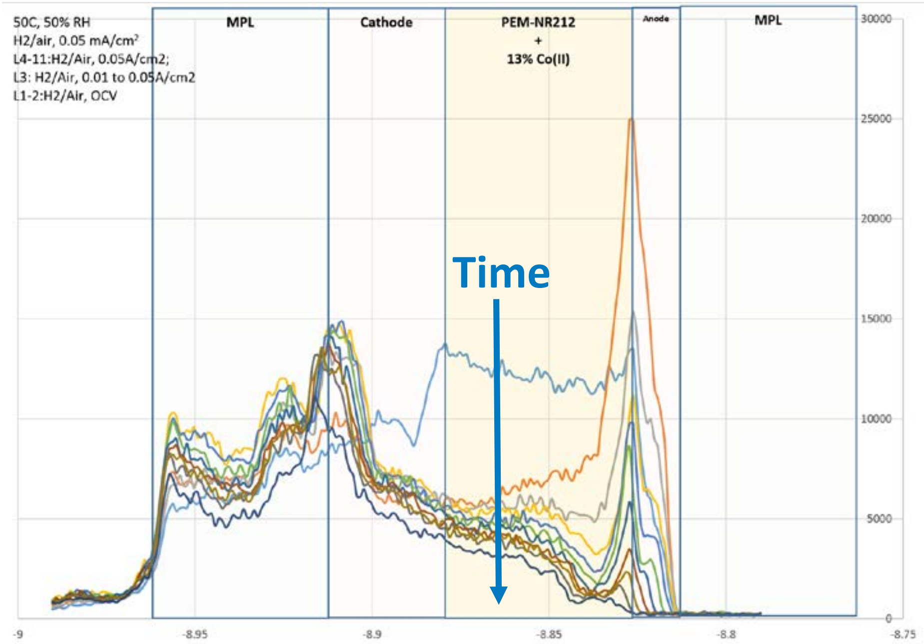
Operando Measurement of Cation Migration (Co)

Convection effects: dry cathode/50% RH anode



- Humidified anode/dry cathode causes Co transport from anode CL/PEM into cathode and MPL
- Fast equilibration into PEM/CL ionomers after exposure to humidified N_2/N_2
- Exposure to dry N_2/N_2 locks profile into place
- Co goes into anode CL when RHs are switched

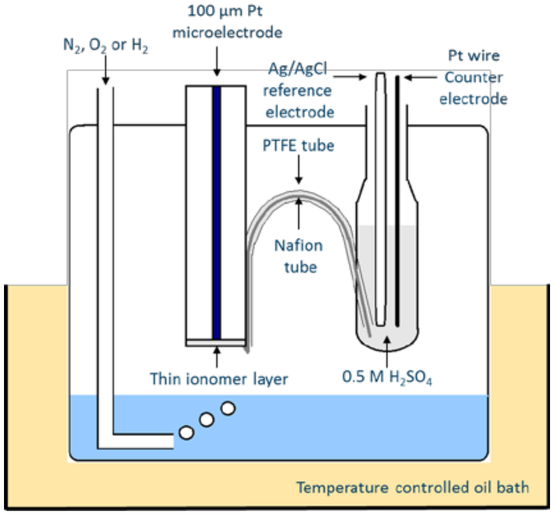
Potential effects: 80% RH in H_2/air at 0.05 mA/cm^2



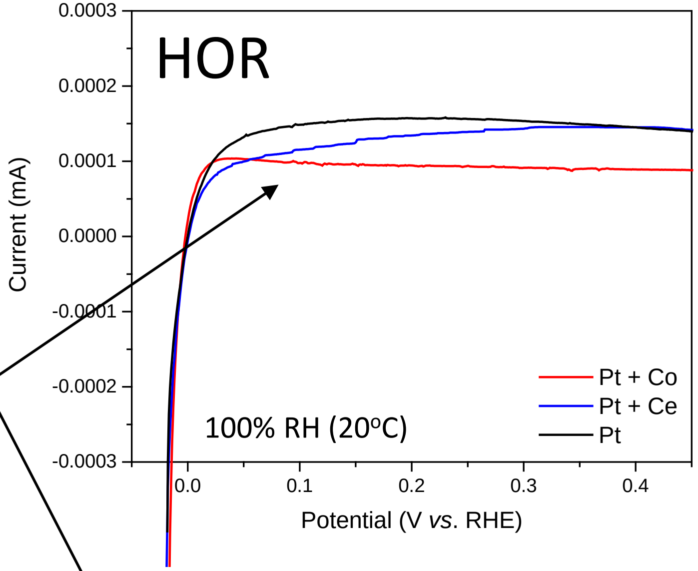
- Significant migration from anode CL/PEM into cathode CL/MPL under load
- No evidence for migration beyond 50 μm cathode MPL

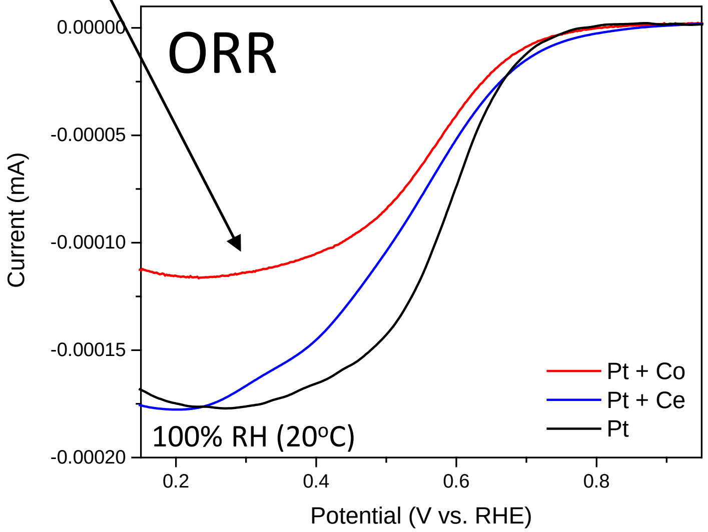
Pt Microelectrode Studies

Schematic of set-up



Significant decrease in Pt surface area (observed in both HOR and ORR) with presence of Co contaminant in ionomer

