U.S. DEPARTMENT OF ENERGY

Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

HyMARC: Addressing Key Challenges to Hydrogen Storage in Advanced Materials Through a Multi-Lab Collaboration

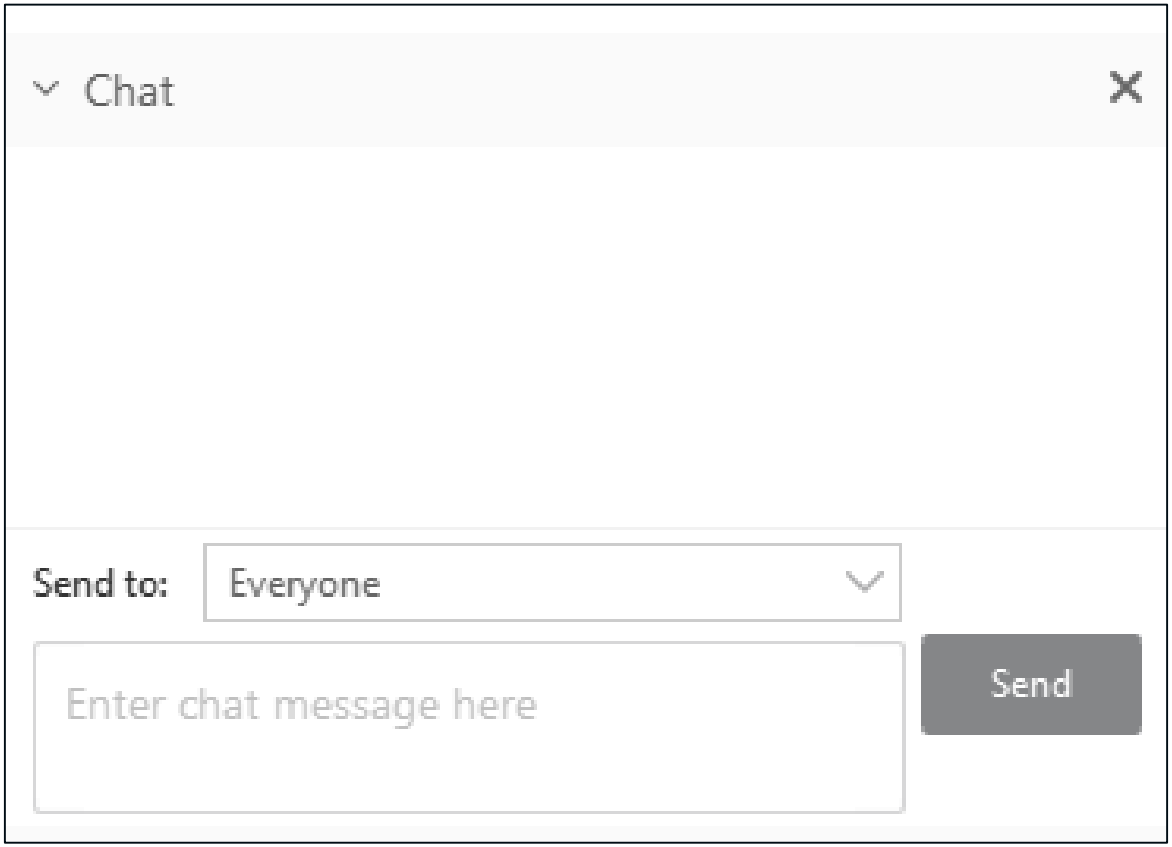
Mark D. Allendorf, Sandia National Laboratories
Tom Gennett, National Renewable Energy Laboratory

Fuel Cell Technologies Office Webinar

January 9, 2019

Question and Answer

- Please type your questions to the chat box. **Send to: (HOST)**



Acknowledgements

We are grateful for the financial support of EERE/Fuel Cell Technologies Office and for technical and programmatic guidance from
Dr. Ned Stetson, Jesse Adams, and Zeric Hulvey

Enabling twice the energy density for onboard H_2 storage

Outline

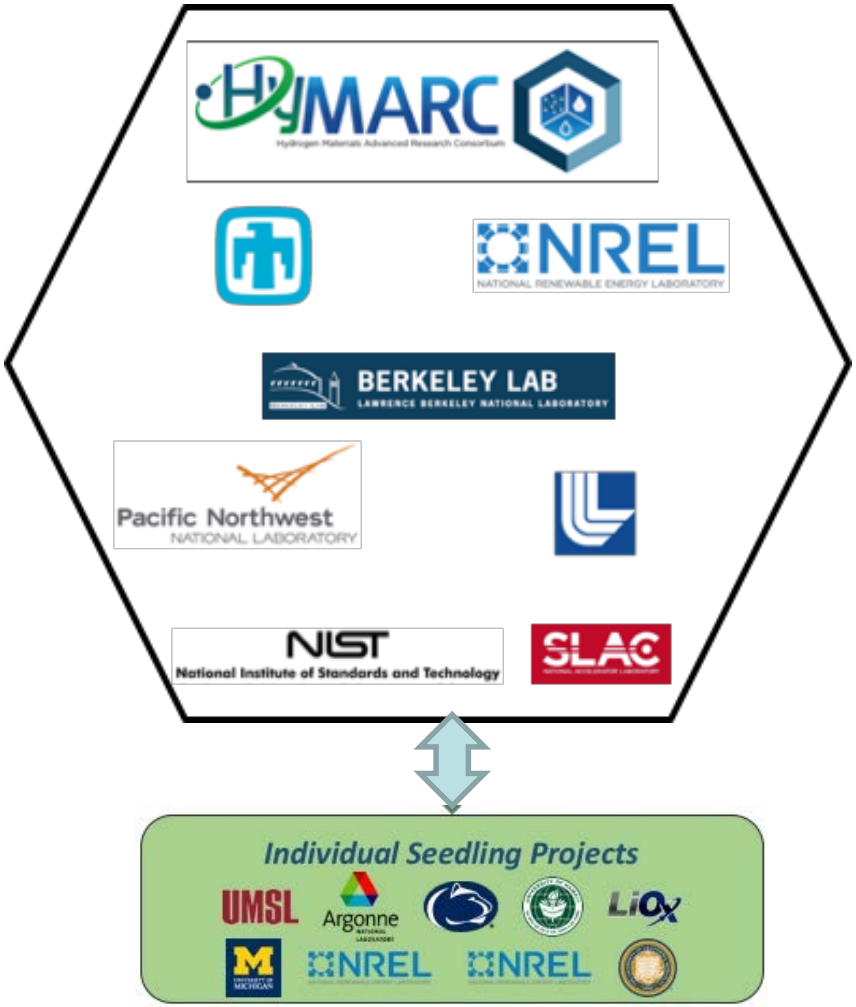
- FCTO Introduction
- HyMARC
  - Objectives & goals
  - Phase 1 accomplishments
    - Moving the state-of-the-art
    - Seedlings
- HyMARC Phase 2
  - Tasks
  - Research projects
- HyMARC Capabilities
  - Modelling
  - Advanced characterization
- HyMARC
  - Examples of on-going research
- Questions and Answers

