U.S. DEPARTMENT OF
ENERGY

Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

FC-PAD: Fuel Cell Performance and Durability Consortium

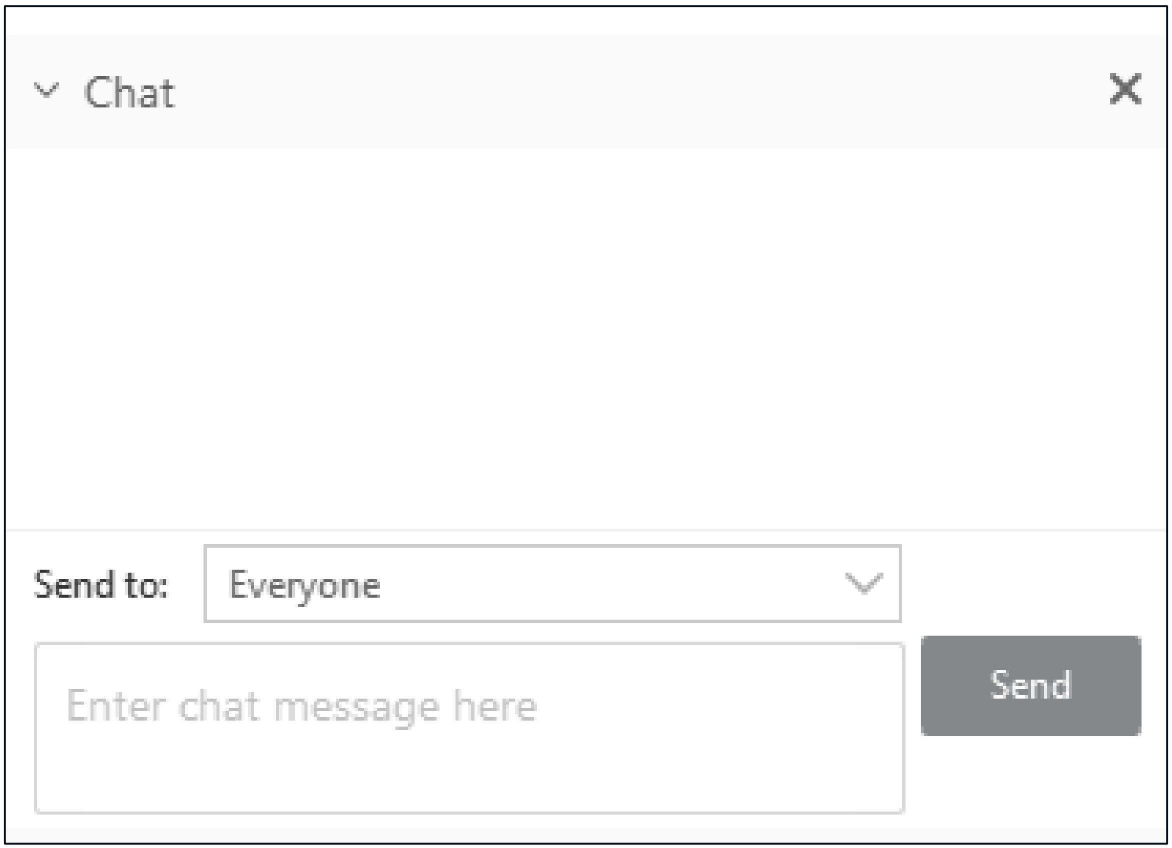
Rod Borup, LANL, Adam Weber, LBL

Fuel Cell Technologies Office Webinar

March 28, 2018

Question and Answer

- Please type your questions to the chat box. **<u>Send to: (HOST)</u>**



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Reminder: FOA Deadlines

Deadline to Submit Concept Papers for Commercial Truck, Off-Road Vehicle, and Gaseous Research Funding Opportunity Announcement

Concept papers for this funding opportunity are due **March 29**, and full applications will be due **May 15**. Applicants must submit a concept paper by the deadline to be eligible to submit a full application. For more information and application requirements, please visit the EERE Exchange website or Grants.gov

Deadline to Submit Concept Papers for H2@SCALE Funding Opportunity Announcement

Concept papers for this funding opportunity are due **April 8**, and full applications will be due **May 29**. Applicants must submit a concept paper by the deadline to be eligible to submit a full application. For more information and application requirements, please visit the EERE Exchange website or Grants.gov

www.energy.gov/eere/fuelcells/fuel-cell-technologies-office-newsletter

FC-PAD Consortium
Fuel Cell Performance and Durability

FC-PAD is funded by:

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy — Fuel Cell Technologies Office (FCTO)

- FC-PAD coordinates activities related to fuel cell performance and durability
  - The FC-PAD core-lab team consists of five national labs and leverages a multi-disciplinary team and capabilities to accelerate improvements in PEMFC performance and durability
  - Advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) at a pre-competitive level
  - The core-lab team consortium was awarded beginning in FY2016
  - Provide technical expertise and harmonize activities with developers

Los Alamos National Laboratory · Argonne National Laboratory · NREL National Renewable Energy Laboratory · Berkeley Lab · Oak Ridge National Laboratory

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*

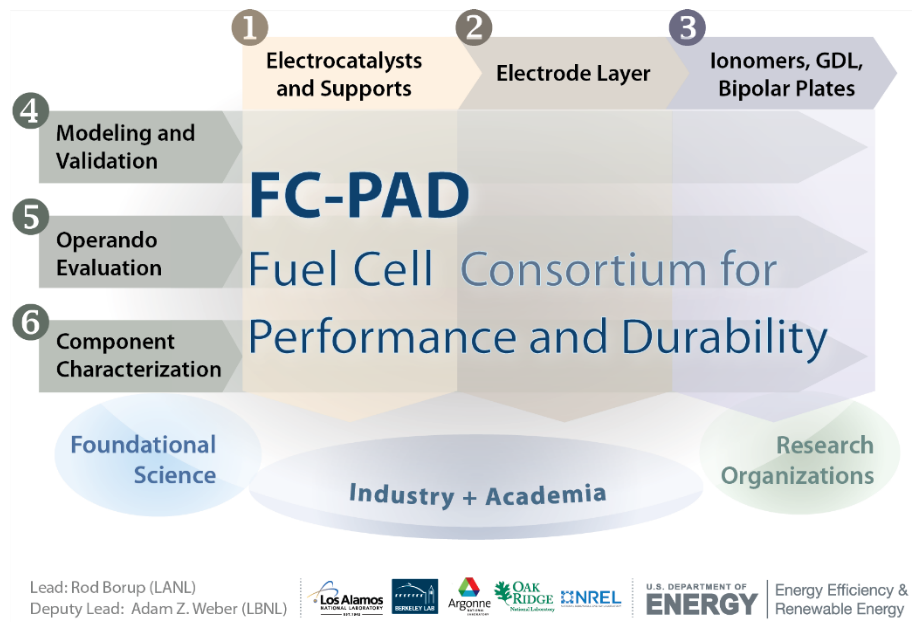
Argonne NATIONAL LABORATORY
Los Alamos NATIONAL LABORATORY
BERKELEY LAB
NREL NATIONAL RENEWABLE ENERGY LABORATORY
OAK RIDGE National Laboratory

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

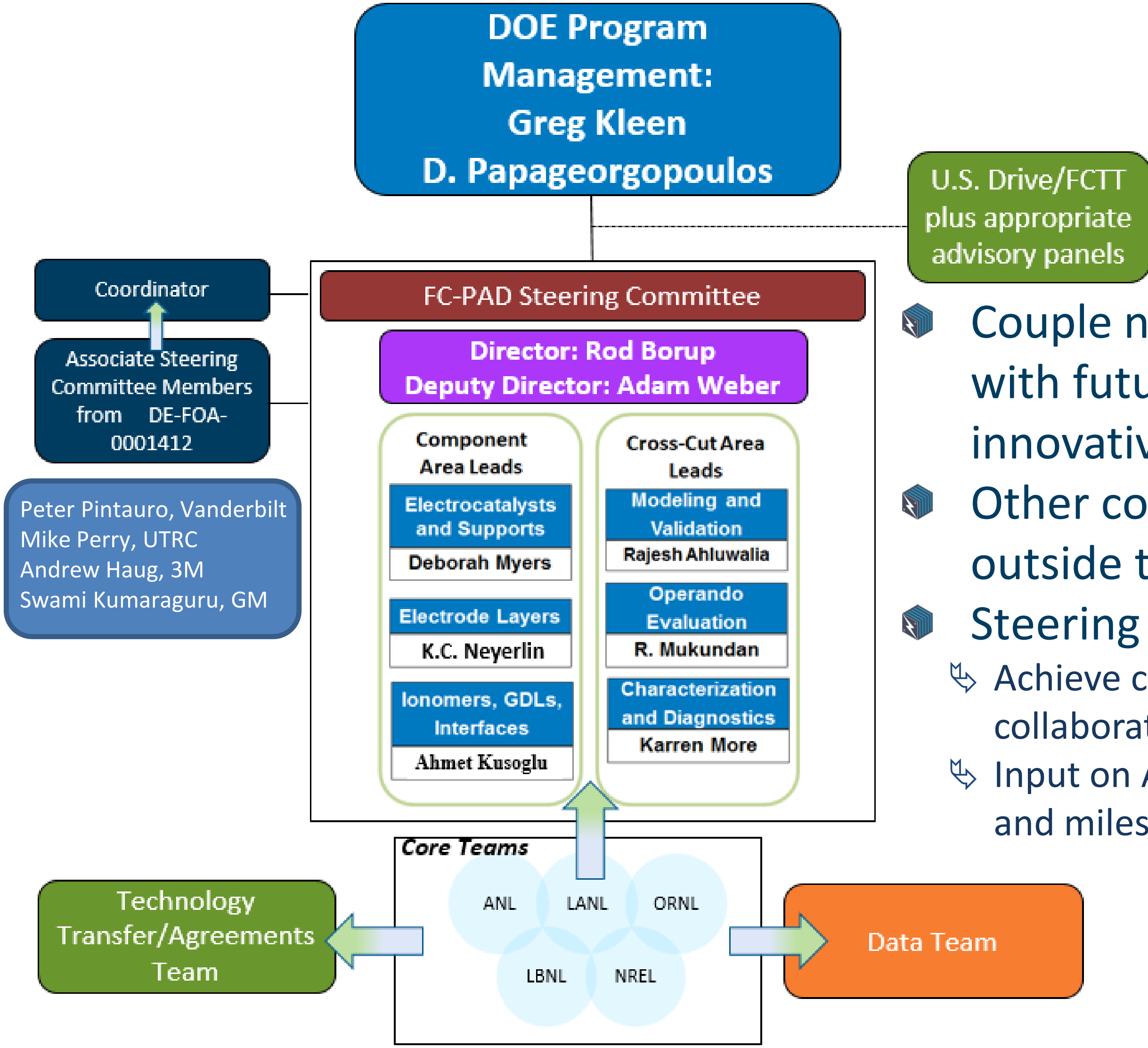
3M
GM
United Technologies Research Center
VANDERBILT

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

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

Argonne National Laboratory

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Nancy Kariuki
Dennis Papadias
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J-K Peng
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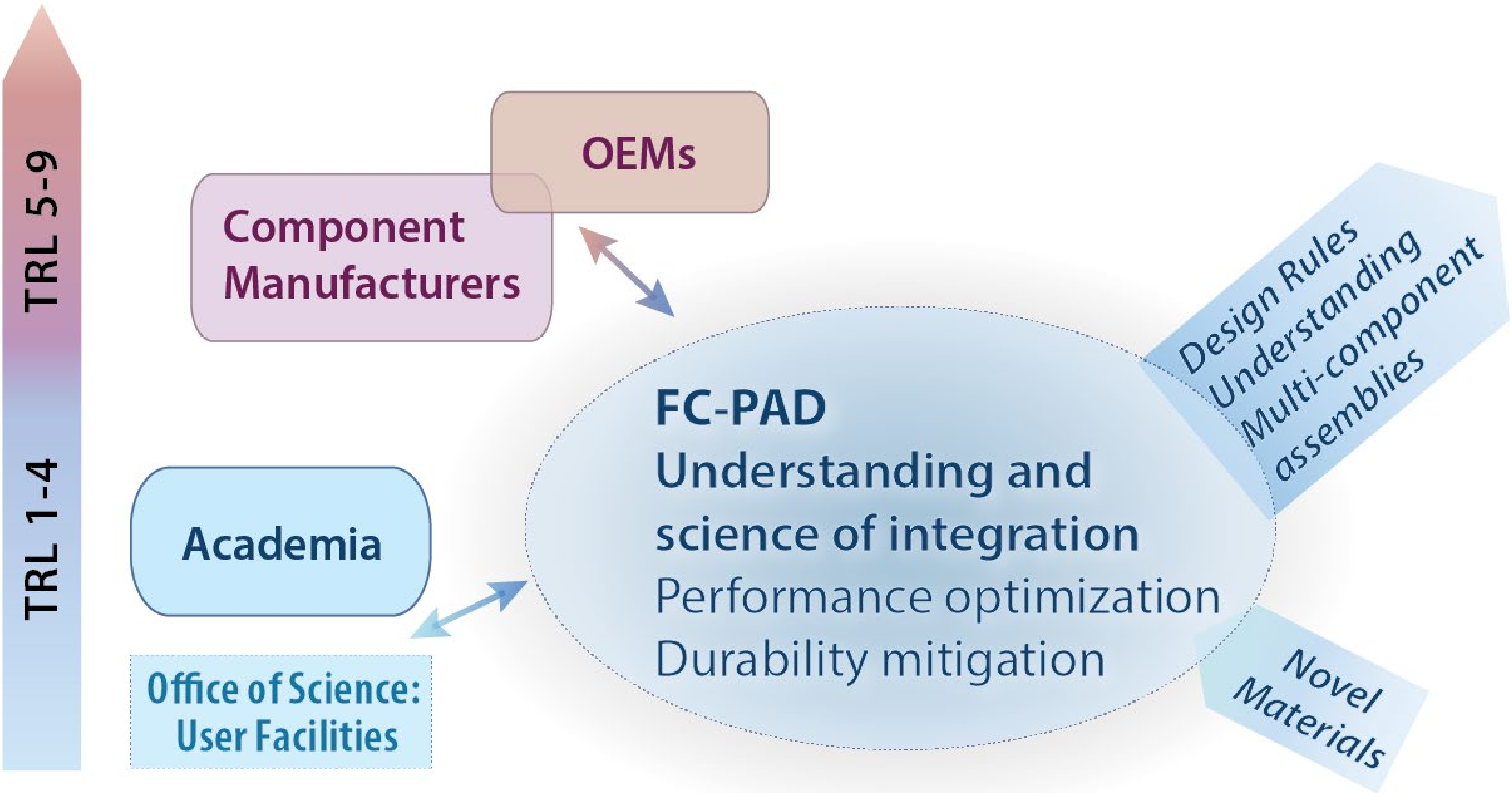
U.S. Department of Energy | Energy Efficiency & Renewable Energy

Dimitrios Papageorgopoulos
Greg Kleen

Fuel Cell FC-PAD Performance and Durability

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 – 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*

FC-PAD Work-Scope Emphasis (Highly Ranked by 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

Fiscal Year 2019 Commercial Trucks and Off-road Applications

FOA: Natural Gas, Hydrogen, Biopower, and Electrification Technologies

FOA Number: DE-FOA-0002044

Topic 4: High-durability, Low Platinum Group Metal (PGM) Membrane Electrode Assemblies (MEAs) for Medium- and Heavy-duty Truck Applications

The Fuel Cell Performance and Durability (FC-PAD) core lab consortium team is available to support DOE awarded projects related to FOA-0002044 with the core capabilities assembled into FC-PAD.

For FC-PAD capabilities, please see:

FC-PAD Website: https://www.fcpad.org/PAD

FC-PAD DOE FCTO AMRs:
https://www.hydrogen.energy.gov/annual_review18_fuelcells.html#performance

FC-PAD Webinars: todays, plus 2016:
https://www.energy.gov/eere/fuelcells/downloads/fcto-consortia-overview-hymarc-and-fc-pad-webinar

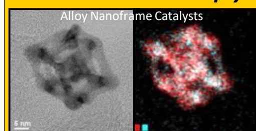
FC-PAD Core National Laboratories are not eligible to participate in proposal development nor discuss the open FOA

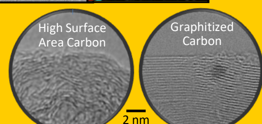
FC-PAD NL Capabilities

Columns: **Structural & Chemical Characterization** | **Performance Testing & Evaluation** | **Modeling & Theory**

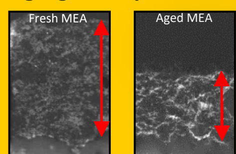
Rows: **Catalyst & Catalyst Support** | **Electrode & MEA** | **Membrane & Ionomer** | **GDL & Cell**

Analytical Electron Microscopy

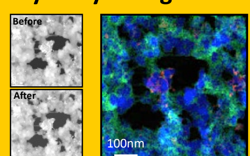




Imaging and spectroscopy



Catalyst-layer degradation



Ionomer mapping

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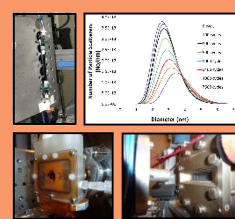
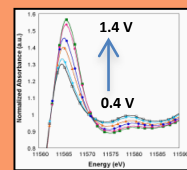
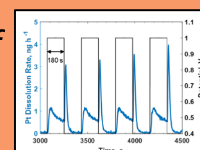
Advanced X-Ray Techniques

Catalyst and support atomic structure and particle size





On-line Analysis of Catalyst Degradation



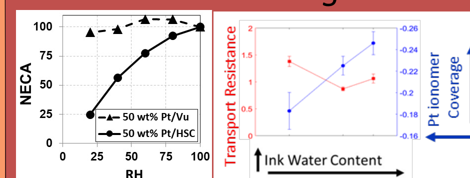
Pt and Co dissolution rate with potential

DMyers@anl.gov

Electrode Fabrication

Ultrasonic spray - electrospinning

Advanced MEA Diagnostics



Transport - Accessibility - Coverage

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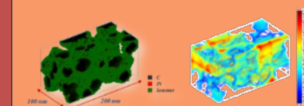
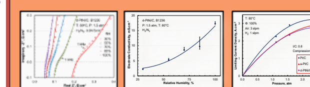
Electrode Simulations



3-D electrode reconstruction and transport



Quantify various losses

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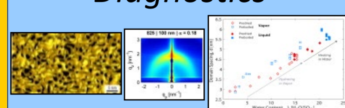
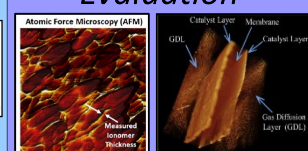
Advanced Component Diagnostics

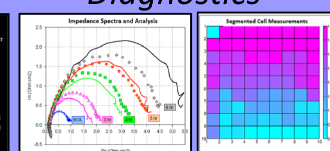


Bulk and thin-film morphology and properties

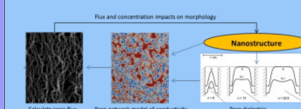
Electrode Structure Evaluation



MEA Component Diagnostics

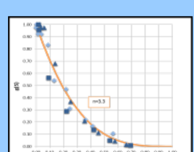


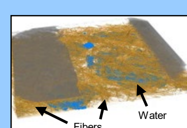
Multiphysics, Multiscale Models



Membrane simulations

Transport property measurements





X-ray tomography

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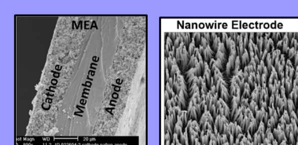
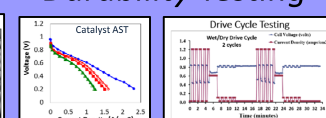
MEA Fabrication



Performance & Durability Testing



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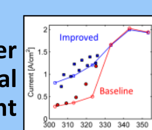
Optimize water and thermal management



