HyMARC: A Consortium for Advancing Hydrogen Storage Materials

HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

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

COVID-19 Pandemic halted all work in February 2020. Milestones to be evaluated after re-opening.

NREL NATIONAL RENEWABLE ENERGY LABORATORY · Sandia National Laboratories · Lawrence Livermore National Laboratory · BERKELEY LAB · ALS ADVANCED LIGHT SOURCE · MOLECULAR FOUNDRY · Pacific Northwest NATIONAL LABORATORY · NIST · SLAC NATIONAL ACCELERATOR LABORATORY





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Project ID #: ST127

Overview

Timeline*

Phase 1: 10/1/2015 to 9/30/2018
Phase 2: 10/1/2018 to 9/30/2022
Project continuation determined annually by DOE.
(*previously a component of NREL's materials development program and supported annually since 2006)

Budget

DOE Budget (Entire HyMARC Team)
Total FY19: $4.3M
Total FY20 (Planned): $6.25M

SNL: $1.15M
NREL: $1.5M (covers NIST and SLAC)
PNNL: $1.1M
LLNL: $0.9M
LBNL (Long): $1.1M
LBNL (Prendergast) $0.5M

Barriers addressed

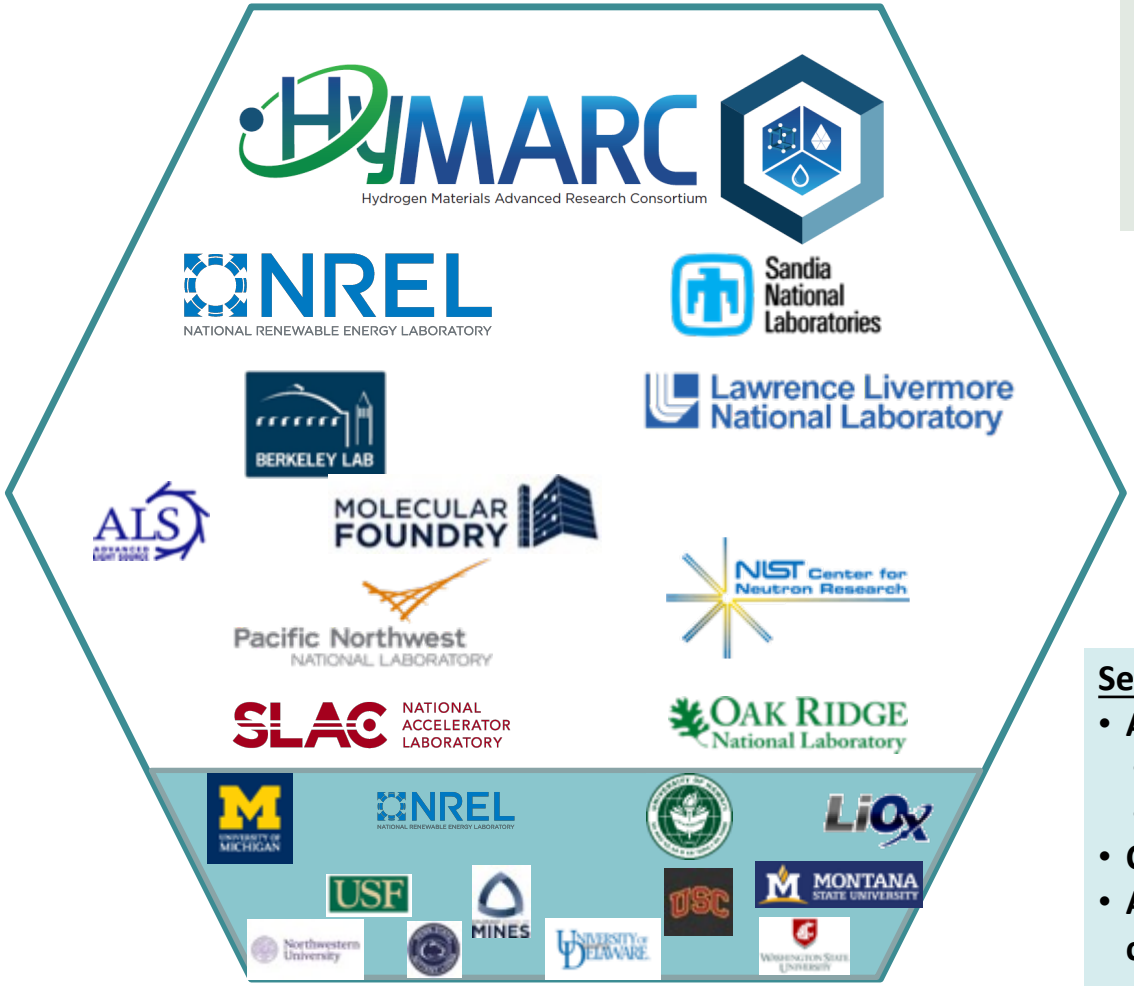
General:
A. Cost, B. Weight and Volume, C. Efficiency,
E. Refueling Time
Reversible Solid-State Material:
M. Hydrogen Capacity and Reversibility
N. Understanding of Hydrogen Physi- and Chemisorption
O. Test Protocols and Evaluation Facilities

Partners/Collaborators

NIST – Craig Brown, SLAC – Michael Toney
HyMARC – SNL, LLNL, LBNL, PNNL team members
H_2ST^2, USA – Hydrogen Storage Tech Team
Colorado School of Mines - Colin Wolden, Brian Trewyn,
Univ. Hawaii – Craig Jensen, Godwin Severa
Université de Genève – Hans-Rudolf Hagemann, Angelina Gigante

HyMARC Energy Materials Network: enhanced, highly coordinated capabilities to accelerate materials discovery

Enabling twice the energy density for hydrogen storage



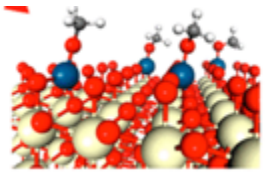
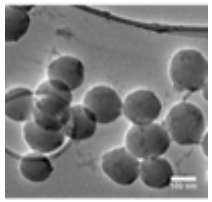
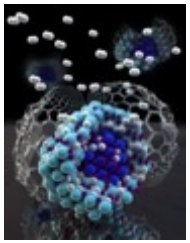
- **Foundational R&D**
- **Computational models**
- **Synthetic protocols**
- **Advanced characterization tools**
- **Validation of material performance**
- **Guidance to FOA projects**
- **Database development**

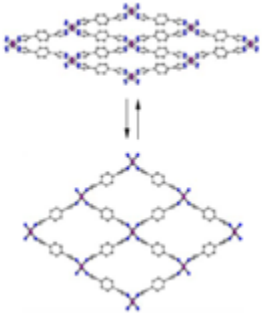
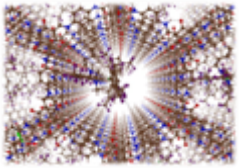
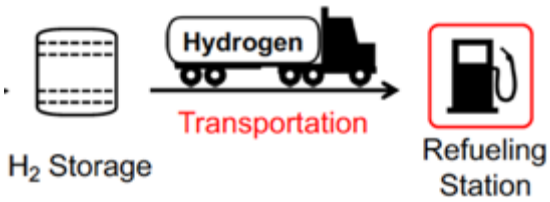
Seedling Projects

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

Organizational Accomplishments HyMARC March 2019—March 2020

- >25 Journal articles published
- HyMARC video for MRS meeting and website
- Numerous invited talks (major international meetings, academic, gov't institutions)
- Major Hydrogen Symposia and workshops organized at major conferences (ACS, MRS, GRC, etc) and for DoE
- Organizational improvements: Face to face meetings, new seedling initiative, kickoff meetings, mentoring, extensive new level of collaboration/cooperation
- > 15 postdocs supported, 8 graduate students
- Global connectivity through extensive network of collaborations
- Multiple awards for PIs, Scientists, Pdocs and Grad students
- Seedling support increased significantly
- COVID-19 Pandemic halted all work in February 2020. Milestones to be evaluated after re-opening.

Tasks with interdisciplinary expertise, focus areas of research

Tom Gennett (NREL)
Co-Director

Mark Allendorf (SNL)
Co-Director

HyMARC

Task 1
Sorbents
Gennett

Task 2
Hydrides
Allendorf

Task 3
Carriers
Autrey

Task 4
Adv. Char.
Parilla
(NREL validation)
Prendergast
(ALS, SLAC, MF)
Bowden
(PNNL NMR)
Brown
(NIST Neutron)
Toney
(SLAC, X-ray)
Rameriez
(ORNL, Vision)

Task 5
Seedling
Support
Allendorf
Gennett
Includes new methane initiative

Task 6
Data Hub
Munch
(NREL)

Focus Areas

Focus Areas

Focus Areas

Focus Areas

Task leads:
Coordinate work
Milestone accounting
Reporting

Focus Areas (new concept):
Multi—lab Research clusters
Defined topic
Dynamic, agile
Duration: as little as 1 year
Applied topics: Go/No-Go
Foundational topics: milestones

User Facility POCs

ALS SLAC NREL NIST EMSL MOLECULAR FOUNDRY OAK RIDGE

How the HyMARC team moved the BAR

- **SORBENTS**
  - New record for room temperature hydrogen adsorption (wt%) in a vanadium based MOF
  - Ability to synthesize monoliths with increased volumetric capacity, both COFs and MOFs
  - Exhibited control of Q_{st} both synthetically and via external stimulus (alter π backbonding)
  - Improved the application of flexible MOFs to hydrogen storage (modeling/synthesis successes)
  - Assessed the performance of different density functionals and ab initio methods for H_2 storage and characterized the origin of errors in binding energies
- **HYDRIDES**
  - Established for the first time that a data science/machine learning approach can be applied to metal hydrides to identify structure-property relationships and unify prior experimental observations
  - Demonstrated >6 wt% reversible capacity (material basis) for Li3N@porous carbon, p(H_2) of 55 bar, and fast desorption kinetics (meets DOE fill time target) at 250 ˚C, a temperature at which the bulk material is unusable
  - Identified three new structure-property relationships:
    - Rate-limiting step for dehydrogenation of complex hydrides is likely a surface process, not bulk-phase transport or nucleation
    - Validated by experiment that an enthalpy-entropy compensation effect exists for hydrides, analogous to sorbents
    - The equilibrium p(H_2) of intermetallics is related to a descriptor that depends only on the elemental composition
- **CARRIERS**
  - Demonstrated a single-site Pt/CeO_2 catalyst that dehydrogenates MeOH and other alcohols 40 times faster than 2.5-nm Pt/CeO_2 and 800 times faster than CeO_2 loaded with 7-nm Pt clusters
  - Demonstrated the viability and efficiency of porous liquids as gas sorbents
  - Demonstrated the plasmonic activation of hydrogen desorption in hydrides from multiple systems
  - Formic acid dehydrogenation on Pd catalysts: determined sensitivity to surface and environment
  - Expanded capabilities of H_2 carrier techno-economic analysis process that allows material-based storage systems to be compared with incumbent technologies
- **CHACTERIZATION**
  - Increase the characterization capacities for structure, chemical composition and electronic structure of sorbents and hydrides
  - Extend thermal capacity measurement capabilities to micro-dosing of stoichiometric amounts of hydrogen
  - Further improve the in-situ/operando characterization capabilities at nearly real-world condition (at relevant temperature and pressure) for the hydrogen adsorption/desorption or release chemical transformation processes
  - Evaluate all OEM of PCT instrumentation and evaluated all mole balance models

Approach and Relevance (Adsorbents)

Approach

- **1.A** Enthalpy/entropy under practical conditions (with NREL, PNNL)
- **1.B Optimization of sorbent binding energies**
  - **1.B.1** Electronic structure computations (LBNL, LLNL)
  - **1.B.2** Strong-binding sites (LBNL, NREL, NIST)
- **1.C** Sorbent packing: MOF monolith synthesis (LBNL, SNL, NREL)
- **1.D** Dynamic sorbent materials (LBNL, NREL)
- **1.E** Multiple H_2 binding (LBNL, NIST)

Relevance

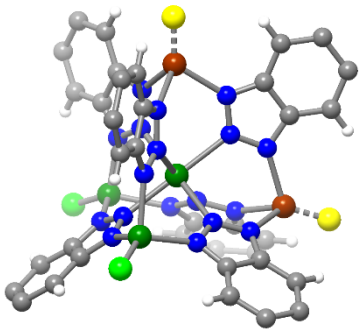
Research and development of metal–organic frameworks with high volumetric and gravimetric H_2 storage capacities (Barrier A – C, E).

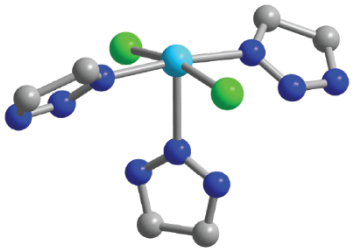
- Adsorption enthalpy in the optimal range of −15 to −25 kJ/mol
- Open metal sites that adsorb more than two H_2 molecules

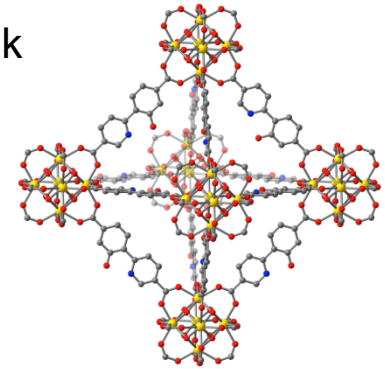
*Focus Areas discussed in this presentation are in black

Accomplishments in FY19 (Adsorbents)

- Determined ΔH_{ads} and ΔS_{ads} for $V_2Cl_{2.8}$(btdd) using variable-temperature DRIFTS (Task 1.A)
- Computed binding energy contributions due to orbital interactions and permanent electrostatics for MOFs with open metal site (Task 1.B.1).
- Located the D_2 adsorption sites in Cu^I-MFU-4*l* using *in situ* powder neutron diffraction (Task 1.B.2)
- Analyzed the H_2 storage capacity of Cu^I-MFU-4*l* at ambient temperatures (Task 1.B.2)
- Synthesized a new triazolate framework with open Cu^I sites that strongly bind H_2 (Task 1.B.2)
- Began synthesis of MOF and COF monoliths (Task 1.C.1)
- Began synthesis of flexible MOFs that could allow for a greater usable capacity, heat management, and desorption without pressure loss.. (Task 1.D.1)
- Improved Cu^I loading and performance in UiO-67-PhOHpydc and demonstrated Mn, Re, and Li metalation (Task 1.E)



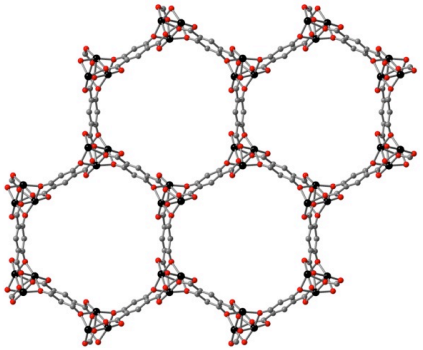




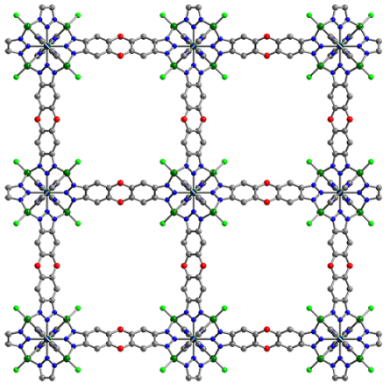
Approach 1.B.2: Sorbents with Optimal Binding Energies

Is it possible to create MOFs that adsorb H_2 with an enthalpy in the optimal range of −15 to −25 kJ/mol?

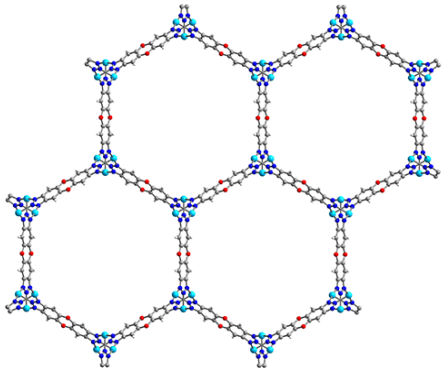
- Values are based upon assumptions about the correlation between adsorption enthalpy and entropy. However, these assumptions are not always valid.



Ni_2(*m*-dobdc)



Cu-MFU-4*l*



$V_2Cl_{2.8}$(btdd)

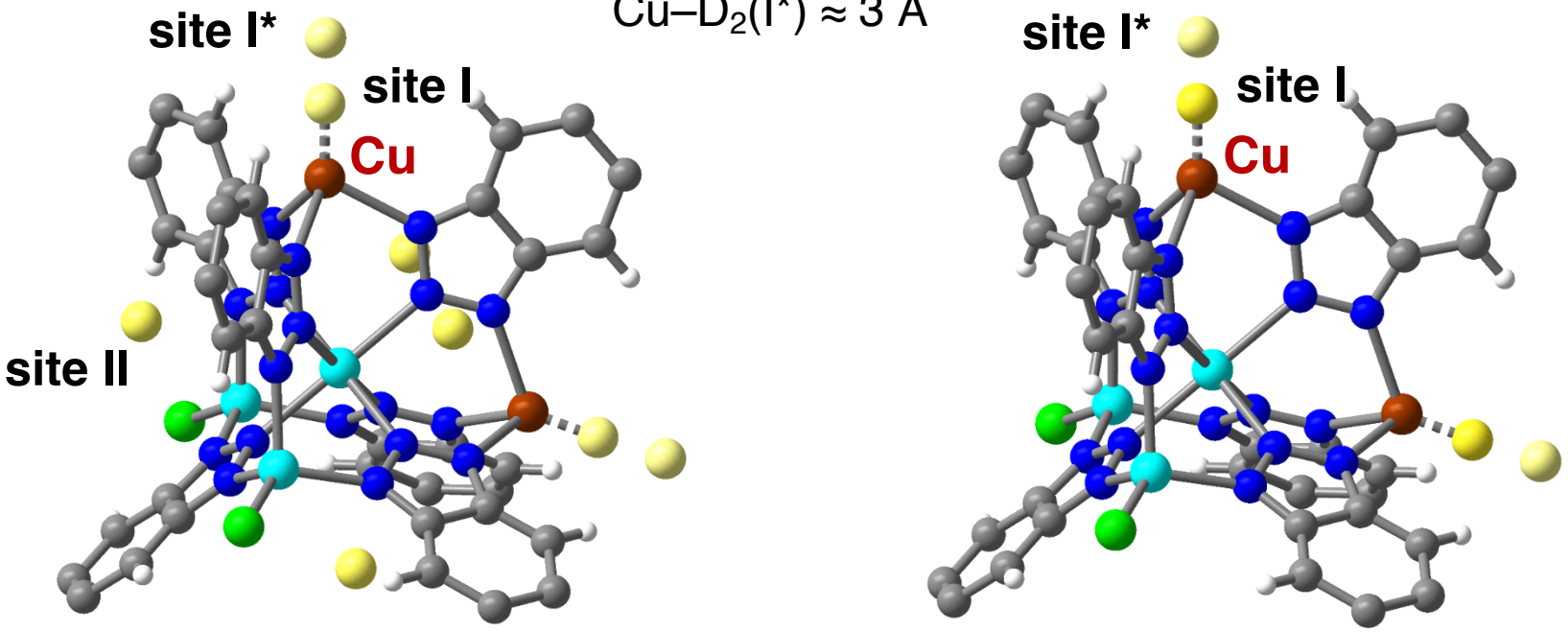
The Lewis-acidic open metal sites are capable of polarizing and accepting electron density from H_2; however, Δ*H* is lower than 15 kJ/mol.

π-Backdonation plays a primary role in strong H_2 binding: therefore, π-basic metals (Cu^{I} and V^{II}) will be incorporated into frameworks.

