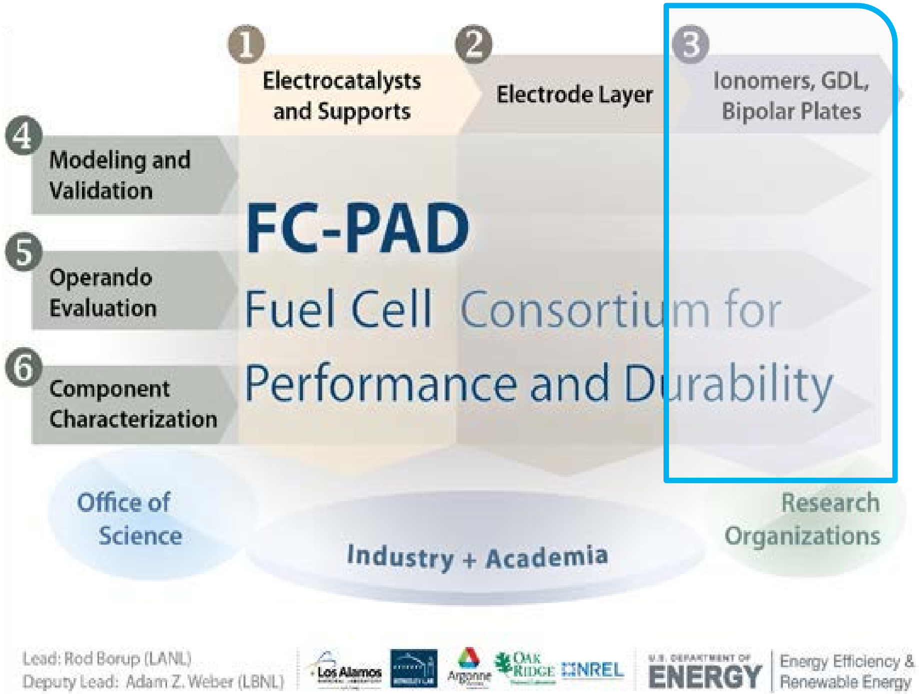
FC-PAD

Fuel Cell – Performance and Durability

FC138 – Ionomers, GDLs, Interfaces

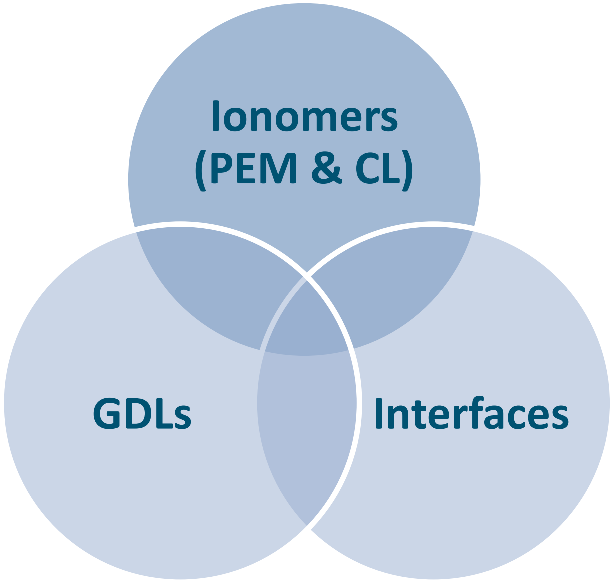
Thrust Coordinator: Adam Weber

FC-PAD Overview & Cross cutting thrusts



- This thrust/presentation focuses on fuel-cell components, their diagnostics, structural characterization as well as modeling, for both performance and durability improvements

- Three thrusts:
  - Components: catalysts, electrodes and ionomer/GDLs
  - Crosscutting: modeling, evaluation and characterization



FC-PAD contributors to this presentation

Argonne National Laboratory

Nancy Kariuki
Debbie Myers
Rajesh Ahluwalia

Berkeley Lab

Adam Weber
Kelsey Hatzell
Lalit Pant
Ahmet Kusoglu
Shouwen Shi

Los Alamos National Laboratory

Rangachary Mukundan
Andrew Baker
Yu Seung Kim
Rod Borup

NREL National Renewable Energy Laboratory

Huyen Dinh
KC Neyerlin

Oak Ridge National Laboratory

Karren More

Collaborations

- Tufts University (GDL imaging)
- PSI (GDL Imaging)
- U Delaware (Membrane durability)
- 3M (Ionomers)
- Colorado School of Mines (Membrane diagnostics)

FC-PAD Thrust 3: Overview

Timeline

- Project start date: 10/01/2015
- Project end date: 09/30/2016

National Labs

- NREL, ANL, LBNL, LANL, ORNL

Partners/Collaborations

(To Date Collaborations Only)

- Tufts University
- U. Delaware
- PSI
- 3M
- Colorado School of Mines
- Partners to be added by DOE DE-FOA-0001412

Barriers

- The ionomer presents challenges in terms of performance and durability
  - Membrane durability additive movement is unknown
  - Local losses associated with ionomer thin films
- Water and thermal management, especially at lower temperatures
- Impact of interfaces and their optimization

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Approach: Fuel-Cell Components

Ionomer membranes (PEM)

In-situ/ex-situ diagnostics
structure-property characterization
Degradation
Reinforcement and Additives

Gas Diffusion Layers (GDLs)

Transport and 3D-structure (imaging)
Water and thermal management
Phase-change kinetics

Ionomer Thin Films (CL)

Ionomer-substrate interactions and thickness effects (confinement)
Transport properties
Formation

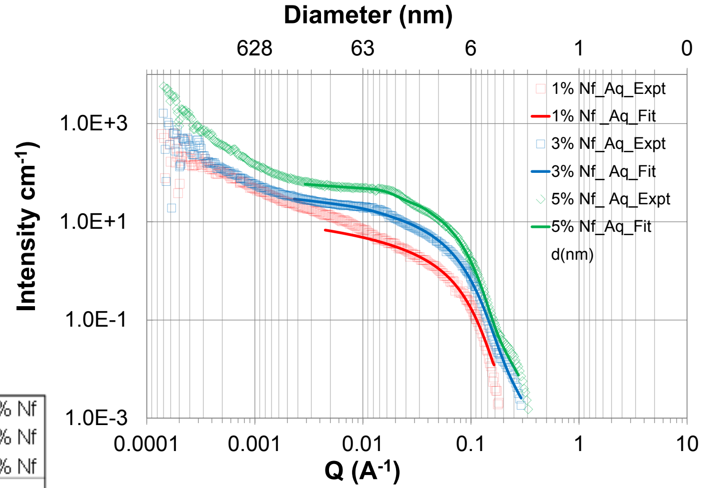
Interfaces

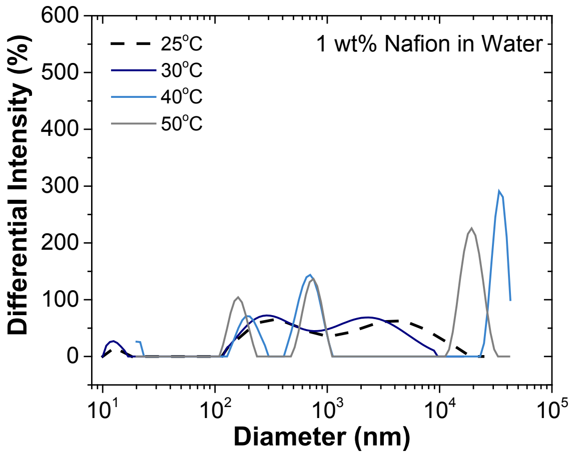
Water and thermal management
GDL/Channel and droplets
CL/MPL and flooding

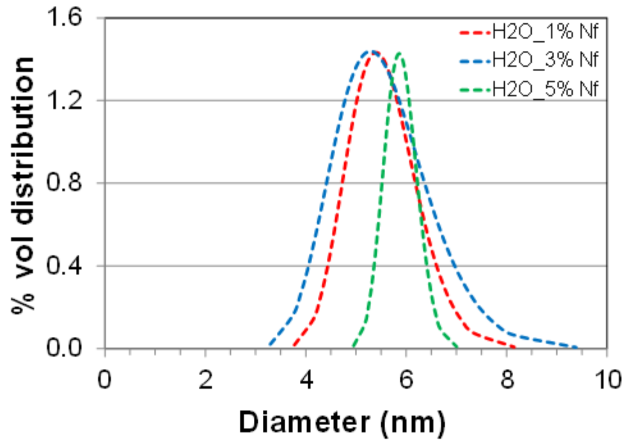
Operando, modeling, and ex-situ diagnostics to elucidate governing behavior and optimize performance and durability

Accomplishments:
Ionomer Dispersions – Processing of PFSA

- Ionomer dispersions
  - Understanding the underlying ink structure enables facile and controlled manufacturing processes for tunable properties
  - Ionomer dispersions demonstrate a thermo-responsive behavior which may yield changes in the structure and size of ionomer unit
- Ionomer dispersions (USAXS)
  - Data indicate that particles size is positively correlated with ionomer content in dilute solutions (1-5 wt%)





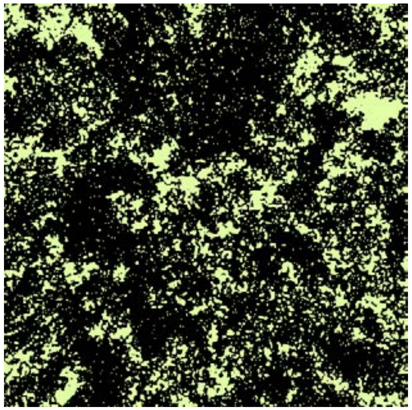


Liquid-to-Solid Material Transformations

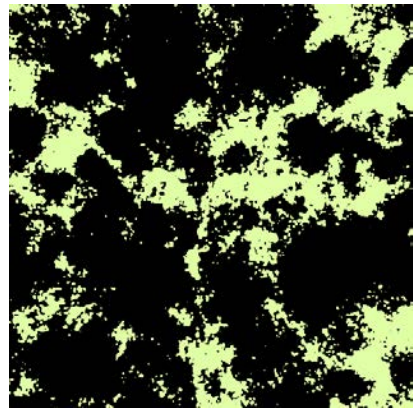
Accomplishments:
Ionomer Dispersions – Solvent Effect