HyMARC performs foundational research, develops capabilities to accelerate materials discovery, and supports Seedling projects

Objectives:

- *Develop* and *Enhance* Hydrogen Storage Core 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

- *Validate* claims, concepts and theories of hydrogen storage materials
- *Accelerate* the path forward to development of hydrogen storage materials for transportation



Principal Investigators and Lead Researchers

Mark Allendorf
Co-Director
SNL PI

Tom Gennett
Co Director
NREL PI

Brandon Wood
LLNL PI

David Prendergast
LBNL PI

Tom Autrey
PNNL PI

Vitalie Stavila

Phil Parilla

Tae Wook Heo

Jeff Long
LBNL PI

Mark Bowden

Craig Brown

Terry Udovic

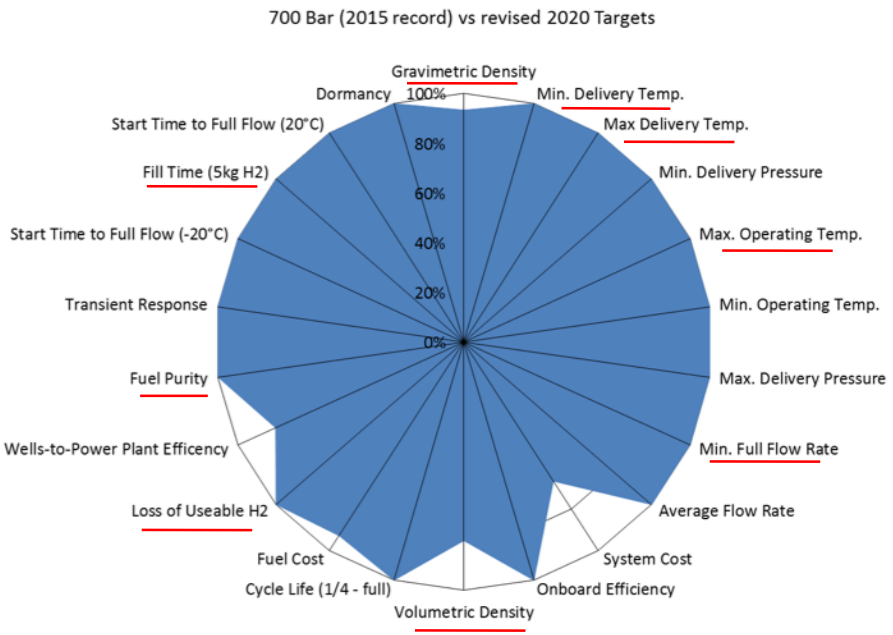
Jeff Urban

HyMARC Phase-1 Activities

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)

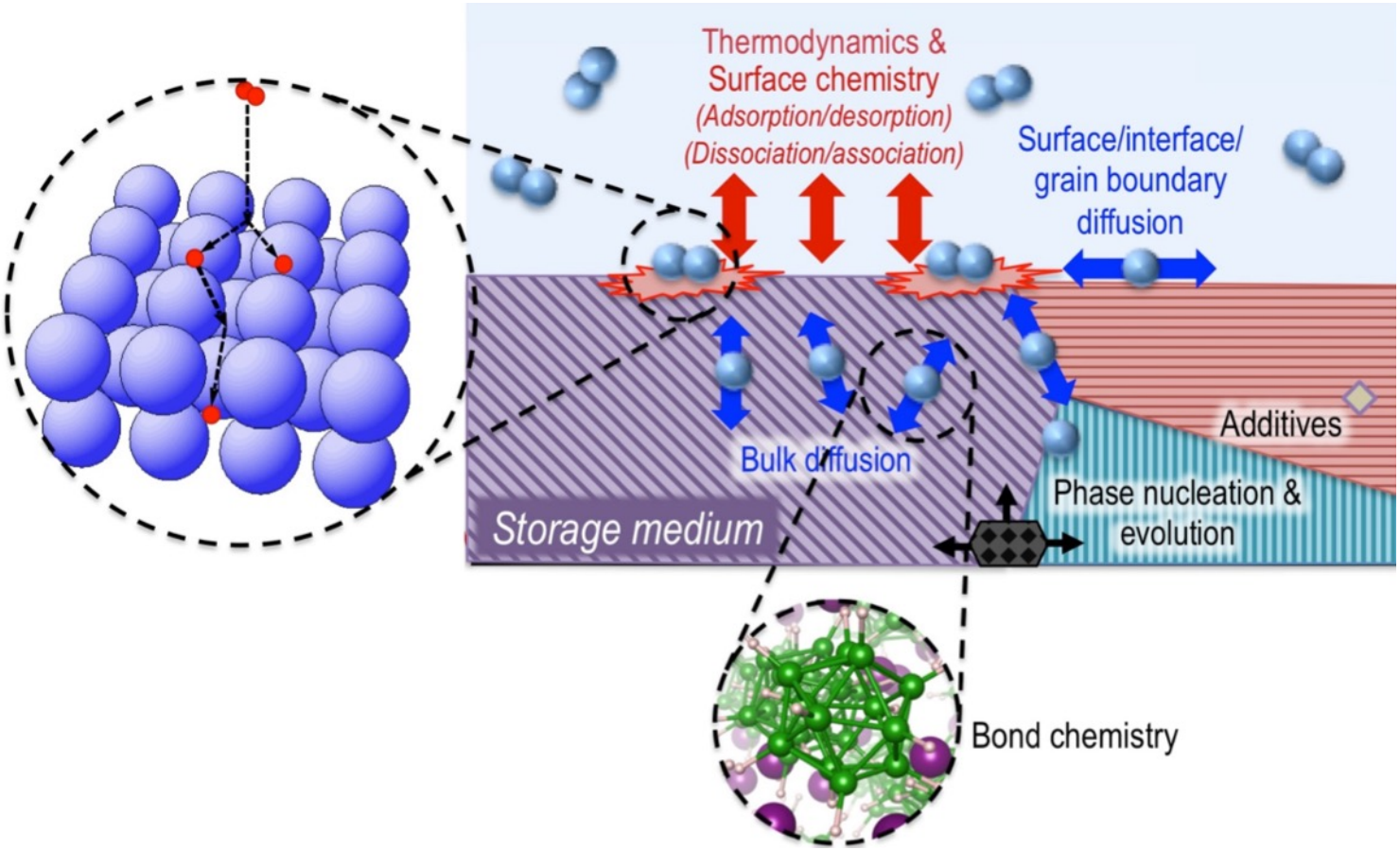
Material development strategies we evaluated indicate progress toward several DOE targets



HyMARC foundational research addresses all phenomena potentially influencing reaction thermodynamics and kinetics

