FUEL CELL PERFORMANCE AND DURABILITY

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

May 2020

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FC-PAD Presentation Outline

- FC-PAD Structure & Landscape
- FC-PAD Organization & Partners
- Relevance, Overview & Objectives
- Approach: Priorities, Milestones, Capabilities
- Durability:
  - Effect of Loading
  - Alloy Degradation
  - Catalyst Support
  - Effect of Upper Potential
- Catalyst Inks to Performance and Catalyst Layer (CL) Analysis:
  - Ink Composition-Solvent Studies
  - Cell Testing
  - Impact of Fabrication
  - Membrane and Ionomer Characterization
  - Cell and CL modeling
- Collaborations
- Future Work
- Summary

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

FUEL CELL PERFORMANCE AND DURABILITY

Approach

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

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

FOA partners

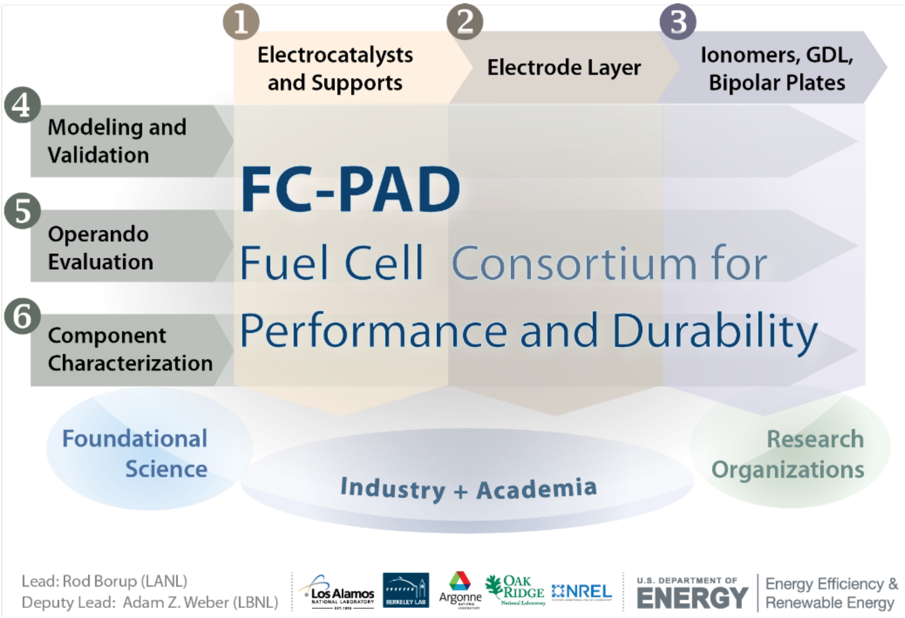
Light-Duty: 3M, GM, VANDERBILT, United Technologies Research Center

Heavy-Duty: GM, Carnegie Mellon University TARTANS, NIKOLA

Objectives

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

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

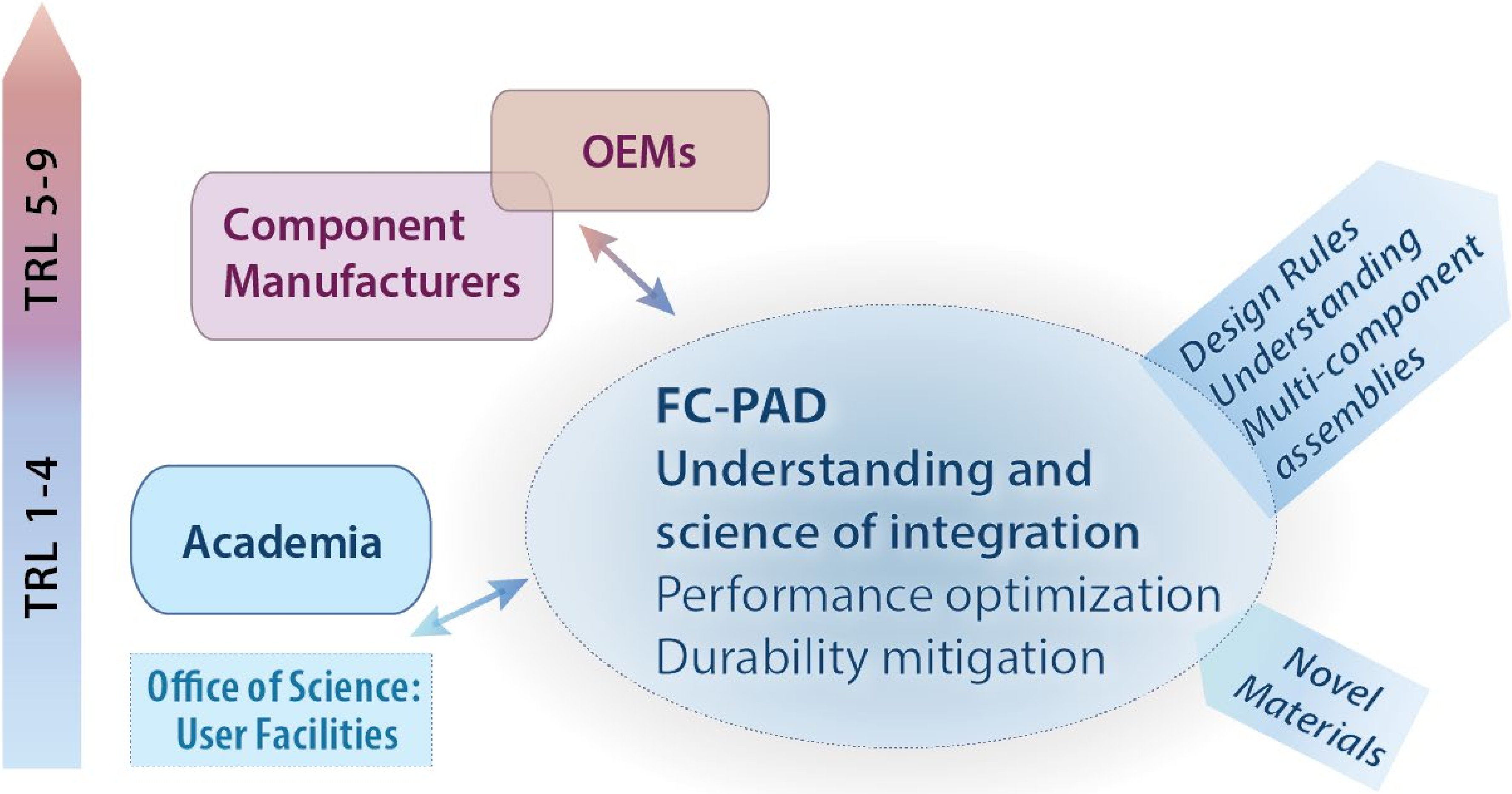
Industry + Academia

Research Organizations

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

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

FC-PAD Landscape

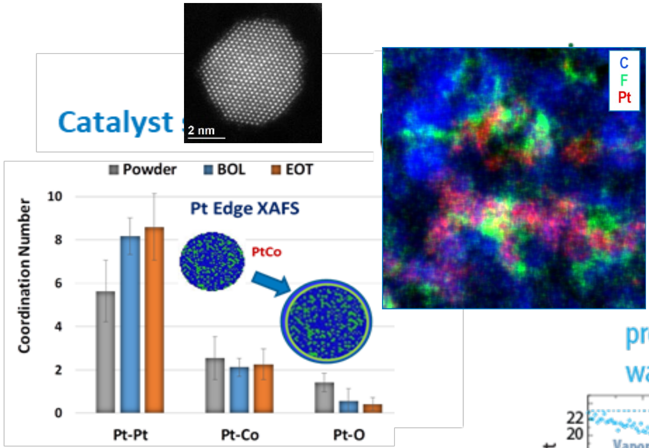


- FC-PAD conducts research at pre-competitive development levels
- Primarily TRL 2, 3, 4
- FC-PAD directly interacts with OEMs, components suppliers and academia

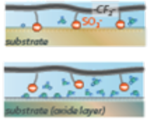
FC-PAD: Exploration of Critical Phenomena

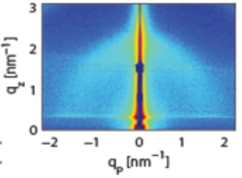
	Reactions and Charge Transport	Mass Transport of Species	Kinetics and cell testing	Durability ASTs: RH, V,T cycling	Durability: Field Testing
relavant phenomena & timescale	nsec - msec local nanostructure	sec - min component function	sec - hrs membrane-electrode	hrs - days fuel-cell	lifetime stack/system

Characterization/Diagnostics



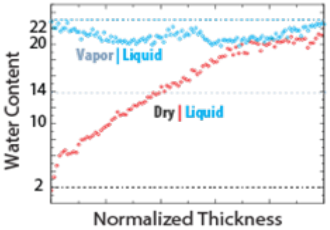
Imaging catalyst layers



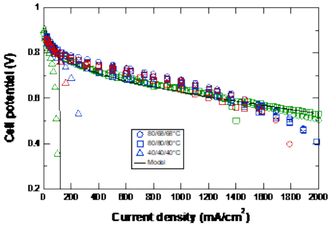


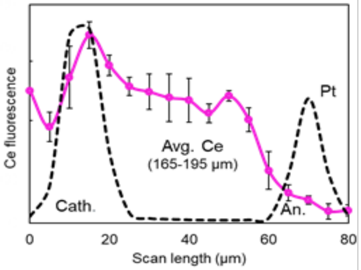
ionomer-Pt/C interactions

probing water & ion transport

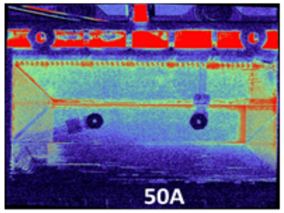


Cell performance and optimization

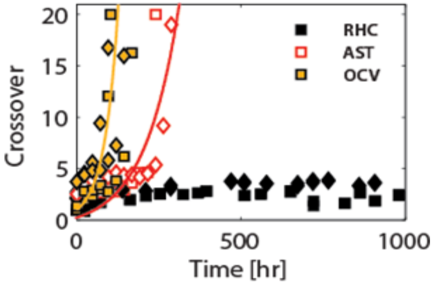




Monitoring, Measuring Degradation and Performance Decay



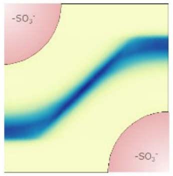
Operando Imaging



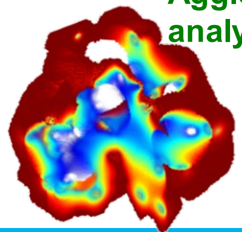
characterization of phenomena fundamental understanding ⟷ *performance-durability interplay: understanding and improvement*

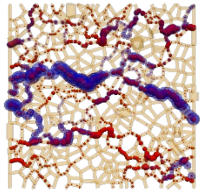
Modeling

Nanoscale

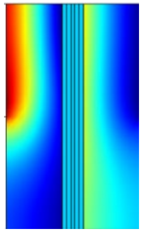


Agglomerate analysis

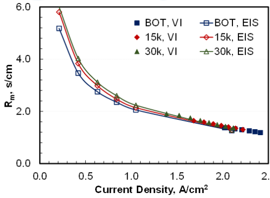




Component Transport

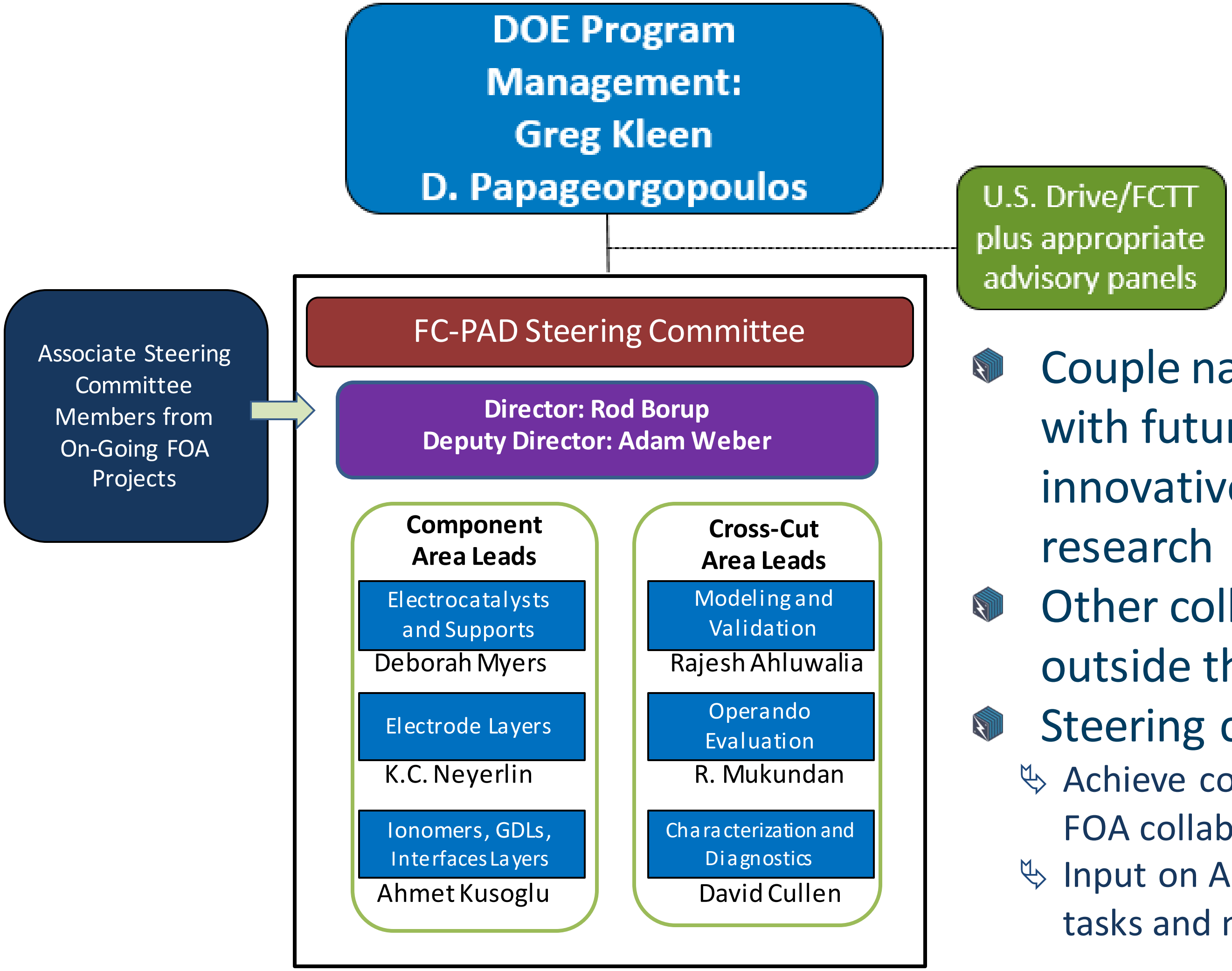


Cell-level performance and durability



Predicting life and decay

FC-PAD Organization



DOE Program Management:
Greg Kleen
D. Papageorgopoulos

U.S. Drive/FCTT plus appropriate advisory panels

Associate Steering Committee Members from On-Going FOA Projects

FC-PAD Steering Committee

Director: Rod Borup
Deputy Director: Adam Weber

Component Area Leads

- Electrocatalysts and Supports — Deborah Myers
- Electrode Layers — K.C. Neyerlin
- Ionomers, GDLs, Interfaces Layers — Ahmet Kusoglu

Cross-Cut Area Leads

- Modeling and Validation — Rajesh Ahluwalia
- Operando Evaluation — R. Mukundan
- Characterization and Diagnostics — David Cullen

- 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

New Partners; Heavy Duty Fuel Cell Applications

Reviewer comments: …. open the consortium to other partners to take into account system consideration….

Comment – with move to heavy duty, need to understand operating conditions, cost targets, longer-term degradation mechanisms

Heavy Duty FOA Awards & New Collaborators

NIKOLA™

GM

Carnegie Mellon University
TARTANS

New Heavy Duty Project/Partners

Durable Fuel Cell MEA through Immobilization of Catalyst Particle and Membrane Chemical Stabilizer

GM

3M

MINES

CORNELL UNIVERSITY FOUNDED A.D. 1865

PAJARITO POWDER
FUEL CELL CATALYSTS

Durable High Power Density Fuel Cell Cathodes for Heavy-Duty Vehicles

Carnegie Mellon University
TARTANS

Chemours™

BALLARD®

Durable MEAs for Heavy-Duty Fuel Cell Electric Trucks

NIKOLA™

GT
GEORGIA TECH

Northeastern University

Carnegie Mellon University
TARTANS

FC-PAD Consortium - Overview & Relevance

Timeline

- Project start date: 10/01/2015
- Project end date: 09/30/2020
- Re-competed for FY21

Budget

- FY20 project funding: ~ $3,500,000
- As proposed: 5-year consortium with yearly milestones & Go/No-Go

Partners/Collaborations

- DOE DE-FOA-0001412:
  - (GM, 3M, UTRC, Vanderbilt)
- DOE DE-FOA-0002044:
  - (GM, Nikola, Carnegie Mellon)
- No-cost collaborations listed

Barriers

Heavy-Duty Transportation (2030)

- Durability: 25,000 hour lifetime
- 68% peak efficiency
- $80/kW fuel cell system cost

Light-Duty Transportation (2025)

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

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

- **Catalyst-layer Structure**
  - Correlate electrode microstructure and performance using characterization results and modeling to determine, for example, electrode transport properties
  - Develop/measure key CCL parameters using multiple methodologies with consistent results
  - Show where the ionomer is for different systems
  - Effect of ink composition, processing, and fabrication method on electrode microstructure
- **Performance/Durability (Characterization, Experimental, Modeling)**
  - Understand/improve durability of alloy catalysts: effect of leaching on ionomer properties
  - Understand/improve high current performance: R_{O2}, R_{H2}, different ionomers/carbons
- **New Capability and Modeling Development**
  - Develop novel methods, cells, and analysis techniques for in situ, ex situ and operando characterization of electrode layers and components
  - Develop new high-resolution ionomer imaging and spectroscopy methods and develop and apply algorithms for structural reconstructions
  - Develop novel methods, cells, and analysis techniques for in situ, ex situ and operando characterization of electrode and membrane layers and components
  - Develop new diagnostic methods to understand transport processes
  - Develop and apply Integrated predictive models of coupled performance and durability

FC-PAD Consortium – Relevance & Objectives

- Advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) and their *components* at a pre-competitive level
  - FY20 – shifted emphasis to heavy-duty applications
- 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*
  - *Projects ending FY20*
- *Provide support to DOE-funded FC-PAD projects from FOA-2044*
  - *Projects initiated FY20*

Target Comparison between Light-Duty and Heavy-Duty

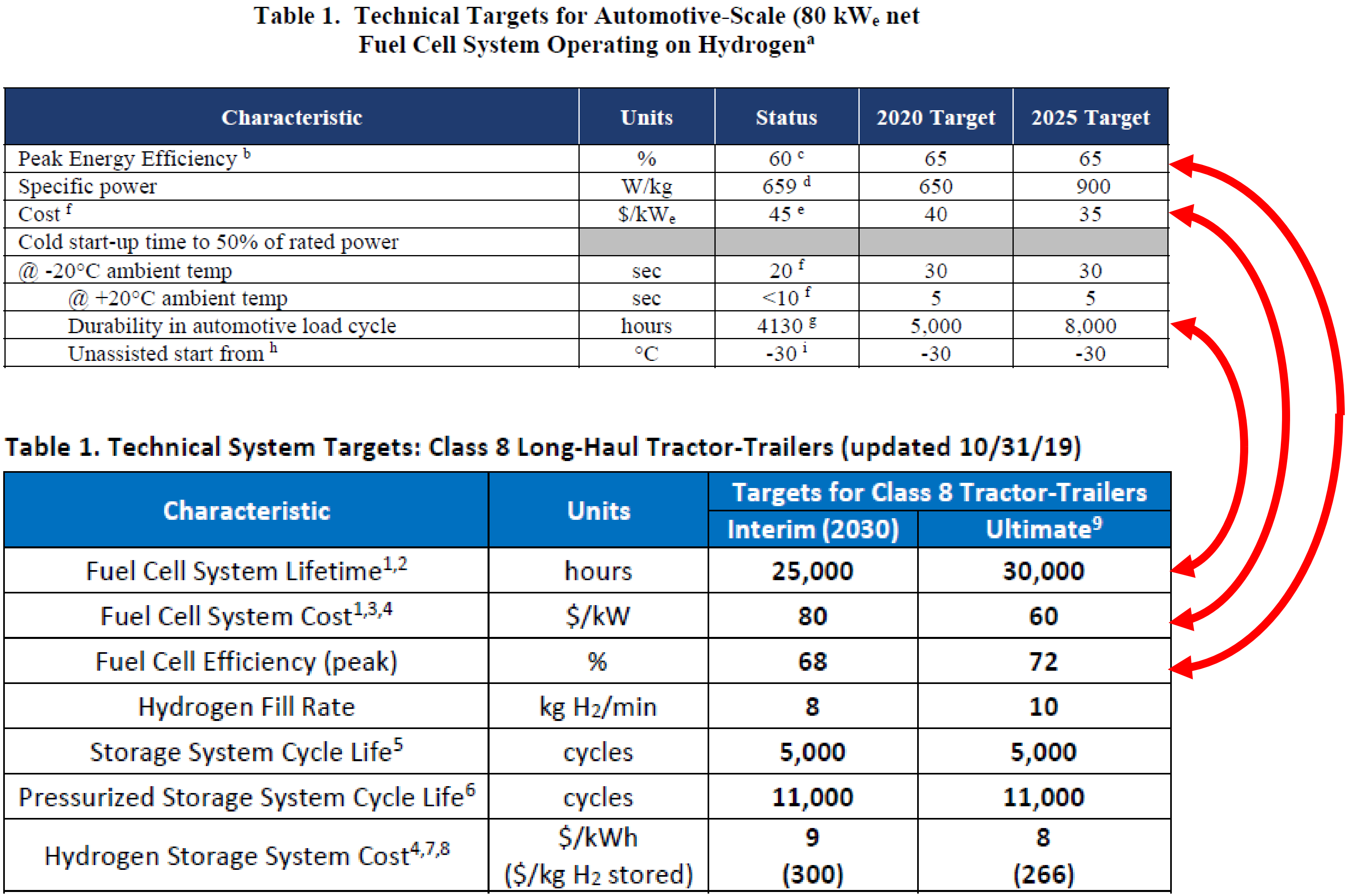


Table 1. Technical Targets for Automotive-Scale (80 kW$_e$ net Fuel Cell System Operating on Hydrogen[a]

Characteristic	Units	Status	2020 Target	2025 Target
Peak Energy Efficiency [b]	%	60 [c]	65	65
Specific power	W/kg	659 [d]	650	900
Cost [f]	$/kW$_e$	45 [e]	40	35
Cold start-up time to 50% of rated power				
@ -20°C ambient temp	sec	20 [f]	30	30
@ +20°C ambient temp	sec	<10 [f]	5	5
Durability in automotive load cycle	hours	4130 [g]	5,000	8,000
Unassisted start from [h]	°C	-30 [i]	-30	-30

Table 1. Technical System Targets: Class 8 Long-Haul Tractor-Trailers (updated 10/31/19)

Characteristic	Units	Targets for Class 8 Tractor-Trailers	
		Interim (2030)	Ultimate[9]
Fuel Cell System Lifetime[1,2]	hours	25,000	30,000
Fuel Cell System Cost[1,3,4]	$/kW	80	60
Fuel Cell Efficiency (peak)	%	68	72
Hydrogen Fill Rate	kg H_2/min	8	10
Storage System Cycle Life[5]	cycles	5,000	5,000
Pressurized Storage System Cycle Life[6]	cycles	11,000	11,000
Hydrogen Storage System Cost[4,7,8]	$/kWh ($/kg H_2 stored)	9 (300)	8 (266)

FY2020 Q1 - Q2 Joint Milestones

Q1 Milestone Name/Description	Due Date	Comments
Enhance the visibility of FC-PAD by presentations and publications. Distribute, present and publicize FC-PAD results. (ANL, LANL, LBNL, NREL, ORNL) Expected results: 33 presentations at ECS, submission opinion article to 'Current Opinion in Electrochemistry'.	12/31/2019	✓ Completed ✓ Current Opinion article published

Q2 Milestone Name/Description	Due Date	Comments
Enhance the visibility of FC-PAD by presentations and publications. Distribute, present and publicize FC-PAD results. (ANL, LANL, LBNL, NREL, ORNL)	3/31/2020	✓ Submission of FC-PAD perspectives article to 'Nature Energy'. ✓ Revision re-submitted
Quantify importance of operational variables for MEA durability for heavy duty applications. Define expected number of duty cycles for 1,000,000 miles of operation, SD/SU and design ASTs to reflect . (LANL, ANL) Examine operational variables including: For Catalyst AST: CL Loading, UPL, Temperature, RH for catalyst ASTs For Membrane AST: Time at OCV, RH and RH swing, Temperature	3/31/2020	✓ Completed ✓ Data included in AMR
Comparison MEA fabrication techniques to validate applicability of lab-scale MEA production. Spray versus gravure (NREL, ORNL, LANL, ANL) Compare performance and characteristics of lab-produced MEAs (spray) to MEAs produced by mass-manufacturable techniques (roll-coating, Gravure, draw-down-bar), in term of performance, impedance, porosity, CL distribution and elemental/ionomer mapping	3/31/2020	✓ Completed ✓ Data included in AMR

FY2020 Q3 - Q4 Joint Milestone

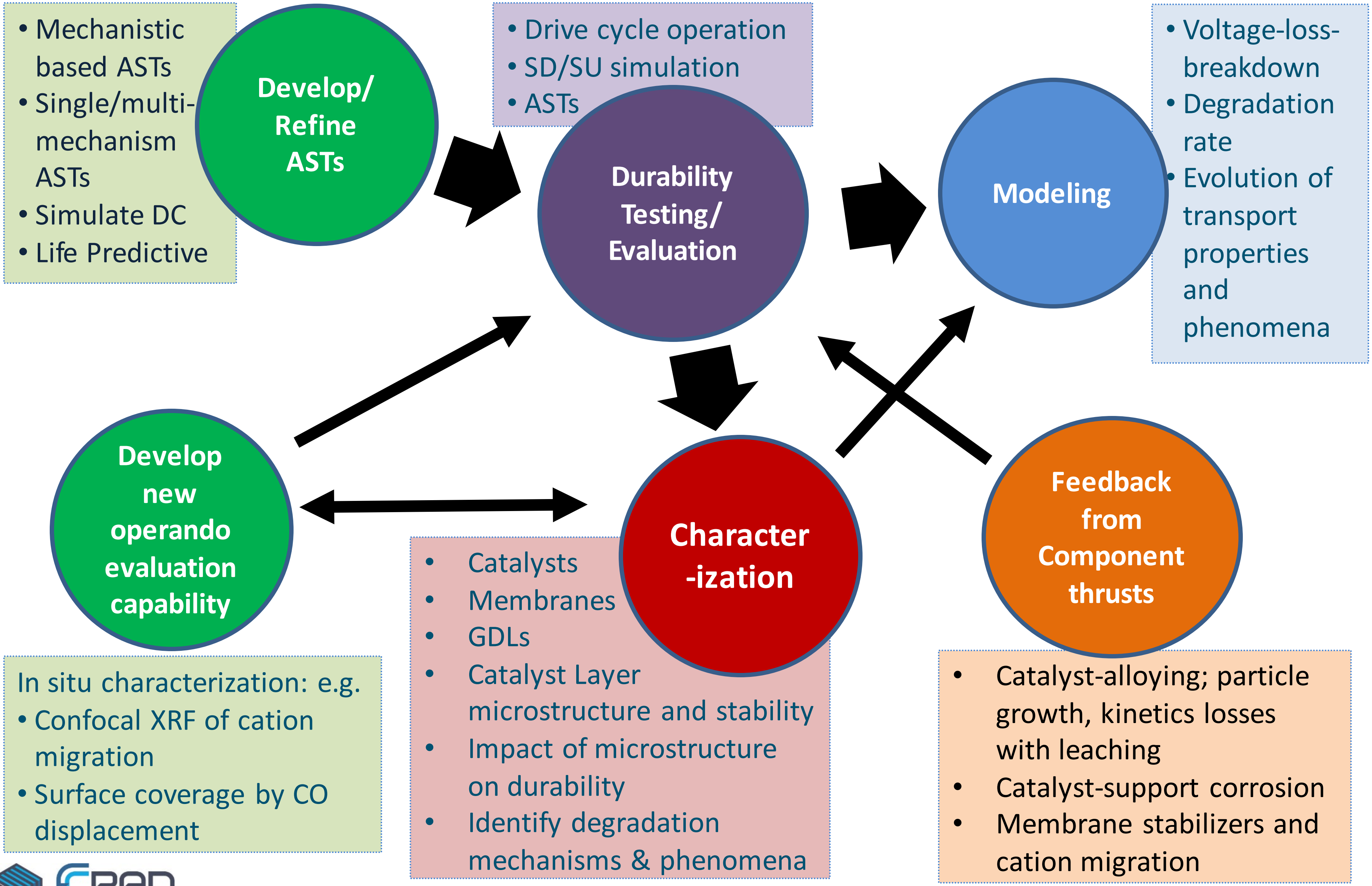
Q3 Milestone Name/Description	Due Date	Comments
Comparison MEA fabrication techniques to validate applicability of lab-scale MEA production: spray versus roll-to-roll/gravure/draw-down bar. (ANL, LANL, LBNL, NREL, ORNL) Compare catalyst layer structure (XCT, ionomer mapping, impedance, catalyst layer porosity) for PtCo/HSAC (or other current advanced ~~alloy~~ catalysts). Also validate and compare in situ performance characteristic including VIR, resistances, impedance and durability.	6/30/2020	✓ Partially Completed ✓ Varying MEA fabrication techniques compared ✓ Characterization under-way ✓ Data included in AMR

Q4 Milestone Name/Description	Due Date	Comments
Propose ASTs for heavy-duty fuel cell applications on catalysts and membranes, with substantiating modeling and experimental data. (ANL, LANL, LBNL, NREL, ORNL) Define expected time at maximum operating temperature (via system analysis and FC-PAD Heavy Duty partners). Define membrane AST to reflect expected maximum operating temperatures for Class 8 vehicles. Evaluate heavy-duty vehicle expected idle time and normal load and their effect on membrane durability. Define catalyst AST (at loadings of 0.1, 0.2, 0.4 mgPt/cm^2) to reflect expected number of duty cycles for 1,000,000 miles of operation. Conduct all proposed ASTs on current SOA materials with post-characterization.	9/31/2020	✓ In Progress ✓ Loading of 0.1, 0.2, 0.3 ✓ Data included in AMR

FY2020 EOY GO/NO-GO

Description	Criteria
Heavy-Duty drive-cycle and AST recommendations	• Develop Heavy-Duty Vehicle MEAs demonstrating improved durability. Demonstrate 4x-cycle life improvement at high current density in heavy-duty MEAs compared to LDV state-of-art MEAs (LDV SOA MEAs defined as total Pt loading of 0.125 mgPt/cm^2, cycle life defined as 30 mV voltage degradation). • Propose new MEA drive cycle, and catalyst/membrane ASTs to reflect heavy-duty operation, including operation simulating time and temperature for high loads (95 – 105 C), and time and temperature simulating extensive idle (~ < 60 C). • Catalyst ASTs will detail upper potential, lower potential, cycle time (including rise/fall slope), operating temperature, and relative humidity. • Membrane ASTs will define operating temperature and stressors related to OCV and radical generation plus mechanical swelling/de-swelling. • These protocols will be develop in collaboration with new project partners related to heavy-duty FOA projects.

Durability Approach: Materials-based Solutions to Decrease Degradation



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

Develop/ Refine ASTs

- Drive cycle operation
- SD/SU simulation
- ASTs

Durability Testing/ Evaluation

Modeling

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

Develop new operando evaluation capability

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

Character-ization

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

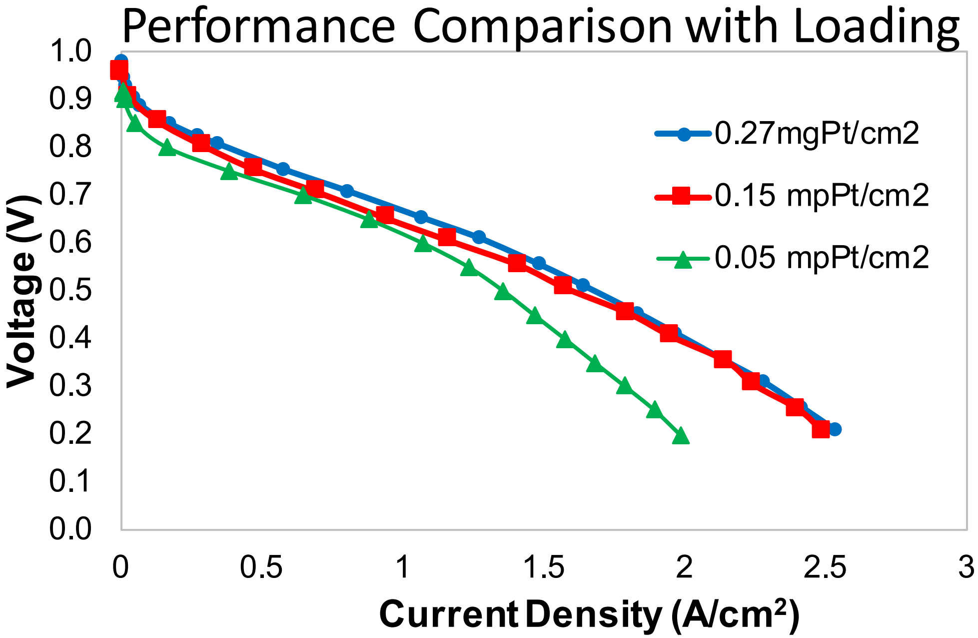
Feedback from Component thrusts

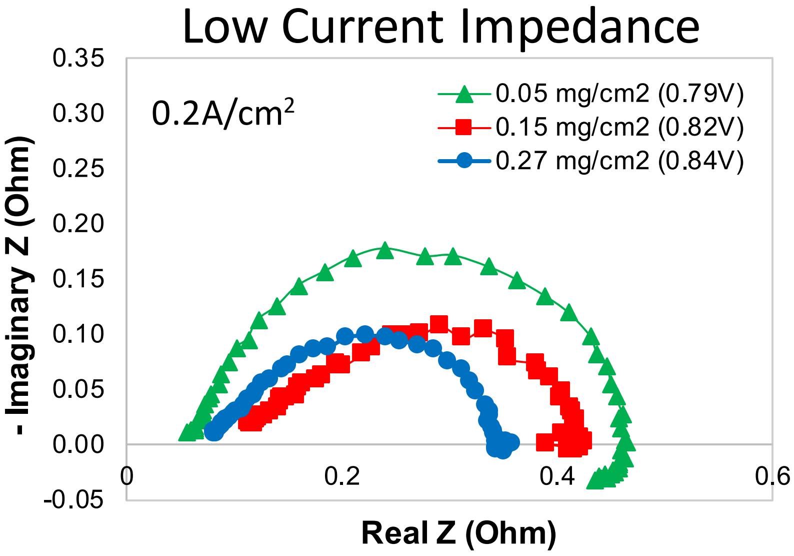
- Catalyst-alloying; particle growth, kinetics losses with leaching
- Catalyst-support corrosion
- Membrane stabilizers and cation migration

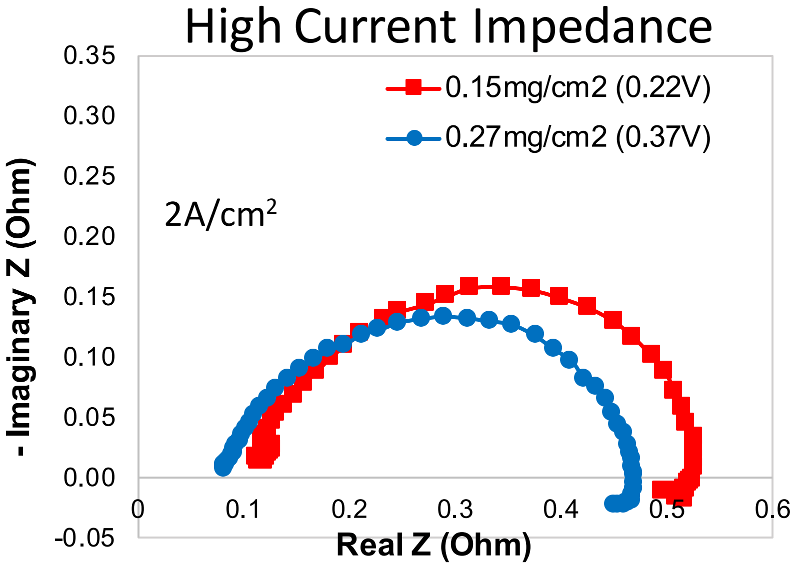
Re-Focus on Heavy-Duty MEAs, Durability and Performance

Higher Loading Durability - Effect of loading

Durability Performance: High Loading - Effect of Loading





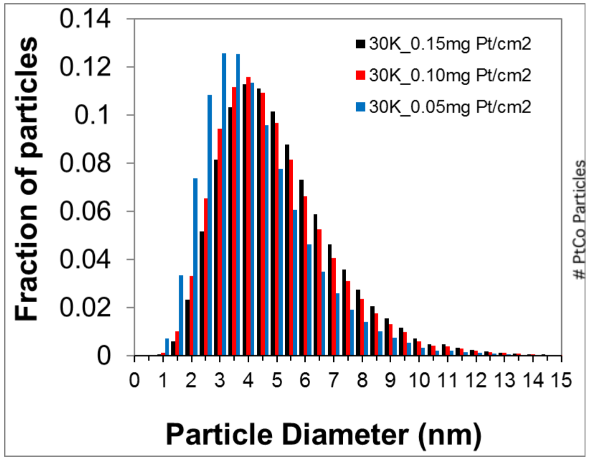


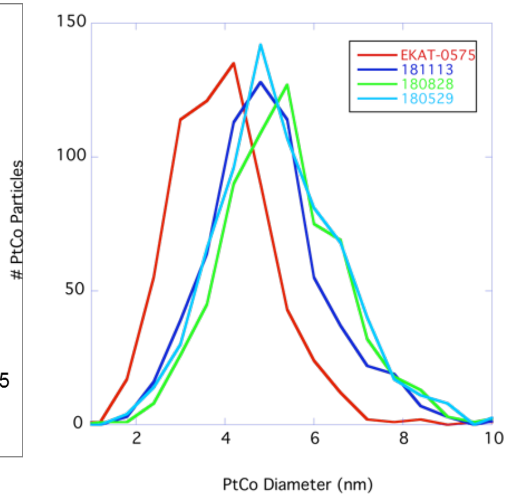
- Loading improves kinetic performance but Mass activity decreases (worse utilization of Pt) from 977mA/mg @ 0.05mg/cm^2 0.495mA/mg @ 0.27 mg/cm^2. Diminishing returns
- Mass transport does not improve at high loadings and thicker electrodes lose any benefit at high current densities

80C, 100% RH, 150 kPa

SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

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





Mean diameter after AST (SAXS)

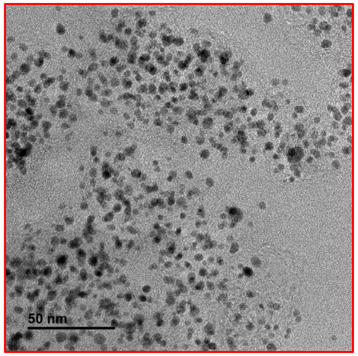
0.05 mg/cm^2: 4.5 nm
0.10 mg/cm^2: 5.2 nm
0.15 mg/cm^2: 5.5 nm

Pt:Co at% in electrode (EDS)

BOL : Pt:Co = 75:25
30K (0.05) : Pt:Co = 80:20
30K (0.10) : Pt:Co = 85:15
30K (0.15) : Pt:Co = 87:13

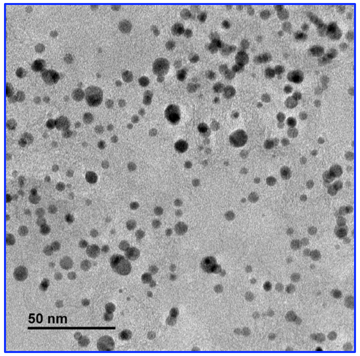
- Higher loading results in slightly larger growth in Pt particle size (both SAXS and TEM)
- On average Co is retained better in the lower loaded electrode
- Larger lattice contraction loss for lower loading (EXAFS data, not shown) coupled with smaller particle growth indicate larger particles retain Co better than smaller particles

