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

Mark D. Allendorf, P.I.
Sandia National Laboratories
Livermore, CA
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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:	$1,250K
• FY16 DOE Funding:	$2,430K
• FY17 DOE Funding:	$2,823K
• FY18 DOE Funding:	$3,025K
• Total DOE Funds Received:	$9,528K

Partners

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

Relevance/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

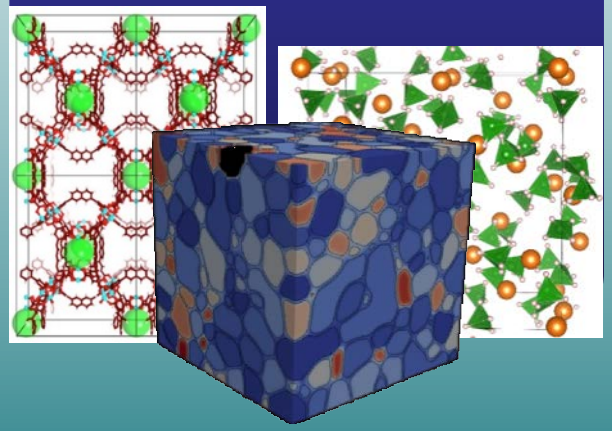
HyMARC will deliver **community tools and capabilities:**

