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

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

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

HyMARC

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

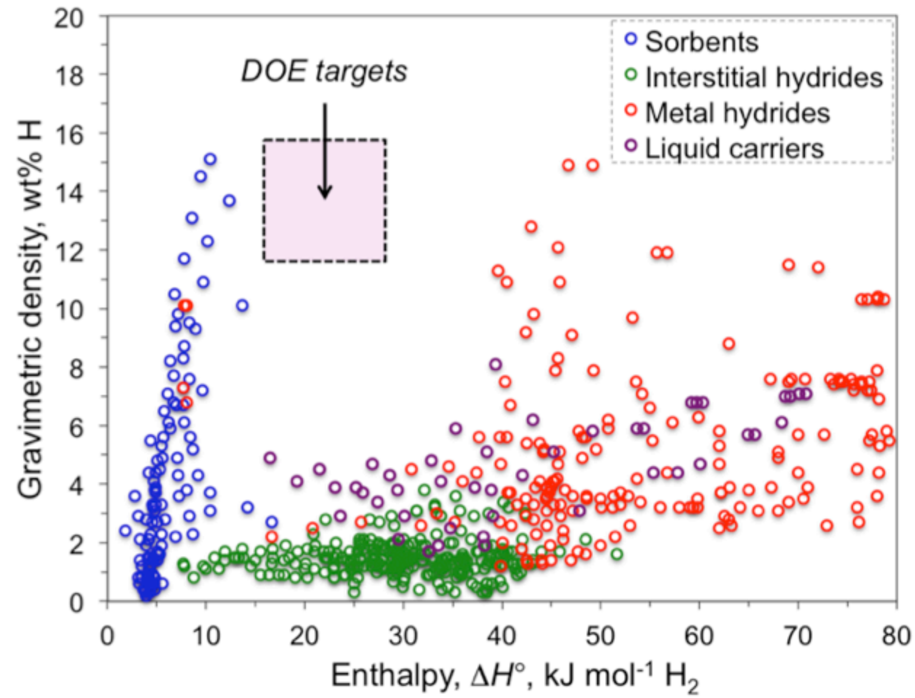
- Volumetric capacity at operating temperature is too low
- Increased usable hydrogen capacity needed
- Distribution of H_2 binding sites and ΔH at ambient temperature not optimized

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

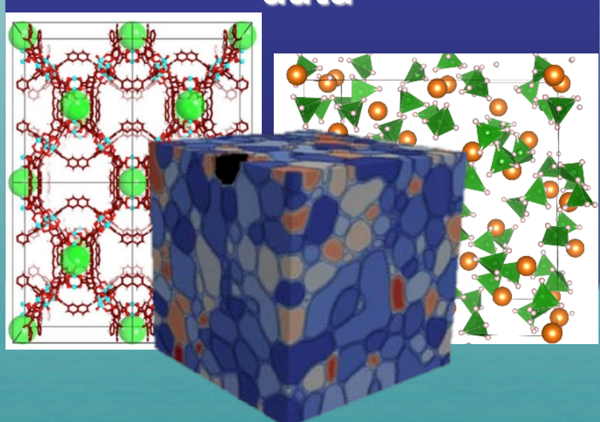
HyMARC will deliver **community tools and capabilities:**

