FC137 – FC-PAD: Electrode Layers and Optimization

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Tuesday, June 6th 2017

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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

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*

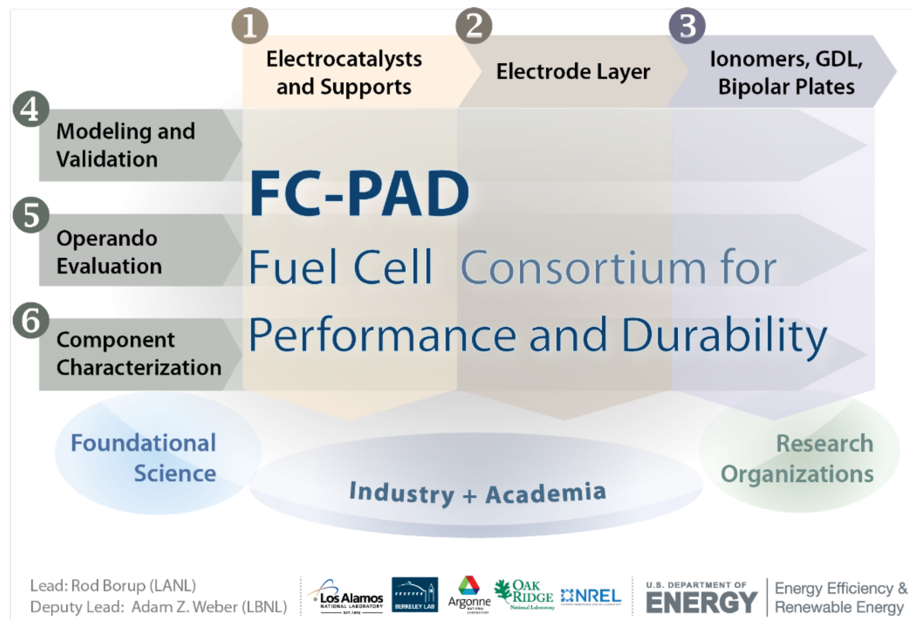
Argonne National Laboratory · Los Alamos National Laboratory · Berkeley Lab · NREL National Renewable Energy Laboratory · Oak Ridge National Laboratory

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 Consortium - Overview

Fuel Cell Technologies Office (FCTO)

- FC-PAD coordinates activities related to fuel cell performance and durability
  - The FC-PAD team consists of five national labs and leverages a multi-disciplinary team and capabilities to accelerate improvements in PEMFC performance and durability
  - The core-lab team consortium was awarded beginning in FY2016; builds upon previous national lab (NL) projects
- Provide technical expertise and harmonize activities with industrial developers
- FC-PAD serves as a resource that amplifies FCTO's impact by leveraging the core capabilities of constituent members

Los Alamos NATIONAL LABORATORY

Argonne NATIONAL LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB

OAK RIDGE National Laboratory

FC-PAD Consortium – Relevance & Objectives

Overall Objectives:

- Advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) at a pre-competitive level
- Develop the knowledge base and optimize structures for more durable and high-performance PEMFC components
- Improve high current density performance at low Pt loadings
  - Loading: 0.125 mg Pt/cm^2 total
  - Performance @ 0.8 V: 300 mA / cm^2
  - Performance @ rated power: 1,000 mW / cm^2
- Improve component durability (e.g. membrane stabilization, self-healing, electrode-layer stabilization)
- *Provide support to DOE Funded FC-PAD projects from FOA-1412*
- *Each thrust area has a sub-set of objectives which lead to the overall performance and durability objectives*

FC-PAD Overview & Relevance

Timeline

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

Budget

FY17 project funding: $5,150,000
As proposed: 5-year consortium with quarterly, yearly milestones & Go/No-Go
Total Expected Funding: $25M (NLs only)

Partners/Collaborations

(To Date Collaborations Only)

- EWii Fuel Cells, Umicore, NECC, GM, TKK, USC, JMFC, W.L. Gore, Ion Power, Tufts, KIER, PSI, UDelaware, 3M, CSM, SGL, NPL, NIST, CEA, Ulorraine, UTRC, U Alberta
- Partners added by DOE DE-FOA-0001412

Barriers

- Cost: $40/kW system (2020), $30/kW (ultimate); $14/kW$_{net}$ MEA (2020)
- 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

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

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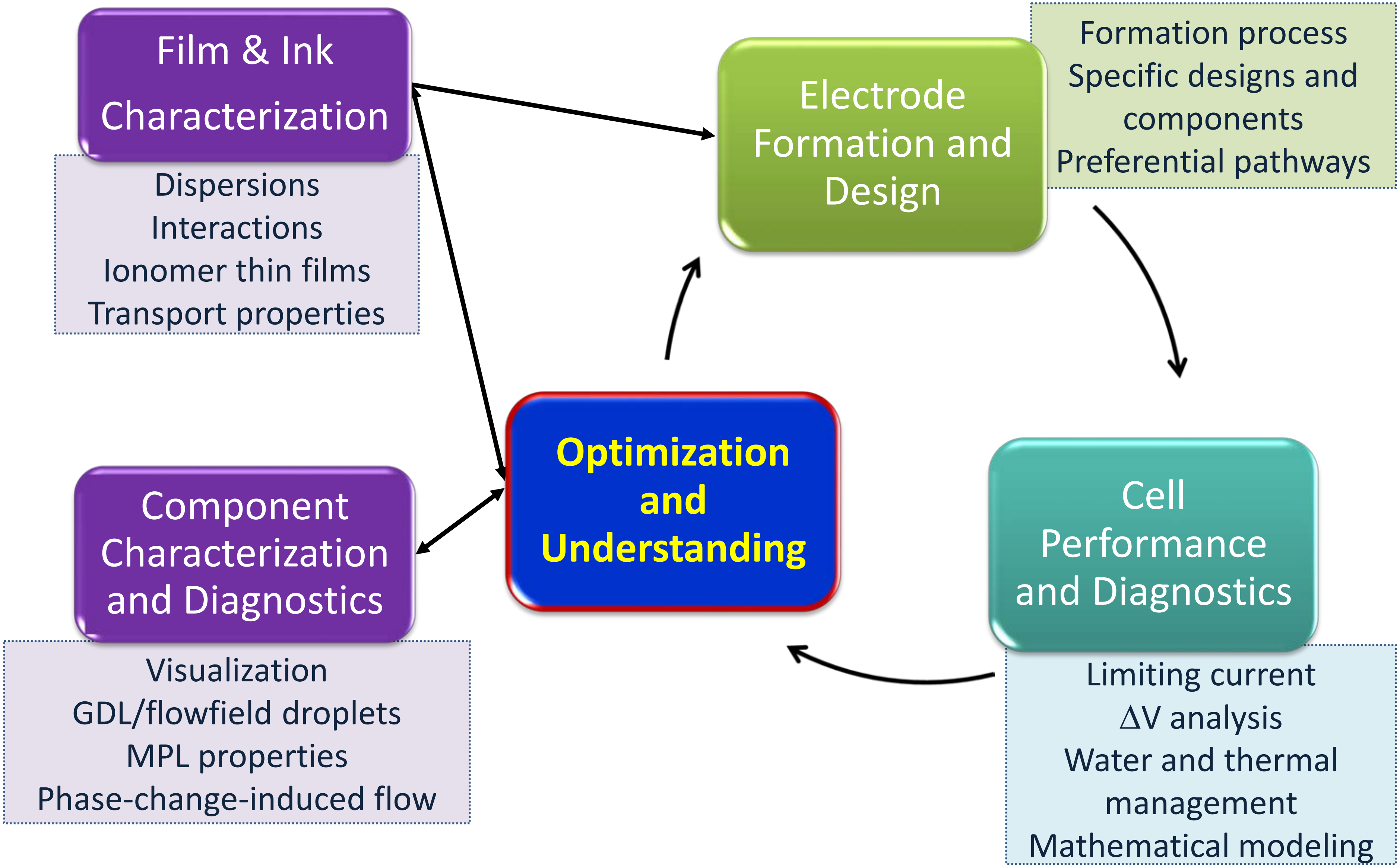
Objective: How we get there

- Develop the knowledge base and optimize structures for more durable and high-performance PEMFC components
- Understanding Electrode Layer Structure
  - Characterization
- New Electrode Layer Design and Fabrication
  - Stratified (Spray, Embossed, Array), Pt - Deposition, Jet Dispersion
- Defining/Measuring Degradation Mechanisms
  - Membrane, Catalyst Pt-alloy dissolution

FC-PAD Presentations

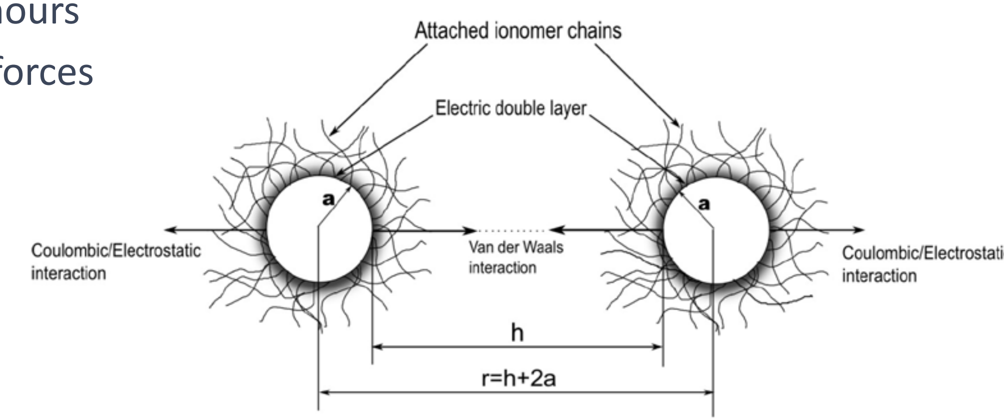
- **FC135: FC-PAD: Fuel Cell Performance and Durability Consortium (Borup, LANL)**
  - Overview, Framing, Approach, and Highlights/**Durability**
- **FC136: FC-PAD: Components and Characterization (More, ORNL)**
  - Concentrate on **Catalysts** and **Characterization**
- **FC137: FC-PAD: Electrode Layers and Optimization (Weber, LBNL)**
  - Concentrate on **Performance** - MEA construction and modeling
- **FC155 (3M), FC156 (GM), FC157 (UTRC), FC158 (Vanderbilt) FOA-1412 Projects**

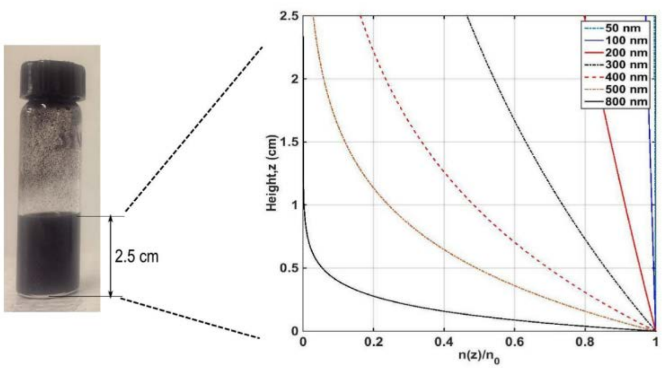
Approach: Electrode Layers and Optimization

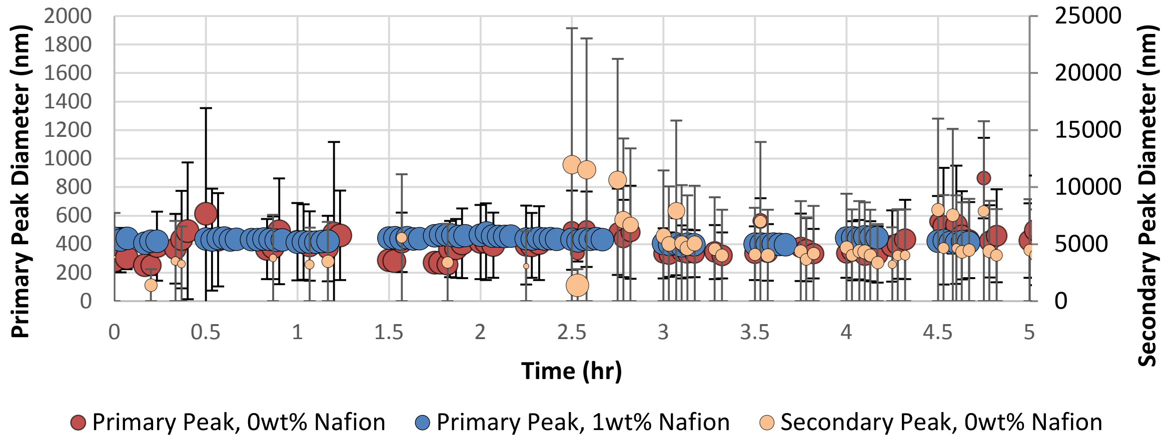


Ink Stability

- Inks are unstable
  - Model and experiments demonstrate large carbon aggregates that drop out of suspension
    - Secondary peak forms after a couple of hours
    - Governed by collisions and interparticle forces
      - Settling
  - Ionomer helps to stabilize the ink
    - Depends on solvent ratio



