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

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Livermore, CA
June 7, 2017

HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

Project ID: ST127

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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 DOE Funding: $2,250K
- FY17 Planned DOE Funding: $3,000K
- Total DOE Funds Received: $6,000K

Partners

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

Relevance: 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

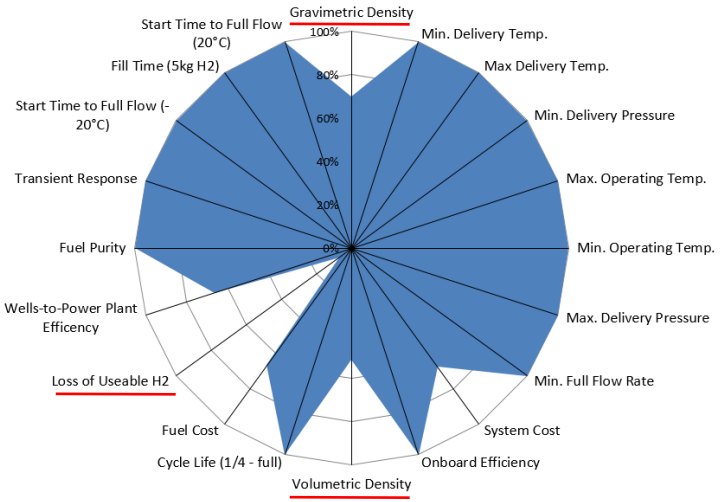
Metal hydrides

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

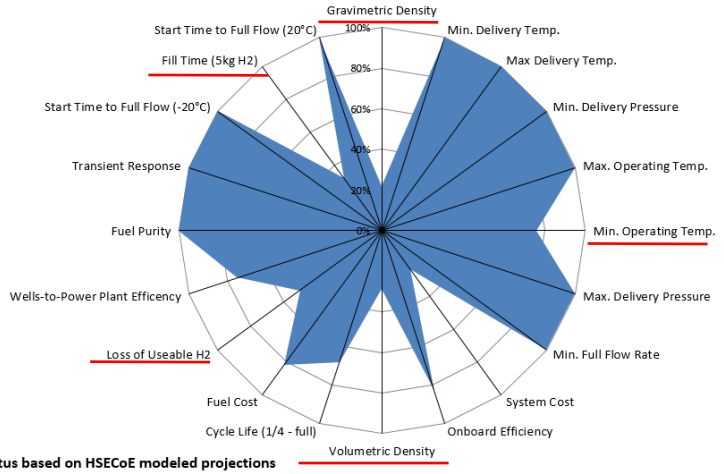
*DOE Engineering Center of Excellence

Projected MOF-5 System Compared Against 2020 Targets
(100 bar, 80-160K, Type I Tank, Hexcell - loose powder)



Status based on HSECoE modeled projections

Projected Sodium Alanate (SAH) System Compared Against 2020 Targets *(dual tank)*



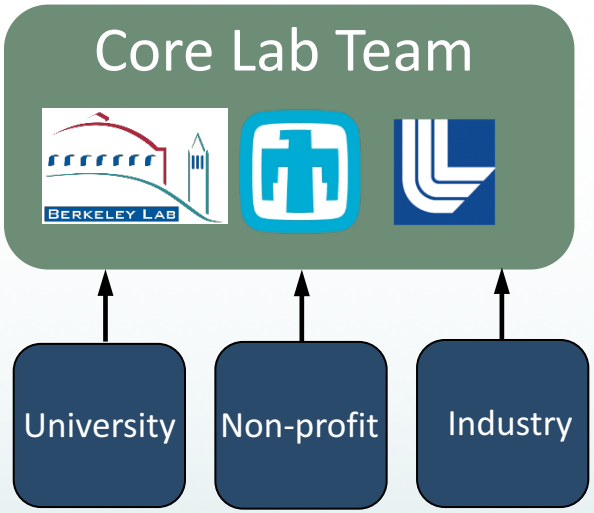
Status based on HSECoE modeled projections

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

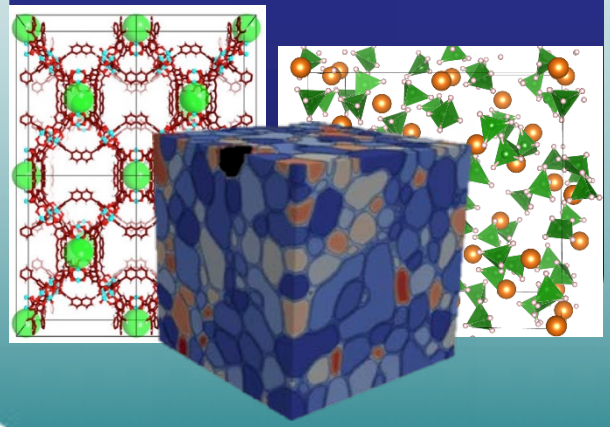
Foundational understanding of phenomena governing thermodynamics and kinetics limiting the development of solid-state hydrogen storage materials

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

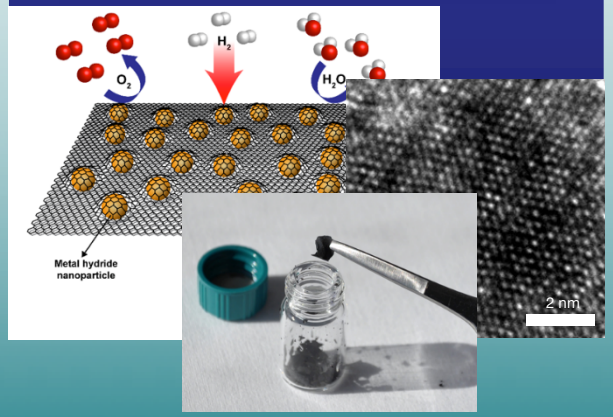
- **Computational models and databases** for high-throughput materials screening
- **New characterization tools and methods** (surface, bulk, soft X-ray, synchrotron)
- **Tailorable synthetic platforms** for probing nanoscale phenomena



