Sandia National Laboratories

HyMARC Hydrogen Materials Advanced Research Consortium

H_2FC Hydrogen and Fuel Cells Program

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

Mark Allendorf (PI), Vitalie Stavila (Presenter), James White, Chun-Shang Wong, Andreas Schneemann, Annabelle Benin, Pavithra Wijeratne, Lennie Klebanoff, Robert Kolasinski, Farid El Gabaly, Catalin Spataru, Xiaowang Zhou

Sandia National Laboratories, Livermore, CA, USA

Annual Merit Review Meeting, Crystal City, VA – May 1, 2019

Enabling twice the energy density for hydrogen storage

Project ID# ST128

SAND#2019-3249

Overview

Timeline

- Project start date: 09/17/2018

SNL R&D Budget

- FY18 Phase 1 Funding: $895,000
- FY18 Phase 2 Funding: $783,890
- FY19 Phase 2 Funding: $450,000
- Total Phase 2 Funding: $1,233,890

Barriers

- Lack of Understanding of Hydrogen Physisorption and Chemisorption (Barrier O)
- System Weight & Volume (Barrier A)
- Cost, Efficiency, Durability (Barrier F)
- Charging/Discharging Rates (Barrier E)

Core Team

HyMARC Hydrogen Materials Advanced Research Consortium

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

Relevance

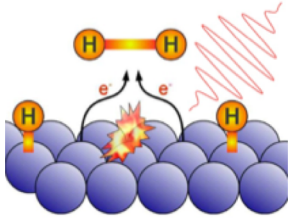
Identifying and addressing foundational knowledge gaps

⇒ Understanding the physical and chemical influences that can **improve thermodynamics of sorbents and complex metal hydrides**

⇒ Elucidated **surface/interface phenomena in complex metal hydrides** that impact H_2 storage

⇒ Identified species critical to **hydrogen transport through surfaces and interfaces**

⇒ Probed the underlying **mechanisms for additive effects on kinetics**



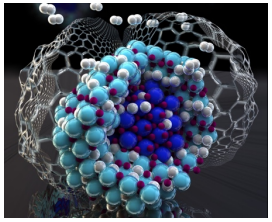
Discovery of new material concepts for hydrogen storage

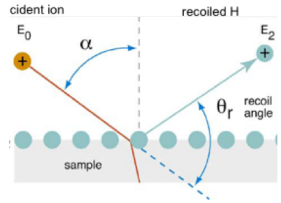
⇒ **Mitigated intermediate formation** in hydrogen storage reactions through doping and nanostructuring

⇒ Demonstrated **molecularly dispersed metal borohydride species**

⇒ Applied **SNL multiscale codes to discover new materials** and new mechanisms of storing hydrogen, provide input for database development

⇒ Developed catalysts for low-temperature, **carbon-neutral hydrogen generation**

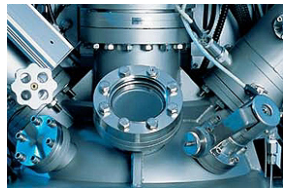




Development of new capabilities

⇒ Developed techniques to **detect and monitor hydrogen on surfaces**

⇒ Coupled X-ray spectroscopy with spectral theory to **probe electronic structure**

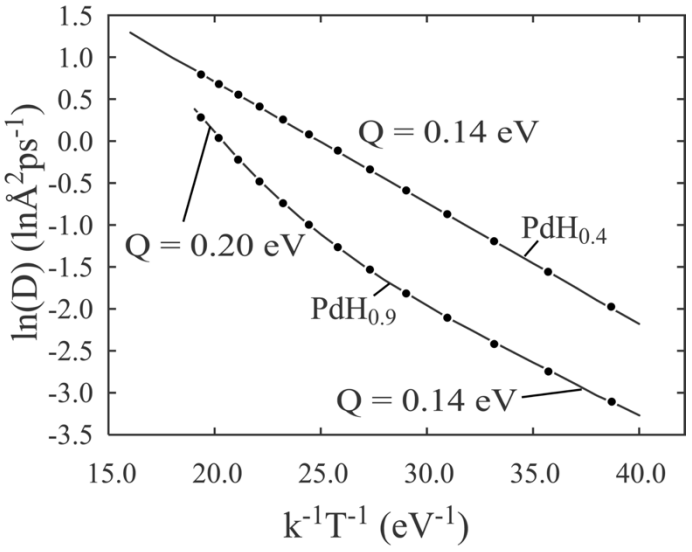


Seedling interactions and validation

⇒ Collaborated with seedling projects to **assess novel materials concepts for hydrogen storage**

Phase 1 Accomplishments: Established MD modeling framework to predict hydrogen transport

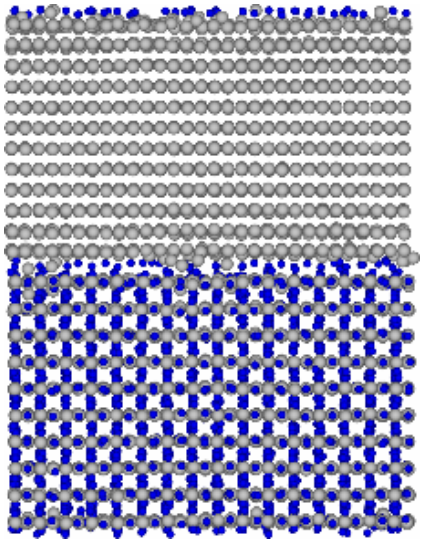
Accurate Model of H Diffusion in Pd



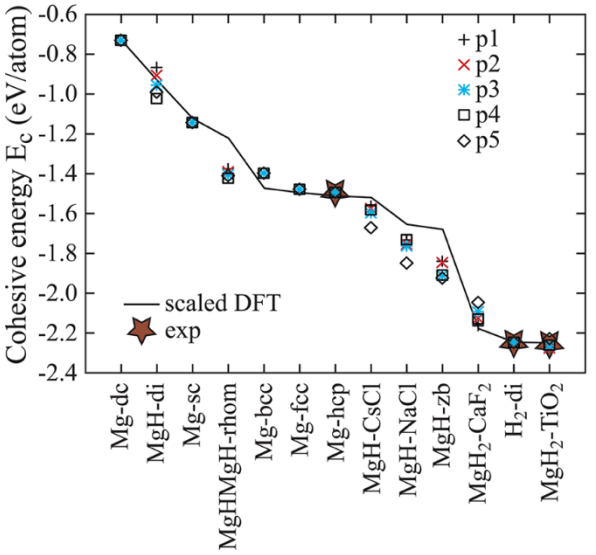
Approach validated with experiments on palladium hydride

Developed Reliable Mg-H Force Field

MgH_2/Mg interface



Energy trends

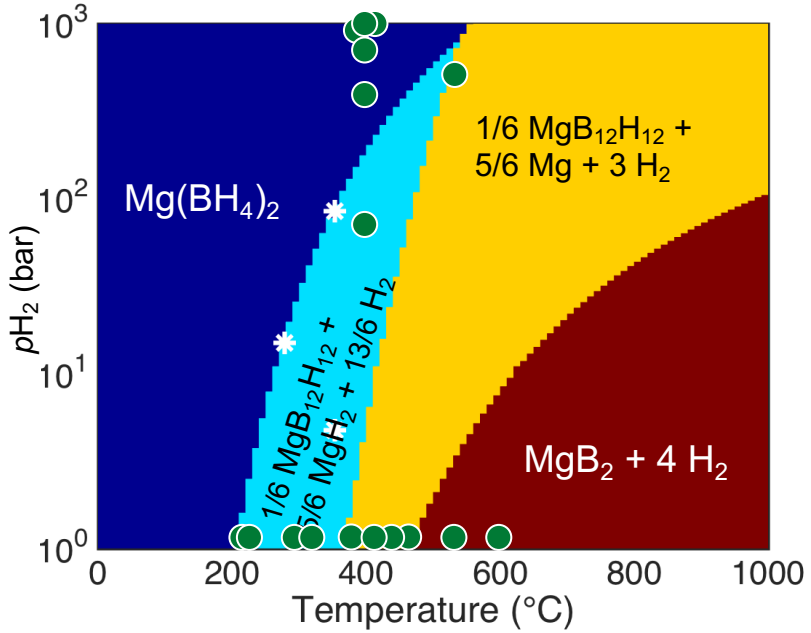


- H diffusion in Al: X.W. Zhou, F. El Gabaly, V. Stavila, M.D. Allendorf, *J. Phys. Chem. C*, **2016**, *120*, 7500.
- H diffusion in bulk Pd: X.W. Zhou, T.W. Heo, B.C. Wood, V. Stavila, S. Kang, M.D. Allendorf, *Scripta Mater*, **2018**, *149*, 103.
- PdH_x bulk: X.W. Zhou, T.W. Heo, B.C. Wood, V. Stavila, S. Kang, M.D. Allendorf, *MRS Adv.*, **2017**, *2*, 3341;
  X.W. Zhou, T.W. Heo, B.C. Wood, V. Stavila, S. Kang, M.D. Allendorf, *J. Appl. Phys.*, **2018**, *123*, 225105.
- Mg-H force field: X.W. Zhou, S. Kang, T.W. Heo, B.C. Wood, V. Stavila, M.D. Allendorf, *ChemPhysChem*, **2019**, *20*, 1.

⇒ Sandia Molecular Dynamics modeling tools provide activation barriers and pathways as input to kinetic hydrogen transport models developed at LLNL.