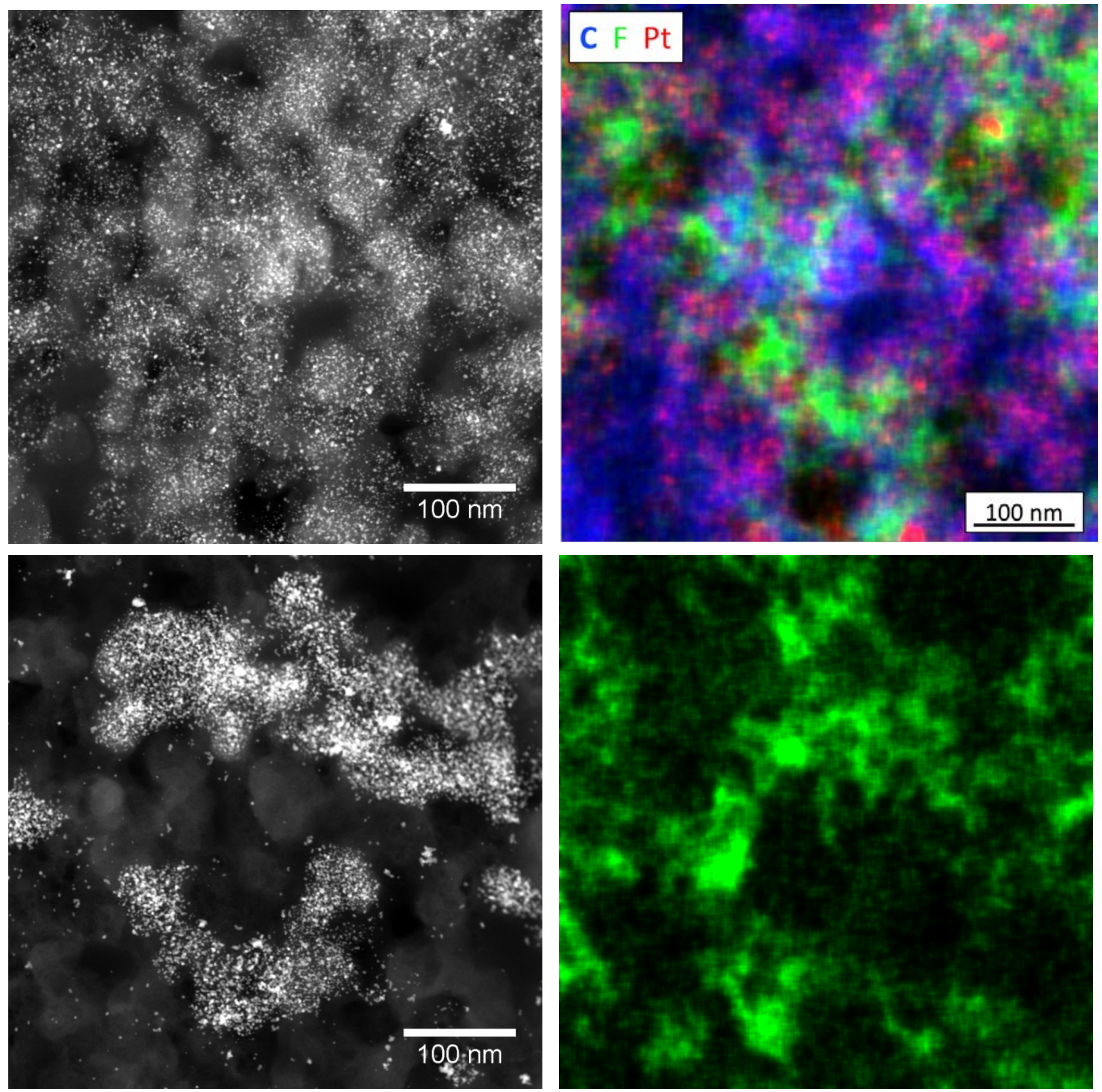




Interparticle forces and interactions key towards understanding CL formation

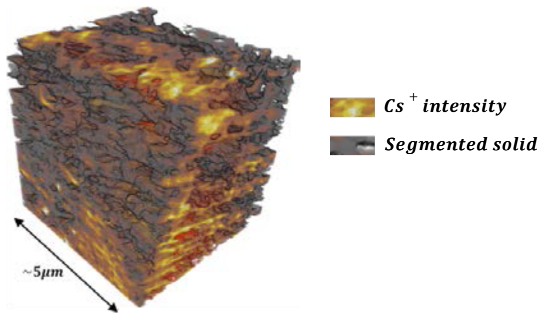
Catalyst Layer Structure

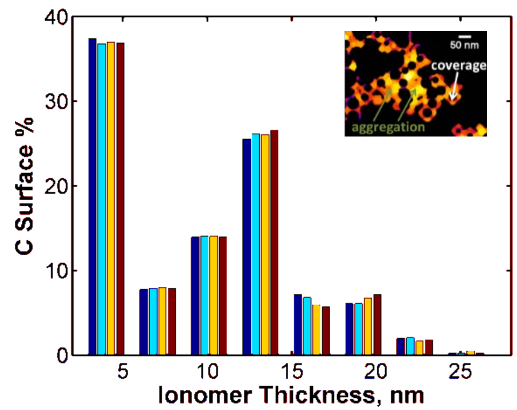
- Catalyst structures are heterogeneous
  - Impacts analysis of transport phenomena
  - Ionomer preferentially interacts with Pt/V



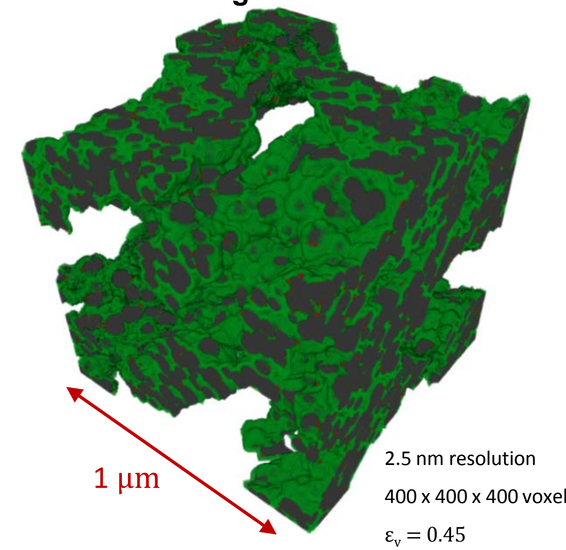
Electrode Microstructure Analysis

- Developed method to reconstruct electrode microstructure from multiple data
  - Nano-CT, TEM, USAXS data
    - C, Pt, pore size distributions
    - Ionomer visualized and computed

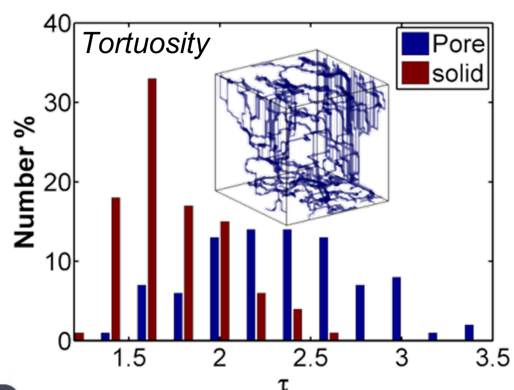


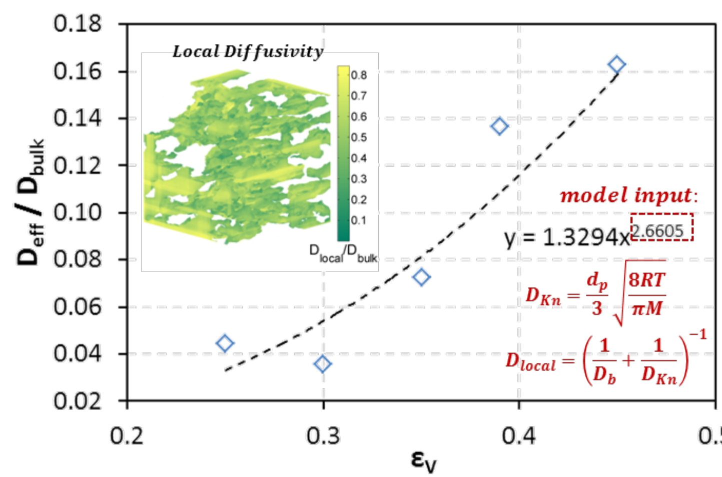


Resulting Microstructure



- Simulate transport through the domain
  - Elucidate transport bottlenecks

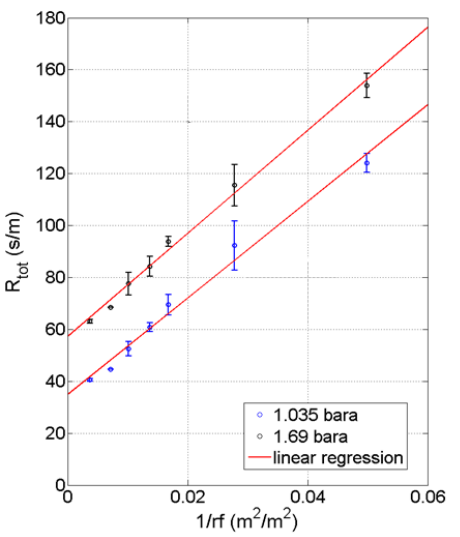


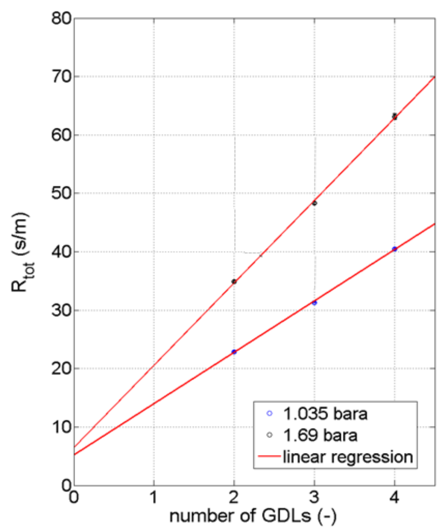


Local Transport Resistance

- Hydrogen limiting current can be used to yield more information

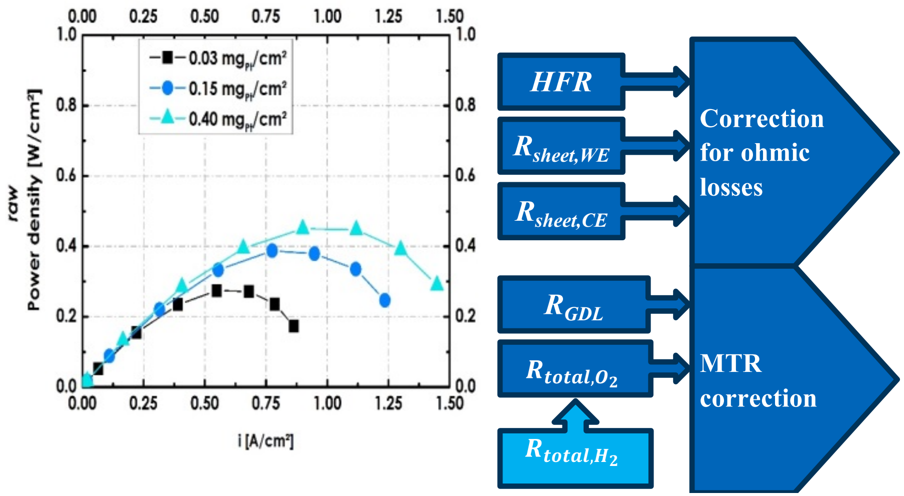
Pressure (bar)		1.035		1.69	
R (s/cm)		R_{GDL}	R_{cl}	R_{GDL}	R_{cl}
Method	GDL stacking	8.79	9.96	14.11	12.22
	local resistance	8.67	12.80	14.24	18.02



