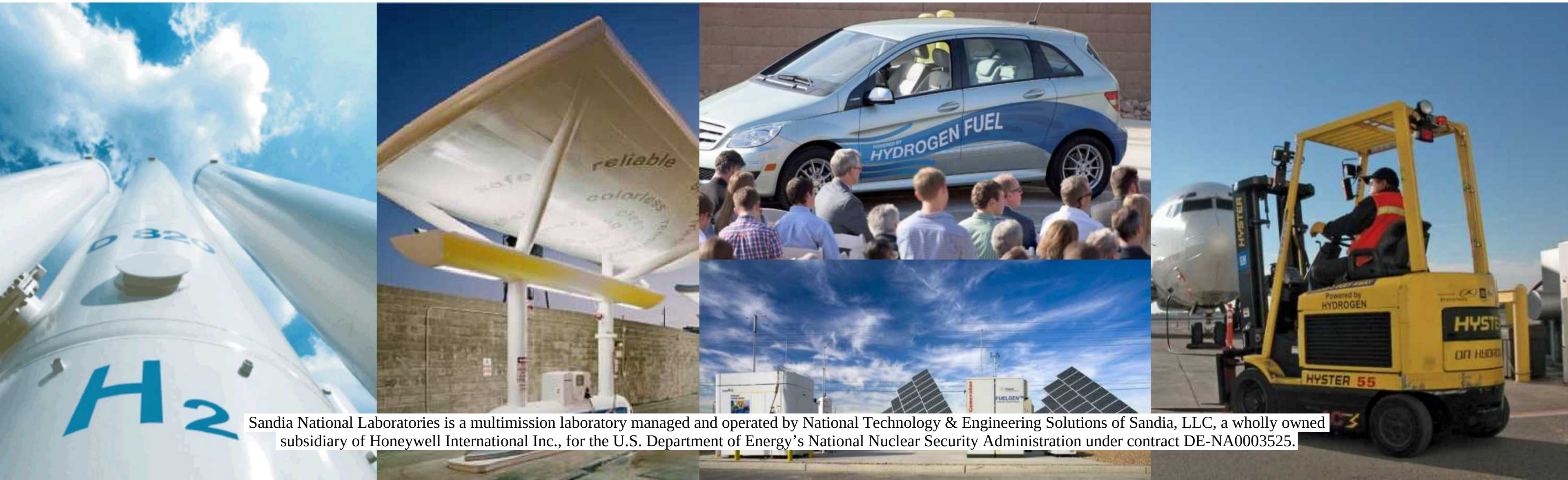
SAND2019-1802PE

Hydrogen Materials Advanced Research Consortium (HyMARC): Sandia Technical Effort

Mark D. Allendorf, Sandia National Laboratories

Tech Team Meeting

February 20-21, 2019



Outline

Summary of Phase 1 accomplishments

Metal hydrides research (Task 2) overview

Task 1: Sorbents

- MOF monolith synthesis

Task 2: Metal Hydrides

- Phase Diagrams for ternary borohydrides and eutectics
- Atomistic simulations of molecular interactions in Mg-B-H systems
- Experimental probing of surface and buried interface chemistry of complex "non-ideal" systems
- Modulation of B-B and B-H bond strength in borohydrides
- Non-innocent hosts for metal hydride nanoencapsulation
- Searching for efficient solid-state hydrogen storage materials using ML technique

Task 3: Carriers

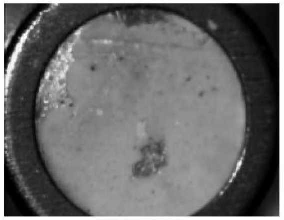
- Aqueous organic carriers

Phase 1: HyMARC moved the bar for specific materials and strategies related to metal hydrides

- Thermodynamics: validated thermodynamic model for the Mg-B-H system
- Nanoconfinement (porous host): $Mg(BH_4)_2$@(6-nm C) H_2 desorption T reduced by >100 °C
- Desorption kinetics: discovered key role of surface oxides in H_2 release from complex hydride
- Interface engineering: Li_3N@(6nm-C) H_2 cycling T reduced by >180 °C (bulk is 430 °C)
- Reversibility: demonstrated reversible H_2 desorption from $Mg(BH_4)_2$ at temperatures <300 ˚C

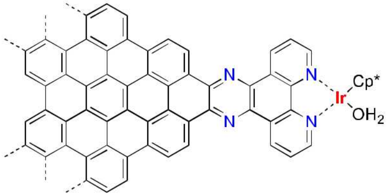
Synthetic capabilities: New sample formats for encapsulated metal hydrides, MgB_2 nanoparticles, graphene nanostructures

Atomic/Molecular
(0 – 1 nm)



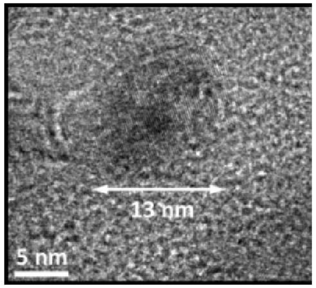
$Mg(BH_4)_2$ film on Au for LEIS measurements

Molecular and microscales
(0.5 – 2 nm)

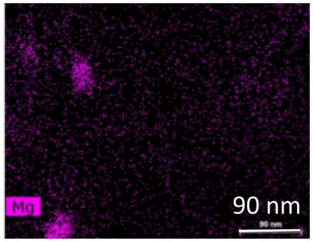


Model systems: GNR+(H_2 dissoc. catalyst)

Mesoscale
(2 - 100 nm)



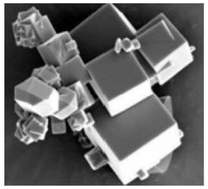
$Mg(BH_4)_2$@rGO



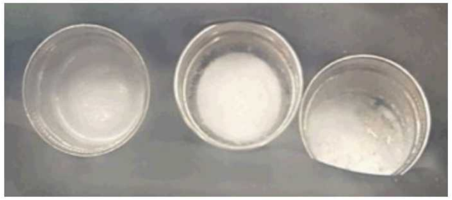
MgB_2 nanoparticles
Encapsulation
Strain effects
Nanoscaling

Grains
(up to ~ 10 µm)

Macroscale/Bulk



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)

High-pressure hydrogen station provides access to pressures at 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
  - Validation of Seedling Go/No-go results

- **More than 75 samples for Seedling projects processed during Phase 1**

HyMARC collaborated extensively in Phase 1 with Seedling Projects. These interactions continue in Phase 2

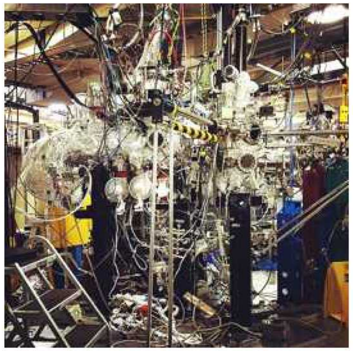
The HyMARC team assists individual projects with:

- A designated HyMARC point-of-contact
- Technical expertise concerning specific scientific problems
- Access to HyMARC capabilities

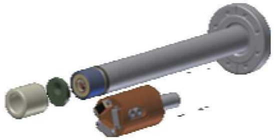
- ***Development of Magnesium Boride Etherates as Hydrogen Storage Materials*** (U. Hawaii)
  - Instability in MgB_2 B sheets explained (LLNL modeling investigation)
  - High-P hydrogenation, XRD, and FTIR performed for > 60 samples
  - Joint paper accepted**+REF**
- ***Electrolyte Assisted Hydrogen Storage Reactions*** (LiOx Power)
  - High-P experiments and sample characterization
  - Joint paper on eutectics **+REF**
- ***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

Characterization tools: expanded and extended to <u>in-situ</u>, <u>in-operando probing</u> and <u>mesoscale resolution</u>

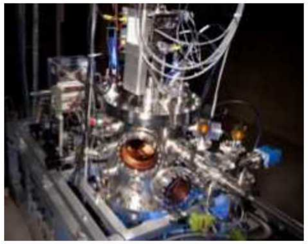
Atomic/molecular
(0 – 1 nm)



AP-XPS
ALS/BL 11.0.2



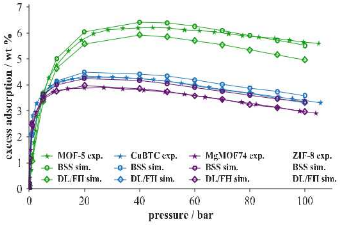
XAS In-situ flow cell
(1 bar, max. 250˚C)

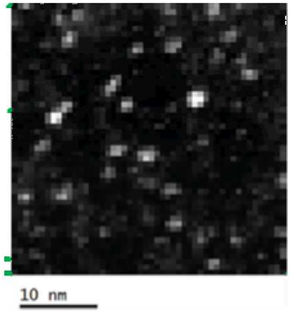


Lab-based
AP-XPS

Molecular/microstructure
(0.5 – 2 nm)

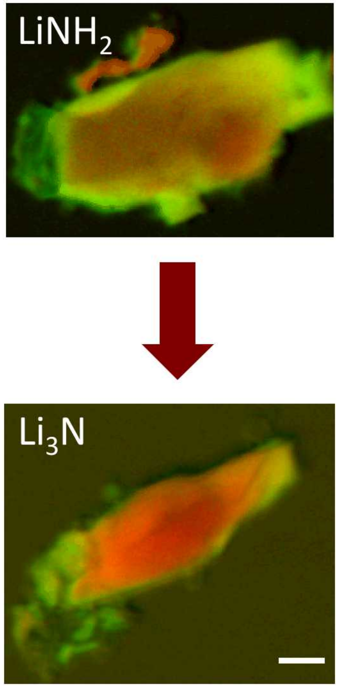
Microporosimetry/BET





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)

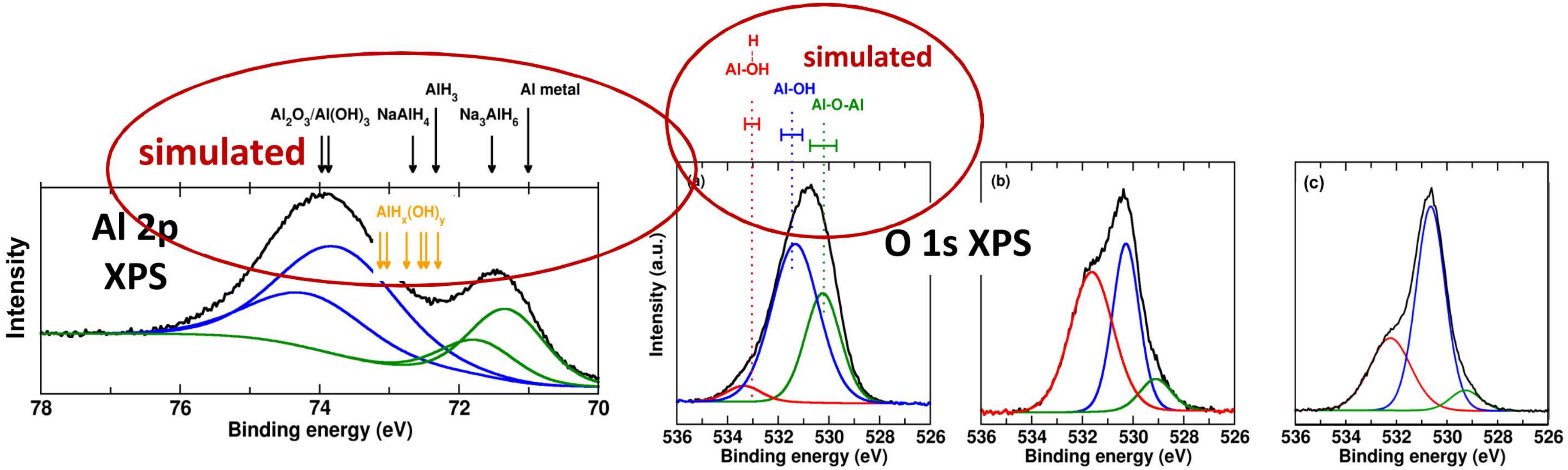
H-D exchange

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

Length (m)