Ionomer (F map) Area %

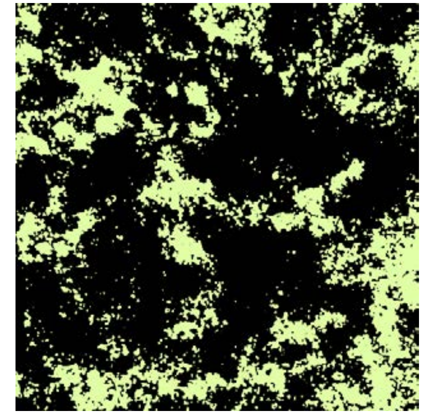
H_2O/IPA **28.9%**



NMP **29.5%**



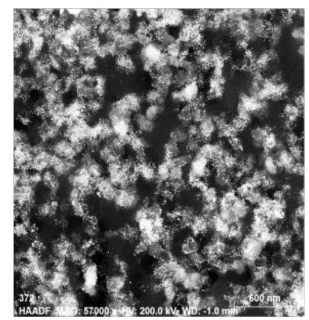
Glycerol **32.6%**

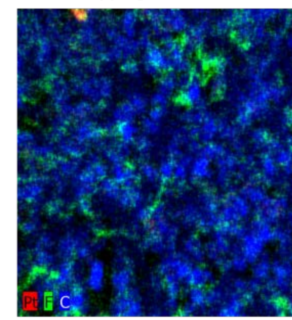


- Electrode morphology
  - conventional vs. LANL's technologies
    - Element mapping indicates that Pt electrocatalysts are more uniformly distributed in the LANL-developed electrodes

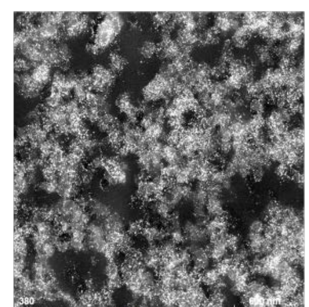
TEM Image of Fuel Cell Electrode **Element Mapping of Fuel Cell Electrode**

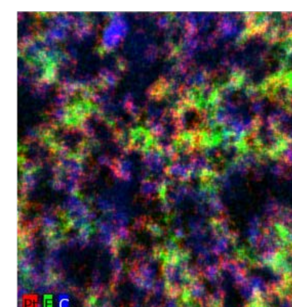
Conventional Ionomer Dispersion





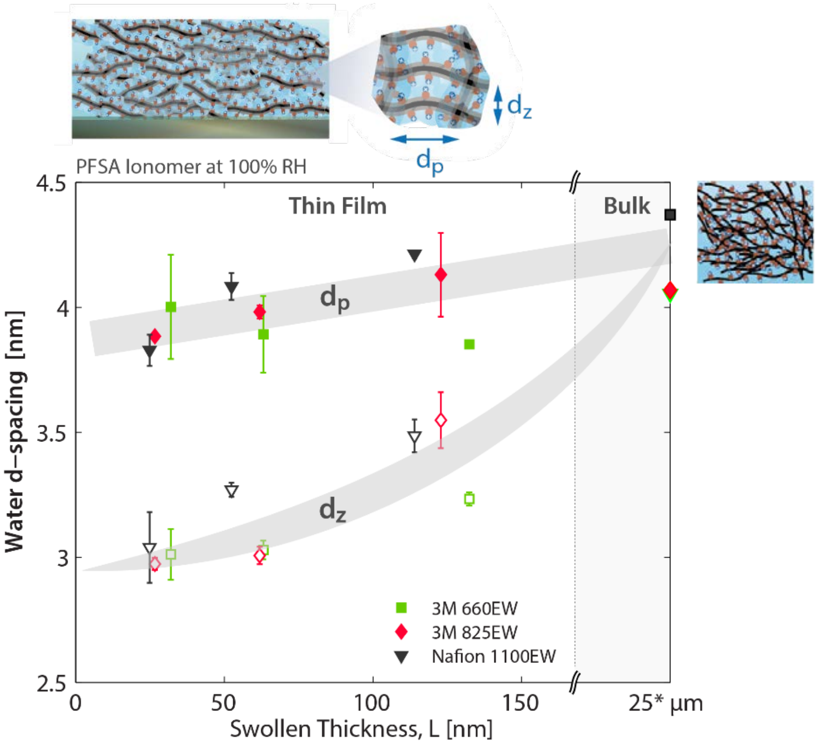
LANL's Ionomer Dispersion



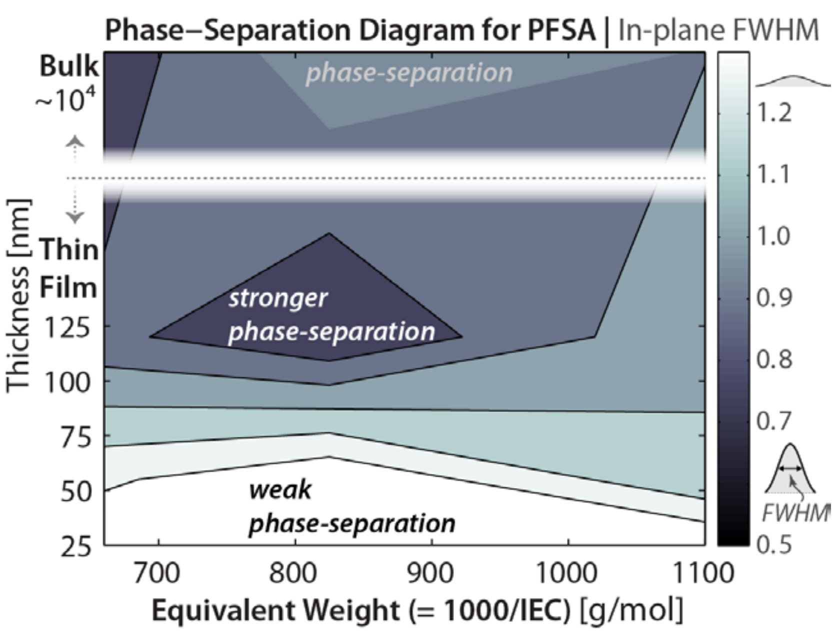


Accomplishments: Ionomer Thin Films – Impact of EW/Chemistry

- Anisotropy increases for thin films due to confinement
  - Domains are closer and better-packed in thickness direction
  - Impacts transport behavior



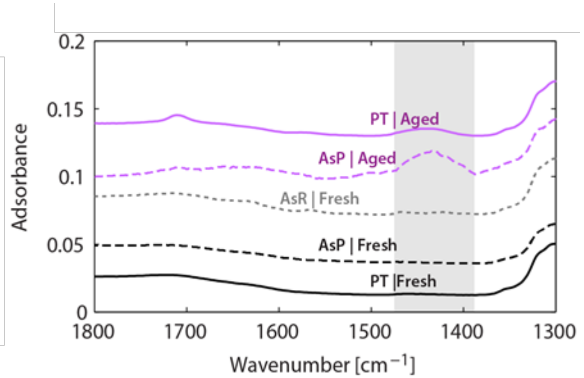
- Phase-separation diagram
  - Generated from a large structure/ swelling dataset on PFSAs
  - Thickness-EW interplay in thin films
    - Shorter side-chain and/or lower EW demonstrate stronger phase separation

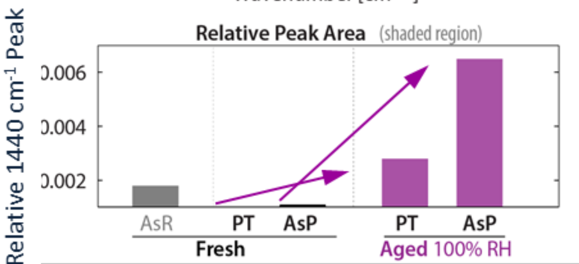


Kusoglu et al. Advanced Functional Materials (2016)

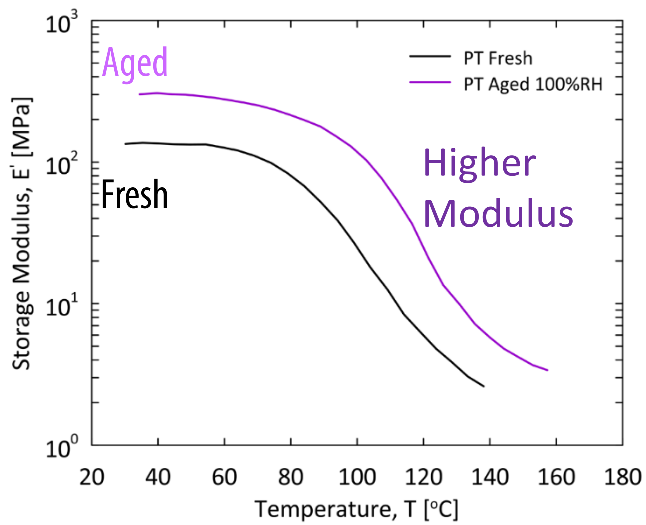
Accomplishments: Membrane – Impact of Ageing and Contamination

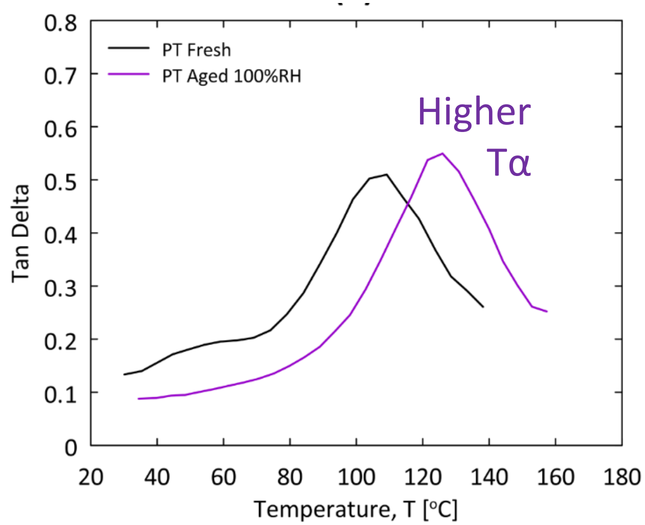
- Hygrothermal ageing of pretreated and processed Nafion
  - Significant reduction in water uptake and conductivity upon ageing w/contaminant



