# Hydrogen Materials Advanced Research Consortium


**Sponsor: DOE—EERE/Fuel Cell Technologies Office**


**Consortium Director:** Dr. Mark D. Allendorf

**Partner Laboratories:**

Sandia National Laboratories

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# Presentation topics

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

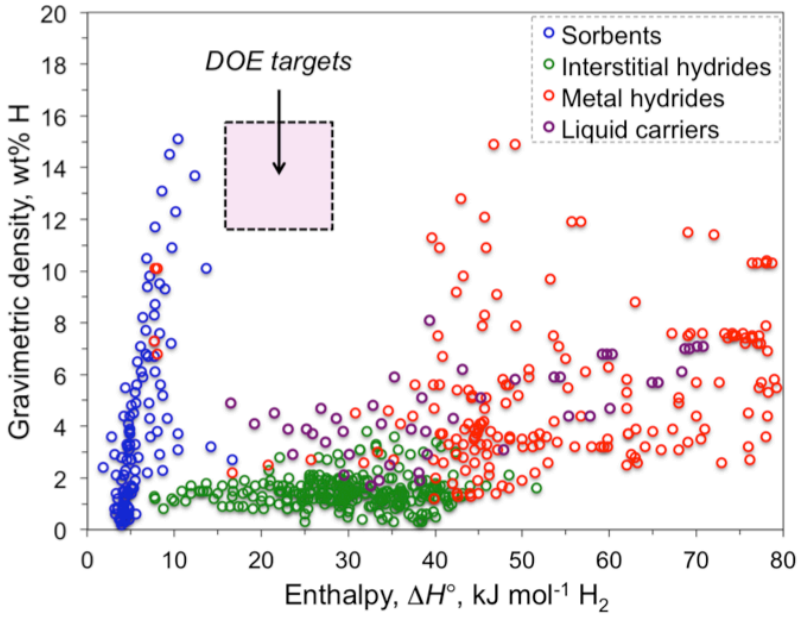
# Critical Scientific Challenges (Identified by NREL PI meeting, Jan. 2015)

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

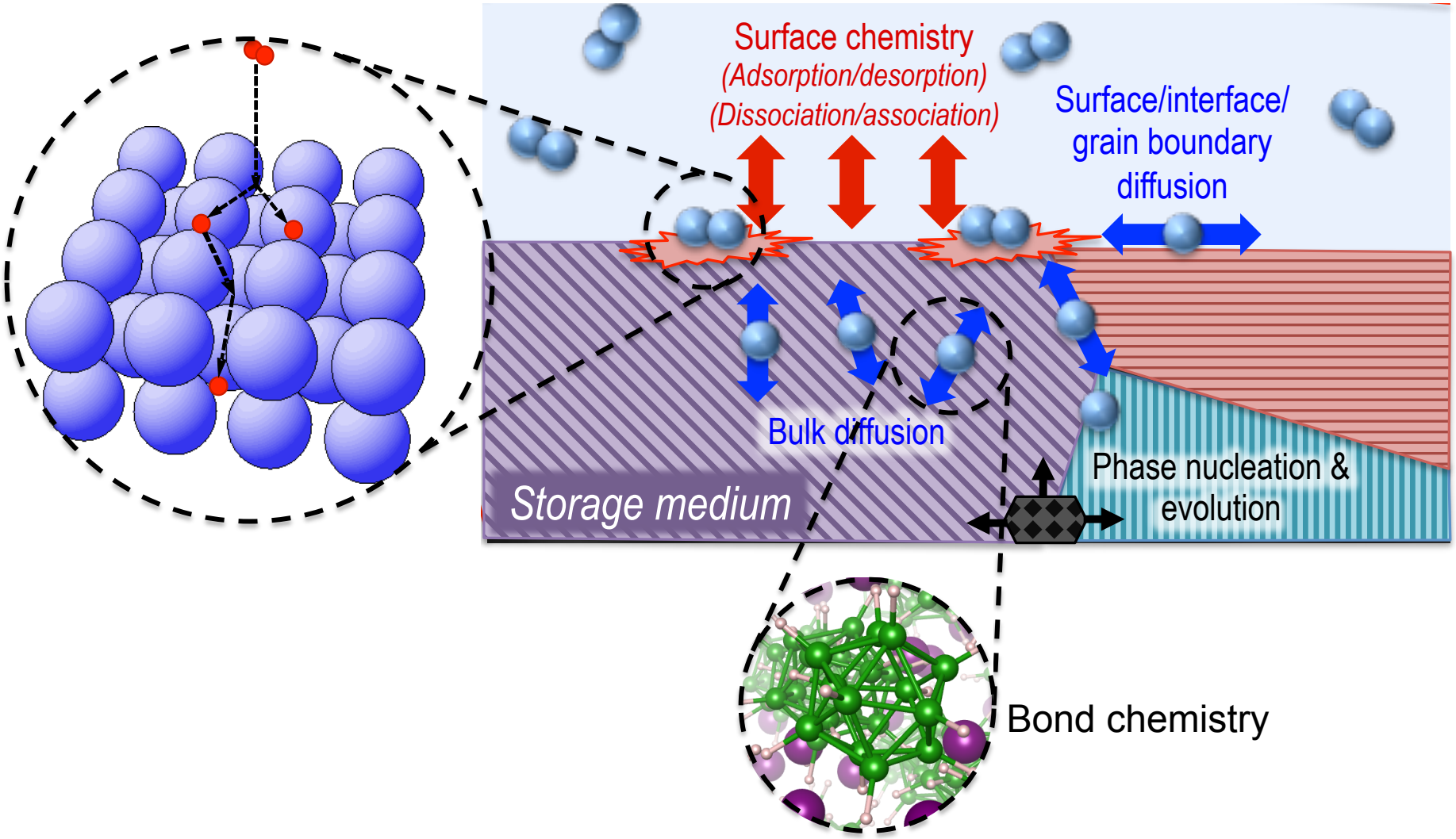
- Volumetric capacity at operating temp.
- Increased usable hydrogen capacity needed
- Distribution of $H_2$ binding sites and ΔH at ambient temperature not optimized