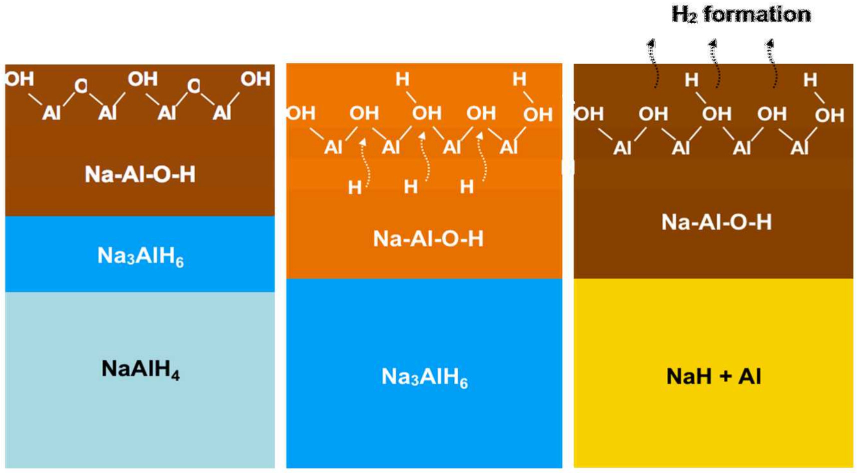
$NaAlH_4$ surface chemistry understood using tools that probe the surface, near surface, and bulk material

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**

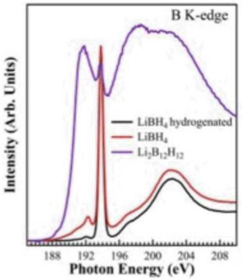


Reaction progress

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

Atomic/molecular
(0 – 1 nm)

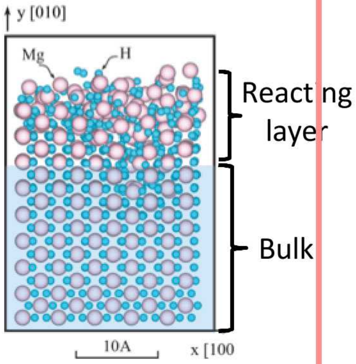
Computational Spectroscopy



Example:
$NaAlH_4$ surface chemistry: role of oxide

Molecular/micro
(0.5 – 2 nm)

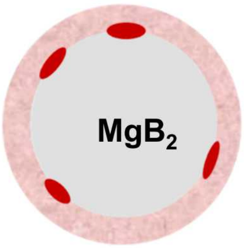
Surface chemistry
Interatomic potentials

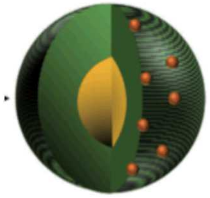


Example:
Time-dependent simulations of MgH_2 formation

Mesoscale
(2 - 100 nm)

Nucleation kinetics
Phase microstructures

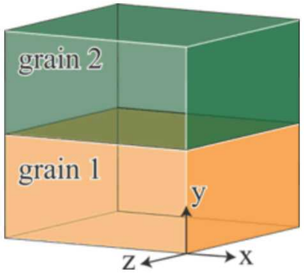




Example:
Nano-alloying of Ni-doped Mg

Grains
(≤ 10 μm)

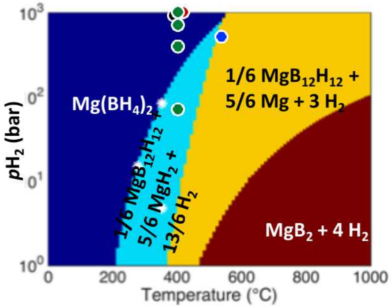
Grain boundaries
Particle size effects
Stress/strain



Examples:
H diffusion in PdH_x
Diffusion in $NaBH_4$

Macroscale/Bulk

Thermodynamics

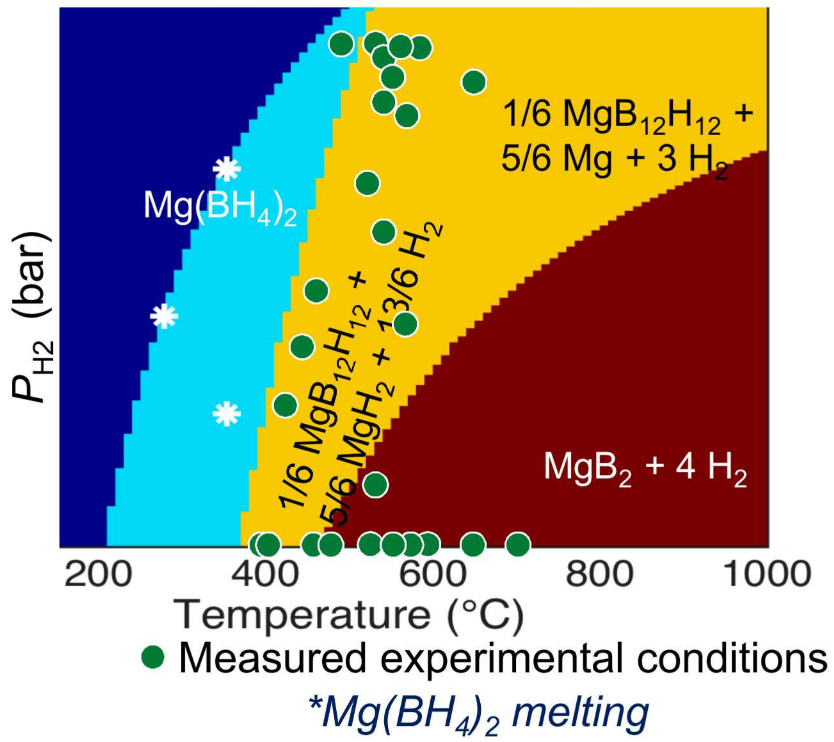


Example:
$Mg(BH_4)_2$ phase diagram

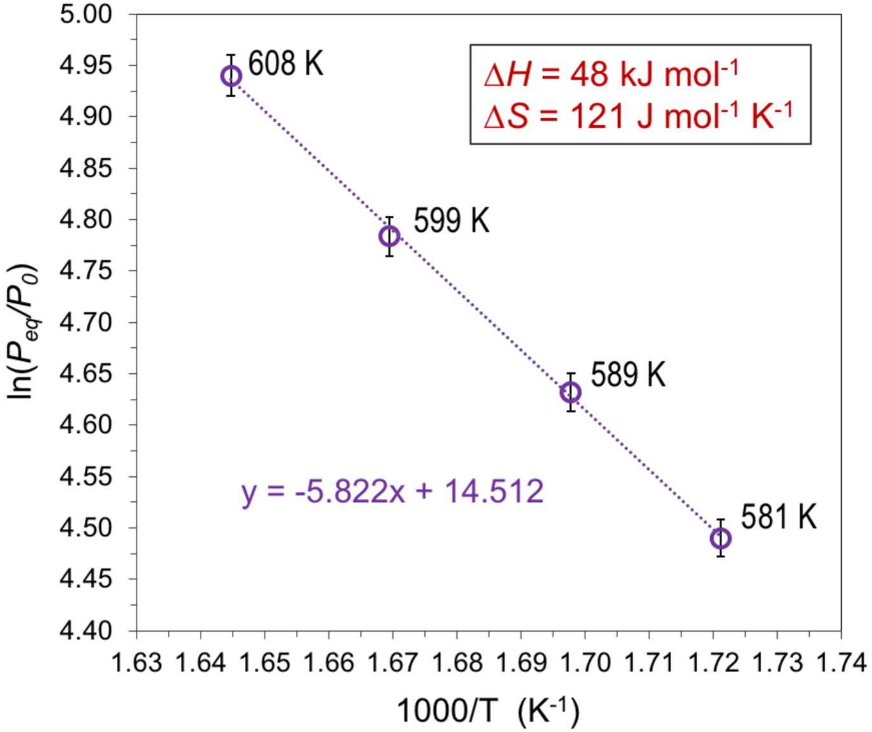
10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2}

Length (m)

Phase diagram for bulk magnesium borohydride



$Mg(BH_4)_2$ Phase Diagram



Direct vant's Hoff measurements, $Mg(BH_4)_2$

Kinetic products

$3Mg(BH_4)_2 \rightarrow 2MgH_2 + Mg(B_3H_8)_2 + 2H_2$

$5Mg(BH_4)_2 \rightarrow 4MgH_2 + MgB_{10}H_{10} + 11H_2$

Thermodynamic products

$6Mg(BH_4)_2 \rightarrow 5MgH_2 + MgB_{12}H_{12} + 13H_2$

$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$

ΔH and ΔS values measured under high-hydrogen pressure

Sandia was lead on two major publications from HyMARC Phase 1 document perspectives: 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*

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**

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)

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

"Nanostructured Metal Hydrides for Hydrogen Storage"

Topics include:

- **Classes of nanostructured metal hydrides**
- **Synthesis routes**
- **Structure**
- **Morphology**
- **Thermodynamics**
- **Kinetics**
- **Mechanistic effects**
- **Future directions in nanohydride research**

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)

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)

Sandia Phase 2 Focus Areas activities involving Sandia

Task 1 Sorbents:

1.C Optimizing Sorbent Packing

1.F Nanoscale Defects in Sorbents (to begin in FY20)

Task 2 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

Task 3 Hydrogen carriers:

3.B Aqueous organic carriers

3.C Eutectic systems as hydrogen carriers

The Phase 2 hydride task builds on discoveries and developments in HyMARC Phase 1

- **Thermodynamics**
  - Ternary systems (e.g. Mg-Li-B-H)
  - Experimental data + computational modeling → new phase diagrams

- **Strategies for thermodynamic tuning**
  - Nanoscaling: 1) non-innocent hosts; 2) strain; 3) microstructure
  - Eutectics

- **Kinetic mechanisms using multiscale modeling**
  - Activation of MgB_2 by defects
  - Targeted additives for B-B and B-H activation

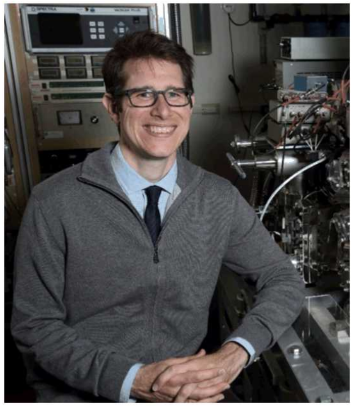
- **Advanced diagnostics**
  - Probes of all relevant length scales XAS+XPS+LEIS
  - DOE/BES user Approved Programs:
    - Molecular Foundry
    - Advanced Light Source

- **Integrated spectroscopy and theory**
  - Computed XAS spectra enable data interpretation and feature assignment
  - Team with Molecular Foundry (Prendergast), LLNL (Wood)

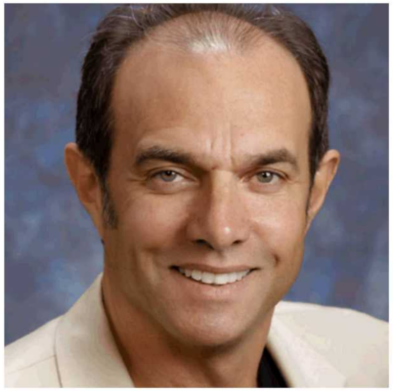
Sandia team

Mark Allendorf
Co-Director
SNL PI

Vitalie Stavila
Hydrides
Carriers



Rob Kolasinski
Surface probes



Lennie Klebanoff
Additives
Mechanisms

Jim White
Mechanisms
Synchrotron meas.

