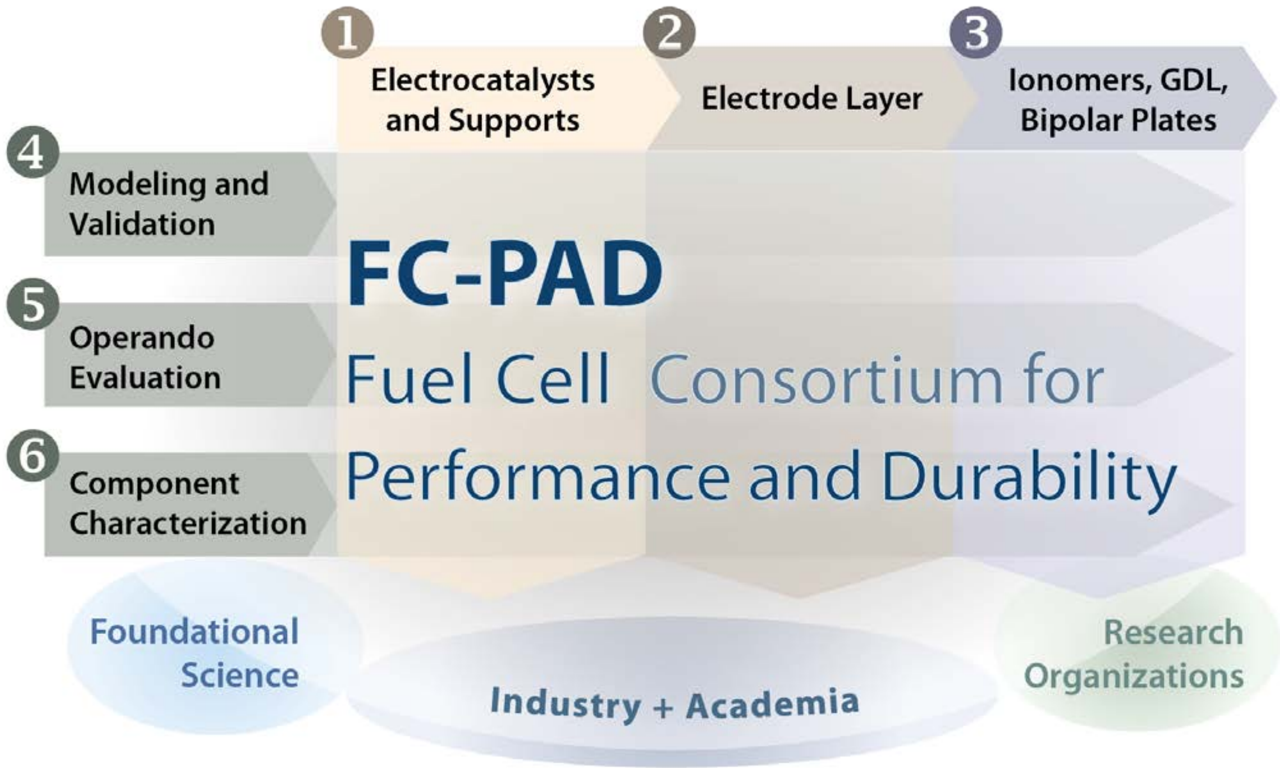


Lead: Rod Borup (LANL)
Deputy Lead: Adam Z. Weber (LBNL)

Los Alamos National Laboratory | Berkeley Lab | Argonne National Laboratory | Oak Ridge National Laboratory | NREL | U.S. Department of Energy | Energy Efficiency & Renewable Energy

The National Lab FC-PAD consortium capabilities are available to support collaborations

Thrust areas are broken into component and cross-cutting thrust areas:

Component areas:

Electrocatalysts and Supports
Electrode Layers
Ionomers, Gas Diffusion Layers, Bipolar Plates, Interfaces

Cross-cutting areas:

Modeling and Validation
Operando Evaluation: Benchmarking, ASTs, and Contaminants
Component Characterization and Diagnostics

FC-PAD Thrust Areas, Coordinators, and Individual National Lab 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 (yellow): Electrode Layers – ANL, LBNL; Component Characterization and Diagnostics – ANL, LANL

High Activity (green): all other X cells

Thrust Area 1: Electrocatalysts and Supports Overview

- **Primary Participants**
  - Argonne and Los Alamos

- **Thrust Area Coordinator**
  - Deborah Myers, Argonne National Laboratory

- **Subtasks**
  - Catalyst and catalyst support durability and degradation mechanisms
  - Catalyst/support interactions
    - X-ray scattering
  - Ex-situ analysis of catalyst instability on cathode-catalyst-layer properties

- **Materials**
  - State-of-the-art commercial catalysts
  - Catalysts and supports arising from materials development projects within FCTO and BES portfolio, where sufficient quantities are available
  - Materials which have demonstrated the ability to reach the DOE beginning-of-life performance targets or those demonstrating the potential to meet the targets in *ex situ* measurements

Focus, goals, and activities of Thrust Area 1

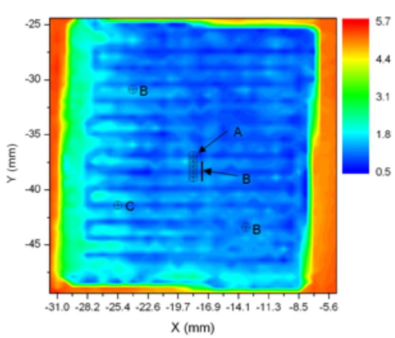
- **Catalyst and catalyst support durability and degradation mechanisms**
  - Elucidate catalyst and support degradation mechanisms as a function of catalyst and support physicochemical properties and cell operating conditions
  - Quantify catalyst and support stability during accelerated stress tests and start-up and shut-down transients using in-cell measurements
  - Determine stability of catalyst components against dissolution, catalyst and support composition and structural changes induced by cell testing, particle size distribution changes with time using operando X-ray techniques and microscopy, and oxide growth kinetics and steady-state coverages using electrochemical and spectroscopic techniques

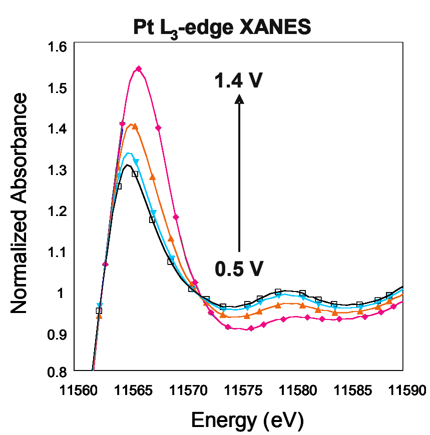
- **Catalyst/support interactions**
  - Understand interplay between the catalyst and support properties and their mutual interactions
  - Determine the effects of carbon type (e.g., high, medium, and low surface area) and carbon dopants on the strength of the catalyst/support and ionomer/support interactions
  - Investigate the impact of these interactions on catalyst and support stability, durability, and performance