- **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

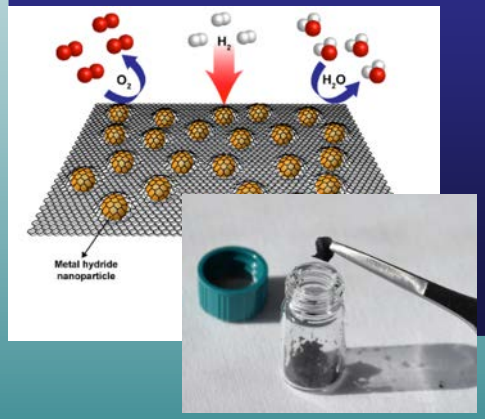
Core Lab Team

BERKELEY LAB

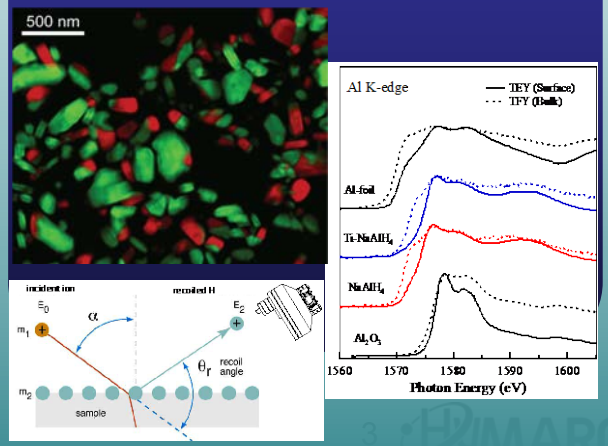
Theory, simulation, & data



Controlled synthesis



In situ characterization

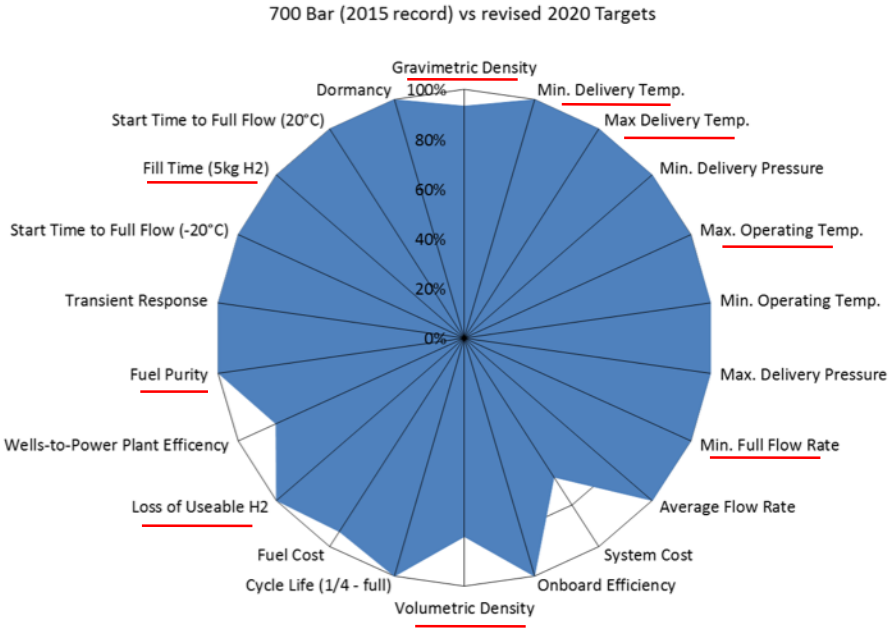


Relevance: HyMARC is accelerating materials discovery and moving the bar relative to compressed H_2

Accelerating materials discovery

- **Strategy assessments:** identified most promising material improvement strategies