Phase 1 Accomplishments: Experimental/theory phase diagram for bulk $Mg(BH_4)_2$

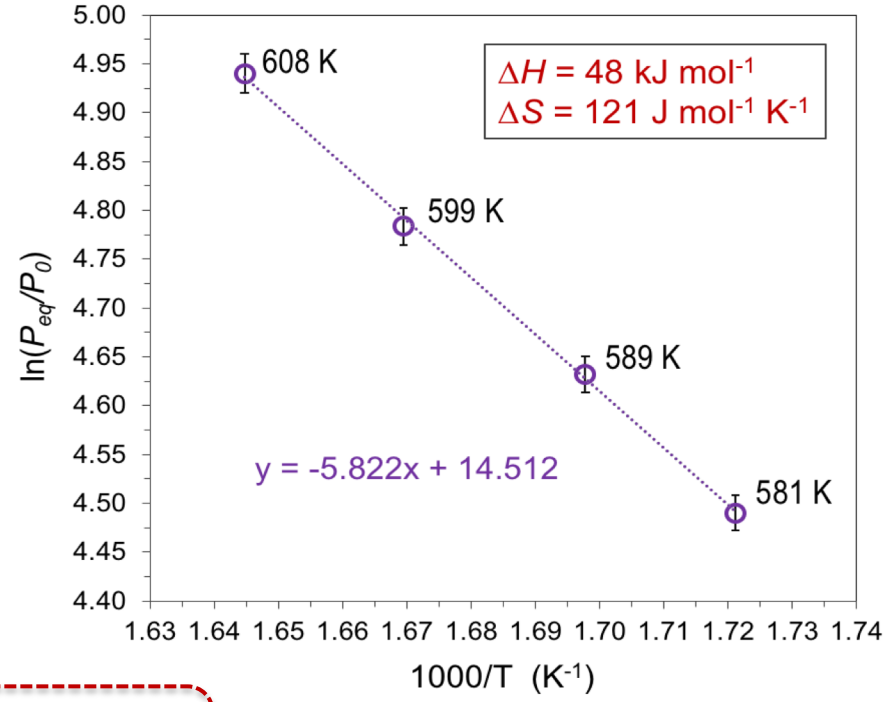
$Mg(BH_4)_2$ Phase Diagram



● Measured experimental conditions

Direct van't Hoff measurements, $Mg(BH_4)_2$

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



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

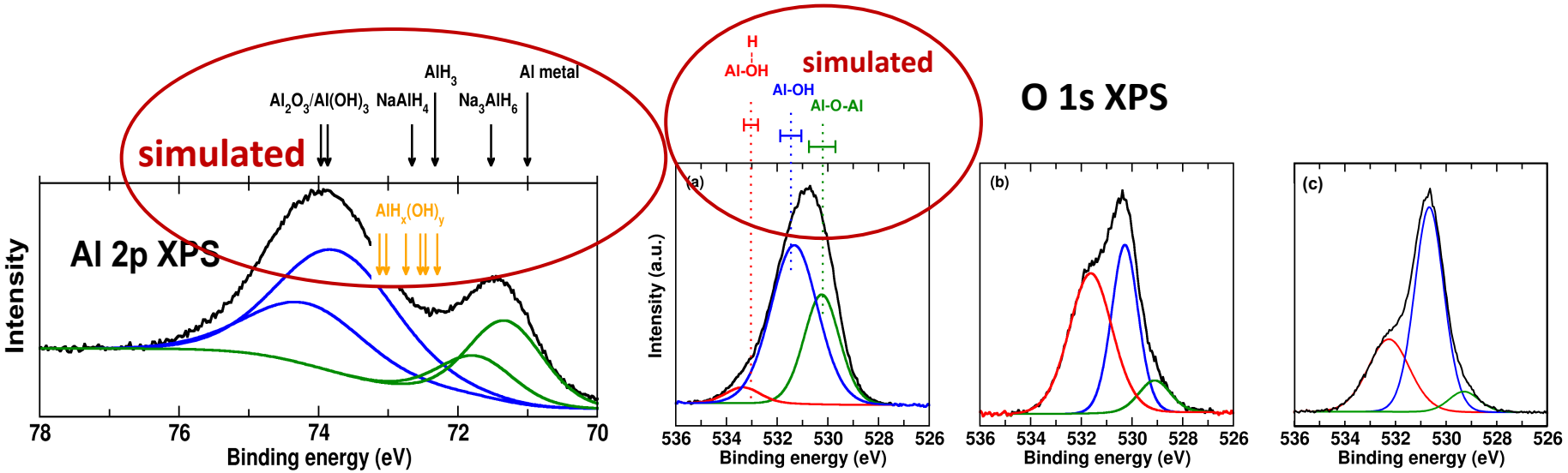
$6Mg(BH_4)_2 \rightarrow 5MgH_2 + MgB_{12}H_{12} + 13H_2$

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

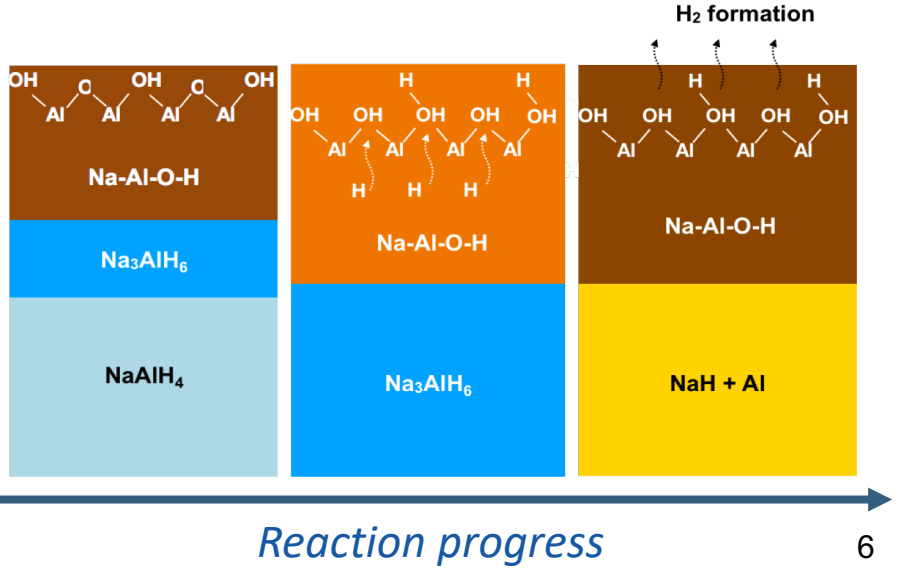
Accurate experimental ΔH and ΔS values obtained for initial dehydrogenation of magnesium borohydride; values consistent with HyMARC theory predictions

Phase 1 Accomplishments: $NaAlH_4$ surface chemistry understood using tools that probe surface composition

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



- Simulated XPS spectra show that past work has incorrectly assigned chemical species, which do not always follow formal oxidation state!
- Near-surface region chemistry involves oxide film on Na_3AlH_6, which evolves as hydrogen enriches and then depletes during dehydrogenation
- Surface hydroxides serve as low-barrier sites for H-H combination and H_2 release



Coordination and Collaboration:
Sandia collaborates with Phase 2 seedling projects

The Sandia HyMARC team assists the H_2 storage community with:

⇒ Technical expertise concerning specific scientific problems

⇒ Provides well-characterized sorbents and hydrides for joint studies

⇒ Access to HyMARC modeling and experimental capabilities

As of 03/31/2019, Sandia has performed high-pressure hydrogenations on ≈110 samples from the US and international collaborators

Sandia is providing support to seedling projects:

- ***Development of Magnesium Boride Etherates as Hydrogen Storage Materials*** (U. Hawaii)
  - Explored jointly instability in MgB_2 boron sheets
  - High-pressure hydrogenation, XRD, and FTIR performed for > 60 samples
  - Joint paper accepted in *ChemPhysChem*
- ***Electrolyte-Assisted Hydrogen Storage Reactions*** (LiOx Power and HRL Labs)
  - High-P experiments and sample characterization
  - Joint paper on eutectics published in *J. Phys. Chem. C*
- ***Atomic-Layer Deposition Synthesis of 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. Mich.)
  - Crystal engineering of Open Metal Sites in Metal-Organic Frameworks

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 of Hydrogen Storage Reactions

2.B Solid Interfaces and Surfaces

2.C Activation of Bonds in Hydride Materials to Improve Kinetics (e.g., B-B, B-H)

2.D Nanoscaling to Improve Thermodynamics and Kinetics

2.E Microstructural Impacts of Complex Metal Hydride Reactions

2.F Machine Learning and Data Science

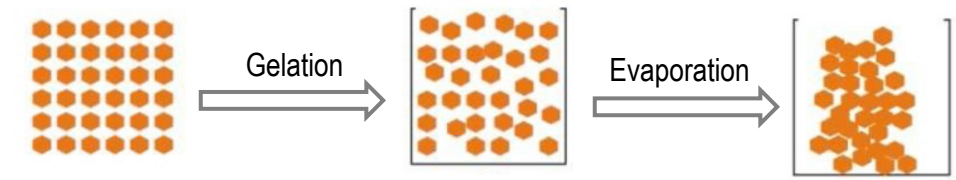
Task 3-Hydrogen Carriers:

3.B Aqueous Organic Carriers

3.C Eutectic Systems as Hydrogen Carriers

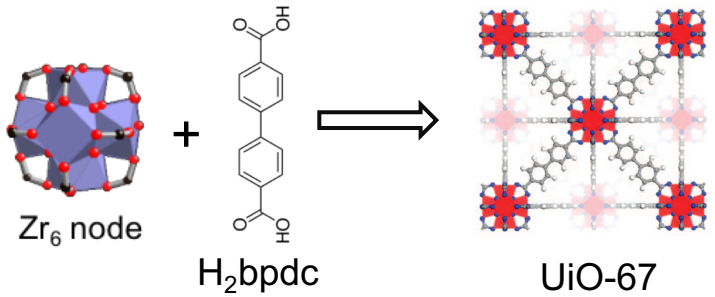
Sorbents: 1.C. Optimizing sorbent packing

Synthesis of high-density MOF monoliths

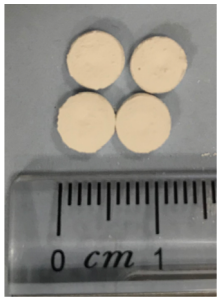


volumetric CH_4 and H_2 uptake is twice that of HKUST-1 powder due to the high bulk density of the monolith sample.

D. Fairen-Jimenez et al., *Nat. Mater.* **2018**, *17*, 174.

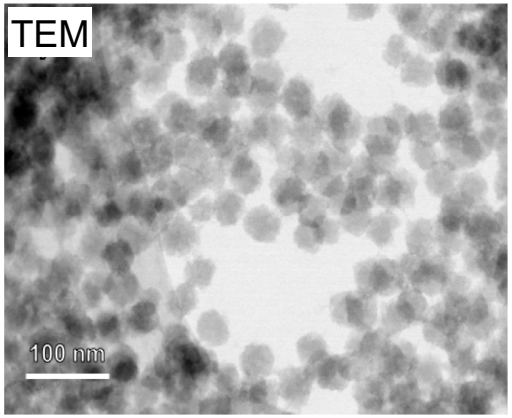


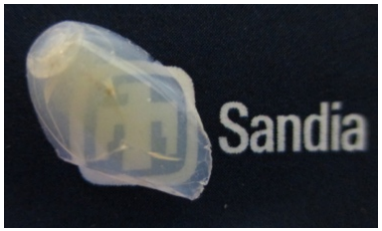
Sol-gel



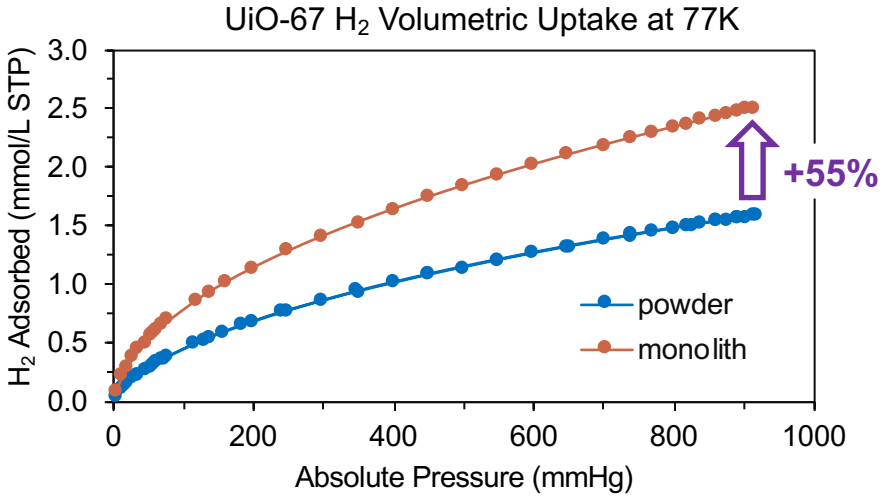
UiO-67 monolith, d=0.31 g/cm^3

UiO-67 powder d=0.20 g/cm^3





Manuscript describing synthesis of UiO-66-NDC monolith accepted:
T. Wang *et al.*, *Chem. Commun*, 2019, in press.