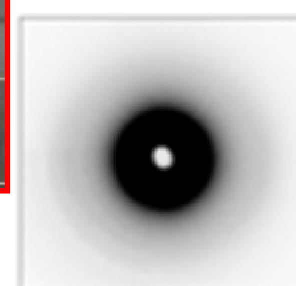
- **Ex-situ analysis of catalyst instability on cathode-catalyst-layer properties**
  - Quantify the impact of catalyst degradation on the properties defining the performance of the cathode catalyst layer (e.g., impact of base metal leaching from Pt alloy catalyst on proton conductivity, oxygen permeability, and water uptake in ionomer)

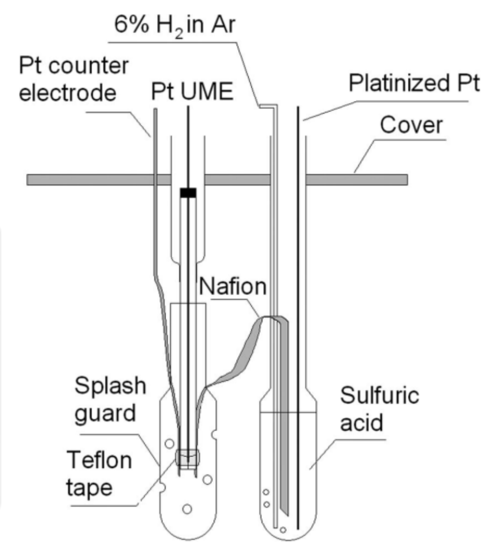
Key Capabilities Relevant to Thrust Area

- Dissolution measurements using electrochemical techniques coupled with ICP-MS
- Operando X-ray absorption and scattering for catalyst component oxidation state and oxide structure and metal and carbon particle/agglomerate size
- Aqueous and in-cell electrochemical measurements of platinum oxidation kinetics and extent of oxidation
- Solid-state ultra-microelectrode electrochemical cell for measurement of oxygen permeability through ionomer layers
- X-ray fluorescence for changes in catalyst composition with AST cycling
- X-ray tomography for changes in micro- and nano-structure with AST cycling
- On-line CO_2 detection from MEAs for quantification of carbon corrosion
- TEM, HR-TEM, EDAX of supports and catalysts









Thrust Area 2: Electrode Layers Overview

- **Primary Participants**
  - ANL, LBNL, LANL, NREL
- **Thrust Area Coordinator**
  - Shyam Kocha, National Renewable Energy Lab
- **Objectives**
  - Understand transport losses in low loaded catalyst layers at high current densities
  - Understand transport losses in alloy catalysts at high current densities with development of novel diagnostics
  - Design novel electrodes that overcome these problems
    - Stratified catalyst layers; Electrode structures using advanced catalysts (eg. EFTECS)
  - Coordinate with performance/durability modeling and characterization
- **Subtasks**
  - *Low Pt-loaded electrode layers*
  - *Transport in low-loaded catalyst layers*
  - *Electrode-layer designs and fabrication*
  - *Electrode-layer degradation*

Thrust Area 2: Electrode Layers

Low Pt-loaded electrode layer*s:* This subtask area will concentrate on improving the performance of low Pt loaded electrode layers at high current densities and limiting the degradation losses at the electrode layer level, including electrocatalyst and support composition/morphology changes and electrode-structure changes. Such electrode layers also include NSTF ones.

Transport in low-loaded catalyst layers: The impact of different catalyst-layer compositions (including low equivalent-weight ionomer) will be explored to ascertain how transport phenomena change. Applying existing diagnostics using limiting current and developing new techniques, the transport limitations will be quantified and the resistance better defined.

Electrode-layer designs and fabrication: The formation of electrode layers is still a black art. Altering the ionomer-solvent-catalyst ink composition, solvent removal methods, and/or ionomer properties, such as equivalent weight, will be explored in coordination with Thrust 1 activities. To increase high-current-density performance, new electrode-layer structures will be explored including those involving a very thin first layer coating the catalyst surfaces to provide local conductivity with a minimal transport barrier and a second phase of a solid network to provide bulk ionic conductivity.

Electrode-layer degradation*:* We will examine the origins of the changing transport losses by examining how changing properties of the electrode layer, the surface properties of the carbon support, protonic conductivity of the ionomer, and pore morphology impact durability.

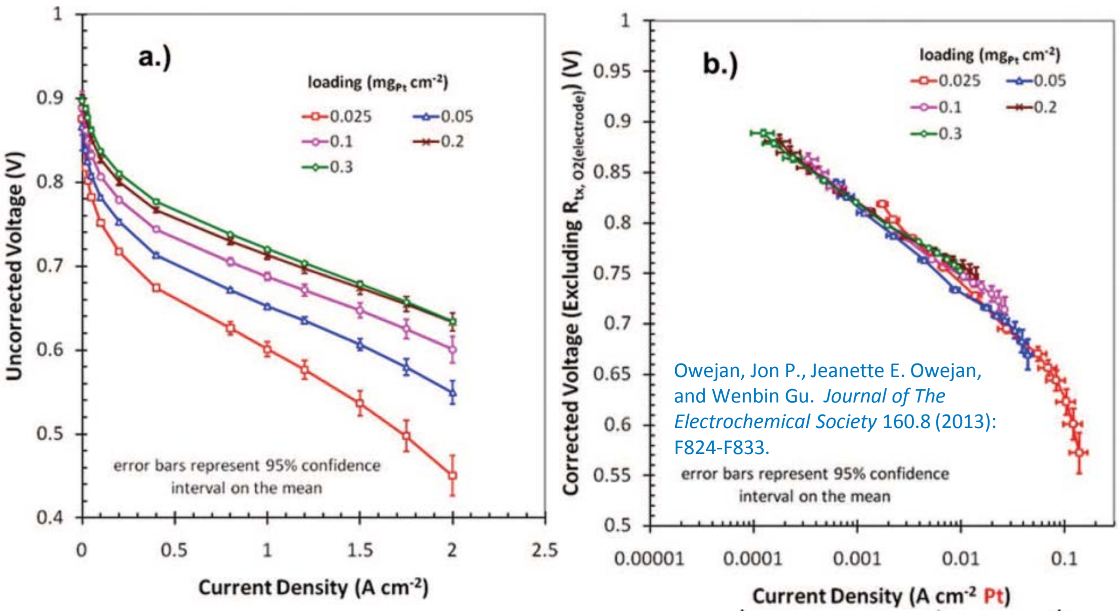
Automated Diagnostics

Automated gas mixing for oxygen limiting current and the development/investigation of CO limiting current as a diagnostic