- **Missing/inaccurate data:** e.g. thermodynamic data essential for material assessment
- **Modeling tools:** filling major gaps in understanding of key processes
- **Enabling Seedling Projects by providing:**
  - Access to experimental resources essential to their success (e.g., hi-P reactors and PCT)
  - Computational modeling in support of experiments (outside Seedling budget)
  - Assisting with data interpretation (e.g., computational spectroscopy)

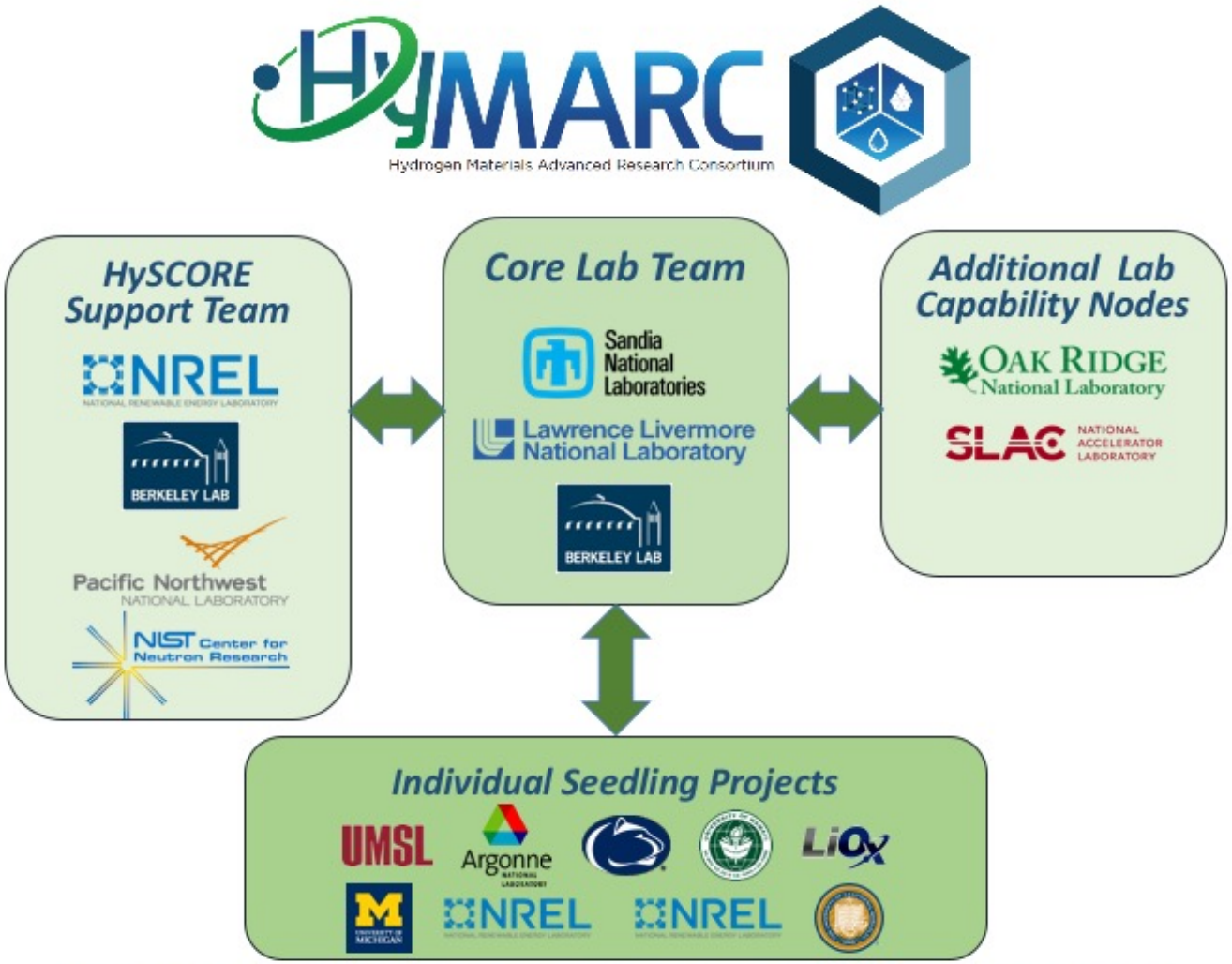
Material development strategies we evaluated indicate progress toward several DOE targets