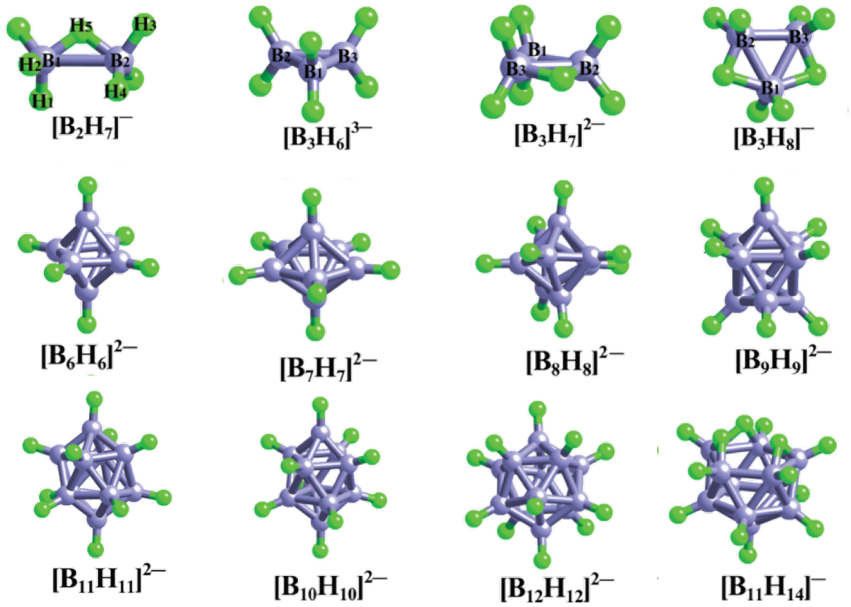


⇒ Used established methodology to synthesize UiO-66-NDC and UiO-67 monoliths

⇒ Found >50% increase in volumetric H_2 uptake in monolith compared to UiO-67 powder

Approach: Molecular dynamics simulations of hydride multicomponent systems

Arachno- , *Nido-* and *Closo*-Borates



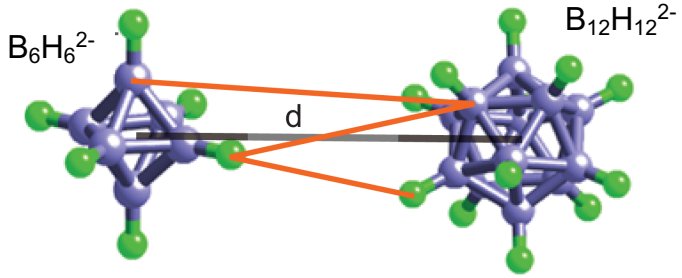
Overcoming the complexity arising from dynamic behavior of a large number of interacting molecules and species.

- *Too many atoms for ab-initio DFT calculations.*
- *Use DFT to develop accurate intermolecular potentials.*
- *Then, use MD to predict phase interaction energies.*

DFT derived potentials

- Predict interaction energies between reactants and newly formed products
- The MD simulations capture the molecular nature of the solids involved
- In molecular dynamics simulations, species are distinguished by combination of molecules and atoms, not just atoms

Capture molecular and ionic forces



⇒ The objective is to develop accurate phase energetics and pathways to predict the thermodynamics and kinetics of multicomponent hydrogen storage reactions.

Accomplishments: 2.A Metal hydride thermodynamics

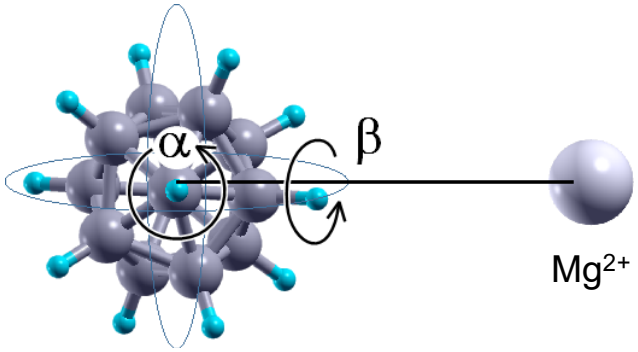
Force field modeling of relevant borohydride species

Initial stage of hydrogen desorption:

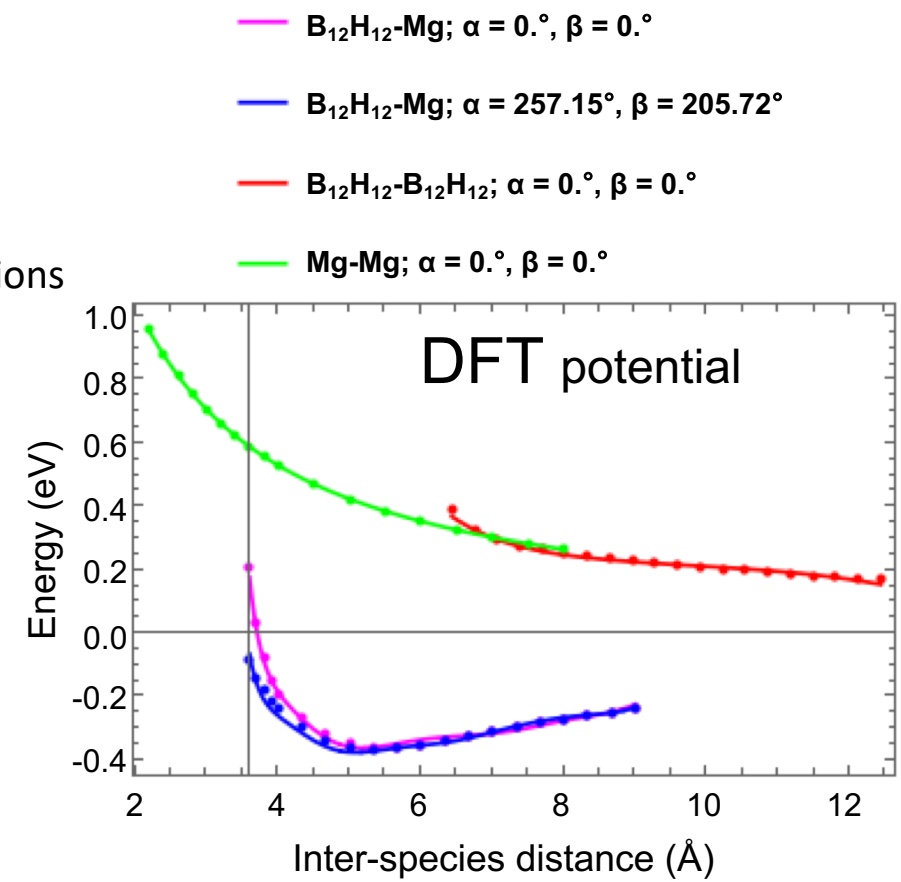
$$6Mg(BH_4)_2 \rightarrow 5MgH_2 + MgB_{12}H_{12} + 13H_2$$

- ✓ Completed DFT training sets on relevant species: **H_2, Mg^{2+}, MgH_2, BH_4^-, $B_{12}H_{12}^{2-}$** (> 700 cases)
- ✓ Completed force field parameterization software
- ✓ Fitted Mg-Mg, Mg-H_2, H_2-H_2 ,Mg-MgH_2, MgH_2-MgH_2, Mg-BH_4, BH_4-BH_4, Mg-$B_{12}H_{12}$, $B_{12}H_{12}$-$B_{12}H_{12}$, interactions

Rotation-dependent molecular interactions



α,β: multiples of π/7.

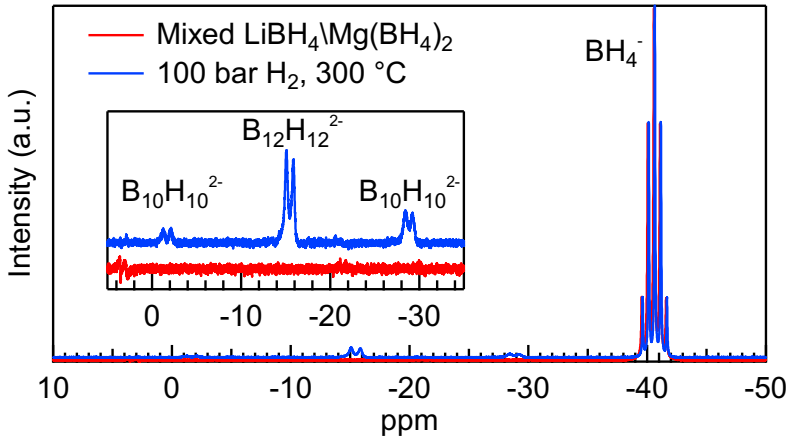


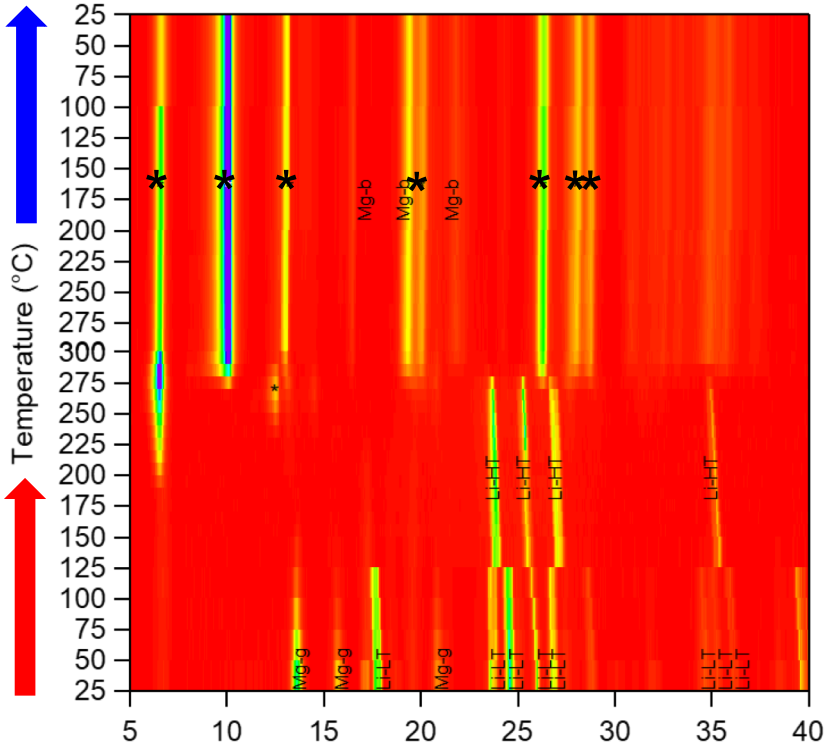
⇒ The predicted DFT potentials will allow MD simulations of the thermodynamics and kinetics of multicomponent boron-based hydrogen storage materials.

Accomplishments: 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
- VTXRD at 10 bar H_2 reveals a new phase in both 3:1 and 1:3 (Li:Mg) mixtures
- ^{11}B NMR results show that stable intermediates $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ form in $LiBH_4$-$Mg(BH_4)_2$ eutectics even under 100 bar H_2 backpressure

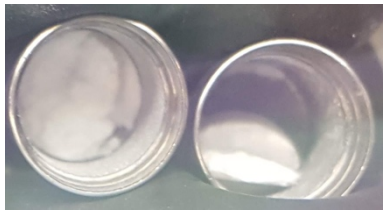




* New Li-Mg-BH_4 phase
$LiBH_4$-orthorhombic (Li-LT) $LiBH_4$-hexagonal (Li-HT)
γ-$Mg(BH_4)_2$ (Mg-g) β-$Mg(BH_4)_2$ (Mg-b)

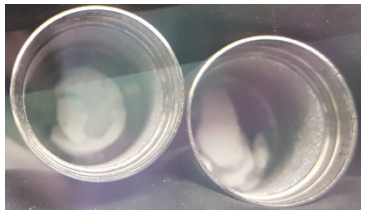
⇒ Created an unexpected new crystal phase under the conditions thought to generate a Li-Mg borohydride eutectic.