Accomplishment 1.B.2: *In situ* Powder Neutron Diffraction of Cu-MFU-4*l*

$Cu–D_2(I) \approx 1.6$ Å

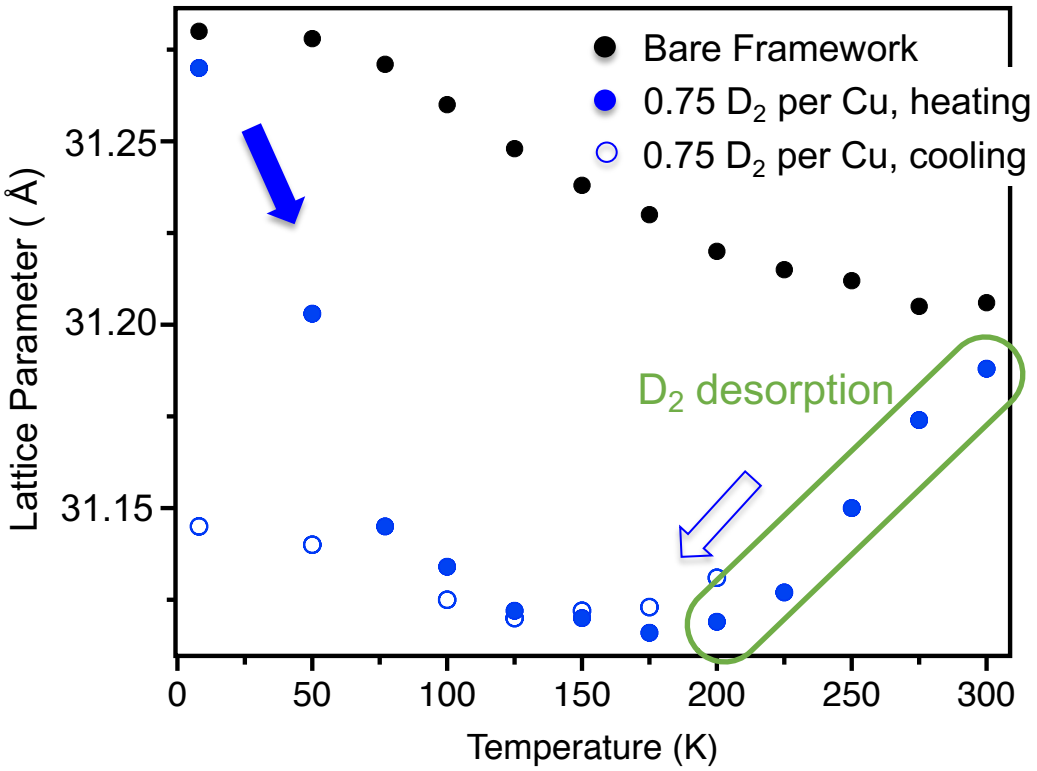
$Cu–D_2(I^*) \approx 3$ Å



- Sample dosed with 0.75 D_2/Cu at 40 K and then cooled to 7 K
- Occupation of two distinct D_2 sites near Cu^+ is apparent
- Occupancy of site I increases upon dosing at successively higher *T*

Barnett, Evans, Su, Jiang, Chakraborty, Banyeretse, Martinez, Trump, Tarver, Dods, Drisdell, Hurst, Gennett, FitzGerald, Brown, Head-Gordon, Long, *Submitted.*

Activated D_2 Binding in Cu^I-MFU-4*l*

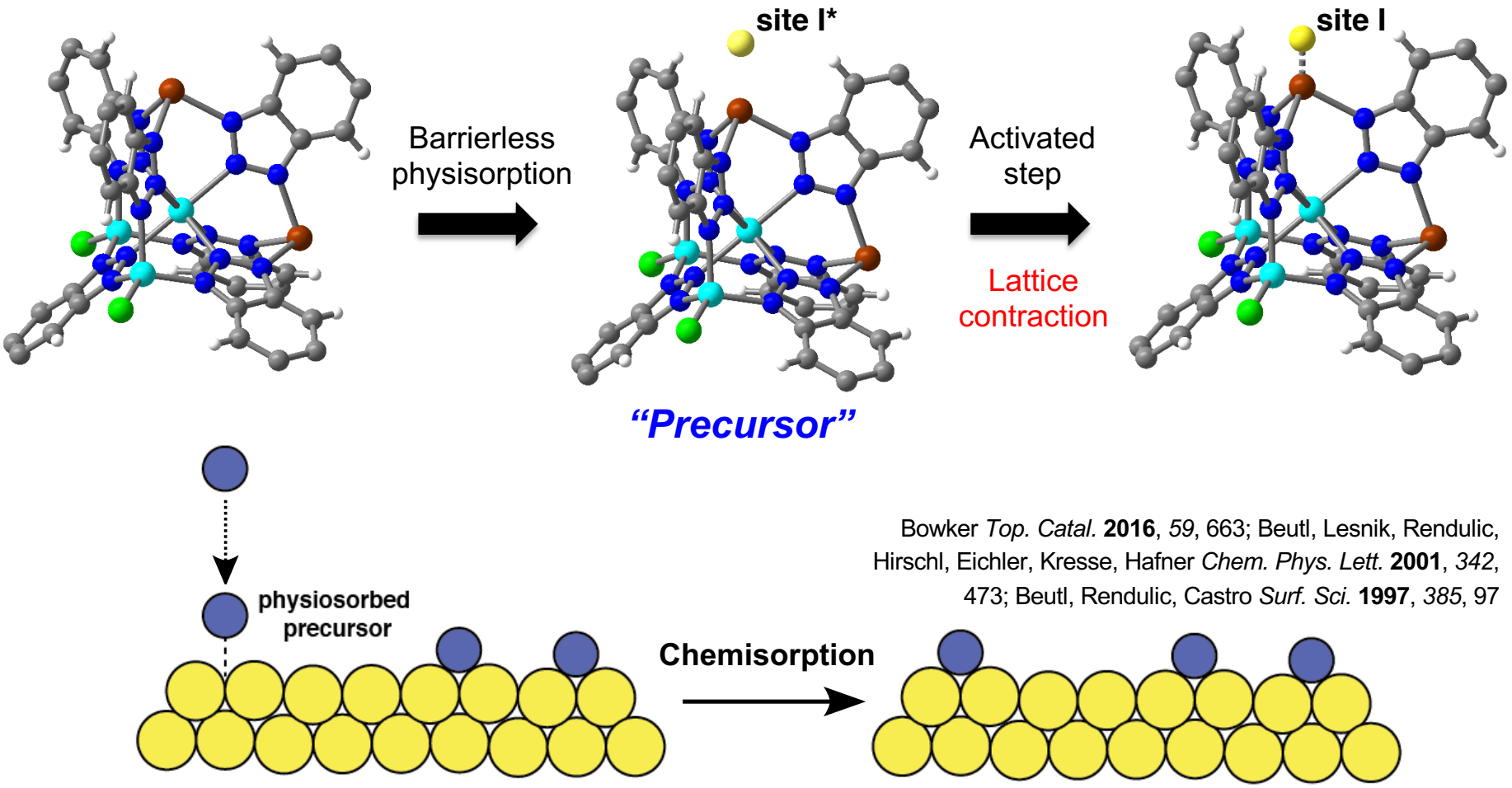


Dosing temp.	Site I occ. (D_2 per Cu)	*a* (Å)
none (bare MOF)	–	31.2744(14)
40 K	0.10(2)	31.2174(10)
77 K	0.48(2)	31.1652(10)
300 K	0.602(14)	31.1505(6)

- Significant lattice contraction with strong D_2 binding
- Spontaneous desorption begins around 200 K
- Hysteresis observed on cooling below 100 K

Barnett, Evans, Su, Jiang, Chakraborty, Banyeretse, Martinez, Trump, Tarver, Dods, Drisdell, Hurst, Gennett, FitzGerald, Brown, Head-Gordon, Long, *Submitted.*

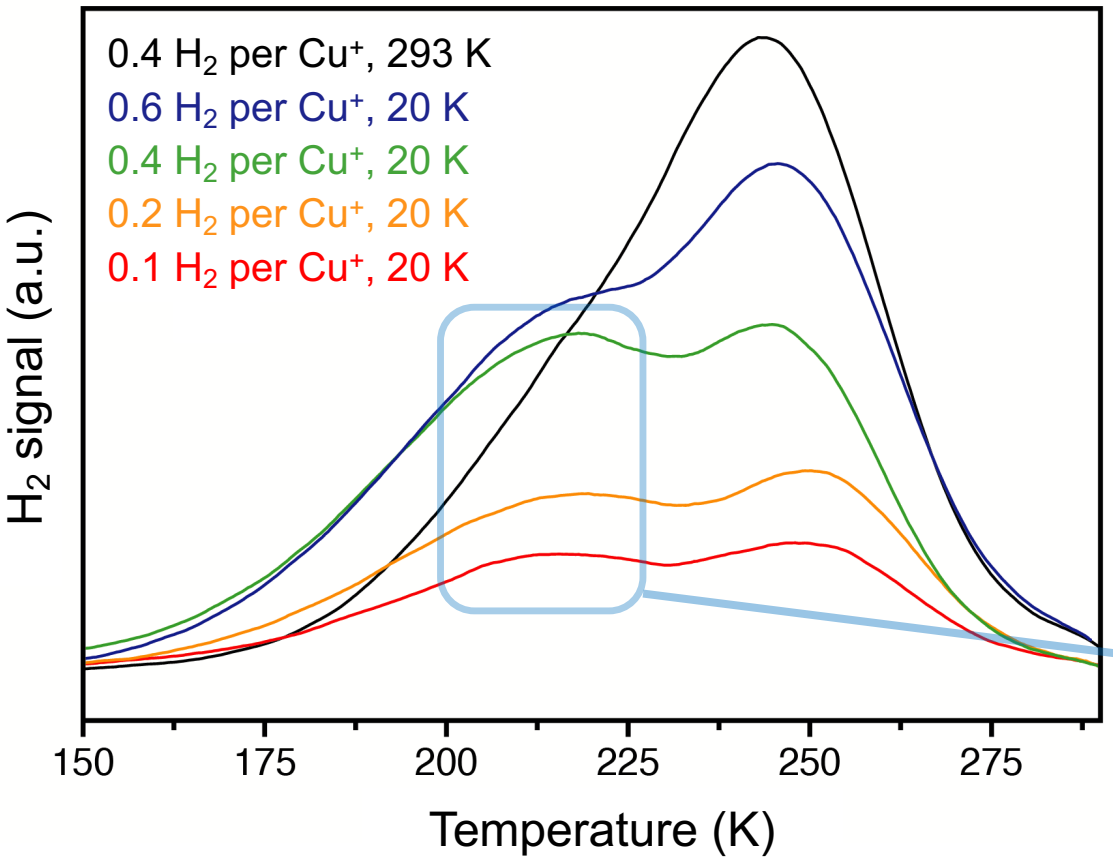
Elucidating the Mechanism of H_2 Chemisorption

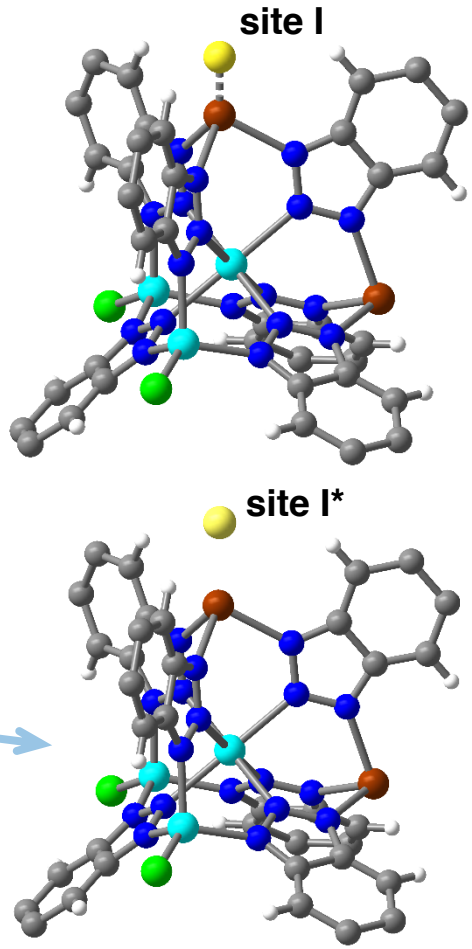


Bowker *Top. Catal.* **2016**, *59*, 663; Beutl, Lesnik, Rendulic, Hirschl, Eichler, Kresse, Hafner *Chem. Phys. Lett.* **2001**, *342*, 473; Beutl, Rendulic, Castro *Surf. Sci.* **1997**, *385*, 97

- Precursor state corresponds to local energy minimum en route to chemisorption
- Such states have been observed for dissociative and non-dissociative adsorption of various substrates (*e.g.*, H_2, N_2, O_2, CO)

Direct Observation of Precursor Using TPD



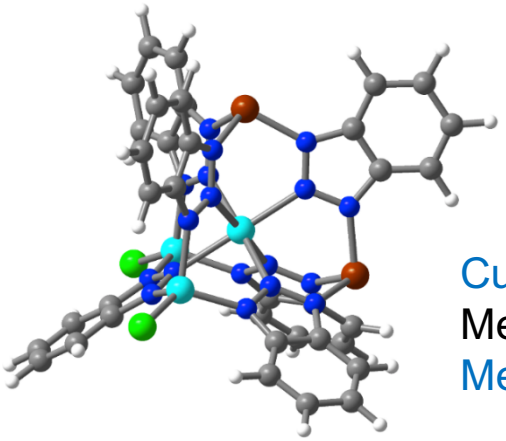


- New desorption peak around 200 K can be assigned to precursor state

Barnett, Evans, Su, Jiang, Chakraborty, Banyeretse, Martinez, Trump, Tarver, Dods, Drisdell, Hurst, Gennett, FitzGerald, Brown, Head-Gordon, Long, *Submitted.*

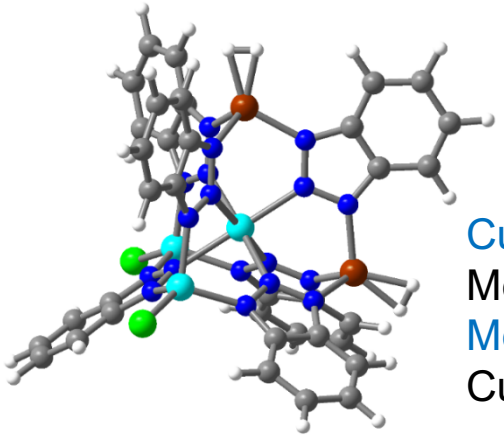
DFT Optimizations of Cu^{I}-MFU-4/ Cluster Models

Question: Why is there an activation barrier to adsorption at an open metal site?



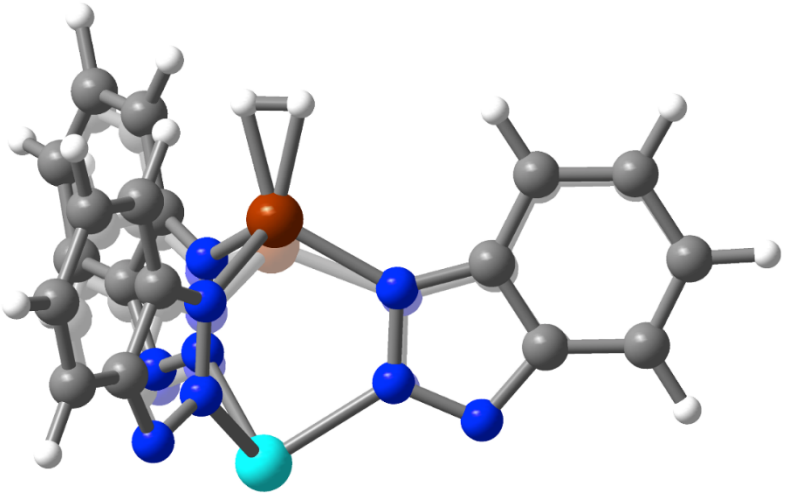
Cu–Zn(O_h) = 3.27 Å
Mean Cu–N = 1.96 Å
Mean N–Cu–N = 108.6°

Bare cluster



Cu–Zn(O_h) = 3.49 Å
Mean Cu–N = 2.00 Å
Mean N–Cu–N = 101.2°
Cu–H_2 = 1.70 Å

Cluster with adsorbed H_2



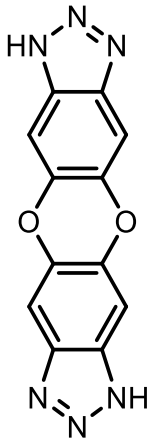
Significant Structural Distortions upon H_2 Adsorption

- Cu moves away from center of cluster upon binding H_2
- Bonds between N and central Zn shorten by a mean value of 0.03 Å

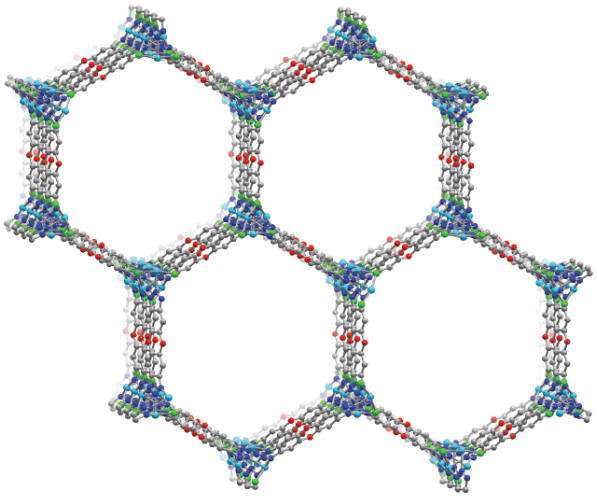
Previous Results: $V_2Cl_{2.8}$(btdd) Contains Open V^{2+} sites

Hypothesis: Increasing orbital interactions with H_2 will allow us to access this range

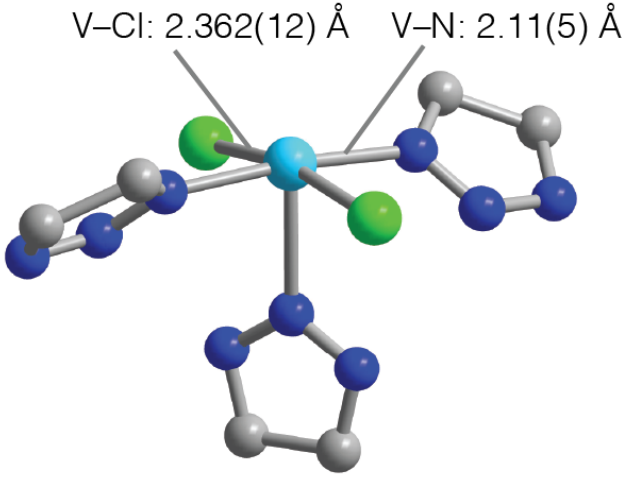
- Square pyramidal V^{2+} sites exhibit appropriate electronic structure



H_2btdd



$V_2Cl_{2.8}$(btdd)



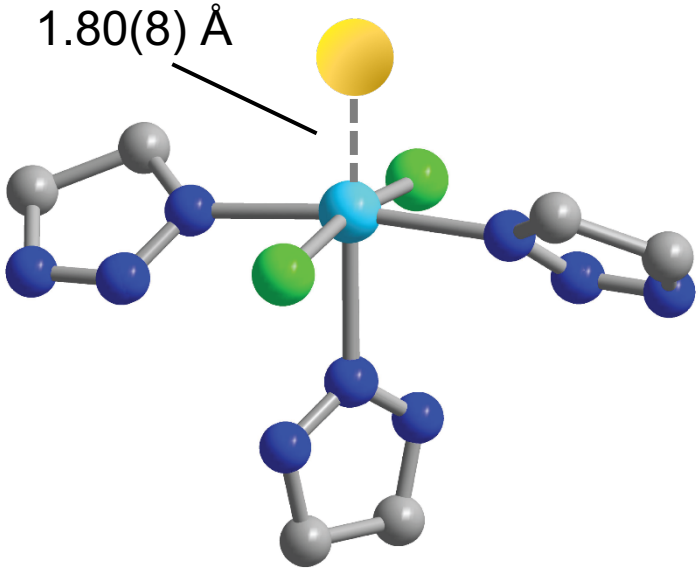
5-coordinate V^{II} site

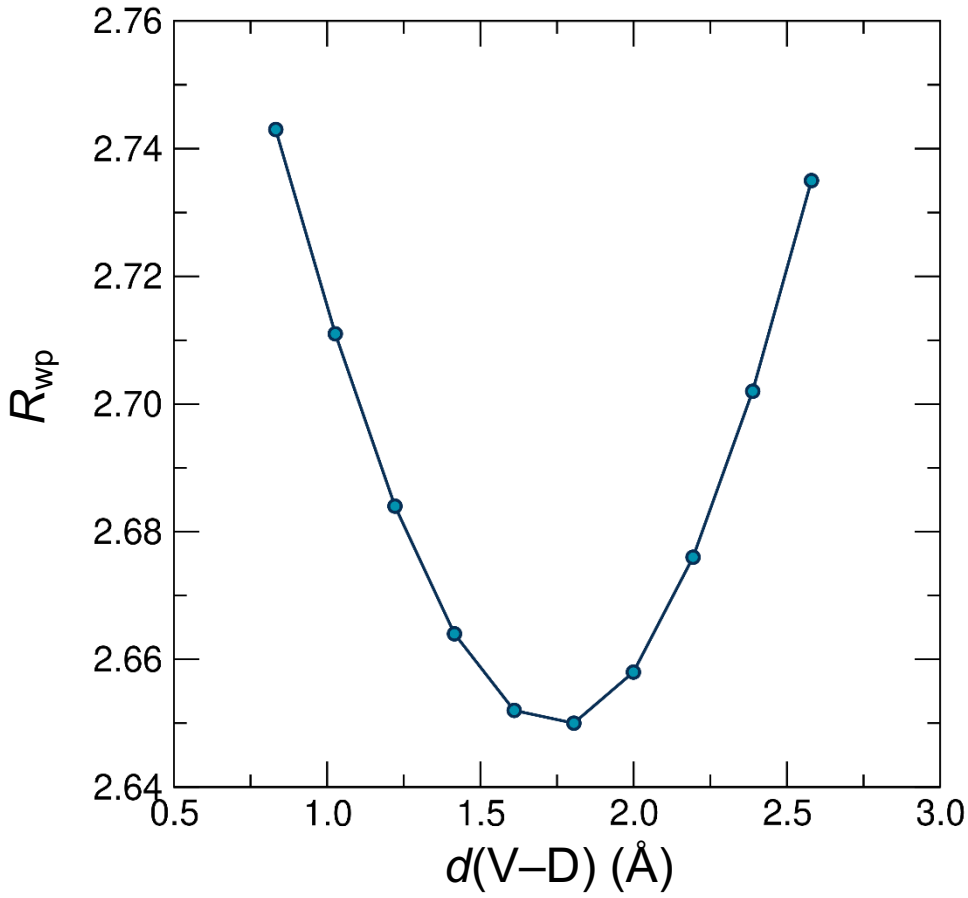
- Triazolate linker stable to the highly reducing V^{2+} (unlike carboxylate linkers)
- $SA_{Langmuir}$ = 3290 m^2/g, SA_{BET} = 1930 m^2/g

Jaramillo, Reed, Jiang, Oktawiec, Mara, Forse, Lussier, Murphy, Cunningham, Colombo, Shuh, Reimer, Long. *Nat. Mater.* **2020**, DOI: 10.1038/s41563-019-0597-8