Moving the bar for specific materials or strategies

- Interface engineering: Li_3N@(6nm-C) H_2 cycling T reduced by >180 °C (bulk is 430 °C)
- Nanoconfinement (porous host): $Mg(BH_4)_2$@(6-nm C) H_2 desorption T reduced > 100 °C
- Nanoencapsulation: $Mg(BH_4)_2$@rGO >10 wt% (record for nanoscale hydride)
- Thermodynamics tuning: U. Hawaii Seedling project (MgB_2 etherates): advances to Phase 2

Approach: The HyMARC Core Lab team addresses foundational research objectives and supports Seedling projects

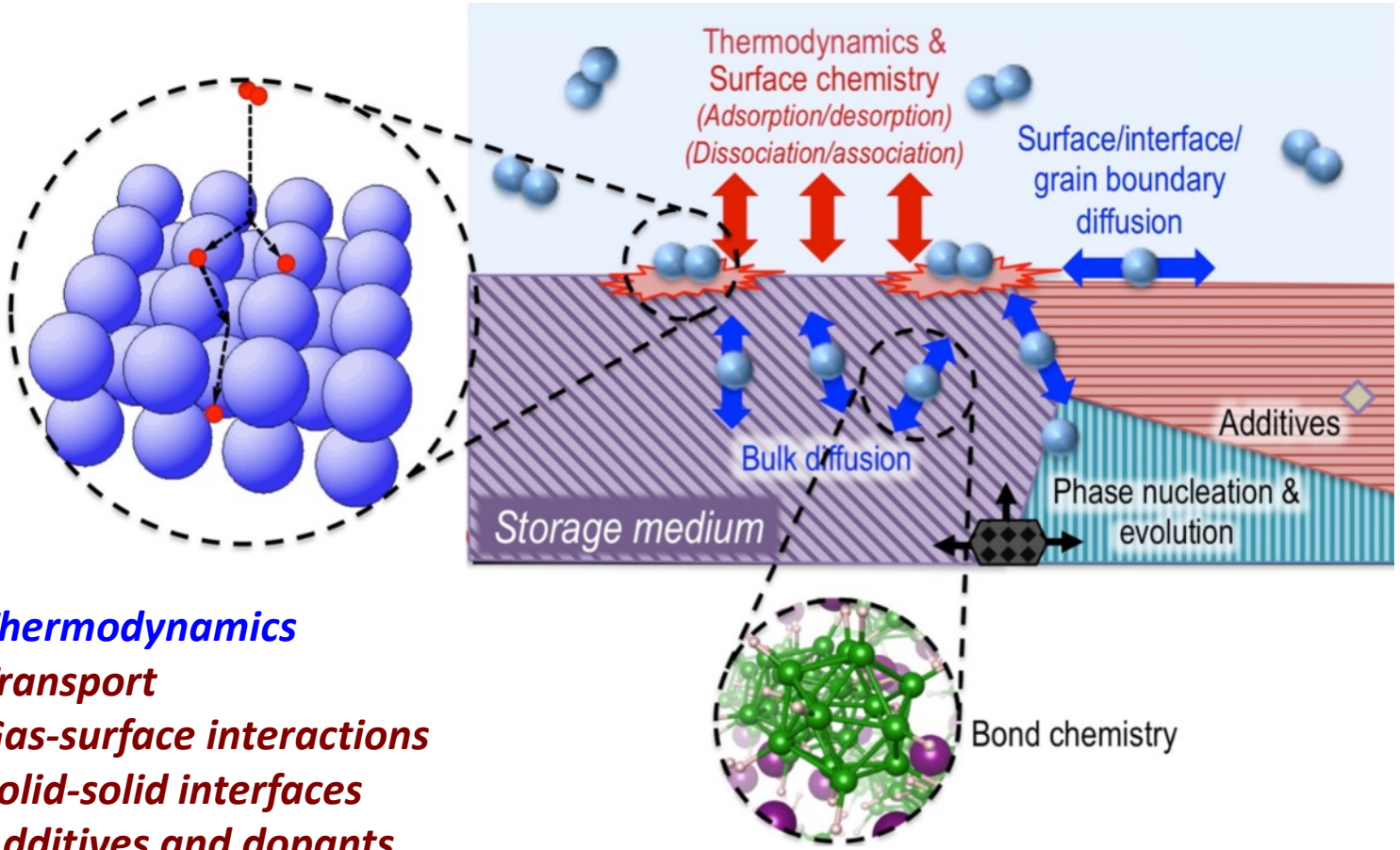


Enabling twice the energy density for hydrogen storage

Approach: HyMARC/Core Team tasks target 1) thermodynamics and 2) all 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

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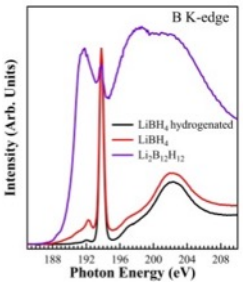
Accomplishments overview: technical themes highlighted in the consortium partner presentations

- **New capabilities developed or enhanced:**
  1. Modeling
  2. Characterization
  3. Synthesis
- **BES User Facilities and international collaborations build foundational understanding**
- **Seedling Project success enabled and enhanced**
- **Communication: making HyMARC results accessible to the hydrogen storage community**
  - Workshops
  - Sorbent Perspective
  - Nanohydride review

Accomplishment: modeling tools that now cover all relevant length scales and many important phenomena

Atomic/molecular (0 – 1 nm)

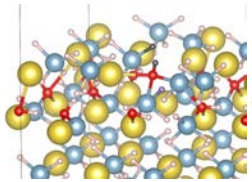
Computational Spectroscopy

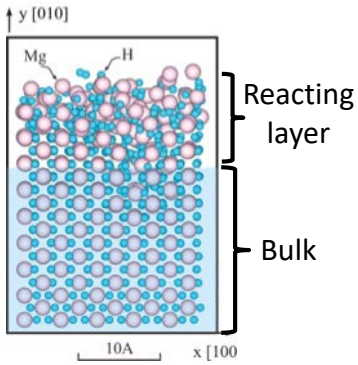


Example: $NaAlH_4$ surface chemistry: role of oxide

Molecular/micro (0.5 – 2 nm)

Surface chemistry Interatomic potentials

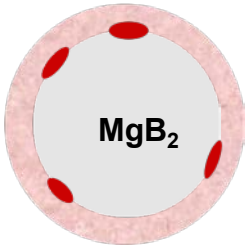


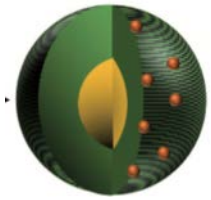


Example: Time-dependent simulations of MgH_2 formation

Mesoscale (2 - 100 nm)

Nucleation kinetics Phase microstructures

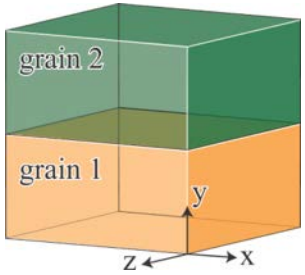




Example: Nano-alloying of Ni-doped Mg

Grains (≤ 10 μm)

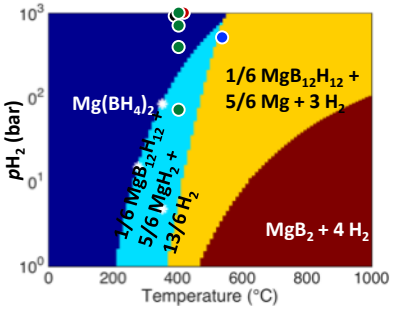
Grain boundaries Particle size effects Stress/strain



