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

Presenter: Rod Borup

Tuesday, June 6th 2017

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FC-PAD: Consortium to advance fuel cell performance and durability

Approach

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

FCPAD
FUEL CELL PERFORMANCE
AND DURABILITY

Objectives

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

Consortium fosters sustained capabilities and collaborations

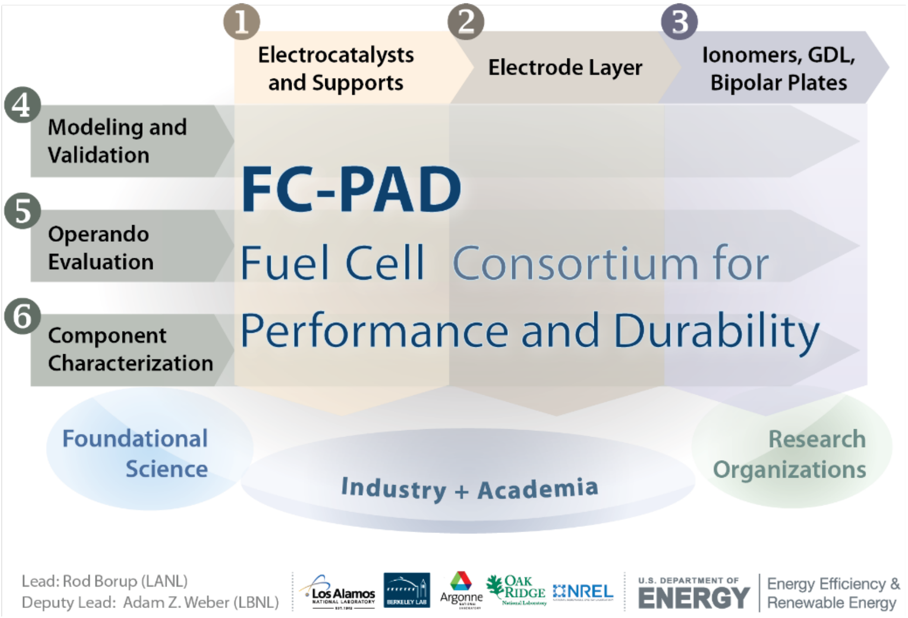
Core Consortium Team*

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

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

3M
GM
United Technologies Research Center
Vanderbilt

Structured across six component and cross-cutting thrusts



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

FC-PAD Consortium - Overview

Fuel Cell Technologies Office (FCTO)

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

Los Alamos NATIONAL LABORATORY

Argonne NATIONAL LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB

OAK RIDGE National Laboratory

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

FC-PAD Consortium – Relevance & Objectives

Overall Objectives:

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

FC-PAD Overview & Relevance

Timeline

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

Budget

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

Partners/Collaborations
(To Date Collaborations Only)

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

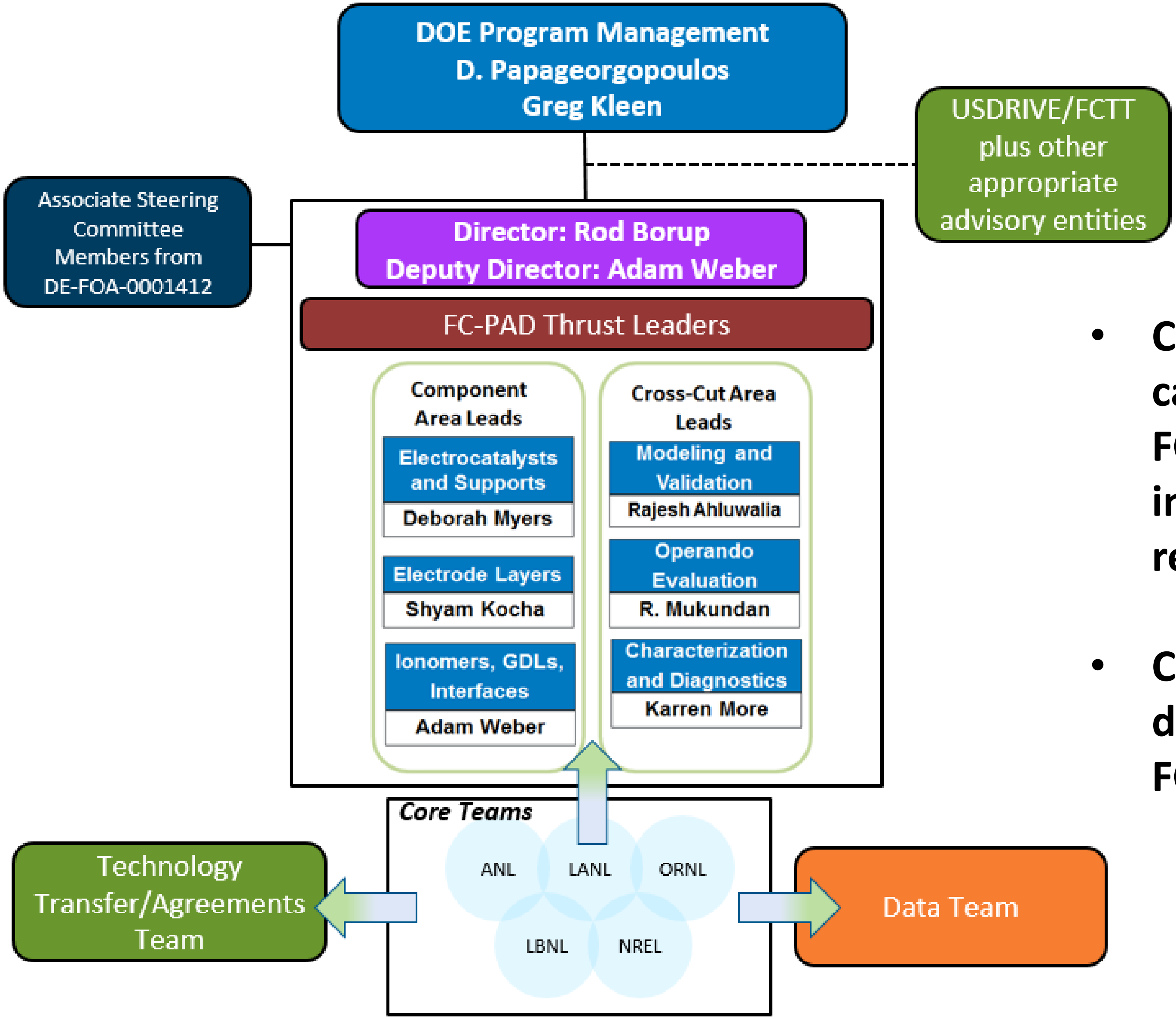
Barriers

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

- **Mitigation** of Transport Losses
- **Durability** targets have not been met

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

FC-PAD Organization



DOE Program Management
D. Papageorgopoulos
Greg Kleen

USDRIVE/FCTT plus other appropriate advisory entities

Associate Steering Committee Members from DE-FOA-0001412

Director: Rod Borup
Deputy Director: Adam Weber

FC-PAD Thrust Leaders

Component Area Leads

Electrocatalysts and Supports	Deborah Myers
Electrode Layers	Shyam Kocha
Ionomers, GDLs, Interfaces	Adam Weber

Cross-Cut Area Leads

Modeling and Validation	Rajesh Ahluwalia
Operando Evaluation	R. Mukundan
Characterization and Diagnostics	Karren More

Core Teams

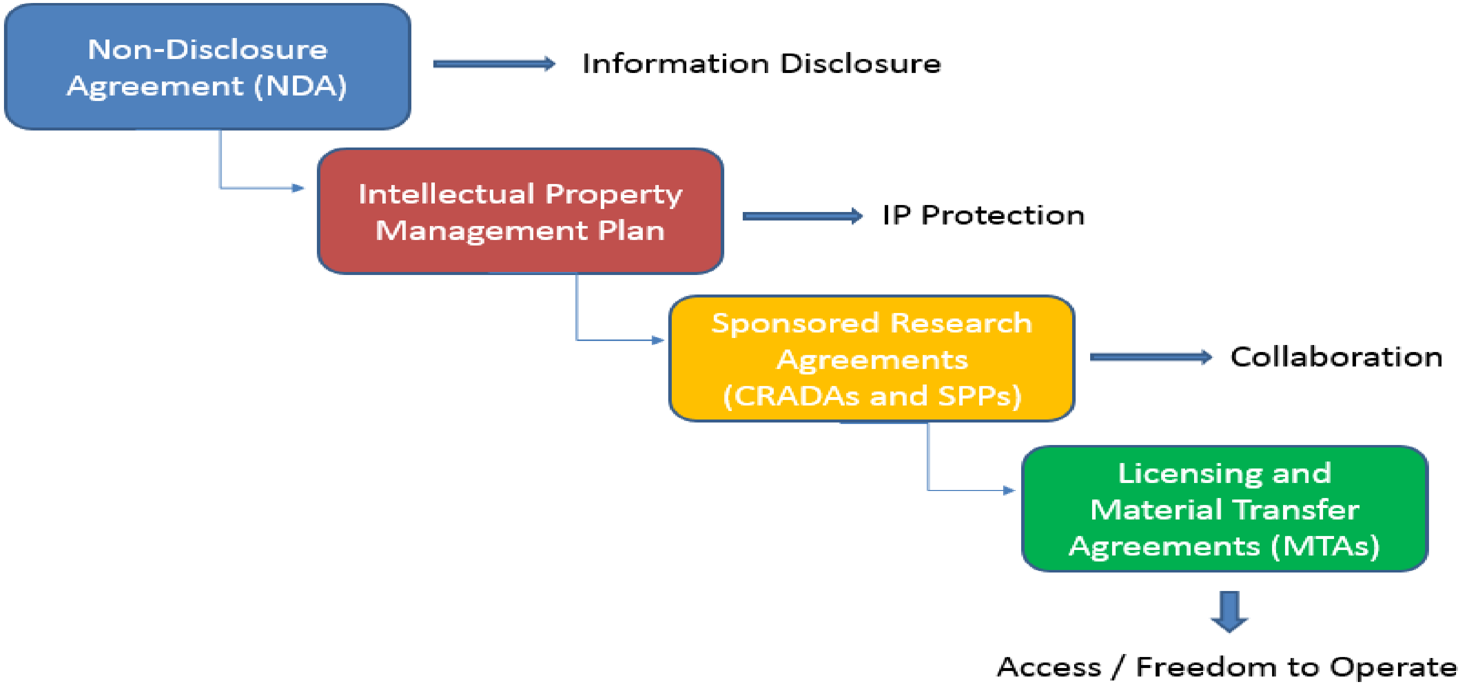
Technology Transfer/Agreements Team

Data Team

- Couple national lab capabilities with future FOAs for an influx of innovative ideas and research
- Collaborations are also desired outside the FOA process

Technology Transfer and Agreement Update – FC-PAD

- Multi-Lab Non Disclosure Agreement (NDA) – Executed
- Project-specific NDA Agreements – 3 of 4 are Executed
- Intellectual Property Management Plan (IPMP) - In process
- Material Transfer Agreement (MTA) – In process
- CRADA Template – Complete. Previously agreed upon format. Available for use.
- Tech Transfer & Agreements group conference call held in March to discuss TT/A strategy and status update



FC-PAD Thrusts, Coordinators, NL Roles

DOE: Dimitrios Papageorgopoulos
Greg Kleen

Director: Rod Borup
Deputy Director: Adam Weber

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

🟨 **Moderate Activity**

🟩 **High Activity**

- Coordination between thrusts
  - Standardization of materials
  - Input from associate steering committee members, FCTT, AMR reviewers
  - Promote coordination between FOA projects (as possible)
  - Achieve consensus for no-cost, non-FOA Collaborations from FC-PAD Core

Objective: How we get there

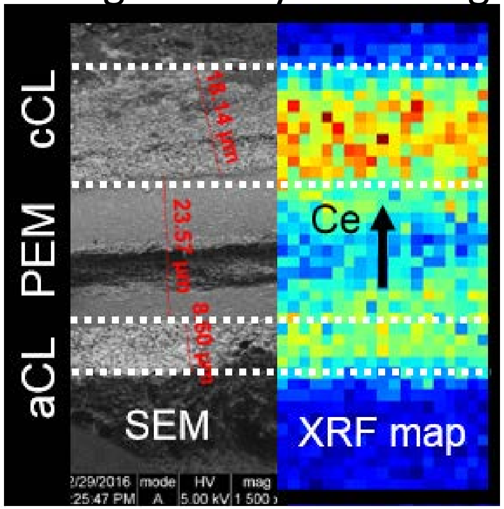
- **Develop the knowledge base and optimize structures for more durable and high-performance PEMFC components**
- **Understanding Electrode Layer Structure**
  - Characterization
- **New Electrode Layer Design and Fabrication**
  - Stratified (Spray, Embossed, Array), Pt - Deposition, Jet Dispersion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