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FC-PAD FUEL CELL PERFORMANCE AND DURABILITY

Examples of NL FC-PAD Capabilities
(From Jan 2016 Webinar)

- Dissolution measurements using electrochemical techniques
- X-ray absorption spectroscopy for catalyst component oxidation state and oxide structure
- Electrochemical measurements of platinum oxidation kinetics and oxidation
- Small angle X-ray scattering for in situ and operando nanoparticle size distribution during potential cycling, humidity cycling, in-cell and model systems
- Anomalous small angle X-ray scattering for evolution of intra-particle catalyst component structure
- Solid-state electrochemical cell for oxygen permeability through ionomer layer measurements
- X-ray fluorescence for changes in catalyst composition with AST cycling
- On-line CO_2 detection from MEAs for quantification of carbon corrosion
- Advanced high-resolution imaging and spectroscopy (TEM, STEM, EDS, EELS, *in situ*, etc.)
- Synthesis capabilities including electro-spinning, spray coating, de-cal transfer, vapor deposition, ALD
- H_2/Air & H_2/O_2 VI performance evaluation, crossover, cyclic voltammetry, AC impedance
- Setups for water transport and interactions
- Structural properties including scattering and x-ray techniques and mechanical properties
- Synthesis and characterization of ionomer thin films
- Segmented cells
- Contamination and leachates

FC-PAD Collaboration with USCAR:
A case study in FC-PAD Characterization Capabilities

Characterization of commercial fuel cell components from Toyota Mirai to set bench-mark State-of-Art materials, performance and durability

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

MEA Component Summary From Toyota Mirai

Cathode

- PtCo/C: Pt = 87mole%, 0.32 mg_{Pt}/cm^2
- Cathode layer ~ 9 μm; decreases to ~ 8.1 μm
  - 300 h: 4.86 nm – Pt-Pt: 2.747
  - 3000 h: 4.96 nm – Pt-Pt: 2.745

Anode

- Anode layer ~ 2.3 μm; 0.050 mg_{Pt}/cm^2

GDLs

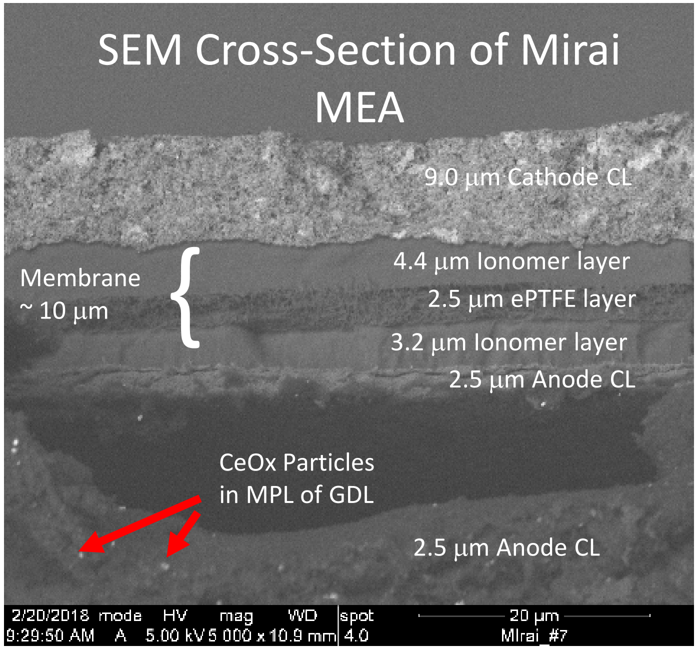
- Anode: ~ 150 μm total with ~ 60 μm MPL
- Cathode: ~ 160 μm total with ~ 40 μm MPL
  - High concentration of CeOx in MPLs
    - ~ 60 $\mu g_{Ce}/cm^2$ on the cathode;
    - ~ 120 $\mu g_{Ce}/cm^2$ on the anode

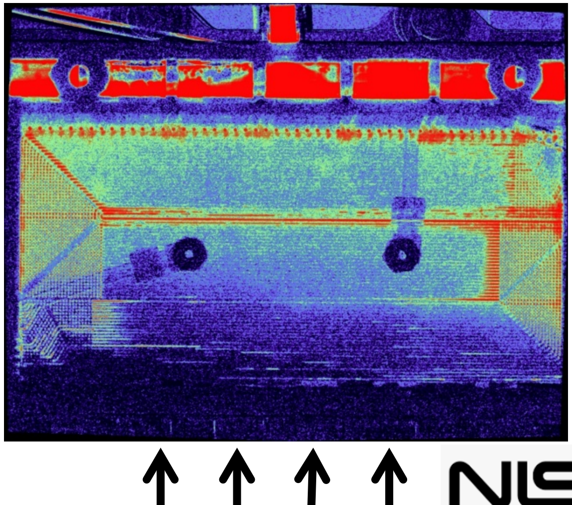
Membrane

- ~ 10 – 10.5 μm with ePTFE; Nafion side chain
- Ionomer EW: ~ 901 ± 1 g/meq by acid-base titration

Bipolar Plate

- Cathode Ti foil; with Ti mesh; ~ 80 nm carbon coating
- Anode serpentine; ~ 80 nm carbon coating





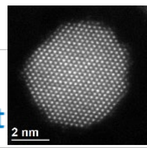
NIST

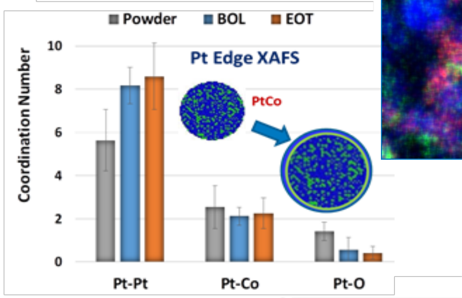
FC-PAD: Exploration of Critical Phenomena

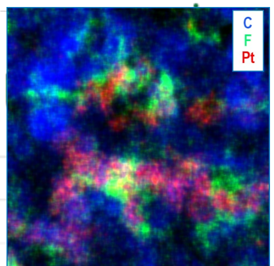
	Reactions and Charge Transport	Mass Transport of Species	Kinetics and cell testing	Durability ASTs: RH, V,T cycling	Durability: Field Testing
relavant phenomena & timescale	nsec - msec local nanostructure	sec - min component function	sec - hrs membrane-electrode	hrs - days fuel-cell	lifetime stack/system

Characterization/Diagnostics

Catalyst

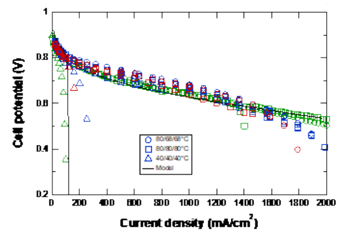


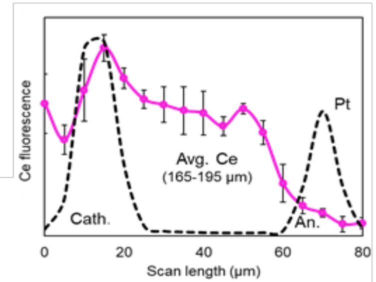




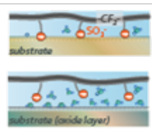
Imaging catalyst layers

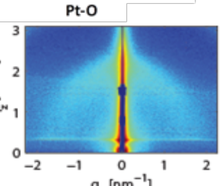
Cell performance and optimization





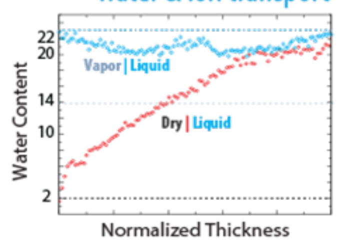
Monitoring, Measuring Degradation and Performance Decay

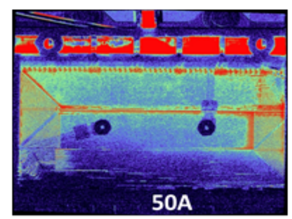




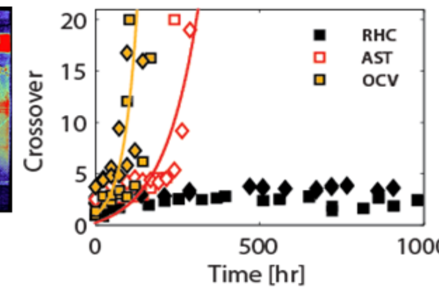
ionomer-Pt/C interactions

probing water & ion transport





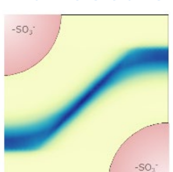
Operando Imaging



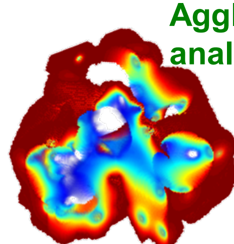
characterization of phenomena fundamental understanding ↔ *performance-durability interplay: understanding and improvement*

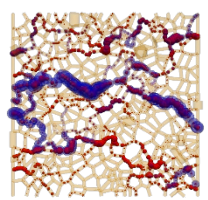
Modeling

Nanoscale

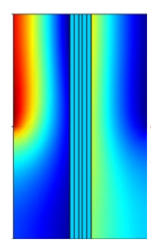


Agglomerate analysis

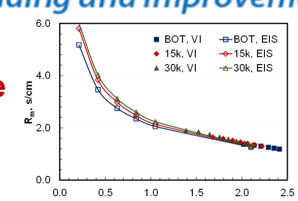




Component Transport



Cell-level performance and durability

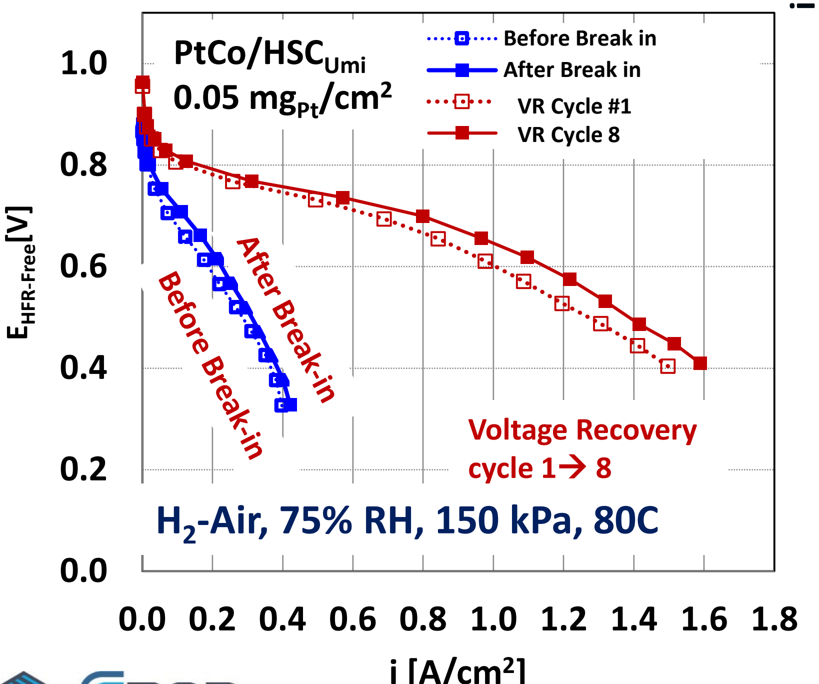


Predicting life and decay

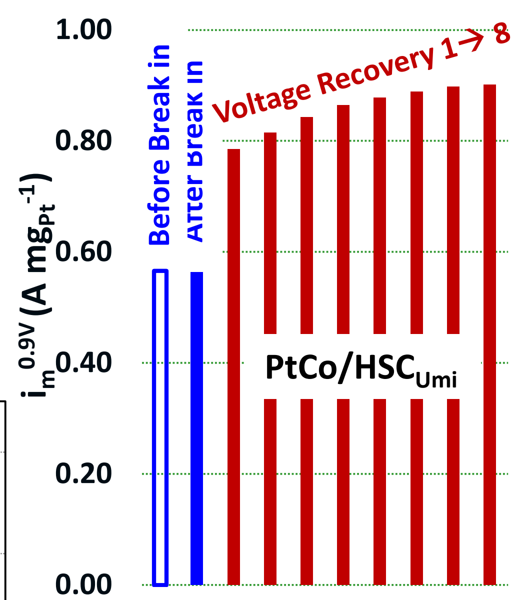
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

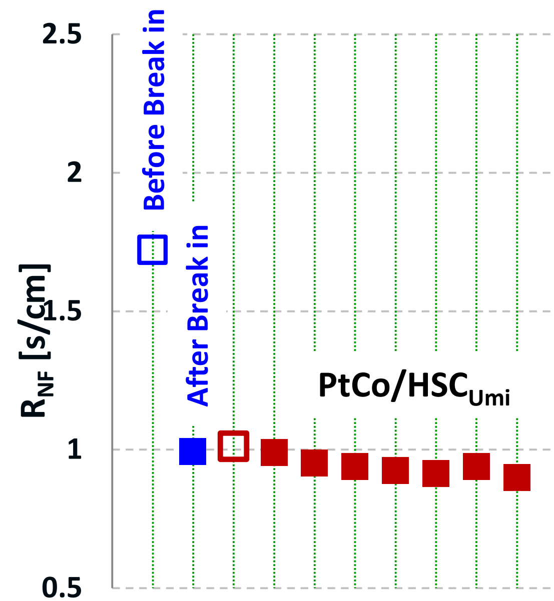
Transport Measurements Related to Conditioning

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



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

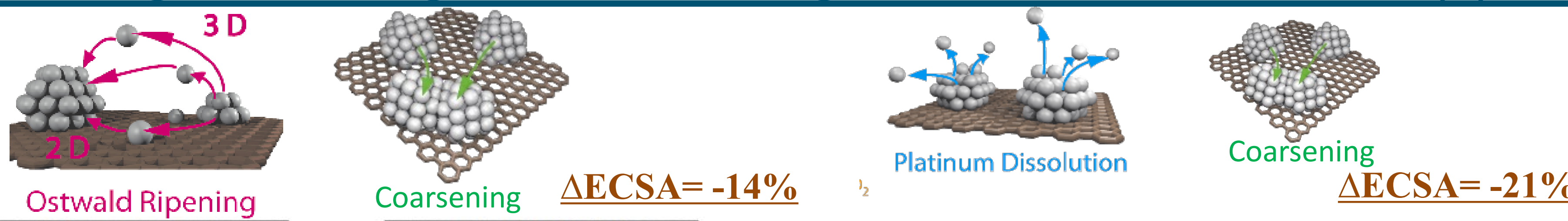


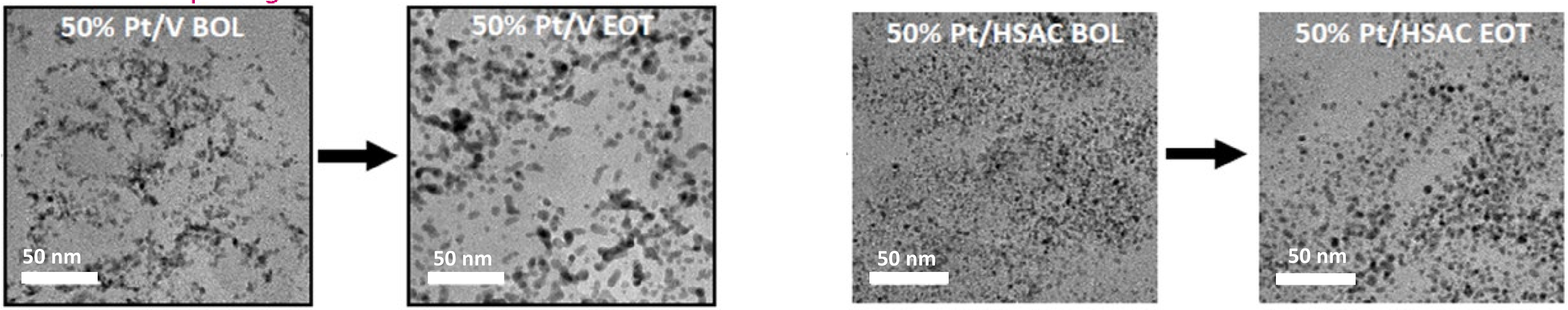


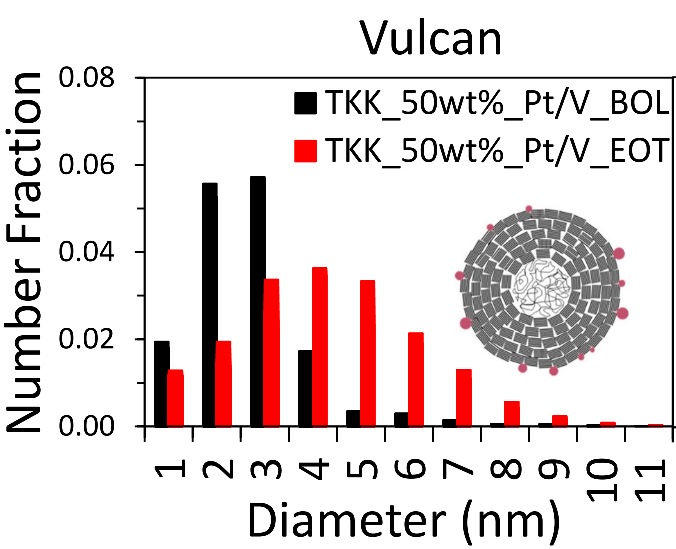
Suggests that break-in impacts local effects and voltage recovery more than macroscopic effects

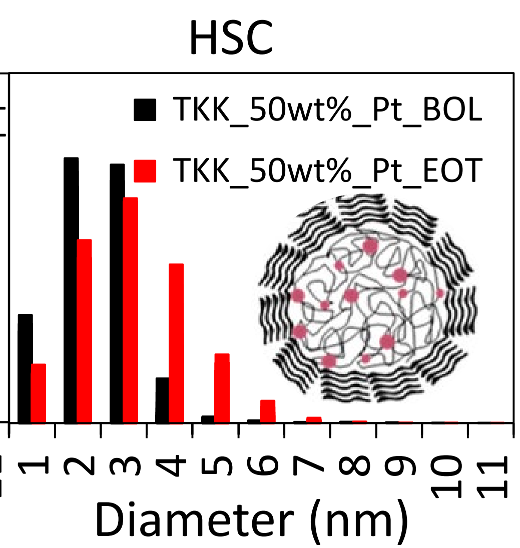
First voltage recovery cycle is crucial for improved H_2/Air performance