BOL (EKAT 0574)



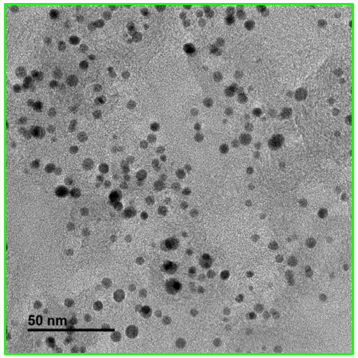
PtCo particle size = 4.2 nm

$0.05 mg_{Pt}/cm^2$
30,000 cycles



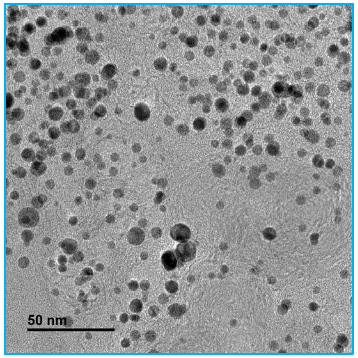
PtCo particle size = 5.1 nm

$0.10 mg_{Pt}/cm^2$
30,000 cycles



PtCo particle size = 5.5 nm

$0.15 mg_{Pt}/cm^2$
30,000 cycles



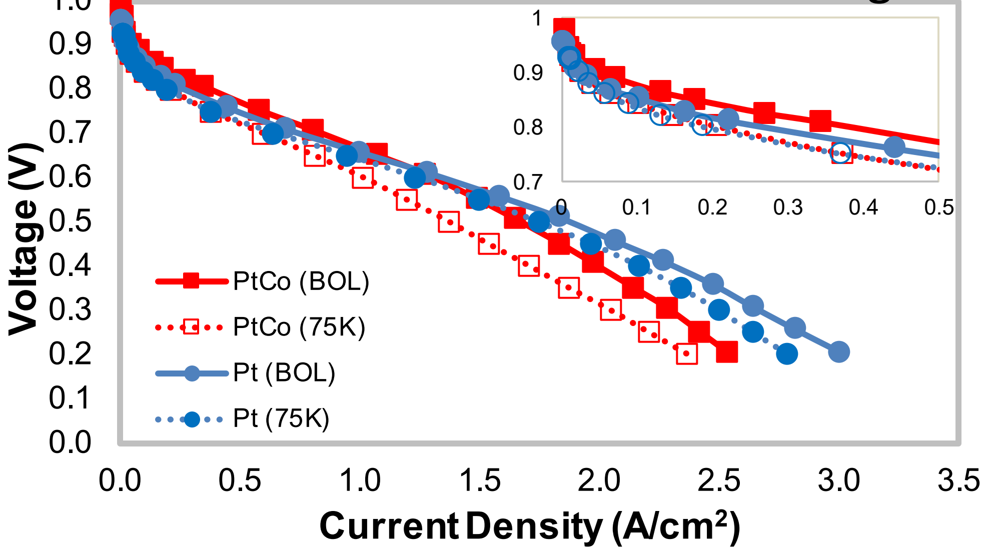
PtCo particle size = 5.6 nm

SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

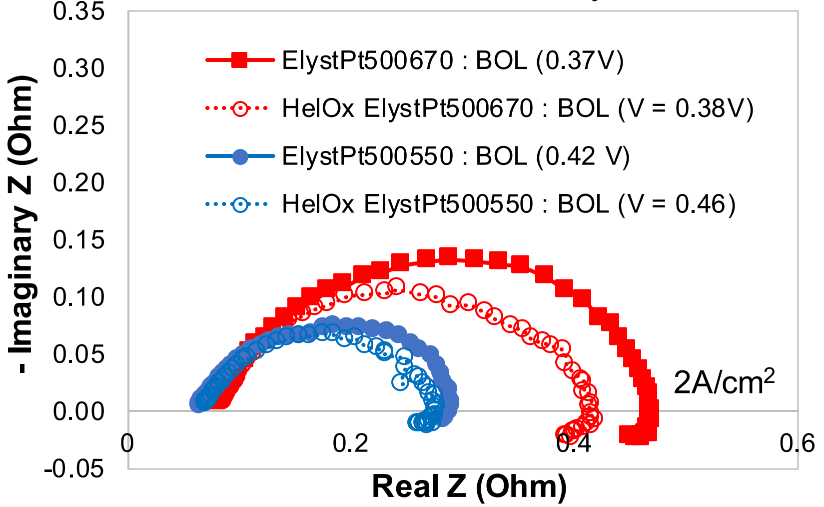
Effect of Alloys

Durability Performance: High Loading - Effect of Alloying

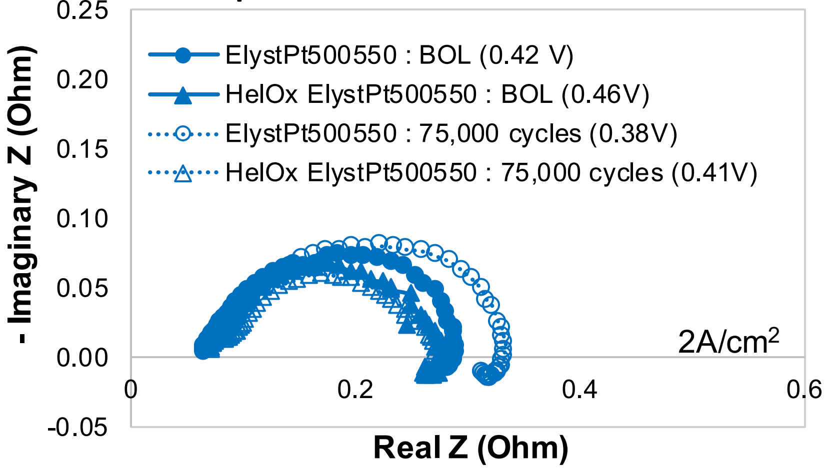
Performance of Pt and PtCo During AST



Pt and PtCo BOL Impedance



Pt Impedance BOL and After AST



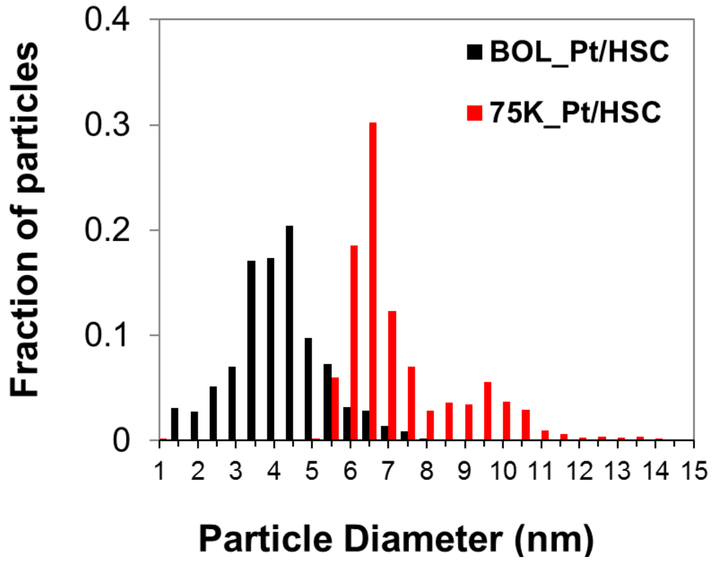
- Kinetic performance of PtCo is better than that of Pt at BOL: higher alloy mass activity
- No kinetic advantage at EOL of using alloy catalyst: significant loss in kinetic performance of alloy catalyst
- Transport resistance of PtCo alloys higher than Pt

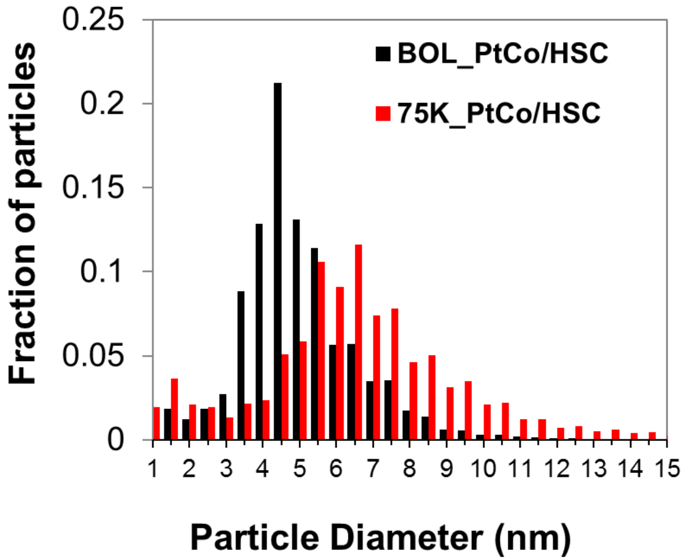
ElystPt500550 (Pt) and
ElystPt500670 (PtCo)

80C, 100% RH, 150 kPa Loading = 0.25mg/cm²

SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

Durability Characterization: High Loading - Effect of Alloying





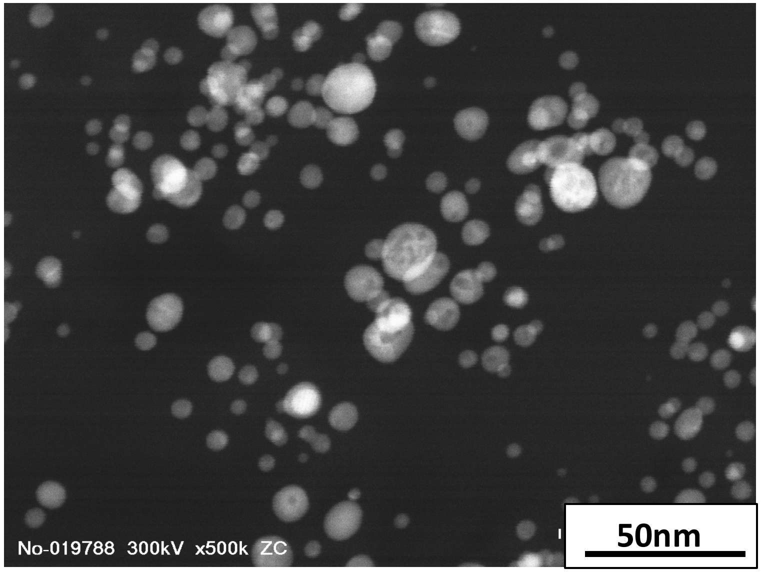
- PtCo has a larger initial particle diameter and grows less
- Pt has a smaller initial particle diameter and grows more (Pt has larger particle size than PtCo after 75,000 cycles)
- Particle size increase does not have an effect on high current performance at high loadings

	Mean diameter (nm)		
Sample	**BOL**	**EOT**	**Δd (nm)**
Pt/HSC 0.25mgPt/cm^2	4.3	7.5	3.2
PtCo/HSC 0.27mgPt/cm^2	5.2	6.8	1.6

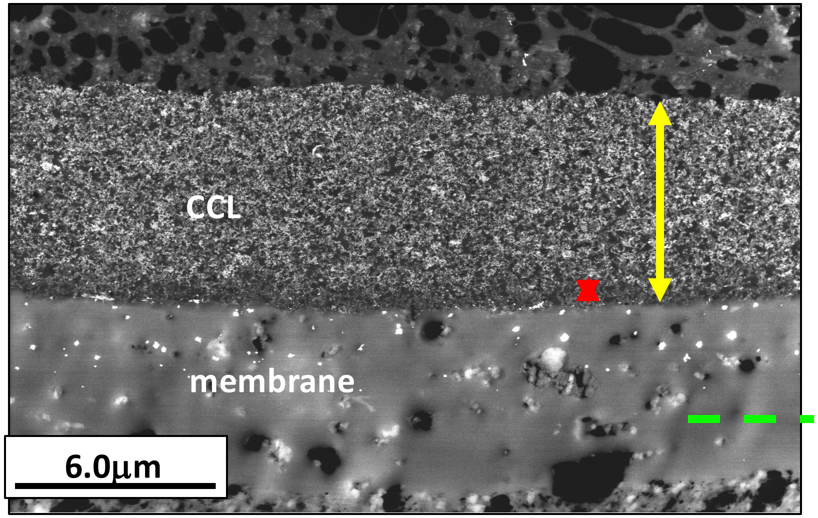
TEM shows 6.8 nm Pt and 6.4 nm PtCo particles after 75,000 cycles

SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

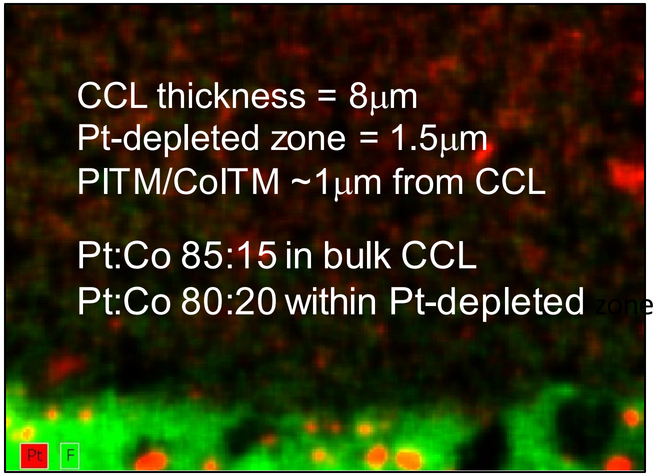
Durability Characterization: High Loading - Effect of Alloying



- Larger PtCo particles exhibit a "spongy" or "core-shell" morphology
- Large PtCo particles (Core shell)
- CCL porosity is similar
- Ionomer more aggregated in PtCo than Pt (I/C 0.95 in PtCo and 0.83 in Pt)
- Both Pt and Co measured ITM (In The Membrane)



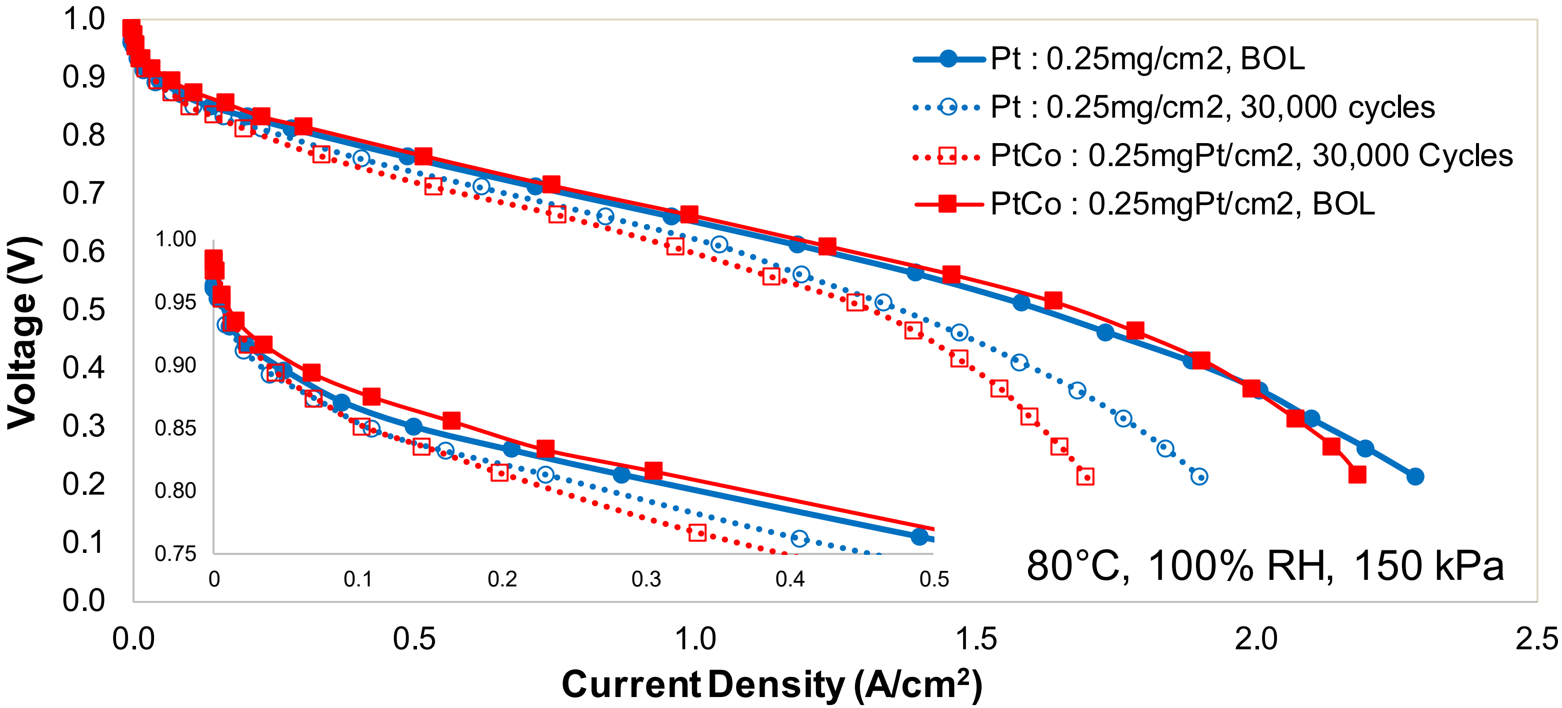
CCL thickness = 7μm
Pt-depleted zone = 1μm
PITM ~4μm from CCL



CCL thickness = 8μm
Pt-depleted zone = 1.5μm
PITM/CoITM ~1μm from CCL

Pt:Co 85:15 in bulk CCL
Pt:Co 80:20 within Pt-depleted zone

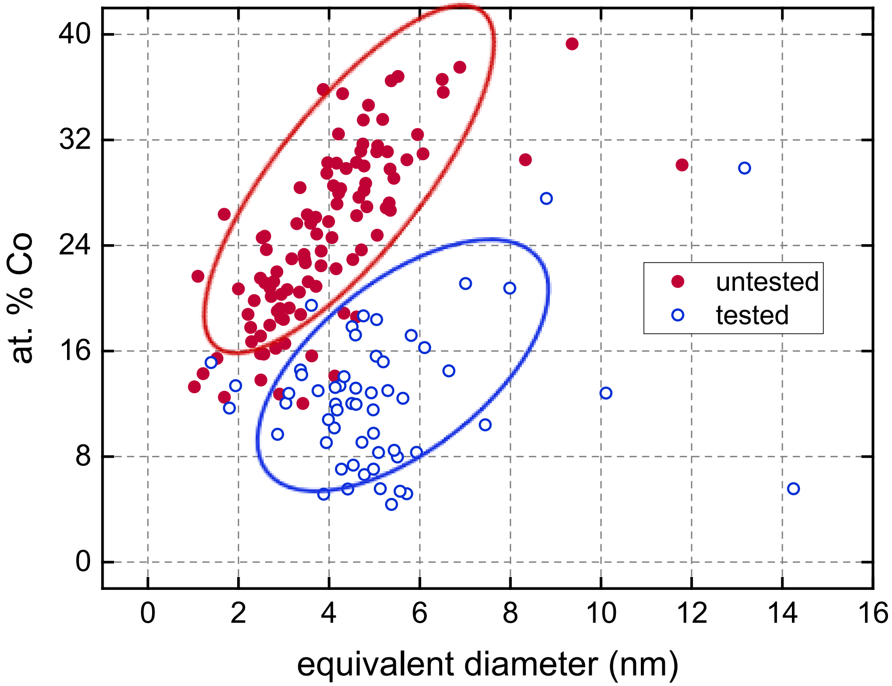
Durability Performance : High Loading: Effect of Alloying

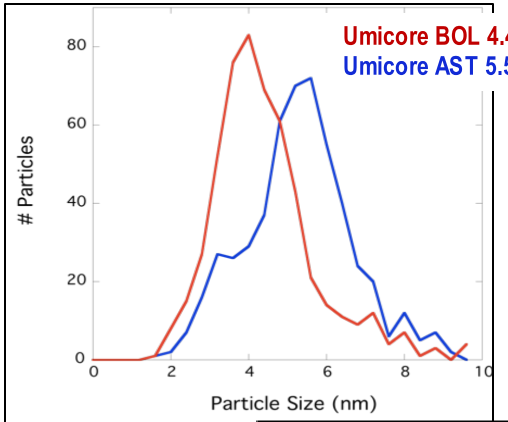


- TEC10E50E and TEC36E32E confirm results observed with Umicore catalysts
- PtCo alloy catalysts lose kinetic advantage after durability cycles
- Mass transport in Pt catalysts better during all stages of the AST

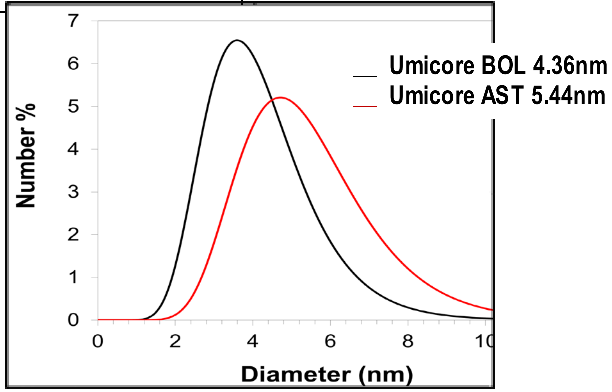
SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

Umicore - PtCo Catalyst in CCL After Catalyst Cycling AST

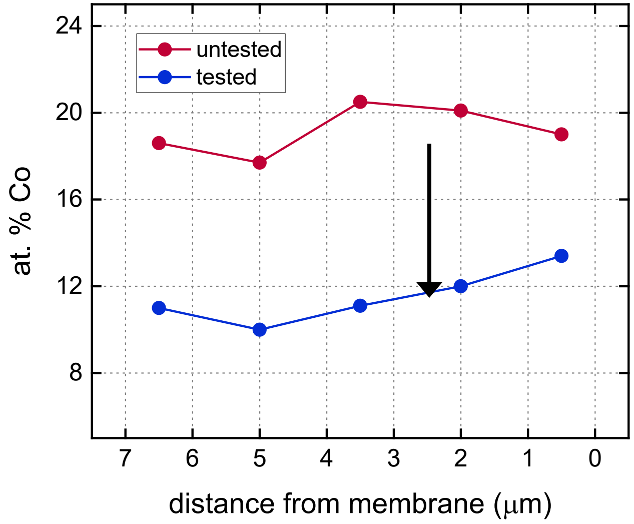




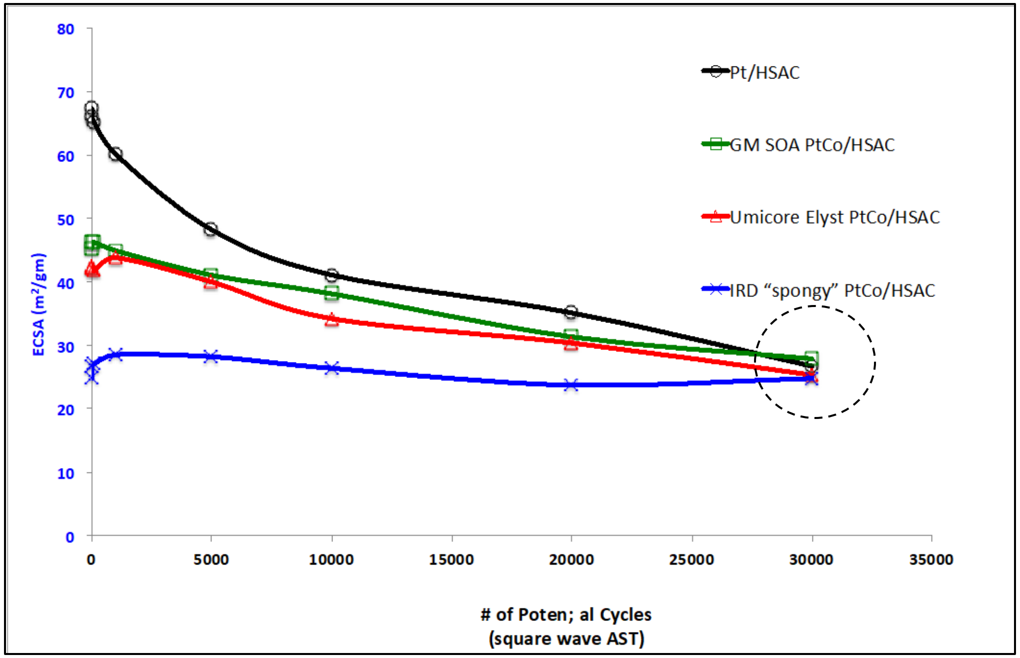
SAXS particle sizes agree with TEM



~30% Co loss from CCL into membrane during AST

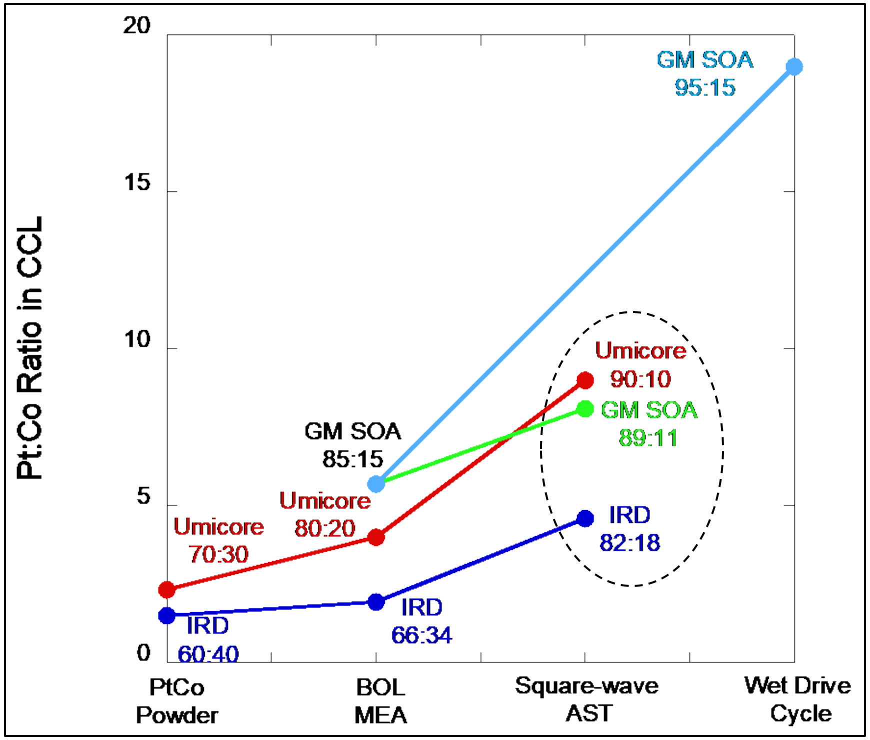


Co Dissolution/Migration (Loss) During Electrocatalyst AST



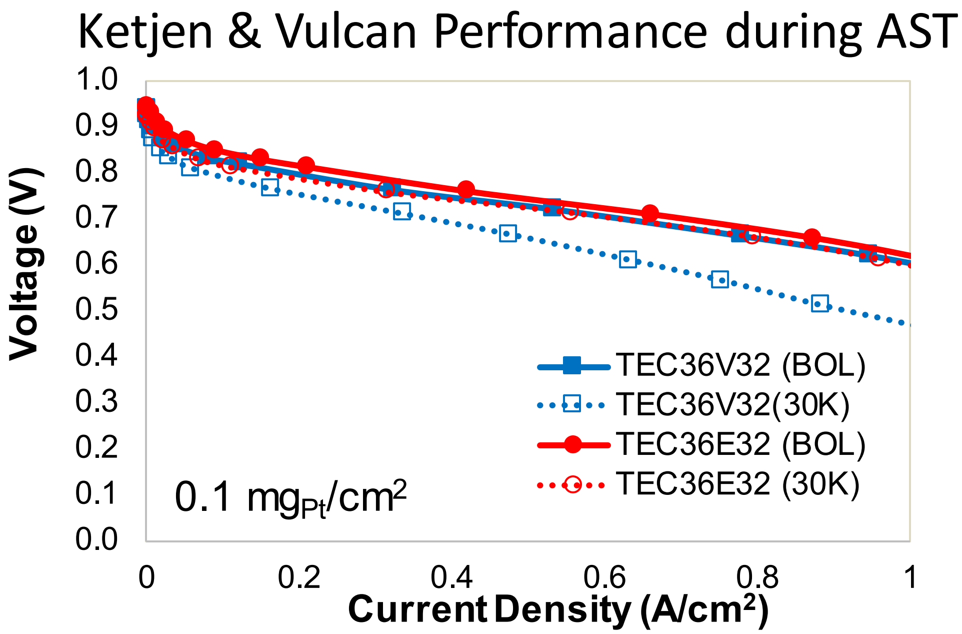
SOA PtCo exhibits improved initial performance (ECSA) compared to other PtCo/HSAC catalysts, but after 30,000 cycles, ECSA values are the same

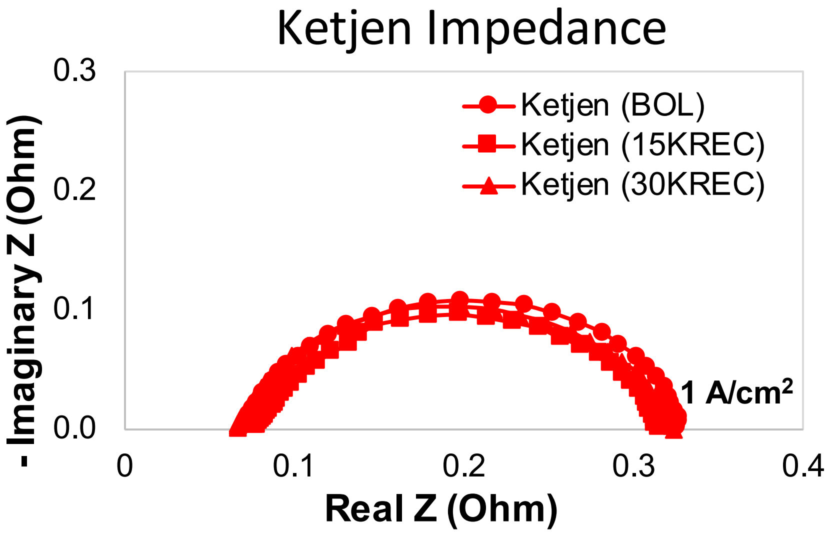
Performance (ECSA) loss can be directly attributed to extensive Co loss from catalyst/CCL into membrane during AST

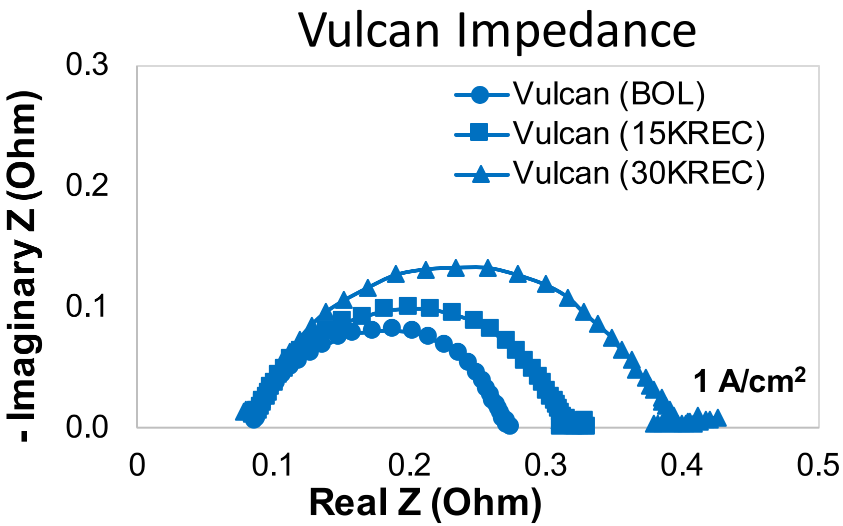


Effect of support on catalyst durability

Durability Performance
Effect of Carbon Support (porous/solid)


Ketjen & Vulcan Performance during AST


Ketjen Impedance


Vulcan Impedance

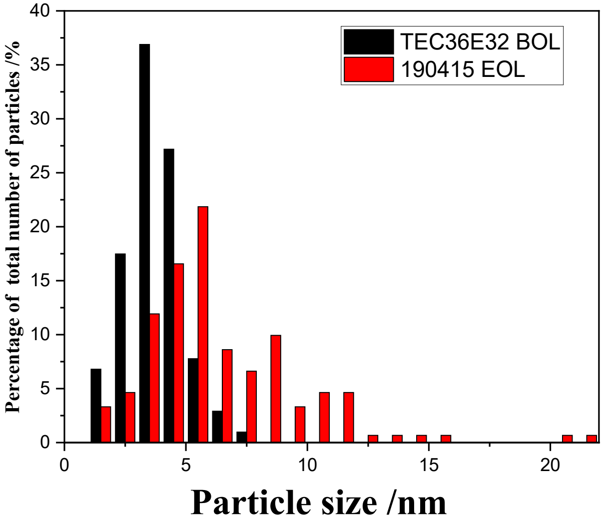
- Kinetic performance of TEC36E32 is better than that of TEC36V32 consistent with higher ECSA and mass activity
- Transport of TEC36V32 better than transport of TEC36E32 consistent with greater RO_2
- Durability of TEC36E32 superior to that of TEC36V32 especially in transport region where even a sight improvement is observed

TEC36V32 and TEC36E32

80C, 100% RH, 150 kPa

SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

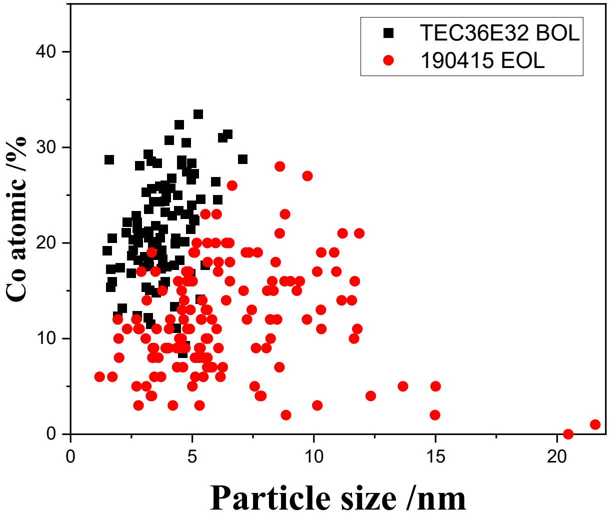
Durability Characterization
Effect of Carbon Support (porous/solid)



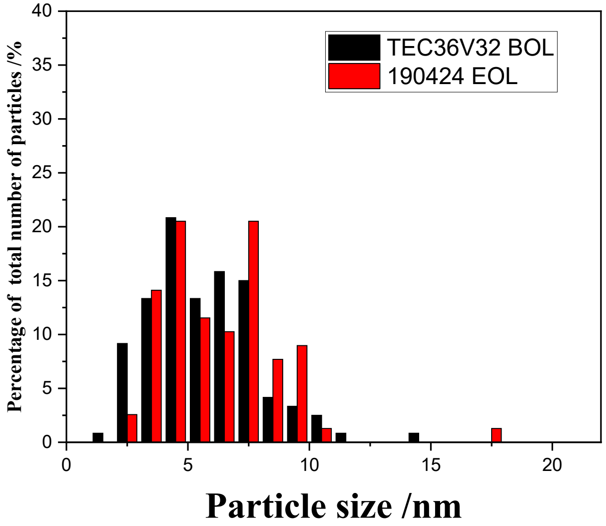
TEC36E32

TEM:
Avg : 3.8 nm → 6.4 nm
Pt:Co : 81:19 → 89:11

SAXS/WAXS
Size : 4.6nm → 5.7 nm
Pt:Co : 82:18 → 96:04



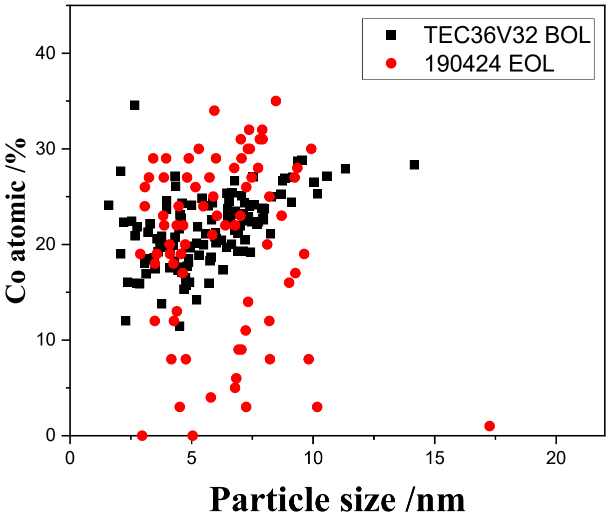
- Porous carbon slows Pt growth while Vulcan support retains more Co



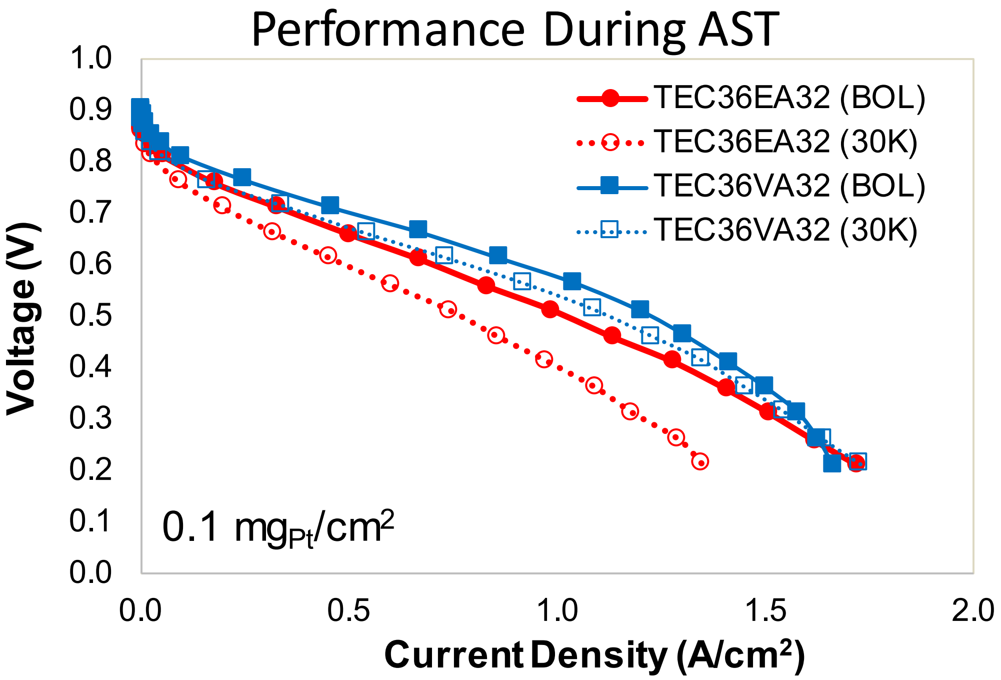
TEC36V32

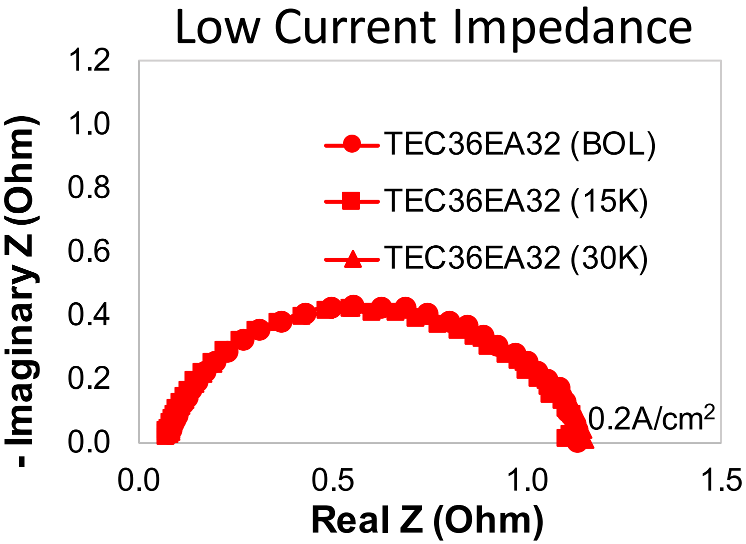
TEM:
Avg : 5.7 nm → 6.5 nm
Pt:Co : 73:27 → 80:20

