

Hydrogen Materials Advanced Research Consortium



Sponsor: DOE—EERE/Fuel Cell Technologies Office



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Partner 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)

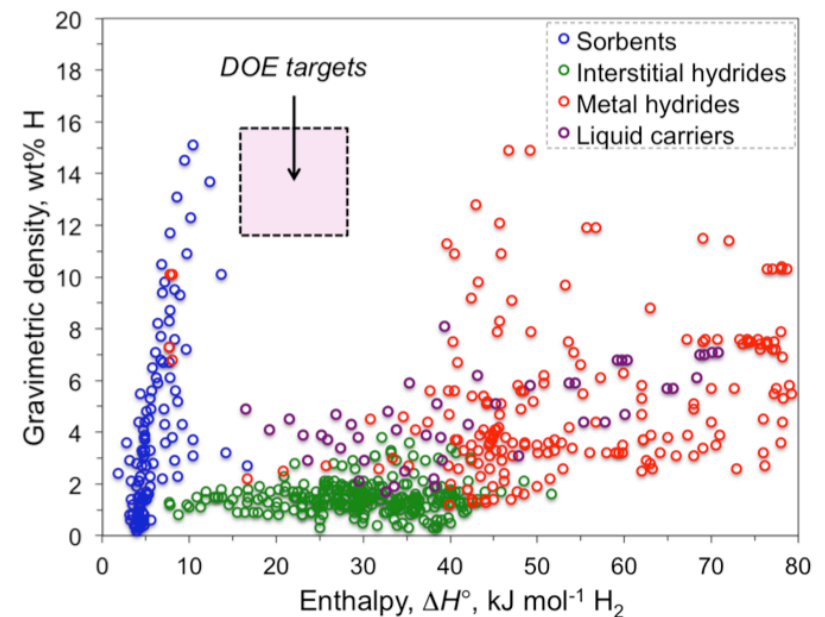


Sorbents: Eng. COE target: 15 – 20 kJ/mol

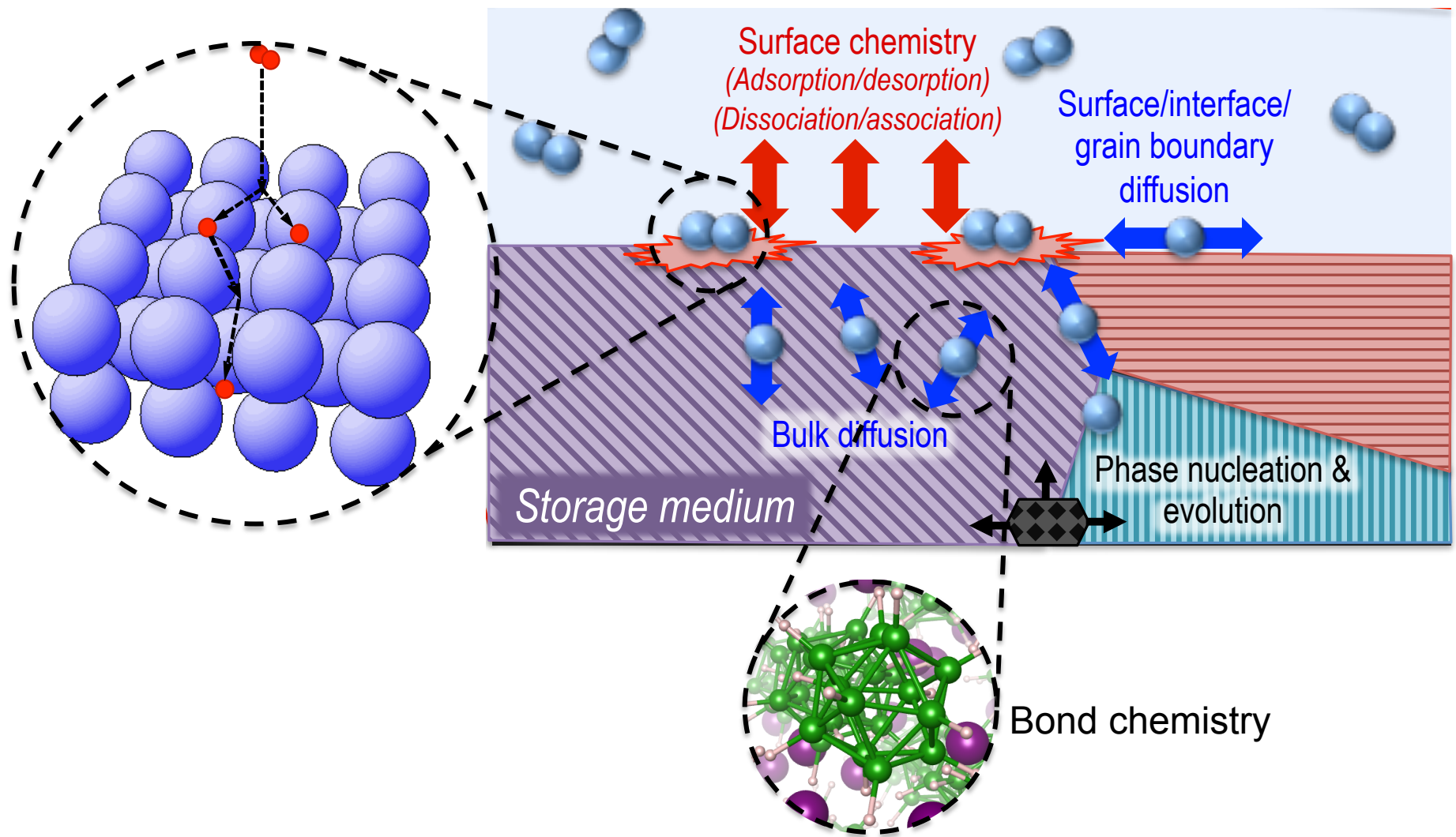
- Volumetric capacity at operating temp.
- Increased usable hydrogen capacity needed
- Distribution of H₂ binding sites and ΔH at ambient temperature not optimized