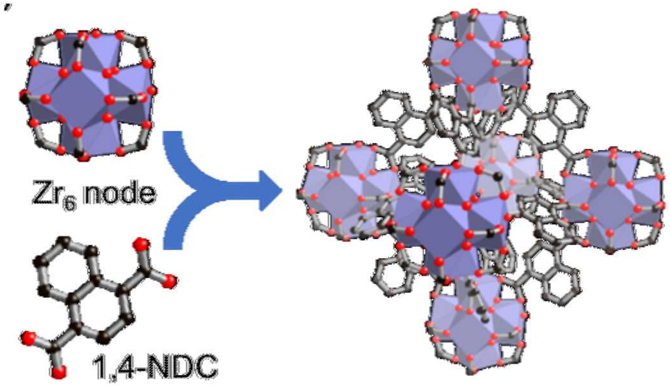
Xiaowang Zhou
Force field development

Annabelle Benin
MOF monoliths

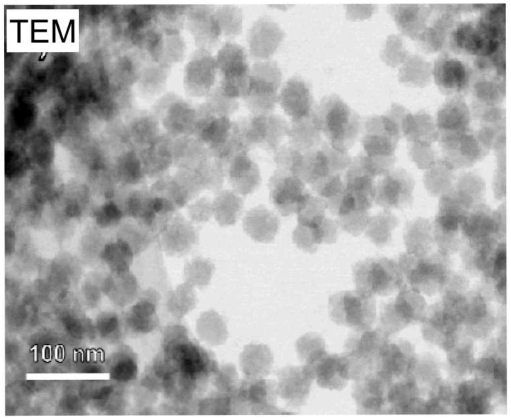
Sapan Agarwal
Machine Learning

Sorbents: 1.C. Optimizing sorbent packing

Synthesis of UiO-66-1,4-NDC monolith

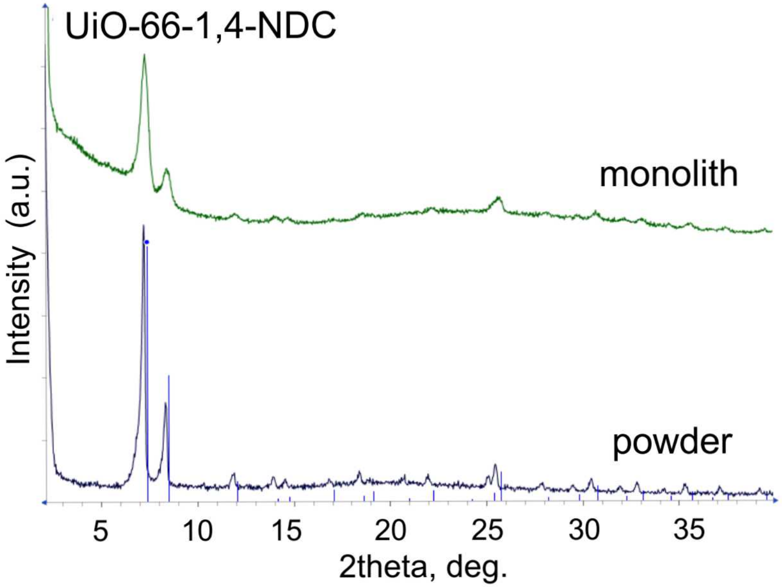


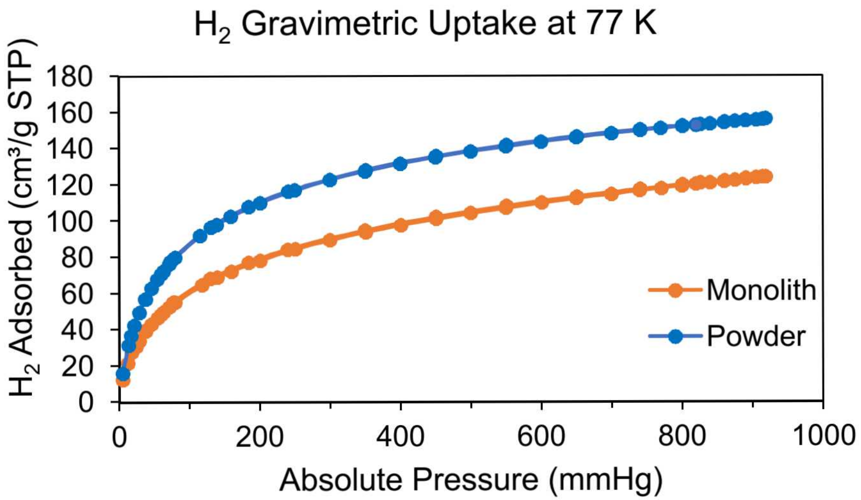
UiO-66-1,4-NDC



monolith

powder



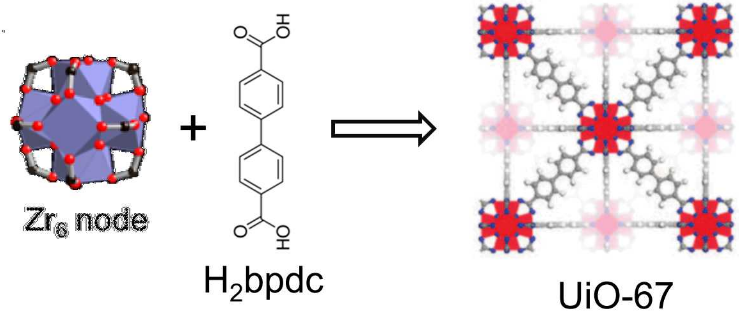


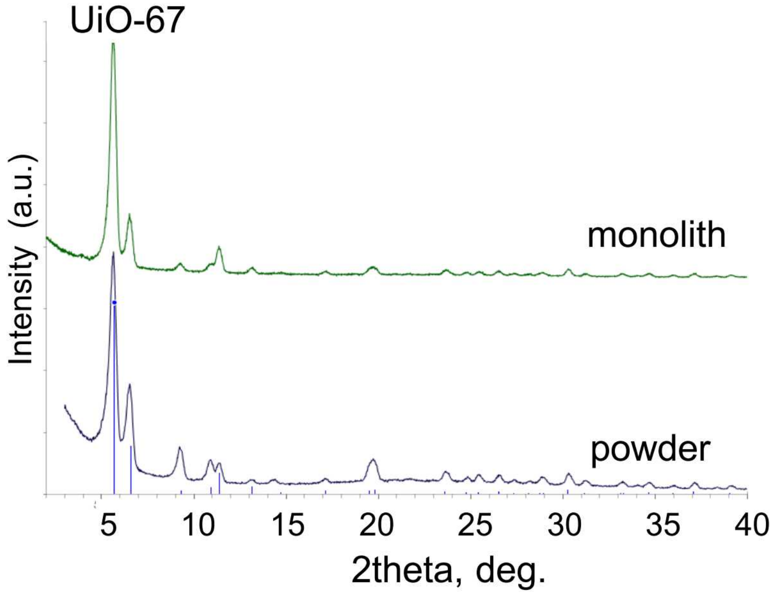
⇒ Showed that the UiO-66-1,4-NDC monolith is composed of sub-100 nm particles

⇒ UiO-66-1,4-NDC monolith shows a lower hydrogen uptake compared to powder

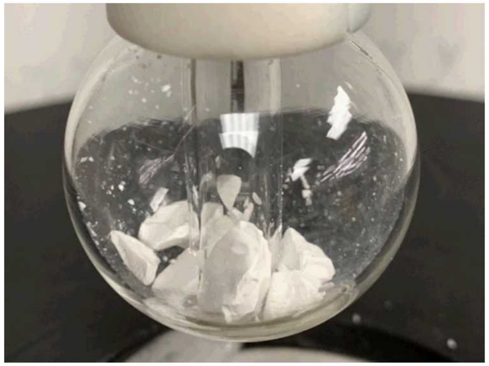
Task 1. Sorbents: 1.C. Optimizing sorbent packing

Synthesis of UiO-67 monolith

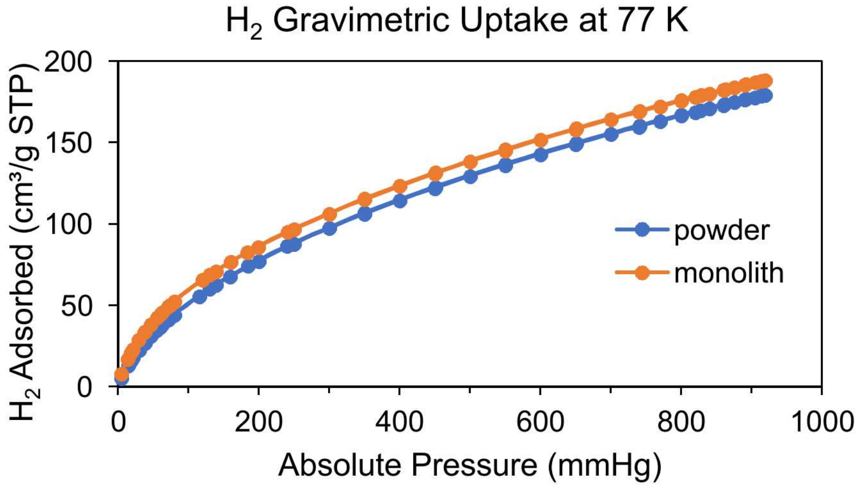




powder



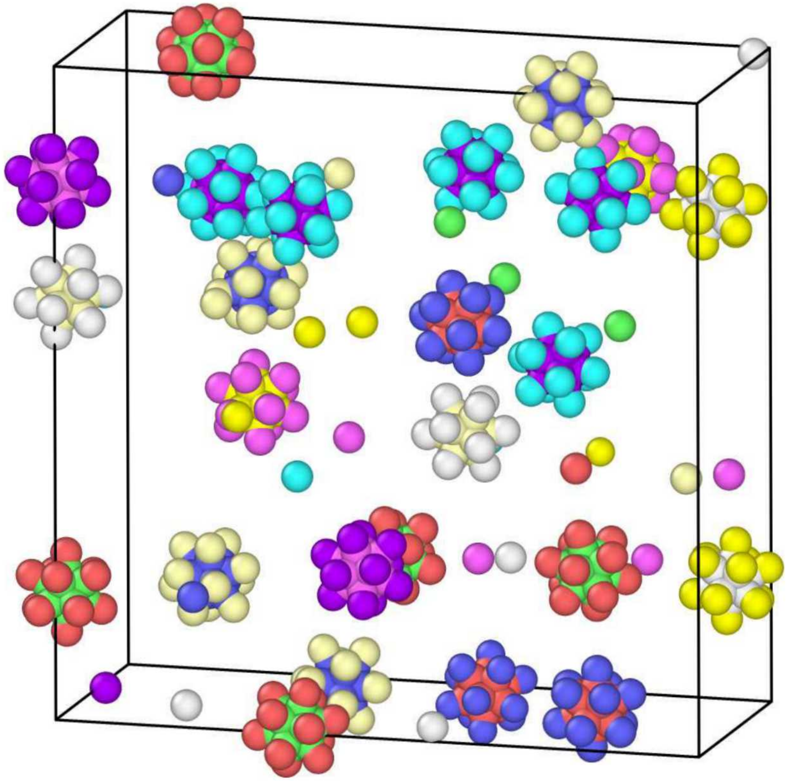
monolith



⇒ Successfully synthesized a UiO-67 monolith with a gravimetric hydrogen uptake similar to that of powder UiO-67

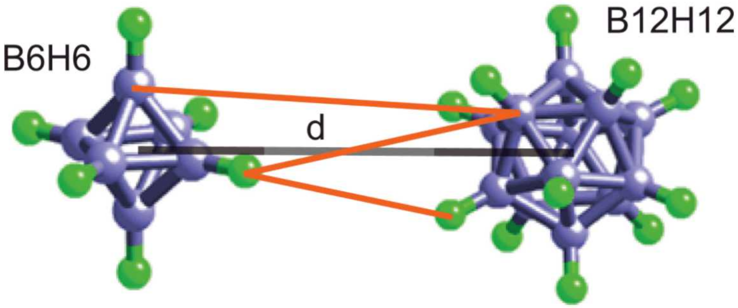
2. Hydrides: Molecular dynamics simulations of complex molecular systems

Molecular Systems



- Computational systems contain molecules rather than atoms
- Molecular forces equal sum of atomic forces between molecules
- In molecular dynamics simulations, species are distinguished by combination of molecules and atoms, not just atoms