Accomplishment: Neutron Diffraction Characterization of V–D_2

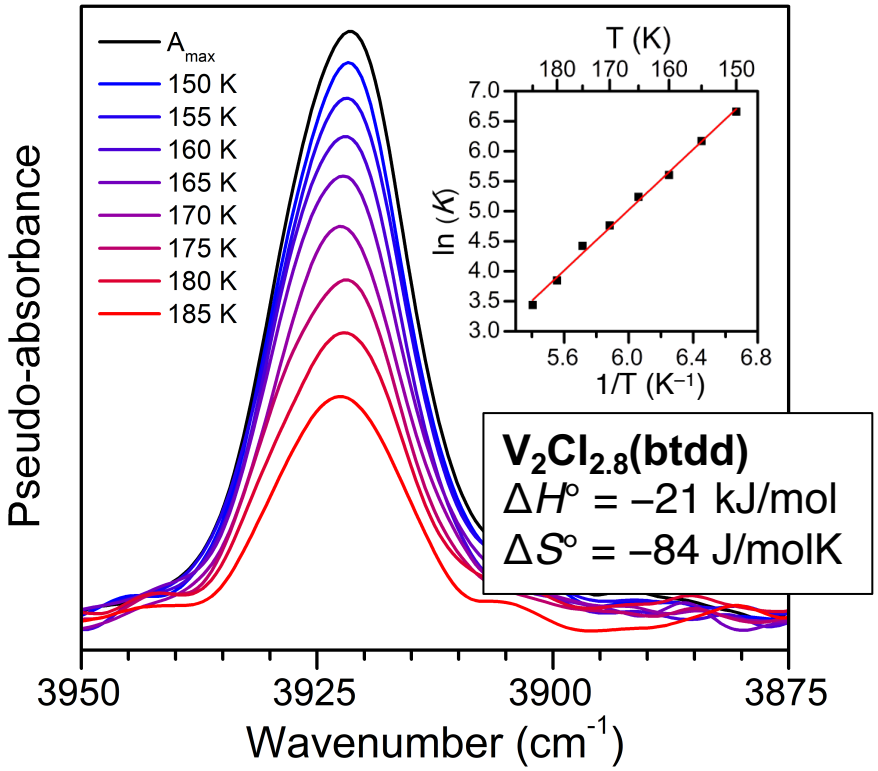
$V_2Cl_{2.8}$(btdd) + 0.75 equiv. D_2

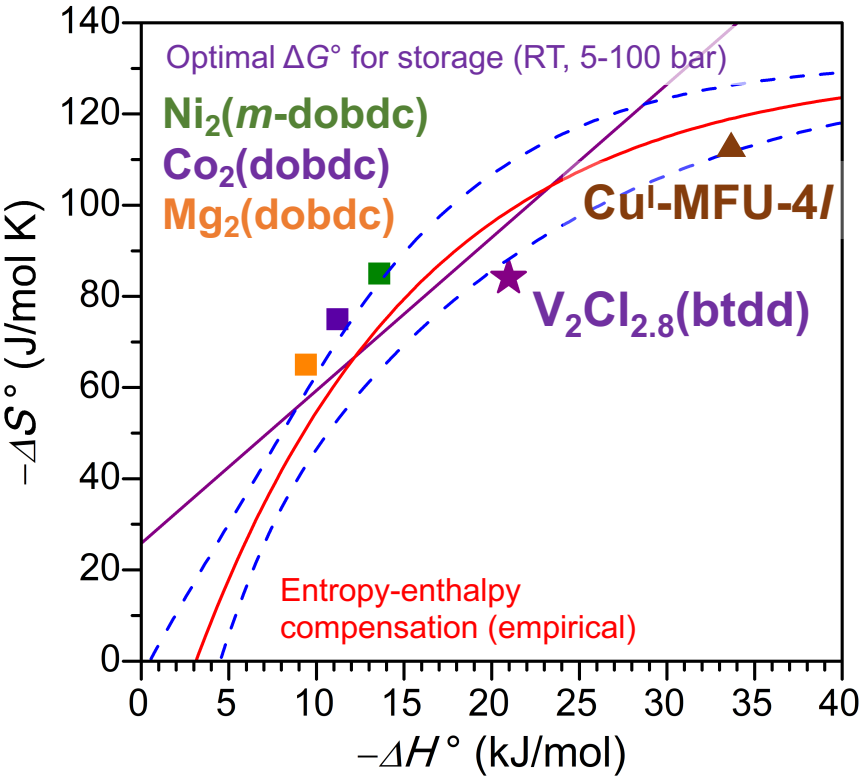




- V–D_2 can be resolved despite disorder with V^{III}–Cl sites
- d(Cu–D_2) = 1.60(3) Å in Cu^{I}–MFU-4*l*; d(Ni–D_2) = 2.18(4) Å

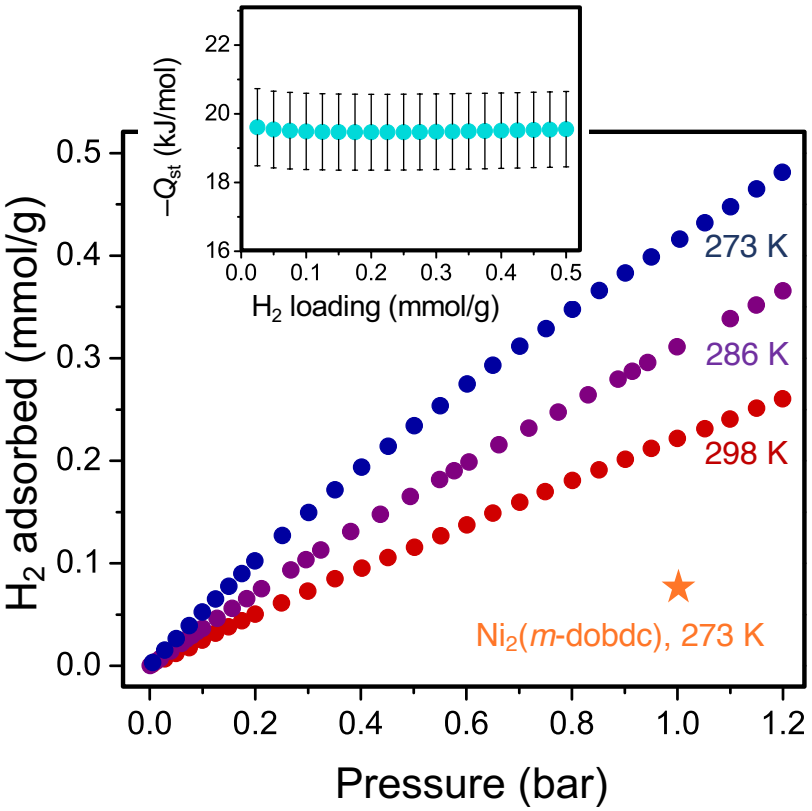
Variable-Temperature IR Spectra of H_2

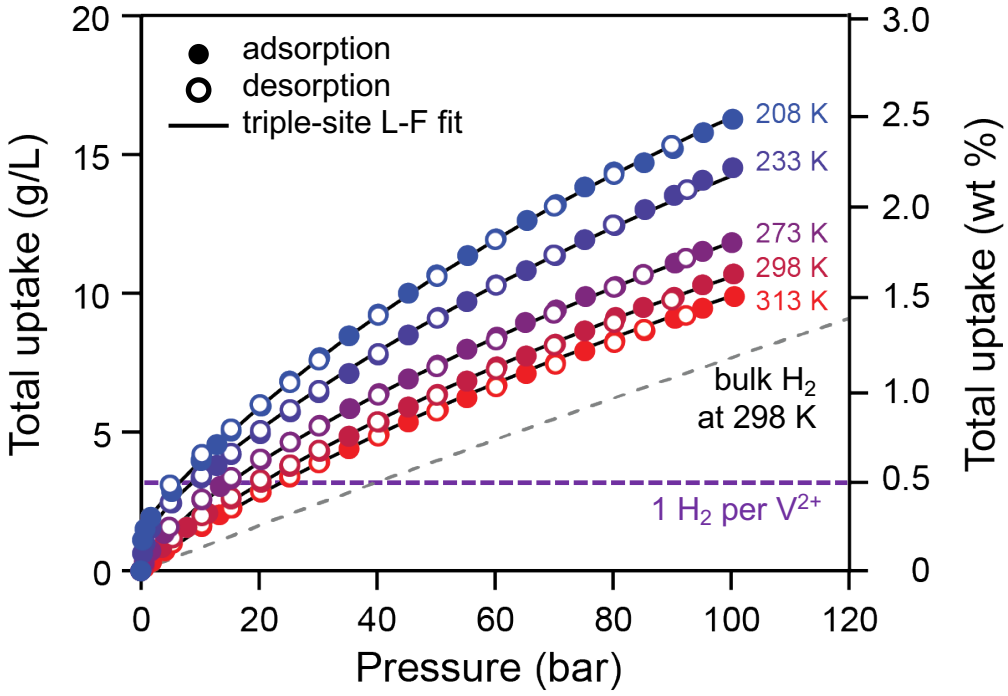




- First example of a MOF with ΔH in the optimal range between –15 and –25 kJ/mol
- Enthalpy-entropy relation distinct from M_2(dobdc) family

Low- and High-Pressure Ambient H_2 Isotherms





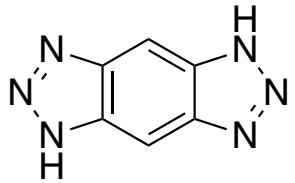
- Gravimetric total uptake for $V_2Cl_{2.8}$(btdd) surpasses Ni_2(*m*-dobdc) at 298 K and 100 bar (1.64 *vs.* 0.98 wt %)
- Initial steep uptake can be observed below 233 K where V^{2+} sites do not contribute to usable capacity

Future Plans (Task 1.B)

MOF	ΔH from DRIFTS[a] (kJ/mol)	Q_{st} from isotherms (kJ/mol)	Total H_2 uptake at 298 K, 100 bar (g/L)	Usable capacity at 298 K, 5–100 bar (g/L)
Comp. H_2	—	—	7.7	7.3
Ni_2(*m*-dobdc)	−13.7	−12.3	11.9[b]	11.0[b]
Cu^I-MFU-4*l*	−33.6	−32.7	11.0[b]	9.3[b]
$V_2Cl_{2.8}$(btdd)	−21.0	−19.5	10.7[b]	9.6[b]
HKUST-1[c]	n.d.	−6.9	9.8	9.0

[a]Diffuse reflectance infrared Fourier transform spectroscopy, [b]Applied single crystal density, [c]HKUST-1 monolith prepared in Task 1.C.1

- Gain a complete understanding of H_2 adsorption in these V^{II} and Cu^I systems
- Post-synthetically reduce $V_2Cl_{2.8}$(btdd) to access an all vanadium(II) framework (vanadium density of 4.4 mmol/g)
- Synthesis of V_2Cl_2(bbta): greater gravimetric capacity (6 mmol/g) with likely binding enthalpy ~20 kJ/mol



H_2bbta

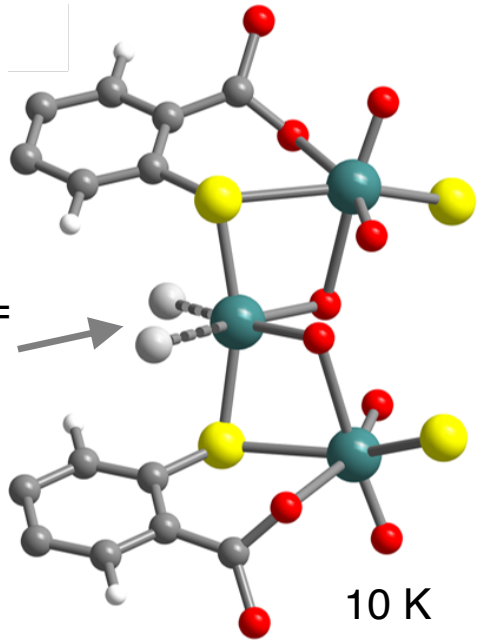
Any proposed future work is subject to change based on funding levels

Approach 1.E: Binding of Multiple H_2 per Metal Cation

Is it possible to create MOFs with open metal sites that adsorb more than two H_2 molecules?

- This is a long-standing "holy grail" in MOF chemistry
- Highly complex synthetic challenge

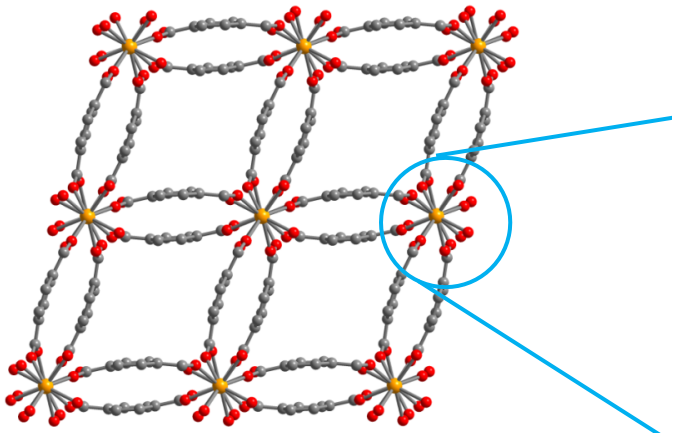
Mn_2(dsbdc) adsorbs two H_2 at a Mn^{2+} site: Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long *Chem. Commun.* **2016**, *52*, 8351.



Questions:

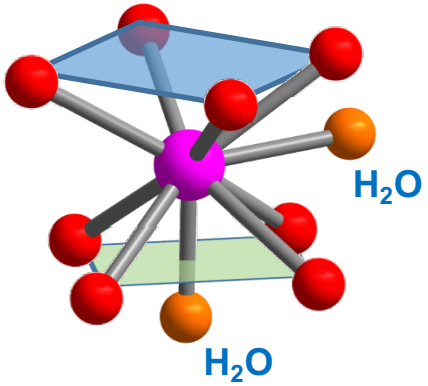
- Can we access multiple open sites per metal at secondary building units in MOFs?
- Can MOFs with the f-elements (coordination numbers up to 15) bind multiple H_2 per metal?

Accomplishment 1.E: A New 3-Dimesional Uranium MOF—$U(bdc)_2(H_2O)_2$



$U(bdc)_2(H_2O)_2$

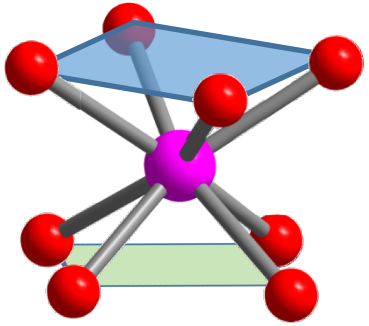
As-synthesized
$U(bdc)_2(H_2O)_2$
(Single-crystal XRD)



Bi-capped square antiprism

activation

Activated $U(bdc)_2$
(Powder XRD)

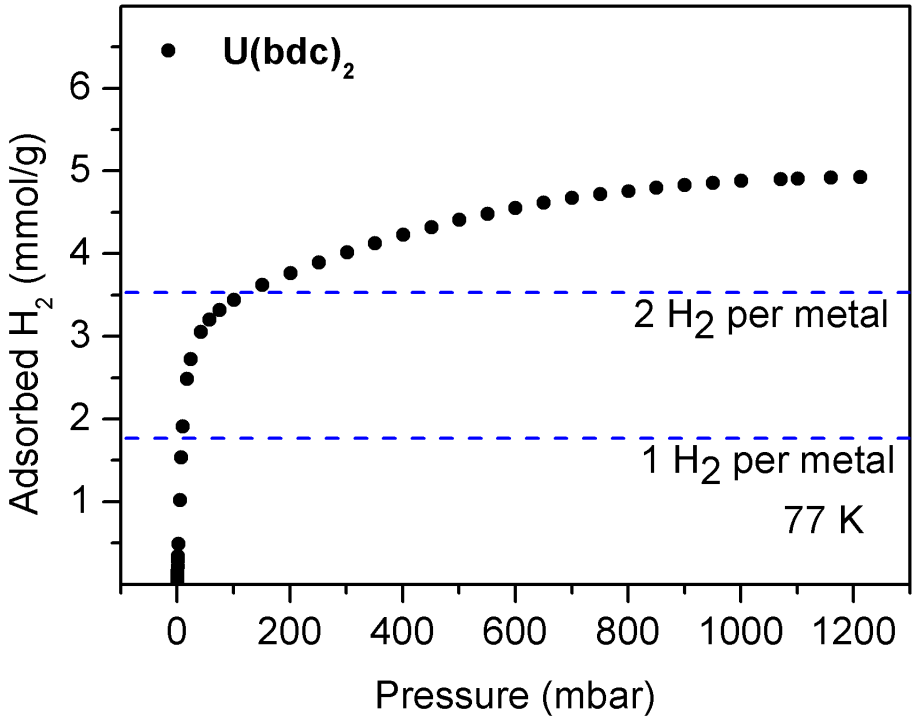


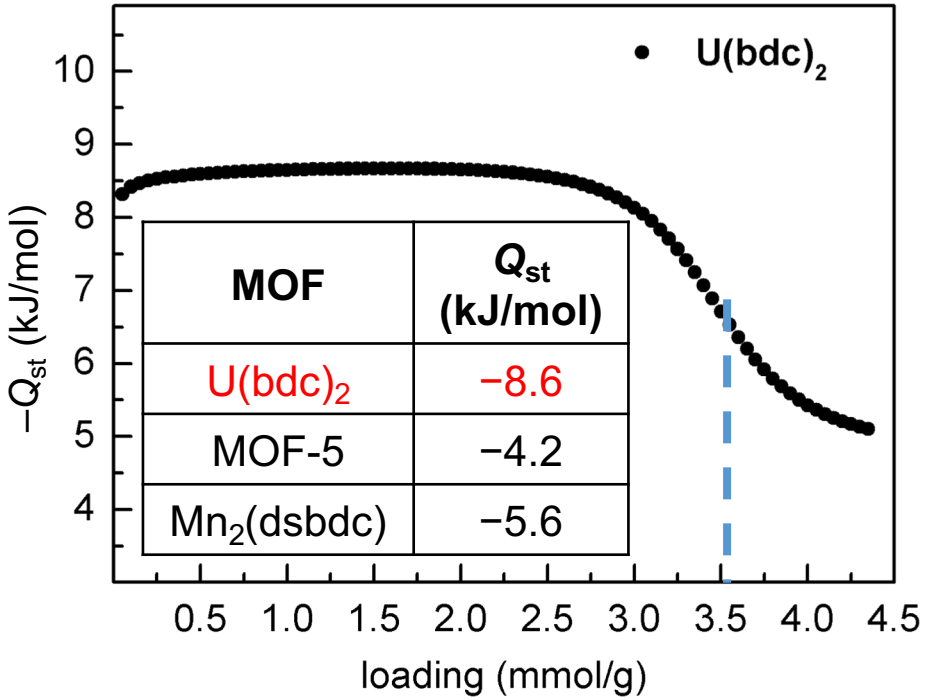
Square antiprism

- Langmuir surface area = 570 m²/g
- Each uranium is coordinated by two H_2O (TGA shows desolvation step at 130 °C)
- Can we access two open metal sites for H_2 binding in activated $U(bdc)_2$?

Halter, D. P.; Klein, R. A.; Boreen, M. A.; Trump, B. A.; Brown, C. M.; Long, J. R. *Angew. Chem. Int. Ed.*, submitted.

Low-Pressure H_2 Adsorption in $U(bdc)_2$

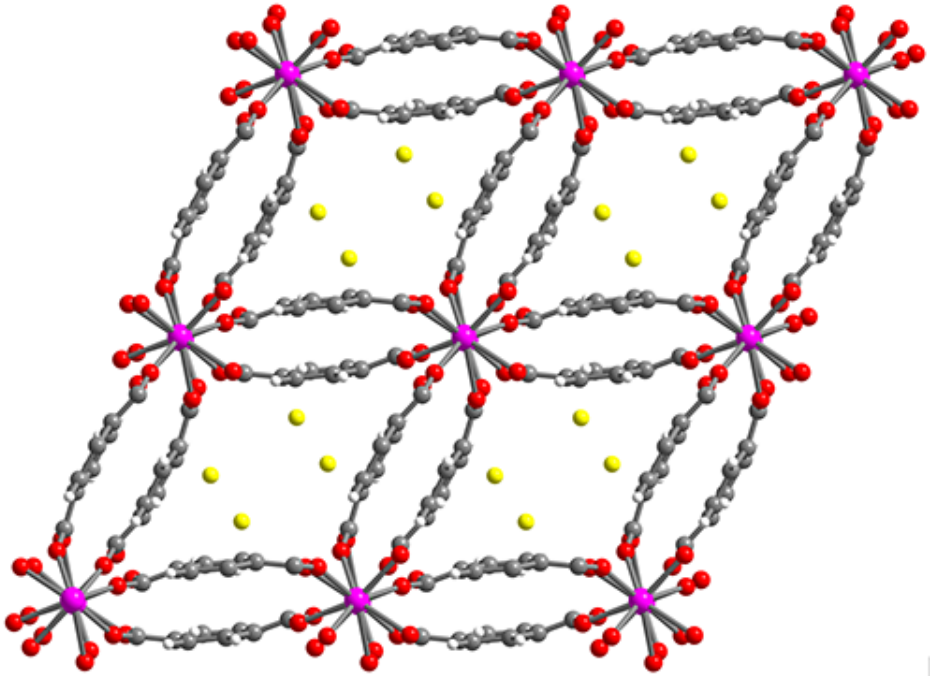




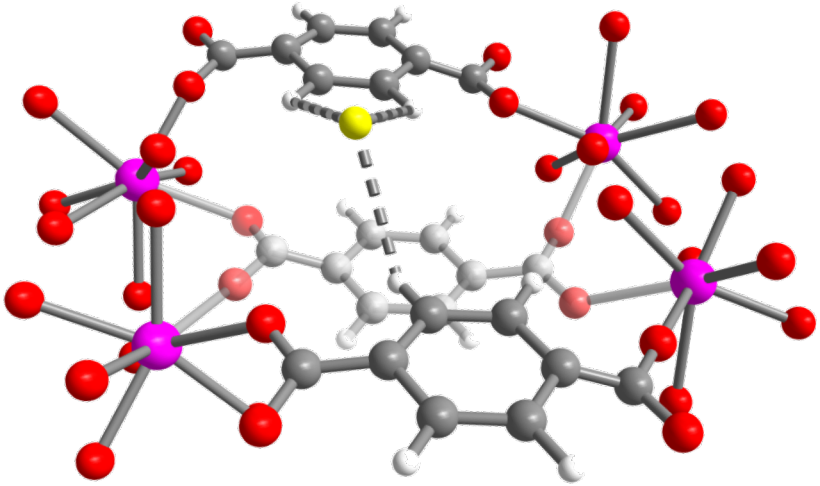
- Strong H_2 binding to theoretical capacity of 2 H_2 per metal
- Inflection point matches theoretical capacity of 2 H_2 per metal

Halter, D. P.; Klein, R. A.; Boreen, M. A.; Trump, B. A.; Brown, C. M.; Long, J. R. *Angew. Chem. Int. Ed.*, submitted.