Changes During Conditioning: Effect of Carbon Support





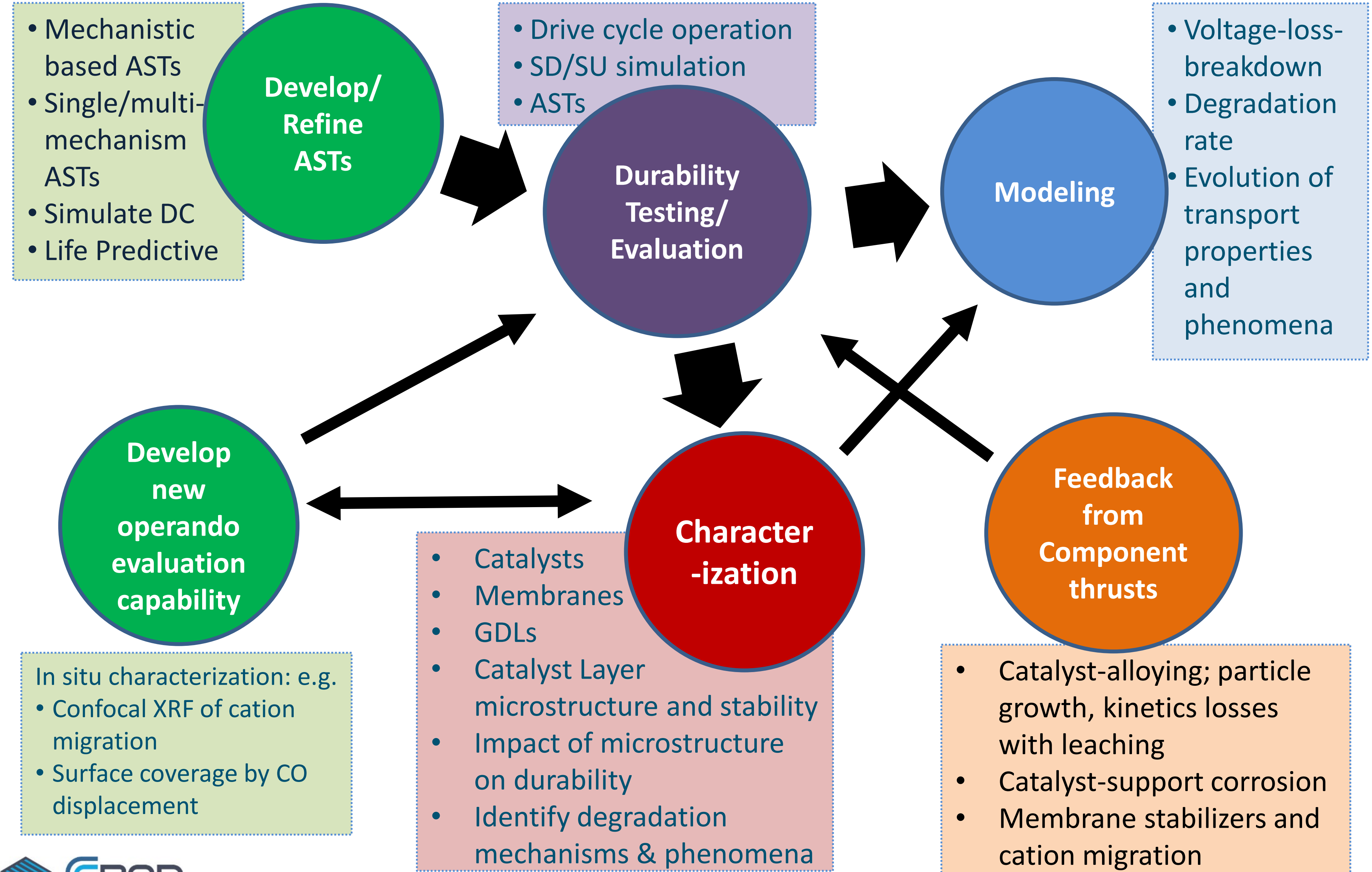




Pt/Vulcan$_{TKK}$ vs. Pt HSC$_{TKK}$

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

Durability Approach:
Materials-based Solutions to Decrease Degradation



- Mechanistic based ASTs
- Single/multi-mechanism ASTs
- Simulate DC
- Life Predictive

- Drive cycle operation
- SD/SU simulation
- ASTs

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

In situ characterization: e.g.
- Confocal XRF of cation migration
- Surface coverage by CO displacement

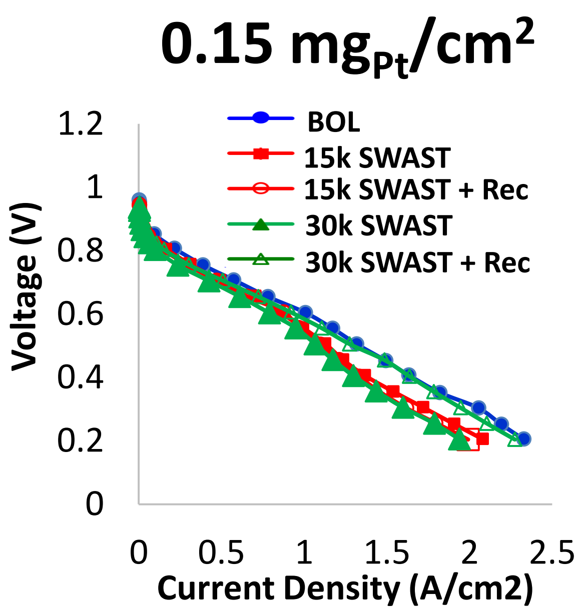
- Catalysts
- Membranes
- GDLs
- Catalyst Layer microstructure and stability
- Impact of microstructure on durability
- Identify degradation mechanisms & phenomena

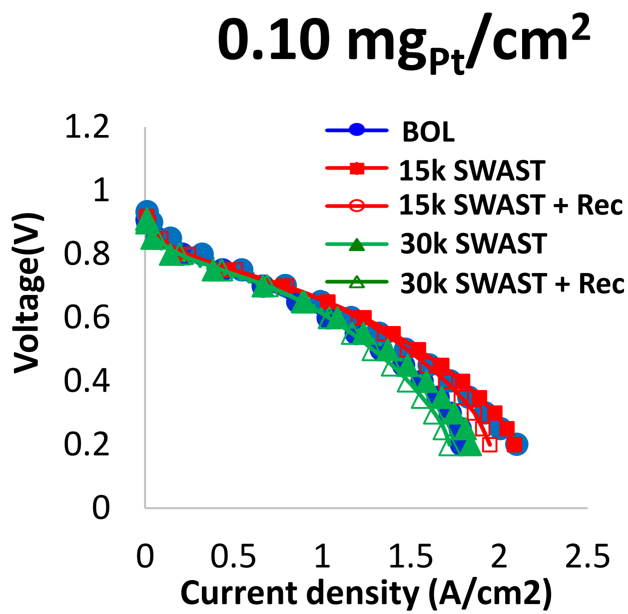
- Catalyst-alloying; particle growth, kinetics losses with leaching
- Catalyst-support corrosion
- Membrane stabilizers and cation migration

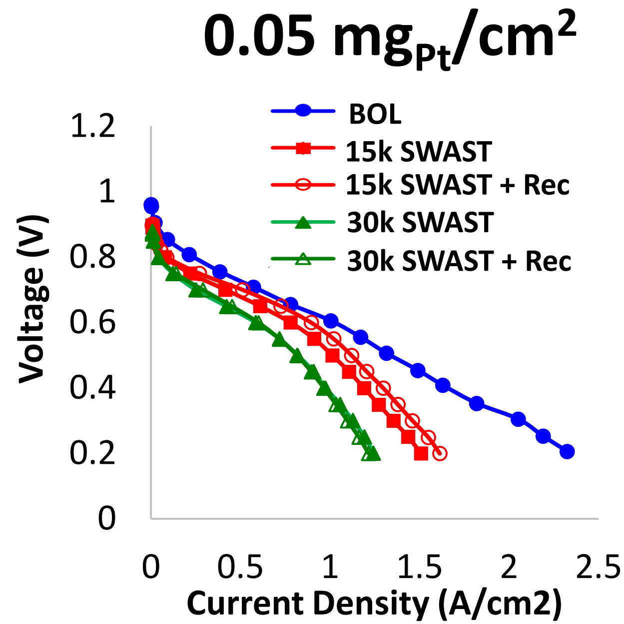
Durability: PtCo Cathode - Effect of Loading

(0.15 to 0.05 mg_{Pt}/cm^2)

80 °C, 100% RH, 150KPa

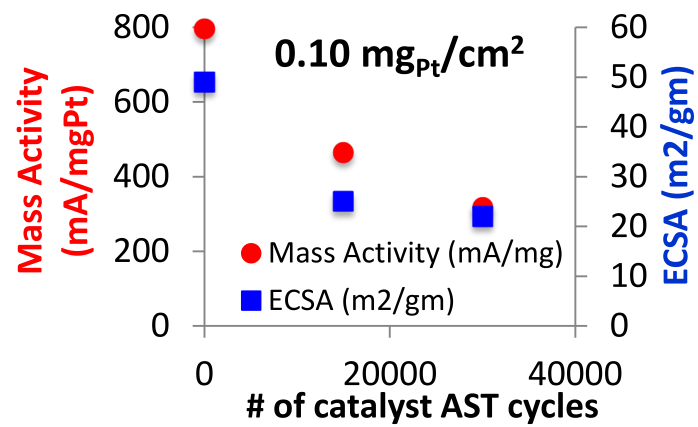






- After recovery @ 30,000 cycles, mainly kinetic losses observed
- ECSA and mass activity decrease
- Local transport still most significant loss at high current density

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



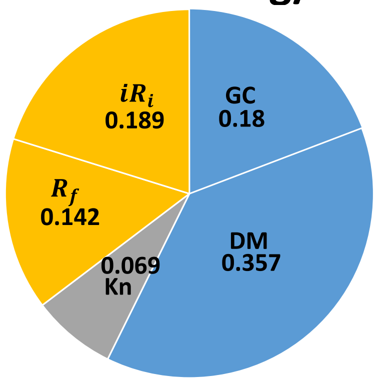
Square Wave Catalyst AST (0.6 – 0.95V)
80°C, 100% RH, 150kPa

Catalyst Degradation Loss Breakdown

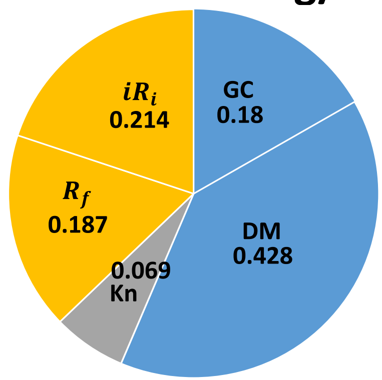
R_m at Limiting Current Density (i_L): 1.5 atm, 4% X(O_2), 80°C, 90% RH

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

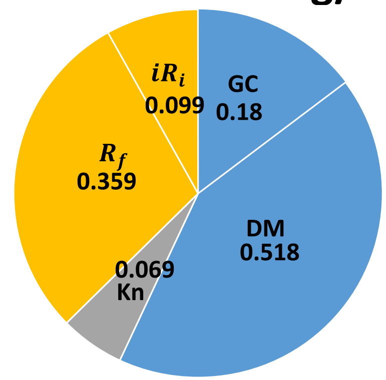
BOL



i_L=615 mA/cm², R_m=0.937 s/cm

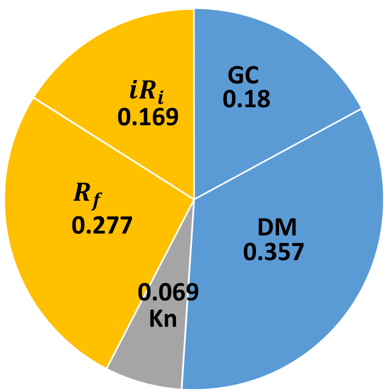


i_L=535 mA/cm², R_m=1.077 s/cm

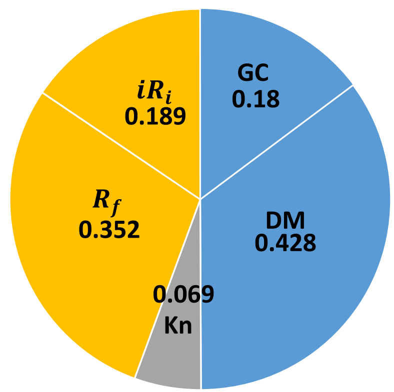


i_L=471 mA/cm², R_m=1.224 s/cm

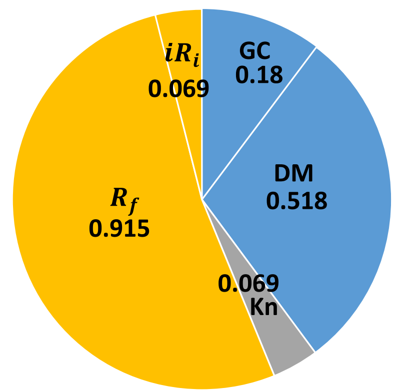
30k Cycles



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)

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

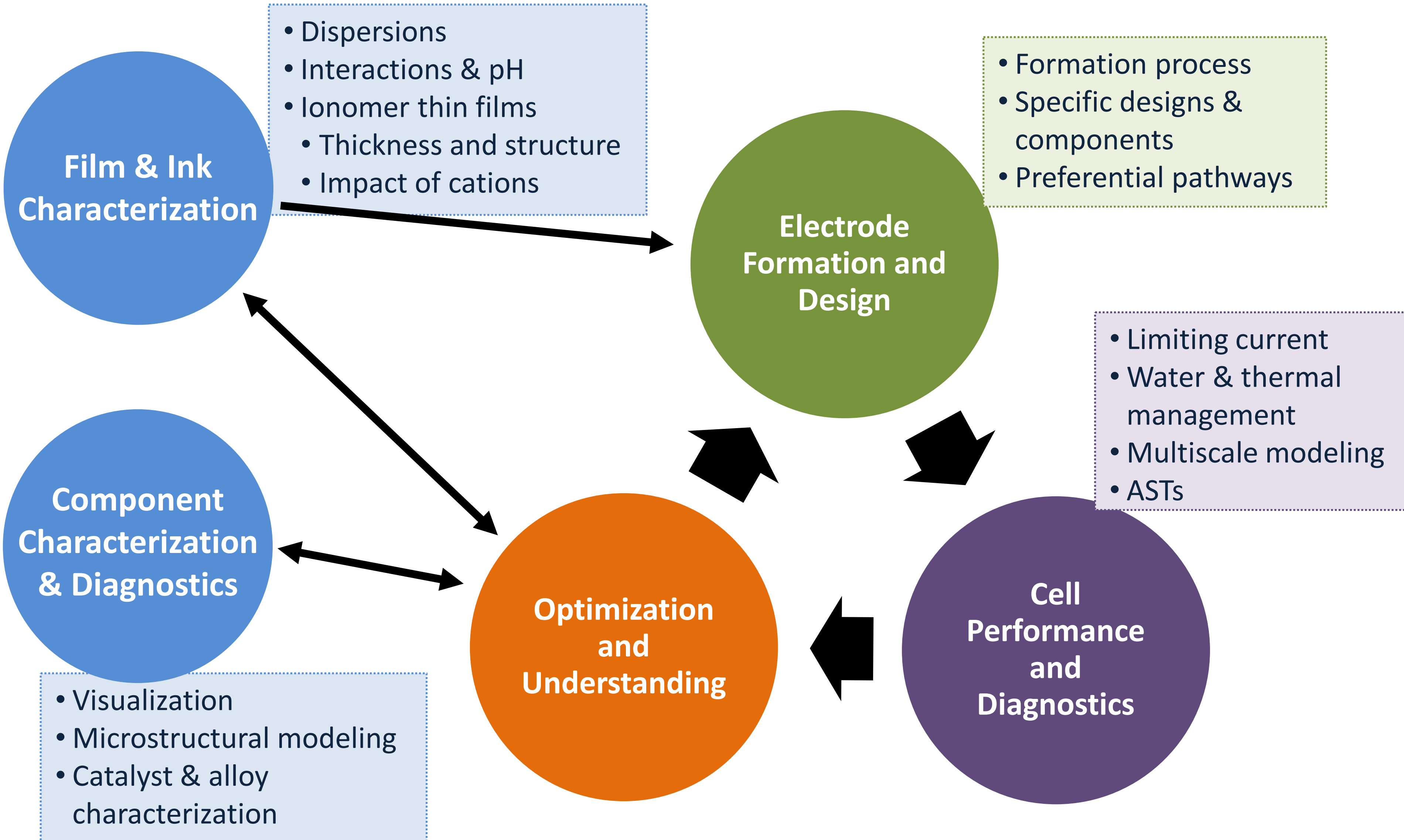
GC DM MPL/CCL CCL

R_f = **Ionomer Film Resistance**

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

FC-PAD FUEL CELL PERFORMANCE AND DURABILITY

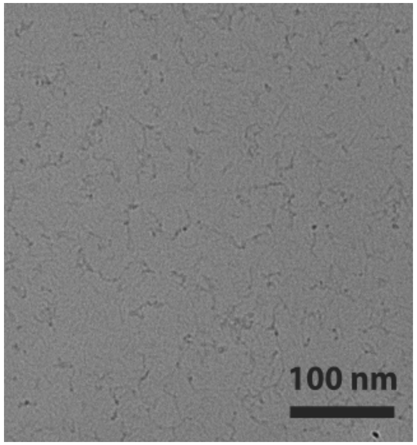
Approach: Electrode Layers and MEA Exploration



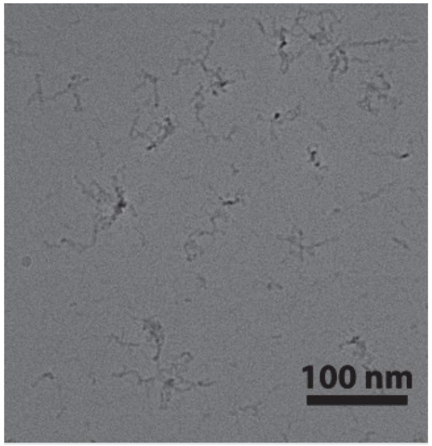
Agglomerates: Dispersions

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

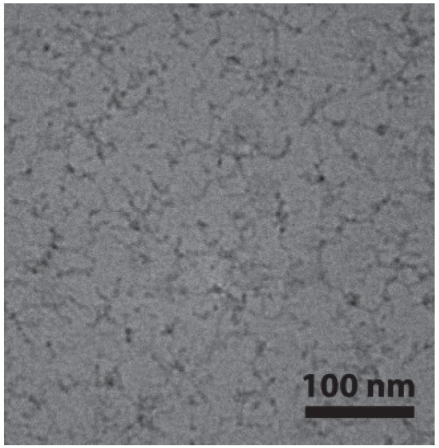
50% H_2O, 0.2 wt-%



90% H_2O, 0.2 wt-%

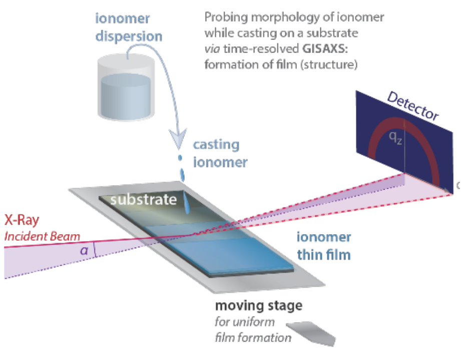


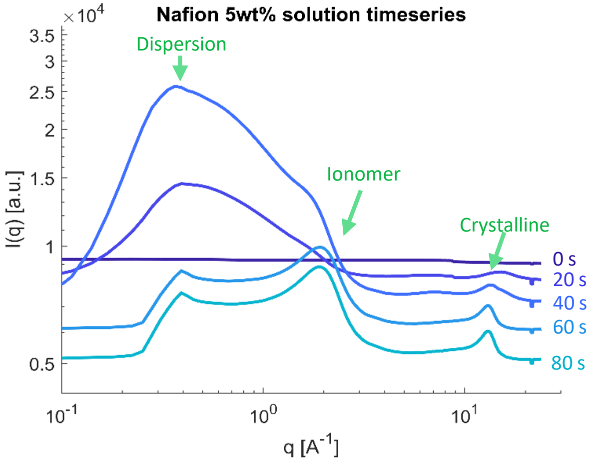
90% H_2O, 2 wt-%



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

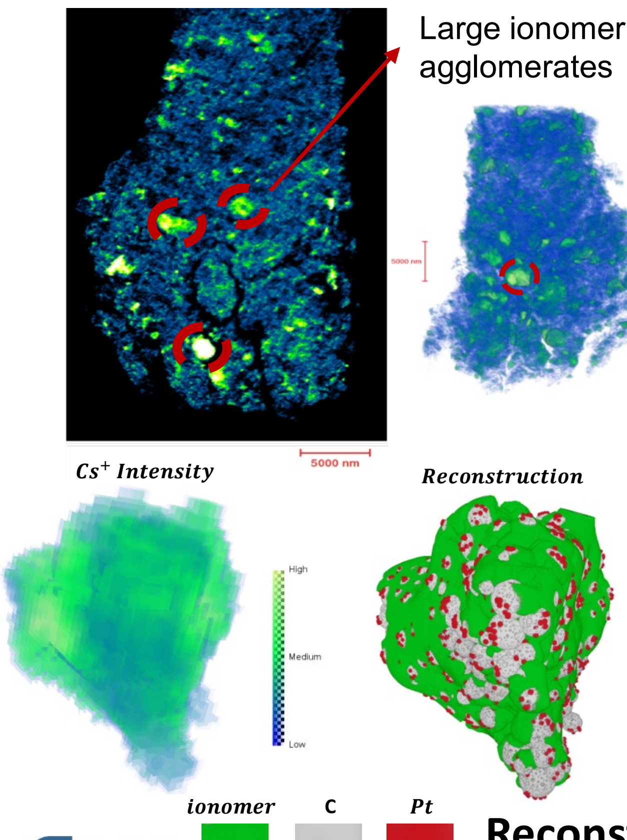




Characterization of Aggregates and Agglomerates

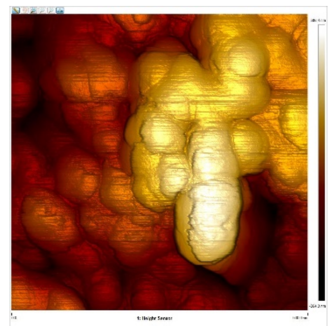
- Ionomer and Pt/C exhibit different aggregation behavior, resulting in various heterogeneities within electrode that can be detected with various methods
  - Multiple techniques used to measure ionomer and carbon aggregates and agglomerates
    - Ionomer thin films plus larger agglomerates (globules)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