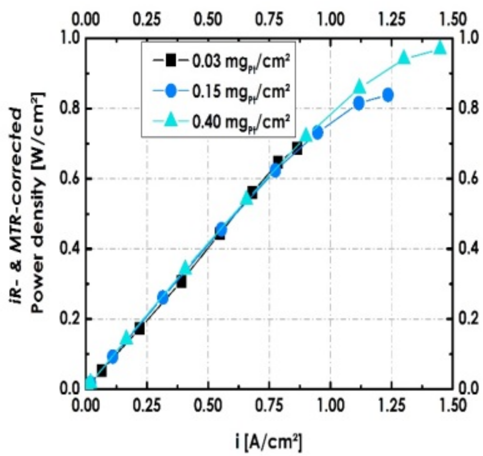


- Stacking allows single loading testing
- Resistance values depend on technique
  - Suggests not all Pt is active

- Can use H_2 data to correct polarization curves for mass-transport resistance



80°C, 90 % RH
H_2/air, 140 kPa_{abs}



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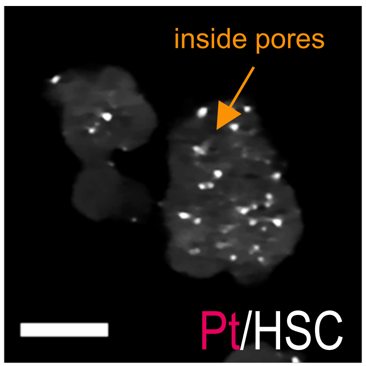
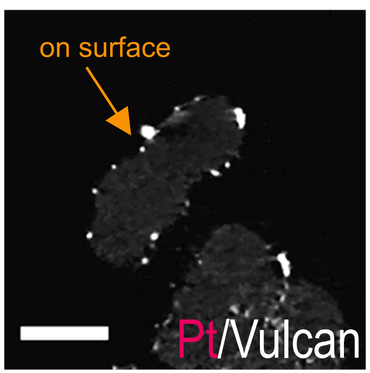
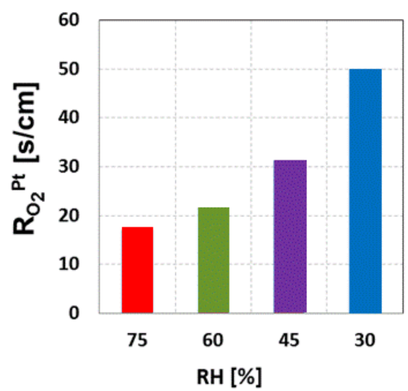
Local Transport Resistance

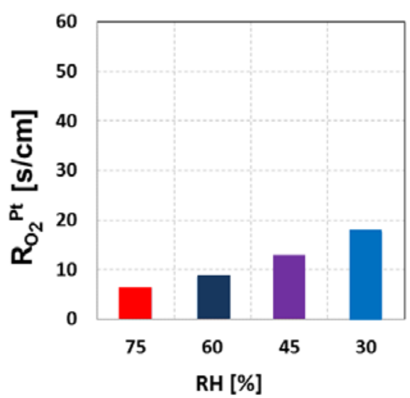
- Use oxygen limiting current to measure the local transport resistance
  - Value depends on accurate measurement of ECA
    - Varies depending on carbon support
  - Pt/V is a better baseline for novel ionomers

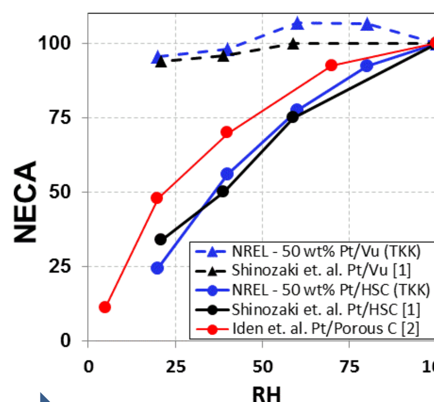


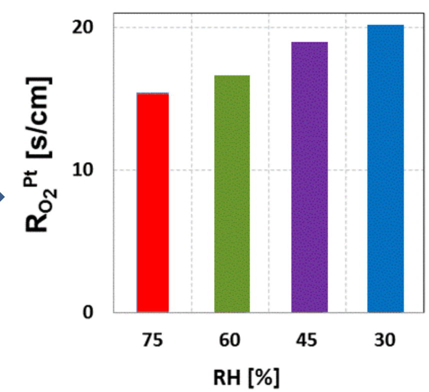


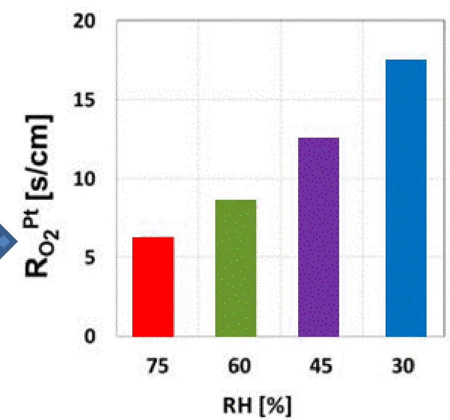
20 wt.% Pt









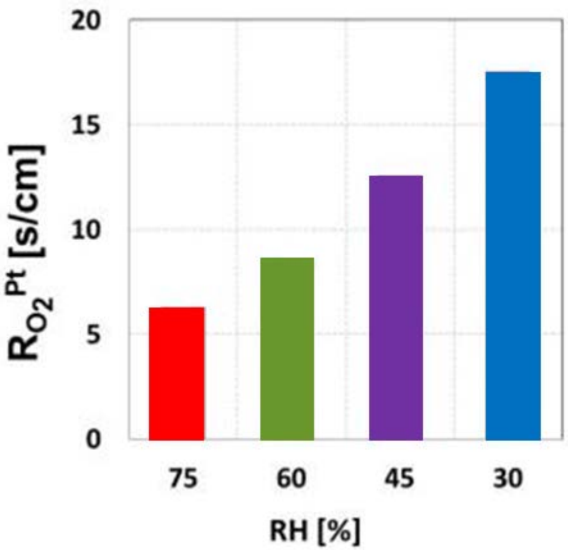


Greszler et al., *JES*, 159(12):F831-F840 (2013)

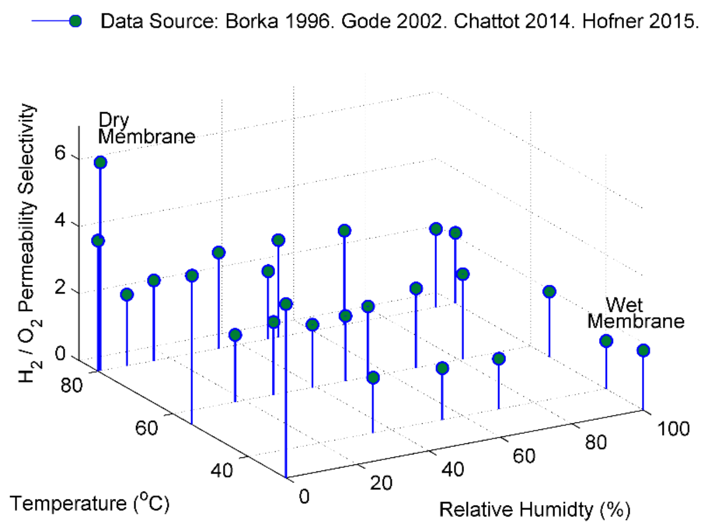
Local Transport Resistance

- Comparison of hydrogen- and oxygen-derived local transport resistance
  - Hydrogen is lower and less humidity and more temperature dependent than oxygen
    - Consistent with ionomer difference in bulk permeability
    - Driven by change in (bulk) diffusivity

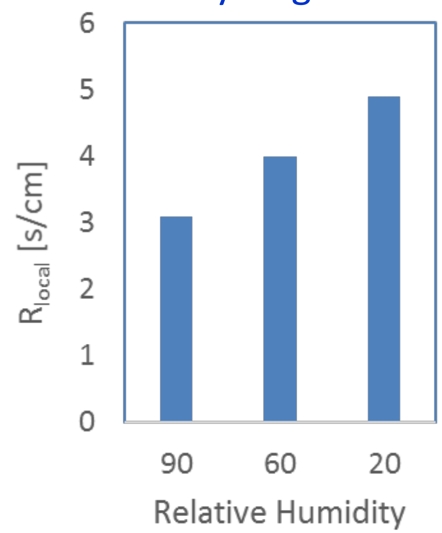
Oxygen



Bulk Nafion



Hydrogen

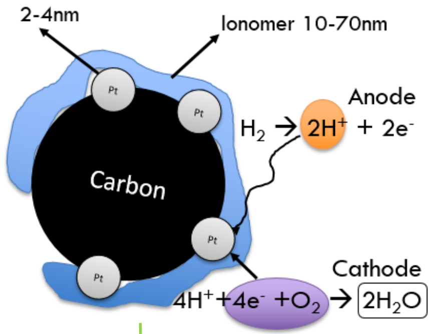


Gas	Liq/dry	
	D sel (D liq/D dry)	S sel (S Liq/ S dry)
H2	61.5	1.0
O2	739.1	0.2

Diagnostics suggest ionomer-related transport is limiting

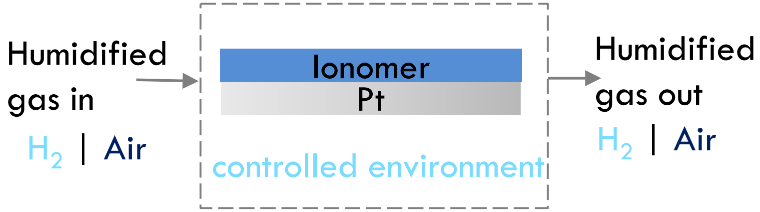
Influence of Environment on Ionomer Thin Film

'Real' catalyst-layer phenomenon

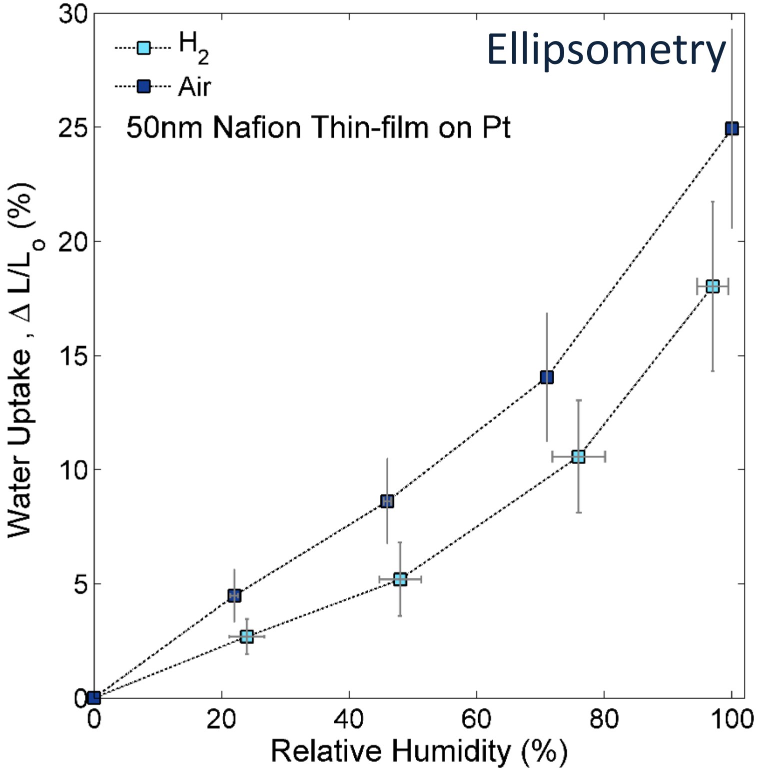


studied using

Model experimental system



Water uptake of Nafion thin-film supported on Platinum substrate in reducing and oxidizing environments



GISAXS

Lower critical angle & film density

↓

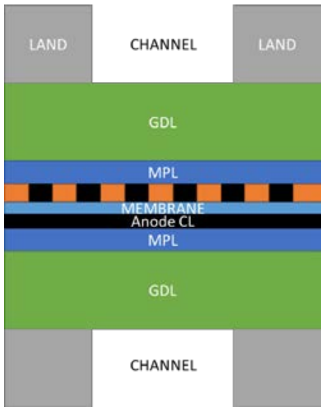
Higher critical angle & film density

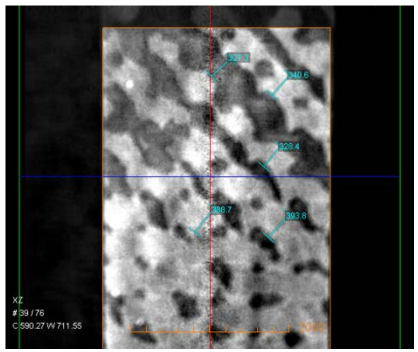
- Oxidizing gas (Air) facilitates Pt-O growth, while reducing gas (H_2) removes it
  - Reducing environment promotes Pt surface, resulting in ionomer densification
  - Reversible process, related to ionic and water interactions with the surface