Metal hydrides: Eng. COE target: ≤ 27 kJ/mol H₂

- 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 H₂ storage

focuses activities on two overarching aspects of storage materials

“Effective thermal energy for H₂ release”

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

Thermodynamics of uptake and release
Tasks 1

- Sorbents
- Hydrides

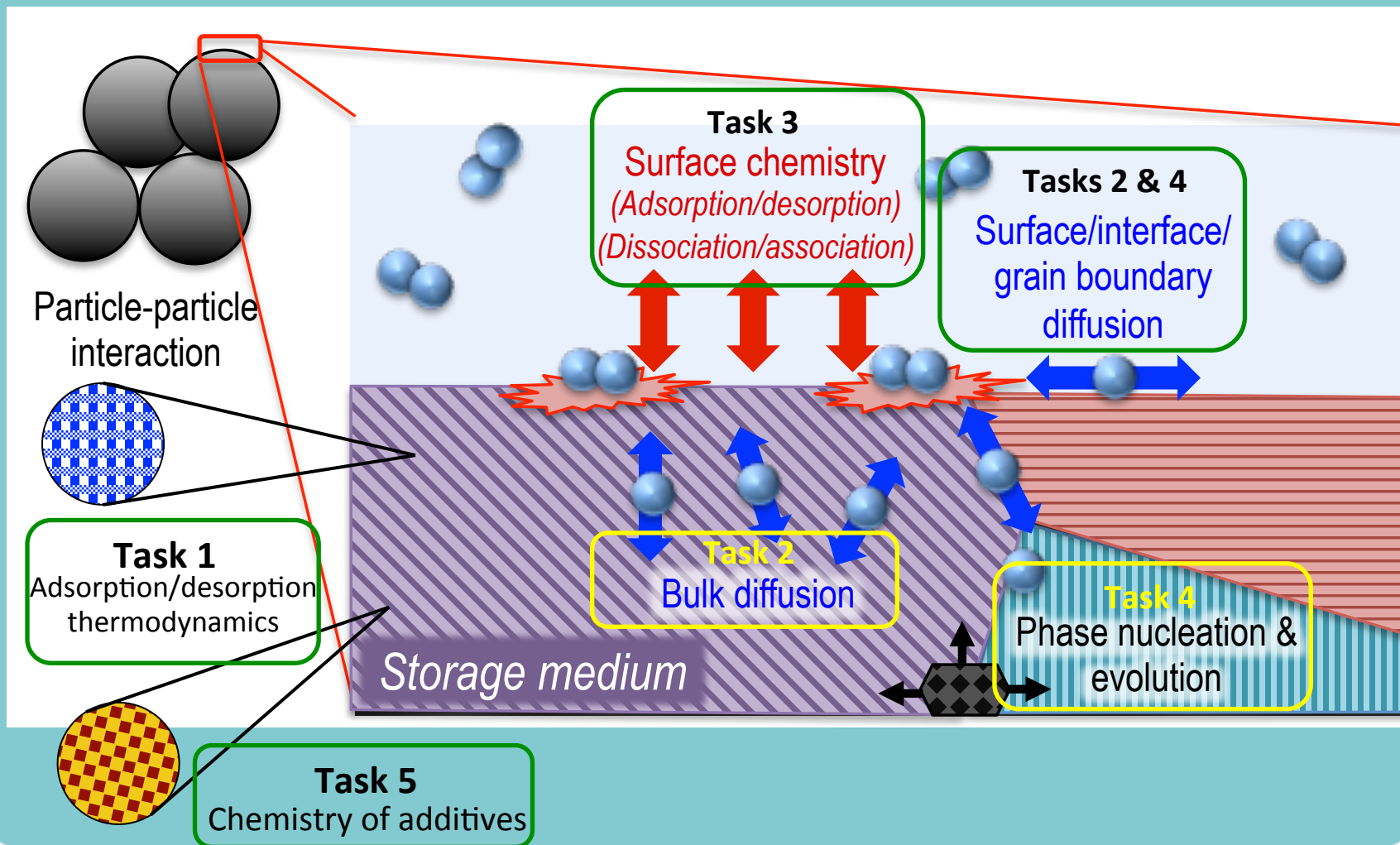
Kinetics of uptake and release
Tasks 2, 3, 4, and 5