Examples: H diffusion in PdH_x Diffusion in $NaBH_4$

Macroscale/Bulk

Thermodynamics



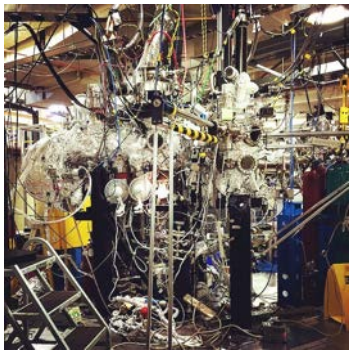
Example: $Mg(BH_4)_2$ phase diagram

10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2}

Length (m)

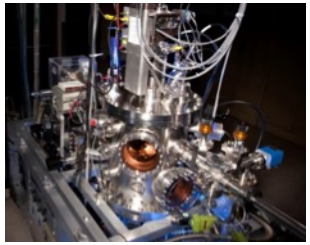
Accomplishment: characterization tools expanded and extended to in-situ, in-operando probing and mesoscale resolution

Atomic/molecular (0 – 1 nm)



AP-XPS
ALS/BL 11.0.2

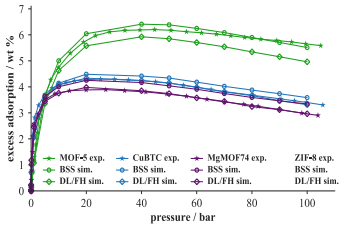
XAS In-situ flow cell (1 bar, max. 250˚C)

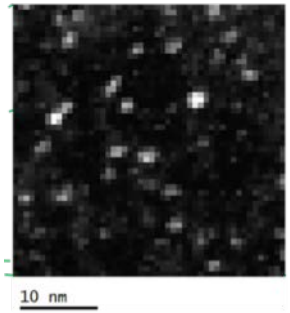


Lab-based AP-XPS

Molecular/micro (0.5 – 2 nm)

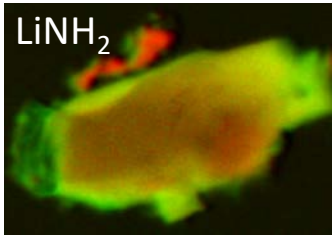
Microporosimetry/BET

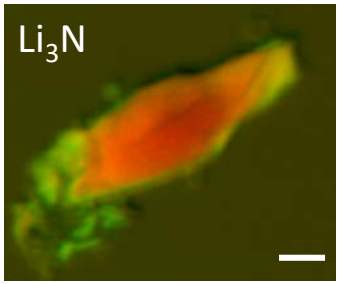




He bubbles seen by AC-TEM
STEM res. 63 pm

Mesoscale (2 - 100 nm)





STXM (30 nm res.)
LBNL/ALS

Grains (≤ 10 µm)

Macroscale/Bulk

Ultrahigh Pressure Reactor (1000 bar)

H-D exchange

10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2}

Length (m)

Accomplishment: >400 hours of synchrotron and neutron beam time at 5 international user facilities in the US, Canada, and Japan

	Shifts (8 h)	Samples
ALS Berkeley, CA (BES user facility): Approved Program continues		
STXM	9	Partially dehydrog. Li_3N and $LiNH_2$+2LiH (N K edge)
XAS	6	TiF_3/$TiCl_3$ doped MgB_2; oxidation of MgB_2; B-doped C aerogels
ALS Berkeley, CA (BES user facility): General User Proposal approved		
AP-XPS	12.5	$Mg(BH_4)_2$ *in situ* desorption: pure & partially oxidized samples
SLAC/SSRL Stanford, CA (BES user facility): General User Proposal approved		
TXM	3	MgB_2 and $Mg(BH_4)_2$
UVSOR Myodaiji, Okazai, Japan (all travel expenses covered by UVSOR)		
STXM	6	partially hydrogenated MgB_2 and partially dehydrogenated $Mg(BH_4)_2$ (B K edge)
CLS/REIXS	14	MgB_2; $TiCl_3$/TiF_3-doped MgB_2; nano-MgB_2; B-doped C aerogels
NIST Gaithersburg, MD		
NVS, INS		$Mg(BH_4)_2$, MOF-74 samples
Diffraction		M-closoborates (e.g $B_{12}H_{12}$) samples
ORNL/Spallation Neutron Source/VISION: General User Proposal approved		