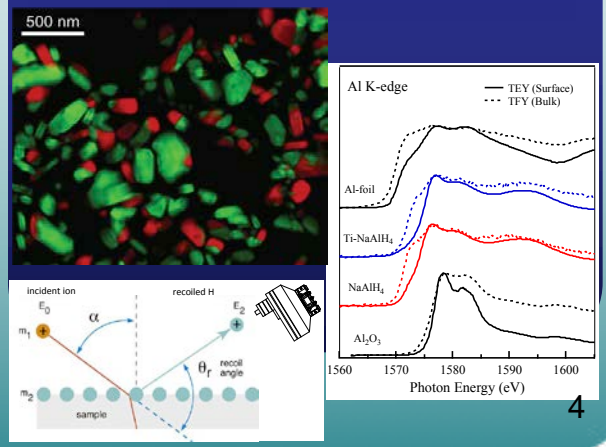
Theory, simulation, & data



Controlled synthesis



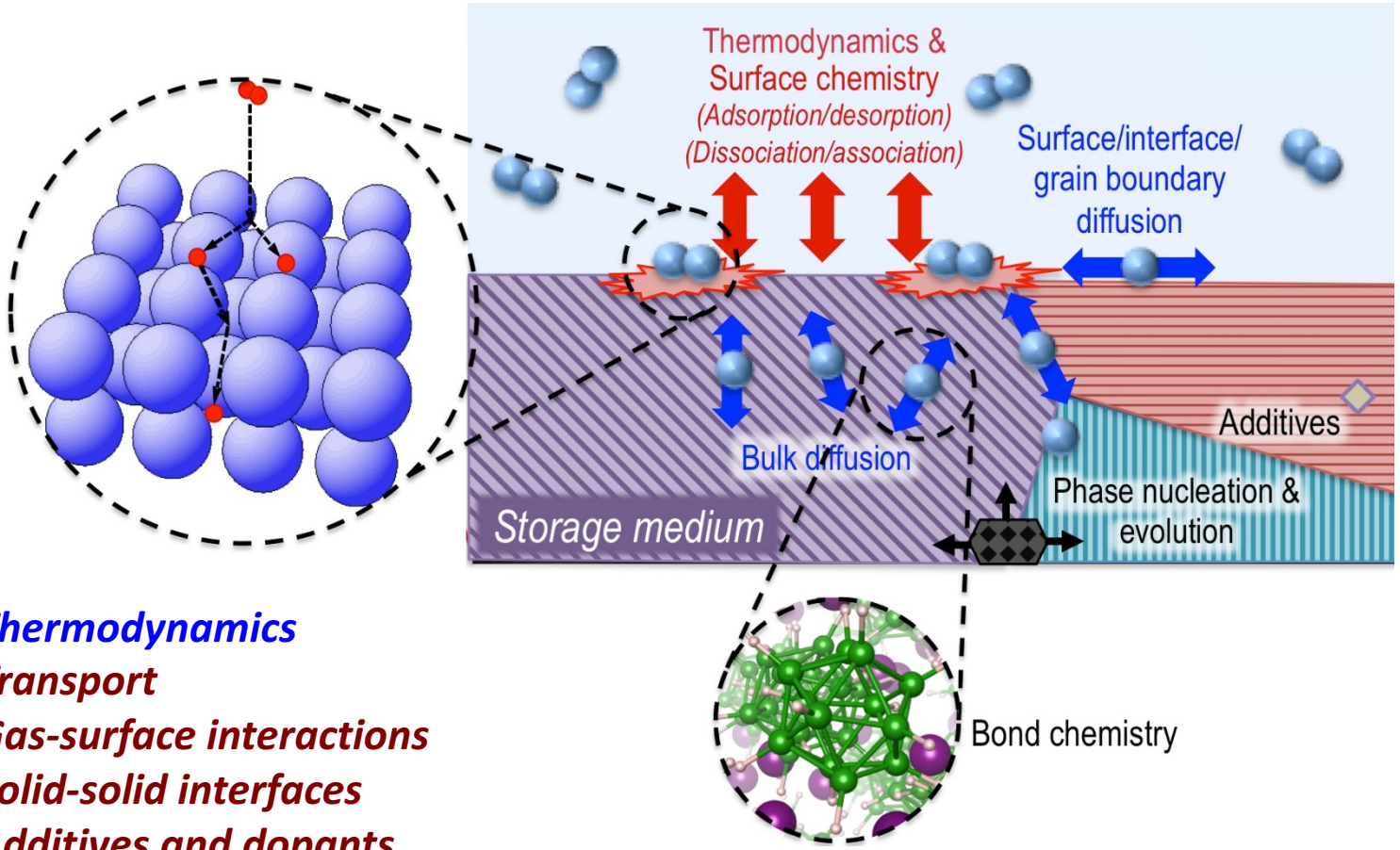
In situ characterization



Relevance: HyMARC tasks target thermodynamics and all major phenomena potentially influencing reaction 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

Approach: HyMARC is part of a network of laboratories interacting closely with individual projects

"Seedling" projects

Core National Laboratory Team

HySCORE: Characterization and Validation Team

- **Applied material development**
  - Novel material concepts
  - High-risk, high-reward
- **Concept feasibility demonstration**
- **Advanced development of viable concepts**

- **Material development tools**
  - Foundational R&D
  - Computational modeling development
  - Synthetic/characterization protocol development
- **Guidance to FOA projects**
- **Database development**

- **Characterization Resources**
  - Validation of Performance
  - Validation of "Theories"
- **"User-facility" for FOA projects/HyMARC**
- **Characterization Method Development**

Accomplishments overview: technical themes highlighted in the consortium partner presentations

- **New capabilities development**
- **Foundational understanding**
- **Intense collaborations among HyMARC partners**
- **ALS projects: 3-year Approved Program launched**
- **$Mg(BH_4)_2$: a HyMARC-HySCORE collaboration**
- **The HyMARC payoff: supporting the FOA Seedling Projects**