FC-PAD Presentations

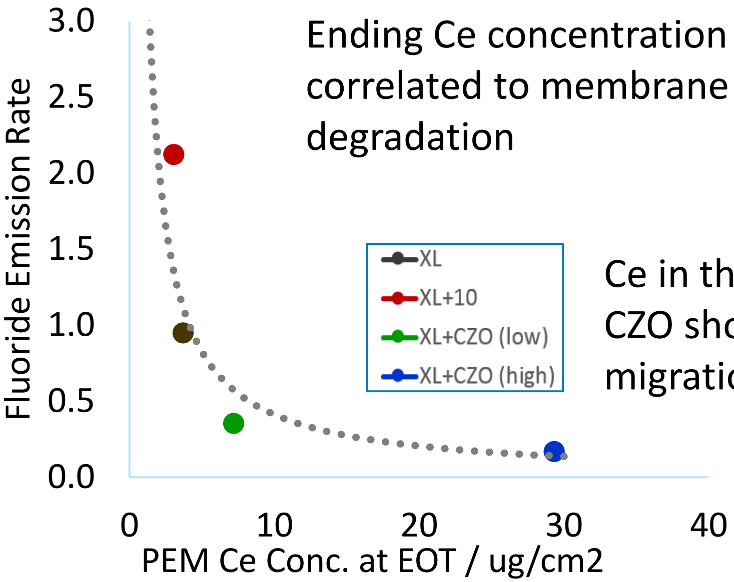
- **FC135: FC-PAD: Fuel Cell Performance and Durability Consortium (Borup, LANL)**
  - Overview, Framing, Approach, and Highlights/**Durability**
- **FC136: FC-PAD: Components and Characterization (More, ORNL)**
  - Concentrate on **Catalysts** and **Characterization**
- **FC137: FC-PAD: Electrode Layers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

Membrane Additives (Ce)
Evaluating Migration and Stabilization

Ce Migration between PEM and CL during Drive cycle testing:

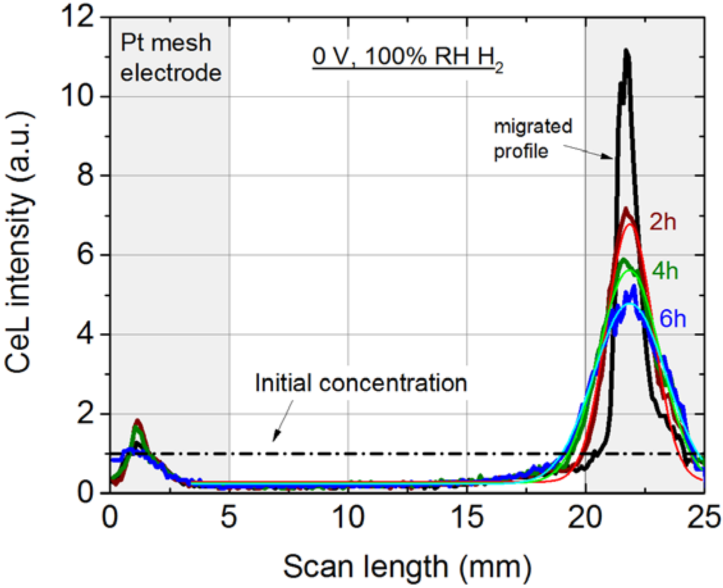


- After MEA synthesis, Ce is equilibrated between the PEM and CLs
- During fuel cell operation, AST testing, Ce migrates to catalyst layers
- In conductivity cell, with applied potential, Ce migrates to cathode
- After 100% RH H_2 pump, Ce contents in cathode CL exceed ionic equilibrium
- After 50% RH H_2 pump, very little Ce measured in CLs



Ending Ce concentration correlated to membrane degradation

Ce in the form of CZO shows lower migration

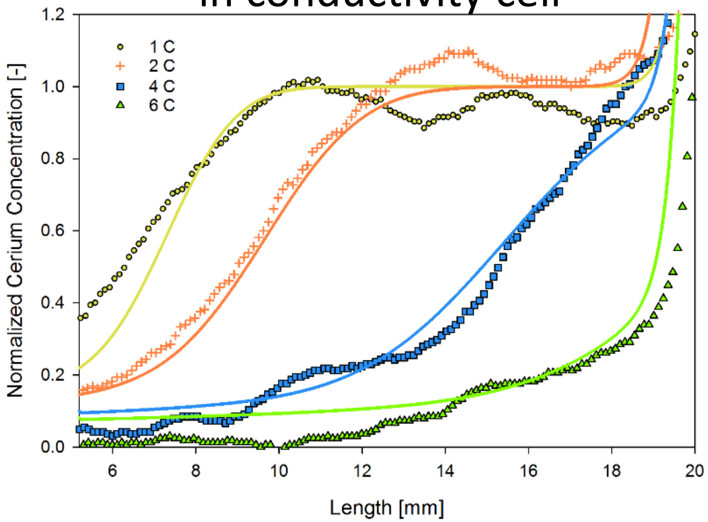


After Ce migration, potential relaxation shows diffusion

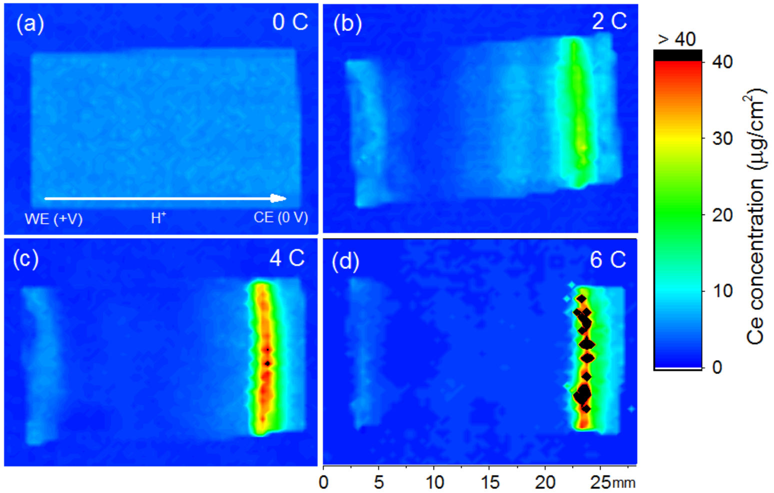
Baker, et al., *ECS Trans.*, **75**, 2016

Evaluating Cerium Migration Coefficients

Measured/Modeled Ce Migration in conductivity cell



Ce Migration between PEM and CL



- Operation results in cerium migration into the cathode CL due to proton flux
- Performance decay compared to a Ce-free MEA was attributed to Ohmic losses in CL ionomer
- Migration due to concentration and water gradients have also been identified

Defining Cerium Migration Coefficients

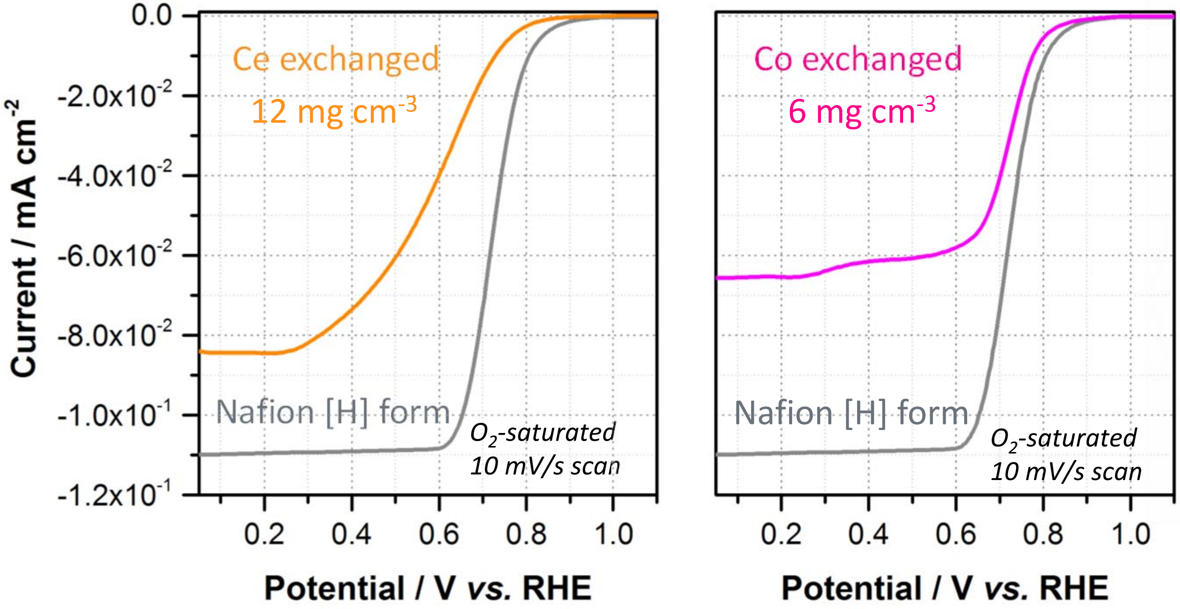
$$\frac{\partial c}{\partial t} + \nabla . \left(-D \nabla c - z u_m F c \nabla \phi_{ionic} \right) = 0$$

Parameter	100% RH	50 % RH
Diffusion Coefficient [x10^{-10} m^2 s^{-1}]	0.686	0.041
Mobility [x10^{-15} s mol kg^{-1}]	7.2±0.8	0.68±0.04

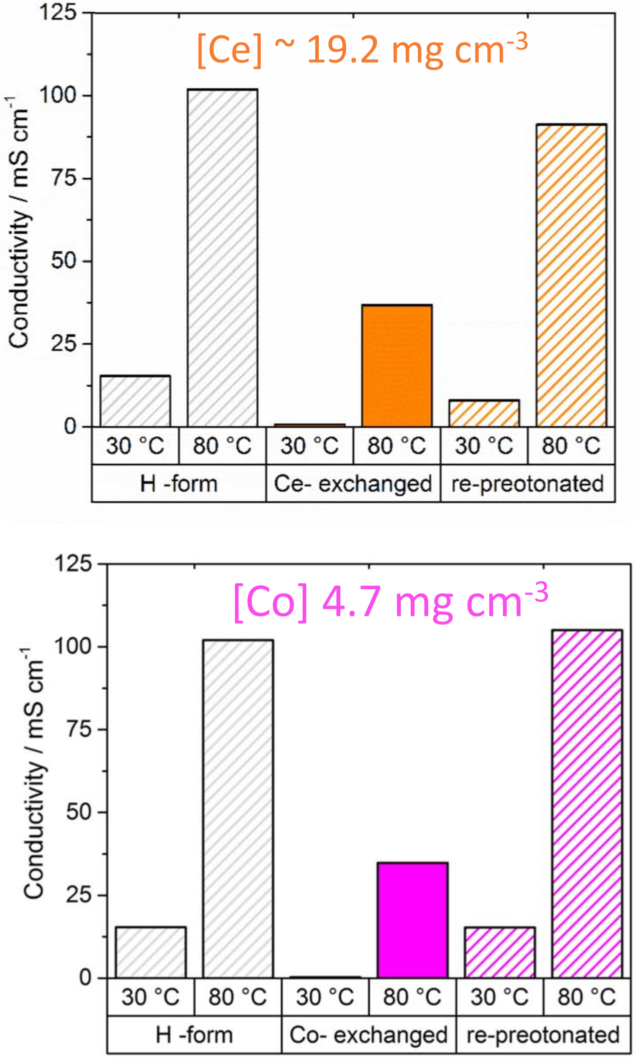
$$D_{eff} = \frac{D_o}{1 - {c}/{c_{sat}}} \qquad u_m = \frac{D_{eff}\, n}{RT}$$