Nano X-ray tomography

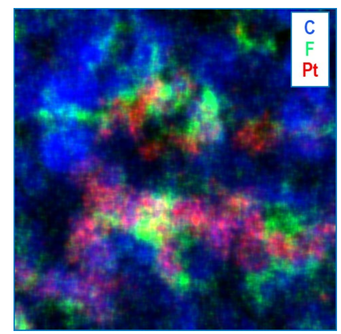


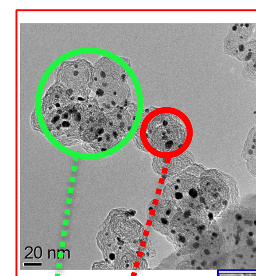
Reconstruction

AFM

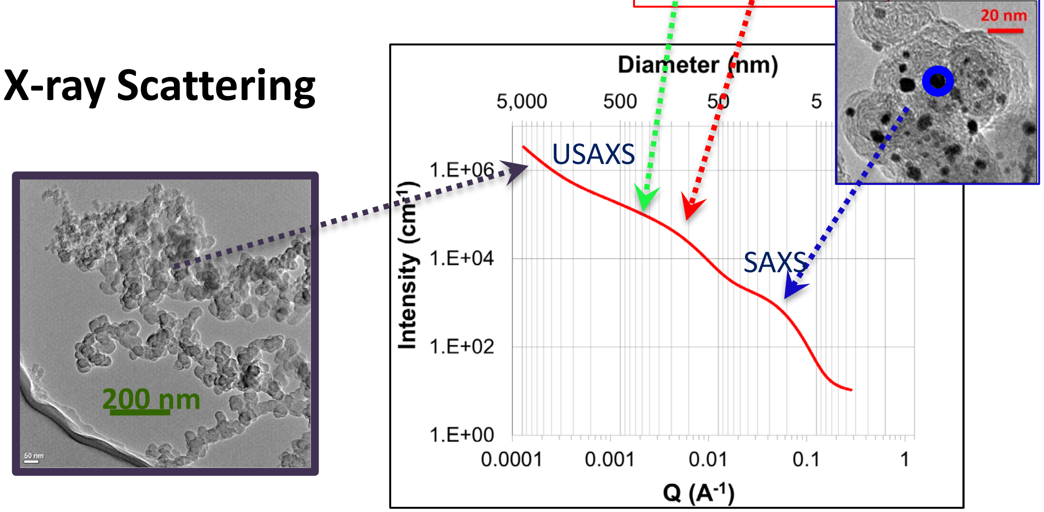


STEM



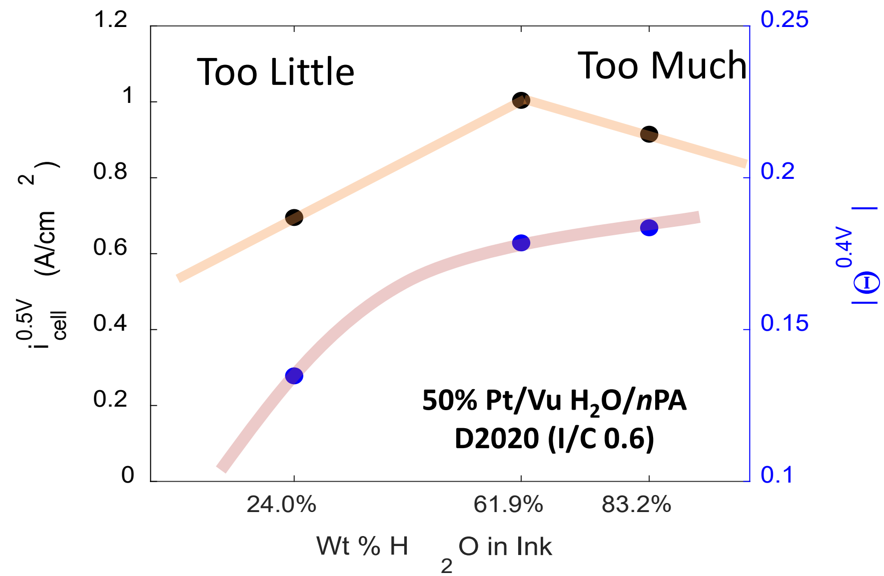


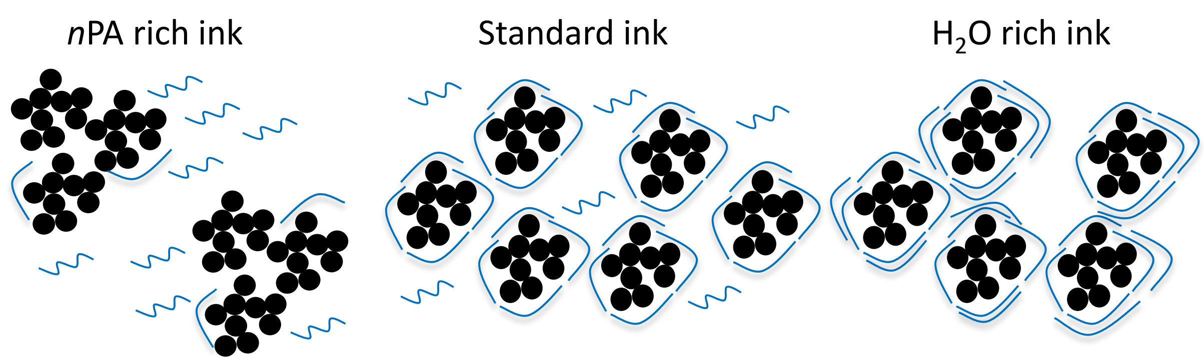
X-ray Scattering

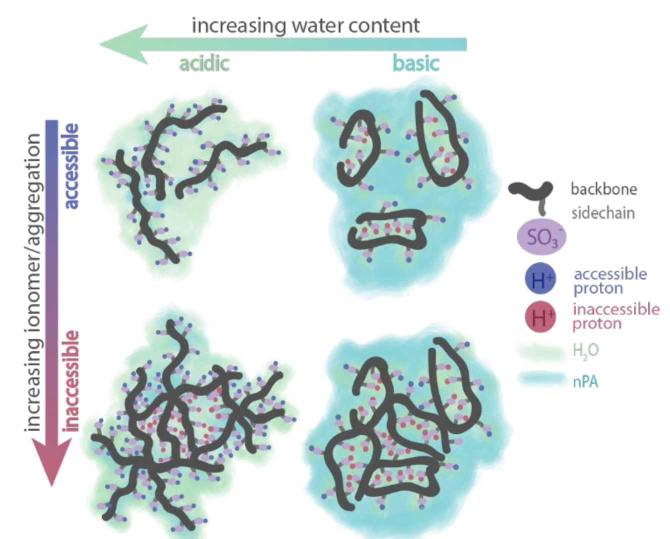


Case Study: Ink Solvent Ratio Effect on Performance

- 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 Ratio Effect on Performance

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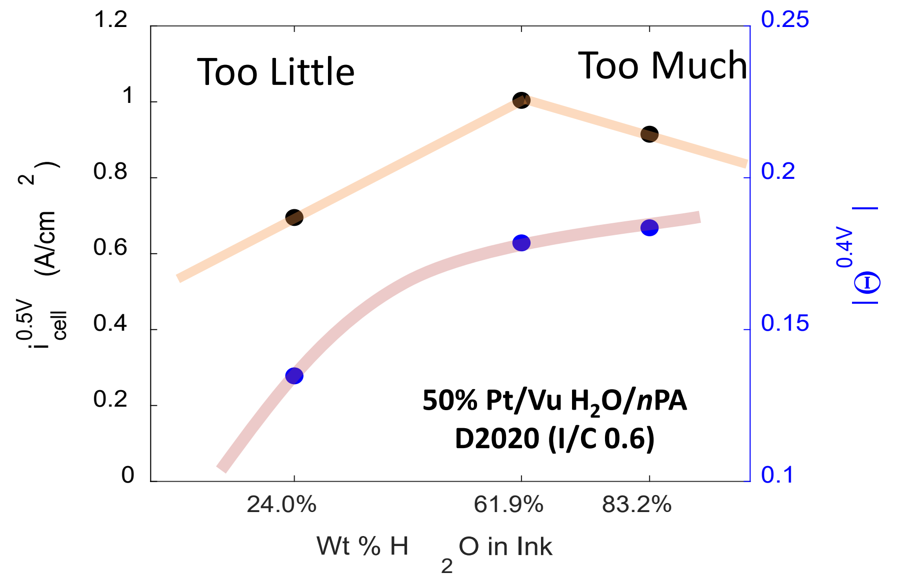
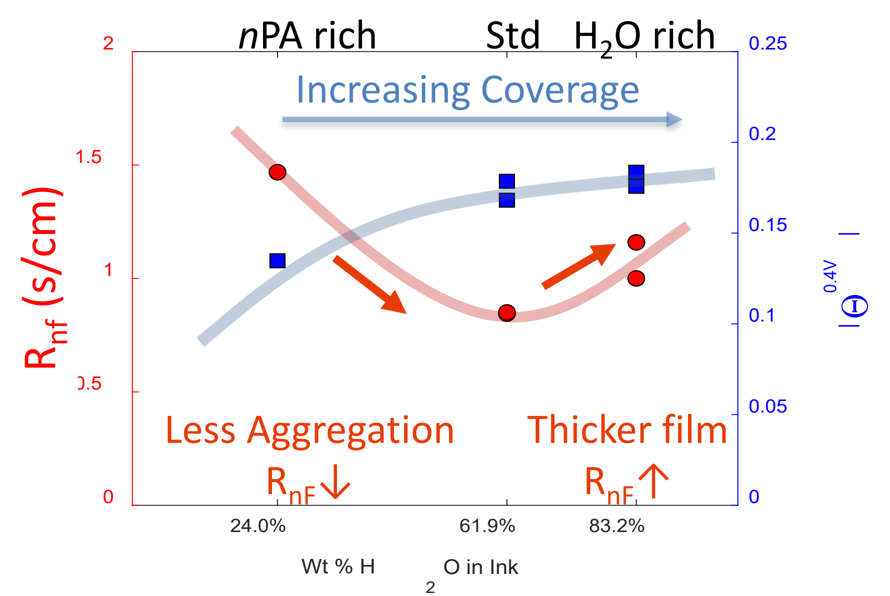
- Slightly water-rich ink exhibits best performance due to trade-off between coverage and structure
  - High water contents - aggregation of side-chains and looser structure
  - High propanol contents - clustering and reverse-micelle structure
- Larger solvent effects in O_2 transfer-limited region
  - 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

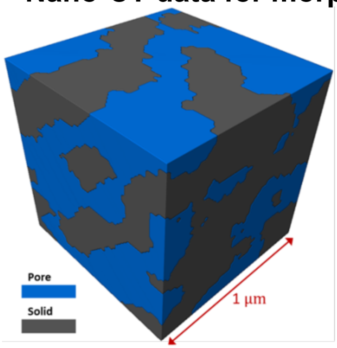


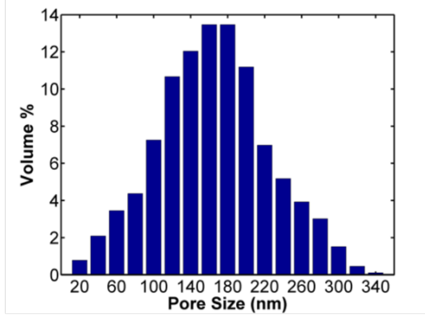


Electrode Microstructure Reconstruction

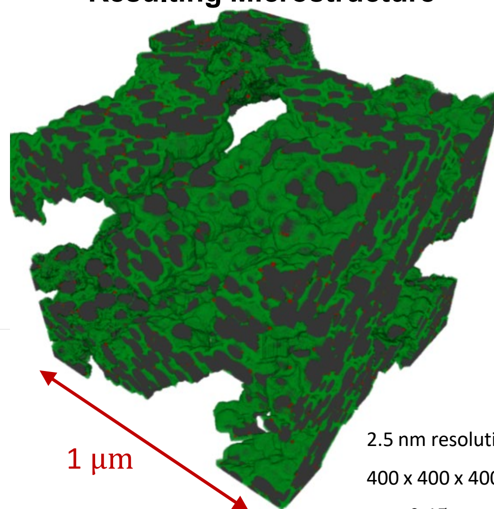
Method to reconstruct electrode microstructure from multiple datasets

Nano-CT data for morphology of the secondary pores





Resulting Microstructure

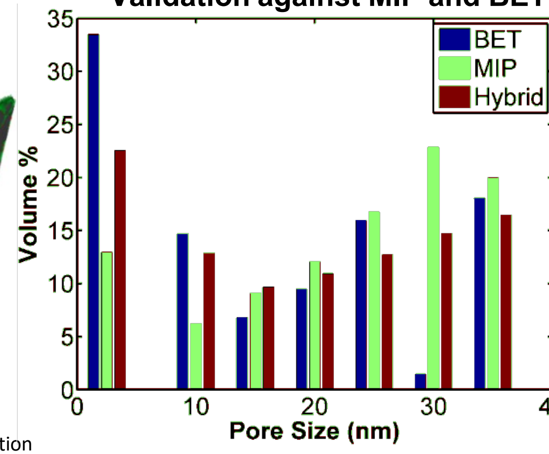


2.5 nm resolution

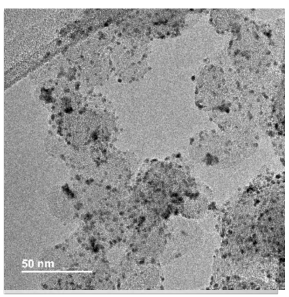
400 x 400 x 400 voxels

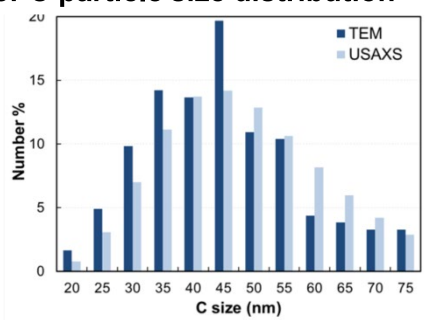
$\varepsilon_v = 0.45$

Validation against MIP and BET

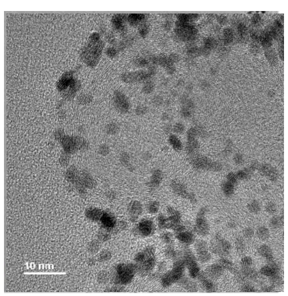


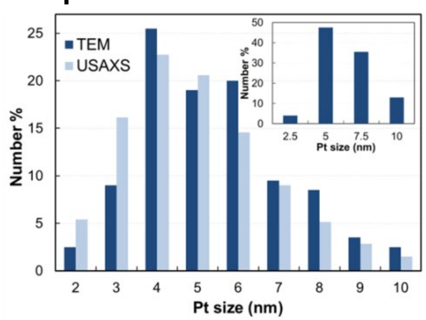
TEM and USAXS data for C particle size distribution



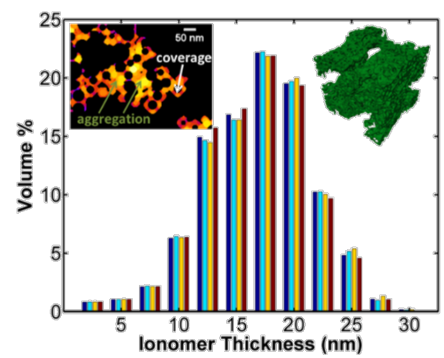


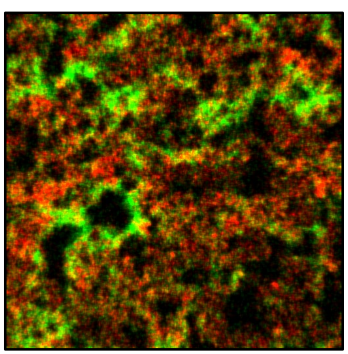
TEM and USAXS data for Pt particle size distribution





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

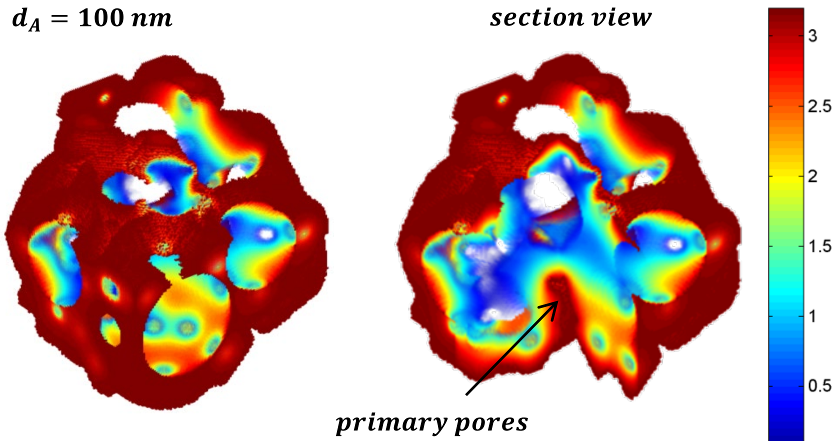


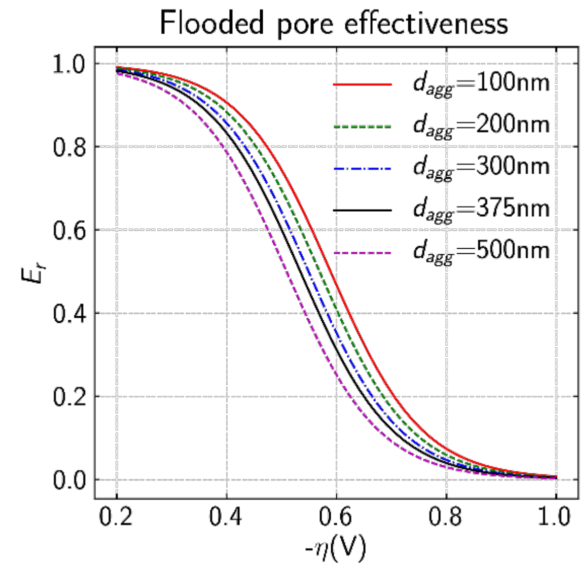


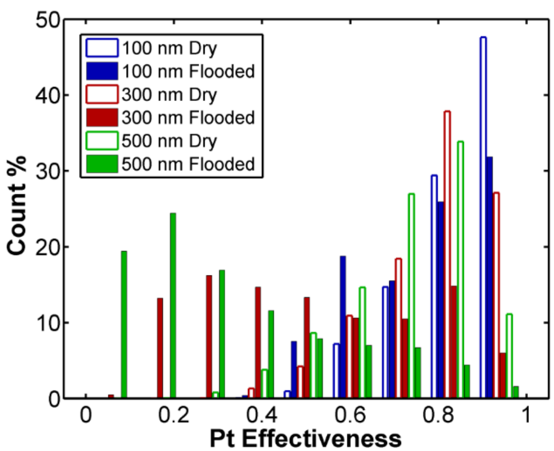
Microstructural Modeling

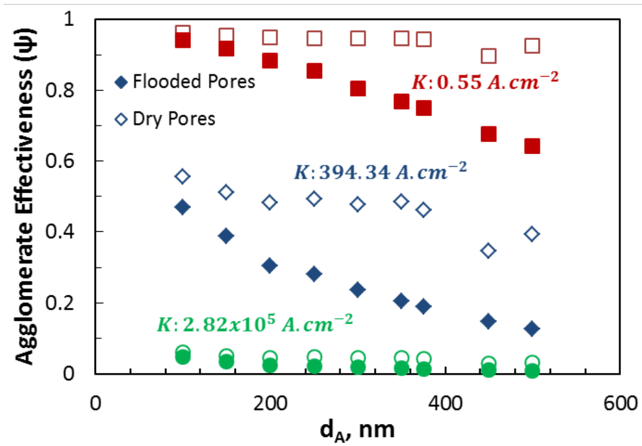
$$Effectiveness\ Factor, Er = \frac{Actual\ reaction\ rate}{Rate\ if\ not\ slowed\ by\ diffusion}$$