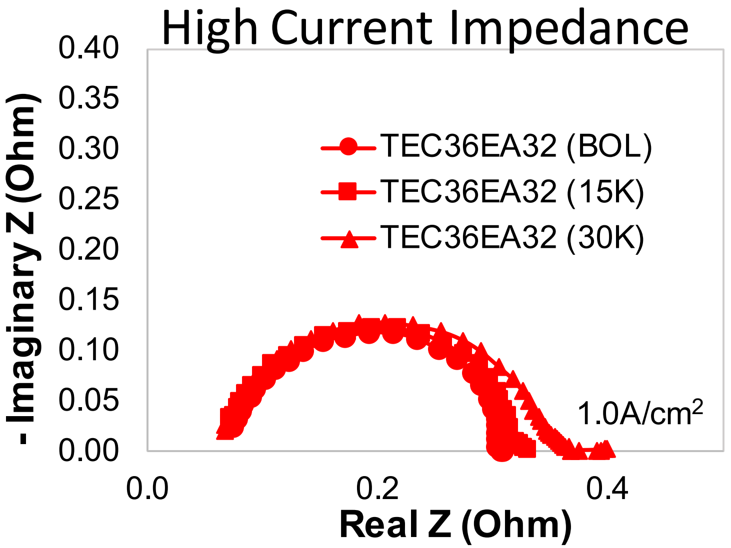
SAXS/WAXS
Size : 5.9nm → 8.3 nm
Pt:Co : 73:27 → 81:19



Durability Performance Graphitized Carbons(porous/solid)







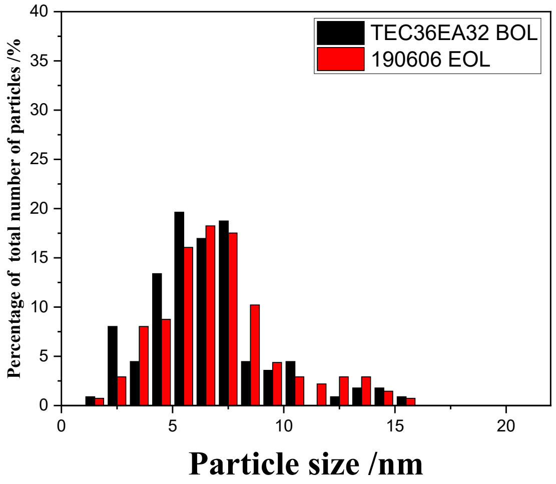
- Performance of graphitized carbons significantly lower due to larger particle size and lower ECSA
- Performance of TEC36VA32 (I/C = 0.4) better than transport of TEC36EA32 (I/C = 0.5)
- Kinetic and Mass transport resistances show little change

TEC36VA32 and TEC36EA32

80C, 100% RH, 150 kPa

SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

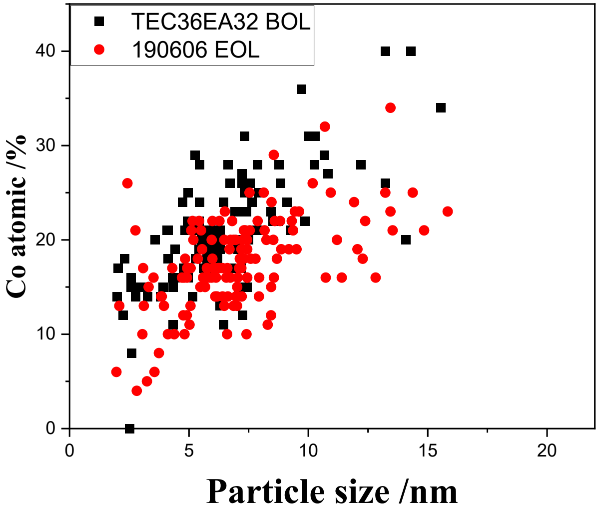
Durability Characterization
Graphitized carbon(porous/solid)



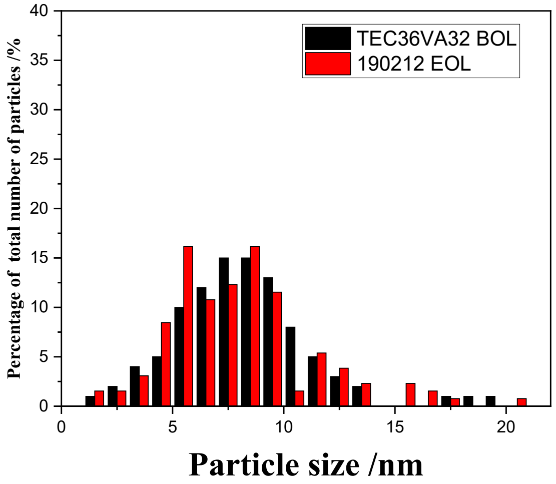
TEC36EA32

TEM:
Avg : 6.5 nm → 7.1 nm
Pt:Co : 74:26 → 79:21

SAXS/WAXS
Size : 2.9nm → 8.8 nm
Pt:Co : → 80:20



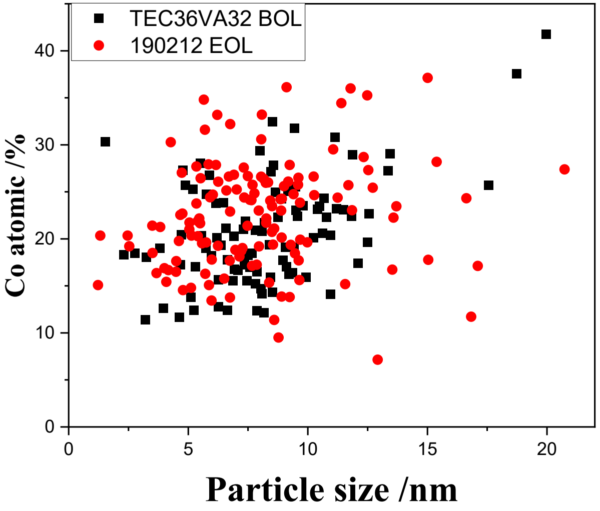
- Little change in catalyst particle size or Co content (TEM). USAXS shows particle size growth



TEC36VA32

TEM:
Avg : 8.2 nm → 8.0 nm
Pt:Co : 74:26 → 78:22

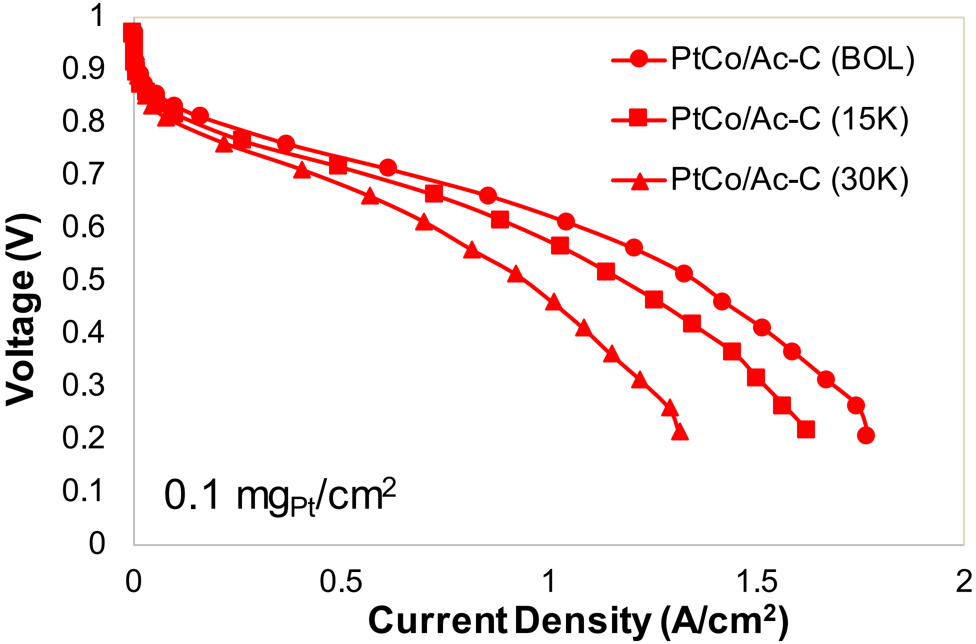
SAXS/WAXS:
Size : 9.9nm → 10.4 nm
Pt:Co : 78:22 → 79:21



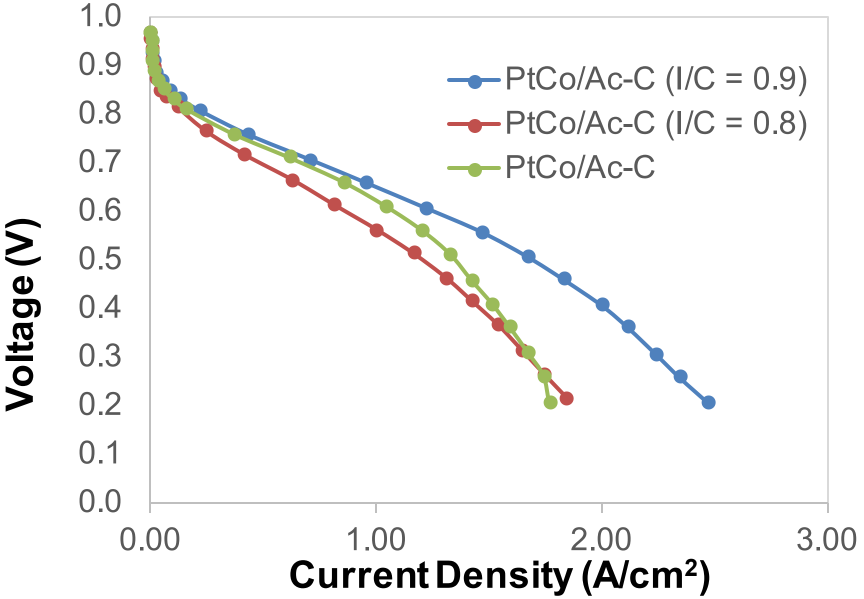
SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

Durability Performance
Acetylene Black

Performance During AST



Ionomer/C Effect on Performance

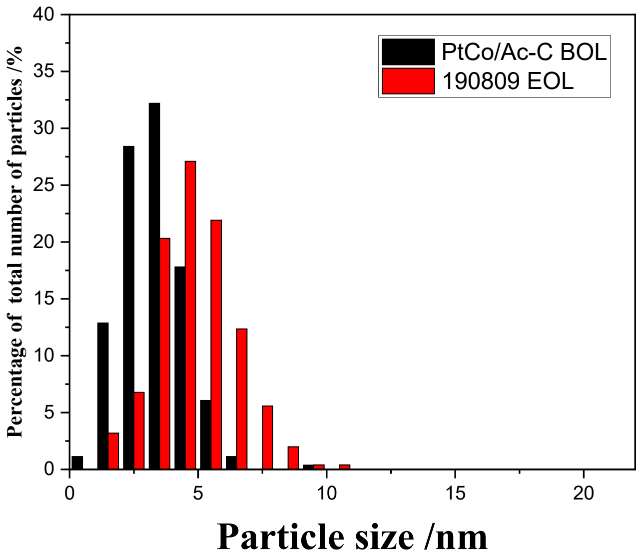


- Unoptimized MEA performance was lower and durability poor
- MEA optimization significantly enhanced performance
- Repeat of durability underway

80C, 100% RH, 150 kPa

SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

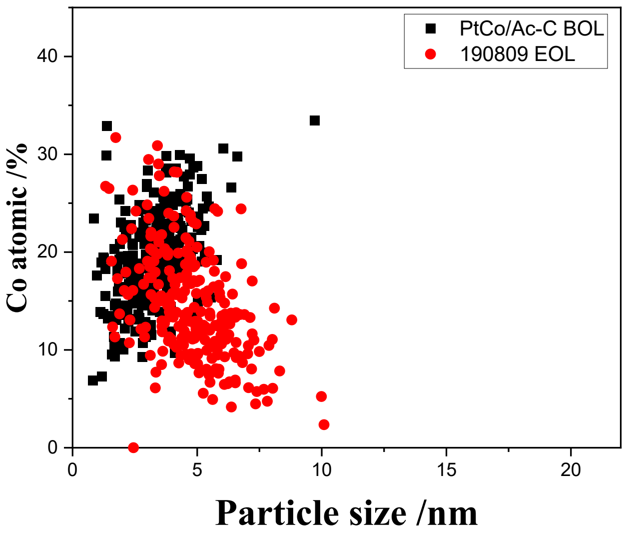
Durability Characterization
Acetylene Black



PtCo/Ac-C

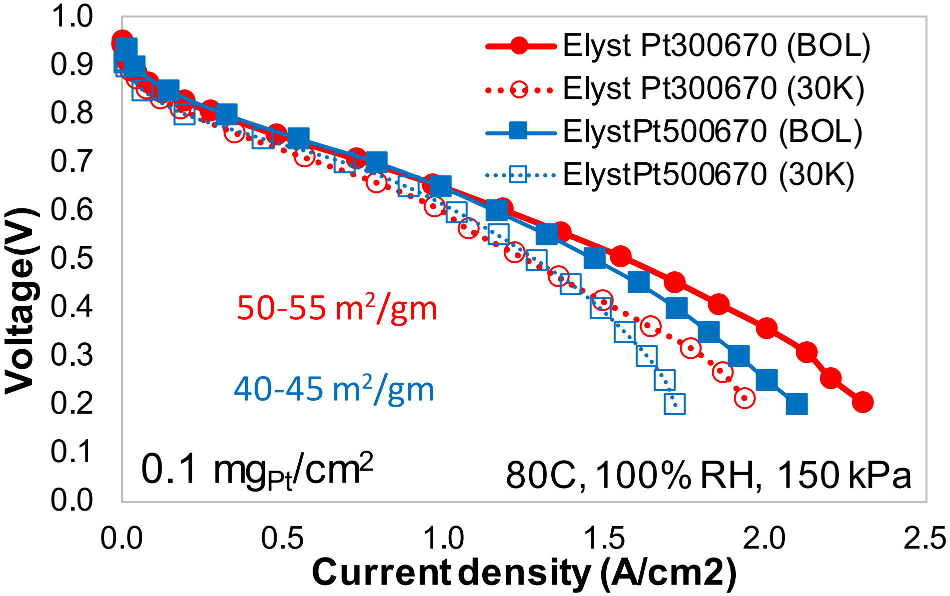
TEM:
Avg : 3.3 nm → 4.8 nm
Pt:Co : 80:20 → 90:10

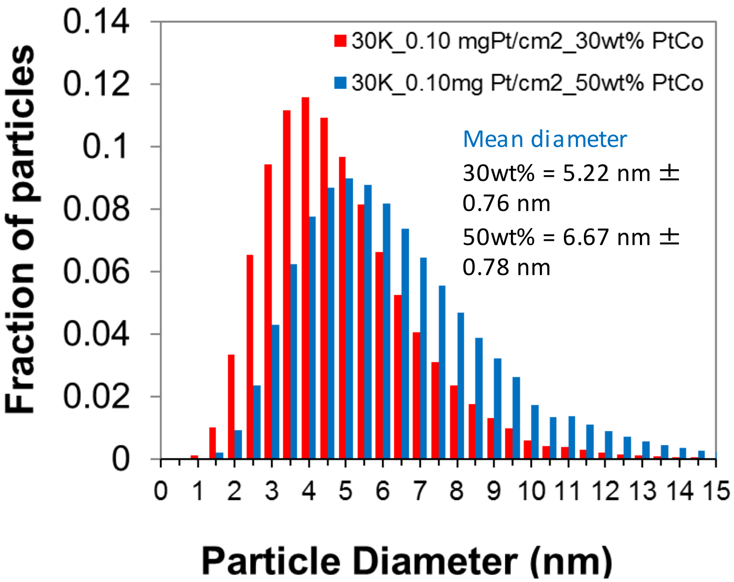
SAXS/WAXS
Size : 2.4nm → 4.3 nm
Pt:Co : → 88:12



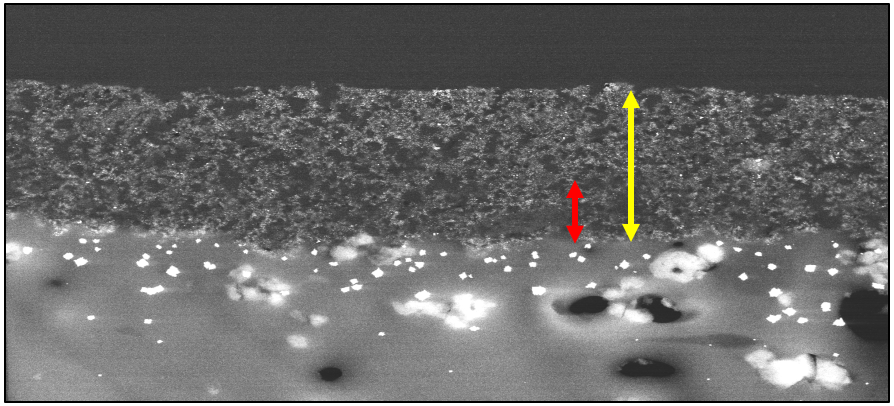
- Smallest Pt particle sizes at both BOL and EOL of any catalyst tested
- At BOL the Co content of the particles increases with increasing particle size consistent with other catalysts
- At EOL most of the larger particles have lower Co content. Probably due to dissolution and reprecipitation of Pt

Durability : Effect of Catalyst Pt/C ratio





- Pt(50%)/C has lower BOL performance than Pt(30%)/C due to larger starting particle size of 5.2nm vs 4.2nm and increased RO_2.
- The Pt(50%) shows a slightly larger growth during durability (28% vs 24%) despite its larger initial particle size
- The Pt(50%)/C catalysts shows better Co retention. Pt in the membrane was observed and a 1-1.5um depletion layer was also observed close to the catalyst layer



ELYSTPt500670 and ELYSTPt300670

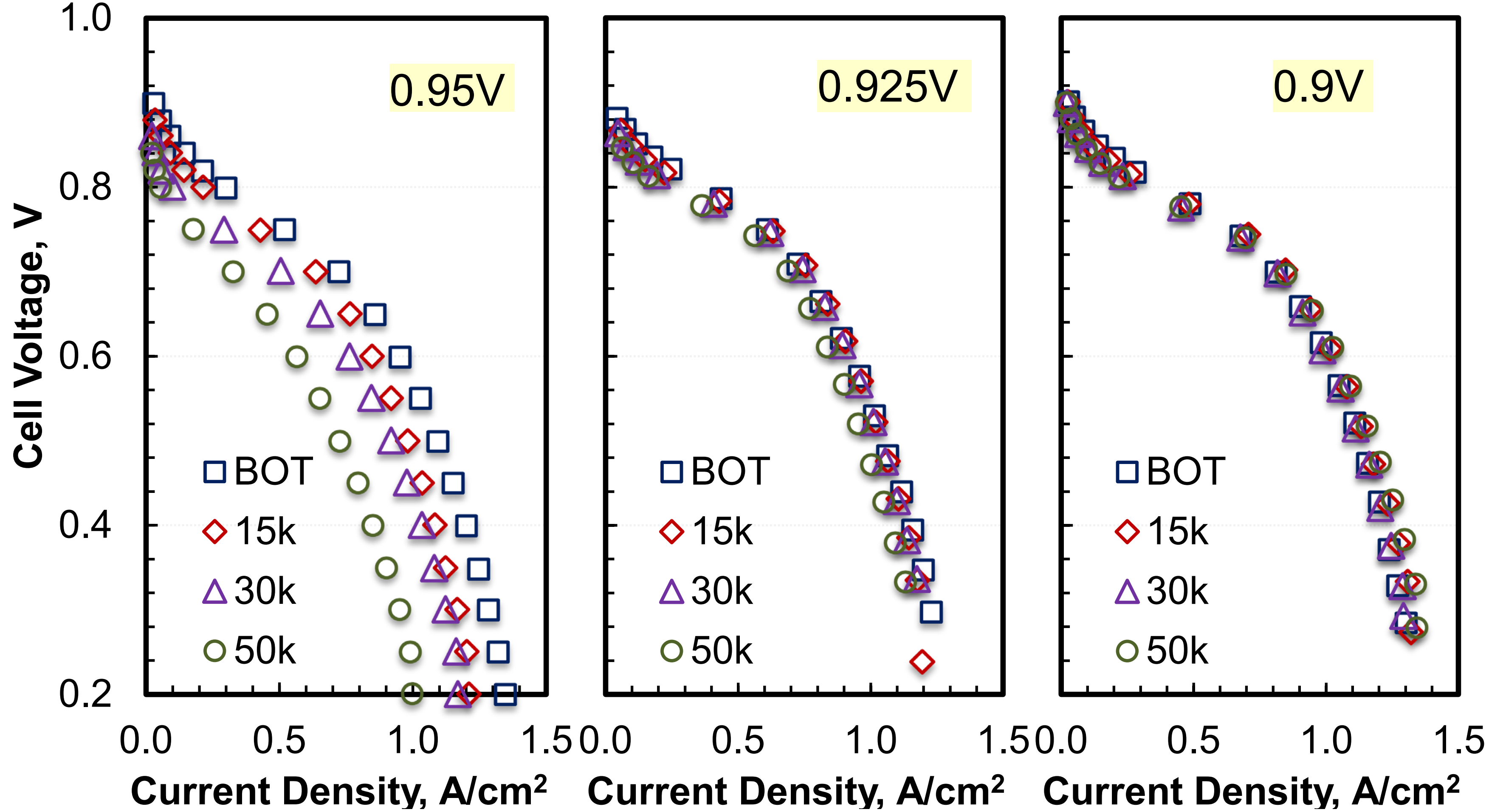
SW AST = Square Wave Catalyst AST (0.6 – 0.95V)

Effect of Upper potential

Cell Degradation in Catalyst AST: Effect of Upper Potential Limit

Degradation can be controlled by clipping cell voltage

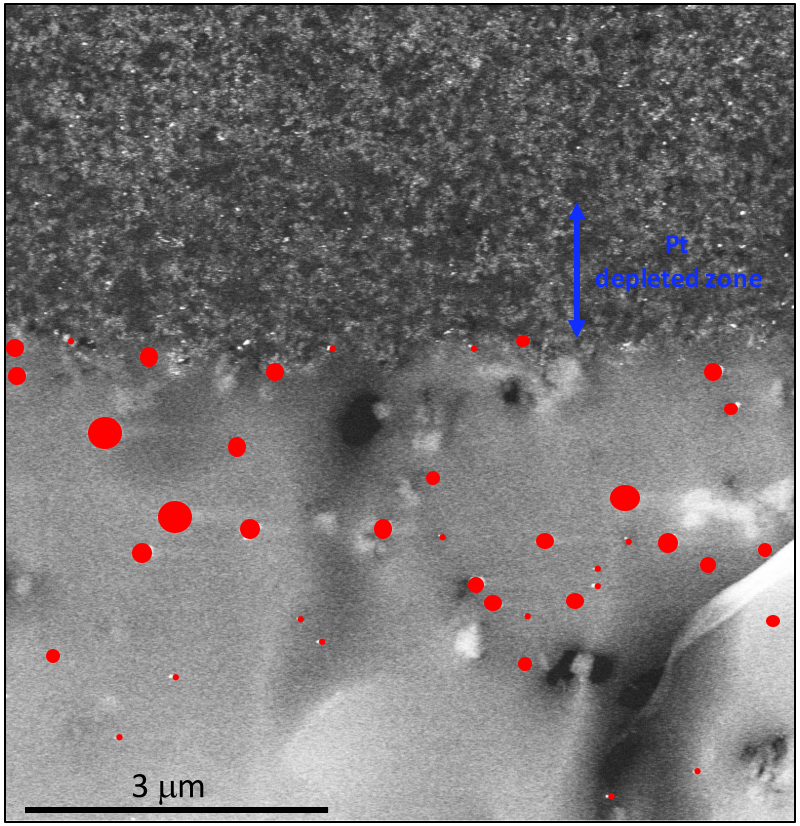
- After 50k AST cycles: $\Delta V(0.90V\ UPL) < \Delta V(0.925V\ UPL) \ll \Delta V(0.95V\ UPL)$
- After 50k cycles at 0.90V UPL, no loss in cell voltage for current densities up to 1.25 A/cm^2



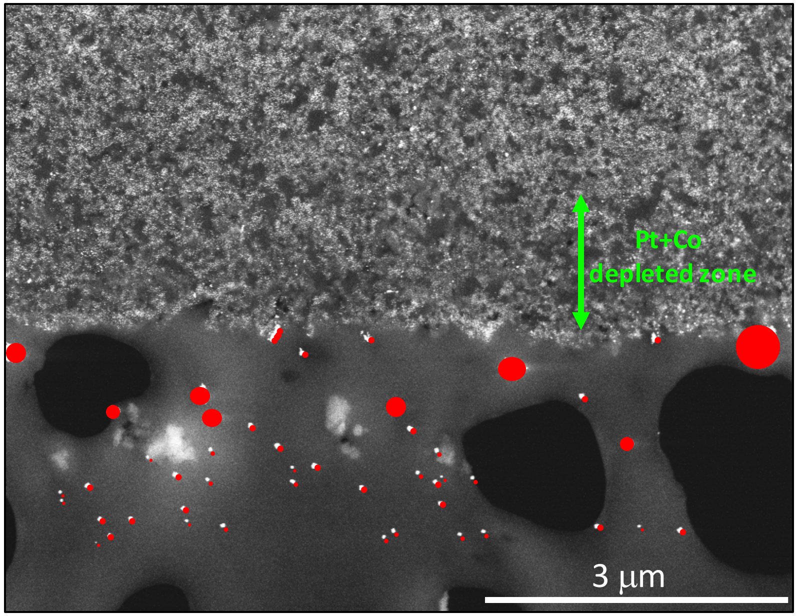
Polarization curves in a differential cell at 1.5 atm, 80^{o}C, 100% RH, 10% X(O_2)

Durability : Catalyst Characterization (upper potential effect)

30,000 cycles 0.6-**0.925**V (LANL190422)



30,000 cycles 0.6-**0.95V** (LANL180828)



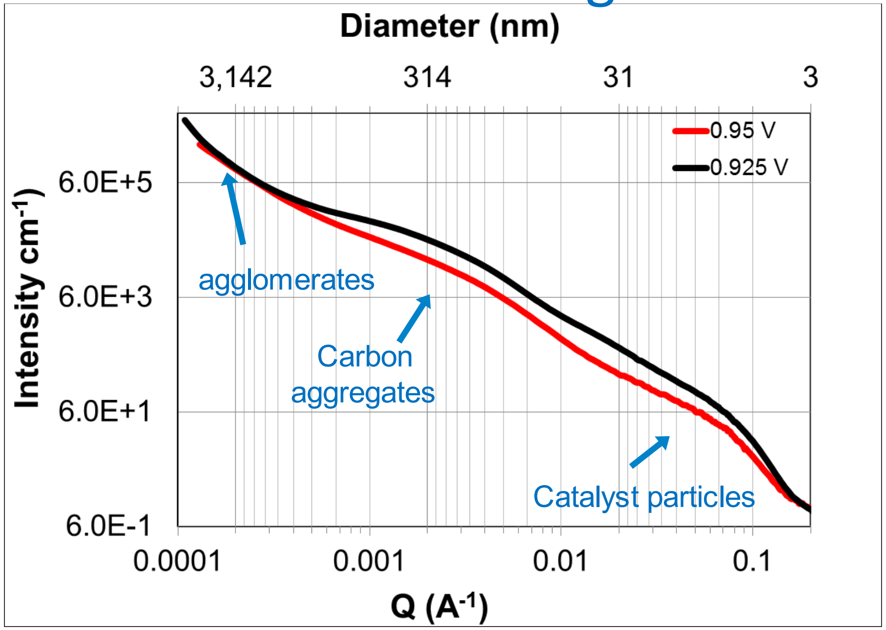
The amount of PITM and depth of Pt migration into membrane are both *greater* for lower voltage (**0.925V**) MEA

The amount of Co dissolution into membrane is *greater* for higher voltage (**0.95V**) MEA

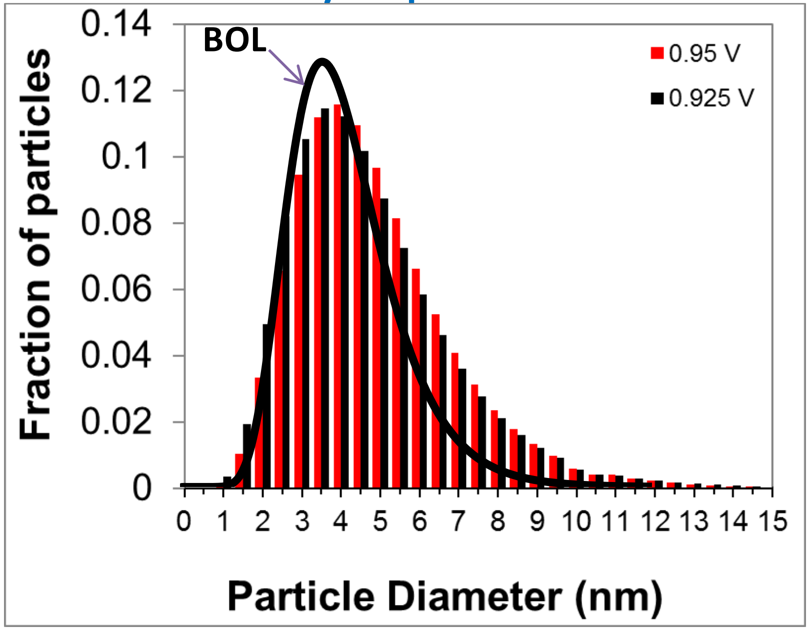
Durability : Catalyst Characterization (upper potential effect)

MEA: 30K cycles; 0.1mgPt/cm^2; PtCo/HSC (ElystPt300670)

Scattering data



Catalyst particle: PSD



- Scattering by catalyst nanoparticles at q > 0.01 (A^{-1}):
  - Cycling the electrodes to UPL of 0.925 V or 0.95 V results in PSD shifted to slightly larger particle sizes for UPL of 0.95 V
  - Mean particle diameter slightly larger for the electrode cycled to high UPL

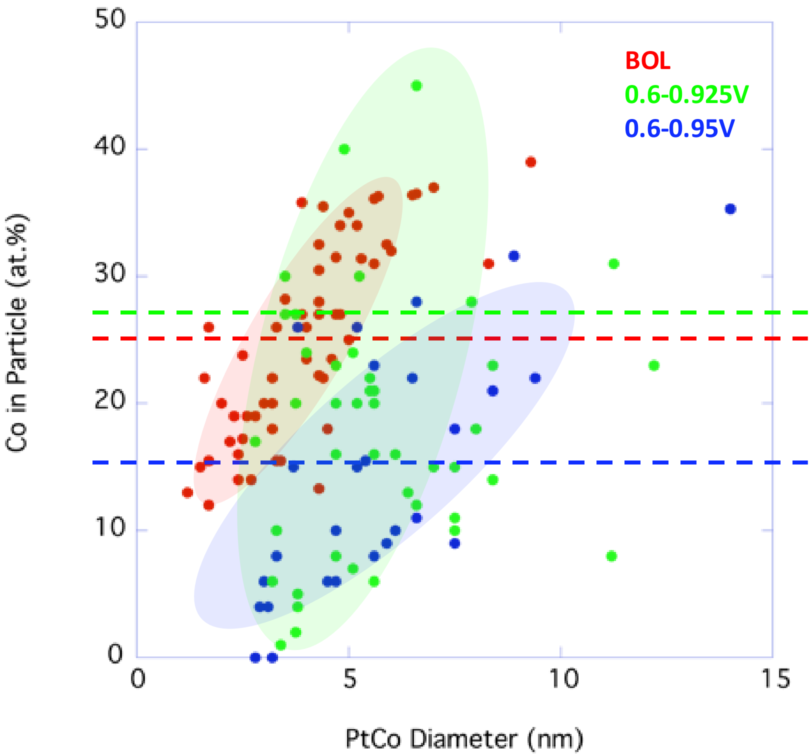
Mean diameters

BOL = 4.2 nm ± 0.6 nm

0.925 V$_{UPL}$= 5.0 nm ± 0.8 nm

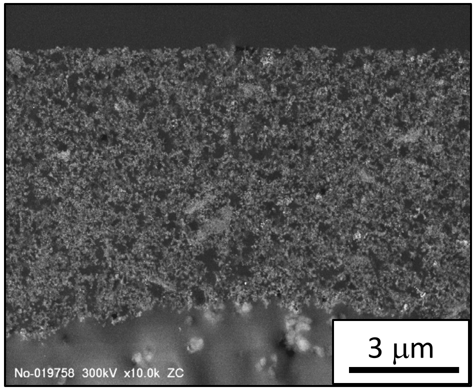
0.950 V$_{UPL}$ = 5.2 nm ± 0.8 nm

Durability : Catalyst Characterization (upper potential effect)

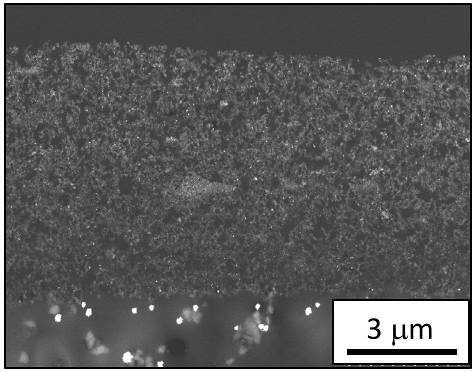


- Larger particles retain more Co
- More Co retained in 0.925V cycled sample (especially in Pt depleted zone)
- Thickness change also correlates with voltage (more carbon corrosion at higher voltages)

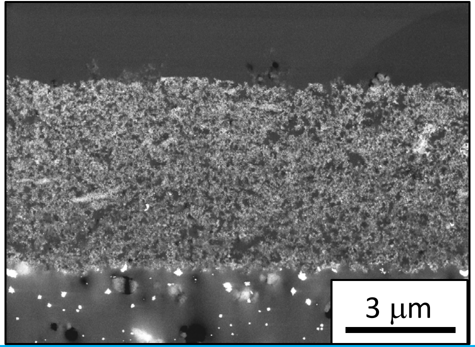
BOL (EKAT 0575)



30,000 cycles 0.6-**0.925**V



30,000 cycles 0.6-**0.95V**

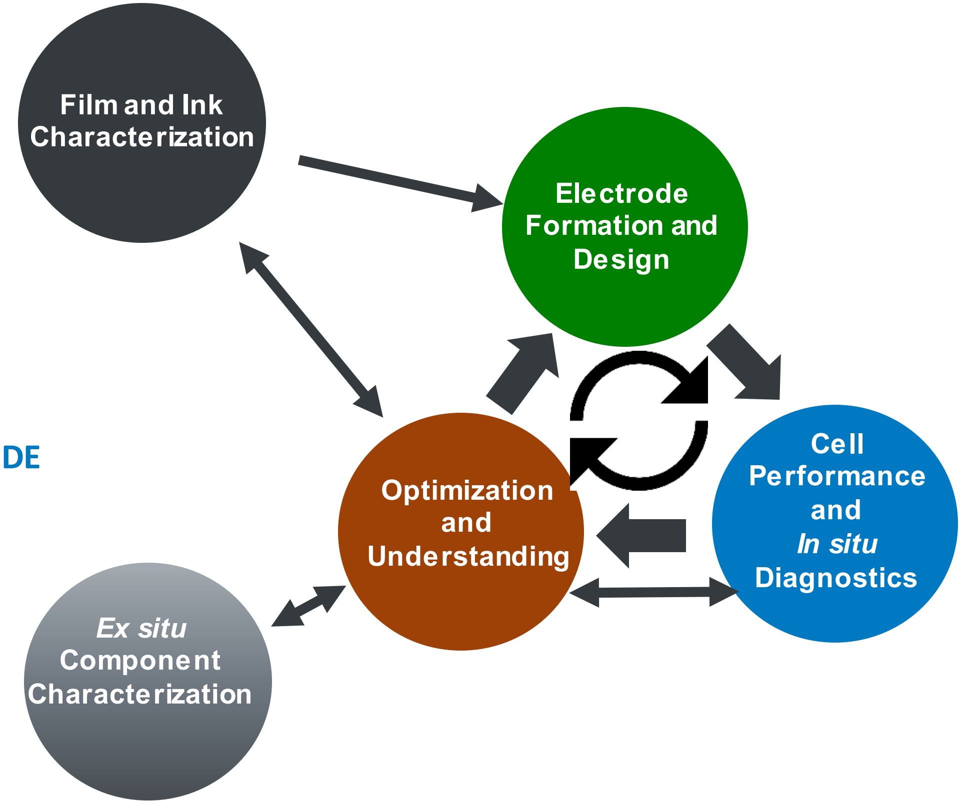


Electrode Structure

Ink Composition-Solvent Studies

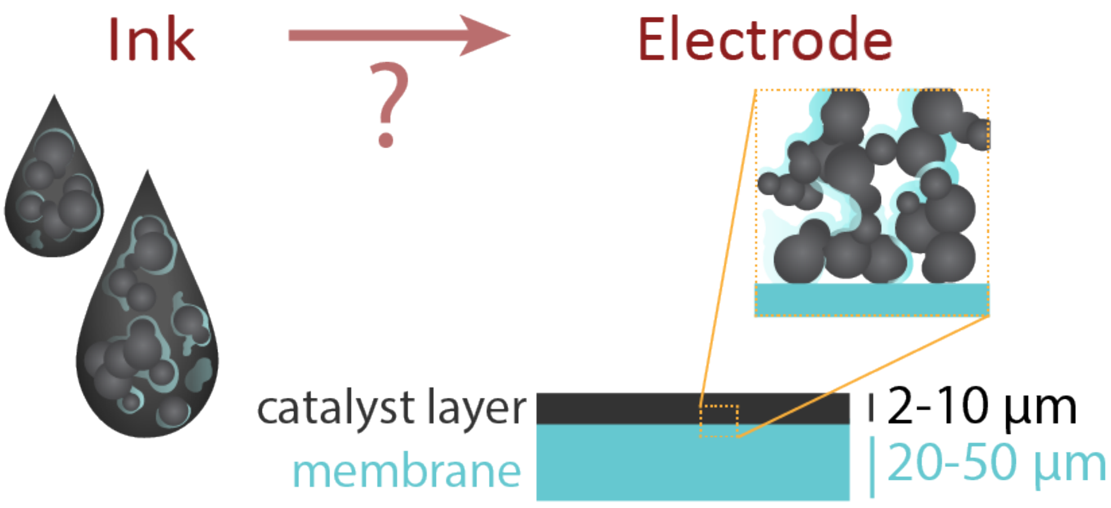
Electrode Layers and MEA Characterization:
Electrode Input Variables and Optimization

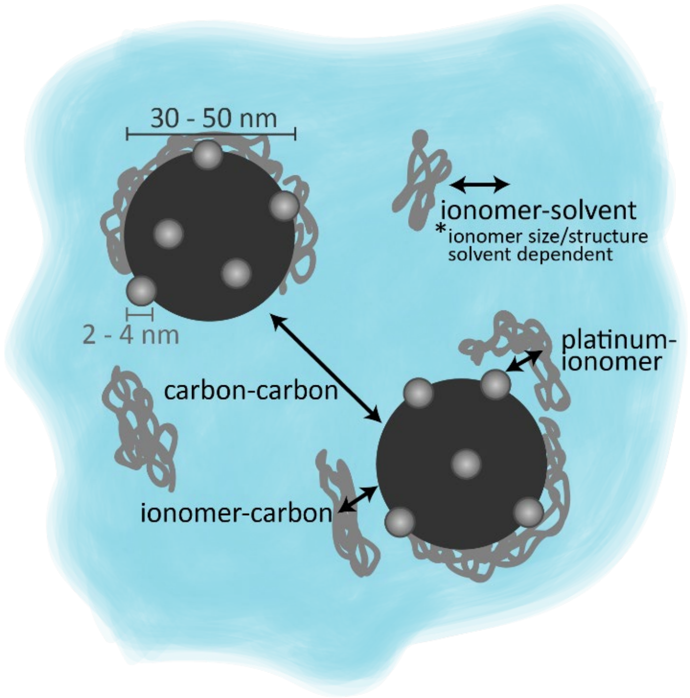
RDE	**Intrinsic Catalytic Properties**
Materials Sets	**Catalyst/support type, Membrane, Ionomer chemistry, I/C ratio, DM**
Dispersion Method	**Ultrasonic, Shear Mixing, Solvent(s)**
Coating Method	**Spray Coating, Roll-to-Roll, CCM vs GDE**
MEA Conditioning	**Procedure, Duration**
Data Acquisition	**Conditions, Measurement Direction**
MEA	**Functional Device Properties**



How does ionomer distribution affect performance?