- **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

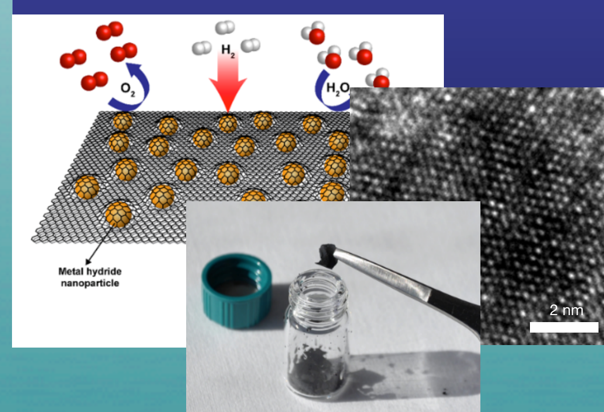
Core Lab Team

University | Non-profit | Industry

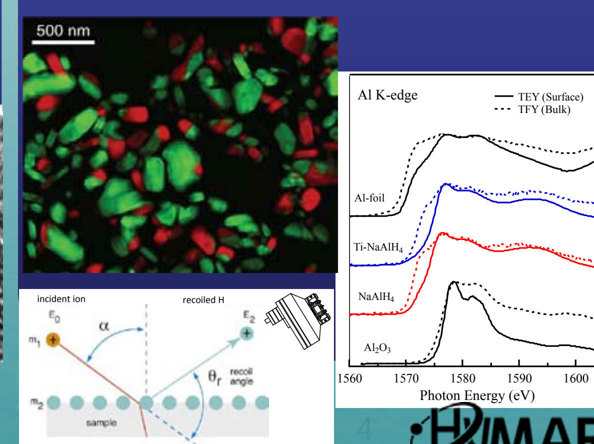
Theory, simulation, & data



Controlled synthesis



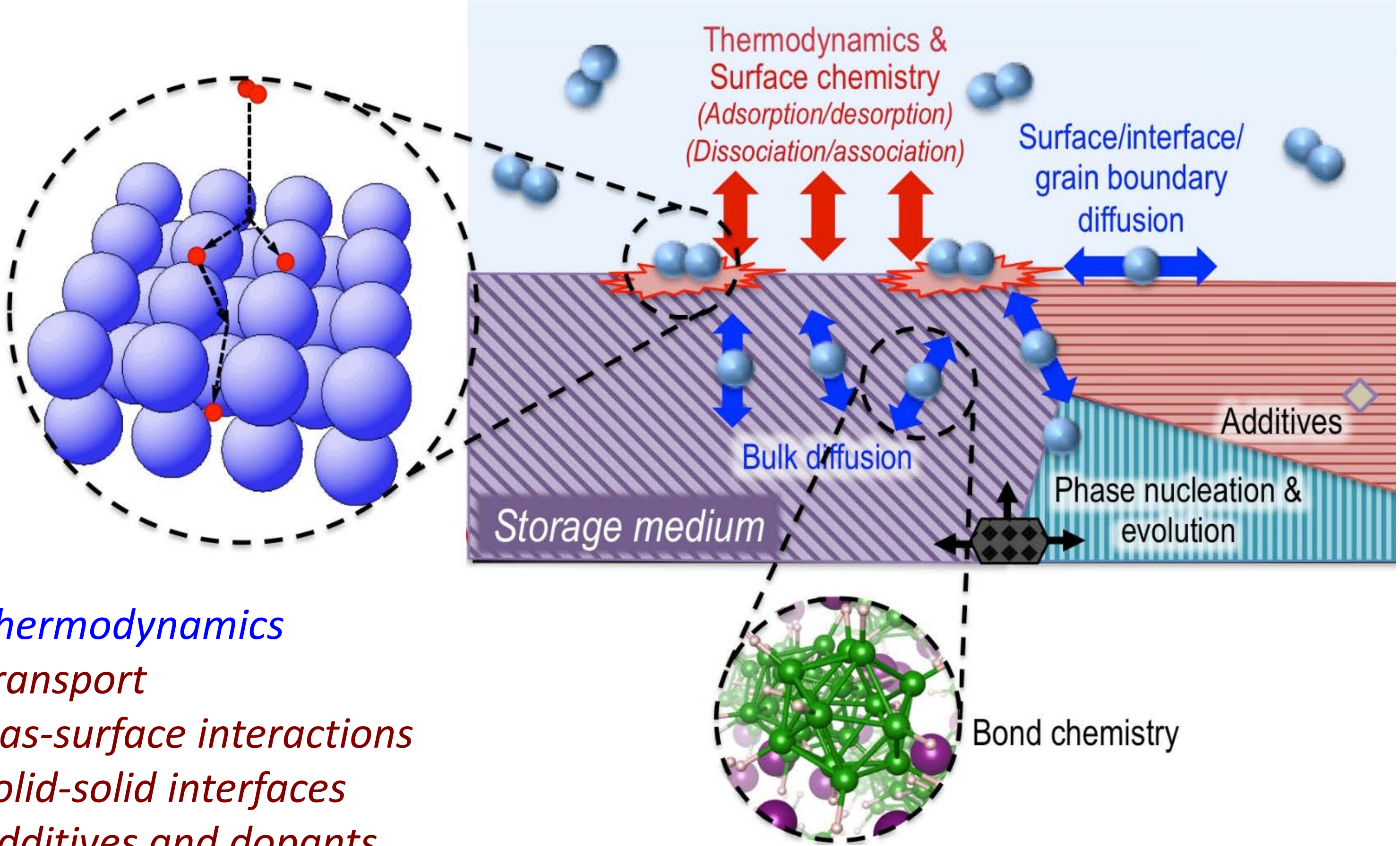
***In situ* characterization**



Approach: HyMARC tasks target thermodynamics and kinetics

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

Thermodynamics **Kinetics**



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

Lawrence Livermore National Laboratory

Sandia National Laboratories

BERKELEY LAB

Brandon Wood
LLNL Lead

Mark Allendorf
Director
SNL Lead
Vitalie Stavila
Deputy

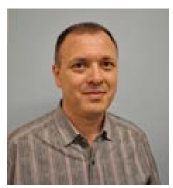
Jeff Urban
LBL Lead
David Prendergast
Deputy