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

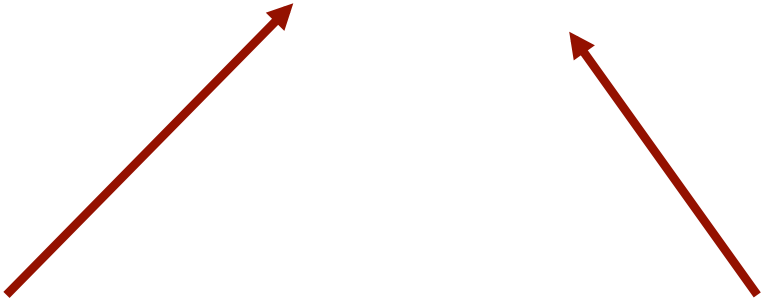
- Multi-physics software, methods, and models optimized for high-throughput material screening using the large-scale parallel computing facilities of the three partners
- Sustainable, extensible database framework for measured and computed material properties
- Protocols for synthesizing storage materials 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"

$$\Delta E(T) = \Delta H°(T) + E_a$$



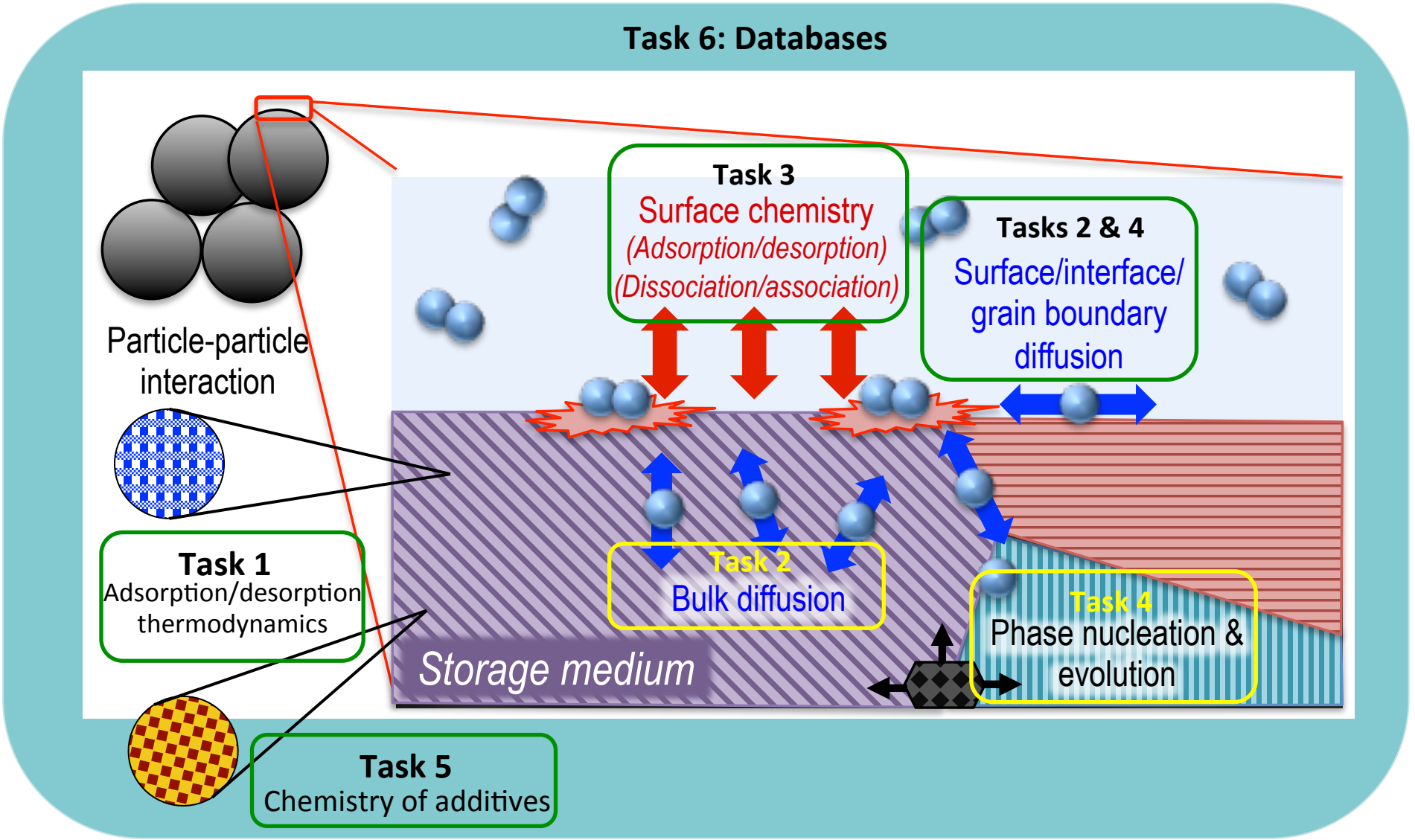
**Thermodynamics of uptake and release**
**Tasks 1**