Motivation





- Many poorly-understood interactions in inks that control catalyst layer morphology
- Need to better clarify impact of ionomer in ink and catalyst-layer formation process

K. B. Hatzell, M. B. Dixit, S. A. Berlinger, A. Z. Weber, *J. Materials Chemistry A*, **5**, 20527 - 20533 (2017)

Ionomer Thin Films: Casting Methods

Spin-Casting

Rapid film formation by casting solution on a spinning substrate

Drop Casting

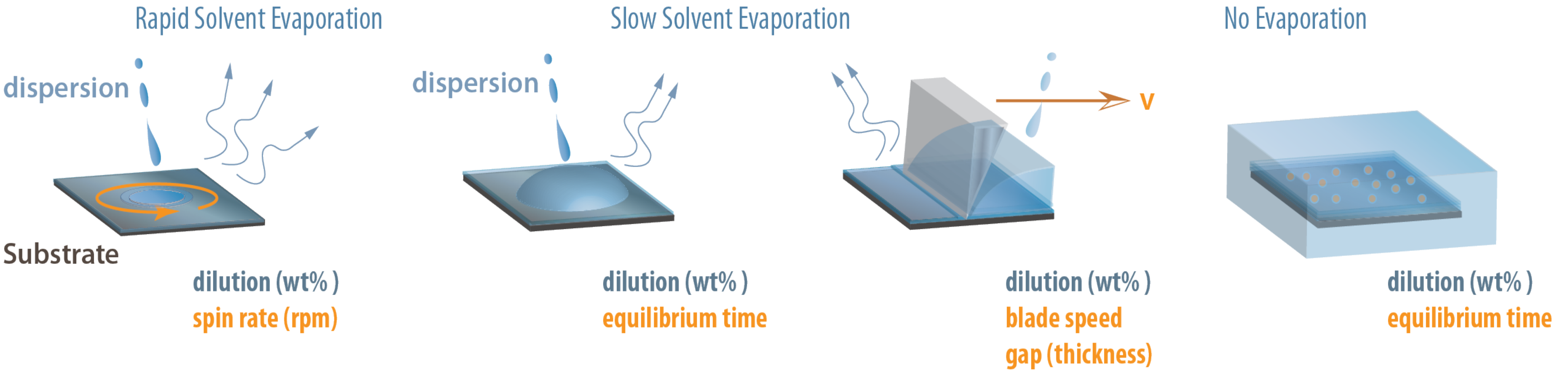
Forming a film upon evaporation of solution cast on a surface

Blade Coating

Film formation by uniformly distributing the solution

Self-Assembly

Adsorbtion of film on the substrate in an equilibrated ionomer solution



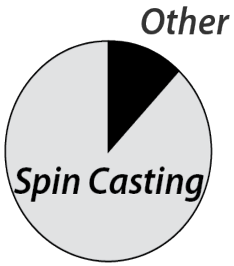
dilution (wt%)
spin rate (rpm)

dilution (wt%)
equilibrium time

dilution (wt%)
blade speed
gap (thickness)

dilution (wt%)
equilibrium time

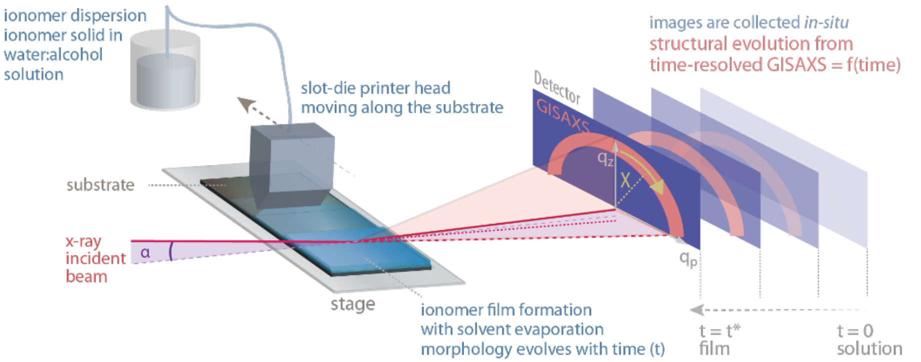
In PFSA Literature



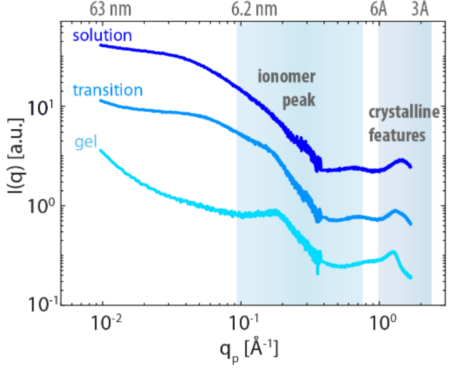
Morphology of Ionomer during Casting

- In-situ casting device implement at the ALS beamline 7.3.3. for grazing-incidence x-ray scattering (GIXS)
- Monitor films from dispersion to film state (on a substrate)
  - Solution and solid in single run
- Origins of film formation
  - Fundamental understanding
- Linkage to casting-ink studies and catalyst-ionomer film formation
- Evolution of the features: kinetics
  - Aggregates, gel behavior
  - Crystallinity, Phase-separation
  - Domain size and connectivity, anisotropy

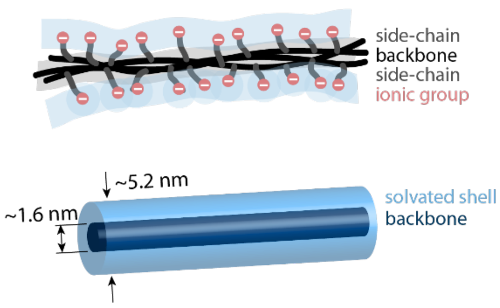
Schematics of *in-situ* GIXS technique for monitoring ionomer film morphology during casting

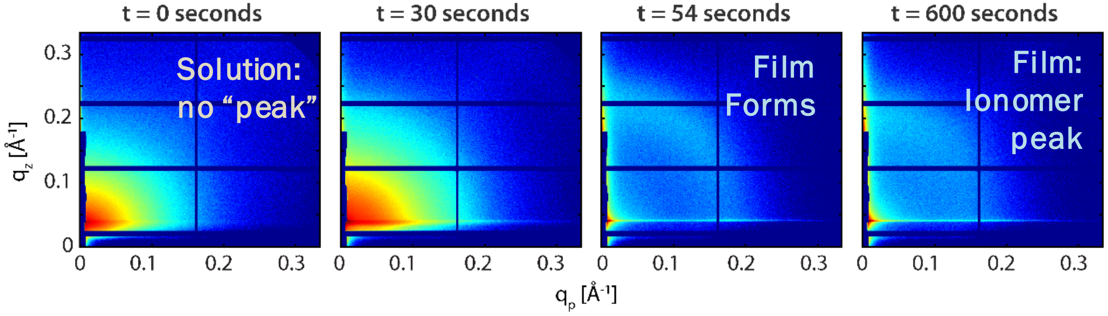


GIXS profiles at selected phases



Structural representation of ionomer aggregate





P. J. Dudenas and A. Kusoglu, *Macromolecules*, 52 (2019) 7779-7785

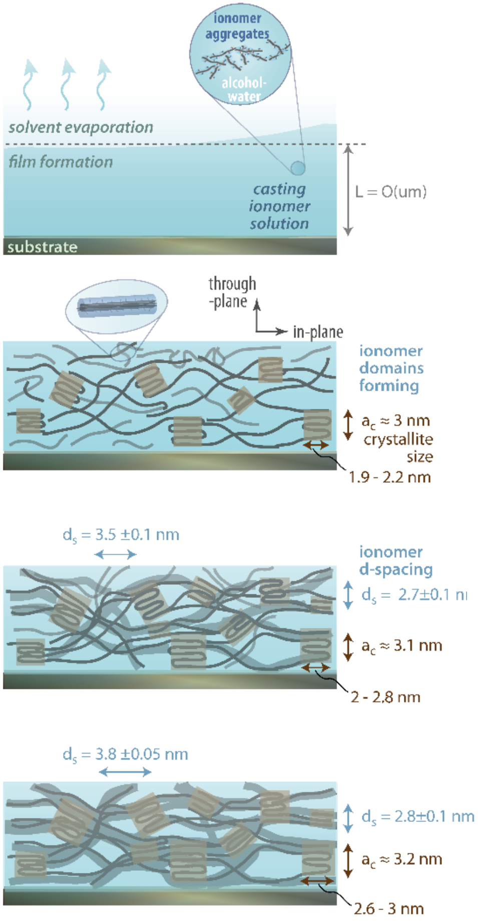
Structural Evolution (Stage I-IV)

Stage I
solution phase:
dispersion behavior
solvent evaporation begins
core-shell cylindrical aggregates

Stage II
sol-gel transition:
phase-separation begins
crystallization starts and increases rapidly with preferential anisotropy

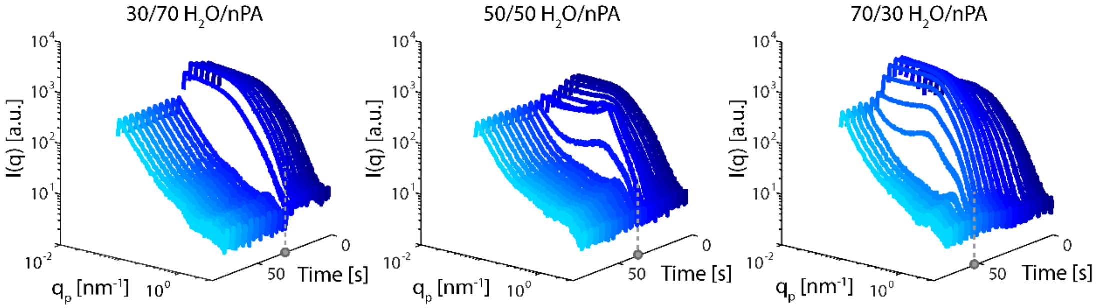
Stage III
gel phase & film formation:
domains grow & coalesce
enhanced phase-separation with increasing d-spacing
crystallite ripening

Stage IV
film drying:
phase-separation complete
d-spacing is decreasing (drying)
crystallite ripening continues



- Understanding of the stages of film formation
  - I. Solution
  - II. Sol-Gel transition and crystallization
  - III. Film formation and phase-separation
  - IV. Film drying and network formations

Morphological Evolution of Nafion ionomer film in solutions

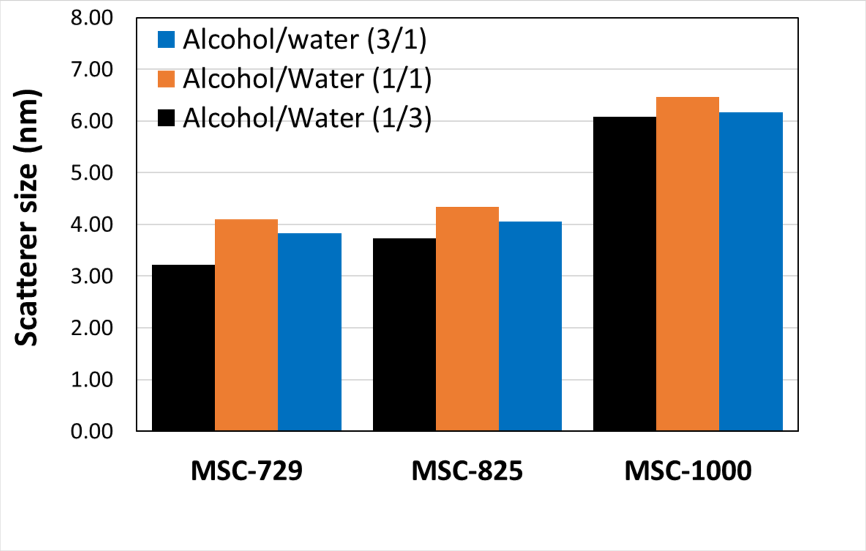


- Factors controlling ionomer film properties and functionality
  - A new avenue to control and alter film functionality
  - Effect of Solvent Composition on Film Structure

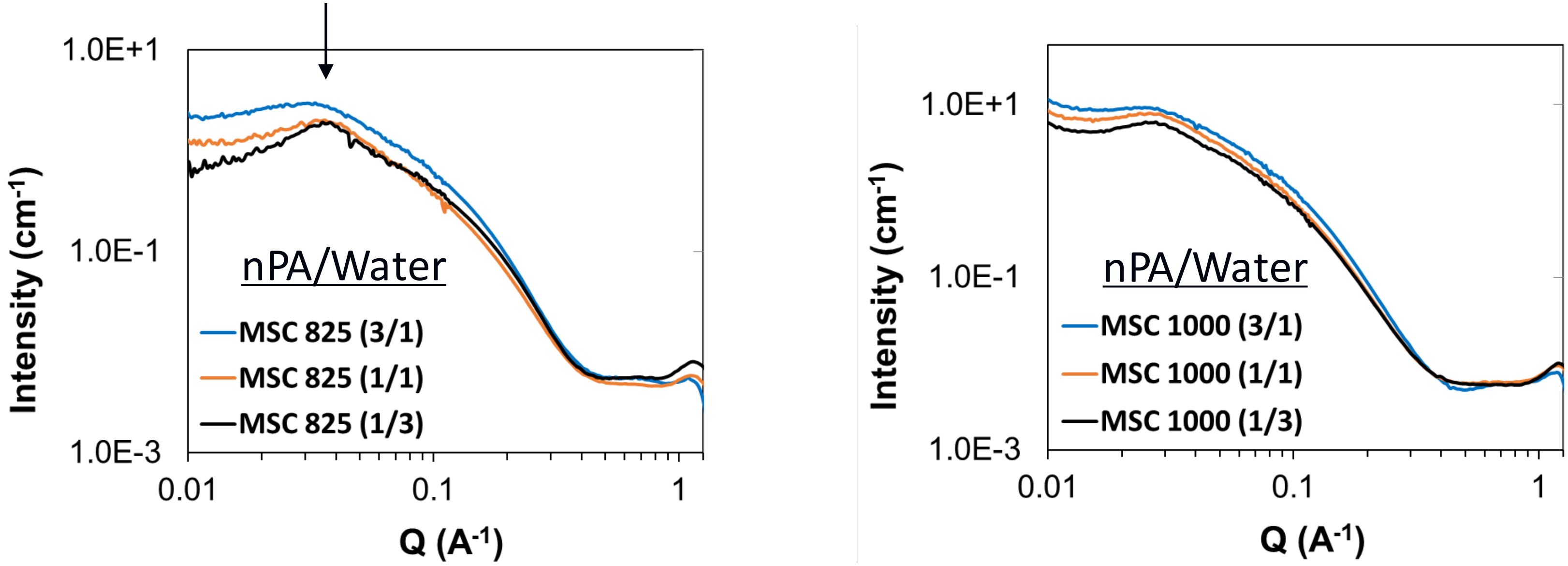
P. J. Dudenas and A. Kusoglu, *Macromolecules*, 52 (2019) 7779-7785

Effect of Solvent on Ionomer Structure

- Rod–like ionomer aggregates of 3-7 nm diameter in solvent mixtures
  - ✓ Large variation in diameter with EW
  - ✓ Slight variation with nPA:water
- Ordering of rod-like aggregates increases with increasing water content of ink
- 825 EW aggregates are more aligned/ordered than 1000 EW aggregates

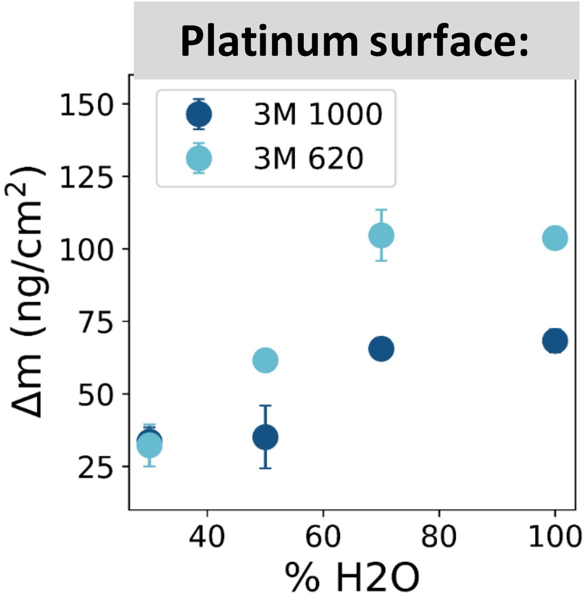


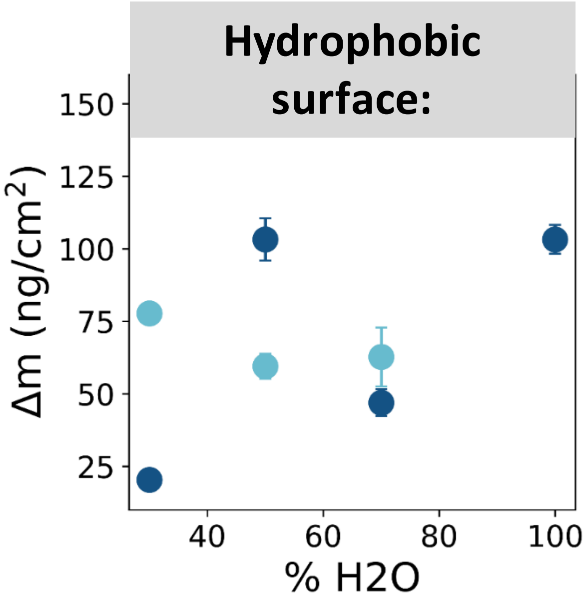
Ordering of rod-like ionomer aggregates

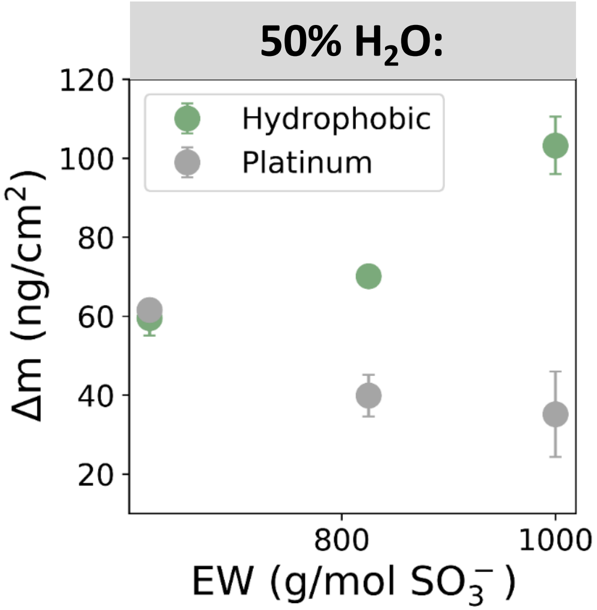


Probing Fundamental Interactions in Inks

- Quartz Crystal Microbalance (QCM) – adsorption dynamics on model surfaces


Platinum surface:

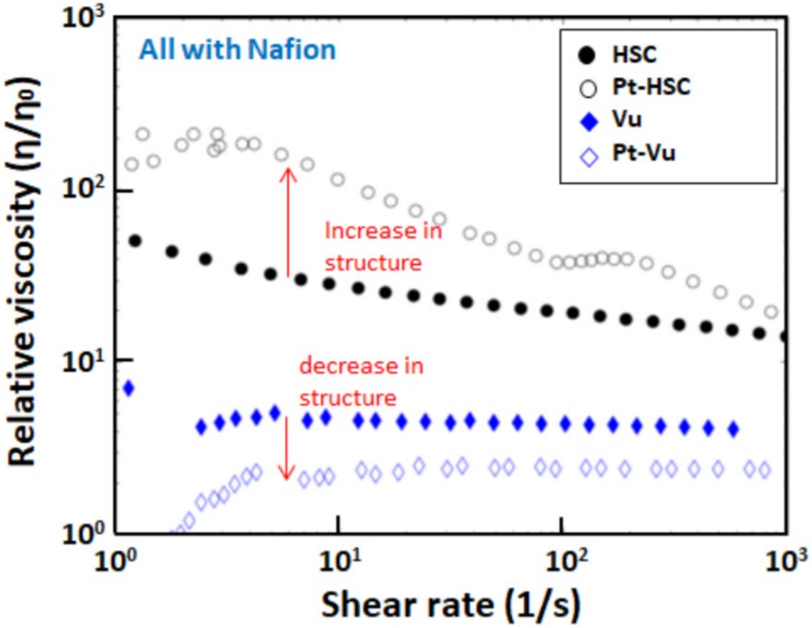

Hydrophobic surface:


50% H_2O:

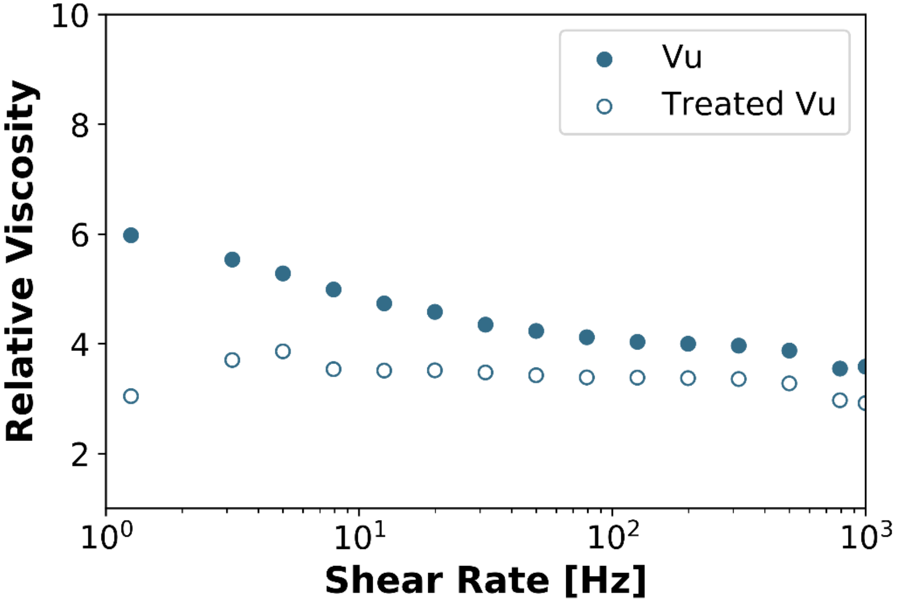
Adsorption **strongly affected** by solvent choice and EW

Higher EW more sensitive to surface type

Carbon Support Effect on Catalyst-Ionomer Ink Rheology

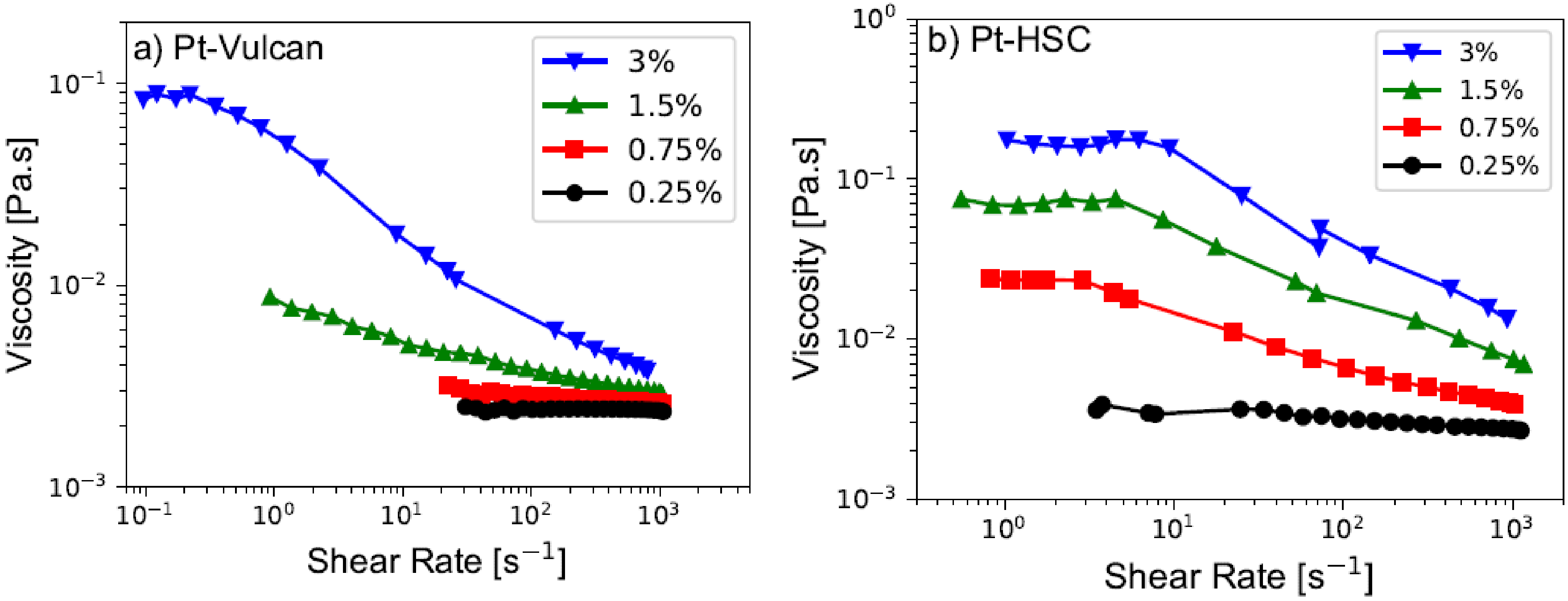


NREL AMO AMR 2017



- Treated carbon with similar platinum treatment process
- Similar viscosity shift (though smaller)
  - Currently testing with QCM

Catalyst-Ionomer Ink Rheology



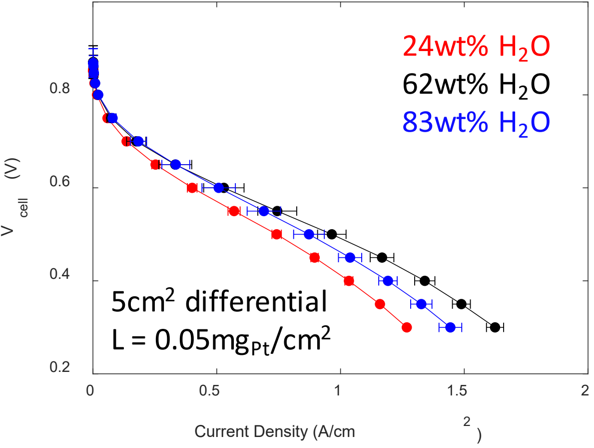
Khandavalli et al. ACS Appl. Mater. Interfaces. 10 (2018) 43610–43622

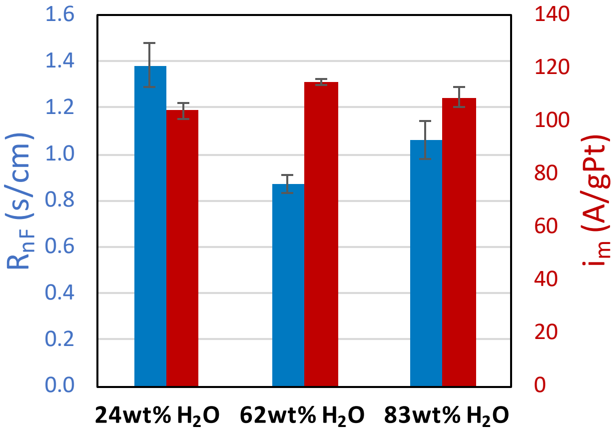
- Pt-HSC tend to have more shear thinning behavior – more structure in solution

Cell Testing

Ink Solvent Effects on Pt/Vu CCMs

H_2/Air, 80°C, 150kPa, 75%RH





Electrode Fabrication Details

50wt% Pt/Vu (TKK) catalyst

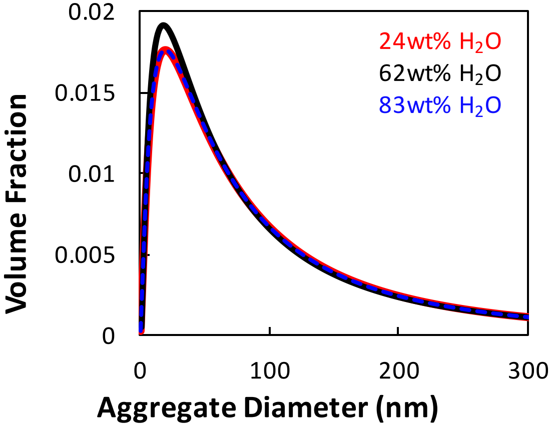
3 different H_2O:nPA ink ratios

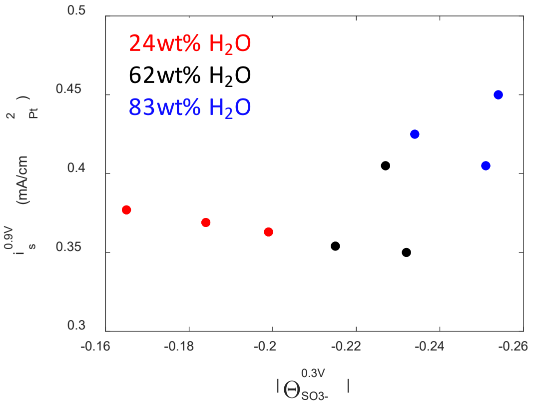
D2020 Ionomer (I:C 0.6)

Ultrasonic sprayed CCMs on Nafion 211

Conditioned with 3 VR cycles

USAXS





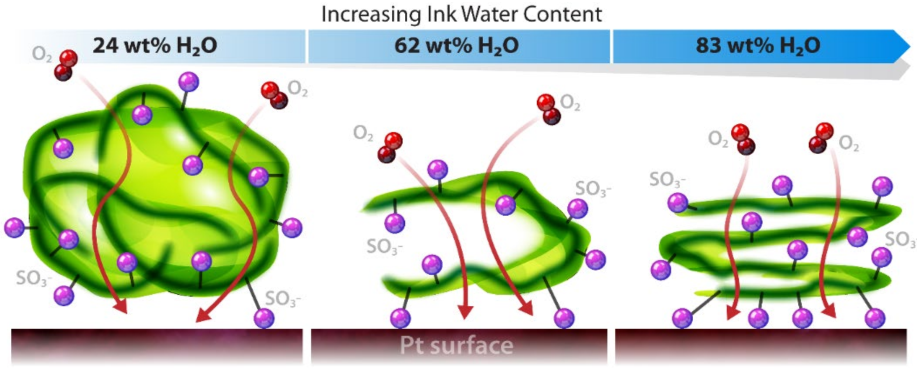
- Ink content mainly affects O_2 transport
- Insignificant effect on mass activity
- Similarly sized catalyst aggregates
  - Aggregation does not explain effect
- Specific Activity does not strongly depend on sulfonate coverage $(\Theta_{SO_3^-})$
  - No evidence of site blocking

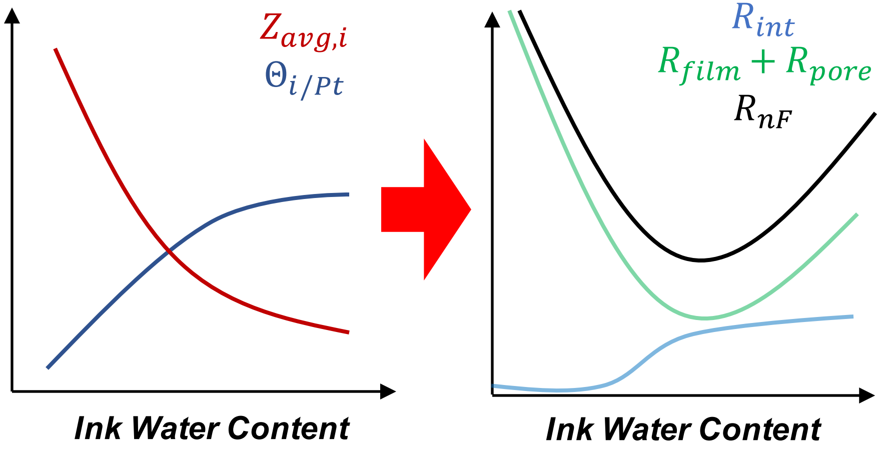
How does ink formulation (H_2O:nPA ratio) affect ionomer distribution in and its interactions with catalyst particles?

T. Van Cleve *et al. ACS Appl. Mater. Interfaces* 2019, 11, 50, 46953-46964

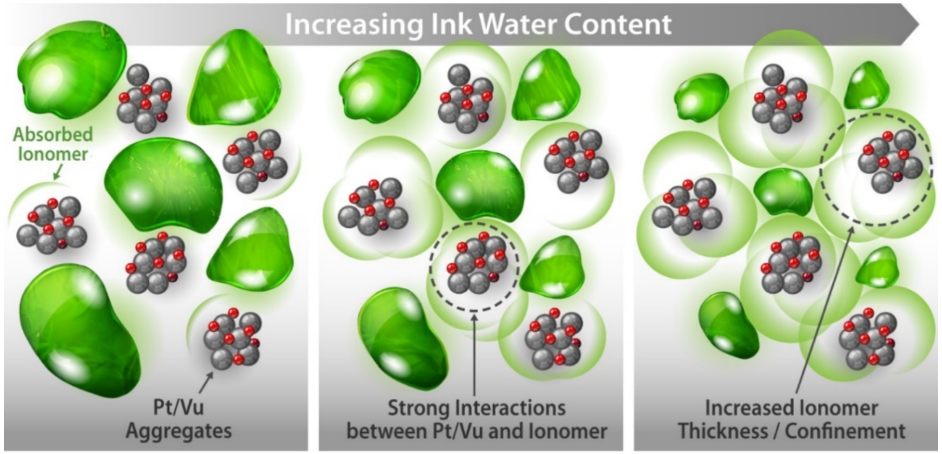
Understanding Solvent Effects on Pt/Vu Electrode Structure and Performance

Catalyst/Ionomer Interface





Electrode Microstructure

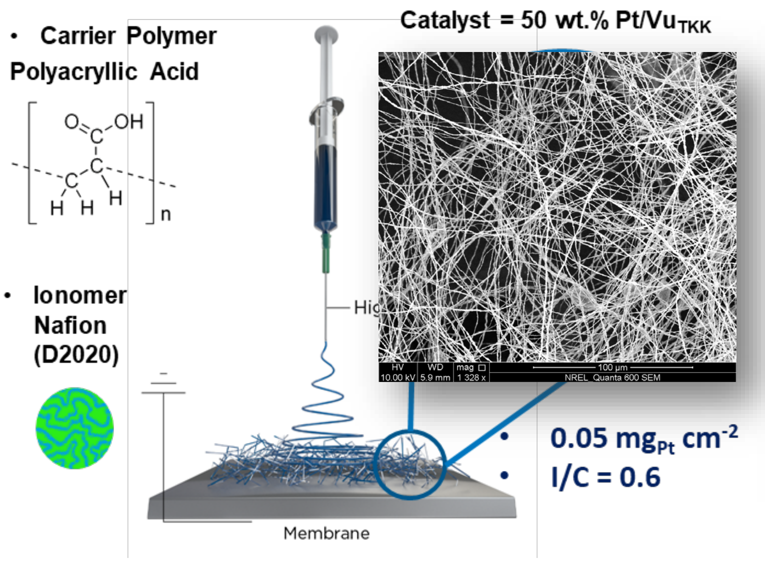


General Trends with Increasing wt% H_2O

- Ionomer coverage on Pt increases (EC)
- Ionomer aggregation decreases (DLS)
- Complex O_2 transport balances microscale (ionomer break-up) and nanoscale (Pt / ionomer interface and orientation) phenomena

T. Van Cleve *et al. ACS Appl. Mater. Interfaces* 2019, 11, 50, 46953-46964

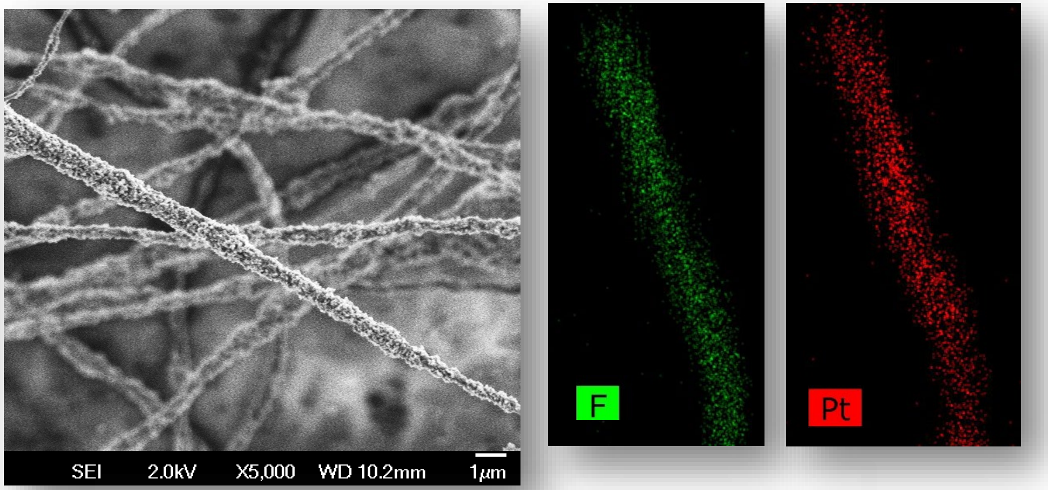
Fabrication Method and Electrode Structure (Electrospinning)

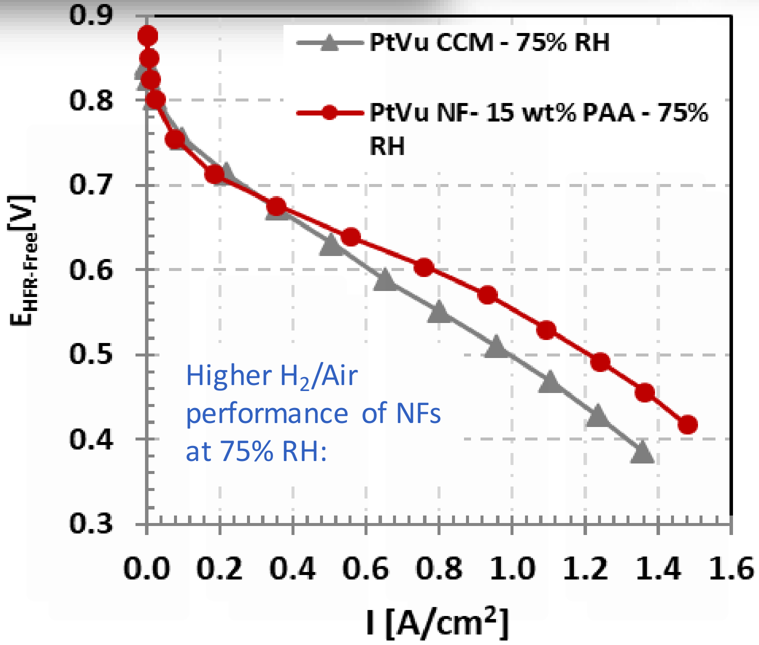


- **Carrier Polymer Polyacryllic Acid**
- **Ionomer Nafion (D2020)**

Catalyst = 50 wt.% Pt/Vu$_{TKK}$

- **0.05 mg$_{Pt}$ cm^{-2}**
- **I/C = 0.6**





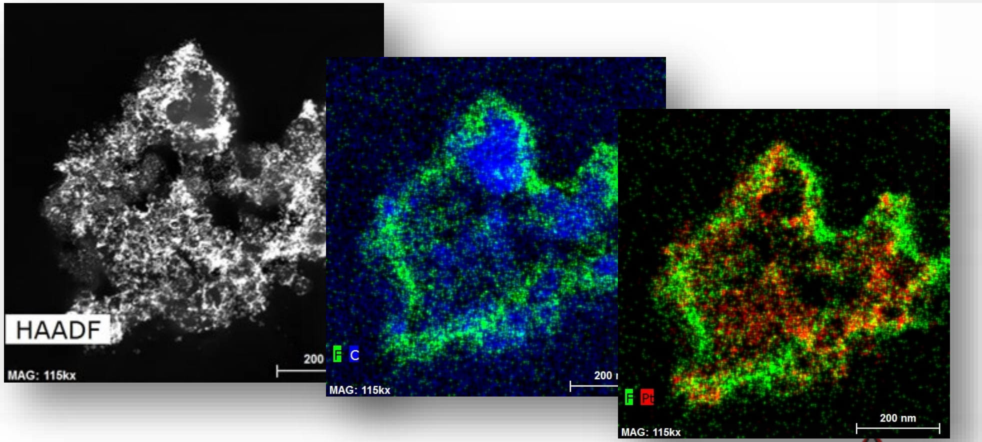
Higher H_2/Air performance of NFs at 75% RH:

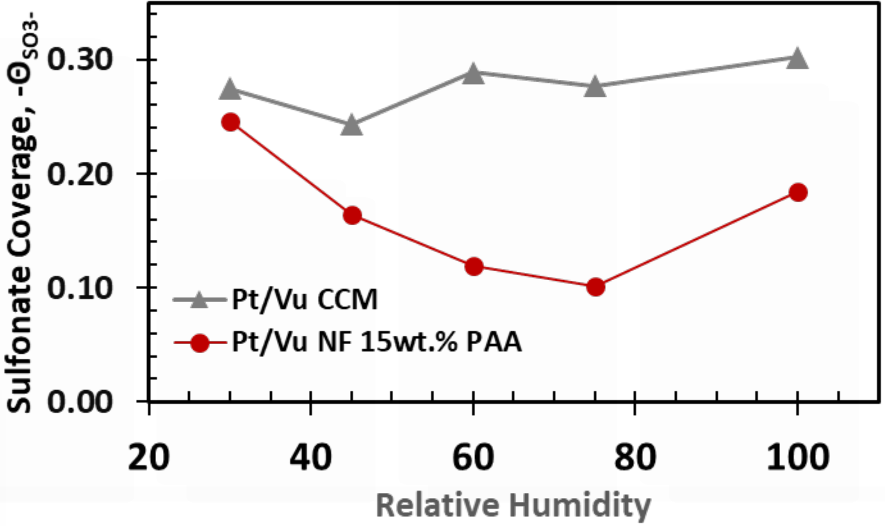
Complementary in-situ and ex-situ approaches are needed to understand materials and process improvements: Extend our current understanding and utilization of various ex situ microscopic characterization and in situ electrochemical diagnostic techniques towards studying and optimizing new electrode designs

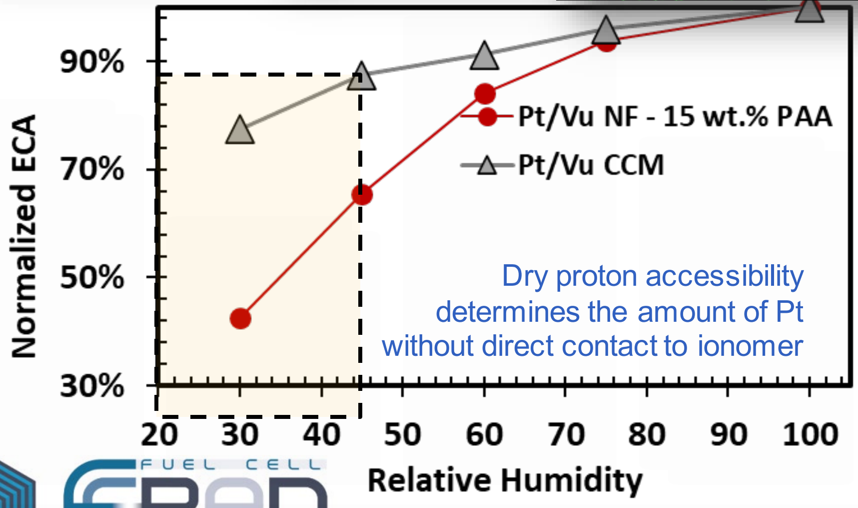
Fabrication Method and Electrode Structure (Electrospinning)

- Fabrication method can aid in altering interactions and properties

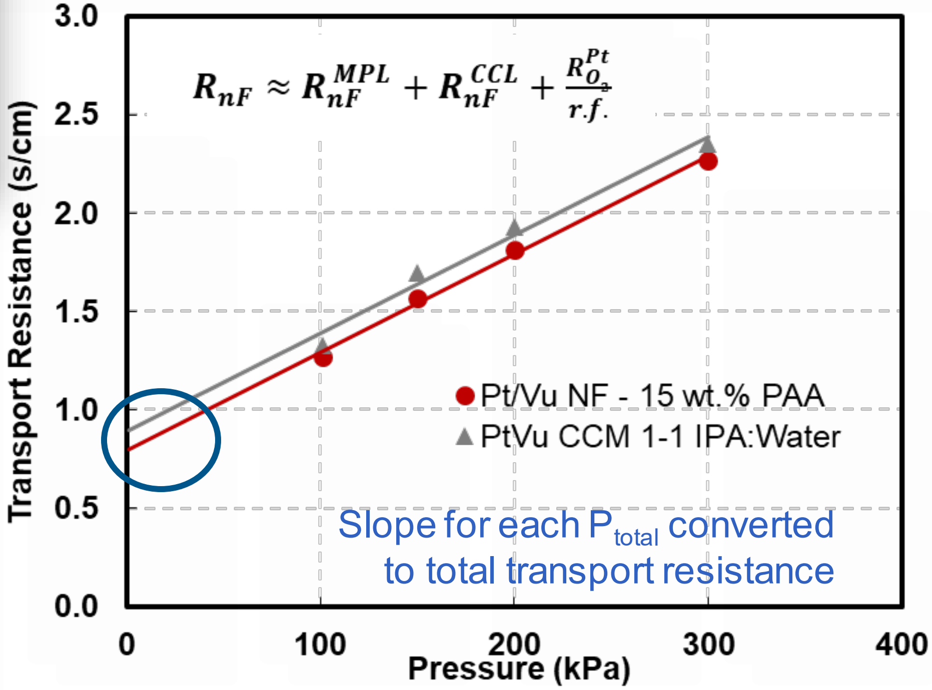
Combined approach needed for understanding Ionomer coverage and proton accessibility of the Platinum active sites in nanofibers and other electrode structures.







Dry proton accessibility determines the amount of Pt without direct contact to ionomer



Slope for each P_{total} converted to total transport resistance

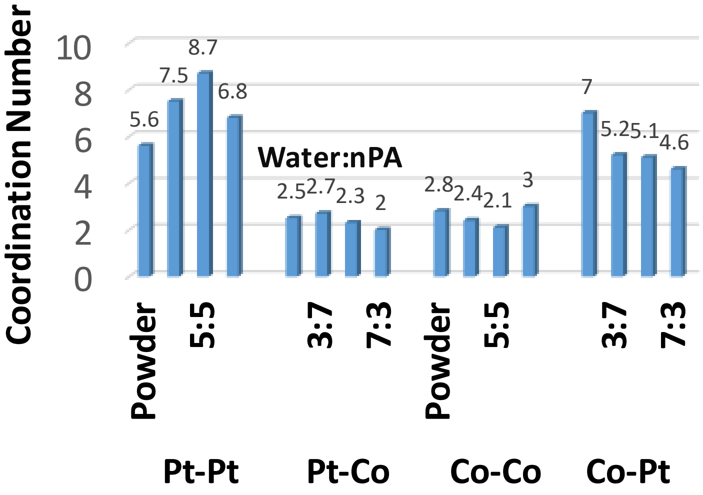
Sample Matrix – I/C and Solvent Effect

Catalyst	Ionomer Type	I/C	Ink Solvent nPA:Water	Form/ Characterization
30 wt% Pt/HSC	3M 825 EW	0.7	5:5	Ink/USAXS
30 wt% Pt/HSC	PFSA 1000	0.7 0.9 1.2	7:3 , 3:7 5:5 7:3, 5:5, 3:7	Ink/USAXS
46.7 wt% Pt/Vulcan TEC10V50E	PFSA 1000	0.6	8:2, 3:4, 2:8	Electrodes before and after pol curves/USAXS
30 wt% PtCo/HSC	3M 825 EW	0.7	7:3, 5:5, 3:7	Ink/USAXS and XAFS
30 wt% PtCo/HSC	PFSA 1000	0.7 **0.9** 1.2	7:3 **7:3, 5:5, 3:7** 7:3, 5:5, 3:7	Ink/USAXS Electrodes/USAXS, XAFS, nano-CT
16.4 wt% PtNi/HSC (ANL)	PFSA 1000	0.9	7:3. 5:5, 3:7, 4:6, 2:8	Ink/USAXS
14.4 wt% PtNi/Vulcan (ANL)	PFSA 1000	0.9	7:3. 5:5, 3:7, 4:6, 2:8	Ink/USAXS

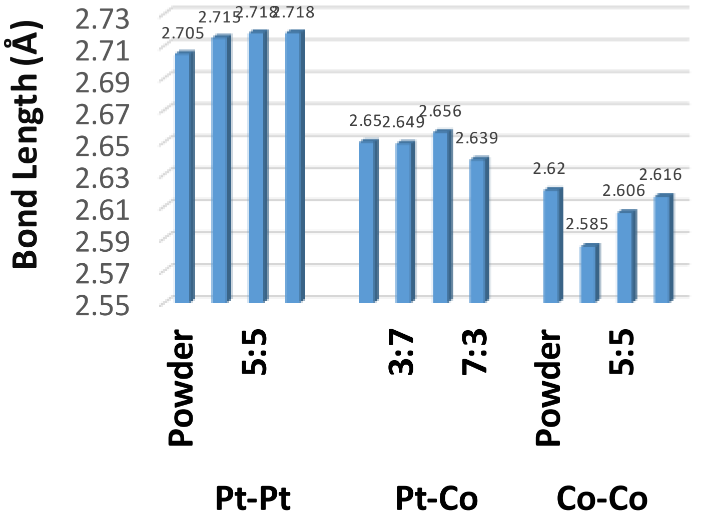
PtNi/HSC and PtNi/Vulcan provided by V. Stamenkovic, FC140

Effect of Ionomer Type on PtCo Structure

3M 825 EW

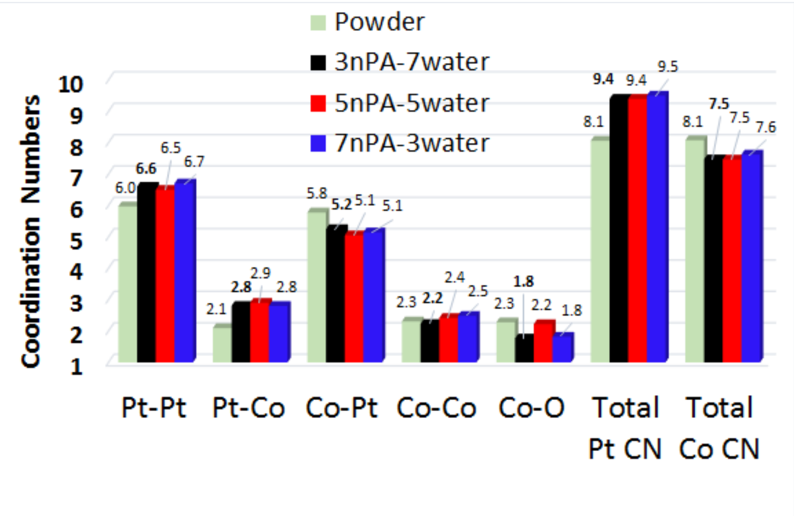


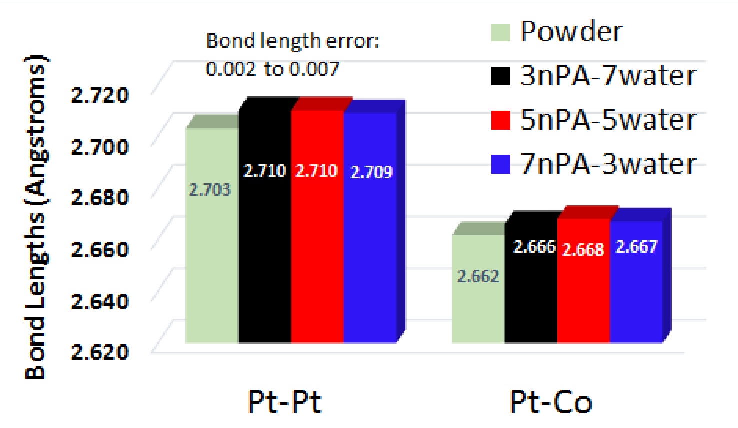
Pt-Pt bond length in Pt catalyst: 2.758Å



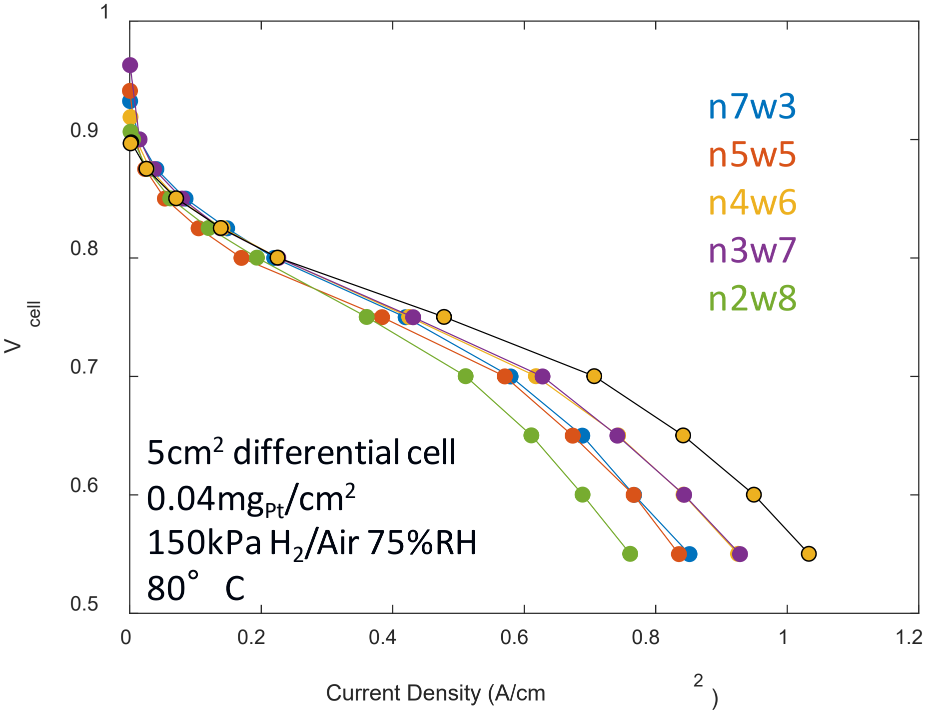
- Number of Pt-Pt bonds and Pt-Pt bond length increases from powders to inks indicative of loss of Co from particles
- **3M 825 EW Ionomer: Co leaching increases with increasing water content in inks**
- **3M 825 EW ionomer causes more Co leaching than PFSA 1000 EW ionomer and more loss of Pt-Pt contraction**

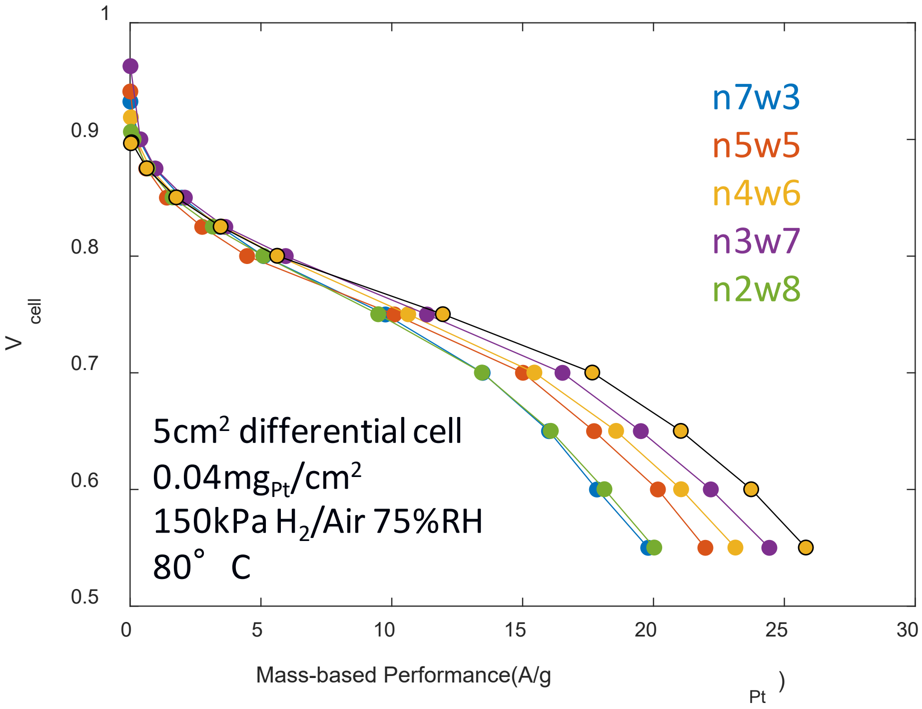
PFSA 1000 EW




Bond length error: 0.002 to 0.007

Solvent Ratio Impact on PtCo/HSC Performance

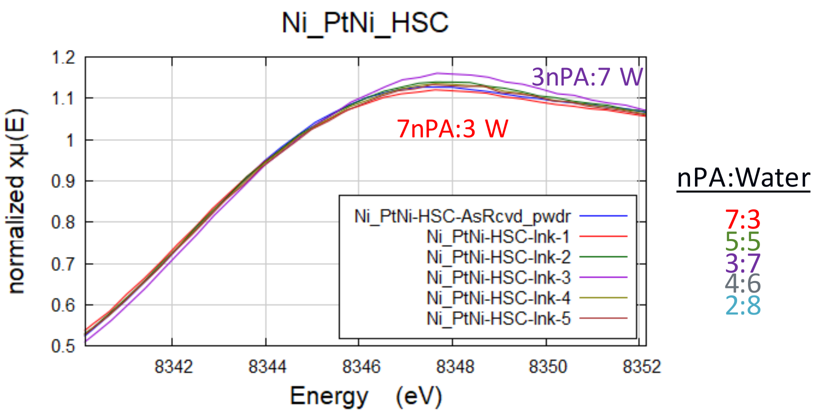


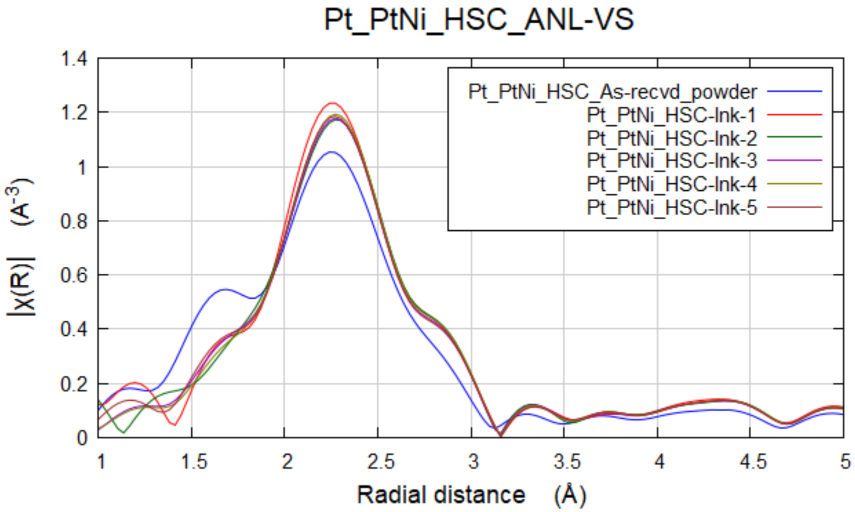


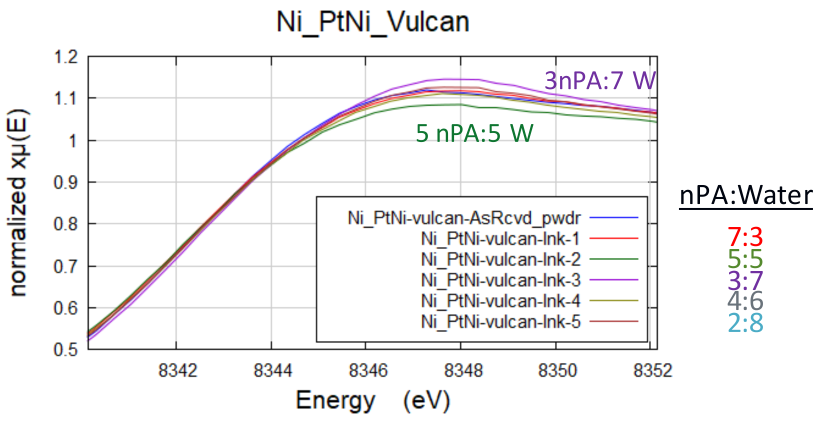
- Similar dependence on ink content for PtCo/HSC and Pt/Vu

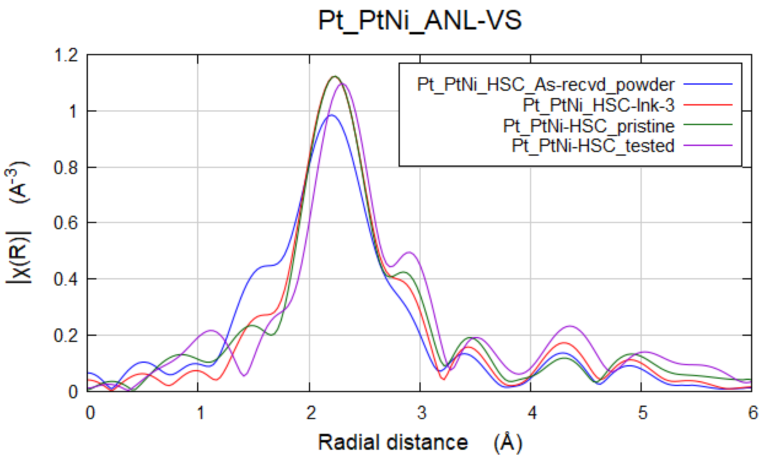
Place holder

Effect of Ink Solvent on PtNi







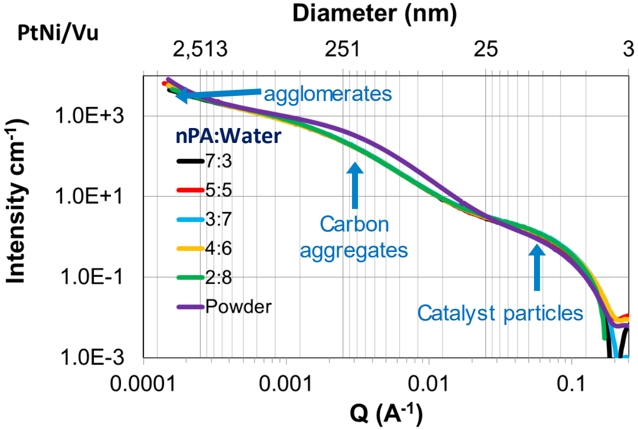


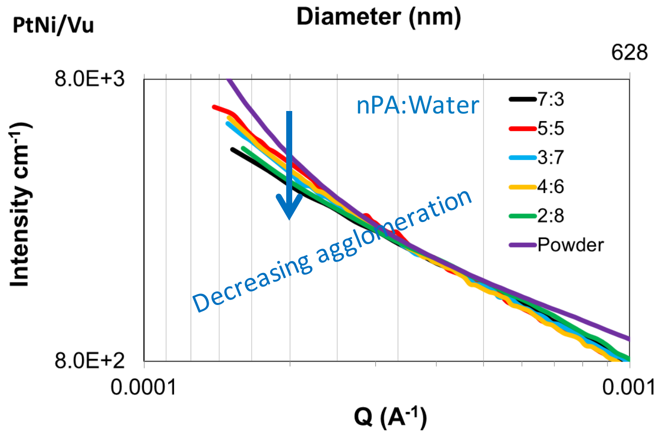
Highest extent of Ni leaching into ink observed for 3 nPA:7 Water

Effect of Solvent on Agglomerate Break-up: ANL-PtNi, HSC vs Vulcan

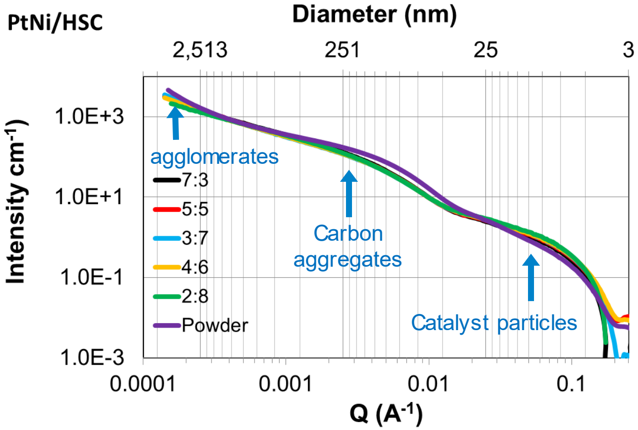
PtNi/Vu and PtNi/HSC, I/C =0.9

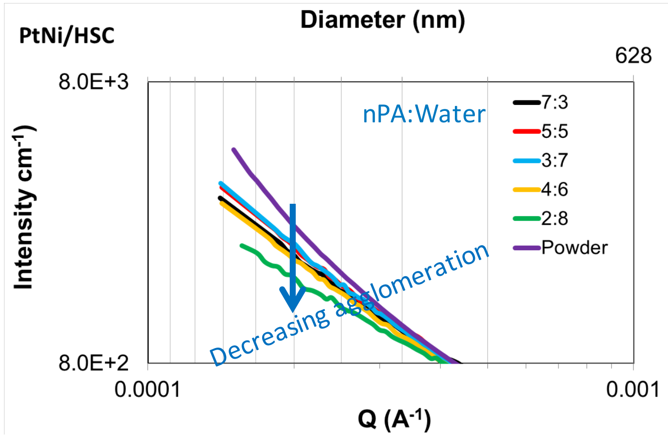
ANL_PtNi/Vu





ANL_PtNi/HSC

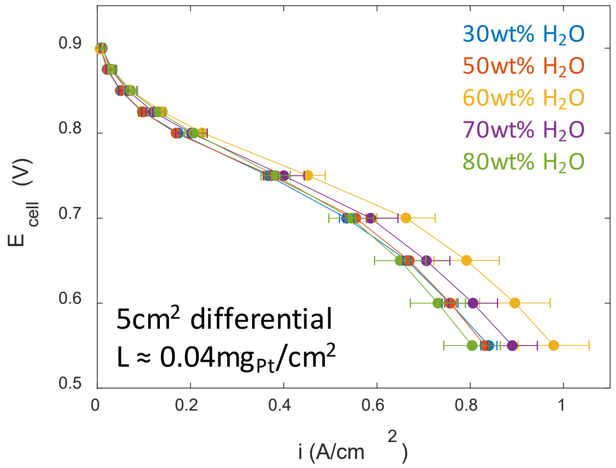




- Aggregate scattering not influenced by type of solvent
- General trend: Better break-up of carbon agglomerates with **increasing water content in the inks (HSC and Vulcan)**
- **Opposite of solvent effect seen for Pt/C**

Ink Solvent Effects on PtCo/HSC CCMs

H_2/Air, 80°C, 150kPa, 75%RH



- Same performance trends observed on Pt/Vu and PtCo/HSC
- Best O_2 transport for 60 and 70wt% water CCMs

Electrode Fabrication Details

30wt% PtCoHSC (Umicore) catalyst

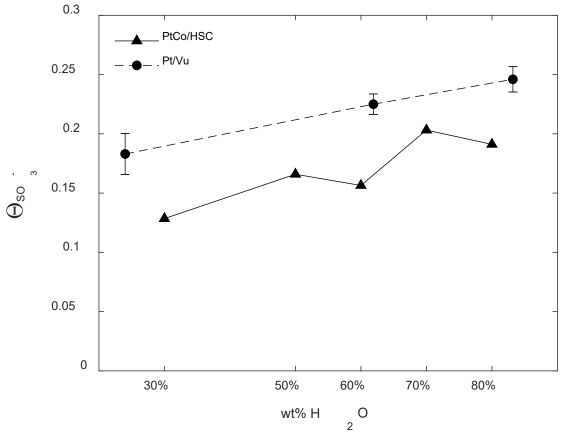
5 different H_2O:nPA ink ratios

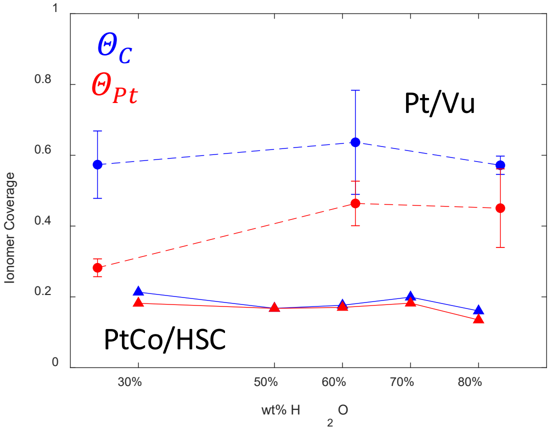
D2020 Ionomer (I:C 0.9)

Ultrasonic sprayed CCMs on Naf 211

Conditioned with 5 VR cycles

Catalyst/Ionomer Interface

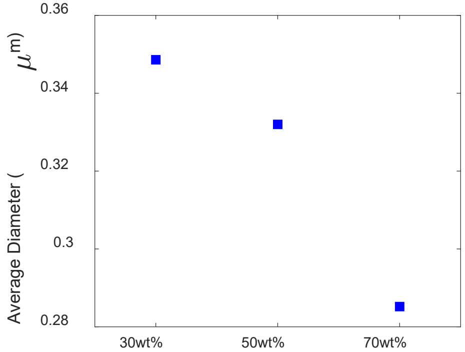


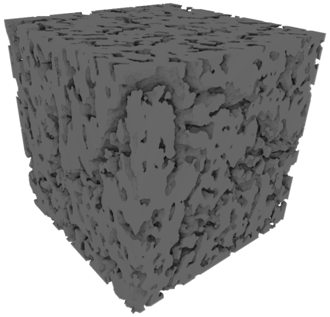


Less catalyst/ionomer interactions on HSC supports

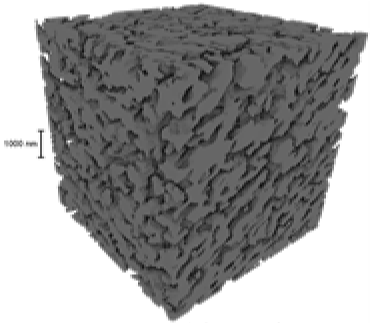
Weaker influence solvents on these interfaces

Electrode Microstructure





30wt% H_2O



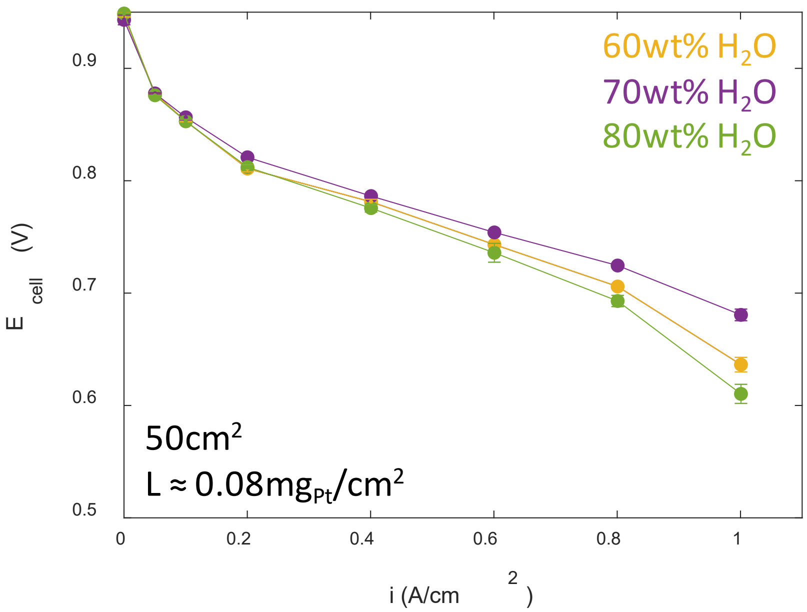
70wt% H_2O

Smaller agglomerates present for water-rich electrodes

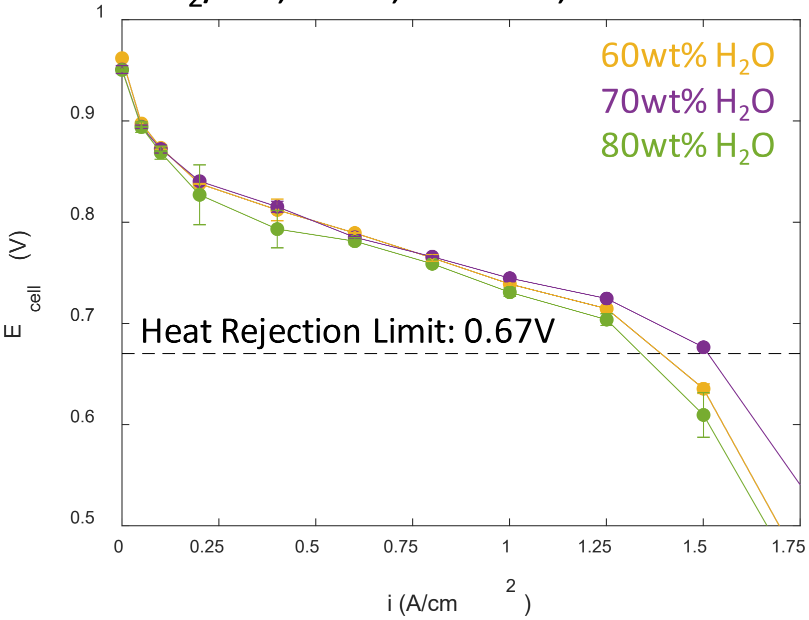
Significance difference in electrode microstructures on HSC supports

$50cm^2$ MEA Performance with Optimized Cell Configuration

H_2/Air, 80°C, 150kPa, 100%RH



H_2/Air, 94°C, 250kPa, 65%RH



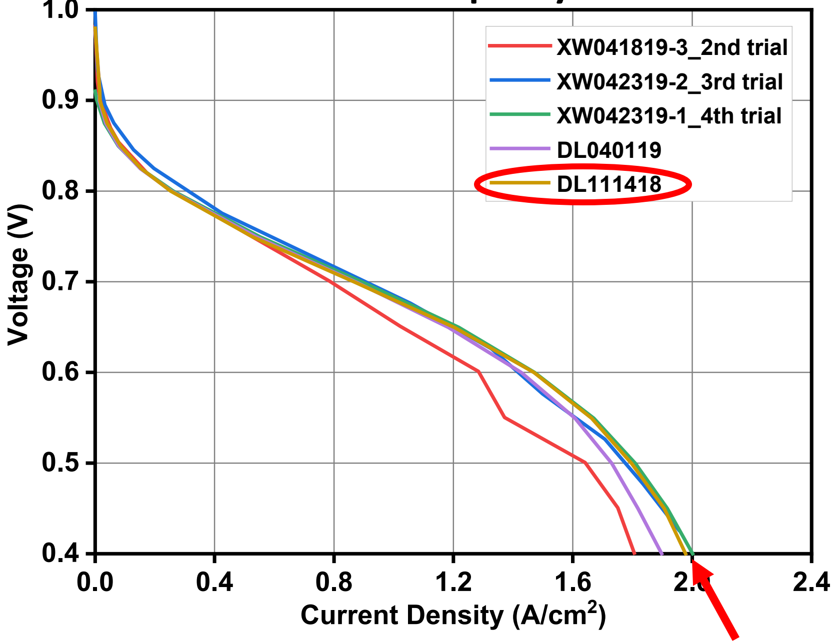
2020 DOE Targets	**Units**	**Target**	**60wt%**	**70wt%**	**80wt%**
Mass Activity at $0.9V_{iR\text{-free}}$ (anodic/cationic scan)	A/mg_{PGM}	**0.44**	1.186 1.008*	1.164 0.989*	1.020 0.867*
Current Density at 0.8V	A/cm^2	**0.3**	0.27	0.32	0.27
Power at 0.67 V, 250 kPa_{abs}	W/cm^2	**1**	0.93	1.02	0.90
PGM Loading	mg/cm^2	**0.125**	0.11	0.11	0.11

Possible to exceed DOE targets with industrially available catalysts by only modifying ink formulation

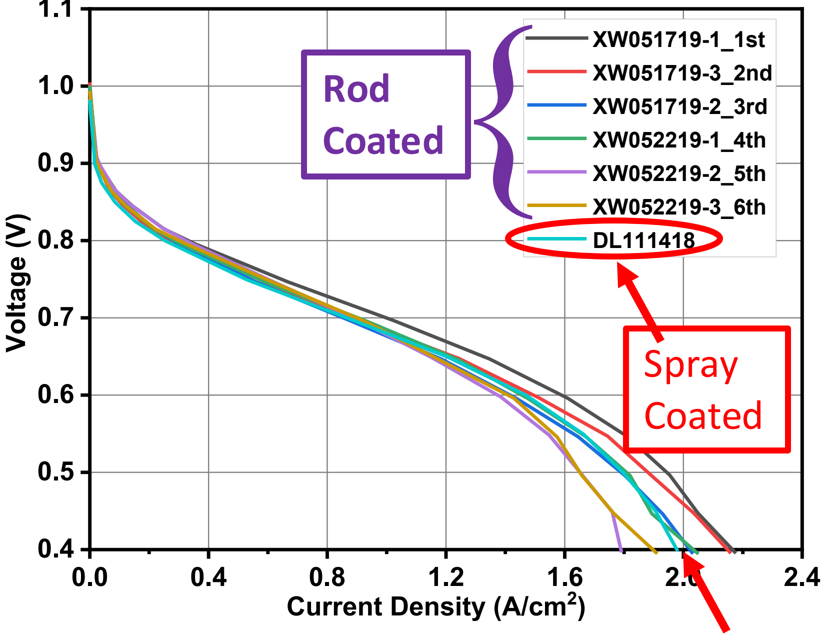
Impact of Fabrication

Electrodes: Sprayed versus Rod-coated (TEC10E20E)

Cathode sprayed



Rod-coated using IPA



Rod-coating comparable performance to **sprayed CCM**

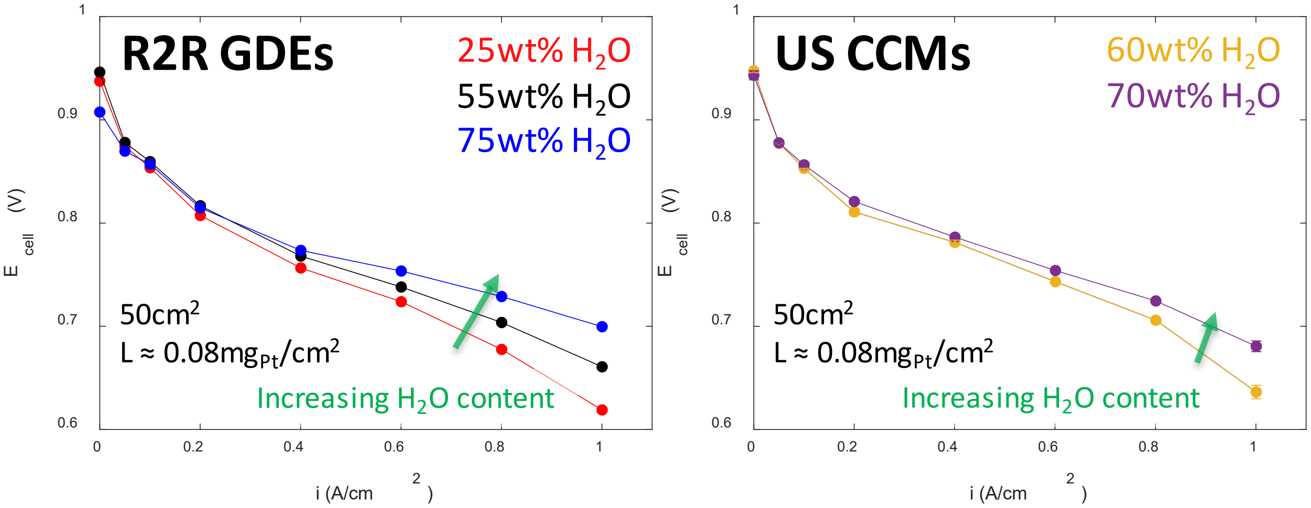
- IPA/water ratio matters:
  - At same IPA/water ratio, diluted ink shows similar performance
- NPA and IPA are equivalent in terms of performance

