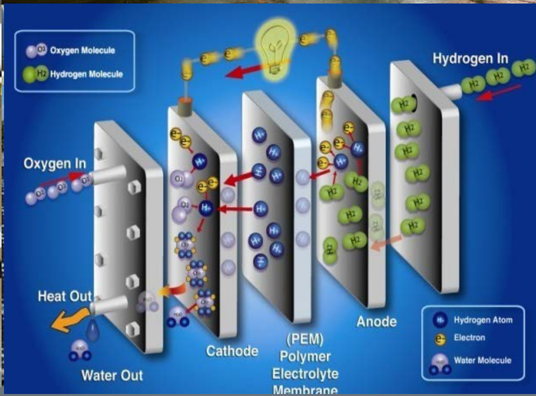
Fuel Cell Technologies Office Webinar

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



FCTO Lab Consortia Overview: ElectroCat and HyMARC

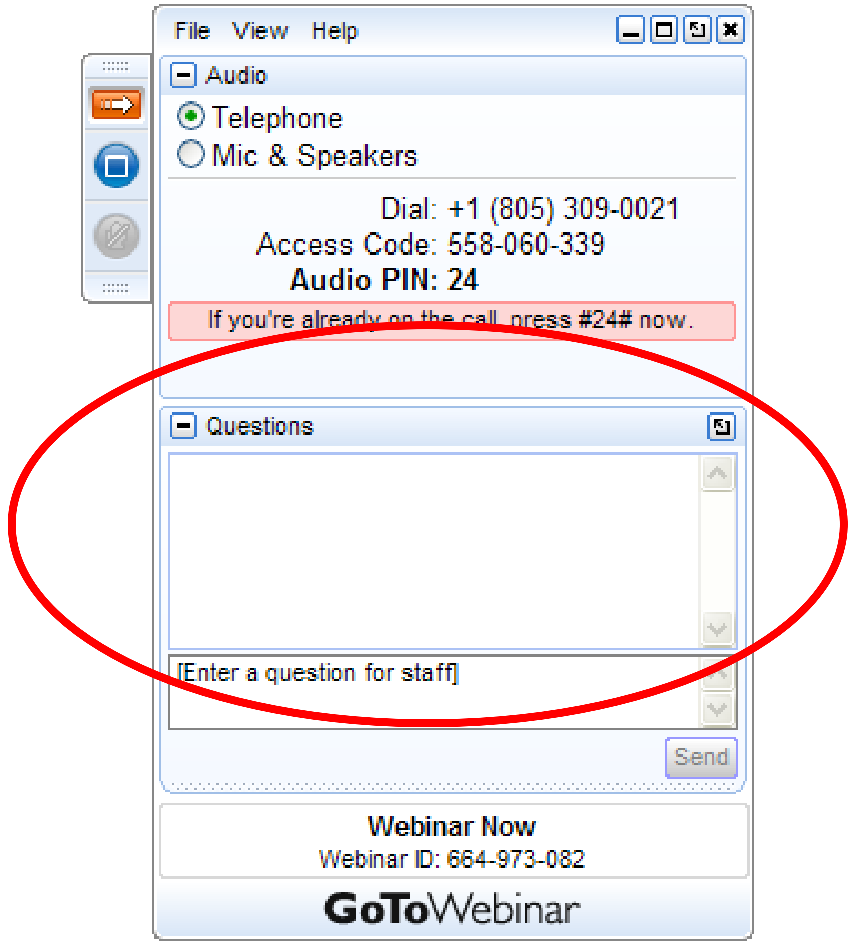
Tuesday, November 8th, 2016

Presenter(s)

Debbie Myers – ANL (ElectroCat)
Piotr Zelenay – LANL (ElectroCat)
Mark Allendorf – SNL (HyMARC)

Question and Answer

Please type your questions into the question box



Webinar Topics

- Summary of the organization of two Fuel Cell Technologies Office consortia within DOE-EERE's Energy Materials Network
  - Electrocatalysis Consortium (ElectroCat)
  - Hydrogen Materials—Advanced Research Consortium (HyMARC)
- Current/planned scientific activities and capabilities
- Role of individual projects selected to work with these consortia
- Utilizing existing consortia capabilities
- Upcoming FY17 Funding Opportunity Announcement (FOA)

ElectroCat
Electrocatalysis Consortium

FCTO Lab Consortia Overview: ElectroCat

Purpose, scope, and capabilities of ElectroCat

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

November 8, 2016

Steering Committee

Los Alamos National Laboratory — Piotr Zelenay

Argonne National Laboratory — Debbie Myers

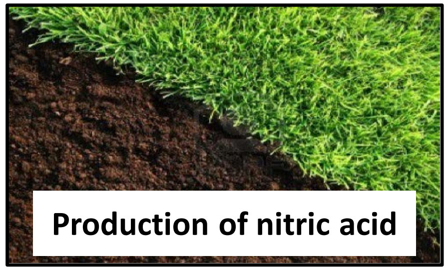
Oak Ridge National Laboratory — Karren More

NREL National Renewable Energy Laboratory — Huyen Dinh

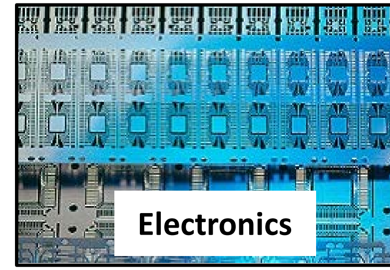
Dimitrios Papageorgopoulos and Adria Wilson, DOE-EERE-FCTO

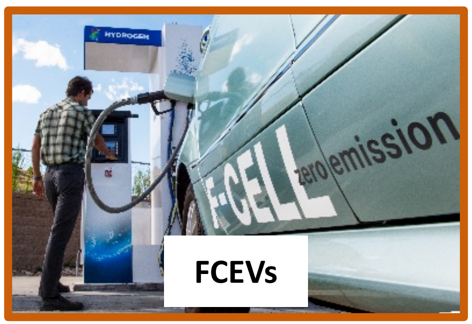
ElectroCat Materials Domain: Electrocatalysts


Petroleum refining

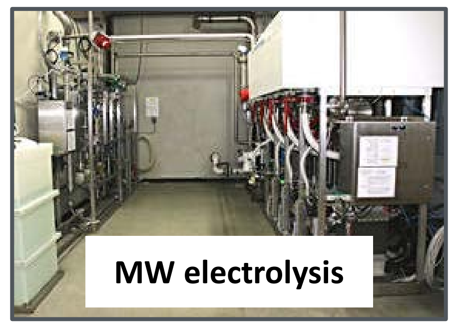

Production of nitric acid


Vehicle Pollution Control


Electronics



FCEVs

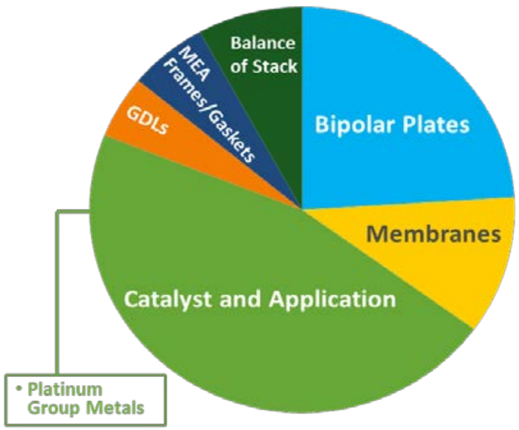

MW electrolysis

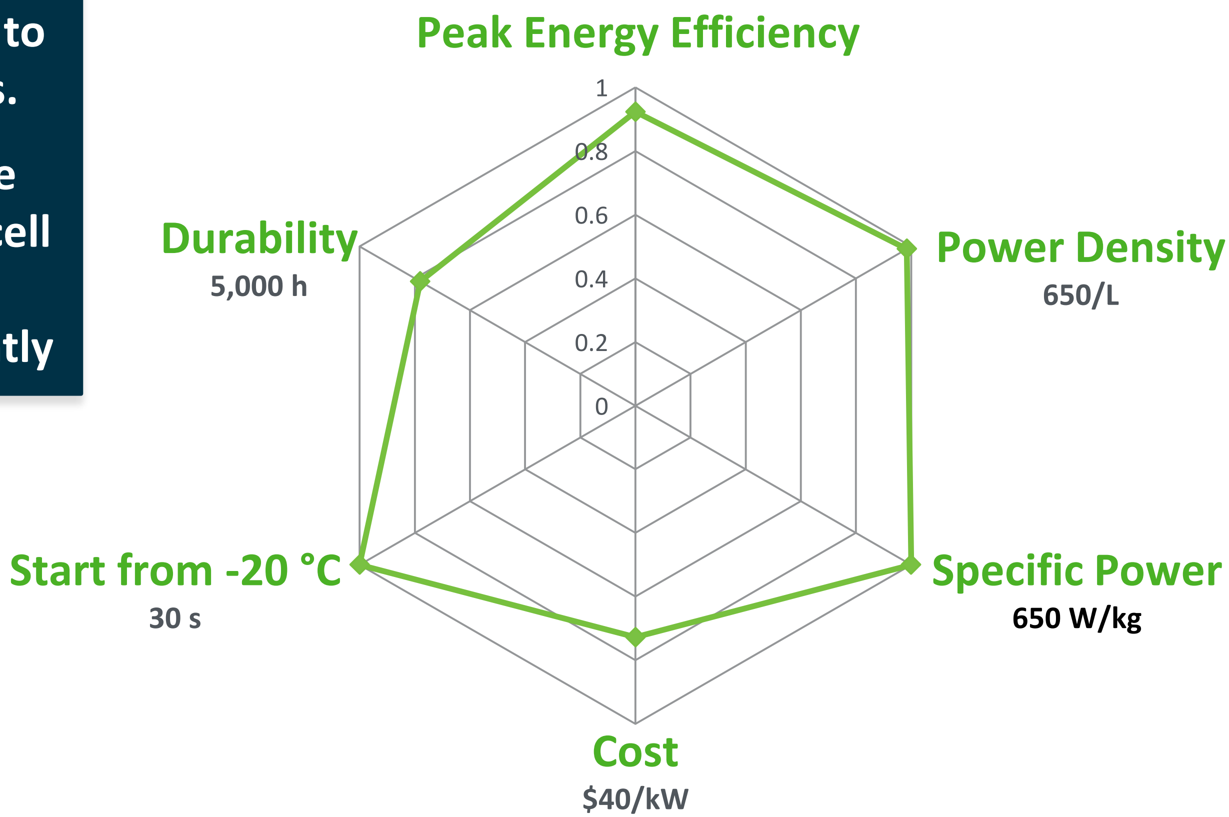
Project Focus: PGM-free catalysts for automotive fuel cells

Problem Statement

Fuel cell system targets set to be competitive with ICEVs.

Durability <u>and</u> cost are the primary challenges to fuel cell commercialization and must be met concurrently





PGM-free catalysts lag behind platinum in efficiency, durability, cost, and ease of integration into membrane electrode assemblies.

PGM-free *vs.* PGM Cathodes: Targeting Competitiveness

Technical Targets: Electrocatalysts for Transportation Applications			
Characteristic	**Units**	**2015 Status**	**2020 Targets**
Platinum group metal total content (both electrodes)	g/kW (rated, gross) @ 150 kPa (abs)	0.16	0.125
Platinum group metal (PGM) total loading (both electrodes)	mg_{PGM}/cm^2 (electrode area)	0.13	0.125
Mass activity	A/mg_{PGM} @ 0.9 $V_{iR\text{-}free}$	> 0.5	0.44
Loss in initial catalytic activity	% mass activity loss	66	< 40
Loss in performance at 0.8 A/cm^{2*}	mV	13	< 30
Electrocatalyst support stability	% mass activity loss	41	< 40
Loss in performance at 1.5 A/cm^2	mV	65	< 30
PGM-free catalyst activity	**A/cm^2 @ 0.9 $V_{IR\text{-}free}$**	**0.024 A/cm^2**	**> 0.044***

*Equivalent to PGM catalyst mass activity target of 0.44 A/mg_{PGM} at 0.1 mg_{PGM}/cm^2

PGM-free containing MEAs need to meet DOE performance and durability targets

ElectroCat Electrocatalysis Consortium

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Strategy: Research Priorities

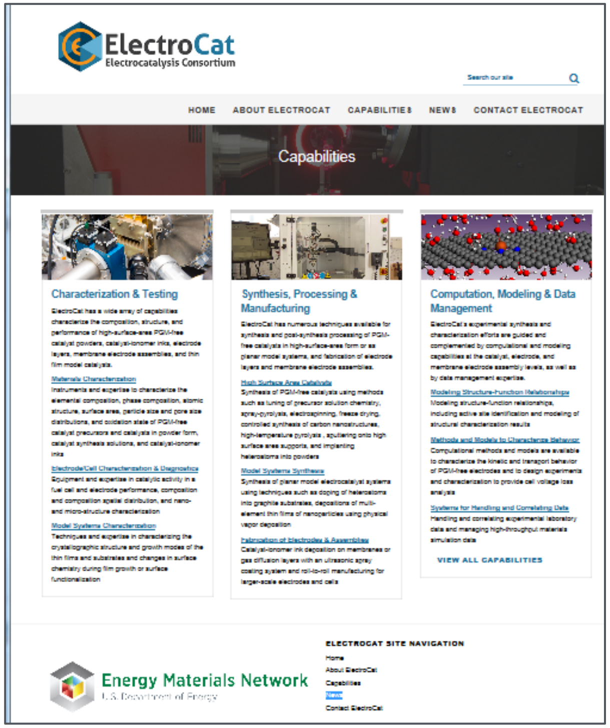
Materials Discovery & Development	**Catalysts** for oxygen reduction in low-temperature PEMFCs and PAFCs
	Catalysts for oxygen reduction and hydrogen oxidation in AMFCs
	Development of **electrodes and MEAs** that are compatible with PGM-free catalysts
Tool Development	Optimization of **atomic-scale** and **meso-scale models** of catalyst activity to predict macro-scale behavior
	High-throughput techniques for catalyst synthesis
	High-throughput techniques for characterization of catalysts, electrodes, and MEAs
	Aggregation of data in an easily searchable, public database to facilitate the development of catalyst materials and MEAs

Introduction to FOA

- High-performing and durable PGM-free catalysts and electrodes to significantly reduce fuel cell cost primarily for automotive applications
- Goal is durable PGM-free oxygen reduction reaction catalysts that achieve activity of 0.044A/cm^2 at 0.9 V in a PEMFC MEA by 2020
- Proposed projects are expected to leverage specified collaboration with one or more ElectroCat national lab-based capabilities, which include:
  - catalyst synthesis, characterization, processing, and manufacturing
  - high-throughput, combinatorial techniques
  - advanced computational tools
- Projects for this topic will be up to 3 years with interim go/no-go decision points
- Interested applicants are encouraged to interface with the ElectroCat Steering Committee to determine potential for collaboration **before** the FOA is released

ElectroCat Capabilities Overview

http://www.electrocat.org/capabilities/



Synthesis, Processing and Manufacturing

Synthesis and post-synthesis processing of PGM-free catalysts in high-surface-area form or as planar model systems, and fabrication of electrode layers and MEAs

- ✓ High surface area catalysts
- ✓ Model systems synthesis
- ✓ Fabrication of electrodes and membrane-electrode assemblies

Characterization and Testing

Composition, structure, and performance of high-surface-area PGM-free catalyst powders, catalyst-ionomer inks, electrode layers, membrane electrode assemblies, and thin film model catalysts.