Molecular and Atomic Forces

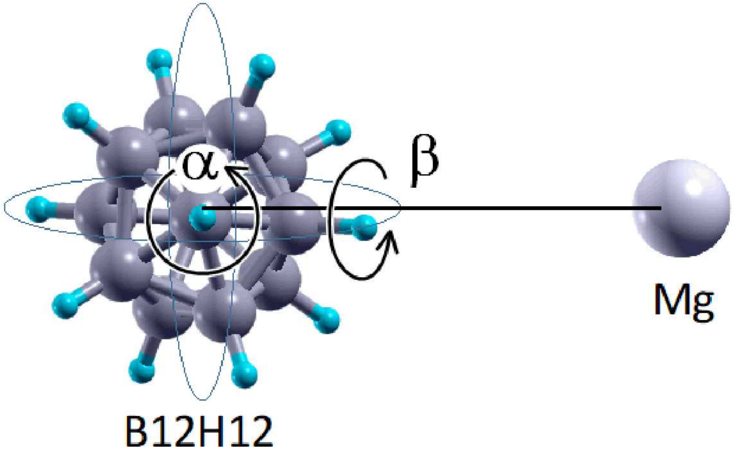


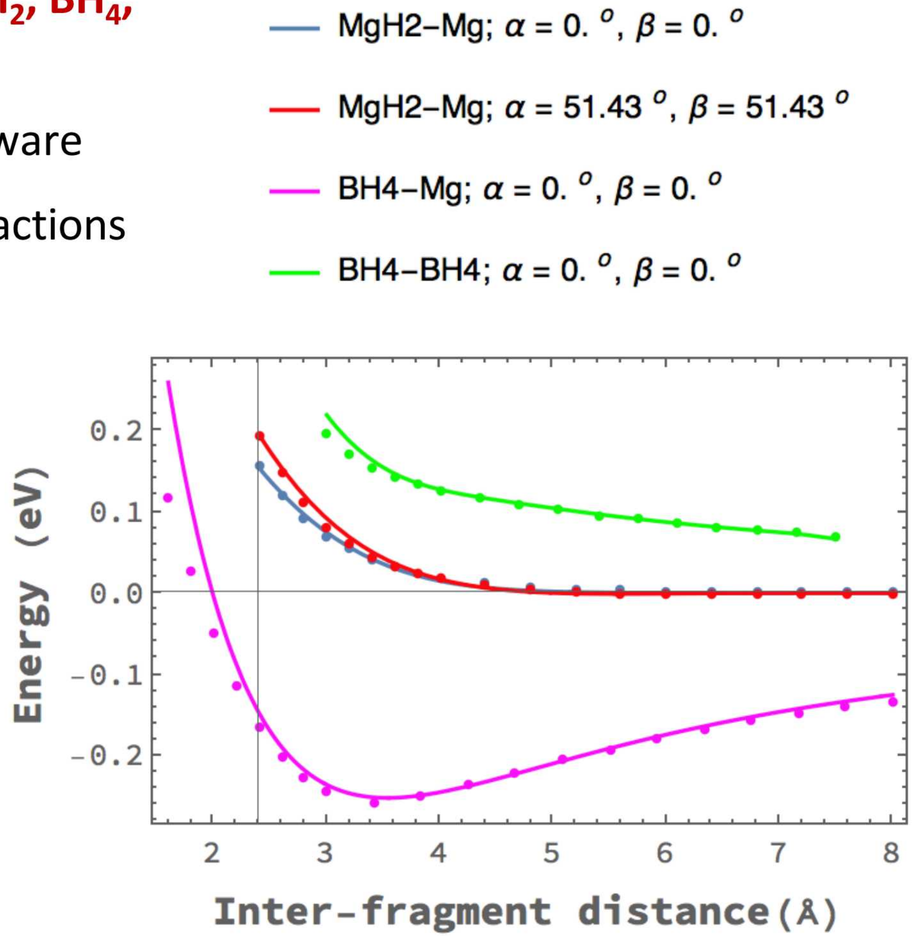
⇒ Developed MD approaches to predict complex transformations in metal borohydrides upon hydrogen release and uptake

2. Hydrides: Progress on Mg, H_2, BH_4^-, MgH_2, and $B_{12}H_{12}^{2-}$ force field modeling

- ✓ Completed DFT training sets on **H_2, Mg, MgH_2, BH_4, $B_{12}H_{12}$** (> 700 cases)
- ✓ Completed force field parameterization software
- ✓ Fitted Mg-MgH_2, Mg-BH_4, and BH_4-BH_4 interactions

Rotation-dependent molecular interactions





⇒ Established energetics and inter-fragment distances for relevant species in the magnesium borohydride system

Hydrides: 2.A. Metal hydride thermodynamics

$LiBH_4$-$Mg(BH_4)_2$ eutectics

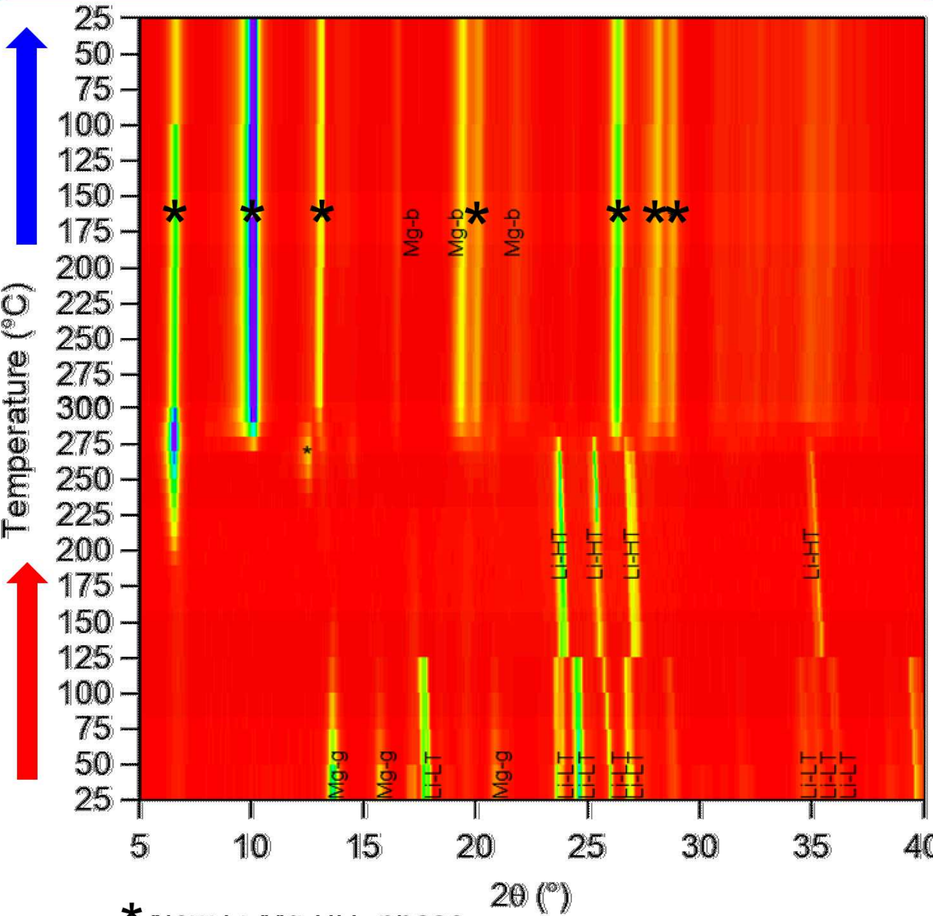
- Investigated eutectic melting of varying ratios of $LiBH_4$ (m.p.=280 ° C) and $Mg(BH_4)_2$ (m.p.=360 ° C)
- Induce melting at high H_2 pressure (1000 bar) to suppress dehydrogenation reaction
- Variable Temperature XRD under 10 bar H_2 reveals a new, Li-Mg borohydride phase in both 3:1 and 1:3 (Li:Mg) mixture

1000 bar, 200° C

3:1 1:3

1000 bar, 250° C

3:1 1:3



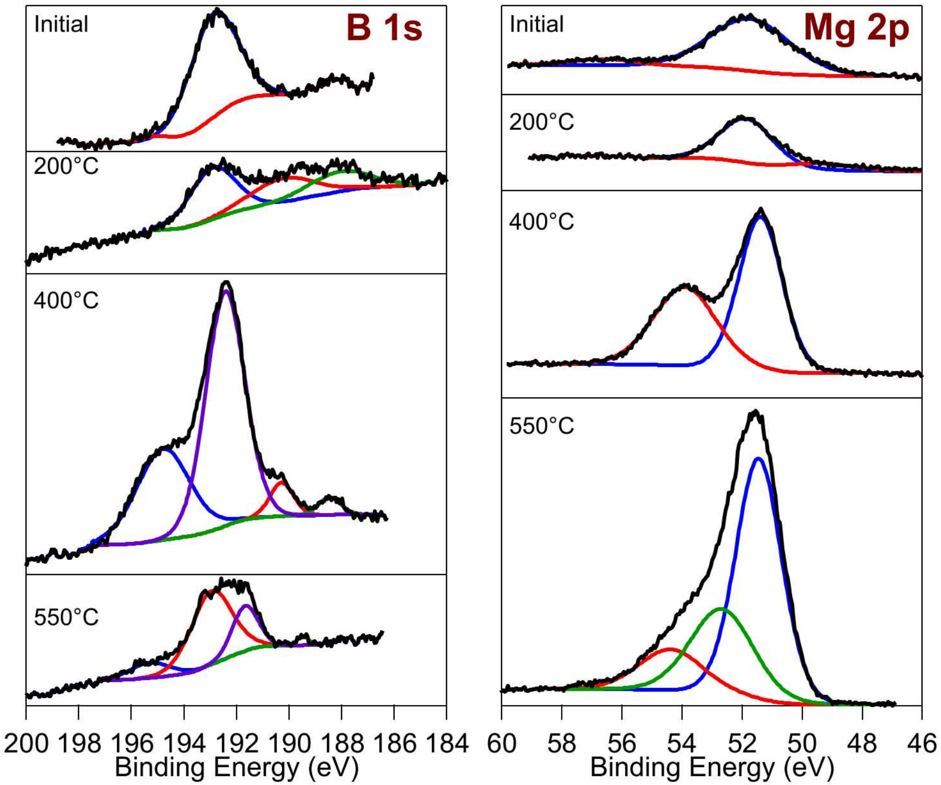
* New Li-Mg-BH_4 phase
$LiBH_4$- orthorhombic (Li-LT) $LiBH_4$- hexagonal (Li-HT)
γ-$Mg(BH_4)_2$ (Mg-g) β-$Mg(BH_4)_2$ (Mg-b)

⇒ Created an unexpected new phase of Li-Mg borohydride under the conditions known to generate a Li-Mg borohydride eutectic

Hydrides: 2.B Solid Interfaces and Surfaces

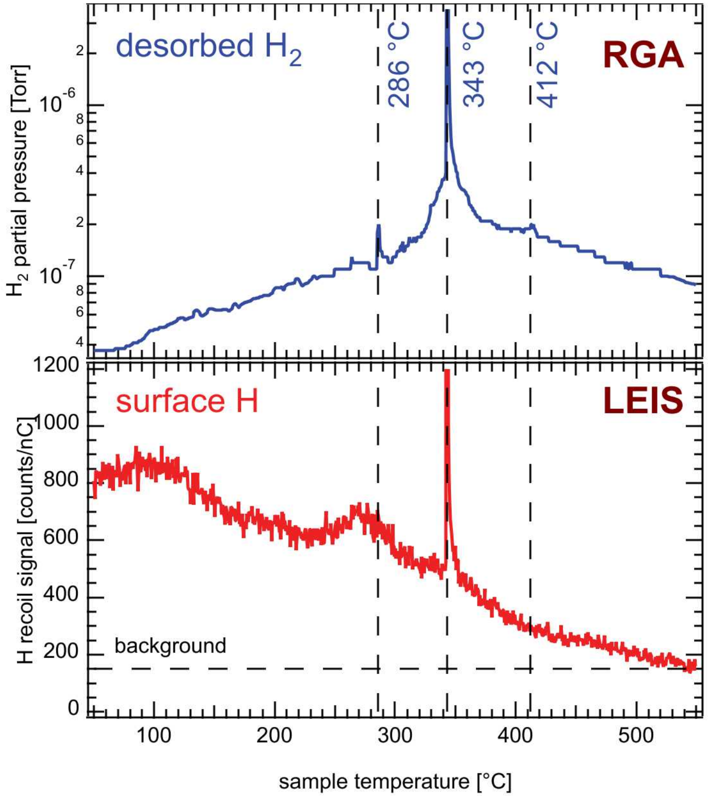
In situ surface characterization of $Mg(BH_4)_2$

XPS data



- Concentration of boron species elevated at near peak desorption
- Magnesium segregates to surface – implications for reversibility upon full desorption

RGA and LEIS data



- 2 keV Ne^+ scattering parameters optimized for H detection (less sensitive for O, B)
- H, Mg and 2 background channels monitored to provide absolute peak height

⇒ Demonstrated XPS, LEIS, and RGA can track hydrogen transport to the surface and subsequent desorption during $Mg(BH_4)_2$ dehydrogenation reaction

Hydrides: 2.C Activation of bonds in hydrides

Combining XAS and TEM to understand additive reactions

For the TiF_3/MgB_2 system, FTIR and XRD tell us TiF_3 has disappeared, but no products were observed.