1000 bar, 200 °C



3:1 1:3

1000 bar, 250 °C

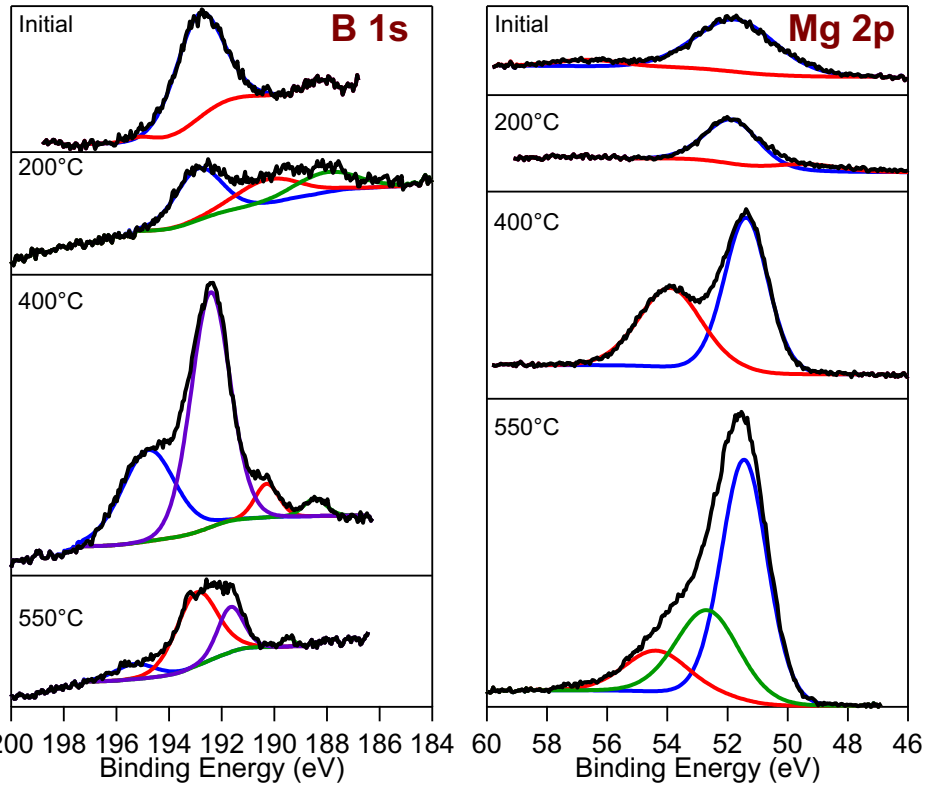


3:1 1:3

Accomplishments: 2.B Solid Interfaces and Surfaces

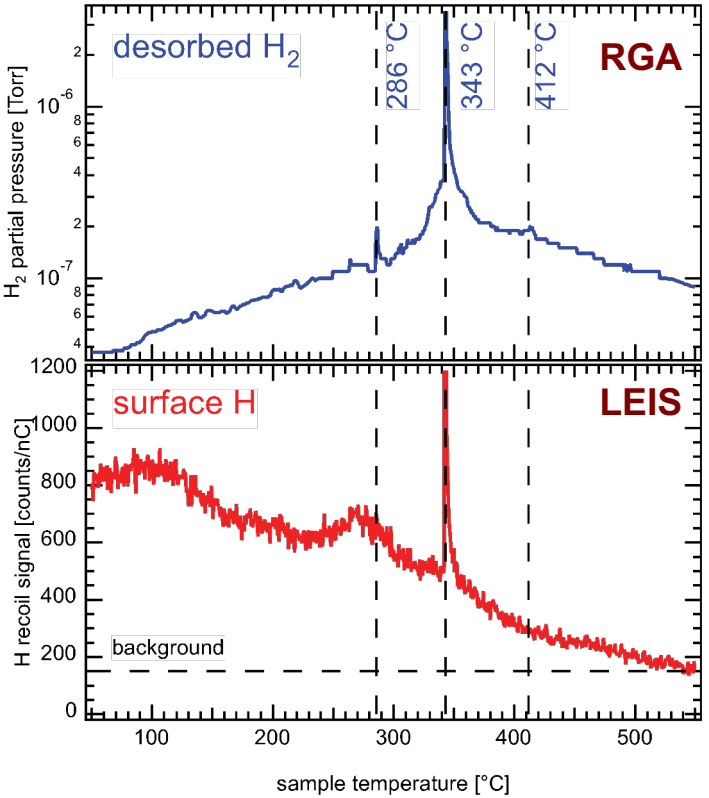
In situ surface characterization of $Mg(BH_4)_2$

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

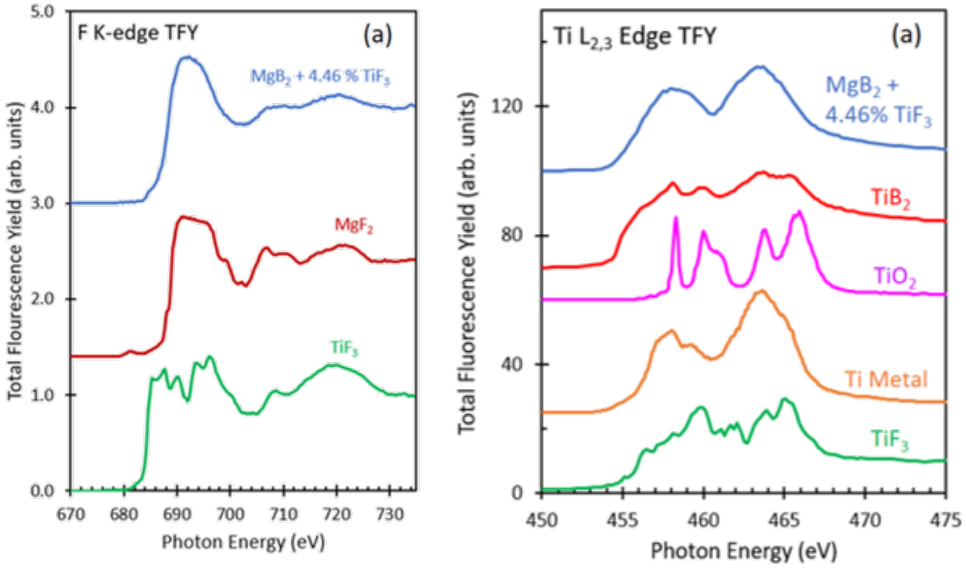
⇒ Demonstrated that XPS, LEIS, and RGA can track hydrogen transport to the surface and subsequent desorption during $Mg(BH_4)_2$ dehydrogenation reaction

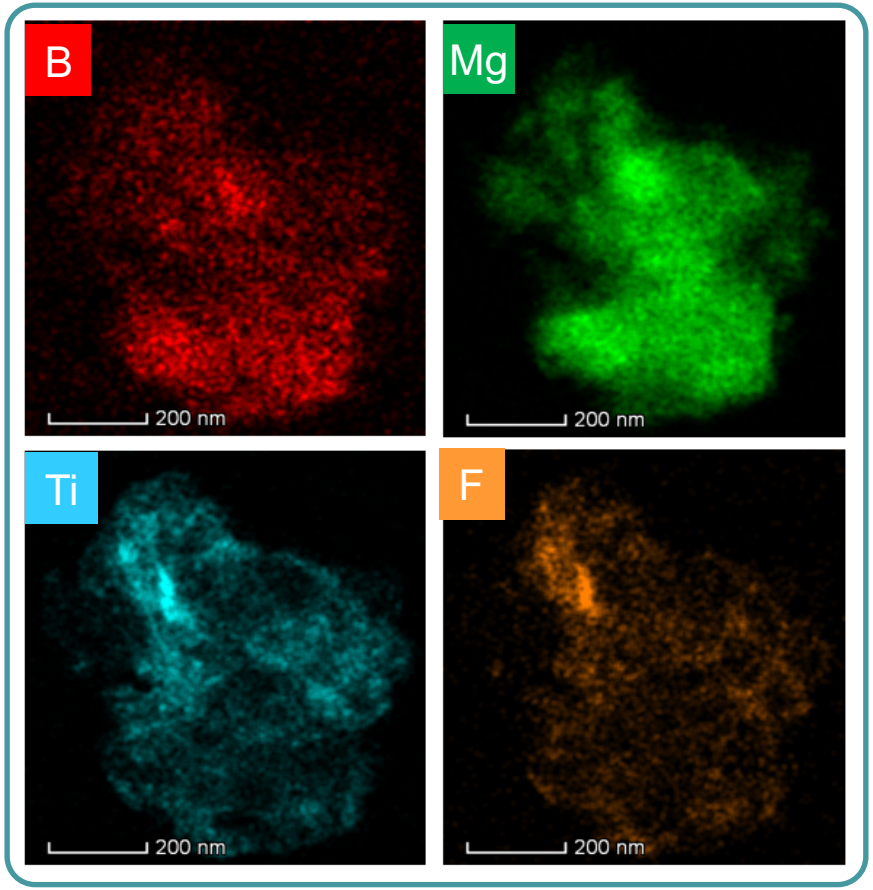
Accomplishments: 2.C Activation of bonds in hydrides

Combining XAS and TEM to understand additive reactions

TiF_3 is a promising additive for metal borohydrides, yet its role in hydrogenation of MgB_2 is unknown. We found that in the ≈5mol%TiF_3/MgB_2 additive system TiF_3 fully reacts with MgB_2:

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





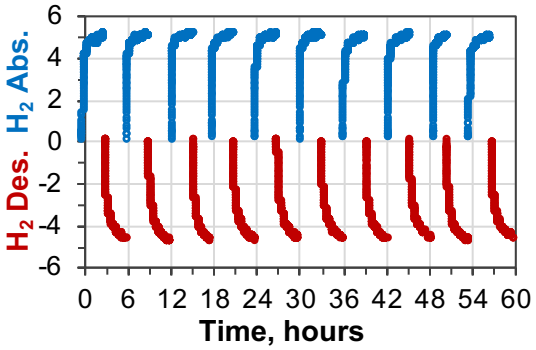
⇒ XAS reveals the formation of MgF_2 and metallic Ti with no evidence of titanium boride.

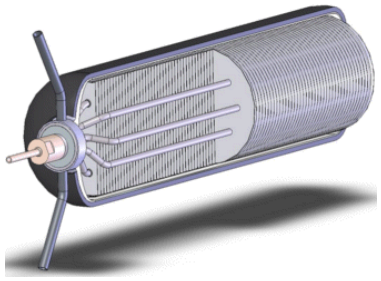
⇒ TEM shows that Ti and F are spread throughout the MgB_2 material. The fluorine is generally spatially associated with the titanium species.

Accomplishments: 2.D Nanoscale Metal Hydrides

Engineering requirements for nanoscale hydrides

Design Parameters	Ti-$NaAlH_4$	bulk-Li_3N	KH-6nm-Li_3N
Reversible capacity. wt%	4.5	8.2	**5.4**
Thermal cond., W m^{-1} K^{-1}	9.0	1.0	**9.6**
Density of hydride bed, kg m^{-3}	720	710	**760**
Total system mass, kg	329	312	**252**
Total hydride mass, kg	164	112	**116**
Tank outer diameter, m	0.47	0.46	**0.45**
Tank length, m	2.23	2.21	**2.19**
System volume, m^3	0.310	0.256	**0.227**
% 2025 Gravimetric Target	31	33	**40**
% 2025 Volumetric Target	45	55	**62**

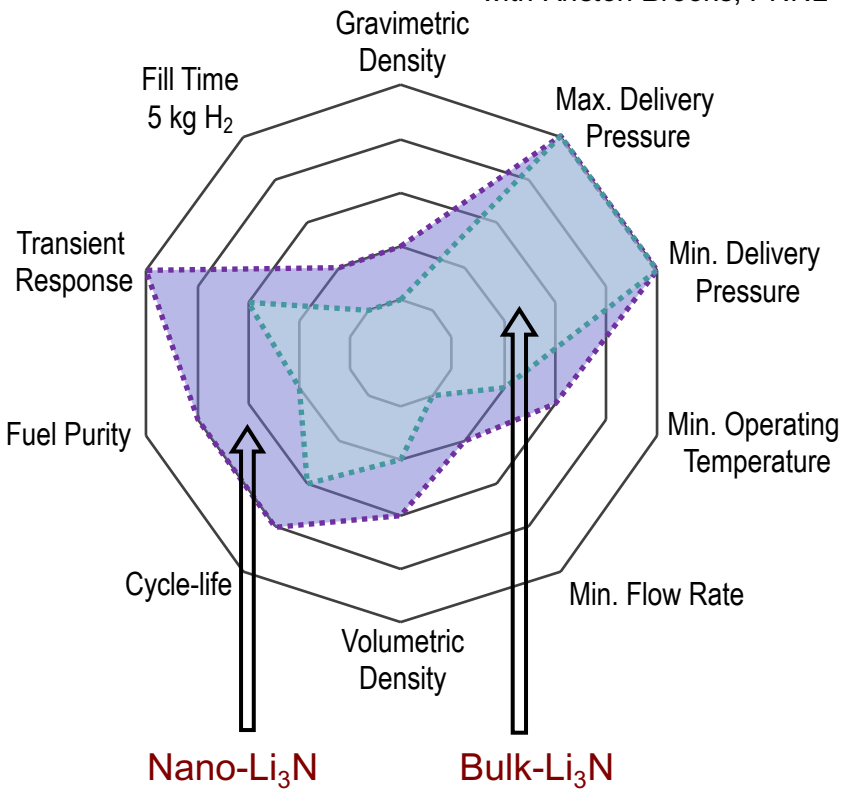




MHFE-SAH tank design

MHFE model on Li_3N@6nm-Carbon

with Kriston Brooks, PNNL

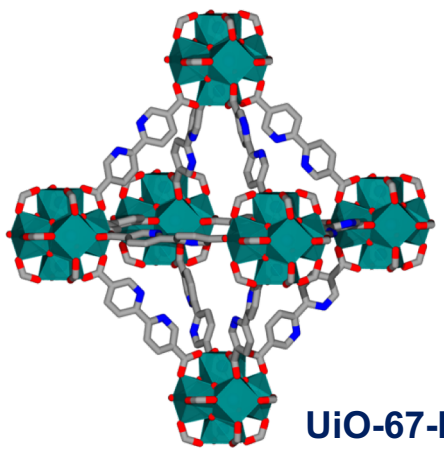


For additional details, see ST128a

⇒ Used HSCOE Metal Hydride Finite Element model to reveal non-intuitive tradeoffs and benefits of using nanoscale metal hydrides in an operational H_2 storage tank

