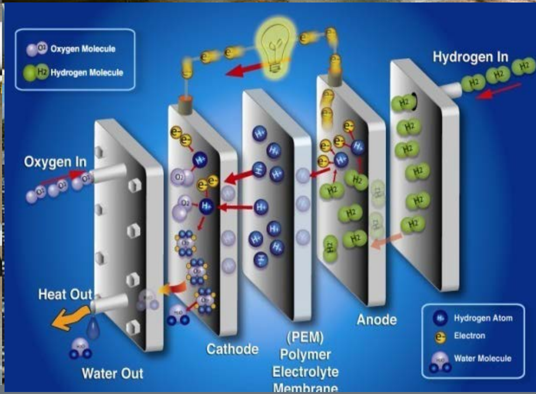
FCTO Consortia Overview Webinar (HyMARC and FC-PAD)

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



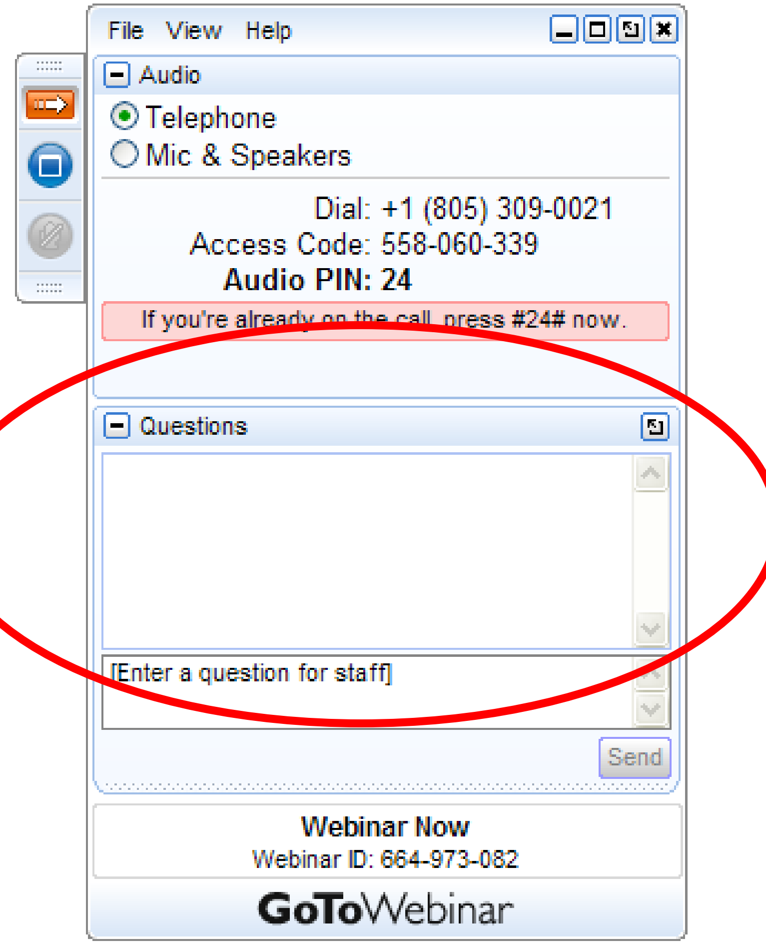
Presenters:
Mark Allendorf - Sandia National Laboratory
Rod Borup – Los Alamos National Laboratory

DOE Host:
Ned Stetson – DOE Fuel Cell Technologies Office
Dimitrios Papageorgopoulos - DOE Fuel Cell Technologies Office

U.S. Department of Energy
Fuel Cell Technologies Office
January 7th, 2016

Question and Answer

- Please type your questions into the question box



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Hydrogen Materials Advanced Research Consortium

Sponsor: DOE—EERE/Fuel Cell Technologies Office

Consortium Director: Dr. Mark D. Allendorf

Partner Laboratories:

Sandia National Laboratories

Mail Stop 9161, Livermore, CA 94551-0969. Phone: (925) 294-2895. Email:mdallen@sandia.gov

Lawrence Livermore National Laboratory

POC: Dr. Brandon Wood Phone: (925) 422-8391. Email: brandonwood@llnl.gov

Lawrence Berkeley National Laboratory

POC: Dr. Jeff Urban; phone: (510) 486-4526; email: jjurban@lbl.gov

Presentation topics

- **Concept, objectives, goals, organizational structure of HyMARC**
- **Overview of partner capabilities**

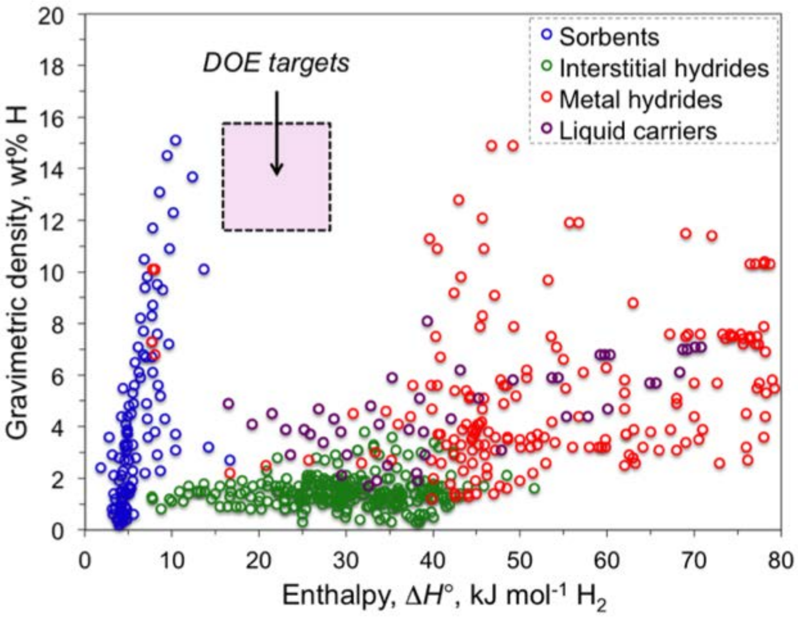
Critical Scientific Challenges (Identified by NREL PI meeting, Jan. 2015)

Sorbents: Eng. COE target: 15 – 20 kJ/mol

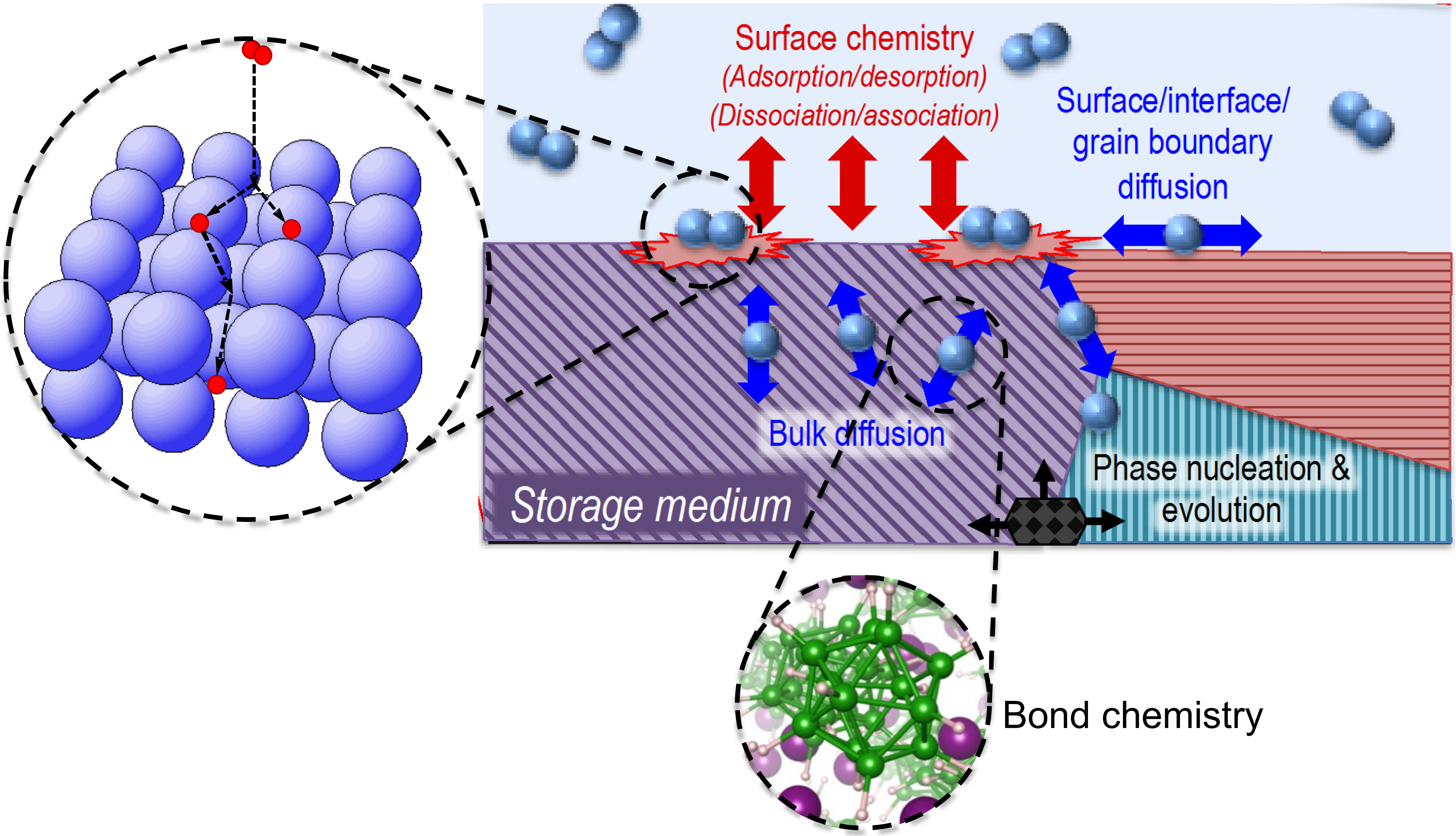
- Volumetric capacity at operating temp.
- Increased usable hydrogen capacity needed
- Distribution of H_2 binding sites and ΔH at ambient temperature not optimized

Metal hydrides: Eng. COE target: ≤27 kJ/mol H_2

- Poor understanding of limited reversibility and kinetics
- Role of interfaces and interfacial reactions
  - Solid-solid
  - Surfaces
- Importance and potential of nanostructures



Need for multiscale modeling approaches to address both thermodynamic and kinetic issues



HyMARC Objective

HyMARC will provide the fundamental understanding of phenomena governing thermodynamics and kinetics necessary to enable the development of on-board solid-phase hydrogen storage materials

These resources will create an entirely new DOE/FCTO Capability that will enable accelerated materials development to achieve thermodynamics and kinetics required to meet DOE targets.

Ambitious HyMARC goal: a set of ready-to-use resources

- Multi-physics software, methods, and models optimized for high-throughput material screening using the large-scale parallel computing facilities of the three partners
- Sustainable, extensible database framework for measured and computed material properties
- Protocols for synthesizing storage materials in bulk and nanoscale formats
- Ultra high-pressure synthesis and characterization facilities (700 bar and above)
- *In situ* and *ex situ* spectroscopic, structural, and surface characterization methods, tailored for hydrogen storage and, where necessary, adapted for facile use of ALS soft X-ray probes

HyMARC will purposefully make consortium assets (people, software, and hardware) as accessible as possible, thereby maximizing the impact of FCTO investments and providing a platform for leveraged capabilities with other DOE offices.

A simple conceptual framework for energetics of H_2 storage focuses activities on two overarching aspects of storage materials

"Effective thermal energy for H_2 release"

$$\Delta E(T) = \Delta H^{\circ}(T) + E_a$$

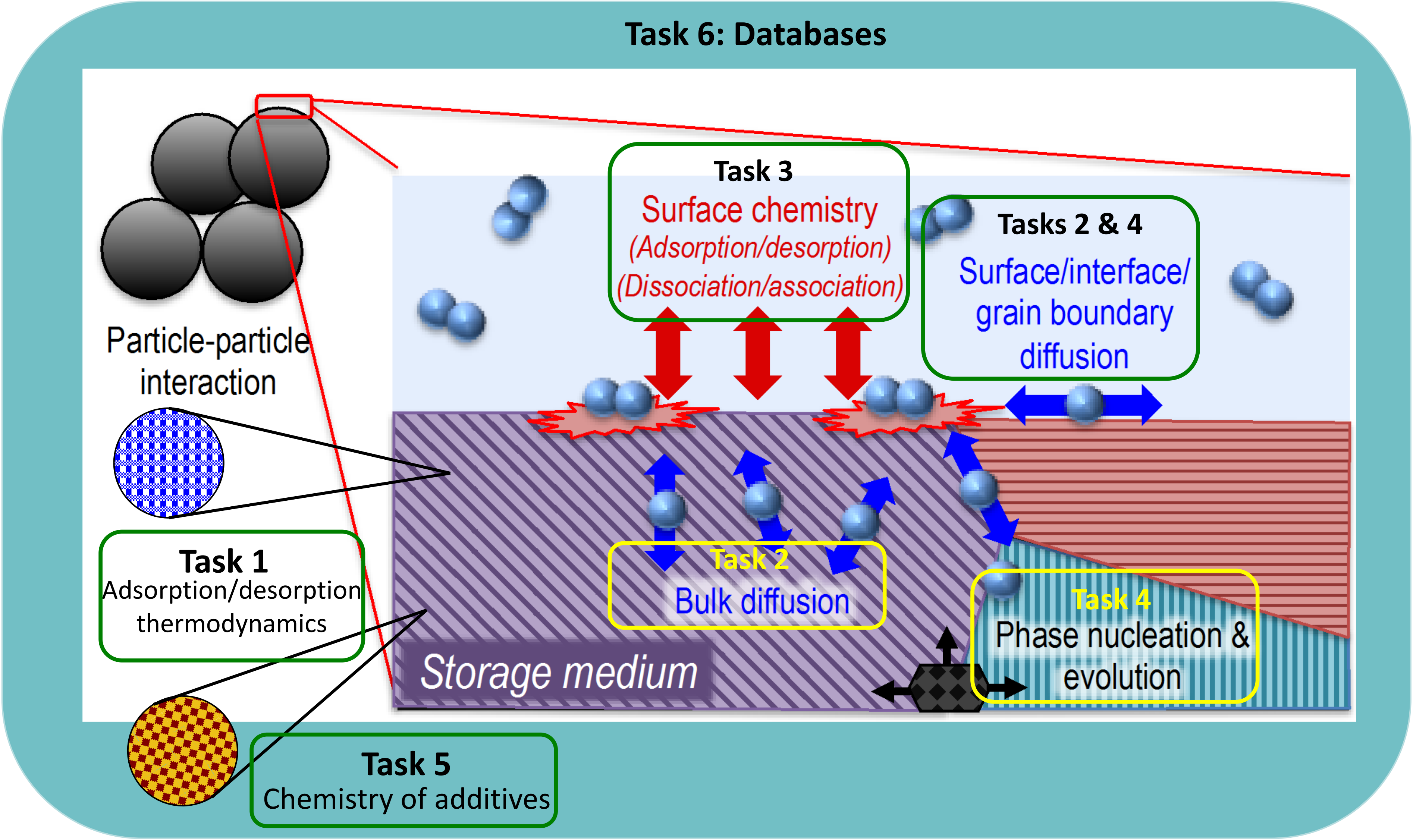
Thermodynamics of uptake and release
Tasks 1

