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

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June 8, 2016

Project ID: ST127

Overview

Timeline

Project Start Date: 9/17/2015
Phase 1 end date: 9/30/2018

Barriers

A. System Weight and Volume
E. Charging/Discharging Rates
O. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Budget

- FY15 DOE Funding: $750K
- FY16 Planned DOE Funding: $2,250K
- Total DOE Funds Received: $3,000K

Partners

- Sandia National Laboratories
- Lawrence Livermore National Laboratory
- Lawrence Berkeley National Laboratory

Relevance: Critical scientific roadblocks must be overcome to accelerate materials discovery for vehicular hydrogen storage

Critical issues identified by PIs at NREL meeting, Jan. 2015:

Sorbents

Target desorption enthalpy*: 15 – 20 kJ/mol

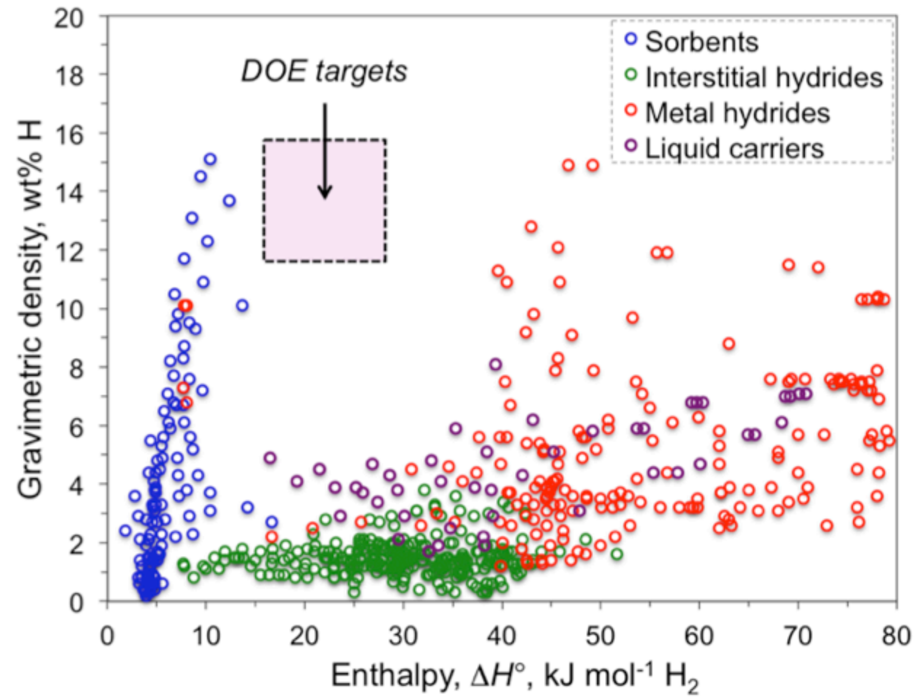
- Volumetric capacity at operating temperature is too low
- Increased usable hydrogen capacity needed
- Distribution of H_2 binding sites and ΔH at ambient temperature not optimized

Metal hydrides

Target desorption enthalpy*: ≈ 27 kJ/mol H_2

- Limited reversibility and slow kinetics not understood
- Role of interfaces and interfacial reactions
  - Solid-solid
  - Surfaces
- Importance and potential of nanostructures

*DOE Engineering Center of Excellence



Source: DOE Hydrogen Storage Materials Database

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

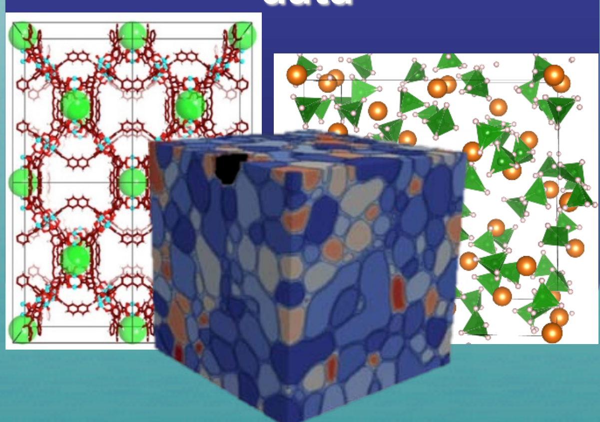
HyMARC will deliver **community tools and capabilities:**