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

Thermodynamics Kinetics



Phase 1: Some Examples of how HyMARC moved 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)
- Sorbent Capacity: Ni (m-dodbc) Highest volumetric/gravimetric room temperature capacity to date.
- Hydrides: Improved reversibility of $Mg(BH_4)_2$ to temperatures below 200 ˚C
- Binding energies: Established ability to alter hydrogen binding energies approaching 15 kJ/mole in sorbent materials
- Desorption control: Established that desorption temperatures can be controlled with dynamic sorbent materials (e.g. phonon vibrational modes, expansion, etc.)
- Multiple molecular H_2 adsorption: First sorbent material with validated existence of two hydrogen molecules adsorbed per metal center

Two major publications from HyMARC Phase 1 document perspectives on sorbent strategies and nanoscale metal hydrides

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)

Energy & Environ. Sci. **2018**, *11*, 2784

"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**

Chem. Rev. **2018**, *22*, 10775

"Nanostructured Metal Hydrides for Hydrogen Storage"

Topics include:

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

HyMARC is currently collaborating with Phase 2 Seedling Projects and facilitating their research

The HyMARC team assists individual projects with:

- **A designated HyMARC point-of-contact**
- **Technical expertise concerning specific scientific problems**
- **Access to HyMARC capabilities**
  - **Note that HyMARC collaborates and is *not* an analytical service**

- ***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

- ***Electrolyte Assisted Hydrogen Storage Reactions*** (Liox Power)
  - High-P experiments and sample characterization

- ***ALD Synthesis of Novel Nanostructured Metal Borohydrides*** (NREL)
  - $Mg(BH_4)_2$ nanoparticle samples sent to NREL for ALD coating

- ***Optimized Hydrogen Adsorbents via Machine Learning & Crystal Engineering*** (U. MI)
  - Discussions on crystal engineering of OMS in MOFs

HyMARC Phase 2 Task Structure

Task 1: Sorbents

- **PI: Tom Gennett (NREL, Golden, CO)**

Task 2: Metal Hydrides

- **PI: Mark Allendorf (Sandia, Livermore, CA)**

Task 3: Hydrogen Carriers

- **PI: Tom Autrey (PNNL, Richland, WA)**

Note: webinar on the hydrogen carrier activities was presented on Dec. 6th. (https://www.energy.gov/eere/fuelcells/downloads/hydrogen-carriers-bulk-storage-and-transport-hydrogen-webinar).

Task 4: Advanced Characterization Capabilities

- **PI: Phil Parilla (NREL, Golden, CO) and David Prendergast (Molecular Foundry, LBNL)**

Task 5: Research Support for Seedling Projects

- **PI's: Mark Allendorf and Tom Gennett**

Task 6: HyMARC Data Hub

- **PI: Kristin Munch (NREL, Golden, CO)**

HyMARC Phase 2 Focus Areas: designated high-priority research topics

Sorbents:

1.A Enthalpy / Entropy
1.B Optimizing Sorbent Binding Energies
1.C Optimizing Sorbent Packing
1D. Dynamic Sorbent Materials
1.E Multiple Hydrogens Per Metal
1.F Nanoscale Defects in Sorbents

Metal hydrides:

2.A Thermodynamics
2.B Solid Interfaces and Surfaces
2.C Activation of bonds in hydride materials to improve kinetics (e.g. B-B, B-H, etc.)
2.D Nanoscaling to Improve Thermodynamics and Kinetics
2.E Microstructural Impacts of Complex Metal Hydride Reactions
2.F Machine Learning and Data Science

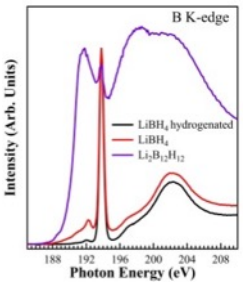
Advanced Characterization:

4.A High-Temperature Validated PCT System
4.B PCT Calorimetry,
4.C NMR Spectroscopy
4.D *In-situ* and *ex-situ* Synchrotron, Neutron and DRIFTS Techniques

HyMARC Modeling capabilities: tools that now cover all relevant length scales and many important phenomena

Atomic/molecular (0 – 1 nm)

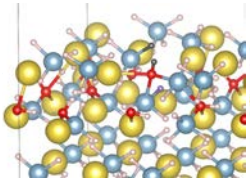
Computational Spectroscopy

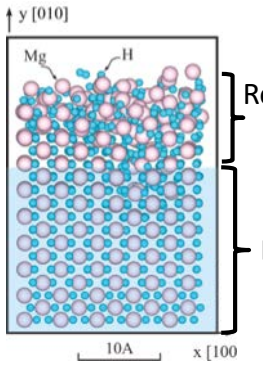


Example: $NaAlH_4$ surface chemistry: role of oxide

Molecular/micro (0.5 – 2 nm)

Surface chemistry Interatomic potentials

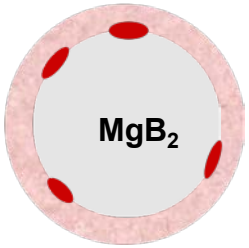


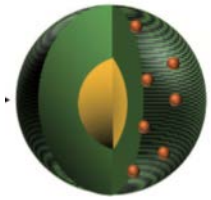


Example: Time-dependent simulations of MgH_2 formation

Mesoscale (2 - 100 nm)

Nucleation kinetics Phase microstructures

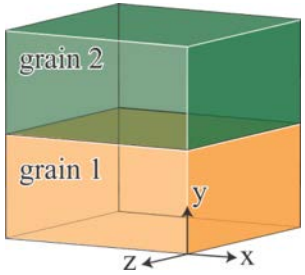




Example: Nano-alloying of Ni-doped Mg

Grains (≤ 10 μm)

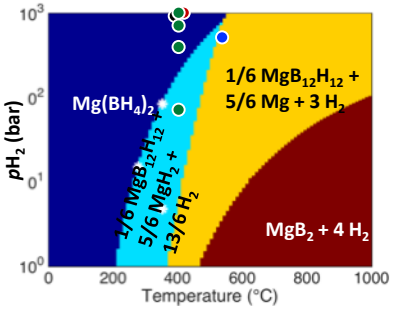
Grain boundaries Particle size effects Stress/strain



Examples: H diffusion in PdH_x Diffusion in $NaBH_4$

Macroscale/Bulk

Thermodynamics



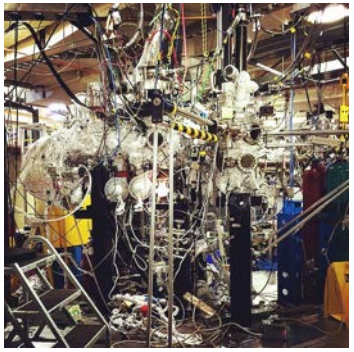
Example: $Mg(BH_4)_2$ phase diagram

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

Length (m)