- Surface reactions
 - Mass transport
 - Solid-solid interfaces
 - Additives
-
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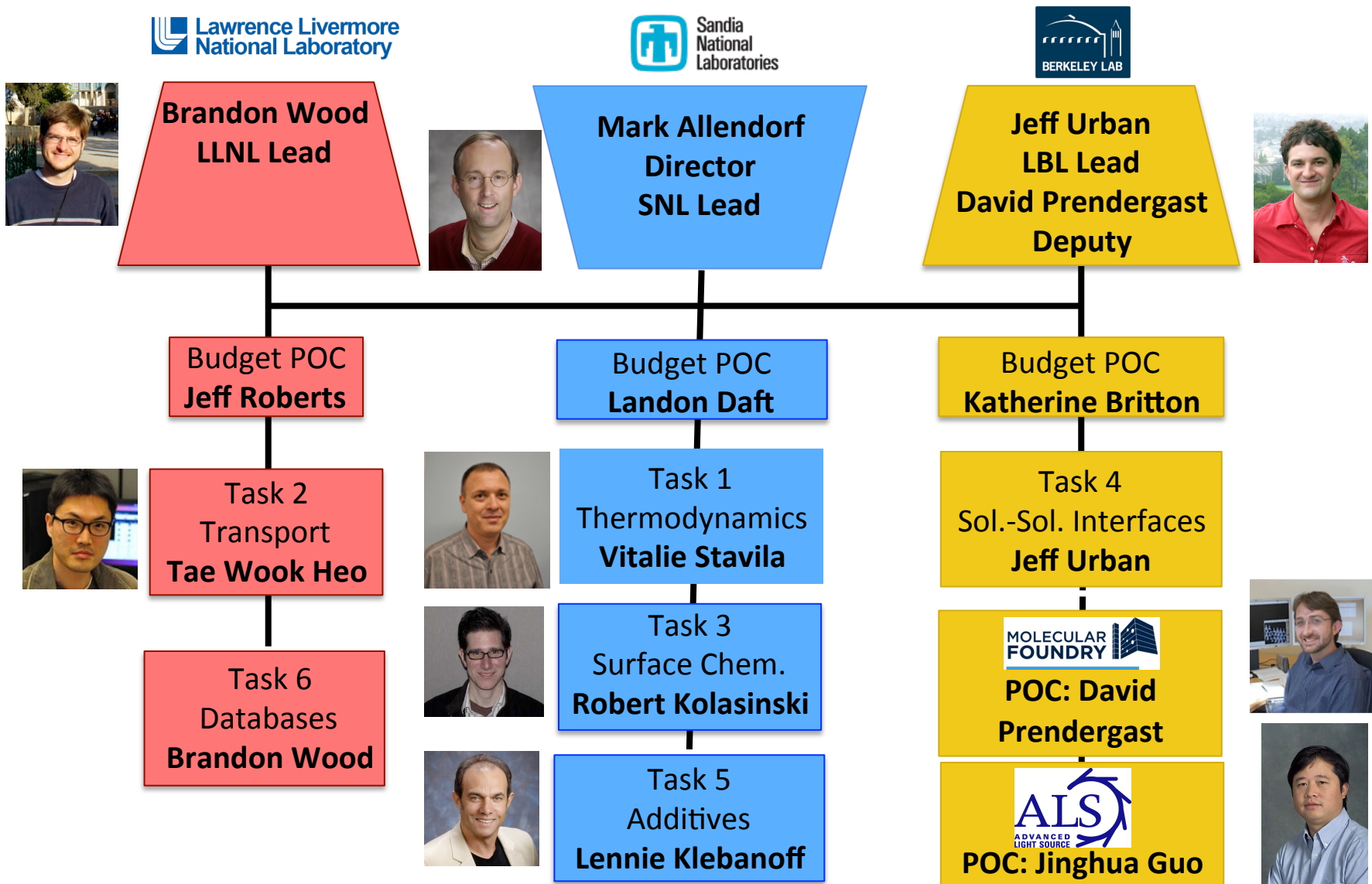
HyMARC tasks address the critical scientific questions limiting the performance of solid-state storage materials



Task 6: Databases









Organizational structure of Core Team




All consortium partners and their unique capabilities contribute to each task



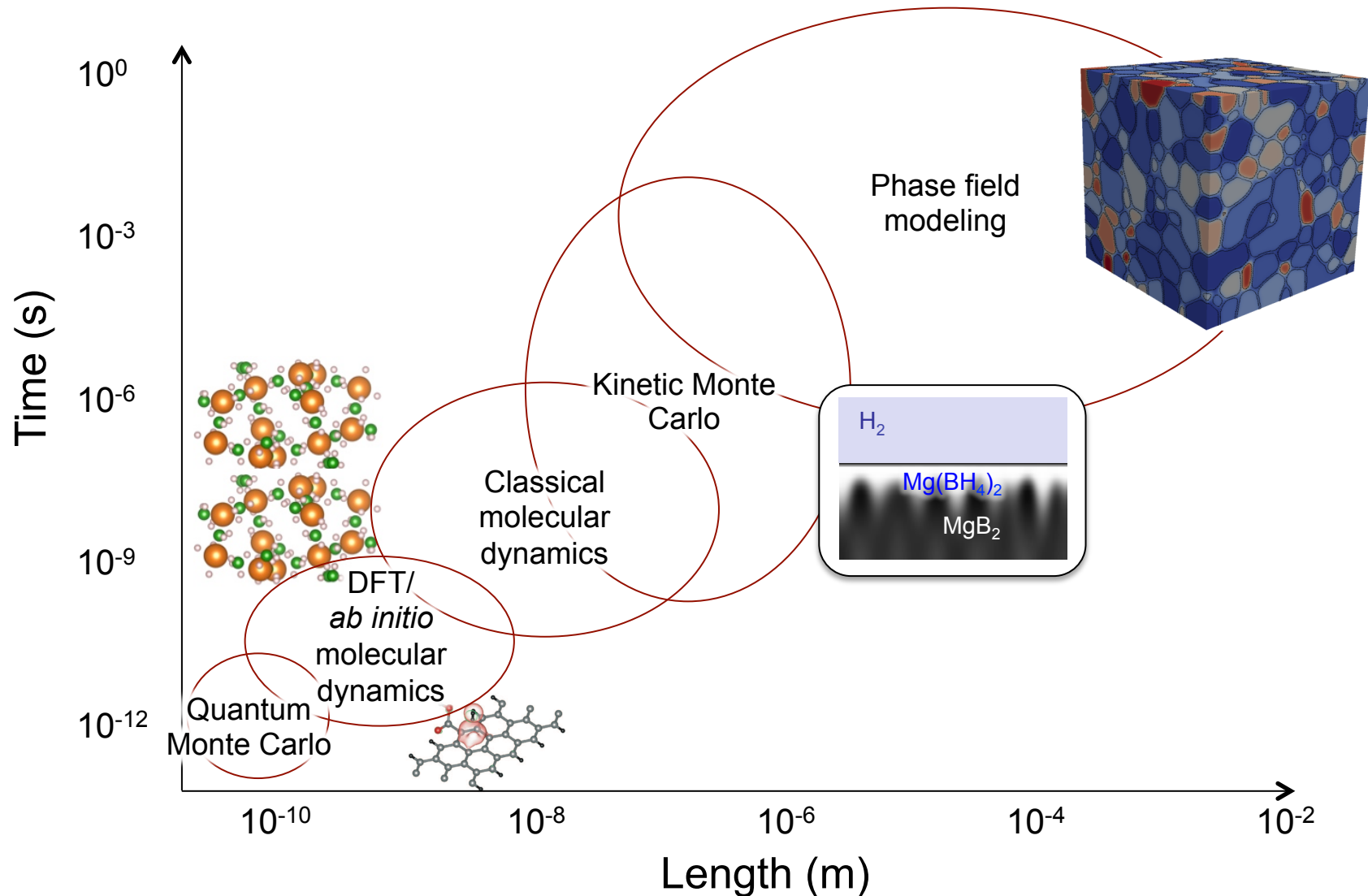
	Task 1	Task 2	Task 3	Task 4	Task 5	Task 6
 Sandia National Laboratories	Synthesis of bulk and nanoscale metal hydrides and MOFs					
		LEIS	LEIS, XPS		LEIS, XPS	
	Ultra-high pressure reactor	Atomistic modeling of large systems	XPS & AP-XPS	Atomistic modeling		
 Lawrence Livermore National Laboratory	Tailored graphene sorbents	XAS, XES		XAS, XES	XAS, XES	Database concepts
	Multi-scale modeling tools					
 BERKELEY LAB	Graphene Nanobelts	Soft x-ray characterization tools 				CoRE Database
	Encapsulated metal hydrides	Modeling for x-ray spectroscopies 				
	Lewis acid/base sorbent chemistry			Electron microscopies 	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
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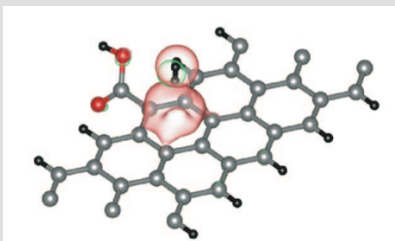
A suite of techniques for multiscale simulations are a key capability of the HyMARC Core Team