Accomplishment: enhanced internal and external communications

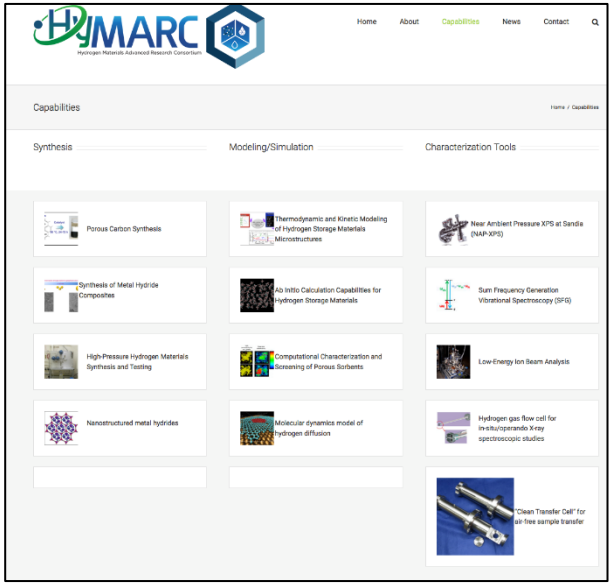
HyMARC web site is online

- Descriptions of all capabilities
- Contact portal
- News
- Will eventually provide links to databases

https://hymarc.org/

Other team communications

- Individual monthly webinars focused on modeling with 2 Seedling projects
- PNNL/HySCORE webinars (biweekly) r.e. modeling borohydrides + bilateral site visits
- Theory group webinars (biweekly) for HyMARC – HySCORE coordination
- Task meetings (monthly with in-person participation by all three labs)
- HyMARC-HySCORE-DOE steering committee conference calls (monthly)



Accomplishment: extensive suite of modeling capabilities. Many are ready for use by internal and external collaborations

- **Forcefield evaluation tool:** Developed a **comprehensive Mathematica tool** for fitting properties of various hydrides that is easily adapted to a range of material systems of interest for hydrogen storage. This tool allows new potentials to be fully evaluated in as little as one day.

The Journal of Physical Chemistry

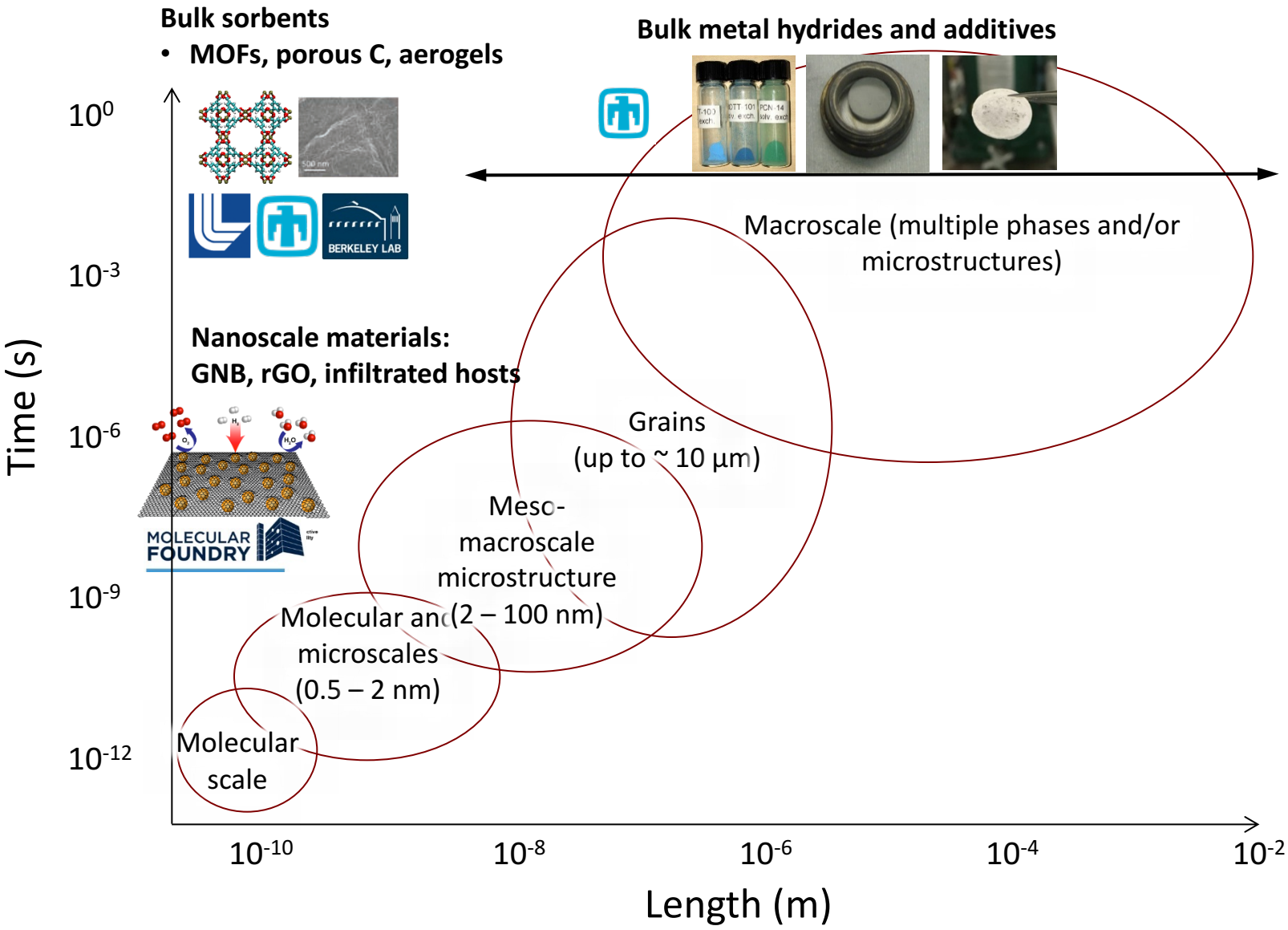
Molecular Dynamics Simulations of Hydrogen Diffusion in Aluminum

X.W. Zhou, F.El Gablay, V. Stavila, and M.D. Allendorf
Sandia National Laboratories, Livermore, California, 94550, U.S.