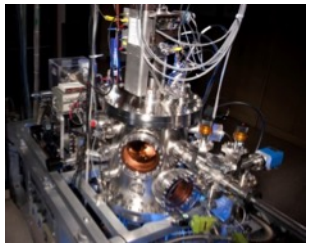
Characterization tools: expanded and extended to in-situ, in-operando probing and mesoscale resolution

Atomic/molecular (0 – 1 nm)



AP-XPS
ALS/BL 11.0.2

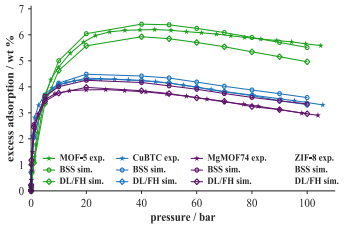
XAS In-situ flow cell
(1 bar, max. 250˚C)

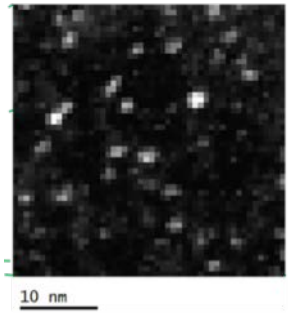


Lab-based
AP-XPS

Molecular/micro (0.5 – 2 nm)

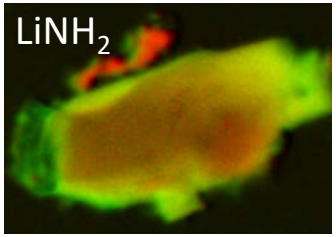
Microporosimetry/BET

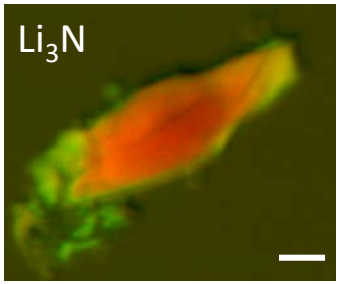




He bubbles seen by
AC-TEM
STEM res. 63 pm

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}

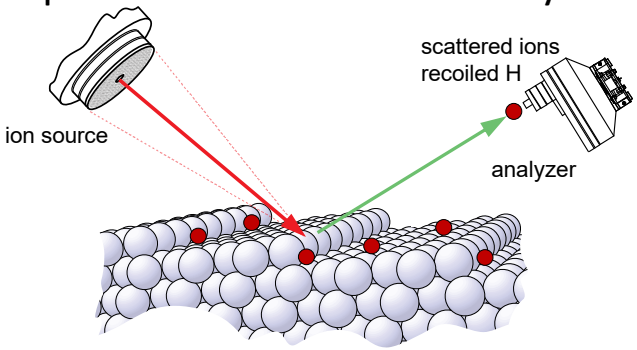
Length (m)

HyMARC surface characterization capabilities include unique instrumentation to directly probe hydrogen on surfaces

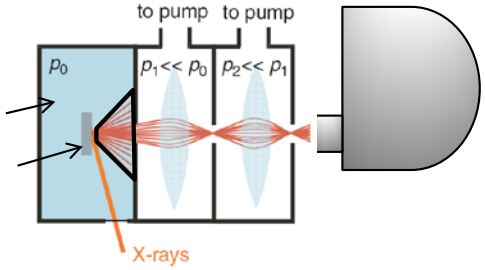
Motivation:

Surfaces are believed to play an important role in hydrogen storage reactions; exact role and mechanisms remain unclear

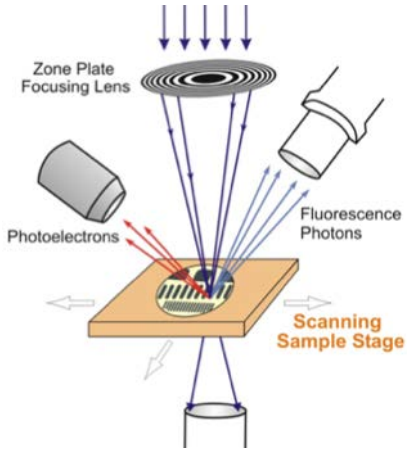
Technical Approach: *In-situ* techniques enable us to probe the surface chemistry for H_2 storage materials



Low energy ion scattering (LEIS):
Determine surface composition, H surface conc.
(First monolayer only, <1 nm)



Ambient pressure XPS:
Characterize O, Na, Al, and Ti binding
(Surface and near sub-surface, <10 nm)



Scanning trans. x-ray microscopy (STXM):
Distribution of Ti within particles
(Bulk)

What we can learn:

⇒ ***What is the exact surface composition of H_2 storage materials?***

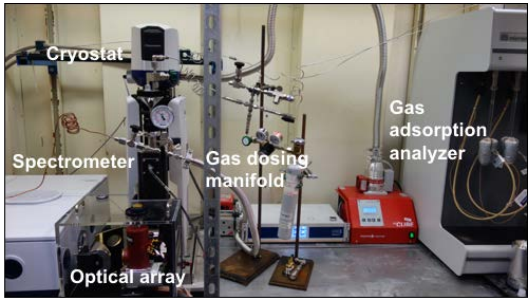
⇒ ***How do surfaces respond to temperature and H_2 environments?***

⇒ ***What is the spatial distribution of species of interest?***

⇒ ***Can surfaces be modified to improve H_2 storage properties?***

Extended Characterization Capabilities

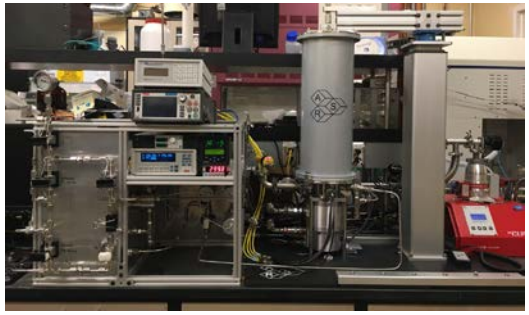
DRIFTS



Diffuse reflectance system coupled to cryostat and gas adsorption analyzer

Can collect data at 15-373 K and 0-100 bar (controlled dosing up to 1.2 bar)

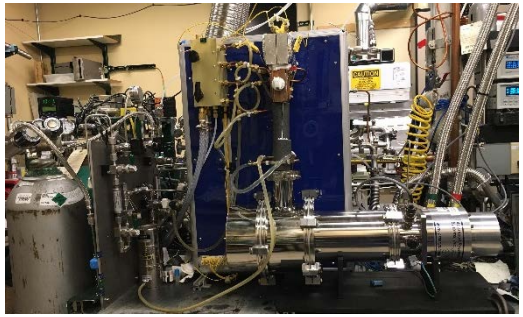
Thermal Conductivity



H_2, He (other gases possible) from vacuum to 100 bar
Temperature Range: 40 K to 375 K

Sample types include solids & compressed pucks & powder

Variable Temperature PCT



Modified PCT Pro system with capabilities of hydrogen pressures up to 200 bar, and a controlled temperature range from 40 – 350 K. (other gases possible including CH_4)

High-pressure hydrogen station provides access to pressures in current fueling stations