- **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

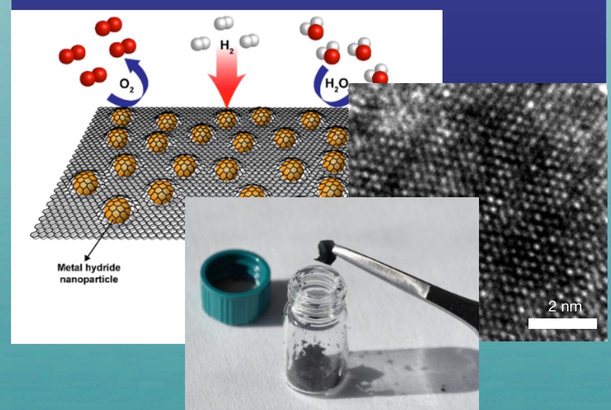
Core Lab Team

University | Non-profit | Industry

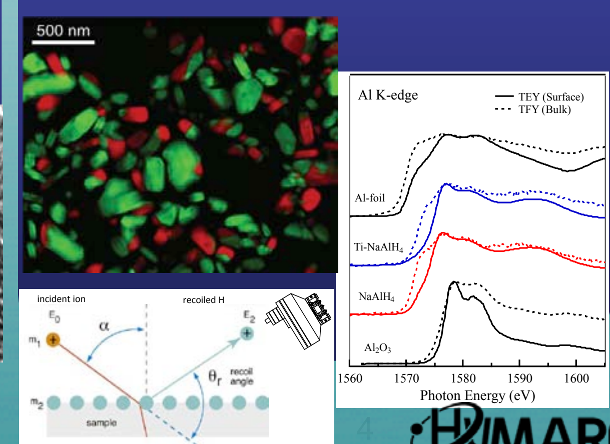
Theory, simulation, & data



Controlled synthesis



In situ characterization



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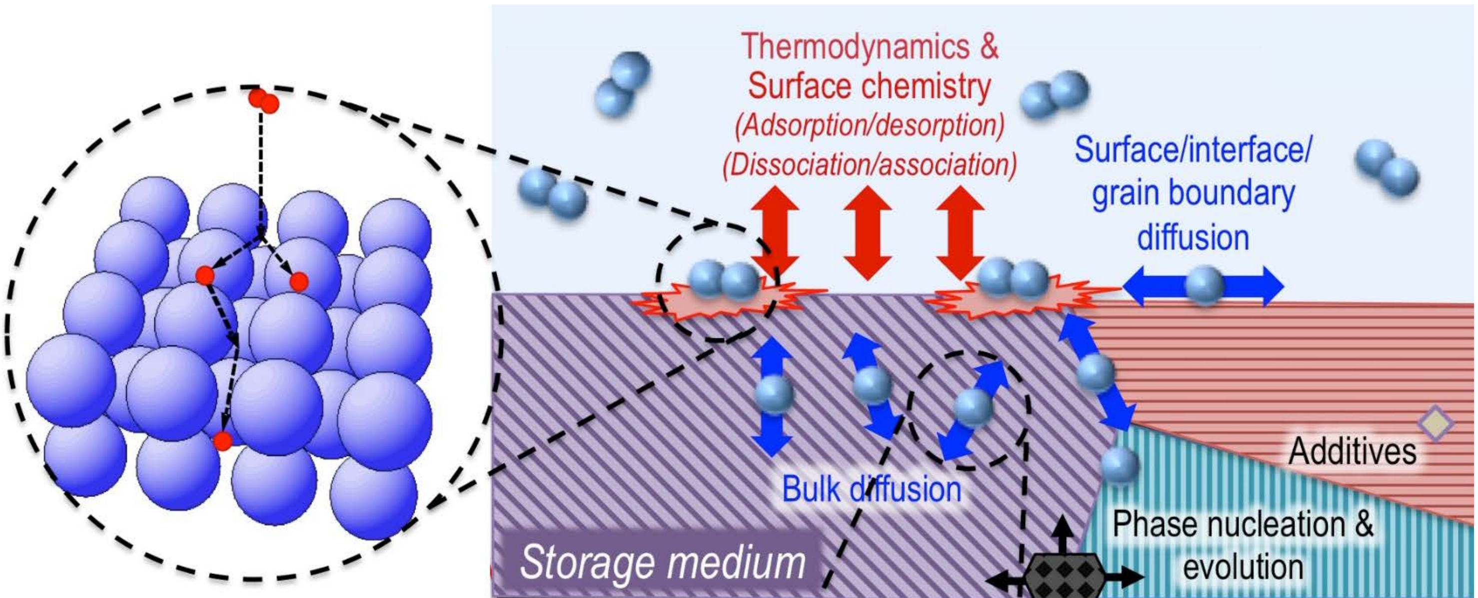
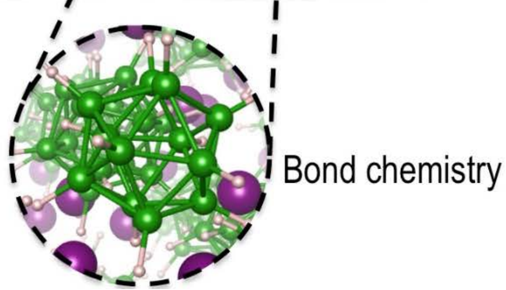
Approach: HyMARC tasks target thermodynamics and kinetics

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

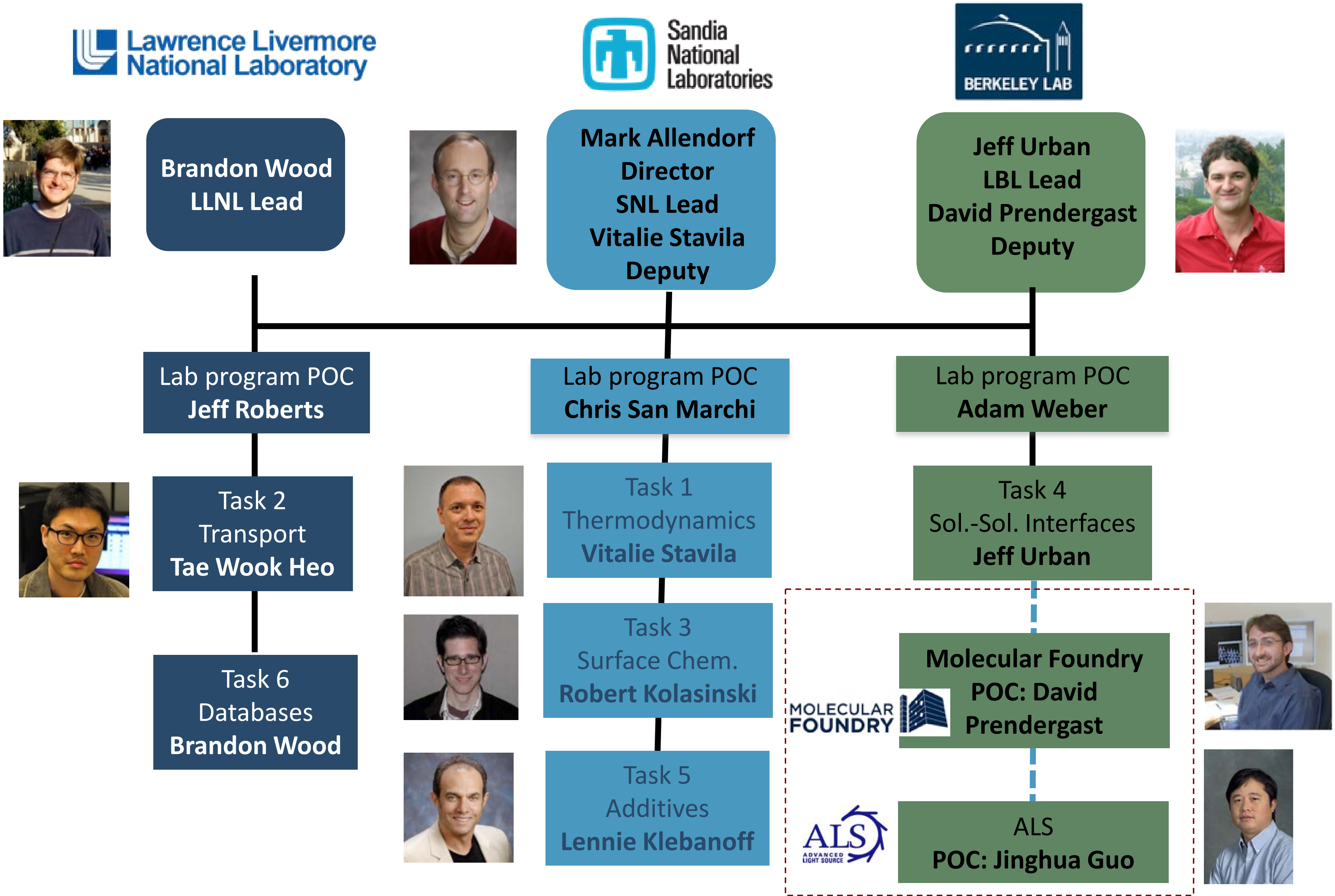
Thermodynamics ($\Delta H^{\circ}(T)$) **Kinetics** (E_a)