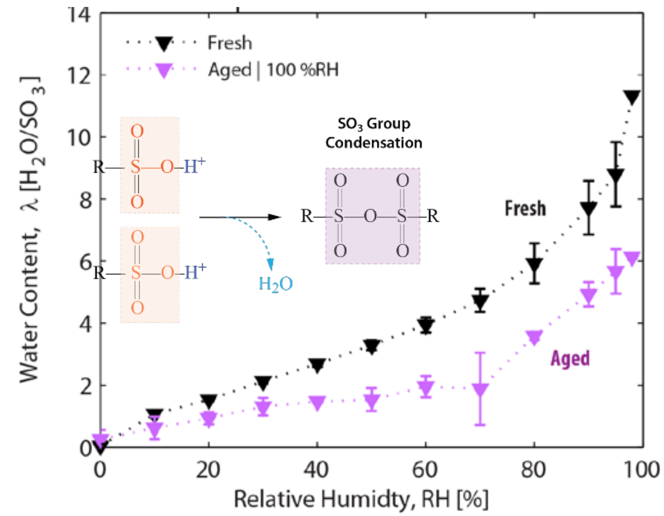


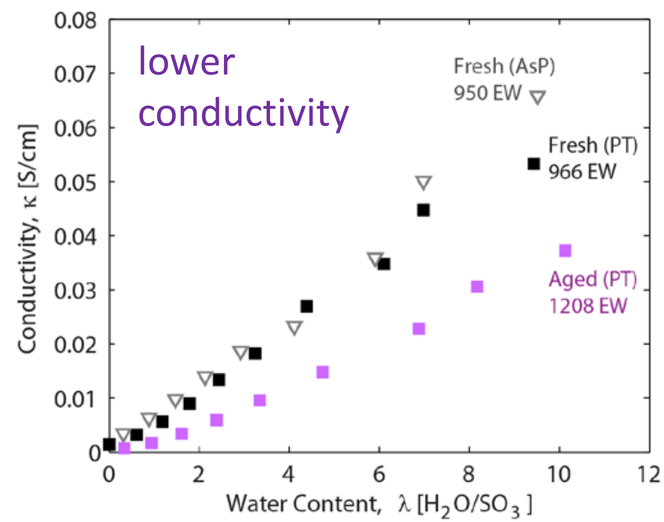
Ionic group condensation ➔ Crosslinks ➔ higher modulus





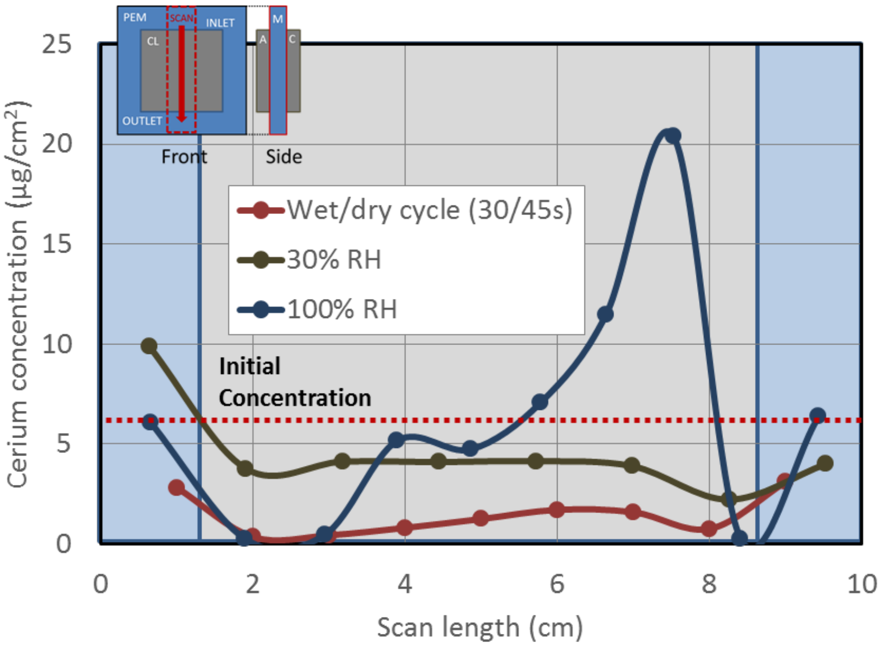
Less ionic groups + high modulus ➔ less water uptake

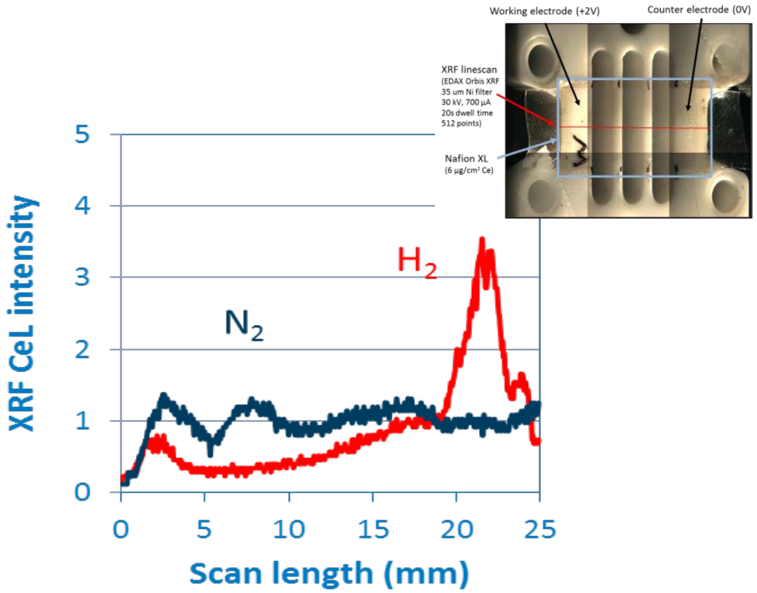




FUEL CELL PERFORMANCE AND DURABILITY

Accomplishments:
Membrane – Cerium Migration and Washout

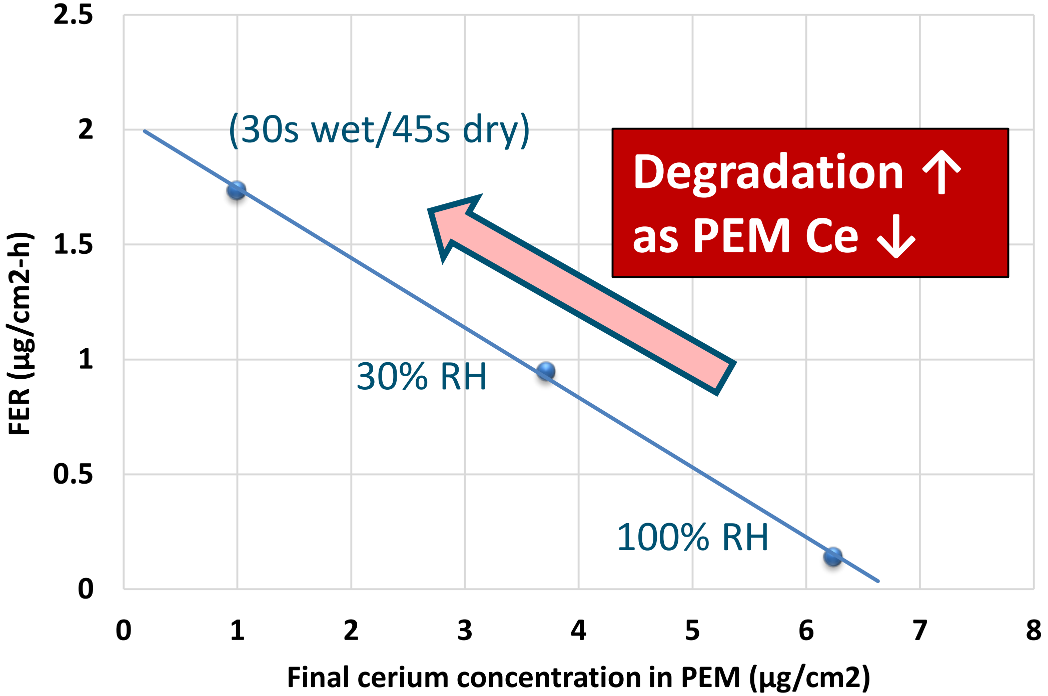




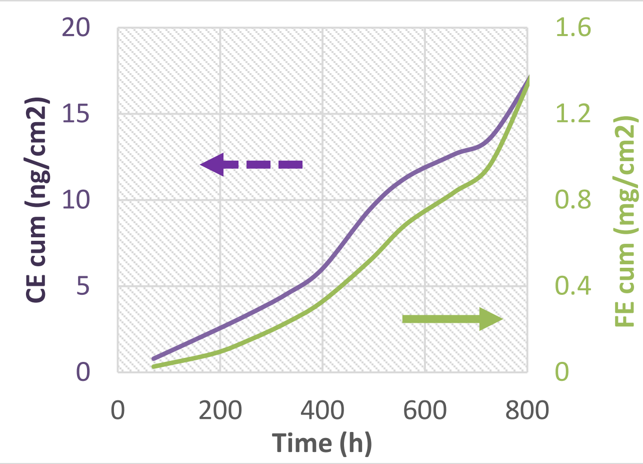
- XRF studies demonstrate that cerium
  - Moves with proton flux more so than with potential gradients
  - In plane profiles reveal very different cerium migration profiles
    - 100% RH: cerium gradient follows humidified gasses from inlet to outlet
    - 30% RH: diffusion drives uniform migration
    - Wet/dry cycling: significant reduction in PEM cerium with in-plane gradient

Accomplishments: Membrane – Cerium Migration and Washout

- Cerium is an effective radical scavenger, but it is mobile in operating cells
  - Key is to understanding migration and washout mechanisms
    - Implications for performance loss and radical scavenging
  - Cerium migration from PEM increases degradation
  - Cerium migrates into the CLs as a byproduct of degradation



- **Cerium and fluoride release are correlated**
- Cerium maybe released from the MEA as part of side-chain polymer fragment