J. Phys. Chem. C 2016, 120, 7500−7509

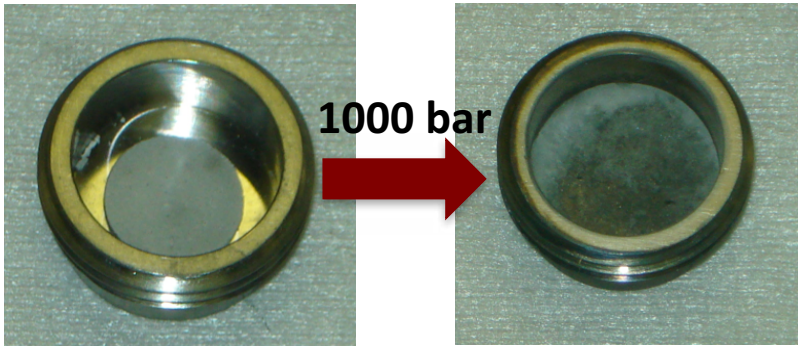
- **Ready for use: Finite-temperature free energy model of hydride phases** (based on ab initio dynamics)
- **Ready for use:** Multiphase **phase-fraction model of hydrides.** Predicts phase composition at intermediate stages of (de)hydrogenation
- **Ready for use: mechanical stress-strain model.** Predicts effects on hydride thermodynamics
- **Ready for use:** Semi-empirical **kinetic models of hydrogen surface reaction and diffusion**

Accomplishment: Synthesis capabilities summary: bulk materials, dopants, sorbents, and nano-scale platforms

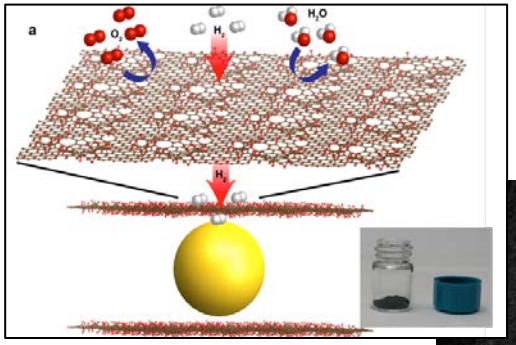


Accomplishment: Selected highlights of synthesis and method development

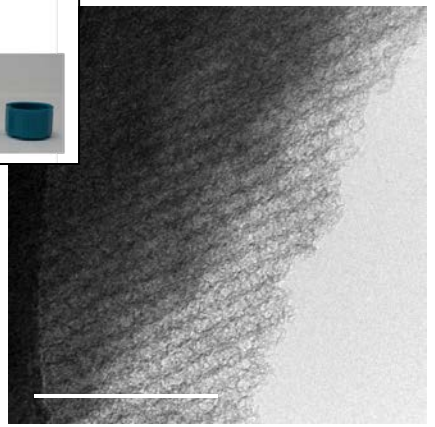
- Ultra-high pressure reactor now online and available for use by Independent Projects SNL, HySCORE, Seedling projects



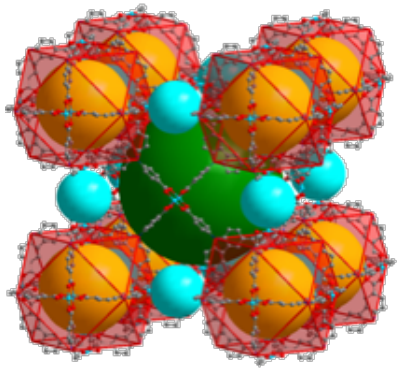
- Complex hydrides incorporated in Reduced Graphene Oxide (rGO) hosts LBL/Urban-Fischer, LLNL/modeling



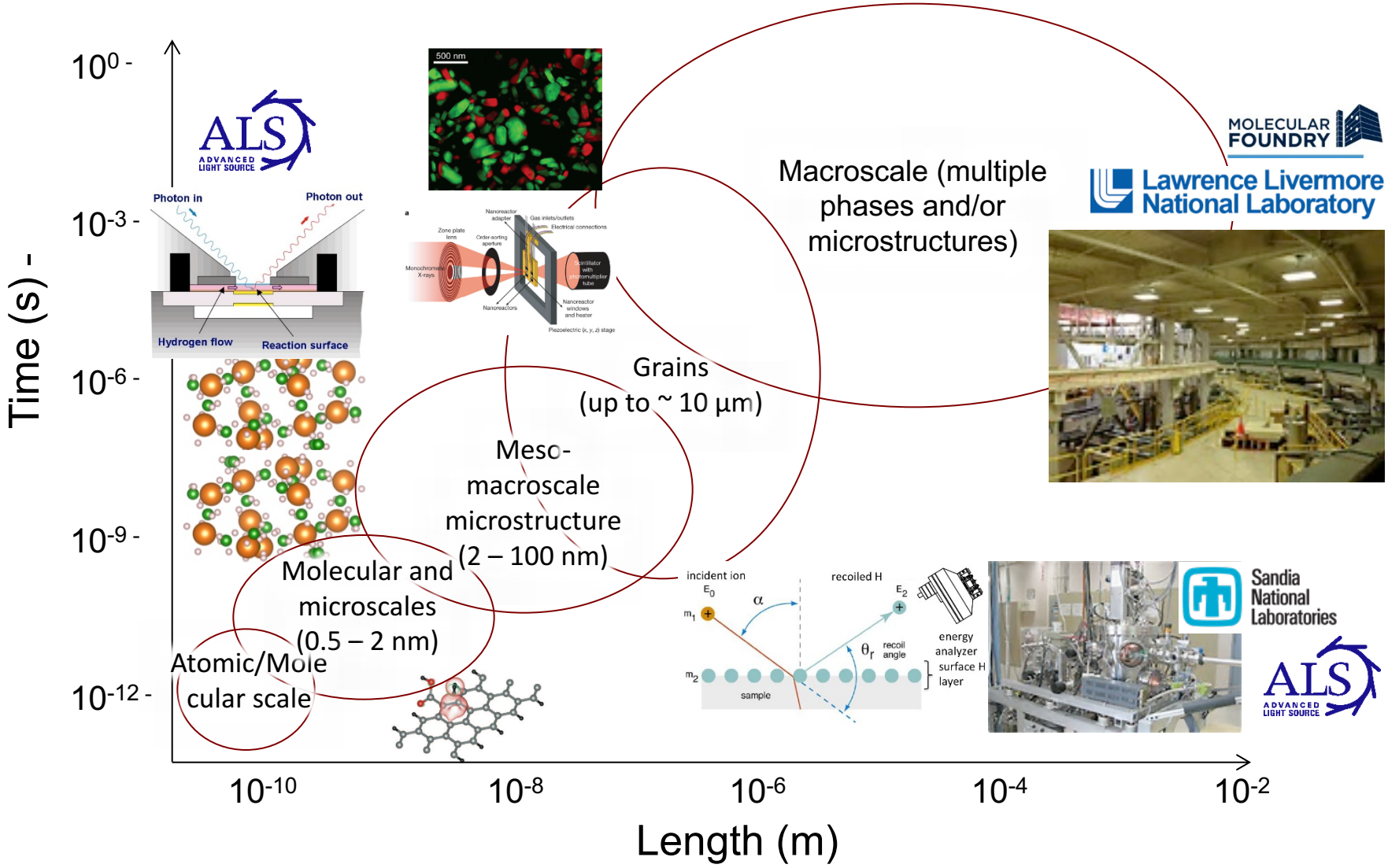
- Boron and nitrogen-doped carbon aerogels and templated carbons as sorbents and hosts for metal hydrides SNL, UMSL (Seedling), LLNL (Baumann)