Accomplishment: New sample formats for encapsulated complex hydrides, MgB_2 nanoparticles, graphene nanostructures

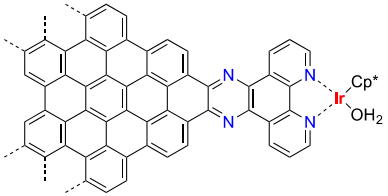
Atomic/Molecular (0 – 1 nm)

Molecular and microscales (0.5 – 2 nm)

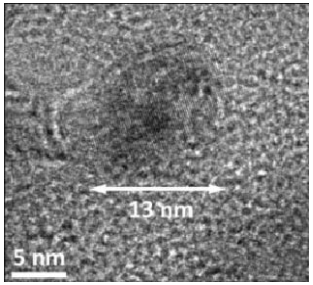
Mesoscale (2 - 100 nm)

Grains (up to ~ 10 µm)

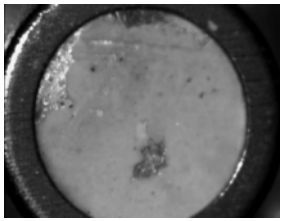
Macroscale/Bulk



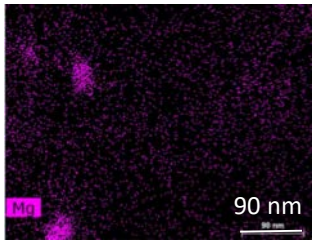
Model systems: GNR+(H_2 dissoc. catalyst)



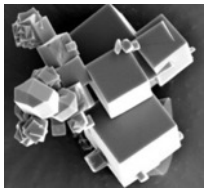
$Mg(BH_4)_2$@rGO



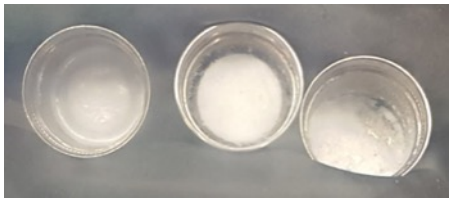
$Mg(BH_4)_2$ film on Au for LEIS measurements



MgB_2 nanoparticles
Encapsulation
Strain effects
Nanoscaling



High-purity MOFs for model validation



New thermodynamics: Liquid-phase $Mg(BH_4)_2$

10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2}

Length (m)

Accomplishment: Two major publications document Go/No-go milestones

HyMARC FY17/Q2 Go/No-go Milestone

Rank improvement strategies for sorbents. Decision criterion: select 2 with greatest potential for increasing ΔH°. Top strategies:

- ***Open metal sites in MOFs***
- ***Lewis acid/Lewis-base sites***

HyMARC FY18/Q4 Go/No-go Milestone

Rank improvement strategies for hydrides. Decision criterion: select 2 with greatest potential for reducing effective ΔH

(article addresses a major strategy considered in the Go/No-go)

Submitted to *Energy & Environ. Sci.*

"An Assessment of Strategies for the Development of Solid-State Adsorbents for Vehicular Hydrogen Storage"

Topics include:

- **Usable gravimetric and volumetric capacities**
- **The importance of binding strength**
- **Theoretical calculations of H_2 physisorption**
- **Considerations for adsorbent synthesis and characterization**
- **Revisiting the results of the 2010 HSCoE final report**
- **Perspectives on current material strategies**

Submitted to *Chem. Rev.*

Nanostructured Metal Hydrides for Hydrogen Storage

Topics include:

- **Classes of nanostructured metal hydrides**
- **Synthesis routes**
- **Structure**
- **Morphology**
- **Mechanistic effects**

Collaborations and Coordination: HyMARC is actively collaborating with Seedling Projects and facilitating their research

Improving communications: Designated point-of-contact identified for each Seedling Project