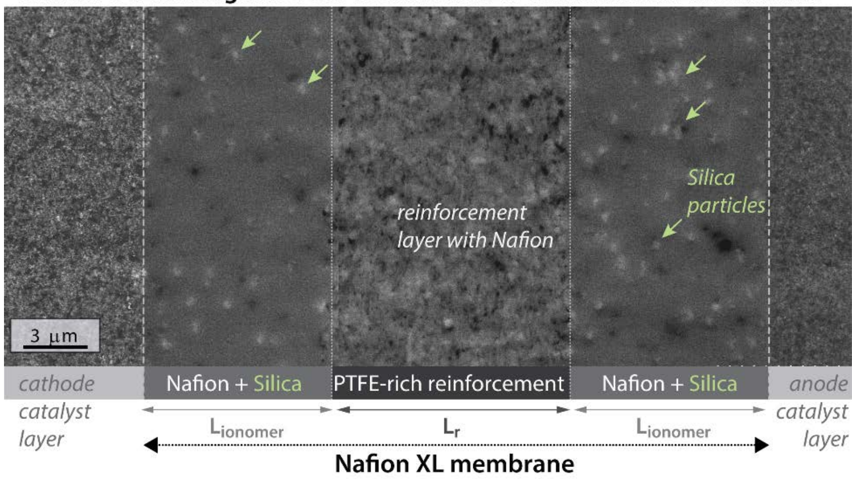


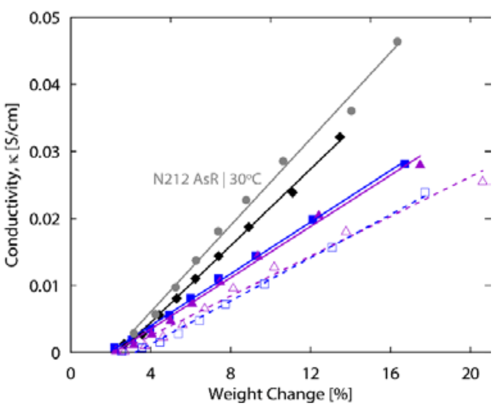
CE_{cum} = cumulative cerium emissions
FE_{cum} = cumulative fluoride emissions

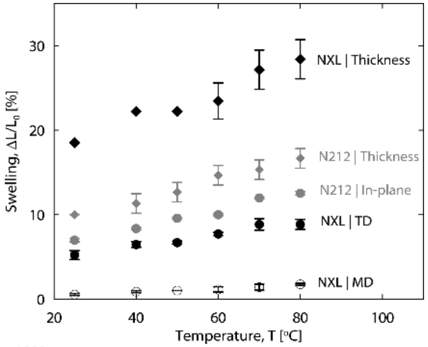
Accomplishments:
Membrane – Nafion XL Composite Membranes

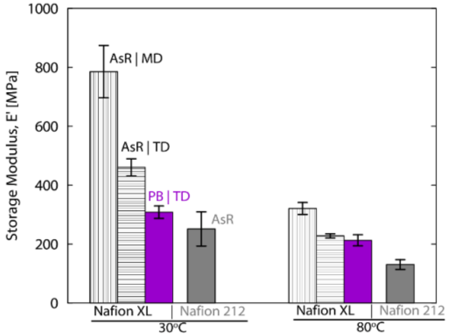
- Strong anisotropy in Nafion XL
  - Conductivity
    - N212: Preboiled > As Received
    - XL: Preboiled > As Received (in the plane)
    - XL: Preboiled < As Received(thickness)
  - Opposite trends for modulus
- Dramatic impact of conditioning

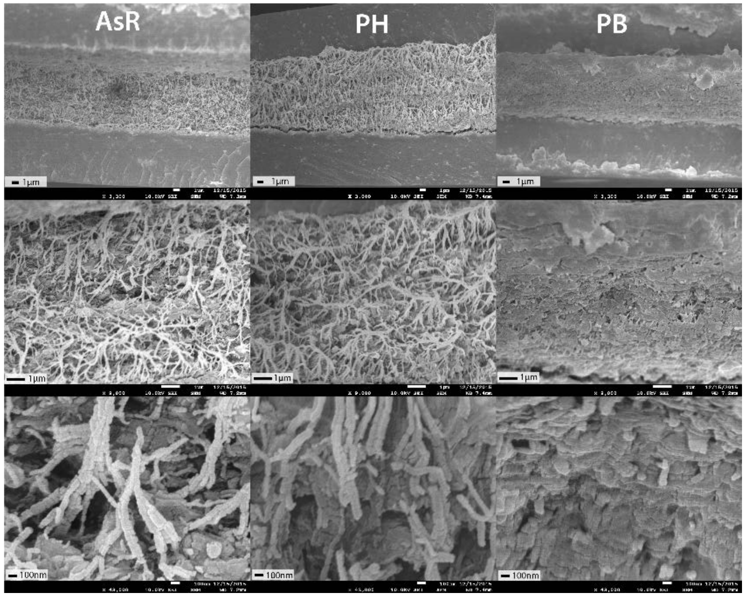
HADF-STEM image of cross-sectioned MEA with Nafion XL membrane





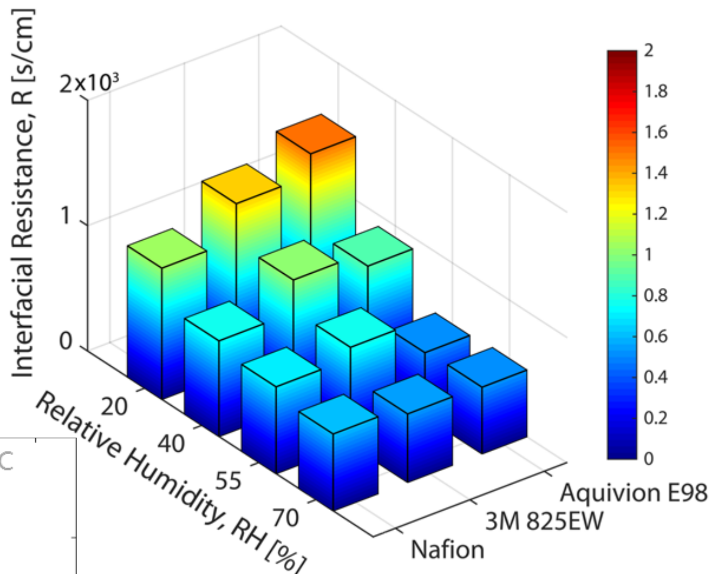


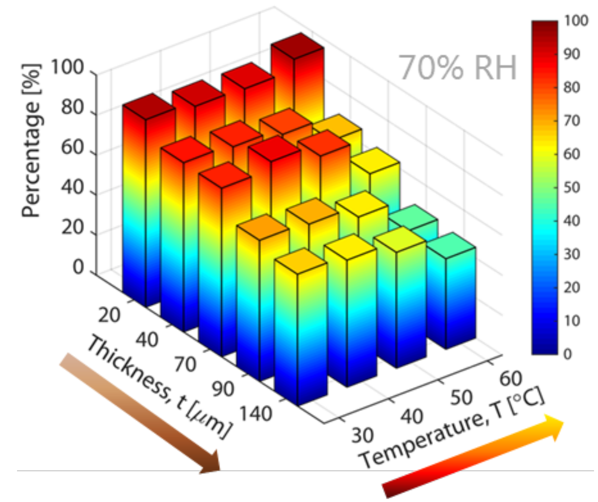


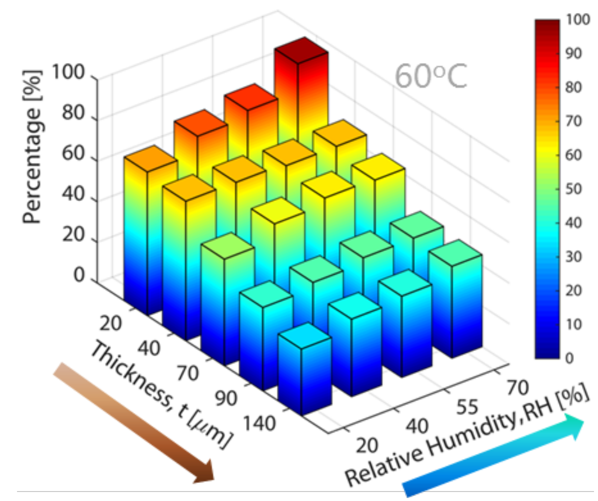


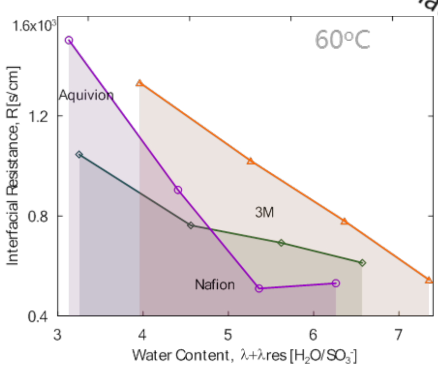
Accomplishments:
Interface – Membrane Interfacial Resistance

- All PFSA ionomers exhibit large interfacial resistance
  - Increases with lower humidity and shorter side chain
- Interfacial resistance dominates transport response
  - Larger fraction at lower temperature
  - Larger fraction at higher humidity