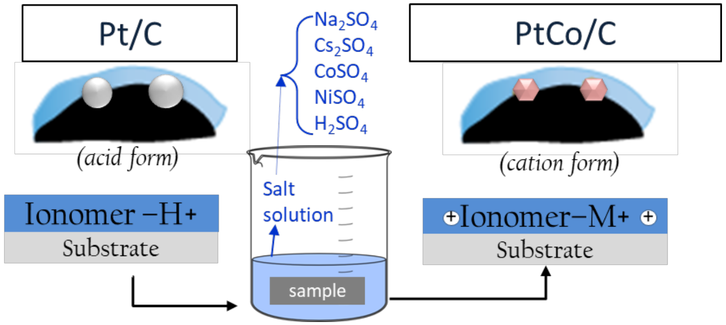


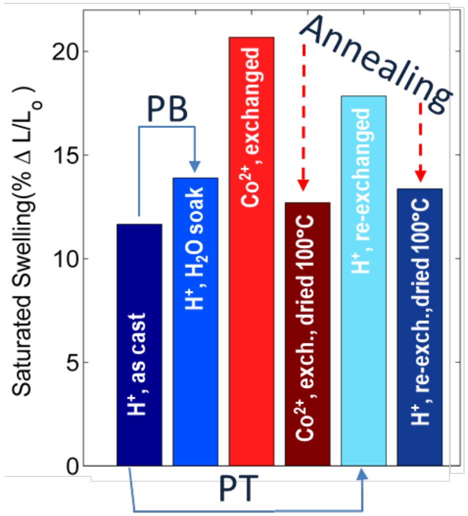


- Ionomer solution (0.05 wt.% Nafion) mixed with contaminants Co (as $CoClO_4$, target Co 5 mg/cm^3) and Ce (as $Ce(SO_4)_2$, target Ce 15 mg/cm^3) and allowed to exchange overnight
- Submicron (ca. 500 nm) thin-film of ionomer solution spin-cast onto 100 µm electrode at 1000 rpm
- Co-contaminated Nafion layer reduces limiting current for both HOR and ORR
- Ce-contaminated Nafion layer does not affect limiting current, but inhibits reaction until mass transport limited

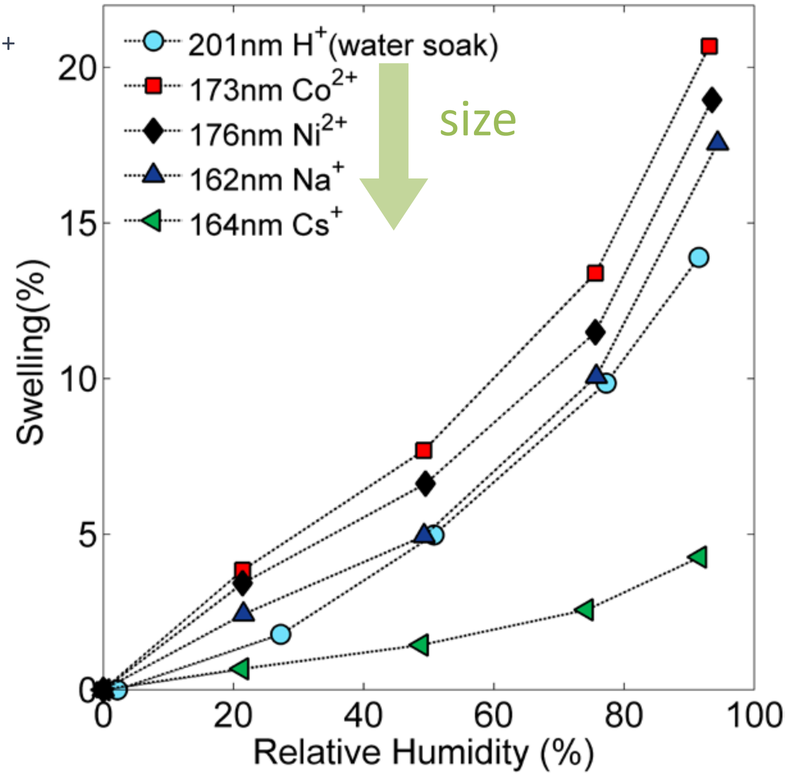
Impact of Cation on Ionomer Thin Films

- Different salt solutions employed to investigate impact of cation
- Impacted by cationic exchange, hydration dynamics depend on:
  - Coordination number and shell
    - Strength of binding(ΔHhyd): $Cs^+ < Na^+ << H^+ << Co^{2+} \sim Ni^{2+}$
  - Ionic radius: $H^+ << Ni^{2+} < Co^{2+} < Na^+ < Cs^+$
- Ionomer thin-film uptake impacted by processing:
  - Increases with water soaking (PB)
  - Increases with acidic re-exchanging (PT)