Sandia high-pressure H_2 station

- Up to 1000 bar H_2 and 400 ˚C
- Holds up to 4 different samples at once
- Employed for:
  - Synthesis of metal hydrides that cannot be synthesized in another way
  - Destabilization of $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ compounds
  - Hydrogenation of metal borides, *e.g.* MgB_2, MgB_2-etherates
  - Stability of hydrides and sorbents under high-pressure H_2

Synthetic capabilities: New sample formats for encapsulate complex hydrides, MgB_2 nanoparticles, graphene nanostructures

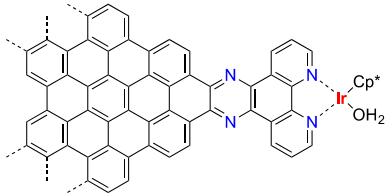
Atomic/Molecular (0 – 1 nm)

Molecular and microscales (0.5 – 2 nm)

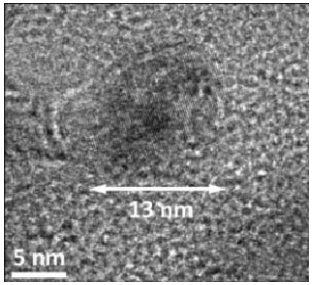
Mesoscale (2 - 100 nm)

Grains (up to ~ 10 µm)

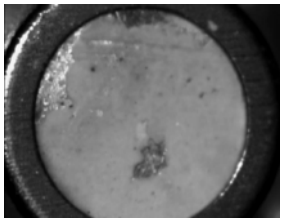
Macroscale/Bulk



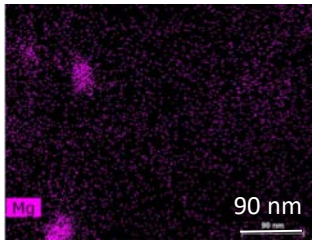
Model systems: GNR+(H_2 dissoc. catalyst)



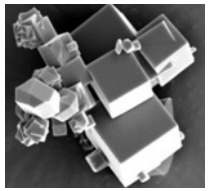
$Mg(BH_4)_2$@rGO



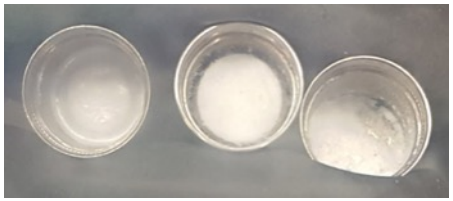
$Mg(BH_4)_2$ film on Au for LEIS measurements



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)

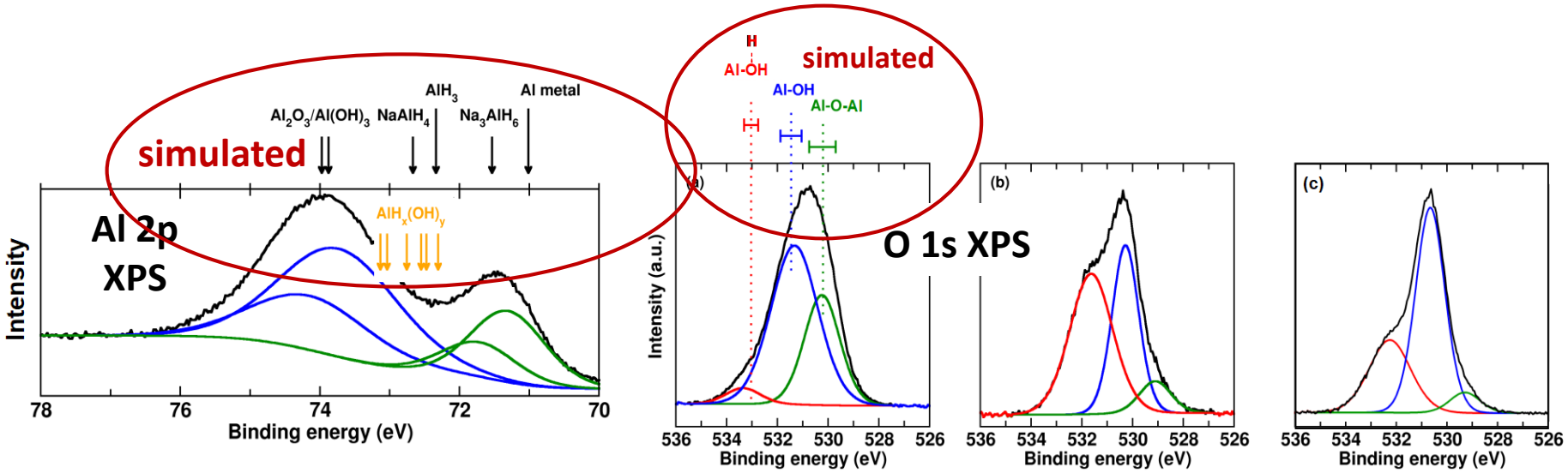
HyMARC has access to several user facilities

Joint experiments may be planned on a limited basis

Examples of experimental progress

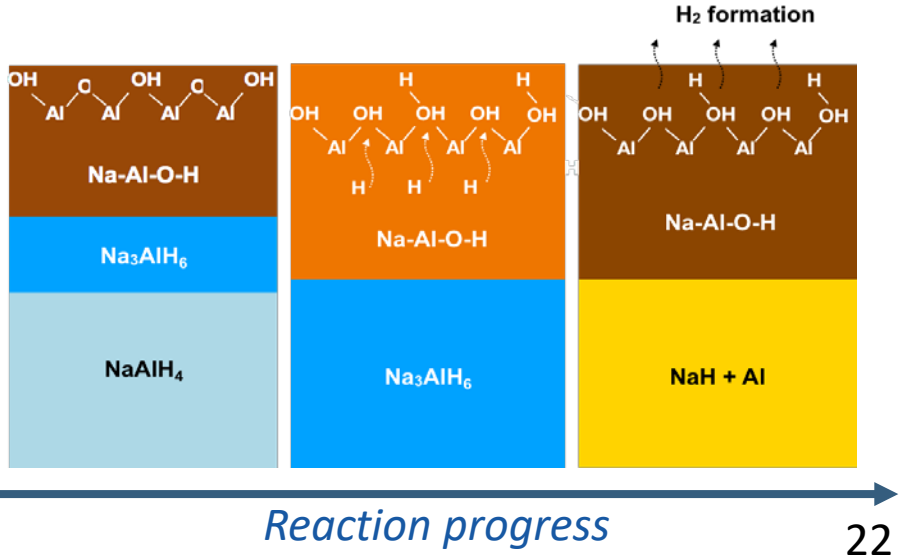
$NaAlH_4$ surface chemistry understood using tools that probe the surface, near surface, and bulk material

Novel approach mixes AIMD with XPS simulations via LLNL/LBNL collaboration to interpret SNL AP-XPS and obtain a reliable picture of how surface chemistry evolves