Direct numerical simulation of O_2 transport in multi-phase agglomerate









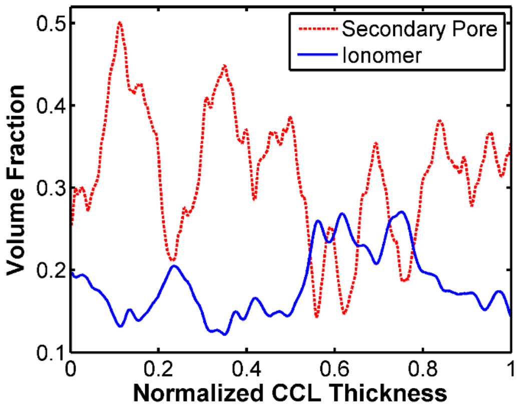
$$c^r_{O_2} = 34.1\ mol.m^{-3}$$

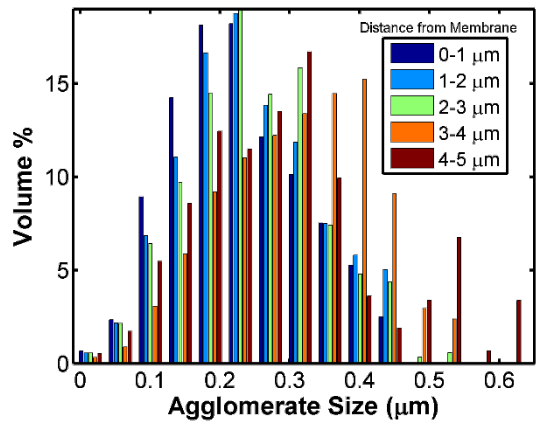
$$i = K\left(\frac{c_{O_2}}{c^r_{O_2}}\right)$$

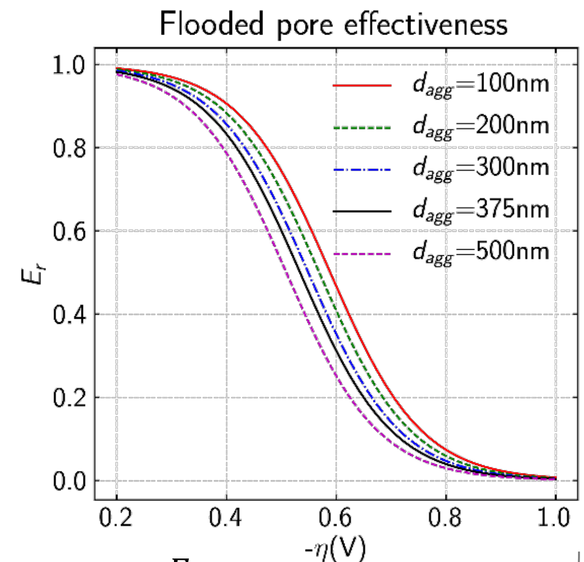
- Catalyst effectiveness is generally smaller if particles are closer to agglomerate center, at higher current density, and if pores are flooded

Multiscale Modeling

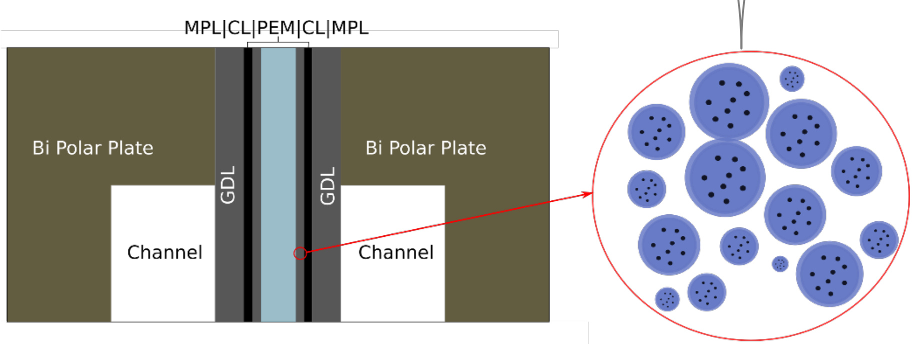
$$Effectiveness\ Factor, Er = \frac{Actual\ reaction\ rate}{Rate\ if\ not\ slowed\ by\ diffusion}$$







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

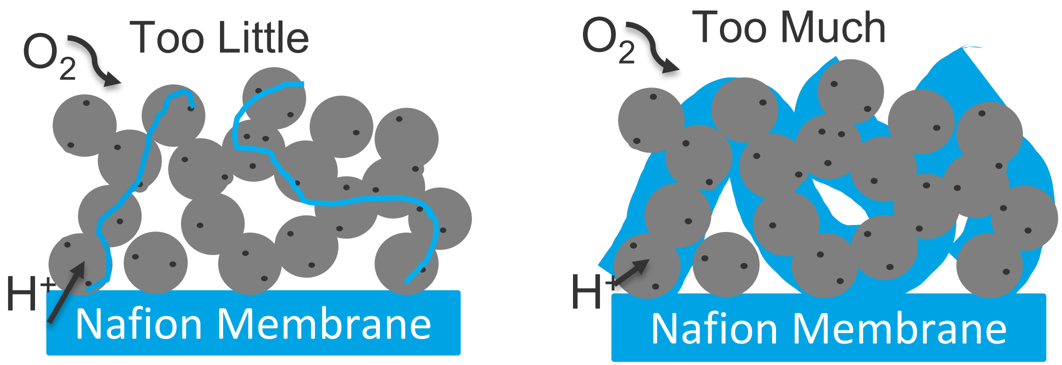


Agglomerate distribution

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

Optimizing CL Structure (Ionomer Distribution)

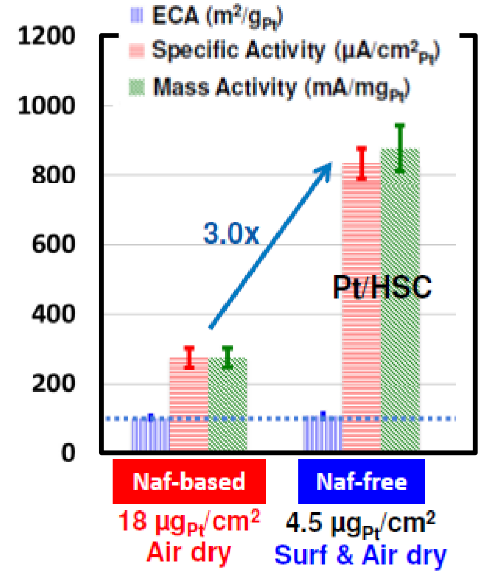
Control ionomer content & distribution



- Poor H^+ Transport
- Lower Pt utilization

- Decreased O_2 transport
- Site and Pore Blockage

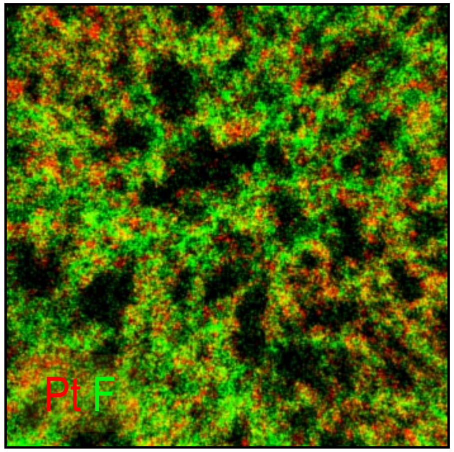
Ionomer Inhibits ORR

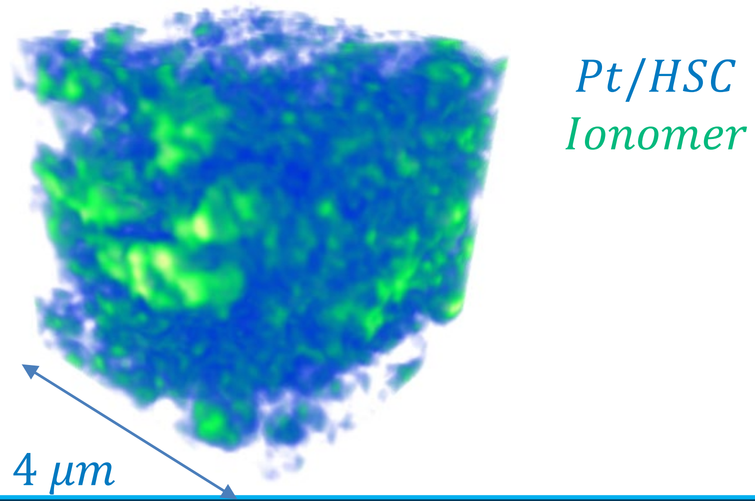


Challenge: Difficult to control and characterize

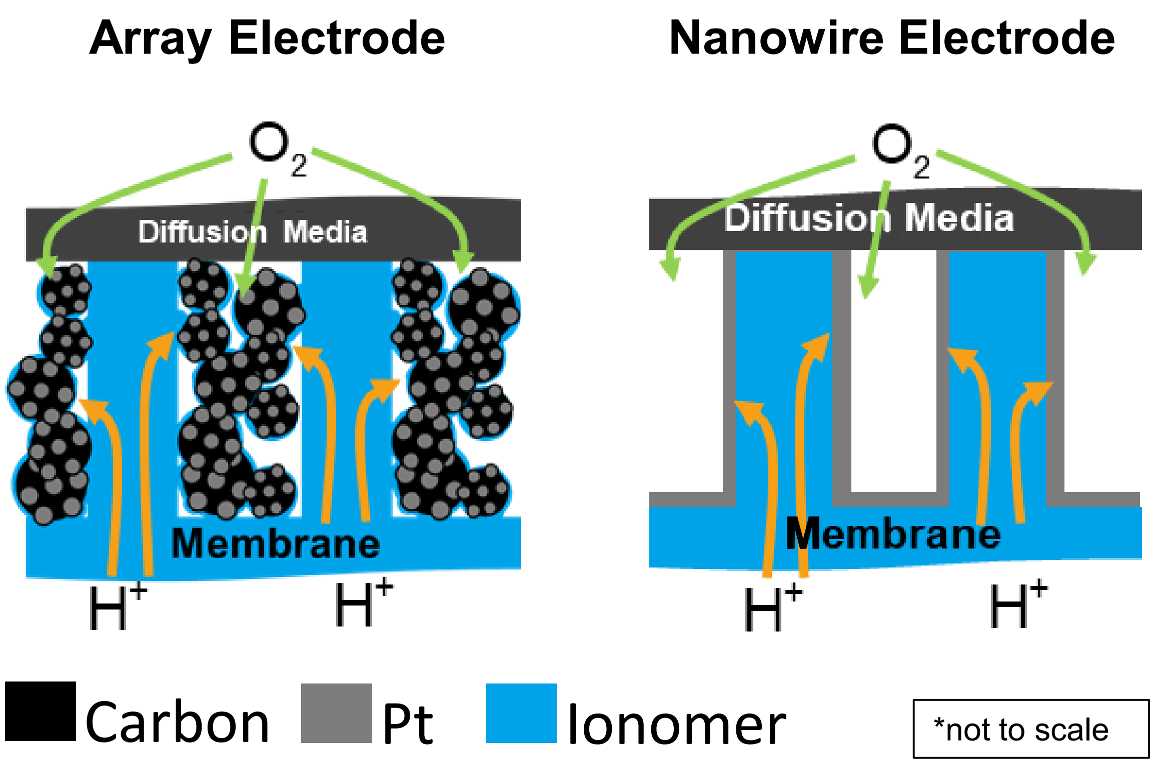
SEM elemental map

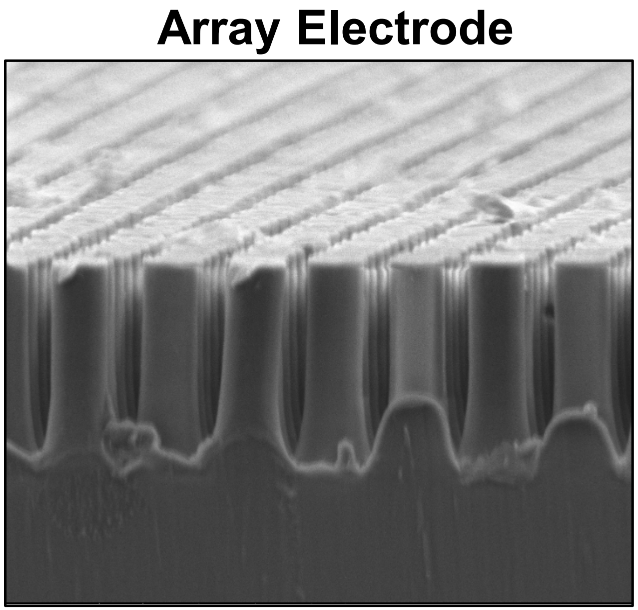
Umicore 0.1 mg PtCo/HSC - Bulk I:C 0.9

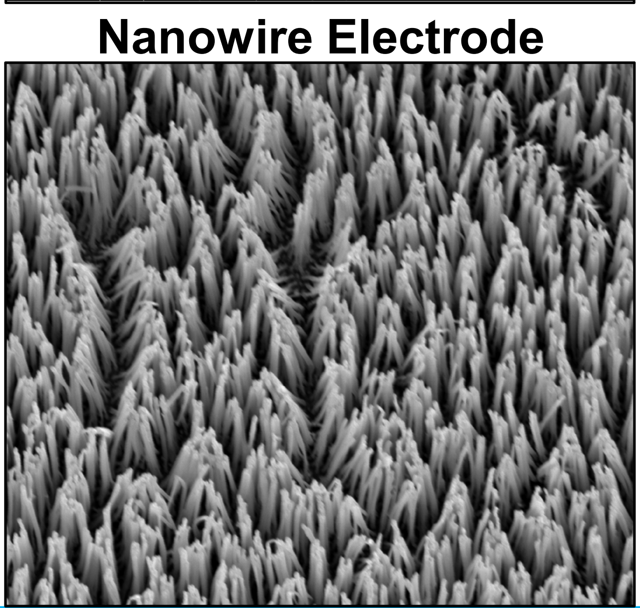




Ordered Array Electrode







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

FC-PAD Support to FOA-1412 Projects

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

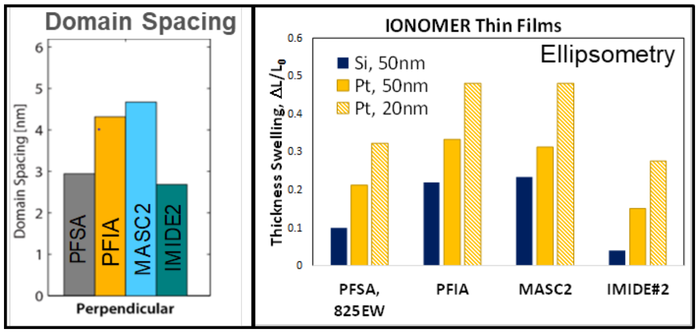
FC-PAD support to: Novel ionomers and electrode structures for improved PEMFC electrode performance at low PGM loadings

P.I.: Andrew Haug- Project ID: FC155

3M

Component understanding

Ionomer morphology and properties



PFSA & IMIDE#2 more dense and oriented

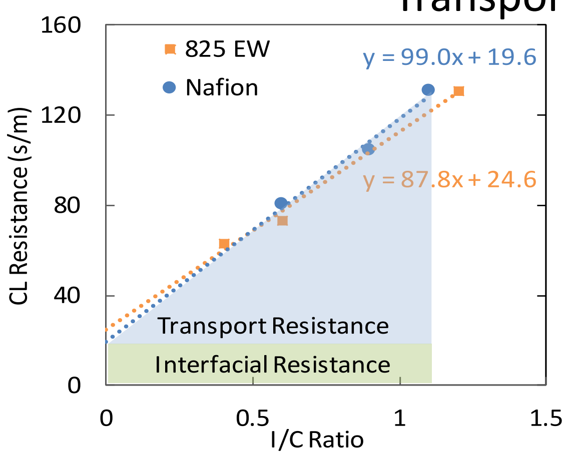
Examine processing conditions and CL structure

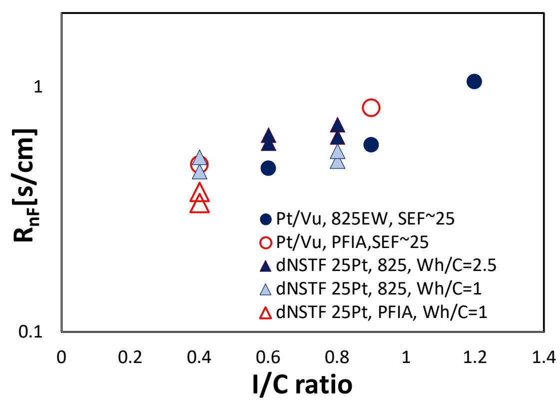
	Type 1 vs	Type 2	>400nm Agglomeration
C-type	HSC	XC72	7X
%M/C	XC72	10V50E	50X
I/C	0.8	0.4	3X
Ionomer	825	PFIA	~2X
Electrode	**dNSTF,** XC72, I/C=0.4	10V50E Baseline	**~75X** (500X for HSC)

dispersed NSTF results in higher agglomeration

- ## Phenomena elucidation

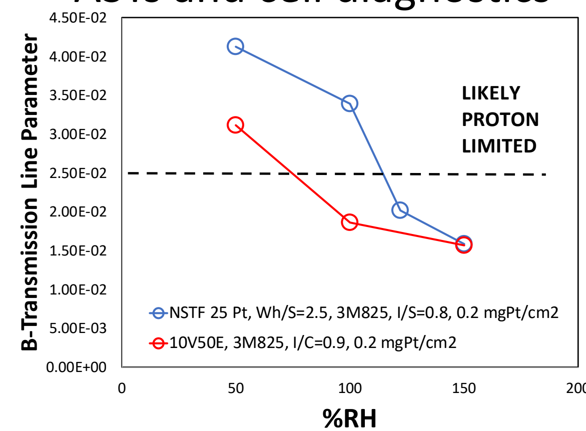
Transport analysis





3M ionomers and dNSTF result in lower local resistance

ASTs and cell diagnostics

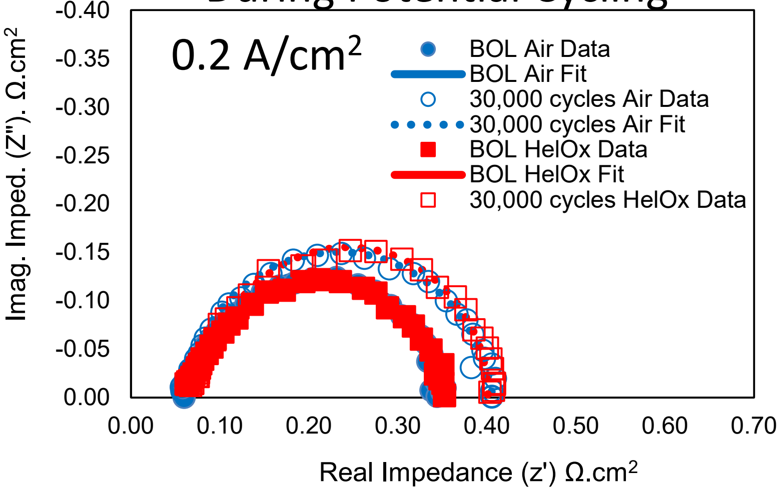


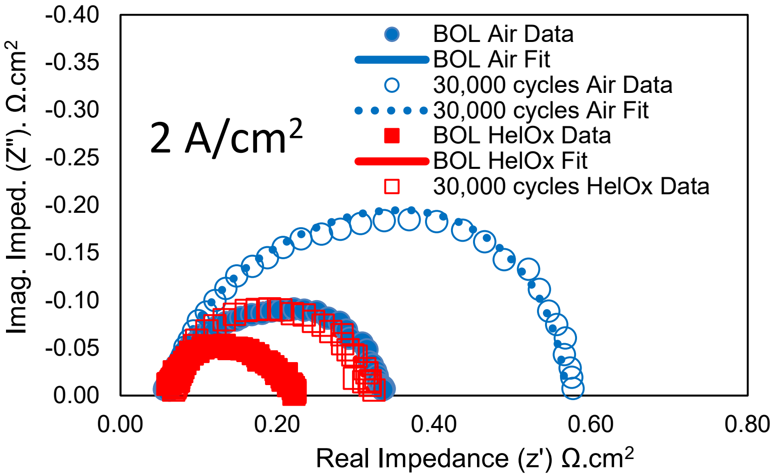
Better water management and durability with dNSTF and apparently proton limited