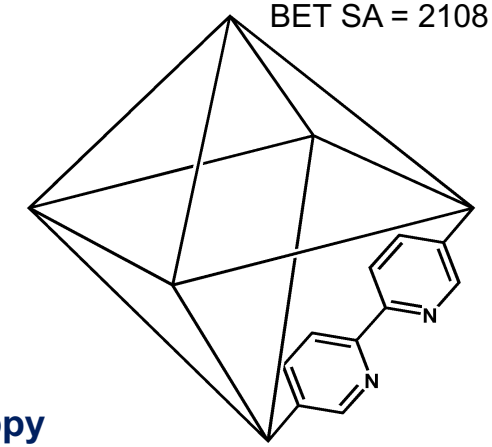
Accomplishments: 2.D Nanoscale Metal Hydrides

Molecularly dispersed $Mg(BH_4)_2$ species



UiO-67-bpy

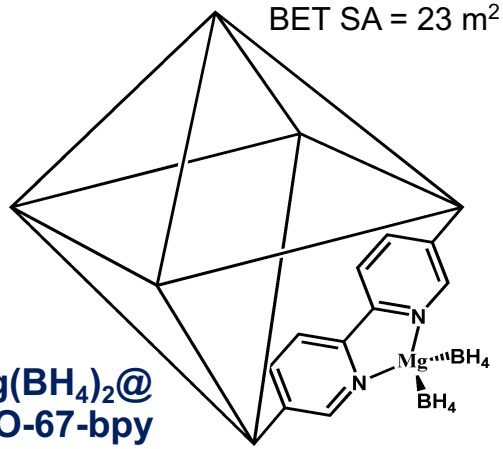
BET SA = 2108 m^2 g^{-1}



$Mg(BH_4)_2$

$(CH_3)_2S$

BET SA = 23 m^2 g^{-1}

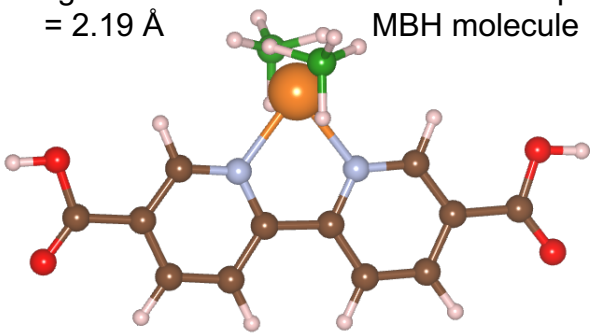


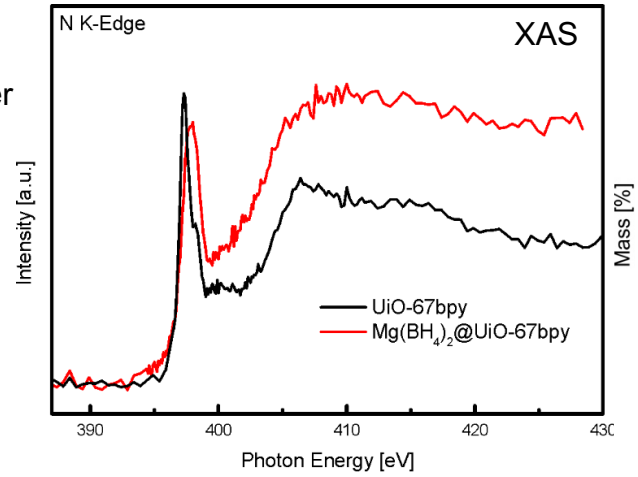
$Mg(BH_4)_2$@ UiO-67-bpy

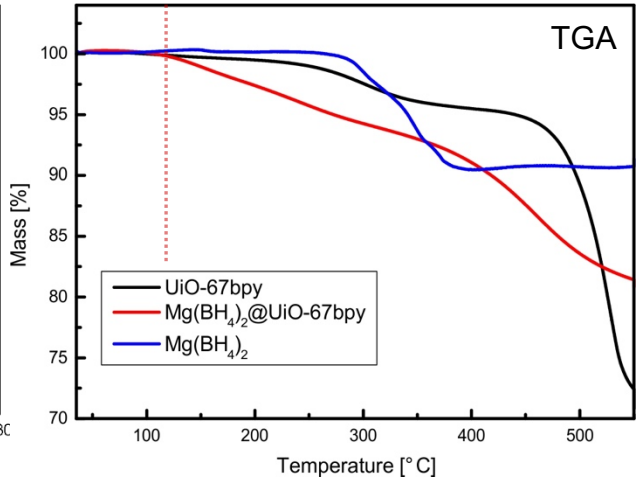
DFT *cis*-bpy/$Mg(BH_4)_2$

Mg-N dist. = 2.19 Å

ΔE = -1.54 eV per MBH molecule





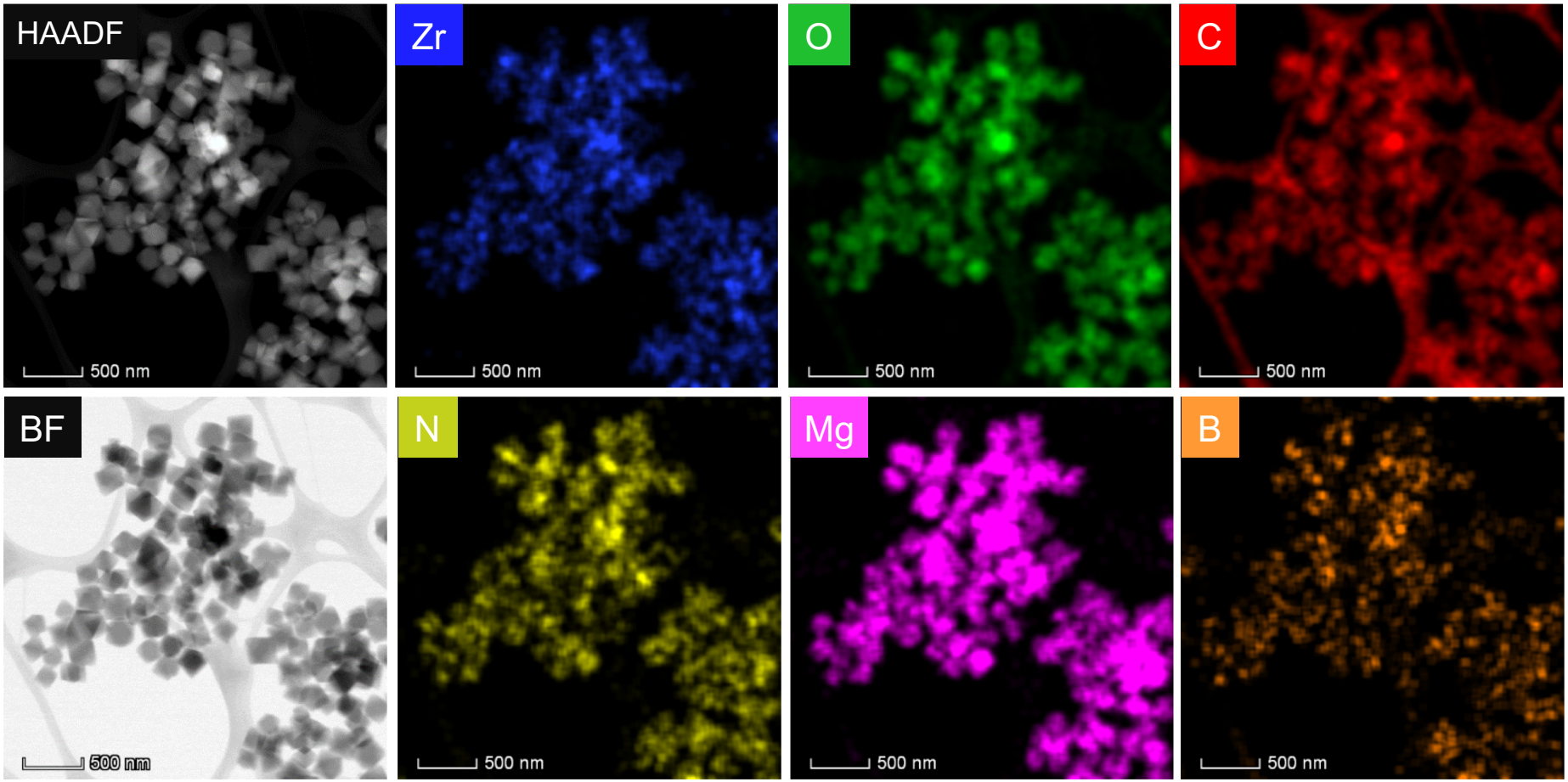


⇒ XAS measurements and computational spectroscopy reveal that $Mg(BH_4)_2$@UiO-67-bpy is composed of molecular $Mg(BH_4)_2$ species coordinated to bipyridine groups

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

Accomplishments: 2.D Nanoscale Metal Hydrides

Aberration–corrected TEM on $Mg(BH_4)_2$@UiO-67bpy

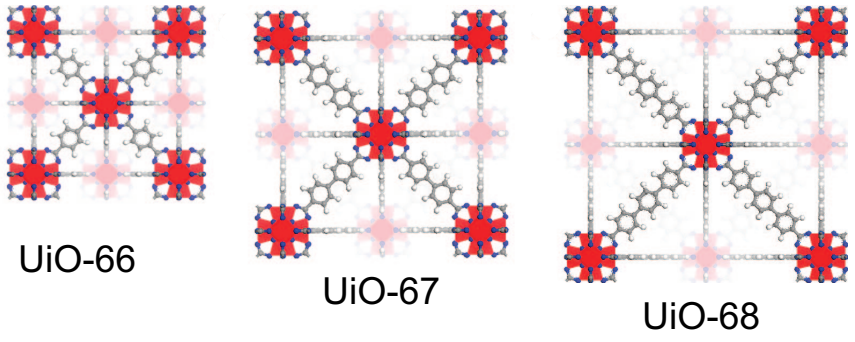


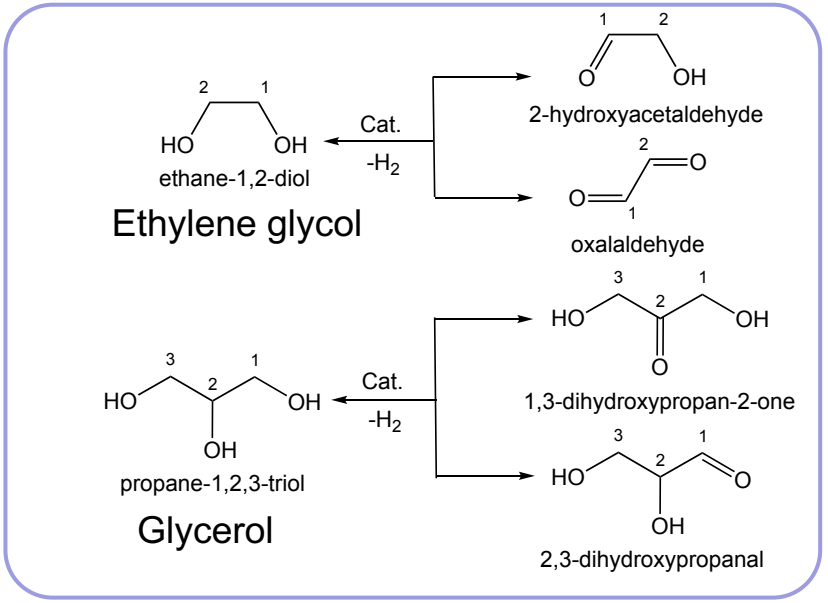
⇒ Aberration-corrected TEM/EDS measurements (Titan AC-STEM) reveal that both Mg and B atoms are homogeneously distributed within the UiO-67-bpy crystals, suggesting $Mg(BH_4)_2$ exists as molecular species within the MOF pores