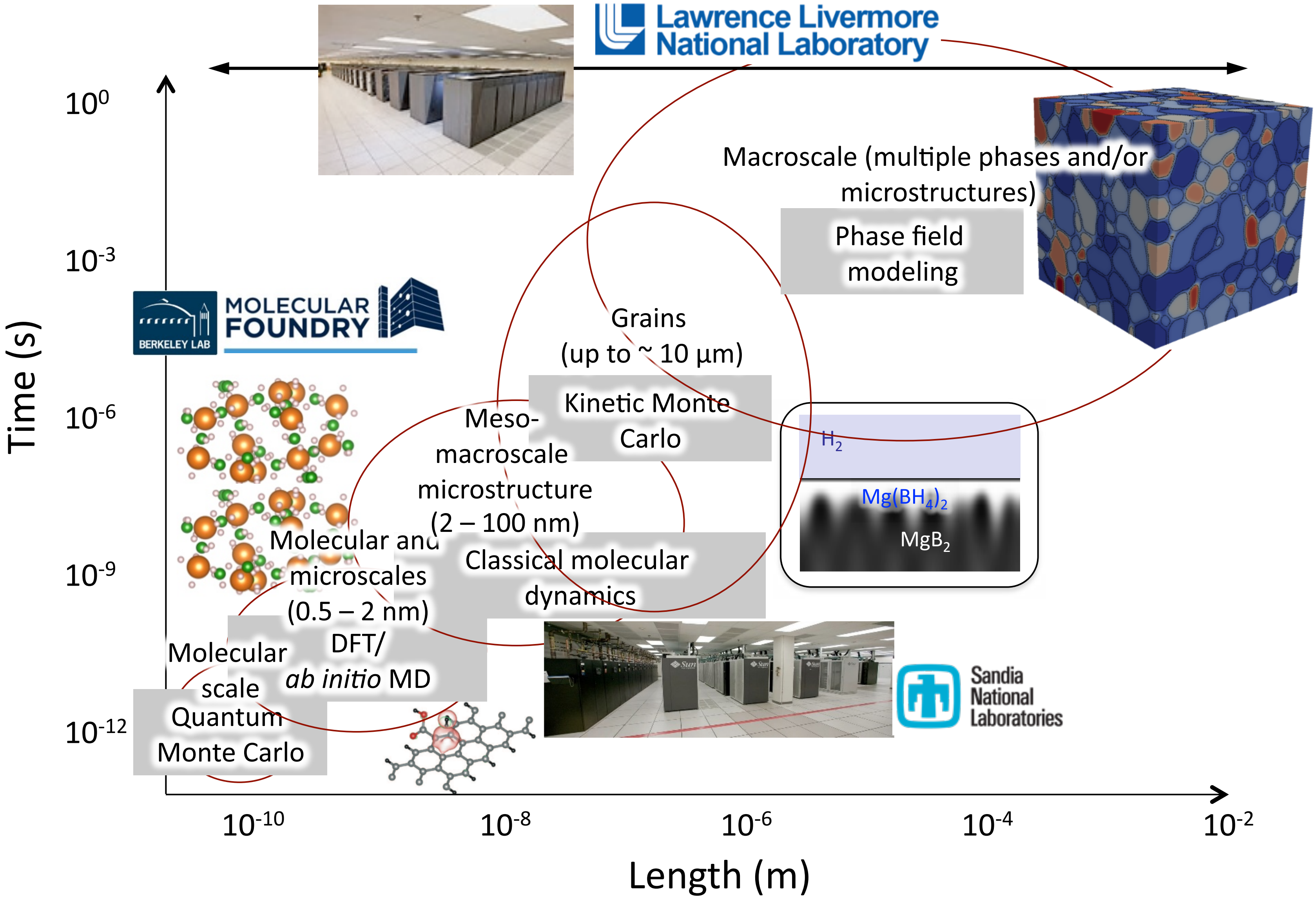


Task 1: Thermodynamics
Task 2: Transport
Task 3: Gas-surface interactions
Task 4: Solid-solid interfaces
Task 5: Additives and dopants
Task 6: Materials informatics

Technical approach: Organizational structure of Core Lab Team



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



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	Metal hydrides
• Thermodynamics of H_2 release Library of sorbents with representative structural motifs: • MOFs with open metal sites • Porous carbons • Doped materials	• 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. $Mg(BH_4)_2$

"Simple" Complex hydrides:
- **Phase segregation**
- **Bulk → Nano**
- **Graphene nanobelts, templates, colloidal synthesis**

Complex systems, e.g. $Mg(BH_4)_2$:
- **"Molecular" species (e.g. $B_{12}H_{12}$)**