FC-PAD support to: Fuel Cell Membrane-Electrode-Assemblies with Ultra-Low Pt Nanofiber Electrodes

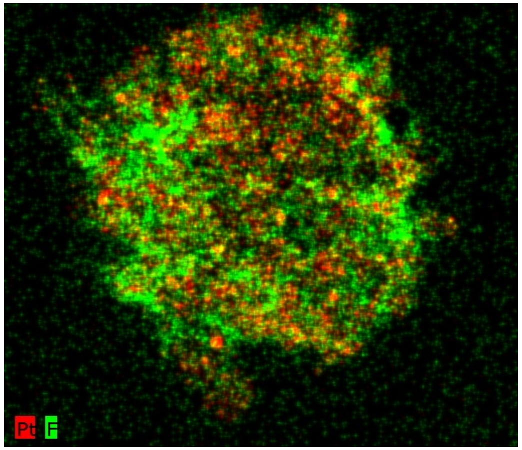
PI: Peter Pintauro - Project ID: # FC158

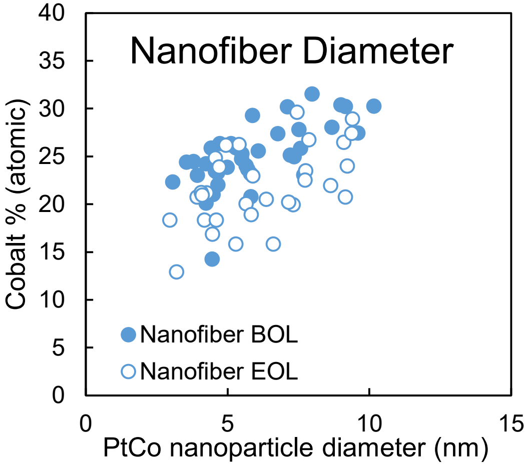
Quantify Kinetic and Transport Losses During Potential Cycling

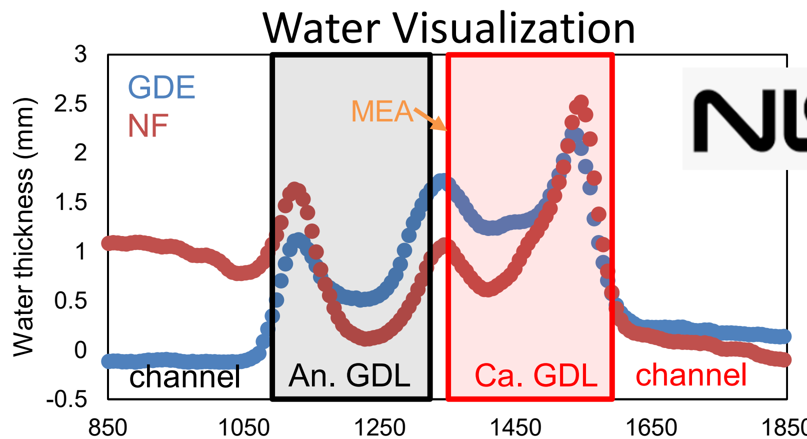




Characterization of Nanofiber Electrodes







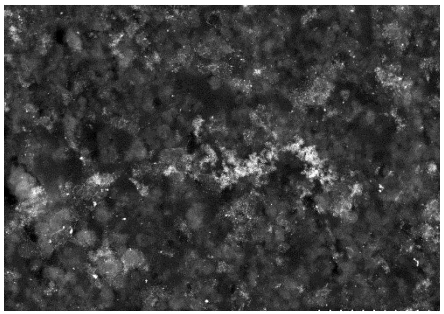
➢ Better water management and better durability of nanofiber MEAs

FC-PAD support to: High performance PEFC electrode structures

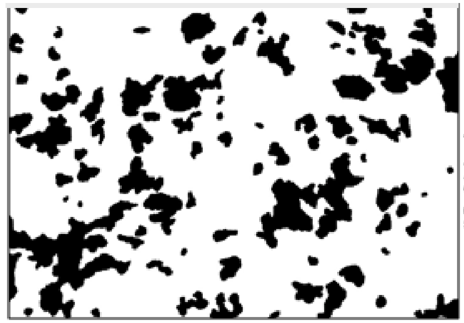
P.I.: Mike L. Perry - Project ID: FC157

United Technologies Research Center

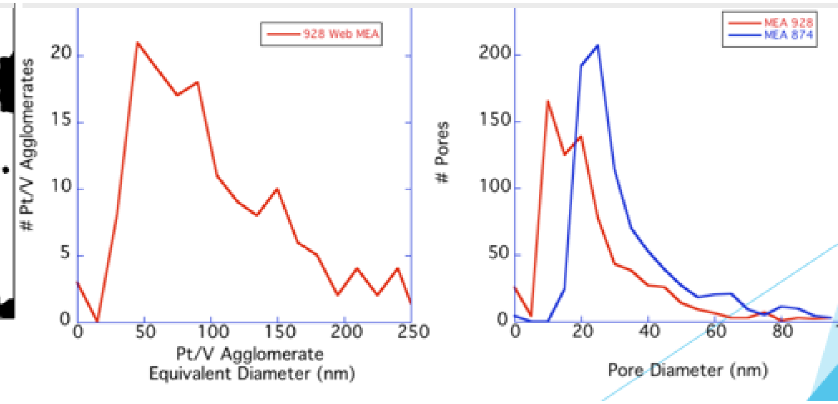
STEM to estimate agglomerate size



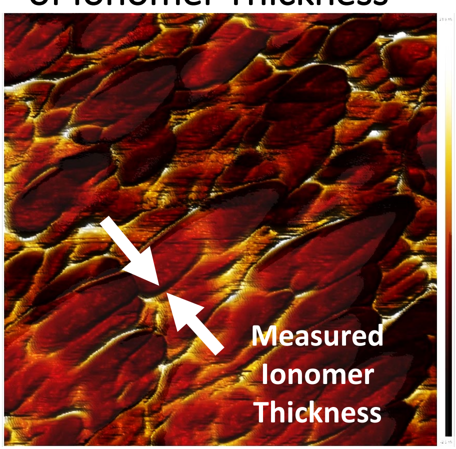
Digitized images



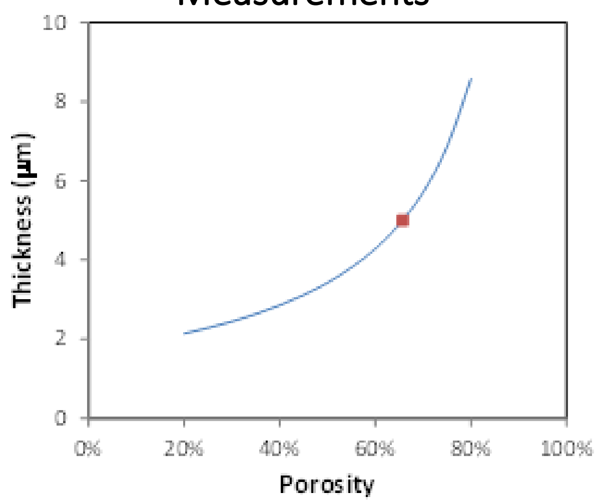
Agglomerate Distribution by slicing through smaller dimension of agglomerate chains.



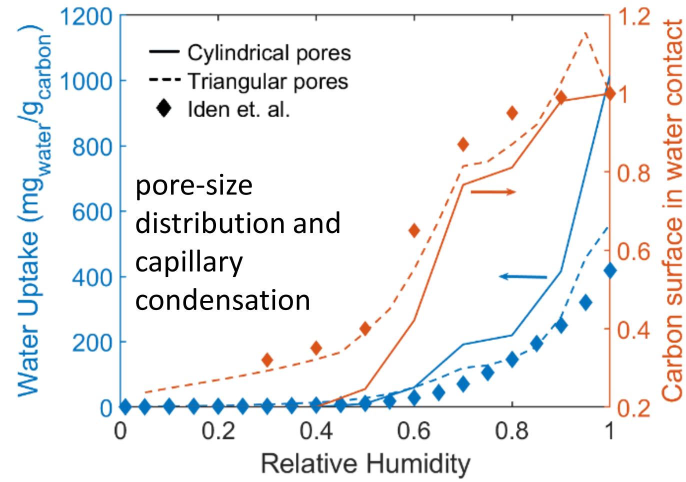
AFM Measurements of Ionomer Thickness



Catalyst Layer Porosity Measurements



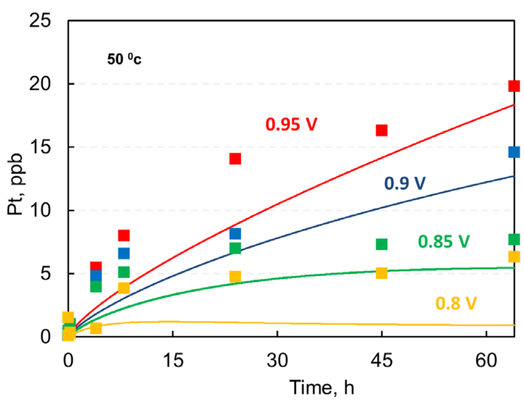
Modeling porous carbons for optimization of catalyst utilization

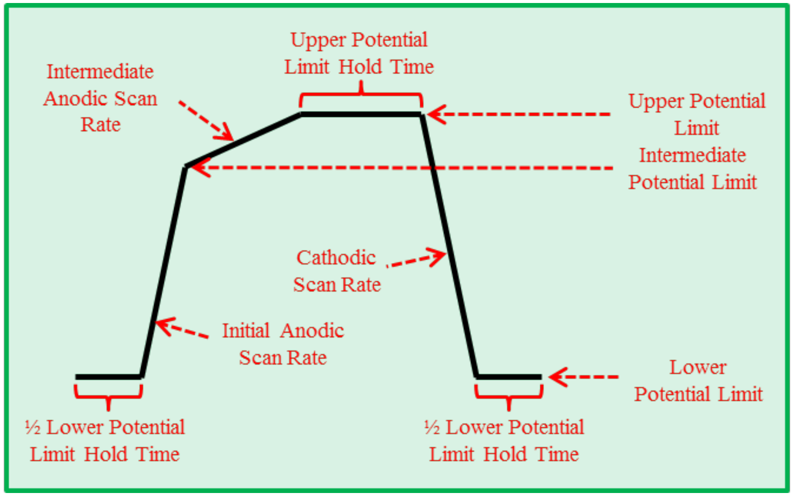


FC-PAD support to: Durable High Power Membrane Electrode Assembly with Low Pt Loading

P.I.: Swami Kumaraguru - Project ID: FC156

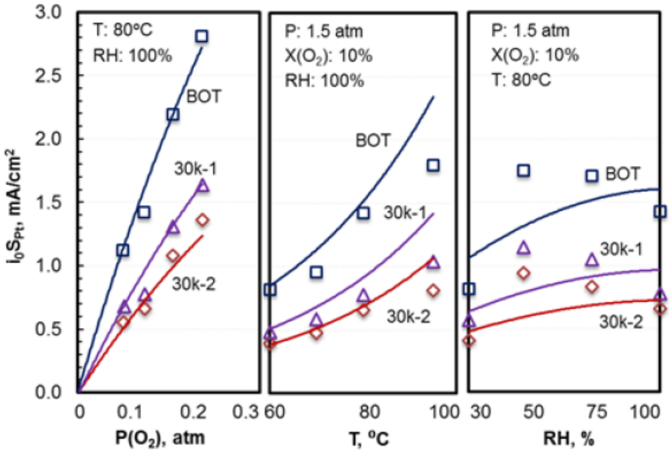
Pt Dissolution (half-cell)



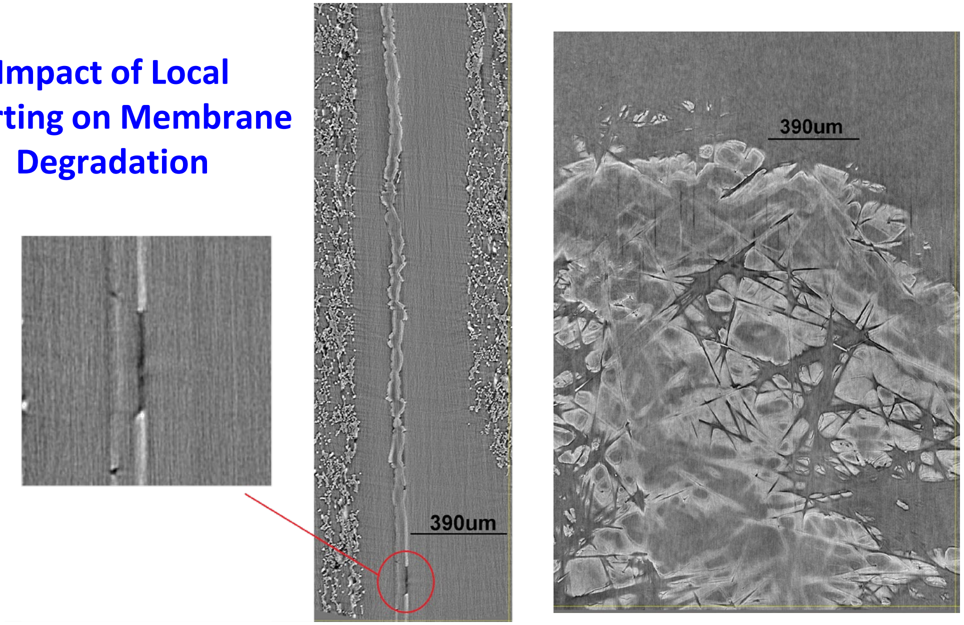


H_2-N_2 voltage cycling to identify operational limitations

Model framework development to identify root cause of durability losses



Impact of Local Shorting on Membrane Degradation



FC-PAD Planned Work Related to 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

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
- **Selected 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
  - 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

Acknowledgements

FC-PAD acknowledges funding from:
DOE EERE: Energy Efficiency and Renewable Energy
Fuel Cell Technologies Office (FCTO)

- Fuel Cells Program Manager & Technology Manager:
  - Dimitrios Papageorgopoulos
  - Greg Kleen
- Organizations we have collaborated with todate
- 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, LANL-Center for Integrated Nanotechnologies
  - NIST: BT-2

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2019 AMR – April 29 – May 1

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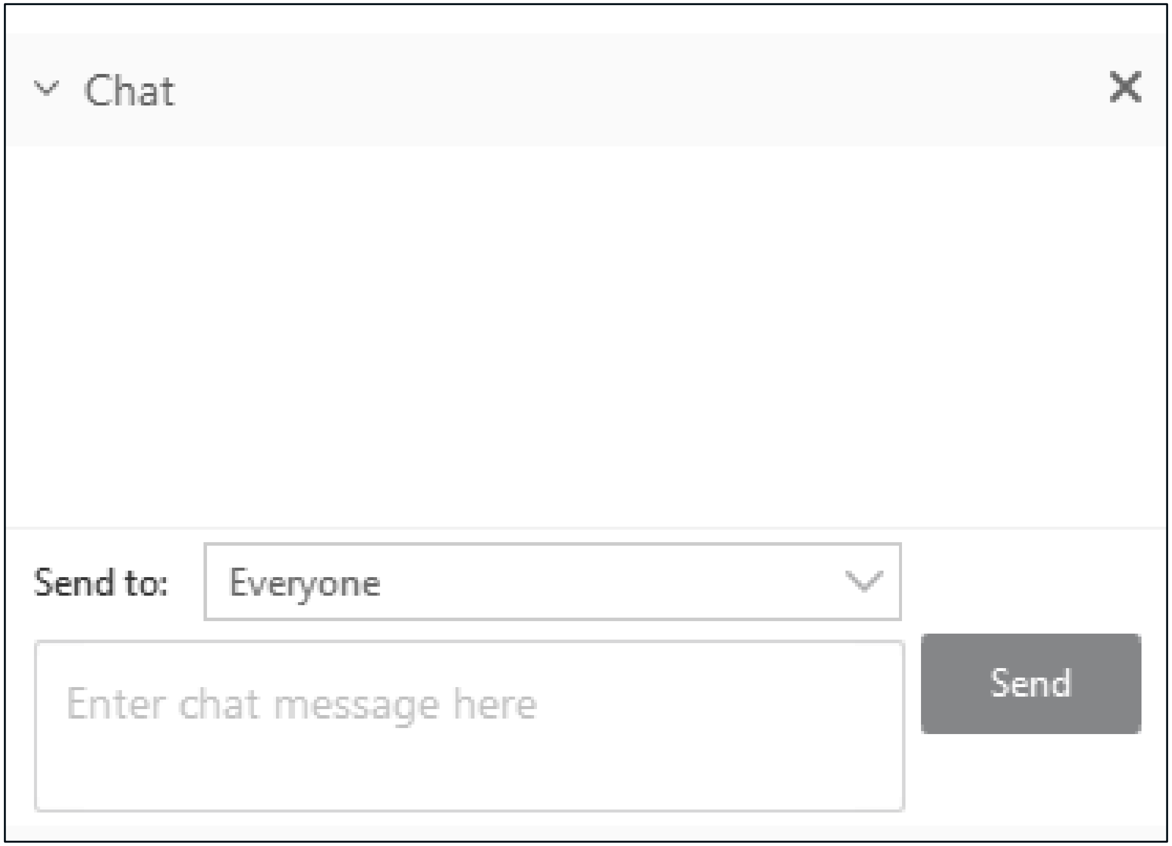
Question and Answer

- Please type your questions to the chat box. **Send to: (HOST)**



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Thank you

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hydrogenandfuelcells.energy.gov