- Ultra-high surface area MOFs – testing the Chahine rule SNL (Stavila, Benin), LBL (Haranczyk)

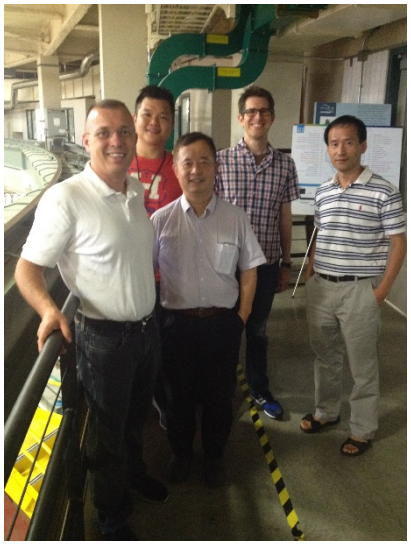


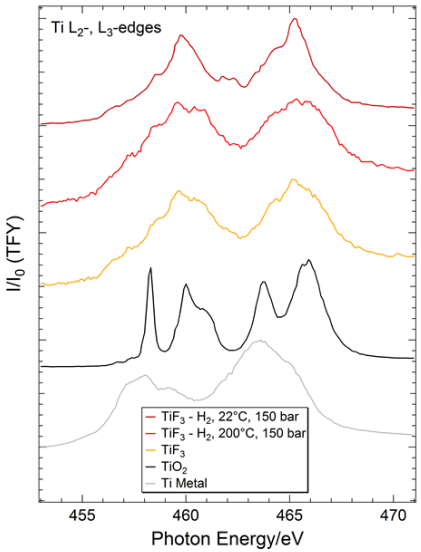
Accomplishments: Characterization: state-of-the-art tools probing bulk and surface chemistry, microstructure, phase composition



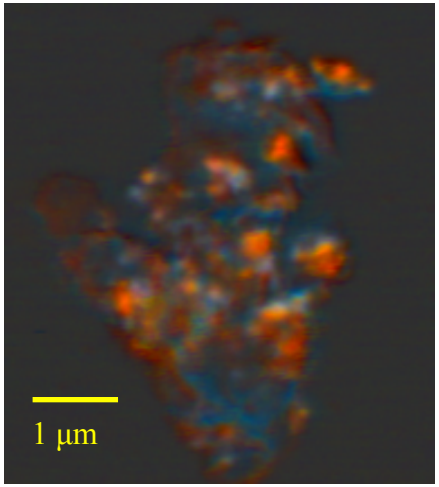
Accomplishment: HyMARC ALS Approved Program provides guaranteed access for 3 years (effective July 2016) to two beamlines

- 5% of time on BL 5.3.2.2 (Scanning Transmission X-ray Microscopy--STXM)
- 6% of time on BL 7.3.1 (X-ray Absorption Spectroscopy)
- HyMARC supports a full-time postdoc
- “Clean transfer cell” supplied to ALS

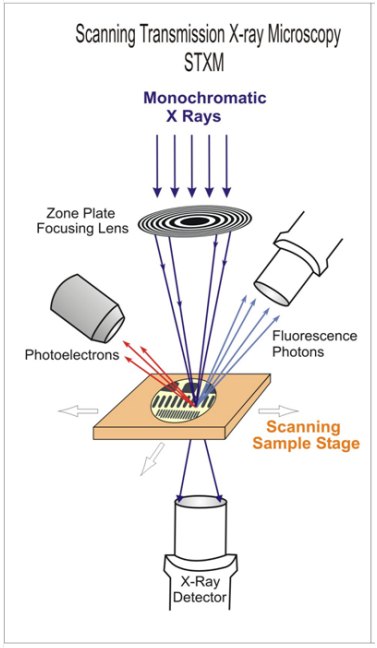




X-ray Absorption Spectroscopy



STXM mapping of additives in hydride crystallites



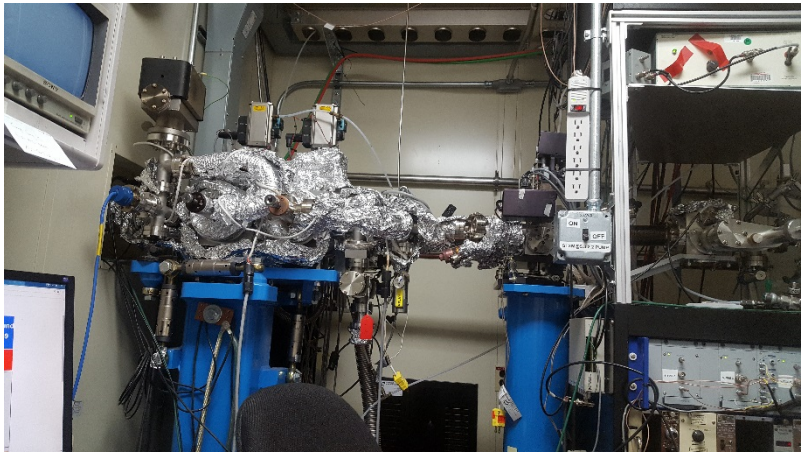
Accomplishment: A major ALS method development and scoping effort was launched starting in July 2016