- 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

**Brandon Wood**
**LLNL Lead**

**Mark Allendorf**
**Director**
**SNL Lead**

**Jeff Urban**
**LBL Lead**
**David Prendergast**
**Deputy**

Budget POC
**Jeff Roberts**

Budget POC
**Landon Daft**

Budget POC
**Katherine Britton**

Task 2
Transport
**Tae Wook Heo**

Task 1
Thermodynamics
**Vitalie Stavila**

Task 4
Sol.-Sol. Interfaces
**Jeff Urban**

Task 3
Surface Chem.
**Robert Kolasinski**

**POC: David Prendergast**

Task 5
Additives
**Lennie Klebanoff**

**POC: Jinghua Guo**

Task 6
Databases
**Brandon Wood**

# All consortium partners and their unique capabilities contribute to each task

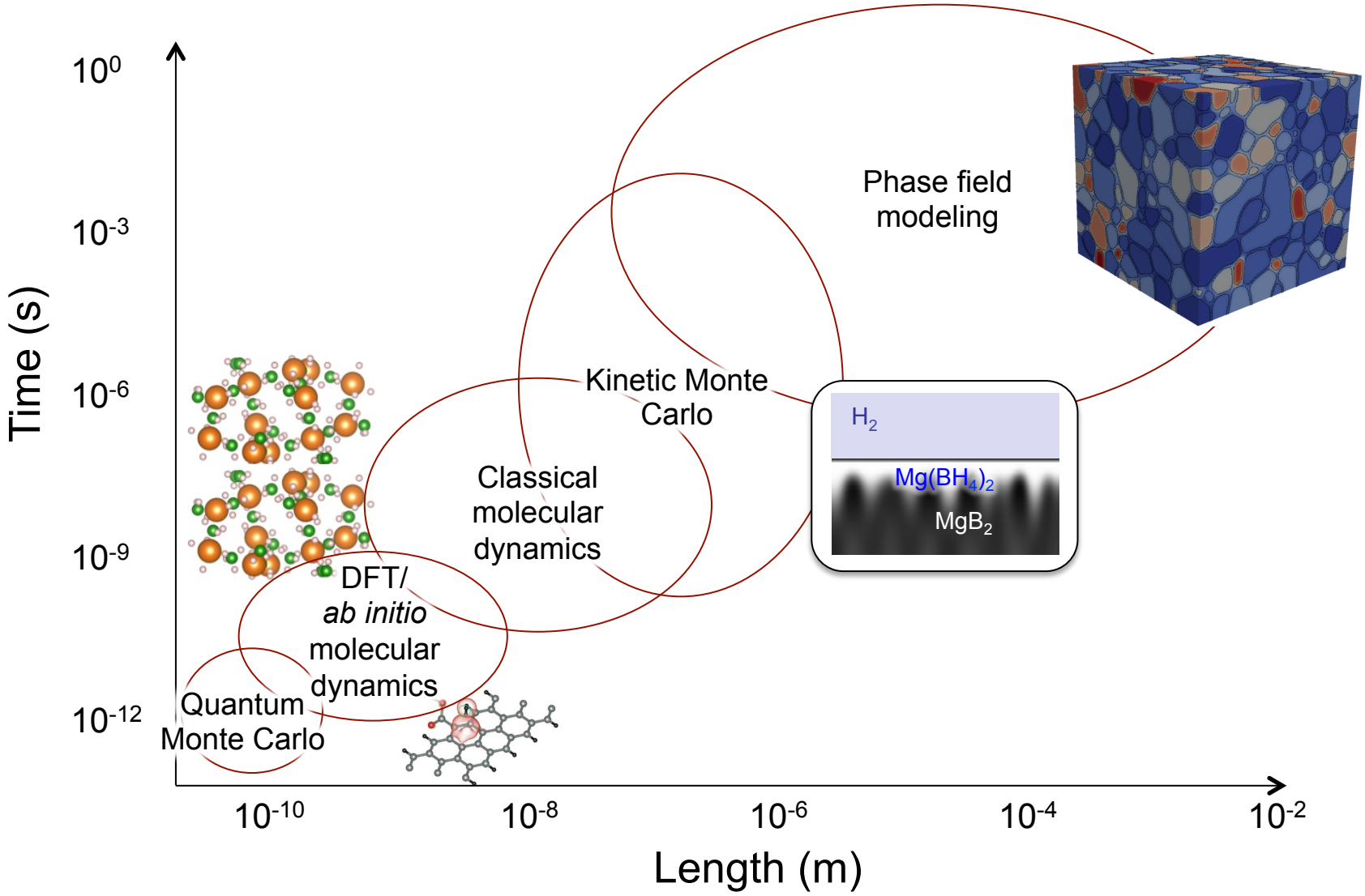
| | Task 1 | Task 2 | Task 3 | Task 4 | Task 5 | Task 6 |
|---|---|---|---|---|---|---|
| | Synthesis of bulk and nanoscale metal hydrides and MOFs | | | | | |
| Sandia National Laboratories | | LEIS | LEIS, XPS | | LEIS, XPS | |
| | Ultra-high pressure reactor | Atomistic modeling of large systems | XPS & AP-XPS | Atomistic modeling | | |
| Lawrence Livermore National Laboratory | Tailored graphene sorbents | XAS, XES | | XAS, XES | XAS, XES | Database concepts |
| | Multi-scale modeling tools | | | | | |
| BERKELEY LAB | Graphene Nanobelts | Soft x-ray characterization tools (ALS) | | | | CoRE Database |
| | Encapsulated metal hydrides | Modeling for x-ray spectroscopies (MOLECULAR FOUNDRY) | | | | |
| | Lewis acid/base sorbent chemistry | | | Electron microscopies (MOLECULAR FOUNDRY) | Catalytic nanoparticles on mesoporous supports | |