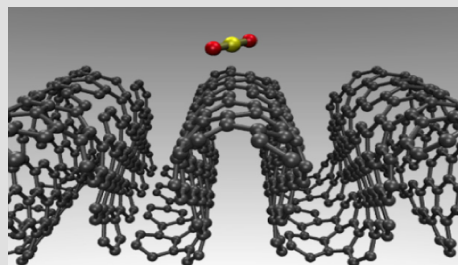
Quantum Monte Carlo for accurate sorbent energetics

Stochastic quantum method for beyond-DFT accuracy for H₂-metal energetics and Lewis acid-base interactions

Carbon sorbents



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



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

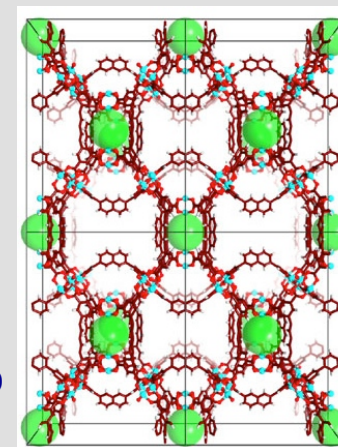
Chemical
functionalization
(edge and
surface)

Curvature
and strain

Metal-organic frameworks (MOFs)

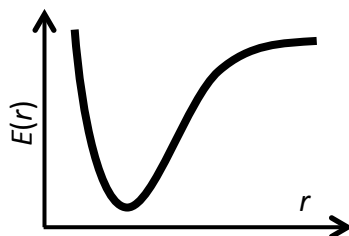
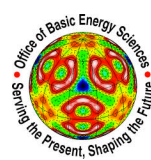
Open metal sites