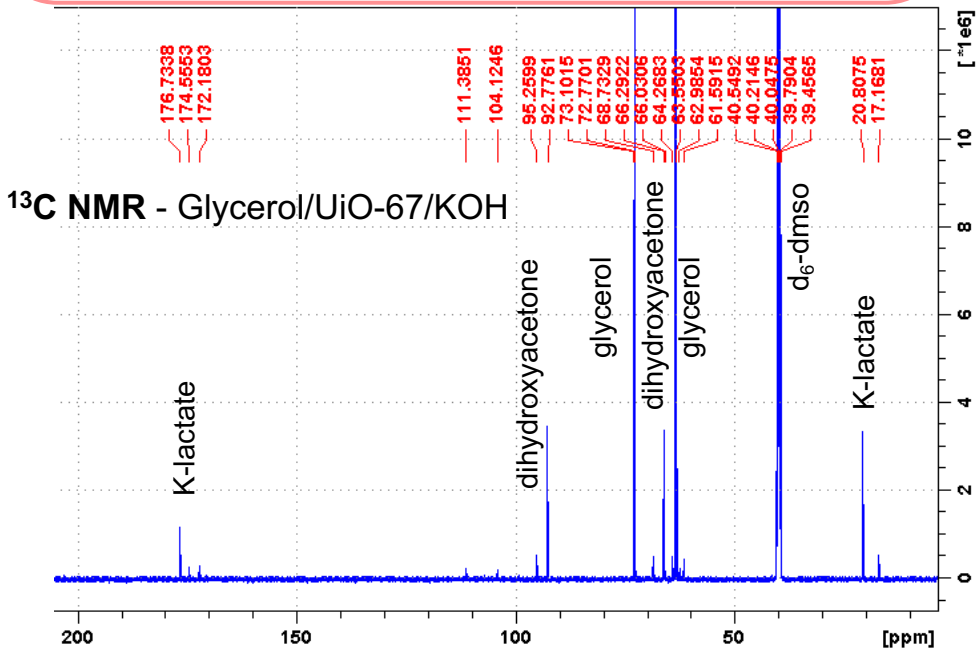
Accomplishments: 3.B Aqueous organic carriers

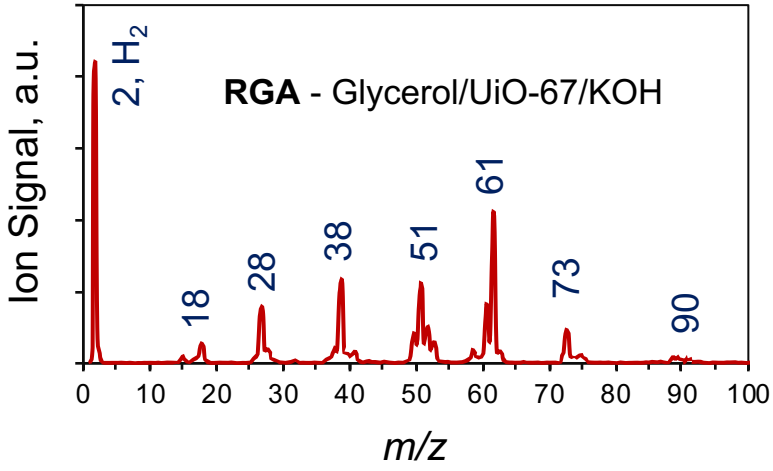
Catalytic H_2 production from polyalcohols

Catalytic MOFs stable under H_2O and H_2







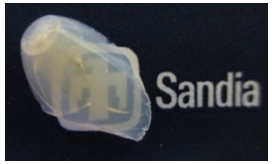


⇒ Demonstrated MOF-catalyzed hydrogen production from ethylene glycol and glycerol.

Summary and Conclusions

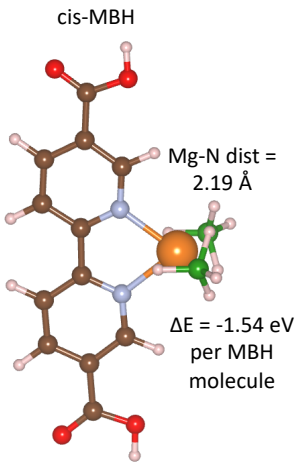
Sorbents

- Developed synthetic routes to monoliths of several Zr-based MOFs, including UiO-66-1,4-NDC, UiO-67, and NU-1000.
- Demonstrated a ≈55% higher volumetric hydrogen uptake in UiO-67 monolith compared to the powder version of this material.



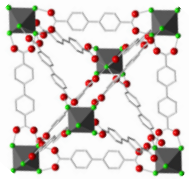
Metal Hydrides

- Established a molecular dynamics modeling framework to provide the fundamental basis for theory predictions of energetics and kinetics 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 react with MgB_2 and how the B-B bonding is disrupted.
- Used HSECoE models to determine the benefits of using nanoconfined metal hydrides (*e.g.* nano-Li_3N) in an operational hydrogen storage tank.
- First synthesis of molecularly dispersed $Mg(BH_4)_2$ within the pores of a non-innocent functionalized MOF.



Hydrogen Carriers

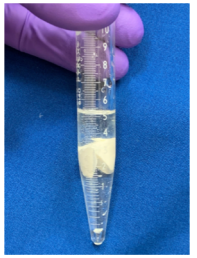
- Demonstrated a catalytic acceleration of hydrogen production from polyols.



Future Work

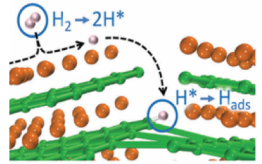
Sorbents

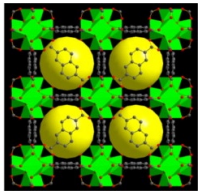
- Establish new methods for powder compaction, including MOF gel and monolith formation
- Probe the effect of structural defects on H_2 storage properties of MOFs.



Hydrides

- Activation of B-B and B-H bonds: *Test the performance of additives predicted by theory to be efficient in activating B-B and B-H bonds*.
- Investigate hydrogen storage properties of molecularly dispersed $Mg(BH_4)_2$ and expand the methodology to other complex metal hydrides
- Reversible capacity (milestone): Demonstrate >6% reversible capacity for at least one Li-N-H or Mg-N-H phase, based on predicted composition from phase diagram, with reasonable kinetics at a temperature of ≤ 300 ˚C.



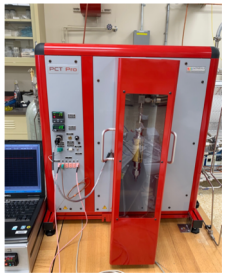


Carriers

- Carrier material approaches: Establish catalytic processes for reversible hydrogen generation from alcohols and polyols.

Advanced characterization

- Test and validate newly installed PCTPro system at Sandia for temperatures of up to 450 ˚C and pressures of up to 100 bar H_2.



Seedling interactions

- Provide support to current and future HyMARC seedling projects.

Acknowledgements

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

HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for hydrogen 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

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under Contract No. DE-NA-0003525.

Technical Back-Up Slides

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

- **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

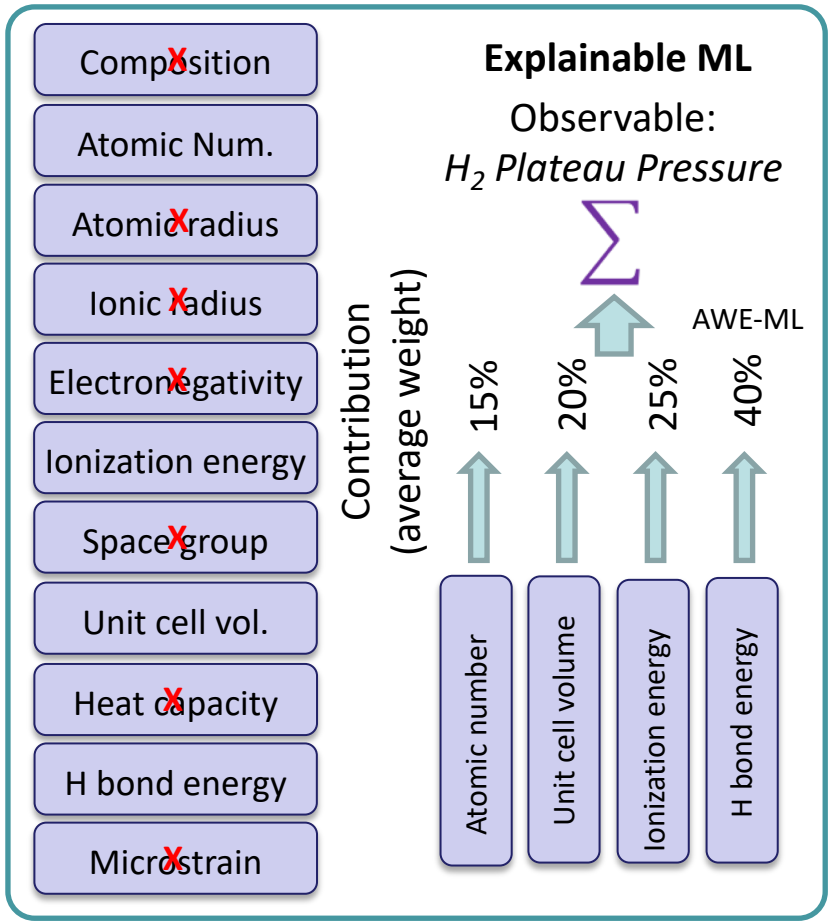
FIZ Karlsruhe ICSD

ASM INTERNATIONAL
ASM Alloy Phase Diagram Database

FactSage

Thermophysical Properties of Matter Database

Explainable Machine Learning Framework

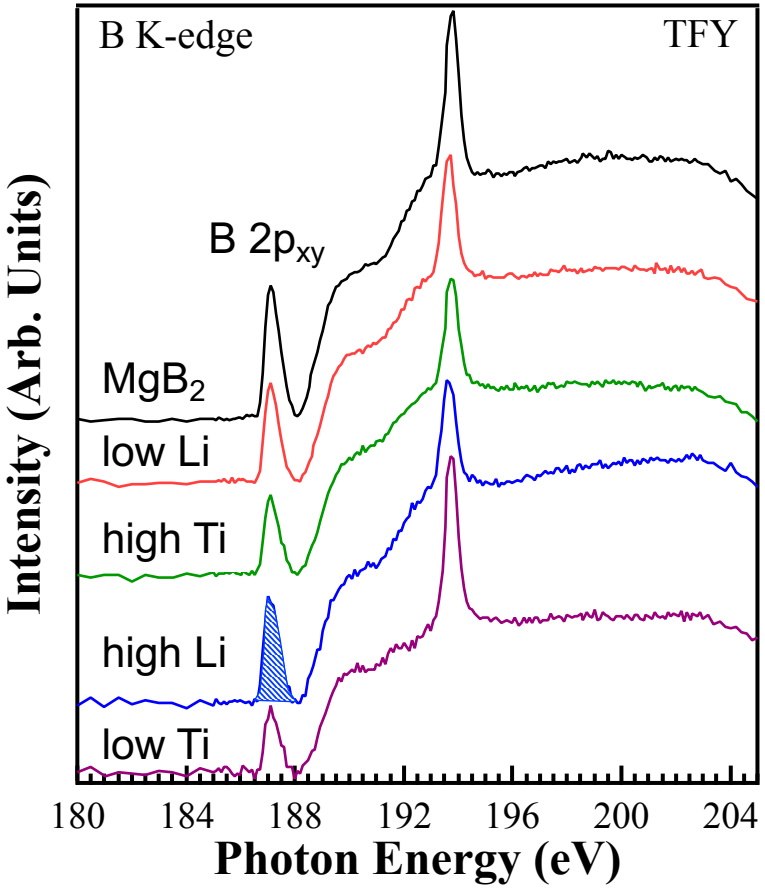


Accomplishments: 2.C Activation of bonds in hydrides

Does disrupting the B-B ring promote MgB_2 hydrogenation?