Backup Slides

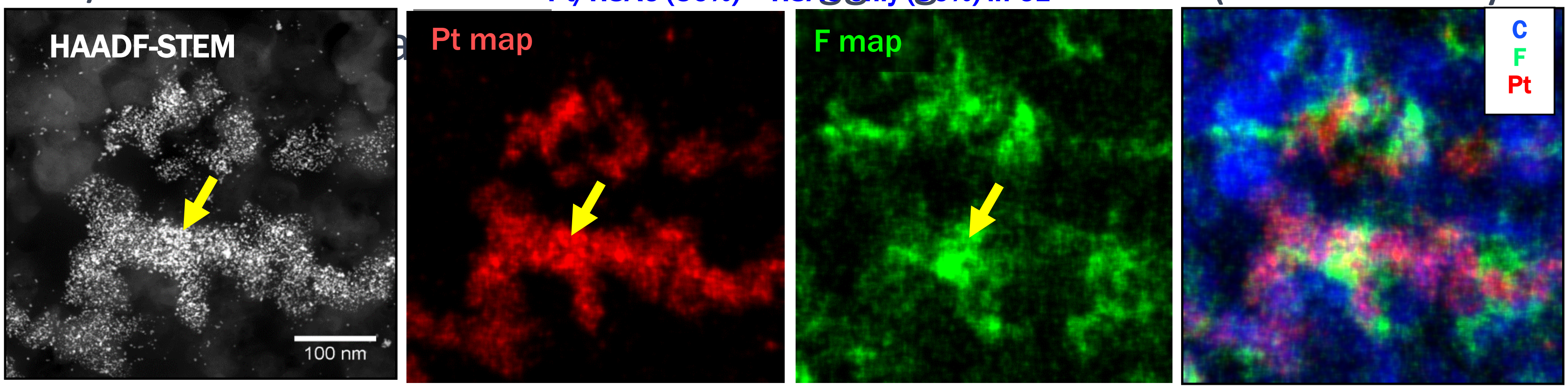
Ionomer Dispersion within Catalyst Layers

Comparing Ionomer+C and Ionomer+Pt/C

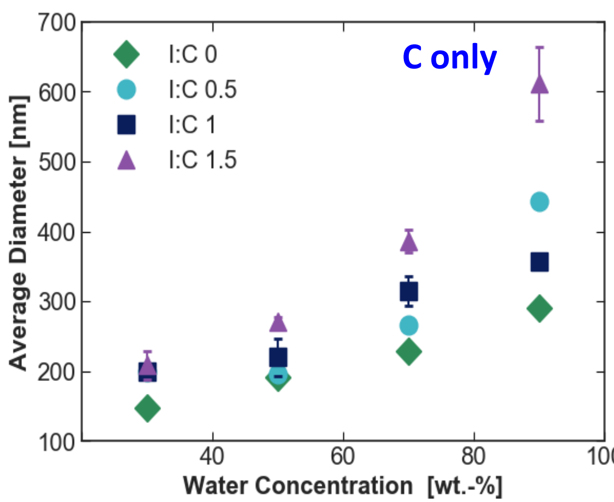
- Increased interactions when Pt added
  - Evidence for ionomer predominantly associated with Pt/C regions
    - Pt/ionomer interactions dominate aggregation in inks (measured by

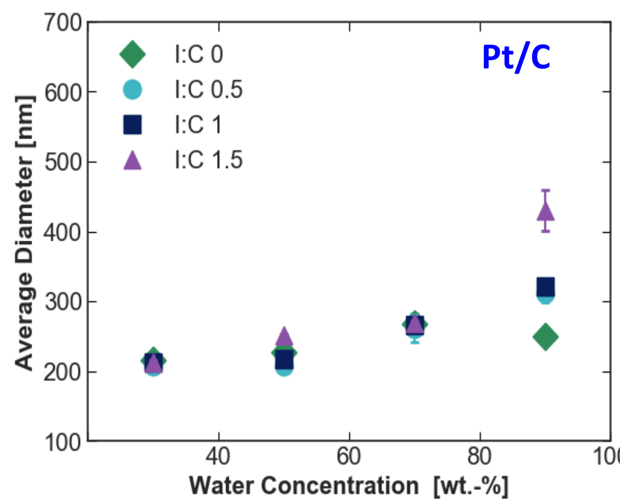
Pt/HSAC (50%) + HSAC-only (50%) in CL

CL



Ink

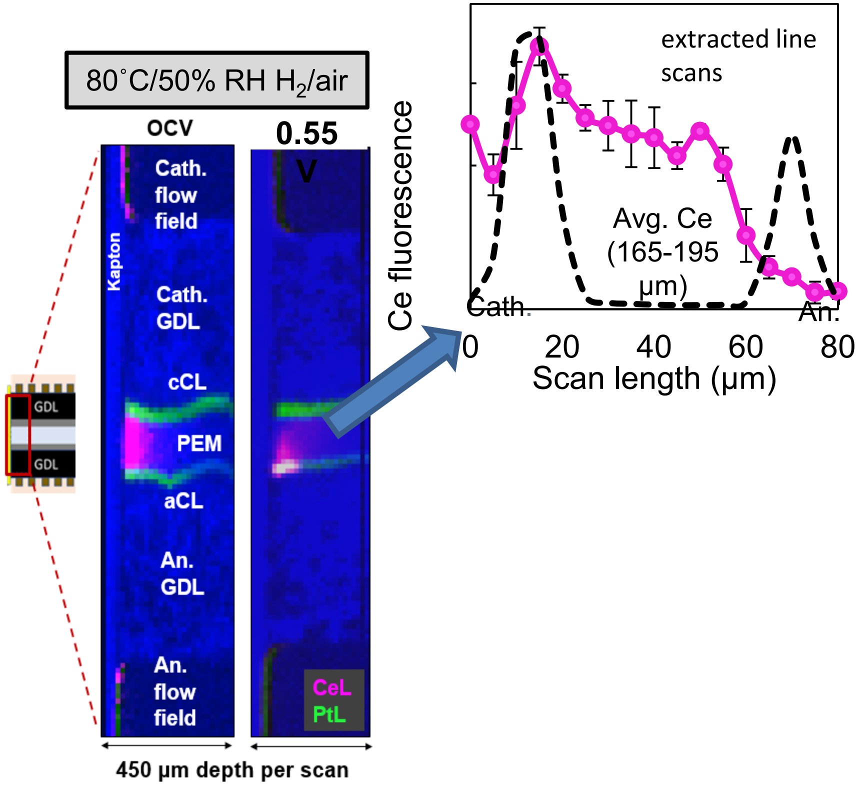




Higher agglomeration without Pt

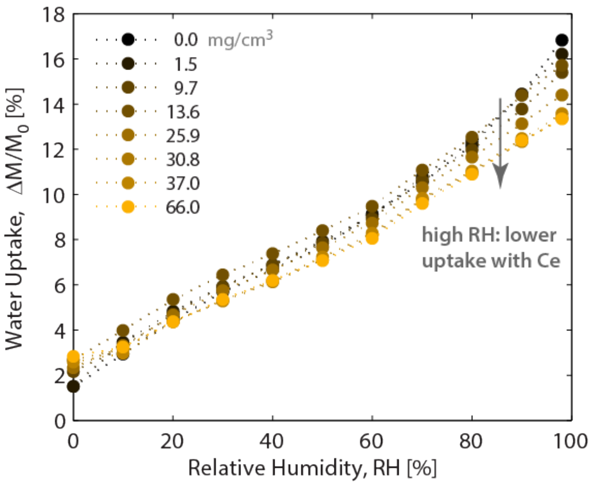
Ce Migration: Membrane Properties

Confocal Raman: observe Ce migration during and after applied potential

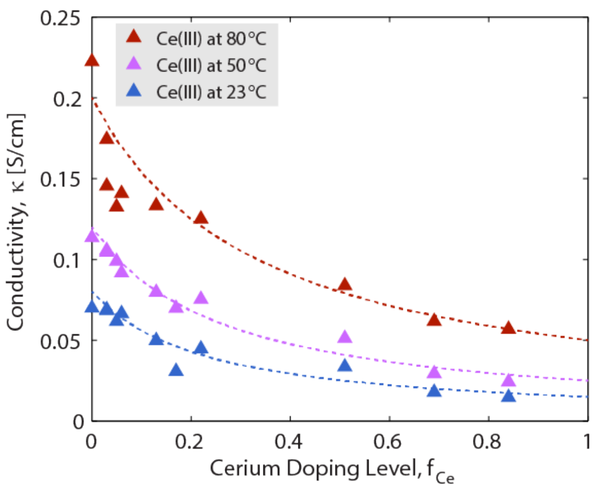


- Ce moves towards cathode during operation
- Removing load redistributes Ce ~ 5 minutes; half that of migration

Membrane water uptake and conductivity

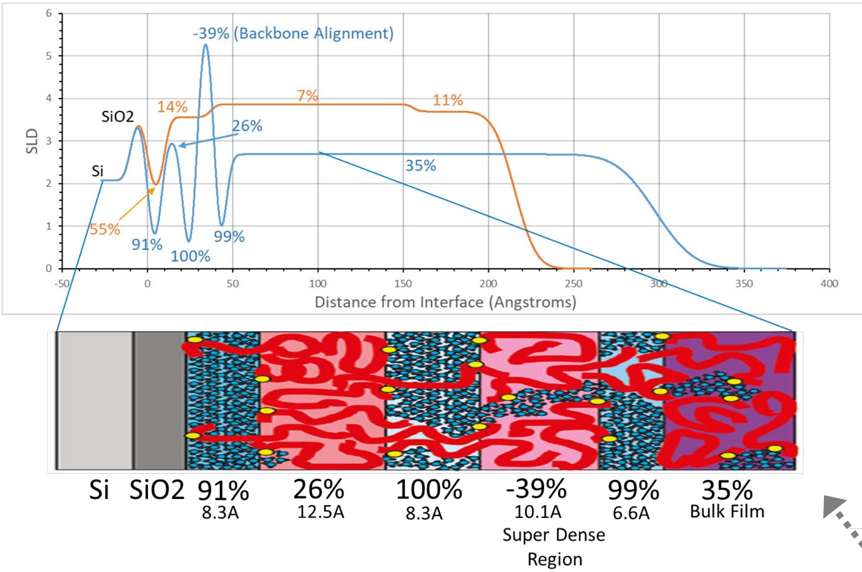


- Ce impacts membrane water uptake properties
  - Decreased water uptake

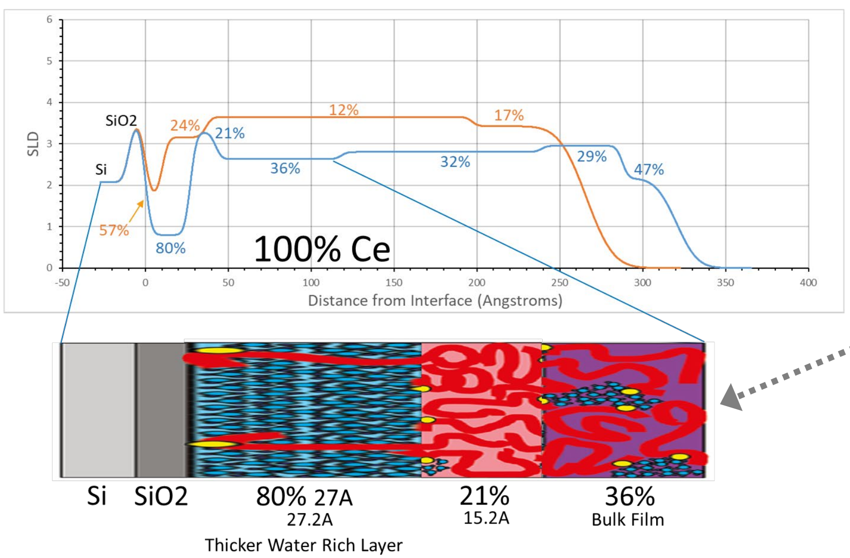


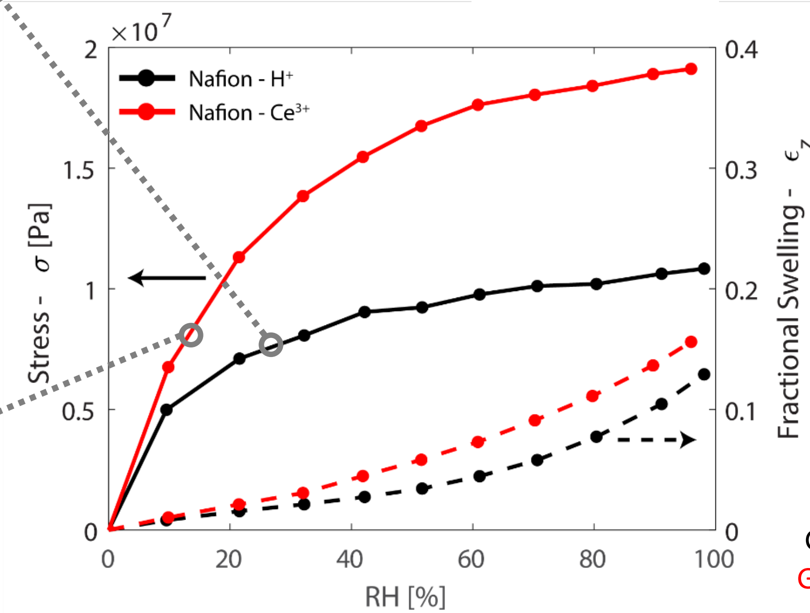
- Decrease in conductivity in liquid water with Ce doping
  - Increased activation energy with loading

Ionomer Thin films: Cerium Doping



- Clear connection between structure and thermodynamic/mechanical properties, which is altered by cation identity
  - Similar structures in the dry state, which manifests in similar mechanical response and swelling at low RH
  - At high water content, the more interspersed water results in higher stress and modulus for the Ce-exchanged film
- Swelling response agrees with more water in Ce-exchanged film





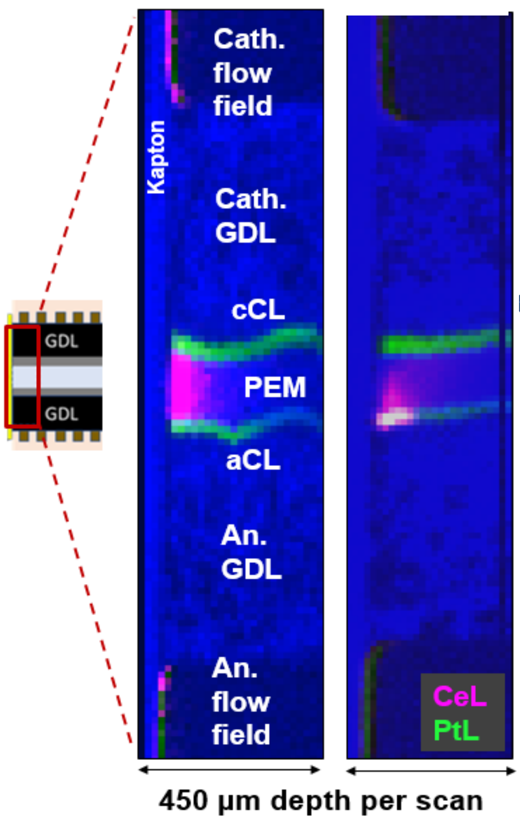
G_H= 304 Mpa

G_{Ce} = 323 MPa

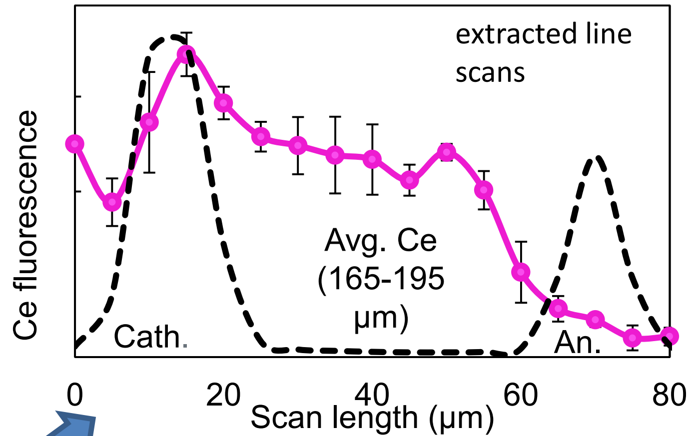
Cation (Ce) Migration: Experiments

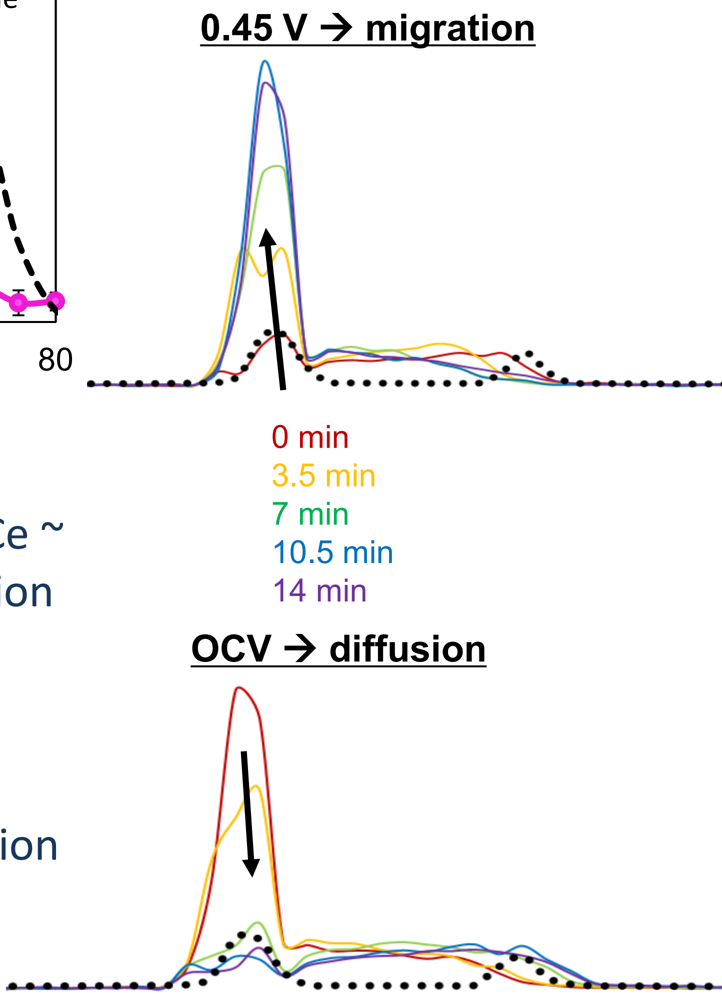
Observing Ce migration during and after applied potential