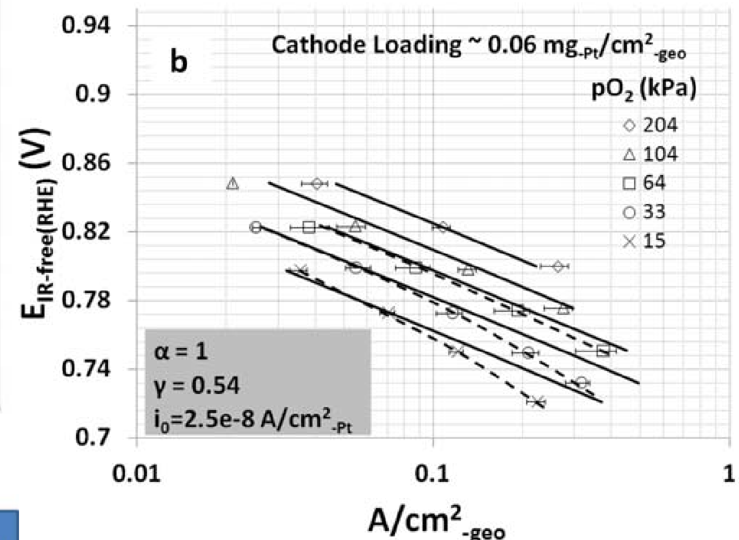
Automated potentiostats
-ideal for durability studies
-voltage cycling and automated CV collection
-helpful for Pt oxide measurements
-useful for CO limiting current measurements

HFR-Free Potential Control
-Used to match potentials where kinetic data and oxide coverage data is taken

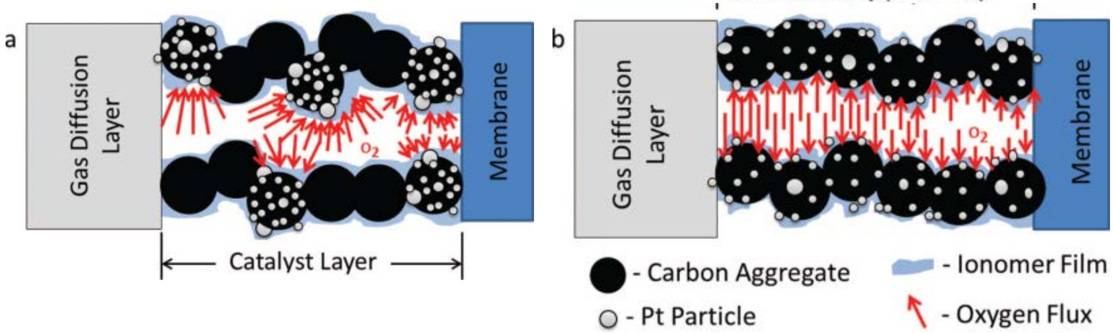
MEA Performance Diagnostics Motivation



Unpredicted voltage loss at low Pt loadings correlate with a reduction in total Pt surface area



Subramanian, N. P., et al. *Journal of The Electrochemical Society* 159.5 (2012): B531-B540.



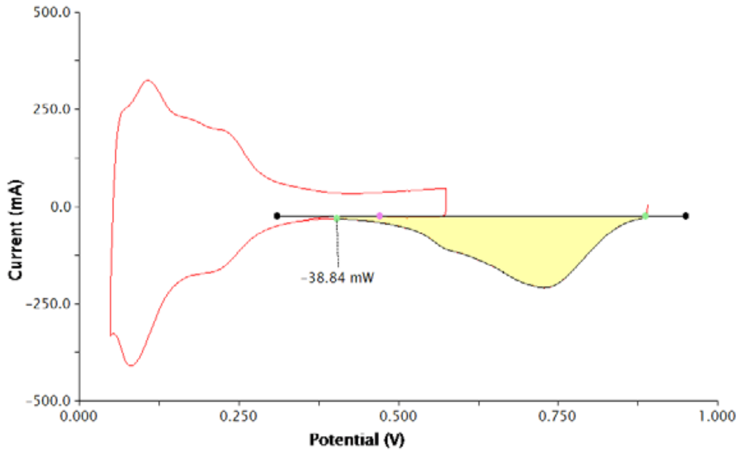
Accounting for oxide coverage kinetics at low potentials does not account for the entire voltage loss

Goal

- To understand the cause of the unanticipated voltage losses observed at high current density and low Pt loading
- Electrochemical Kinetics and/or Electrode Design
- Requires pressurized DI system/ vacuum system and HFR-Free Potential Control

Pt and advanced Pt catalyst - oxide coverage dependent kinetics

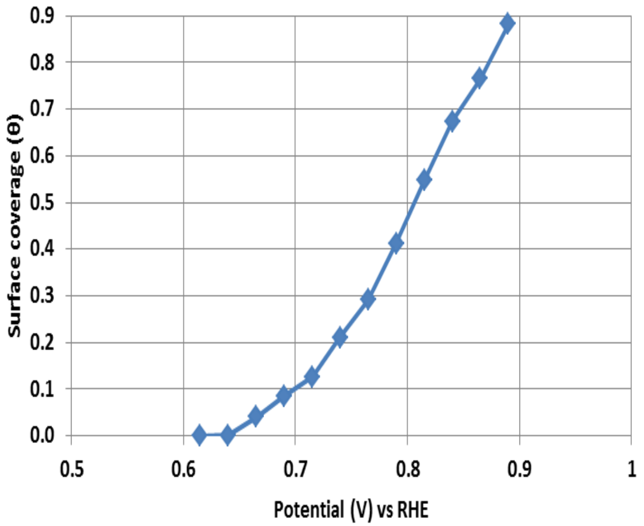
- Local transport resistance cannot be quantified without the assessment of oxide coverage dependent kinetics
- Experiments utilizing this technique are underway for state-of-the-art Pt alloy catalysts.



Oxide coverage measured through integration of oxide reduction peak – PtVu repeat

Requires HFR-free potential control and programmable potentiostat capability is preferred

$$i = i_0 \left(\frac{p_{o2}}{p_{o2,\text{ref}}} \right)^{\gamma} (1 - \theta) \exp\left(\frac{-\alpha F \eta}{RT} \right) \exp\left(-\frac{\omega\theta}{RT} \right)$$



Calculated oxide surface coverage for Pt/V

Subramanian, N. P., et al. *Journal of The Electrochemical Society* 159.5 (2012): B531-B540.