Microelectrode Performance with Cations dosed into Nafion

Micro-electrode ORR with Cations



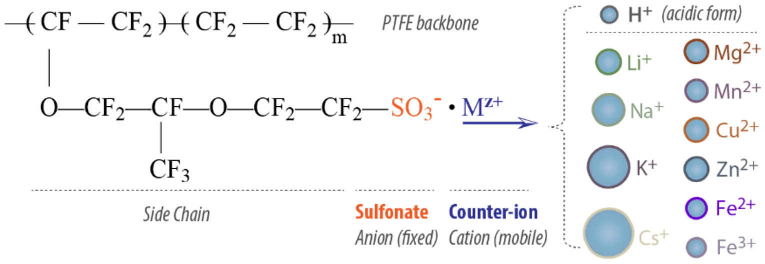
2 probe conductivity cell



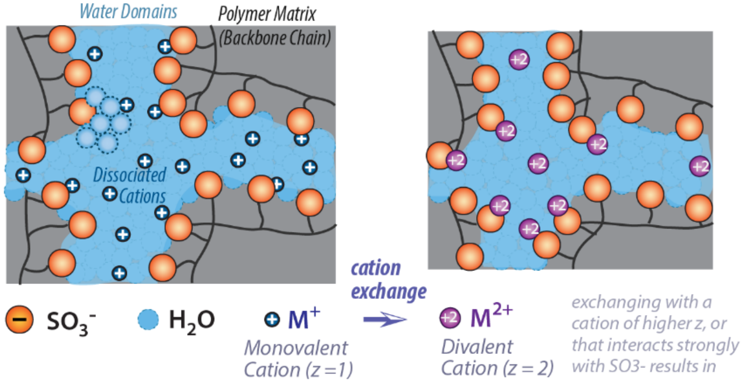
- 100 µm Pt microelectrode with a ~5 µm thin film
- Sharp decrease in $E_{1/2}$; 0.60 V vs. 0.73 V
- Lower limiting current with contaminated ionomers 8.2×10^{-2} (Ce), 6.2×10^{-2} (Co) and 6.3×10^{-2} (Ni) mA cm^2 *vs.* 1.1×10^{-1} mA cm^{-2}

- [Ce] based on measured migration into CCL
    - Ni, Co concentrations based on measured TEM after ASTs

Cation changes to PFSA Conductivity: Water/Cation - What Controls Conductivity?



$$-(CF-CF_2)-(CF_2-CF_2)_m- \quad O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3^- \cdot M^{z+}$$



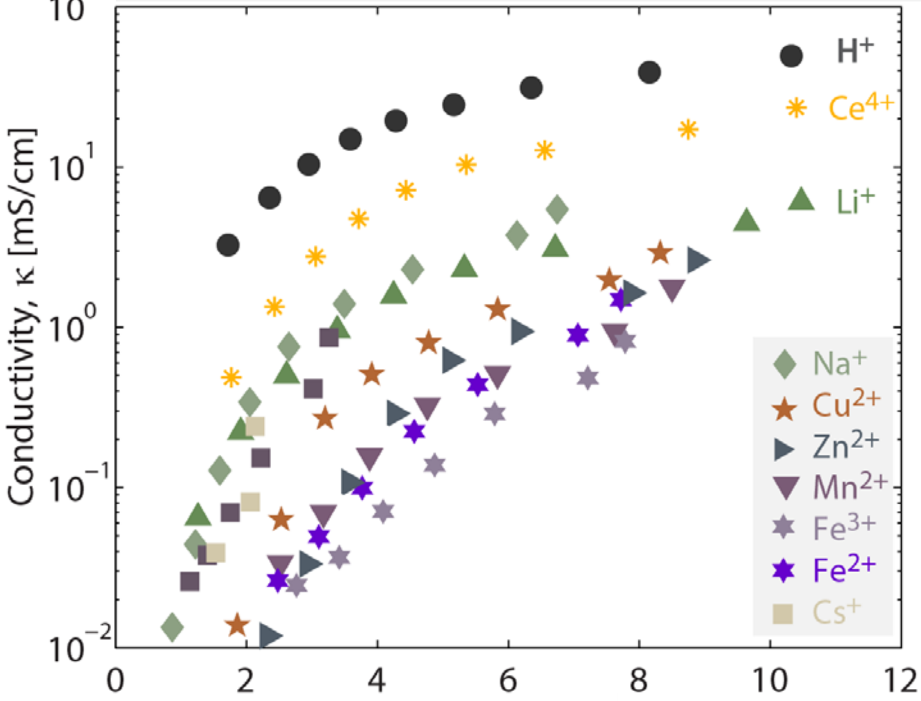
exchanging with a cation of higher z, or that interacts strongly with SO3- results in

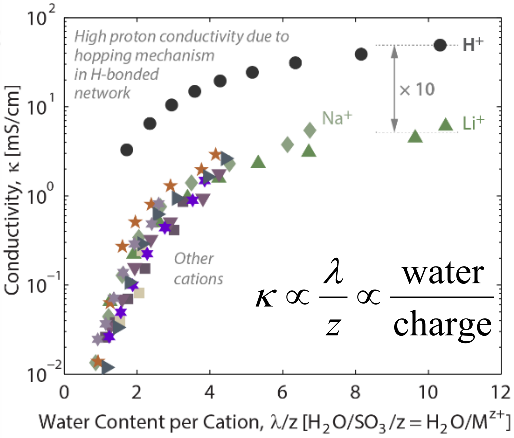
cation concentration = c_{M^+} → cation concentration = $c_{M^{2+}}$ ↓

water content = $\lambda = H_2O/SO_3^-$ → water content = $\lambda = H_2O/SO_3^-$ ↓

ion conductivity $\propto \lambda/z \sim \lambda$ → ion conductivity $\propto \lambda/z \sim \lambda/2$ ↓

Conductivity *scales with water per charge*





$$\kappa \propto \frac{\lambda}{z} \propto \frac{\text{water}}{\text{charge}}$$

- Cation Solvation (local interactions)
  - **Dominant at low RH** (hydration)

$$\kappa_{\text{local}} = F \cdot \underbrace{z}_{\text{cation charge number}} \cdot \underbrace{c_{M^+}}_{\text{cation concentraton}} \cdot \underbrace{\mu_{M^+}}_{\text{cation mobility}}$$

- Ionomer network (mesoscale)
  - **Dominant at high RH** (hydration)

$$\kappa_{\text{eff}} = \underbrace{\kappa_{\text{local}}}_{\text{Cation interactions}} \times \frac{\phi_{\text{water}}}{\underbrace{\tau}_{\text{Polymer Network}}}$$

Shi, Weber, and Kusoglu (2016), *Electrochim. Acta*, 220, p 517-528

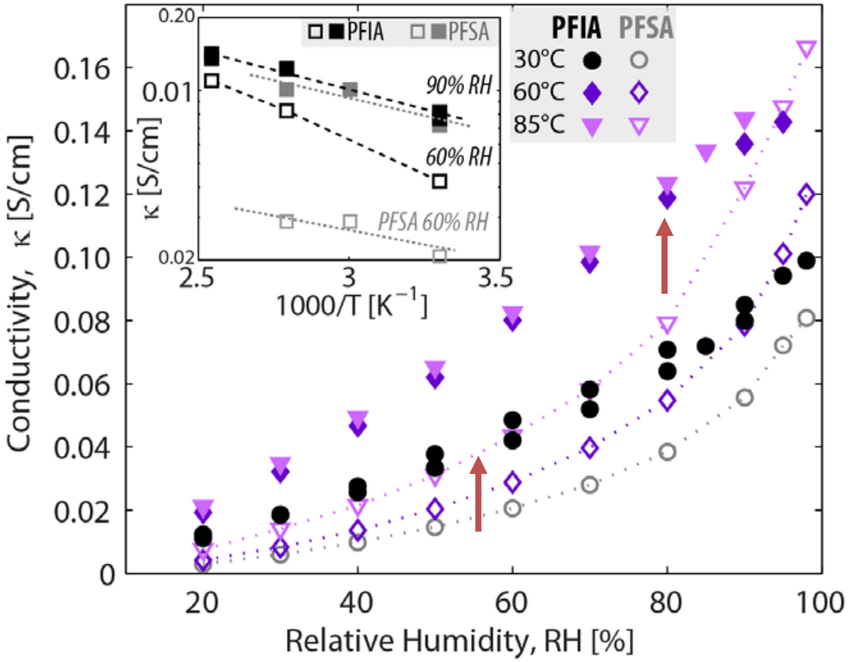
PFIA Membrane: Proton Conductivity

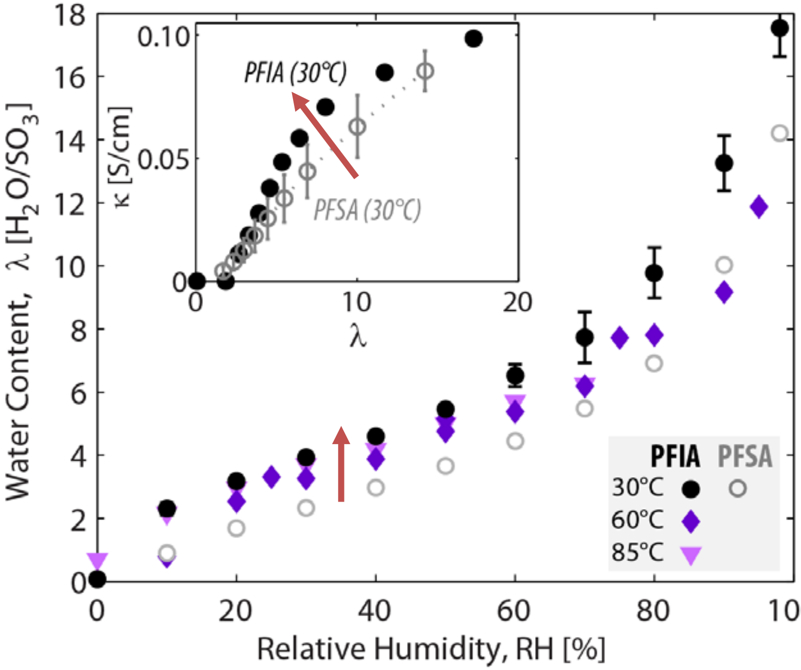
Conductivity: PFIA (*vs PFSA*)

- Higher conductivity at mid-RH
  - even at the same water content
  - Presence of a different mechanism: owing to the additional protogenic group
- Better high-T conductivity

Uptake: PFIA

- Similar to PFSA, slightly higher lambda
- More hydrophilic side-chains
  - Help formation of H-bonded network
  - Even at low RH, explains the conductivity

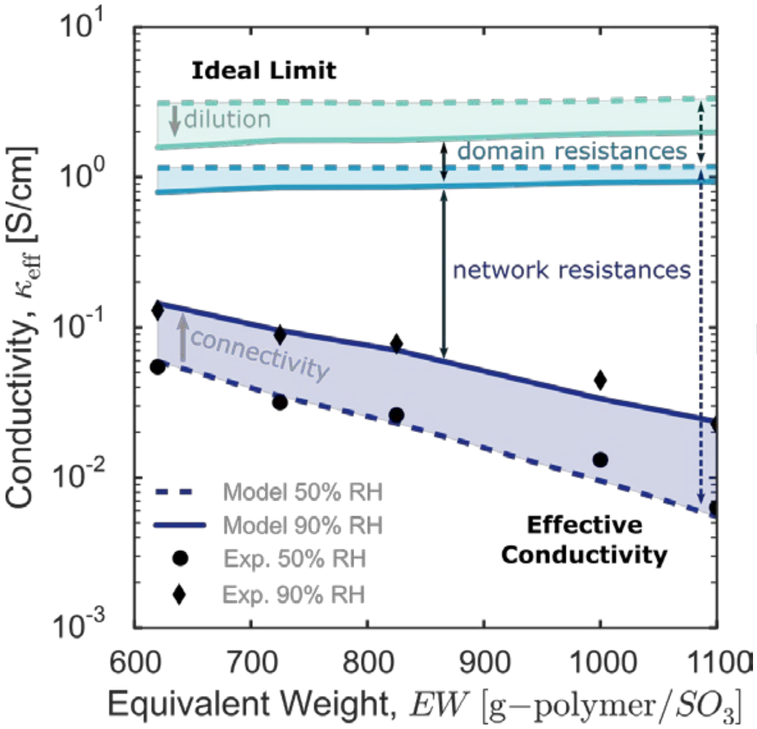


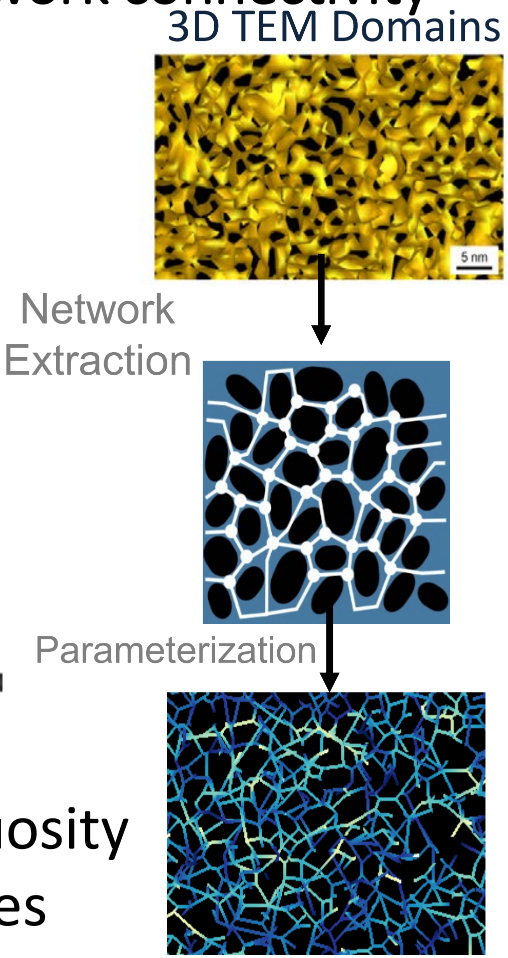


Modeling Membrane Conductivity - Multiscale ionomer model - Impact of Equivalent Weight