Approved Program activities: method development and experiments using model materials

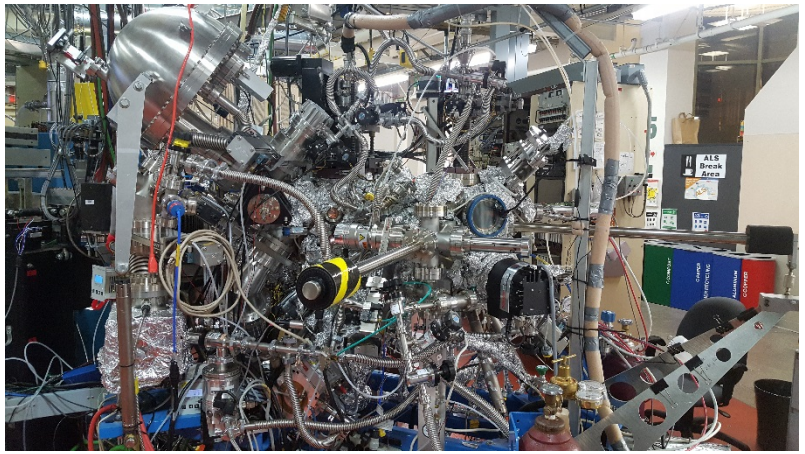
- **STXM (BL 5.3.2.2)**
  - First large-scale data collection was completed
  - 15 8-hour shifts
  - Initial samples: Ti-doped $NaAlH_4$, Li_3N, and Mg nanoparticles
- **XAS/XES (BL 6.3.1.2)**
  - Broad range of hydrides and decomposition products

AP-XPS at the ALS (BL11.0.2)

- In very high demand
- Obtained access via Director's Discretionary time
- Submitted 1-year General User proposals for AP-XPS and ptychography



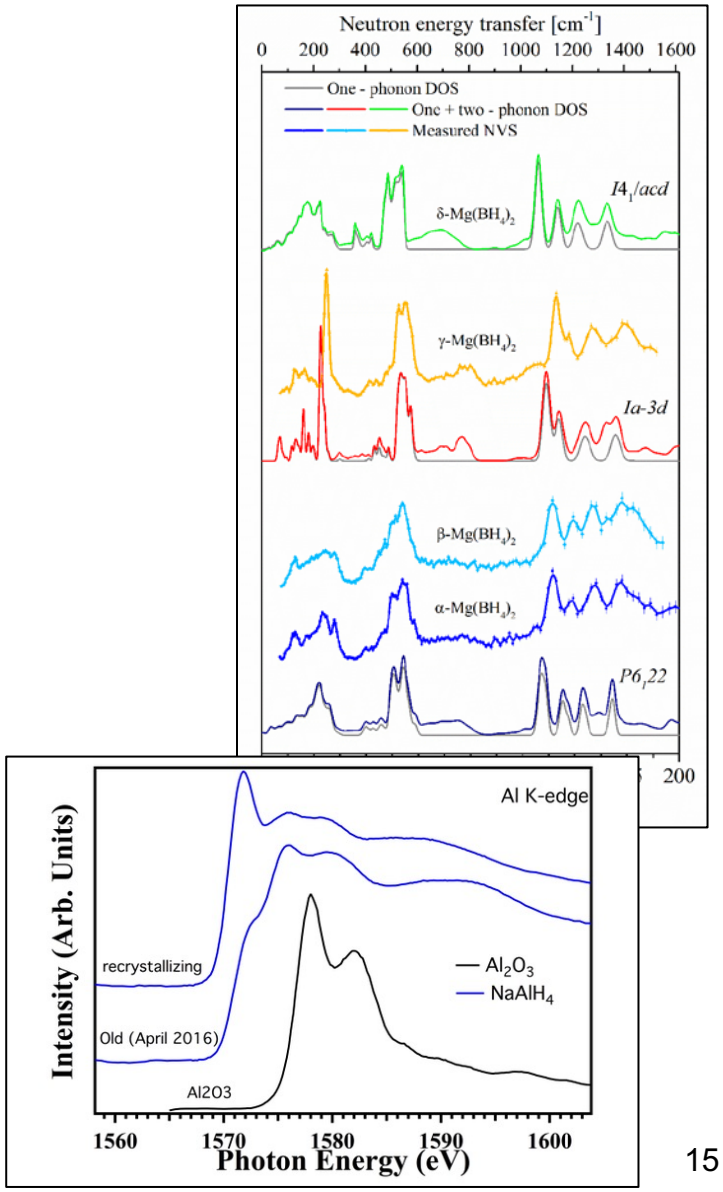
STXM instrument on BL 5.3.2.2



AP-XPS instrument on BL 11.0.2

Accomplishment: spectroscopic standards library to facilitate understanding of novel storage materials

- **HyMARC-HySCORE collaboration**
  - PNNL/Autrey: NMR
  - NIST/Udovic: NVS
  - LBNL-Molecular Foundry/Prendergast: computational spectroscopy
  - XAS (ALS): LBNL/Guo; LLNL/Lee; SNL/White
  - SNL/Stavila, Benin, White (hydride and MOF sample prep)
  - IR/Raman (SNL): Klebanoff
- **XAS data collected to date:**
  - Al K-edge data: Al foil, Al_2O_3, $LiAlH_4$, $NaAlH_4$, Ti-doped $NaAlH_4$
  - Na K-edge data: NaOH, $NaHCO_3$, $NaNH_2$, NaH, $NaBH_4$, $NaAlH_4$, and Ti doped $NaAlH_4$
  - $TiCl_3$, TiF_3
  - KH-doped Li-Mg-N-H
  - α-, β- and γ-$Mg(BH_4)_2$
- **NVS data:** α-, β- and γ-$Mg(BH_4)_2$ at 4 K
- **NMR:** borohydride intermediates (B_xH_y)
- **First publication:** ***PCCP*** 2016**, 18**, 25546



Collaborations

- **Dr. Tom Autrey (PNNL):** NMR of borohydride systems
- **Drs. Tom Gennett, Katie Hurst, Phil Parrila:** high-accuracy H_2 sorption measurements
- **Prof. Martin Head-Gordon (LBNL):** quantum-chemistry calculations/physisorption
- **Prof. Jeff Long (LBNL):** porosimetry, high-pressure FTIR
- **Dr. Terry Udovic, Dr. Craig Brown (NIST):** neutron spectroscopies and diffraction