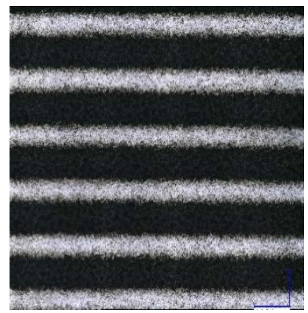
Ionomer undergoes changes with local surface conditions and environment

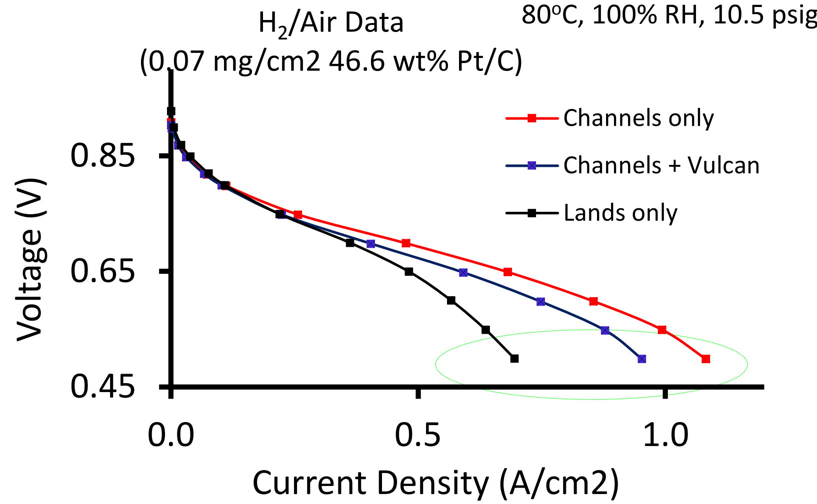
Electrode Structure: Stratified

- Optimize catalyst-layer structure
  - Irregular thickness and porosity: enhanced gas and water transport in and out of MEA
    - Minimize local resistance effects?



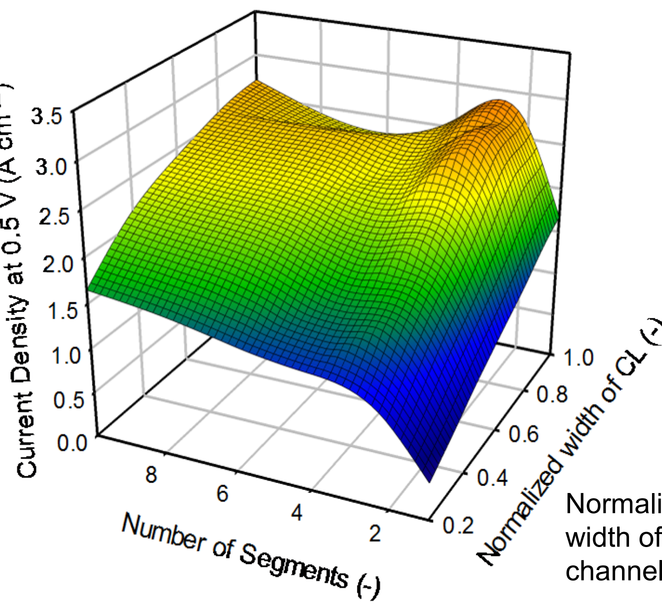




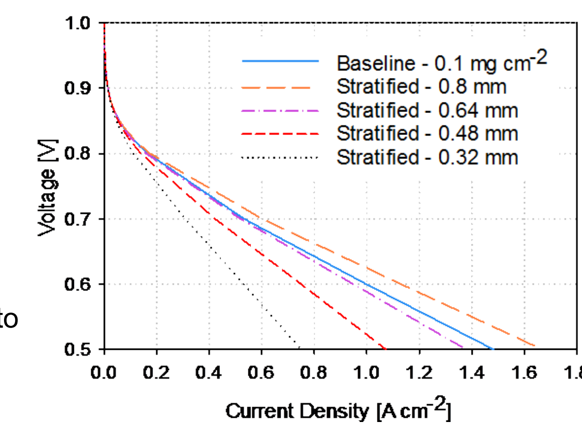


- Need catalyst under channel
- Strong HFR dependence

- Model guided design
  - Model shows gains for stratified CL at high current densities
    - Best gains for ~2 stratified CL segments per channel

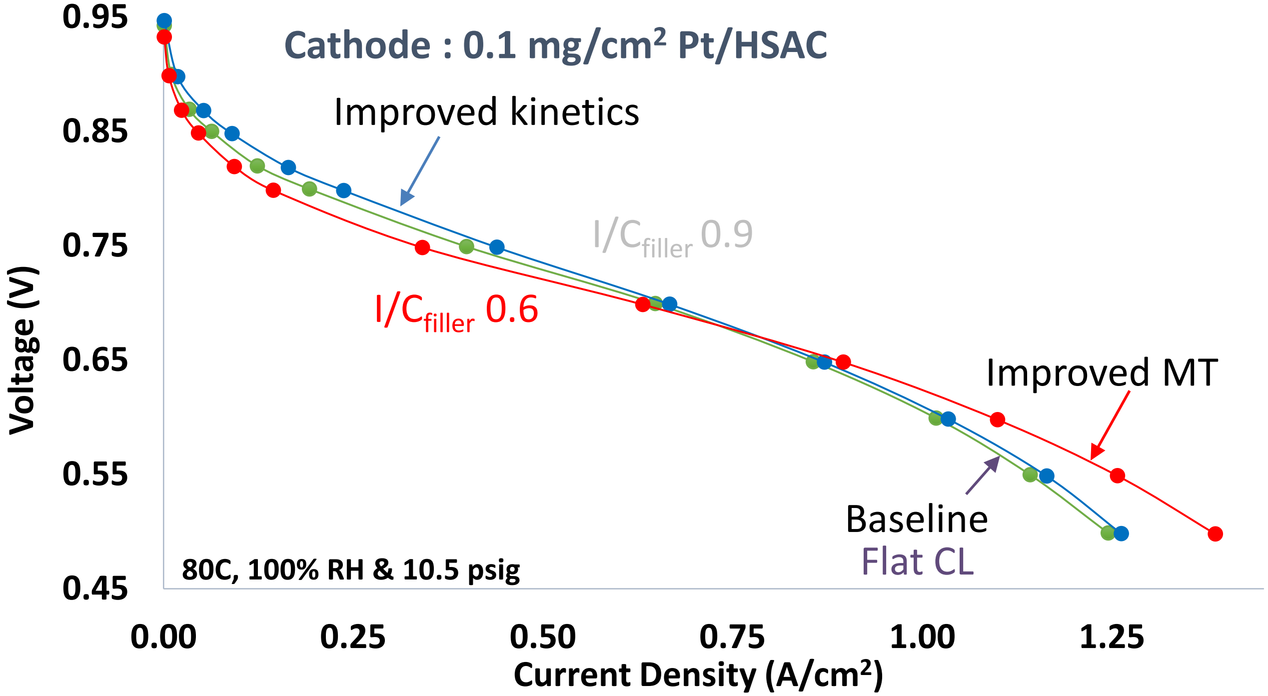


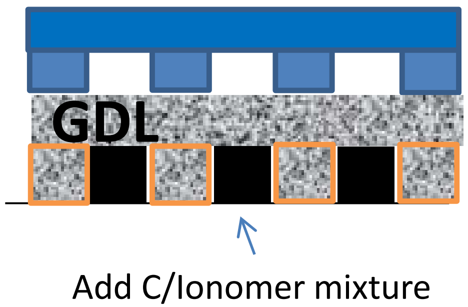
Normalized to width of the channel



[1] T. E. Springer, M. S. Wilson, and S. Gottesfeld, *J. Electrochem. Soc.*, **140** (12), 3513–3526 (1993).
[2] R. Borup and T. Rockward, U.S. DOE Annual Merit Review, Project ID: FC052 (2015); https://www.hydrogen.energy.gov/pdfs/review15/fc052_rockward_2015_p.pdf

Electrode Structure: Stratified

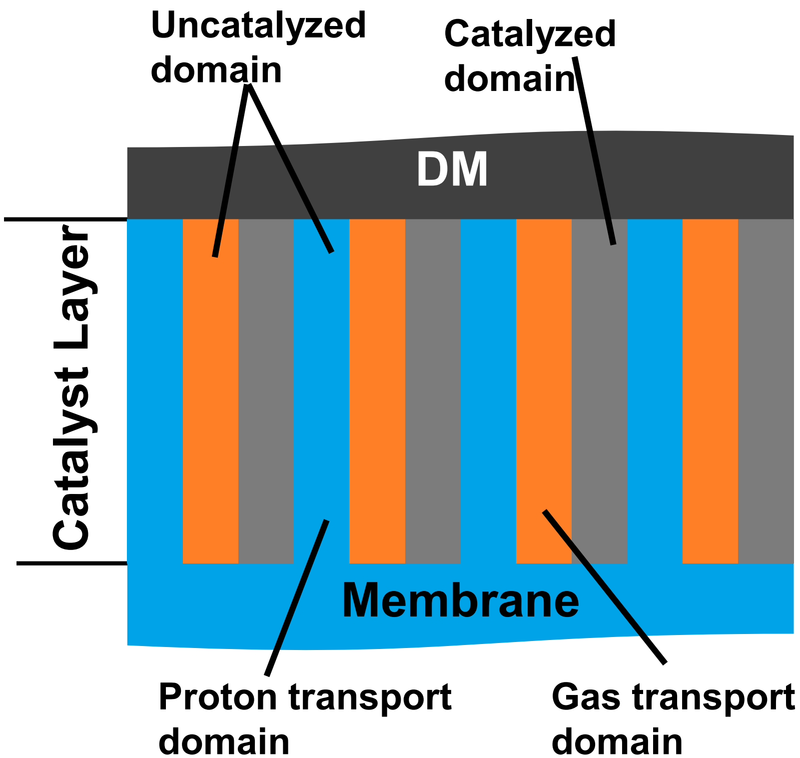


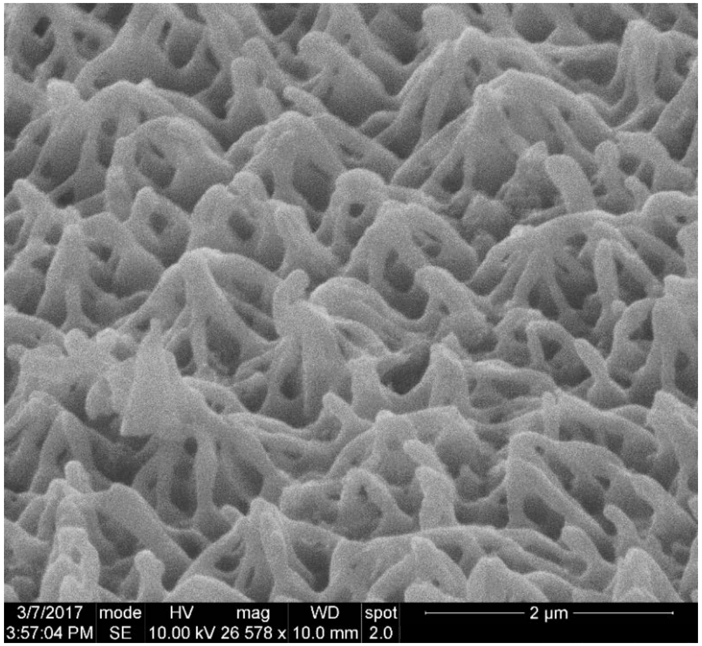


- Need filler to improve performance
  - Kinetic improvement at high I/C ratio suggests higher Pt utilization
  - Mass-transport improvement with low I/C ratio is likely due to reduced water retention and better utilization of Pt
  - Carbon filler made of Ketjen 300J better than Vulcan