Lab program POC
Jeff Roberts

Lab program POC
Chris San Marchi

Lab program POC
Adam Weber

Task 2
Transport
Tae Wook Heo



Task 1
Thermodynamics
Vitalie Stavila

Task 4
Sol.-Sol. Interfaces
Jeff Urban

Task 3
Surface Chem.
Robert Kolasinski

MOLECULAR FOUNDRY

Molecular Foundry
POC: David Prendergast

Task 6
Databases
Brandon Wood

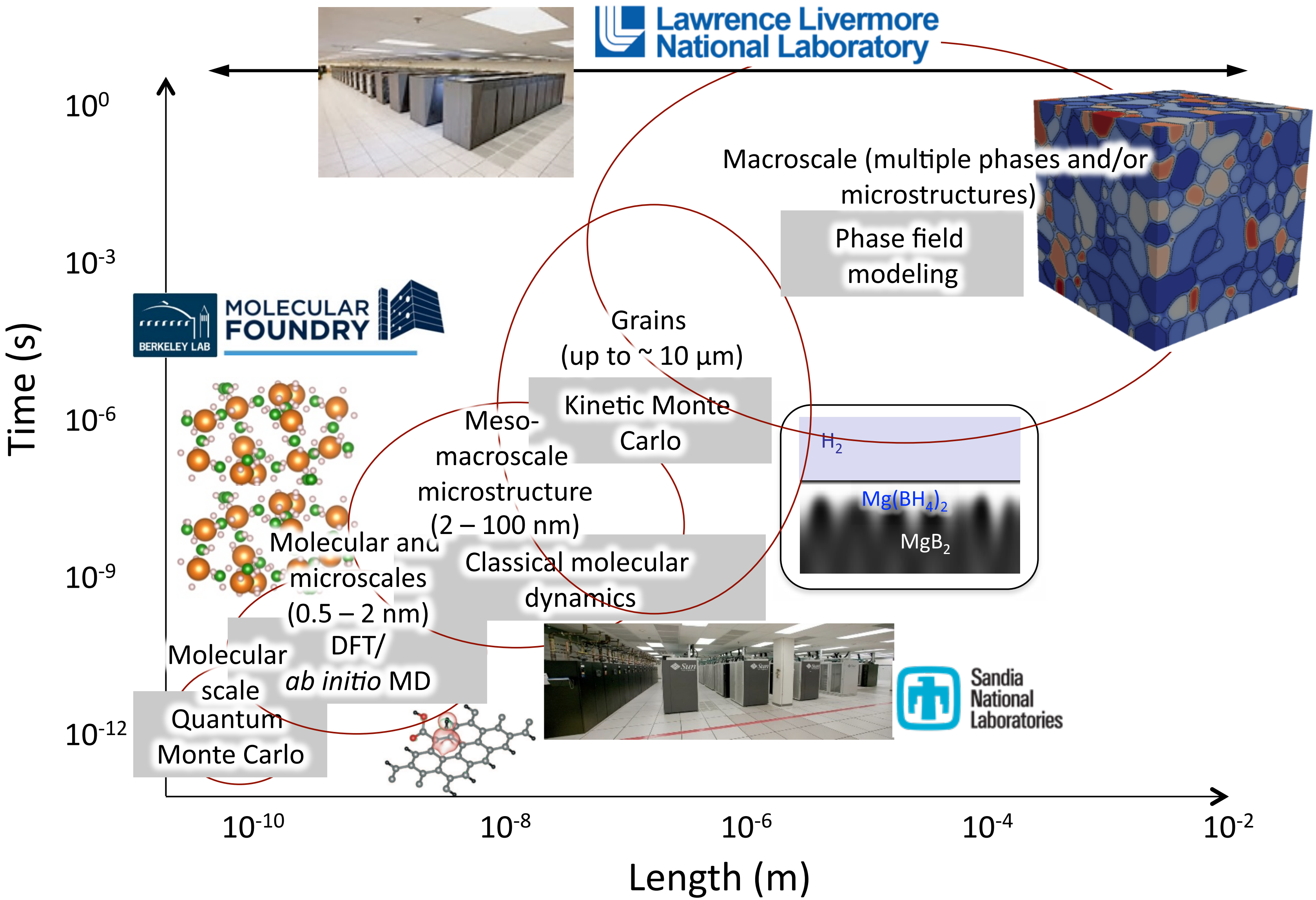
Task 5
Additives
Lennie Klebanoff

ALS ADVANCED LIGHT SOURCE

ALS
POC: Jinghua Guo

HyMARC

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. $Mg(BH_4)_2$

Phase segregation

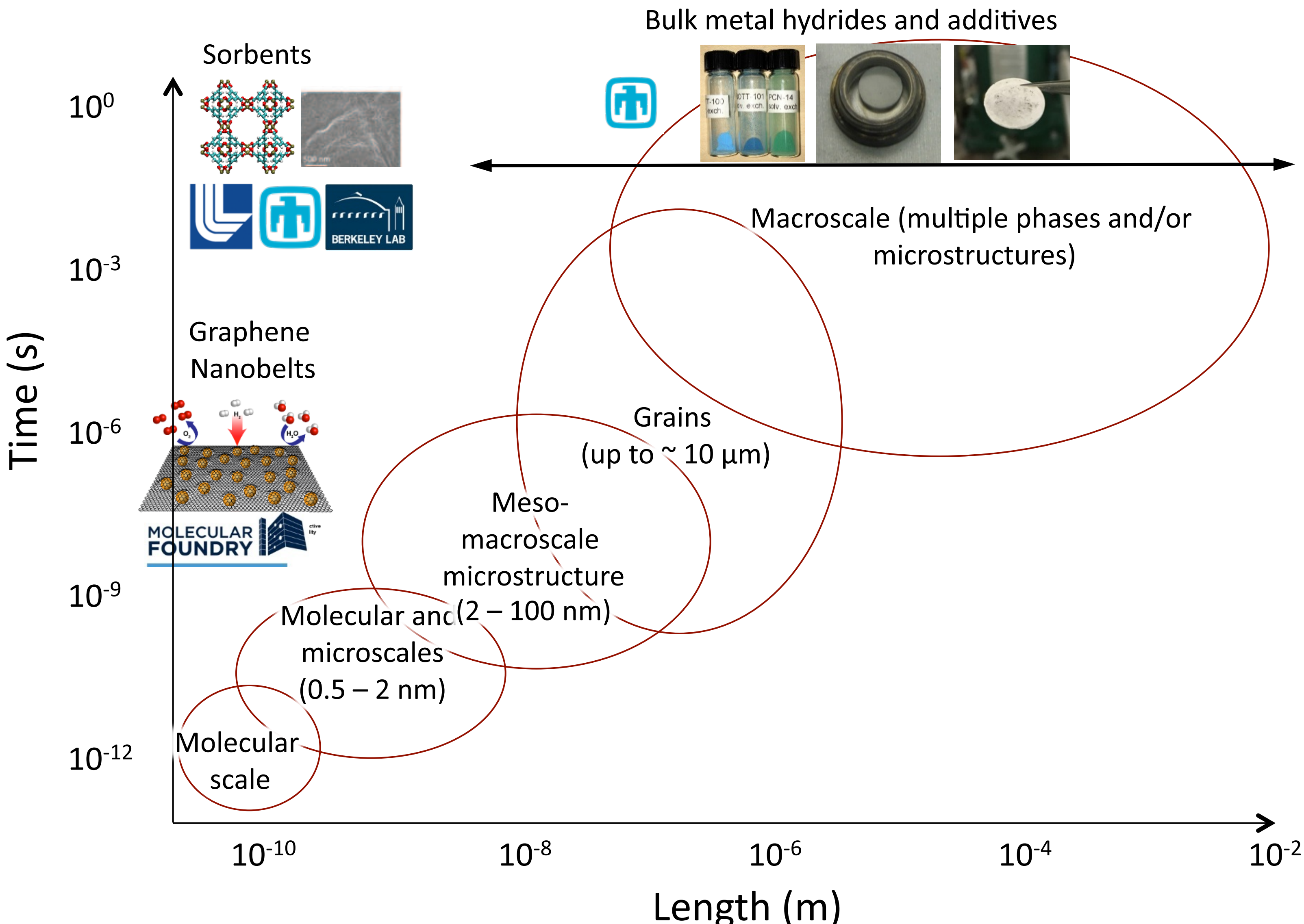
"Molecular" species (e.g. $B_{12}H_{12}$)