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

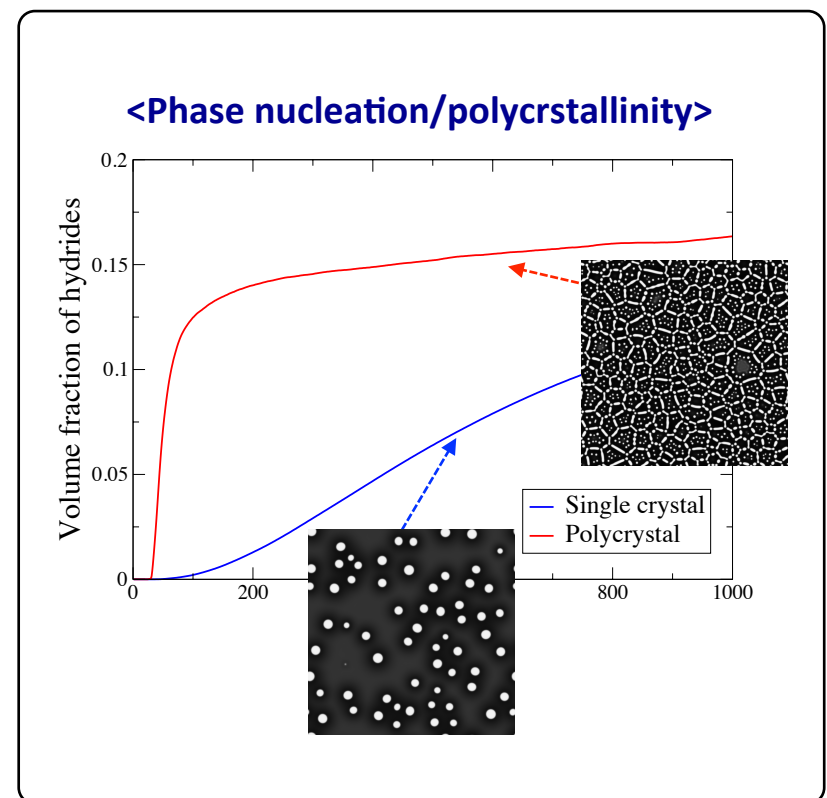
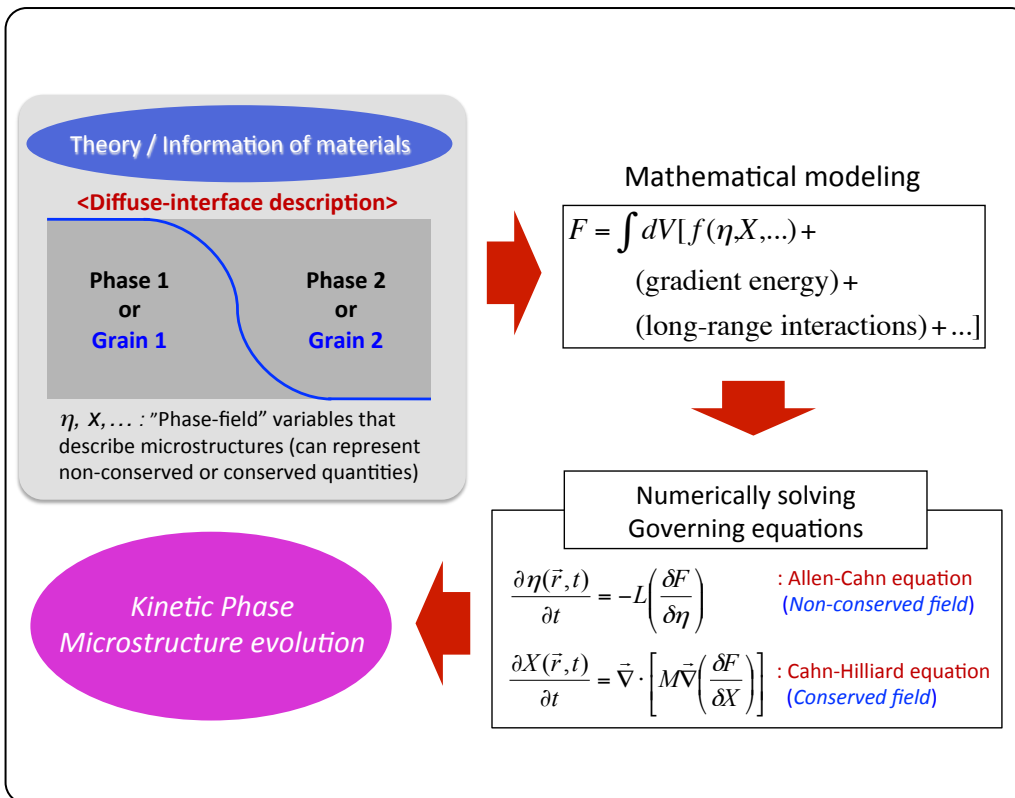


Phase-field modeling (PFM): Solid-state phase transformation kinetics

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



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

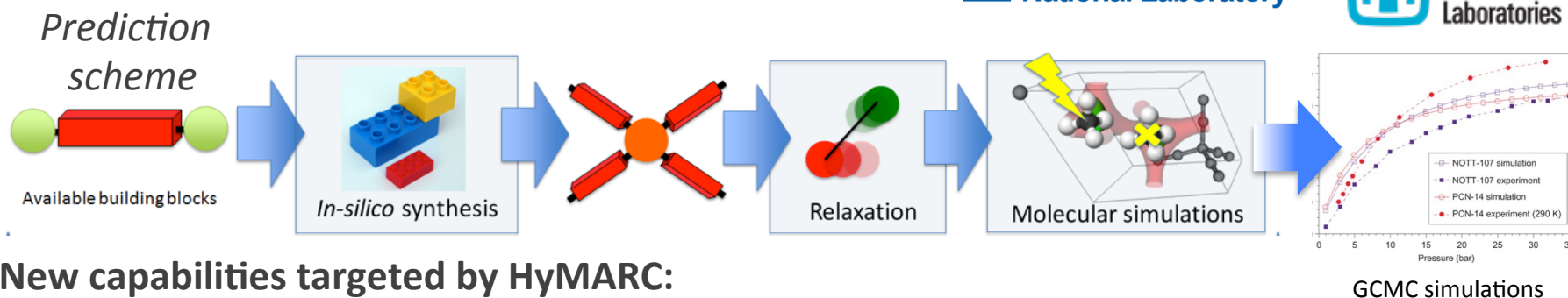
T.W. Heo, S. Bhattacharyya, L.-Q. Chen, *Phil. Mag.*, **93**, 1468 (2013)

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

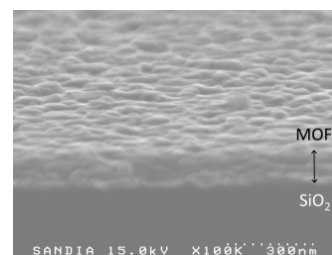
Goal: validated theoretical models that can serve as the basis for high-throughput computational material design