In situ Neutron Diffraction Studies of $U(bdc)_2$ with D_2



4 D_2 per pore = 2 D_2 per U



Binding pocket: 3 C–H bonds

- Loading from neutron diffraction data is consistent with that observed in H_2 isotherms
- Unexpectedly there are no D_2–U interactions

Halter, D. P.; Klein, R. A.; Boreen, M. A.; Trump, B. A.; Brown, C. M.; Long, J. R. *Angew. Chem. Int. Ed.*, submitted.

Accomplishments in FY20 (Adsorbents)

- **Mechanism of H_2 chemisorption in Cu^I-MFU-4*l*:** Used powder neutron diffraction and temperature-programmed desorption to characterize a metastable, adsorbed precursor intermediate in Cu^I-MFU-4*l*
- ***In situ* powder neutron diffraction:** Resolved V–D_2 bond distance in $V_2Cl_{2.8}$(btdd) despite disorder with V^{III}–Cl sites. Bond distance is compatible with strong binding
- **Multiple H_2 per metal:** Synthesized MOFs with multiple open sites per metal by harnessing larger ionic radii and high coordination numbers of the *f*-elements

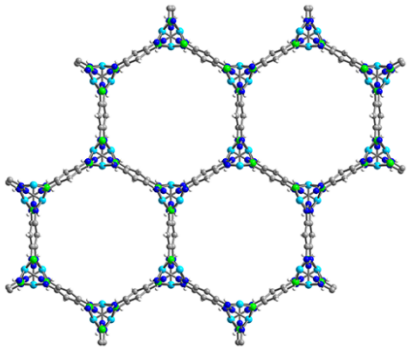
- Obtained valuable insight into the mechanistic pathway of activated H_2 chemisorption in Cu^I-MFU-4*l* from DFT simulations of the Cu^I nodes
- Measured high-pressure H_2 adsorption isotherms for $V_2Cl_{2.8}$(btdd), which corroborated binding enthalpy within an optimal operation range
- Demonstrated N_2-induced flexibility at 77 K in two new Zn(bdp) derivatives
- Confirmed photochemical release of CO from Mn carbonyl complexes ligated by bipyridine (bpy) in the zirconium framework UiO-67-bpy. Confirmed photochemical release of H2 from Cu sites in a metalated COF.
- Verified the synthesis of HKUST-1 monolith, which exhibits volumetric H_2 uptake 50% greater than the powder form. Completed monolith synthesis of COF materials.

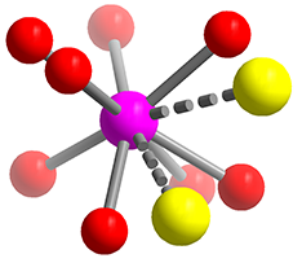
Summary (FY20 Internal Adsorbents Milestones)

Task	Milestone	Due	Status
1.B.1	**Electronic structure computations:** Develop a computational protocol to asses thermochemical effects (enthalpy and entropy) in hydrogen adsorption.	9/2020	30%
1.B.2	**Optimal binding energies:** Synthesize a derivative of Cu^{I}-MFU-4/ or V_2Cl_2(btdd) with a modified ligand and measure H_2 heat of adsorption.	9/2020	30%
1.C.1	**MOF monoliths:** Synthesize at least 2 monolith MOFs that outperform the volumetric storage capacity of monolith HKUST-1 at temperatures above 150 K and < 100 bar.	9/2020	30%
1.D.1	**Flexible MOFs:** Synthesize at least 2 different M(bdp) (M other than Co) frameworks and locate step pressures at 77 K.	9/2020	50%
1.E	**Multiple H_2s per metal:** Demonstrate either (a) binding of three H_2 to a single metal center, or (b) binding of multiple H_2 to a single metal center, with a maximum heat of adsorption of at least 8 kJ/mol.	9/2020	25%

Future Directions (Adsorbents)

- Use ^{65}Cu solid-state NMR to investigate whether thermodynamic or kinetic cooperativity between proximal Cu^{I} centers influences H_2 binding in Cu^{I}-MFU-4*l*
- Synthesize V-based MOFs with shorter linkers for greater volumetric H_2 storage capacities and a target binding enthalpy of ~20 kJ/mol
- Explore functionalized M(bdp) variants to tune the step pressure at ambient temperatures
- Explore new MOFs with *f*-elements featuring multiple accessible metal binding sites
- Optimize synthetic conditions of MOF-74-type monoliths to increase volumetric H_2 storage capacities
- Predict usable capacities from anharmonic free energy estimates in MOFs





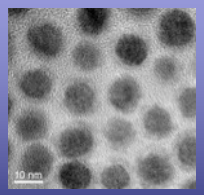
Any proposed future work is subject to change based on funding levels

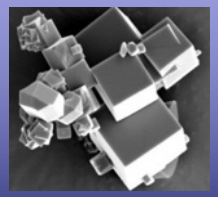
We employ a synergistic approach to identify and test new metal hydride storage material concepts

Objective: develop models at all relevant length scales to identify rate-limiting processes and to tune the ΔH and ΔS of hydrogen uptake and release by metal hydrides

Reproducible synthesis of well-characterized metal hydrides

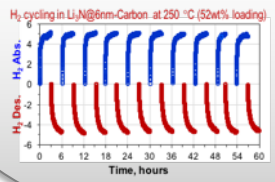
Synthesis

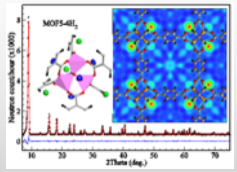




Phase purity, control over size/shape, doping, additives, crystallinity

Characterization

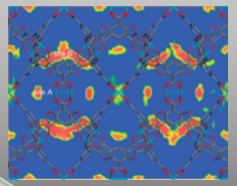


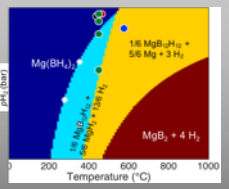


PCT, XAS, STXM, MAS-NMR, NVS

Measure thermodynamic and kinetic properties and determine reaction pathways

Model validation





DFT, MD, thermodynamics, phase field…

Provide high-accuracy validation of computational models

Model validation

27

Relevance: hydride challenges HyMARC is addressing

DOE Target	Target Value*	Current Strategies and *Materials Under Consideration*
Grav. Density (g H_2/g system)	5.5	Eutectics; metastable hydrides; systems analysis *$Mg(BH_4)_2$+$LiNH_2$ eutectic; nano-$LiAlH_4$; Li_3N (bulk and nano)*
Vol. Density (g H_2/L)	40	Improve nanoscale hydride loading & packing density *Li_3N@(porous C); $Mg(BH_4)_2$+$LiNH_2$ eutectic*
Min/Max Deliv. *T* (˚C)	-40/85	Predict accurate phase diagrams; ID rate-limiting steps *Li_3N; high-entropy alloys*
Min./Max. Deliv. *P* (bar)	5/12	Machine learning to discover hydrides w/ desirable thermo. *High-entropy alloys; nanoscale hydrides*
Min Full Flow Rate (g/s/kW)	0.02	Nanoscaling to improve kinetics *Li_3N@(porous C); $LiAlH_4$@(porous C); "molecular" $Mg(BH_4)_2$*
Fill time (min)	3 – 5	Reduce energy barriers for H_2 uptake (multiple strategies) *Li_3N@(porous C); 2$LiNH_2$+MgH_2*
Loss of Useable H_2	SAE J2579	Eliminate kinetic dead ends to improve reversibility *Li_3N@(porous C); nano-$LiAlH_4$*
Fuel purity	SAE J2719	Change reaction pathways; chemical trapping *Li_3N@(porous C); $Mg(BH_4)_2$CMK-3 porous C*

*2025 targets

Relevance: $Li_3N/(LiNH_2+LiH)$ is currently our most promising hydride with potential to meet most DOE 2025 targets

Objective: meet DOE 2025 gravimetric and fill-time targets

1) ✓ Perform system analysis on bulk and nanoscale hydride to understand differences
2) ✓ Identify the rate-limiting step for H_2 release
3) Design new materials with accelerated kinetics/increased capacity that meet targets

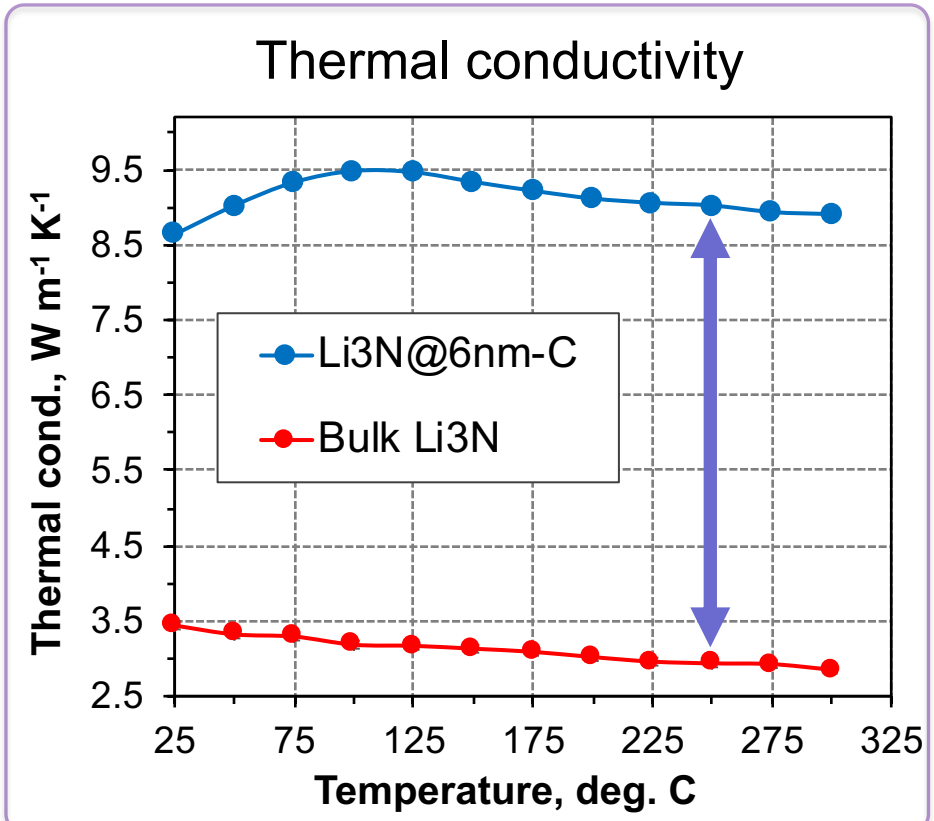
Why Li-N-H?

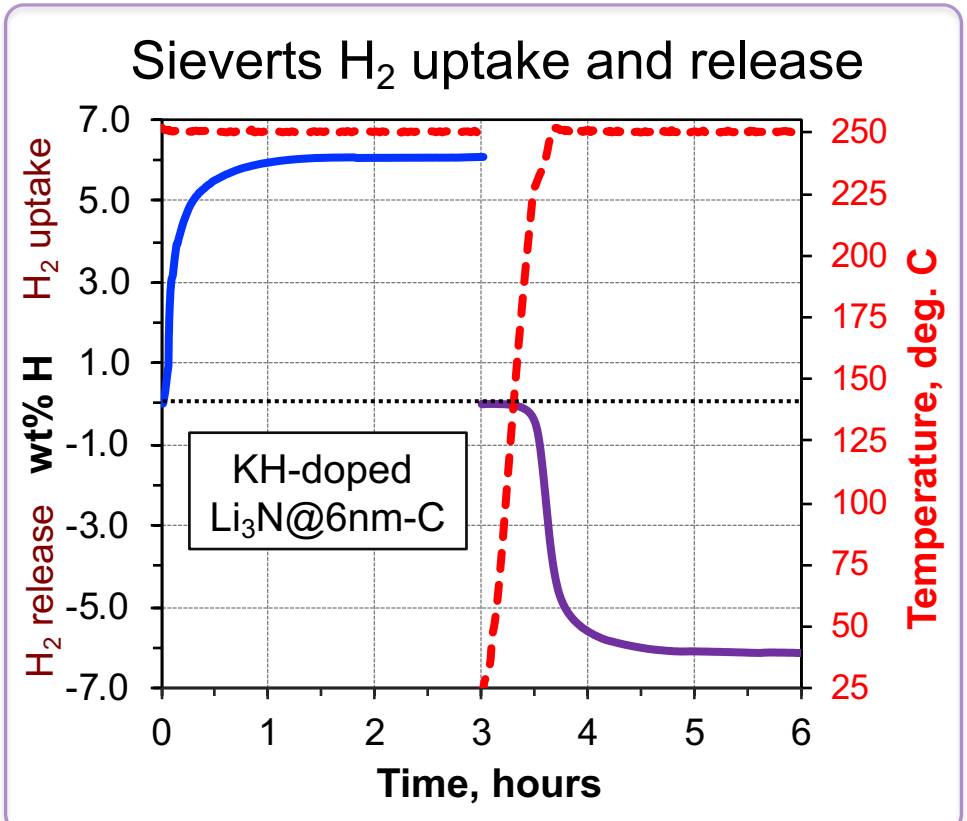
- Bulk total H capacity : ~10.5 wt.%
- Bulk reaction: $Li_3N + 2\ H_2 \rightleftharpoons Li_2NH + LiH + H_2 \rightleftharpoons LiNH_2 + 2\ LiH$
- Fully reversible at 250 ˚C (J. Wang *et al. MRS Bull.* 2013, 38, 480)
- Nano KH-doped Li_3N@(6-nm porous carbon)
  - Meets 9/2019 milestone: 6.1 wt% reversibility at 250 ˚C

Approach:

- Synthesize bulk Li_3N and nanoscale Li_3N with controlled size, known H_2 release kinetics
- Probe atomic, nano, and mesoscales using X-ray spectroscopies and microscopy
- Use systems analysis to compare bulk vs. nanoscale hydride

Accomplishment: Thermal conductivity and kinetics of hydrogen uptake and release for KH-doped Li_3N@6nm-C





Take-home lessons:

- **Thermal conductivity of nanoconfined KH-6nm-Li_3N@Carbon material is about 2.9-3.2 times higher compared to that of bulk Li_3N**
- **The material can be reversibly cycled at 250 ˚C and 10.5 MPa hydrogen pressure)**

Accomplishment: full systems analysis using US06 drive cycle for KH-doped Li_3N@using newly measured kinetics

- Finite element analysis/US06 Drive Cycle
- Li_3N@6-nm-Carbon
- Experimental data inputs:
  - Hydride loading
  - Enthalpy, entropy of reaction
  - H_2 desorption kinetics (E_a)
  - Thermal conductivity

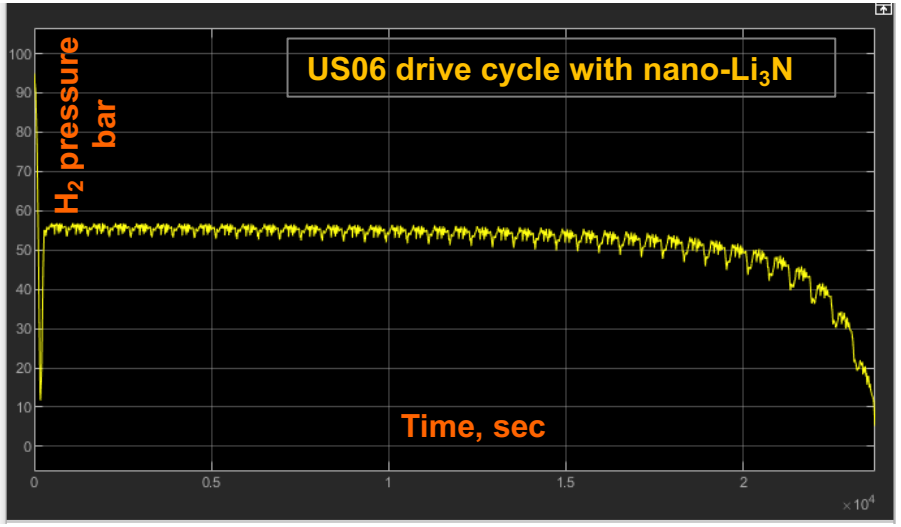
Key results

- Li_3N@6-nm-Carbon can sustain a demanding US06 cycle
- Bulk Li_3N cannot produce an H_2 generation rate high enough to start the vehicle

Take home lesson: a nanohydride out-performs a bulk material under relevant engineering conditions

→ Motivates follow-on work

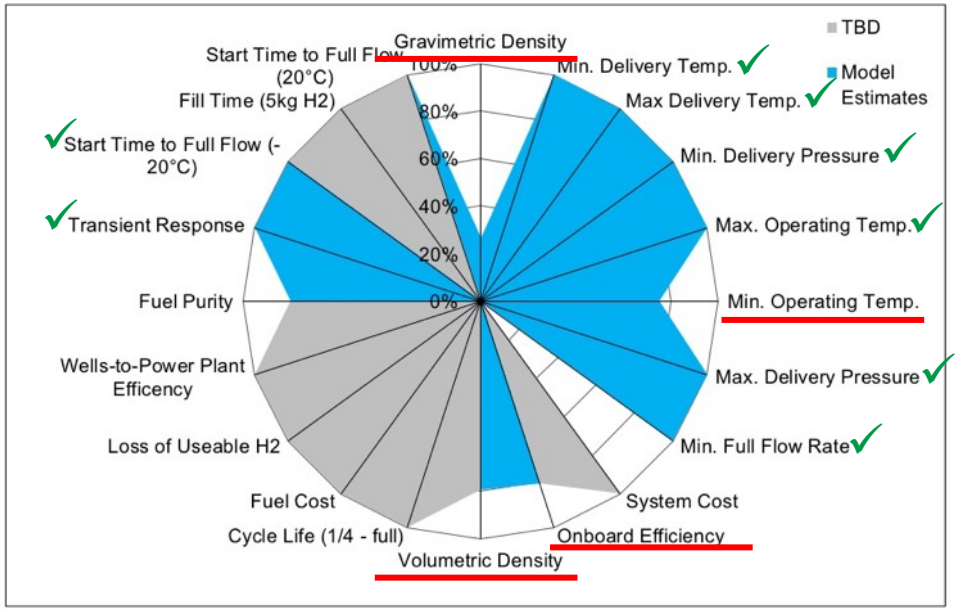
- Smaller pores
- Additional kinetic data
- Expanded systems analysis



System mass (kg)	466.5	
System volume (m^3)	0.236	
H_2 combustor	1	
Mass of H_2 burned	1.845	
Tank outer diameter (m)	0.428	
Tank length (m)	1.646	
Number of coolant tubes	115	
Total hydride mass (kg)	122.06	
Tank mass (kg)	300.97	
Maximum temperature (deg. C)	282.75	
% DOE 2025 Gravimetric Target	**27**	**11 (bulk)**
% DOE 2025 Volumetric Target	**79**	**31 (bulk)**

Accomplishment: Comparison with DOE targets determined by systems model including kinetics using US06 drive cycle

- Of the 13 targets in the evaluation (shaded blue):
  - 9 are 100%
  - 3 are ≥ 75%
- Predicted $P(H_2)_{max}$ = 55 bar at 250 ˚C; DOE target = 12 bar
- Grav. Capacity is 30% of target
  - Due to burner weight of burner and cooling tubes



Take-home lessons:

- Assessing system performance based on one DOE target (e.g. bulk wt%) is overly simplistic
- Systems analysis and material design should be performed in parallel

Next step: Expand systems study to answer the question *"Can the number of cooling tubes and burner weight be reduced so that Grav. Capacity can be increased while maintaining other targets at or close to 100%?"*

Accomplishment: Comparison of systems model (chemical thermodynamics) with DOE targets for various hydrides

Metal hydride finite-element analysis (assumes kinetics are not rate-limiting)

	Measured inputs			Predicted			
Material / Property	H capacity (wt%)	κ(bed)	ΔH kJ/mol	T_{max} (recharge) (˚C)	H_2 burn (kg)	% Grav Target(2)	% Vol Target(2)
Ti-doped $NaAlH_4$(1)	4.5	8.96	40.8	197	1.77	16.6	43.2
$2LiBH_4/MgH_2$	9.7	0.89	44.2	242	1.97	16.4	40.1
KH-doped $2LiNH_2$-MgH_2	4.0	2.10	39.5	216	1.69	11.6	29.2
KH-doped Li_3N (bulk)	8.2	0.96	67.3	493	3.60	11.3	31.2
6nm-Li_3N@C	6.1	8.32	42.1	283	1.84	25.4	74.8
KH-6nm-Li_3N@C	6.4	9.61	41.7	256	1.82	27.2	79.3

(1) From HSEngCOE (2) 2025 (2) DOE 2025 target

Take-home lessons:

- **Capacity trend predicted: KH-6nm-Li_3N@C > 6nm-Li_3N@C > KH-doped Li_3N (bulk)**
- **Trend is result of thermodynamics only (kinetics are not included in this modeling)**