Rod method/Ink by:
Applied Catalysis B: Environmental
Volume 56, Issues 1–2, 2005, 9-35

	Pt loading (mg/cm^2)	ECSA (m^2/g) HUPD	MA (A/mg)	HFR (Ω)
DL111418	0.0955	78.30	0.557	0.012
XW051719-1_1st	0.1080	81.25	0.614	0.012

Ink Solvent Effects on PtCo/HSC R2R GDEs

H_2/Air, 80°C, 150kPa, 100%RH



Roll-to-Roll GDE Fabrication

30wt% PtCo/HSC (Umicore)

3 different H_2O:nPA ink ratios

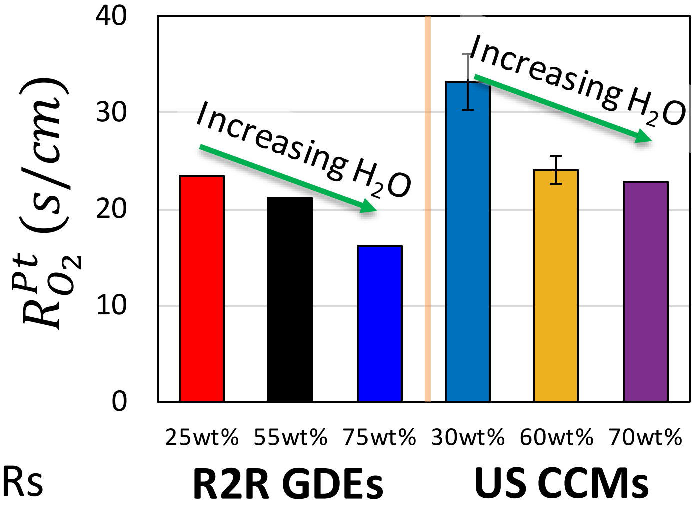
D2020 Ionomer (I:C 0.9)

Slot-die coated on H23C8 GDL

Hot-pressed on Nafion 211

Same anodes as ultrasonic spray CCMs (50wt% Pt/HSC with 0.1mgPt/cm2 loading, I:C 0.9)

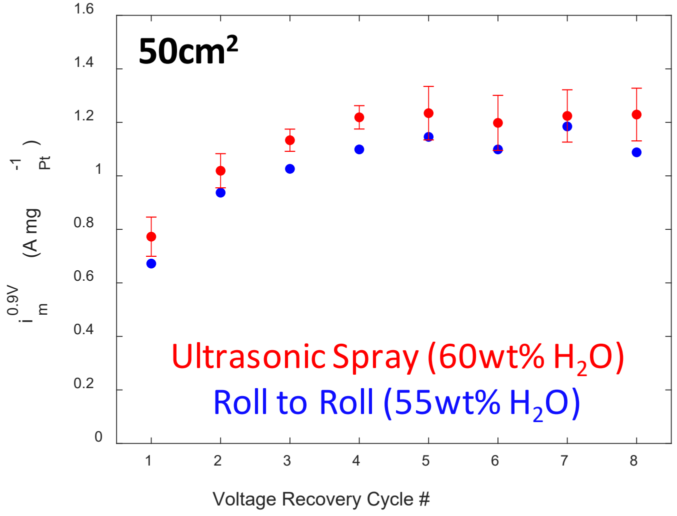
75%RH
after 4 VRs



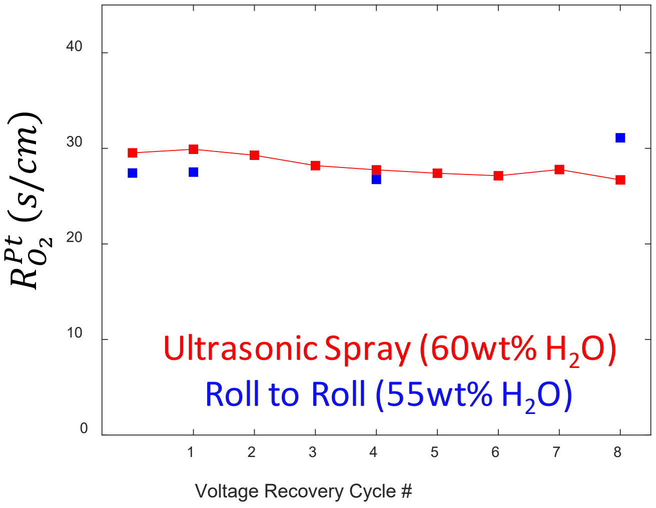
- Both R2R GDEs and US CCMs show better H_2/Air performance for water-rich inks compared to nPA-rich inks
- Performance improvements correspond with lower local O_2 transport resistances ($R_{O_2}^{Pt}$) for water-rich formulations

Effect of Conditioning on R2R PtCo/HSC Performance

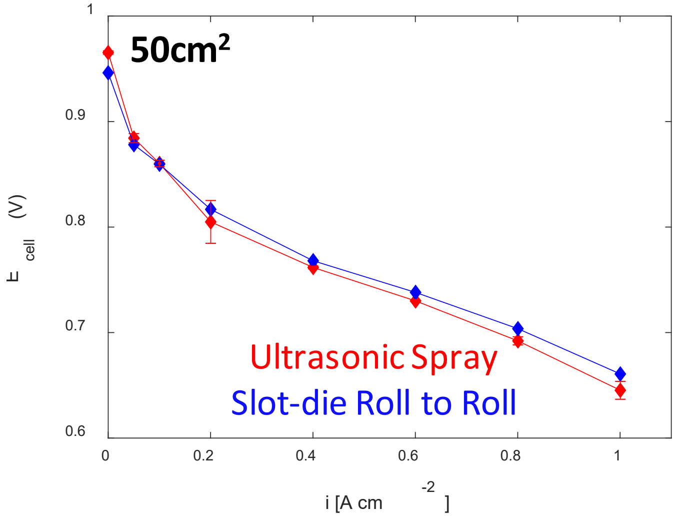
H_2/O_2, 80°C, 150kPa, 100%RH



80°C, 75%RH



H_2/Air, 80°C, 150kPa, 100%RH



- 55wt% H_2O R2R GDEs exhibits similar performance and conditioning trends compared with prior work on 60wt% H_2O sprayed CCMs[1,2]
- Peak activity achieved after 5 VR cycles without affecting R_{O_2}
- For these formulations, electrode fabrication has little effect on mass activity, O_2 transport, and H_2/Air Performance

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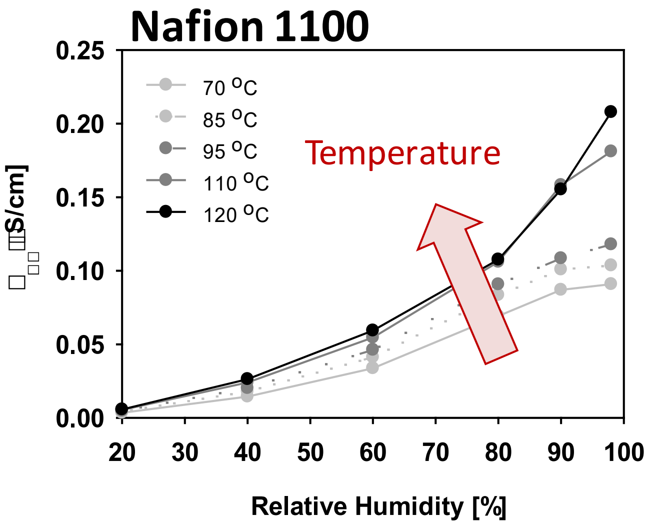
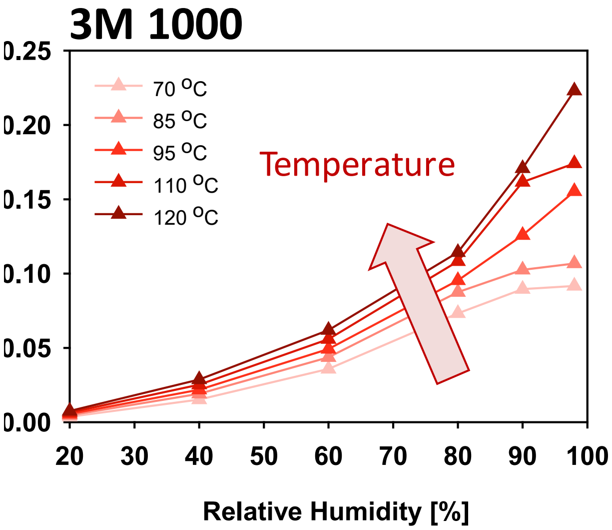
[1] *S. Kabir et al. ACS Appl. Mater. Interfaces* 2019, 11, 48, 45016-45030

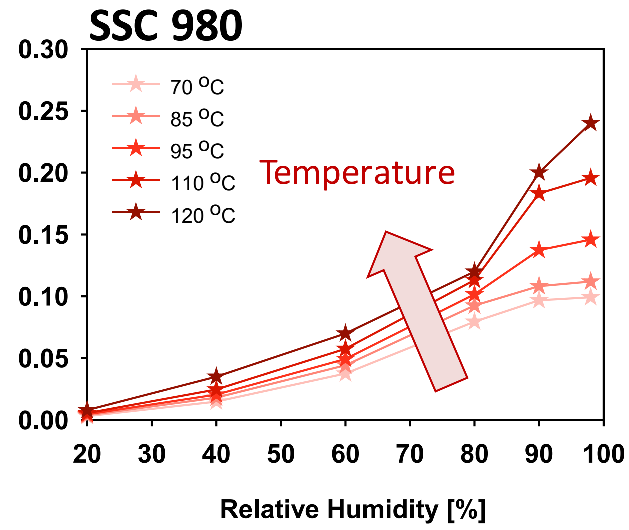
[2] *T. Van Cleve et al PtCo Ink Series [manuscript in preparation]*

Membrane and Ionomer Characterization

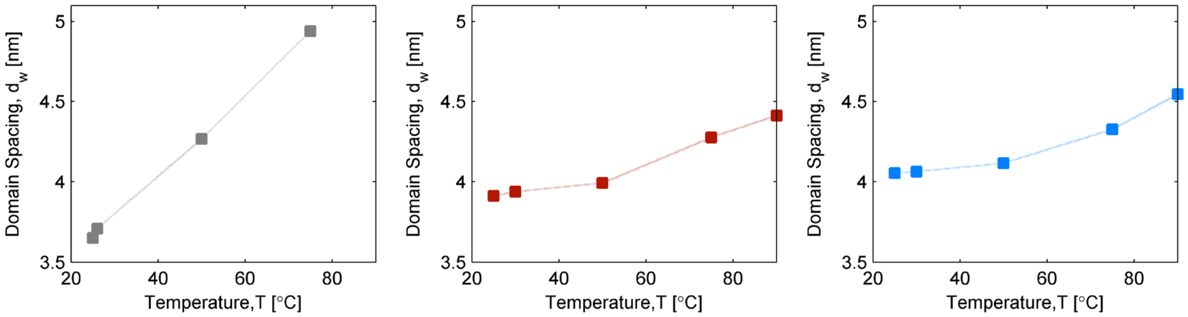
High-Temperature Conductivity of PFSAs

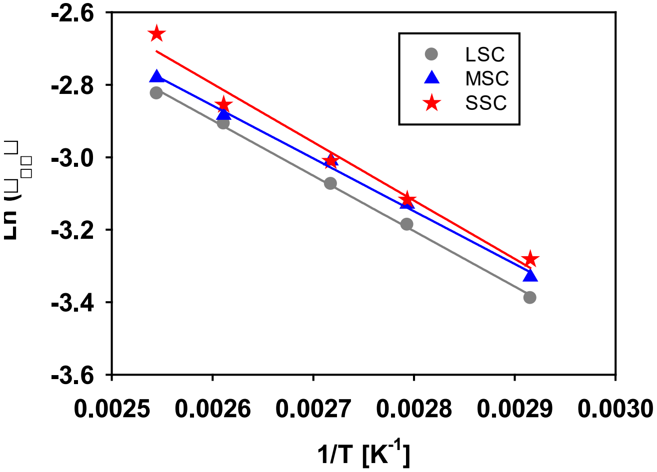






- Proton conductivity and d-spacing increase with temperature



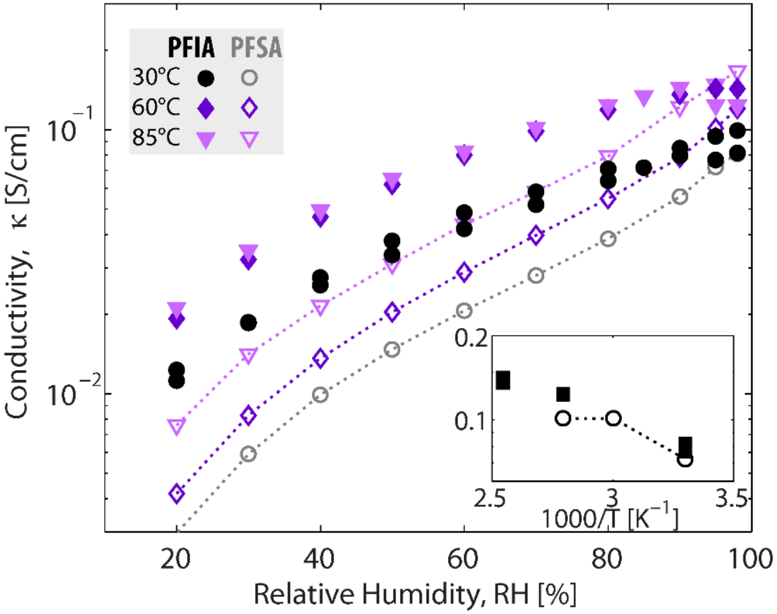


- Membrane nanostructure in water during heating
  - Side-chain affects the nano-domain swelling

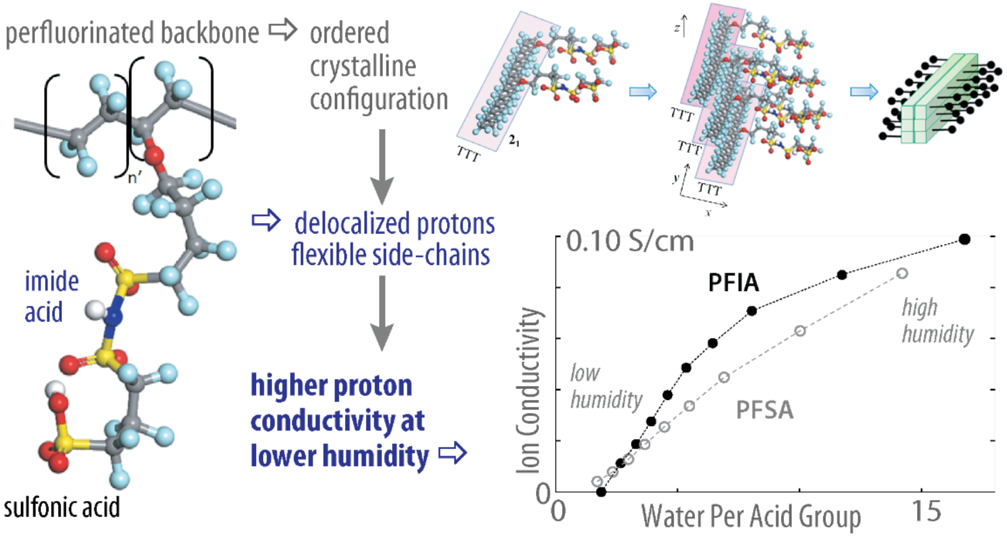
Similar activation energies:
Minor dependence on side-chain

Multi-acid side-chain PFIA: Structure-Transport

- Structural origins if transport in PFIA
  - perfluorosulfonic imide side chain
  - Increasing IEC for the same backbone
  - backbone of the polymer froms into an unusually highly ordered more crystalline configuration, giving rise to both inter- and intraside chain interactions
- Higher conductivity at low RH
  - Even at the same water content
  - Better high-Temp conductivity
- Presence of a different mechanism
  - Help formation of H-bonded network
  - higher proton conductivity at lower RH conditions owing to dynamic changes in its local molecular environment and more flexible side chains with better-dispersed, smaller water clusters forming the hydrophilic domains



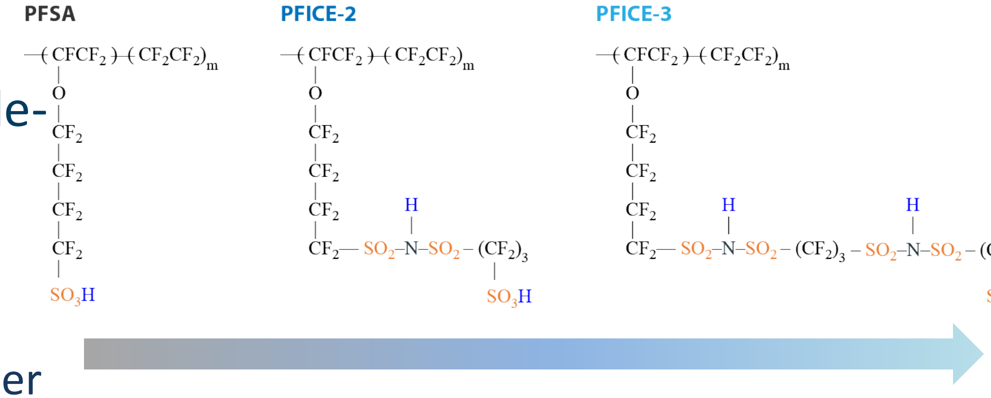
Perflourosulfonic Imide Acid side chain (PFIA) ionomer

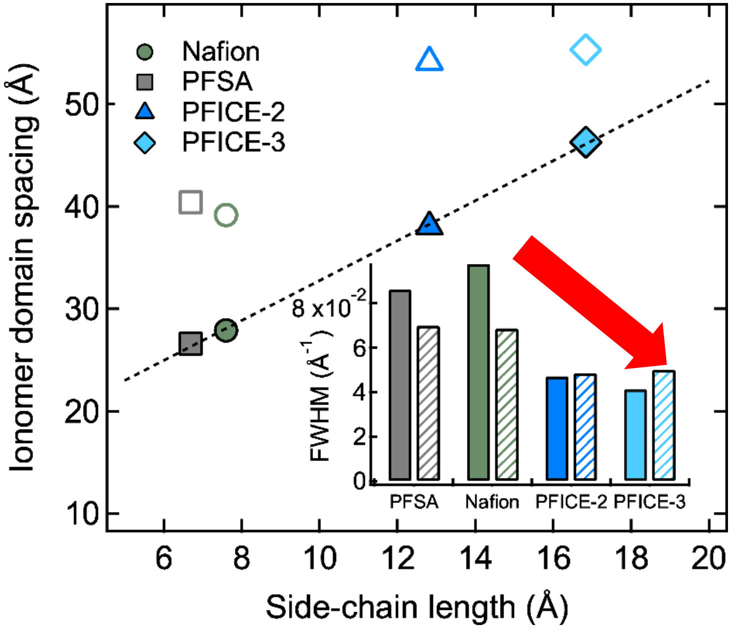


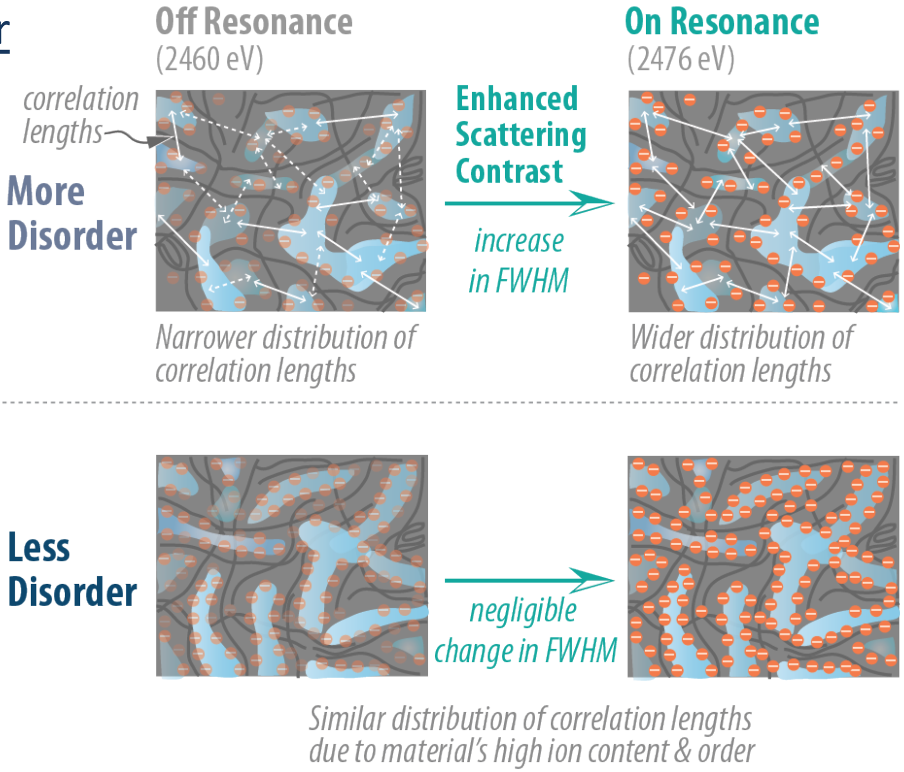
Kusoglu et al. Chem. Mater. 2020, 32, 1, 38-5

PFICE vs. PFSA Ionomers – Dry vs. Hydrated

- Nano-domain swelling with water
- PFICE has more acid groups on side-chain, and preserves order (peak FWHM)
  - With Larger d-spacing in dry /wet
  - Narrower peak in both states → better phase-separation → <u>structural order</u>







Off Resonance (2460 eV)

On Resonance (2476 eV)

correlation lengths

More Disorder

Enhanced Scattering Contrast

increase in FWHM

Narrower distribution of correlation lengths

Wider distribution of correlation lengths

Less Disorder

negligible change in FWHM

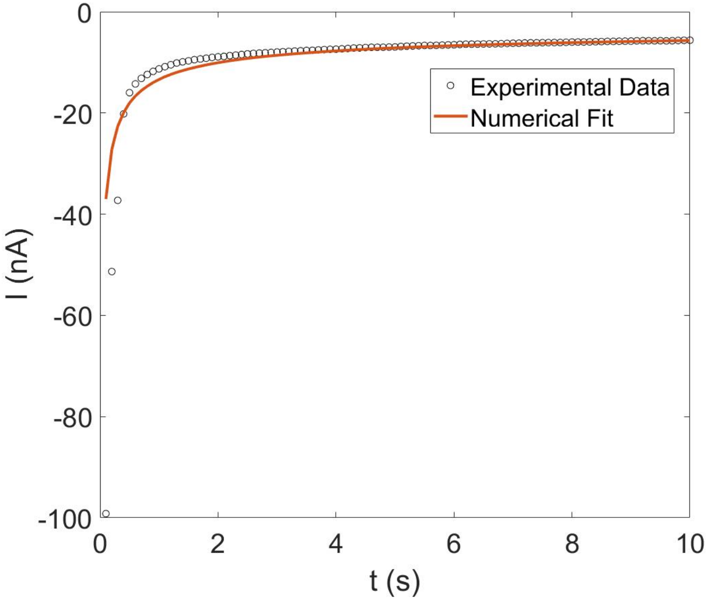
Similar distribution of correlation lengths due to material's high ion content & order

FUEL CELL PERFORMANCE AND DURABILITY

G.M. Su, I.A. Cordova, M.A. Yandrasits, M. Lindell, J. Feng, C. Wang, A. Kusoglu, JACS, 2019, 141, 13547-13561

Analyzing Ionomer Properties Using Microelectrodes

- Oxygen diffusivity and solubility in Nafion 211 calculated from mass transport-limited current
  - This fitting procedure allows for a more accurate determination of membrane properties
    - The diffusion equation was solved numerically for the Pt electrode-membrane geometry
    - Least-squared error fitting was used to optimize the fit and produce a curve accurate over longer time domains



Calculated numerical best-fit curve of current vs time. This was used to determine the D and S of the membrane.

Species	Diffusivity (m^2/s)	Solubility ($mol/(m^3*bar)$)	Permeability ($mol/(m*s*bar)$)
Oxygen	6.02×10^{-12}	270	1.63×10^{-9}

Microscale Model of Membrane Transport Properties

- **Stefan-Maxwell-Onsager Theory**

$$c_i \nabla \mu_i = \sum_{j \neq \mathrm{M}} K_{ij}(\boldsymbol{v}_j - \boldsymbol{v}_i)$$

c_i: concentration

μ_i: electrochemical potential

K_{ij}: friction coefficient

$\boldsymbol{v}_i$: velocity

- **Complete description of membrane transport properties**

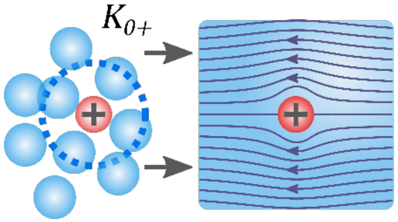
  ↳ $\alpha_{00}, t_{\mathrm{H}^+}, \xi, \kappa = f(K_{ij})$

- **Rigorous description of interspecies interactions and transport couplings**

Types of friction coefficients:

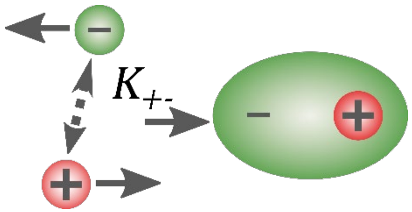
1) Solvent/ion

- **Predicted by Stokes flow**



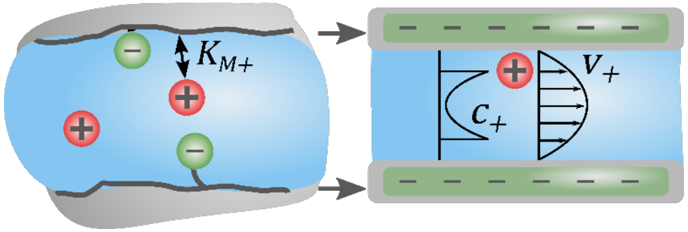
2) Ion/ion

- **From Debye-Hückel-Onsager Theory**



3) Solvent/ and ion/membrane

- **Hydrodynamic flow through pores**



Microscale Model of Membrane Transport Properties

Electrolyte Properties
- dilute ion-water diffusivity
- ion-ion diffusivity
- viscosity

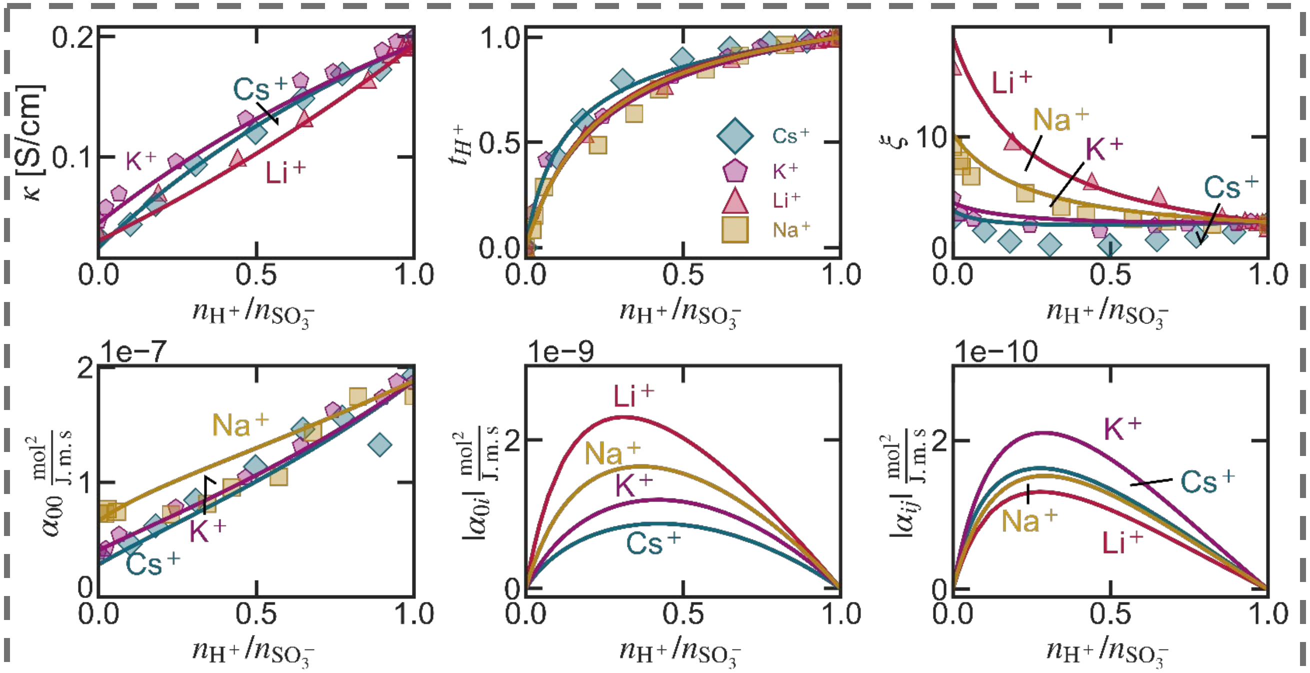
Model Schematic

Microscopic Transport
- species friction
- membrane friction

Macroscopic Transport
- conductivity
- transference number
- osmotic coefficient
- water permeability

Membrane Properties
- water uptake
- domain spacing (SAXS)
- *tortuosity*
- *pore shape*

Validation



A. Crothers et al., JECS, **167**, 013548 (2020). doi: 10.1149/1945-7111/ab6724

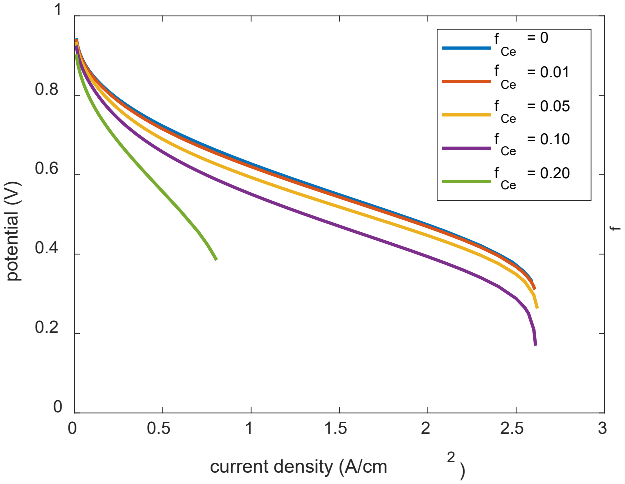
Cell and CL Modeling

Cerium-Ion Transport Model

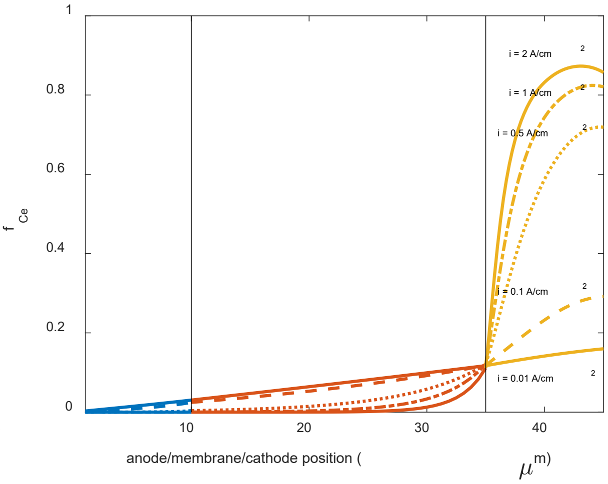
Dilute Solution Theory

- Nernst-Planck Equation
- Can work for low cerium content
- Early limiting current densities at higher cerium contents
- Migration term dominates

Polarization Curves

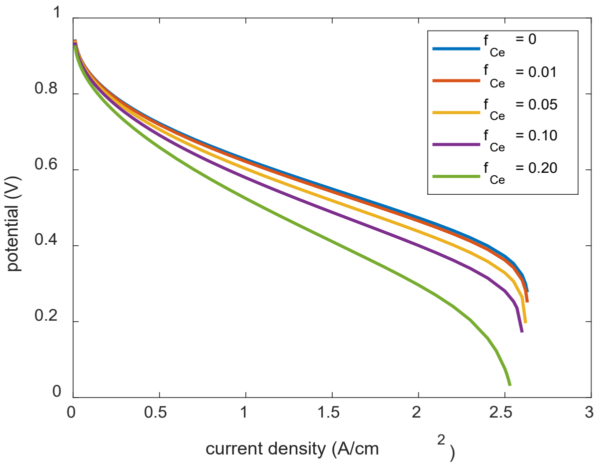


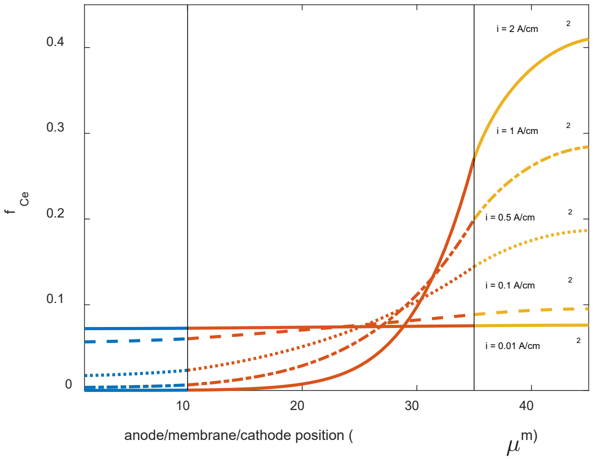
Cerium Distribution



Concentrated Solution Theory

- Takes into account effect of water on Ce ion transport
- Uniform across fuel cell at low current densities.
- Captures mass transfer limited behavior for high Ce content





Simulation conditions:

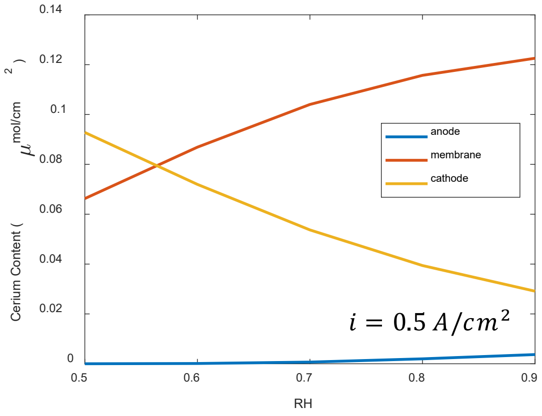
- T = 80ºC, p = 1 bar, RHa = RHc = 90%
- Feed/air flow = 60/100 sccm

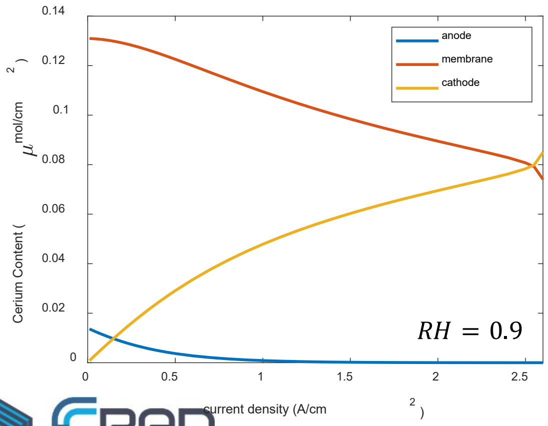
- Cerium concentration = 10% of SO_3^- sites

Cerium-Ion Transport Model

Operating Conditions

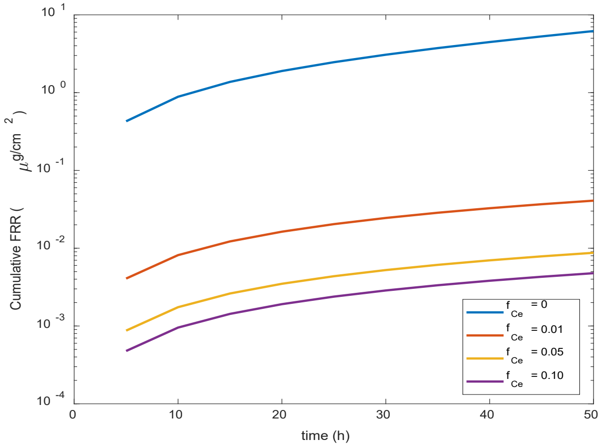
- As RH ↓, cerium in cathode ↑
  - Higher λ draws cerium towards anode and membrane: Better mitigation of peroxide at anode, improves conductivity
- As current ↑, cerium in cathode ↑

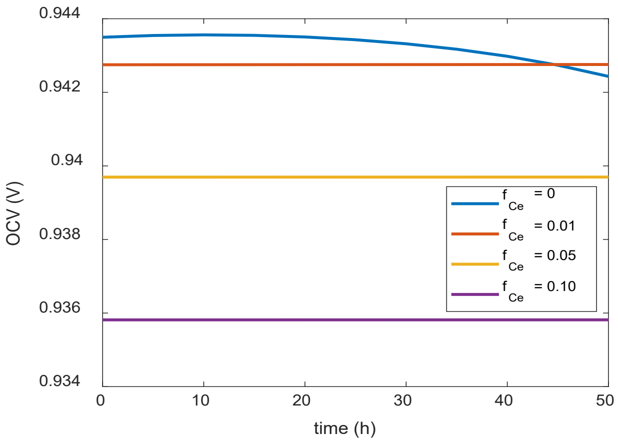




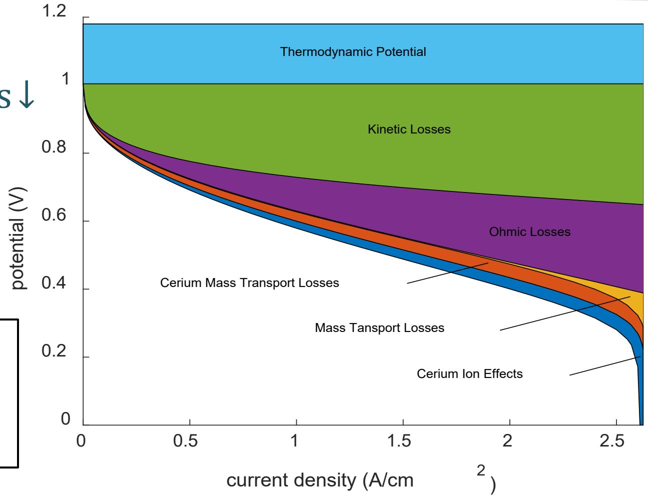
Transient Effects

- Order of magnitude decrease in FRR with 1% cerium in membrane
  - Further ↓ in FRR as cerium ↑
  - Acceleration of degradation rate with time
- All cerium cases show no OCV decay, while base case with no cerium does
  - OCV ↓ with cerium content ↑





- **Voltage Loss Breakdown**
  - As cerium ↑, activity of protons ↓
  - Cerium changes transport properties, contributing additional losses

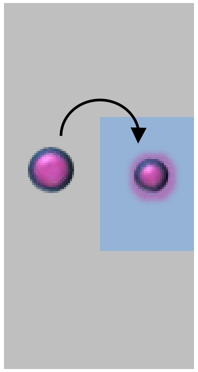


Simulation conditions:

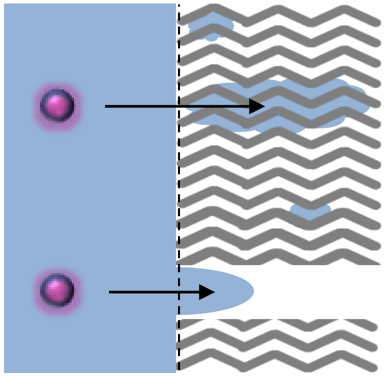
- Cerium concentration = 10% of $SO3^-$ sites
- T = 80ºC, p = 1 bar, RHa = RHc = 90%
- Feed/air flow = 60/100 sccm

Modeling Iron Movement

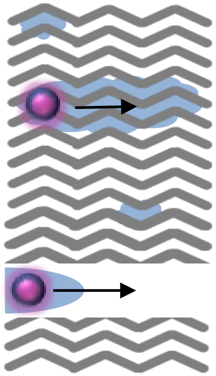
1) iron corrosion
BPP → $H_2O_{aq,channel}$