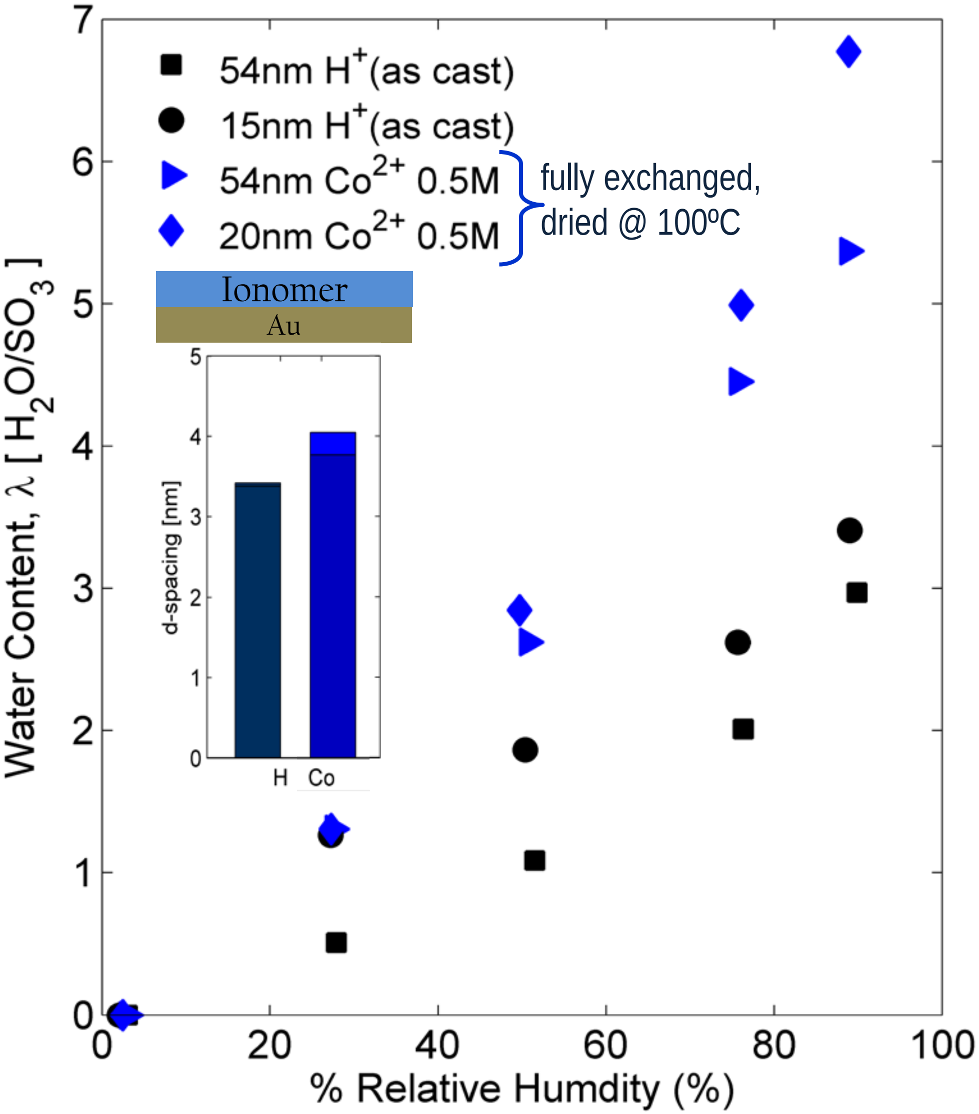


~200nm Nafion thin-film on Si/SiO_2



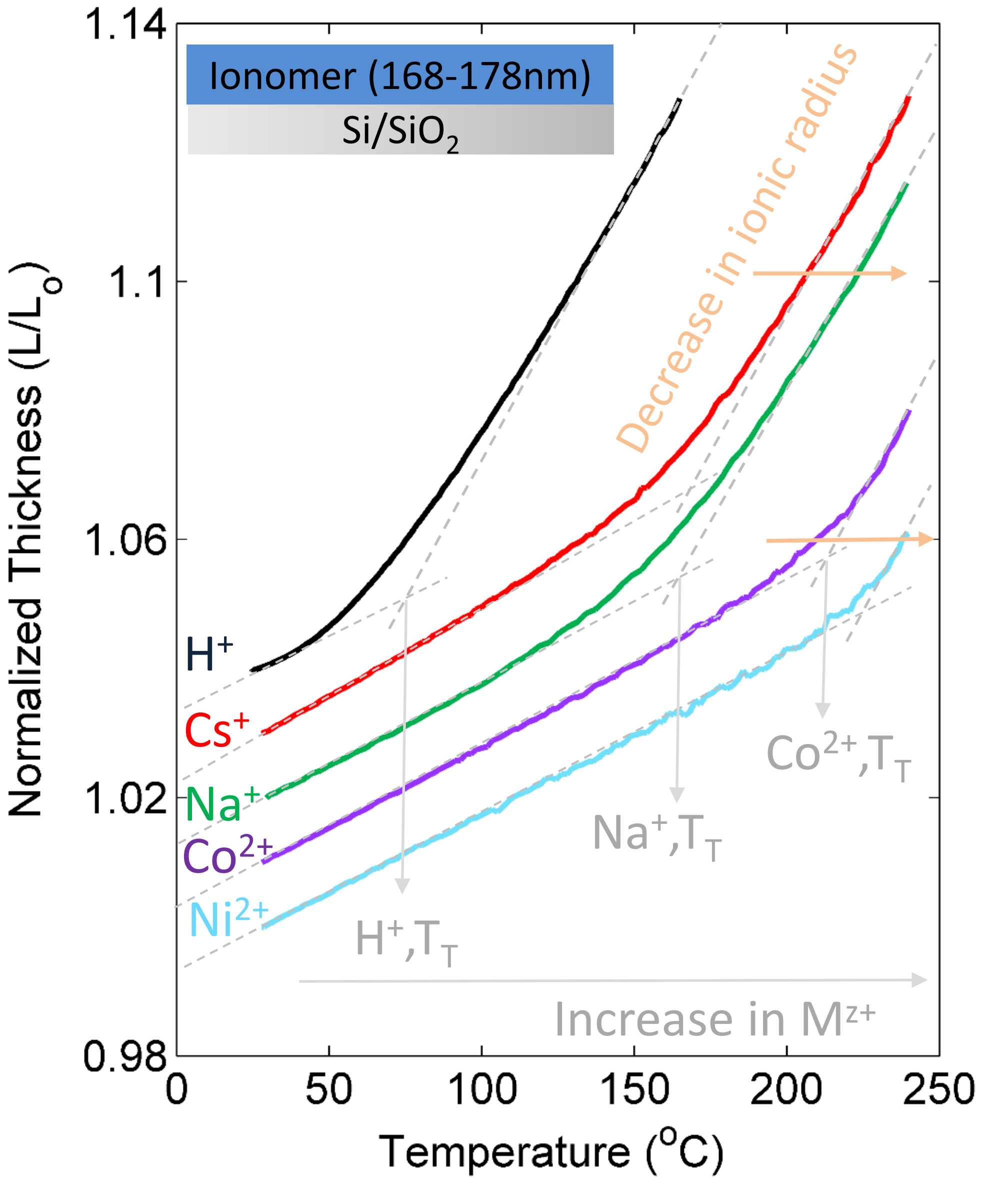
Impact of Cation on Ionomer Thin Films

- Water uptake below 50 nm increased due to anisotropic ionomer structure
  - Agrees with d-spacing from GISAXS
- Increase in Co^{2+} fully doped films possible due to CO^{2+} higher
  - Hydration energy (~1000 vs 2000 kJ/mol)
  - Water bond length (~250 vs 200 pm)
  - Residence time of water with Co^{2+} [*]



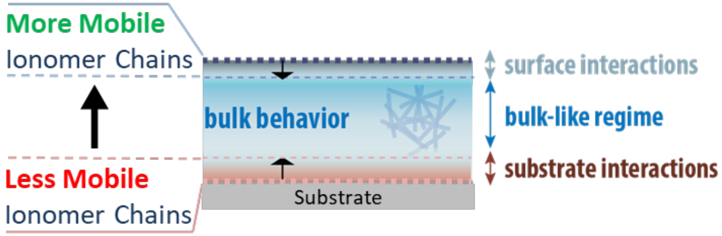