# 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

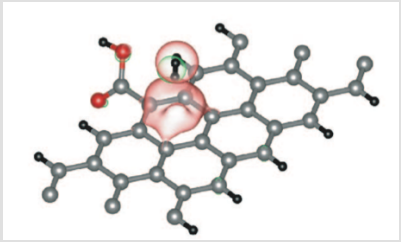
# A suite of techniques for multiscale simulations are a key capability of the HyMARC Core Team



# Quantum Monte Carlo for accurate sorbent energetics

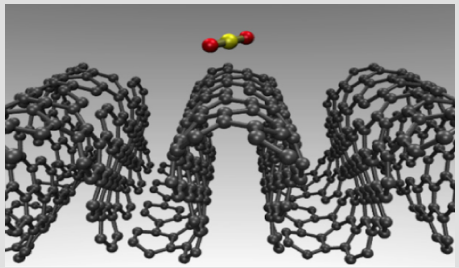
Stochastic quantum method for beyond-DFT accuracy for $H_2$-metal energetics and Lewis acid-base interactions

## Carbon sorbents



Chemical functionalization (edge and surface)

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



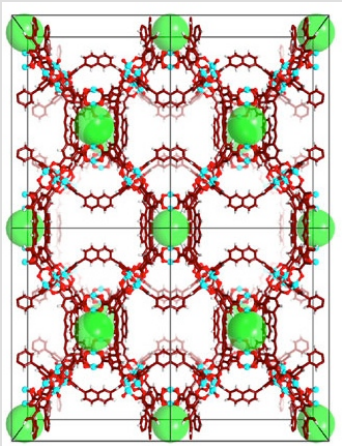
Curvature and strain

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

## Metal-organic frameworks (MOFs)

Open metal sites

Organic linkers

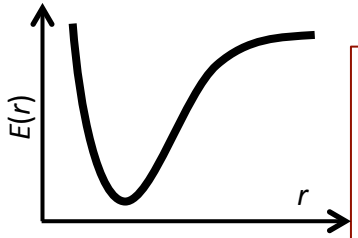


Crystal structure/ coordination

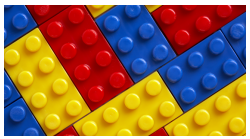
QMCPACK

Office of Basic Energy Sciences · Serving the Present, Shaping the Future

National Science Foundation




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



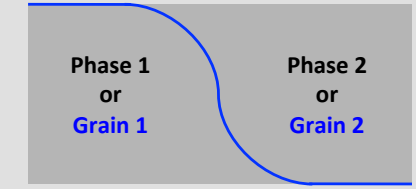
# Phase-field modeling (PFM): Solid-state phase transformation kinetics

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

## General Framework

Theory / Information of materials

<Diffuse-interface description>




$\eta, X, \ldots$ : "Phase-field" variables that describe microstructures (can represent non-conserved or conserved quantities)

Mathematical modeling

$$F = \int dV[f(\eta, X, \ldots) + (\text{gradient energy}) + (\text{long-range interactions}) + \ldots]$$