- Model predictive across range of EWs
- Network and cation-polymer interactions cause resistances
- Increased conductivity at low EW from better network connectivity

- **Ideal limit decreases with RH because of dilution of cations**
- **Network losses increase at low RHs**
- **Extracted conductive network skeleton from 3D TEM**
- **Effective membrane resistance: 0.11 S/cm (0.071 S/cm Experiment*) without any fitting**

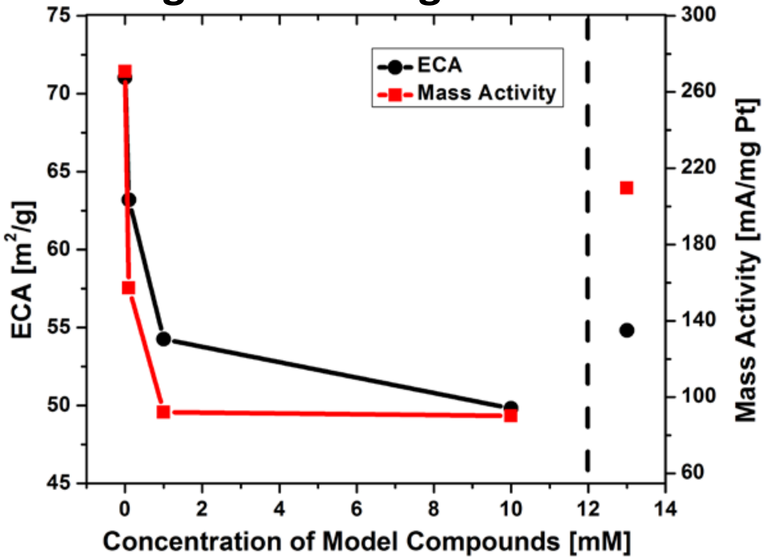


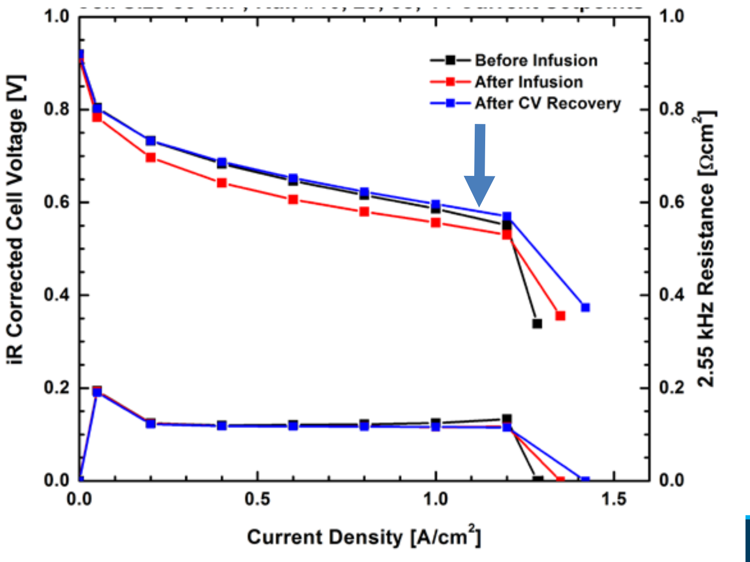


Shows inherent tortuosity of PFSA membranes

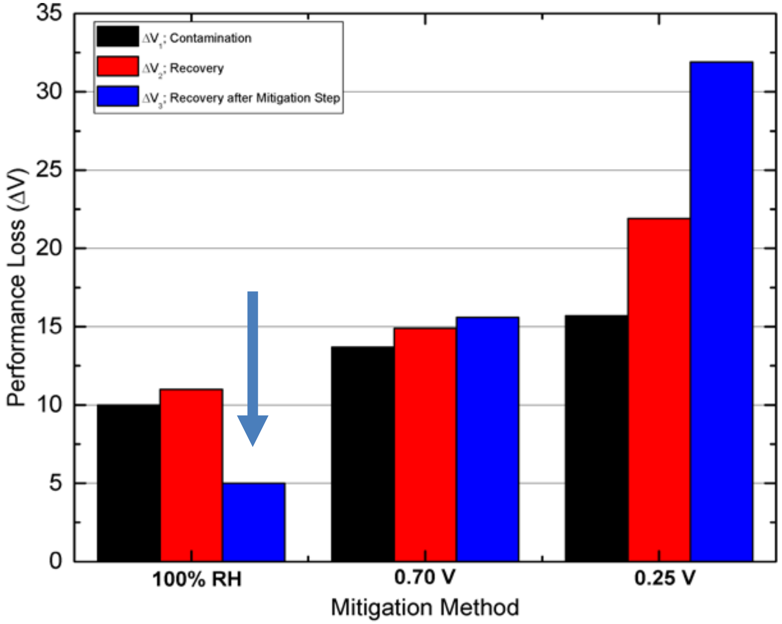
Technical Accomplishments:
Effect of Operating Conditions with Sulfate Contamination

Sulfate used to simulate membrane degradation fragments





In-situ infusion experiments to characterize effects of SO_4^{2-} contamination



- Performance loss due to sulfate contamination is observed at cell potentials below 0.7 V
- Neither high (0.7 V & OCV) nor low cell potentials (0.25V) led to recovery
- Increasing RH led to partial recovery
- CV cycling shows recovery

2016 Reviewer Comments

Reviewer: ‘ … suggested that the projects shift focus to a foundational understanding of degradation causes and novel fuel cell testing techniques. ‘

- This is a primary focus of the FC-PAD consortium.

Reviewer: ‘The project will likely have difficulty accessing SOA materials sets. ‘

- As a consortium, stronger access to materials than previously. GM, 3M, Vanderbilt have all provided materials to date. Other materials (e.g. advanced membranes, catalysts) obtained under non-analysis agreements (useful for benchmarking)

Reviewer: ‘The path forward to work with DOE-funded project teams is not clear. The extent to which the collaboration with new partners will be made is not clear.’

- Interactions with FOA-1412 projects should be more clear now that activities have started and work has been defined.

Reviewer: ‘Integration of new partners and coordination of the whole consortium could be a weakness if strong communication means are not clearly set.’

- POCs have been set. Steering committee set.

Reviewer: ‘… be very difficult to manage such activities unless a robust intellectual property/non-disclosure/confidential disclosure agreement is in place.’

- Technology Transfer and Agreement update was given. Progress made during FY17; more progress needs to occur. FC-PAD faces similar legal issues that other EERE consortium face (e.g. LightMat, HydroGen). Agreements between the various consortia being shared and duplicated as possible.

Collaborations (From FOA-1412)

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

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

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

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

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

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

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

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

Support Distribution

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

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

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

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

Collaborations (non-FOA activities)

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

Collaborations (non-FOA activities)

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

Future Work

Other details in FC136, FC137 presentations

- **Increase Integration of FOA projects**
  - NL support mostly just starting; activities need to ramp-up
- **Continue outreach to develop new collaborators**

- **Membrane, membrane additives and cation effects**
  - Beam line work to measure cerium profile during in situ fuel cell operation
  - Stabilize Ce in localized areas of the membrane (CZO, Ce stabilized within fibers or capsules)
- **Microelectrode work**
  - Measurements with 10 – 100 nm thin ionomer film
  - Lower concentrations of Ni, Co, Ce to define lower limit of effect
- **Micro continuum model for domain-scale physics**
  - Include nanoscale interactions: electrostatics, solvation, finite size, image charge, dispersion forces
  - Model effect of elected cations relevant to leaching, for thin film ionomers
  - Incorporate isolation of nanoscale and mesoscale resistances
- **Fuel Cell durability testing**
  - Verify/validate differential cell hardware
  - Revamp durability protocols for use in differential hardware
  - Develop validated AST for GDLs
- **Contaminants**
  - Better define reversible degradation mechanisms
  - SO_4^{2-} desorption conditions

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

Summary

- **Relevance**: **Advance performance and durability of PEMFCs**
- **Approach**: **Coordinate activities related to fuel cell performance and durability**
  - *Collaborate and support industrial and academic developers (4 FOA awarded projects)*
- **Accomplishments and Progress (selected):**
- **FY17: 20 publications, 61 presentation, 2 Invention disclosures**
  - Membrane & Ionomer
    - Membrane Additive Migration: Measured and modeled migration and diffusion coefficients
    - PFIA water uptake and conductivity comparisons with PFSA
    - Micro-continuum model - high inherent tortuosity of PFSA from 3D TEM (0.11 vs. 0.071 S/cm)
    - Microelectrode studies: Reduction in O2 diffusion from cations due to Ce, Ni Co
  - Fuel Cell Testing/Diagnostics (drive cycle, AST, limiting current), contaminant studies
    - Fuel Cell testing and catalyst cycling ASTs > 3 types of PtCo
    - SD/SU protocol on E-carbon, V-carbon and advanced-carbon based MEAs
  - Pt and Pt-alloy catalysts; Electrode Structure
    - Support structure, corrosion
    - Pt and alloy component dissolution measurements
    - Characterization of MEA/Ionomer Structure
  - Multiple variations of electrode designs to optimize high current density performance
    - Stratified (Spray, Embossed, Array), Pt - Deposition, Jet Dispersion

Acknowledgements

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

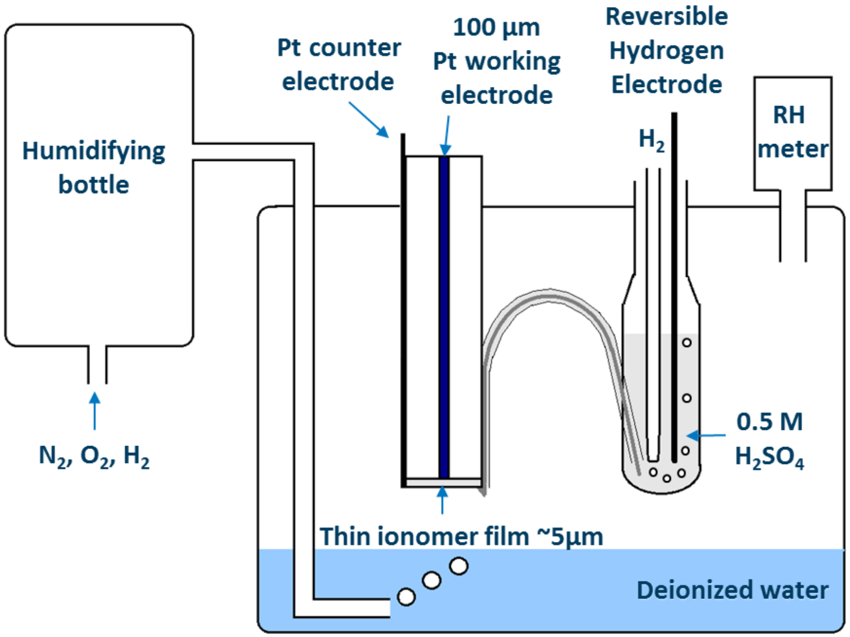
- Fuel Cells Program Manager & Technology Manager:
  - Dimitrios Papageorgopoulos
  - Greg Kleen