Bulk → Nano

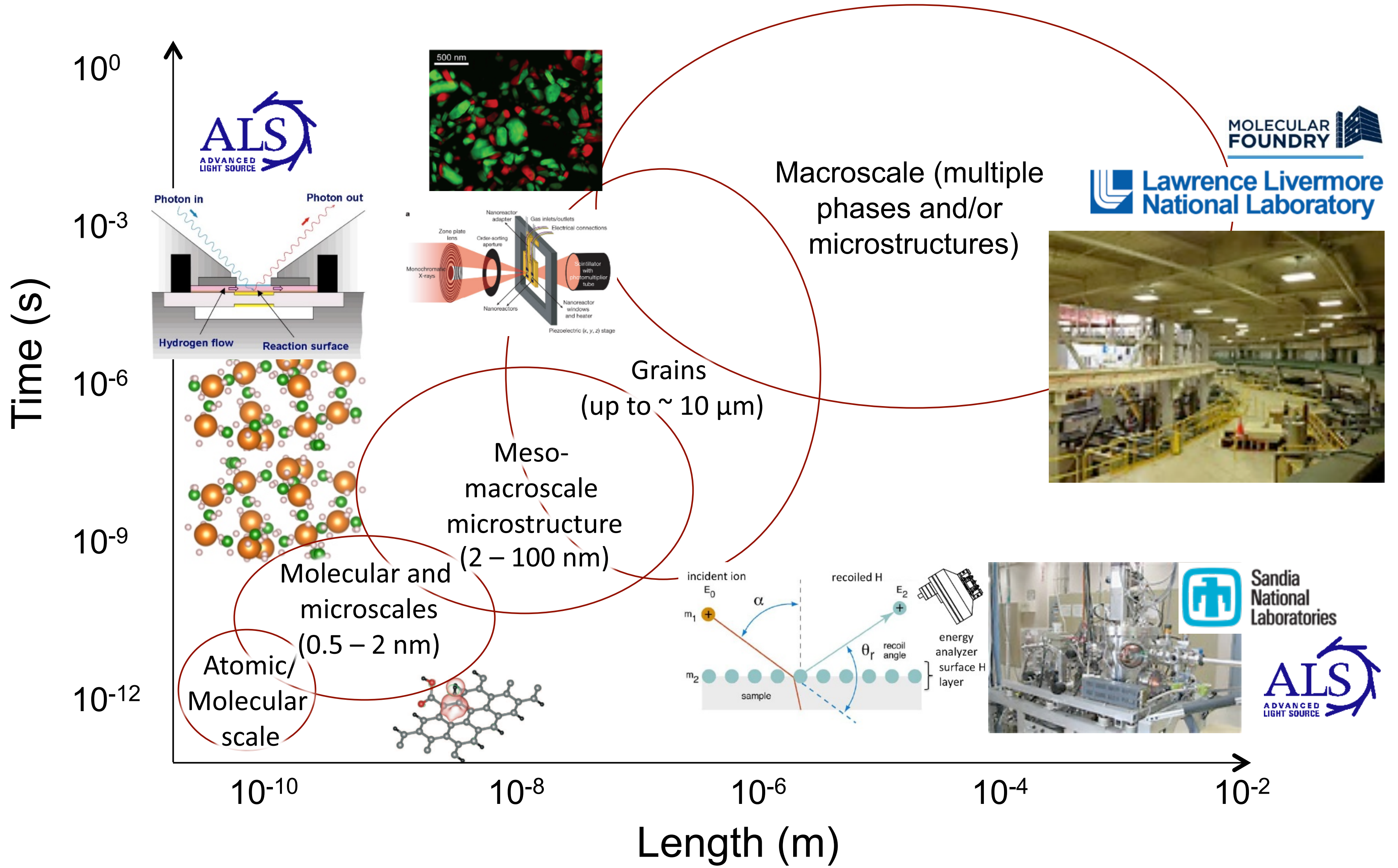
Graphene nanobelts, templates, colloidal synthesis

HyMARC

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



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

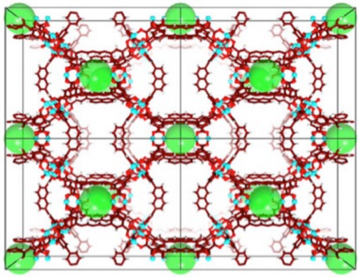
PI team

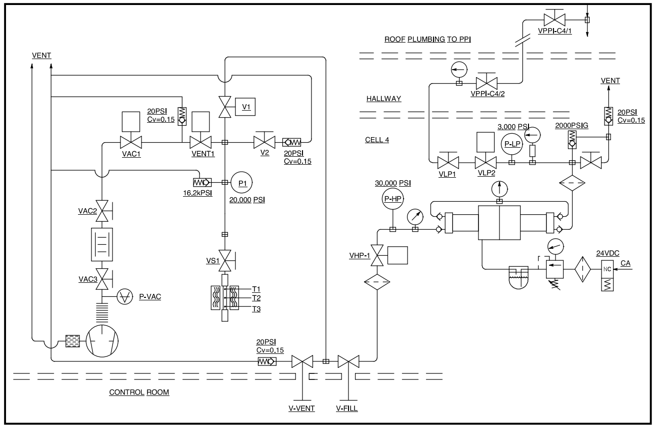
- **Sandia:** Stavila (Task lead), Allendorf
- **LLNL:** Baumann, Bonev, Campbell, Heo, Morales-Silva, Lee, Wood
- **LBL:** Urban, Fischer (UC-Berkeley), Somorjai