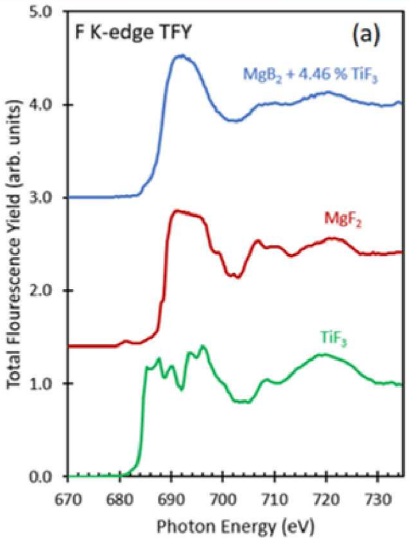
We turned to XAS (ALS) and TEM (Sandia) to figure it out.

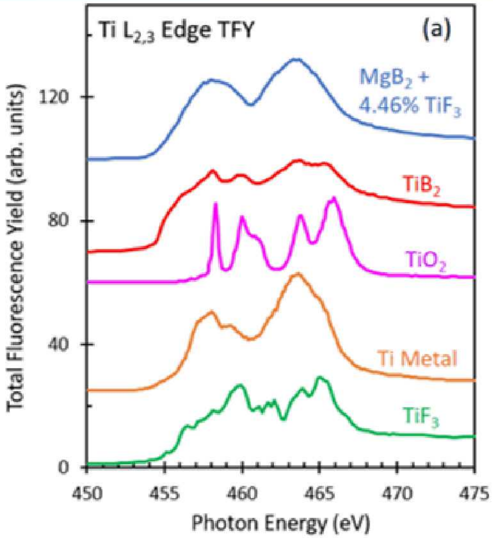
XAS reveals the formation of MgF_2.

XAS shows the formation of metallic Ti, with no evidence for titanium borides.

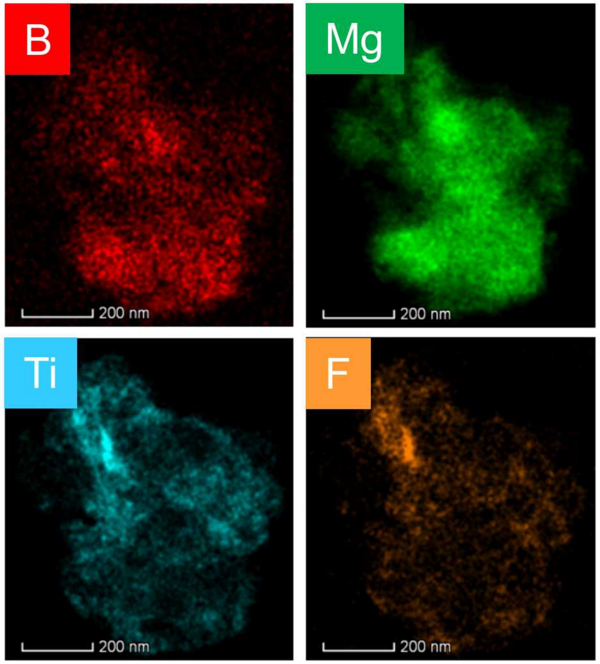
$$TiF_3 + 3/2MgB_2 = Ti + 3/2MgF_2 + 3B$$

TEM shows no evidence for discrete particulate phases of Ti or MgF_2. Rather, the Ti and F are smeared out within the MgB_2 as a film. The F is generally spatially associated with the Ti, so when the reaction took place, the resulting Ti metal and MgF_2 did not distribute completely uniformly within the MgB_2.





-- in collaboration with Yi-Sheng Liu, Jinghua Guo of LBNL and ALS

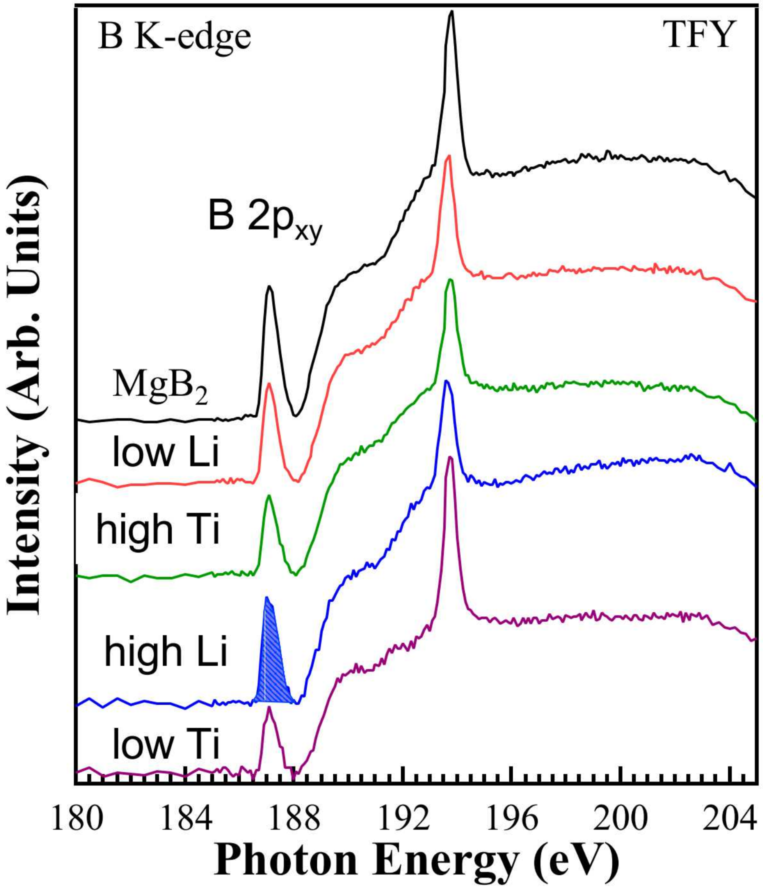


Hydrides: 2.C Activation of bonds in hydrides

Does disrupting the B-B ring promote MgB_2 hydrogenation?

The B $2p_{xy}$ intensity arises from the MgB_2 B-B ring. Use LiH and TiH_2 additives to disrupt it.

"low" = 0.25 mole fraction; "high" = 0.47 mole fraction



Sample	Integrated B $2p_{xy}$ Area
MgB_2	0.44
MgB_2 + low Li	0.31
MgB_2 + high Li	0.36
MgB_2 + low Ti	0.20
MgB_2 + high Ti	0.25

It looks like both Li and Ti additives reduce the B-B ring signal, but Ti disrupts it more, as predicted by LLNL theory.

Now have samples to assess affect of B-B ring disruption on H_2 uptake in MgB_2

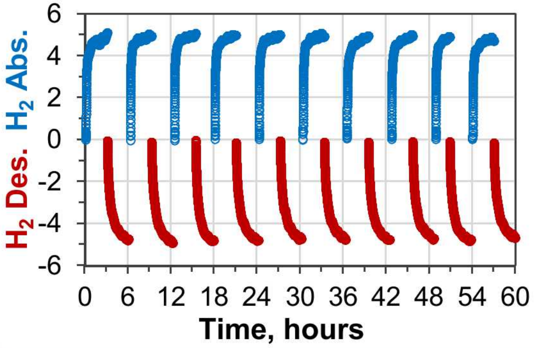
-- in collaboration with Yi-Sheng Liu, Jinghua Guo of LBNL and ALS

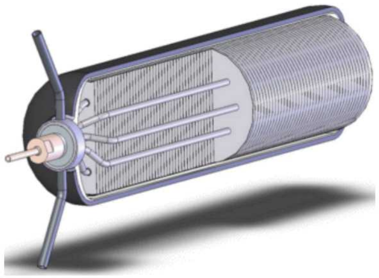
Next Steps: Sieverts H_2 uptake measurements on the Li/MgB_2 and Ti/MgB_2 samples to see if B-B bond disruption leads to faster hydrogenation of the MgB_2 sample.

Hydrides: 2.D Nanoscale Metal Hydrides

Engineering requirements for nanoscale hydrides

Design Parameters	Ti-$NaAlH_4$	6nm-Li_3N	KH-6nm-Li_3N
Reversible capacity. wt%	5.6	5.1	6.2
Thermal cond., W m^{-1} K^{-1}	9.0	8.9	9.6
Density of hydride bed, kg m^{-3}	720	675	740
System mass, kg	331	432	418
Total hydride mass, kg	125	129	113
Tank outer diameter, m	0.47	0.50	0.45
Tank length, m	2.23	2.23	2.19
System volume, m^3	0.38	0.42	0.37
% 2025 Gravimetric Target	38	29	40
% 2025 Volumetric Target	49	45	51