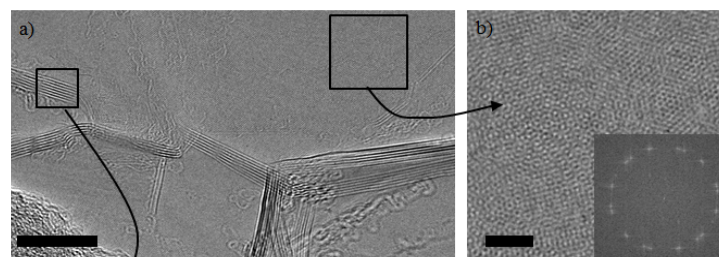
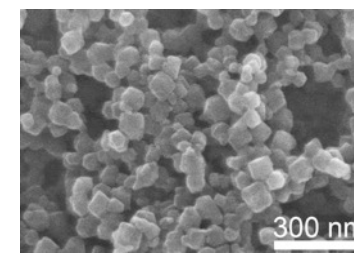
New capabilities targeted by HyMARC:

- 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 , \rightarrow complex hydrides/no “molecular” species (e.g. NaAlH_4)
 \rightarrow Hydrides with highest complexity (phase segregation+molecular species; e.g. $\text{Mg}(\text{BH}_4)_2$)

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



Phase minimization strategies: overcome transport problems due to phase segregation

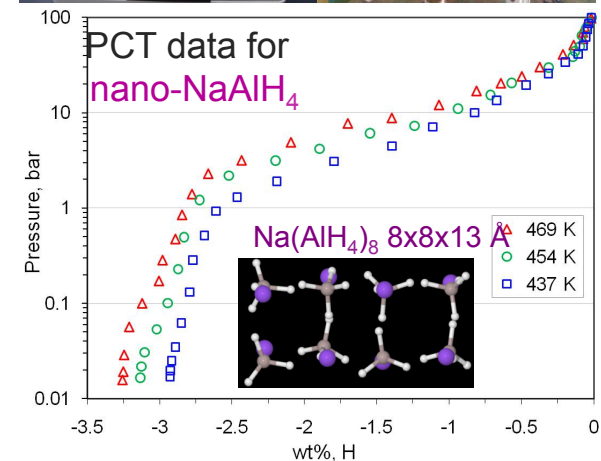
Doping and defect creation: solid solutions to minimize the number of solid phases

Entropy tuning: crystalline-to-amorphous transitions to improve ΔG°

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.

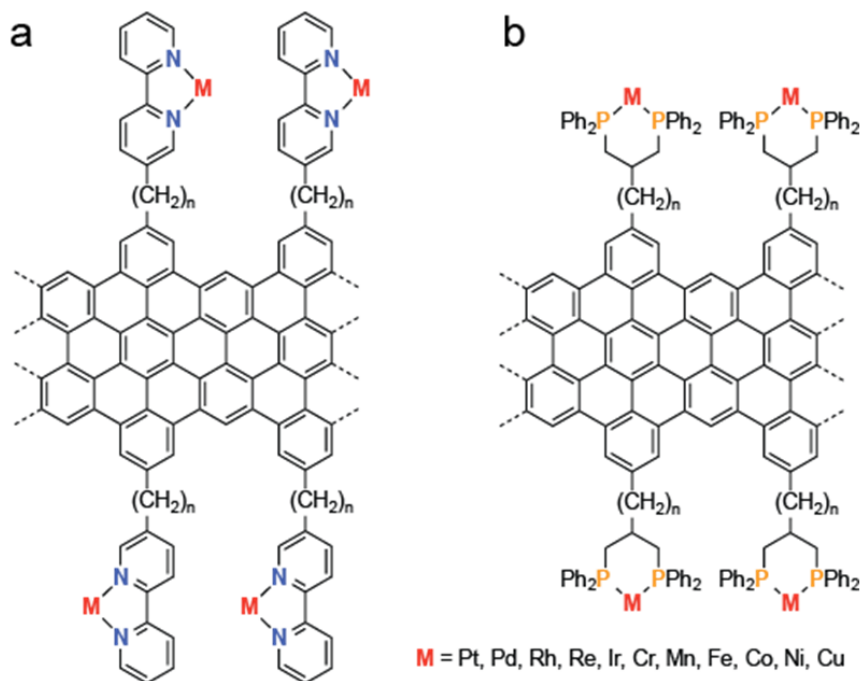
Top right: ultra-high pressure cell

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

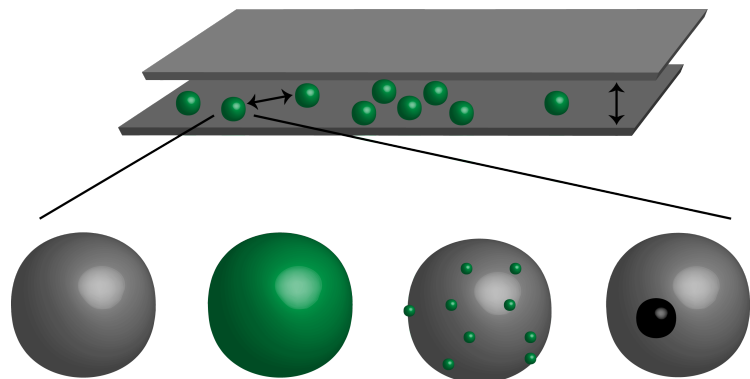
Quite adaptive: catalytic metals, or chelating and ED/EWD groups