- Sorbents
- Hydrides

Kinetics of uptake and release
Tasks 2, 3, 4, and 5

- Surface reactions
- Mass transport
- Solid-solid interfaces
- Additives

HyMARC tasks address the critical scientific questions limiting the performance of solid-state storage materials



Organizational structure of Core Team

HyMARC

Lawrence Livermore National Laboratory

Brandon Wood
LLNL Lead

Budget POC
Jeff Roberts

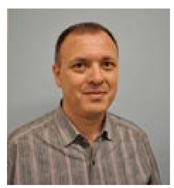
Task 2
Transport
Tae Wook Heo

Task 6
Databases
Brandon Wood

Sandia National Laboratories

Mark Allendorf
Director
SNL Lead

Budget POC
Landon Daft



Task 1
Thermodynamics
Vitalie Stavila

Task 3
Surface Chem.
Robert Kolasinski

Task 5
Additives
Lennie Klebanoff

BERKELEY LAB

Jeff Urban
LBL Lead
David Prendergast
Deputy

Budget POC
Katherine Britton

Task 4
Sol.-Sol. Interfaces
Jeff Urban

MOLECULAR FOUNDRY
POC: David Prendergast

ALS ADVANCED LIGHT SOURCE
POC: Jinghua Guo

All consortium partners and their unique capabilities contribute to each task

HyMARC

<table>
<tr><th></th><th>Task 1</th><th>Task 2</th><th>Task 3</th><th>Task 4</th><th>Task 5</th><th>Task 6</th></tr>
<tr><td rowspan="3">Sandia National Laboratories</td><td colspan="5">Synthesis of bulk and nanoscale metal hydrides and MOFs</td><td></td></tr>
<tr><td></td><td>LEIS</td><td>LEIS, XPS</td><td></td><td>LEIS, XPS</td><td></td></tr>
<tr><td>Ultra-high pressure reactor</td><td>Atomistic modeling of large systems</td><td>XPS & AP-XPS</td><td>Atomistic modeling</td><td></td><td></td></tr>
<tr><td rowspan="2">Lawrence Livermore National Laboratory</td><td>Tailored graphene sorbents</td><td>XAS, XES</td><td></td><td>XAS, XES</td><td>XAS, XES</td><td>Database concepts</td></tr>
<tr><td colspan="5">Multi-scale modeling tools</td><td></td></tr>
<tr><td rowspan="3">BERKELEY LAB</td><td>Graphene Nanobelts</td><td colspan="4">Soft x-ray characterization tools (ALS Advanced Light Source)</td><td>CoRE Database</td></tr>
<tr><td>Encapsulated metal hydrides</td><td colspan="4">Modeling for x-ray spectroscopies (Molecular Foundry)</td><td></td></tr>
<tr><td>Lewis acid/base sorbent chemistry</td><td></td><td></td><td>Electron microscopies (Molecular Foundry)</td><td>Catalytic nanoparticles on mesoporous supports</td><td></td></tr>
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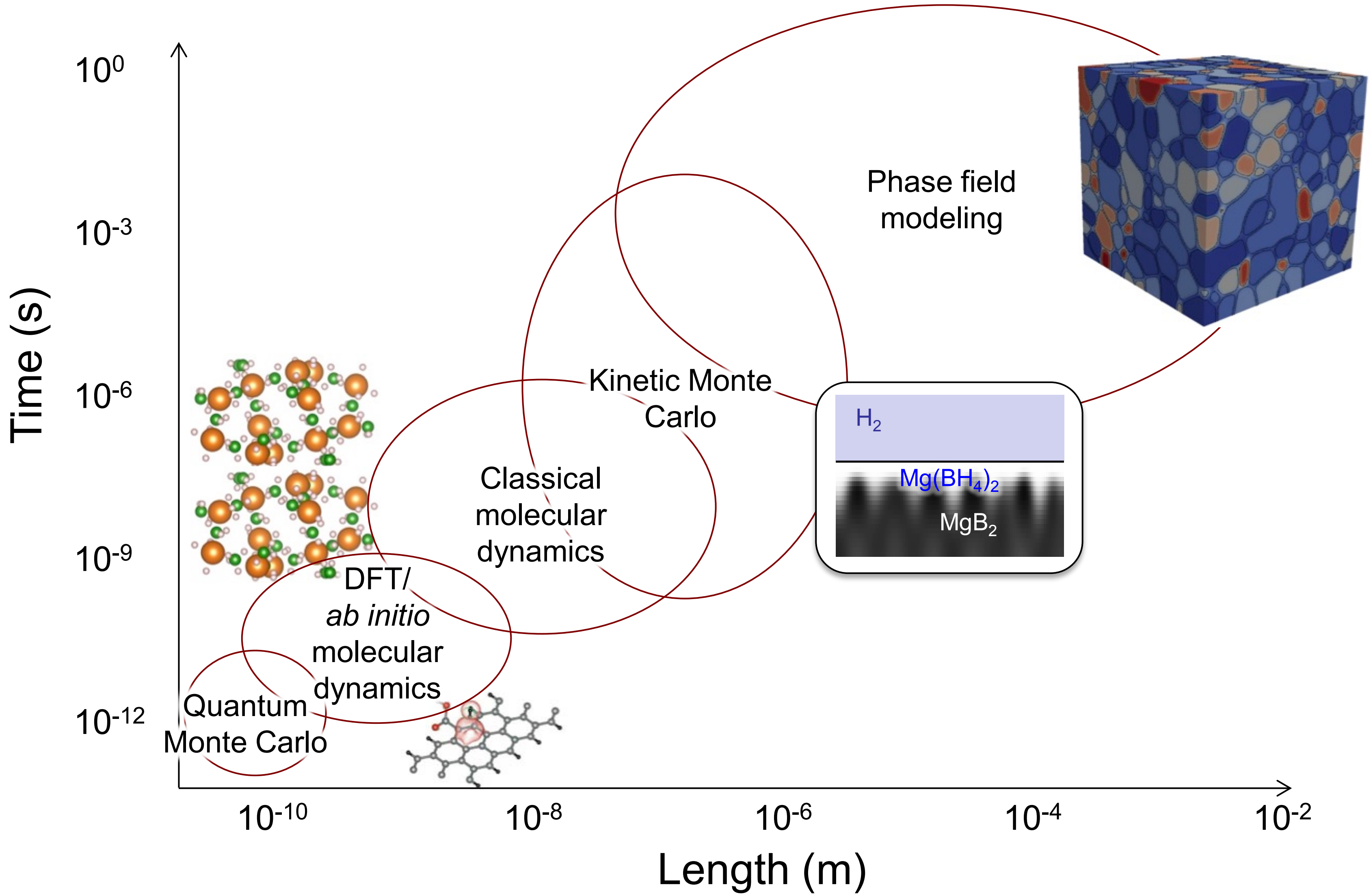
Overview of HyMARC capabilities and selected approaches

The following slides illustrate unique existing capabilities within the HyMARC Core Team and some of the approaches we are using to address critical barriers to the development of successful solid-state storage materials

- Quantum Monte Carlo for accurate sorbent energies
- Phase-field modeling (PFM): Solid-state phase transformation kinetics
- Sorbent suite for model testing and validation
- Bulk and nanoscale metal hydrides synthesis and characterization
- Modified graphene nanoribbons: functional catalysis
- Hierarchical integrated hydride materials
- Low-energy ion scattering for detecting hydrogen on surfaces
- Ambient-pressure X-ray Photoelectron Spectroscopy (AP-XPS)
- Soft X-ray spectroscopy and microscopy at the Advanced Light Source
- Theory and modeling: computational spectroscopy and x-ray spectroscopy
- Community tools, including databases

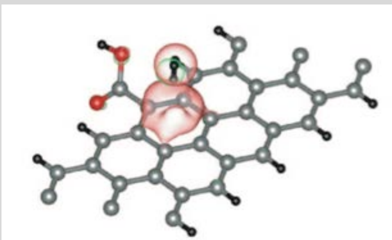
A suite of techniques for multiscale simulations are a key capability of the HyMARC Core Team



Quantum Monte Carlo for accurate sorbent energetics

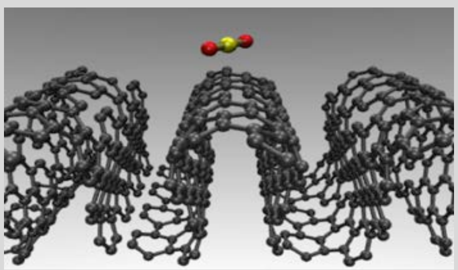
Stochastic quantum method for beyond-DFT accuracy for H_2-metal energetics and Lewis acid-base interactions

Carbon sorbents



Chemical functionalization (edge and surface)

Ulman et al., J. Chem. Phys. 140, 174708 (2014)



Curvature and strain

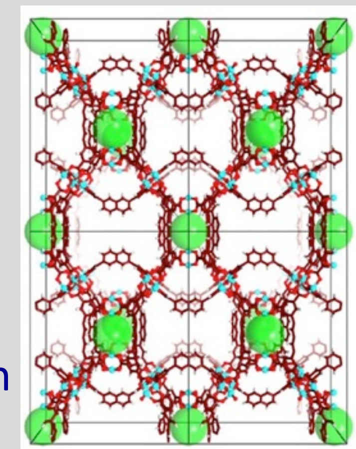
Dutta et al., J. Phys. Chem. C 118, 7741 (2014)

Metal-organic frameworks (MOFs)

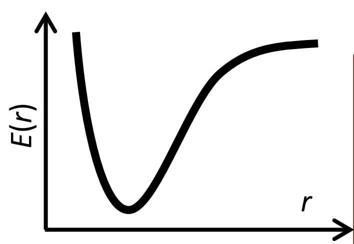
Open metal sites

Organic linkers

Crystal structure/coordination



QMCPACK

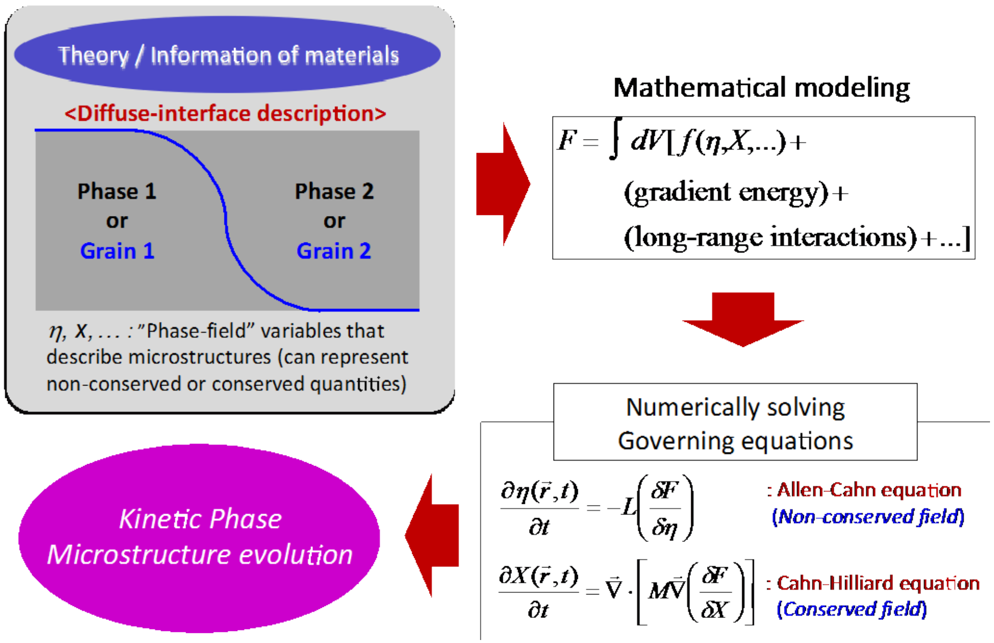


Generate fitted potentials (or benchmarked DFT functionals) for integration with Zeo++ porosity modeling and CoRE database for isotherm prediction

Phase-field modeling (PFM): Solid-state phase transformation kinetics

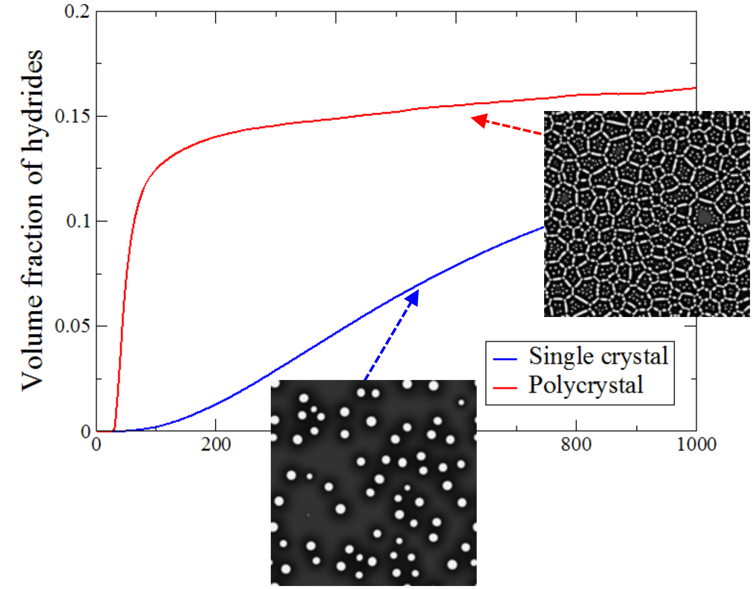
Combine **thermodynamics**, **mass transport** (bulk, surface, and interface), **mechanical stress**, and **phase nucleation/growth** to **model solid-state reaction kinetics**