- Organizations we have collaborated with to date

- User Facilities
  - DOE Office of Science: SLAC, ALS-LBNL, APS-ANL, LBNL-Molecular Foundry, CNMS-ORNL, CNM-ANL
  - NIST: BT-2

Back-up Slides

Microelectrode Experimental setup



ORR measurements:

- ORR performance of a 100 µm Pt microelectrode with a ~5 µm thin film
- Measurements done in a O_2-saturated environment, 10 mV/s scan rate
- 25° C, 100% RH
- Thickness measured using laser profilometry
- Concentration of contaminants on deposited Nafion film measured by XRF:
  - Target [Ce] ~ 15 mg cm^{-3}
  - Target [Co], [Ni] ~ 4.7 mg cm^{-3}

Conductivity measurements:

- Performed in a temperature/ humidity controlled chamber using a 2 probe conductivity cell
- NR211 exchanged in $5x10^{-3}$ M $Ce(SO_4)_2$, $5x10^{-4}$ M $CoClO_4$ or $5x10^{-4}$ M $NiClO_4$ solutions for 30 min
- Concentration measured by XRF: same targets as above
- Re-protonation in 0.5 M H_2SO_4, only traces of contaminants remaining

Target CL ionomer concentration calculations

- **Ce concentration in the CL ionomer**
  - 2,000h OCV hold at 100% RH → **15 mg_{Ce}/cm^3 [1]**
    - **Migration due to degradation is minimized at 100% RH**

- **Co and Ni concentrations in the CL ionomer:**
  - Co:F = Ni:F = 1:1000 [2]
  - [F] = 3.8 mg/cm^2 for a 25 µm membrane [3] → 1.52 $g_F/cm^3 = 8x10^{-2}\ M_F/cm^3$
  - [Co] = [Ni] = $8x10^{-5}\ M_{Co/Ni}/cm^3$ → **4.71 $mg_{Co/Ni}/cm^3$**

Contaminant ion	Concentration in CL ionomer (mg/cm^3)
Ce	15 [1]
Co	4.7 [2,3]
Ni	4.7 [2,3]

[1] Baker, A. M. *et al. J. Electrochem. Soc.* **163,** F1023–F1031 (2016).
[2] Personal communication with David Cullen, March 17, 2017
[3] Rodgers, M. P. *et al. Chem. Rev.* **112,** 6075–6103 (2012).

What Controls Conductivity?

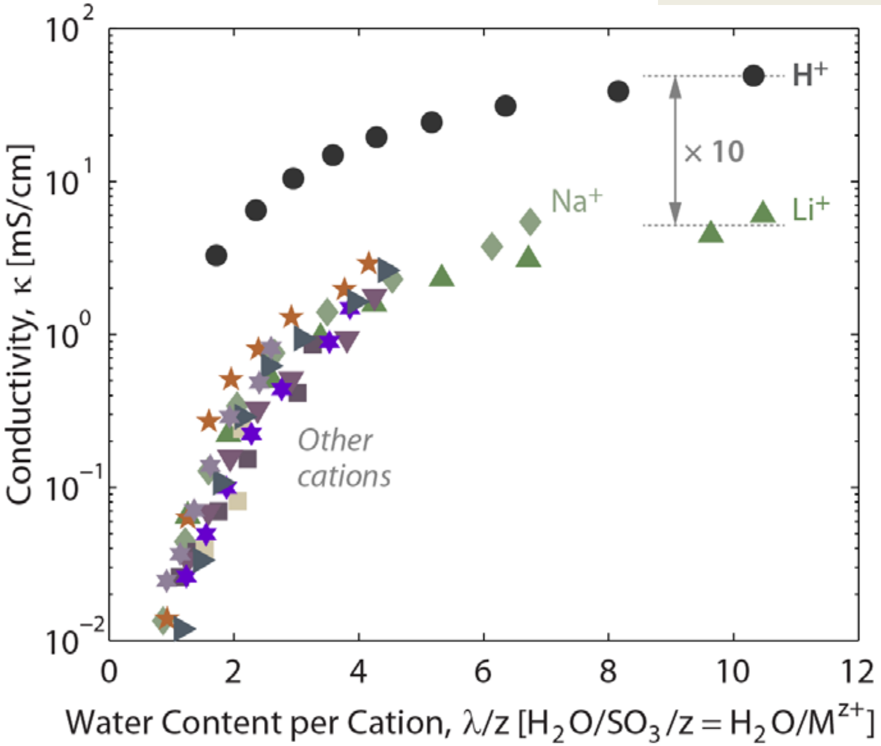
- Cation Solvation (local interactions)
  - **Dominant at low RH** (hydration)

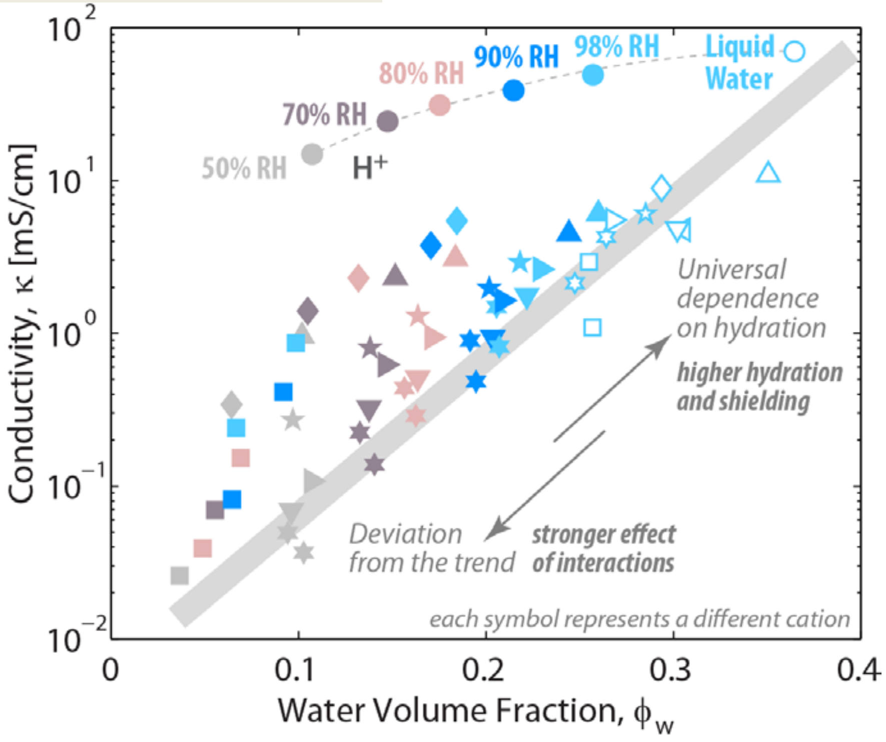
$$\kappa_{\text{local}} = F \cdot \underbrace{z}_{\substack{\text{cation}\\ \text{charge}\\ \text{number}}} \cdot \underbrace{c_{M^+}}_{\substack{\text{cation}\\ \text{concentraton}}} \cdot \underbrace{\mu_{M^+}}_{\substack{\text{cation}\\ \text{mobility}}}$$

- Ionomer network (mesoscale)
  - **Dominant at high RH** (hydration)

$$\kappa_{\text{eff}} = \underbrace{\kappa_{\text{local}}}_{\substack{\text{Cation}\\ \text{interactions}}} \times \frac{\phi_{\text{water}}}{\underbrace{\tau}_{\substack{\text{Polymer}\\ \text{Network}}}}$$

Conductivity *scales with water per charge*, not per poly(anion)





FY17 Milestones (Selected Joint)

FC-PAD Annual Milestone (Joint Milestone for all NL's; Shared Fate)

Milestone Name/Description	End Date
Local platinum resistance vis H2 and O2 limiting current measurements on at least 4 different MEAs compared	12/30/2016
Compare high density performance of 4 different cathode (including stratified) electrode layers, including variations on higher land versus channel catalyst loadings, microstructural Pt layer densification, electrode layer thickness masking creating micron size electrode features and effect of Nafion electrospun fibers. *Down-select MEA designs which do not show a path to equivalent or better performance to traditional SOA electrode layer designs*	6/30/2017
Benchmark and characterize the durability and performance of a series of Pt-X/C (minimum 3 different types of SOA Pt alloys; catalysts meeting 400 mA/mg-Pt ORR mass activity BOL performance) catalysts and electrode layers using FCTT catalyst AST and drive cycle protocols and compare with that of Pt/C catalysts; quantify the degree of degradation of Pt-based alloy catalysts and define the life-time (BOL to EOL) performance advantage of Pt-X alloys over Pt. Dealloying will be quantified by post-cycling TEM characterization and ex situ XAFS, WAXS, etc. evaluation.	9/30/2017

Joint between LBNL/NREL

Joint between LANL/NREL

Joint between All labs

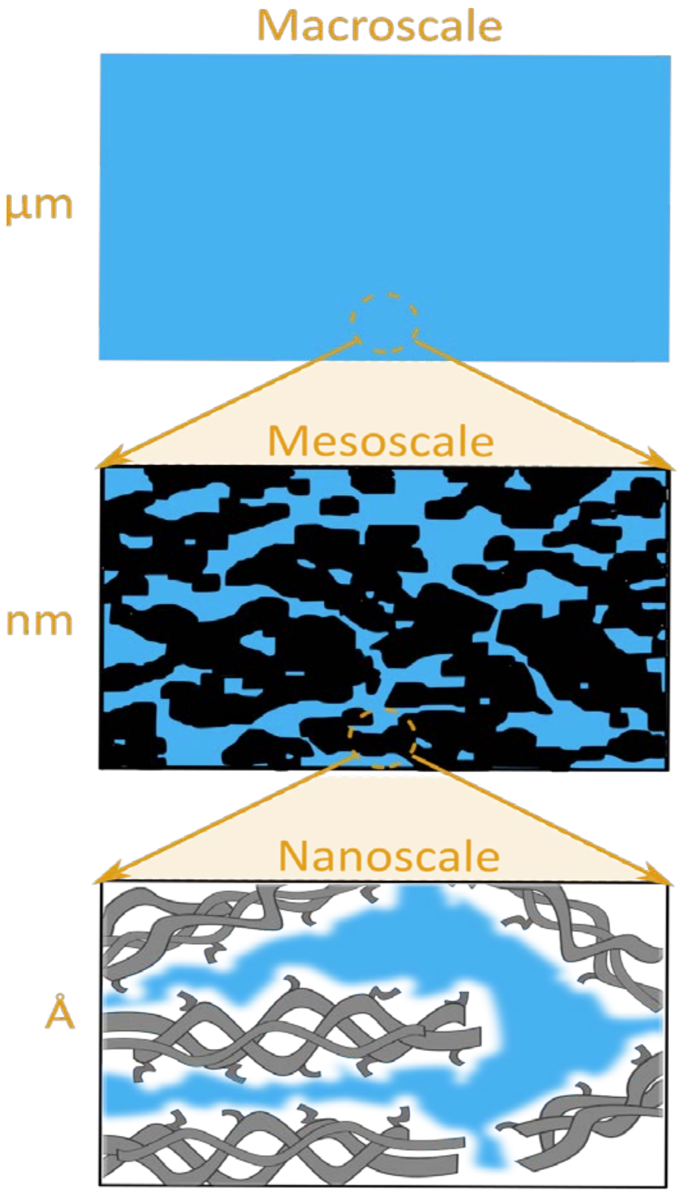
Supplemental Slides

Ce Additive Samples

Sample Name	Ce contents
XL	As received Nafion XL PEM (6 μg/cm^2 ion-exchanged Ce)
XL+10 (doped)	Nafion XL PEM doped with additional 10 μg/cm^2 Ce using Ce acetate solution
XL+18 (doped)	Nafion XL PEM doped with additional 18 μg/cm^2 Ce using Ce acetate solution
XL+CZO-low	Nafion XL PEM with 10 μg/cm^2 CZO added to the cathode CL
XL+CZO-high	Nafion XL PEM with 55 μg/cm^2 CZO added to the cathode CL

Backup: Multiscale Methodology

- **Use micro continuum model for domain-scale physics**
  - Incorporate nanoscale interactions:
    - Electrostatics, solvation, finite size, image charge, dispersion forces
  - Electrochemical potential is driving force
    - Ion mobility modified for confinement and dielectric friction
- **Upscaling via the mesoscale**
  - Parallel channel model used initially
  - Fitting only tortuosity (no nanoscale fitting parameters)
- **Model allows isolation of nanoscale and mesoscale resistances**