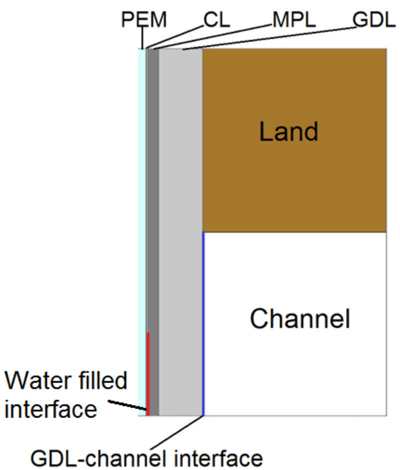


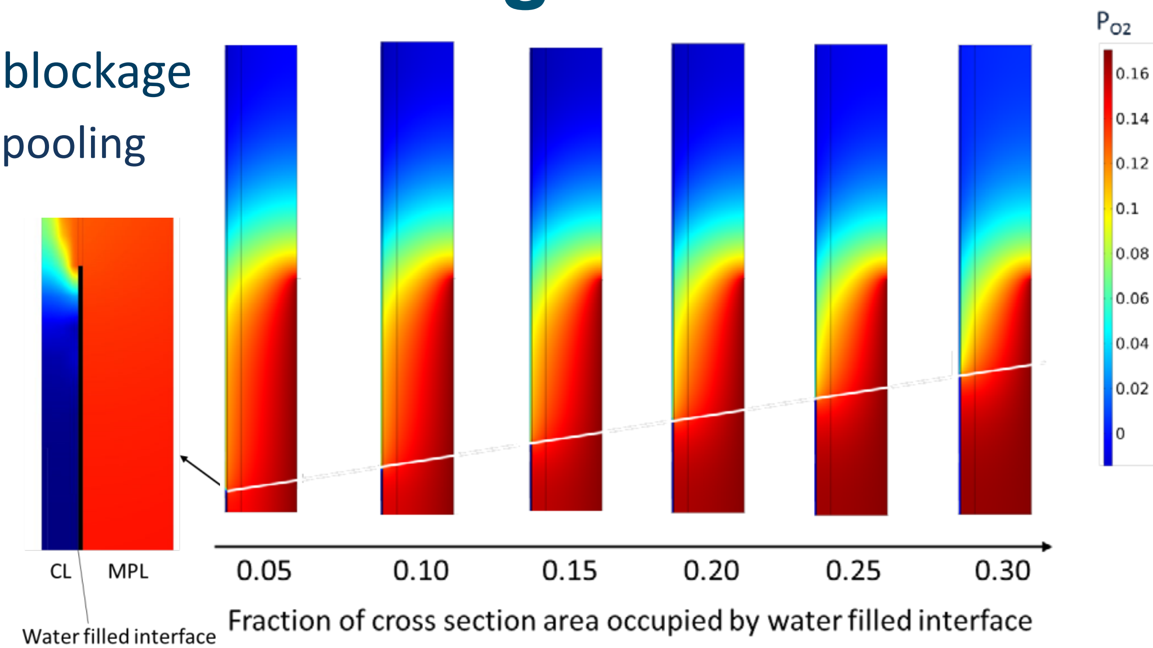




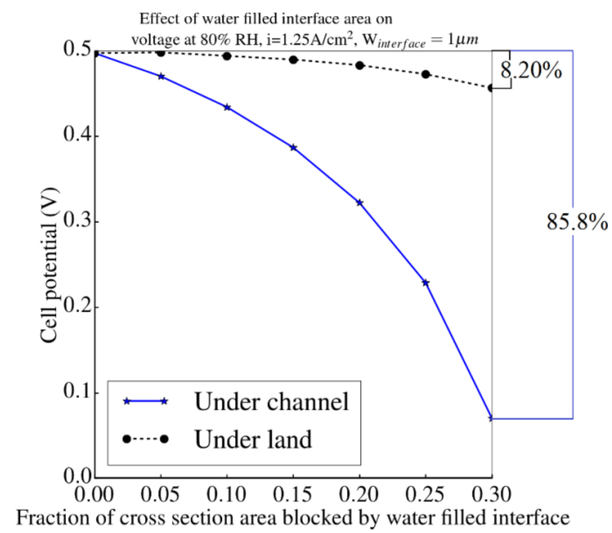
Accomplishments: Interface – Impact of blockage at MPL/CL

- Examine impact of interfacial blockage
  - Due to manufacturing or water pooling





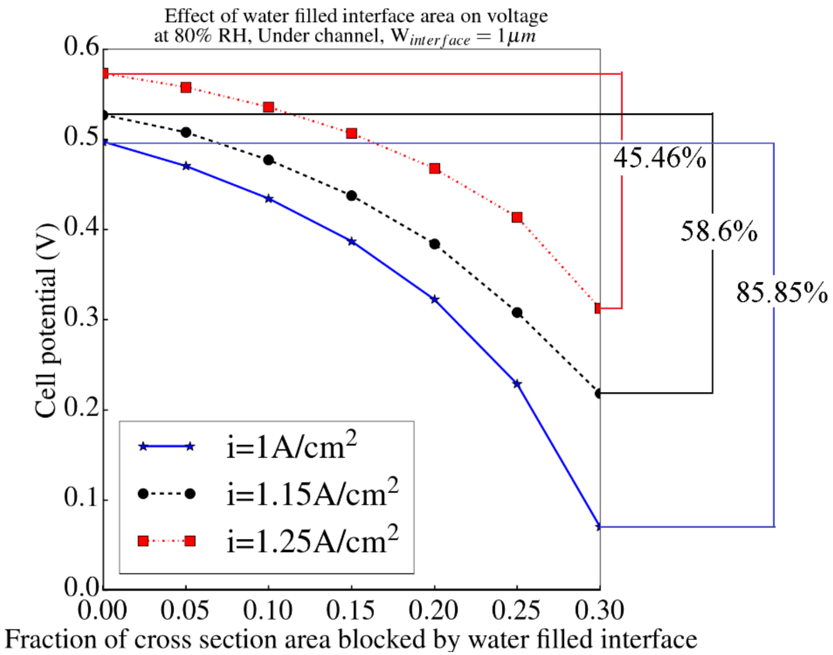
- Nonlinear decrease in performance
  - Drop in performance is much higher if the water filled interfaces are under channel compared to under land



Accomplishments:
Interface – Impact of blockage at MPL/CL

Constant Current

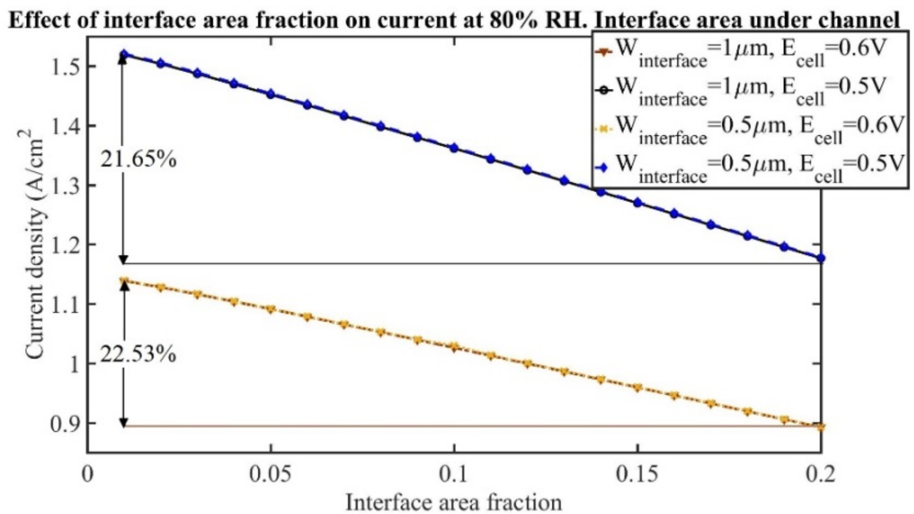
- Mimics cell in stack



- Nonlinear and more severe change in cell potential driven by need for higher average current density
  - Impacts even at 5-10 %

Constant Potential

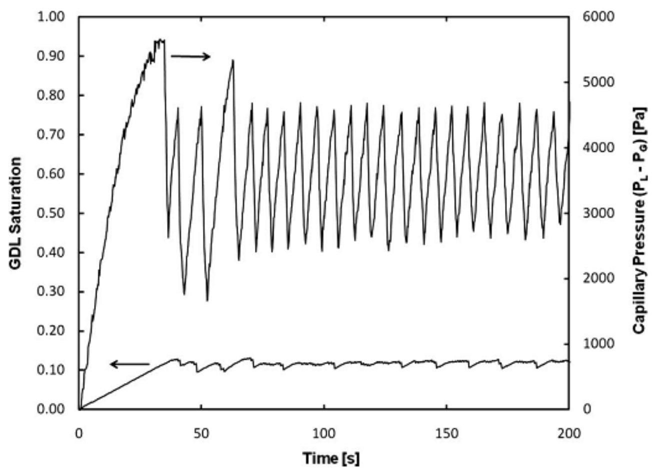
- Mimics single cell



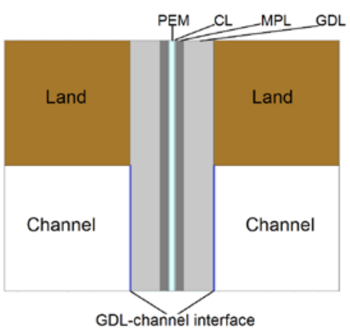
- Almost linear change in average current density driven by blocking off of reaction area
  - Interface width not significant as long as wide enough

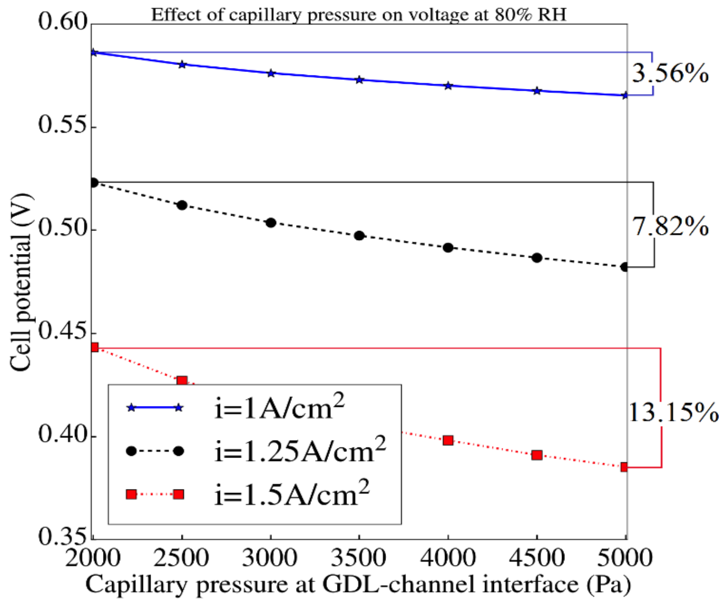
Accomplishments: Interface – GDL/Channel Water Droplets