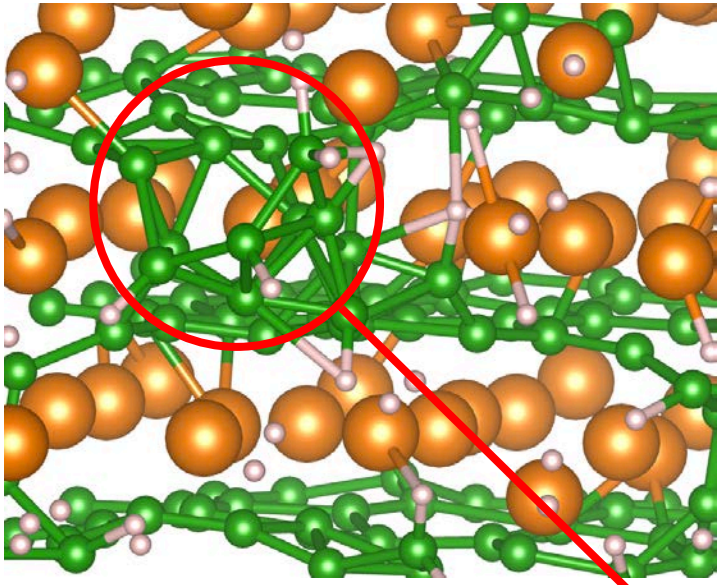
- **Simulated XPS shows that past work has incorrectly assigned chemical species, which does not always follow oxidation state!**

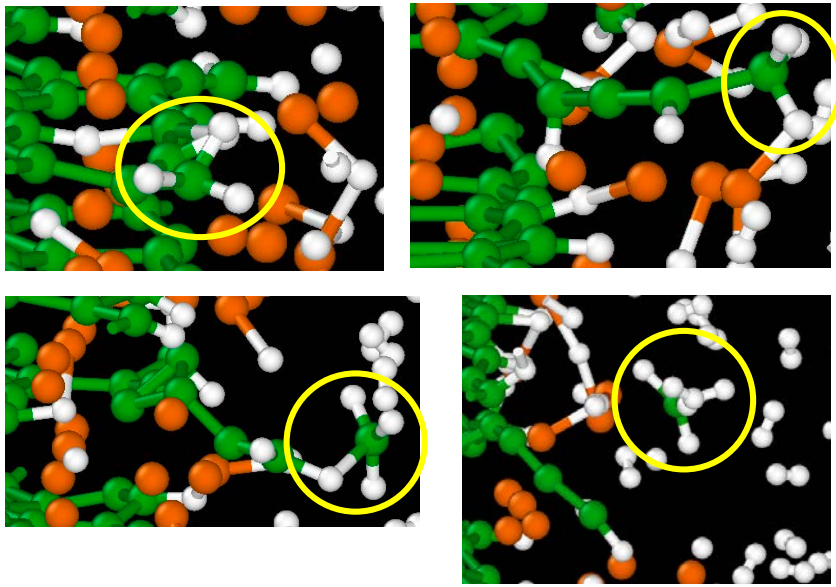
- **Near-surface region chemistry involves oxide film on Na_3AlH_6, which evolves as hydrogen enriches and then depletes during dehydrogenation**

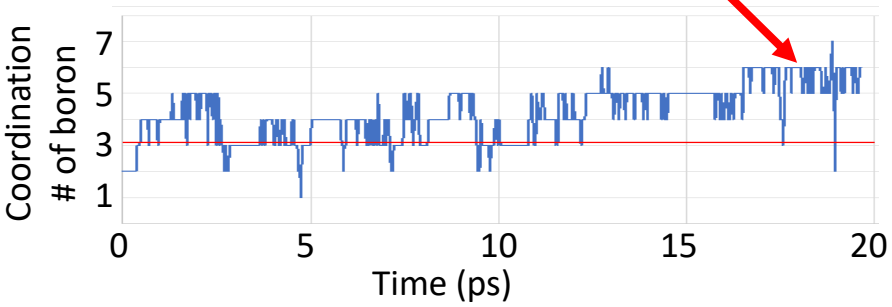


Understanding MgB_2 decomposition

HPC-enabled capability to directly observe chemical reactions upon hydrogenation of MgB_2 edges under high pressure illustrates competing pathways for B_xH_y formation. -Utilized to improve strategies for performance/design of new materials