80˚C/50% RH H_2/air



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

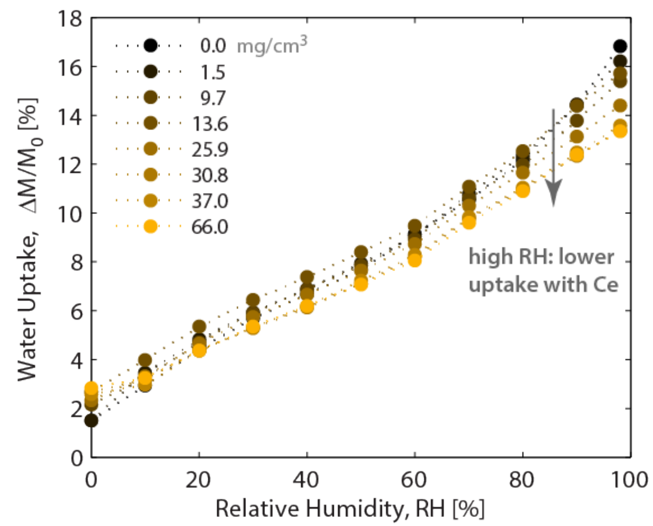


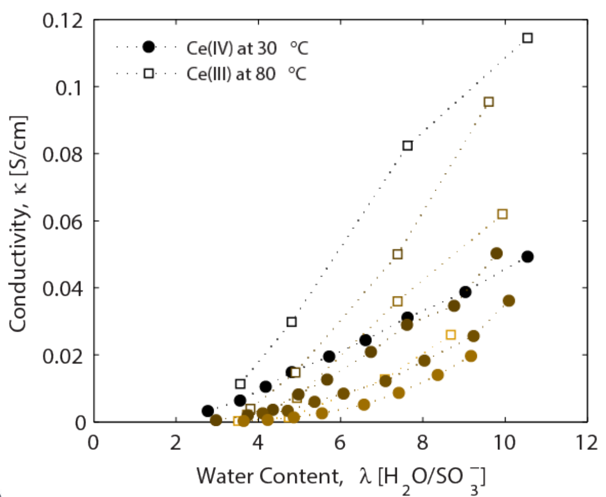


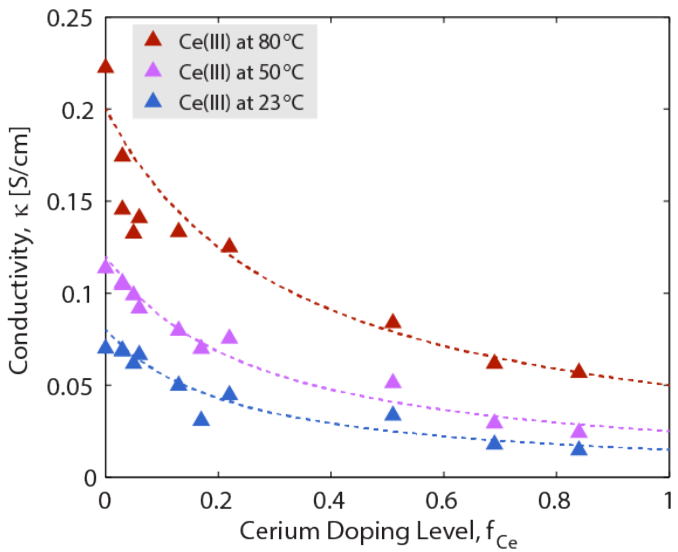
- Removing load redistributes Ce ~ 5 minutes; half that of migration
- Ce moves towards cathode during operation - balance between diffusion and migration

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



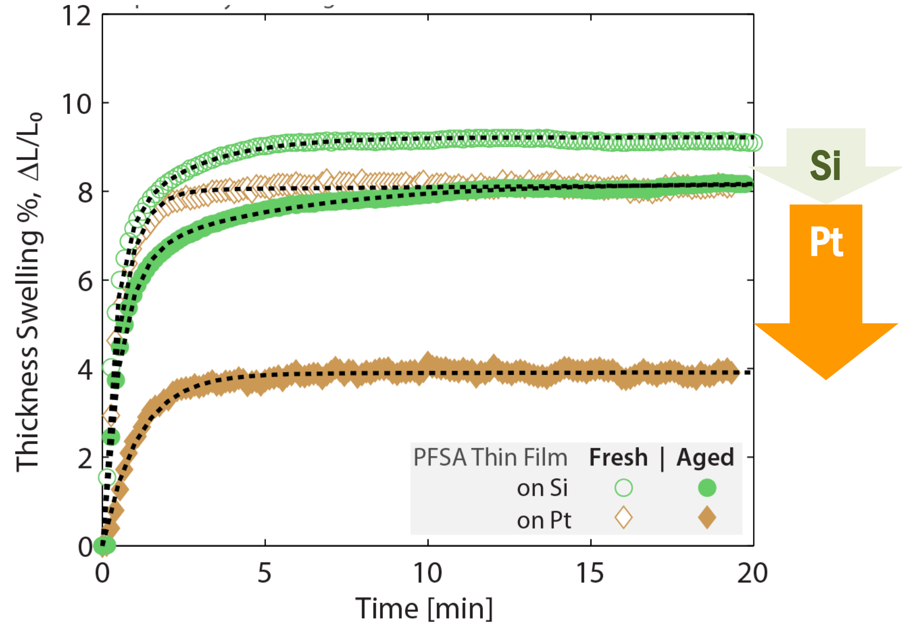


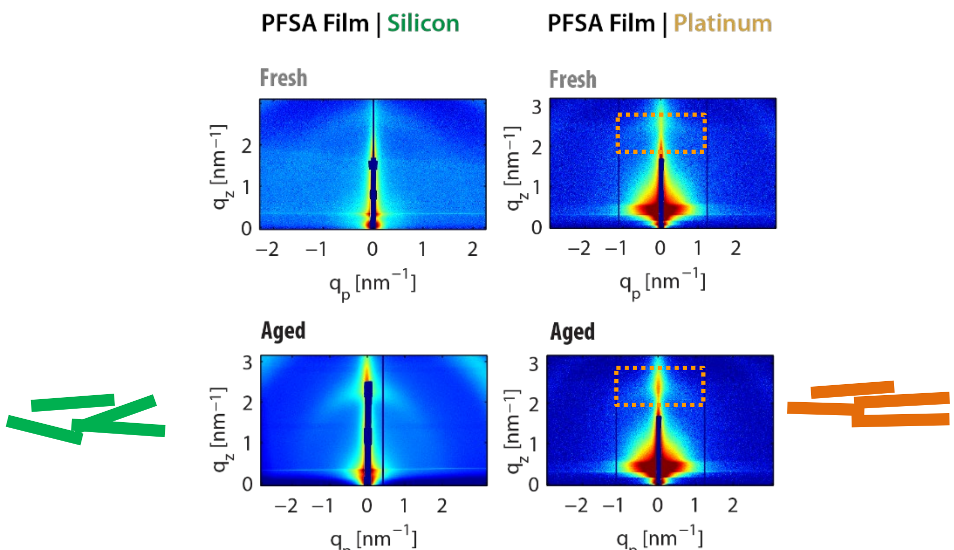


Ionomer Thin Films: Impact of Ageing

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

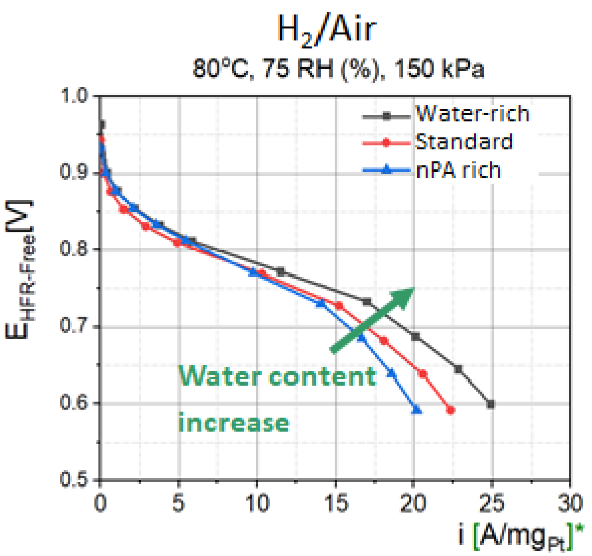
	Fresh film	Aged Film
Swelling	Si > Pt	Si >> Pt ↓
Swelling Kinetics	Si > Pt	Si >> Pt ↓
Domain Orientation	Si < Pt	Si << Pt ↑

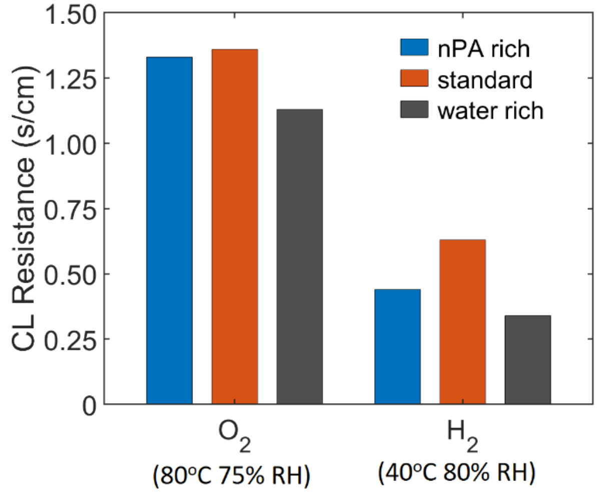


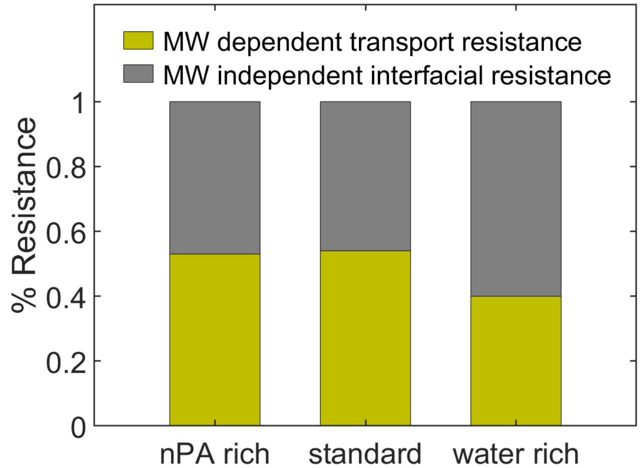


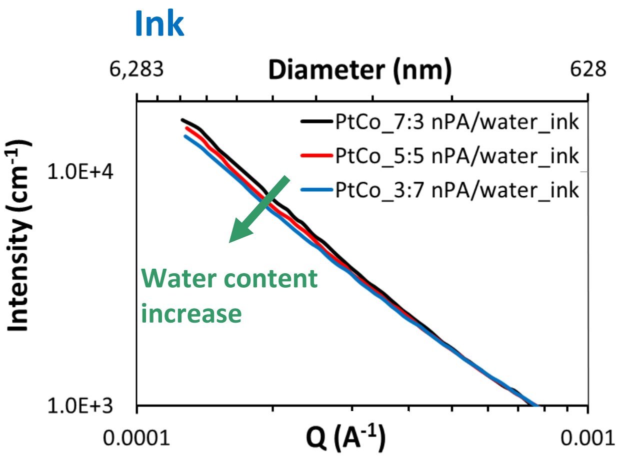
M Tesfaye, D. Kushner, A. Kusoglu, ***ACS Applied Polymer Materials*** (Accepted Manuscript)

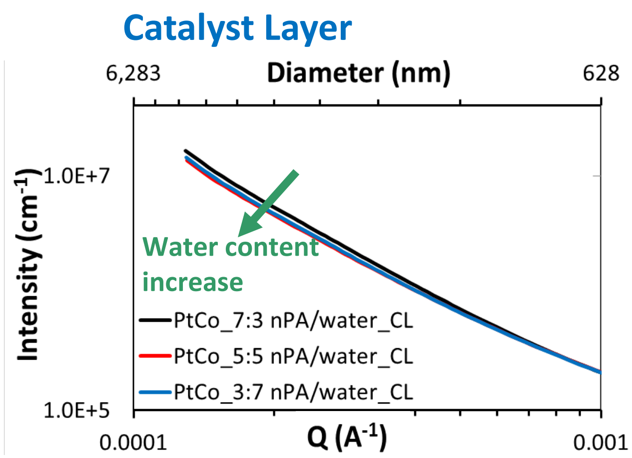
Case Study: Ink Solvents







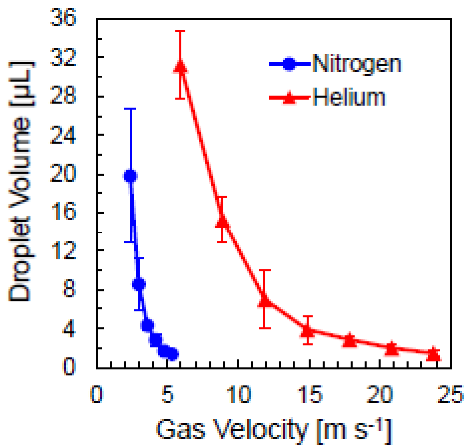


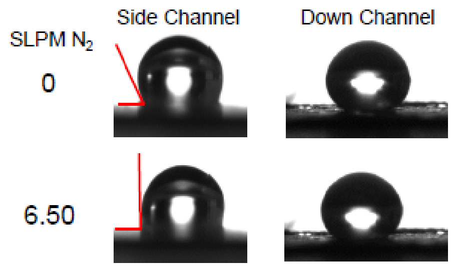


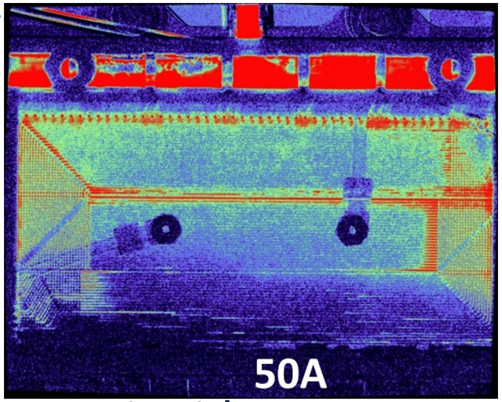
- Performance improvement with water-rich ink
  - Reduction in non-Fickian and MW dependent transport percentage of resistance
  - Decrease in agglomerate size both ink and CL

Water Management

- 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

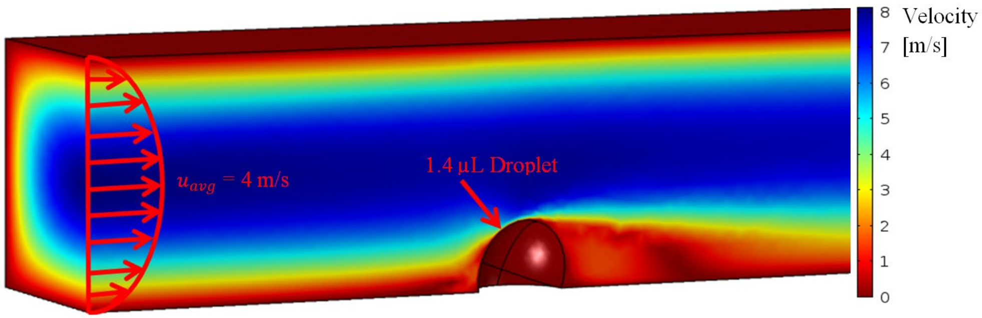




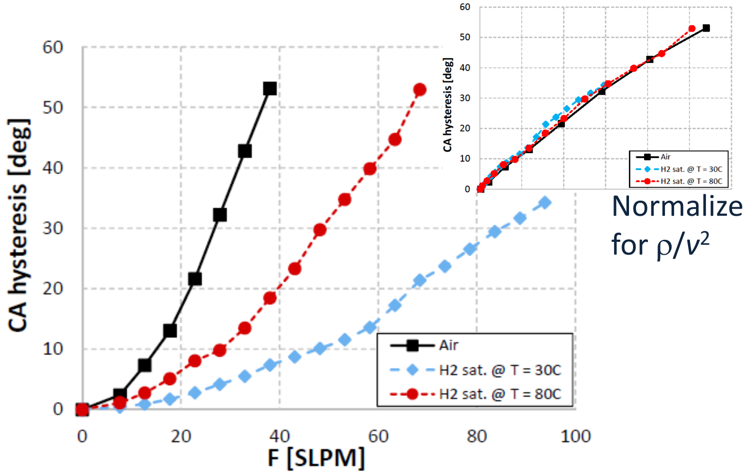


Liquid water on anode in Mirai

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



Coupled flow and deformation model

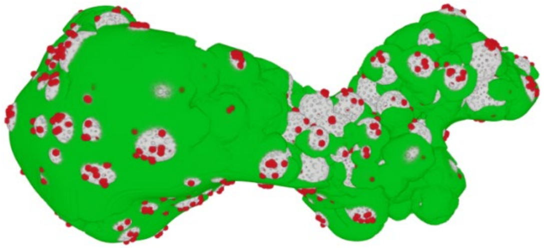


Normalize for ρ/v^2

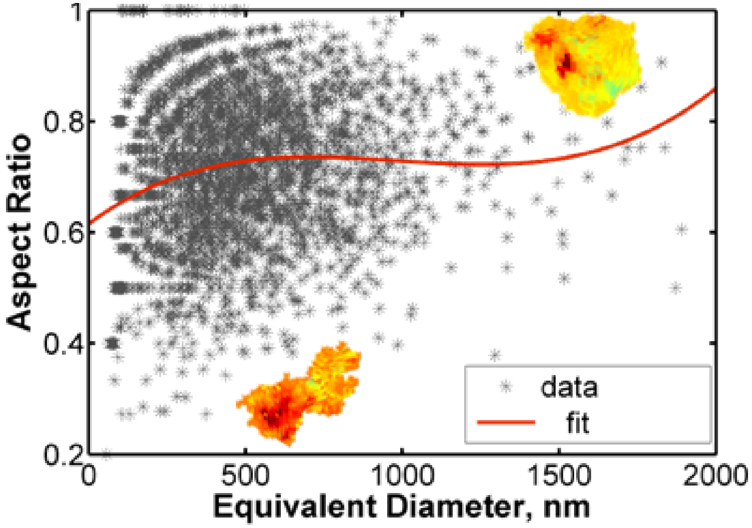
Modeling of Microscale Transport-Catalyst Layer Agglomerates

- Explore agglomerate structures and understand mechanisms limiting of transport

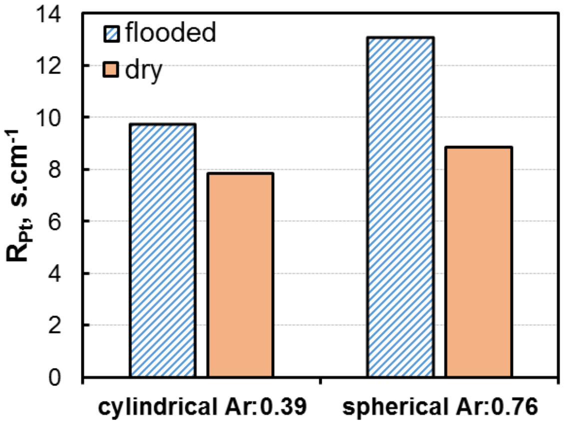
Agglomerates identified by applying binary separation algorithm to segmented phase contrast images

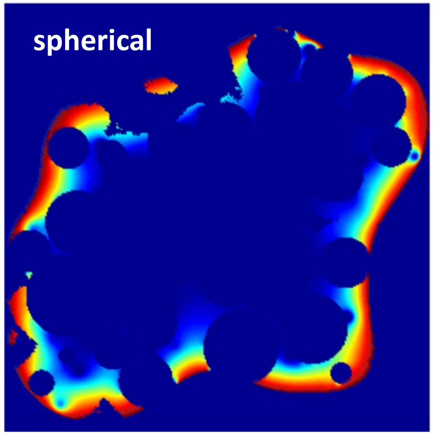


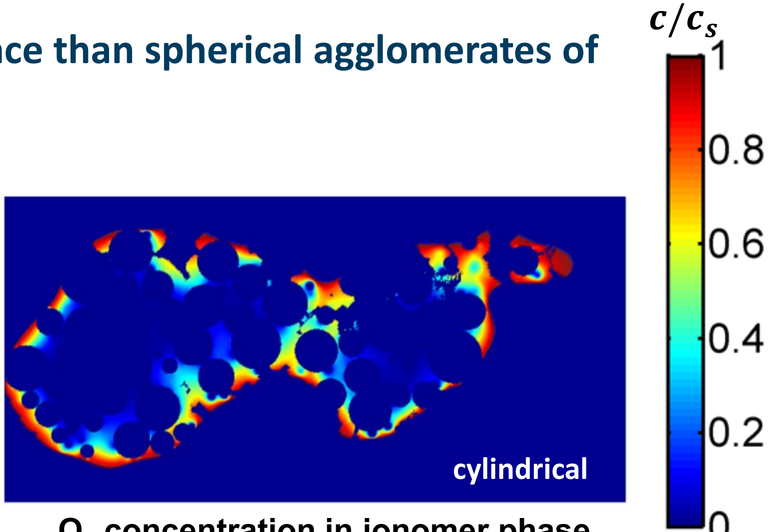
Reconstructed agglomerate includes porous C, Pt, and ionomer distributions from absorption contrast images



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)