We previously showed that H-H bond breaking does not limit the rate of MgB_2 hydrogenation. New evidence suggests that it is necessary to disrupt B-B ring in MgB_2 to achieve faster hydrogenation.

"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

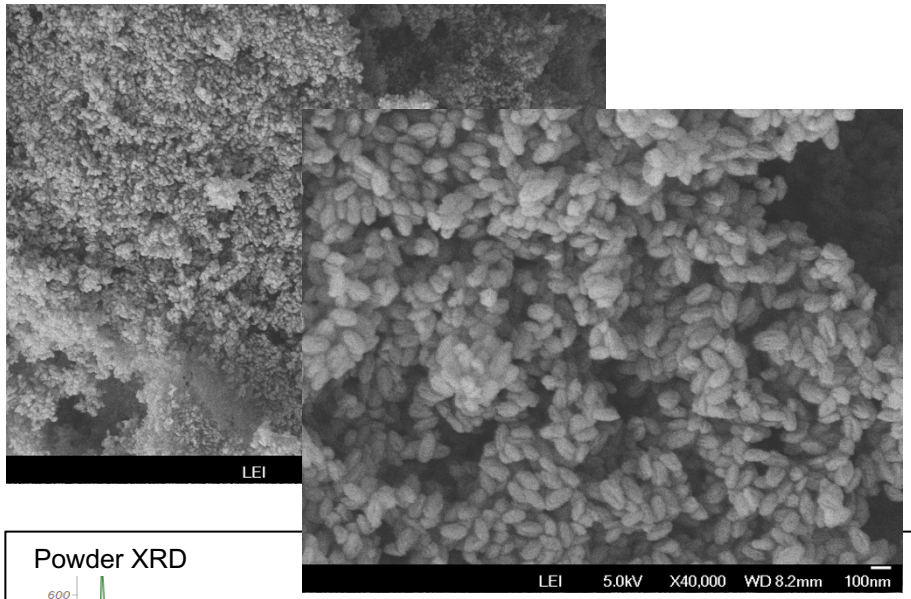
Both Li and Ti additives reduce the B-B ring signal, but Ti disrupts it more, as predicted by LLNL theory.

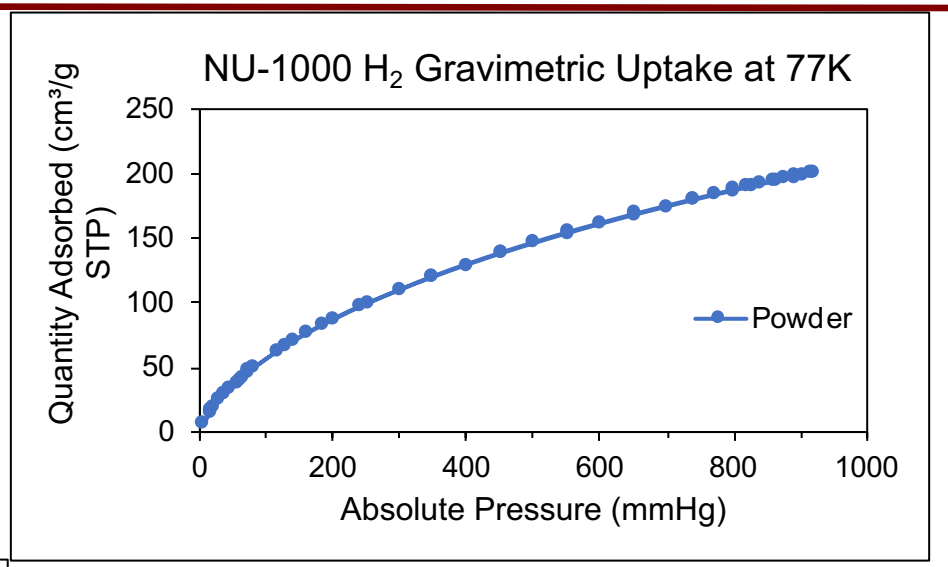
Next Steps: Sieverts H_2 uptake measurements to see if B-B bond disruption leads to faster hydrogenation of the MgB_2 sample.

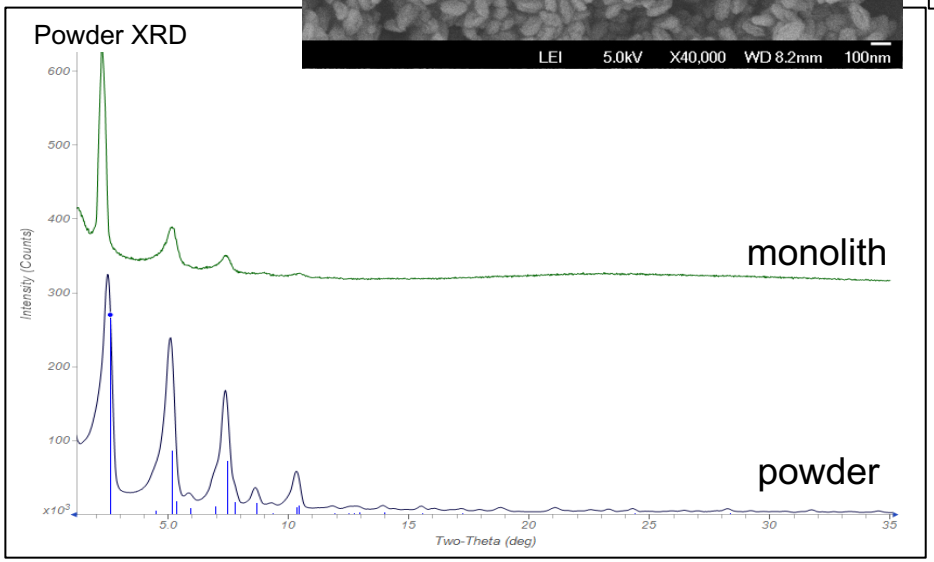
⇒ Our data indicate that the B-B ring structure can be disrupted through the use of additives, possibly promoting hydrogenation of MgB_2 to magnesium borohydride.

Accomplishments: 1.C. Optimizing sorbent packing

Synthesis of NU-1000 monoliths

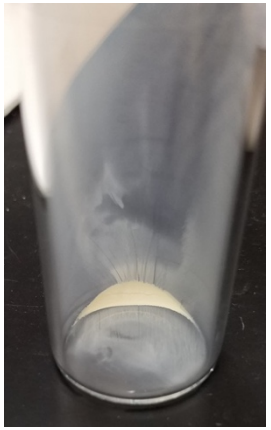






Scale-up effort underway

powder



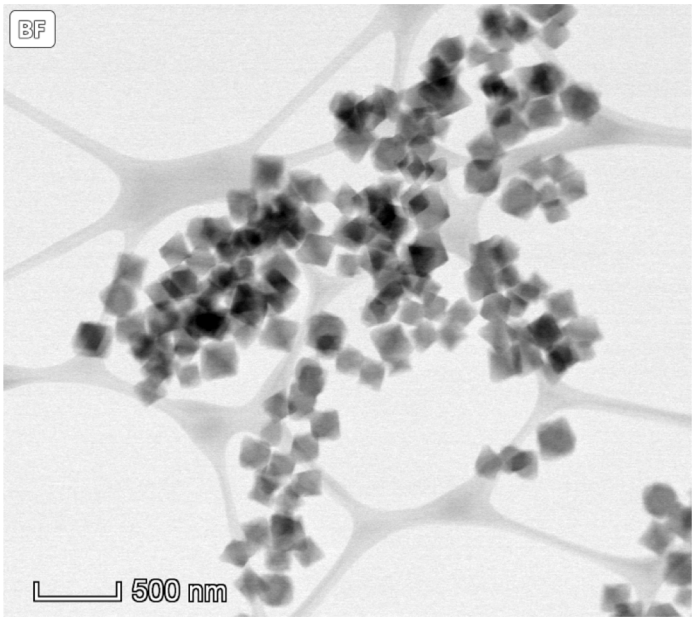
monolith

⇒ Successfully synthesized NU-1000 monolith composed of 100-200 nm particles

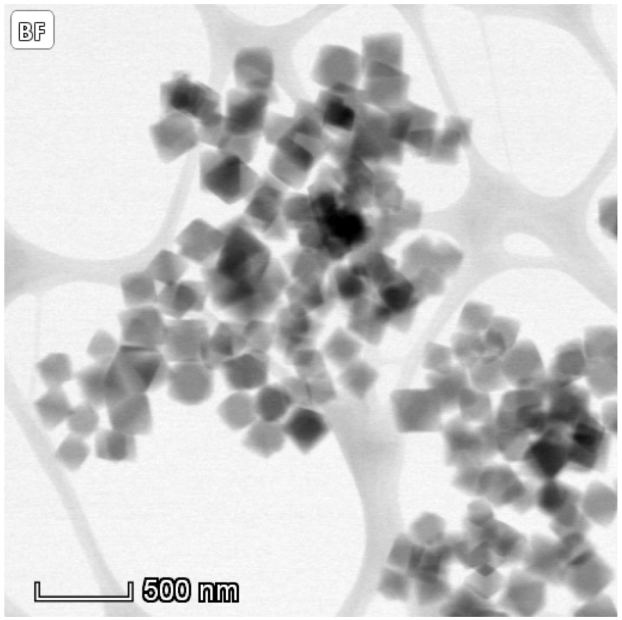
Accomplishments: 2.D Nanoscale Metal Hydrides

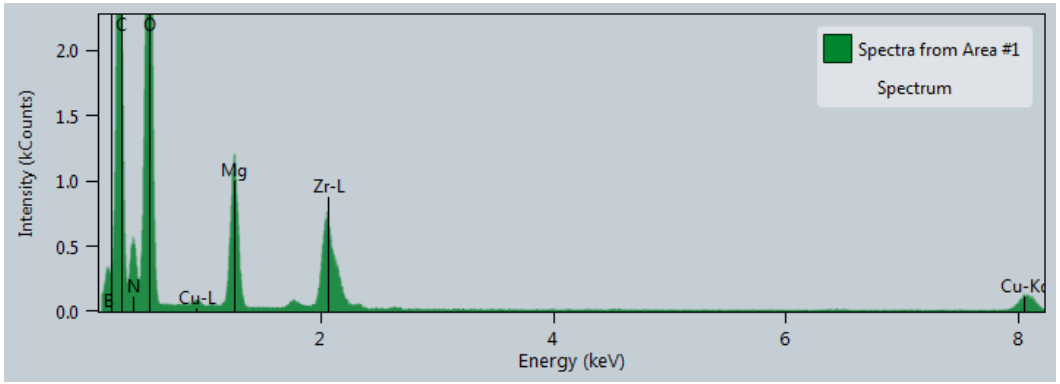
TEM/EDS on nanoconfined $Mg(BH_4)_2$@UiO-67bpy