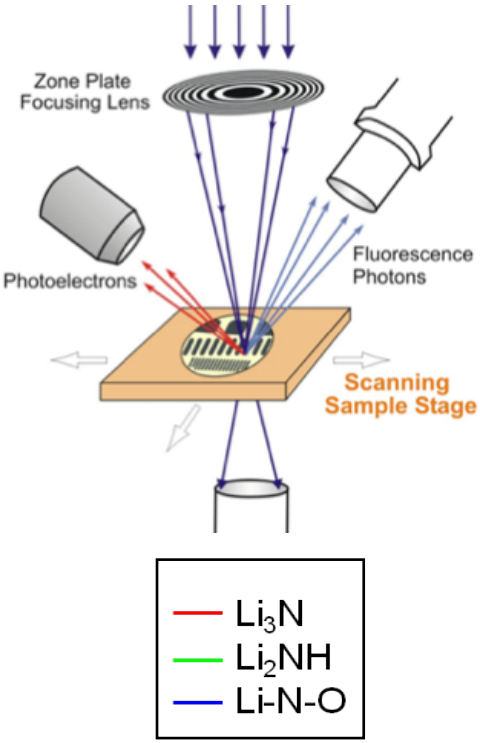
Next step

- **Extend full systems model including kinetics to other hydrides**

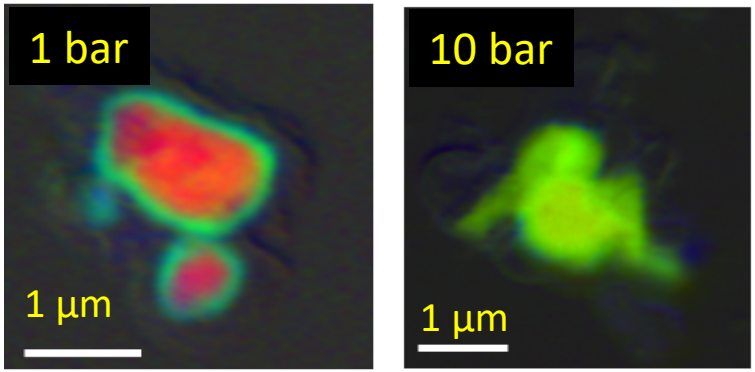
Accomplishment: Phase nucleation and growth at buried interfaces in Li-N-H revealed for the first time

If we can identify the chemical step limiting the rate of H_2 release from $LiNH_2$, we may be able to design a material with a lower release temperature

Nitrogen composition maps measured by Scanning Transmission X-Ray Microscopy (STXM)



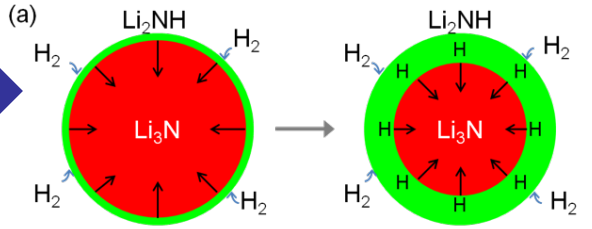
Hydrogenation at 200 ˚C



Mechanism hypotheses

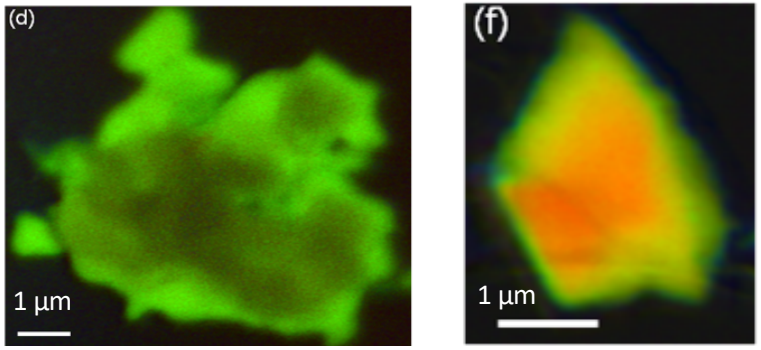
Very little $LiNH_2$ detected

$LiNH_2$ → Li_2NH is fast



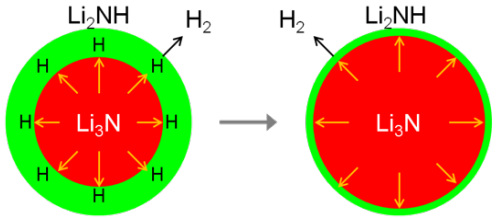
Dehydrogenation at 400-450 ˚C

Inverted core-shell chemical map



Interior dehydrogenates first

→ Slow surface chemistry?



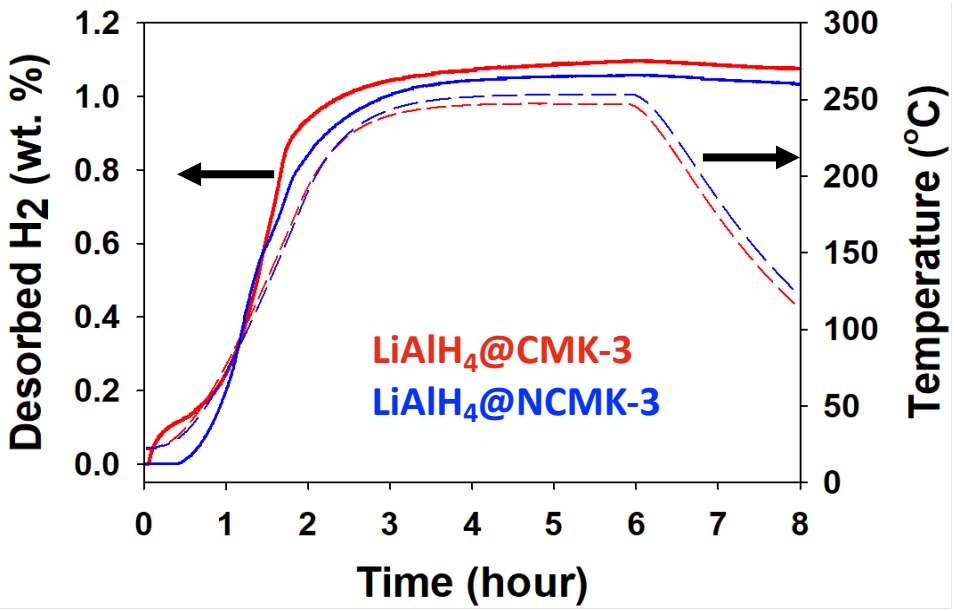
Take home message: conventional assumption that H_2 release at surface is fast is incorrect

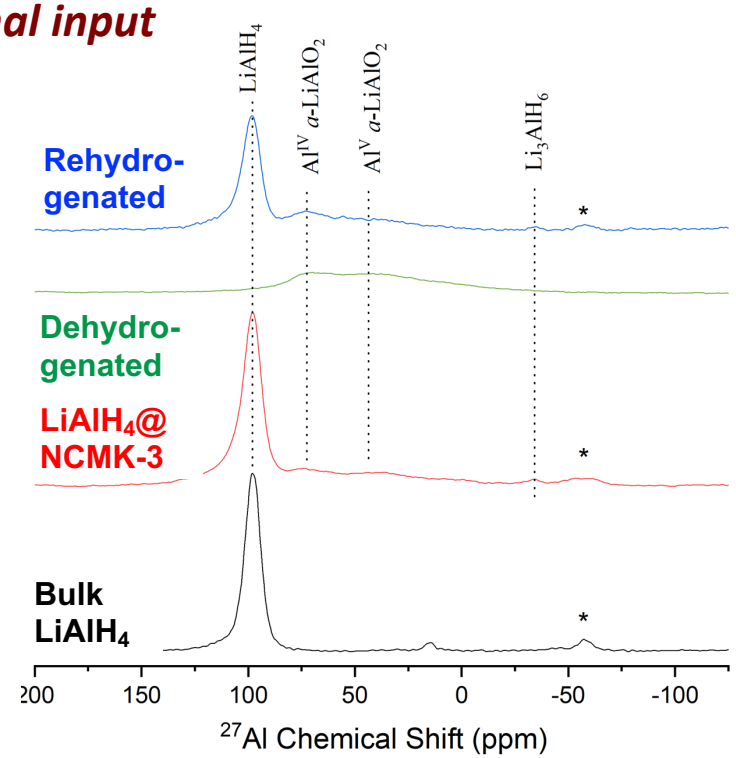
→ Possible reasons will be assessed by computational modeling underway

Publication: J. L. White, V. Stavila et al. *Adv. Mater. Interfaces*, 2020, *7*, 1901905

Accomplishment: First demonstration of reversible H_2 release and uptake by a metastable hydride ($LiAlH_4$)

Thermodynamic stabilization of metastable metal hydrides can enable reversible H_2 release with low thermal input





Key results:

- Nano-$LiAlH_4$@C decomposition mechanism: 1 step, not 2 based on ^{27}Al MAS NMR
- Volatiles are primarily H_2 with trace Et_2O
- ^{27}Al MAS NMR: desorbed $LiAlH_4$@NCMK-3 sample can be rehydrogenated at 1000 bar H_2 and 50 ˚C

Multi-gram quantities synthesized

Accomplishment: $LiAlH_4$ reversibility observed by nanoscaling: infiltrating N-doped carbon host

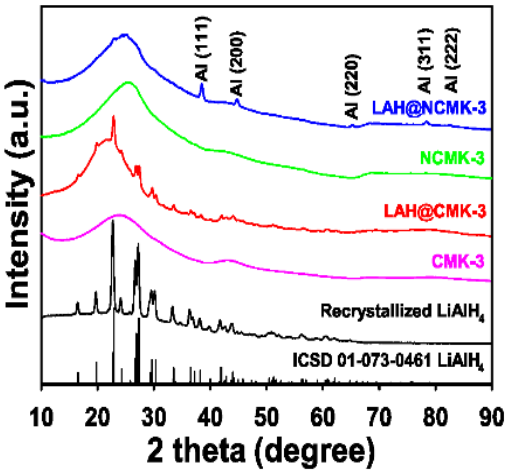
High-capacity hydrides $LiAlH_4$ (10.4 wt%) and AlH_3 (10.1 wt%) have fast desorption kinetics and could potentially meet DOE targets but are metastable as bulk materials

- **Decomposition reaction**

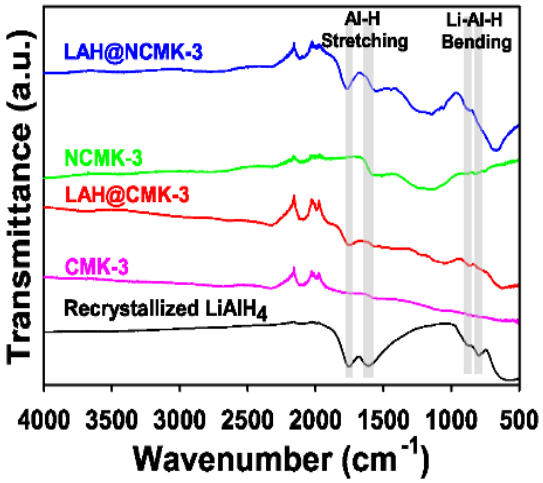
$LiAlH_4$@(porous C) → Al(0) + LiH + 1.5H_2

- **Only $LiAlH_4$ in the nitrogen-functionalized carbon ($LiAlH_4$@NCMK-3) can be rehydrogenated**
- **Reactive N sites identified by NMR**
  - **Pyridinic N and pyrrolic N**

Powder XRD

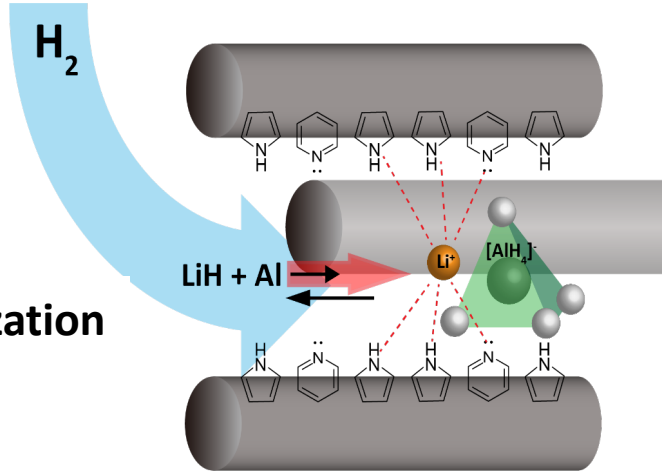


FTIR



Take-home lesson: Porous hosts hosts are not simple scaffolds that "support" metal hydride nanoparticles, but can enable reversible H_2 uptake and release can be rehydrogenated at 1000 bar H_2 and 50 ˚C

Next steps: Establish the degree of thermodynamic stabilization and determine the enthalpy and entropy of the process



Accomplishment: Borohydride-amide interactions observed suggest eutectic formation upon heating

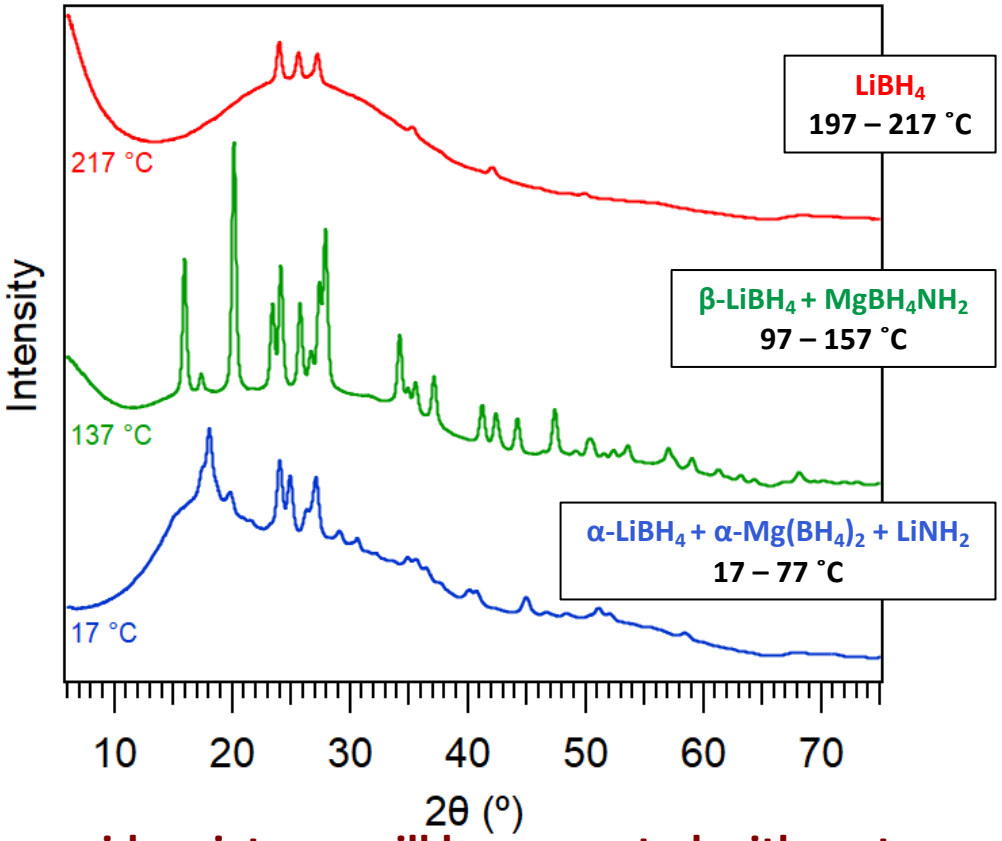
Objective: synthesize metal hydride eutectics with favorable thermodynamics and protic-hydridic interactions. Low onset of H_2 desorption (100 ˚C) was observed in a related dual cation/anion system. (Liu, Y., et al. *Int. J. Hydr. Energ.* 2018, **43**, 13981)

Approach:

- Synthesize $Mg(BH_4)_2$-$LiNH_2$ mixtures; evaluate H_2 storage properties using PCTPro (SNL)
- Observe phase evolution as a function of temperature by XRD (SNL, SSRL)
- Demonstrate eutectic melting occurs by high-pressure calorimetry (SNL)

Results:

- $Mg(BH_4)_2$-$LiNH_2$ exhibits 3 phase regimes upon heating
- New $MgBH_4NH_2$ phase observed is evidence that a eutectic forms



Take-home lesson: If successful, borohydride-amide mixtures will be generated with up to 13.0 wt% H_2 and low onset temp.

Path forward: Assess kinetics and thermodynamics using PCT/Sieverts and TGA/DSC analysis

Accomplishment: "Explainable" machine learning demonstrated as a new tool for discovery of new metal hydrides

Objective: Identify non-evident structure-property relationships and use these to discover or design new hydrogen storage materials

Approach: M. Whitman, V. Stavila et al. *J.Phys. Chem. Lett.* (2020) 11, 40

1) Data: HydPARK (compositions, ΔH, $\{P_{eq}, T\}$, H wt.%), "cleaned" to remove duplicates and incomplete entries

2) Features: generated by Magpie
Generate structurally agnostic features for each of the ~ 400 *complete* entries in HydPARK

"$LaNi_5$"

|||

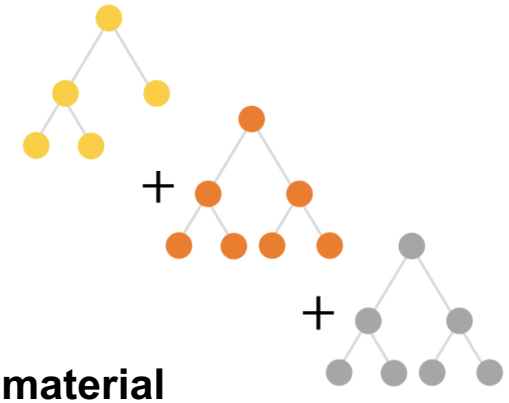
$\{v_{pa}^{Magpie}, \text{Feat\#2}, \ldots, \text{Feat\#145}\}$

An example feature describing a material generated by Magpie code:

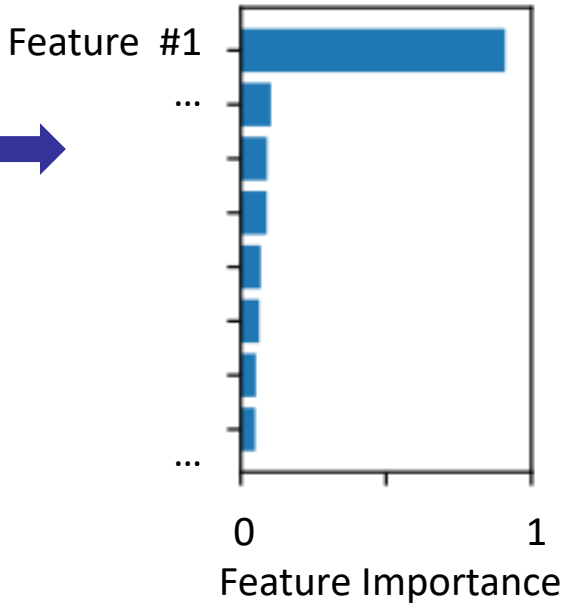
$$v_{pa}^{Magpie} = \sum_i f_i v_i$$

$f_i \equiv$ **composition fraction of element *i***
$v_i \equiv$ **ground state volume per atom of elemental solid *i***

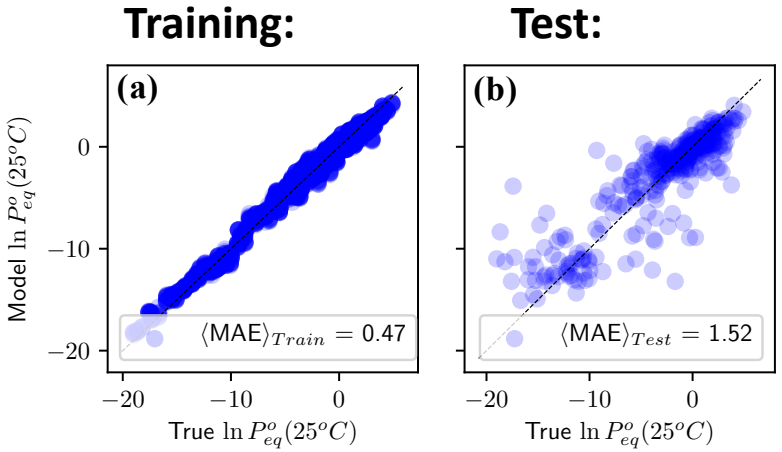
3) Model: Gradient Boosting Trees
Train a model to minimize the mean squared error of its equilibrium pressure predictions

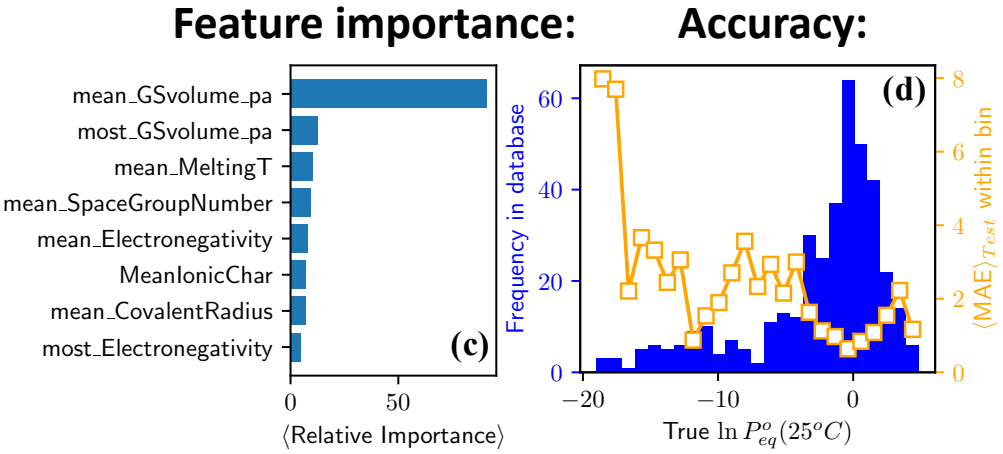


4) Feature Importance (Explainability)
An overall ranking of showing which features contribute most to model predictions

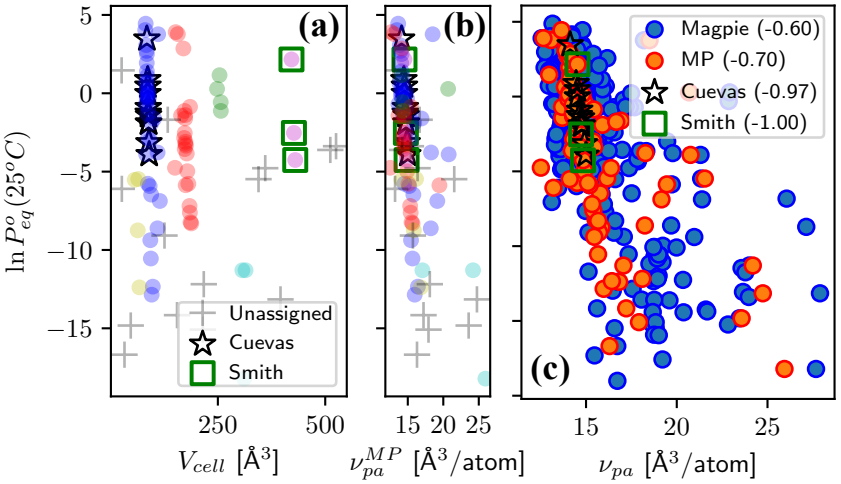


Accomplishment: ML identifies structure-property relationship predicting equilibrium P based only on material composition





Explainable ML model relates HydPARK data and published results (Cuevas, Smith) to a single feature (ν_{pa}^{Magpie}) related only to composition



This permits *a prioi* design of novel materials exhibiting a desired property value:

The model predicts that a known intermetallic (UNi_5) (unknown hydriding properties) would be one of the least stable hydrides. DFT calculations support this prediction.