- ***Development of Magnesium Boride Etherates as Hydrogen Storage Materials*** (U. Hawaii)
  - Instability in MgB_2 B sheets explained (LLNL modeling investigation)
  - High-P hydrogenation, XRD, and FTIR performed for 43 MgB_2(etherate) samples
- ***"Graphene-wrapped" Complex Hydride Materials*** (Argonne National Lab.)
  - Go/No-Go 3 samples processed at Sandia (March 2018)
- ***Surface-Functionalized Mesoporous Carbons for Thermodynamic Stabilization and Reversibility of Metal Hydrides*** (Univ. Missouri, St. Louis)
  - XPS, FTIR, publication (Chem. Mater.); samples shipped to us
- ***Developing A Novel Hydrogen Sponge with Ideal Binding Energy and High Surface Area for Practical Hydrogen Storage*** (Penn State Univ.)
  - Measured H_2 isotherms (low- and high-P)
- ***Electrolyte Assisted Hydrogen Storage Reactions*** (Liox Power)
  - 1) High-P experiments and sample characterization; 2) Go/No-go tests underway
- ***ALD Synthesis of Novel Nanostructured Metal Borohydrides*** (NREL)
  - $Mg(BH_4)_2$ nanoparticle samples sent to NREL for ALD coating
- ***Fluorinated COFs: A Novel Pathway to Enhance Hydrogen Sorption*** (NREL)
  - Modeling study; paper submitted
- ***Optimized Hydrogen Adsorbents via Machine Learning & Crystal Engineering*** (U. MI)
  - Discussions on crystal engineering of OMS in MOFs
- ***Super-Metalated Frameworks as Hydrogen Sponges*** (UC Berkeley)
  - Discussions concerning use of high-pressure reactor and PCT

Collaborations with external research groups are vigorous

DOE BES User Facilities

- **Dr. A.J. (Timmy) Ramirez-Cuesta (SNS/ORNL):** neutron vibrational spectroscopy
- **Dr. Simon Bare (SLAC/SSRL):** synchrotron measurements

Advice and assistance writing/submitting General User Proposals for these facilities

Academia and Government

- **Prof. Torben Jensen (Aarhus University, Denmark):** metal borohydride intermediates
- **Prof. Stefan Kaskel (Technical University Dresden):** high surface-area MOFs
- **Prof. H.-C. Yu (U. Michigan): Phase-field model development**
- **Prof. Nobuhiro Kosugi, Director, UVSOR: synchrotron measurements**
- **Prof. Eun Seon Cho, KAIST: experimental measurements of strain effects**

Several manuscripts published, accepted, or underway

HyMARC is making the results of its research available to the community using multiple communication channels

Conferences and workshops

- ACS Spring 2018 symposium "Hydrogen Energy: Production, Storage & Application," March 13 – 17, 2018, New Orleans, LA (V. Stavila, T. Autrey, organizers)
- 2017 Advanced Light Source Users meeting "Surmounting Fundamental Challenges to Vehicular Hydrogen Storage," Oct. 4 – 5, 2017, Berkeley, CA (M. Allendorf, F. El Gabaly, J. Guo organizers)
- Machine learning workshop: "Application of Machine Learning and Data Analytics for Energy Materials Network Consortia 2018," May 2 – 3, 2018, Livermore, CA (B. Wood, organizer)

Presentations

- 14 contributed presentations at conferences (ECS, APS, MRS, ACS, GRC)
- 20 invited presentations

Journal publications

- 8 published since last AMR
- 2 invited reviews submitted (*Energy Environ. Sci.* and *Chem. Rev.*)

Progress toward Milestones

Project Milestone	Type	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	% Complete	
Use QMC, DFT, and force fields to compute H_2 binding and select appropriate levels of theory for MOFs. Revised milestone: Compute H_2 binding curves with different computational methods for model MOFs to establish protocol for accurate physisorption calculations	PM	12/31/17	3/31/18		70%	LLNL and LBNL are working on finite-size/extended system corrections based on MOF-74. Study of different DFT functionals on model noncovalent systems published in recent sorbent review.
Sensitivity analysis of local binding and second-sphere effects	PM	3/31/17		9/30/17	100%	Completed by Maciek Haranczyk (LBNL) for open metal sites in MOFs. Results to appear in sorbent perspective
Rank improvement strategies for sorbents. Decision criterion: select 2 with greatest potential for increasing ΔH°	GNG	3/31/17		3/31/17	100%	Strategy and results reported at AMR. Manuscript for submission to *En. Env. Sci.* in progress
Modify LEIS instrument to enable laser-induced thermal desorption	PM	6/30/17		6/30/17	100%	Demonstrated feasibility of ion beam-based desorption technique
Evaluate additive/composite strategies for improving effective ΔE	PM	9/30/17	9/30/18		75%	Evaluation of multiple strategies in progress
Prototype hydride surface and interface chemistry kinetic models	M	9/30/17		9/30/17	100%	
Amorphous phases and defects model formalism	PM	12/31/17		12/31/17	100%	

Progress toward Milestones (cont.)