- ✓ Materials Characterization
- ✓ Electrode/Cell Characterization & Diagnostics
- ✓ Model Systems Characterization

Computation, Modeling and Data Management

Guiding and complementing experimental efforts with computational and modeling capabilities at the catalyst, electrode, and membrane electrode assembly levels, as well as by data management expertise.

- ✓ Modeling structure-function relationships
- ✓ Methods and models to characterize behavior
- ✓ Systems for handling and correlating data

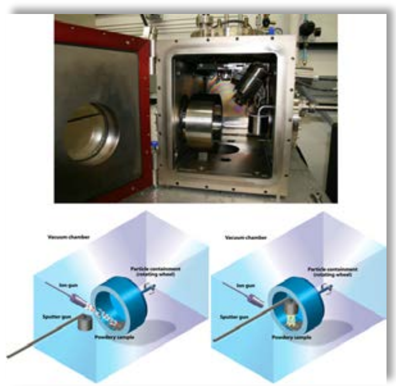
Synthesis, Processing and Manufacturing Capabilities

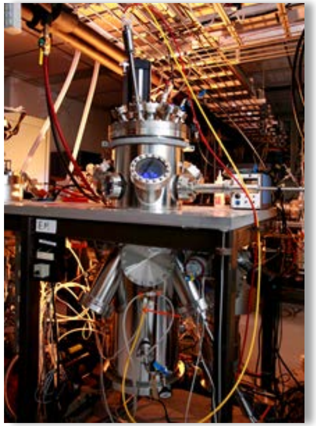
High Surface Area Catalysts

- PGM-free Catalyst Synthesis, Analytical Characterization, and Electrochemical and Fuel Cell Testing (LANL)
- Sputter Deposition of Thin Films and High Surface Area Catalysts (ORNL)
- Powder Sputter and Implant System (NREL)
- High-throughput Synthesis of PGM-free Catalysts and Electrodes (ANL)

Model Systems Synthesis

- Controlled Functionalization of Model Catalysts (LANL)
- Sputter Deposition of Thin Films and High Surface Area Catalysts (ORNL)
- High-throughput (HT) Thin Film Fabrication and Characterization (NREL)





Fuel Cell Fabrication

- Membrane-Electrode Assembly Fabrication (LANL)
- High-throughput Synthesis of PGM-free Catalysts and Electrodes (ANL)
- High-throughput Approaches to Scaling PGM-free Electrodes (NREL)
- Manufacturing Porous Electrodes (ORNL)

Characterization and Testing Capabilities

Materials Characterization

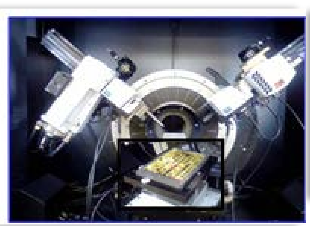
- PGM-free Catalyst Synthesis, Analytical Characterization, and Electrochemical and Fuel Cell Testing (LANL)
- X-Ray Characterization Techniques (LANL)
- X-Ray Photoelectron Spectroscopy (ORNL)
- Electron Tomography (ORNL)
- Analytical Electron Microscopy (ORNL)
- In situ Electron Microscopy (ORNL)
- Structure/Composition-Function Relationships and Active Sites (ANL)
- In situ and Operando Atomic, Nano-, and Micro-structure Characterization (ANL)
- Combinatorial Hydrodynamic Screening of PGM-free Catalyst Activity and Stability (ANL)
- High-throughput Characterization of PGM-free Catalysts and Electrodes (ANL)

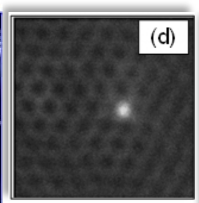
Electrode and Cell Characterization

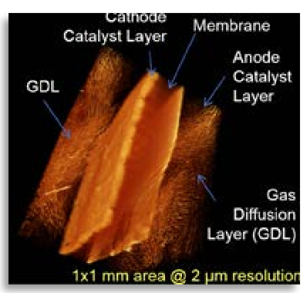
- Operando Differential Cell Measurements of Electrochemical Kinetics and Transport (NREL)
- PGM-free Catalyst Synthesis, Analytical Characterization, and Electrochemical and Fuel Cell Testing (LANL)
- Electrode Microstructure Characterization and Simulation (ANL)
- Electron Tomography (ORNL)
- Analytical Electron Microscopy (ORNL)
- In situ and Operando Atomic, Nano-, and Micro-structure Characterization (ANL)
- Segmented Cell System Optimized for R&D Combinatorial Studies (NREL)
- In situ Fluoride and Carbon Dioxide Emission Measurements (LANL)
- Segmented Cell and Neutron Imaging (LANL)
- High-throughput Characterization of PGM-free Catalysts and Electrodes (ANL)

Model Systems Characterization

- Controlled Functionalization of Model Catalysts (LANL)
- X-Ray Photoelectron Spectroscopy (ORNL)
- High-throughput (HT) Thin Film Fabrication and Characterization (NREL)







Computation, Modeling & Data Management

Catalyst Modeling

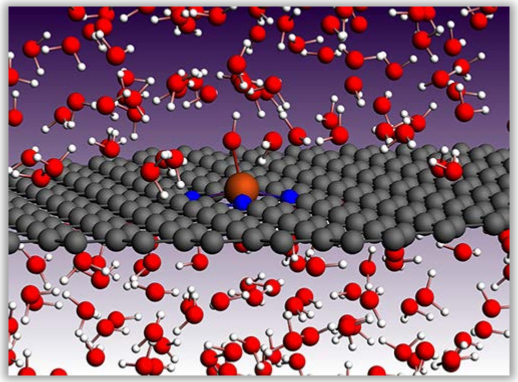
- Multi-scale Modeling
- Rational Design of PGM-free Catalysts (LANL)

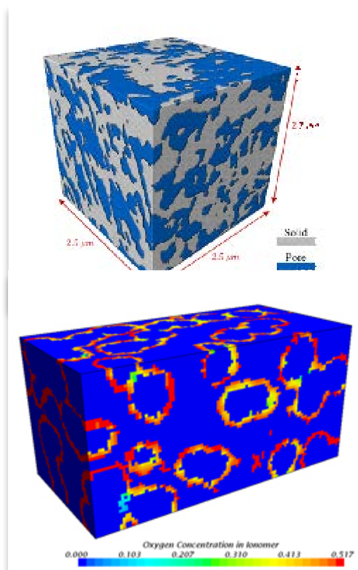
Electrode/Fuel Cell Performance Modeling

- Electrode Microstructure Characterization and Simulation (ANL)
- Modeling Kinetic and Transport Processes in PGM-free Electrodes (ANL)

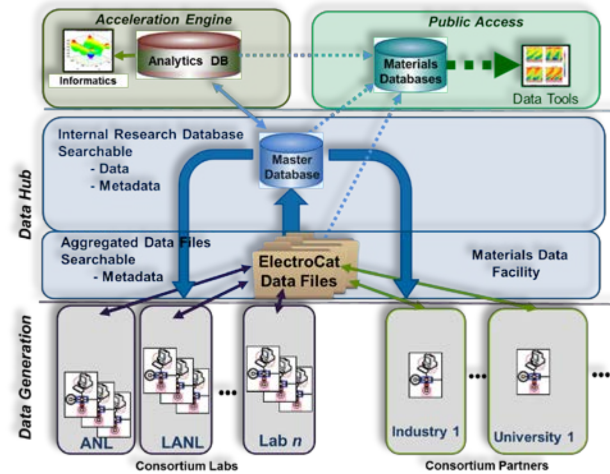
Data Management

- Experimental and Computational Materials Data Infrastructure (NREL)
- Materials Data Facility and Globus (ANL)





Oxygen transport



Capability Navigation

Materials Characterization

PGM-free Catalyst Synthesis, Analytical Characterization, and Electrochemical and Fuel Cell Testing

The expertise in PGM-free catalyst synthesis, characterization, and fuel cell testing at LANL is built on decades-long experience and proven results, and is the most important capability within LANL's PGM-free program by far.

ELECTRODE/CELL CHARACTERIZATION | HIGH SURFACE AREA CATALYSTS | MATERIALS CHARACTERIZATION | SYNTHESIS/PROCESSING/MANUFACTURING

Title

Laboratory: LANL, ANL, ORNL, or NREL

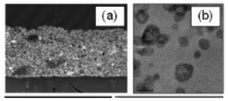
Capability Expert: *Person to contact with specific questions about capability*

Capability Details:

- Title
- Class
- Description
- Capability Bounds
- Unique Aspects
- Availability
- References
- Benefit
- Illustrative Graphic

Analytical Electron Microscopy

Laboratory:	Oak Ridge National Laboratory (ORNL)
Capability Expert:	Karren L. More
Capability Details:	
Title:	High-resolution analytical scanning transmission electron microscopy (STEM)
Class:	Characterization
Description:	High-resolution transmission electron microscopy (TEM) and aberration-corrected scanning transmission electron microscopy (STEM) are microscopy methods used to characterize the atomic-scale structure of PGM-free catalysts (typically in powder form) and the material constituents (catalyst and ionomer) comprising membrane electrode assemblies (MEAs). STEM instruments are typically equipped with multiple detectors, including high angle annular dark field (HAADF) detectors to perform what is commonly referred to as Z-contrast STEM imaging (where Z refers to the atomic number), bright field (BF) detectors, and spectrometers (e.g., an electron energy loss spectrometer (EELS) and an energy dispersive X-ray spectrometer (EDS)). These detectors and spectrometers, when used in combination, enable the simultaneous study of the atomic structure and chemistry of novel PGM-free catalyst systems and their interfaces with other MEA constituents from the bulk-scale to the single atom level. Compositions and chemistries can be acquired and mapped (spectral imaging) across multiple length scales and directly correlated with the atomic structure determined through HAADF/BF-STEM imaging.
Capability Bounds:	NA
Unique Aspects:	A full suite of scanning transmission electron microscopes (STEM) is available at ORNL for conducting imaging and spectroscopic analysis of PGM-free catalysts and membrane electrode assemblies (MEAs) from the bulk-scale to the single-atom level, including the identification of unique morphologies of catalyst particles and insight towards understanding the atomic structure of catalytically active sites. Unique microscopes include low-voltage (60kV) and high-voltage (200kV) aberration-corrected STEM instruments equipped with high-energy resolution electron energy loss spectroscopy (EELS) and high spatial-resolution energy dispersive X-ray spectroscopy (EDS), which enable a broad range of structural, chemical, and
Availability:	Instruments in ORNL's Materials Characterization Center (MCC) are available for partnership with industry through Strategic Partnership Projects (SPP), cooperative research and development agreements (CRADAs) via full-cost recovery (hourly fee), and direct project collaborations to facilitate new materials discovery and understanding; instruments in ORNL's Center for Nanophase Materials Sciences (CNMS – a U.S. DOE Office of Science User Facility) are accessible through a peer-reviewed proposal process (no cost if results are publishable and full-cost recovery if data is proprietary). All instruments in the MCC and CNMS are available for characterization of PGM-free catalysts and MEAs.
References:	G. Wu, K.L. More, C.M. Johnston, and P. Zelenay, "High-Performance Electrocatalysts for Oxygen Reduction Derived from Polyanilene, Iron, and Cobalt," *Science* **332** 443-447 (2011). W. Gao, G. Wu, M.T. Janicke, D.A. Cullen, R. Mukundan, J.K. Baldwin, E.L. Brosha, C. Garlande, P.M. Ajayan, K.L. More, A.M. Dattlebaum, and P. Zelenay, "Ozonated Graphene Oxide Film as a Proton Exchange Membrane," *Angewandte Chemie International Edition* **53** [14] 3588-3593 (2014). G. Wu, K.L. More, P. Xu, H.L. Wang, M. Ferrandon, A.J. Kropf, D.J. Myers, S. Ma, C.M. Johnston, and P. Zelenay, "A Carbon-nanotube-supported Graphene-rich Non-precious Metal Oxygen Reduction Catalyst with Enhanced Performance Durability," *Chemical Communications* **49** 3291-3293 (2013).
Benefit:	ORNL's unique STEM instruments provide capabilities for the complete analytical and structural characterization of PGM-free catalysts and MEAs at multiple length scales to correlate structure and chemistry with material performance.



- **Questions about capabilities:**

  Contact@ElectroCat.org

  (to Steering Committee members)

- **Questions about FOA:**

  http://energy.gov/eere/fuelcells/subscribe-news-and-financial-opportunity-updates

- **Note:** If you intend to interact with ElectroCat through a FOA-awarded project, please do not contact either Steering Committee members or capability experts after the FOA has been released

Thank you

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Piotr Zelenay
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hydrogenandfuelcells.energy.gov

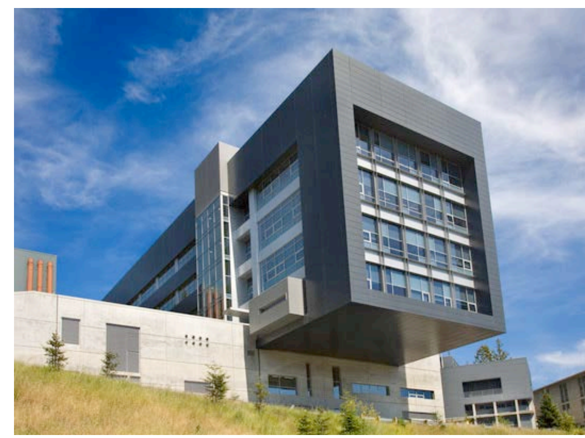
Introduction to FOA - HyMARC

- High-risk, high-reward seedling projects to develop innovative and novel onboard rechargeable hydrogen storage material concepts for use in automotive applications enabling higher capacity and lower cost storage systems
- Projects will work collaboratively with the HyMARC core team
- Multi-phase, stage-gated projects, up to 3 years total length, and $250k-1M in DOE funding
- Projects must demonstrate the development of materials that meet agreed upon quantitative metrics to continue past the initial seedling phase (12-18 months)

HyMARC: A Consortium for Advancing Solid-State Hydrogen Storage Materials

Mark D. Allendorf, P.I., Sandia National Laboratories

November 8, 2016



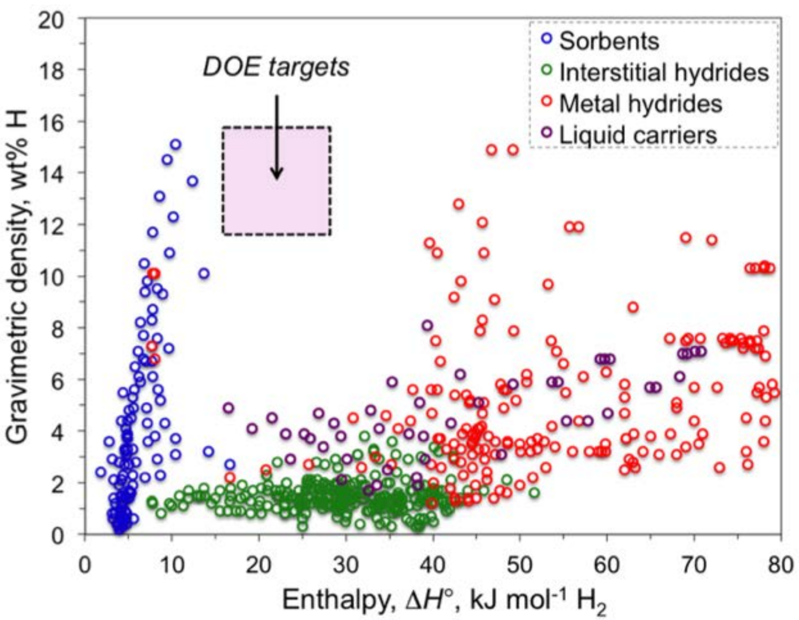
Critical Scientific Challenges (Identified by NREL PI meeting, Jan. 2015)