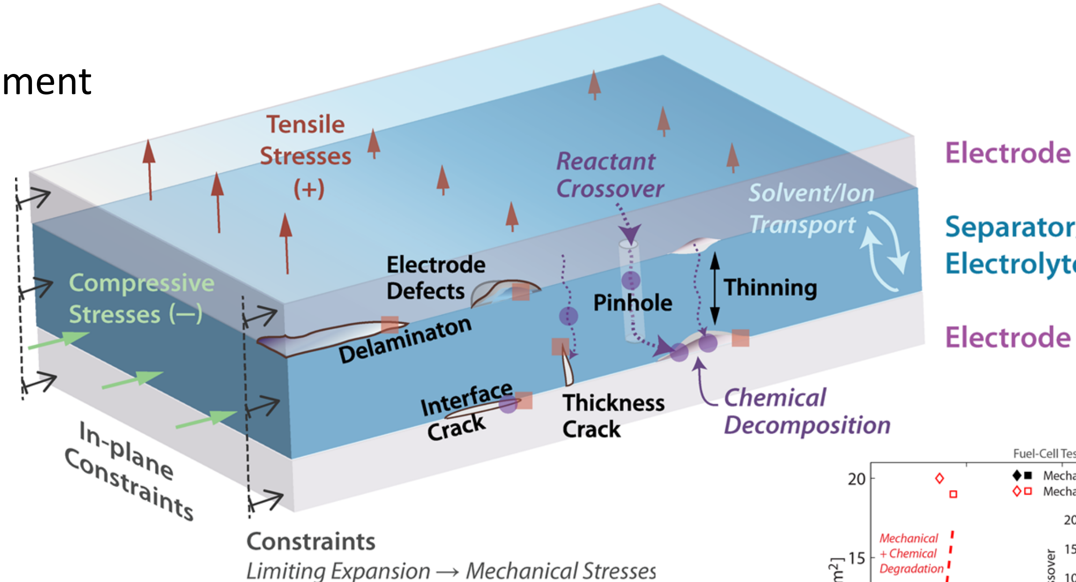
Thrust Area 3: Ionomers, Gas Diffusion Layers, Bipolar Plates, and Interfaces
Overview

- **Participants**
  - LBNL and LANL
- **Thrust Area Coordinator**
  - Adam Weber, Lawrence Berkeley National Lab
- **Objectives**
  - *Membranes and Ionomer films*
    - *Examine SOA membranes including stabilization and reinforcement*
      - *Stability of Ce; crack propagation; structure-function*
    - Thin-film properties
      - Casting conditions and solvents, chemistry, substrate,
  - *GDLs*
    - *Examine water-transport controls and impacts;*
      - *in-situ and AST characterization*
  - *Bipolar plates*
    - *Examine leachate ions and corrosion products and contact resistance*
  - *Interfaces*
    - GDL/channel droplet interface; CL interface and areas of high porosity

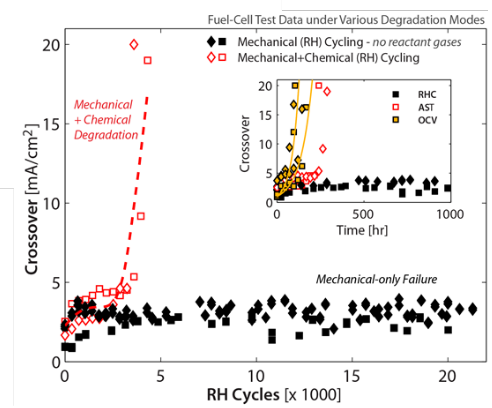
Bulk Membranes

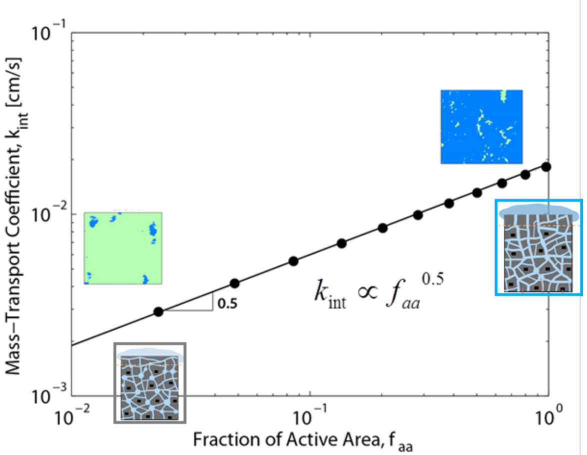
Structure/function/performance across length scales

- Durability concerns
  - Mechanical reinforcement
  - Cerium migration



Localized **Chemical** stressors
higher rate of degradation and crossover
Localized **Mechanical** stressors
stress concentration, damage initiation





- Transport and uptake of polymers
  - Impact of interfacial phenomena

Structure/Property Investigation of Ionomers

PFSA ionomers: Parameter space influencing their structure/property relationship and functionalities

Chemistry
Side-chain
Backbone
(IEC/EW)

Dispersion
Solution

Casting (*Thickness*)

Membrane (~*μm*)

Thin Film (~*nm*)
Substrate
Confinement

Processing
Pre-stretching
Reinforcement

Annealing
Heat-treatment
ion-exchange
- *cations*

Environment
RH, T, p, pH

Time
ageing
relaxation

Degradation
physical
chemical
mechanical

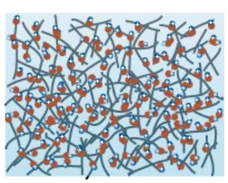
Structure
- *Morphology*
- *Crystallinity*
- *Nano-domains*
- *Surface*

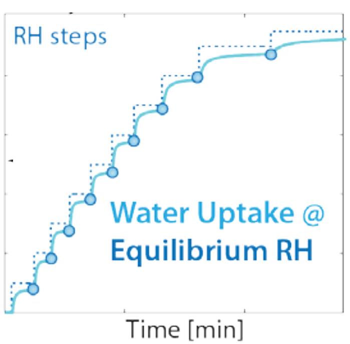
Properties
Transport
- *Uptake/Swelling*
- *Diffusion, Mobility*
- *Conductivity (ion)*
- *Permeability*

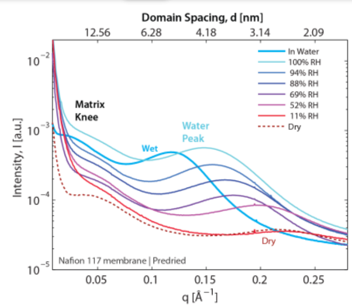
Thermal
- *Conductivity, T_g, T_m*

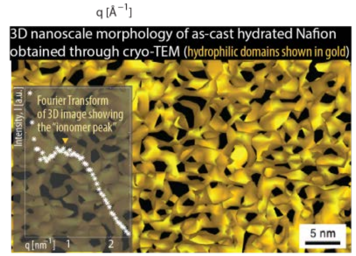
Mechanical
- *Stress-Strain response*
- *Modulus, Strength*
- *Viscous Behavior*
- *Break strain, Fracture*

Polymers / Chemistry → **Environmental conditions** → **Morphology (SAXS, TEM)** → **Diagnostics/Properties (Transport)** → **Structure-Property Correlations**