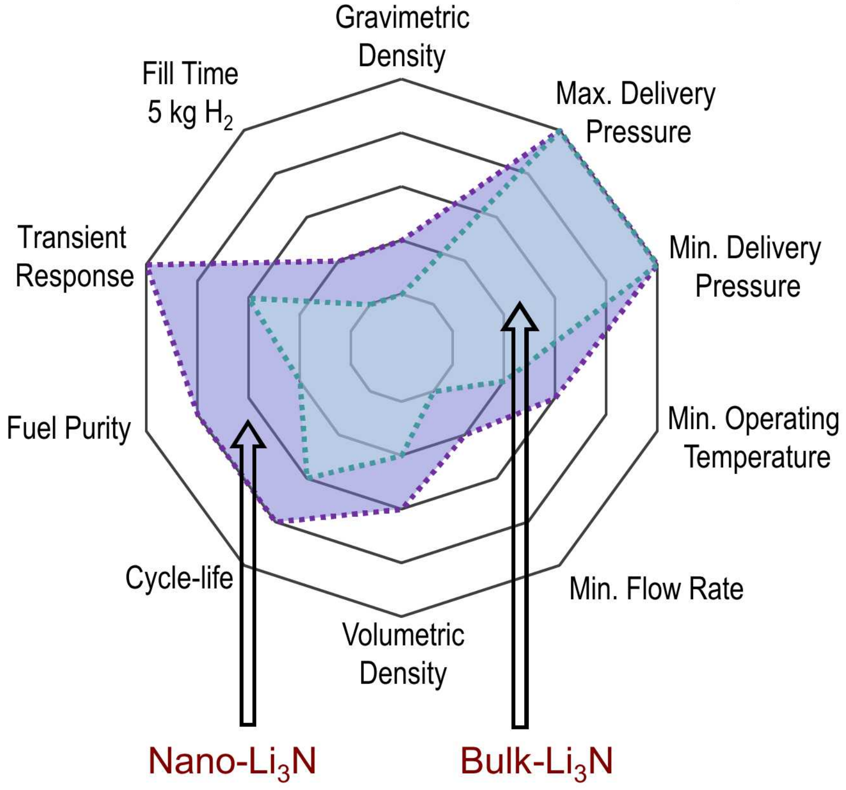




MHFE-SAH tank design

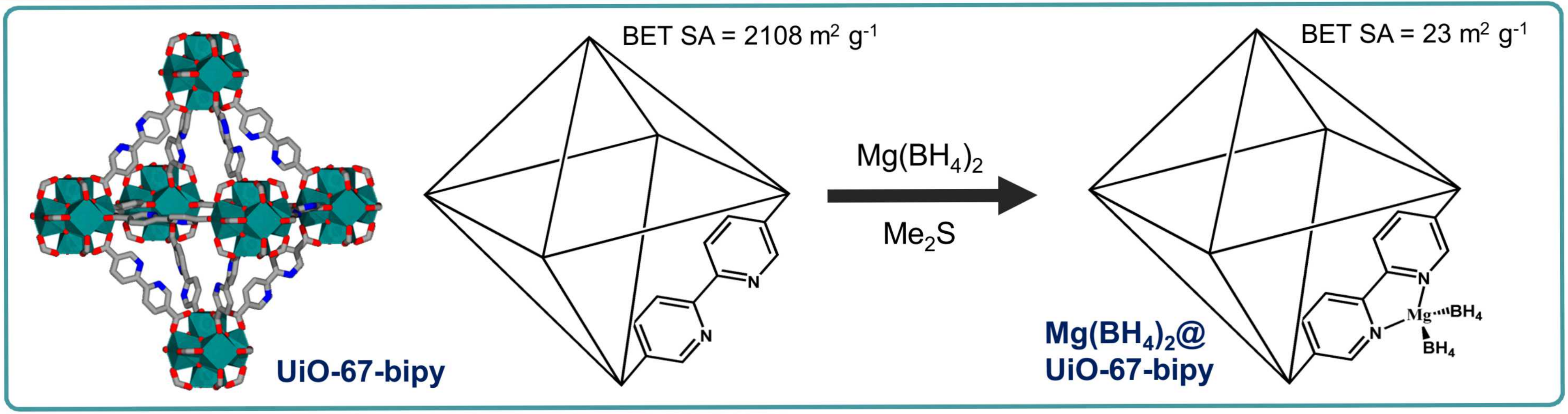
MHFE-SAH model on Li_3N@6nm-Carbon

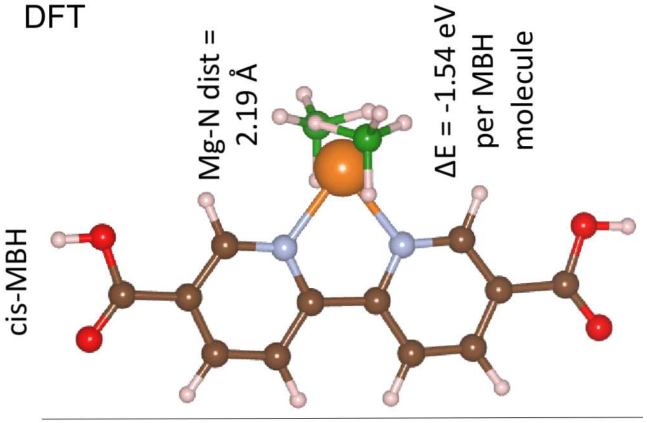
with Kriston Brooks, PNNL

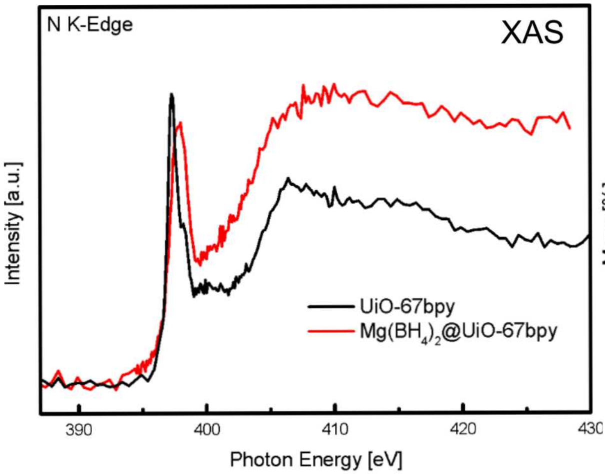


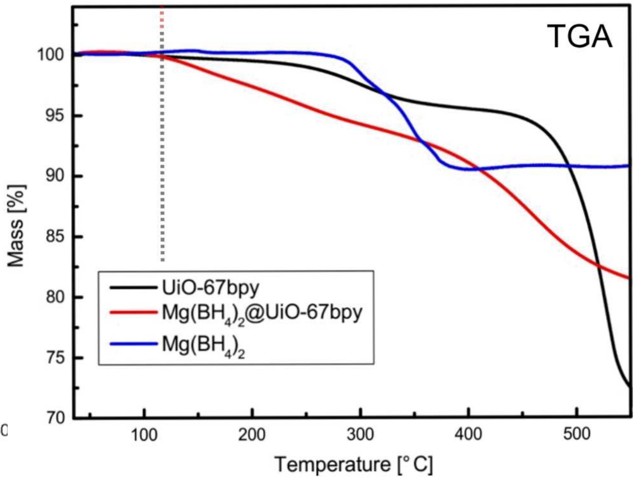
⇒ Used MHFE-SAH model developed in HSECoE to determine the benefits of using nanoscale lithium nitride in an operational hydrogen storage tank

Task 2. Metal Hydrides: 2.D Nanoscaling to Improve Thermodynamics and Kinetics





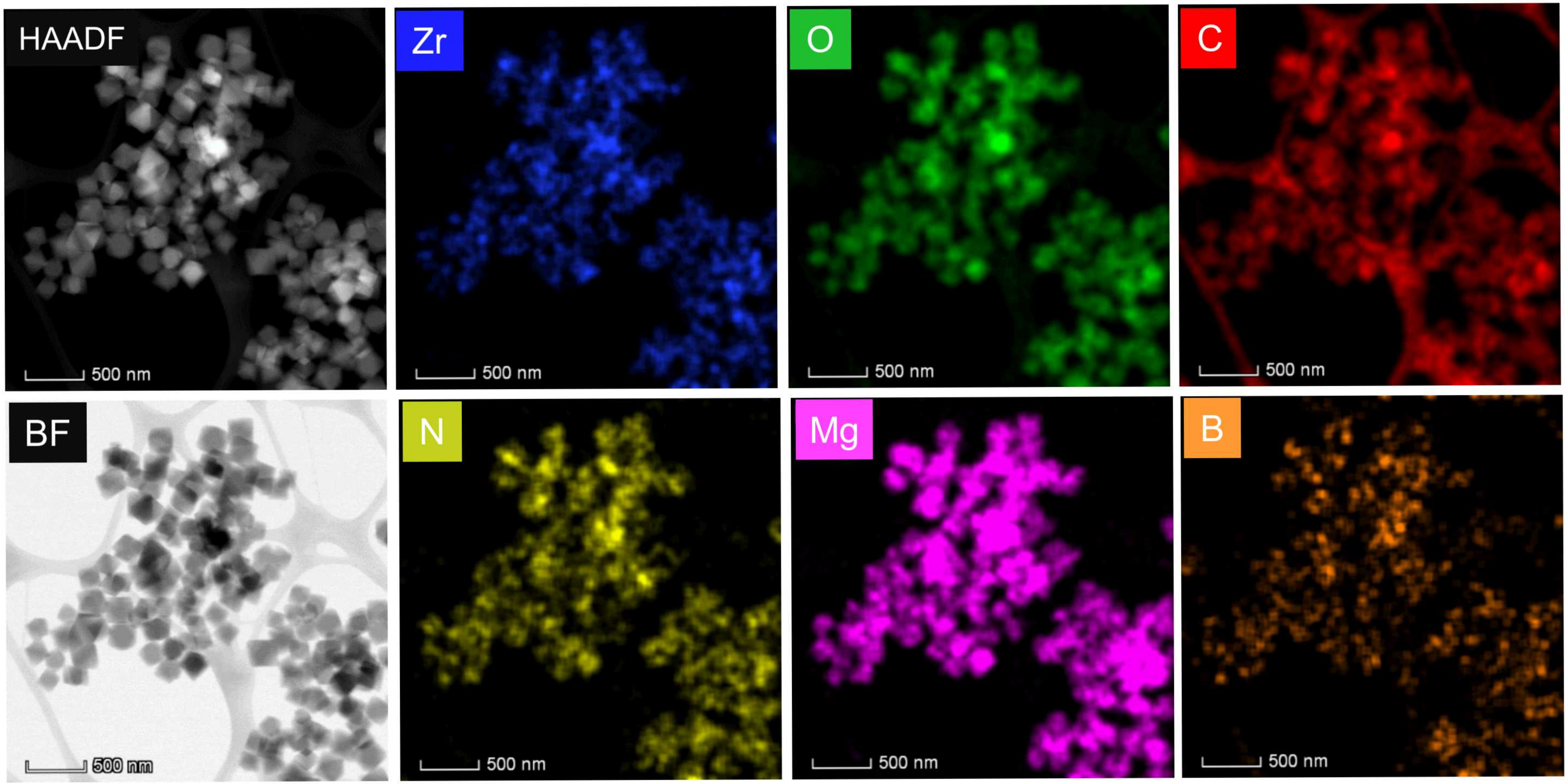




⇒ XAS measurements and computational spectroscopy reveal that $Mg(BH_4)_2$@UiO-67-bipy is composed of molecular $Mg(BH_4)_2$ species coordinated to bipyridine groups

⇒ Hydrogen release starts as low as 120 deg. C, >100 deg. C lower than bulk.

Task 2. Metal Hydrides: 2.D Nanoscaling to Improve Thermodynamics and Kinetics



⇒ TEM EDS measurements (Titan, aberration correction) reveal that both Mg and B atoms are homogeneously distributed within the UiO-67-bipy crystals, suggesting $Mg(BH_4)_2$ exists as molecular species within MOFs

Task 2. Hydrides: 2.F Development of machine-learning for discovery of new metal hydrides

HyMARC Hydrogen Materials Advanced Research Consortium

Sandia National Laboratories

Lawrence Livermore National Laboratory

- **Team: Sandia (lead), LLNL**
- **Objective:** develop a new HyMARC capability to efficiently search for the promising metal hydrides to complement an ongoing seedling effort (U. Michigan; Siegel)
- **Strategy:** apply Sandia's new "Explainable Machine Learning" tool to identify relationships between material features and observables such as plateau pressure
- **Status:** new postdoc hired (UC Berkeley); will start in June 2019

Hydrogen Storage Materials Database

FIZ Karlsruhe ICSD

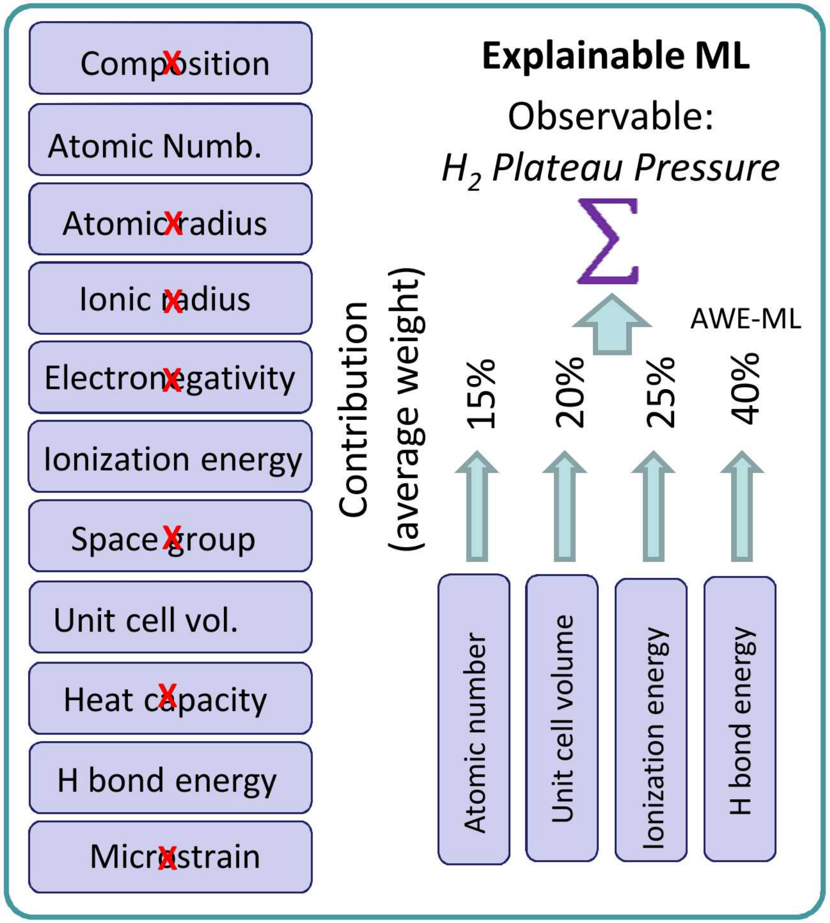
ASM International

ASM Alloy Phase Diagram Database

FactSage

Thermophysical Properties of Matter Database

Explainable Machine Learning Framework



~~Composition~~

Atomic Numb.