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

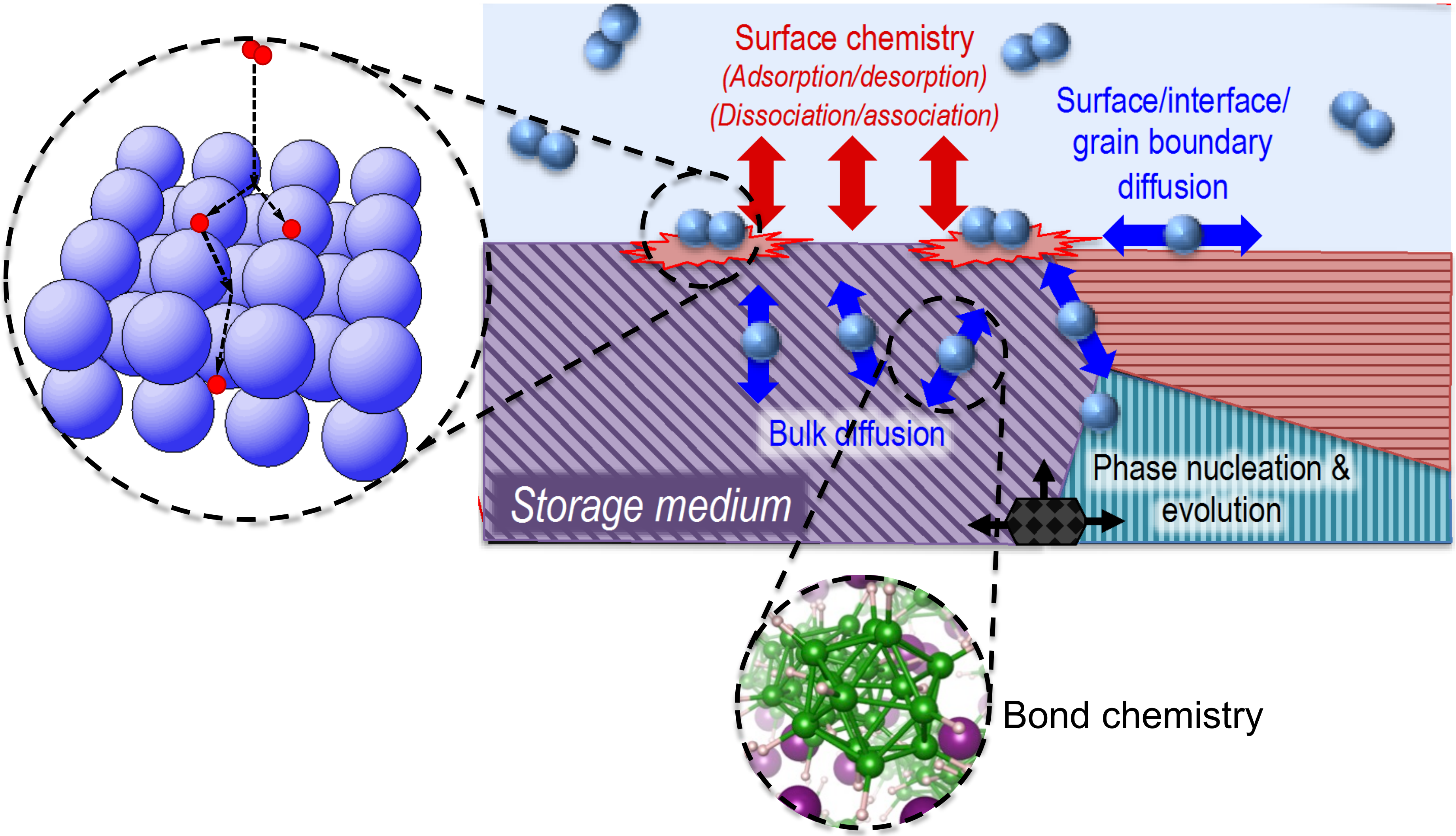
- Volumetric capacity at operating temp.
- Increased usable hydrogen capacity needed
- Distribution of H_2 binding sites and ΔH at ambient temperature not optimized

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



Objective: accelerate discovery of breakthrough storage materials by providing **capabilities** and **foundational understanding**

Foundational understanding of phenomena governing thermodynamics and kinetics limiting the development of solid-state hydrogen storage materials

HyMARC will deliver **community tools and capabilities:**

- **Computational models and databases** for high-throughput materials screening
- **New characterization tools and methods** (surface, bulk, soft X-ray, synchrotron)
- **Tailorable synthetic platforms** for probing nanoscale phenomena

Core Lab Team

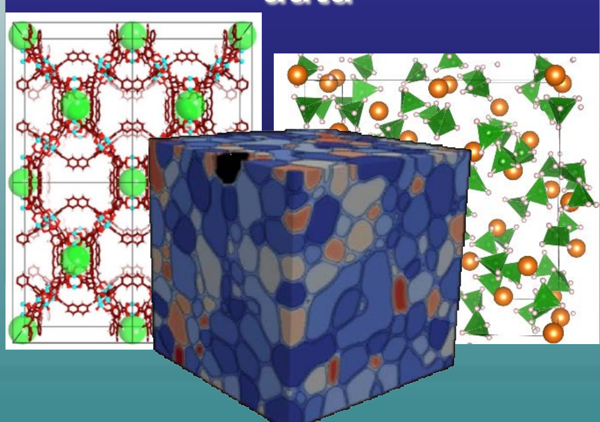
BERKELEY LAB

University → Core Lab Team

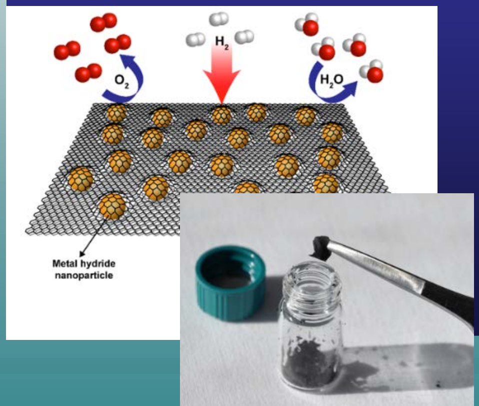
Non-profit → Core Lab Team

Industry → Core Lab Team

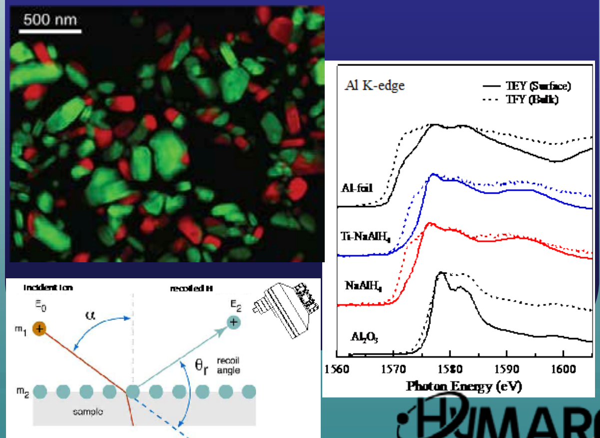
Theory, simulation, & data



Controlled synthesis



In situ characterization



HyMARC

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

Technical approach: Organizational structure of Core Lab Team

Lawrence Livermore National Laboratory

Brandon Wood
LLNL Lead

Lab program POC
Jeff Roberts

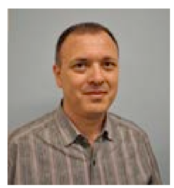
Task 2
Transport
Tae Wook Heo

Task 6
Databases
Brandon Wood

Sandia National Laboratories

Mark Allendorf
Director
SNL Lead
Vitalie Stavila
Deputy

Lab program POC
Chris San Marchi



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

Lab program POC
Adam Weber

Task 4
Sol.-Sol. Interfaces
Jeff Urban

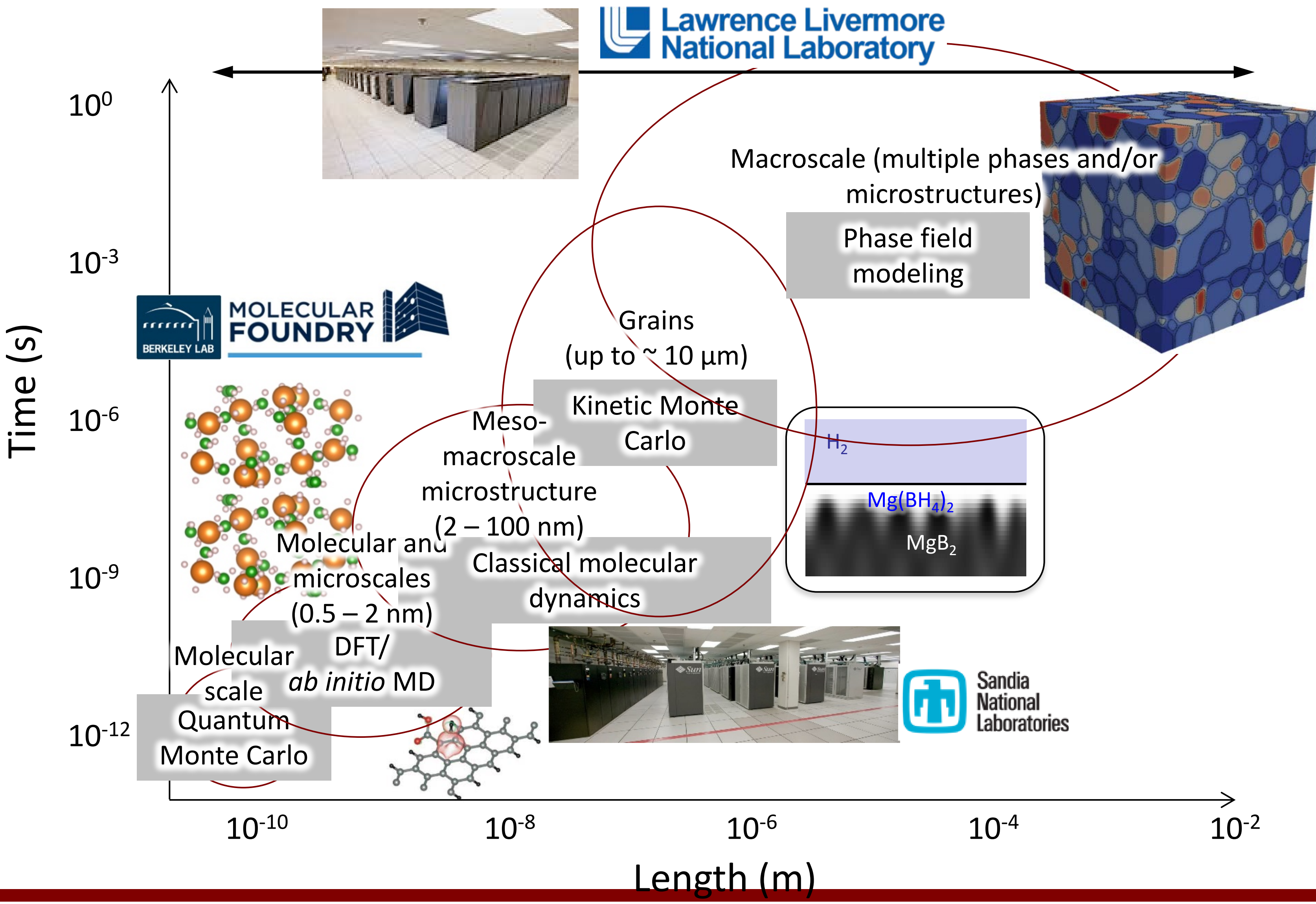
MOLECULAR FOUNDRY

Molecular Foundry
POC: David
Prendergast

ALS ADVANCED LIGHT SOURCE

ALS
POC: Jinghua Guo

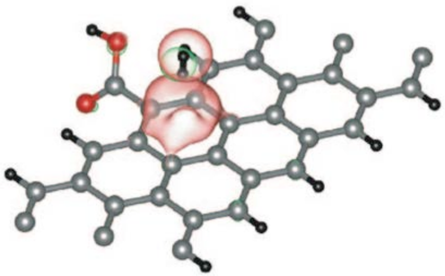
Technical approach/Modeling capabilities: high-performance National Lab computing allows simulations at all relevant length scales



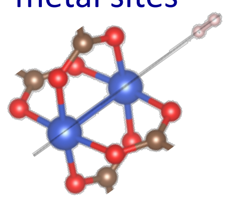
Accurate physisorption energetics

H_2 physisorption energetics with high-accuracy quantum chemistry and electronic structure methods

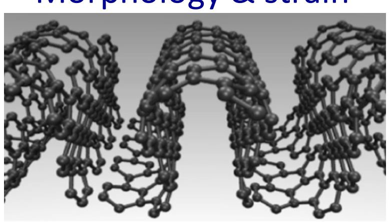
Chemical substitution/ functionalization