[*]*Chem. Rev. 1993, 93, 1157-1204*

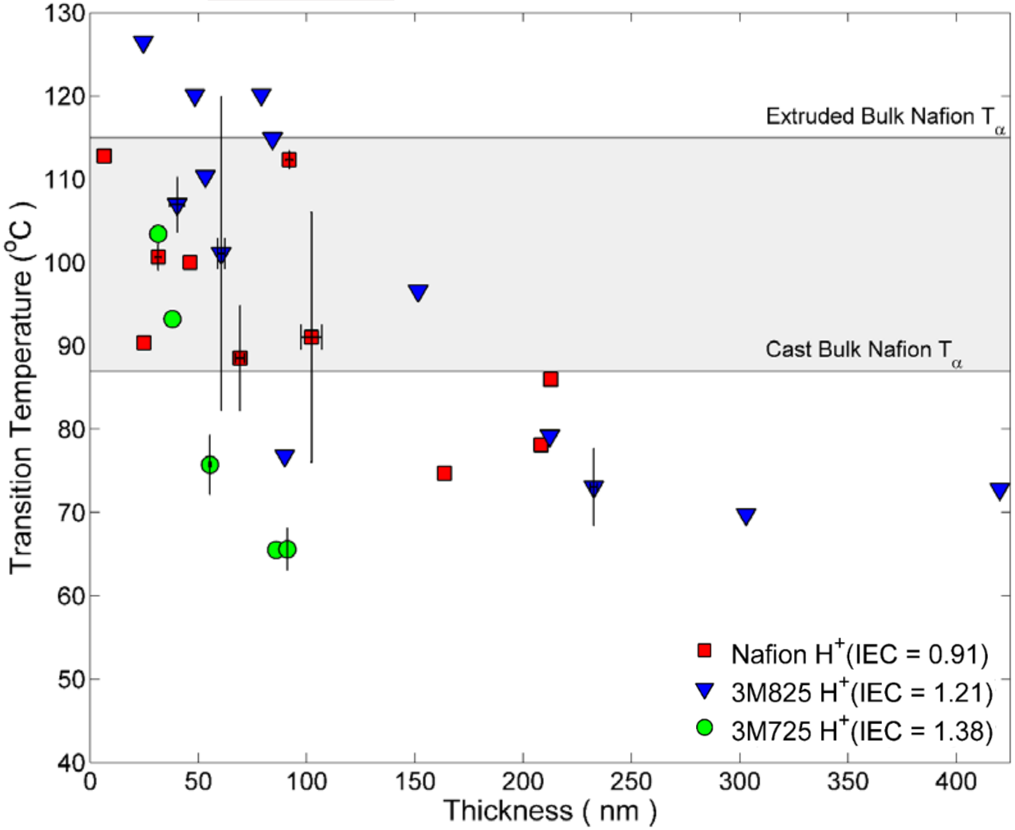
Impact of Cation on Ionomer Thin Films



- Cation form impacts thin-film transition temperature (T_T), which represents mobility
  - Increase in cation charge → increase in T_T due to ionic crosslinking
  - M^{2+} correlated better with ionic radius than M^{1+}
- Thickness dependence of T_T in M^{1+} is not strong, indicating dominating influence of ion-dipole interaction between M^+ --- $^-SO_3$ moieties over adsorption with substrate