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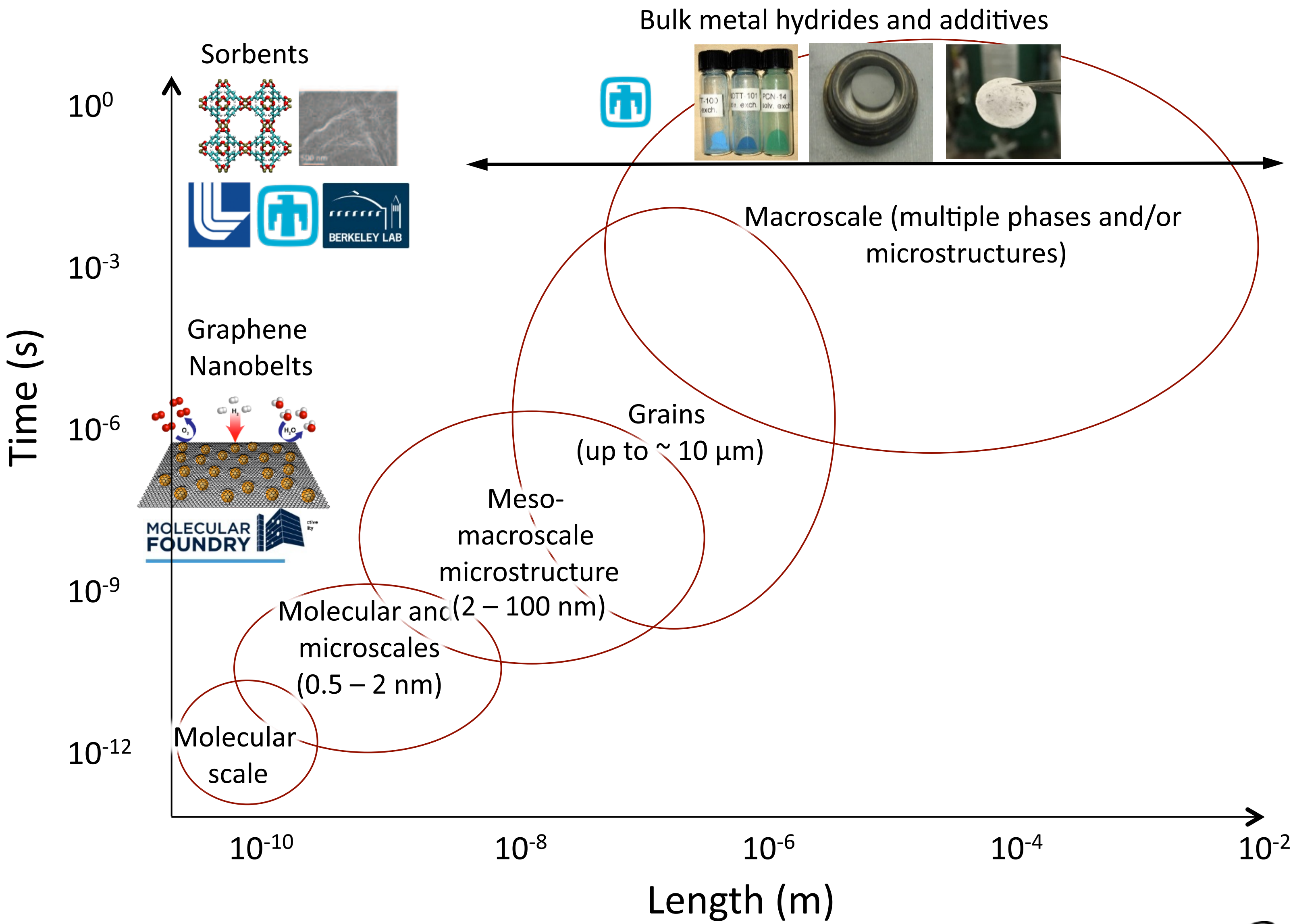
Technical approach/Synthesis capabilities: bulk materials, dopants, sorbants, and nano-scale platforms



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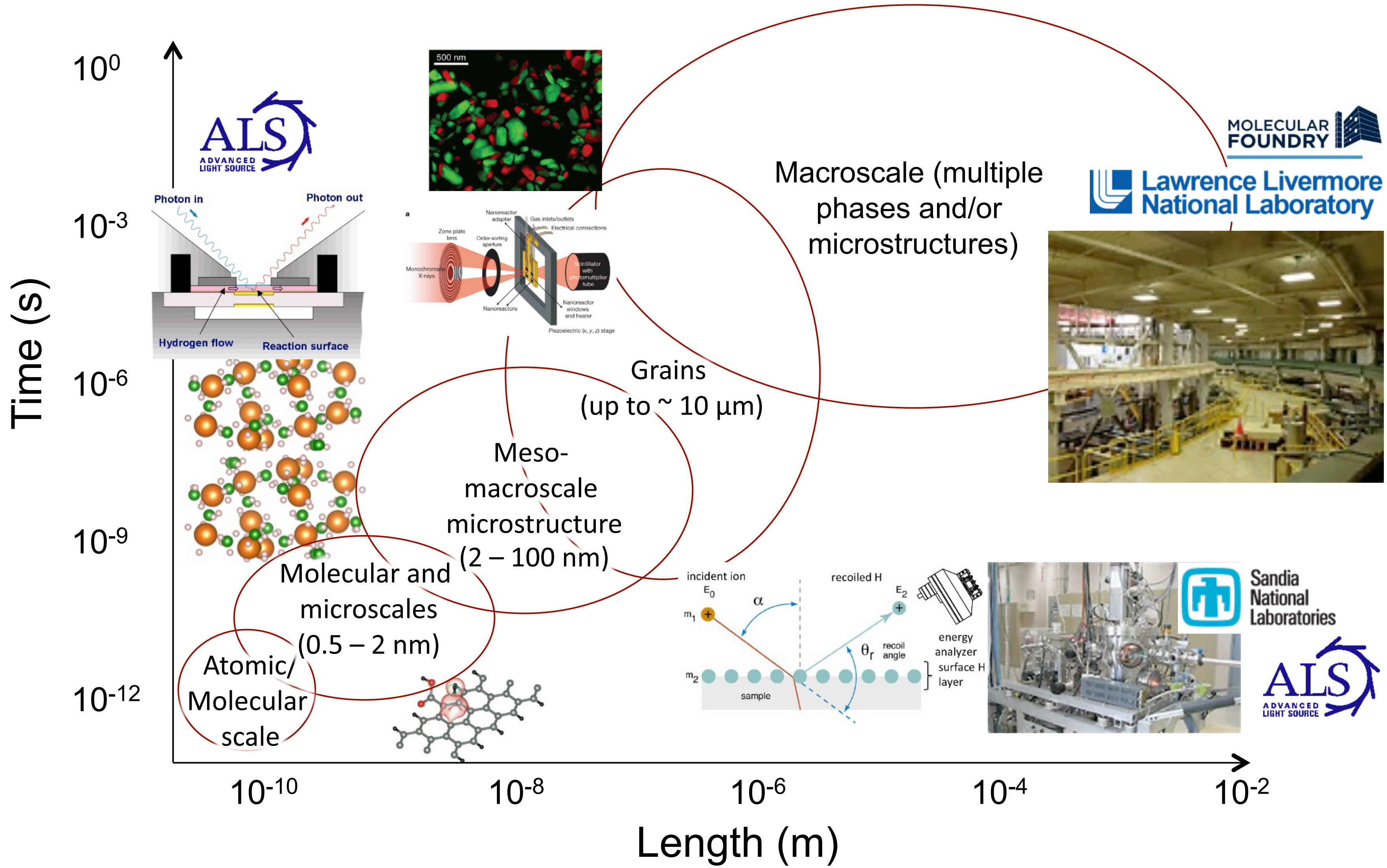
Technical approach/characterization: state-of-the-art tools probing bulk and surface chemistry, microstructure, phase composition