HySCORE

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

DOE BES User Facility

- **Prof. Lizhi Ouyang (Tennessee State University):** amorphous metal hydride models
- **Prof. Marcello Baricco (University of Turin, Italy):** IEA Task-32 theory review article
- **Prof. Torben Jensen (Aarhus University, Denmark):** metal borohydride intermediates
- **Prof. Stefan Kaskel (Technical University Dresden):** high surface-area MOFs
- **Dr. Nico Fisher (Univ. Cape Town, South Africa):** In-situ time-resolved XRD
- **Prof. Pasit Pakawatpanurut (Mahidol Univ., Thailand):** Metal hydride synthesis
- **Prof. H.-C. Yu (U. Michigan): Phase-field model development**
- **Dr. M Otani (AIST, Japan): Hybrid quantum-classical simulations of borohydride interfaces**

Academia & Government

- **Agiltron, Inc. (**Dr. Jing Zhao)**: SBIR to develop Mg-(reduced graphene oxide) technology**
- **Liox Inc. (**Dan Addison): metal *closo*-boranes

Industry

Mark Allendorf is representing HyMARC at the IEA Task 32 meetings ("Hydrogen-Based Storage") and attended meetings in Berlin (Dec. 2016) and Hawaii (March 2017)

Collaborations: HyMARC is actively collaborating and facilitating new FY17-18 Seedling Projects

- ***Development of Magnesium Boride Etherates as Hydrogen Storage Materials*** (Dr. Godwin Severa, PI; Univ. of Hawaii)
  - Cody Sugai visiting for 1 month to perform high-pressure studies of Mg borohydride etherate regeneration
- ***"Graphene-wrapped" Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials*** (D. -J. Liu, PI; Argonne Nat'l Lab)
  - LLNL is collaborating with the ANL project team to understand the thermodynamics and electronic structure of hydrides under confinement
  - Technical discussions with Jeff Urban's group at LBL underway
- ***Fundamental Studies of Surface-Functionalized Mesoporous Carbons for Thermodynamic Stabilization and Reversibility of Metal Hydrides*** (Prof. Eric Majzoub, PI; Univ. Missouri, St. Louis)
  - Grad student Waruni Jayawardana visited for 3 weeks to perform XPS and high-pressure gas sorption measurements of N-doped porous carbon samples
- ***Developing A Novel Hydrogen Sponge with Ideal Binding Energy and High Surface Area for Practical Hydrogen Storage*** (Prof. Michael Chung, PI; Penn State Univ.)
  - Postdoc visit to SNL (April 2017)
- ***Electrolyte Assisted Hydrogen Storage Reactions*** (Dr.Channing Ahn, Caltech)
  - Technical discussions underway

Progress toward FY17 Milestones

Milestone (revised)	Description	Status*
Q3 FY16	Demonstrate in-situ soft X-ray AP-XPS, XAS, XES tools, with sample heating	100
Q4 FY16	Identify hydride mobile species and diffusion pathways	100
Q4 FY16	Synthesize library of nanoparticles: 1 – 5 nm, 5 – 10 nm, >10 nm for one prototype hydride	100
12/31/17	Use QMC, DFT, and force fields to compute H_2 binding and select appropriate levels of theory for MOFs.	50
9/30/17	Sensitivity analysis of local binding and second-sphere effects	20
3/31/17 Go/No-go	Rank improvement strategies for sorbents. Decision criterion: select 2 with greatest potential for increasing $\Delta H°$	100
6/30/17	Modify LEIS instrument to enable laser-induced thermal desorption	100
9/30/17	Evaluate additive/composite strategies for improving effective ΔE	20
9/30/17	Prototype hydride surface and interface chemistry kinetic models	100

*% Complete

Remaining Challenges and Barriers

Integration of diverse models to create an integrated framework is a major undertaking

We have initiated discussions with developers of the AMPE code at LLNL to collaborate on strategies for model integration, with full implementation planned in Phase II pending project renewal.

Access to ALS facilities is limited, particularly for beam lines that can probe light elements such as boron

We made use of Director's Discretionary Time to gain access for limited, but high-impact, experiments (e.g., AP-XPS of Ti-doped $NaAlH_4$). These provide the basis for General User Proposals that we are submitting. We are also considering facilities at other light sources

A single database framework that can integrate experimental and theory data, as well as past data archived within the DOE Hydrogen Storage Materials Database

We are working within the broader Energy Materials Network to engage with other consortia to develop common database formats and activities. This will make the best use of limited resources and facilitate data sharing.

The broad diversity of HyMARC activities and potential storage materials will be difficult to address, even within a large consortium such as ours

HyMARC leadership, in consultation with DOE, will be making decisions later in FY17 concerning which activities to bring to conclusion and redirect resources to focus on the highest-priority areas.

Proposed future work

- - Initiate database development activities (Task 6) pending identification of common platform for EMNs by DOE
- - Submit General User Proposals to upcoming ALS proposal calls to gain access to beam lines 11.0.2 (AP-XPS, STXM, and ptycography; light elements B, N, O, Mg, Al) and 8.0.1 (XAS, light elements including B, C, N, O, Na)
- - Broaden access to neutron facilities at ORNL/Spallation Neutron Source:
  - - Submitting Programmatic and General User proposals for access to VISION and NOMAD
  - - Planning to fund postdoc to reside at the SNS
- - Initiate model integration activity, in collaboration with AMPE code developers at LLNL
- - Convene consortium partner PIs, task leads, and BES user facility POCs to prioritize research activities and redirect resources as needed