Understanding Ionomer Thin-Films





Increase in Ionomer Confinement

Increase in Substrate Interaction Impact

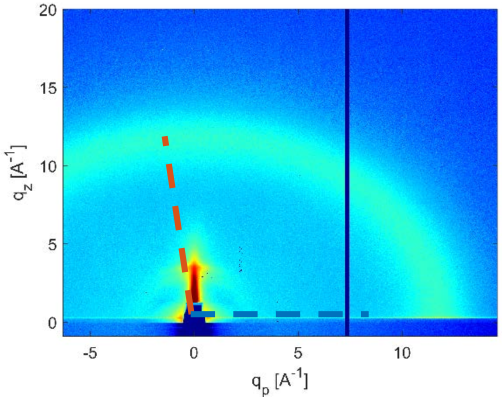
- Ionomer thin-films experience:
  - Finite size effects (confinement)
  - Substrate impacts (physical adsorption & polymer chain interaction with substrate)
  - Free surface interactions (higher configurational freedom near air/polymer interface)
- Transition temperature (T_T) increases with decreasing thickness
  - Greater impact of substrate
  - Demonstrates less mobility and hence expected worse transport properties
- Need to design polymers with free volume to counteract tendencies

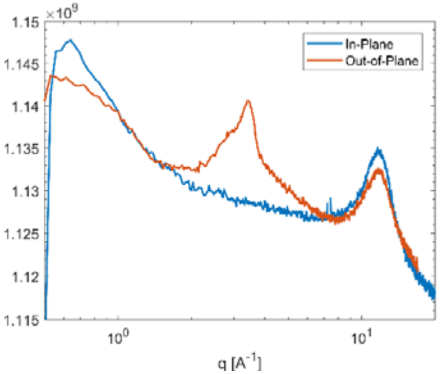
Ionomer Thin-film Characterization

Grazing-incidence X-ray Scattering

- GISAXS beamline – ALS, LBNL

➢ 2D GIWAXS probes in-plane and out-of-plane ordering → Confinement induced anisotropic domain ordering





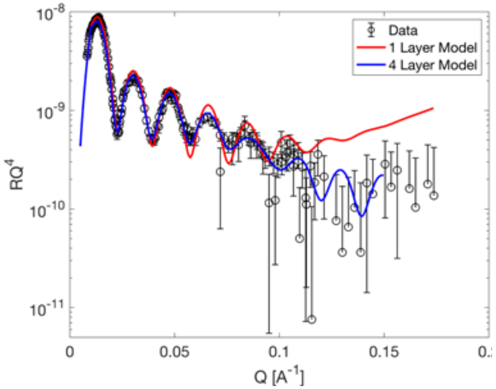
Neutron Reflectivity (NR)

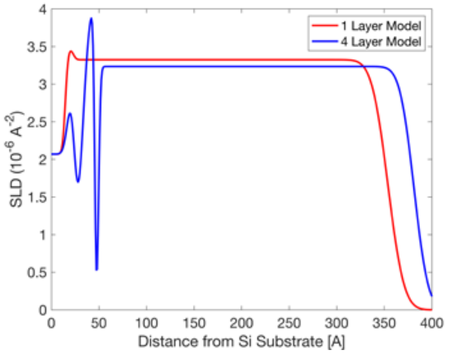
- Asterix Beamline – LANSCE, LANL

➢ Through-plane scattering length density

➢ Sensitive to local density fluctuations

➢ Local hydration at the substrate-film interface is evident





Collaborations (FOA-1412 Partners)

- Core FC-PAD team consists of five national labs
- Each lab has one or more thrust roles and coordinators

Interactions with DOE Awarded FC-PAD Projects (FOA-1412)

POC assigned for each project to coordinate activities with PI

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

- 35% of National Lab budget supports FOA projects
  - Equal support to each project across FC-PAD
- Two in-person FC-PAD meetings held annually - include FOA members with individual sessions held to discuss interactions and progress
- Project-by-project details vary, but some hold bi-weekly conference calls with FOA project member and national labs

Collaborations (Non-FOA activities)

Institutions	Role
Umicore	Supply SOA catalysts, MEAs
EWii	Supply SOA catalysts, MEAs
University Carlos III of Madrid	Microscale simulations
TKK	Supply SOA catalysts
Johnson Matthey	Catalysts and CCMs
GM	Supply SOA catalysts, MEAs
Ion Power	Supply CCMs
W.L. Gore	SOA Membranes (in collaboration with GM)
ANL–Materials Science Division Group	SOA catalyst
Tufts University	GDL imaging
KIER	Micro-electrode cell studies
University of Delaware	Membrane durability
Vanderbilt University	Ink studies
PSI – Paul Scherrer Institute	GDL imaging

Collaborations (Non-FOA Activities)

Institutions	Role
University of Waterloo	GDL modeling
University of Alberta	GDL and flowfield modeling; ink studies
3M	Ionomers
Colorado School of Mines	Membrane diagnostics
SGL Carbon	GDL Supplier
NPL - National Physical Laboratory	Reference electrodes for spatial measurements
NIST – National Institute of Standards and Tech.	Neutron imaging
University of Arkansas-Little Rock	Catalysts
Simon Fraser University	Ionomer
Chemours	Ionomer
NREL-EFTECS project	Catalyst