UiO-67bpy (before)



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





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

Accomplishments: 2.D Nanoscale Metal Hydrides

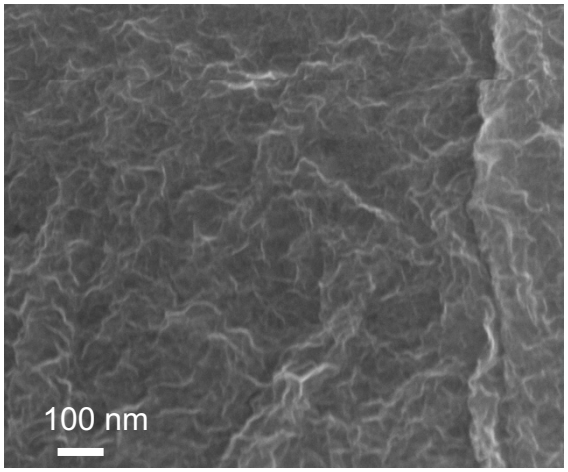
$Mg(BH_4)_2$ nanoconfinement in porous hosts

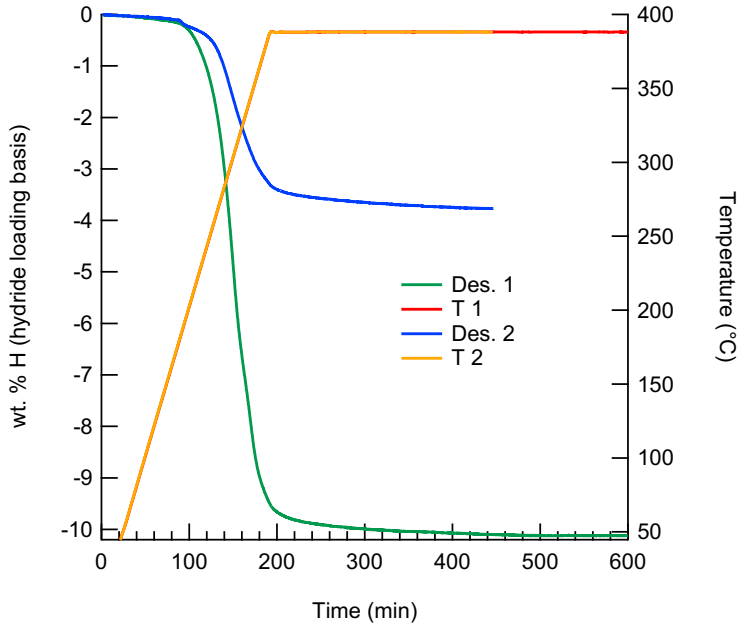
- $Mg(BH_4)_2$ found to melt stably (without decomposition) at ~367 °C with high H_2 backpressures (>350 bar)

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 Graphene Aerogel





Accomplishments: 1.B. Sorbent binding energies

MOF stability under high-pressure hydrogen

MOF	Metal Ion	Initial BET S.A. (m^2/g)	Initial pore volume (cm^3/g)	Post-testing pore volume (% change)	
				0.5 to 10 MPa H_2, 1000 cycles	70 MPa H_2, 1 cycle
MOF-5	Zn(II)	3320	1.387	1.388 (0%)	1.385 (0%)
MOF-177	Zn(II)	4490	1.958	1.954 (0%)	1.912(-2%)
HKUST-1	Cu(II)	1700	0.712	0.697 (-2%)	0.712 (0%)
NOTT-100	Cu(II)	1250	0.609	0.574 (-6%)	0.603(-1%)
Mg-IRMOF-74-I	Mg(II)	1430	0.573	0.570 (0%)	0.583(+2%)
Mg-IRMOF-74-II	Mg(II)	2280	1.027	0.910 (-11%)	1.044(+2%)
Ni_2(m-dobdc)	Ni(II)	1090	0.542	0.527 (-3%)	0.531(-2%)
Ni-IRMOF-74-I	Ni(II)	1200	0.510	0.430 (-16%)	0.462 (-10%)
Ni-IRMOF-74-II	Ni(II)	1520	0.651	0.640 (-2%)	Not tested
Ni-IRMOF-74-III	Ni(II)	1925	0.924	0.927 (0%)	Not tested
Ni-IRMOF-74-IV	Ni(II)	1460	0.956	0.997 (+4%)	Not tested
Ni-IRMOF-74-V	Ni(II)	1505	1.195	1.217 (+2%)	Not tested

⇒ Stability of a wide range of MOFs under hydrogen was tested; results confirm that most MOFs are stable under both 5 to 100 bar H_2 cycling conditions and under 700 bar H_2

Reviewer-Only Slides

Collaboration and Coordination

- T. Udovic and C. Brown (NIST): neutron diffraction/spectroscopy
  - *Exchanged 8 samples for neutron diffraction and NVS studies*
- M. Toney, K. Stone, N. Strange (SLAC): synchrotron XRD and SAXS
  - *Measured XRD and SAXS for 15 samples of bulk and nanoscale metal hydrides*
- T. Autrey and M. Bowden (PNNL): NMR on metal borohydrides and intermediates
- K. Hurst, P. Parilla and T. Gennett (NREL): Validation of MOF H_2 adsorption isotherms
- Timmy Ramirez and David Cullen (ORNL): inelastic neutron scattering, neutron diffraction
- Stephen FitzGerald (Oberlin College): hydrogen binding in MOFs
- Viktor Balema, Vitalij Pecharskij (AMES Lab): metal hydrides, mechanochemistry
- Dhanesh Chandra (University of Nevada, Reno): CALPHAD calculations and phase diagrams
- Martin Dornheim (Helmholtz-Zentrum Hamburg, Germany): high-pressure calorimetry
- Torben Jensen (Aarhus University, Denmark): reversibility aspects of metal hydrides
- Shin-ichi Orimo (Tohoku University, Japan): transport in metal *closo*-borates
- Ping Chen (Dalian University, China): characterization of ternary metal amides
- Stefan Kaskel (Technische Universität Dresden, Germany): high-surface area MOFs
- David Fairen-Jimenez (University of Cambridge, UK): synthesis of MOF monoliths
- Hexiang Deng (Wuhan University, China): MOF stability under hydrogen
- Eun Seon Cho (KAIST, South Korea): strain-induced destabilization of metal hydrides

Publications and Presentations

Patents:

1. V. Stavila, L.E. Klebanoff, "Nanostructured Metal Amides and Nitrides for Hydrogen Storage" US Patent #10000377 granted on 06/19/2018.
2. V. Stavila, J.L. White, "Solid state synthesis of metal borohydrides", US Patent Application #16/000,683 filed on 08/05/2018.

Selected Papers (*from a total of 15 papers co-authored by the Sandia team over the past 12 months*)**:**

1. Schneemann, A.; White, J.L.; *et al*. "Nanostructured Metal Hydrides for Hydrogen Storage." *Chemical Reviews*, **2018**, *118*, 10775-10839. (*cover article*).
2. Allendorf, M.D.; *et al*. "An assessment of strategies for the development of solid-state adsorbents for vehicular hydrogen storage", *Energy Environ. Sci*., **2018**, *11*, 2784-2812. (*hot article*).
3. White, J.L.; *et al.* "Promotion of Dehydrogenation of Ti-Doped $NaAlH_4$ by Dynamic Surface Hydroxides." *ACS Appl. Mater. Interfaces.*, **2019**, *11*, 4930-4941.
4. Jensen, S.; *et al*. "Hydrogenation properties of lithium and sodium hydride – *closo*-borate, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$, composites." *Phys. Chem. Chem. Phys.*, **2018**, *20*, 16266-16275 (*jointly with Aarhus U., Denmark*).
5. Carr, C.; *et al*. "Anomalous H_2 Desorption Rate of $NaAlH_4$ Confined in Nitrogen-Doped Nanoporous Carbon Frameworks." *Chem. Mater.*, **2018**, *30*, 2930-2938. (*collaboration with Seedling project*).
6. Vajo, J.J.; *et al*. "Electrolyte-Assisted Hydrogen Storage Reactions." *J. Phys. Chem. C*, **2018**, *122*, 26845. (*collaboration with Seedling project*).
7. Liu, Y. -S.; *et al*. "In-situ/operando X-ray characterization of metal hydrides," accepted for publication in *ChemPhysChem,* Feb. 7, **2019**. DOI:10.1002/cphc.201801185R1.
8. Zhou, X. W.; *et al*. "An Analytical Bond Order Potential for Mg-H Systems," accepted for publication in *ChemPhysChem* Jan. 12, **2019**, DOI:10.1002/cphc.201800991R1.

Presentations:

14 presentations (1 keynote and 6 invited) at national and International conferences and symposia.

Sandia has led two major publications on *sorbent improvement 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" (Hot Article)

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 2010 HSCoE final report
- Perspectives on current material strategies

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

"Nanostructured Metal Hydrides for Hydrogen Storage" (Journal Cover)

Topics include:

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

Critical Assumptions and Issues

- **Assume that theory is sufficiently validated to allow *de novo* predictions of additive promotion of hydrogen storage reactions**
  - *Will further test and validate the theory in the additive space by performing hydrogen uptake and release experiments for promising additives*
- **Assume that the models for predicting phase diagrams for model metal borohydrides will be transferable other borohydride-based systems**
  - *Will perform DFT and ab initio MD computations to correlate the results*
  - *Will perform experiments to validate theory models*
- **Capability of monitoring the surfaces and interfaces *in situ* during hydrogen release and absorption**
  - *Multiple characterization techniques (spectroscopy, scattering, electron microscopy) will be used to correlate the results and determine mechanisms and hydrogen diffusion pathways*

Data Management Plan

- **All unrestricted data will be preserved long-term on HyMARC Data Hub (datahub.hymarc.org)**
  - *Archivable experimental characterization data will include reference NMR, XAS/XES, XRD, FTIR, NVS*
  - *Archivable experimental testing data will include Sieverts isotherm and PCT data*
  - *Computational data will include reference free energies of bulk compounds, surface energies, elastic tensors, and vacancy formation energies*
  - *Also plan to archive raw ab initio molecular dynamics trajectory data*
  - *Data hub has password-protected data sandboxing for public access or for private internal (HyMARC-only) access*
  - *Data hosted physically on NREL server*
  - *Partner data will be restricted to HyMARC team access prior to publication*
- **Publications are uploaded to OSTI archive with digitally accessible link**

Responses to Reviewer Comments

- **Do the conclusions for the surface oxidation of $NaAlH_4$ necessarily extend to other complex metal hydrides (for example $Mg(BH_4)_2$)?**
  - *The generality of the conclusion that surface oxidation promotes hydrogen desorption, as seen in $NaAlH_4$, is currently under investigation. We have observed surface oxides and hydroxides in the $Mg(BH_4)/MgB_2$ system, and are currently exploring their roles.*
- **There should be a focus on multicomponent composite systems with high capacities.**
  - *In Phase 2 of HyMARC, we initiated a new direction to explore multicomponent materials, including mixed metal borohydrides, borohydride-amide materials, and multicomponent eutectics, in collaboration with the HRL/Liox seedling project.*
- **The research team needs to include a pipeline for materials that is more likely to achieve technical targets.**
  - *HyMARC probes the fundamental limitations to hydrogen storage materials, but we do so with high-capacity families of materials, such as MOFs with open metal sites, metal borohydrides, metal amides, etc. We also assist the seedling projects who are focused on specific high—capacity materials with prospects for meeting the technical targets.*
- **The project needs to develop a list of priorities and provide a strong technical rationale for ranking of such priorities.**
  - *The priorities for Phase 2 of HyMARC have been developed as a result of guidance from DOE, TechTeam and AMR Reviews. Those priorities, as reflected in the Phase 2 Focus Areas, address the most important materials problems inhibiting H_2 storage materials performance.*