~~Atomic radius~~

~~Ionic radius~~

~~Electronegativity~~

Ionization energy

~~Space group~~

Unit cell vol.

~~Heat capacity~~

H bond energy

~~Microstrain~~

Explainable ML

Observable:

H_2 Plateau Pressure

$\sum$

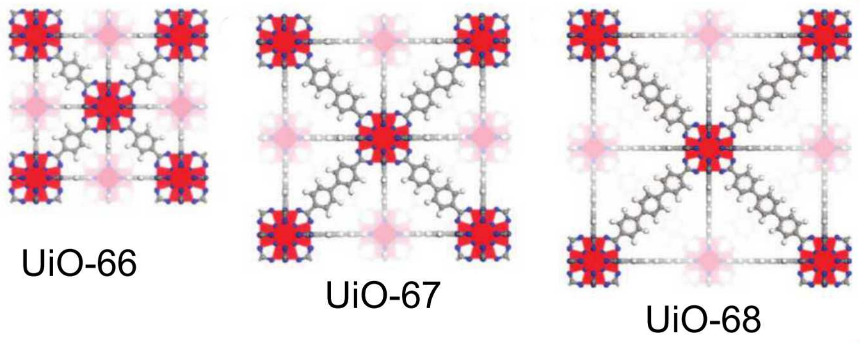
AWE-ML

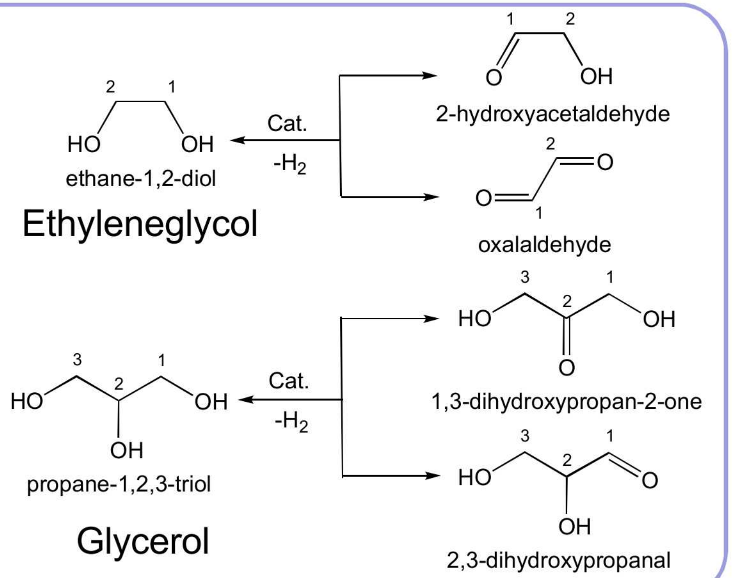
Contribution (average weight)

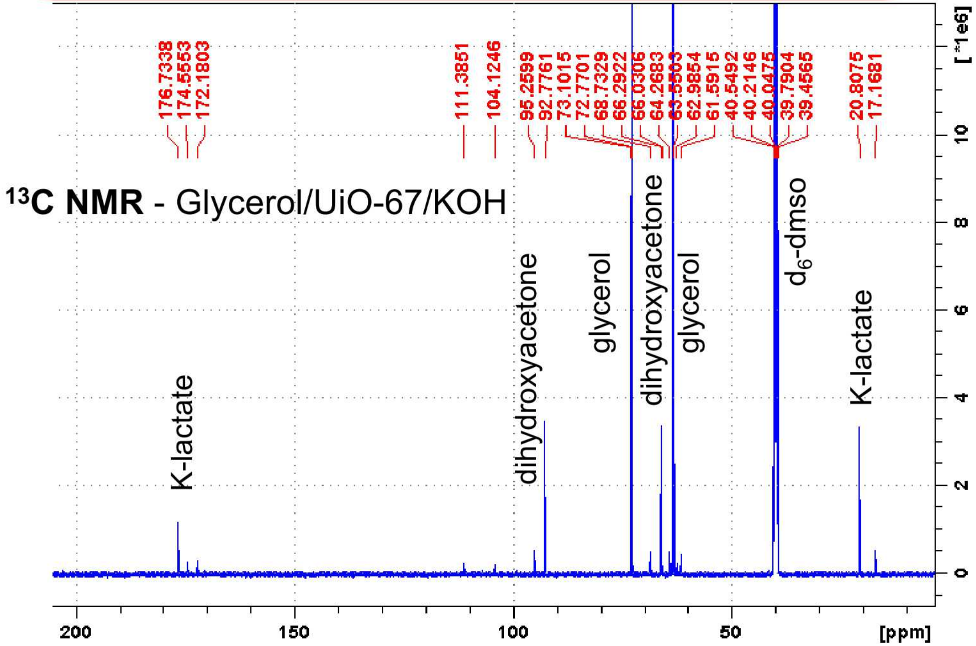
15%	20%	25%	40%
Atomic number	Unit cell volume	Ionization energy	H bond energy

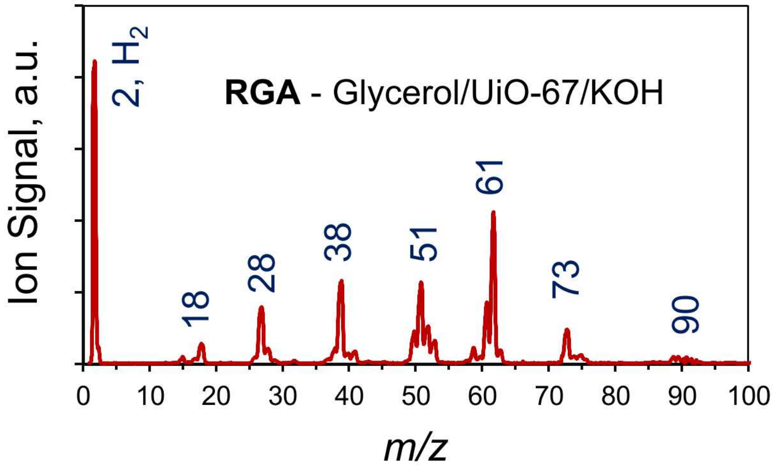
Task 3. Hydrogen Carriers
3.B Aqueous organic carriers

Catalytic MOFs stable under H_2O and H_2






^{13}C NMR - Glycerol/UiO-67/KOH


RGA - Glycerol/UiO-67/KOH

⇒ Demonstrated MOF-catalyzed hydrogen production from polyalcohols

Summary and Conclusions

Sorbents

- Developed synthetic approaches to monolith of several Zr-based MOFs, including UiO-66-1,4-NDC, UiO-67, and NU-1000, in order to improve packing density.
- Demonstrated a slightly higher hydrogen uptake in UiO-67 monolith compared to the powder version of this material.

Hydrides

- A molecular dynamics modeling framework was established to provide the fundamental thermodynamic basis of hydrogen storage reactions.
- Established in situ XPS and LEIS techniques to track hydrogen transport to the surface and subsequent desorption, using $Mg(BH_4)_2$ as an example.
- Established a theory-experimental framework for understanding how additive species may react with MgB_2 and how the B-B bonding could be disrupted.
- Used MHFE-SAH model developed in HSECoE to determine the benefits of using nanoconfined Li_3N in an operational hydrogen storage tank.
- Demonstrated a synthetic approach to creating molecular $Mg(BH_4)_2$ species within the pores of a functionalized MOF.

Hydrogen Carriers

- Demonstrated a catalytic acceleration of hydrogen production from polyalcohols.

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

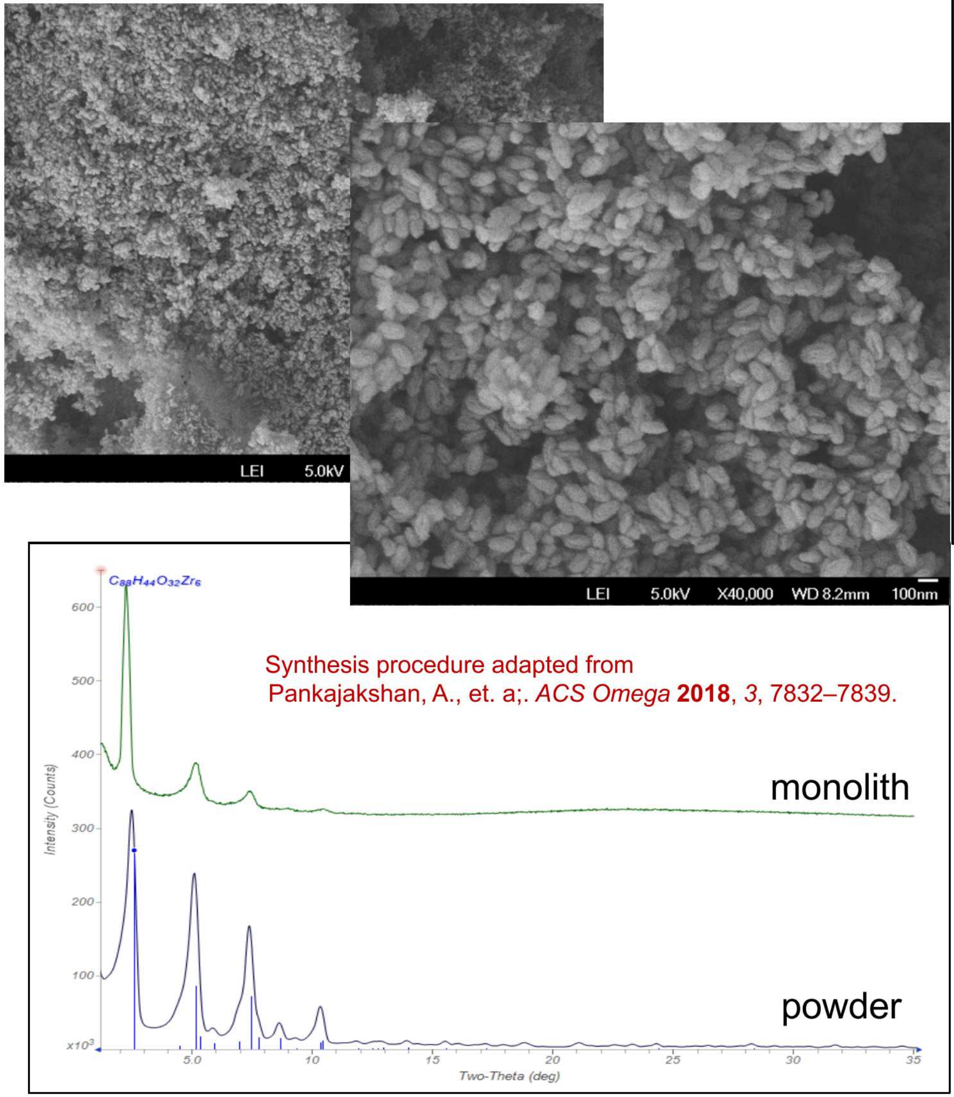
HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

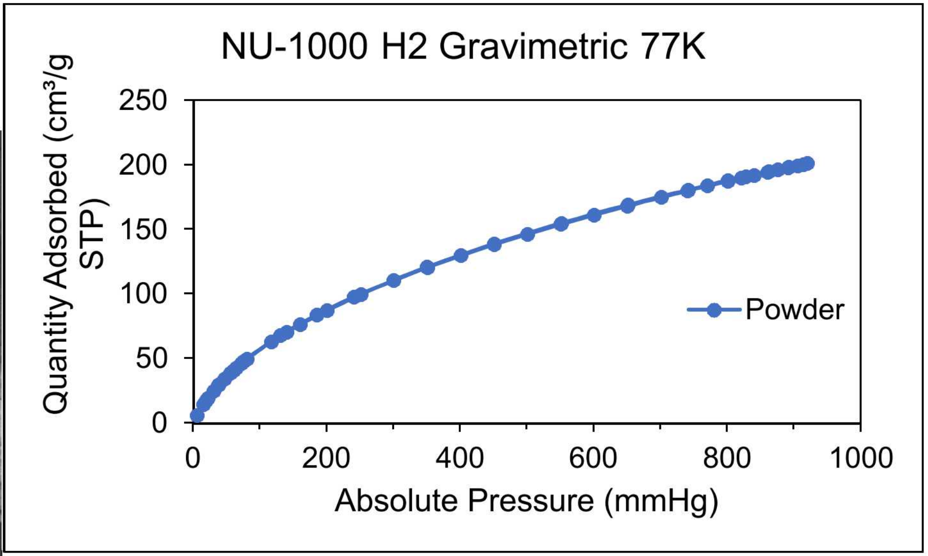
Sandia National Laboratories
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
BERKELEY LAB
Lawrence Berkeley National Laboratory
Lawrence Livermore National Laboratory
Pacific Northwest
NATIONAL LABORATORY
NIST
National Institute of Standards and Technology
SLAC
NATIONAL ACCELERATOR LABORATORY

Back-Up Slides

Synthesis of NU-1000 monolith



Synthesis procedure adapted from Pankajakshan, A., et. a;. *ACS Omega* **2018**, *3*, 7832–7839.