	ν_{pa}	ΔH	E_f	ΔE_{def}	ΔE_H	V/V_0
UNi_5	13.17	-0.60	-285	65.2	-65.8	1.278
$CeNi_5$	13.76	-20.5	-353	49.3	-69.8	1.266
$LaNi_5$	14.38	-36.1	-224	44.3	-80.5	1.256

Take-home lesson: ML allows rapid screening of unexplored composition spaces to identify new materials with thermodynamics appropriate for vehicular storage

M. Whitman, V. Stavila et al.
***J.Phys. Chem. Lett.* (2020) 11, 40**

Sandia National Laboratories

HyMARC collaborates with Phase 2 Seedling Projects to facilitate their efforts to develop new hydride storage materials

The HyMARC team assists individual projects with:

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

- ***Magnesium Boride Etherates as Hydrogen Storage Materials*** (U. Hawaii, G. Severa, Lead)
  - 16 modified MgB_2 samples for ultrahigh-P hydrogenation
  - 10 modified MgB_2 samples for XAS at the ALS
- ***Electrolyte Assisted Hydrogen Storage Reactions*** (LiOx Power, J. Vajo, Lead)
  - 4 samples for ultrahigh-P hydrogenation
- ***ALD Synthesis of Novel Nanostructured Metal Borohydrides*** (NREL, S. Christensen, Lead)
  - 4 samples for ultrahigh-P hydrogenation
- ***Heteroatom-Modified and Compacted Zeolite-Templated Carbons for Gas Storage*** (Montana State Univ., N. P. Stadie, Lead)
  - > 50 AlC_x/BC_x samples and standands for XAS at ALS
- ***MOFs Containing Frustrated Lewis Pairs for Hydrogen Storage at Ambient Temperature*** (Univ. South FL, S. Ma, Lead)
  - 4 metal-organic framework samples for XAS at the ALS
- ***A Reversible Liquid Hydrogen Carrier System Based on Ammonium Formate and Captured CO2*** (Washington State Univ., H. Lin)
  - 4 MOF catalysts synthesized at Sandia were sent for formate catalysis testing

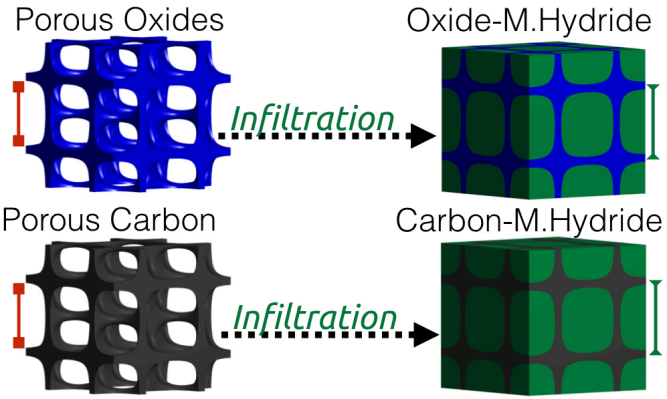
International Collaborations for Metal Hydride Research

- KAIST/Prof. Eun Son Cho: strain effects in hydrides (grad. student at Sandia 6 months)
- Aarhus Univ./Prof. Torben Jensen: Rietveld refinement nanoscale MgB_2)
- Univ. Nottingham/Prof. Sanliang Ling: DFT calculations for machine learning model development (joint paper published in *J. Phys. Chem. Lett.*)
- Univ. Cambridge/Prof. David Fairen-Jimenez: Pd nanoparticles@MOF (samples provided for high-P H_2 isotherm measurements; manuscript in preparation)
- Helmholz-Zentrum/Dr. Martin Dornheim: high pressure calorimetry on metal borohydride samples
- Max Planck Institute Solid State Research/Dr. Betina Lotsch: COFs for "molecular" hydride stabilization (samples of COF materials provided)
- Uppsala Univ./Prof. Martin Sahlberg: synthesis and X-ray diffraction on high-entropy alloys
- Univ. of Geneva/Hans Hagemann, Angelina Gigante: physiochemical properties of "solvent-free" $Mg(B_3H_8)_2$

HyMARC-NSF seedling projects
FY19 SSMC-EMN Supplemental Funding Opportunity

Tunable Isomorphic Architectures for Hydrogen Storage
Prof. Morgan Stefik, Univ. South Carolina
stefik@mailbox.sc.edu

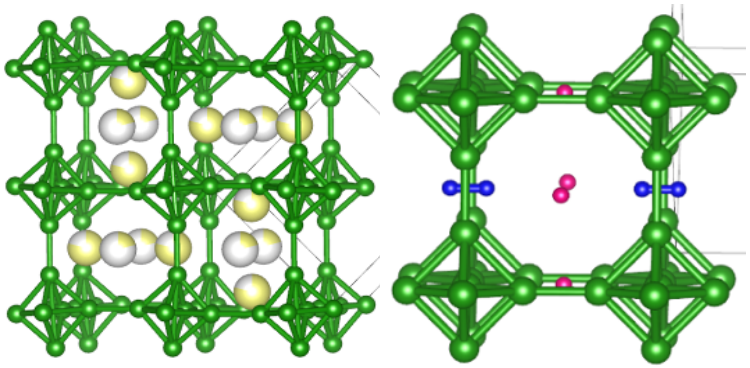
- Visit by graduate student Eric Williams Nov., 2019
- Synthesis of narrow-pore carbons



tunable: interface-chemistry, confinement and length scale

Transition Metal-Free Borides for Hydrogen Storage
FY19 SSMC-EMN Supplemental Funding Opportunity
Prof. Viktor Poltavets, Univ. New Orleans
vpoltave@uno.edu

- Visit by grad. student Roshni Bhuvan Oct-Nov 2019
- High-pressure rehydrogenation of doped-MgB_2
- Samples of Al- and Y-doped MgB_2 received for high-pressure experiments



Transition metal doping in MgB_2

Sandia National Laboratories | Lawrence Livermore National Laboratory | NIST

Summary of Future Task 2 (Hydrides) Work in FY20-21

KH-doped nanoscale Li_3N:

- **Combine systems modeling with experimental data to guide material modifications:**
  - **Effect of using porous carbon with smaller pores (< 6 nm)**
  - **Measure thermal conductivity under hydrogen and obtain additional kinetic data at lower temperatures**
  - **Develop computational models to test mechanism hypotheses, which will provide insight into how to accelerate H_2 uptake and release kinetics**

Systems analysis/materials development

- **Perform sensitivity analysis for several hydride storage materials to understand effects of changing material properties (e.g. hydride loading in porous host) and system operating conditions (e.g. desorption temperature) on overall approach to DOE targets**

Eutectics

- **$Mg(BH_4)_2$-$LiNH_2$ (*13.0 wt%*)**
  - **Perform PCT & calorimetry with synchrotron-based in-situ XRD to determine thermodynamics and phase nucleation properties of new eutectic phases**
- **$LiBH_4$-$Mg(NH_2)_2$ (*10.2 wt%*)**
  - **Synthesize phase-pure $Mg(NH_2)_2$**
  - **Assess reversibility and enthalpy and entropy of hydrogen release and uptake**

Metastable $LiAlH_4$:

- **Develop theory models to assess the thermodynamics of $LiAlH_4$@(porous carbon), including ΔH and ΔS, to understand extent of stabilization. Use these data to define next steps**
- **Extend strategy to AlH_3**

Machine learning:

- **Develop and implement strategies for expanding the metal hydride database**
- **Extend ML approach to high-entropy alloys**

We are grateful for the financial support of EERE/FCTO and for technical and programmatic guidance from Drs. Ned Stetson, Jesse Adams, and Zeric Hulvey

HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

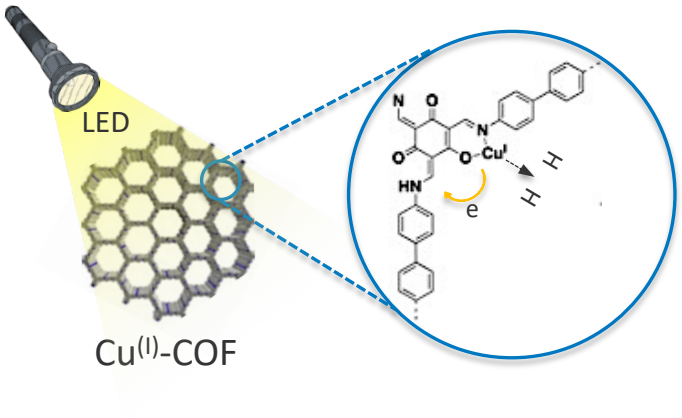
Technical Backup Slides

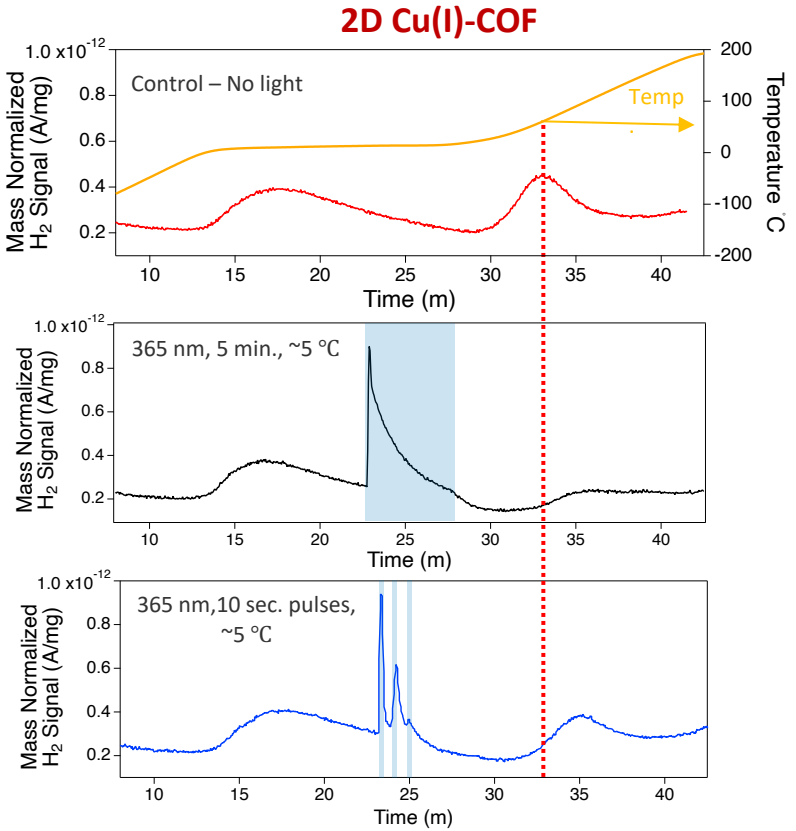
Task 1.D.2. Thermal/photo-responsive sorbent matrices

Relevant technical target: 'Tuning' isosteric heats of H_2 adsorption

Approach:

- Cu loaded into a framework, heat treatment to generate open $Cu^{(I)}$ binding site, enthalpy of H_2 desorption ~15 k/mol
- Photoinduced metal-ligand charge transfer from $Cu^{(I)}$ to Frameworke generates 'transient' $Cu^{(II)}$ with decreased π-backbonding
- H_2 evolves when exposed to light



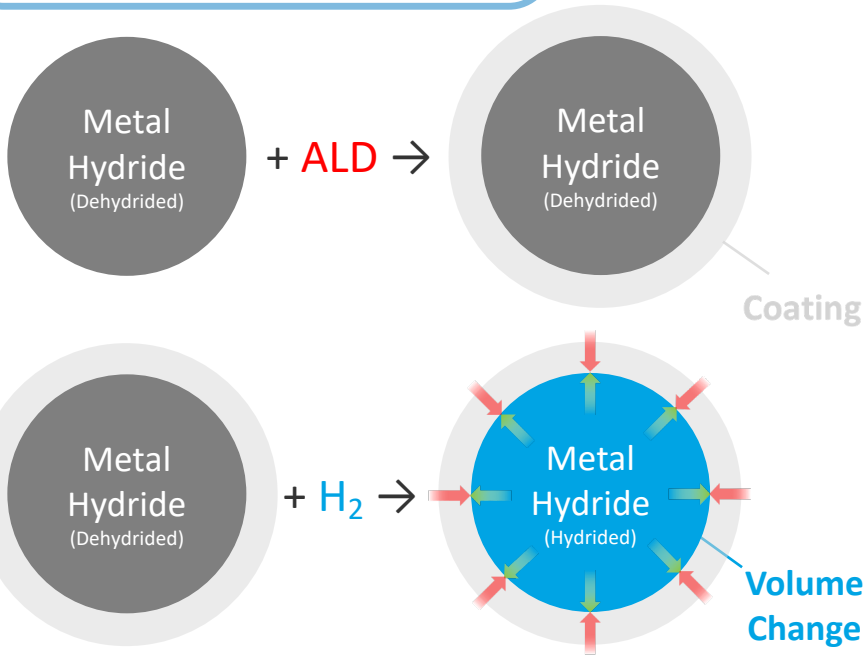


Accomplishment: Successfully demonstrated 'on demand' release of H_2 from sorbent

Project success → 'On demand' ambient temperature H_2 delivery

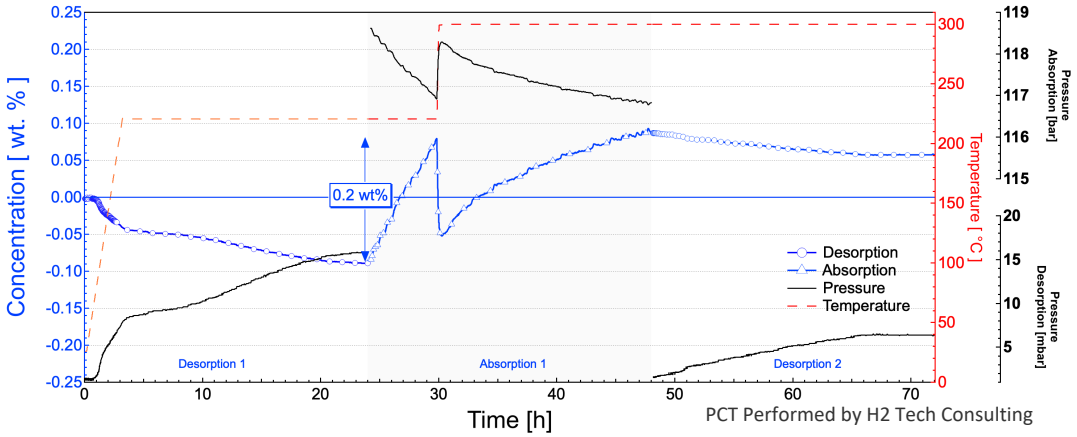
A&P: 2.D.9 Nano-confined metal hydrides under mechanical stress

Relevance: Metal hydrides under applied stress/strain can lead to improved operability performance.

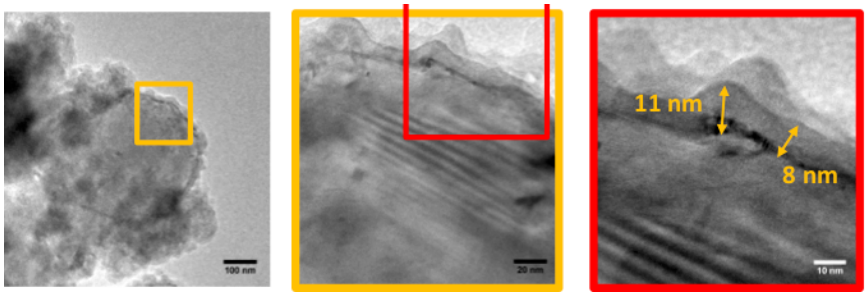


Approach: *Use atomic layer deposition (ALD) to encapsulate metal hydrides for applied stress/strain.*

PCT: ALD Boron Nitride / Magnesium



PCT Performed by H2 Tech Consulting



TEM: Mg coated with BN (Images: A. Gualding)

- Materials Synthesis & Testing
- Low H_2 uptake (0.2 wt%) after charging
- Pursuing Al_2O_3 coatings: better H_2 transport

HyMARC

Sandia National Laboratories

Lawrence Livermore National Laboratory

NREL NATIONAL RENEWABLE ENERGY LABORATORY

Summary of progress toward HyMARC milestones

Milestone	Criteria	End Date	Status
Focus 2.A.1: Phase diagrams/ternary hydrides	*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.*	9/30/2019	Achieved for Li-N-H system
Focus 2.C: Activation of B-B and B-H bonds	Demonstrate computational approach to enable screening of additives to activate B-B bonds in MgB_2.	6/30/2019	Complete
2.F Development of machine-learning for discovery of new metal hydrides	Assemble computational database of metal hydride thermodynamic properties and identify descriptive features using conventional ML classifiers	3/31/2020	Complete

Metal hydride thermodynamics: $Mg(BH_4)_2$ + 0.3 THF

Relevance

Technical target addressed:

usable gravimetric capacity, min/max delivery temperature, operational cycle life

Approach

Materials:

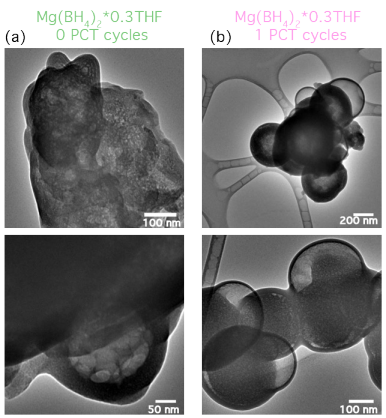
lower melting point of $Mg(BH_4)_2$ by adding THF, to increase H_2 cyclability of the material at 3 wt% and T < 180˚C

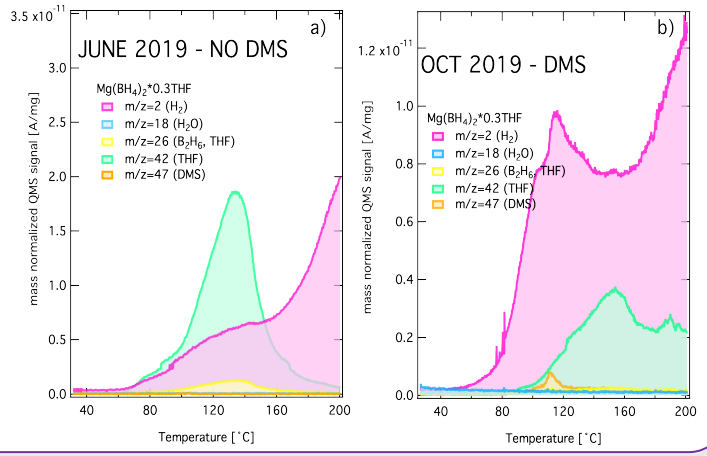
Accomplishments

Moving the bar:

- ✓ Melting point was lowered by ~100 ˚C
- ✓ 3 H_2 cycles were demonstrated by NMR at 1 wt% and T ≤ 180˚C

- ✓ "Dead weight" THF is removed after 1st H_2 desorption
- ✓ TEM shows "encapsulation" after 1st PCT cycle
- ✓ Solvent impurities affect material performance (e.g. DMS)





Collaborations

Team & Efforts:

Pacific Northwest National Laboratory — Tom Autrey (PI), Mark Bowman: NMR, XRD, project coordination