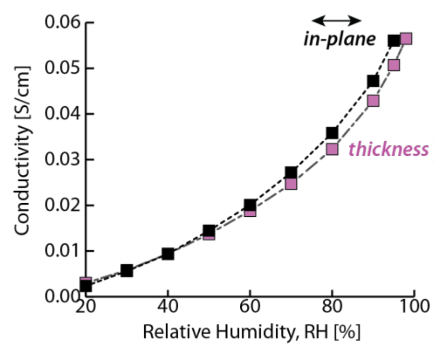


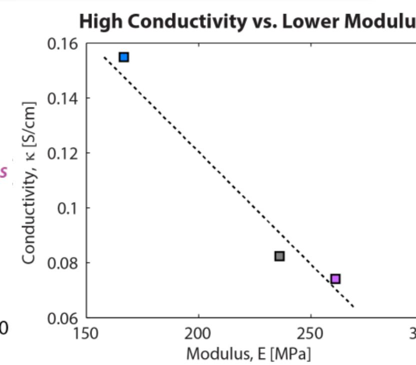






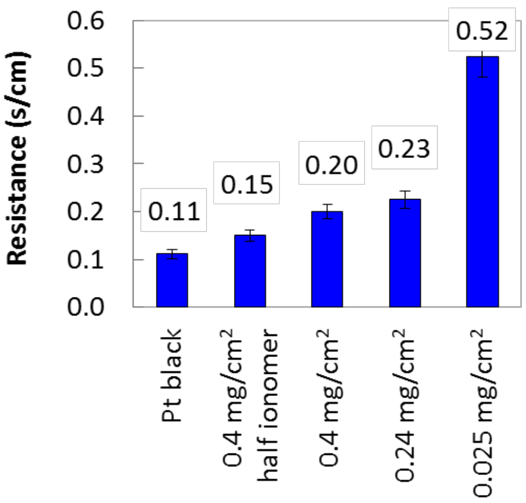
F.I. Allen, L.R. Comolli, A. Kusoglu, M.A. Modestino, A.M. Minor, A.Z. Weber, *ACS Macro Letters*, 4 (2015) 1-5 | DOI: 10.1021/mz500606

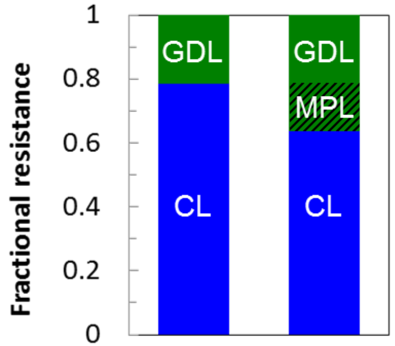




Catalyst Layer Ionomer

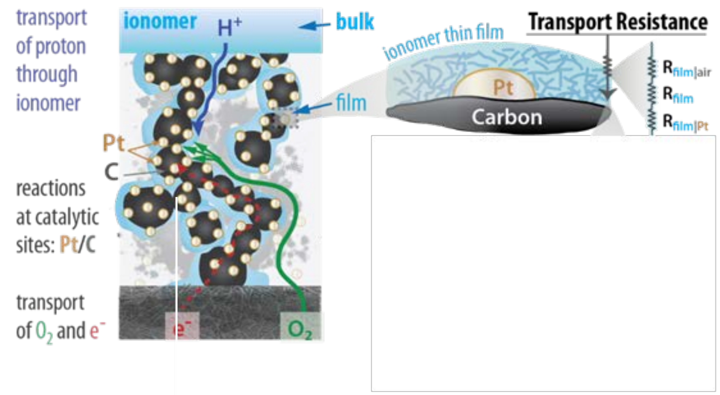
- Measure local resistance

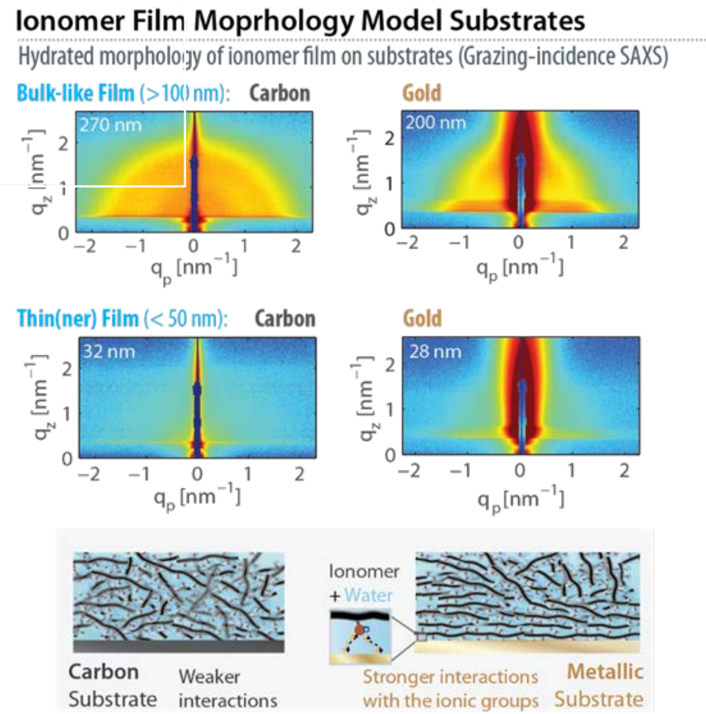




- Correlating resistance to ionomer thin-film structure on model substrates
  - Elucidate limiting phenomena
  - Measure critical transport properties

- Insights will allow for novel strategies and materials to overcome limitations





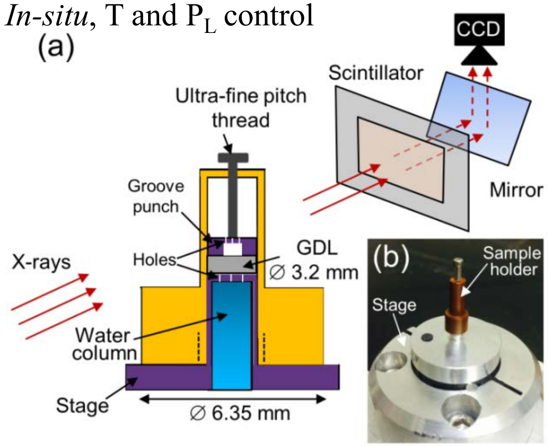
Diffusion Media and Plate Studies

- Measure critical properties and morphology
  - Examine changes as a function of time and operating stressors
  - Examine interfaces in terms of performance and durability concerns

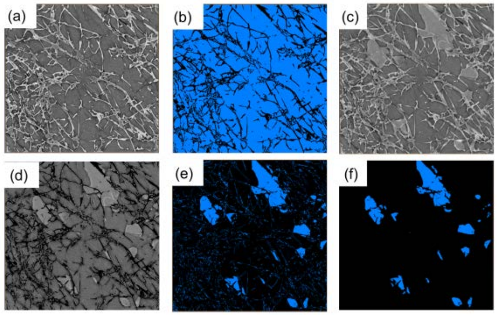
XCT imaging

Morphology and Spatial Distributions

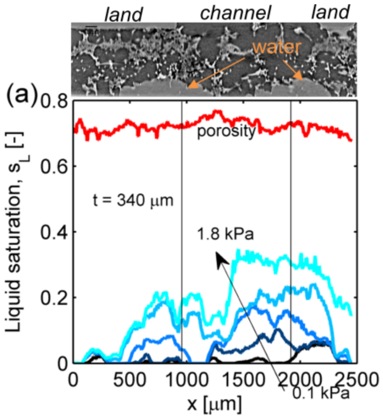
- 1.3 μm resolution
- *In-situ*, T and P_L control