- Droplets result in dynamic pressures at GDL/Channel boundary



  - Simulate to see if have effect on performance

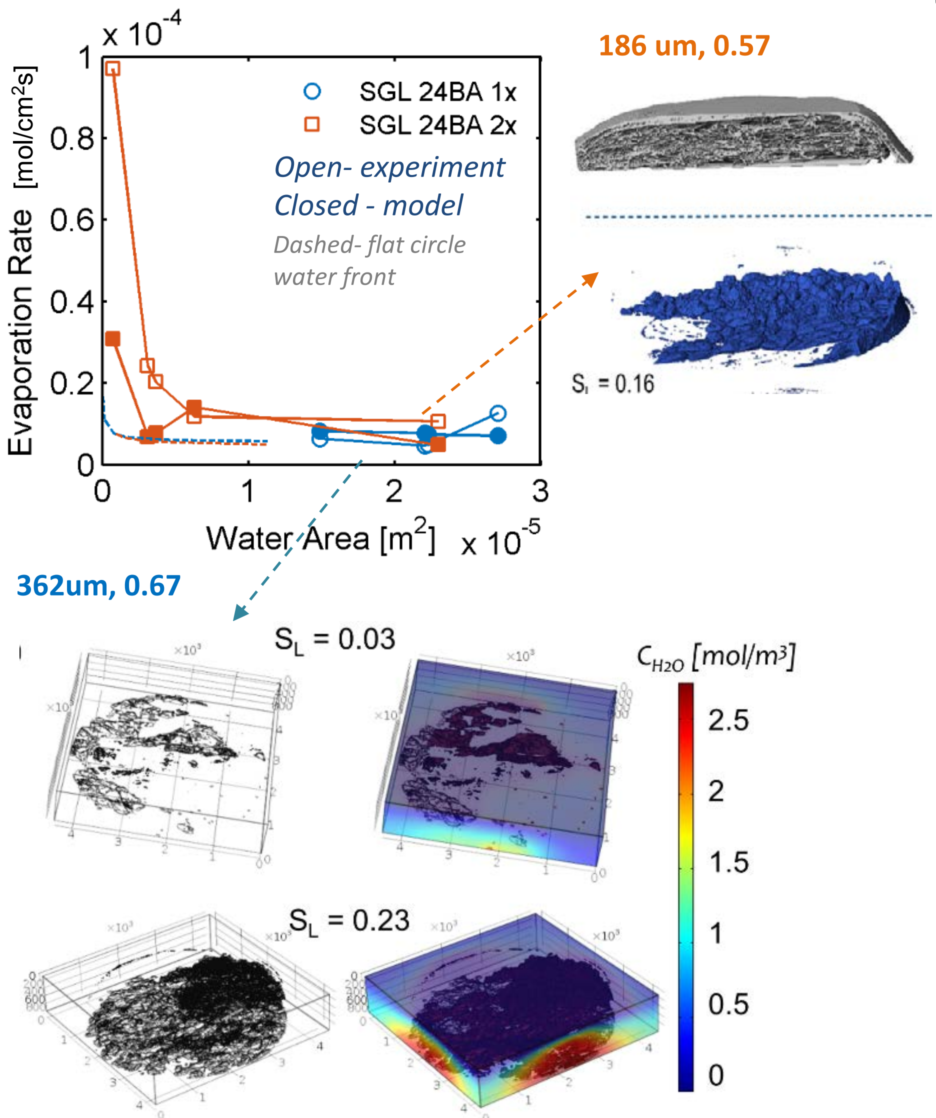




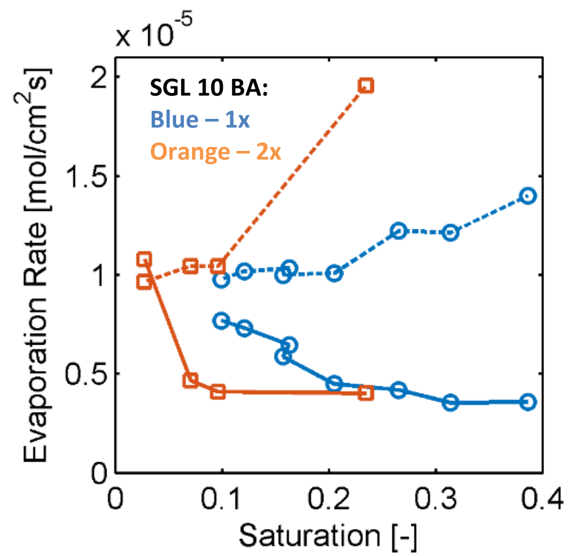
- Performance is sensitive to the boundary condition at higher current densities
  - Relatively linear change so can use time-averaged value

Gostick et al, Impact of Liquid Water on Reactant Mass Transfer in PEM Fuel Cell Electrodes, J Electrochem Soc, v157(4) (2010)

Accomplishments:
GDLs – Imaging and Modeling Water Evaporation

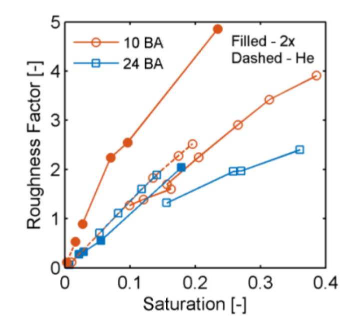


- Study with x-ray tomography and modeling
  - Water roughness factor increases linearly with saturation
  - Evaporation rate
    - Normalized per surface area of water: asymptotes
    - Normalized per geometric area: increases with saturation



Dashed – normalized per geometric cross-section of GDL
Solid – normalized per actual SA of water-front

Roughness Factor = $SA_{\text{water front}}$ / $SA_{\text{cross-section of GDL}}$



FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Proposed Future Work

- **Membranes**
  - Investigation of side-chain chemistry and governing structure-property correlations, especially impact of reinforcement
  - Determine the relationship between cerium migration and durability
    - Understand the relative influence of each migration mechanism
    - Stabilize cerium in the PEM and localize it to areas of highest radical generation
- **Dispersions and Casting**
  - Direct observation of shear-induced transformation of dilute solutions
  - Model study to elucidate interactions during solvent evaporation with different solvents
- **Ionomer thin films**
  - Explore conditioning protocols for thin films relevant to CL preparation and conditioning and elucidate the impact of various carbon substrates
  - Develop a thin-film structure/property model
- **GDLs**
  - Model interactions and examine scale coupling
- **Interfaces**
  - Explore interfacial effects related to conductivity and rougher membrane interfaces
  - Detail model for GDL/Channel interface and droplets

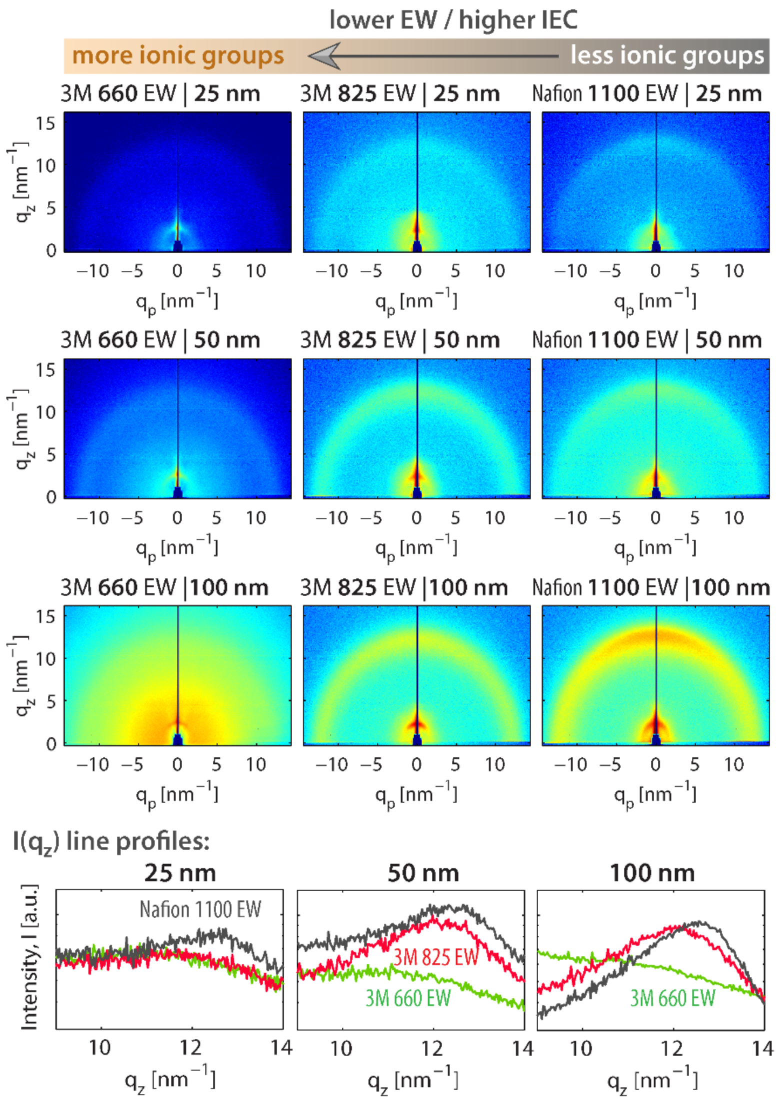
Summary

- Relevance/Objective:
  - Optimize performance and durability of fuel-cell components including ionomers, interfaces, diffusion media, and bipolar plates
- Approach:
  - Use synergistic combination of crosscutting thrusts to explore component properties, behavior, and phenomena
- Technical Accomplishments:
  - Combined modeling and experiment to understand interfaces
    - Examined water-related issues including blockage and droplet conditions
  - New key findings on the role of EW/side-chain on ionomer thin-film morphology and swelling
  - Investigations on Nafion XL composite membrane 's transport/stability behavior
    - Cerium migration and correlation to durability
    - Conditioning-dependent anisotropy
  - Impact of solvent and processing on dispersions
- Future Work:
  - Understand liquid-water movement and interactions in fuel-cell components and cells
  - Explore genesis of membranes and thin films and their associated properties
  - Minimize and stabilize cerium migration in membranes under operation
  - Leverage cross-cutting thrusts to provide knowledge to optimize component durability and performance