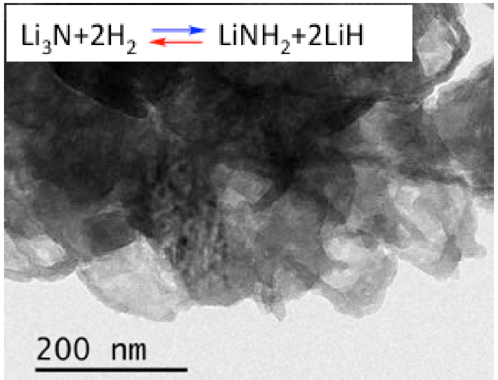
Key Results

- 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

QMCPACK







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

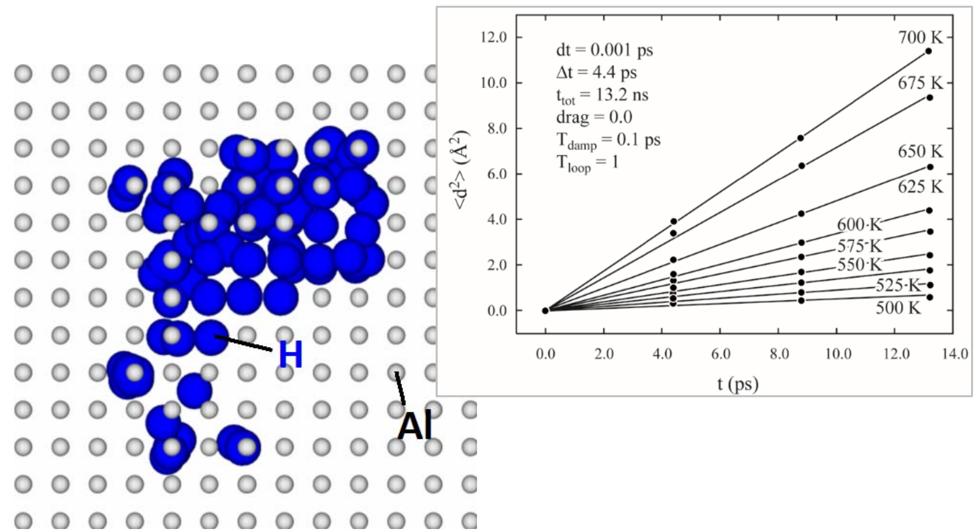
LLNL: Heo (Task lead), Wood

SNL: Zhou, Kolasinski, El Gabaly

Key Results

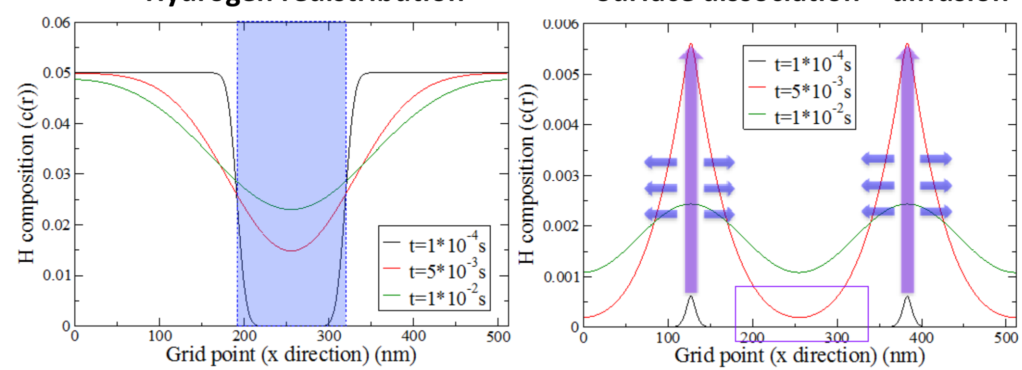
- Robust classical MD for H diffusion
  X. Zhou et al. on line *J. Phys. Chem. C* 2016
- Preliminary mesoscale surface H diffusion model