Raw data

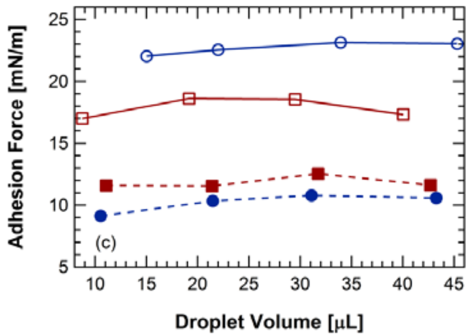


Binary image stacks of GDLs and water



Transport Properties and Phenomena

Durability



Thrust Area 4: Modeling and Validation
Overview

- **Participants**
  - LBNL and ANL

- **Thrust Area Coordinator**
  - Rajesh Ahluwalia, Argonne National Lab

- **Focus**
  - *Model development and validation*
    - *Microstructural models including catalyst layers*
    - *Component degradation models*
    - *Water and thermal management (performance) models*
      - *Multiscale, multiphysics*
  - Develop well-designed test protocols for characterizing the kinetic and transport properties of cell components
  - Optimization and elucidation of performance and durability bottlenecks

Performance Models

Performance Models

1. **1-D Model**: Kinetic study, species transport, temperature distribution
2. **1+1-D Channel Model**: Straight channel, counter or parallel flows. Species concentration and temperature distribution along flow directions
3. **2+1-D Channel Model**: Landing effect, liquid removal by cornering, GDL compression
4. **3-D Channel Model**: Elliptic flow effect, serpentine flow
5. **Cell Model**: Straight or serpentine flow channels with inlet/outlet baffles, non-uniform channel flows
6. **Stack Model**: anode, cathode and coolant manifolds; cell to cell non-uniform pressure, flow and temperature distributions

Component Models and Data Analysis

1) **Impedance Studies (ES, OE):** H_2/N_2, H_2/air

2) **Pt Oxidation (ES, OE):** Cyclic voltammetry

3) **ORR Kinetics (OE)**: H_2/O_2 cell in differential mode

4) **Oxygen Mass Transfer (OE)**: H_2/air in differential mode

5) **Water Transport in GDL and Catalyst Layers (CF, OE)**

6) **Membrane and Ionomer (BOC, OE, ELI)**

Degradation Models

Degradation Models

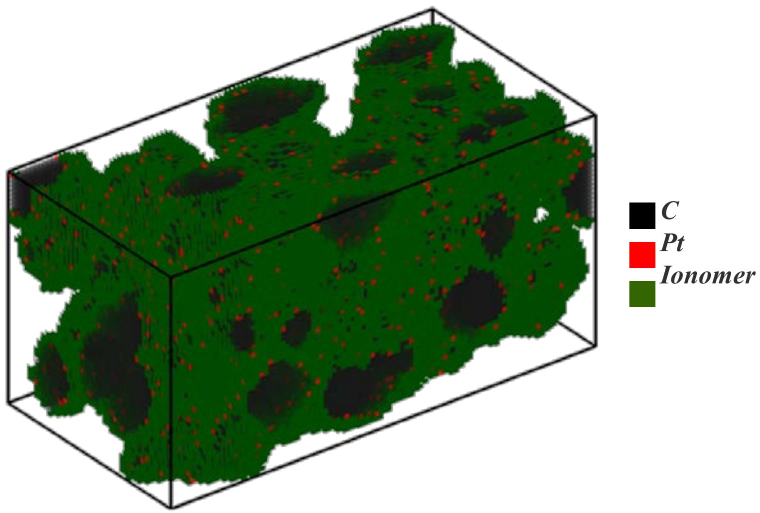
1) **Catalyst:** Pt dissolution, coarsening, base metal leaching
2) **Membrane:** FER, cerium (radical scavenger) transport, Pt in membrane, mechanical/chemical stability, H_2 cross-over
3) **Ionomer**
4) **Catalyst Support:** Potentiostatic and potentiodynamic corrosion rate, SU/SD model
5) **Electrode:** Pore size distribution, thickness, reversible and irreversible degradation
6) **GDL**
7) **Bipolar Plates:** Cation release rate, ICR

Durability Data Analysis

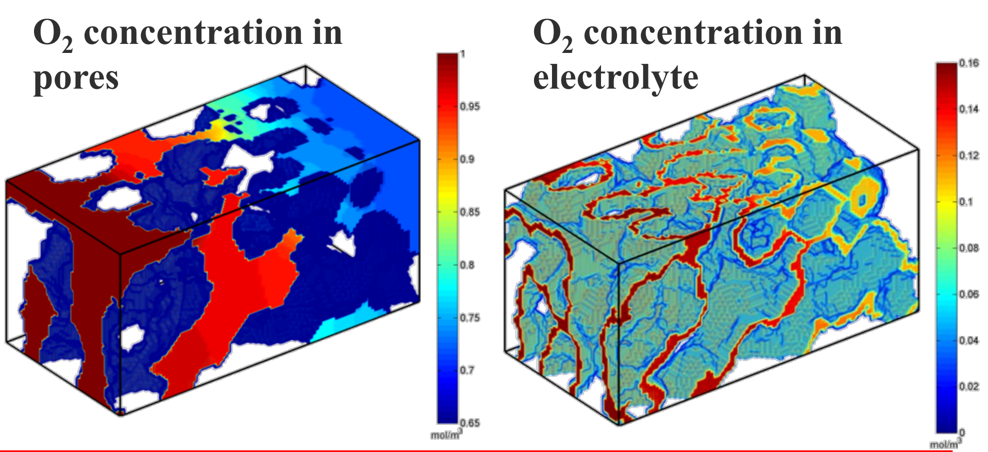
1) **Catalyst (ES):** Stability of $PtCo_x$ and d-$PtNi_3$ alloys
2) **Membrane (BOC):** Durability of chemically-stabilized and mechanically-reinforced membranes
3) **Ionomer (ELI, OE)**
4) **Catalyst Support (ES, OE):** Unified model for carbon support, Non-carbon supports
5) **Electrode (ELI, OE):** Reversible and irreversible degradation, NSTF electrodes
6) **GDL (BOC)**
7) **Bipolar Plates (BOC, OE):** State-of-the-art ceramic, polymer and graphite coated plates