Proposed Future Work

- **Inks and thin films**
  - Examine carbon interactions with different solvents and ionomer chemistry
    - Direct observation of dispersions
  - Measure ionomer thin-film properties under applied potential
  - Evaluate interfaces and impact of carbon type including durability protocols
  - Examine impact of cation doping level
  - Casting and evolution of ionomer thin-film structure
  - Gas permeability measurements
- **Catalysts**
  - Re-examine intrinsic potential-dependent kinetics
    - Elucidate governing binary interactions
    - Direct observation of dispersions
- **Catalyst-layer structure**
  - Continue exploration of different catalyst-layer structures
    - Array, electrospun, HSC/VC layered
  - Incorporation and characterization of novel electrocatalyst materials
  - Microstructural reconstruction and modeling for catalyst layers including multiphase flow
    - Impact of Pt/C agglomerates
  - Directly measure ionomer film/carbon in operating electrodes
  - Local resistance analysis
    - Limiting current under variety of conditions, techniques, ionomers, gases, temperature, humidity

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

Proposed Future Work

- **Advanced Characterization**
  - Multimodal characterization of thin films
  - New low-voltage cryo-STEM
    - Combinatorial EELS and EDS and tomography (4D STEM)
    - Customized in situ cryo-holder to enable improved soft-matter imaging
- **Water and thermal management**
  - Complete impact of conditioning and changes during break-in
  - Detail model for GDL/channel interface and droplets
  - Water visualization in various components
  - Explore impact of carbon type in MPLs
  - Integrate and evaluate various components to elucidate emergent phenomena
  - Translational modeling going from ex situ property data to operando performance
- **Durability**
  - Model synergistic mechanical degradation with crossover and performance
  - Model and measure the movement of chemical scavengers and/or other ions
  - Examine the effect of aging on electrode microstructure
  - Develop stabilized systems of radical scavengers

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

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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:
  - Developed new catalyst-layer architectures
  - Utilized characterization and experimental diagnostics to delineate catalyst layer interactions
  - Experimentally evaluated degradation mechanisms and conditioning effects
  - Completed analysis of Mirai SOA components
  - Developed diagnostics and models for interpreting critical phenomena and data
  - Explored impact of cations from inks to MEAs
- Future Work:
  - Develop the knowledge base to improve catalyst-layer structures for higher fuel cell performance and durability

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

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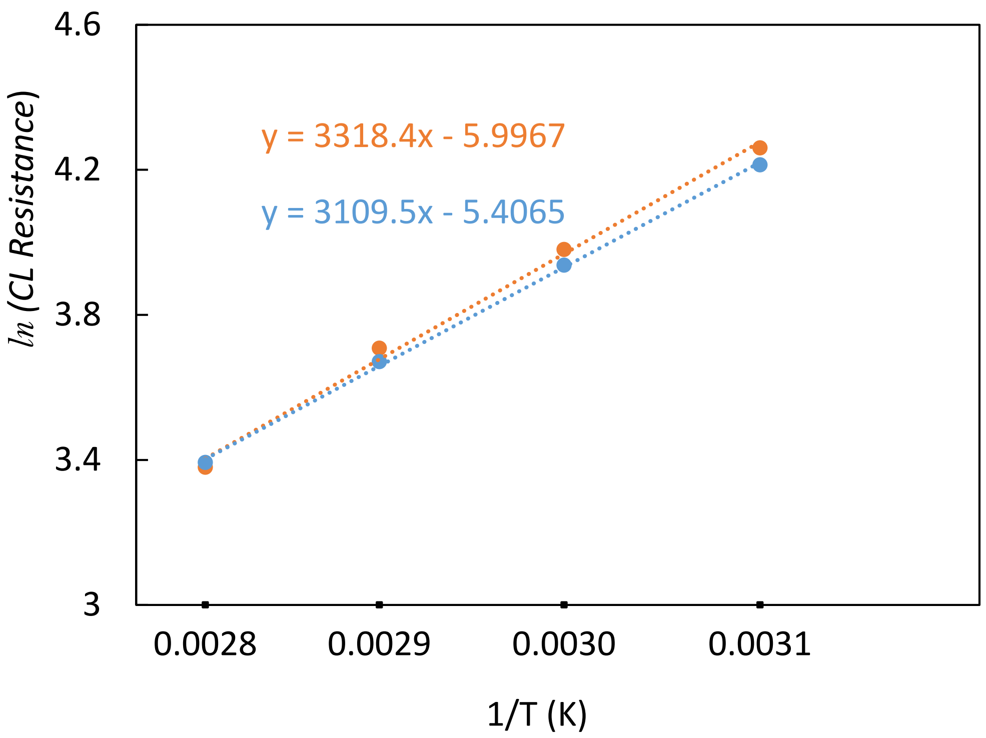
- User Facilities
  - DOE Office of Science: SLAC, LBNL-Advanced Light Source, ANL-Advanced Photon Source, LBNL-Molecular Foundry, ORNL-Center for Nanophase Materials Sciences, ANL-Center for Nanostructured Materials
  - NIST: BT-2

Technical Back-Up Slides

Transport Activation Energy Analysis

- Diffusional activation energy of CL ionomer thin films higher than bulk hydrated Nafion values



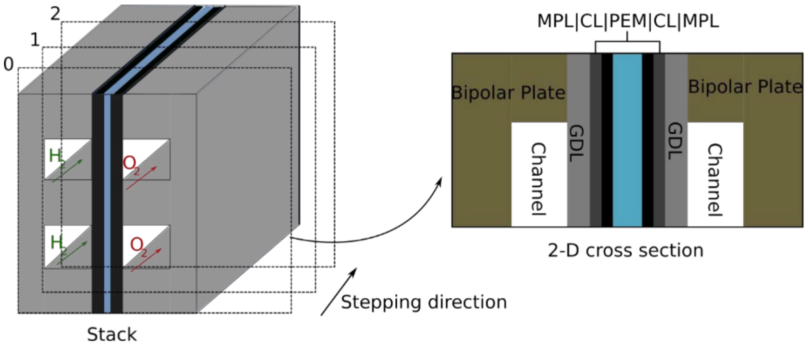
CL Ionomer	Activation Energy (10^{-20} J)
1000 EW	4.58
725 EW	4.29
Nafion (wet)[1]	3.32
Nafion (dry) [1]	6.20
Water[2]	3.33
Argon[3]	0.67
Knudsen	0.22