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

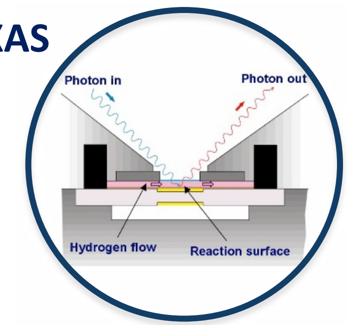
PI team

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

Key Results

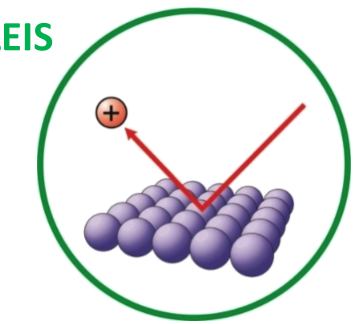
- Proof-of-concept: surface diffusion data using LEIS
- Clean transfer system: air-free XPS/AP-XPS
- In-situ, real-time surface composition monitoring

XAS



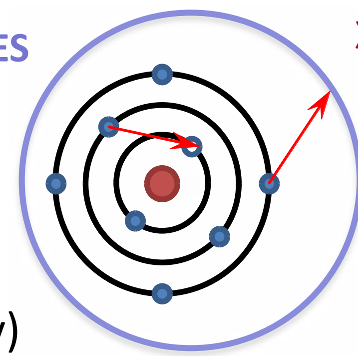
X-ray absorption spectroscopy

LEIS



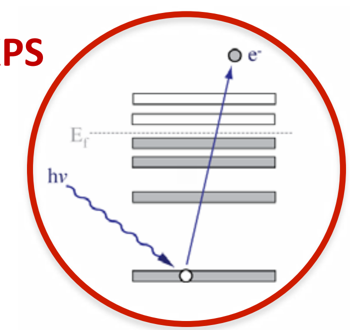
Low Energy Ion Scattering

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

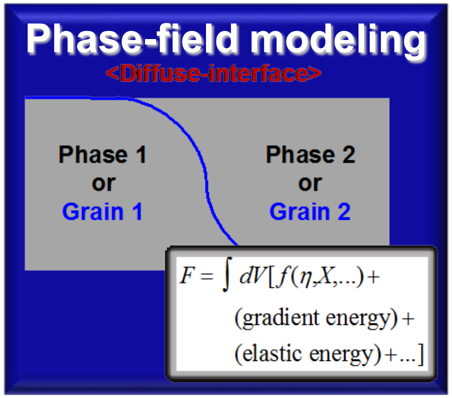
- ALS soft X-ray tools
- SNL, LLNL, MF/NCEM TEM

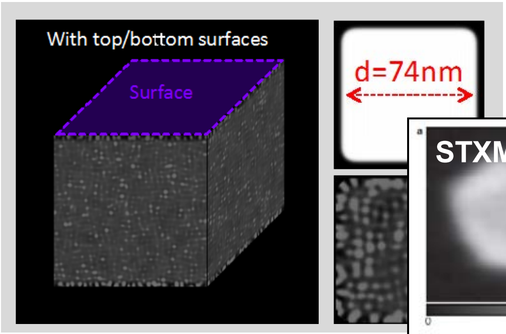
PI team

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

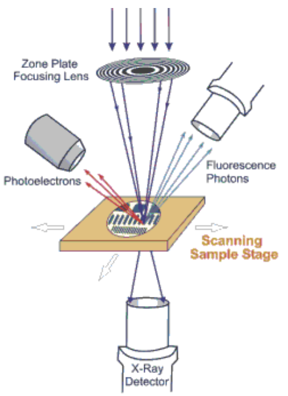
Key results

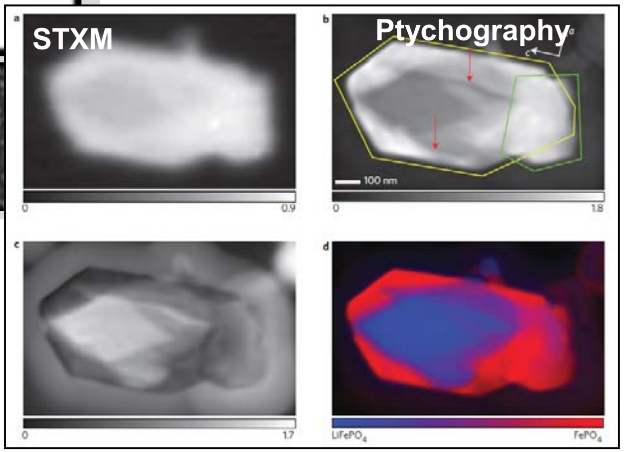
- First STXM measurements
- Phase-field model predictions compare favorably with experiment