Progress toward FY16 Milestones

Milestone	Description	Status (% complete)		
		SNL	**LLNL**	**LBL**
Q1 FY16	**Synthesis:** prepare library of bulk-phase model storage systems for T1-T5	100	100	100
Q2 FY16	**Synthesis:** Size control method for one prototype complex hydride nanostructure	100	100	100
Q3 FY16	**Characterization:** Demonstrate in-situ soft X-ray AP-XPS, XAS, XES tools, with sample heating	33	33	33
Q4 FY16	**Characterization+Theory:** Identify hydride mobile species and diffusion pathways	25	25	50
Q4 FY16	**Synthesis+Characterization:** Synthesize library of nanoparticles: 1 – 5 nm, 5 – 10 nm, >10 nm for one prototype hydride	50	50	50

Details to follow in consortium partner presentations

Accomplishments: Overall Project Level

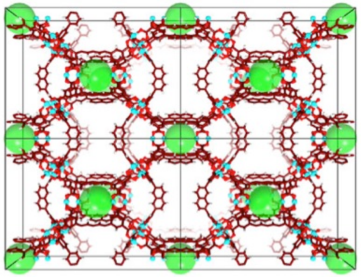
- **Overview Webinar describing HyMARC on 1/7/2016**
- **Staffing: postdocs**
  - *Sandia:* James White (Princeton, chemistry). Storage material synthesis and characterization
  - *LLNL:*
    - ShinYoung Kang (MIT, materials science). First-principles free energy calculations
    - Patrick Shea (Dalhousie Univ. physics). Multiscale transport kinetics
  - *LBL:* Yi-Sheng Liu **(**Tamkang Univ., physics**)**. Soft X-ray spectroscopies
- **BES User Facilities**
  - *Molecular Foundry (LBL):* **user proposal approved**
    - Electron microscopy, computational tools, nanoscale synthesis, various spectroscopies
  - *Advanced Light Source (LBL):* **"Approved Program" submitted**
    - Would provide dedicated time for 3 years
  - *Spallation Neutron Source (Oak Ridge):* **user proposal submitted** for use of VISION vibrational spectrometer
- **Participated in gas sorption round robin coordinated by NREL**

Thermodynamics (Task 1): overview and accomplishments

Establishing structure-property relationships governing hydrogen uptake and release

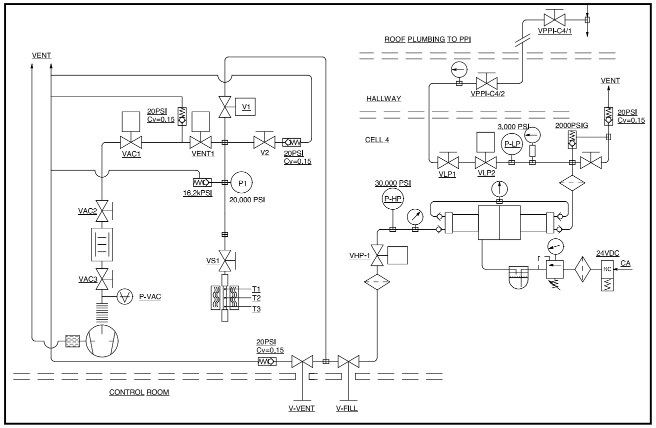
Objectives

- Accurate H_2-sorbant interaction potentials
- Particle morphology & additives in thermo models
- Alloying, amorphization to shift equilibria
- Potential of nanoscaling



Capabilities

- Quantum Monte-Carlo
- New ultrahigh-pressure reactor (>700 bar)
- MOFs, porous carbon synthesis

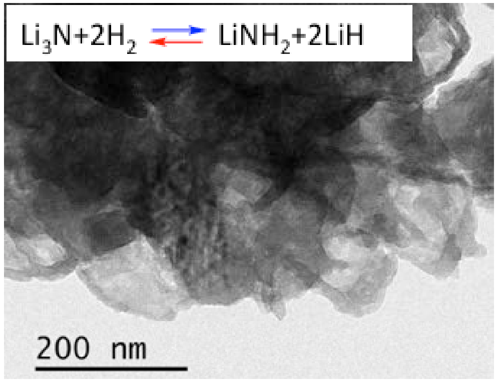


PI team

- **Sandia:** Stavila (Task lead), Allendorf
- **LLNL:** Baumann, Bonev, Campbell, Heo, Morales-Silva, Lee, Wood
- **LBL:** Urban, Fischer (UC-Berkeley), Somorjai

Key Results

- MOF suite for high-P sorption measurements
- High Ti dopant effect on $NaAlH_4$ thermodynamics
- Single-step hydriding of Li_3N@nanocarbon
  Manuscript under review



Kinetics of mass transport (Task 2): overview and accomplishments

Multiscale computational modeling with spatially resolved characterization

Objective: Identify fundamental processes and rate-limiting steps in mass transport

Capabilities

- Ab initio and classical MD
- Kinetic Monte Carlo (kMC)
- Phase-Field Modeling (PFM)
- Low Energy Ion Scattering (LEIS)
- Soft X-ray microscopies

PI team

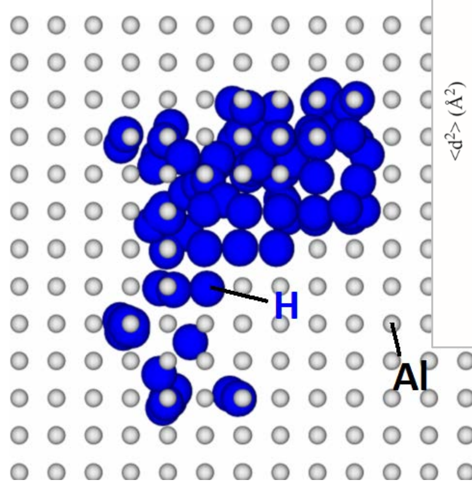
LLNL: Heo (Task lead), Wood

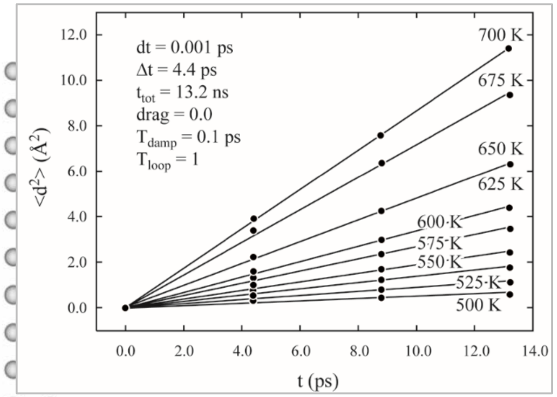
SNL: Zhou, Kolasinski, El Gabaly

Key Results

- Robust classical MD for H diffusion
  X. Zhou et al. on line *J. Phys. Chem. C* 2016
- Preliminary mesoscale surface H diffusion model