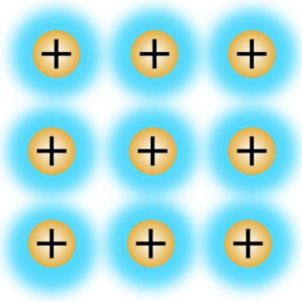


Backup: Nanoscale Physics

- **Electrochemical potential**

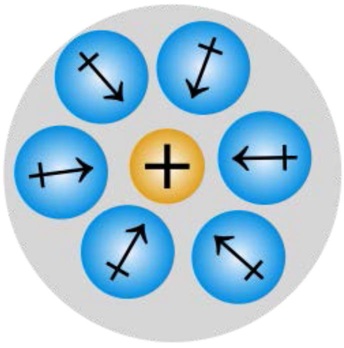
$$\underbrace{\tilde{\mu}_+ = \tilde{\mu}_+^0 + k_b T \ln \rho_+}_{\text{ideal solution}} + \underbrace{z_+ e \Phi}_{\text{electrostatics}} + \overbrace{\mu_{fs}}^{\text{finite size}} + \underbrace{\mu_{solv}}_{\text{solvation}} + \overbrace{\mu_{dsp}}^{\text{dispersion}} + \underbrace{\mu_{img}}_{\text{image charge}}$$

finite size



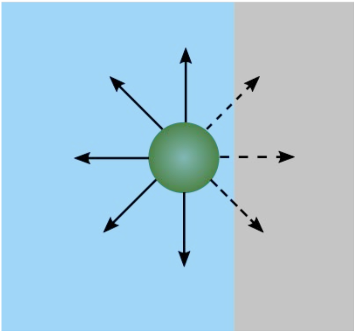
Bikerman 1942

solvation



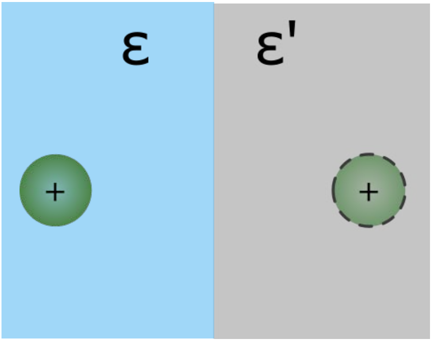
Bontha and Pintauro 1994

dispersion



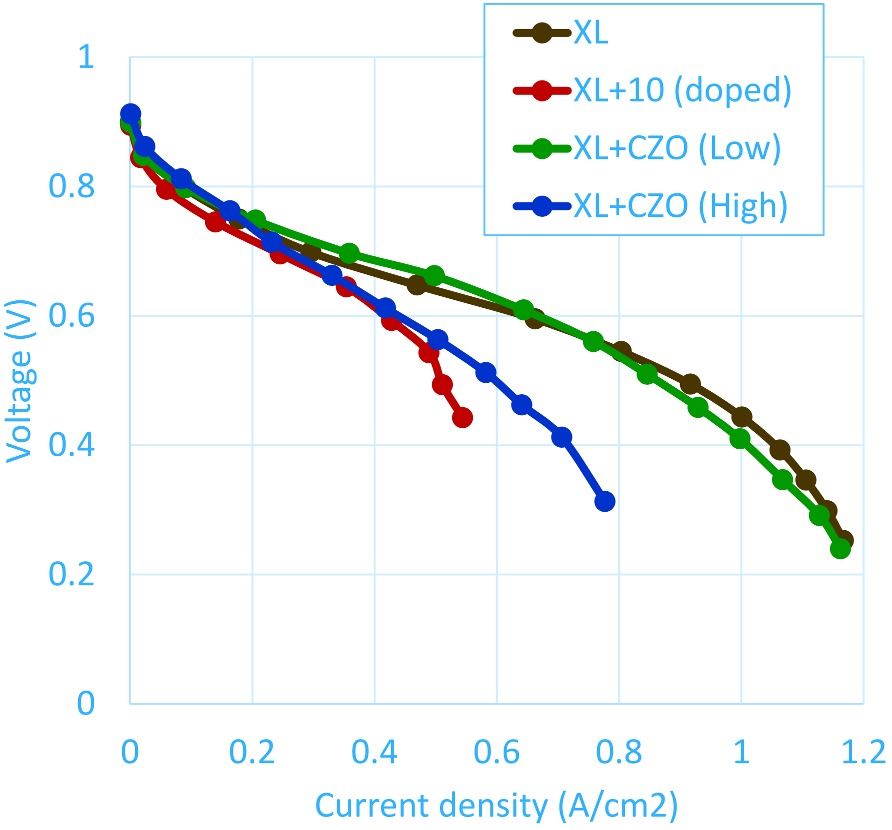
Karraker and Radke 2002

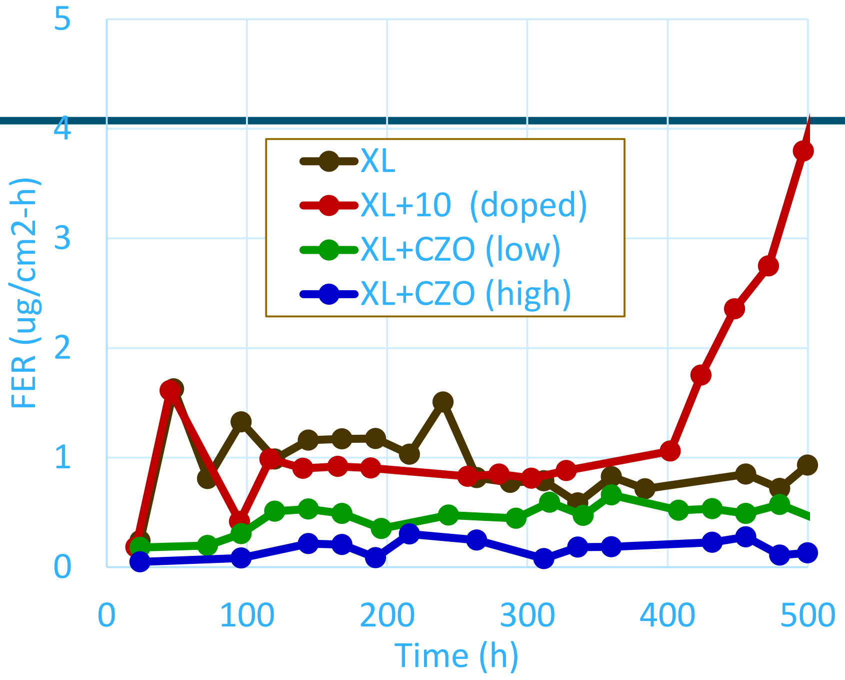
image charge



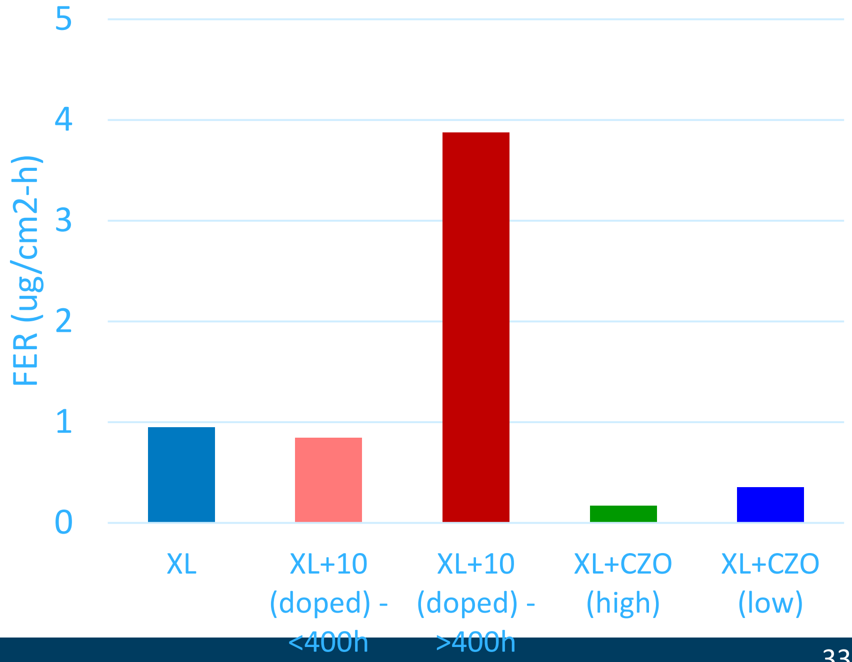
Onsager 1934

BOL polarization and FER

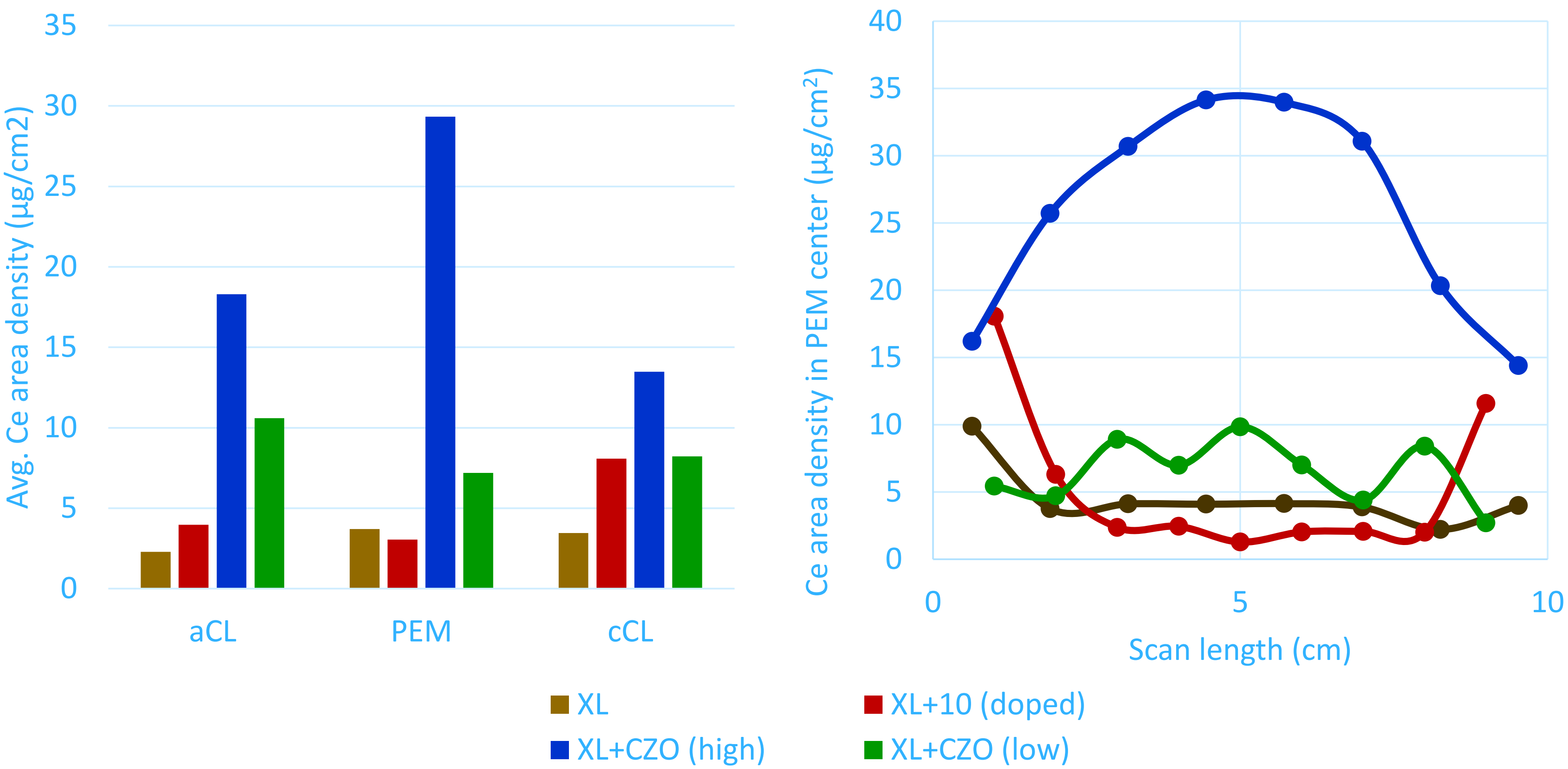




- Increased ion exchange in PEM results in increased ohmic resistance vs CZO which is still in oxide form
- FER is stable and lower than undoped XL until around 300h, when a catastrophic failure occurs. Not sure why this failure occurs