Enhanced performance at high current densities compared to conventional layers

Electrode Structure: Meso-Structured Array

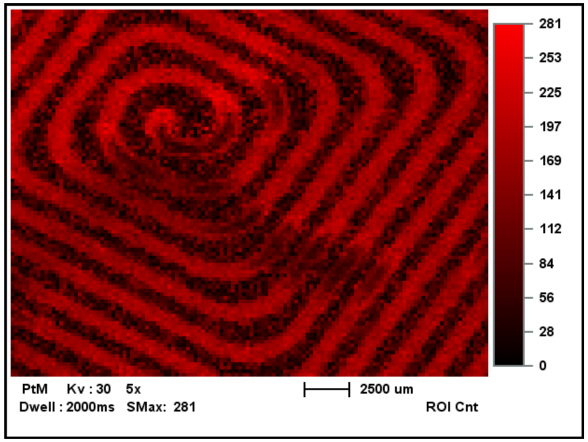




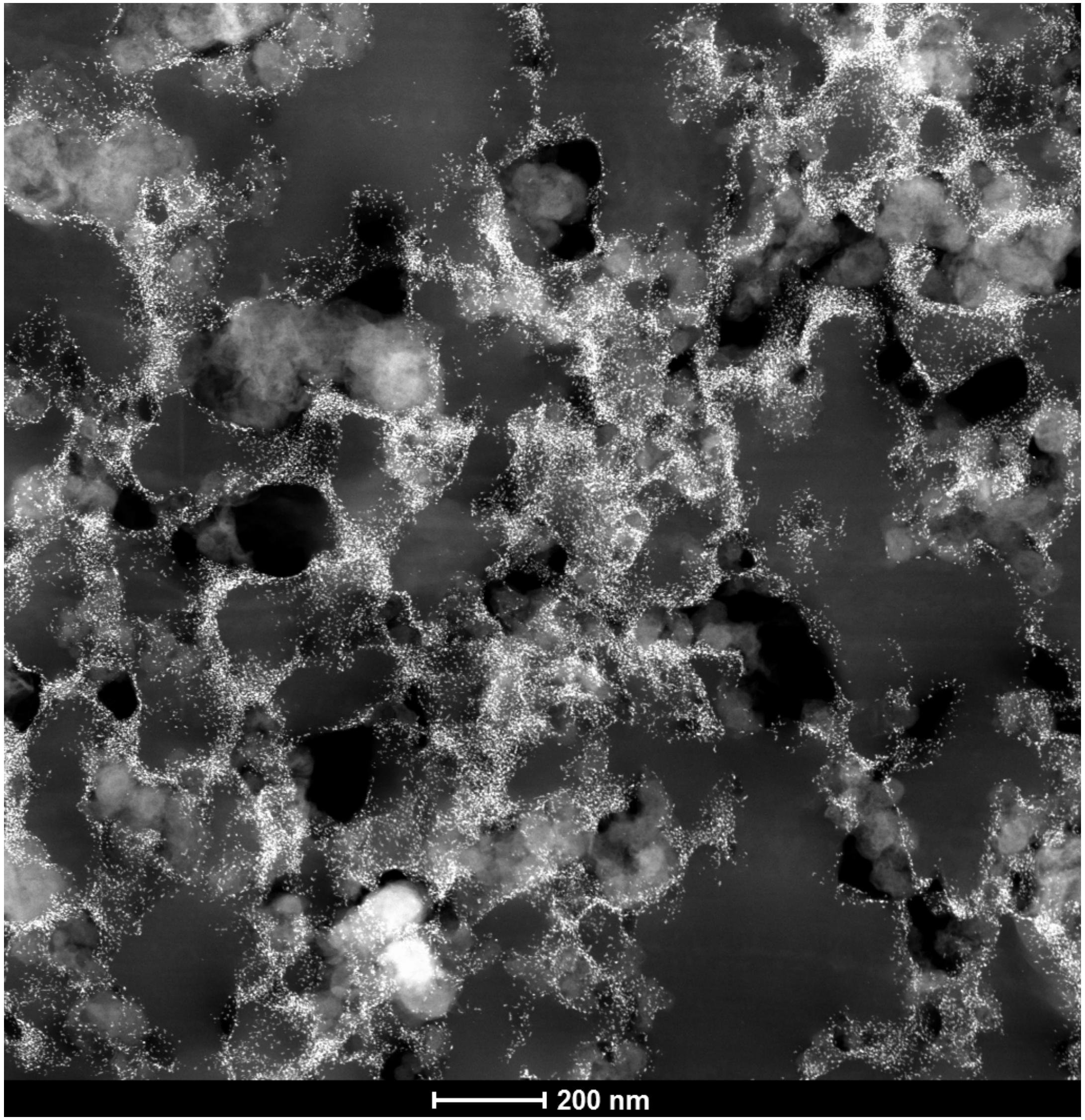
SEM image of oriented Nafion nanofibers of 200nm diameter and 5 µm height

- Electrode functions separated into different elements with a ternary array
- Controlled, low-tortuosity configuration enables transport limitations to be reduced or eliminated
- Nafion nanofibers provide effective proton transport through these low-tortuosity percolating highways
- Allows the catalyst domain to have a lower ionomer/catalyst ratio

Electrode Structure: Controlled Deposition of Pt



Scanning Pt-XRF image of Pt deposited in a spiral on a GDL (catalyzed spiral region roughly 1 mm wide by 10 μm deep)

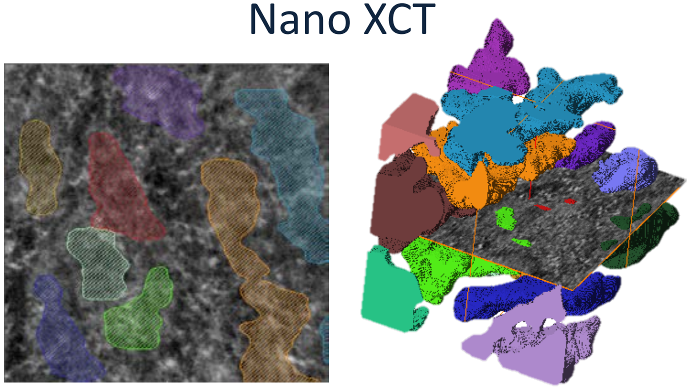


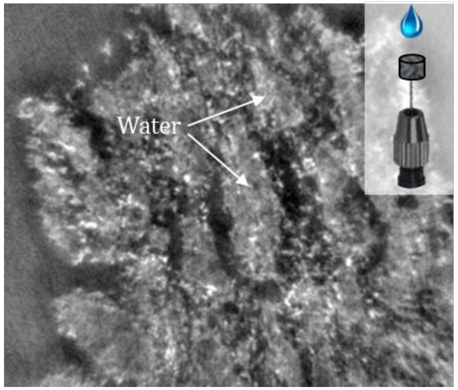
HAADF-STEM image within the spiral depicting Pt catalyst particles with uniform distribution and size (avg. 2 to 3 nm dia.)

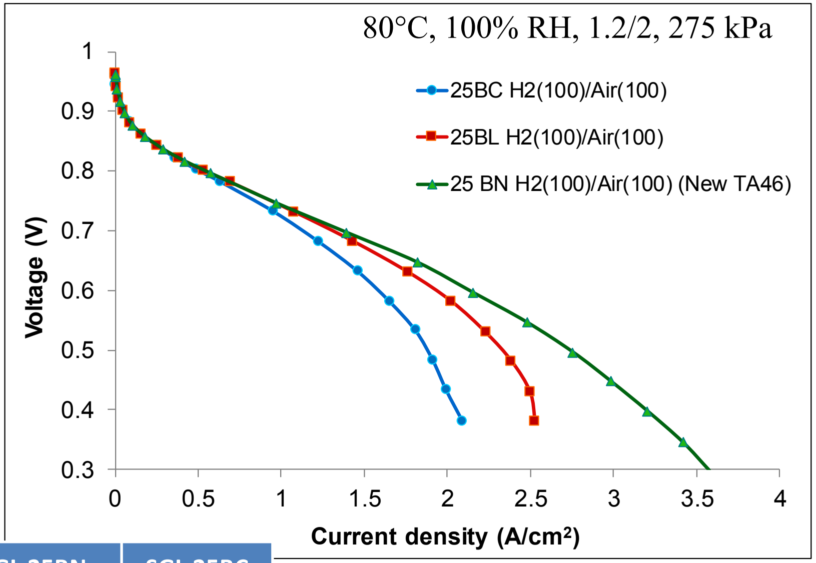
Water Management: Hydrophilic MPLs

- Examine carbon nanotubes (SGL 25BN) in MPL
  - Observe liquid water in nanotubes
  - **Improved performance**
    - Less liquid water throughout the cell
    - Diagnostics demonstrate both easier breakthrough as well as lower adhesion force/detachment velocity from GDL

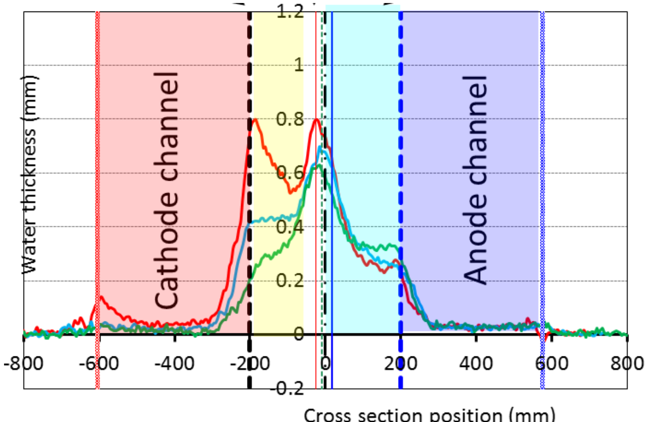
Nano XCT





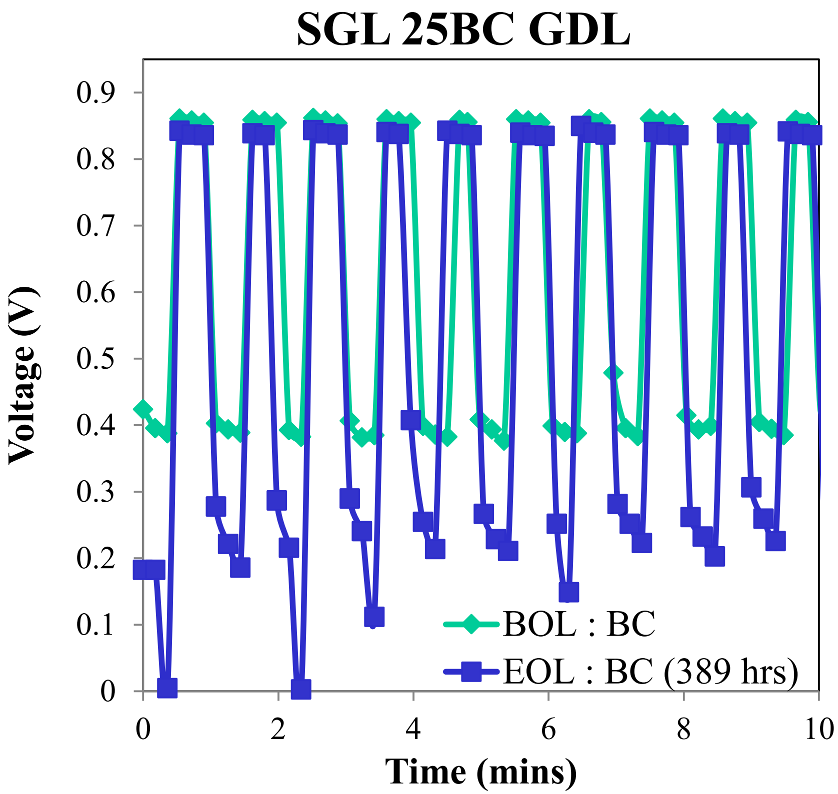


Test	SGL 25BN	SGL 25BC
Detachment velocity	3 m/s	5 m/s
Adhesion Force	7 mN/m	8 mN/m
Breakthrough pressure	4.4 kPa	5.7 kPa