General Framework



Kinetic evolution of microstructure

<Phase nucleation/polycrstallinity>

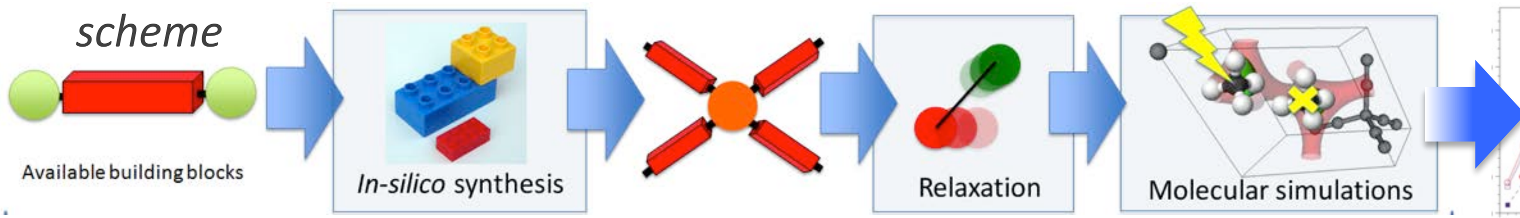


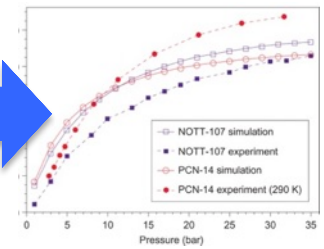
T.W. Heo, S. Bhattacharyya, L.-Q Chen, *Acta Mater.*, **59**, 7800 (2011)
T.W. Heo, S. Bhattacharyya, L.-Q. Chen, *Phil. Mag.*, **93**, 1468 (2013)
T.W. Heo, L.-Q Chen, *Acta Mater.*, **76**, 68 (2014)
T.W. Heo, L.-Q Chen, B.C. Wood, *Comp. Mater. Sci.*, **108**, 323 (2015)

Sorbent suite for model testing and validation

Goal: validated theoretical models that can serve as the basis for high-throughput computational material design

Prediction scheme



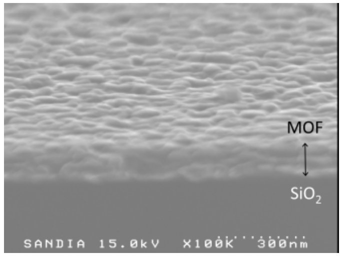


GCMC simulations

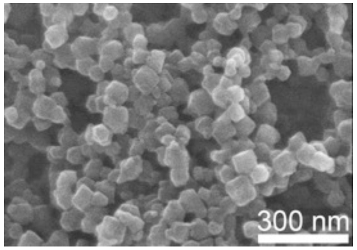
New capabilities targeted by HyMARC:

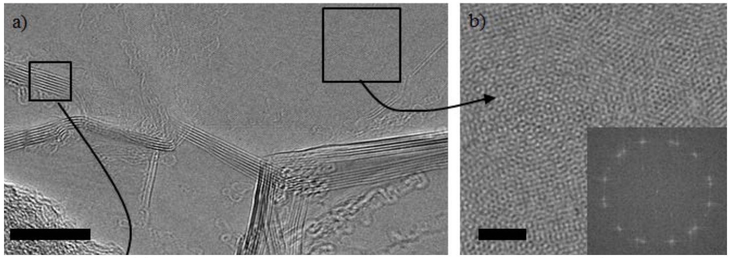
- Accurate simulation of strong adsorption sites
- Library of structural motifs for forcefield development (e.g. open metal sites in MOFs, dopants in porous carbons)
- Models that account for effects of:
  - Morphology (e.g. particle size/shape/aspect ratio, core-shell geometry, etc.)
  - Additives
- Library of established sorbent materials:
  - Powders, thin films, nanoparticles
  - Proven synthetic routes
  - Data for model validation

MOF thin films



MOF NPs





Crystalline *t*-boron nitride aerogel

Bulk and nanoscale metal hydrides

Progression of “Model Systems”

Binary hydrides (e.g. MgH_2, → complex hydrides/no “molecular” species (e.g. $NaAlH_4$)
→ Hydrides with highest complexity (phase segregation+molecular species; e.g. $Mg(BH_4)_2$)

What synthesis-structure-property relationships govern hydrogen uptake and release?

Phase minimization strategies: overcome transport problems due to phase segregation

Doping and defect creation: solid solutions to minimize the number of solid phases

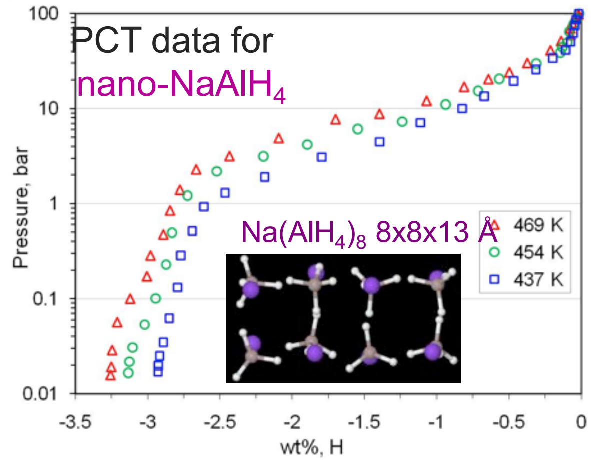
Entropy tuning: crystalline-to-amorphous transitions to improve $\Delta G°$

Ultrahigh H_2 pressures (up to 700 bar) as a new strategy to regenerate metal hydrides

Consortium capabilities for bulk hydride synthesis include:

- High-pressure reactors (up to 2000 bar/500 °C)
- PCT equipment (200 bar/400 °C)
- Extensive ball-milling equipment

Sandia National Laboratories

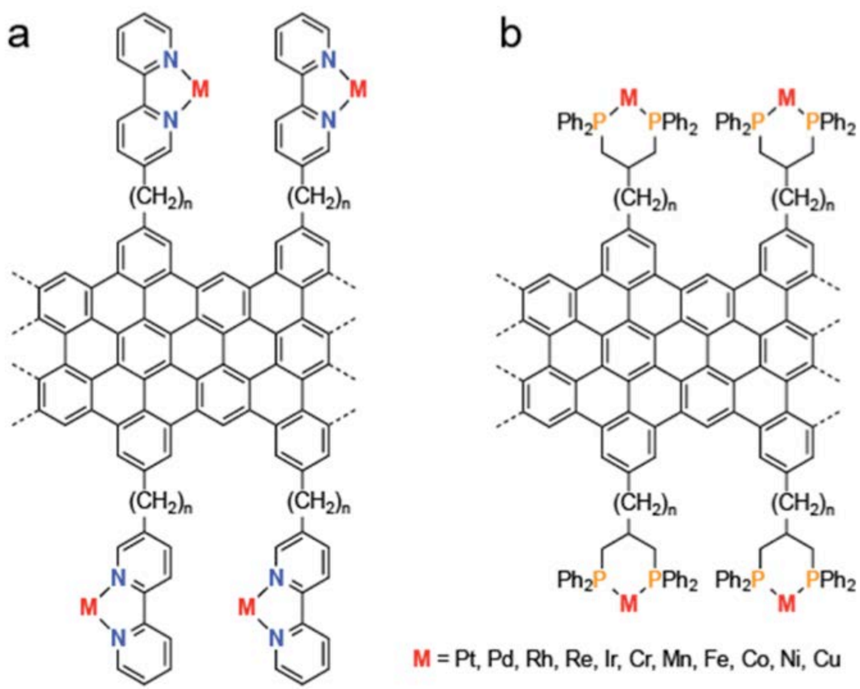


Top left: variable-T ball mill.
Top right: ultra-high pressure cell

Modified graphene nanoribbons for controlled catalysis

GNR: fix the location and chemical identity of catalytic active sites in well-defined materials. Can be integrated with other storage materials

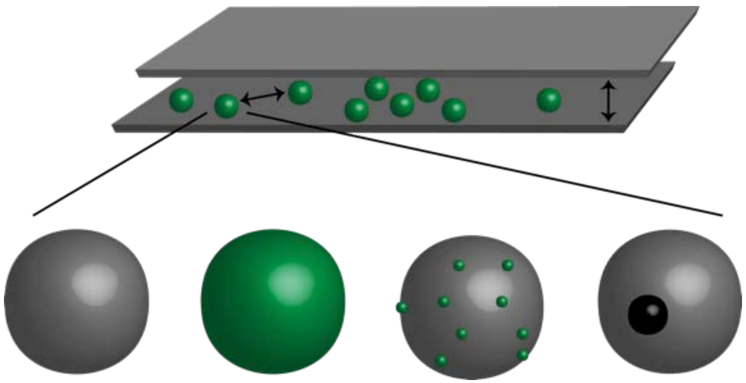
Quite adaptive: catalytic metals, or chelating and ED/EWD groups



Schematic representation illustrating the integration of molecular-defined transition metal catalyst centers via:

a) bipyridine or
b) bindentate phosphine ligands along the edges of atomically defined GNRs.

Hierarchical integrated hydride materials

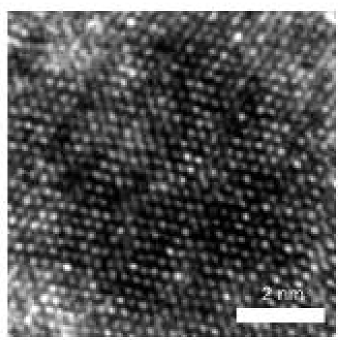


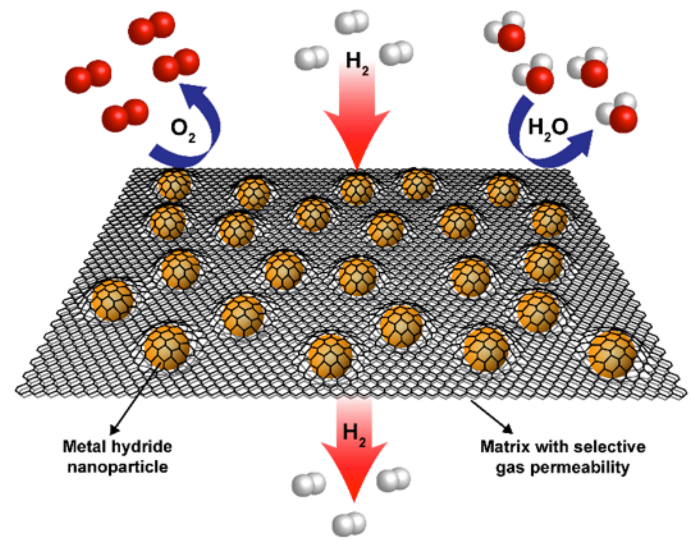
Want to have clear model systems to drive fundamental understanding

Also push the development of advanced materials: from Mg and Al to complex hydrides such as $LiNH_2$, $Mg(BH_4)_2$

Cho, E., Urban, J. J. et al. *Adv. Mater.* **2015**, in press

Want to integrate new classes of materials to provide new options in modifying thermodynamics, understanding pathways





E.S.Cho et al, *submitted* (2015)

Jeon, Moon, et al. Nature Materials (2011)

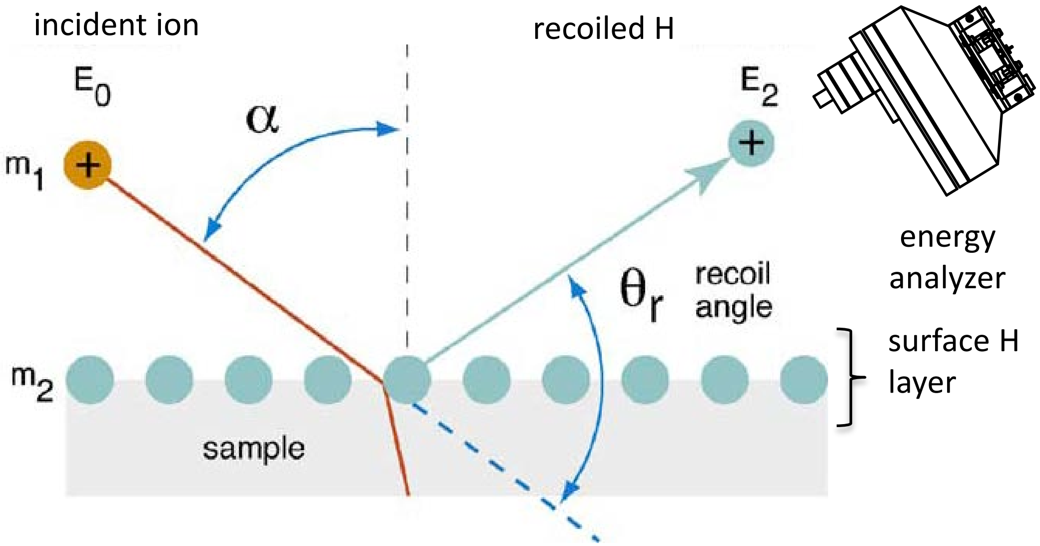
Bardhan, Ruminski, et al. En. Environ. Sci., (2013)

Direct mapping of hydrogen on surfaces by Low Energy Ion Scattering (LEIS) spectroscopy

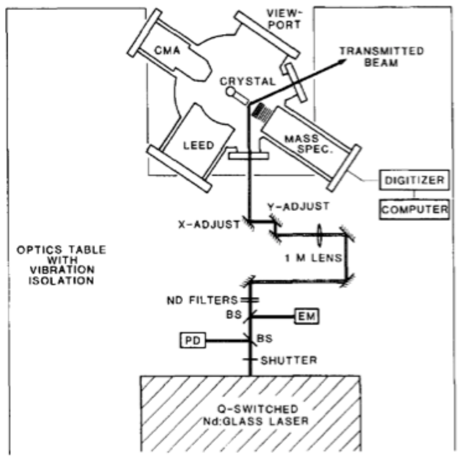
HyMARC

Sandia National Laboratories

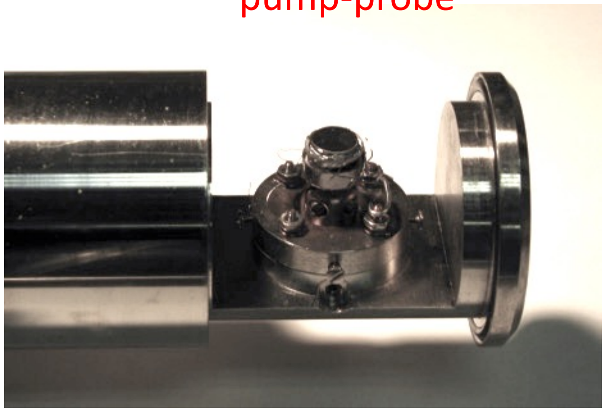
- Optimized for direct sensitivity to H on surfaces (< 0.05 ML)
- High surface specificity
- Distinguishes H and D (exchange experiments)
- Adsorption kinetics on compressed particle beds/thin films (res. ~ 1 – 10 s)
- Atomic doser available to characterize uptake of H_2 vs. H
- Surface diffusion measurement: laser-induced pump probe