Numerically solving Governing equations

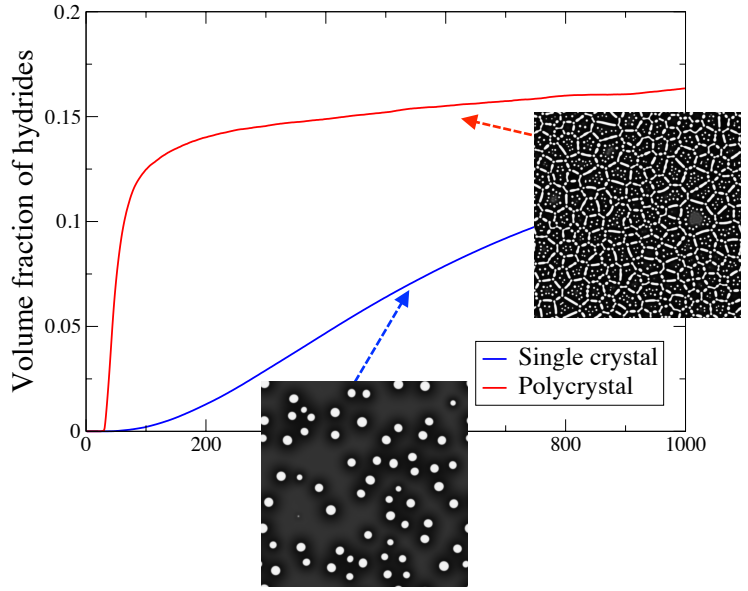
$$\frac{\partial \eta(\vec{r},t)}{\partial t} = -L\left(\frac{\delta F}{\delta \eta}\right)$$ : Allen-Cahn equation (*Non-conserved field*)

$$\frac{\partial X(\vec{r},t)}{\partial t} = \vec{\nabla}\cdot\left[M\vec{\nabla}\left(\frac{\delta F}{\delta X}\right)\right]$$ : Cahn-Hilliard equation (*Conserved field*)

*Kinetic Phase Microstructure evolution*

## Kinetic evolution of microstructure

<Phase nucleation/polycrstallinity>





**T.W. Heo**, S. Bhattacharyya, L.-Q Chen, *Acta Mater.*, **59**, 7800 (2011)

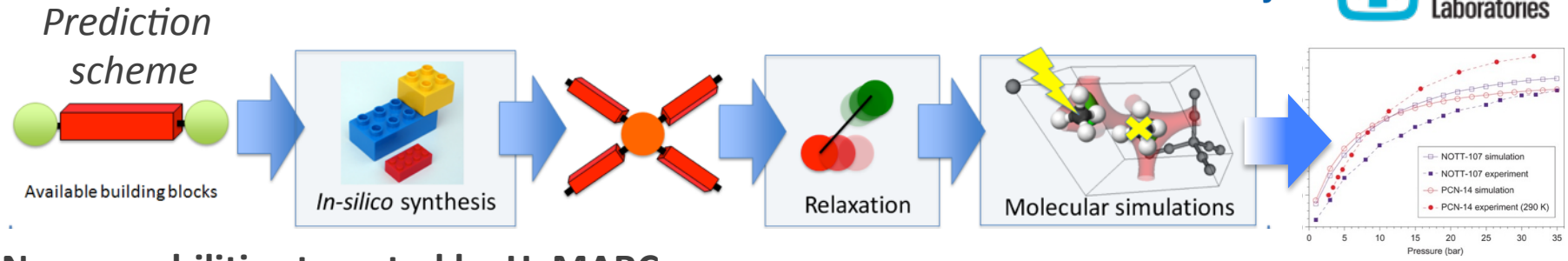
**T.W. Heo**, S. Bhattacharyya, L.-Q. Chen, *Phil. Mag.*, **93**, 1468 (2013)

**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***

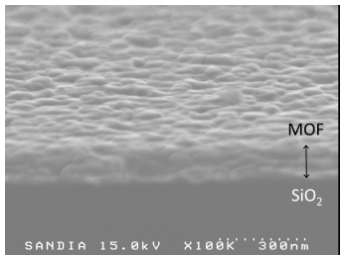



GCMC simulations

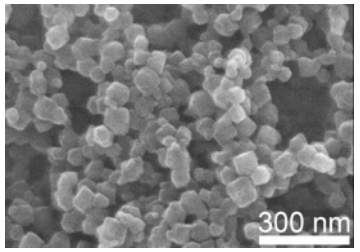
**New capabilities targeted by HyMARC:**

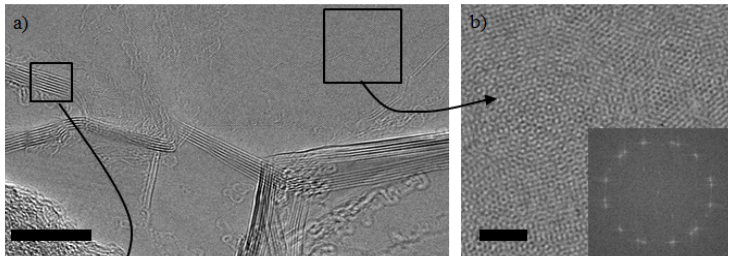
- Accurate simulation of strong adsorption sites
- Library of structural motifs for forcefield development (e.g. open metal sites in MOFs, dopants in porous carbons)
- Models that account for effects of:
  - Morphology (e.g. particle size/shape/aspect ratio, core-shell geometry, etc.)
  - Additives
- 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?***

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**Phase minimization strategies:** overcome transport problems due to phase segregation