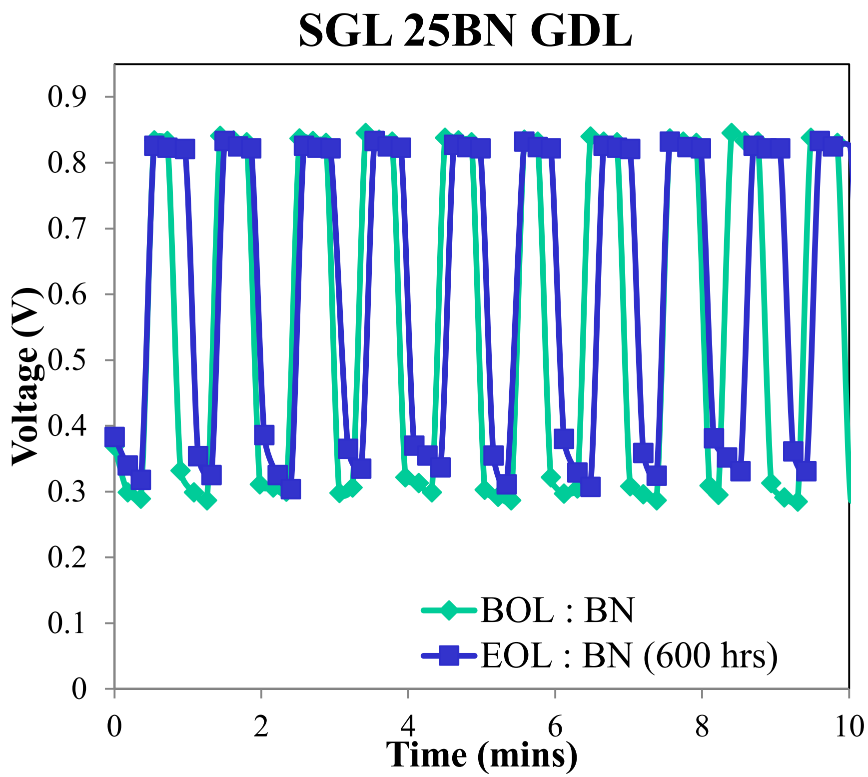


Neutron Imaging

Water Management: Hydrophilic MPLs



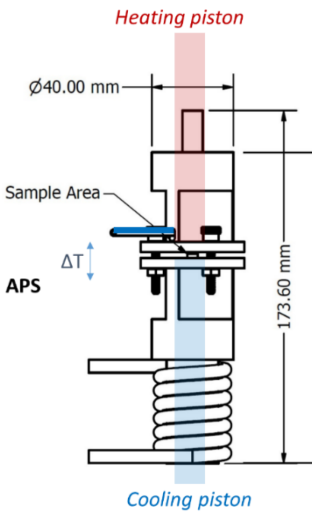
Flooding ended test after 389 hours

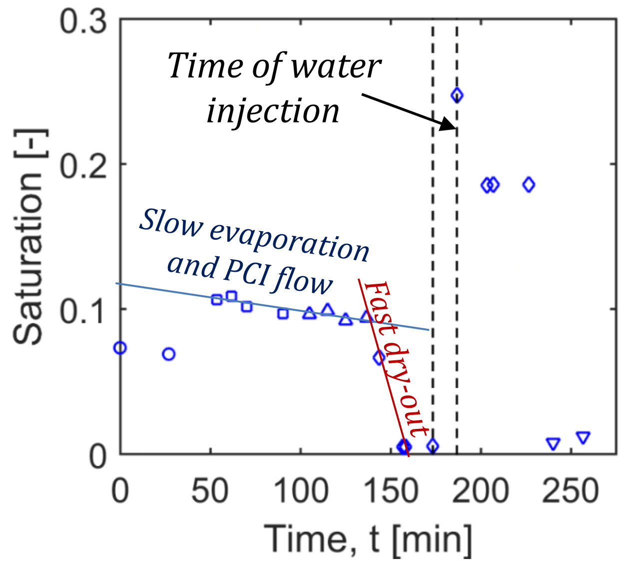


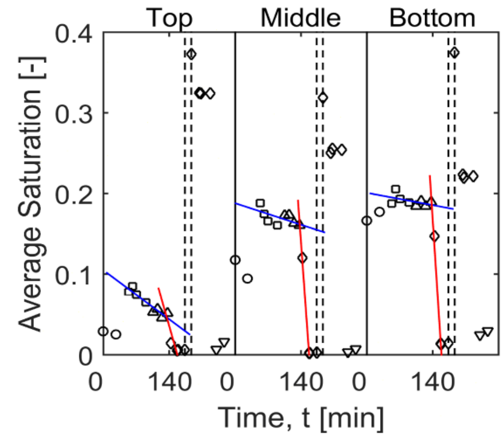
Slightly improved high current performance after 600 hours

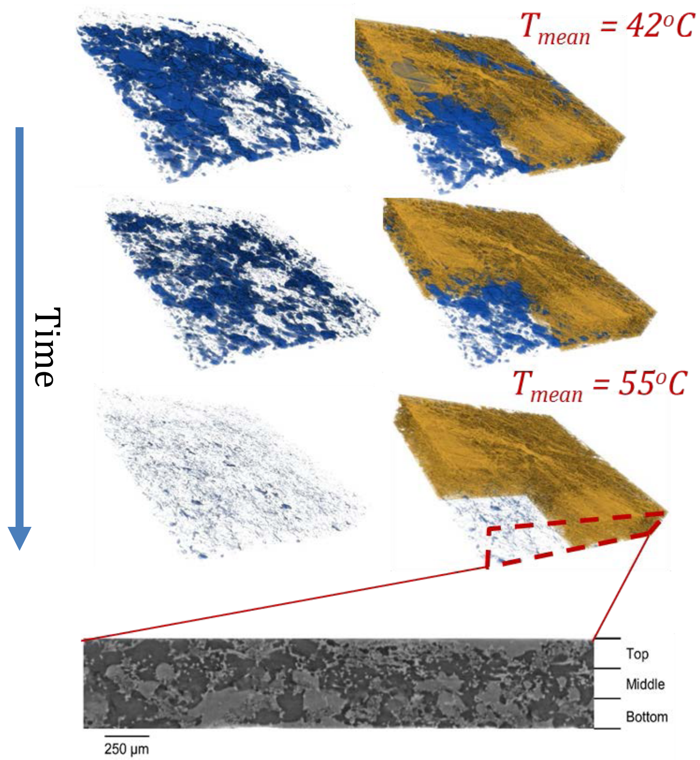
- Carbon nanotubes demonstrate *increased durability* performance under drive cycle
  - Mass-transport losses related to GDL develop during testing

Water Management: Phase-Change-Induced Flow

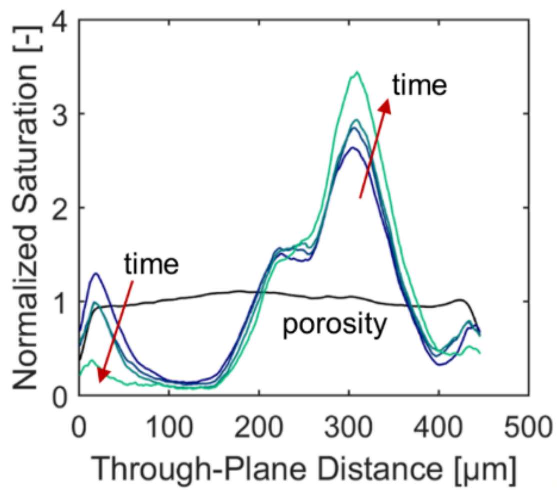








- PCI flow observed and quantified
  - Slow until becomes disconnected then rapid evaporation
  - Major role in water and thermal management

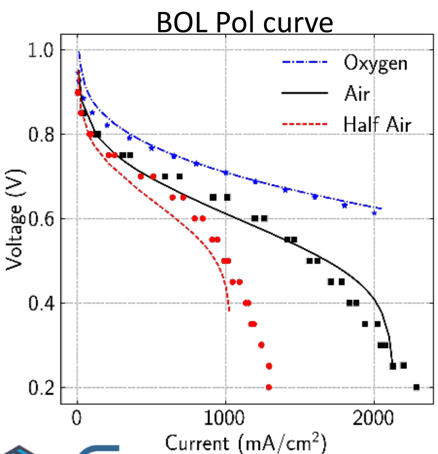


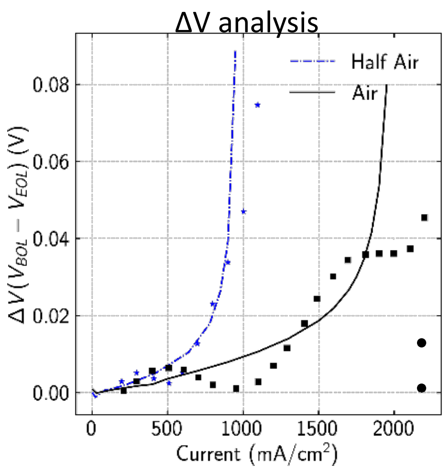
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

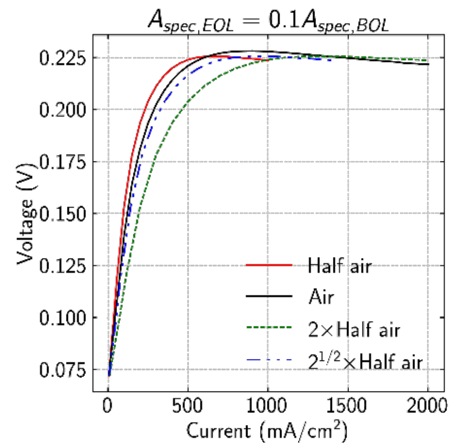
Modeling ΔV Analysis Performance Diagnostic

- Shape of the ΔV curves, magnitude of ΔV, and reaction order may be used to uniquely identify limiting mechanism:

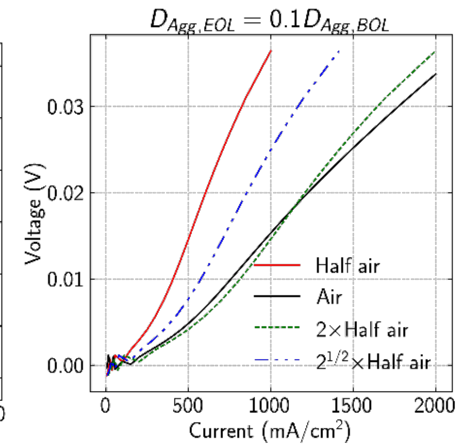
Limitation	Order	Sensitivity	Shape
Kinetics	1/2	High sensitivity to specific area	Logarithmic
CL diffusion	1	Low sensitivity to diffusivity	Exponential
GDL-MPL Diffusion	1	High sensitivity to diffusivity	Exponential
CL proton conductivity	0	High sensitivity to ionomer conductivity	Linear



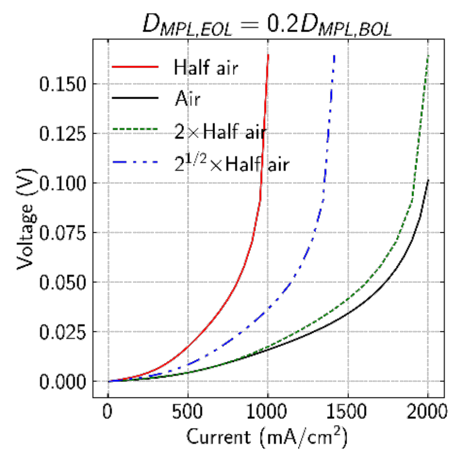




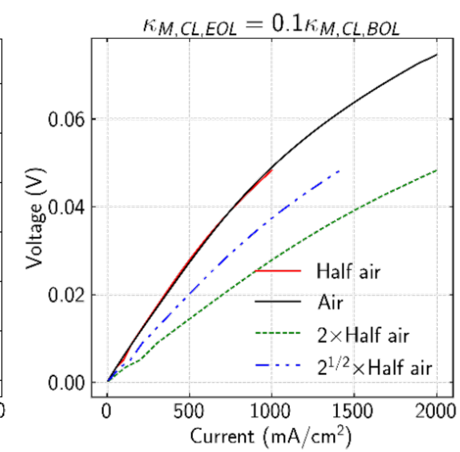
Kinetics limited



D_{agg} limited



D_{MPL} limited



κ_m limited in CL

Analysis of experimental ΔV shows kinetic and transport limited

Kinetic and transport parameters are adjusted to determine relative fractions and values

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Collaborations (From FOA-1412)

- The core FC-PAD team consists of five national labs
  - Each Lab has one or more thrust roles and coordinators

<u>Interactions with DOE Awarded FC-PAD Projects (FOA-1412)</u>

Assigned a POC for each project to coordinate activities with project PI:

3M PI: Andrew Haug – FC-PAD POC: Adam Weber

GM PI: Swami Kumaraguru – FC-PAD POC: Shyam Kocha

UTRC PI: Mike Perry – FC-PAD POC: Rod Borup

Vanderbilt PI: Peter Pintauro – FC-PAD POC: Rangachary Mukundan

- 35% of the National Lab budget defined as support to the Industrial FOA projects
- Support to these projects is primarily just beginning
- Equal support to each project
- Agreed upon 1-year SOW by ~ Feb 2017