R. Kolasinski, N. C. Bartelt, J. A. Whaley, & T. E. Felter, *Phys. Rev. B* **85**, 115422 (2012).



laser-induced desorption pump-probe

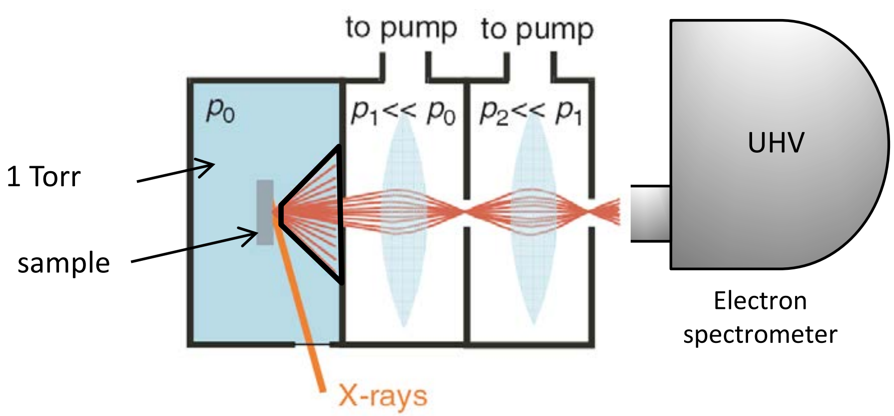


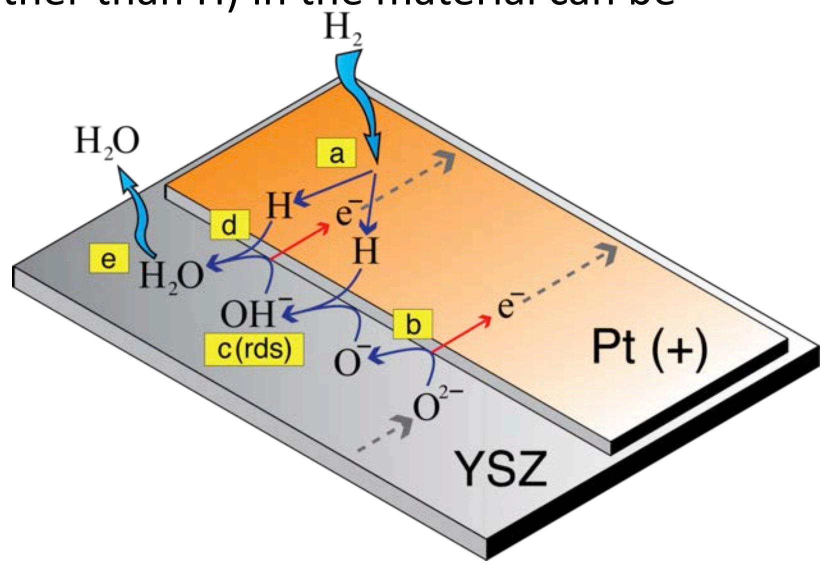
clean sample transfer container

Ambient-Pressure X-ray Photoelectron Spectroscopy (AP-XPS)

- Chemical information about the surface composition and oxidation state
- Environments of up to 1 Torr of gas pressure
- Sample heating up to 1000°C
- Use to study dehydrogenation of ‘loaded’ hydrogen storage materials
- Composition and bonding state of all elements (other than H) in the material can be monitored *in-situ*

AP-XPS at the ALS: Beamlines 9.3.2 and 11.0.2, 95-2000 eV





In previous AP-XPS studies, we have described the mechanism of hydrogen utilization in operating Pt-based SOFCs

F. El Gabaly et al., Chemical Communications 48, 8338–8340 (2012)

AP-XPS: Rev. Sci. Instrum. 73, 3872 (2002); Rev. Sci. Instrum. 81, 053106 (2010).

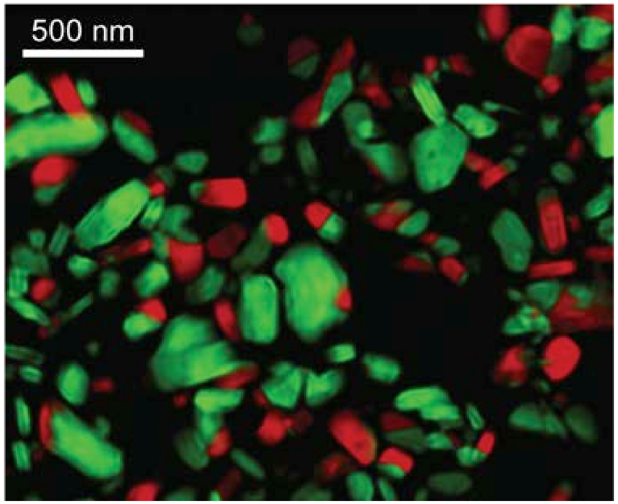
Soft X-ray spectroscopy and microscopy at the Advanced Light Source

We will apply these tools to understand phase nucleation at interfaces and growth at the nano- and mesoscales

Beam tools we will access:

- X-ray absorption (XAS) and X-ray emission (XES) spectroscopies
  - Composition, oxidation state, bonding environment
- Microscopy tools for phase and composition:
  - Scanning Transmission X-ray Microscopy (STXM; ~20 nm resolution)
  - Ptychography (3 nm resolution possible)

STXM image of $Li_xFe(II,III)PO_4$



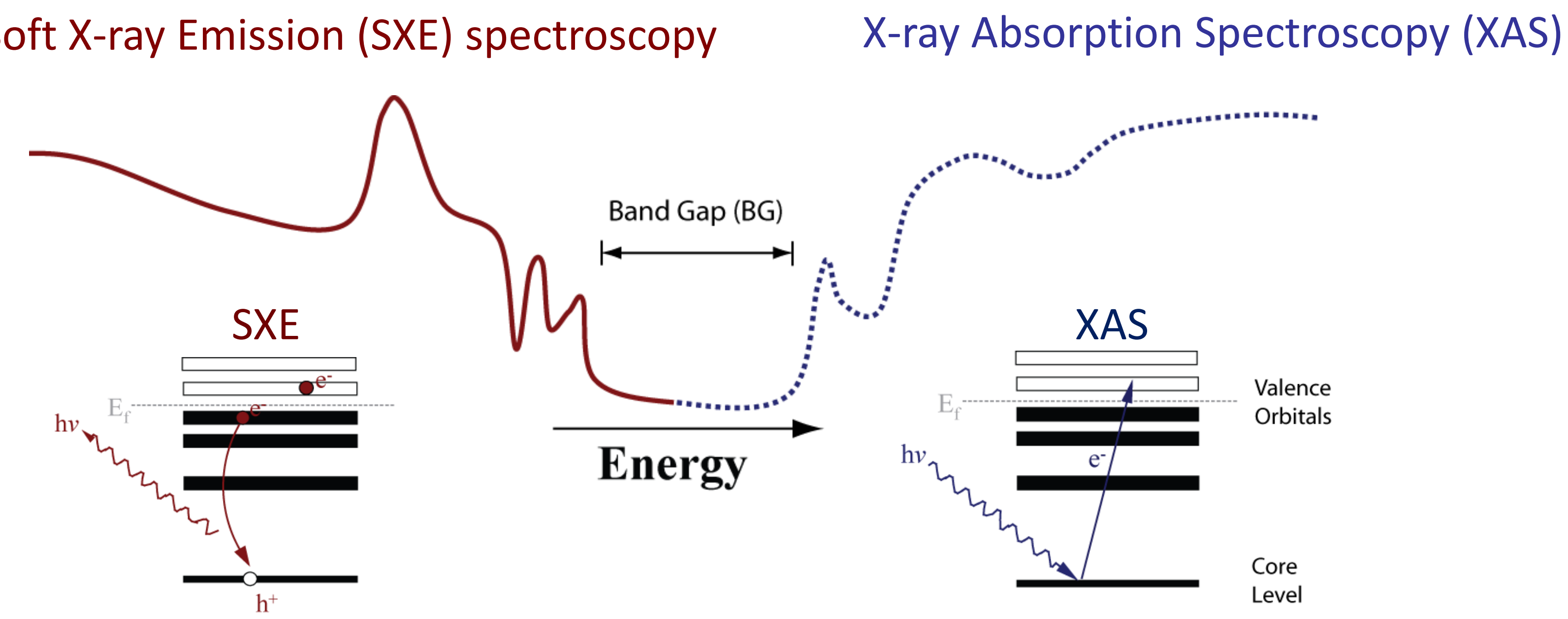
Ptychography STXM image of a Li_xFePO_4 electrode quenched at 68% state of charge. The green and red regions represent $FePO_4$ and $LiFePO_4$ fractions, respectively

F. El Gabaly et al., Nature Materials, **2014**, *13*, 1149–1156.

HyMARC is developing a clean-transfer system to eliminate ambient exposure of samples during transfer from glove-boxes to AP-XPS and STXM (collaboration with LBNL and ALS).

Theory and modeling: computational spectroscopy & x-ray spectroscopy

X-ray Emission Spectroscopy (XES) and X-ray Absorption Spectroscopy (XAS) enable element-specific tracking of the course of hydrogen storage reactions



- Measurement of the occupied DOS
- Resolve structure of filled electronic density of states states

- Element-specific technique
- Orbital angular momentum-resolved probe of the unoccupied electronic DOS

Community tools

Open-source software	Distributed/federated database development

Phase fraction prediction code (thermodynamics)

Phase field modeling for hydrogen storage in hydrides (kinetics)

Kinetic Monte Carlo (transport)

What properties belong in the materials database?

Computational:
- Crystallographic/structural quantities
- Enthalpy, entropy, surface energy, elastic moduli
- Defect formation energies & mobilities
- Computational spectroscopy (e.g., XAS/XES, XPS)

Experimental:
- Absorption isotherms (P, T, size) & time-dependent uptake
- Transport (surface, bulk)
- Characterization data from all tasks

We gratefully acknowledge the
EERE Fuel Cell Technologies Office for funding HyMARC

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

FC-PAD Consortium

Fuel Cell Performance and Durability

FC-PAD is funded by:

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

Fuel Cell Technologies Office (FCTO)

- FC-PAD will coordinate activities related to fuel cell performance and durability
  - The FC-PAD core-lab 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 NL projects
- Provide technical expertise and harmonize activities with industrial developers
- FC-PAD will serve as a resource that amplifies FCTO's impact by leveraging the core capabilities of constituent members

FUEL CELL FCPAD PERFORMANCE & DURABILITY

Los Alamos NATIONAL LABORATORY

BERKELEY LAB

Argonne NATIONAL LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

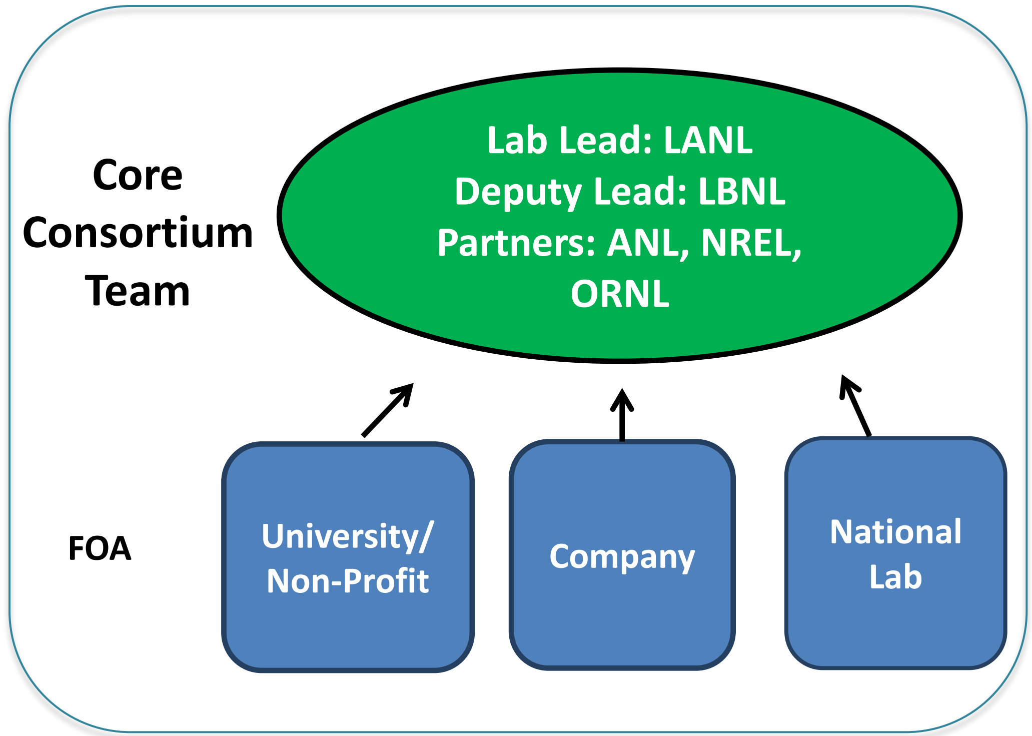
OAK RIDGE National Laboratory

FC-PAD Consortium

Approach:

Create a high-functioning team with core activities and projects

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



Consortium will foster sustained capabilities and collaborations

FC-PAD Consortium

Overall Objectives:

- Advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) at a pre-competitive level to further enable their commercialization
- Develop the knowledge base and optimize structures for more durable and high-performance PEMFC components, while simultaneously reducing cost
- Improve high current density performance at low Pt loadings (0.125 mg/cm^2 total)
- Improved component durability (e.g. membrane stabilization, self-healing, electrode-layer stabilization)

MEA Performance and Durability Metrics

- 5000 hours of operation under simulated vehicle power cycling and shut-down/start-up cycling with < 10% loss in rated power
- Specifically, developing MEAs with SOA catalysts that demonstrate performance > $1 W/cm^2$ with Pt loading < $0.125 mg/cm^2$

Technical Targets: Membrane Electrode Assemblies			
Characteristic	**Units**	**2015 Status**	**2020 Targets**
Cost	$\$ / kW_{net}$	17	14
Durability with cycling	Hours	2,500	5,000
Startup/shutdown durability	Cycles	–	5,000
Performance @ 0.8 V	mA / cm^2	240	300
Performance @ rated power (150 kPa abs)	mW / cm^2	810	1,000
Robustness (cold operation)		1.09	0.7
Robustness (hot operation)		0.87	0.7
Robustness (cold transient)		0.84	0.7

FC-PAD Consortium Structure

FC-PAD Management Structure:

Six Component and Cross-cutting Thrusts

<u>Component Thrusts:</u>

Electrocatalysts and Supports

Electrode Layers

Ionomers, Gas Diffusion Layers, Bipolar Plates, Interfaces

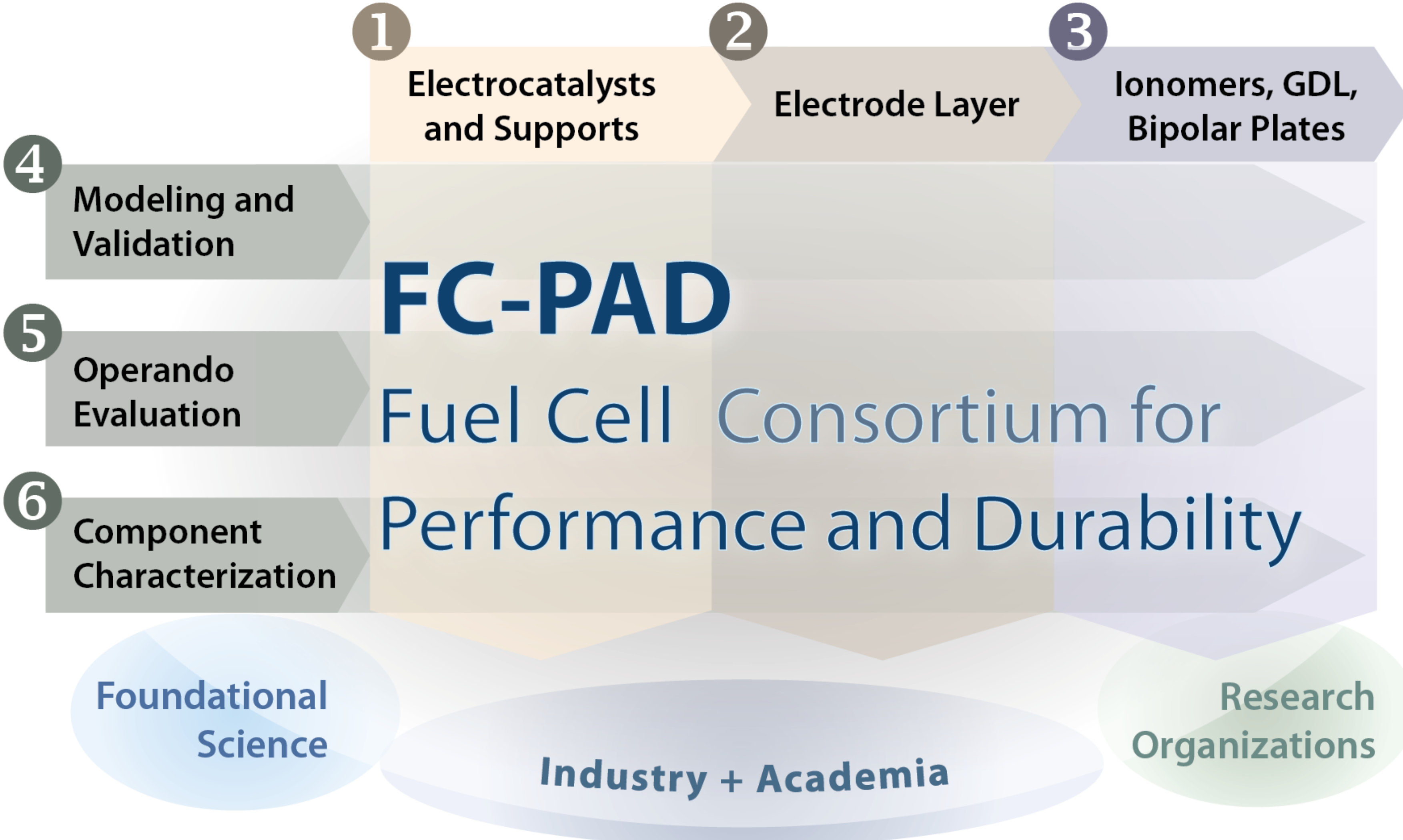
<u>Cross-cutting Thrusts:</u>

Modeling and Validation

Operando Evaluation: Benchmarking, ASTs, and Contaminants

Component Characterization and Diagnostics

- The National Lab FC-PAD consortium capabilities are available to support collaborations awarded in **DE-FOA-0001412**
- Collaborations are also desired outside the FOA process



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

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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 (yellow cells) **High Activity** (green cells)

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Thrust Area Coordination

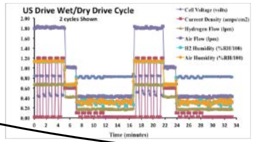
Example
Carbon Corrosion
during drive cycle
ANL, LANL, ORNL

Thrusts 1, 2, 3 - Components
Catalysts, Membranes, GDLs

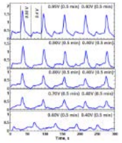
Samples ↕ Component Design

Thrust 5. Operando Evaluation

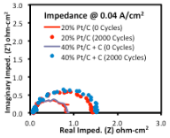
Durability Testing



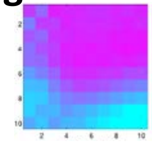
NDIR



EIS



Segmented Cell

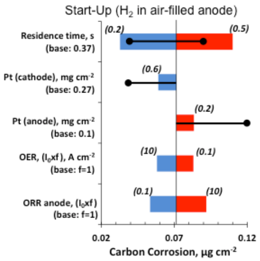


Data Feedback ↔

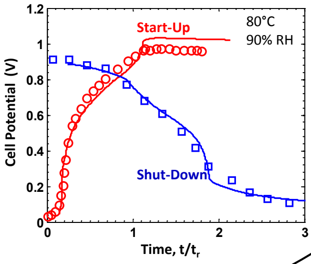
↔ Samples Data

Thrust 4. Modeling Validation

Model Output

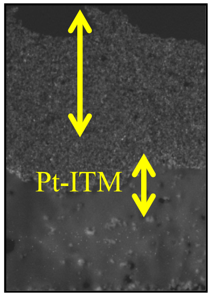


Parametric model

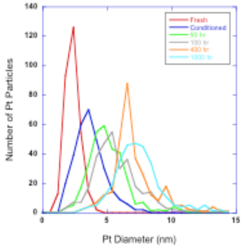


Thrust 6. Characterization

STEM



TEM



Coordination with DE-FOA-0001412 Projects and Interested Developers

- Coordination with the appropriate thrust areas
  - Determined by DOE, project subject, participant interest
- Multi-lab NDAs (Non-Disclosure Agreements)
  - Speed the processes for interacting with the national labs
- FC-PAD will hold annual Working Group Meetings related to durability and transport - experts from industry and academia can openly discuss issues and assess the current SOA

Data Sharing: Internal plus Open Web-Site

- Internal with hierarchical authorization
- Updated minimum quarterly with presentations, publications, refined data
- Searchable site to help disseminate data to developers

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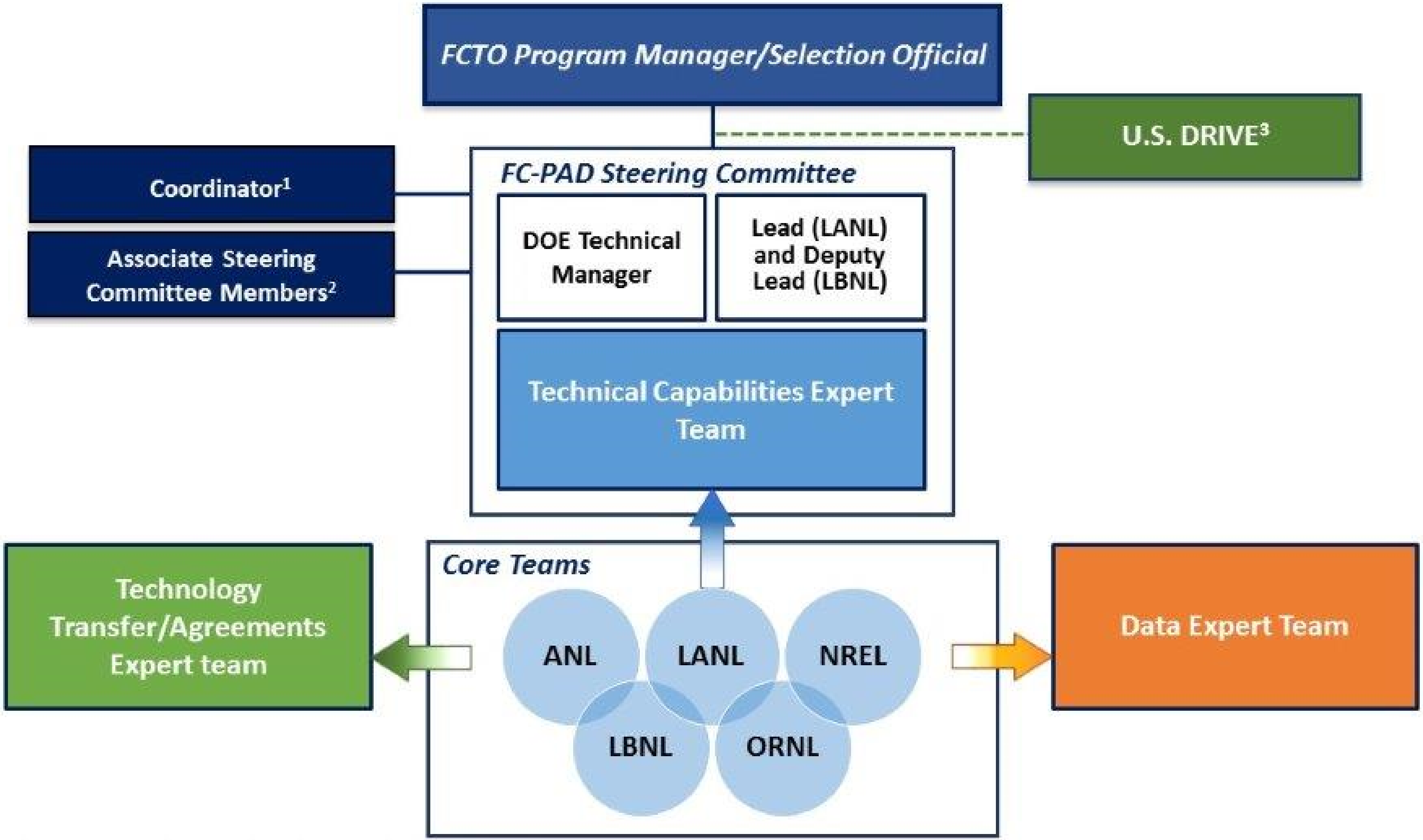
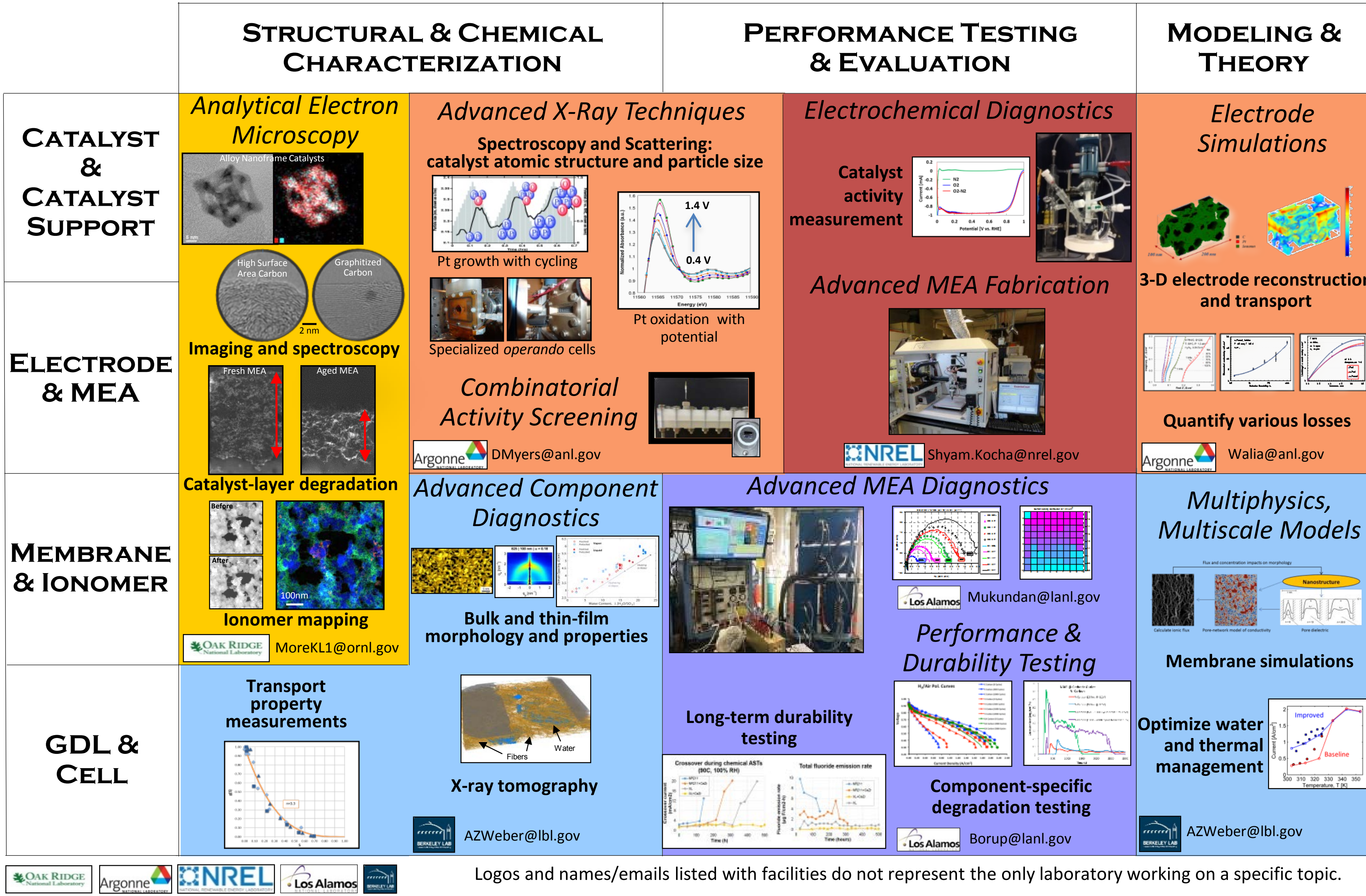
Coordination of FC-PAD



[1]Single point of contact for external partners to connect with the Consortium
[2]From industry/university/lab projects selected through FOA
[3]And other advisory entities as appropriate (e.g., HTAC, NAS)

FC-PAD NL Capabilities



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

Examples of NL 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 oxygen permeability through ionomer layer measurements
- 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
- Setups for water transport and interactions
- Structural properties including scattering and x-ray techniques and mechanical properties
- Synthesis and characterization of ionomer thin films
- Segmented cells
- Contamination and leachates

Thrust 1: Electrocatalysts and Supports

Catalyst and catalyst support durability and degradation mechanisms

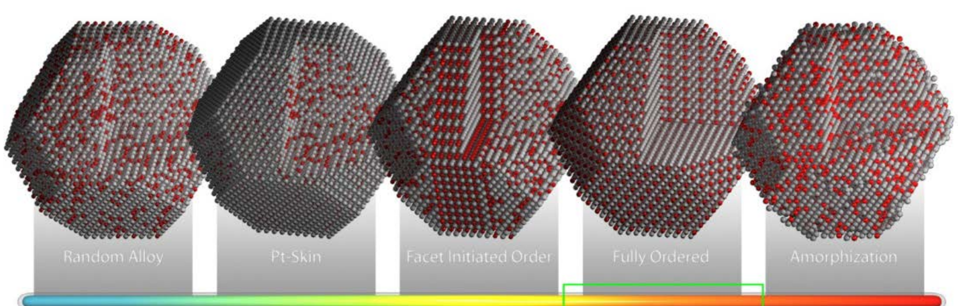
- Elucidate catalyst and support degradation mechanisms as a function of catalyst and support physicochemical properties and cell operating conditions
- Quantify catalyst and support stability during accelerated stress tests and start-up and shut-down transients using in-cell measurements
- Determine stability of catalyst components, catalyst and support composition and structural changes