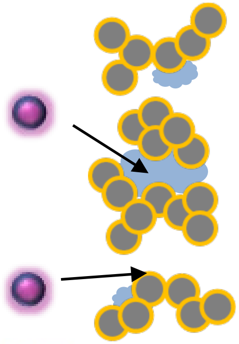
2) channel → DM
transport across interface



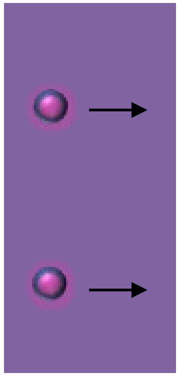
3) transport
within DM



4) transport in CL once
ions reach ionomer



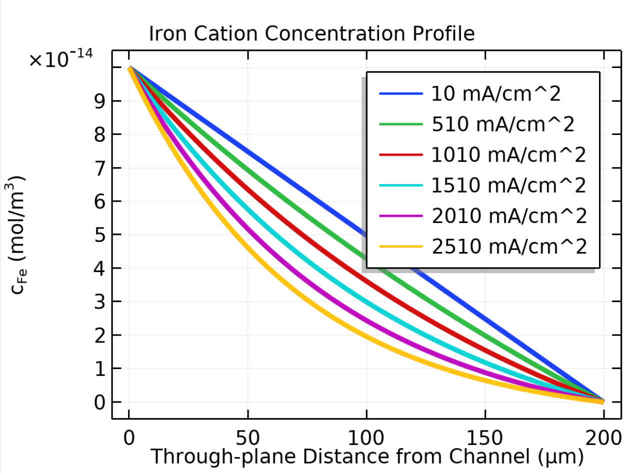
5) transport in PEM

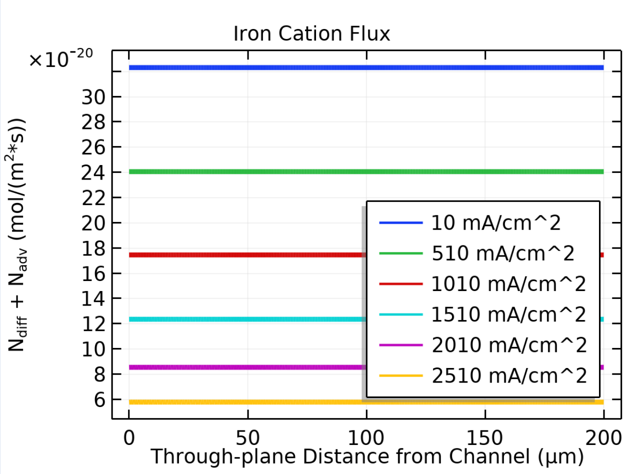


Modeling Iron Movement

- Assume liquid-water pathway from channel to PEM with iron water droplets
  - Increasing cell current density increases liquid water velocity, decreases iron flux to MEA

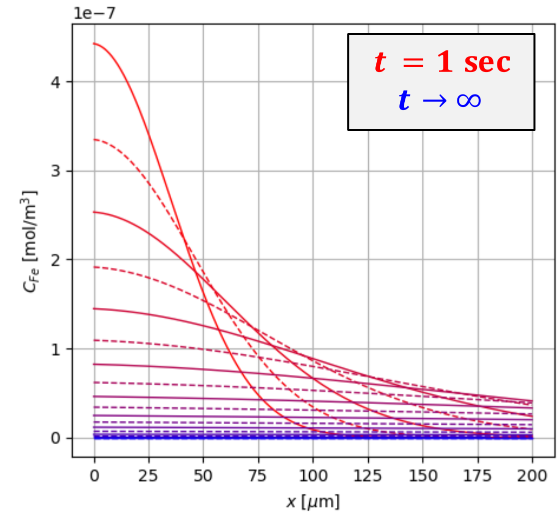
Continuous Droplets

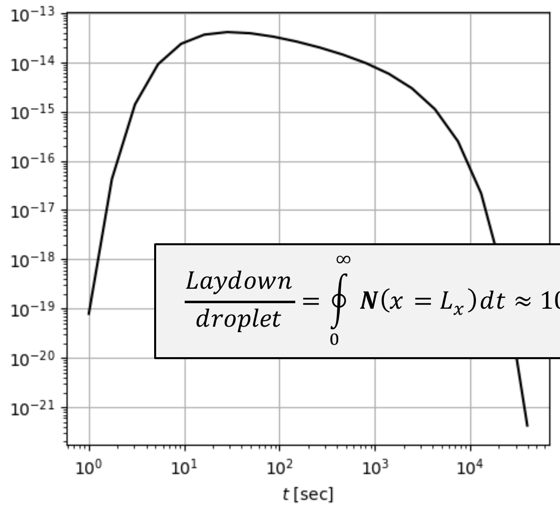




Periodic Droplets

$$u_x = 1 \times 10^{-6} \left[\frac{m}{s}\right]$$

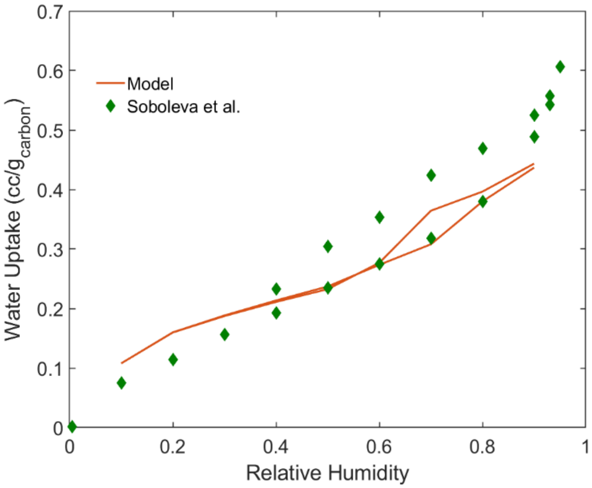


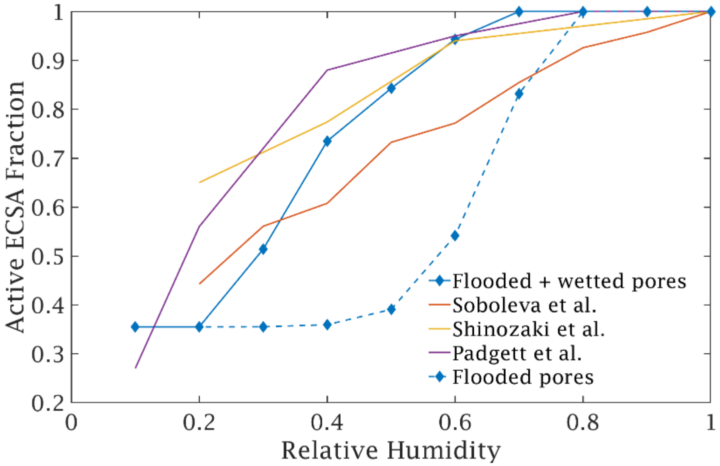


$$\frac{Laydown}{droplet} = \oint_0^{\infty} \boldsymbol{N}(x = L_x)\,dt \approx 10^{-12} \left[\frac{mol}{m^2}\right]$$

ECSA Dependence on RH in HSC

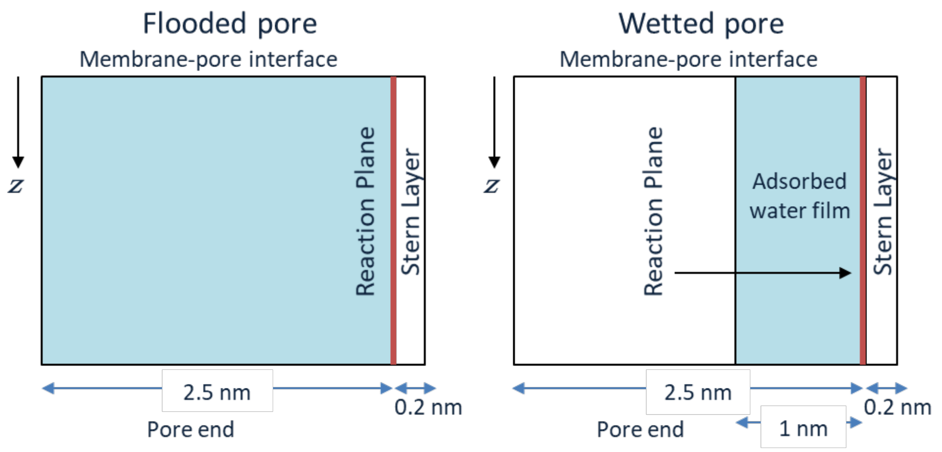
- Modeled water update in high-surface carbon – in agreement with experiments
  - ➢ Model predicts proton conduction via adsorbed water films in addition to water-filled pores
  - N2-BET data (from literature) and SEM imaging studies utilized for carbon pore size distribution
  - Interaction between carbon surface and water molecules implemented using Lennard-Jones 6-12 potential
  - Good match of ECSA dependence on RH with experiments obtained when proton conduction through adsorbed water film of monolayer thickness and above considered
- Pt particles having in contact with adsorbed water films are also active

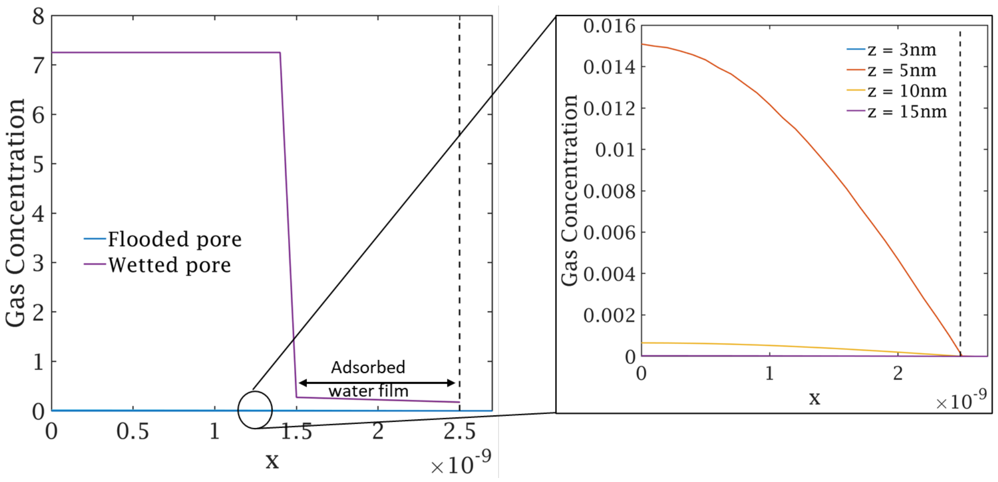




Transport Processes in Pt/C Pores

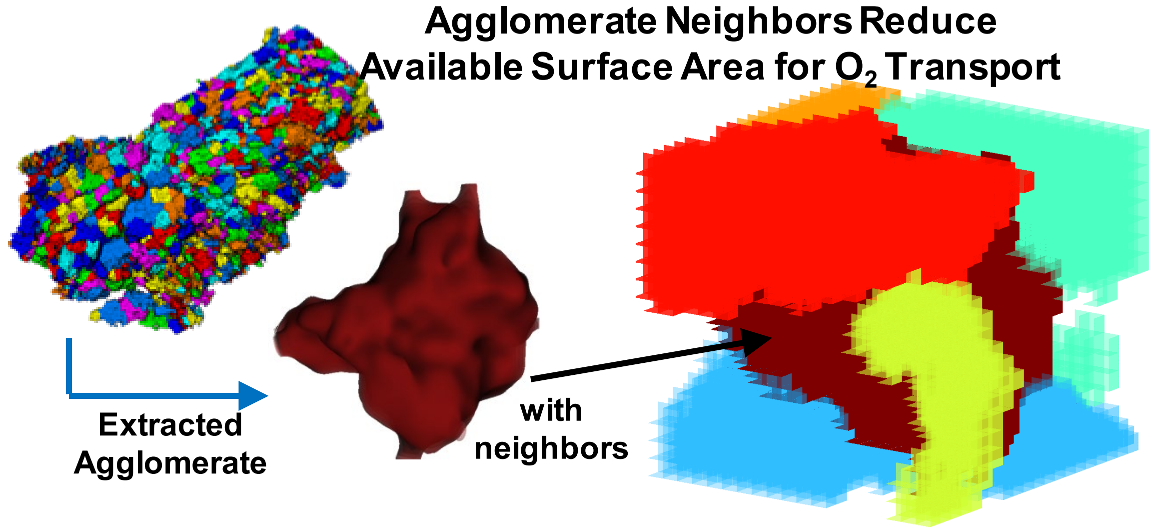
- Modeled proton and gas transport in flooded and wetted pores
- Mesoporous carbon (with wetted pores) performs better at mid-high RH
  - Governing equations for transport include Poisson Boltzmann, Poisson Nernst Planck and Fick's diffusion law
  - Butler-Volmer kinetics-based ORR reaction
  - Double-layer included using Guoy-Chapman-Stern theory without any adsorption in IHP
  - Current in wetted pores up to 3 times higher than flooded pores (Vapplied – Vpzc = -0.2V)

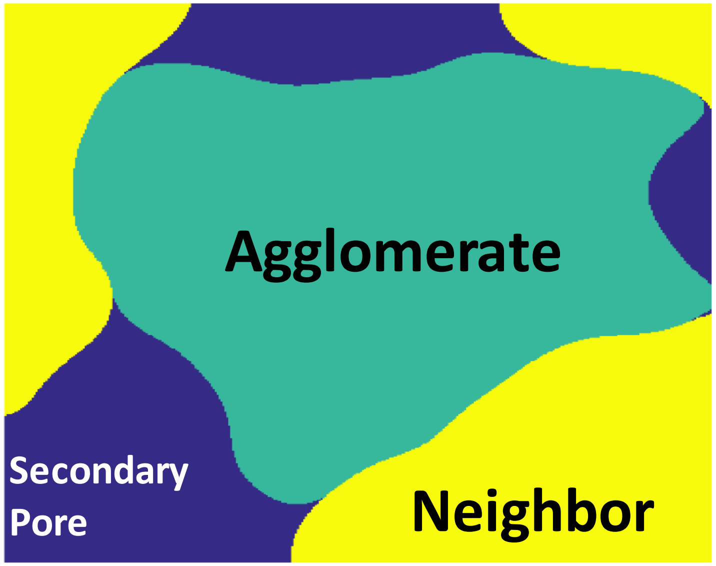




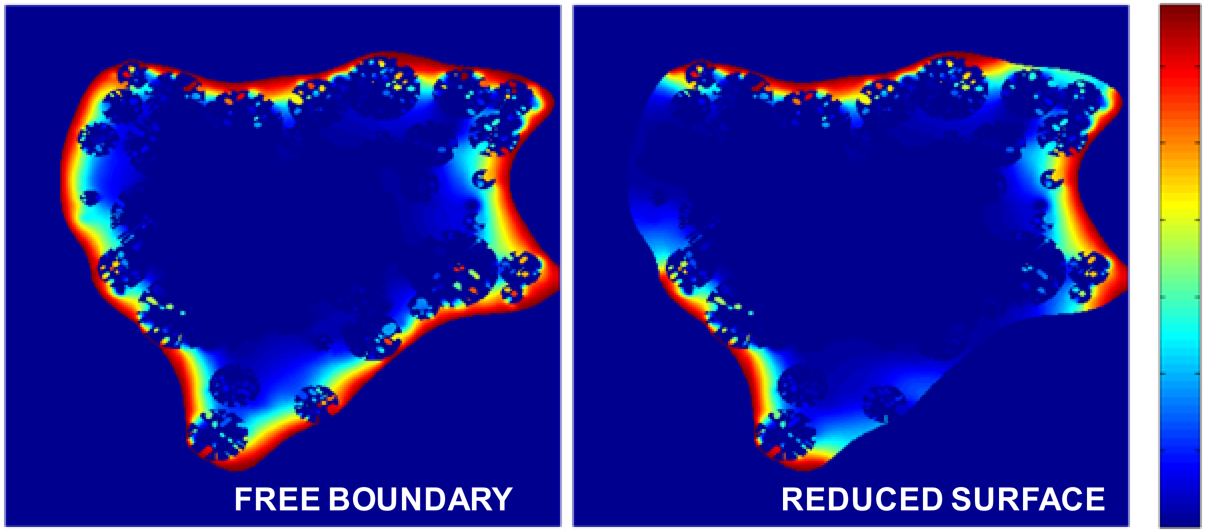
FUEL CELL PERFORMANCE AND DURABILITY

Available Surface Area for O_2 Transport

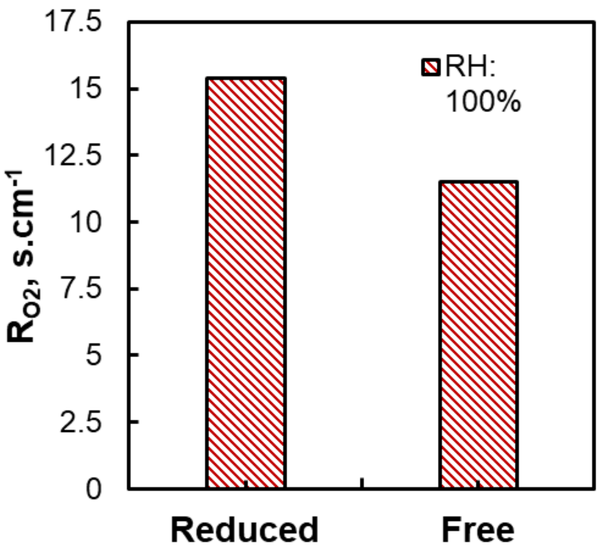

Agglomerate Neighbors Reduce Available Surface Area for O_2 Transport



Available agglomerate surface area has significant impact on the limiting current resistance



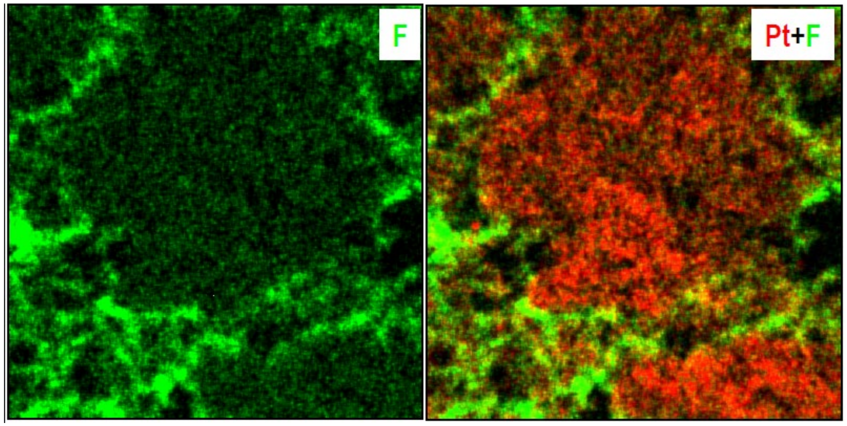
Scaled O_2 Concentration w.r.t Air



Coupled O_2 and Charge Transport

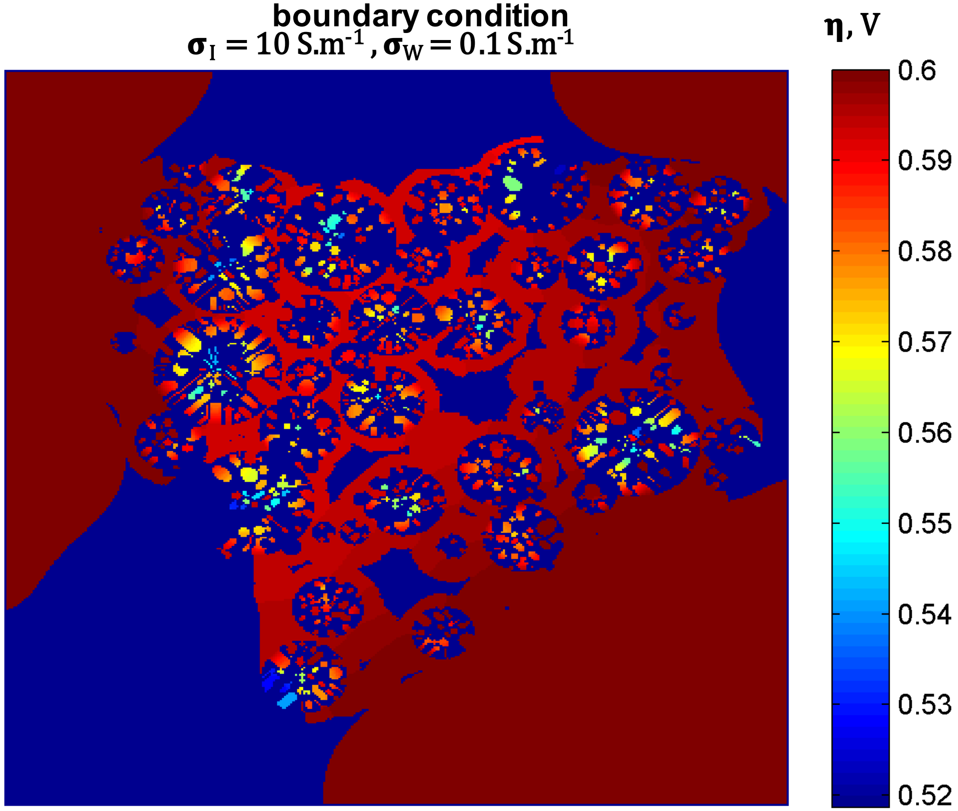
Ionic potential field inside the agglomerate is strongly dependent on the ionomer distribution and proton conductivity of ionomer and liquid water

Example of poor ionomer distribution and penetration in an agglomerate



Ionic potential assigned at the neighbor agglomerates as boundary condition

$\sigma_I = 10\ S.m^{-1}, \sigma_W = 0.1\ S.m^{-1}$



Objectives

- Identify optimum agglomerate structures
- Criterion: Highest current density for given potential

Collaborations (FOA-1412 Partners)

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

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

POC assigned for each project to coordinate activities with PI

FC-PAD work related to those presented in those AMRs

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

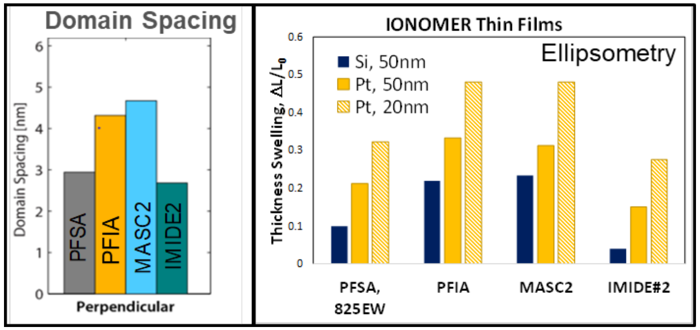
- 30% of National Lab budget supports FOA projects
  - Equal support to each project
- Two in-person FC-PAD meetings held annually - include FOA members with individual sessions held to discuss interactions and progress

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

Component understanding

Ionomer morphology and properties



PFSA & IMIDE#2 more dense and oriented

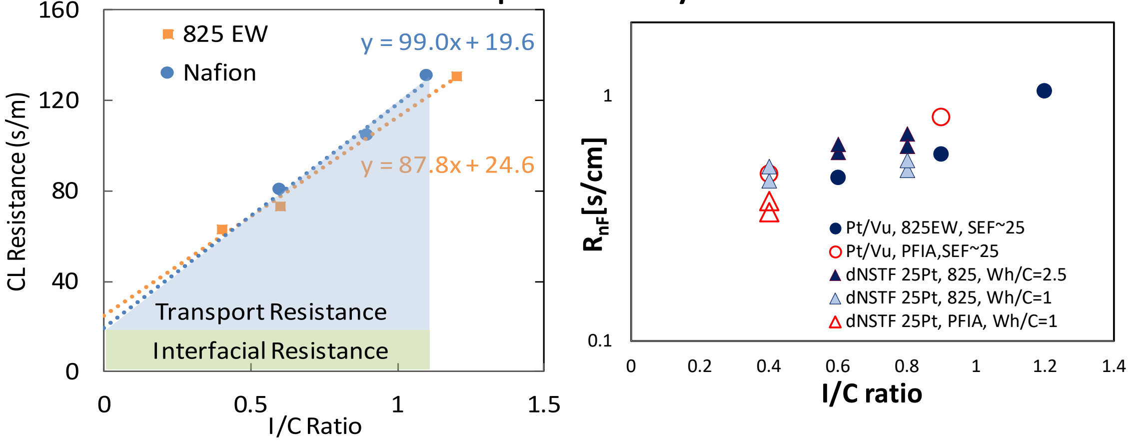
Examine processing conditions and CL structure

	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

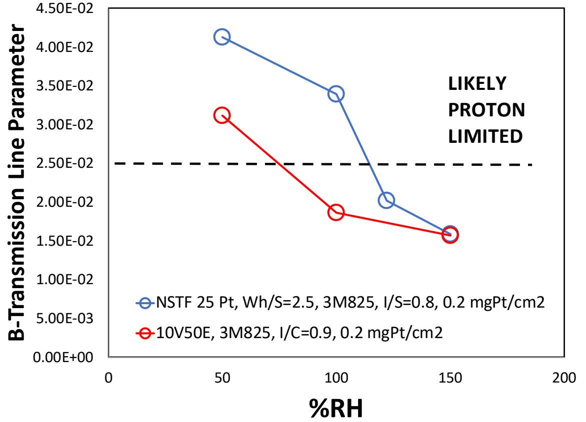
Phenomena elucidation

Transport analysis



3M ionomers and dNSTF result in lower local resistance

ASTs and cell diagnostics

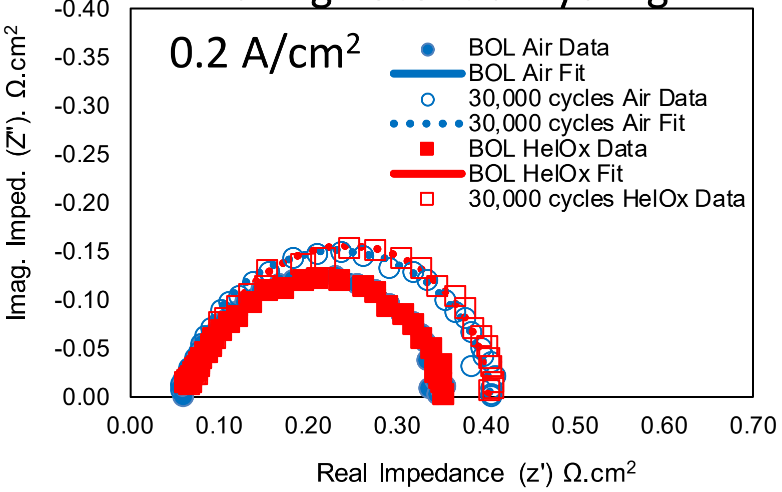


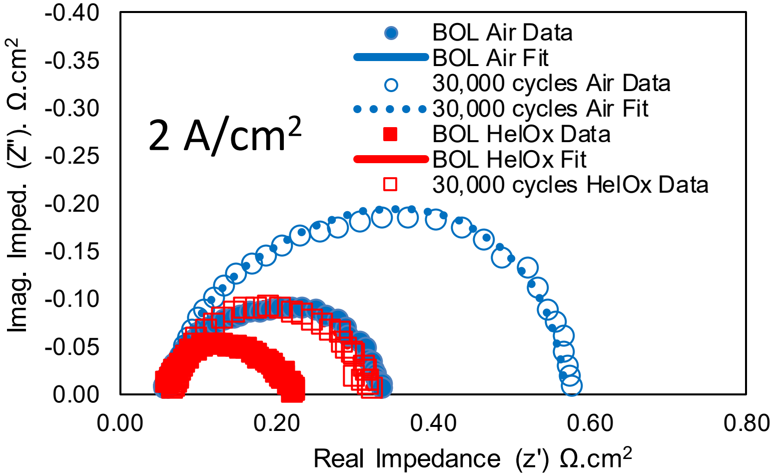
Better water management and durability with dNSTF and apparently proton limited

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

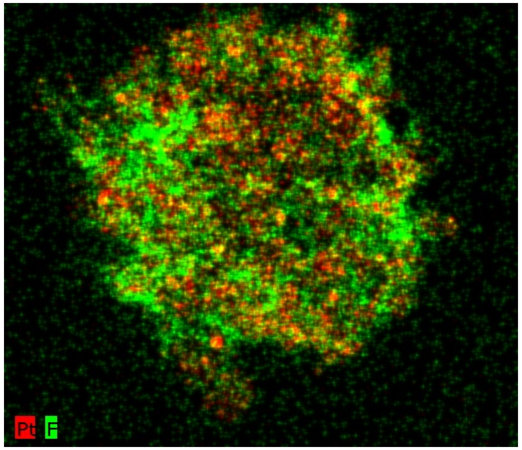
PI: Peter Pintauro - Project ID: # FC158

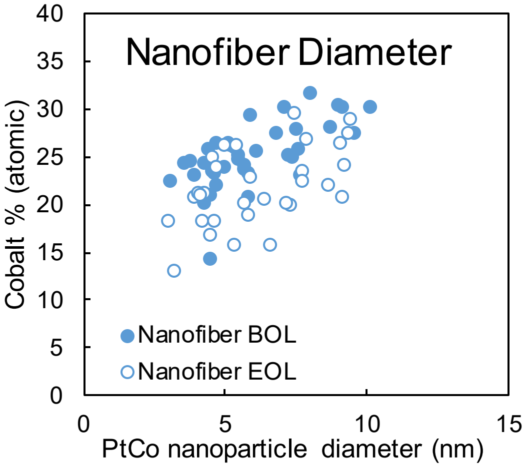
Quantify Kinetic and Transport Losses During Potential Cycling



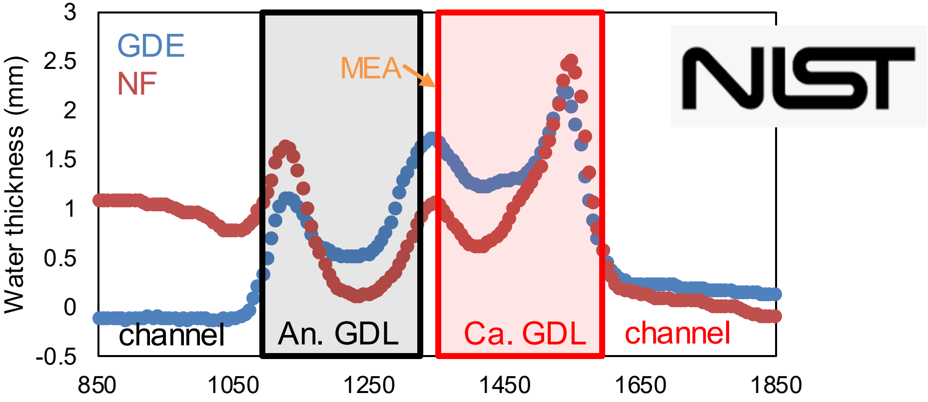


Characterization of Nanofiber Electrodes





Water Visualization



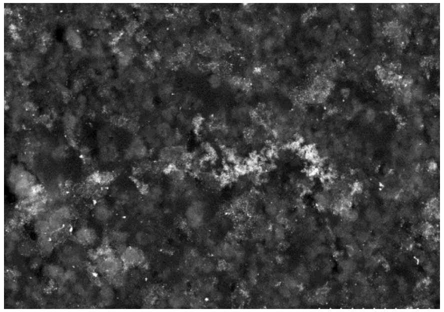
- ➢ Better water management and better durability of nanofiber MEAs

FC-PAD support to: High performance PEFC electrode structures

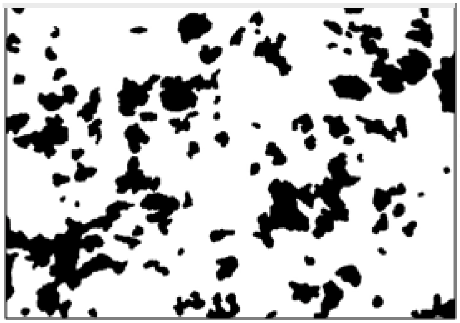
P.I.: Mike L. Perry - Project ID: FC157

United Technologies Research Center

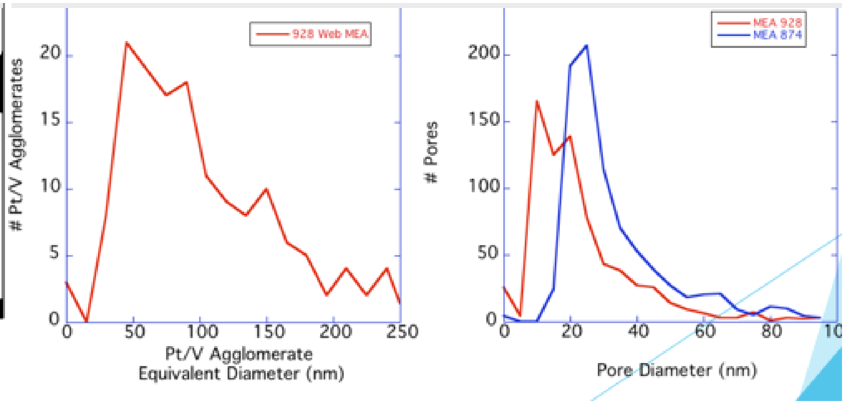
STEM to estimate agglomerate size



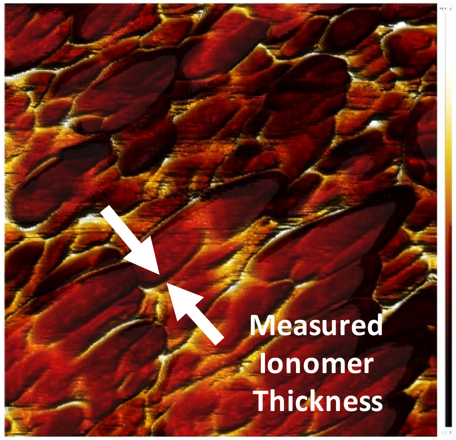
Digitized images



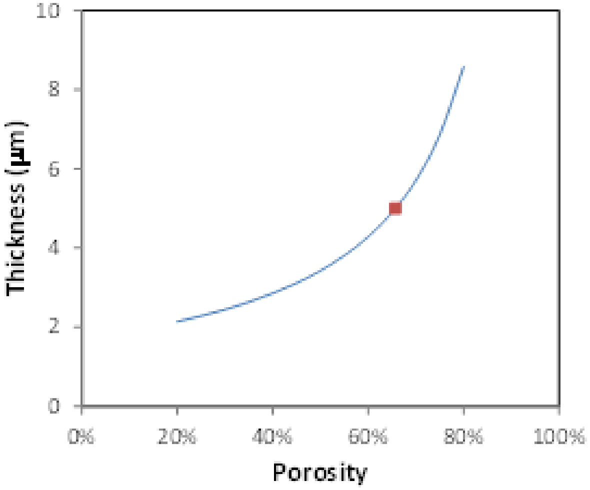
Agglomerate Distribution by slicing through smaller dimension of agglomerate chains.



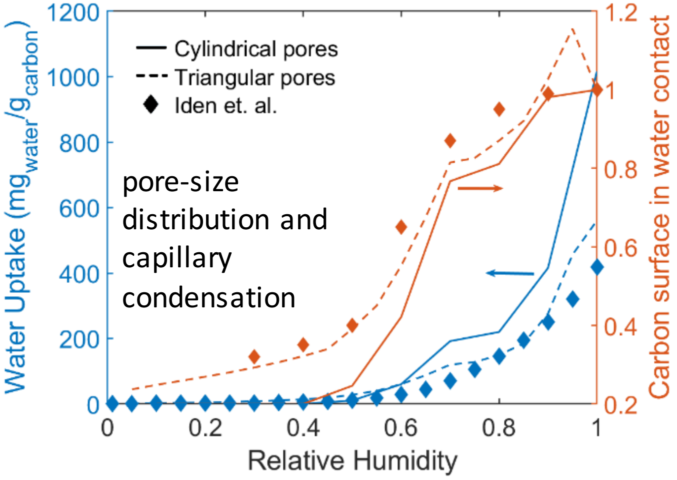
AFM Measurements of Ionomer Thickness



Catalyst Layer Porosity Measurements



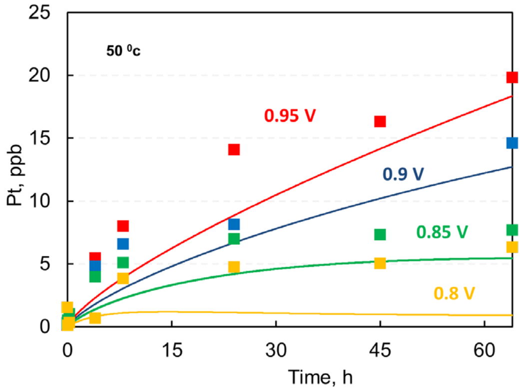
Modeling porous carbons for optimization of catalyst utilization

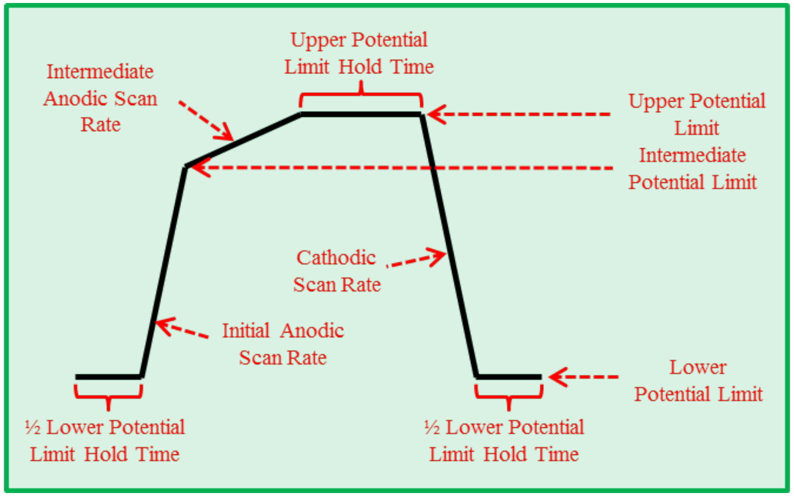


FC-PAD support to: Durable High Power Membrane Electrode Assembly with Low Pt Loading

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

Pt Dissolution (half-cell)





Intermediate Anodic Scan Rate

Upper Potential Limit Hold Time

Upper Potential Limit

Intermediate Potential Limit

Cathodic Scan Rate

Initial Anodic Scan Rate

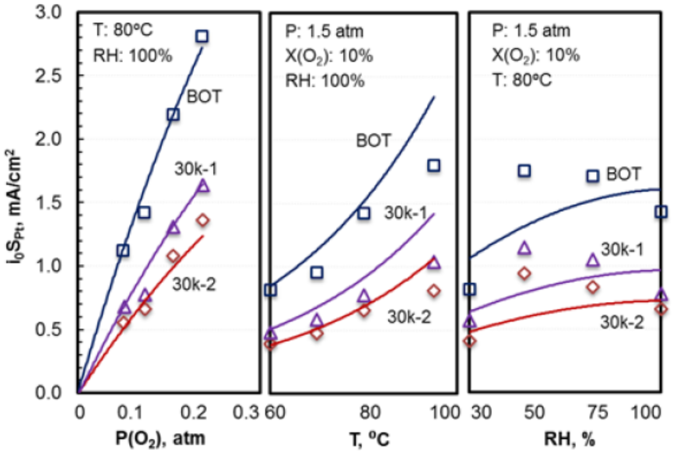
Lower Potential Limit

½ Lower Potential Limit Hold Time

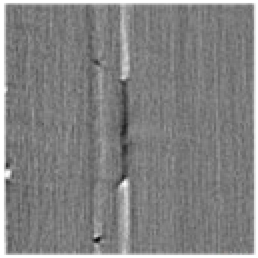
½ Lower Potential Limit Hold Time

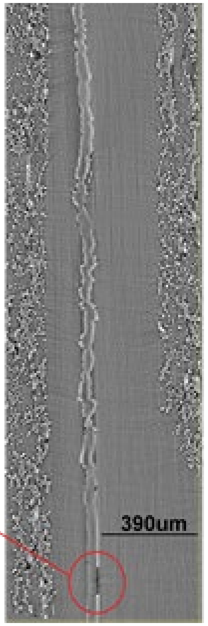
H_2-N_2 voltage cycling to identify operational limitations

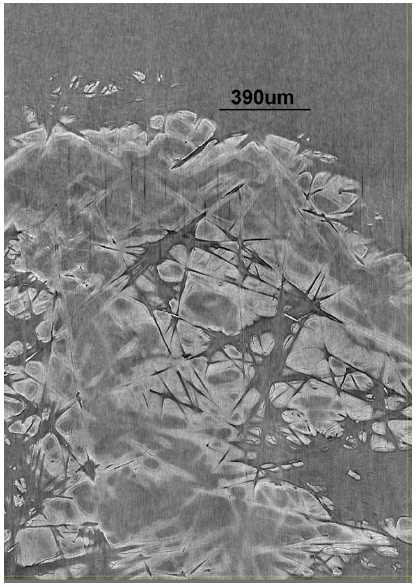
Model framework development to identify root cause of durability losses



Impact of Local Shorting on Membrane Degradation







Collaborations (Non-FOA activities)

Institutions	Role
Umicore	Supply SOA catalysts, MEAs
UC Irvine	GDL imaging
University Carlos III of Madrid	Microscale simulations
TKK	Supply SOA catalysts
Johnson Matthey	Catalysts and CCMs
CEA (and ID-FAST EU Consortium)	Membrane studies
Ion Power	Supply CCMs
Xi'an Jiaotong University	CL mesoscale modeling
NIST – National Institute of Standards and Tech.	Neutron imaging
NYU	Novel Ionomers
University of Alberta	Flowfield and droplet modeling
US Drive	Mirai analysis
3M	Membrane chemistry
LEMTA, CNRS/Université de Lorraine	Shut-down/Start-up testing

Collaborations (Non-FOA activities)

Institutions	Role
CIEMAT	**Electrosprayed CLs**
U Waterloo	**GDL Modeling**
Penn State U	**Ionomer thin films**

Future Work: Heavy-Duty Applications

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

- Much longer lifetimes (1,000,000 miles; 25,000-30,000 hrs)
- Focus on improved efficiency - higher operating temperatures (better kinetics), higher emphasis on lower stack power density (higher voltage)
  - 68% - 72% peak efficiency
- Cost targets are less stringent depending upon efficiency and durability payback
  - Initial $80/kW fuel cell system cost, ultimate $60/kW fuel cell system cost
- Explore relationships between operating conditions, conductivity and membrane durability.
  - Operating temperature in the range of 100–120 C and relative humidity in the range of 20–30%.