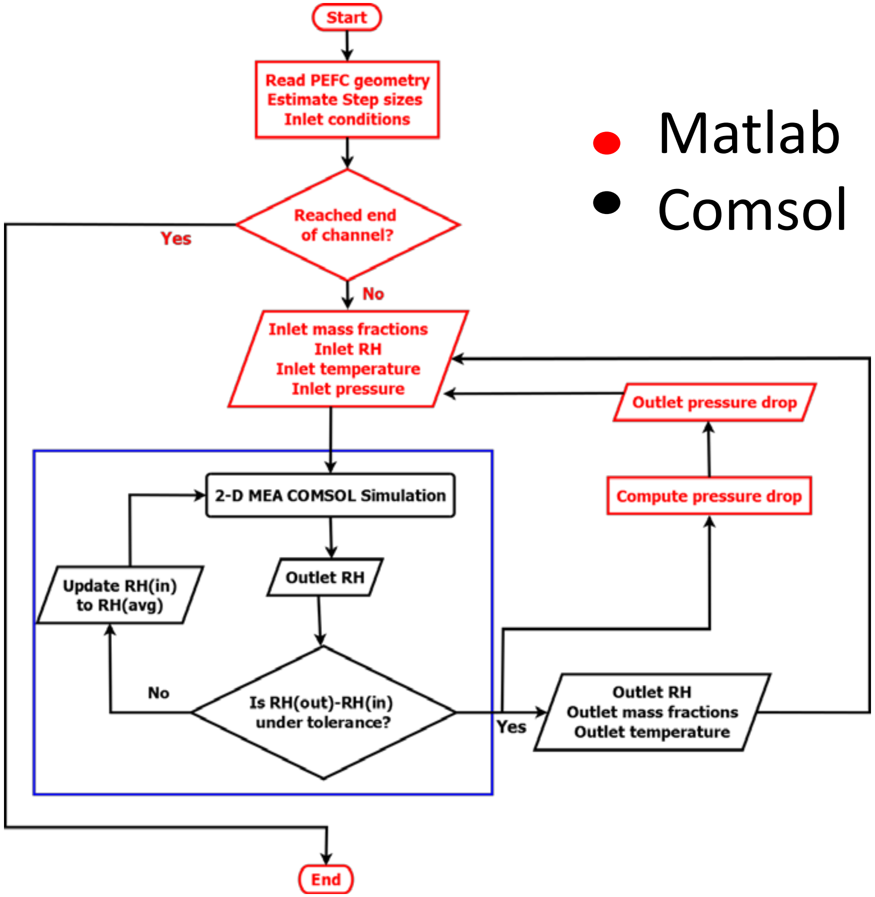
** Linear fit curve equations are color coded with legend*

1. *Schalenbach et. al., J. Phys. Chem. C 2015, 119, 25145–25155*
2. *Wilke-Chang correlation*
3. *Chapman-Enskog correlation*

Development of 1+2D Integral Cell Model

- 1+2D stepping based model
  - 2-D MEA cross section model in COMSOL
  - Along the channel stepping in MATLAB
  - Can account for down the channel changes in concentration, RH, pressure and temperature
  - In-plane transport not incorporated
  - Suitable for low stoich (integral) cell conditions





Start

Read PEFC geometry
Estimate Step sizes
Inlet conditions

Reached end of channel?

Yes

No

Inlet mass fractions
Inlet RH
Inlet temperature
Inlet pressure

2-D MEA COMSOL Simulation

Outlet RH

Is RH(out)-RH(in) under tolerance?

No

Update RH(in) to RH(avg)