<u>Support Distribution</u>

	3M %
LANL	20%
LBNL	39%
ANL	10%
NREL	19%
ORNL	12%

	GM %
LANL	11%
LBNL	25%
ANL	15%
NREL	37%
ORNL	11%

	UTRC %
LANL	48%
LBNL	26%
ANL	14%
NREL	0%
ORNL	12%

	Vanderbilt %
LANL	64%
LBNL	0%
ANL	15%
NREL	10%
ORNL	12%

Collaborations (non-FOA activities)

Institutions	Role
Umicore	Supply SOA catalysts, MEAs
IRD Fuel Cells	Supply SOA catalysts and/or MEAs
Ford	Ionomer imaging studies
TKK	Supply SOA catalysts
Johnson Matthey	Catalysts and CCMs (as part of FC106)
GM	Supply SOA catalysts and/or MEAs
Ion Power	Supply CCMs
GM/W.L. Gore	Supply SOA catalysts, SOA Membranes,
ANL–HFCM Group	SOA catalyst
Tufts University	GDL, MPL imaging
KIER	Micro-electrode cell studies
U Delaware	Membrane durability
Vanderbilt U.	Ink studies
PSI – Paul Scherrer Institute	GDL imaging

Collaborations (non-FOA activities)

Institutions	Role
NTNU – Norwegian Technical University	GDL imaging
UTRC	Cell diagnostics
3M	Ionomers
Colorado School of Mines	Membrane diagnostics
SGL Carbon	GDL Supplier
NPL - National Physical Laboratory	Reference electrodes for spatial measurements
NIST – National Inst. of Standards and Tech	Neutron imaging
U. Alberta	GDL and flowfield modeling; ink studies

Proposed Future Work

- **Inks**
  - Model study to elucidate interactions of ionomer with particle surfaces and solvents
    - Elucidate governing binary interactions
    - Direct observation of dispersions
  - Measure ionomer thin-film properties under applied potential
- **Catalyst-layer structure**
  - Continue exploration of different catalyst-layer structures
    - Stratified, array, electrospun, HSC/VC layered, specific Pt deposition
  - Microstructural modeling for catalyst layers
  - Local resistance analysis
    - Limiting current under variety of conditions, techniques, ionomers, gases, temperature, humidity
- **Water and thermal management**
  - Explore conditioning protocols and understand how each step impacts performance
  - Model interactions and examine scale coupling
    - Compare to segmented cell data
    - Detail model for GDL/Channel interface and droplets
  - Water visualization in various components
  - Explore impact of carbon type in MPLs

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

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**:
  - Examined water transport throughout MEA
  - Developed new catalyst-layer architectures
    - Stratified and array electrodes with variations in loadings
    - Pt deposition where it is needed
  - Unraveling origin of local resistance
    - Hydrogen and oxygen limiting current suggests ionomer film and its local morphology are dominant cause
  - Developed new diagnostics and models for interpreting critical phenomena and data
  - Explored ink stability and dispersions and fabrication methods
- **Future Work**:
  - Optimize catalyst-layer structure for high performance at low loadings
  - Elucidate critical bottlenecks for performance and durability from ink to formation to conditioning to testing
  - Multiscale modeling of cell and components
  - Explore genesis of membranes and thin films and their associated properties

Acknowledgements

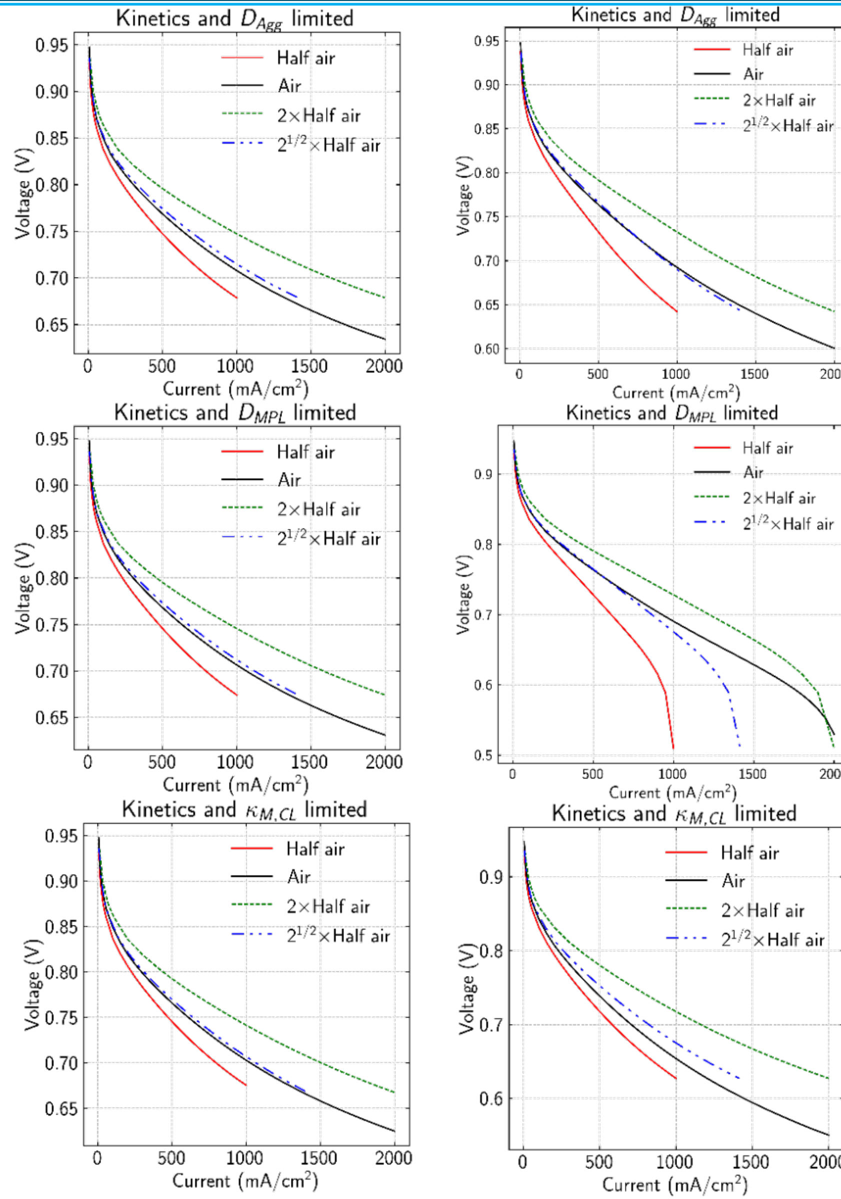
DOE EERE: Energy Efficiency and Renewable Energy Fuel Cell Technologies Office (FCTO)

- Fuel Cells Program Manager & Technology Manager:
  - Dimitrios Papageorgopoulos
  - Greg Kleen
- Organizations we have collaborated with to date
- User Facilities
  - DOE Office of Science: SLAC, ALS-LBNL, APS-ANL, LBNL-Molecular Foundry, CNMS-ORNL, CNM-ANL
  - NIST: BT-2

Technical Back-Up Slides

Modeling ΔV Analysis Performance Diagnostic

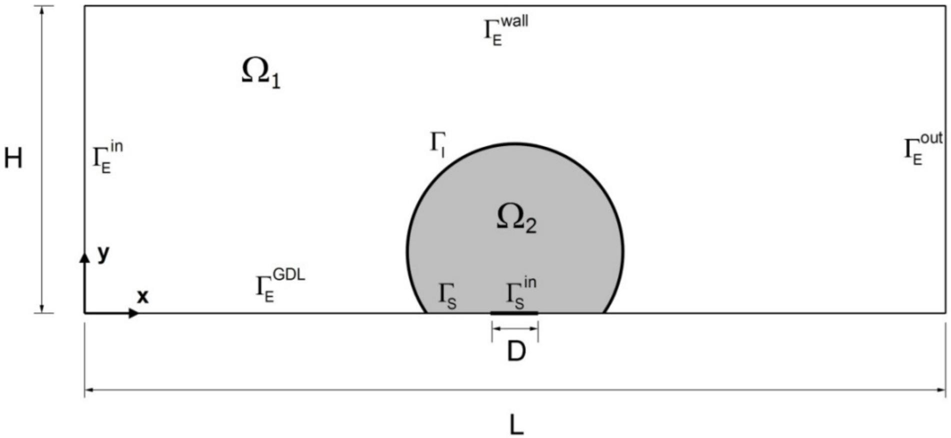
- Reaction order analysis at BOL
  - Kinetics limitations are kept same at BOL & EOL
  - Other limitations are increased from BOL to EOL
  - The reaction order is different from BOL to EOL due to changing contribution of kinetics and other limitations
    - Kinetic effects are prominent at BOL, skewing the reaction orders towards 1/2. Other effects become more prominent at EOL.
  - See change in order due to different mechanisms at different potentials
- Different effects need to be decoupled to be uniquely identified
  - Need for mathematical model

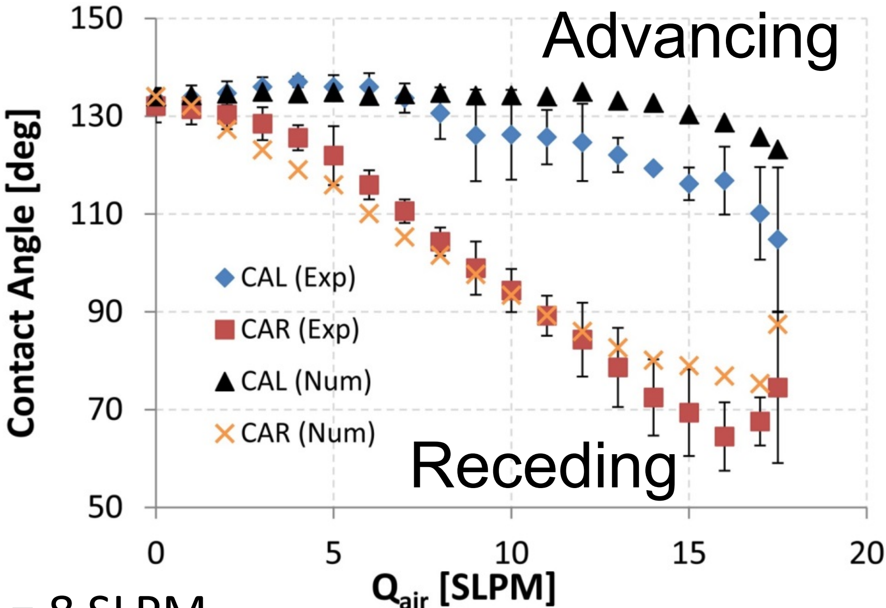


BOL EOL

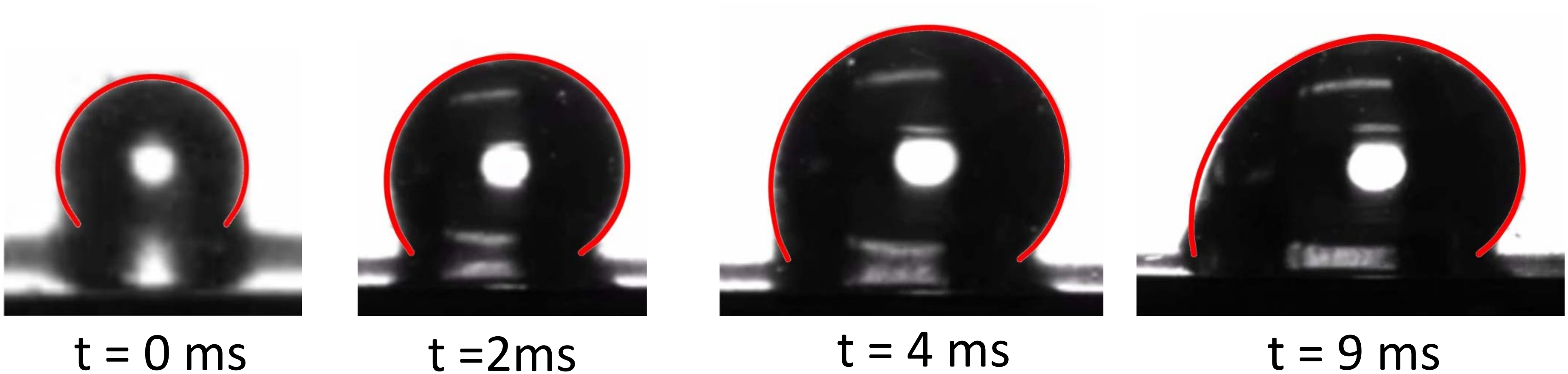
Droplets in Channel

- Develop model for water droplet movement in channels
  - Need to couple to physics within the domain
  - Look at different flow regimes and interactions