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

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

Hierarchical integrated hydride materials



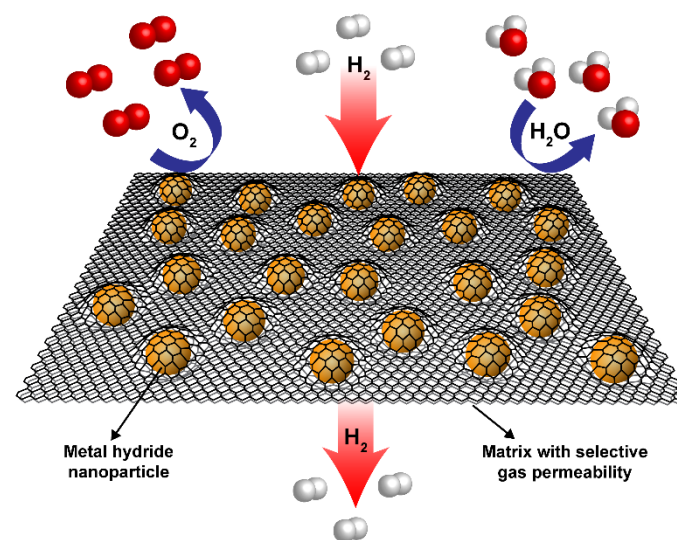
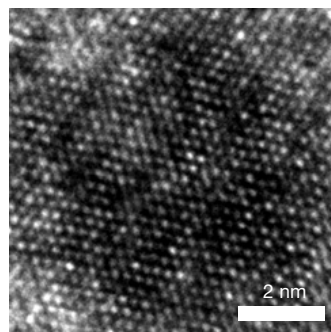
Want to have clear model systems to drive fundamental understanding



Also push the development of advanced materials: from Mg and Al to complex hydrides such as LiNH_2 , $\text{Mg}(\text{BH}_4)_2$

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



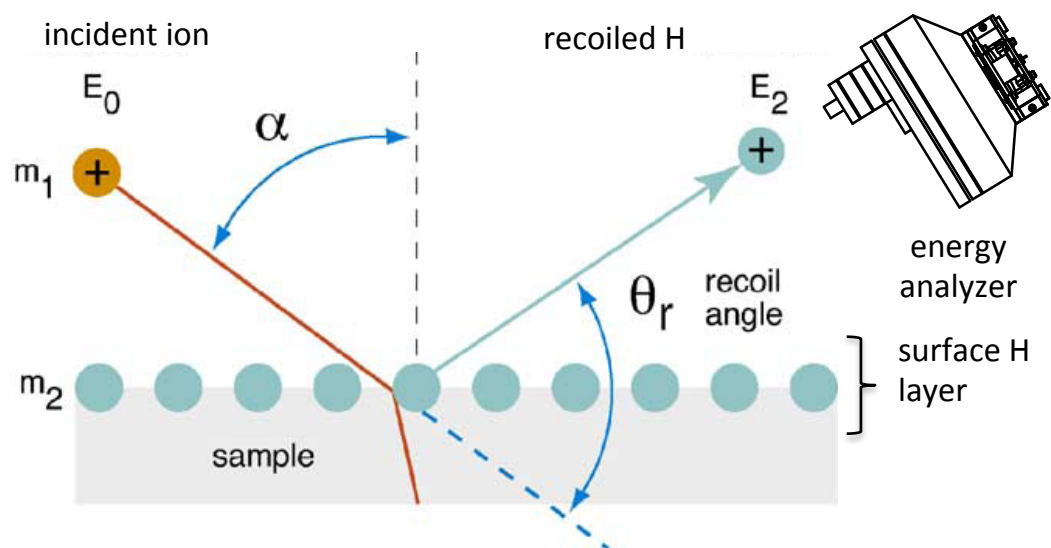
E.S.Cho et al, *submitted* (2015)

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

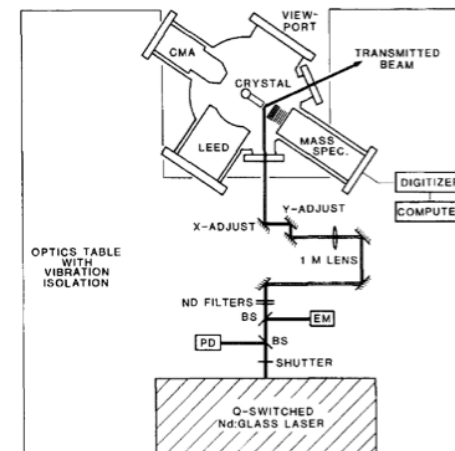
Bardhan, Ruminski, et al. *En. Environ. Sci.*, (2013)

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

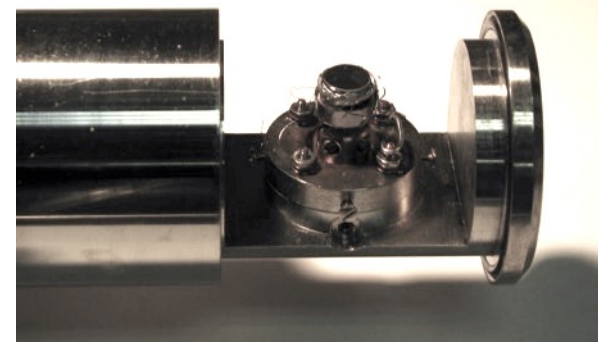
- Optimized for direct sensitivity to H on surfaces (< 0.05 ML)
- High surface specificity
- Distinguishes H and D (exchange experiments)
- Adsorption kinetics on compressed particle beds/thin films (res. $\sim 1 - 10$ s)
- Atomic doser available to characterize uptake of H_2 vs. H
- Surface diffusion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