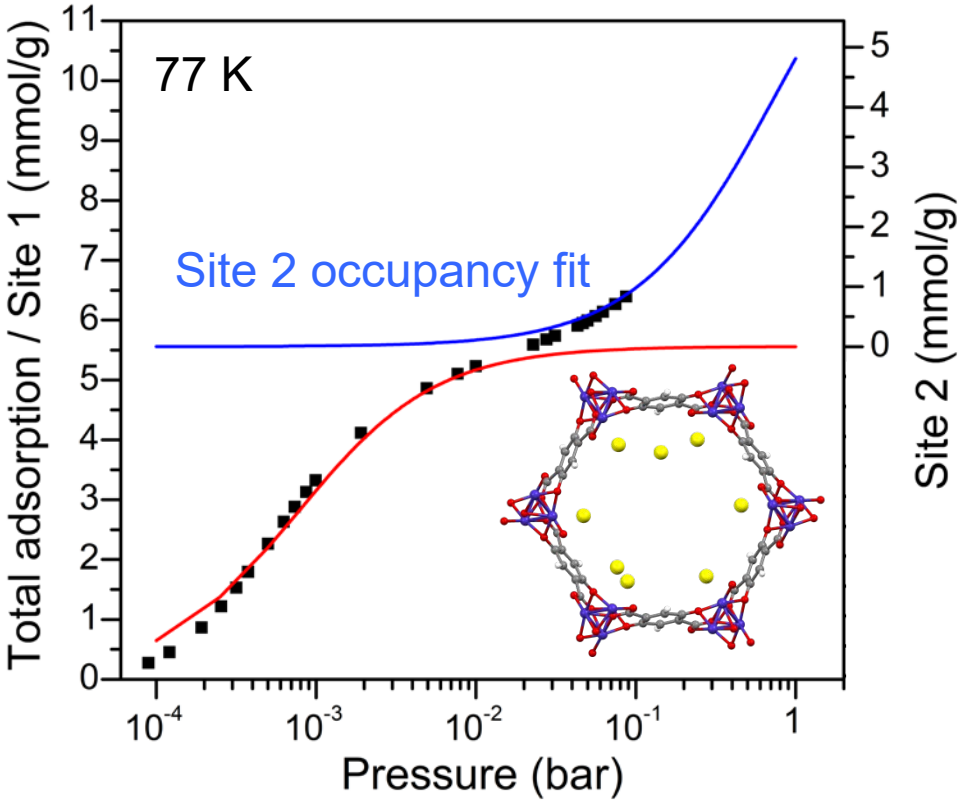


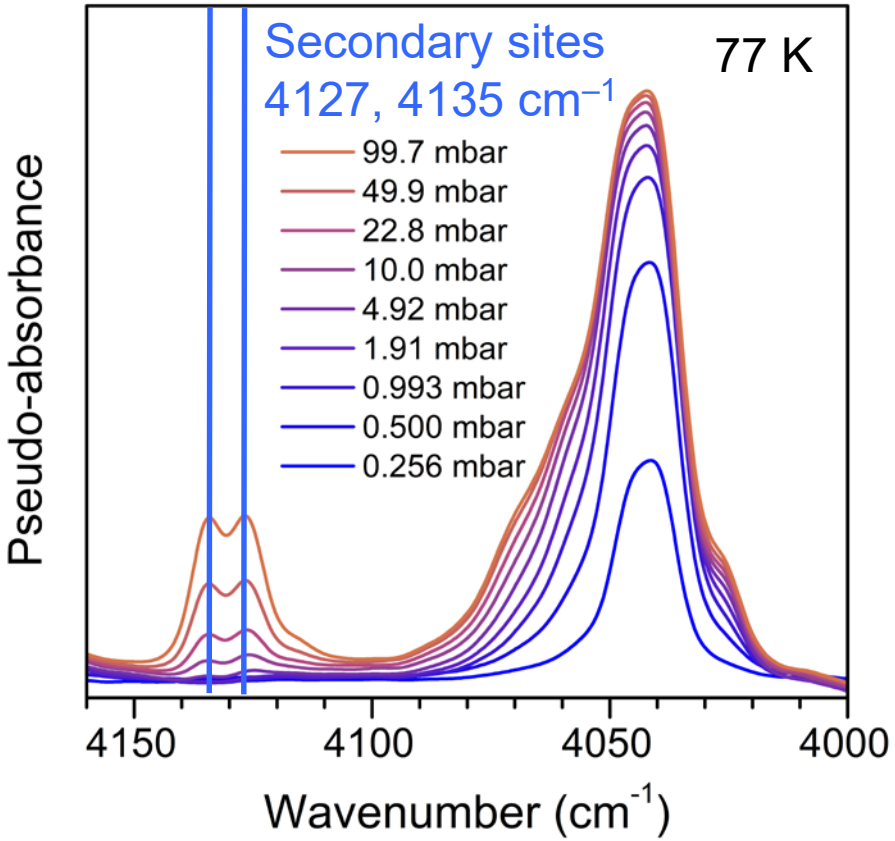
- **AIMD simulations show that chemistry occurs preferentially at exposed edge planes, in agreement with our previous experiment-theory study**

  Ray et al. *PCCP* 19, 22646, 2017

- **Mg-rich edges lead to smaller molecules; B-rich edges lead to closo-borane formation**

DRIFTS: Deconvoluting H_2 Isotherm Data for Co_2(dobdc)





- At low pressures spectra indicate only adsorption at Co^{2+} site (Site 1)
- Secondary physisorption sites (Site 2) are populated after Site 1 is filled

Summary

HyMARC National Laboratory team activities

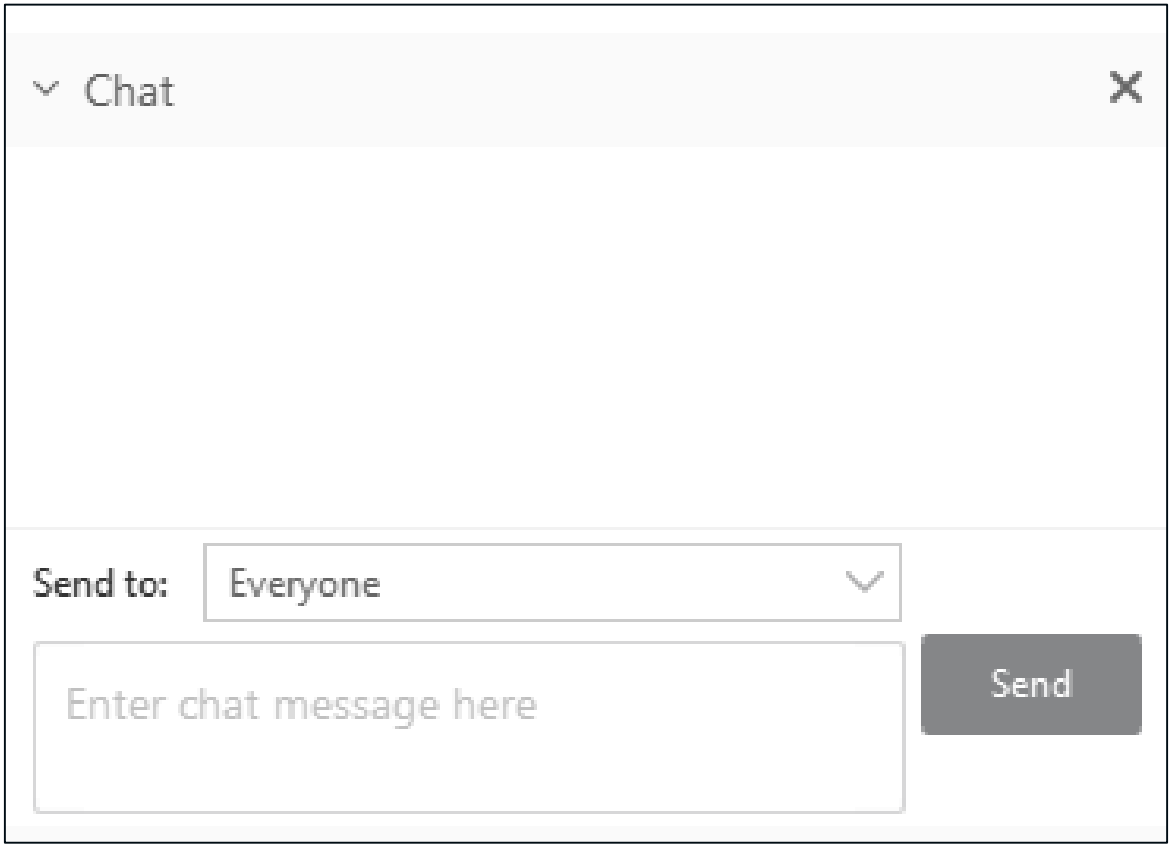
- Foundational research to accelerate materials discovery
- Development of advanced characterization tools
- Computational modeling across all relevant length scales
- Innovative material synthesis

HyMARC researchers collaborate and assist DOE-Fuel Cell Technologies Office Seedling projects

- Scientific expertise
- Joint experiments
- Access to cutting-edge capabilities when needed
- Validation measurements

Question and Answer

- Please type your questions to the chat box. **Send to: (HOST)**



Save the Date and Sign up for Our Newsletter

All relevant DOE offices and other federal agencies working on hydrogen and fuel cell technologies at Annual Merit Review (AMR)