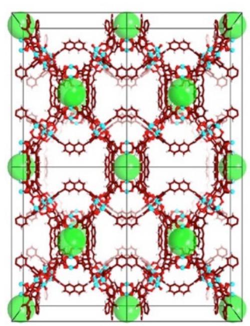
Open metal sites

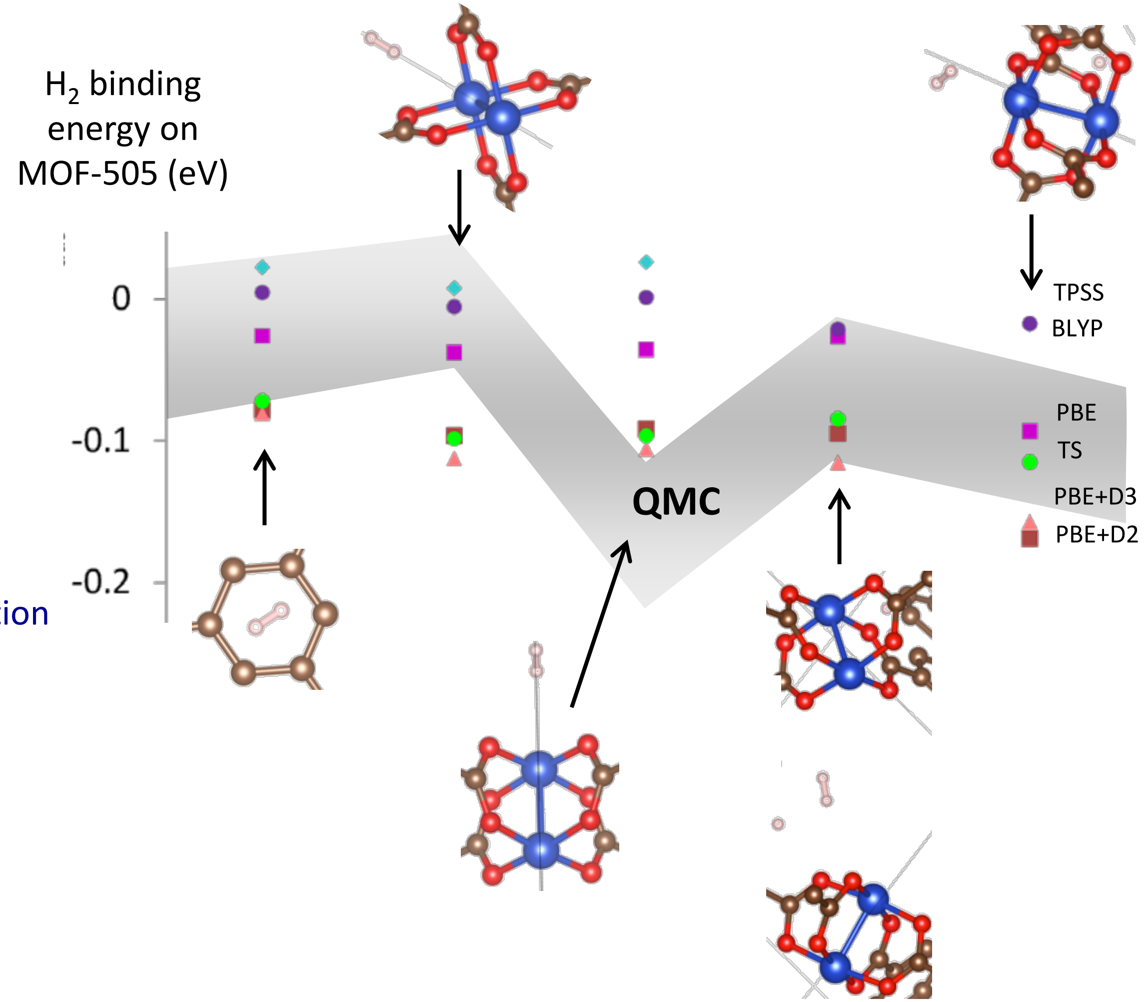


Morphology & strain



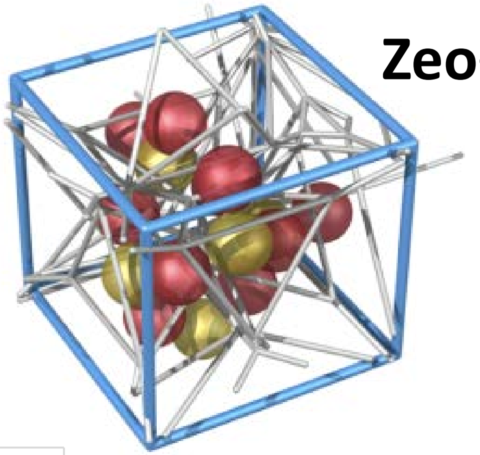
Crystal structure/coordination



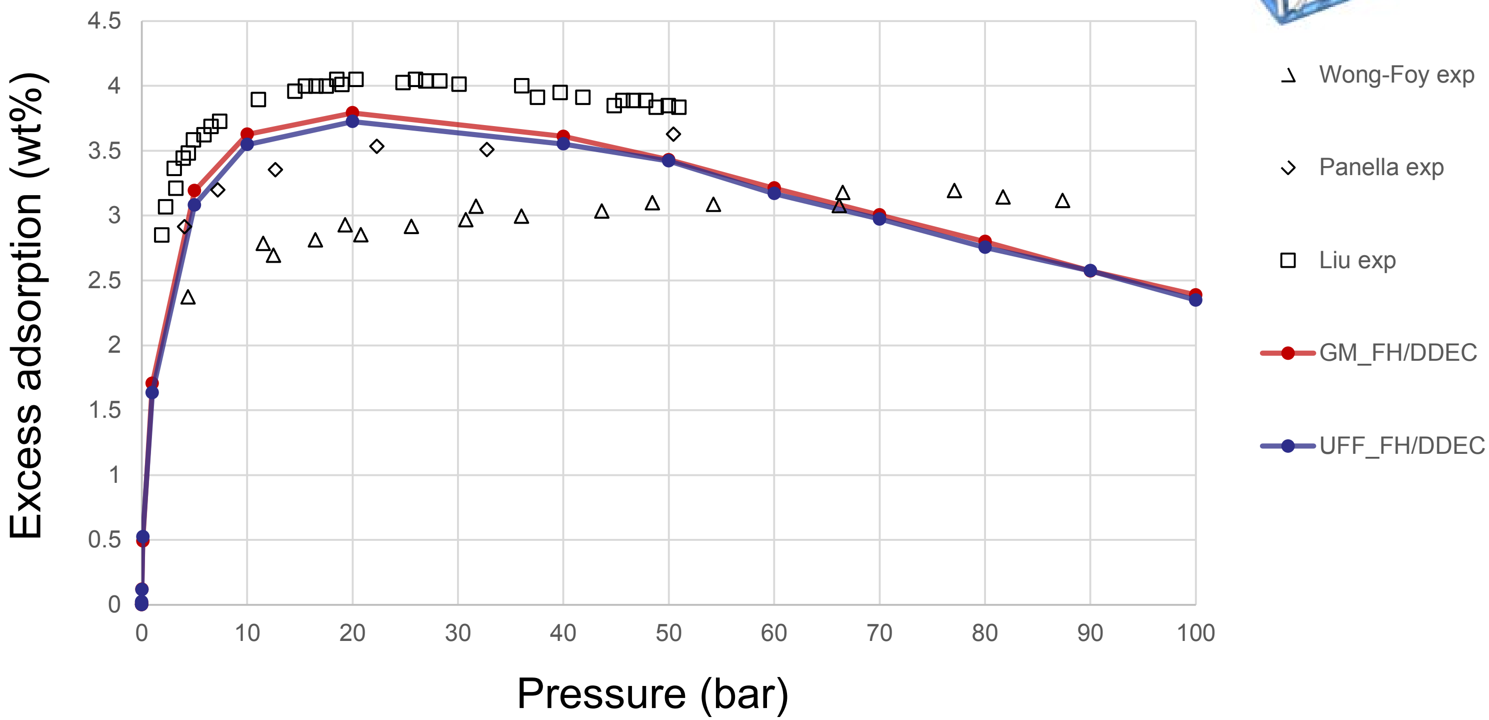


Sorbent characterization & H_2 uptake

- Surface area and porosity characterization
- Isotherm prediction

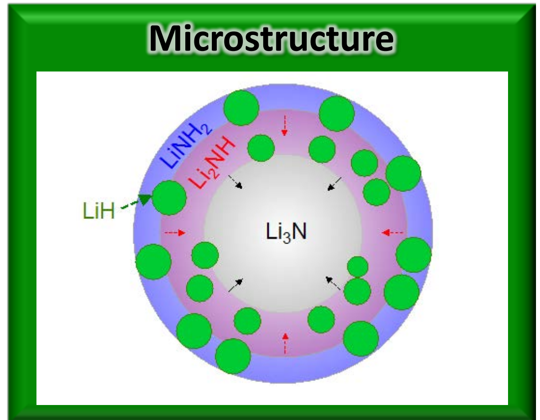


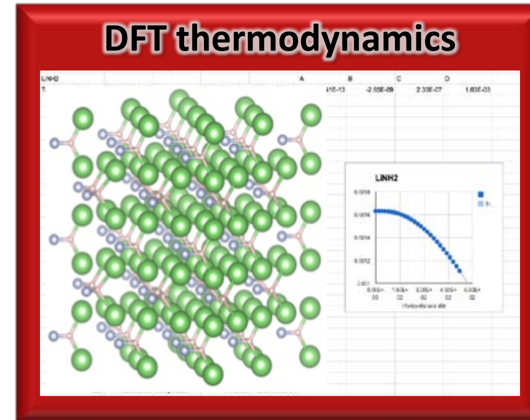
CuBTC/ HKUST-1 at 77 K

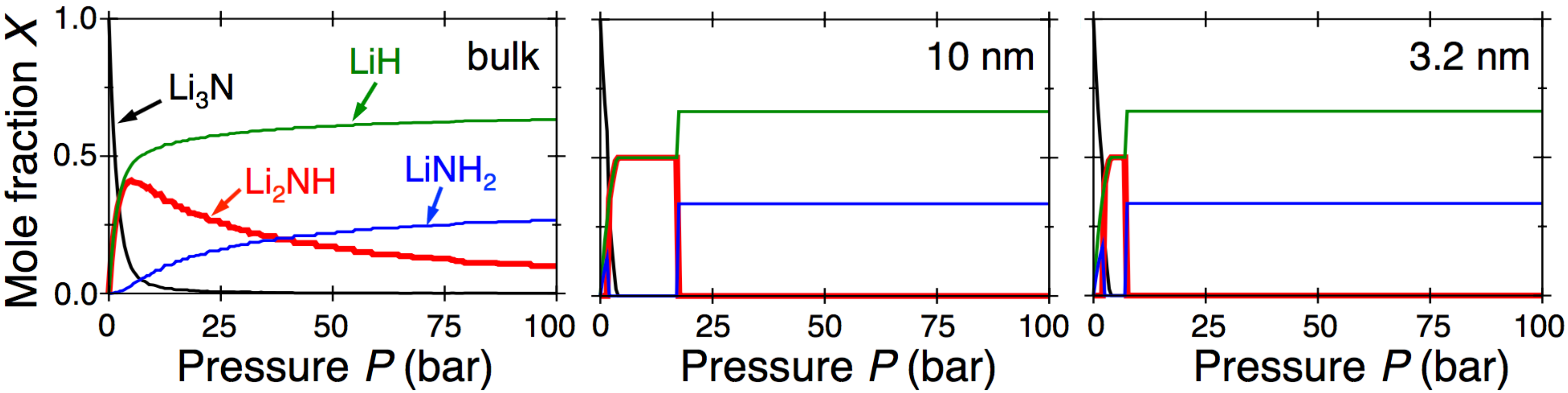


Ab initio thermodynamics

- Reaction free energy
- Effects of mechanical stress and nanosizing
- Phase diagram prediction
- Phase fractions at intermediate (de)hydrogenation



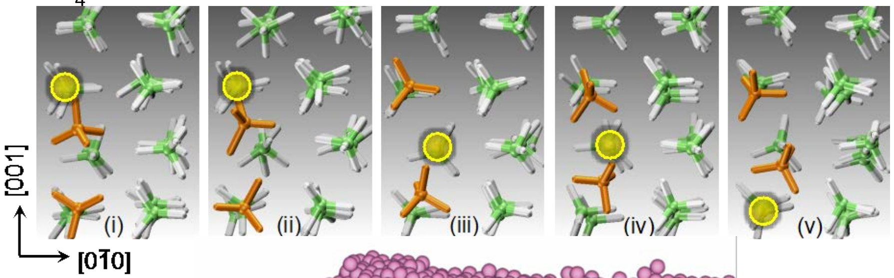




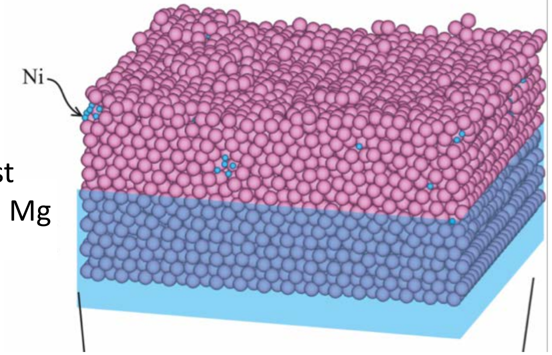
Multiscale mass transport simulations

- *M*olecular dynamics (*ab initio* & classical)
- Defect formation and migration barriers
- Non-equilibrium diffusion
- Polycrystalline effective diffusion

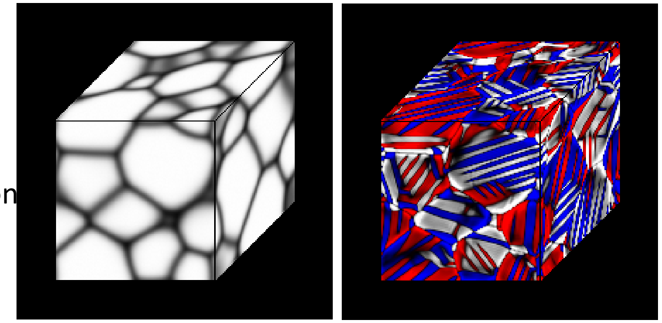
AlH_4 structural diffusion



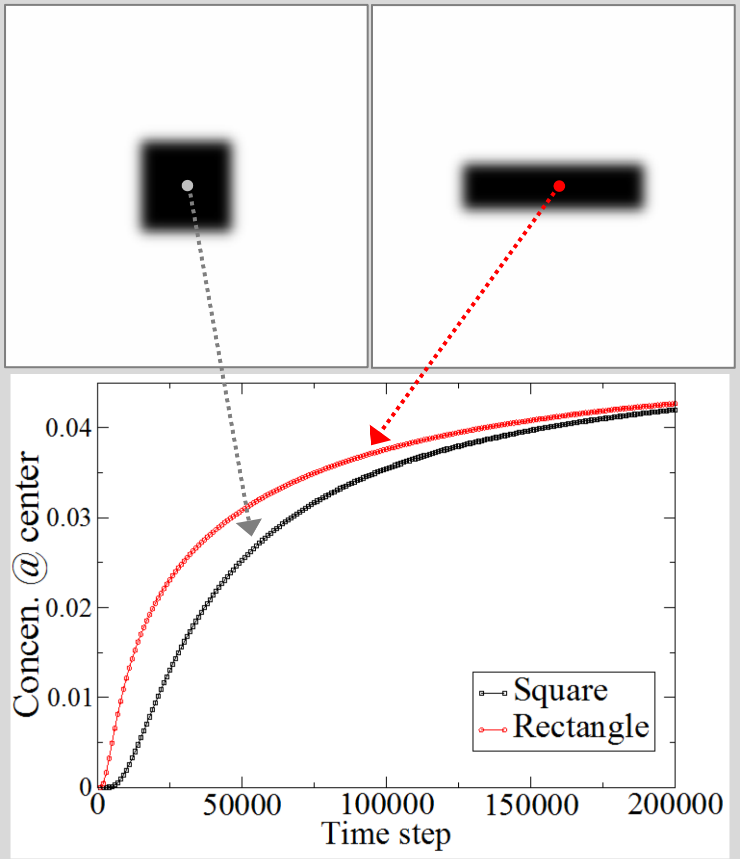
Ni catalyst clustering in Mg



Polycrystalline models for effective diffusion



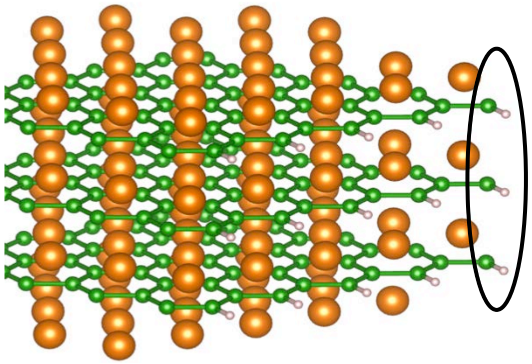
Non-equilibrium surface H diffusion on metals



Interface simulations

- Simulations of interfaces with gas (H_2), liquids, or solids
- Electronic and chemical properties