FC-PAD Thrust 3

Technical Back-Up Slides

Ionomer Thin Films Crystallinity



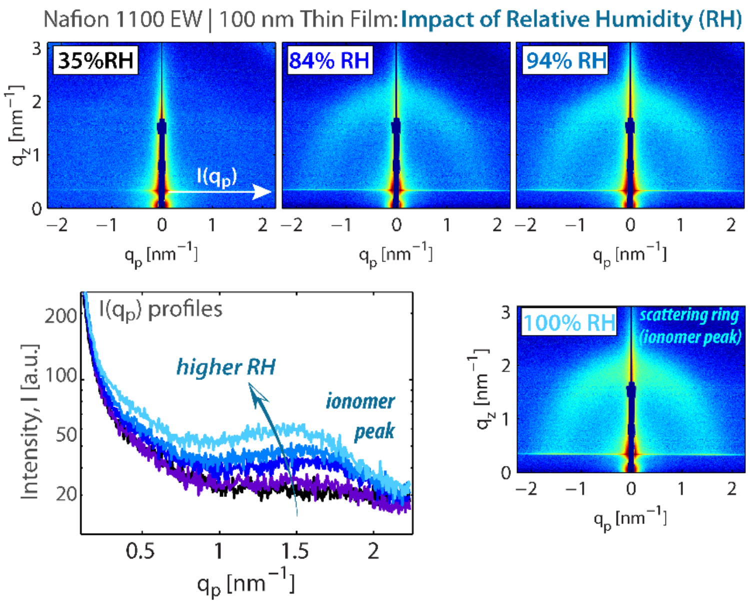
Crystallinity in Thin Films

- Impact of thickness
  - Ionomer thin films possess crystallinity for bulk-like thicknesses (100 nm or higher)
  - Nafion vs 3M thin films
  - Lowering EW tend to reduce crystallinity in ionomer thin films, similar to that observed in bulk membranes
    - This in agreement with the higher swelling observed in lower-crystalline films such as 3M PFSAs (< 825 EW) compared to Nafion 1100 EW

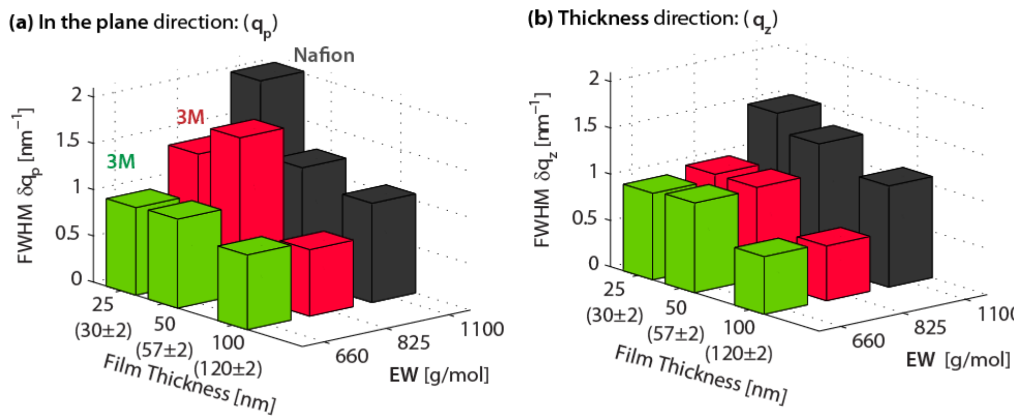
Kusoglu et al. Advanced Functional Materials (2016)

Ionomer Thin Films: Impact of EW/Chemistry

- Grazing-incidence X-ray scattering (GISAXS) under humidification
  - Weaker phase-separation with reduced film thickness (< 50 nm)
    - RH effect is similar to that for bulk membrane, increases water d-spacing

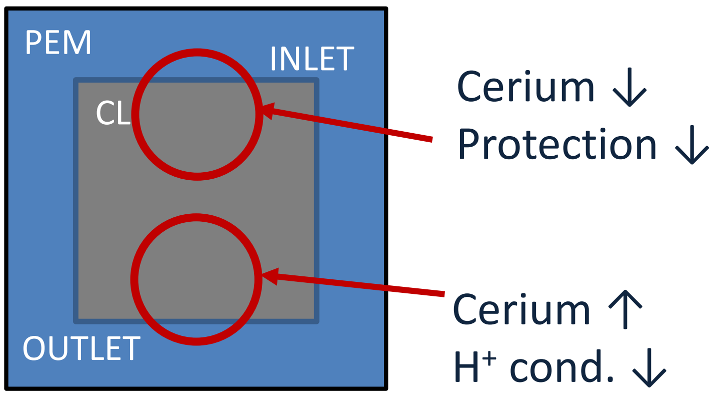


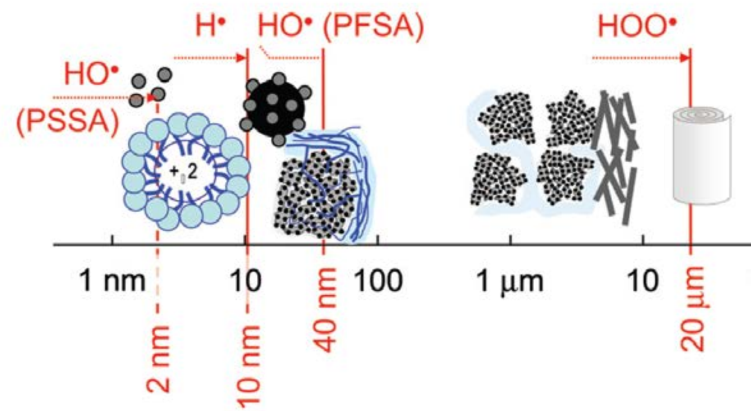
- Comparison of Nafion and 3M PFSA thin films (20 to 100 nm)
  - Most striking difference is phase-separation and alignment
    - Full-width half-max (FWHM) is decreases with EW (also side-chain?)
- Key role of side-chain and EW in ionomer film morphology
  - more critical than observed in bulk



Effects of cerium migration on performance

- In-plane gradients in PEM cerium will reduce the ability of cerium to protect the inlet, while decreasing proton conductivity near the outlet



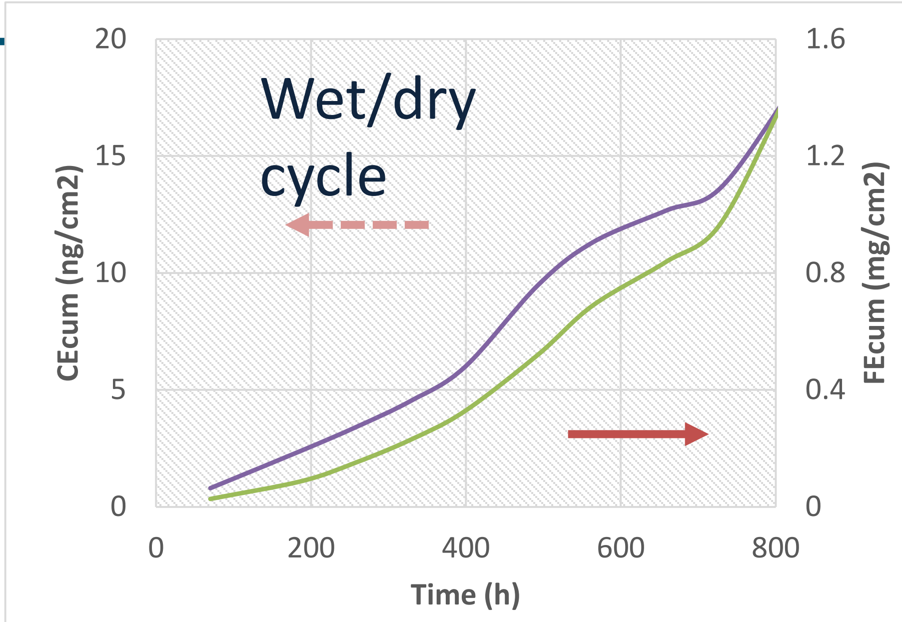


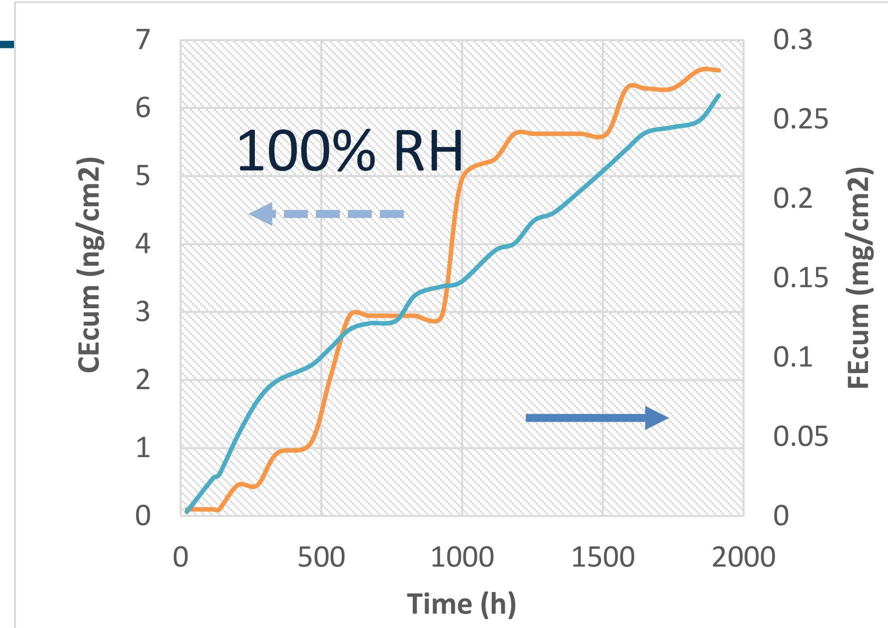
Gubler, et al., *J. Electrochem. Soc.*, **158**, 2011