Project Milestone	Type	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	% Complete	
Sensitivity analysis of morphology and microstructure	PM	3/31/18		3/31/18	100%	Completed analysis, reported in LLNL AMR slides
Rank improvement strategies for hydrides. Decision criterion: select 2 with greatest potential for reducing effective ΔH	GNG	3/31/18		3/31/18	50%	Nanoscaling and Dopants addressed experimentally
Rank improvement strategies for hydrides. Decision criterion: select 2 with greatest potential for reducing effective ΔH	GNG	3/31/18		3/31/18	50%	Nanoscaling and Dopants addressed experimentally
Parameterize integrated kinetic model for representative B-N-Al-hydrides	PM	6/30/18			75%	Thermodynamic parameters completed. Some kinetic parameters have been calculated for Na-Al-H and Mg-B-H
Compute sorbent isotherms from QMC data using CoRE database of MOFs Milestone delayed until Phase 2 due to lack of personnel with requisite expertise	PM	9/30/18			0%	Not started
Public release of codes, databases, synthetic protocols, characterization methodologies optimized for storage materials Revised language: Public release of databases, synthetic protocols, characterization methodologies optimized for storage materials	M	9/30/18			0%	Not started. Release of codes is a time-consuming process that will be difficult to complete for codes that as of the date of this report are not ready.

Remaining Challenges and Barriers

Access to ALS facilities remains limited, particularly for beam lines that can probe light elements such as boron and for in-operando measurements

An ALS General User Proposal was accepted to allow access to the AP-XPS. We initiated a relationship with SLAC/SSRL (AP-XPS and other tools) and with UVSOR (STXM for B) to provide alternatives

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

A Data Management Plan will be developed in the remainder of FY18 with assistance Energy Materials Network that will employ 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 are challenging to address

We are planning a new organizational structure for HyMARC Phase 2 that will employ "Focus Groups" that address hot topics or major roadblocks with small, dynamic teams, with the intention of making rapid progress by concentrating resources in specific areas

Proposed future work

- **To the extent possible, integrate submodels to enable more comprehensive approach to predicting hydride kinetics and behavior**
- **Initiate Data Management Plan with assistance of Kristin Munch (NREL) and using platform and utilities previously developed for other EMNs**
- **Initiate renewal process for ALS Approved Program (2nd 3-years)**
- **Complete and submit as many publications as possible to fully document the Phase 1 progress**
- **Submit additional General User Proposals to SLAC/SSRL and ORNL/SNS to expand access**
- **Update HyMARC web site to include HySCORE capabilities and updated publication list**
- **Initiate model integration activity, in collaboration with AMPE code developers at LLNL**
- **Write and submit proposal for HyMARC Phase 2**
- **Write and submit final report**

Any proposed future work is subject to change based on funding levels

Summary

Model development is moving at a fast pace; several new capabilities now operational

- Finite-T hydride thermodynamics
- Grain boundary model
- Particle morphology model
- Solid mechanics/strain effects model
- Surface chemistry model

Advanced characterization capabilities and methods are now on line

- H/D exchange, AC-TEM, and AP-XPS capabilities at Sandia now available to HyMARC
- A vigorous experimental program at BES and other user facilities is providing many new insights
- Surface chemistry instrumentation suite probes all relevant length scales
- New user proposals approved for access to ORNL/VISION, SSRL

New synthetic methods provide materials and data targeted at specific phenomena

- rGO demonstrated as hosts for complex hydrides
- Effects of high-pressure cycling on sorbents evaluated
- New insights into metal borohydride chemistry

These new capabilities are generating foundational understanding that is changing our view

- Role of surface oxide and –OH
- New strategies for altering hydride thermodynamics (e.g., strain, nanoencapsulation)
- Effects of high-P cycling on MOF sorbents
- Understanding of which bond-breaking events must be targeted for additive development

Robust collaborations within HyMARC, with Seedling projects, and international partners are ensuring an interdisciplinary approach focused on cutting-edge materials discovery

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HyMARC
Hydrogen Materials Advanced Research Consortium

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

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).