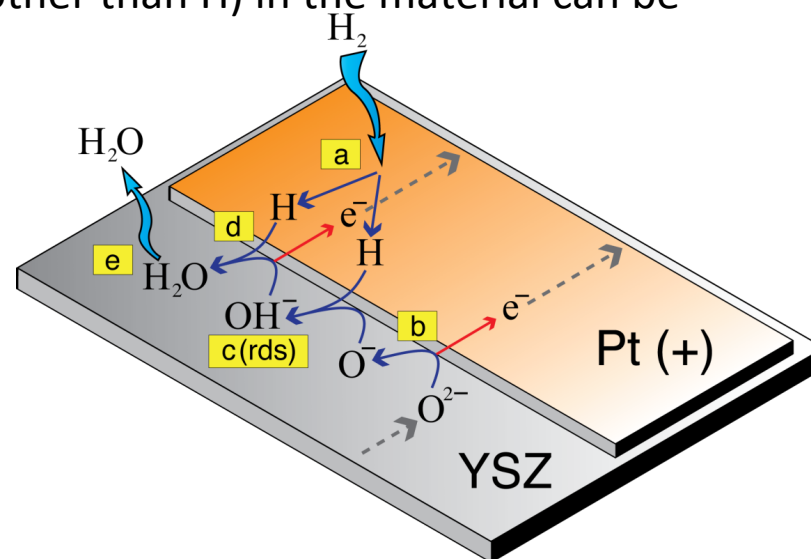
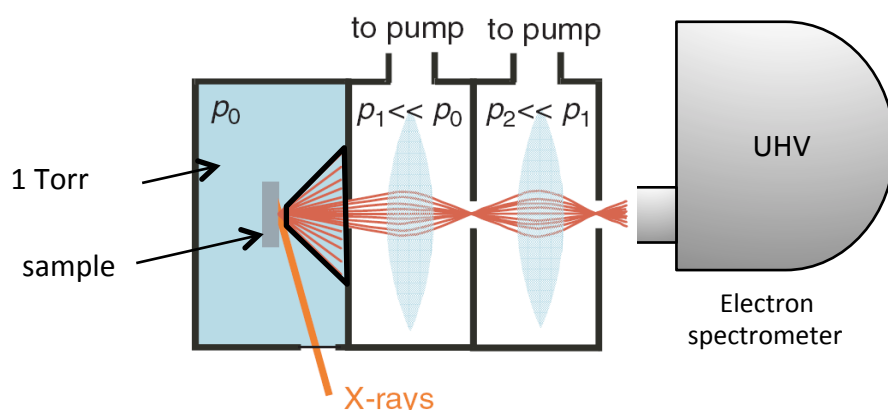
Ambient-Pressure X-ray Photoelectron Spectroscopy (AP-XPS)



- 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)

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



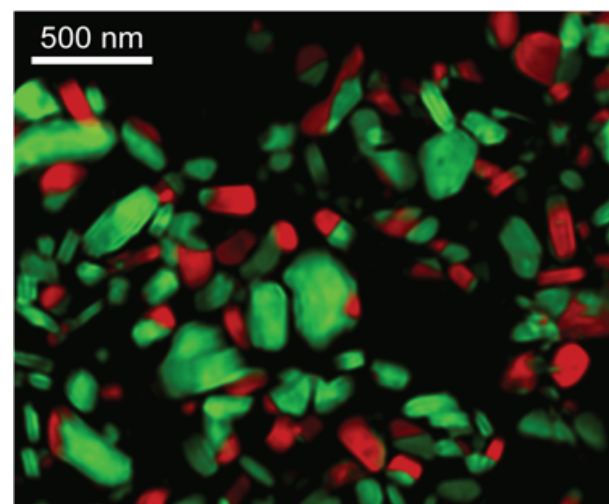
We will apply these tools to understand phase nucleation at interfaces and growth at the nano- and mesoscales



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 $\text{Li}_x\text{Fe(II,III)PO}_4$



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

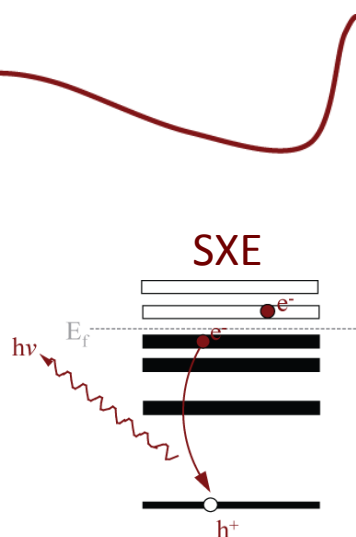
F. El Gabaly et al., Nature Materials, 2014, 13, 1149–1156.

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

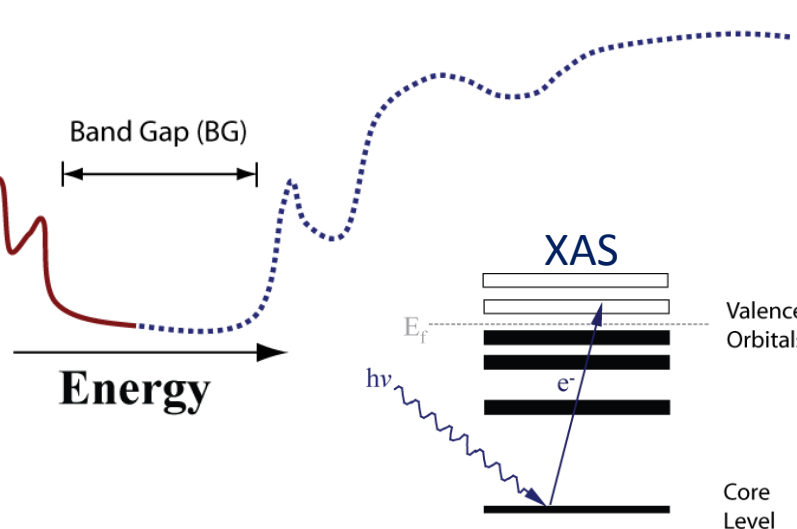
X-ray Emission Spectroscopy (XES) and X-ray Absorption Spectroscopy (XAS) enable element-specific tracking of the course of hydrogen storage reactions

Soft X-ray Emission (SXE) spectroscopy



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

X-ray Absorption Spectroscopy (XAS)



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

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