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

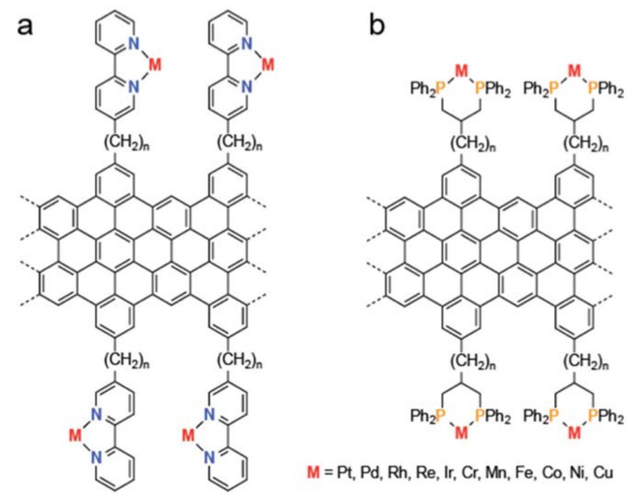
PI team

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

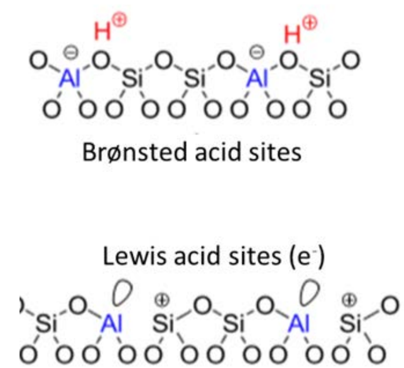
Key results

- 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



HyMARC

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:
    - $\Delta H_f°$,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

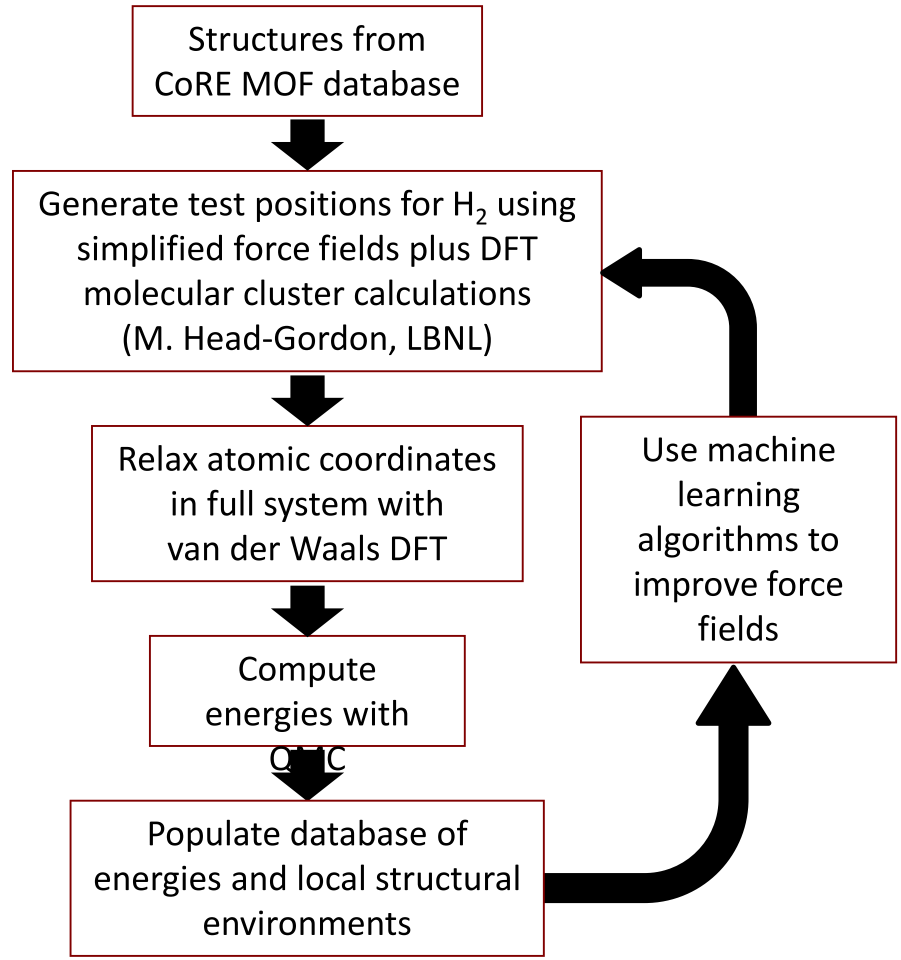
PI team

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

Characterization Team

- **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

DOE BES User Facility

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

Industry

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

Academia

- **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

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!

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

HyMARC

Lawrence Livermore National Laboratory

Sandia National Laboratories

BERKELEY LAB
Lawrence Berkeley National Laboratory