2019 AMR – April 29 – May 1
Crystal City, VA
www.hydrogen.energy.gov

Sign up to receive hydrogen and fuel cell news and updates

www.energy.gov/eere/fuelcells/fuel-cell-technologies-office-newsletter

Thank you

Mark Allendorf
mdallen@sandia.gov

Eric Parker
DOEFuelCellWebinars@ee.doe.gov

Thomas Gennett
thomas.gennett@nrel.gov

Ned Stetson
Ned.stetson@ee.doe.gov

hydrogenandfuelcells.energy.gov

Additional slides if needed

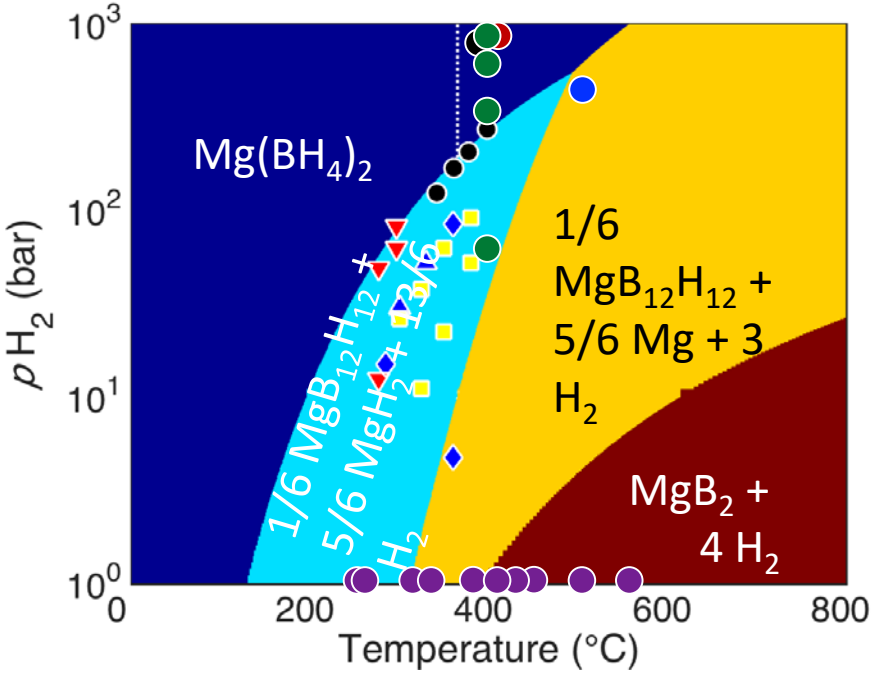
Select onboard hydrogen storage targets

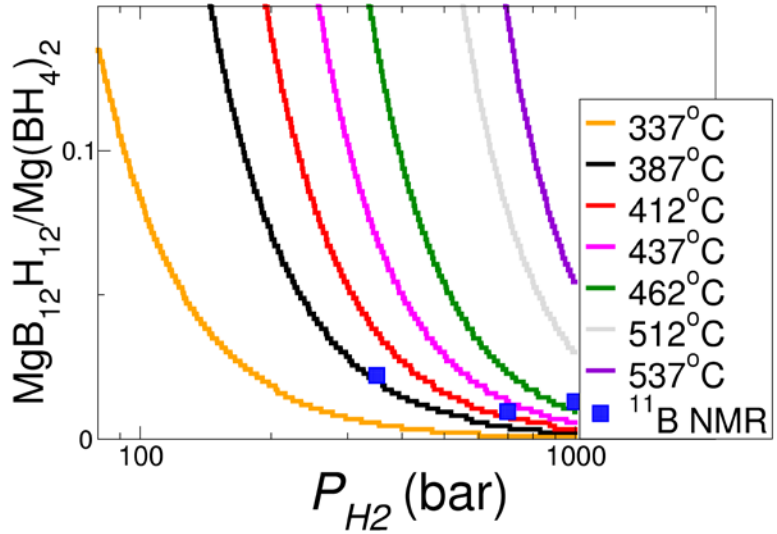
Storage Parameter	Units	2020	2025	Ultimate
System Gravimetric Capacity Usable, specific-energy from H_2 (net useful energy/max system mass)	kWh/kg ($kg\ H_2$/kg system)	1.5 (0.045)	1.8 (0.055)	2.2 (0.065)
System Volumetric Capacity Usable, specific-energy from H_2 (net useful energy/max system volume)	kWh/L ($kg\ H_2$/L system)	1.0 (0.030)	1.3 (0.040)	1.7 (0.050)
Storage System Cost	$\$/kWh_{net}$ ($\$/kg\ H_2$)	10 (333)	9 (300)	8 (266)
Durability/Operability				
Min/max delivery temperature	° C	-40/85	-40/85	-40/85
Min/max delivery pressure	Bar (abs)	5/12	5/12	5/12
Charging/Discharging Rates				
System fill time	Minutes	3-5	3-5	3-5
Minimum full flow	(g/s)/kW of FC	0.004	0.004	0.004
Dormancy (at 95% of capacity)				
Min time to first release	Days	7	10	14
Max boil-off loss after 30 days	%	10	10	10

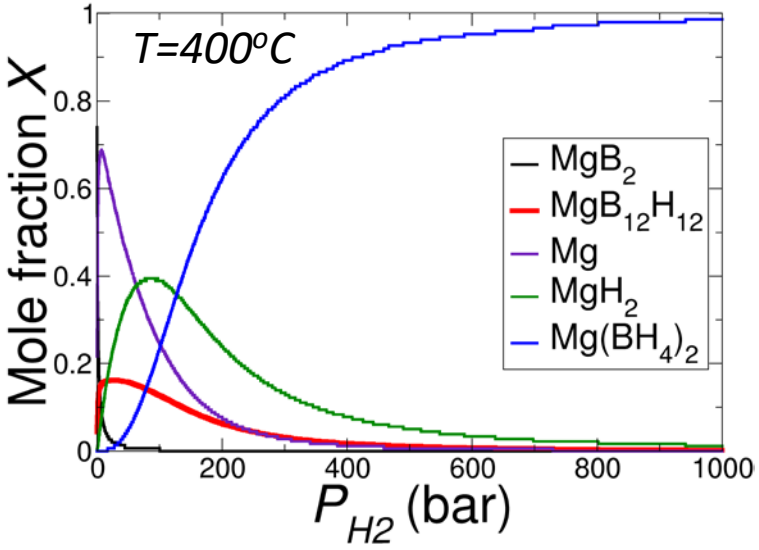
For the complete set of onboard hydrogen storage targets, see:
https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles

Accurate Mg-B-H phase diagram prediction

LLNL, Sandia, and PNNL are working together to predict, measure, and validate phase diagram of Mg-B-H, focusing on high-pressure regime







- **New method gives computed entropy and enthalpy within 3% and 12% of experiments, respectively,**
  up from 11% and 50% for standard DFT
- **Phase equilibrium between $Mg(BH_4)_2$ and $MgB_{12}H_{12}$**
  is correctly predicted to within 10 ° C!