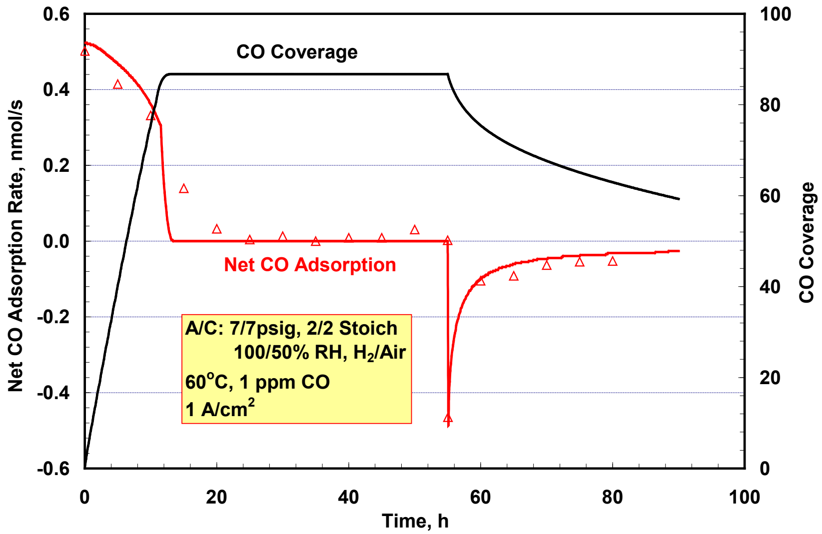
ES: Electrocatalyst and Support; ELI: Electrode Layer Integration; BOC: Membranes, GDL, BP; MPAD: Modeling Transport and Durability; OE: Operando Evaluation; CD: Characterization and Diagnostics

Electrode Microstructure Simulations and Impurity Effects



Subtask 4.5: Electrode Microstructure
1) Numerical Reconstruction Algorithm
2) Multi-Physics Model
3) 3-D Computed Tomography (CD)





Impurity Effects

1) Fuel Impurities (OE)

2) Air Impurities (OE)

3) System Generated Impurities (OE)

4) Cell Generated Impurities (OE)

Thrust Area 5: Operando Evaluation: Benchmarking, ASTs, and Contaminants Overview

- **Participants**
  - LANL and NREL
- **Thrust Area Coordinator**
  - Rangachary Mukundan, Los Alamos National Lab
- **Focus**
  - Performance and durability benchmarking
  - Operational effects on durability
    - Segmented cell studies, drive cycle
  - AST protocol development and validation
    - Freeze protocol
    - SD/SU protocol
    - Refined membrane and catalyst AST
  - Analysis of reversible degradation mechanisms
    - Quantify effect of Pt-oxidation, surface contamination and mass transport effects
  - Contaminants and impurities
    - Air, fuel and system contaminants

Thrust Area 5: Operando Evaluation: Benchmarking, ASTs, and Contaminants

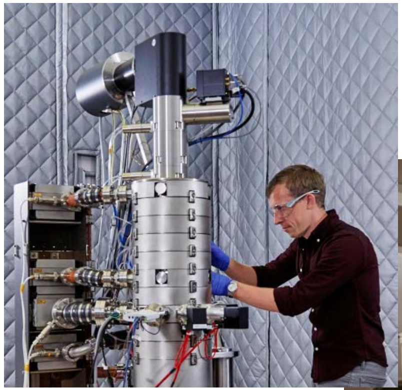
- **Provide durability testing to catalyst, membrane, GDL, bi-polar plate and MEA developers**
  - Perform Stress tests on MEAs
    - Track membrane degradation through Fluoride release, membrane thinning and HFR changes
    - Track catalyst degradation through ECSA, Mass Activity, performance loss, Pt particle size growth and Pt deposition within the membrane
    - Track catalyst support degradation through CO2 emission, Surface characterization, catalyst layer thinning, catalyst layer morphology changes, electrode capacitance changes, and mass transport losses (Impedance and HelOx measurements)
    - Track GDL degradation through surface characterization, pore size characterization and mass transport losses
    - Track Bi-polar plate degradation through contaminant measurements (ICP-MS), and contact resistance changes
- **Provide performance characterization**
  - Perform power cycling on MEAs under various operating conditions including sub-zero operation, in the presence of contaminants and in segmented cells
  - Quantify voltage losses in MEA and attribute them to materials properties using in situ electrochemical characterization, ex situ materials characterization and fuel cell models

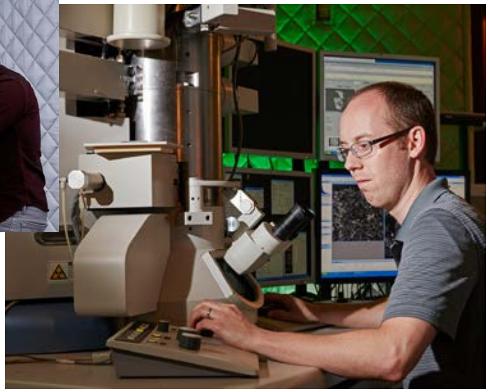
Thrust Area 6: Component Characterization & Diagnostics Overview

- **Participants**
  - ORNL, ANL, LANL, NREL, LBNL
- **Thrust Area Coordinator**
  - Karren More, Oak Ridge National Lab
- **Focus/Objectives**
  - *Comprehensive Materials Benchmarking – sub-Å to μm-level Understanding*
    - Characterize component structure, chemistry, and composition *before & after* durability testing
    - Systematic approach to understand the effects of testing variables/protocols on material's stability and performance
  - *Coordination across all six thrusts for durability/performance characterization*
    - *Advanced Electron Microscopy (ORNL)*
    - *Neutron and X-ray Studies (ANL, LBNL, NIST)*
    - *Component Diagnostics (LANL, NREL)*
    - *Provide experimental input and validation of durability models/simulations*
  - *Development of new techniques/protocols/capabilities*
    - *Characterization targeted towards specific fuel cell materials/components and test protocols*
    - *Operando studies and development of unique tools*

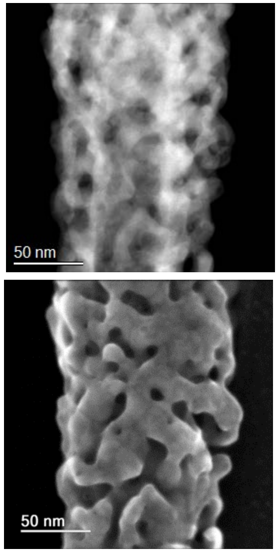
Atomic Resolution Imaging and Spectroscopy

- Advanced analytical scanning transmission electron microscopy (STEM)
  - Atomic resolution imaging
  - Electron Energy Loss Spectroscopy
  - Energy Dispersive Spectroscopy
  - *In situ* microscopy and tomography