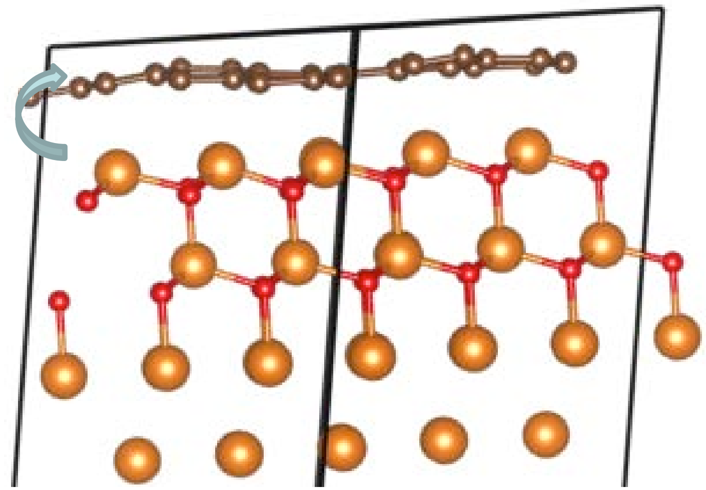
Gas-surface interactions



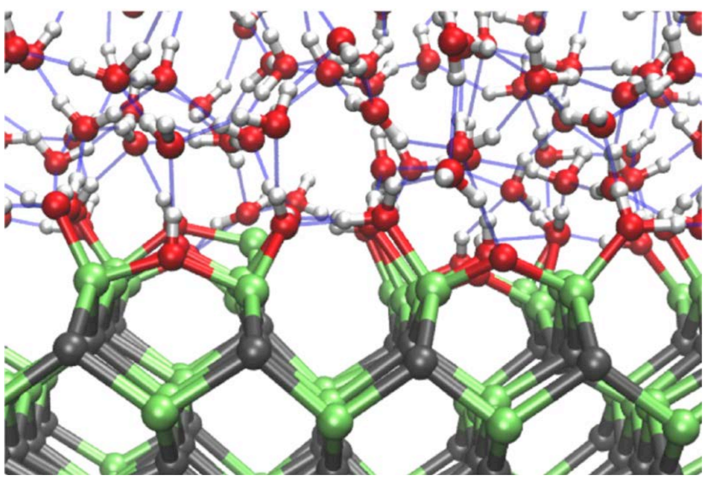
H_2 dissociation on MgB_2

Heterogeneous solid interfaces

$Dr = 0.125e$ per C



Graphene-MgO-Mg interfaces

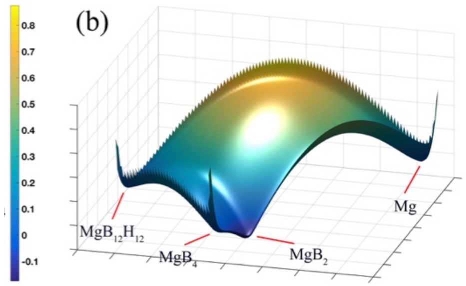


Solid-liquid interfaces

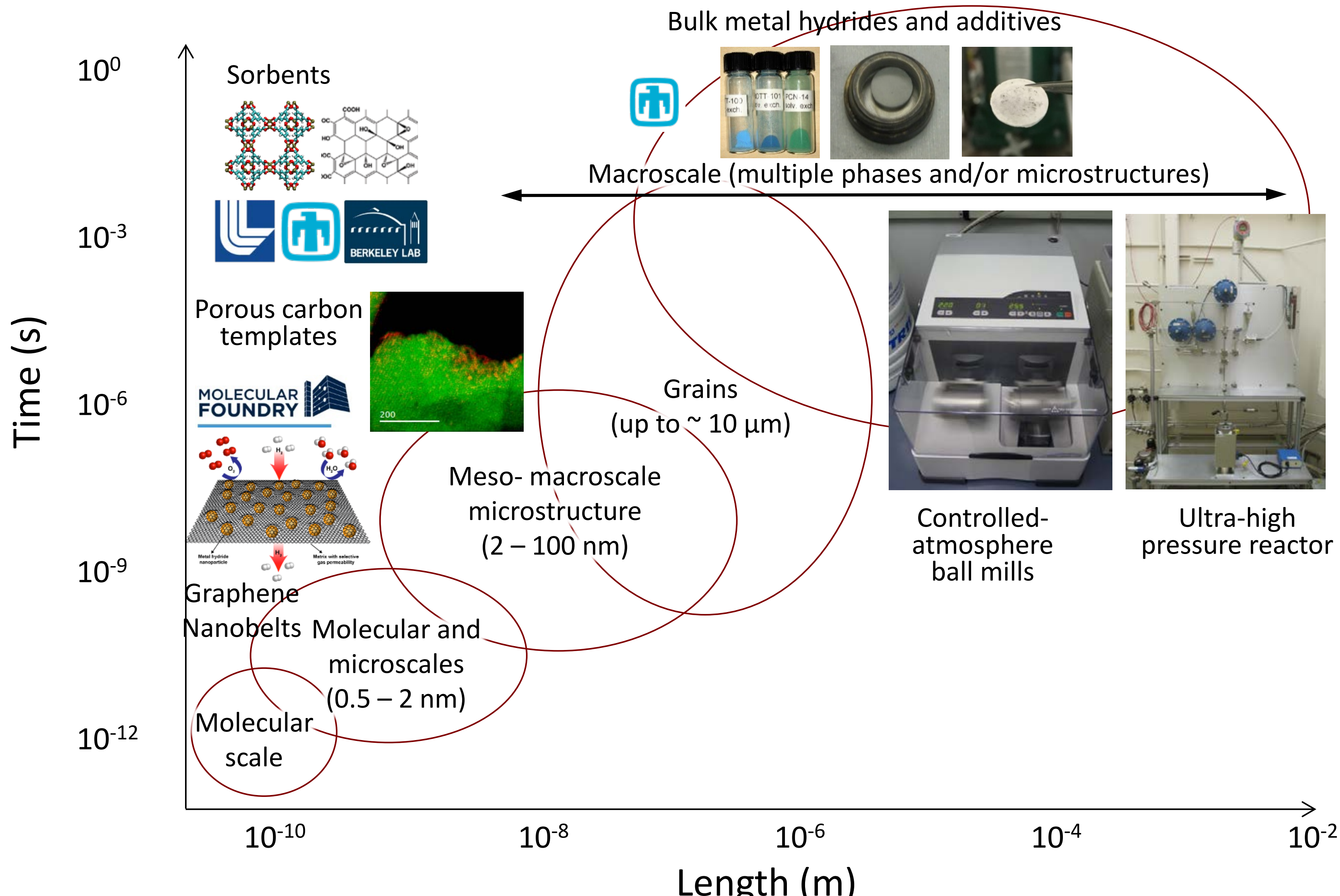
Surface oxide-solvent interface

HyMARC capabilities summary: Modeling and simulation

- **Accurate physisorption energies** (beyond-DFT, QMC, hybrid/vdW DFT)
- **Sorbent characterization and hydrogen uptake** (porosity, GCMC)
- **Quantum chemistry and electronic structure** (DFT)
- ***Ab initio* thermodynamics** (DFT, GCLP, CALPHAD)
- **Multiscale mass transport** (AIMD, KMC, phase field)
- **Computational spectroscopy** (DFT)
- **Interface simulations with gas/liquid/solid** (DFT, AIMD, MD, continuum)
- **Solid-state phase transformation kinetics** (phase field)
- **Kinetic modeling and fitting** (continuum)



Synthesis capabilities: bulk materials, dopants, sorbants, and nano-scale platforms



Technical approach/storage materials: build and validate capabilities using simple "model" systems, then progress to higher complexity

Effective thermal energy for H_2 release: $\Delta E(T) = \Delta H^{\circ}(T) + E_a$

Sorbents

- Thermodynamics of H_2 release

Library of sorbents with representative structural motifs:

- MOFs with open metal sites
- Porous carbons
- Doped materials

Metal hydrides

- Thermodynamics
  - Bulk vs. nano
- Kinetics of uptake and release
- Surface reactions
- Mass transport
- Solid-solid interfaces
- Additives

A progression of model systems will enable development of new capabilities:

Increasing complexity

Binary hydrides → "Simple" Complex hydrides → Complex systems, e.g. $Mg(BH_4)_2$

Phase segregation

"Molecular" species (e.g. $B_{12}H_{12}$)

Bulk → Nano

Graphene nanobelts, templates, colloidal synthesis

Bulk and nanoscale metal hydrides

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

Phase minimization strategies: overcome transport problems due to phase segregation

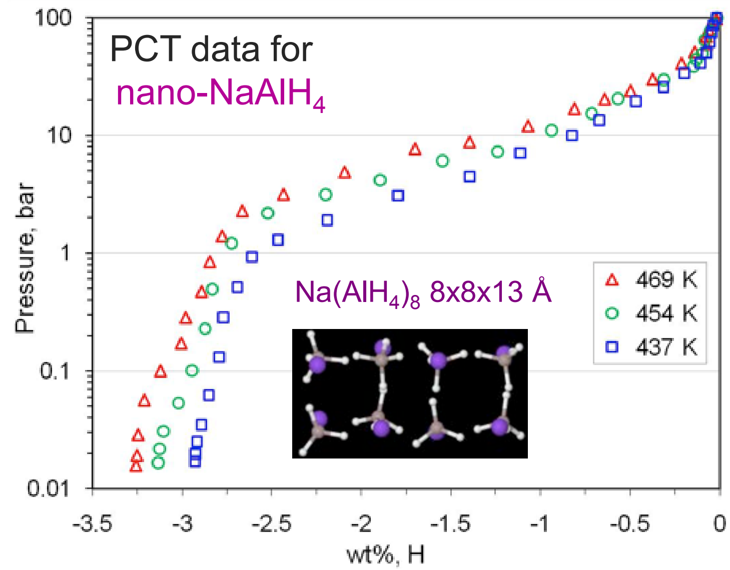
Doping and defect creation: solid solutions to minimize the number of solid phases

Entropy tuning: crystalline-to-amorphous transitions to improve Δ*G*°

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

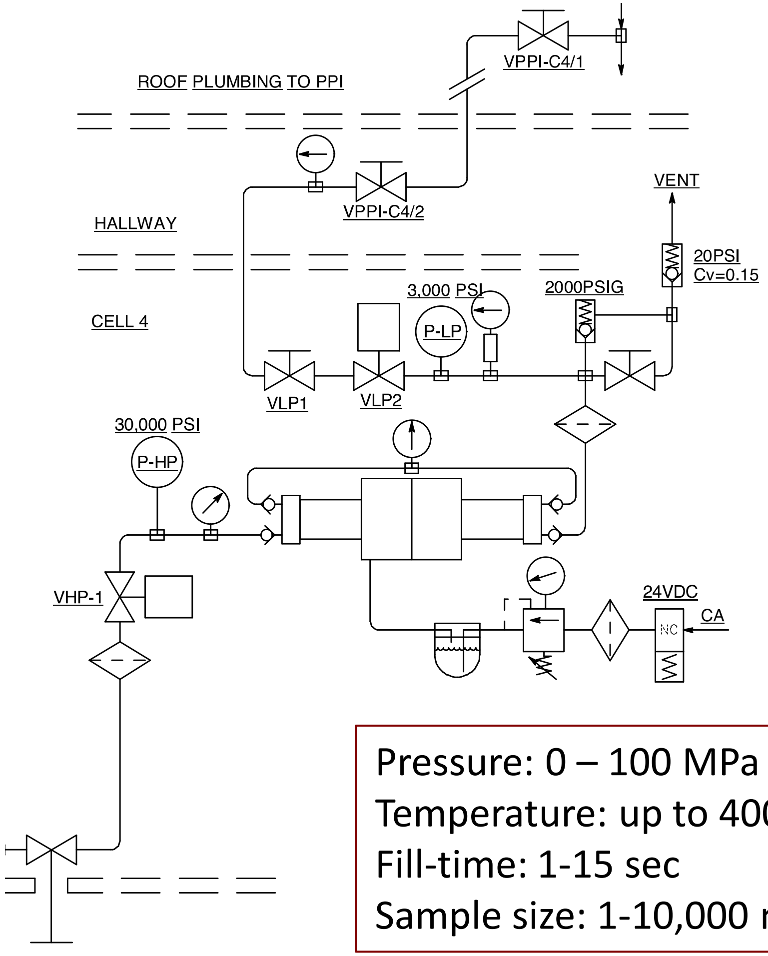
Consortium capabilities for bulk hydride synthesis include:

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



New capability: high-pressure station

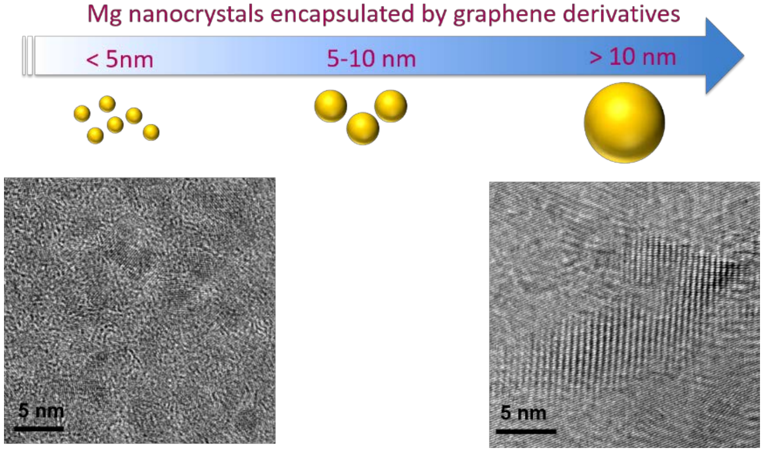
Redesigned and upgraded the Sandia high-pressure hydrogen station (pressures up to 1000 bar H_2)



Pressure: 0 – 100 MPa
Temperature: up to 400 °C
Fill-time: 1-15 sec
Sample size: 1-10,000 mg

Synthesis of Metal Hydride Composites

- Scalable bottom-up synthetic route
- Atomically defined, tunable graphene-based materials as stabilizing support for metal hydride and complex hydride nanoparticles
- Demonstrated using Mg and MgH_2 nanocrystals
  - Graphene oxide (GO) sheets as encapsulation layer
  - Selectively permeable to hydrogen
- Extension to complex metal hydrides underway



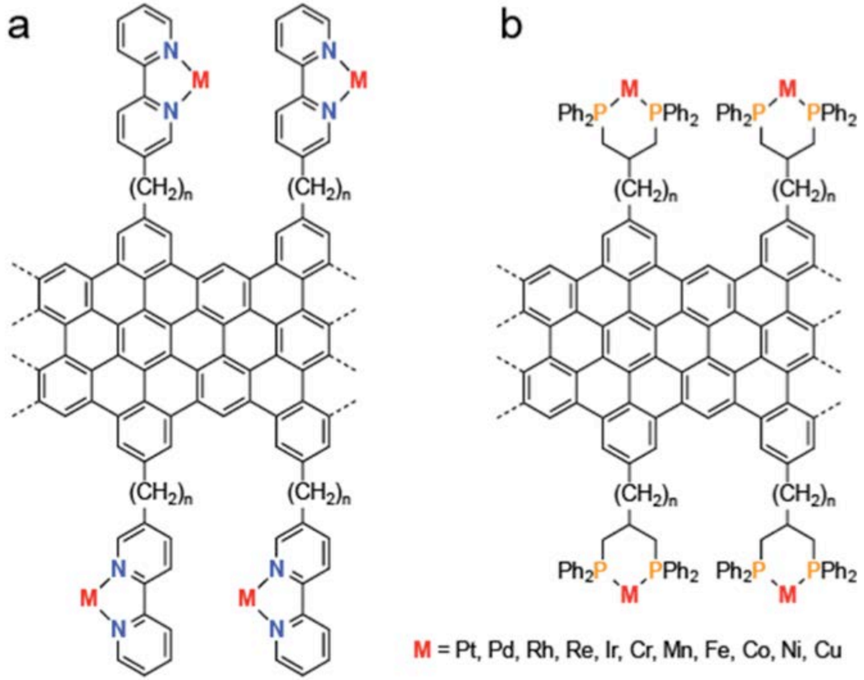
1. Jeon, K.J. et al. *Nat Mater* **10**, 286-290 (2011).
2. Ruminski, A.M.et al. *Energ Environ Sci* **6**, 3267-3271 (2013).
3. Cho, E.S. et al. *Nat Commun* **7**, 10804 (2016).