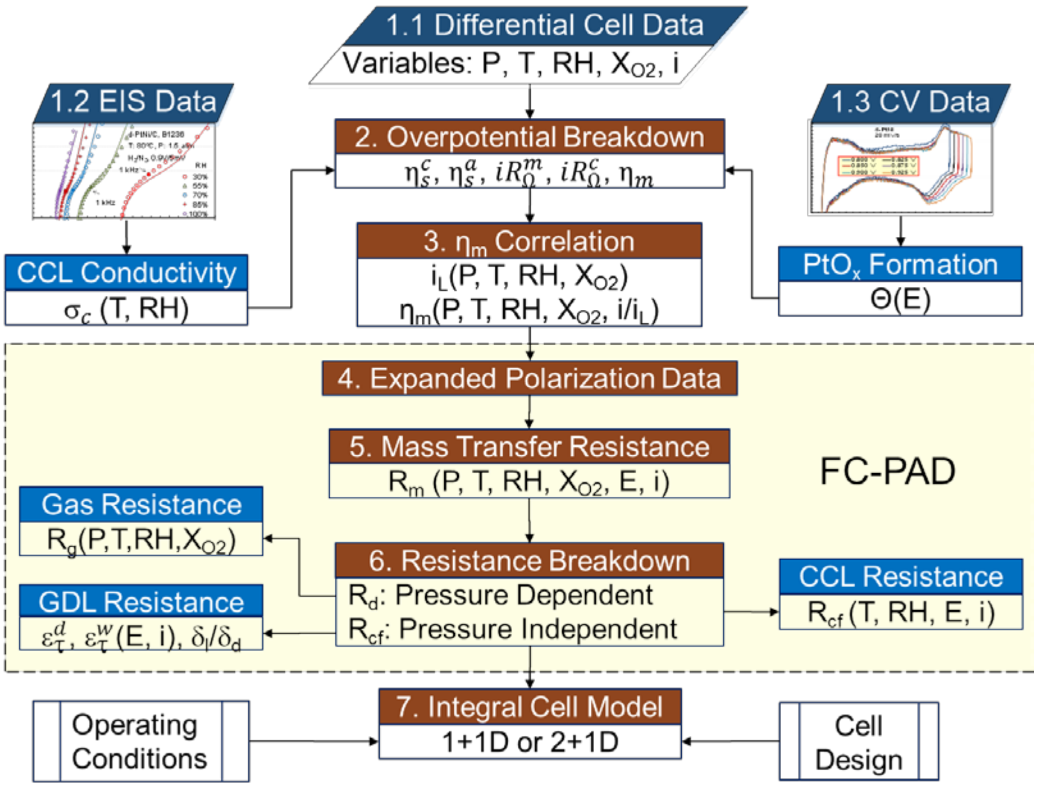


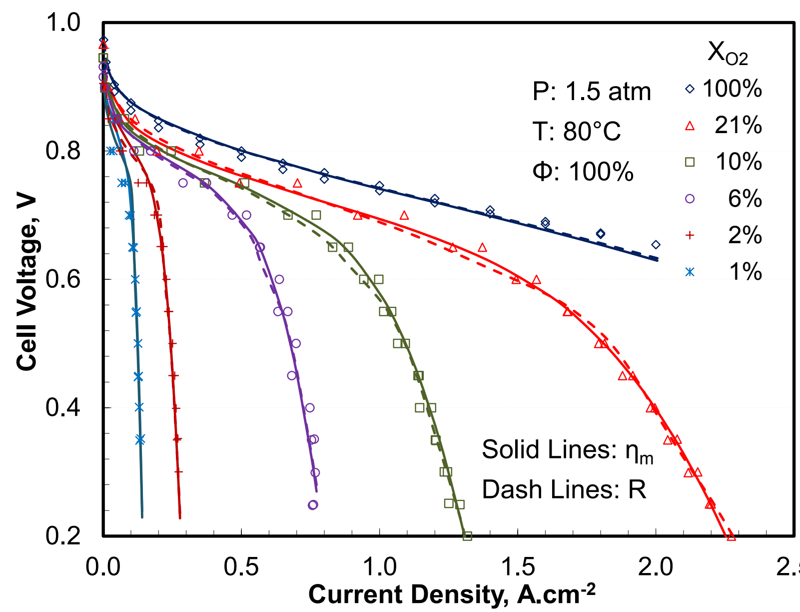
- Droplet growth with Q_w = 2.5 SLPM, Q_{air} = 8 SLPM



From Differential Data to Integral Cell Model

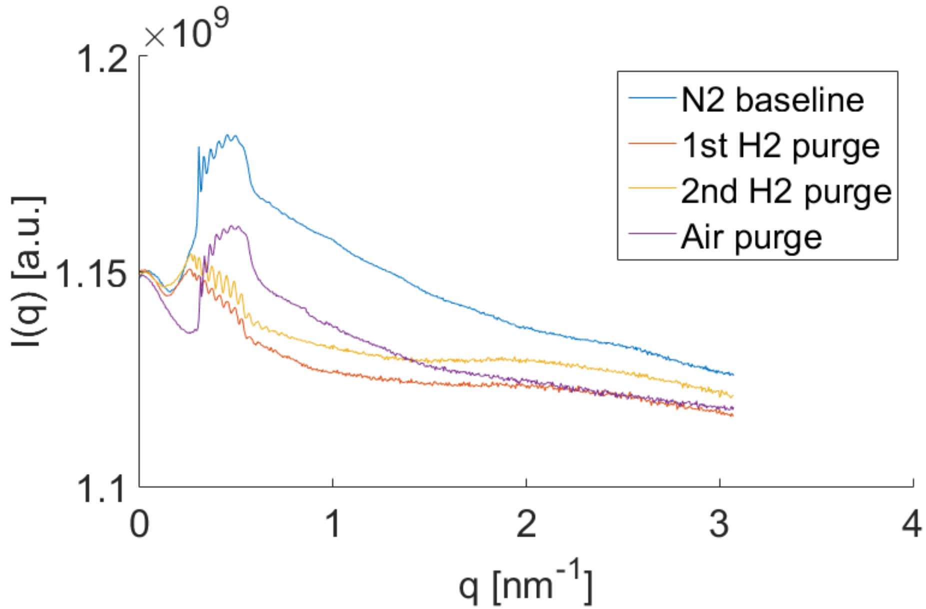
- Determine resistances from differential cell data
  - Develop governing correlations
- Predict integral cell performance using differential-trained correlations



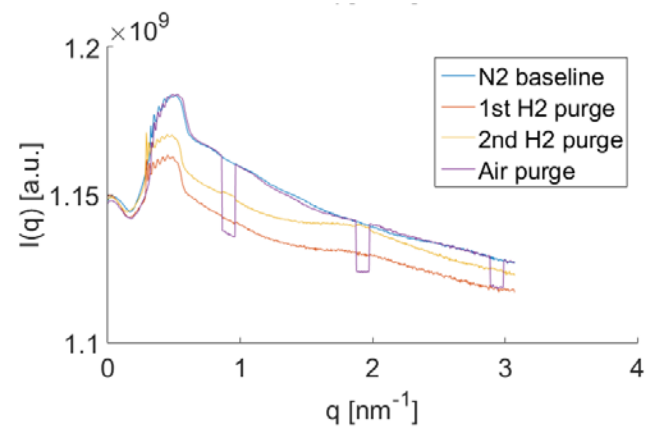


Ionomer Thin Films

α = 0.16 – right above critical angle



α = 0.18

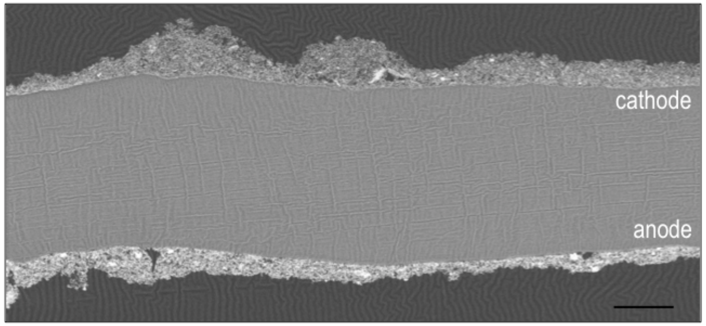


- GISAXS under flowing hydrogen to reduce Pt-oxides
  - Peak at ~0.5 1/nm is the paracrystalline peak of the platinum surface
    - Strong in N_2, it disappears upon purging chamber with H_2. This would indicate x-rays are not penetrating all the way through the film
    - Reappears in air, showing a reversibility
  - H_2 is interacting with Nafion and/or Pt substrate, increasing the film density and therefore the critical angle

Impact of Fabrication Method

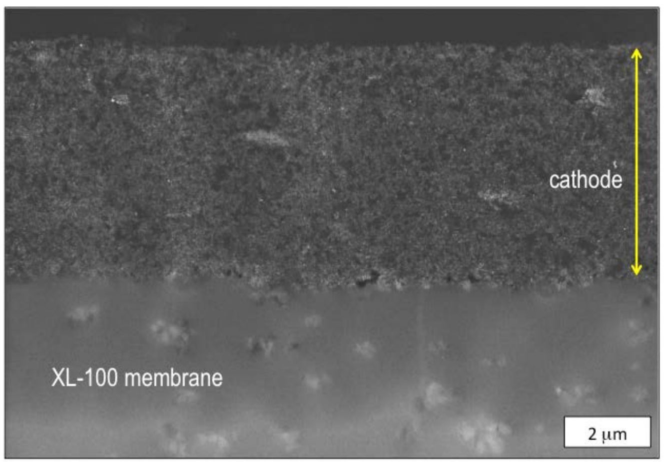
- NREL Fabrication: Spray Coating
  - Stratified

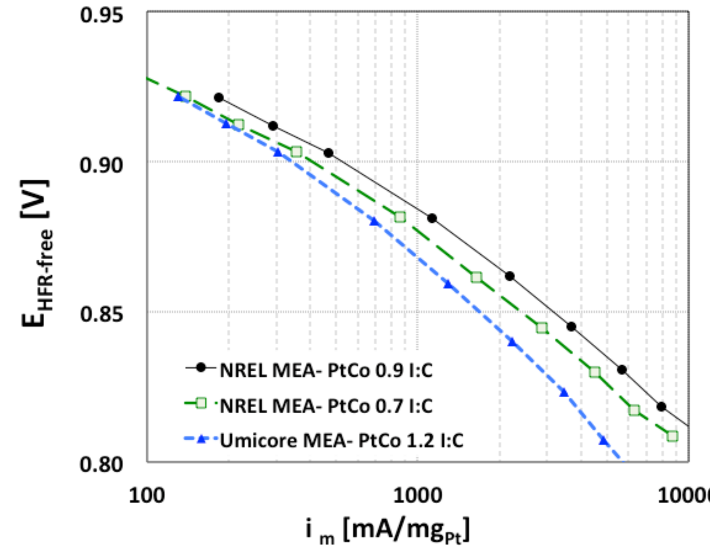
CL thickness non-uniform – ranging from 2μm to 10μm thick

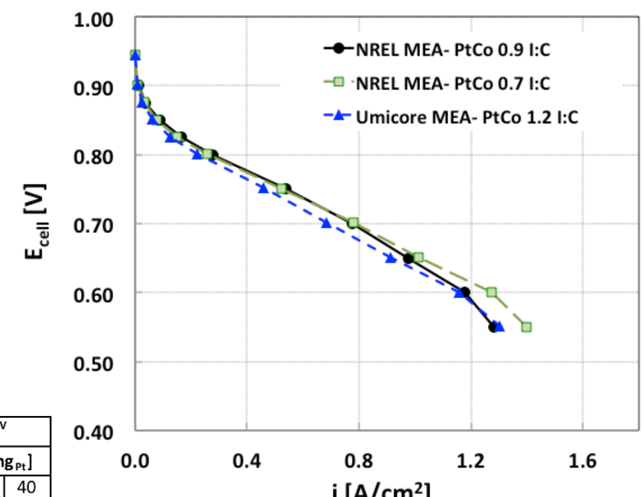


- Umicore Fabrication: Proprietary non-spray

CL thickness very uniform - 6μm







MEA	Loading $[mg_{Pt}/cm^2]$	ECSA $[m^2_{Pt}/g_{Pt}]$			$i_m^{0.9V}$ $[mA/mg_{Pt}]$		
NREL Fab,test MEA- PtCo 0.9 I:C	0.10	37	±	2	514	±	40
NREL Fab, test MEA- PtCo 0.7 I:C	0.10	36	±	1	388	±	47
Umicore Fab, NREL test MEA- PtCo 0.95 I:C	0.10	40	±		336	±	
Umicore Fab, test MEA- PtCo 0.95 I:C	0.14	50	±		475	±	35