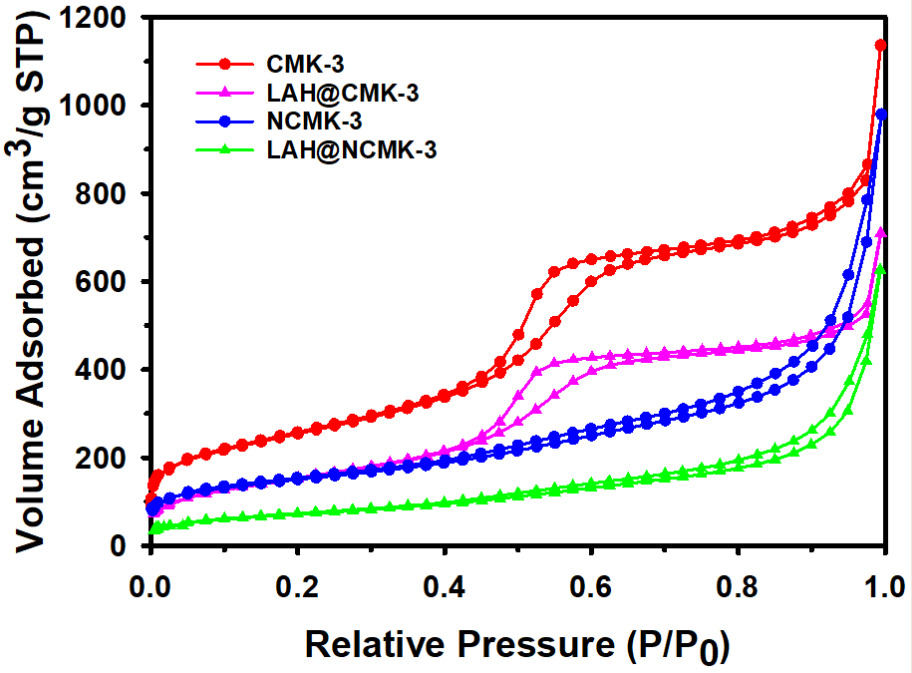
University of Hawai'i — Craig Jensen (PI), Sunil Shrestha: material synthesis, H_2 cycling (PCT), NMR

NREL Transforming ENERGY — Tom Gennett, Noemi Leick, Robert Bell: TPD, TEM

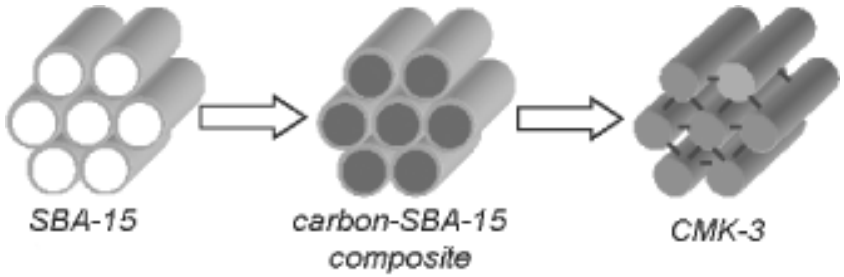
Future Work:

Find another additive/system that enables H_2 wt% > 1

Accomplishment: Metastable hydride stabilized and cycled $LiAlH_4$ confinement within N-functionalized porous carbons



Nitrogen adsorption/desorption isotherms at 77 K of $LiAlH_4$ infiltrated mesoporous carbon scaffolds

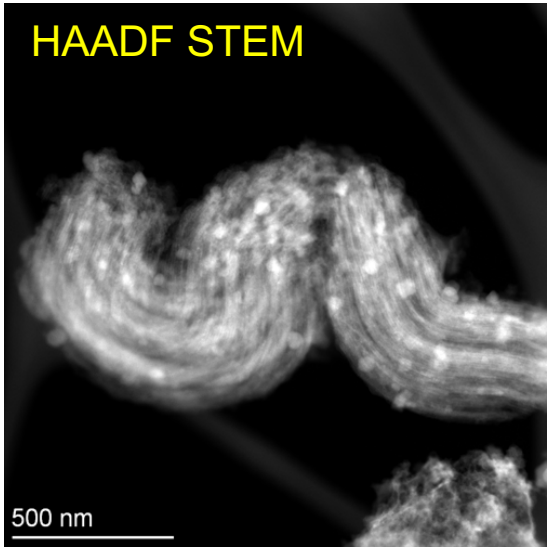


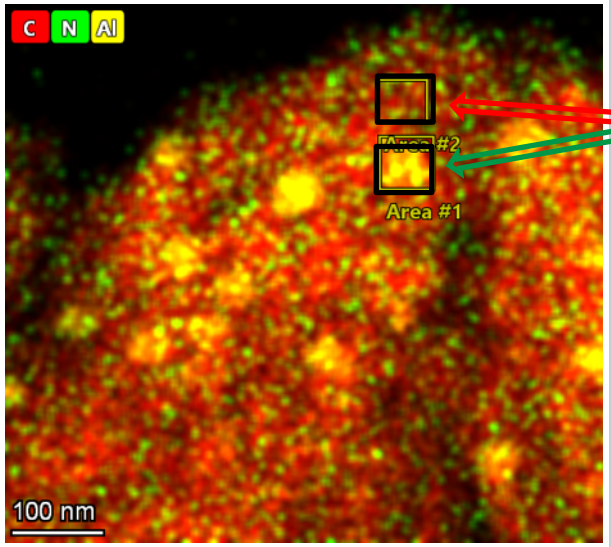
Sample	BET surface area (m^2 g^{-1})	Total volume (cm^3 g^{-1})
CMK-3	911	1.76
LAH@CMK-3	560	1.10
NCMK-3	534	1.51
LAH@NCMK-3	261	0.97

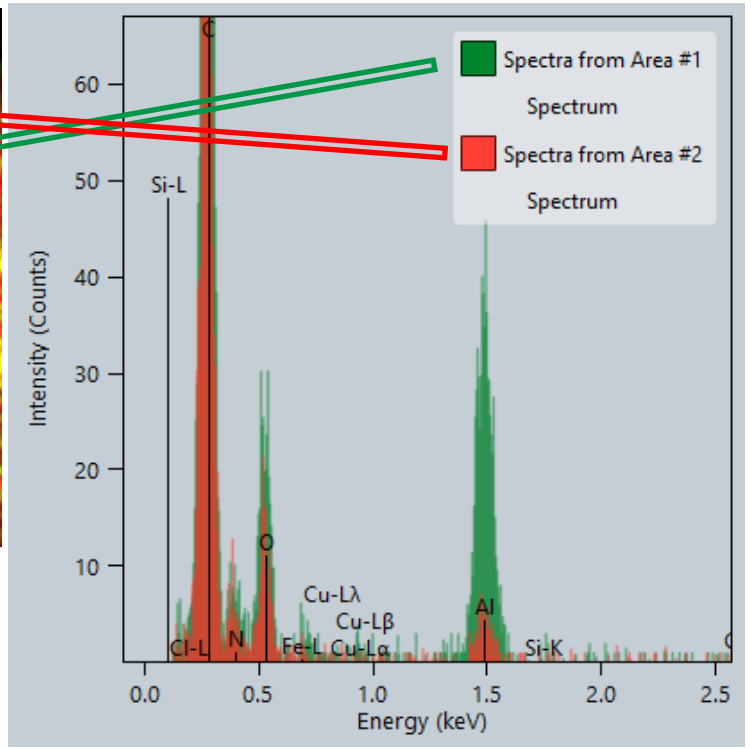
Summary of calculated BET surface area and total pore volumes with nitrogen adsorption / desorption isotherms

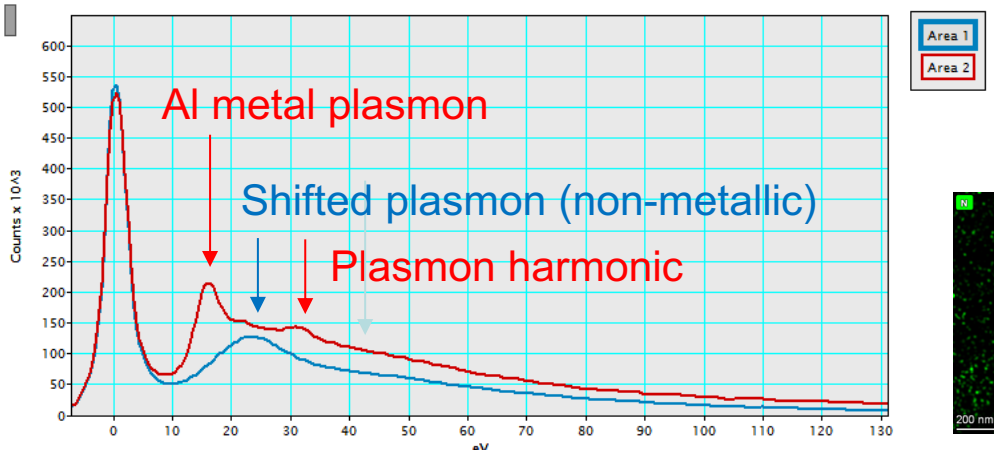
⇒ **Successfully synthesized lithium alanate nanoparticles confined in 6 nm CMK-3 carbons**

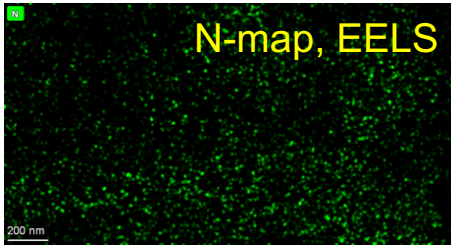
TEM and EDS confirm presence of $LiAlH_4$ nanoclusters

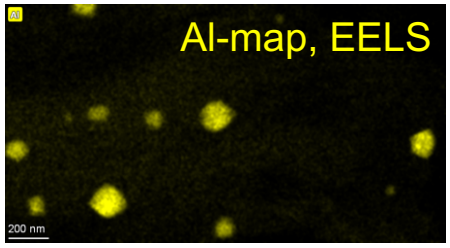












- STEM images of rehydrogenated $LAlH_4$@NCMK-3 reveal the distribution of Al species
- EELS composition maps confirm presence of metallic Al (plasmon peak at 15 eV and 2nd harmonic at 30 eV), as well as alanate particles (plasmon peak at 24 eV)

Assessment of $Mg(BH_4)_2$ phases to improve strategies for materials engineering

Fundamental study designed to address these DOE Technical Targets:

1. min/max delivery temperature (thermodynamics)
2. cycle life (reversibility)
3. charging/discharging rates (kinetics)

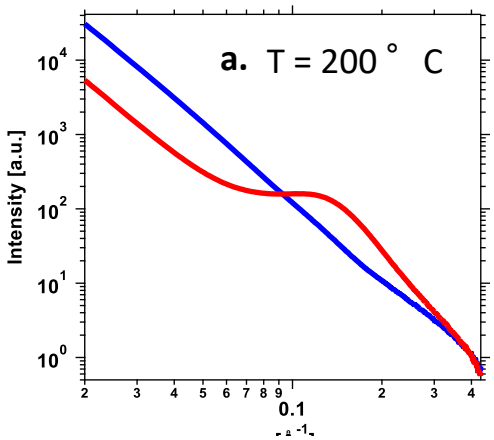
Porous γ-$Mg(BH_4)_2$ used as starting material for modifying dehydriding/rehydriding properties via additives – ALD, etherates, metals (Ti, Co, Ni), eutectic mixtures, etc.

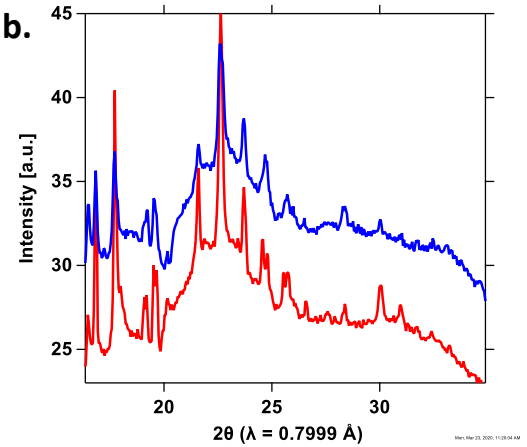
Non-porous hexagonal: α → (180 ˚C) β

Porous cubic: γ → (160 ˚C) ε → (180 ˚C) β

Residual porosity?

Structural refinement of ε-phase may also provide bridge between α and γ decomposition routes





β generated from α

β generated from γ

SAXS[a]/WAXS[b] at SSRL indicates intrinsic porosity is maintained throughout decomposition of γ-phase

-residual porosity is not necessarily externally available

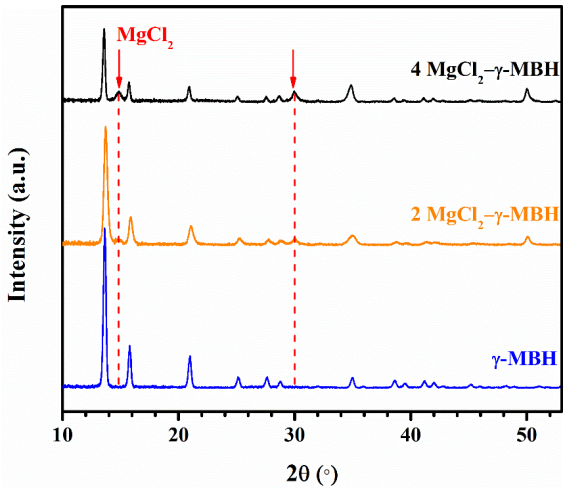
-can infiltrate the pores in the γ-phase and destabilize intermediates

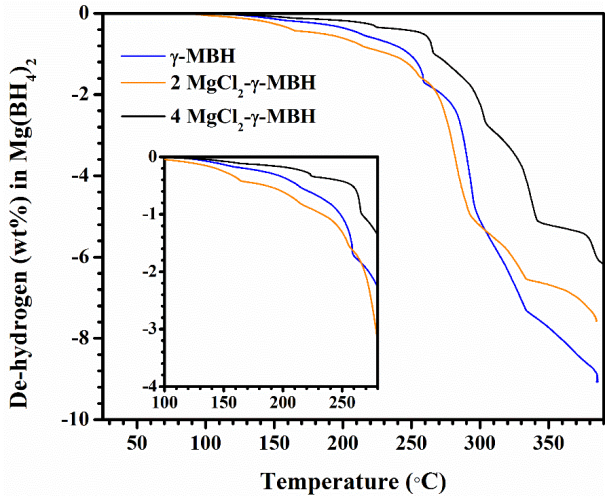
Example: SAXS/WAXS shows 100 ALD cycles of trimethylaluminum (TMA) on γ-$Mg(BH_4)_2$ generate MgH_2 and Mg metal ~100 ˚ C lower than neat γ-$Mg(BH_4)_2$

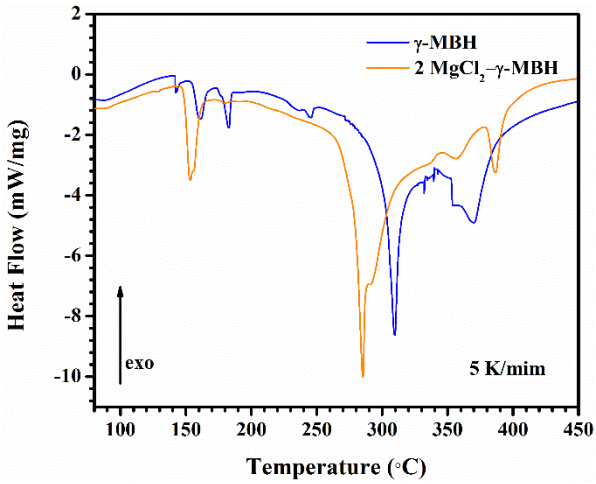
Design and synthesis of $MgCl_2$ – decorated $Mg(BH4)_2$

Relevant DOE Technical System Targets

STORAGE PARAMETER	Units	2020	2025
System Gravimetric Capacity	kg H_2/kg system	4.5%	5.5%
System Volumetric Capacity	kg H_2/L system	3%	4%
Min (max) delivery pressure	bar	5 (12)	5 (12)
Operating ambient temperature	°C	-40/60	-40/60
System fill time	min	3–5	3–5





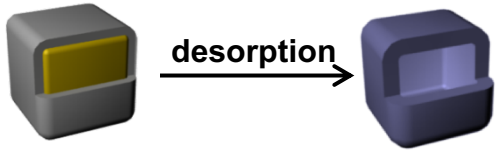


Results:

- **Larger amount of hydrogen release in 2 $MgCl_2$-γ-MBH < 250 °C**
- **Dehydrogenation of 2 $MgCl_2$-γ-MBH starts at ~100 °C**

γ-MBH/$MgCl_2$ — **B and Mg K-edge of XAS** — **Pure γ-MBH**

Right Surface: Boron oxide and $MgCl_2$
Bulk: Boron oxide and $MgBH_4$
Left Surface: Boron oxide, Cl, MgCl(OH) Bulk: Mg, and B_nH_m **but <u>no boron oxide</u>**



Right Surface: Boron oxide and MgO
Bulk: Boron oxide and $MgBH_4$
Left Surface: Boron oxide
Bulk: Mg, Cl, B_nH_m, **and <u>boron oxide</u>**

B-B bond activation for accelerate H_2 uptake kinetics

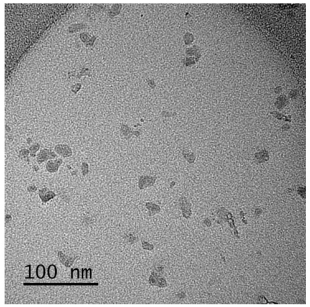
Published work: "Investigating Possible Kinetic Limitations to MgB_2 Hydrogenation"
*International Journal of Hydrogen Energy **44** (2019) 31239-31256 (Sandia, LLNL,LBNL)*

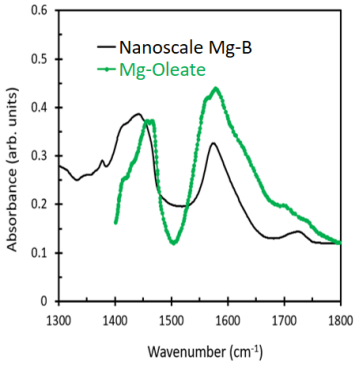
What We Learned (from Pd, Fe and TiF_3 additives with MgB_2):

- ✓ **H-H bond dissociation does not limit the rate of hydrogenation of MgB_2**
- ✓ **Surface diffusion of hydrogen atoms cannot be a limiting factor for MgB_2 hydrogenation**
- ✓ **Experiment and theory (LLNL) demonstrates nucleation kinetics can supersede thermodynamics in determining additive reaction pathways (shown for TiF_3/MgB_2).**

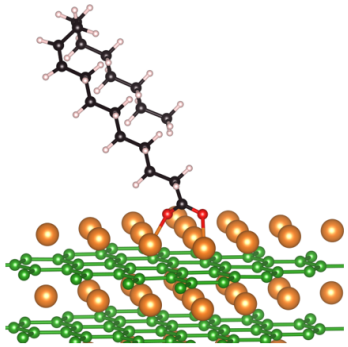
Nanoscale Mg-B:

Ball milling MgB_2 in oleic acid/oleylamine produces Mg-B nanosheets…

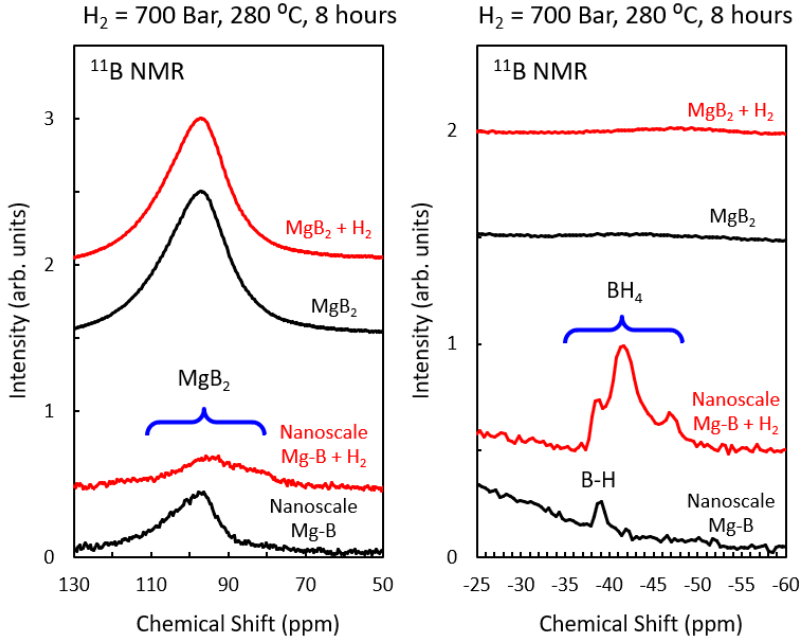




oleate binds to Mg^{2+}…



… predicted by LLNL theory



Nanoscale Mg-B hydrogenates to BH_4 at temperatures well below MgB_2

Publications

- A. Schneemann, L.F. Wan, A.S. Lipton, Y.-S. Liu, J.L. Snider, A.A. Baker, J.D. Sugar, C.D. Spataru, J. Guo, A.S. Autrey, M. Jørgensen, T.R. Jensen, B.C. Wood, M.D. Allendorf, and V. Stavila, "Limit of nanoconfinement? 'Molecular' magnesium borohydride captured in a noninnocent metal-organic framework," submitted to *ACS Nano* (2020).
- B.C. Wood, T.W. Heo, S. Kang, S. Li, and L.F. Wan, "Beyond idealized models of nanoscale metal hydrides for hydrogen storage," *Ind. Eng. Chem. Res*., in revision (2020) [invited article].
- S. Jeong, T.W. Heo, J. Oktawiec, R. Shi, S. Kang, J.L. White, A. Schneemann, E.W. Zaia, L.F. Wan, K.G. Ray, Y.-S. Liu, V. Stavila, J. Guo, J.R. Long, B.C. Wood, and J.J. Urban, "A Mechanistic Analysis of Phase Evolution and Hydrogen Storage Behavior in Nanocrystalline $Mg(BH_4)_2$ within Reduced Graphene Oxide," *ACS Nano*, in press (2020).
- M. Jørgensen, P.T. Shea, A.W. Tomich, J.B. Varley, M. Bercx, S. Lovera, R. Černý, W. Zhou, T.J. Udovic, V. Lavallo, T.R. Jensen, B.C. Wood, and V. Stavila, "Understanding Superionic Conductivity in Lithium and Sodium Salts of Weakly Coordinating Closo-Hexahalocarbaborate Anions," *Chem. Mater.*, in press (2020).
- T.W. Heo and B.C. Wood, "On thermodynamic and kinetic mechanisms for stabilizing surface solid solutions," *ACS Appl. Mater. Interf.* **11**, 48487 (2019).
- T.W. Heo, K.B. Colas, A.T. Motta, and L.-Q. Chen, "A phase-field model for hydride formation in polycrystalline metals: Application to δ-hydride in zirconium alloys," *Acta Mater.* **181**, 262 (2019).
- Y.-S. Liu, L.E. Klebanoff, P. Wijeratne, D.F. Cowgill, V. Stavila, T.W. Heo, S. Kang, A.A. Baker, J.R.I. Lee, K.G. Ray, J.D Sugar, and B.C. Wood, "Investigating possible kinetic limitations to MgB_2 hydrogenation", *Int. J. Hydrogen Energy* **44**, 31239 (2019).
- L.F. Wan, E.S. Cho, T. Marangoni, P.T. Shea, S. Kang, C. Rogers, E.W. Zaia, R.R. Cloke, B.C. Wood, F.R. Fisher, J.J. Urban, and D. Prendergast, "Edge-functionalized graphene nanoribbon encapsulation to enhance stability and control kinetics of hydrogen storage materials," *Chem. Mater.* **31**, 2960 (2019).
- X.W. Zhou, S. Kang, T.W. Heo, B.C. Wood, V. Stavila, and M.D. Allendorf, "An analytical bond order potential for Mg-H systems," *ChemPhysChem* **20**, 1404 (2019).
- S. Kang, T.W. Heo, M.D. Allendorf, and B.C. Wood, "Morphology-dependent stability of complex metal hydrides and their intermediates using first-principles calculations," *ChemPhysChem* **20**, 1340 (2019).