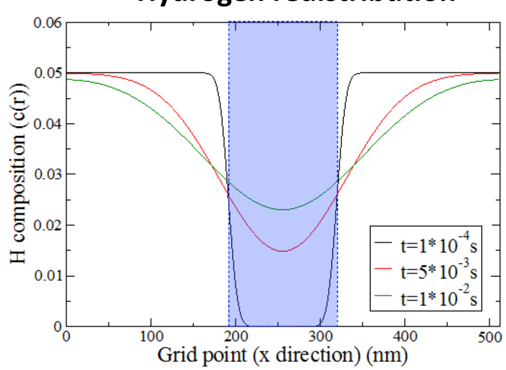
Atomistic modeling of H diffusion



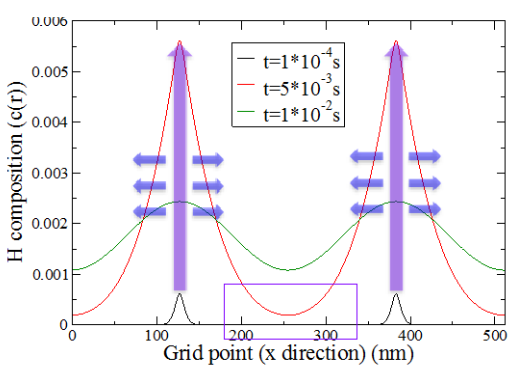


Mesoscale modeling of surface H diffusion

Hydrogen redistribution



Surface dissociation + diffusion



Surface chemistry (Task 3): overview and accomplishments

Multi-technique approach to provide comprehensive picture of key properties/phenomena

Objectives

- Probe both thermodynamics and kinetics
- Data for model development
- New sample handling capabilities
- Methods specific to storage materials
- Realistic sample formats wherever possible

Capabilities

- Low Energy Ion Scattering (LEIS)
- XPS, AES
- Soft x-ray tools: AP-XPS, XAS

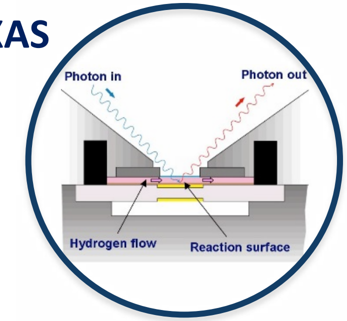
PI team

- **Sandia:** Kolasinski (Task lead), El Gabaly
- **LLNL:** Heo
- **LBL/ALS:** Guo (ALS), Prendergast (MF), Fischer (Berkeley)

Key Results

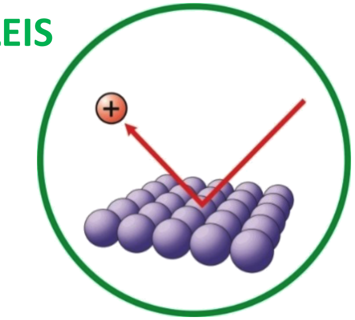
- Proof-of-concept: surface diffusion data using LEIS
- Clean transfer system: air-free XPS/AP-XPS
- In-situ, real-time surface composition monitoring

XAS



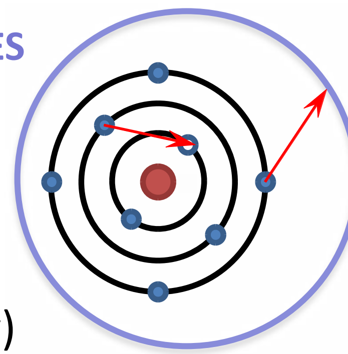
X-ray absorption spectroscopy

LEIS



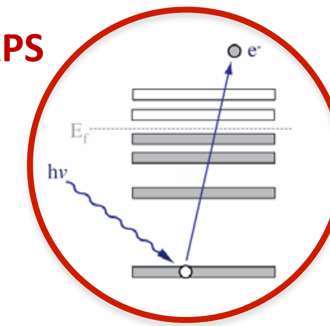
Low Energy Ion Scattering

AES



Auger Electron Spectroscopy

XPS



X-ray Photoelectron Spectroscopy

Internal interfaces (Task 4): overview and accomplishments

Computational models, characterization tools, and methods designed for storage materials

Objectives

- **Interface energetics and dynamics** using LLNL Phase Field Modeling approach and other codes
- **Phase/composition** using new X-ray microscopies (2 – 25 nm resolution)
- **Experimental methodologies** needed to apply new diagnostic tools

Capabilities

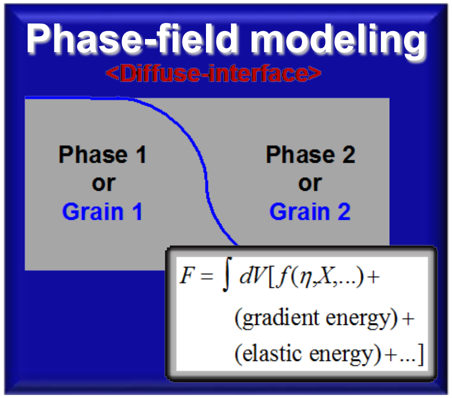
- ALS soft X-ray tools
- SNL, LLNL, MF/NCEM TEM