Modified graphene nanoribbons: functional catalysis

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

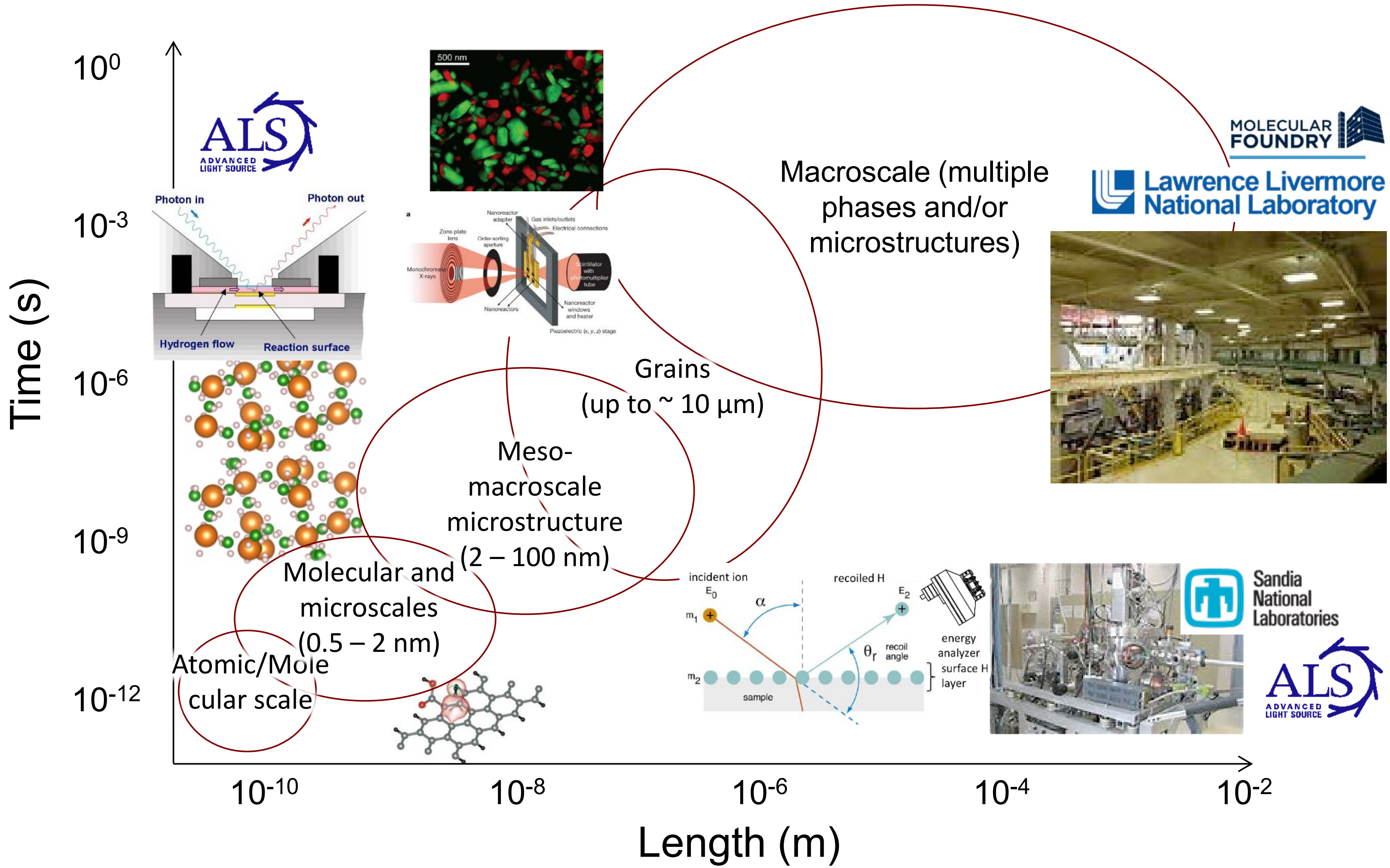
Quite adaptive: catalytic metals, or chelating and ED/EWD groups



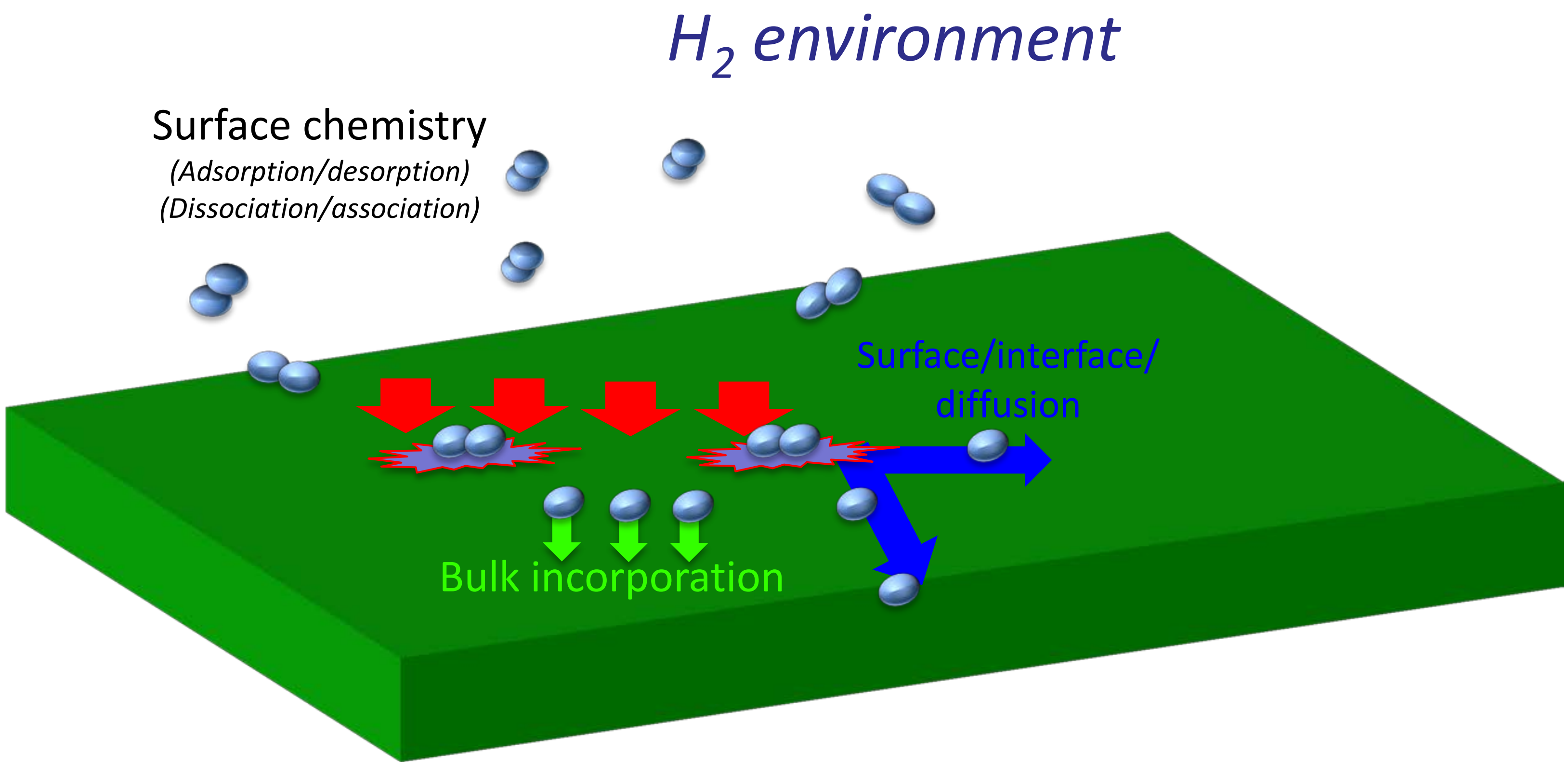
Schematic representation illustrating the integration of molecular-defined transition metal catalyst centers via:

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

Characterization: state-of-the-art tools probing bulk and surface chemistry, microstructure, phase composition



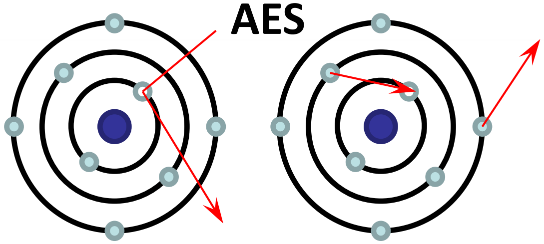
Surface: key to hydrogen storage



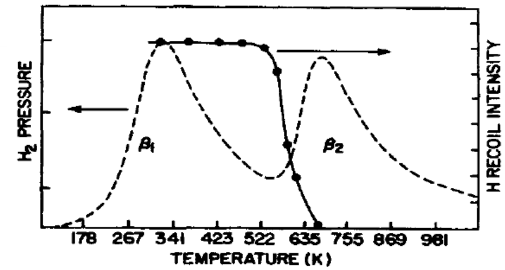
Schematic by Brandon Wood(LLNL)

Detecting hydrogen is challenging with most surface analysis techniques

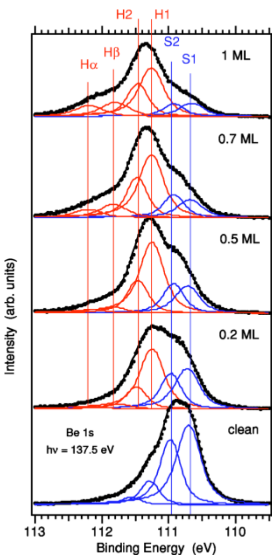
AES



TDS

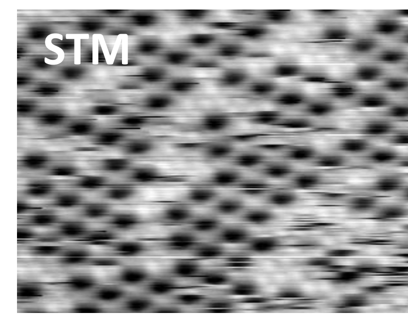


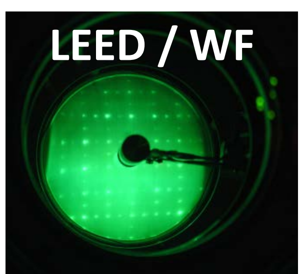
XPS

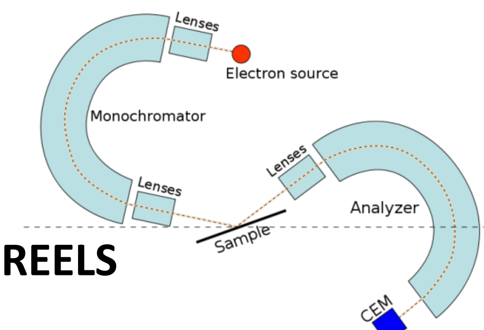


Detecting H poses unique challenges:

- Direct detection impossible with most surface techniques (AES, XPS)
- Detectable signal overwhelmed by substrate (LEED, STM, HREELS)
- Ambiguous/difficult to interpret. (TDS)

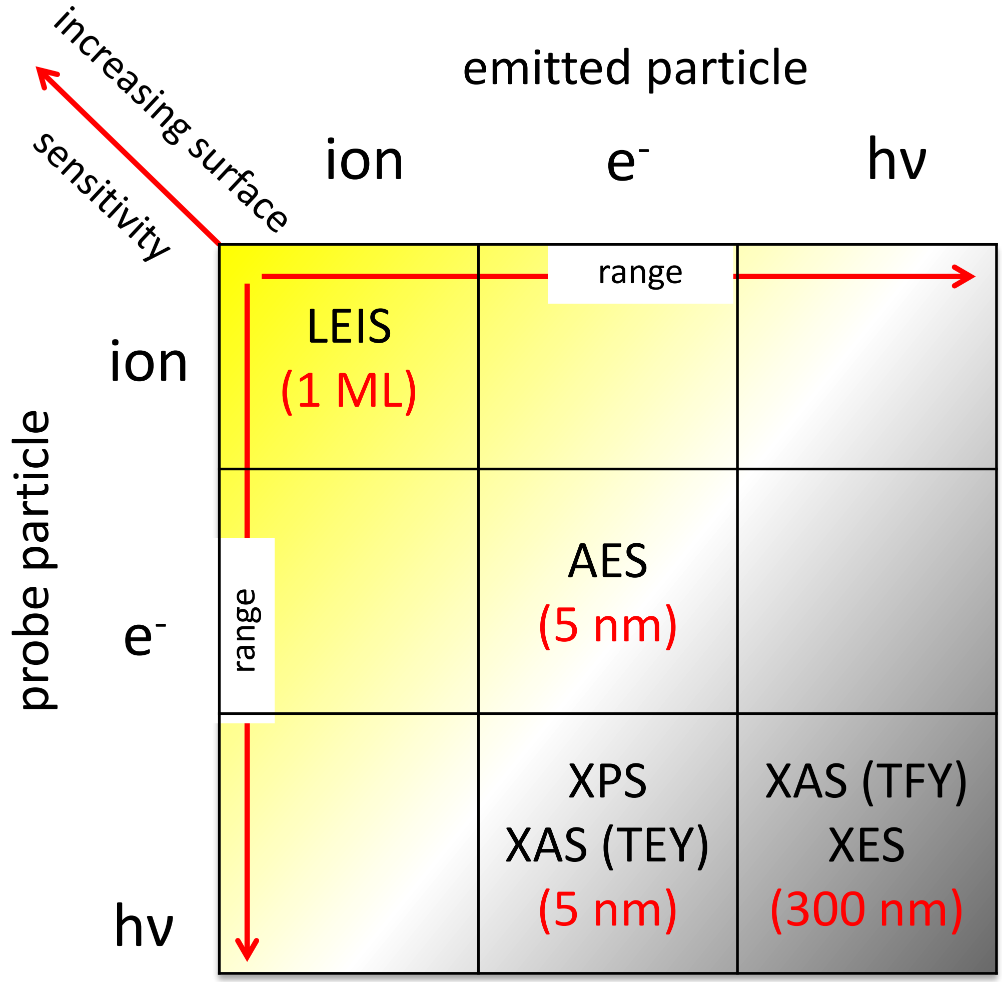


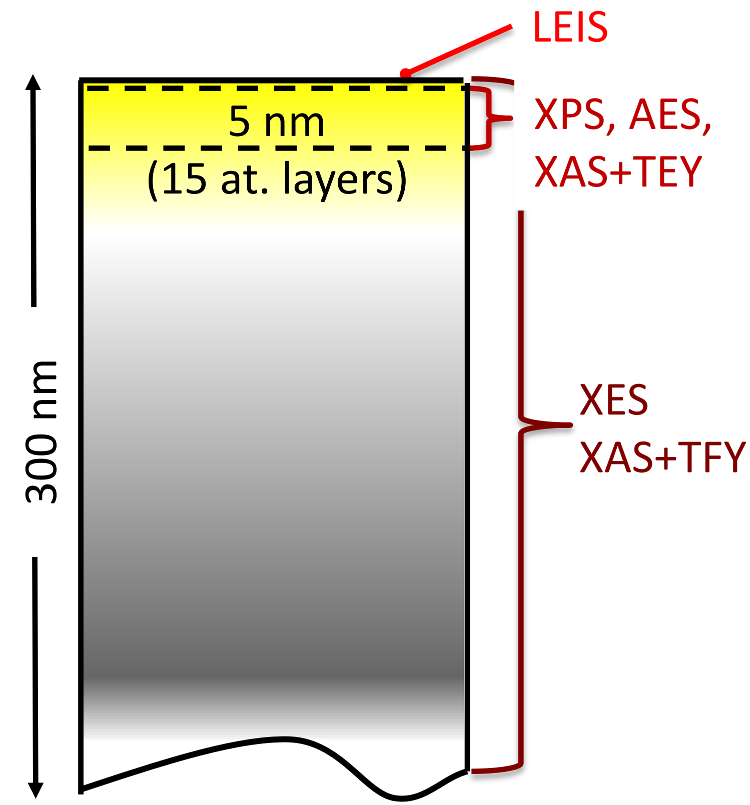




HREELS

Surface sensitivity of the HyMARC analysis probes: information depth depends on particle range





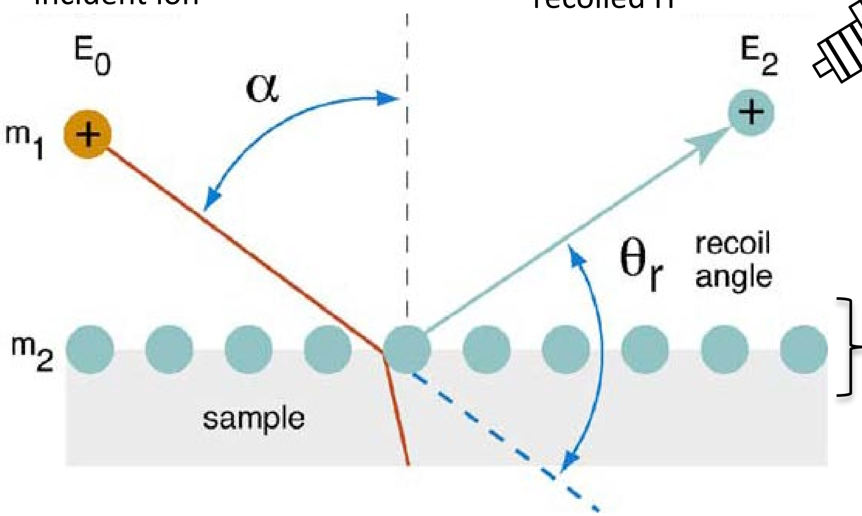
TFY: total fluorescence yield

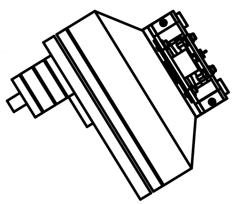
TEY: total electron yield

HyMARC surface analysis techniques provide access to a range of length scales that complement the modeling tools we are developing.