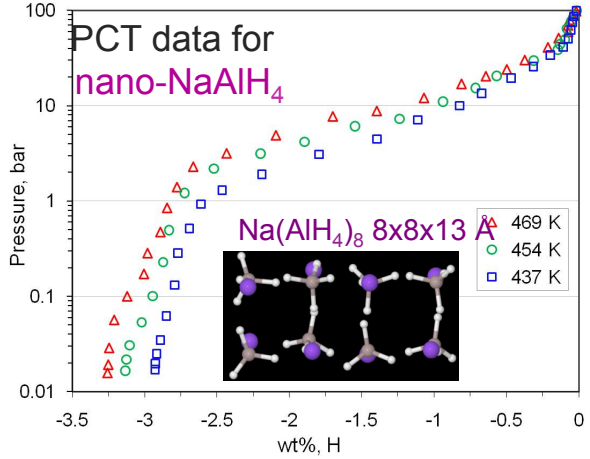
**Doping and defect creation:** solid solutions to minimize the number of solid phases

**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



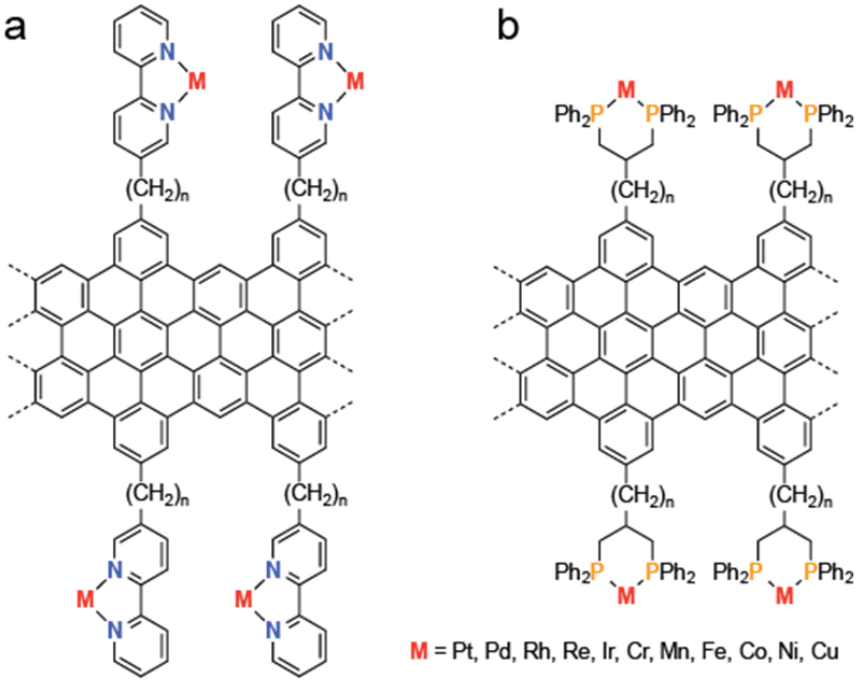

Top left: variable-T ball mill.
Top right: ultra-high pressure cell

# 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

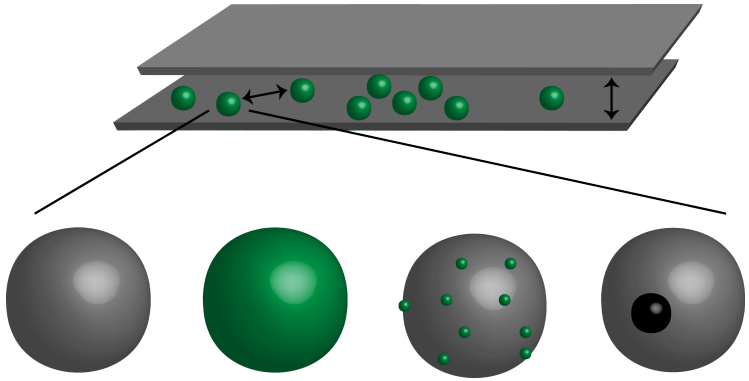
Quite adaptive: catalytic metals, or chelating and ED/EWD groups




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.

# Hierarchical integrated hydride materials

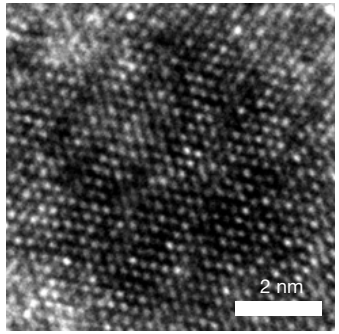


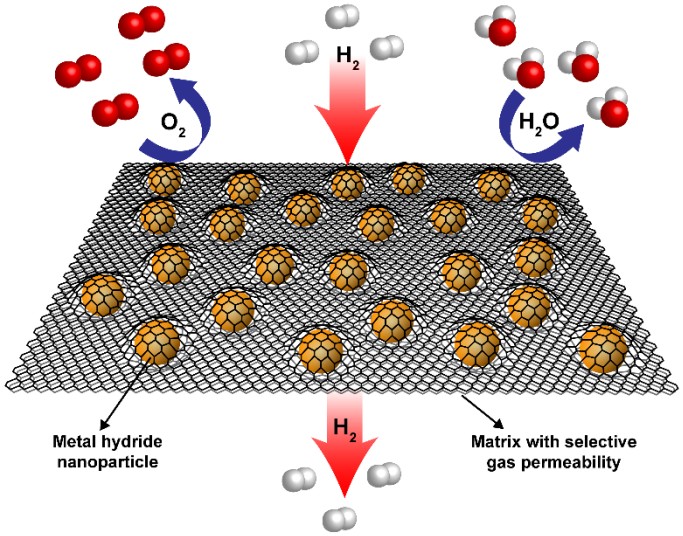
Want to have clear model systems to drive fundamental understanding