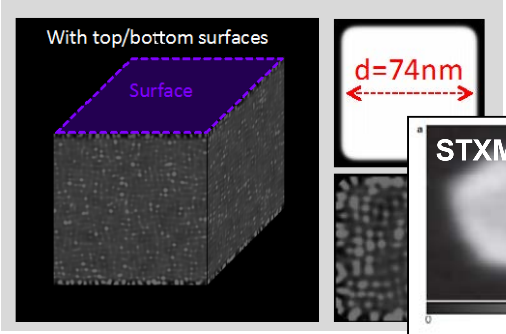
PI team

- **LBL:** Urban (Task lead), Guo, Prendergast
- **LLNL:** B. Wood, T.-W. Heo, J.Lee
- **Sandia:** F. El Gabaly, X. Zhou, V. Stavila

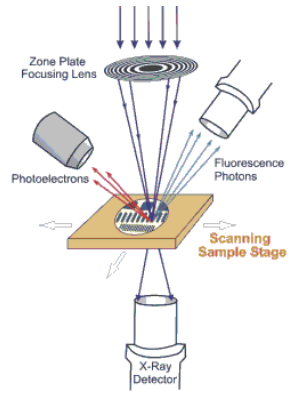
Key results

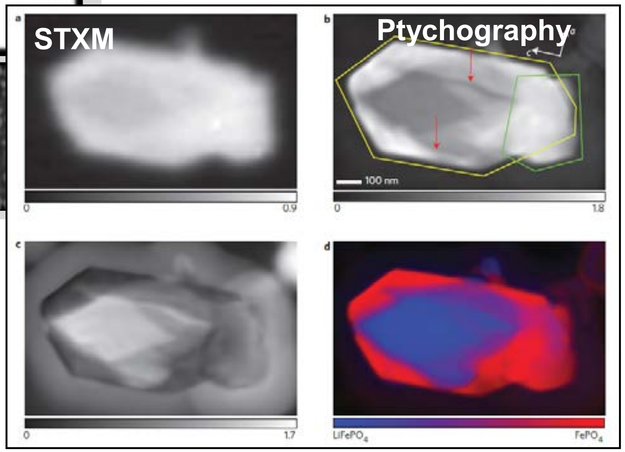
- First STXM measurements
- Phase-field model predictions compare favorably with experiment





Scanning Transmission X-Ray Microscopy (STXM)





D. A. Shapiro, *et al.*, *Nature Photonics, 2014*

Additives (Task 5): overview and accomplishments

New material platforms to provide atomic-scale control of additives

Objectives

- Determine catalytic activity of bulk catalysts
- Create new material platforms for probing effects of additives
- Evaluate influence of acidic sites on H_2 adsorption

Capabilities

- XPS, AES, LEIS, electron microscopies
- Soft X-ray methods

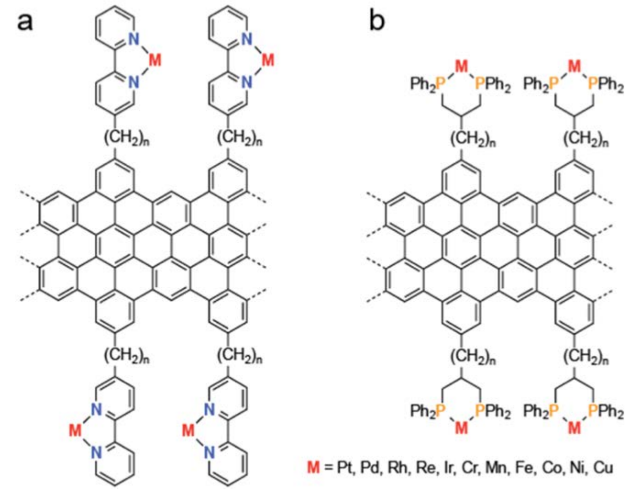
PI team

- **Sandia:** L. Klebanoff (Task lead), R. Kolasinski, V. Stavila
- **LBL:** F. Fischer, G. Somorjai, J. Urban
- **LLNL:** B. Wood, J. Lee

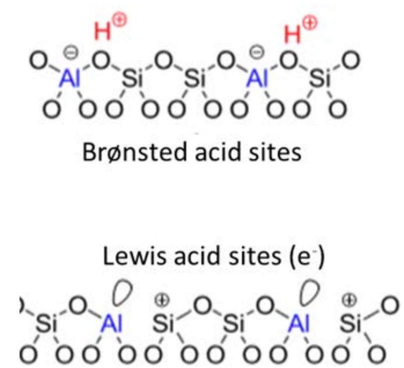
Key results

- XAS, XES shown sensitive to low mole % additives
- Assessed catalytic activity of bulk $TiCl_3$ and TiF_3
- Synthesized Al-Doped silicate model systems for probing acid-base catalysis

Metal-functionalized Graphene Nanobelts



Brønsted and Lewis acid sites



Toward the hydrogen storage materials genome (Task 6): summary

Community tools and databases to accelerate materials discovery

FY16 planning activities

- Workflow proposed for high-throughput MOF screening using CoRE database (currently testing on subclass of MOFs)
- Database content discussions:
  - DFT quantities:
    - ΔH_f°, S(vib), zero-point energy
    - Energy of low-index surfaces
    - Elastic moduli
  - *Ab initio* MD trajectories (80 °C)
  - Computed XAS and IR spectra
  - Thermodynamic and kinetic measurement data
  - Measured X-ray absorption spectra