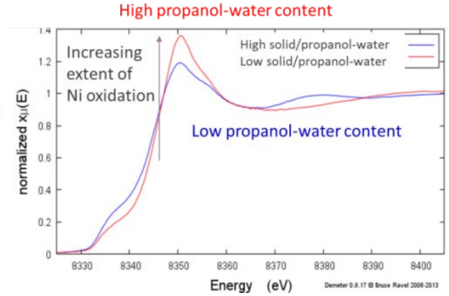
Catalyst/support interactions

- 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)





Thrust 2: Electrode Layers

Low Pt-loaded electrode layers:

- 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

Transport in low-loaded catalyst layers:

- Examine impact of different catalyst-layer compositions to ascertain how transport phenomena change
- Apply existing and develop new diagnostics to quantify the transport limitations and better define the resistance

Electrode-layer designs and fabrication for improved performance:

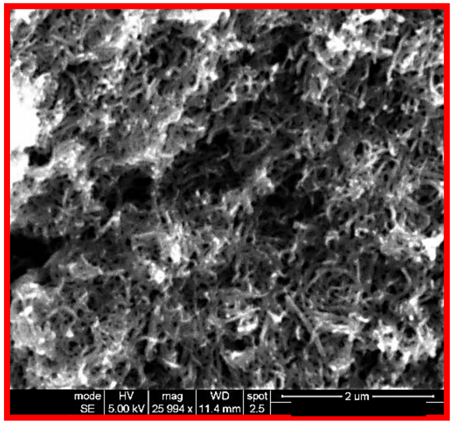
- Thin first layer coating catalyst surfaces to provide local conductivity with a minimal transport barrier and second phase to provide bulk ionic conductivity
- Optimizing ionomer-solvent-catalyst ink composition, solvent removal methods, and/or ionomer

Electrode-layer degradation:

- Examine the origins of the changing transport losses by examining how changing properties of the electrode layer

Automated Diagnostics

Ionomer coated MWCNTs



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

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

Gas Diffusion Layers

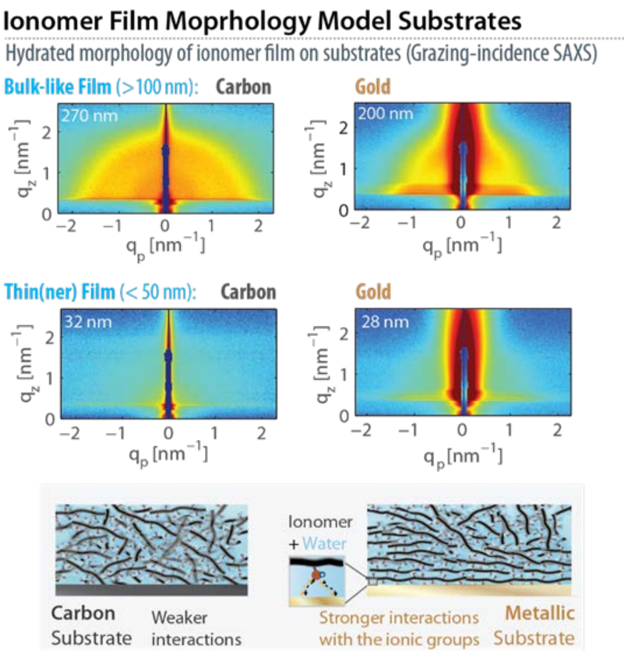
- Examine water-transport controls and impacts;
  - in-situ and AST characterization

Bipolar plates

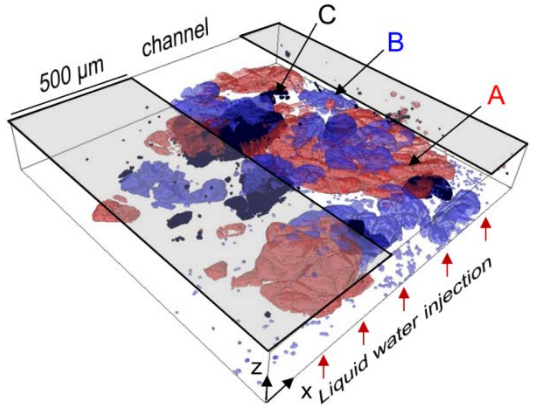
- Examine leachate ions and corrosion products and contact resistance

Interfaces

- GDL/channel droplet interface; CL interface and areas of high porosity



GDL Microcapillary Measurements



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Thrust 4: Modeling and Validation

Model development and validation

- Microstructural models including catalyst layers
- Component and cell performance models for improved water and thermal management
  - Multiscale, multiphysics
- Component degradation models including mechanical failure and dissolution

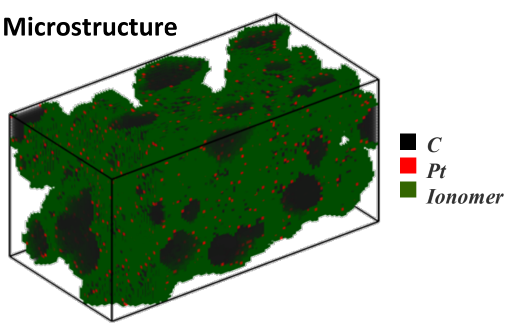
Analysis

- Development of well-designed test protocols for characterizing the kinetic and transport properties of cell components

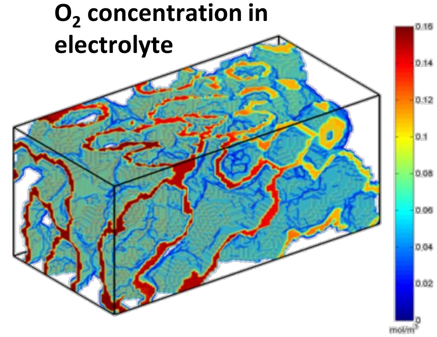
Model deployment

- Elucidation of performance and durability bottlenecks and pathways to overcome them
  - Optimization of operating conditions
  - Sensitivity analysis of component material and transport properties

Microstructure



O_2 concentration in electrolyte



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

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

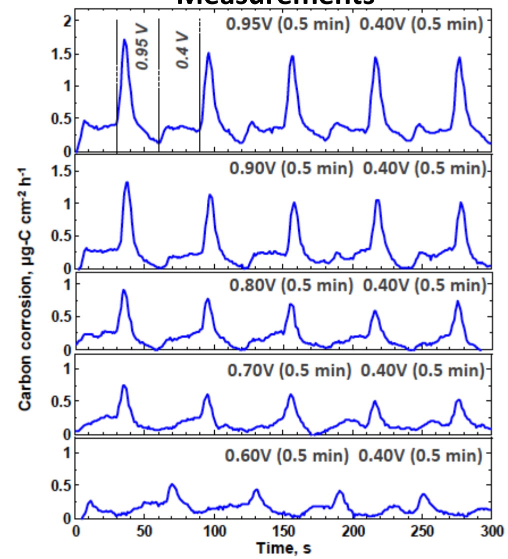
Durability testing

- ASTs: Catalyst, membrane, GDL, bi-polar plate and MEAs

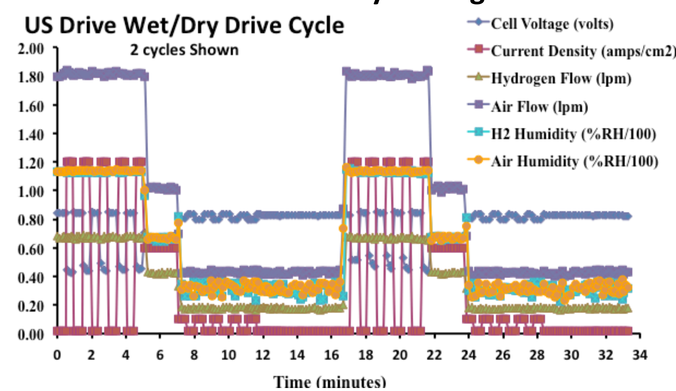
Performance characterization

- Drive cycle, VIR, Impedance

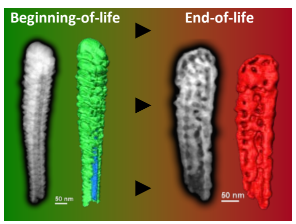
In situ Carbon Corrosion Measurements

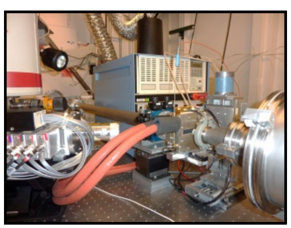


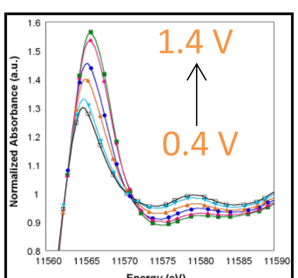
Durability Testing



Thrust 6: Component Diagnostics and Characterization







Comprehensive Materials Benchmarking – sub-Å to mm-level Understanding

- Characterize component structure, chemistry, and composition <u>before & after</u> 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
- Neutron and X-ray Studies
- Component Diagnostics
- 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

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Acknowledgements and Additional Information

FC-PAD is funded by:

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

Fuel Cell Technologies Office (FCTO)

Additional Information Available On-line:

From **DE-FOA-0001412:** http://energy.gov/eere/fuelcells/fc-pad

Detailed FC-PAD slides by thrust area:

http://energy.gov/sites/prod/files/2015/12/f27/fcto_fc-pad_organization_activities_0.pdf

Fuel Cell Technologies Office Multi-Year RD&D Plan:

http://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

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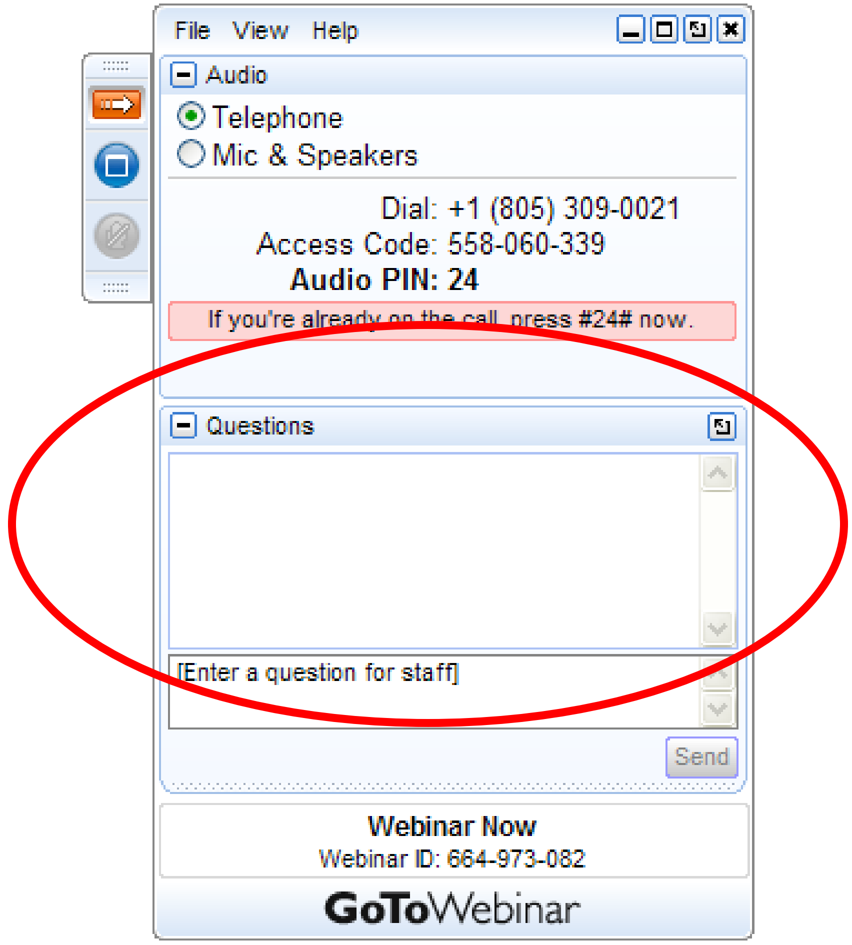
Question and Answer

- Please type your questions into the question box



Thank You

Presenters:

- Mark Allendorf (HyMARC) - Sandia National Laboratory
  - mdallen@sandia.gov
- Rod Borup (FC-PAD) – Los Alamos National Laboratory
  - Borup@lanl.gov

DOE Host:

- Ned Stetson – Hydrogen Storage Program Manager
  - Ned.Stetson@ee.doe.gov
- Dimitrios Papageorgopoulos – Fuel Cell Program Manager
  - Dimitrios.Papageorgopoulos@ee.doe.gov

Webinar Recording and Slides:
(http://energy.gov/eere/fuelcells/webinars)
Newsletter Signup
(http://energy.gov/eere/fuelcells/subscribe-news-and-financial-opportunity-updates)

Supplemental

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

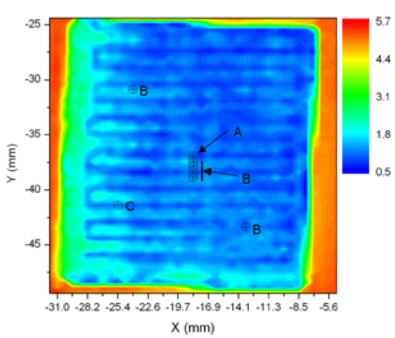
- **Catalyst and catalyst support durability and degradation mechanisms**
  - Elucidate catalyst and support degradation mechanisms as a function of catalyst and support physicochemical properties and cell operating conditions
  - Quantify catalyst and support stability during accelerated stress tests 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

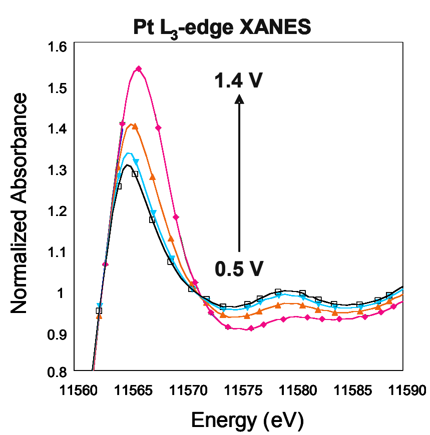
- **Catalyst/support interactions**
  - Understand interplay between the catalyst and support properties and their mutual interactions
  - Determine the effects of carbon type (e.g., high, medium, and low surface area) and carbon dopants on the strength of the catalyst/support and ionomer/support interactions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

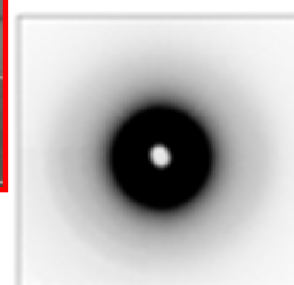
- **Ex-situ analysis of catalyst instability on cathode-catalyst-layer properties**
  - Quantify the impact of catalyst degradation on the properties defining the performance of the cathode catalyst layer (e.g., impact of base metal leaching from Pt alloy catalyst on proton conductivity, oxygen permeability,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

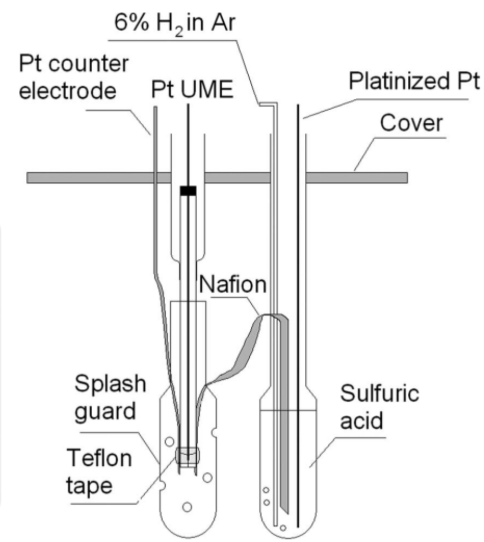
Key Capabilities Relevant to Thrust Area

- 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.