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



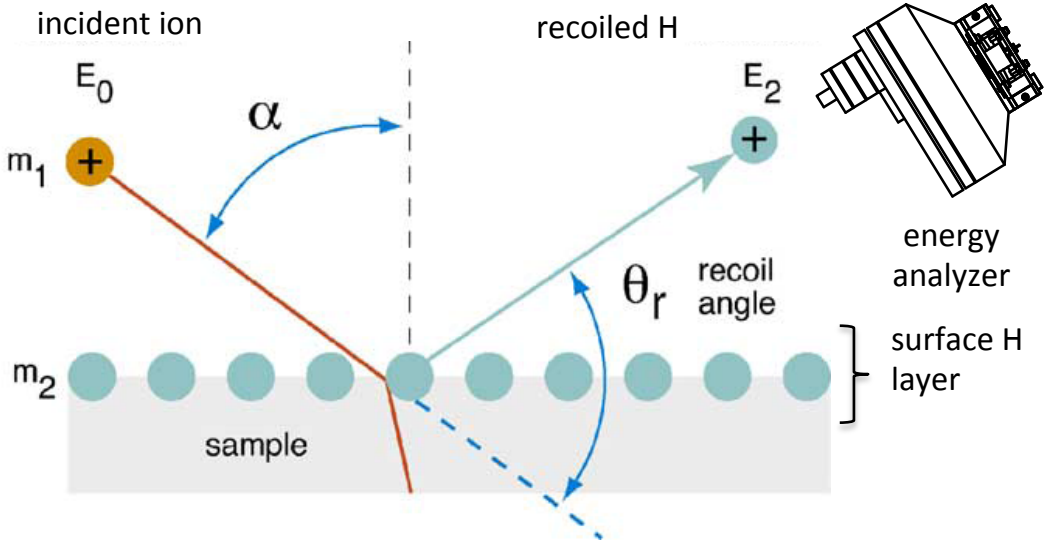

E.S.Cho et al, *submitted* (2015)

*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

- 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).

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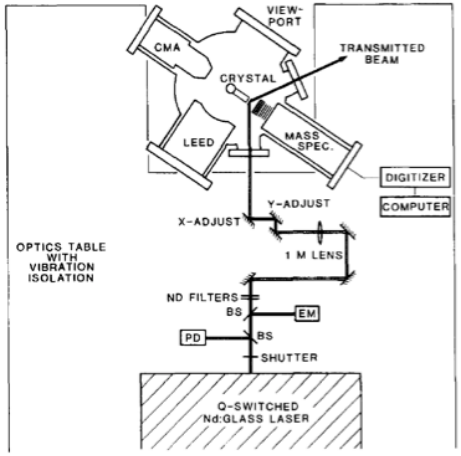
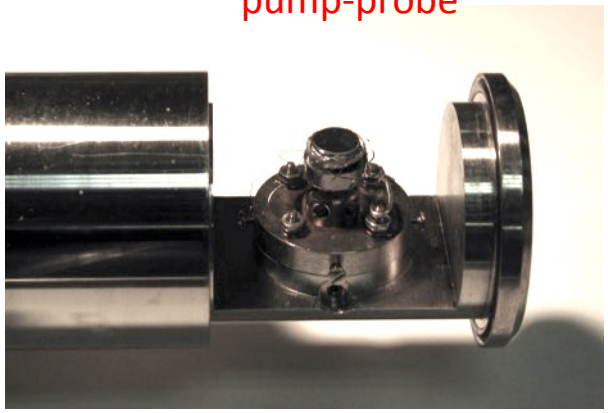