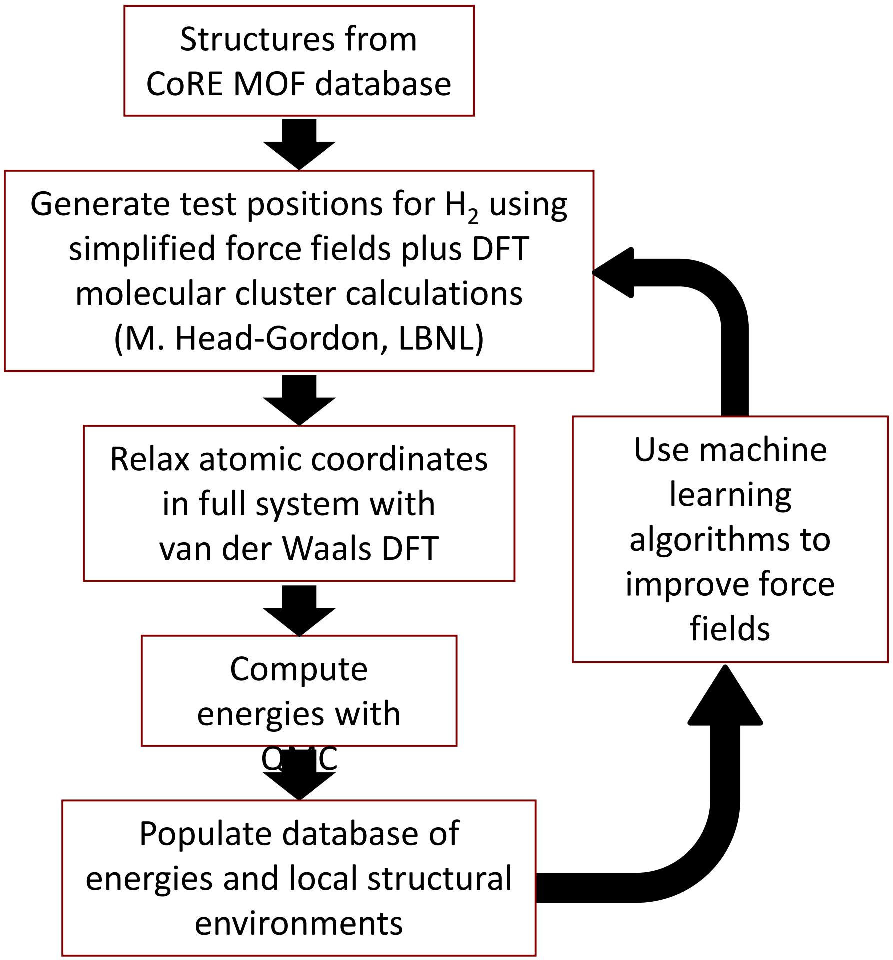
PI team

LLNL: B. Wood (Task lead), M. Morales

LBL: M. Haranczyk, D. Prendergast, J. Urban

Sandia: V. Stavila, M. Allendorf

Example: workflow for high-throughput MOF sorbents



Database activities are scheduled to ramp up in Y2 & Y3

Collaborations external to HyMARC

- **Dr. Tom Autrey (PNNL):** NMR of borohydride systems
- **Dr. Tom Gennett, Katie Hurst:** high-accuracy hydrogen sorption measurements
- **Prof. Martin Head-Gordon (LBL):** quantum-chemistry calculations/physisorption
- **Prof. Jeff Long (LBNL):** porosimetry, high-pressure FTIR
- **Dr. Terry Udovic, Dr. Craig Brown (NIST):** neutron spectroscopies and diffraction

Characterization Team

- **Dr. A.J. (Timmy) Ramirez-Cuesta (SNS/ORNL):** neutron vibrational spectroscopy

DOE BES User Facility

- **Dr. Viktor Balema (Sigma-Aldrich):** synthesis of hydride samples; mechanochemistry

Industry

- **Dr. Nico Fisher (Univ. Cape Town, South Africa):** In-situ time-resolved XRD of GNR-Mg composites during absorption/desorption at process-relevant P & T
- **Prof. Stefan Kaskel (Technical University Dresden)**
  - Student visited SNL-CA for 5 weeks for high-P H_2 uptake measurements
- **Prof. E. Majzoub (Univ. MO St. Louis):** nanoscale hydrides, templating carbons
- **Prof. Pasit Pakawatpanurut (Mahidol Univ., Bangkok, Thailand):** Metal hydride synthesis/characterization
  - Visiting student interns planned
- **Dr. Aaron Thorton (CSIRO Australia) and Prof. Berend Smit (UC Berkeley/EPFL):** High-throughput computational screening of MOFs

Academia

Remaining Challenges and Barriers

Theory

- QMC calculations require relaxed geometries, requiring high-level *ab initio* methods
  - Strategy: established collaboration with Prof. Martin Head-Gordon (UCB/LBL)
- Experimental data concerning time evolution of internal interfaces is unavailable
  - Strategy: develop soft x-ray microscopies to image these
- Unknown sensitivity analysis input parameter ranges for hydrides
  - Strategy: use materials testing and high-accuracy simulations of simple hydrides to inform reasonable input ranges

Synthesis

- Narrow size distribution of hydride nanoparticles
  - Strategy: use host materials will narrow pore size distribution
- Achieving high density of acid sites in a realistic material
  - Strategy: learn from doped silicas and translate to carbons or MOFs

Characterization

- X-ray microscopies at LBL/ALS not configured for air-free sample handling
  - Strategy: Air-free sample holder design under development
- ALS is a user facility; hence access is limited
  - Strategy: submit proposals to SLAC and Canadian Light Source/Saskatoon for time

Proposed future work

Milestone	Description	Current status
Q3 FY16 PM	**Characterization:** Demonstrate in-situ soft X-ray AP-XPS, XAS, XES tools, with sample heating	67 (33)
Q4 FY16 PM	**Characterization+Theory:** Identify hydride mobile species and diffusion pathways	100 (25)
Q4 FY16 SMART	**Synthesis+Characterization:** Synthesize library of nanoparticles: 1 – 5 nm, 5 – 10 nm, >10 nm for one prototype hydride	100 (50)
Q5 FY17 PM	**Theory:** Compute H_2 binding curves by QMC for inclusion in database	100 (15)
Q6 FY17 PM	**Theory:** Perform sensitivity analysis of local binding and second-sphere effects	100 (0)
Q6 FY17 Go/No-go	**Sorbents:** rank improvement strategies: open metal sites; acid sites; polarization effects; phase change materials. Decision criterion: select 2 with greatest potential for increasing ΔH°	100 (10)

PM = Progress milestone

Summary

- **HyMARC is up and running!**
- **Testing and development of new computational tools underway:**
  - Quantum Monte Carlo
  - Charge and field effects model
  - DFT thermodynamics prediction protocol
  - Phase nucleation, phase fraction, interfaces
  - *Ab initio* molecular dynamics
  - Multiscale surface chemistry
  - Phase-field code
- **New synthetic capabilities are being developed and tested:**
  - Graphene nanobelts (LBL)
  - Acid-functionalized sorbents
  - Size-tunable hydrides in porous carbon hosts
  - Sorbent suite (MOFs and porous carbons)
- **Advanced characterization tool development well underway**
  - Soft x-ray techniques at Advanced Light Source (hardware, sample handling, theory)
  - Surface chemistry characterization suite already generating new insights
  - User proposals submitted to Molecular Foundry, ALS, and SNS/VISION

***Our definition of success*:**

1) ***Significant advances in foundational understanding that accelerate materials discovery***
2) ***Community tools, including predictive multiscale models, high-resolution in-situ characterization tools, material synthesis, and databases***

We gratefully acknowledge EERE/FCTO for financial support!

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BERKELEY LAB
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