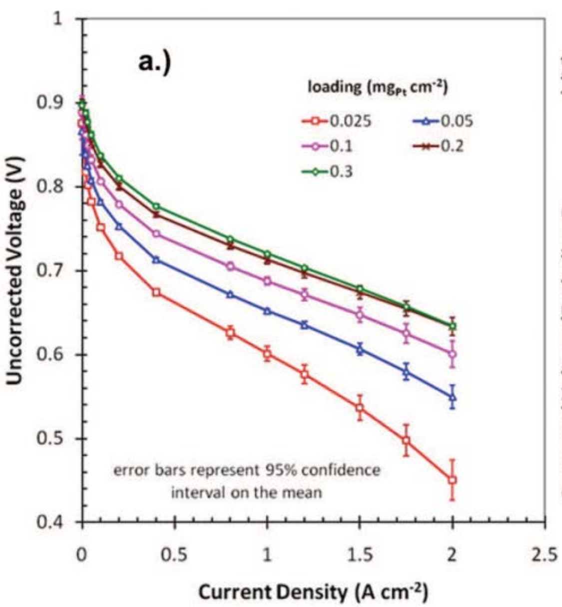
Automated Diagnostics

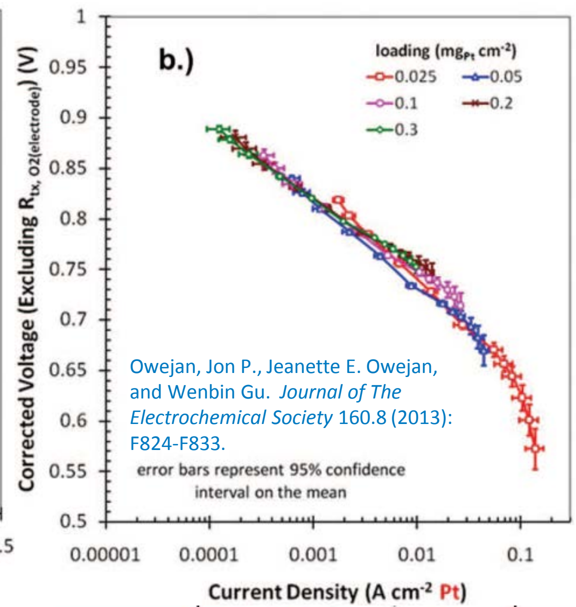
<u>Automated gas mixing</u> for oxygen limiting current and the development/investigation of CO limiting current as a diagnostic

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

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

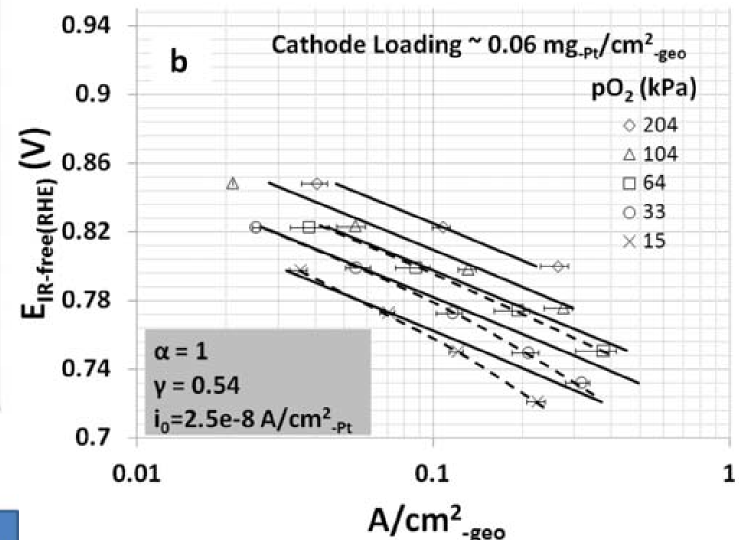
MEA Performance Diagnostics Motivation



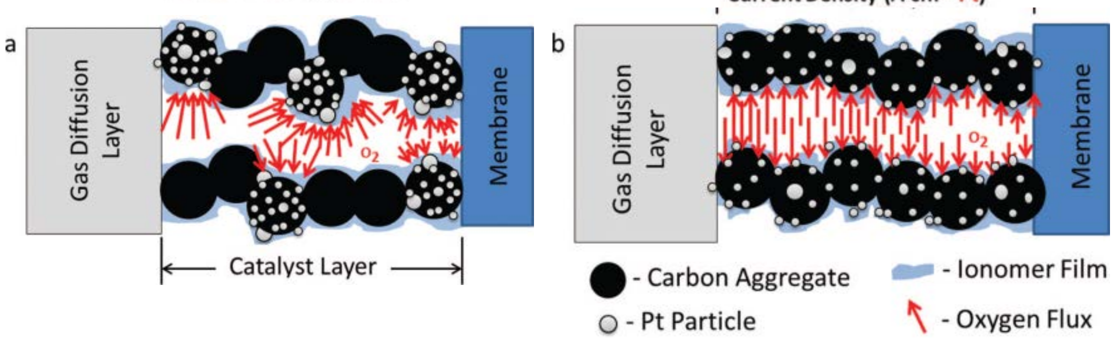


Owejan, Jon P., Jeanette E. Owejan, and Wenbin Gu. *Journal of The Electrochemical Society* 160.8 (2013): F824-F833.

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.



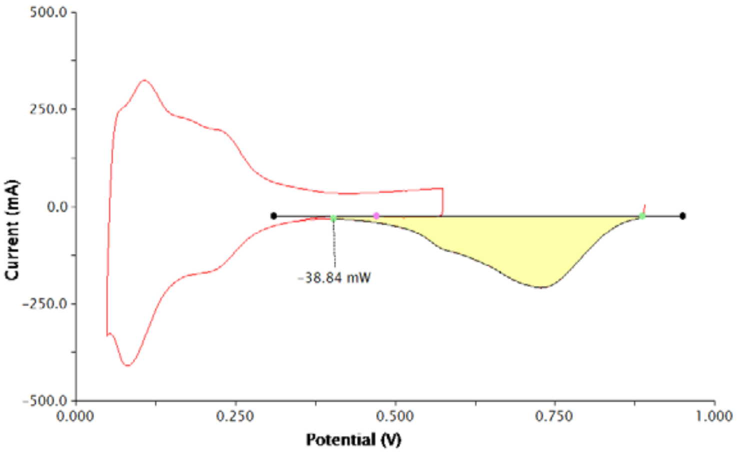
Accounting for oxide coverage kinetics at low potentials does not account for the entire voltage loss

<u>Goal</u>

- 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

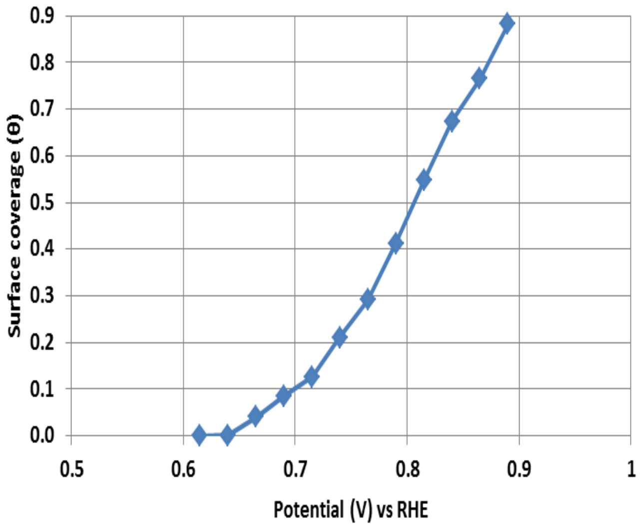
Pt and advanced Pt catalyst - oxide coverage dependent kinetics

- 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



Calculated oxide surface coverage for Pt/V

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

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

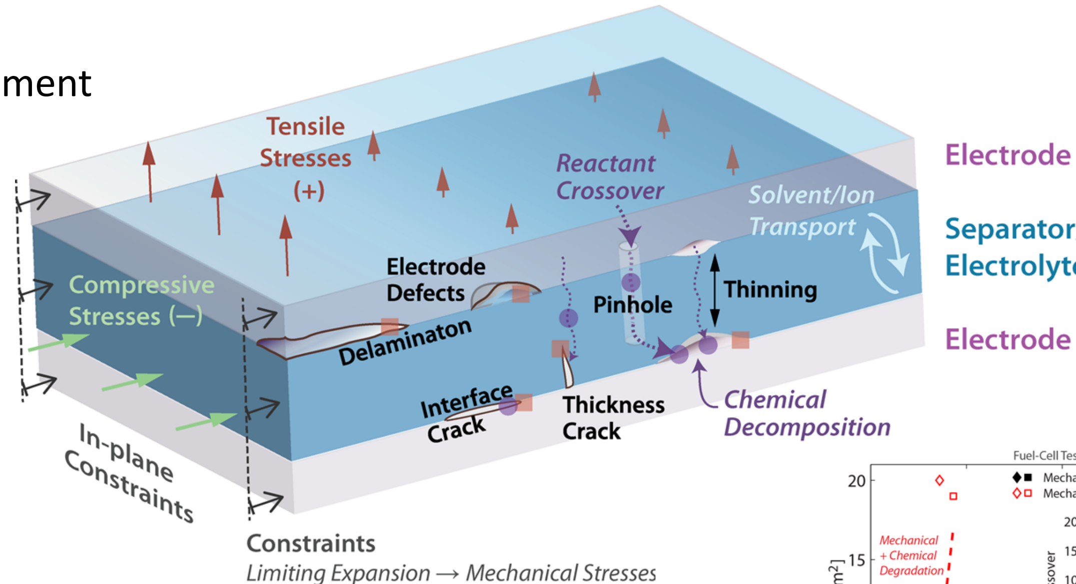
Thrust Area 3: Ionomers, Gas Diffusion Layers, Bipolar Plates, and Interfaces
Overview

- **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

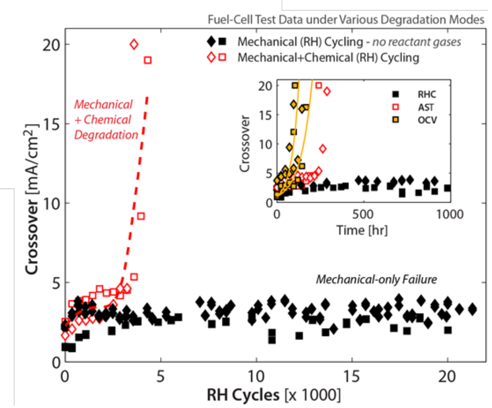
Bulk Membranes

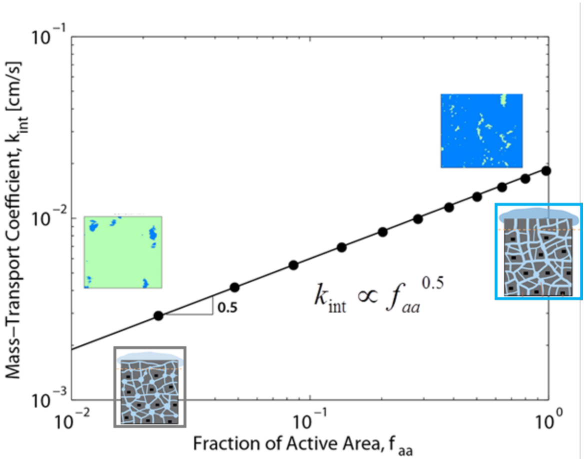
Structure/function/performance across length scales

- 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

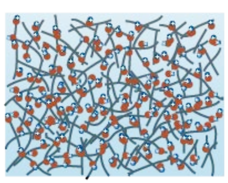
Structure
- *Morphology*
- *Crystallinity*
- *Nano-domains*
- *Surface*

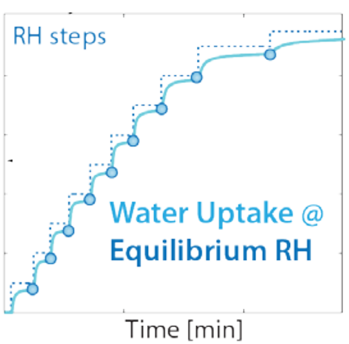
Properties
Transport
- *Uptake/Swelling*
- *Diffusion, Mobility*
- *Conductivity (ion)*
- *Permeability*

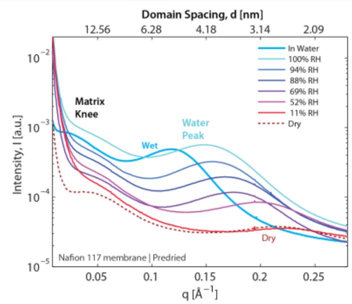
Thermal
- *Conductivity, T_g, T_m*

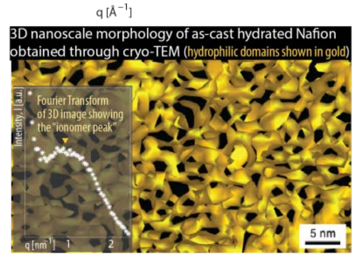
Mechanical
- *Stress-Strain response*
- *Modulus, Strength*
- *Viscous Behavior*
- *Break strain, Fracture*