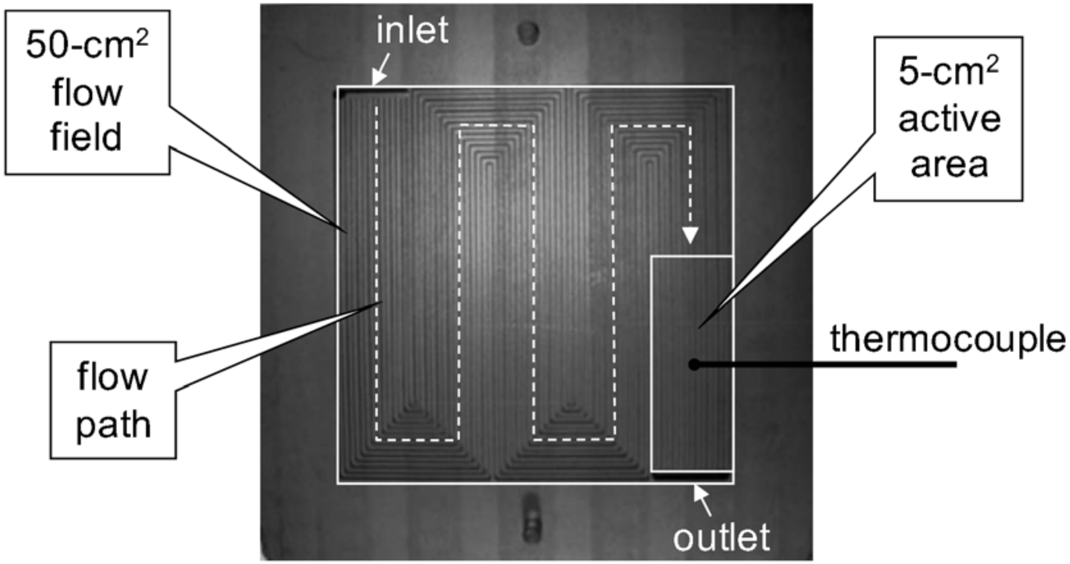
Ce migration



- Catastrophic failure results in a lot of the Ce being depleted from the PEM and going into the CLs
- Agrees with the degradation/stabilization mechanism we discussed in our JECS paper last year (Big FER→Ce depletion from PEM→Ce stabilization in CLs)

Cell Hardware

- 5 cm^2 differential cell
- Loadings of 0.05 to 0.125 mg_{Pt}/cm^2_{elec} and a constant loading of 0.2 mg_C/cm^2_{elec} (i.e. electrodes diluted with like carbon)
- Measure limiting currents as a *f*(pO2, RH) while keeping p_{total}= 101kPa_{abs}



D. R. Baker, D. A. Caulk, K. C. Neyerlin, and M. W. Murphy, *Journal of The Electrochemical Society*, 156, B991 (2009).

Hardware
Active Area 5, 50 cm^2
Triple Serpentine FF
Spray Coated CCMs

Operating Conditions
0.90 V
80°C
100 kPa PO_2
Stoic~9.0
100 %RH

Protocol
Anodic Sweep
5 mins/point

# of Samples >20

Publications and Presentations

<u>Publications Relevant to FC-PAD from Consortium Members:</u>

1. **Iryna V. Zenyuk, Prodip K. Das, and Adam Z. Weber, 'Understanding Impacts of Catalyst-Layer Thickness on Fuel-Cell Performance via Mathematical Modeling,' *Journal of the Electrochemical Society*, 163 (7), F691-F703 (2016). doi: 10.1149/2.1161607jes.**
2. **Ahmet Kusoglu, Thomas J. Dursch, and Adam Z. Weber, 'Nanostructure/Swelling Relationships of Bulk and Thin-Film PFSA Ionomers,' *Advanced Functional Materials*, 26, 4961-4975 (2016). doi: 10.1002/adfm.201600861.**
3. **Shouwen Shi, Adam Z. Weber, and Ahmet Kusoglu, 'Structure/property relationship of Nafion XL composite membranes,' *Journal of Membrane Science*, 516, 123-134 (2016). doi: 10.1016/j.memsci.2016.06.004**
4. **Iryna Zenyuk, Dilworth Y Parkinson, Liam G Connolly, and Adam Z Weber, 'Gas-Diffusion-Layer Structural Properties under Compression via X-Ray Tomography,' *Journal of Power Sources*, 328, 364-376 (2016). doi: <u>10.1016/j.jpowsour.2016.08.020</u>**
5. **Shouwen Shi, Adam Z. Weber, Ahmet Kusoglu, 'Structure-Transport Relationship of Perfluorosulfonic-Acid Membranes in Different Cationic Forms,' *Electrochimica Acta*, 220, 517-528 (2016). doi: 10.1016/j.electacta.2016.10.096**
6. **Iryna Zenyuk, Adrien Lamibrac, Jens Eller, Dilworth Parkinson, Federica Marone, Felix Büchi, Adam Z. Weber, 'Investigating Evaporation in Gas Diffusion Layers for Fuel Cells with X-ray Computed Tomography,' *Journal of Physical Chemistry C*, 120(50), 28701-28711 (2016). doi: 10.1021/acs.jpcc.6b10658.**
7. **Ahmet Kusoglu and Adam Z. Weber, 'New Insights into Perfluorinated Sulfonic-Acid (PFSA) Ionomers,' *Chemical Reviews*, 117 (3), 987-1104 (2017). doi: 10.1021/acs.chemrev.6b00159**
8. **Franz B. Spingler, Adam Phillips, Tobias Schuler, Michael C. Tucker, Adam Z. Weber, 'Investigating Fuel-Cell Transport Limitations using Hydrogen Limiting Current,' *International Journal of Hydrogen Energy*, , (2017). doi: 10.1016/j.ijhydene.2017.01.036**
9. **S. Shukla, S. Bhattacharjee, A. Z. Weber, M. Secanell, 'Experimental and Theoretical Analysis of Ink Dispersion Stability for Polymer Electrolyte Fuel Cell Applications,' *Journal of the Electrochemical Society*, 164 (6), F600-F609 (2017). doi: 10.1149/2.0961706jes**
10. **Lalit M. Pant and Adam Z. Weber, 'Modeling Transport in PEFC Cathode Agglomerates with Double Trap Kinetics,' *Journal of the Electrochemical Society*, 164 (11), E3081-E3091 (2017). doi: 10.1149/2.0081711jes**
11. **Anna T. S. Freiberg, Michael C. Tucker, and Adam Z. Weber, 'Polarization Loss Correction Derived from Hydrogen Local-Resistance Measurement in Low Pt-Loaded Polymer-Electrolyte Fuel Cells,' *Electrochemical Communications*, (2017). doi: 10.1016/j.elecom.2017.04.008**
12. **N Macauley, R Mukundan, DA Langlois, KC Neyerlin, SS Kocha, KL More, Madeleine Odgaard, Rod L Borup, Durability of PtCo/C Cathode Catalyst Layers Subjected to Accelerated Stress Testing, ECS Transactions 75 (14), 281-287**

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Publications Relevant to FC-PAD from Consortium Members:

13. AM Baker, R Mukundan, D Spernjak, SG Advani, AK Prasad, RL Borup, Cerium Migration in Polymer Electrolyte Membranes, ECS Transactions 75 (14), 707-714
14. Shinozaki, K., Morimoto, Y., Pivovar, B.S. and Kocha, S.S., 2016. Suppression of oxygen reduction reaction activity on Pt-based electrocatalysts from ionomer incorporation. *Journal of Power Sources*, *325*, pp.745-751.
15. Shinozaki, K., Morimoto, Y., Pivovar, B.S. and Kocha, S.S., 2016. Re-examination of the Pt Particle Size Effect on the Oxygen Reduction Reaction for Ultrathin Uniform Pt/C Catalyst Layers without Influence from Nafion. *Electrochimica Acta*, *213*, pp.783-790.
16. C. Firat Cetinbas, Rajesh K. Ahluwalia, Nancy Kariuki, Vincent De Andrade, Dash Fongalland, Linda Smith, Jonathan Sharman, Paulo Ferreira, Somaye Rasouli, and Deborah J. Myers, Hybrid approach combining multiple characterization techniques and simulations for microstructural analysis of proton exchange membrane fuel cell electrodes, Journal of Power Sources, 344 (2017), 62-73.
17. Andrew M Baker, Rangachary Mukundan, Dusan Spernjak, Elizabeth J Judge, Suresh G Advani, Ajay K Prasad, Rod L Borup, Cerium migration during PEM fuel cell accelerated stress testing, Journal of The Electrochemical Society 163 (9), F1023-F1031
18. B.T. Sneed, D.A. Cullen, K.S. Reeves, O.E. Dyck, D.A. Langlois, R. Mukundan, R.L. Borup, and K.L. More "3D Analysis of Fuel Cell Electrocatalyst Degradation on Alternate Carbon Supports," submitted to *ACS Catalysis* (under review).
19. Natalia Macauley, Joseph Fairweather, Rangachary Mukundan, D. D. Papadias, Dusan Spernjak, David Langlois, R. Ahluwalia, Karren More and Rodney L. Borup, Accelerated testing of carbon corrosion in PEM fuel cells, submitted
20. Natalia Macauley, Roger W. Lujan, Dusan Spernjak, Daniel S. Hussey, David L. Jacobson, Karren More, Rodney L. Borup, and Rangachary Mukundan, Durability of Polymer Electrolyte Membrane Fuel Cells Operated at Subfreezing Temperatures, *J. Electrochem. Soc. 2016 volume 163, issue 13, F1317-F1329*

Publications and Presentations

Presentations Relevant to FC-PAD from Consortium Members:

1. **A Kusoglu "State of Understanding of PFSA Ionomers and Thin Films," Gordon Research Conference (GRC) Fuel Cells, Easton, MA. August 2016**
2. **A Kusoglu "New Insights into PFSA Ionomers: From Membranes to Thin Films," 3M company, February 2017**
3. **A.Z. Weber, (Keynote) Multiscale Modeling of Polymer-Electrolyte-Fuel-Cell Components, Meeting Abstracts, MA2016-01 (2016) 2211.**
4. **Shum, K.B. Hatzell, L.G. Connolly, O.S. Burheim, D.Y. Parkinson, A.Z. Weber, I.V. Zenyuk, Exploring Phase-Change-Induced Flow in Fuel Cells through X-Ray Computed Tomography, ECS Meeting, 2016.**
5. **T. Schuler, M.C. Tucker, A.Z. Weber, Gas-Transport Resistances in Fuel-Cell Catalyst Layers, ECS Meeting, 2016.**
6. **Adam Z Weber, Lalit Pant, Tobias Schuler, Haui-Suen Shiau, Anna Freiberg, Michael C. Tucker, Anamika Chowdhury, K. C. Neyerlin, Shyam Kocha, Iryna Zenyuk, "Elucidating and Understanding Transport Phenomena in Polymer-Electrolyte Fuel Cells," CARISMA, April, 2017, Newcastle upon Tyne, United Kingdom**
7. **Adam Z. Weber, Tobias Schuler, Franz Spingler, Anna Freiberg, Michael C. Tucker, Anamika Chowdhury, K. C. Neyerlin, and Ahmet Kusoglu, "Ionomer-Associated Transport Resistances in Fuel Cell Electrodes," 21st International Conference on Solid State Ionics, Padua, Italy, June 2017**
8. **Andrew R. Crothers, Shouwen Shi, Peter Dudenas, Ahmet Kusoglu, Adam Z. Weber, "Structure-Transport Relationships of Perfluorinated-Sulfonic-Acid Membrane Interfaces," Polymer-Electrolyte Fuel Cell Components, Asilomar, (2017).**
9. **Andrew R. Crothers, Clayton Radker, Adam Z. Weber, "Elucidating Multiscale, Multiphysics Coupled Transport Phenomena in Polymer-Electrolyte Membranes Structure-Transport Relationships of Perfluorinated-Sulfonic-Acid Membrane Interfaces," Coupled Problems, Rhodes, Greece (2017)**
10. **Pablo A. García-Salaberri, Jeff T. Gostick, Gisuk Hwang, Marcos Vera, Iryna Zenyuk, and Adam Z. Weber, "Multiphysics, Multiphase and Multiscale Modeling of Polymer Electrolyte Fuel Cells: With a Focus on the Gas Diffusion Layers," Coupled Problems, Rhodes, Greece (2017)**
11. **Andrew Shum, Liam Connolly, Kelsey B. Hatzell, Xianghui Xiao, Dilworth Y. Parkinson, Odne Burheim, Adam Z. Weber, Iryna V. Zenyuk, "In-Situ Examination of Phase-Change-Induced Flow in Gas Diffusion Layers and Water Distribution in Microporous Layers using X-Ray Computed Tomography," MRS Fall Meeting, 2016**
12. **Adam Z. Weber, "Understanding Transport in Polymer-Electrolyte-Fuel-Cell Ionomers," Mechanical Engineering Seminar, UC Merced, 2016**