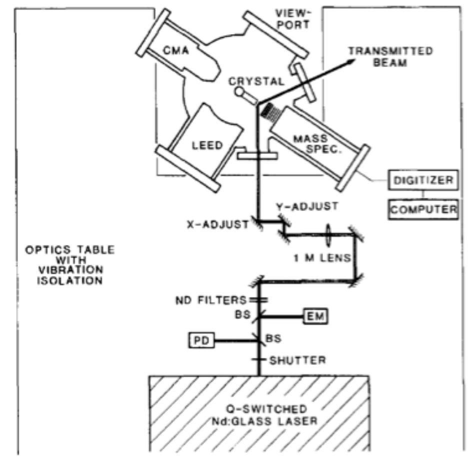
Direct mapping of hydrogen on surfaces by Low Energy Ion Scattering (LEIS) spectroscopy

- 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

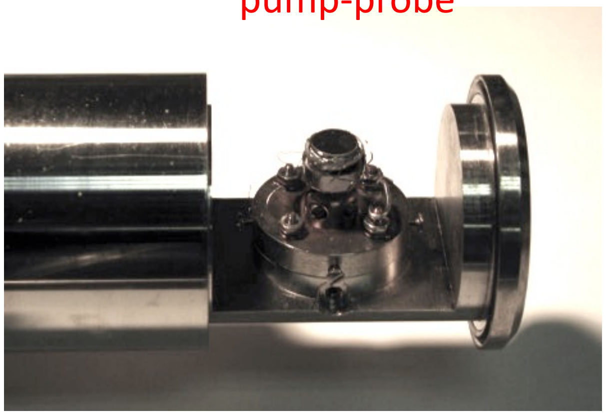




R. Kolasinski et al. *Phys. Rev. B* **85**, 115422 (2012)



laser-induced desorption pump-probe

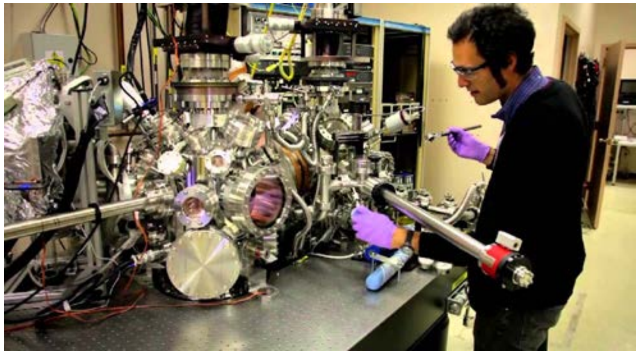


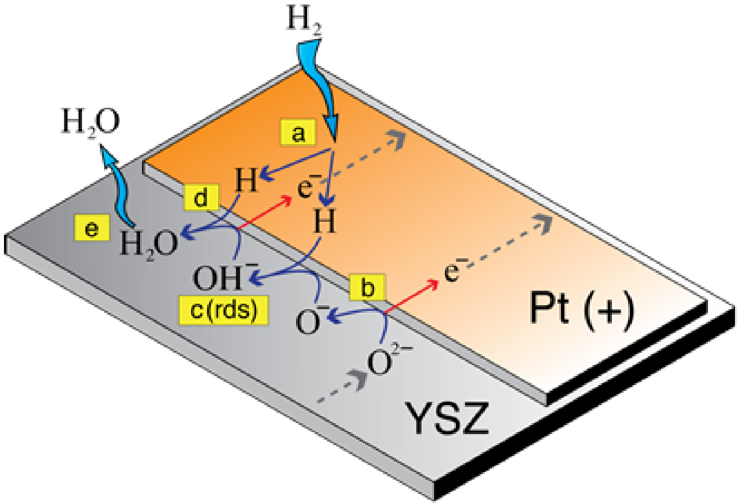
clean sample transfer container

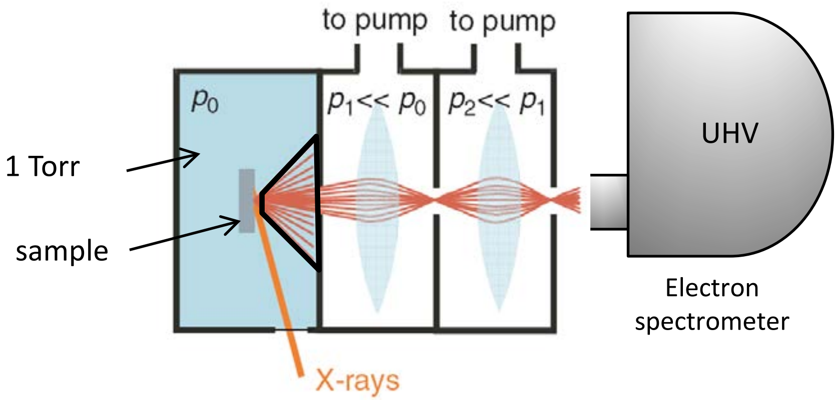
X-ray photoelectron spectroscopy provides unique insight into surface chemistry of storage materials, including oxidation states

- Quantitative surface composition
- Detailed adsorbate binding information
- Reactor chamber available for sample exposure (up to 40 Torr H_2.)
- Near Ambient Pressure XPS allows surface/gas interactions (up to 10 Torr *in situ*)

  - NAP-XPS is at the ALS (LBNL) and under development at SNL, CA):







In previous NAP-XPS studies, we described the mechanism of hydrogen utilization in operating Pt-based SOFCs
F. El Gabaly et al., Chem. Comm. **48**, 8338 (2012)

Summary: HyMARC surface tools

- Sandia, CA:
  - Low Energy Ion Scattering*
  - Auger Spectroscopy*
  - XPS* + reactor chamber

Please ask us about your specific needs!

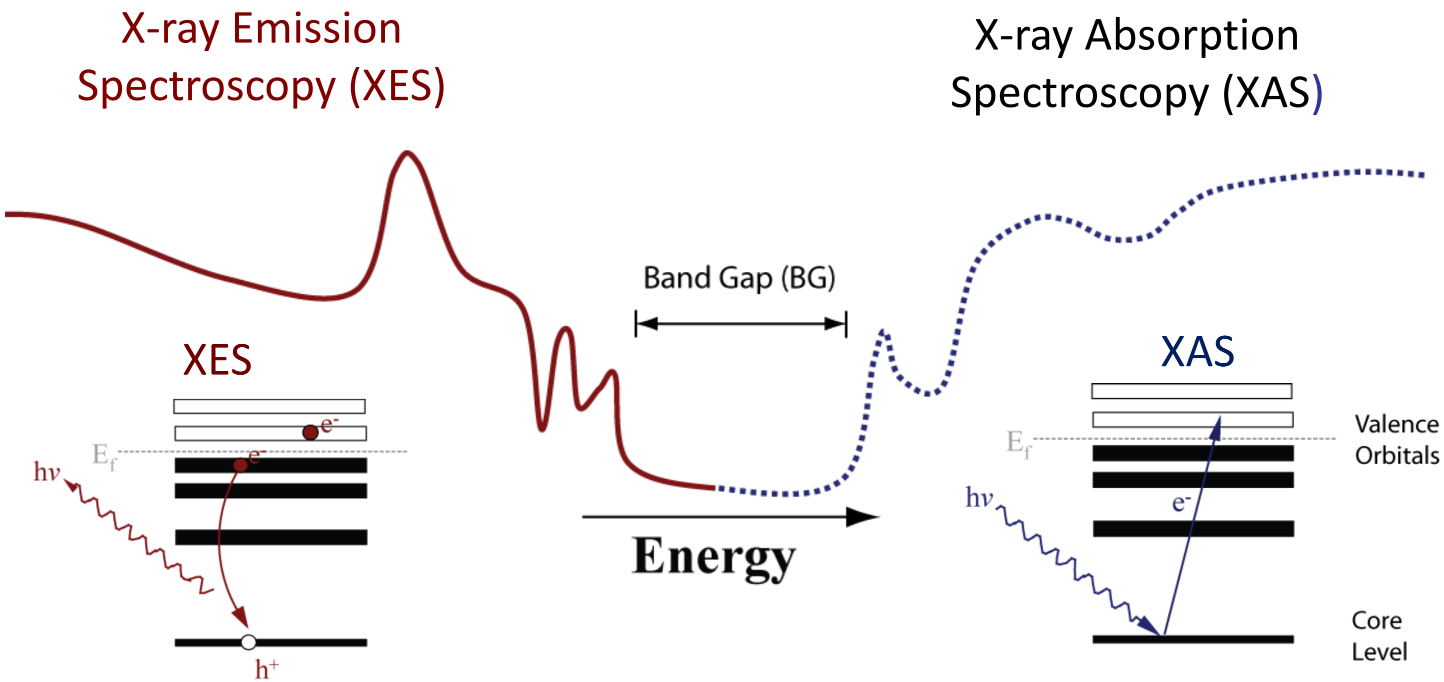
- Advanced Light Source (LBNL):
  - Near-Ambient-Pressure XPS* beamlines *(requires approved ALS user proposal)*

- In development at Sandia, CA:
  - *Lab-based Near-Ambien-Pressure XPS**

**** Clean transfer from glove box available for all techniques***

X-ray Emission and Absorption Spectroscopy

X-ray spectroscopies enable element-specific characterization of the electronic density of states (DOS)

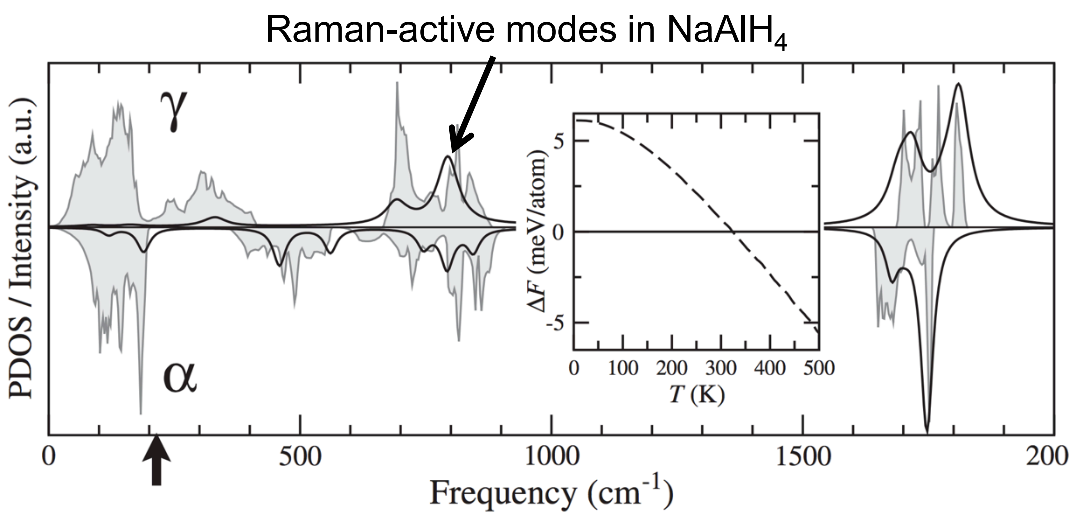


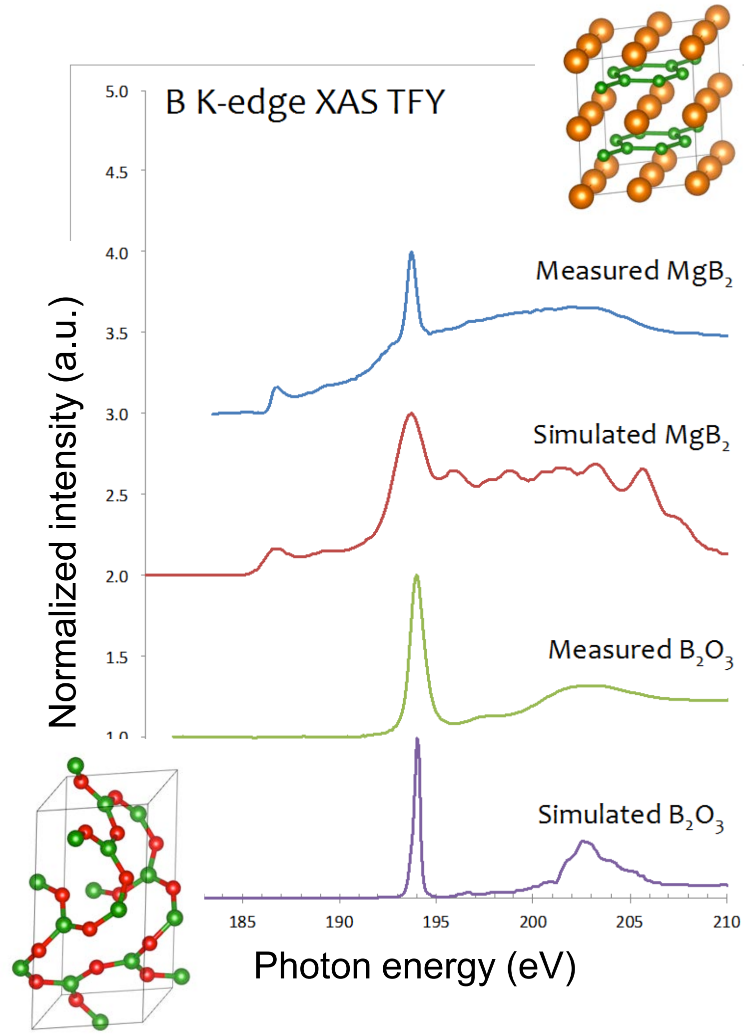
- Measurement of the occupied DOS
- Resolve structure of filled electronic density of states states

- Angular momentum resolved probe of the unoccupied electronic DOS
- Provides structure and bonding information
- Suitable for amorphous and crystalline materials – incl. short range order.