Summary

- **HyMARC communications are greatly enhanced relative to 2016 AMR**
- **Model development is moving at a fast pace; new capabilities:**
  - Materials informatics+hi-accuracy binding energies+GCMC to develop accurate sorbent force fields
  - Finite-T hydride thermodynamics
  - Environment/morphology effects on hydride thermodynamics
  - Solid mechanics/strain effects model
  - Non-equilibrium mass transport models
  - Surface chemistry model
  - Reactive interface phase-field method developed
- **New synthetic methods provide materials and data targeted at specific phenomena**
  - Dopant effects on hydride thermodynamics
  - rGO and GNB demonstrated as hosts for both binary and complex hydrides
  - Ultrahigh pressure effects on sorbents and hydrides
  - New insights into metal borohydride chemistry
- **Advanced characterization capabilities and methods are now on line**
  - A vigorous experimental program at the ALS is providing many new insights
  - Surface chemistry instrumentation suite probes all relevant length scales
  - Programmatic proposal submitted to ORNL-SNS for access to VISION and NOMAD
- **Robust collaborations**
  - Within HyMARC
  - Seedling projects
  - International partners

We are grateful for the financial support of EERE/FCTO and for technical and programmatic guidance from Dr. Ned Stetson

Enabling twice the energy density for onboard H_2 storage

Lawrence Livermore National Laboratory

Sandia National Laboratories

BERKELEY LAB
Lawrence Berkeley National Laboratory

Technical Back-Up Slides

HyMARC Synchrotron Activities at the ALS in FY17

Beamline 5.3.2.2 – Scanning transmission x-ray Microscopy (STXM)

Duration of experiments: 15 shifts (5 days), +9 scheduled shifts prior to FY18

Research highlight: Chemical mapping of Ti-based dopants in NaAlH4

Beamline 6.3.1.2 – X-ray absorption spectroscopy (XAS)

Duration of experiments: 27 shifts (9 days)

Research highlights: Evolution in electronic structure and bonding of (i) TiF_3-doped $NaAlH_4$ & (ii) $MgB_2/Mg(BH_4)_2$ during hydrogenation/dehydrogenation

Beamline 8.0.1.1 –XAS and X-ray emission spectroscopy (XES)

Duration of experiments: 3 shifts (1 day), +6 scheduled shifts prior to FY18

Research highlight: Identification of the composition/bonding within GO encapsulated $Mg(BH_4)_2$ nanocrystals

Beamline 11.0.2 – Ambient Pressure X-ray Photoemission Spectroscopy (AP-XPS)

Duration of experiments: 3 shifts (1 day)

Research highlights: Mechanistic understanding of the roles of Ti and O in the surface dehydrogenation of Ti-doped $NaAlH_4$

Experimental capabilities generated/in development

- A gas cell for XAS/XES of solid state materials under low (~ 1 atm) H_2 pressure and high temperatures (~ 400°C) is almost complete
- Hardware for O_2/H2O-free transfer of air sensitive samples in AP-XPS studies is now fully commissioned

Advanced simulations are critical to the success of the synchrotron experiments

Simulated XAS provides vital predictions/interpretation of materials interfaces during (de)hydrogenation

Personnel involved in experiments: LLNL: A. Baker, J. Lee; SNL: F. El Gabaly, J. White, L. Klebanoff; LBNL: J. Guo, Y.-S. Liu, D. Prendergast

Background for FY17/Q2 Go/No-go Milestone (3/31/2017)

Rank improvement strategies for sorbents. Decision criterion: select 2 with greatest potential for increasing ΔH°. Literature reports and modeling also taken into account.

Downselected strategies

1. Open metal sites (OMS): It is well established for MOFs that H_2 binds more strongly to metal cations with incomplete coordination spheres than to other structural features where only weak physisorption occurs. For example, the highest Q_{st} reported for a MOF without an OMS was 9.5 kJ/mol as of 2012, whereas it is 15.1 kJ/mol for a MOF with OMS and there are several in the 10 – 12 kJ/mol range (see M. P. Suh et al. *Chem. Rev.* 2012, 112, 782–835).
2. Lewis-acid/base sites: OMS in MOFs are Lewis acid sites and are considered as a separate strategy. A related strategy is to incorporate electron-deficient atoms such as boron into porous carbon or other porous materials. This strategy appears promising; Q_{st} values up to ~9 kJ/mol are observed for porous graphene oxide (G. Srinivas et al. *J. Mater. Chem.*, 2011, 21, 11323) and theory predicts that B-doping may raise the adsorption energy of H_2 from 4–8 kJ/mol for pure carbon materials to 15–35 kJ mol; see e.g. Y. Xia et al. *J. Mater. Chem. A*, 2013, 1, 9365). Experimentally, Q_{st} of 12.47 kJ/mol has been reported for a 7.2% B-doped microporous carbon (see Chung et al. *JACS* 2008, 130, 6668). This strategy has not be thoroughly investigated, however.

Other strategies: these were not highly ranked, due either to their small documented effect on Q_{st} or lack of evidence supporting their use for viable storage materials.

1. Frustrated Lewis pairs: Incorporating both Lewis acid and Lewis base atoms to create frustrated Lewis pairs to polarize H_2 has not be thoroughly explored.
2. Polarization by functionalized MOF linkers: ab initio calculations predict that adding electron-donating groups (e.g. CH_3 or NH_2) to the aromatic rings of MOF linkers increases Q_{st} by only ~15%. Electron-withdrawing groups tend to decrease Q_{st}, although systematic studies of N_2 uptake with IRMOF-1-X (X=halide) indicate slightly higher Q_{st} for X=I than X=F (S. T. Meek et al. *J. Phys. Chem. C* 2012, 116, 19765). Larger Q_{st} enhancements were observed by adding amide groups to the linker rings, but the largest increase was 0.7 kJ/mol (13%; see Z. Wang et al. *Chem. Eur. J.* 2010, 16, 212).
3. Brønsted acid sites: There are examples of metal-exchanged zeolites with adsorption enthalpies as high as 17.5 kJ/mol and there are neutron data suggesting values as high as 20-40 kJ/mol might be achievable. However, zeolites are not viable storage materials and Brønsted acid sites in MOFs are rare and are less accessible than in zeolites.
4. Phase-change materials: this is a little-investigated strategy for MOFs and one for which it is difficult to predict how much Qst would be increased, since one cannot readily compare with an analogous, but structurally rigid, structure. There is evidence that structures with large breathing modes bind H_2 more tightly in the ”closed” form, but only a few examples exist. This strategy may have more value for increasing the amount of useable hydrogen, as recently demonstrated by Long et al. for methane storage (Mason et al. *Nature* 2015, 527, 357).