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

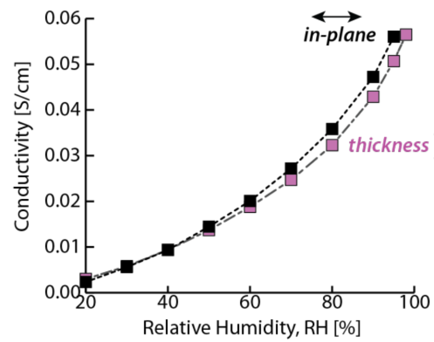


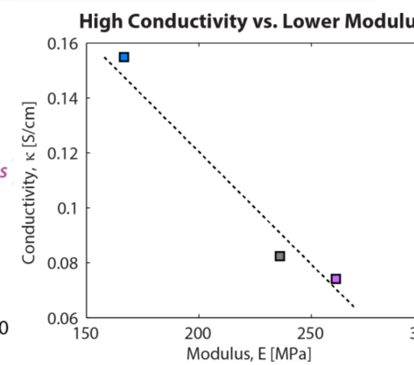






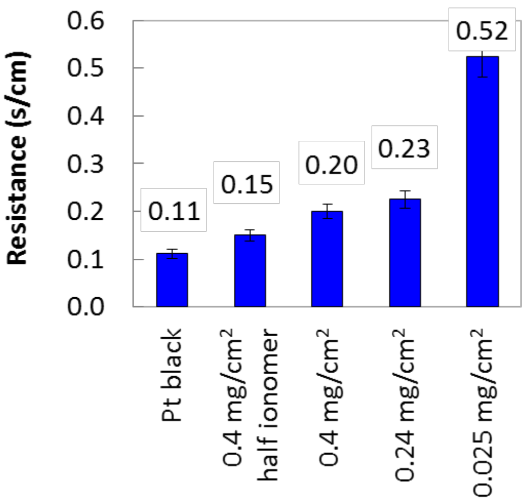
F.I. Allen, L.R. Comolli, A. Kusoglu, M.A. Modestino, A.M. Minor, A.Z. Weber, *ACS Macro Letters*, 4 (2015) 1-5 | DOI: 10.1021/mz500606

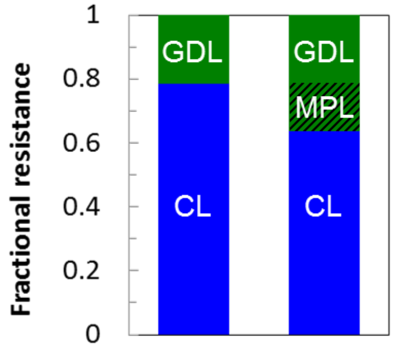


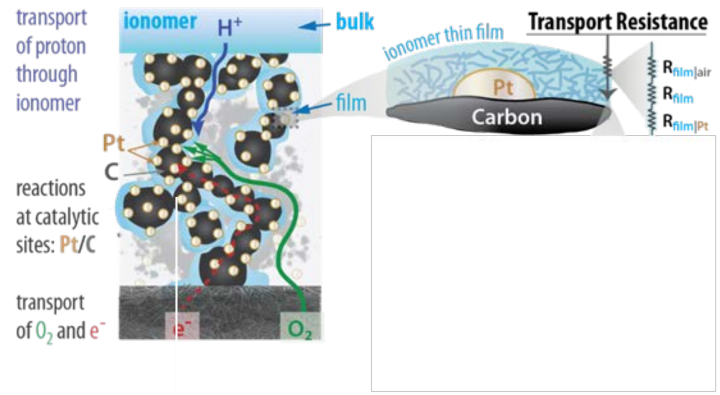


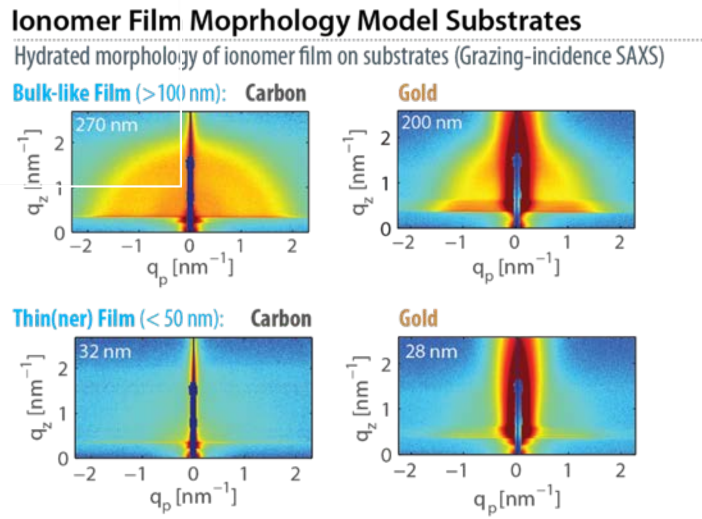
Catalyst Layer Ionomer

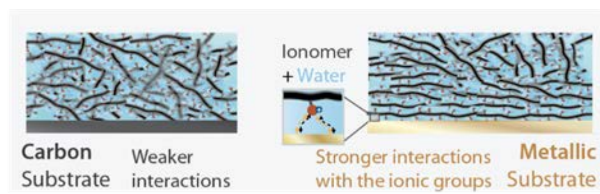
- Measure local resistance











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

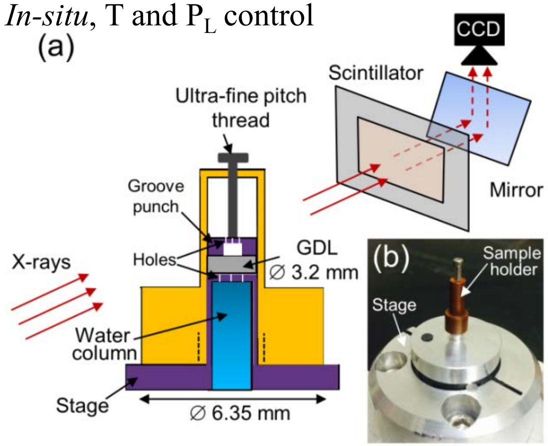
- Insights will allow for novel strategies and materials to overcome limitations

Diffusion Media and Plate Studies

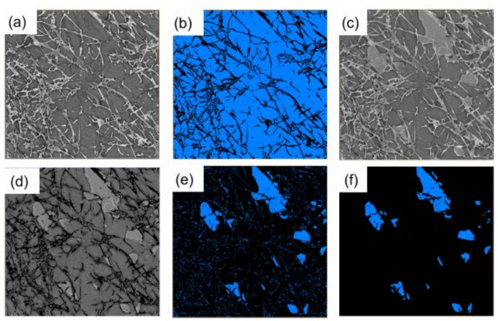
- Measure critical properties and morphology
  - Examine changes as a function of time and operating stressors
  - Examine interfaces in terms of performance and durability concerns

XCT imaging

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

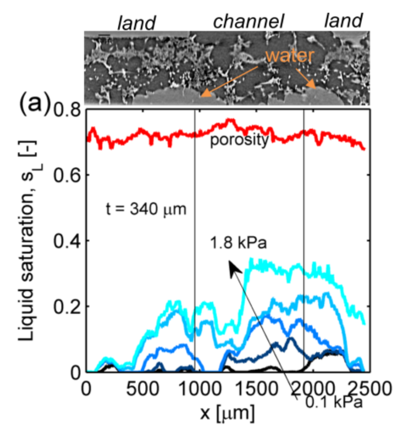


Raw data



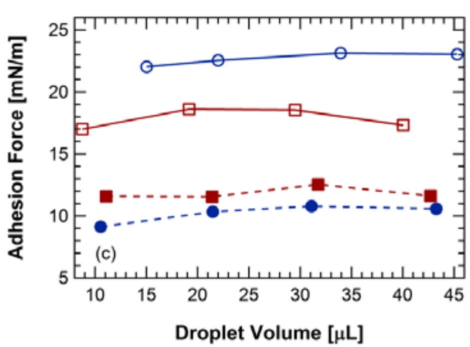
Binary image stacks of GDLs and water

Morphology and Spatial Distributions



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

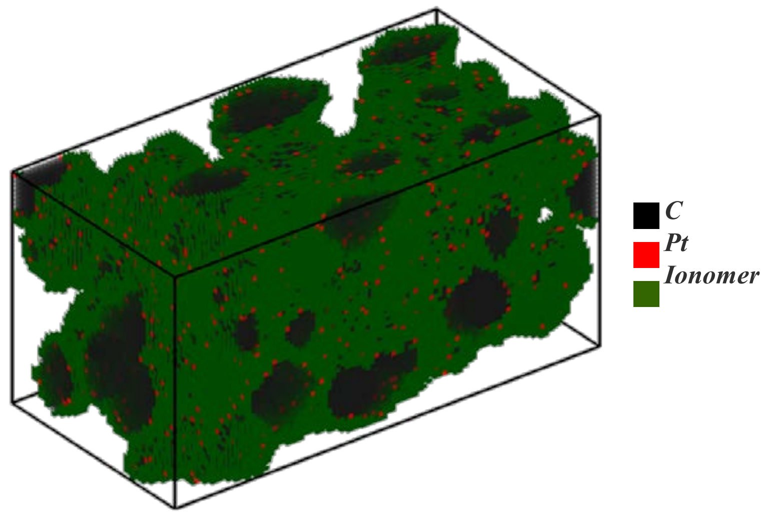
1) **Catalyst:** Pt dissolution, coarsening, base metal leaching
2) **Membrane:** FER, cerium (radical scavenger) transport, Pt in membrane, mechanical/chemical stability, H_2 cross-over
3) **Ionomer**
4) **Catalyst Support:** Potentiostatic and potentiodynamic corrosion rate, SU/SD model
5) **Electrode:** 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

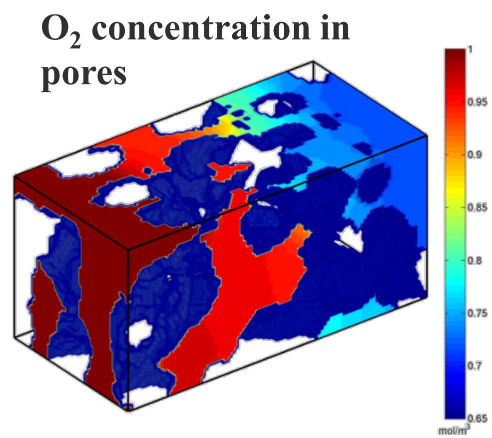


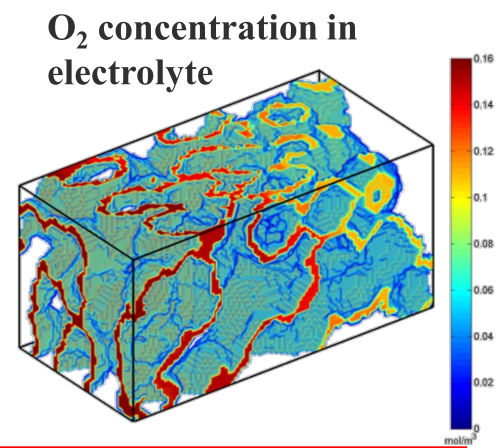
Subtask 4.5: Electrode Microstructure

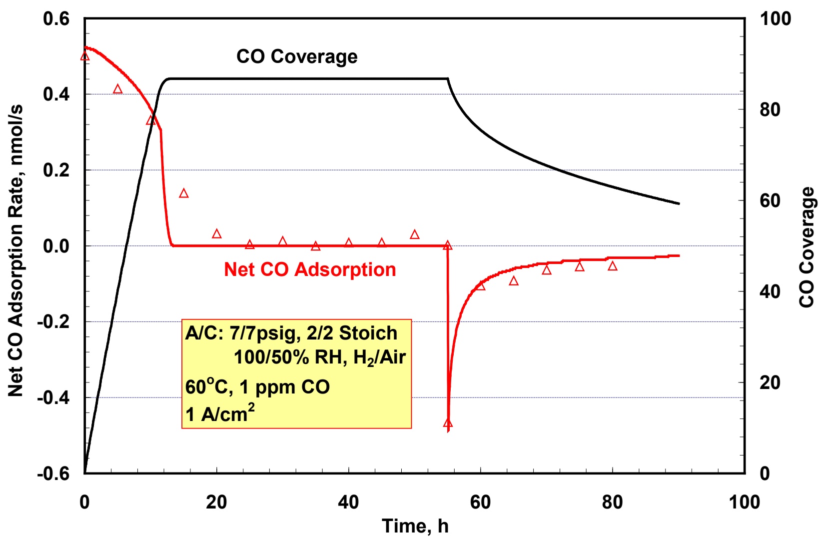
1) Numerical Reconstruction Algorithm

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

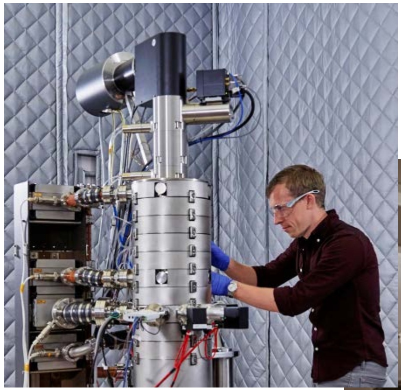
- **Provide durability testing to catalyst, membrane, GDL, bi-polar plate and MEA developers**
  - Perform Stress tests on MEAs
    - Track membrane degradation through Fluoride release, membrane thinning and HFR changes
    - Track catalyst degradation through ECSA, Mass Activity, performance loss, 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

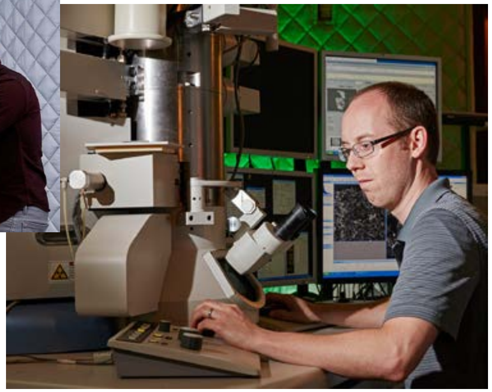
Thrust Area 6: Component Characterization & Diagnostics Overview

- **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*

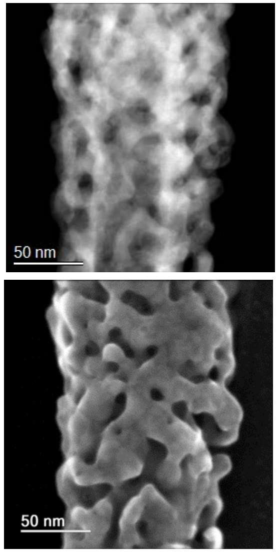
Atomic Resolution Imaging and Spectroscopy

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

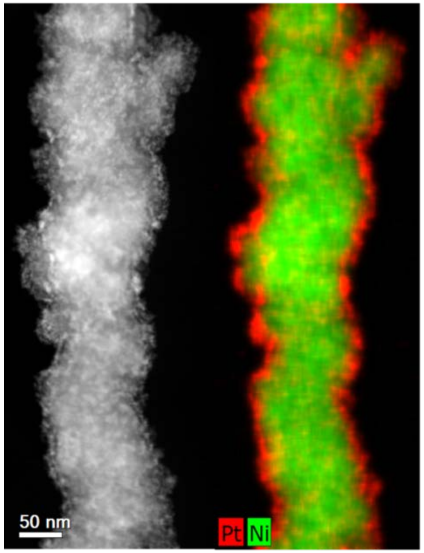




Single Fe atoms in graphene



Porous catalysts



PtNi nanowires (NREL)