Yes

Outlet RH
Outlet mass fractions
Outlet temperature

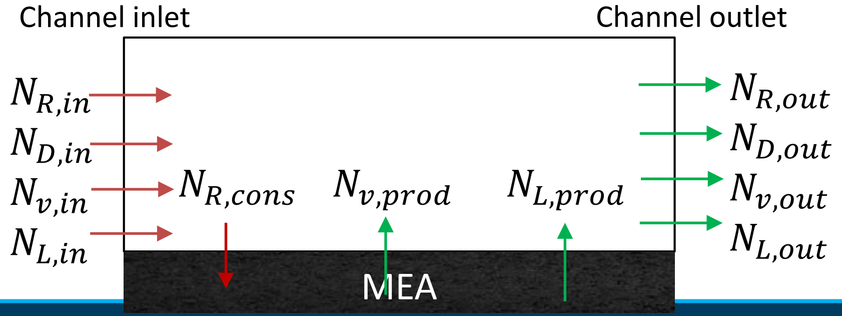
Compute pressure drop

Outlet pressure drop

End

● Matlab

● Comsol



Channel inlet

Channel outlet

$N_{R,in}$

$N_{D,in}$

$N_{v,in}$

$N_{L,in}$

$N_{R,cons}$

$N_{v,prod}$

$N_{L,prod}$

$N_{R,out}$

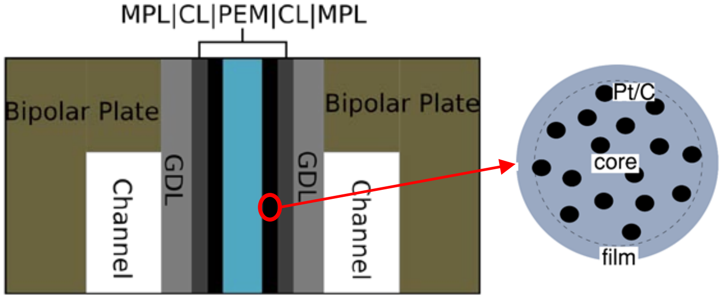
$N_{D,out}$

$N_{v,out}$

$N_{L,out}$

MEA

Development of 2D Differential MEA Model



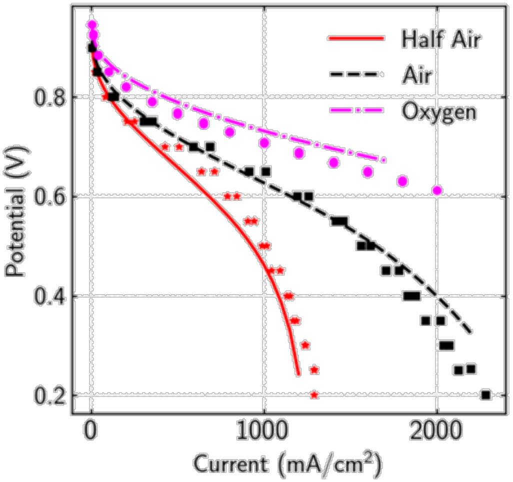
2-D cross section

- 2-D MEA cross-section model
- Doesn't account for along the channel variations
- Suitable for differential conditions (high stoich/flow rate)
- Incorporated physics:
  - Non-isothermal, two-phase model
  - Multicomponent diffusion
  - Electronic and protonic conduction
  - BV kinetics in anode, Tafel with PtOH coverage in Cathode
  - Agglomerate model in cathode

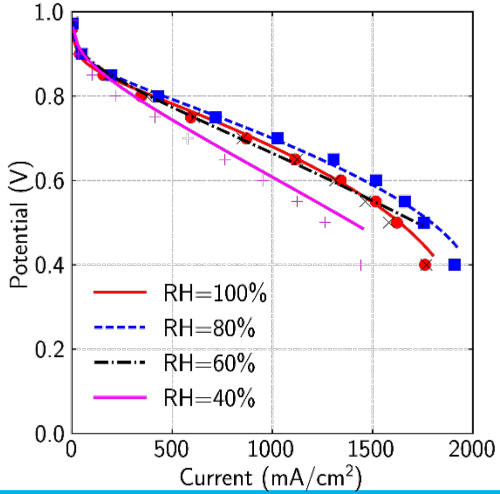
Validation Studies

- **Oxygen concentration sensitivity:**
  - Model able to match experimental trends accurately
- **RH sensitivity:**
  - Can predict cell behavior with RH change
  - Quantitative predictions accurate at higher RH
  - Higher error at lower RH values and high currents

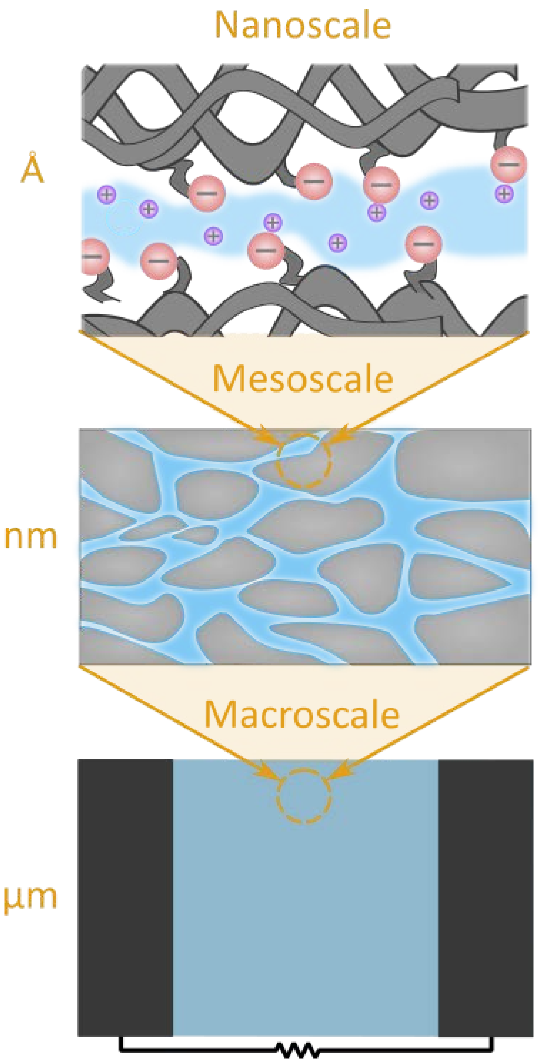
80C, 100% RH, Oxygen concentration sensitivity validation



80C, Air/H_2, RH sensitivity validation

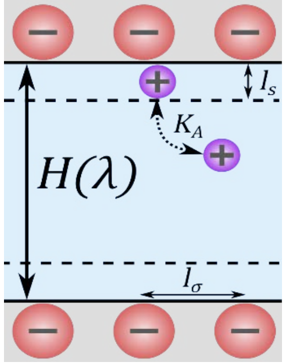


Mesoscale Modeling



- Formalism to bridge nanoscale chemistry to macroscale properties
- Nanoscale model:
  - Concentrated solution transport theory
  - Mean-field interactions
  - Ion dissociation through solvation
  - Swelling
- Mesoscale upscaling model:
  - Resistor network model
  - Heterogeneous domain size distribution
  - Predicts conductivity, water diffusion, and electro-osmosis
- Macroscale predictions:
  - Macroscopically relevant transport properties
  - Account for emergent behavior

Nanoscale domain



Mesoscale resistor network