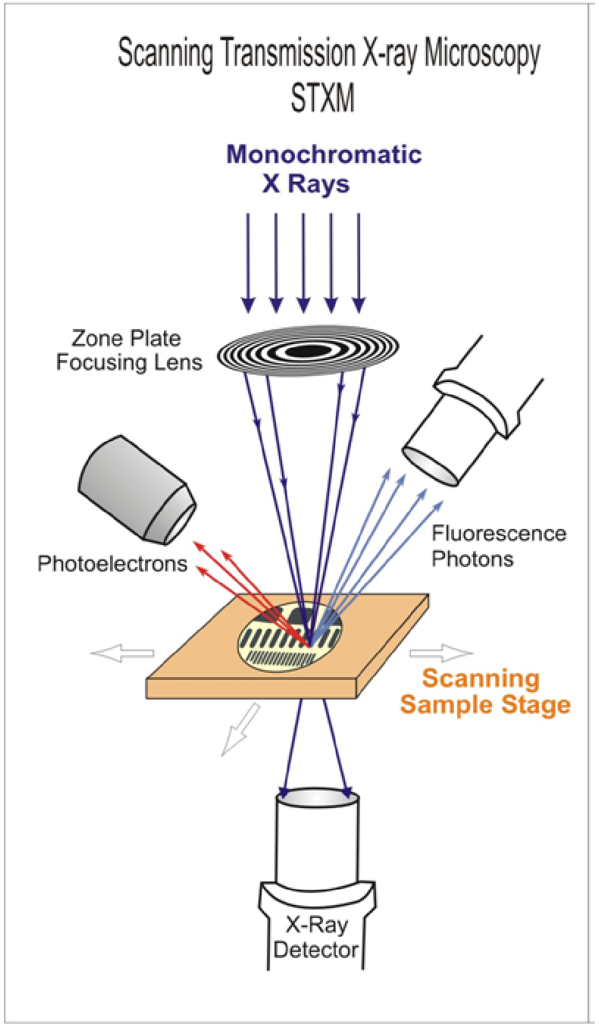
Computational spectroscopy

- X-ray spectroscopic simulations for interpreting XAS, XES, and XPS data
- Infrared and Raman spectroscopic simulations
- Calculation of NMR chemical shifts



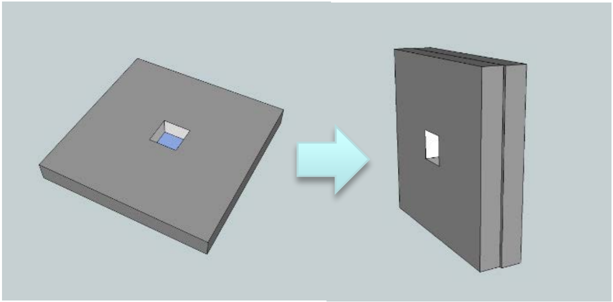


X-ray spectromicroscopy – spatially resolved XAS

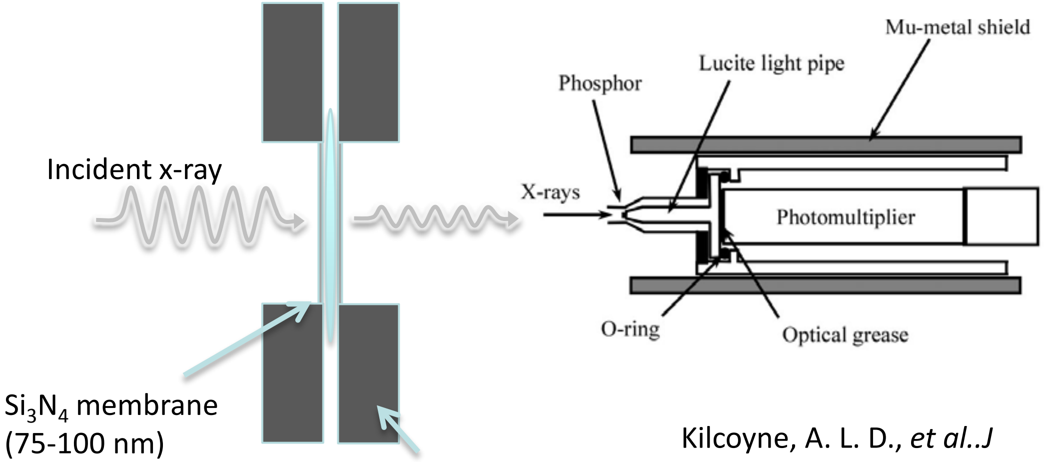


Simple and reliable approach for in situ STXM

Material sealed between two Si_3N_4 membranes



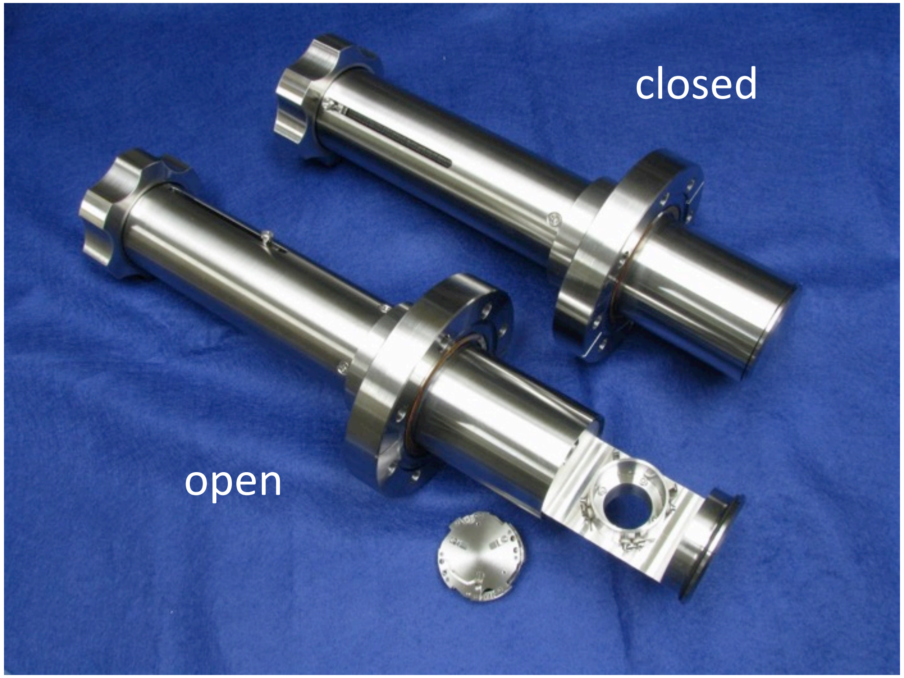
Schematic of experimental set-up

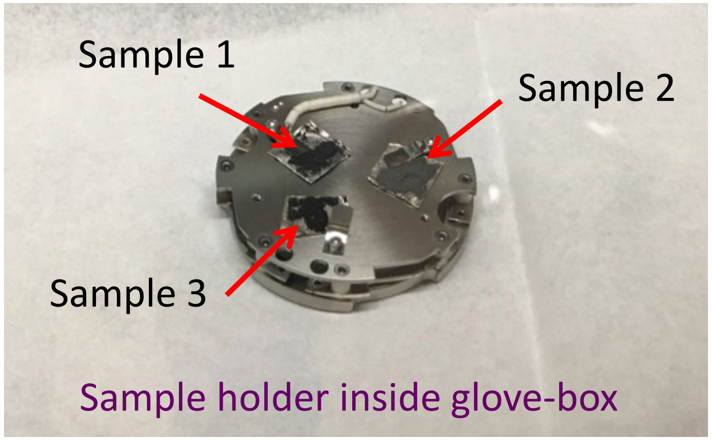


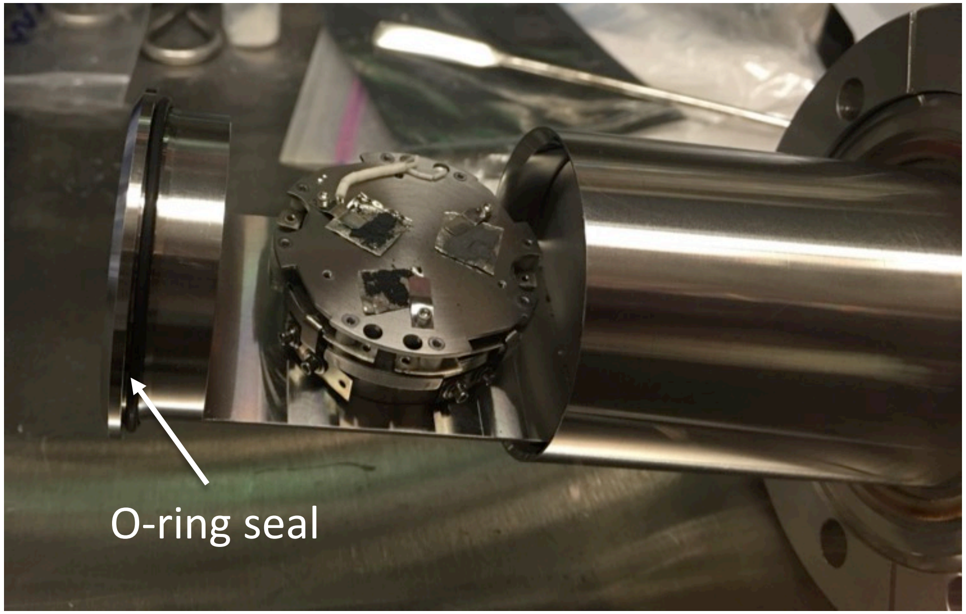
Kilcoyne, A. L. D., *et al..J Synchrotron Rad*. **2003**, 10, 125

- Scan sample - transmitted intensity provides image
- Zone plate: ~ 25 nm resolution

Clean transfer systems ensure materials can be examined without adventitious oxide formation or contamination from air exposure



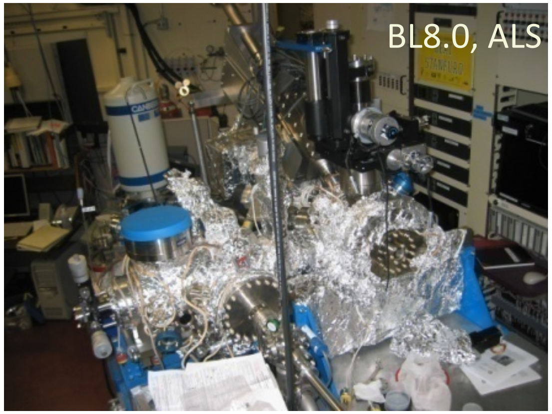




- Designed and fabricated at Sandia
- Transfers samples under inert atmosphere

- Available for XPS systems at Sandia & ALS
- Available for LEIS/AES

Synchrotron techniques implemented under HyMARC

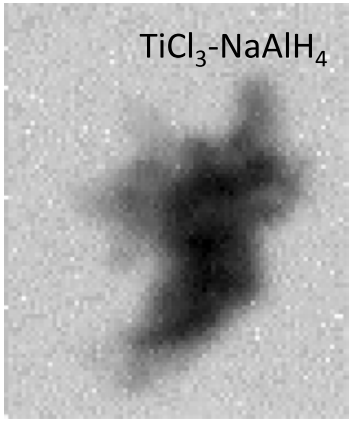


X-ray Emission and Absorption Spectroscopy (XES/XAS)

Beamline 6.3.1.2 (ISAAC), ALS – Approved Program

Beamline 8.0.1.1, ALS – General User Proposal

REIXS beamline, CLS – General User Proposal

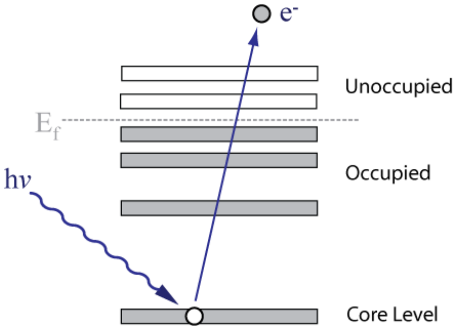


X-ray Spectromicroscopy – Scanning Transmission X-ray Microscopy (STXM)

Beamline 5.3.2.2, ALS – Approved Program

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

Beamline 11.0.2, ALS – Director's Discretion Access



Community tools

Open-source software

Phase fraction prediction code (thermodynamics)

Phase field modeling for hydrogen storage in hydrides (kinetics)

Kinetic Monte Carlo (transport)

Distributed/federated database development

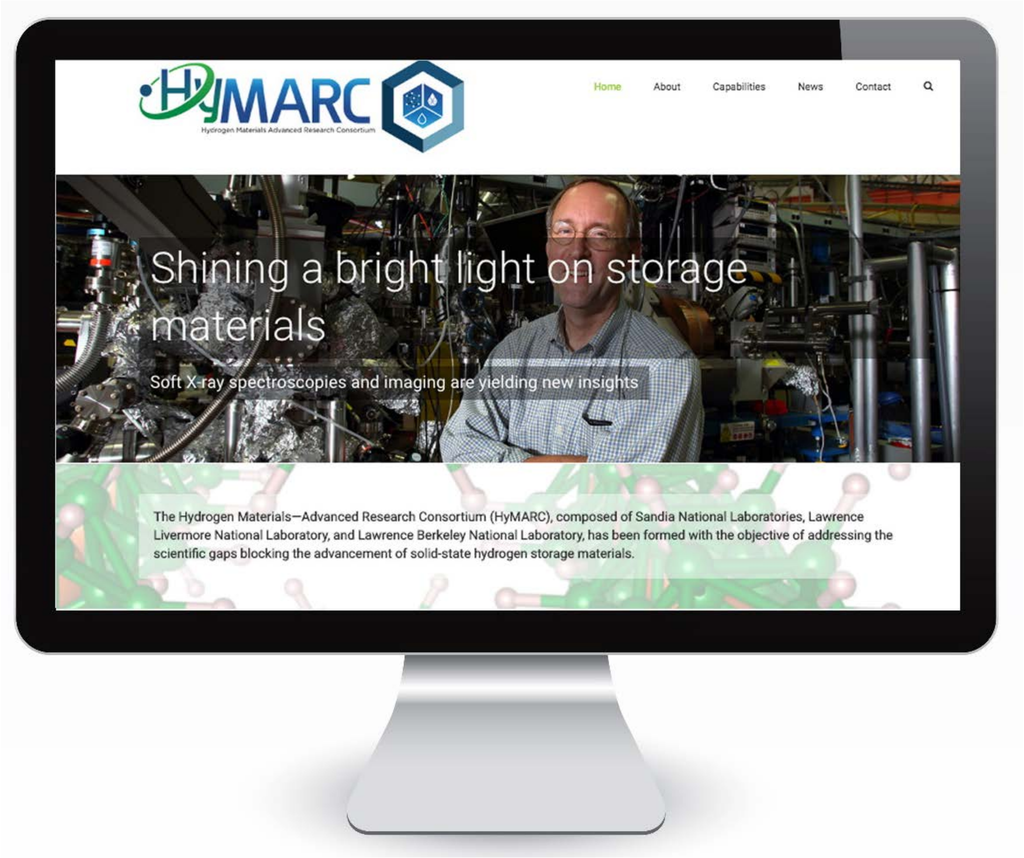
What properties belong in the materials database?

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

HyMARC web site is on line

https://hymarc.org/



- **Capabilities descriptions**
- **Contact information**
- **Recent news**

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

Thank you

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hydrogenandfuelcells.energy.gov

Question and Answer

Please type your questions into the question box