Scale-up effort underway

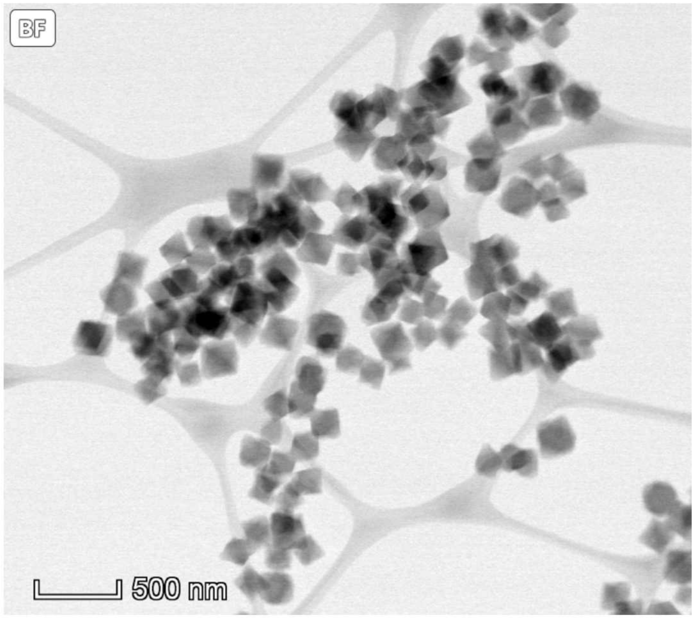
powder

monolith

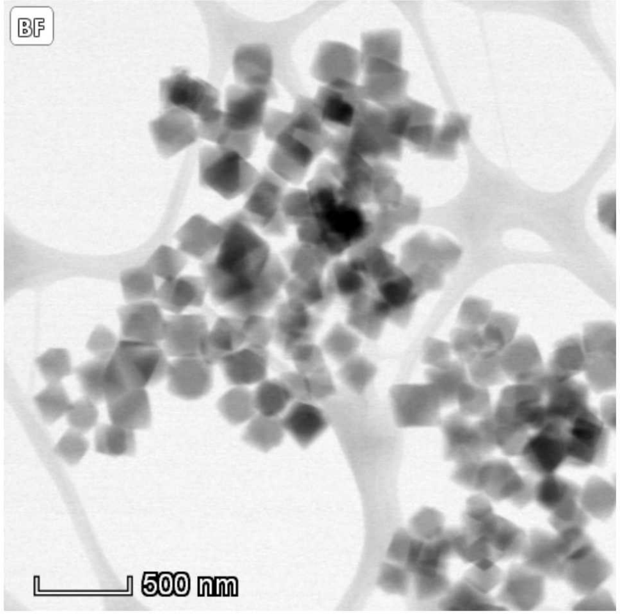
⇒ Successfully synthesized NU-1000 monolith; SEM shows 100-200 nm particles

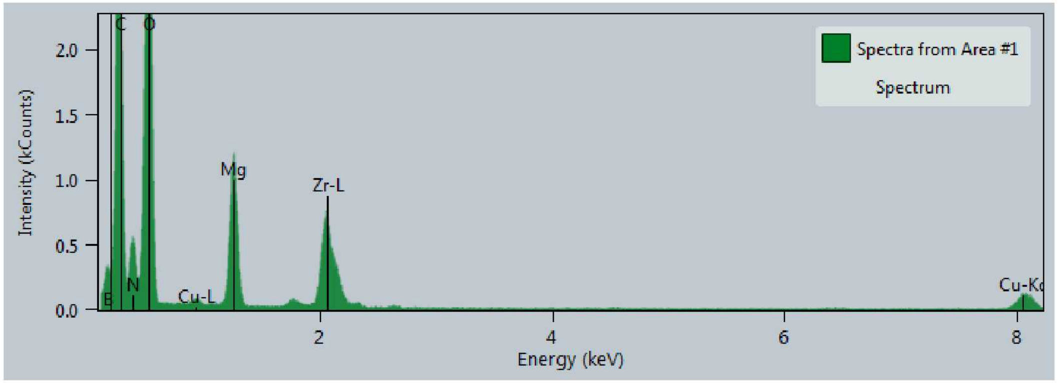
TEM/EDS on nanoconfined $Mg(BH_4)_2$@UiO-67

UiO-67bpy



$Mg(BH_4)_2$@UiO-67bpy





⇒ Morphology of $Mg(BH_4)_2$@UiO-67bpy particles is preserved upon nanoconfinement

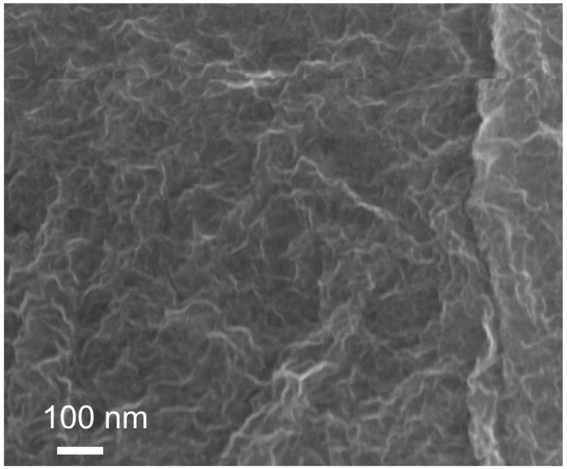
$Mg(BH_4)_2$ nanoconfinement

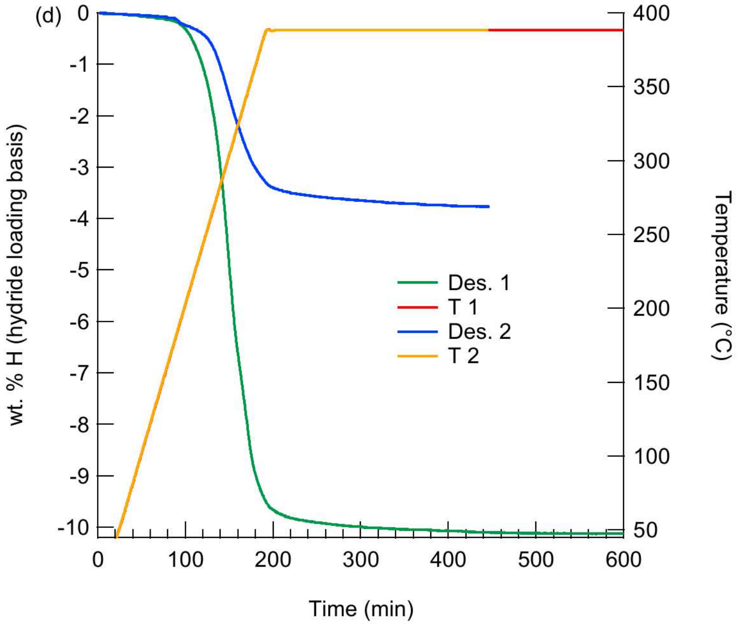
- $Mg(BH_4)_2$ found to melt at ~367 °C with high H_2 backpressures (>350 bar)

Resolidified $Mg(BH_4)_2$ after 1000 bar, 367° C

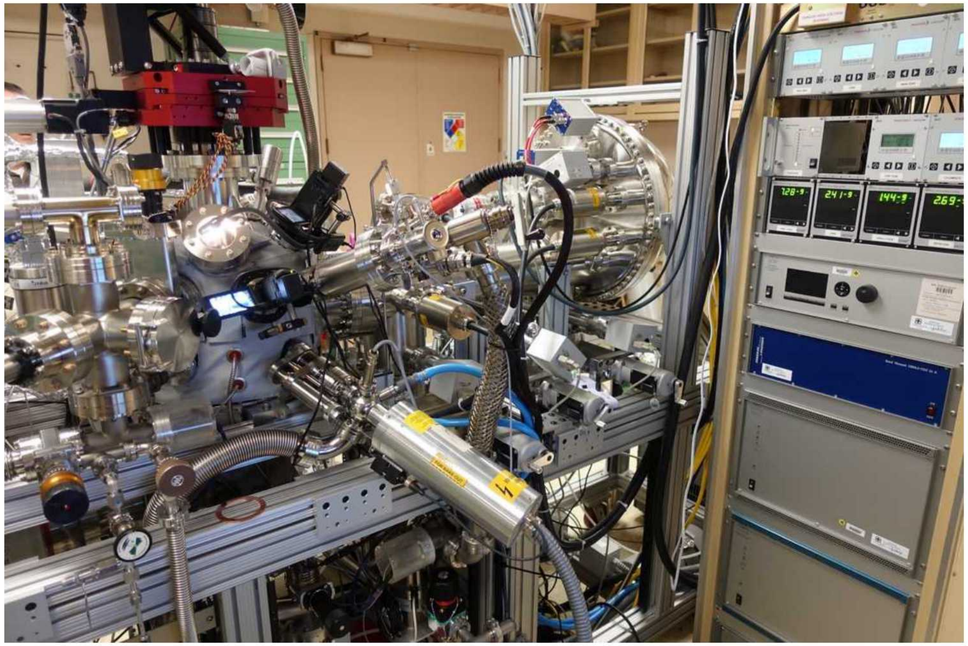
- Use this new knowledge to melt-infiltrate porous carbons, both graphene aerogels and templated carbons (CMK-3, CMK-8)
- Capacity drops by 60% after rehydrogenation at 120 bar H_2

SEM of Infiltrated Aerogel





New capability: AP-XPS system installed at Sandia



- Ambient-pressure XPS Energy Analyzer: 10 Torr, 0.05 eV resolution
- 80 ps/spectrum delay-line electron detector
- In-situ Ar, Ne, He sputtering
- Computer controlled precision 5-axis sample manipulator
  -Al_α and Mg_α ambient-pressure x-ray gun
- Pristine gas delivery system

DESCRIPTION

Ambient pressure Environmental XPS (E-XPS) is used to study surface/gas reactions in close to operating conditions of temperature and pressure). E-XPS measurements reveal 1) the chemical identity of the adsorbed reaction inter-mediates, and 2) the chemical state of the active materials. Traditional XPS can only be used in ultra-high vacuum conditions, allowing only ex-situ hydrogenation experiments and subsequent XPS measurements in vacuum. But the chemical reactivity and surface species can vary greatly with and without gas pressure. Near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) provides this information. In-situ studies with NAP-XPS can reveal the complex coupling between transport, surface reaction rates, and oxidation state changes.

UNIQUE ASPECTS

Unique, in-house designed and fabricated experimental chamber for hydrogen-focused surface studies.