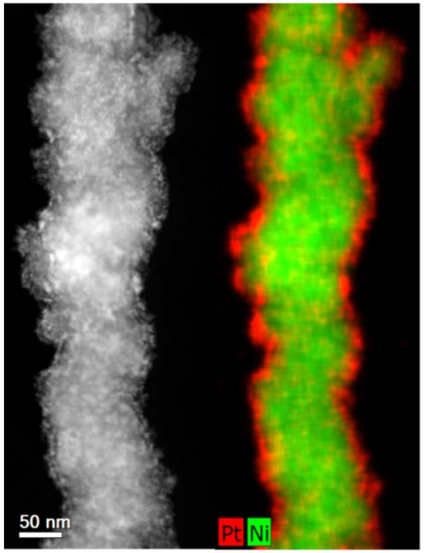




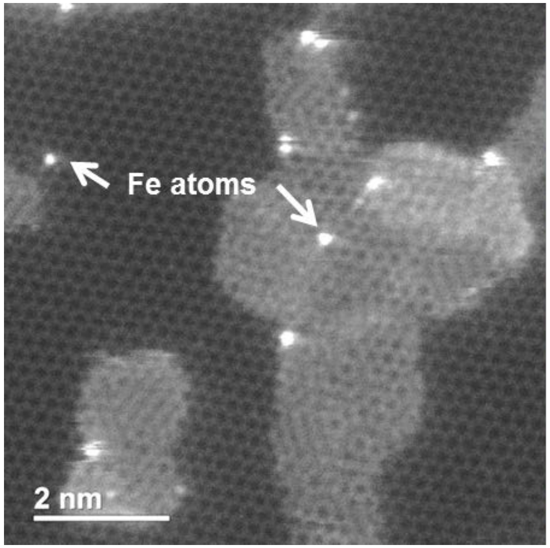
Single Fe atoms in graphene

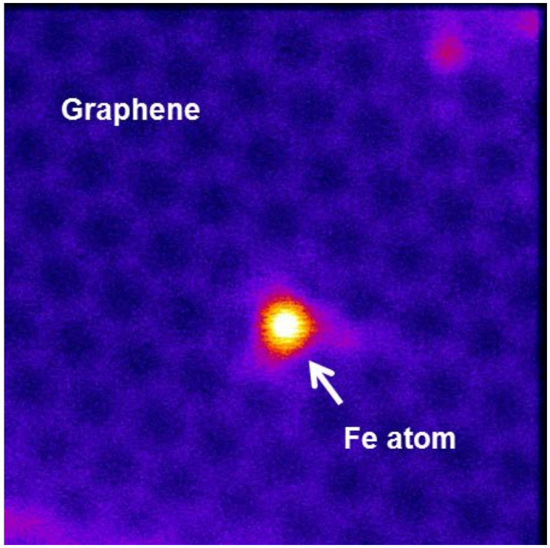


Porous catalysts



PtNi nanowires (NREL)





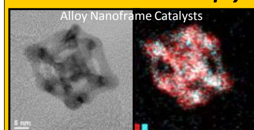
FC-PAD Capabilities

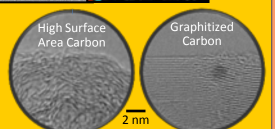
- Dissolution measurements using electrochemical techniques
- X-ray absorption spectroscopy for catalyst component oxidation state and oxide structure
- Electrochemical measurements of platinum oxidation kinetics and oxidation
- Small angle X-ray scattering for in situ and operando nanoparticle size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

FC-PAD Capabilities

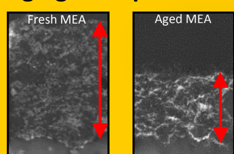
	Structural & Chemical Characterization	Performance Testing & Evaluation	Modeling & Theory
Catalyst & Catalyst Support Electrode & MEA Membrane & Ionomer GDL & Cell			

Analytical Electron Microscopy

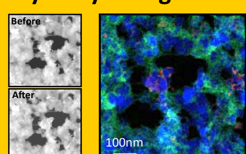




Imaging and spectroscopy



Catalyst-layer degradation

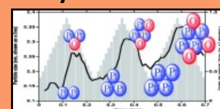


Ionomer mapping

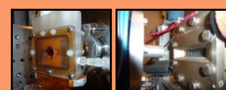
MoreKL1@ornl.gov

Advanced X-Ray Techniques

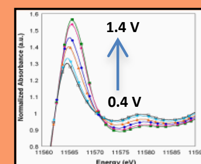
Spectroscopy and Scattering: catalyst atomic structure and particle size



Pt growth with cycling



Specialized *operando* cells



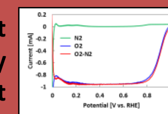
Pt oxidation with potential

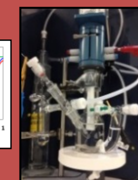
Combinatorial Activity Screening

DMyers@anl.gov

Electrochemical Diagnostics

Catalyst activity measurement

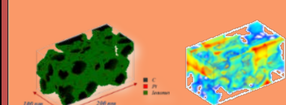




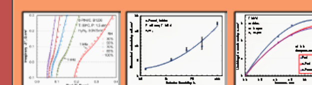
Advanced MEA Fabrication

Shyam.Kocha@nrel.gov

Electrode Simulations



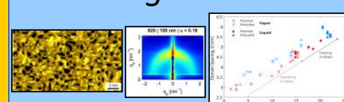
3-D electrode reconstruction and transport



Quantify various losses

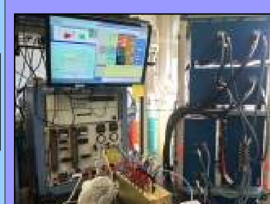
Walia@anl.gov

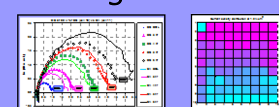
Advanced Component Diagnostics



Bulk and thin-film morphology and properties

Advanced MEA Diagnostics

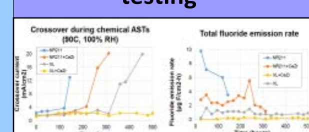


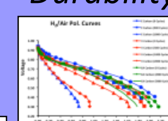


Mukundan@lanl.gov

Performance & Durability Testing

Long-term durability testing

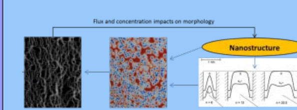




Component-specific degradation testing

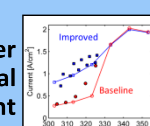
Borup@lanl.gov

Multiphysics, Multiscale Models



Membrane simulations

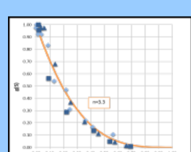
Optimize water and thermal management

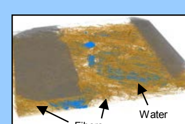


AZWeber@lbl.gov

GDL & Cell

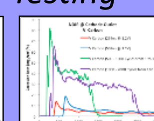
Transport property measurements





X-ray tomography

AZWeber@lbl.gov



Logos and names/emails listed with facilities do not represent the only laboratory working on a specific topic.