FC-PAD Workscope

- Transition to heavy-duty fuel cell operating space and materials
  - Heavy-Duty drive cycles different compared with light-duty
  - Long-haul and delivery also have substantially differing drive cycles
- Refine models, characterization, and diagnostics for heavy-duty operating conditions
- Develop refined ASTs for life-time prediction with 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

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

Future Work:
MEAs & Component for High Efficiency and Durability

- Re-prioritize research directions related to heavy-duty operation
  - Greater efficiency
  - High durability
- Understand the heavy-duty fuel cell operating space and prioritize research directions
  - Examples include:
    - Idle time and fewer start/stops (long haul)
    - Time at high voltage with high power and heat rejection requirements
    - Efficiency hit due to gas crossover through membrane for extended idle
    - Low-power operation with high-power extended spikes.
    - Effect of membrane additives, membrane thickness
    - Catalyst particle size and catalyst alloying under heavy duty operating modes.
- Heavy-Duty Materials, Components and Cell Understanding
  - Material and characterization studies
  - Catalyst layer studies
  - Durability
  - Water and thermal management

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
  - Shifted emphasis to support Heavy-Duty Transportation Applications
- **Approach:**
  - Use synergistic combination of modeling and experiments to explore and optimize component properties, behavior, and phenomena
- **Technical Accomplishments :**
  - Durability measurements at projected heavy-duty loadings
    - Effect of Loading
    - Alloy Degradation
    - Catalyst Support
    - Effect of Upper Potential
  - Catalyst Inks to Performance and Catalyst Layer (CL) Analysis:
    - Ink Composition-Solvent Studies
    - Cell Testing
    - Impact of Fabrication
    - Membrane and Ionomer Characterization
    - Cell and CL modeling
- **Future Work:**
  - Focus on heavy duty applications
    - Emphasis on efficiency and durability
  - Continue to develop the knowledge base to improve catalyst layer structures and component integration for fuel cell performance, efficiency, and durability

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

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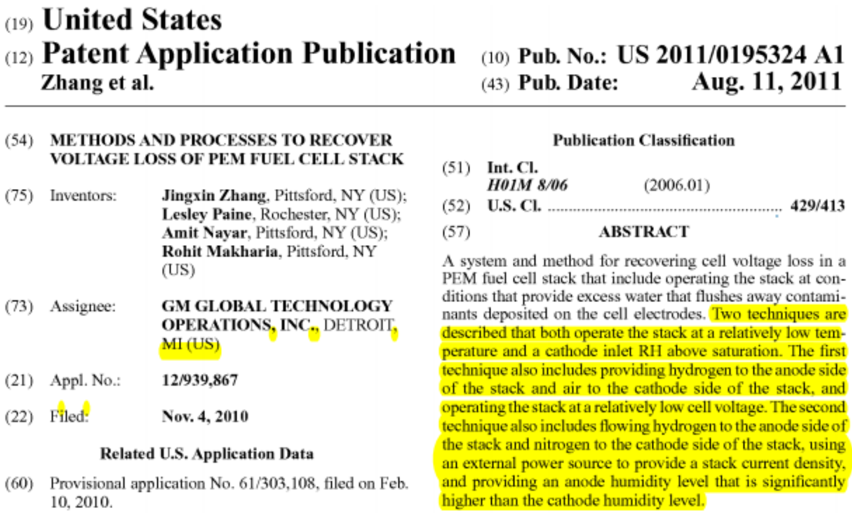
  - Greg Kleen
- Organizations we have collaborated with to date
- User Facilities
  - DOE Office of Science: SLAC, LBNL-Advanced Light Source, ANL-Advanced Photon Source, LBNL-Molecular Foundry, ORNL-Center for Nanophase Materials Sciences, ANL-Center for Nanostructured Materials
  - NIST: BT-2

Technical Back-Up Slides

Experiments

Protocol



(19) **United States**

(12) **Patent Application Publication**

Zhang et al.

(10) **Pub. No.: US 2011/0195324 A1**

(43) **Pub. Date: Aug. 11, 2011**

(54) **METHODS AND PROCESSES TO RECOVER VOLTAGE LOSS OF PEM FUEL CELL STACK**

(75) Inventors: **Jingxin Zhang**, Pittsford, NY (US); **Lesley Paine**, Rochester, NY (US); **Amit Nayar**, Pittsford, NY (US); **Rohit Makharia**, Pittsford, NY (US)

(73) Assignee: **GM GLOBAL TECHNOLOGY OPERATIONS, INC.**, DETROIT, MI (US)

(21) Appl. No.: **12/939,867**

(22) Filed: **Nov. 4, 2010**

Related U.S. Application Data

(60) Provisional application No. 61/303,108, filed on Feb. 10, 2010.

Publication Classification

(51) **Int. Cl.**
H01M 8/06 (2006.01)

(52) **U.S. Cl.** **429/413**

(57) **ABSTRACT**

A system and method for recovering cell voltage loss in a PEM fuel cell stack that include operating the stack at conditions that provide excess water that flushes away contaminants deposited on the cell electrodes. Two techniques are described that both operate the stack at a relatively low temperature and a cathode inlet RH above saturation. The first technique also includes providing hydrogen to the anode side of the stack and air to the cathode side of the stack, and operating the stack at a relatively low cell voltage. The second technique also includes flowing hydrogen to the anode side of the stack and nitrogen to the cathode side of the stack, using an external power source to provide a stack current density, and providing an anode humidity level that is significantly higher than the cathode humidity level.

5cm^2 Differential cell hardware Design from GM Patent

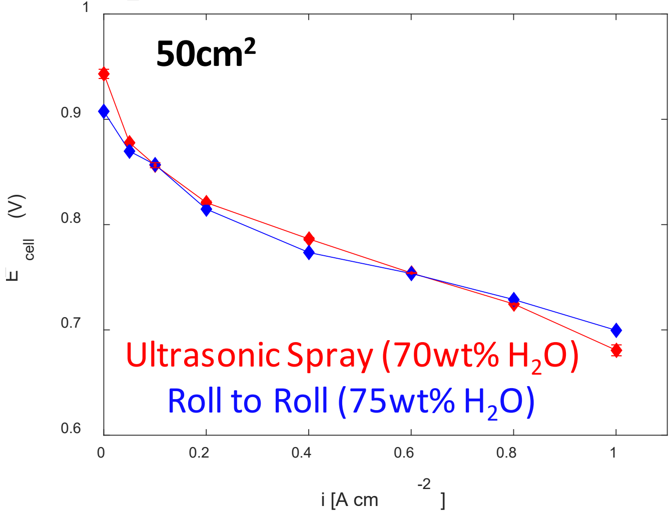
- Recovery Protocol applied before each characterization
  - T_{cell} = 30 °C, T_{anode} = 45 °C, $T_{cathode}$ = 35 °C
  - Operate in H_2 pump mode to slightly negative voltages to desorb impurities, Reduce Pt
  - Operate at high currents in H_2/Air to flush out impurities with generated water, restructure ionomer
- Catalyst AST : 0.6V(3s) - 0.95V(3s), 80°C, 100%RH

Samples Evaluated

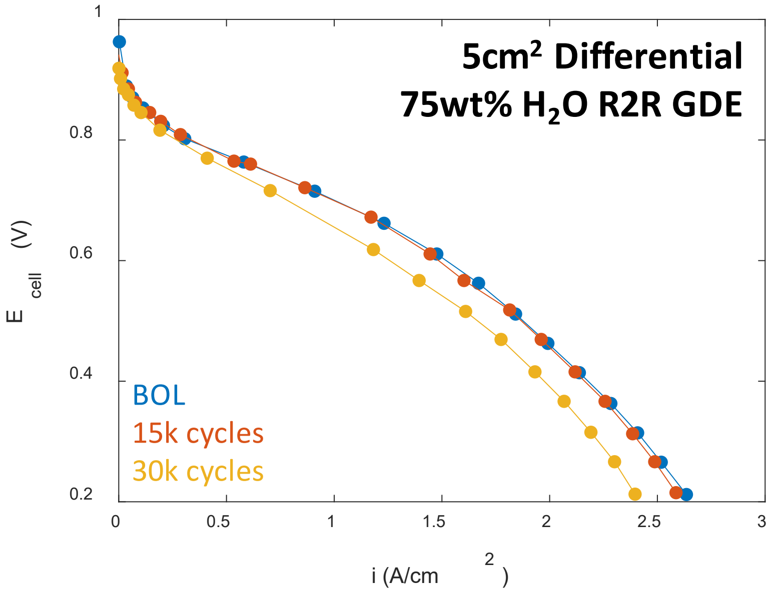
- Umicore samples used for carbon corrosion study
  - EKAT 0424 : 0.1mg$_{Pt}$/cm^2 ELYST Pt300670, I/C = 0.95 (2 samples)
  - EKAT 0428 : 0.1mg$_{Pt}$/cm^2 ELYST 30PtA9029X, I/C = 0.77 (2 samples)
  - EKAT 0428 : 0.1mg$_{Pt}$/cm^2 ELYST Pt200380, I/C = 0.77 (2 samples)
  - EKAT0606 : 0.1mg$_{Pt}$/cm^2 ELYST Pt500550, I/C = 0.83 (5 samples)
  - EKAT0607 : 0.1mg$_{Pt}$/cm^2 ELYST 30PtA9029X, I/C= 0.77 (5 samples)
  - EKAT0608 : 0.1mg$_{Pt}$/cm^2 ELYST Pt500670, I/C = 0.95 (5 samples)
- Umicore samples used for catalyst AST studies
  - EKAT 0574 : 0.05mg$_{Pt}$/cm^2 ELYST Pt300670, I/C = 0.95 (5 samples)
  - EKAT 0575 : 0.1mg$_{Pt}$/cm^2 ELYST Pt300670, I/C = 0.95 (10 samples)
  - EKAT 0576 : 0.15mg$_{Pt}$/cm^2 ELYST Pt300670, I/C = 0.95 (5 samples)
  - EKAT0788 : 0.25mg$_{Pt}$/cm^2 ELYST Pt500550, I/C = 0.83 (5 samples)
  - EKAT0789 : 0.4mg$_{Pt}$/cm^2 ELYST Pt500550, I/C= 0.83 (5 samples)
  - EKAT0790 : 0.25mg$_{Pt}$/cm^2 ELYST Pt500670, I/C = 0.95 (5 samples)
  - EKAT0791 : 0.4mg$_{Pt}$/cm^2 ELYST Pt500670, I/C = 0.95 (5 samples)
- TKK samples received for catalyst AST studies
  - TEC36E32, TEC36V32, TEC36E52, TEC36EA32, TEC36F32, TEC36VA32, TECNiE32

Comparison of High-Performance PtCo/HSC MEAs

H_2/Air, 80°C, 150kPa, 100%RH



- Best performing MEAs (70wt% Spray and 75wt% R2R) exhibit similar H_2/Air polarization performance
- Preliminary durability AST were performed showing losses in … ***<u>O_2 transport?, Mass Activity?</u>***
- Focus on comparing the electrode structure for Spray and R2R MEAs to explain the similarities/differences in performance and durability



[1] S. Kabir et al. *ACS Appl. Mater. Interfaces* 2019, 11, 48, 45016-45030
[2] *T. Van Cleve et al PtCo Ink Series [manuscript in preparation]*

Response to 2019 Reviewer Comments

Strengths

- …. clear objectives, excellent organization for efficient multi-laboratory coordination, different competencies (elaboration, testing and characterization, modeling), means, and different collaborations (e.g., laboratories, universities, and industries).
- …. highlighting of the critical aspects of MEAs that have directly impact on durability, its detailed experimental and computational analysis of relevant MEA operational processes at a range of length scales, its efficient use of DOE resources, and its adequate integration of research partners.
- The composition of the consortium, the coordination of the project, and the well-defined role of the different partners involved are real strengths. … strong focus on publication of the results …. share as much as possible with the international community.
- The multi-laboratory and multi-level approach to studying a broad range of higher-priority degradation and performance mechanisms is a key strength. The outstanding characterization capabilities really drive the in-depth understanding.
- … very strong team and a very clear pathway for development toward FCTO goals.
- … well-articulated project with excellent connections between the national laboratories.
- This project is an outstanding coordinated effort by some of the best folks in the country.
- Experimental resources at the laboratories and knowledge of materials and electrochemist all converged and were coordinated.

Project weaknesses:

- There are no project weaknesses, per se
- It is difficult to find any weaknesses.
- …… however, the coordinated effort needs more than one person to manage such a large and important project. The project team needs someone to assist in "seeing the big picture."
- how information moves between partners ….. not .. clear whether we are seeing the result of several excellent pet projects, or a large volume of information (and possibly materials) is changing hands between the partners.
- ……the real operation vision of the work is missing; what is needed is an operating system with optimized durability and cost. … global optimization is not (component level) …. Optimizing components should be done with a stack-/system-level input.
- The presentation's slides lack clarity for some protocols and conditions, such as the break-in procedure. The value of this work has not been established.
- … its very large scope, which may lead to some loss of focus
- Using only sprayed electrodes appears also to be a weakness
- The project needs more industry input, deeper focus on fewer tasks, and a more holistic approach to study interfaces

FCPAD
FUEL CELL PERFORMANCE AND DURABILITY

Collaborations and Integration Review Comments

1. There is excellent collaboration with other national laboratories.
2. The structure of FC-PAD is based on collaborations. This aspect seems to be very well-thought-out and ….
3. The collaboration between the project's partners is intense and emerges clearly from the presentation.
4. The collaboration between the different partners is well structured and well managed
5. The collaboration between the different partners is well structured and well managed
6. The team has shown good collaboration with partners, both funded through the FOA and unfunded.
7. The rating here might not be fair, but the team did not do a particularly great job in the presentation of describing how the team is integrated.

Comments & Responses

- …system level input, guidance, system level validation & stack-/system-level input
  - Normal input comes from FCTT; GM has been FC-PAD collaborator
  - Three new FC-PAD projects related to heavy-duty; will hopefully get input
  - Generally, Fuel Cell Component R&D projects do not/have not conducted full stack/system level validation
    - EU projects are structured differently, with OEMs conducting validation, but providing little public information

- …. its very large scope…. (also got similar comment ~ last two years)
  - HOWEVER, also got comments about expanding ….
    - …. AEM fuel cells and electrolysis.
    - ….. project should also investigate a PGM- and cobalt-free catalyst.
    - More emphasis on heavy-duty applications

- Using only sprayed electrodes appears also to be a weakness
- Multiple labs make sprayed electrodes
  - Multiple labs also make electrodes by other methods
  - MEAs (not sprayed) often come from Umicore, also Ion Power, IRD, W.L. Gore ….

Special Recognitions & Awards Issued

- David Cullen received the PECASE: Presidential Early Career Awards for Scientists and Engineers
- Kavi Chintam received the LANL 2019 Distinguished Student Award
- Karren More was named 2019 Fellow of the Microscopy Society of America (MSA), Microscopy & Microanalysis 2019

FC-PAD Publications

1. RL Borup, A Kusoglu, KC Neyerlin, R Mukundan, RK Ahluwalia, DA Cullen, KL More, AZ Weber, DJ Myers, **Recent Developments in Catalyst-Related PEM Fuel Cell Durability**, Current Opinion in Electrochemistry, 2020
2. David A. Cullen, K.C. Neyerlin), Rajesh K. Ahluwalia, Rangachary Mukundan, Karren L. More, Rodney L. Borup, Adam Z. Weber, Deborah J. Myers, and Ahmet Kusoglu, **New Roads and Challenges for Fuel Cells in Transportation: Light-Duty Lessons for Heavy-Duty Applications,** submitted to Nature Energy
3. Busra Ergul-Yilmaz, Zhiwei Yang, Mike L. Perry, Karren L. More, Natalia Macauley, Rod Borup, and Tansel Karabacak, **Microstructural Evolution and ORR Activity of Nanocolumnar Platinum Thin Films with Different Mass Loadings Grown by High Pressure Sputtering,** submitted
4. Andrew M. Baker, Andrew R. Crothers, Kavitha Chintam, Xiaoyan Luo, Adam Z. Weber, Rodney L. Borup, Ahmet Kusoglu, **Deconvoluting Morphology and Transport of Multivalent Cation-Exchanged Ionomer Membranes using Ce-PFSA as a Model System,** in review at Macromolecules
5. Siddharth Komini Babu, Dusan Spernjak, Rangachary Mukundan, Daniel S Hussey, David L Jacobson, Hoon T Chung, Gang Wu, Andrew J Steinbach, Shawn Litster, Rod Borup and Piotr Zelenay, **Understanding Water Management in Platinum Group Metal-Free Electrodes using Neutron Imaging,** in review at J. Power Sources
6. Lalit M Pant, Michael R Gerhardt, Natalia Macauley, Rangachary Mukundan, Rodney L Borup, Adam Z Weber, **Along-the-channel modeling and analysis of PEFCs at low stoichiometry: Development of a 1+ 2D model**, Electrochimica Acta 326, 134963 2019
7. S Komini Babu, D Spernjak, J Dillet, A Lamibrac, G Maranzana, S Didierjean, Olivier Lottin, RL Borup, R Mukundan, **Spatially resolved degradation during startup and shutdown in polymer electrolyte membrane fuel cell operation**, v254, Applied Energy, 2019
8. Victoria M. Ehlinger, Ahmet Kusoglu, and Adam Z. Weber, **Modeling Coupled Durability and Performance in Polymer-Electrolyte Fuel Cells: Membrane Effects**, J. Electrochem. Soc., 166 (7), F3255-F3267 2019
9. Julio J. Conde, M. Antonia Folgado, P. Ferreira-Aparicio, Antonio M. Chaparro, Anamika Chowdhury, Ahmet Kusoglu, David Cullen, Adam Z. Weber, **Mass-transport properties of electrosprayed Pt/C catalyst layers for polymer-electrolyte fuel cells**, J. Power Sources, 427, 250-259 2019
10. Yu-Tong Mu, Adam Z. Weber, Zhao-Lin Gu, and Wen-Quan Tao, **Mesoscopic Modeling of Transport Resistances in a Polymer-Electrolyte Fuel-Cell Catalyst Layer: Analysis of Hydrogen Limiting Currents**, Applied Energy, 255, 113895 2019
11. Tim Van Cleve, Sunilkumar Khandavalli, Anamika Chowdhury, Samantha Medina, Svitlana Pylypenko, Min Wang, Karren More, Nancy Kariuki, Deborah Myers, Adam Weber, Scott Mauger, Michael Ulsh, Kenneth Neyerlin, **Dictating Pt-based Electrocatalyst Performance in Polymer Electrolyte Fuel Cells; from Formulation to Application**, ACS Applied Materials & Interfaces, 11 (50), 46953-46964 2019

FC-PAD Publications

12. A. Kusoglu, K. Vezzù, G. Hegde, G. Nawn, A.R. Motz, H.N. Sarode. G.M. Haugen, Y. Yang, S. Seifert, M.A. Yandrasits, S.J. Hamrock, C.M. Maupin, A.Z. Weber, V. Di Noto, A.M. Herring, ‘**ransport and Morphology of a Proton Exchange Membrane Based on a Doubly Functionalized Perflourosulfonic Imide Side Chain Perflourinated Polymer**, Chemistry of Materials, 32, 38-59 2020
13. Andrew R. Crothers, Robert M. Darling, Ahmet Kusoglu, Clayton J. Radke, and Adam Z. Weber, **Theory of Multicomponent Phenomena in Cation-Exchange Membranes, I: Thermodynamic Model and Validation**, J. Electrochem. Soc., 167, 013547 2020.
14. Andrew R. Crothers, Robert M. Darling, Ahmet Kusoglu, Clayton J. Radke, and Adam Z. Weber, **Theory of Multicomponent Phenomena in Cation-Exchange Membranes, II: Transport Model and Validation**, J. Electrochem. Soc., 167, 013548 (2020)
15. Adlai Katzenberg, Anamika Chowdhury, Minfeng Fang, Adam Z. Weber, Yoshiyuki Okamoto, Ahmet Kusoglu, Miguel A. Modestino, **Highly Permeable Perfluorinated Sulfonic Acid Ionomers for Improved Electrochemical Devices: Insights into Structure–Property Relationships**, J. Am. Chem. Soc., 142 (8), 3742-3752 2020
16. Meron Tesfaye, Douglas Kushner, Ahmet Kusoglu, **Interplay between Swelling Kinetics and Nanostructure in Perfluorosulfonic Acid Thin-Films: Role of Hygrothermal Aging,** ACS Appl. Polym. Mater., 1 (4), 631–635 2019
17. D. I. Kushner, A. Kusoglu, N. Podraza, M.A. Hickner, **Substrate-Dependent Molecular and Nanostructural Orientation of Nafion Thin Films**, Advanced Functional Materials, (2019).
18. Peter J. Dudenas and Ahmet Kusoglu, **Evolution of Ionomer Morphology from Dispersion to Film: An in Situ X-ray Study**, Macromolecules, 52, 7779−7785 2019
19. Gregory M. Su, Isvar A. Cordova, Michael A. Yandrasits, Matthew Lindell, Jun Feng, Cheng Wang,, and Ahmet Kusoglu, **Chemical and Morphological Origins of Improved Ion Conductivity in Perfluoro Ionene Chain Extended Ionomers**, J. Am. Chem. Soc. 141, 13547−13561 (2020)
20. Andrew M Baker, Siddharth Komini Babu, Kavitha Chintam, Ahmet Kusoglu, Rangachary Mukundan, Rod L Borup, **Ce Cation Migration and Diffusivity in Perfluorosulfonic Acid Fuel Cell Membranes**, ECS Transactions 92 (8), 429-438 (2019)
21. K Chintam, KL More, KS Reeves, N Macauley, DE Hooks, RL Borup, **Microscopic Analysis of PEMFC Catalyst Layers**, ECS Transactions 92 (8), 95 (2019)
22. Kavitha Chintam, Krysta Waldrop, Andrew M Baker, Michael J Workman, Rangachary Mukundan, Jacob M LaManna, Daniel S Hussey, David L Jacobson, Cenk Gumeci, Nilesh Dale, John James Slack, Rod L Borup, Peter N Pintauro, **Improved Water Management of Electrospun Nanofiber Membrane Electrode Assemblies at High Current Densities Measured in Operando Using Neutron Radiography**, ECS Transactions 92 (8), 395

FC-PAD Publications

23. A. Chowdhury, R. M. Darling, C. J. Radke, and A. Z. Weber, ‘**Modeling Water Uptake and Pt Utilization in High Surface Area**,’ ECS Transactions, 92(8), 247-259 (2019). doi: 10.1149/09208.0247ecst
24. J. G. Petrovick, D. I. Kushner, M. Tesfaye, N. Danilovic, C. J. Radke, and A. Z. Weber, **Mass-Transport Resistances of Acid and Alkaline Ionomer Layers: A Microelectrode Study Part 1 - Microelectrode Development,** ECS Transactions, 92(8), 77-85 (2019). doi: 10.1149/09208.0077ecst
25. J.J. Slack, C. Gumeci, N. Dale, N. Macauley, R. Mukundan, D. Cullen, B. Sneed, K. More, P. N. Pintauro, **Nanofiber Fuel Cell MEAs with a PtCo/C Cathode**, Journal of the Electrochemical Society, 166 (2019) F3202-F3209d
26. Krysta Waldrop, John Slack, Cenk Gumeci, Nilesh Dale, Kimberly Shawn Reeves, David A Cullen, Karren L More, Peter N Pintauro, **Electrospun Particle/Polymer Fiber Electrodes with a Neat Nafion Binder for Hydrogen/Air Fuel Cells**, ECS Transactions 92 (2019) 595-602
27. John J Slack, M Brodt, David A Cullen, Kimberly S Reeves, Karren L More, Peter N Pintauro, **Impact of Polyvinylidene Fluoride on Nanofiber Cathode Structure and Durability in Proton Exchange Membrane Fuel Cells,** Journal of The Electrochemical Society 167 (2020) 054517
28. Kabir, S.; Myers, D. J.; Kariuki, N.; Park, J.; Wang, G.; Baker, A.; Macauley, N.; Mukundan, R.; More, K. L.; Neyerlin, K.C., **Elucidating the Dynamic Nature of Fuel Cell Electrodes as a Function of Conditioning: An ex Situ Material Characterization and in Situ Electrochemical Diagnostic Study.** *ACS Appl. Mater. Interfaces* 2019, *11*, 45016−45030. https://doi.org/10.1021/acsami.9b11365
29. *Wang*, M.; Park, J.; Kabir, S.; Neyerlin, K. C.; Kariuki, N.; Lv, H.; Stamenkovic, V.; Myers, D. J.; Ulsh, M.; Mauger, S. A., **The Impact of Catalyst Ink Dispersing Methodology on Fuel Cell Performance Using In-situ X-ray Scattering**, *ACS Appl. Energy Mater.* 2019, 2(9) 6417-6427. https://doi.org/10.1021/acsaem.9b01037

FC-PAD Presentations

1. Gregory J. Kleen, *Dimitrios C. Papageorgopoulos, Rod L. Borup, Adam Z. Weber* ***(Invited),*** **The FC-PAD Consortium: Advancing Fuel Cell Performance and Durability**, 236th Meeting of the Electrochemical Society, Atlanta, GA, October 2019
2. K.L. More (**invited**), **Advanced Microscopy Methods to Interrogate Materials and Interfaces in Fuel Cell Catalyst Layers,** Advanced Manufacturing and Characterization of Fuel Cells and Electrolyzers Workshop, University of Connecticut, Storrs, CT, September 23-24, 2019.
3. Adam Z. Weber, **Role of Transport Phenomena in Polymer-Electrolyte Fuel-Cell Performance**, 1st International Fuel Cell Conference, Xi'an, China, November. (**invited, plenary**)
4. L. M. Pant, A. Z. Weber, **Numerical Modeling of Hydrogen Fuel Cells using COMSOL,** COMSOL Day, San Jose, CA. April 2020 (**Invited talk**)
5. Derek Richard (**invited**), **Neutron Reflectometry for the Study of Thin-Film Ionomers: Effect of Substrate and Cation Exchange on Ionomer Structure**, UCLA Chemical Engineering Dept., June 2019
6. Lalit M. Pant, Anamika Chowdhury, and Adam Z. Weber, **Development of a Multiscale Approach for Modeling Porous Electrodes**, 236th ECS Meeting, Atlanta, GA. October 2019. (**invited**)
7. Adam Z. Weber, **Fuel Cell Technology**, ISMES Summer School, CalTech, June. (**invited**) D.A. Cullen, K.L. More, **Understanding Electrode Design and Degradation in Fuel Cells,** 257th ACS National Meeting & Exposition, San Diego, CA Aug. 25-29, 2019. (**invited**)
8. D.A. Cullen. **Accelerated Catalyst Development for the Emerging Hydrogen Economy**, UTSI MABE Departmental Series Seminar, Tullahoma, TN Oct. 9th, 2019. (**invited**)
9. D.A. Cullen, S. Cao, M. Chi, K.L. More, A. Weber, D.J. Myers, P. Zelenay, R. Borup, **A new view of fuel cell electrocatalysts through multimodal electron microscopy,** 236th ECS Meeting, Atlanta, GA Oct. 13-17, 2019. (**invited**)
10. D.A. Cullen, **Enabling hydrogen as an energy carrier through analytical electron microscopy**, AVS 66th International Symposium & Exhibition. Columbus, OH Oct. 20-25, 2019. (**invited**)
11. D.A. Cullen, **New opportunities and challenges for hydrogen fuel cells**, University of Cincinnati Department of Chemistry Colloquium, Cincinnati, OH Feb. 21st, 2020 (**invited**)
12. KC Neyerlin (invited) - **Dictating Pt-based electrocatalyst performance in PEFCs: From formulation to application** – ACS Fall 2019 San Diego, CA, August 25th -29th 2019.
13. Michael J. Workman, J. Beau W. Webber, Mike L. Perry, Robert M. Darling, Karren More, Rangachary Mukundan, Rodney L. Borup, **Analysis of PEMFC Electrode Pore Structure – Bridging the Mesoscale Gap,** 236th Meeting of the Electrochemical Society, Atlanta, GA, October 2019

FC-PAD Presentations

14. R. K. Ahluwalia, X. Wang, and C. F. Cetinbas, **Oxygen Transport in Electrodes with Degraded d-PtCo/C Cathode Catalyst**, 236th Meeting of the Electrochemical Society, Atlanta, GA, 16 October 2019
15. Kavitha Chintam, Karren More, Shawn Reeves, Natalie Macauley, Dan Hooks, Rod Borup, **Microscopic Analysis of PEMFC Catalyst Layers,** 236th Meeting of the Electrochemical Society, Atlanta, GA, October 2019
16. K. Chintam, K. Waldrop, A. M. Baker, M. J. Workman, R. Mukundan, J. M. LaManna, D. S. Hussey, D. L. Jacobson, J. J. Slack, P. N. Pintauro , and R. L. Borup, **Improved Water Management of Electrospun Nanofiber Membrane Electrode Assemblies at High Current Densities Measured in *Operando* using Neutron Radiography,** 236th Meeting of the Electrochemical Society, Atlanta, GA, October 2019
17. A. R. Crothers, R. M. Darling, A. Kusoglu, C. J. Radke, A. Z. Weber, **Thermodynamics of Ion and Water Uptake in Phase-Separated Ion-Exchange Membranes**, AIChE Annual Meeting, Orlando, FL. (2019)
18. A. R. Crothers, D. I. Kushner, R. M. Darling, A. Kusoglu, C. J. Radke, A. Z. Weber, **Theory of Multi-Ion Transport and Thermodynamic Phenomena in Solvent-Filled Membranes**, ECS Fall Meeting, Atlanta, GA. (2019)
19. A. Kusoglu, C. Arthurs, D. Kushner, **Characterization of Mechanical Behavior and Stability of Membranes for Energy Conversion Devices**, MRS Meeting, Boston. Dec 2019
20. G.M. Su, I.A. Cordova, M. Yandrasits, M. Lindell, J. Feng, C. Wang, A. Kusoglu, **New Insights into the Morphology of Perfluoro Ionene Chain Extended Ionomers from Resonant X-Ray Scattering and Spectroscopy**, MRS Meeting, Boston. Dec 2019
21. G.M. Su, I.A. Cordova, M. Yandrasits, M. Lindell, J. Feng, C. Wang, A. Kusoglu, **Chemical and Morphological Origins of Improved Transport in PFICE Ionomers**, ECS Meeting, Atlanta, GA. 2019
22. V.M. Ehlinger, A. Kusoglu, A.Z. Weber, **Modeling Impact of Ce on Fuel-Cell Performance and Durability**, ECS Meeting, Atlanta, GA. 2019
23. P.J. Dudenas, A.Z. Weber, A. Kusoglu, **Synchrotron-Based Characterization of Perfluorinated Sulfonic-Acid Ionomers**, ECS Meeting, Atlanta, GA. 2019
24. A.R. Crothers, D.I. Kushner, R.M. Darling, A. Kusoglu, C.J.Radke, A.Z. Weber, **Theory of Multi-Ion Transport and Thermodynamic Phenomena in Solvent-Filled Membranes**, ECS Meeting, Atlanta, GA. 2019
25. I.A. Cordova, A. Kusoglu, G.M. Su, D. Kilcoyne, J. Feng, C. Wang, **Multimodal Resonant X-ray Scattering: Elucidating Electrochemical Membranes**, ECS Meeting, Atlanta, GA. 2019
26. Adam Z. Weber, **Water and Thermal Management in Polymer-Electrolyte Fuel Cells**, 235th ECS Meeting, May, Dallas
27. Nancy N Kariuki, Max Gebhard, Anil U Mane, Magali Ferrandon, Ahmed A Farghaly, Jeffrey W Elam, Nemanja Danilovic, Deborah J Myers, **Highly Active and Durable Ir-Pt Bifunctional Electrocatalyst for Oxygen Evolution and Hydrogen Oxidation Reactions**, 235th ECS Meeting, May 2019, Dallas, TX.

FC-PAD Presentations

28. Sarah A. Berlinger, Bryan D. McCloskey, and Adam Z. Weber, **Understanding Polymer/Particle Interactions in Fuel-Cell Inks using Model Systems**, 236th ECS Meeting, Atlanta, GA. October 2019.
29. John G. Petrovick, Douglas I. Kushner, Meron Tesfaye, Nemanja Danilovic, and Adam Z. Weber, **Mass-Transport Resistances of Acid and Alkaline Ionomer Layers: A Microelectrode Study**, 236th ECS Meeting, Atlanta, GA. October 2019. (Poster)
30. Peter Dudenas, Adam Weber, Ahmet Kusoglu, **Synchrotron-Based Characterization of Perfluorinated Sulfonic-Acid Ionomers**, 236th ECS Meeting, Atlanta, GA. October 2019.
31. Victoria M. Ehlinger, Ahmet Kusoglu, Adam Z. Weber, **Modeling Impact of Ce on Fuel-Cell Performance and Durability**, 236th ECS Meeting, Atlanta, GA. October 2019.
32. Lalit M. Pant, and Adam Z. Weber, **Understanding Heat and Water Management in PEM Fuel Cells**, ASME IMECE conference, Salt Lake City, UT. November 2019.
33. Anamika Chowdhury, Robert M. Darling, Clayton J. Radke and Adam Z. Weber, **Catalyst Layer transport resistance: Role of ionomer content and chemistry**, 236th ECS Meeting, Atlanta, GA. October 2019.
34. Andrew Crothers, Robert Darling, Ahmet Kusoglu, Michael Perry, Clayton Radke, and Adam Z. Weber, **Understanding Transport Phenomena in Fuel-Cell and Flow-Battery Ion-Conducting Membranes,** ENSTIN 2019, Pilanesberg, South Africa, August.
35. A. Chowdhury, J. Petrovick, A. Kusoglu, N. Danilovic, C. J. Radke, A. Z Weber, **Resistances in low-Pt-loaded catalyst layers from a mass transport and ionomer point of view**, European Fuel Cell Durability conference, La Grande Motte, France, September.
36. Sarah A. Berlinger, Clayton J. Radke, Bryan D. McCloskey, Adam Z. Weber, **QCM-D Study of the Solvent-Polymer-Catalyst Particle Interface in Fuel-Cell Inks**, AIChE 2019, Orlando, FL. November 2019.
37. D.A. Cullen, **Atomic-level insights into the next generation of fuel cell catalysts**, CNMS Seminar Series, Oak Ridge, TN Dec. 11th, 2019.
38. D.A. Cullen, **Atomic-level insights into fuel cell catalysts,** Presented at Giner Inc. Newton, MA Dec. 22nd, 2019
39. Andrew M. Baker, Siddharth Komini Babu, Kavitha Chintam, Ahmet Kusoglu, Rangachary Mukundan, Rod L. Borup, **Cerium Migration and Diffusivity in PFSA Fuel Cell Membranes,** 236th Meeting of the Electrochemical Society, Atlanta, GA, October 2019
40. D. Richard, K. Chintam, M. J. Workman, A. Baker, K. L. More, K. S. Reeves, J. Dura, N. Macauley, P. Dudenas, A. Z. Weber, E. Watkins, R. Mukudan, R. L. Borup, **Fundamental Characterization of Catalyst Layer Ionomer Interactions in PEM Fuel Cells,** Fuel Cell Seminar, Nov 5-7 2019, Long Beach, CA
41. V. M. Ehlinger, A. R. Crothers, A. Kusoglu, A.Z. Weber, **Modeling Synergistic Mechanical and Chemical Degradation in Fuel-Cell Membranes**, Chemical and Biomolecular Engineering Colloquium, University of California Berkeley, Berkeley, CA. April 2020
42. A. R. Crothers, A. Kusoglu, C. J. Radke, A. Z. Weber, **Theory of Multicomponent Mass-Transport in Solvent-Filled, Ion-Conducting Membranes**, Chemical and Biomolecular Engineering Colloquium, University of California Berkeley, Berkeley, CA. February 2020

FC-PAD Presentations

43. K. C. Neyerlin, T. Van Cleve, G. Wang, A. G. Star, S. Kabir, L. Osmieri, S. Khandavalli, M. Wang, M. Ulsh, S. A. Mauger, S. Medina, and S. Pylypenko, **Electrode Layer Development and in Situ Diagnostic Characterization in Low Temperature Fuel Cells**, Spring ECS Meeting, Dallas, TX (May 2019).
44. Van Cleve, T; Khandavalli, S; Chowdhury, A; Medina, S; Pylypenko, S; Weber, A; Mauger, S; Neyerlin, K.C. **In situ Electrochemical Techniques to Determine Ionomer Coverage in PEFC Electrodes.** ECS Meeting, Atlanta, GA, Oct 2019.
45. Van Cleve, T; Khandavalli, S; Medina, S; Pylypenko, S; Neyerlin, K.C. **In situ Electrochemical Techniques to Determine Ionomer Coverage in PEFC Electrodes**. AIChE Meeting, Orlando, FL, Nov 2019.
46. Van Cleve, T; Mooney, M; Wang, G; Kabir, S; Neyerlin, K. C. **Effect of Ionomer Coverage on Pt Electrocatalyst Performance in PEFCs.** AIChE Meeting, Orlando, FL, Nov 2019.
47. S. Kabir, S. Khandavalli, T. V. Cleve, S.Medina, S. Pylypenko, N. N. Kariuki, D. Myers, K. L. More, S. A. Mauger, M. Ulsh, and K. C. Neyerlin, **Electrochemical and Rheological Investigations of Catalyst-Solvent-Polymer Ink Formulations for Electrospun Fuel Cell Electrode Structures**, 236th ECS Meeting, (October 13-17) 2019, Atlanta, GA. Abstract MA2019-02 1445
48. S. Kabir, L. Anderson, S. Medina, S. Pylypenko, and K. C. Neyerlin, **Electrospinning and MEA Conditioning As a Tool for Designing Optimized Electrode Structures for Fuel Cell Applications**, 235th ECS Meeting (May 26-31, 2019), Dallas, TX. Abstract #121883
49. Sergio A. Herrera, Rangachary Mukundan, David A. Cullen, Karren L. More, Deborah J. Myers, Rod L. Borup, **Effect of Carbon Support on the Durability of d-PtCo Catalysts in PEM Fuel Cells,** 236th Meeting of the Electrochemical Society, Atlanta, GA, October 2019