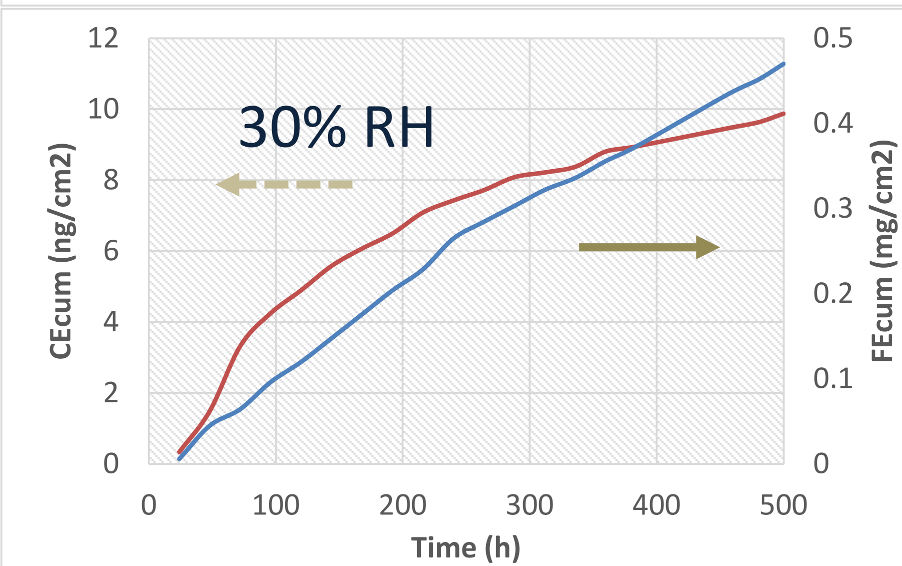
- Through-plane cerium migration into the CLs reduces performance
  - Conductivity loss of CL ionomer
  - Losses are amplified as CL degrades

Cheng, et al., *J. Electrochem. Soc.*, **160**, 2013
Banham, et al., *J. Electrochem. Soc.*, **161**, 2014

PEM: Correlation between Ce and F in effluent water







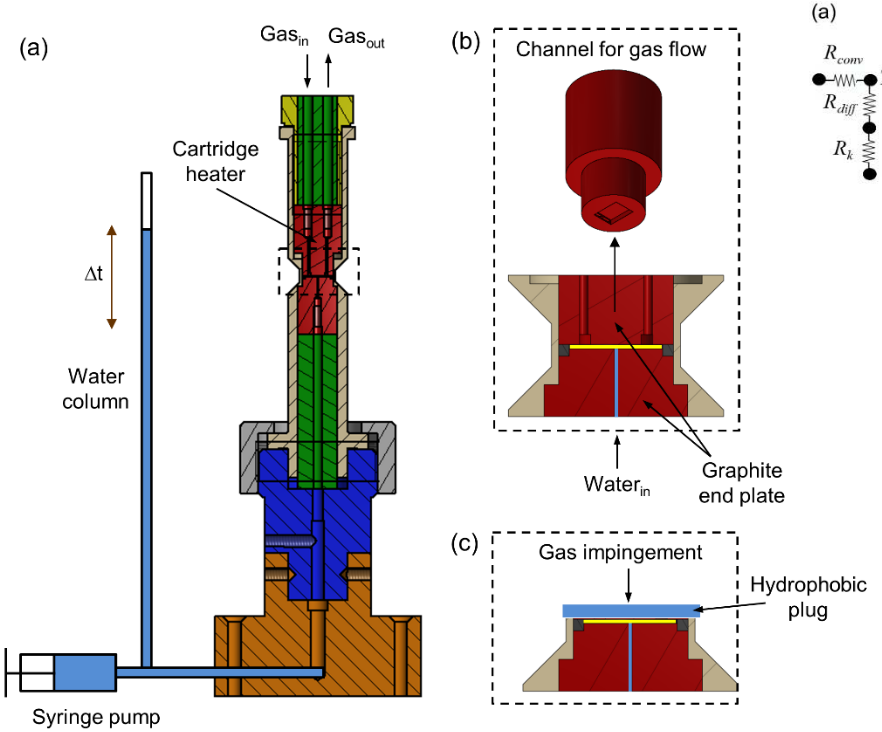
CE_{cum} = cumulative cerium emissions

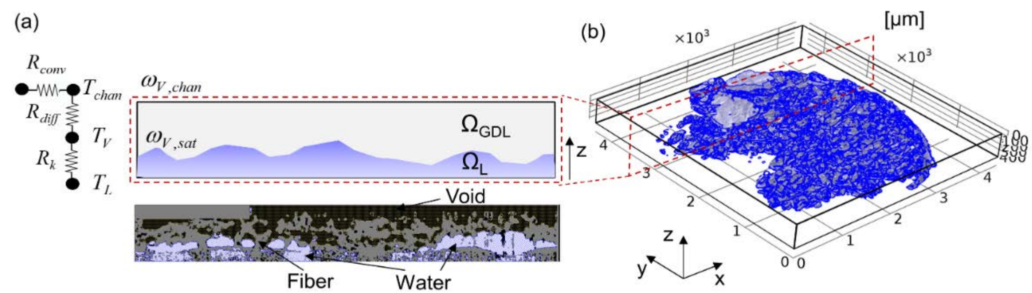
FE_{cum} = cumulative fluoride emissions

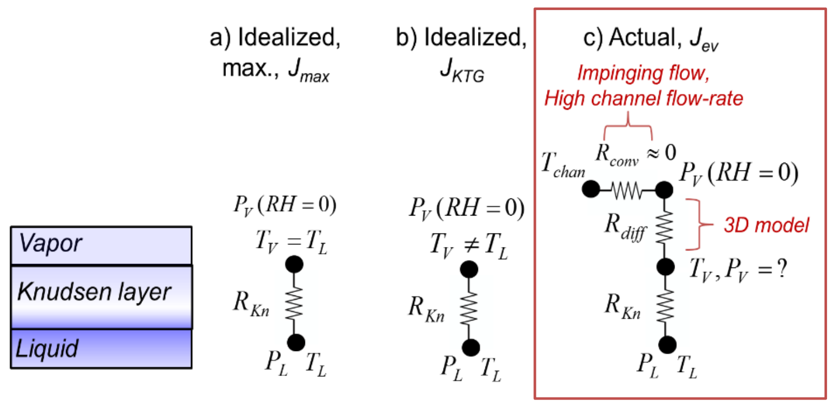
- **Cerium and fluoride release are correlated**
- Cerium is released from the MEA as part of a side chain polymer fragment

GDLs: Experiment and Model Description

- Experimental set-up featured controlled water injection on the bottom and gas flow on top of the GDL
- 3D direct meshing of water fronts
- Stefan-Maxwell diffusion for vapor
- Isothermal, equilibrium thermodynamics

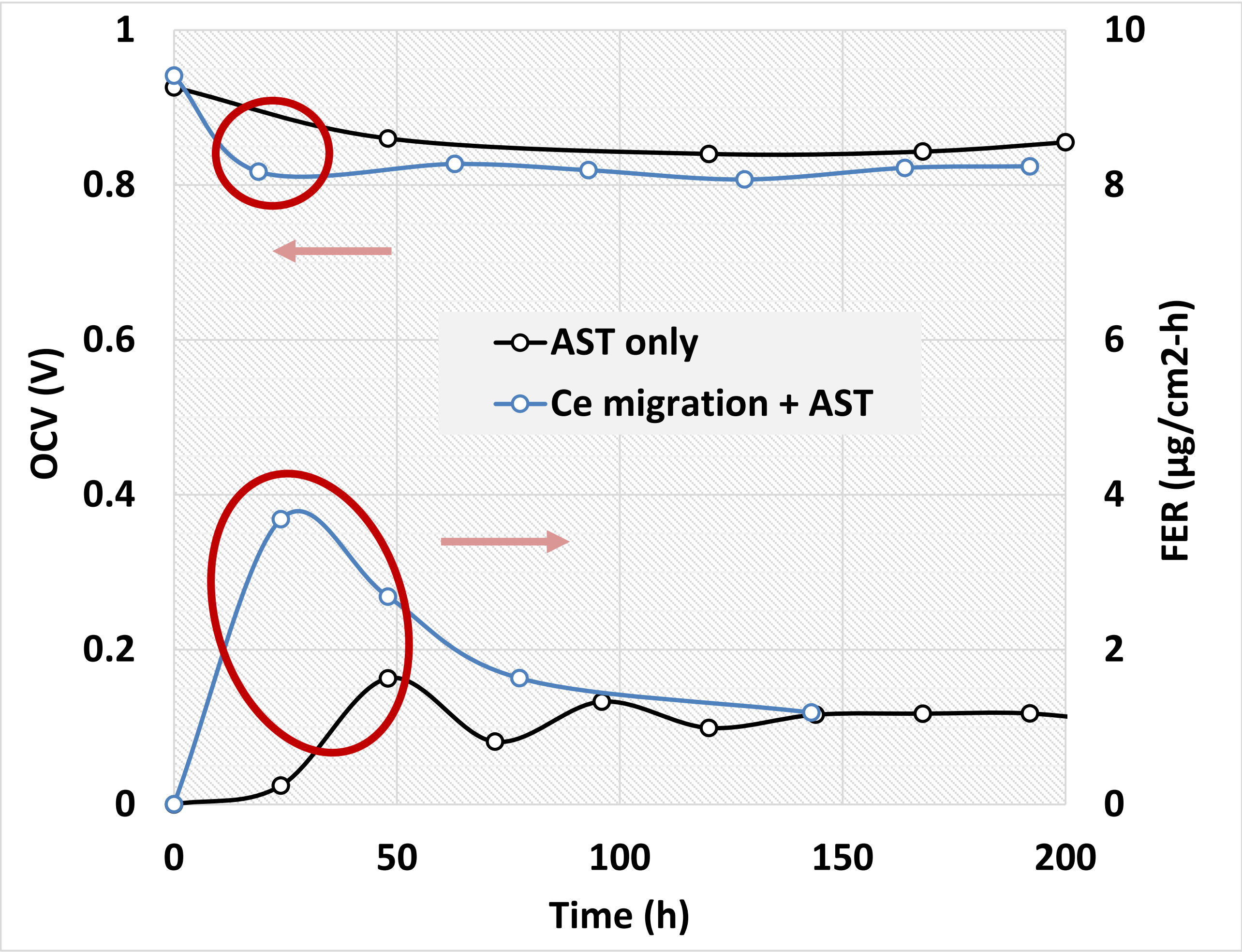






Does cerium migration from the PEM cause greater degradation?

- Performed a cerium migration phase before identical 30% RH AST:



Cerium is moved from the PEM into the CLs without inducing degradation

Initial OCV drop and increase in FER suggest that degradation could be enhanced by cerium migration out of the PEM

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