laser-induced desorption pump-probe

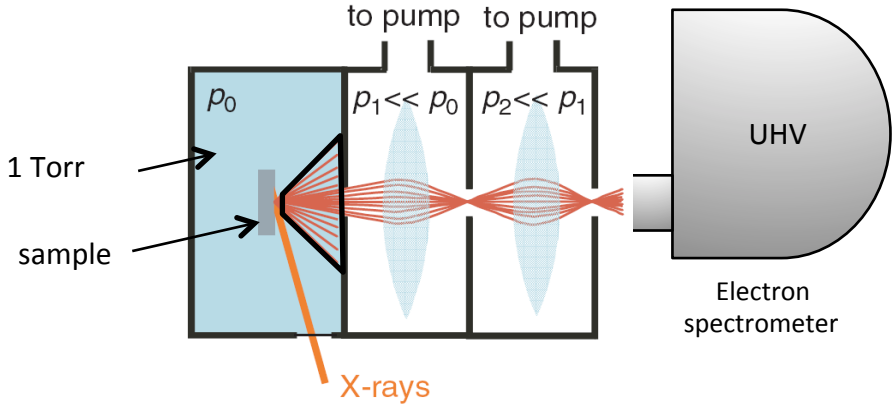


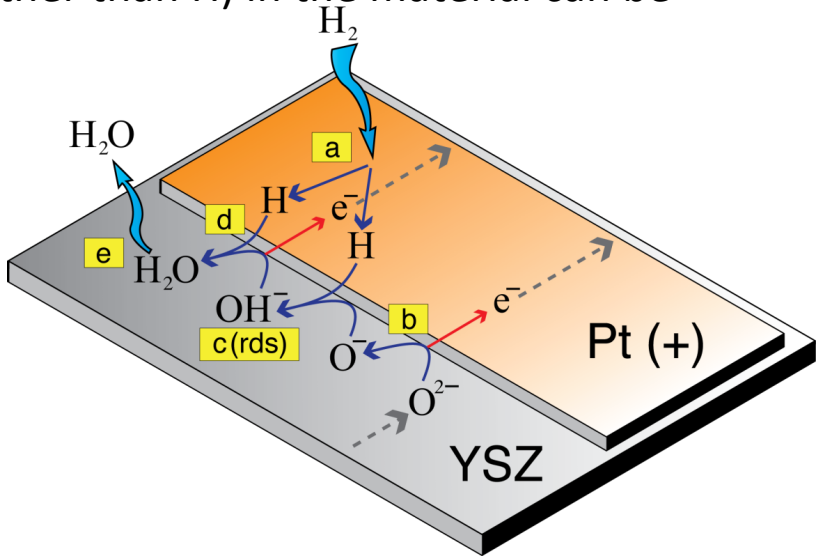
clean sample transfer container

# 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).

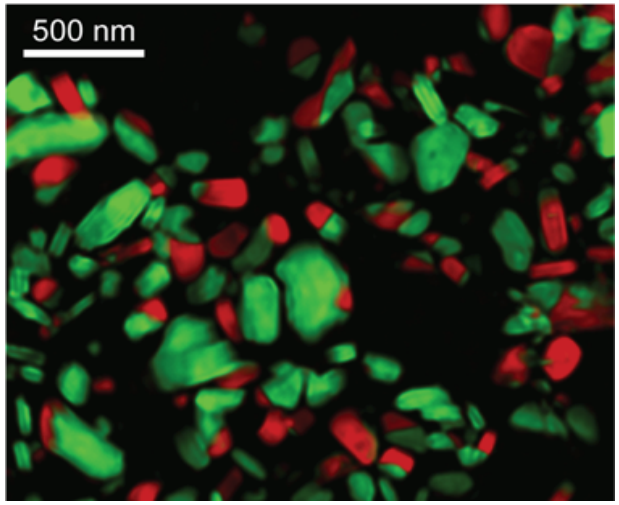
# Soft X-ray spectroscopy and microscopy at the Advanced Light Source

***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.

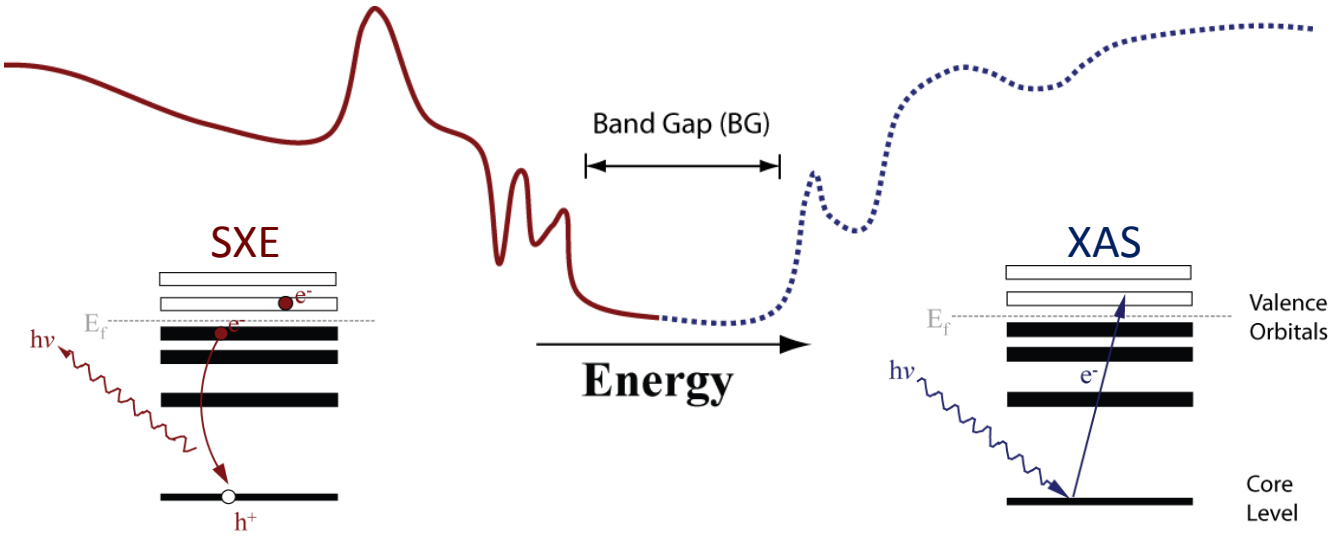
*HyMARC is developing a clean-transfer system to eliminate ambient exposure of samples during transfer from glove-boxes to AP-XPS and STXM (collaboration with LBNL and ALS).*

# 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*

Soft X-ray Emission (SXE) spectroscopy

X-ray Absorption Spectroscopy (XAS)




- 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

**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