Publications and Presentations

Presentations Relevant to FC-PAD from Consortium Members:

13. Ahmet Kusoglu, "Ion-Conductive Polymer for Energy Conversion Devices," Mechanical Engineering Department Seminar, UC Berkeley, February 2017
14. Ahmet Kusoglu, "Structural Characterization of Ionomers using X-rays," Advanced Light Source, Chemical Sciences Seminar Series, Berkeley Lab, Berkeley, CA. July 2016
15. Ahmet Kusoglu, "New Insights into PFSA Ionomers" National Renewable Energy Lab, Golden, CO. 2017
16. A. Kusoglu, S. Shi, A Weber, “Impact of Cation form on Structure/Function Relationships of Perflurosulfonic Acid Ionomers,” APS Meeting, New Orleans, LA. March 2017
17. A. Kusoglu, S. Shi, A Weber, “Impact of Equivalent Weight and Side-Chain on Structure/Functionality of PFSA Ionomers,” ECS Meeting, Hawaii, 2016
18. Iryna V. Zenyuk, Adrien Lamibrac, Jens Eller, Felix N. Büchi, Adam Z. Weber, “Understanding Evaporation in Fuel-Cell Gas-Diffusion Layers with X-ray Computed Tomography,” Interpore, 2016
19. Meron Tesfaye, Bryan D. McCloskey, Adam. Z. Weber, “Gas Permeation Study in Thin and Ultra-thin Ionomer Films,” ECS fall meeting, Hawaii, 2016
20. A. R. Crothers, S. Shi, C. J. Radke, and A. Z. Weber, “Decoupling the influences of molecular- and mesoscales on macroscopic transport properties in perfluorosulfonic-acid membranes,” Fall ECS meeting, Hawaii, 2016
21. I. A. Cordova, C. Wang, A. Z. Weber, R. A. Segalman, M. A. Brady, G. M. Su, “Operando Resonant Soft X-Ray Scattering As a Spatio-Chemical Characterization Technique for Electrochemistry,” Fall ECS meeting, Hawaii 2016.
22. Kelsey Hatzell, Ahmet Kusoglu, Pete Dudenas, Nancy Kariuki, Deborah Myers and Adam Weber, “Indirect and direct observation of ionomer colloidal systems with applications to membrane electrode assemblies for energy conversion systems,” Fall ECS Meeting, Hawaii, 2016
23. Anna Freiberg, Tobias Schuler, Franz Spingler, Michael C. Tucker, and Adam Z. Weber, “Determination and Origin of Local Resistances in PEFC Catalyst Layers,” ISE Annual meeting, Hague, Netherlands, 2016
24. Andrew Shum, Kelsey B. Hatzell, Liam Connely, Odne Burheim, Dilworth Y. Parkinson, Adam Z. Weber, and Iryna V. Zenyuk, “Understanding Phase-Change-Induced Flow in PEFCs Through *In-situ* X-ray Computed Tomography,” ISE Annual meeting, Hague, Netherlands, 2016

Publications and Presentations

<u>Presentations Relevant to FC-PAD from Consortium Members:</u>

25. A. Kusoglu, “Morphology of PFSA ionomers and thin films,” 21st International Conference on Solid State Ionics, Padua, Italy, June 2017
26. R.L. Borup, (Invited) Material Degradation in PEM Fuel Cell Electrodes, 231st ECS Meeting (May 2017)
27. R.L. Borup, (Invited) The FC-PAD Consortium: Advancing Fuel Cell Performance and Durability, 231st ECS Meeting (May 2017)
28. R.L. Borup, (Invited) R Mukundan, T Rockward, M Brady, J Thomson, D Papadias, et al., (Metal) Bipolar Plate Testing, DOE Bipolar Plate Workshop, Feb 2018, Detroit
29. R.L. Borup, (Invited) Rangachary Mukundan, Andrew Baker, Dusan Spernjak, David Langlois, Sarah Stariha, Natalia Macauley, Karren More, Shyam Kocha, Adam Z. Weber, Debbie Myers and R. Ahluwalia, Material Degradation in PEM Fuel Cell Electrodes, CARISMA, April, 2017, Newcastle upon Tyne, United Kingdom
30. R.L. Borup, (Invited) Adam Z. Weber, Deborah Myers, Shyam Kocha, Rajesh Ahluwalia, Rangachary Mukundan, Karren More, The FC-PAD Consortium: Material Degradation in PEM Fuel Cell Electrodes, EMN Meeting on Fuel Cells 2017, Prague, Czech Republic, June, 2017.
31. R.L. Borup, (Invited) A. M. Baker, R. Mukundan, D. Spernjak, E. J. Judge, S. G. Advani, and A. K. Prasad, Membrane Degradation in PEM Fuel Cells: Antioxidant Migration and Recoverable Degradation Losses, 21st International Conference on Solid State Ionics, Padua, Italy, June 2017
32. D. Myers, Structural Characterization of Polymer Electrolyte Fuel Cell Cathode Catalyst Layers, NCNR/LENS Workshop, National Institute of Science and Technology, September 29, 2016. (Invited)
33. Firat Cetinbas, Rajesh Ahluwalia, Nancy Kariuki, Karren More, David Cullen, Brian Sneed, Robert Winarski, Jan Ilavsky, Vincent De Andrade, and Debbie Myers
Structural Characterization and Transport Modeling of Pt and Pt Alloy Polymer Electrolyte Fuel Cell Cathode Catalyst Layers, PRIME 2016, Electrochemical Society Meeting, October 5, 2016.
34. N. N. Kariuki, D.J. Myers, D. Fongalland, A. Martinez, and J. Sharman, Microstructure Analysis of Polymer Electrolyte Membrane Fuel Cell Catalyst-Ionomer Inks and Cathode Catalyst Layers by Small Angle X-ray Scattering, 229th Electrochemical Society Meeting, San Diego, California, June 1, 2016.
35. R.L. Borup, (Invited) FC-PAD: PEM Fuel Cell Durability, Workshop on Recent Advances in PEMFC, CEA, Grenoble, France September 2016
36. Neyerlin, K. C., Jason W. Zack, Natalia Macauley, Rangachary Mukundan, Rod L. Borup, Karren L. More, and Shyam S. Kocha. "Investigation of the Performance of PtCo/C Cathode Catalyst Layers for ORR Activity and Rated Power for Automotive Pemfcs." In *Meeting Abstracts*, no. 38, pp. 2488-2488. The Electrochemical Society, 2016.

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Presentations Relevant to FC-PAD from Consortium Members:

37.Neyerlin, K. C., Jason M. Christ, Jason W. Zack, Wenbin Gu, Swami Kumaraguru, Anusorn Kongkanand, and Shyam S. Kocha. "New Insights from Electrochemical Diagnostics Pertaining to the High Current Density Performance of Pt-Based Catalysts." In *Meeting Abstracts*, no. 38, pp. 2492-2492. The Electrochemical Society, 2016.

38.Kocha, Shyam. "Investigation of the Performance of PtCo/C Cathode Catalyst Layers for ORR Activity and Rated Power for Automotive Pemfcs." In *PRiME 2016/230th ECS Meeting (October 2-7, 2016)*. Ecs, 2016.

39.K.C. Neyerlin (Invited Talk), "Low Pt Resistances", DOE Transport Modeling and Durability Working Group, Lawrence Berkeley National Lab. May 11th and 12th 2016.

40.K.C. Neyerlin (Invited Talk), "Examinations of Kinetic and Transport Losses in Low Pt Electrodes", DOE Catalysis Working Group, Argonne National Lab. July 27th 2016.

41.K.C. Neyerlin (Invited Talk), "Examinations of Kinetic and Transport Losses in Low Pt Electrodes", Gordon Research Conference on Fuel Cells, Stonehill College, Easton MA. August 7th-12th, 2016.

42.Rod Borup, On track for a clean, hydrogen-powered future, Santa Fe New Mexican, October 9, 2016

43.Rod Borup, Forget jetpacks. Where are our hydrogen-powered cars?, The Huffington Post, Dec 13, 2016

44.R Borup, Video: Science in 60–A Clean, Renewable Power Source, LANL (Los Alamos National Laboratory (LANL), Los Alamos, NM (United States))

45.Natalia Macauley, Rod L Borup, Rangachary Mukundan, Mahlon S Wilson, Dusan Spernjak, KC Neyerlin, Shyam S Kocha, Stephen Grot, Performance of Stratified Fuel Cell Catalyst Layer, The Electrochemical Society, Meeting Abstracts, 2490-2490

46.Dusan Spernjak (Invited), Rod L Borup, Daniel S Hussey, Piotr Zelenay, Rangachary Mukundan, Imaging Fuel Cell Components: From Flow Field Channels to Catalyst Layers, The Electrochemical Society, Meeting Abstracts, 2493-2493

47.D.A. Cullen (Invited), B.T. Sneed, and K.L. More, "Fuel Cell Electrode Optimization through Multi-Scale Analytical Microscopy," Microscopy & Microanalysis 2016, Columbus, OH, July 24-28, 2016.

48.D.A. Cullen, B.T. Sneed, and K.L. More, "Fuel Cell Electrode Optimization through Multi-Scale Analytical Microscopy," Gordon Research Conference, Easton, MA, August 7-12, 2016.

Publications and Presentations

Presentations Relevant to FC-PAD from Consortium Members:

49. K.L. More (Invited), "Correlating Structure and Chemistry of PEM Fuel Cell Materials with Performance and Durability using Advanced Microscopy Methods," PRiME 2016, Honolulu, HI, October 3-7, 2016.
50. K.L. More (Invited), ""Correlating Structure and Chemistry of PEM Fuel Cell Materials with Performance and Durability using Advanced Microscopy Methods," University of Illinois – Chicago, November 15, 2016.
51. B.T. Sneed, D.A. Cullen, K.S. Reeves, and K.L. More, "3D STEM Analysis of Ionomer Dispersion and Pore Structures within PEM Fuel Cell Catalyst Layers," MRS Fall Meeting, Boston, MA, November 28 – December 1, 2016.
52. B.T. Sneed, D.A. Cullen, K.S. Reeves, and K.L. More, "Structural and Chemical Study of the Stability of Pt-Based Fuel Cell Electrocatalysts in 3D via Electron Tomography," Pacific Rim Symposium on Surfaces, Coatings, and Interfaces (PAC-SURF), Kohala Coast, HI, December 12-15, 2016.
53. K.L. More (Invited), B.T. Sneed, and D.A. Cullen, "Understanding Fuel Cell Materials Degradation Through the Use of Advanced Microscopy Methods," 231st Meeting of the Electrochemical Society, New Orleans, LA, May 29 – June 2, 2017.
54. K.L. More (Invited), B.T. Sneed, and D.A. Cullen, "Critical interfaces in PEM Fuel Cells: Understanding Behavior Through Advanced Microscopy Studies," 21st International Conference on Solid State Ionics, Padua, Italy, June 18-23, 2017.
55. Mukundan, Rangachary; Spernjak, Dusan; Hussey, Daniel; Jacobson, David L.; Borup, Rod, Application of high resolution neutron imaging to polymer electrolyte fuel cells, Abstracts of Papers, 253rd ACS National Meeting & Exposition, San Francisco, CA, United States, April 2-6, 2017 (2017)
56. R. Mukundan, D. A. Langlois, K. C. Neyerlin, S. S. Kocha, K. L. More, M. Odgaard, and R. L. Borup, Durability of PtCo/C Cathode Catalyst Layers Subjected to Accelerated Stress Testing, 230th Meeting of the Electrochemical Society
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