Publications

- "A Mechanistic Analysis of Phase Evolution and Hydrogen Storage Behavior in Nanocrystalline $Mg(BH_4)_2$ within Reduced Graphene Oxide", S. Jeong, T. W. Heo, J. Oktawiec, R. Shi, S. Y. Kang, J. White, A. Schneemann, E. Zaia, L. F. Wan, K. Ray, Y.-S. Liu, V. Stavila, J.-H. Guo, J. Long, B. Wood, J. Urban, ACS Nano, Accepted, (2020). Doi: 10.1021/acsnano.9b07454
- "Runaway' carbon dioxide conversion leads to enhanced sorption in a nanohybrid porous magnesium metal hydride", S. Jeong, P. Milner, L. F. Wan, Y.-S. Liu, J. Oktawiec, E. W. Zaia, J.-H. Guo, D. Prendergast, J. R. Long, and J. J. Urban, Advanced Materials 2019, 31(44):e1904252. doi: 10.1002/adma.201904252. (Work highlighted in C&E News.)
- "Identifying the Role of Dynamic Surface Hydroxides in the Dehydrogenation of Ti-doped $NaAlH_4$", J. L. White, A. J. E. Rowberg, L. F. Wan, S. Y. Kang, T. Ogitsu, R. D. Kolasinski, J. A. Whaley, A. Baker, J. R. I. Lee, Y. S. Liu, L. Trotochaud, J.-H. Guo, V. Stavila, D. Prendergast, H. Bluhm, M. D. Allendorf, B. C. Wood, F. E. Gabaly, ACS Appl. Mater. Interfaces 2019, 11, 4930-4941.
- "In-Situ/Operando X-ray Characterization of Metal Hydrides", Y. S. Liu, S. Jeong, J. L. White, X. Feng, E. S. Cho, V. Stavila, M. D. Allendorf, J. J. Urban, J.-H. Guo, ChemPhysChem 2019, 20, 1-12.
- "Edge-functionalized graphene nanoribbon encapsulation to enhance stability and control kinetics of hydrogen storage materials" L. F. Wan, E. S. Cho, T. Marangoni, P. Shea, S. Y. Kang, C. Rogers, E. Zaia, R. R. Cloke, B. C. Wood, F. R. Fischer, J. J. Urban, D. Prendergast, Chem. Mater. 2019, 31(8), 2960-2970, DOI: 10.1021/acs.chemmater.9b00494.
- "Efficient Hydrogen Production from Methanol Using A Single-Site Pt_1/CeO_2 Catalyst" L. Chen, K. Hou, Y.-S. Liu, Zh. Qi, Q. Zheng, Y. Lu, J. Chen, J. Chen, Ch. Pao, Sh. Wang, Y. Li, Sh. Xie, F. Liu, D. Prendergast, L. Klebanoff, V. Stavila, M. Allendorf, J.-H. Guo, L. Zheng, J. Su, A. G. Somorjai, JACS, 2019, 141(45), 17995-17999
- W. A. Braunecker, S. Shulda, M. B. Martinez, K. E. Hurst, J. T. Koubek, S. Zaccarine, R. E. Mow, S. Pylypenko, A. Sellinger, T. Gennett, J. C. Johnson, "Thermal Activation of a Copper-Loaded Covalent Organic Framework for Near-Ambient Temperature Hydrogen Storage and Delivery", ACS Materials Lett., 2, 227 (2020)
- C. Sugai, S. Kim, G. Severa, J. L. White, N. Leick, M. B. Martinez, T. Gennett, V. Stavila, C. Jensen "Kinetic Enhancement of Direct Hydrogenation of MgB2 to Mg(BH4)2 upon Mechanical Milling with THF, MgH2, and/or Mg" ChemPhysChem. 10, 1301 (2019)
- S. Jeong, P.J. Milner, L. F. Wan, Y.-S. Liu, J. Oktawiec, E. W. Zaia, A. C. Forse, N. Leick, T. Gennett, J. Guo,

Publications

- Stauch, T.; Chakraborty, R.; Head-Gordon, M. “Quantum chemical modeling of pressure-induced spin crossover in octahedral metal-ligand complexes” ChemPhysChem, **2019**, *20*, 2742.
- Jaramillo, D. E.; Reed, D. A.; Jiang, H. Z. H.; Oktawiec, J.; Mara, M. W.; Forse, A. C.; Lussier, D. J.; Murphy, R. A.; Cunningham, M.; Colombo, A.; Shuh, D. K.; Reimer, J. A.; Long, J. R. “Selective nitrogen adsorption via backbonding in a metal–organic framework with exposed vanadium sites” *Nat. Mater.* **2020**, DOI: 10.1038/s41563-019-0597-8.
- Muller K.W., S. Autrey, and K.P. Brooks. 2018. "Releasing Hydrogen at High Pressures from Liquid Carriers: Aspects for the H2 Delivery to Fueling Stations." *Energy and Fuels*. doi:10.1021/acs.energyfuels.8b01724
- Yu Y., T. He, A. Wu, Q. Pei, A.J. Karkamkar, S. Autrey, and P. Chen. 2019. "Reversible hydrogen uptake/release over sodium phenoxide-cyclohexanolae pair." *Angewandte Chemie International Edition* 58, no. 10:3102-3107. doi:10.1002/anie.201810945
- Hirscher M., S. Autrey, and S. Orimo. 2019. "Hydrogen Energy." *ChemPhysChem* 20, no. 10:1157-1157. doi:10.1002/cphc.201900429
- Grubel K., H. Jeong, C. Yoon, and S. Autrey. 2020. "Challenges and Opportunities for using Formate to Store, Transport and Utilize Hydrogen." *Journal of Energy Chemistry* 41. doi:10.1016/j.jechem.2019.05.016
- Allendorf M.D., Z. Hulvey, T. Gennett, A. Alauddin, S. Autrey, J. Camp, and E. Cho, et al. 2018. "An Assessment of Strategies for the Development of Solid-State adsorbents for Vehicular Hydrogen Storage." Energy and Environmental Science 11, no. 10:2784-2812. doi:10.1039/c8ee01085d
- Tsumori N., Y. Himeda, S. Autrey, and Q. Xu. 2019. "Immobilization of highly active bimetallic PdAu nanoparticles onto nanocarbons for dehydrogenation of formic acid." Journal of Materials Chemistry A 7, no. 32:18835-18839. PNNL-SA-148310. doi:10.1039/c9ta06014f

Presentations

- S. Kang, “Modeling of Thermodynamics and Nucleation Kinetics in the Mg-B-H System,” Orlando, FL, USA, April 2019.
- S. Kang, “Size-dependent lattice parameters of Mg nanoparticles,” KAIST Workshop, Daejeon, South Korea, May 2019.
- S. Kang, “Improved thermodynamics and phase diagram prediction of the Mg-B-H system,” HyMARC Face-to-face Meeting, PNNL, July 2019.
- S. Wan, “Modeling of B-H and B-B bond activation by catalytic additives,” HyMARC Face-to-face Meeting, PNNL, July 2019.
- S. Weitzner, “Modeling the performance and stability of formate synthesis and dehydrogenation catalysts: Atomistic modeling strategies,” HyMARC Face-to-face Meeting, PNNL, July 2019.
- T.W. Heo, “Interfaces, microstructures, and mechanical stress in metal hydrides,” HyMARC Face-to-face Meeting, PNNL, July 2019.
- S. Kang, “Predicting chemical and structural properties of complex interfaces in battery and hydrogen storage materials,” Warsaw, Poland, September 2019.
- B.C. Wood, “Multiscale modeling of reactive interfaces for chemical storage of hydrogen fuel,” American Chemical Society Spring Meeting, Orlando, FL, April 2019 [invited].
- B.C. Wood, “Heading towards a hydrogen-powered future,” Modesto Area Partners in Science Lecture Series, Modesto, CA, September 2019.
- B.C. Wood, “HyMARC: Atomistic modeling of metal hydrides for hydrogen storage,” Helmholtz-Zentrum für Material und Küstenforschung, Geestacht, Germany, July 2019.
- T.W. Heo, “HyMARC: Mesoscale modeling of metal hydrides for hydrogen storage,” Helmholtz-Zentrum für Material und Küstenforschung, Geesthacht, Germany, July 2019.
- B.C. Wood, “Multiscale simulations of metal hydrides for the DOE HyMARC Consortium,” Helmut-Schmidt University, Hamburg, Germany, July 2019.
- B.C. Wood, “Computational hydrogen materials research at the U.S. Department of Energy,” Korea Institute of Science and Technology, Seoul, Korea, May 2019.

Presentations

Presentations

- Veccham, S. P.; Head-Gordon, M. “Assessment of the performance of density functionals for hydrogen storage in sorbents” 2019 National ACS Meetings, Orland, FL, March, 2019.
- Anastasopoulou, A.; Breunig, H. “Techno-economic and life cycle assessment framework for methane storage in advanced porous Materials” 2019 International Symposium on Sustainable Systems & Technology (ISSST), Portland, OR, June, 2019.
- Barnett, B. R. “Structural and kinetic effects of framework-dihyrogen covalency” Nanoporous Materials Seminar, Center for Gas Separations, Berkeley, CA June 26, 2019
- Barnett, B. R.; Long, J. R. “Leveraging π-basicity in metal–organic frameworks for ambient temperature hydrogen storage: structural, thermodynamic, and kinetic insights,” 258th American Chemical Society National Meeting, San Diego, CA, August 27, 2019.
- Furukawa, H. “Design and synthesis of metal–organic frameworks for hydrogen storage applications,” Department Seminar, Tokyo Metropolitan University, Tokyo, Japan, September 10, 2019.
- Barnett, B. R. “Coordination-driven approaches to gas separations and fuel storage in metal–organic frameworks” Department of Chemistry, University of Michigan Ann Arbor, November 25, 2019.
- Barnett, B. R. “Coordination-driven approaches to gas separations and fuel storage in metal–organic frameworks” Department of Chemistry, University at Albany, SUNY, December 5, 2019.
- Barnett, B. R. “Coordination-driven approaches to gas separations and fuel storage in metal–organic frameworks” Department of Chemistry, University of Texas at Austin, December 9, 2019.
- Halter, D. P., “Molecules, Materials, and Methods for Advanced Electrocatalysis, Sustainable Synthesis, and Energy Storage” Sustainable Chemistry Symposium, Mainz, December 11, 2019.
- Barnett, B. R. “Coordination-driven approaches to gas separations and fuel storage in metal–organic frameworks” Department of Chemistry, University of Rochester, January 6, 2020.
- Barnett, B.R. “Coordination-driven approaches to gas separations and fuel storage in metal–organic frameworks” Department of Chemistry, Texas A&M University, January 16, 2020.
- Barnett, B. R. “Coordination-driven approaches to gas separations and fuel storage in metal–organic frameworks” Department of Chemistry and Biochemistry, University of Maryland, College Park, January 13, 2020.

Presentations

- Invited speaker at the International Conference on Boron Chemistry (ICBC-II) Taiyuan, China July 2019 (Autrey)
- Vice chair (chair elect 2021) Gordon Research Conference on Hydrogen-Metal Systems July 2019 (Autrey)
- Edited special addition on Hydrogen Energy: Michael Hirscher, Tom Autrey, Shin-ichi Orimo. Hydrogen Energy. ChemPhysChem. 2019. doi.org/10.1002/cphc.201900429 PNNL-SA-143944.
- Symposium organizer, Energy Storage in Chemical Bonds, ACS National Meeting Spring 2019 (Autrey)
- Symposium organizer Materials, Modeling and Technoeconomic Impacts for Large-Scale Hydrogen and Energy Applications MRS Spring Meeting 2020 (Ginovska)
- Symposium organizer, Hydrogen-Rich Systems: Materials Chemistry for Energy Storage and delivery, Pacifichem 2020 (Bowden)
- "Hybrid and Functionalized MOFs for Fuel Production, Transport, and Storage," M. D. Allendorf, *Hybrid Functional Porous Materials: MOFs, Silica and Conductive Polymers symposium, ACS Fall 2019 Meeting,* San Diego, CA Aug. 25 – 30, 2019. Invited presentation.
- "Understanding Hydrogen Desorption Pathways in Nanoscale Metal Hydrides", V. Stavila, *Gordon Research Conference on Hydrogen-Metal Systems*, Castelldefels, Spain, June 30 – July 5, 2019.
- "Sustainable hydrogen storage in polyalcohols enabled by metal-organic framework catalysts," V. Stavila, L. Klebanoff, J. Su, G. Somorjai, D. Prendergast, T. Autrey, M. Allendorf, *ACS Spring Meeting*, Mar. 31 – Apr. 4, 2019, Orlando, FL.
- "Multiscale modeling of reactive interfaces for chemical storage of hydrogen fuel," B. Wood, T. W. Heo, S. Kang, K. Ray, L. Wan, A. Rowberg, A. Baker, J. Lee, J. White, F. El Gabaly, V. Stavila, L. Klebanoff, *ACS Spring Meeting*, Mar. 31 – Apr. 4, 2019, Orlando, FL.
- M. D. Allendorf: invited presentations at *EuroMOF 2019* (Paris) and Depts. of Chemistry, Univ. Minn., Boston College, and Washington State Univ.

Presentations

- B.C. Wood, “Complex dynamics in metal hydroborates: From hydrogen storage to solid-state batteries,” European Materials Research Society Fall Meeting, Warsaw, Poland, September 2019.
- B.C. Wood, “Probing interfaces in complex metal hydrides through multiscale simulations,” Gordon Research Conference on Metal-Hydrogen Systems, Barcelona, Spain, July 2019 [poster].
- T.W. Heo, “Mesoscale modeling of metal-hydrogen Interactions,” 4th International Symposium on Phase-Field Modelling in Materials Science (PF19), Bochum, Germany, July 2019.
- T.W. Heo, “Mesoscale modeling of mechanical stress, thermal transport, and phase transformations in hydrogen storage materials,” Korea Advanced Institute of Science and Technology, Daejeon, Korea, May 2019 [invited].
- T.W. Heo, “Multiscale modeling of interface kinetics within HyMARC,” DOE Hydrogen and Fuel Cells Program Annual Merit Review Meeting, Washington, D.C., April 2019.
- T.W. Heo, “Mesoscale modeling of phase transformations in metal hydrides for hydrogen storage,” Materials Research Society Spring Meeting, Phoenix, AZ, April 2019.
- S. Wan, “Edge-functionalized graphene nanoribbon encapsulation to enhance stability and control kinetics of hydrogen storage materials,” American Chemical Society National Meeting, Orlando, FL, April 2019.
- S. Wan, “High-throughput study of metal dopants to improve the hydrogenation performance of MgB_2” American Chemical Society National Meeting, Orlando, FL, April 2019.
- S. Wan, “Atomic-scale understanding of the catalytic effects of impurities in hydrogen storage materials,” Gordon Research Seminar, Barcelona, Spain, July 2019.
- B.C. Wood, “Multiscale modeling of reactive interfaces in support of the DOE Energy Materials Network,” Electrochemical Society Spring Meeting, Atlanta, GA, October 2019 [invited].
- B.C. Wood, “Chemical reactions at interfaces: Simulating B-B bond activation in MgB_2,” Borohydride Workshop, Whitefish, MT, October 2019.
- S. Kang, “Thermodynamics vs. kinetics and chemistry vs. materials science,” Borohydride Workshop, Whitefish, MT, October 2019.

Presentations

- Invited presentation: “In-situ/operando soft x-ray spectroscopy of energy materials and catalysis”, Jinghua Guo, European Materials Research Society Spring Meeting, Nice, France (May 27th - 31st, 2019)
- Invited presentation: “In-situ/operando soft x-ray spectroscopy interfacial characterization: R&D and science applications”, Jinghua Guo, INSPIRE: Strategic Upgrades of the IOS Beamline at NSLS-II, Brookhaven National Lab. (September 10th - 11th, 2019)
- Invited presentation: “Soft x-ray spectroscopy (XAS and RIXS) of interfacial phenomena in the chemical transformation”, Jinghua Guo, Beating the Complexity of Matter through the Selectivity of X-rays - Dynamic Pathways in Multidimensional Landscapes, Magnus Haus Berlin, Germany (September 16th - 20th, 2019)
- Invited presentation: “There is plenty of room at the bottom…just no room for error”, Felix Fischer, Department of Chemistry Seminar, Texas A&M University, College Station (November, 7th, 2019).
- Invited speaker: “There is plenty of room at the bottom…just no room for error”, Felix Fischer, Department of Chemistry Seminar, University of Colorado, Boulder (October 28th, 2019).
- Oral presentation: “In-situ/Operando X-ray spectroscopy (XAS and RIXS) characterization of the interfacial charge transfer in energy-storage materials”, Jinghua Guo, MRS fall meeting, Boston (December 4th, 2019).
- Invited presentation: “Soft x-ray spectroscopy for In-situ/operando characterization of energy materials”, Jinghua Guo, The 2020 Annual Meeting of the Physical Society of Taiwan (TPS), Pingtung, Taiwan (February 5th - 7th, 2020)
- Bowden M.E., S. Autrey, M.O. Jones, B. Ginovska, K. Chernichenko, T. Repo, and A.J. Rameriz-Cuesta. 04/03/2019. "Hydrogen chemi-sorption in condensed-phase Frustrated Lewis acid-base Pairs." Presented by M.E. Bowden at ACS National Meeting, Orlando, Florida
- Karkamkar A.J. 07/15/2019. "Hydrogen Release from Solvated Magnesium Borohydride." Presented by A.J. Karkamkar at 2nd International Conference on Boron Chemistry, Taiyuan, China.

Presentations

- Bentley G. et al. “Biologically-based hydrogen production, storage, and release: a high efficiency H_2 production platform” Game Changers LDRD Full Proposal Presentation. May 23, 2019
- Bentley G. et al. “Biological formate-to-H_2 cycle” Face-to-face meeting. PNNL. July 18, 2019
- Bentley G. et al. “Biological H_2 release from formate” HyMARC Seedling. August 21, 2019
- Bentley G. et al. “Biologically-based hydrogen production, storage, and release: a high efficiency H_2 production platform” Xcel Energy. October 17, 2019
- Mow, R. E., Braunecker, W. A., Gennett, T. “Porous liquids Update”, NREL Site Visit, Nov. 15, 2019.
- Braunecker, W. A.,Mow, R. E., Gennett, T. “Dynamic Sorbent Materials”, NREL Site Visit, Nov. 15, 2019.
- Mow, R. E., Braunecker, W. A., Martinez, M. B., Shulda, S., Gennett, T. “Framework Materials as Porous liquids”, 236th ECS Meeting, Oct. 13-17, 2019, Atlanta, GA.
- Mow, R. E., Braunecker, W. A., Martinez, M. B., Shulda, S., Gennett, T. “ Porous liquids from framework materials”, Gordon Research Conference, Aug. 4-9, 2019, Andover, NH
- Braunecker, W. A., Mow, R. E., Gaulding, A., Gennett, T. “ Porous liquids as hydrogen carriers”, HyMARC Face-to-Face Meeting, PNNL, July 18, 19th, 2019.
- Braunecker, W. A., Mow, R. E., Gennett, T. “Carriers: Porous liquids”, NREL Site Visit, April, 2019.
- Braunecker, W. A., Hurst, K. E., Martinez, M. B., Shulda, S., Koubek, J. T., Sellinger, A., Gennet, T., Johnson, J. C., “Hydrogen sorption in fluorinated organic frameworks”, 257th ACS Meeting, Mar. 31-Apr. 4, 2019, Orlando, FL. ENFL - 0607.
- Mow, R. E., Martinez, M. B., Gennett, T., Braunecker, W. A. “ Porous liquid covalent organic frameworks”, 257th ACS, Orlando, FL, Mar. 31-Apr. 4, 2019, ENFL-0446
- Braunecker, W. A. “Fluorinated Organic Materials for Energy Generation, Storage, and Transport Applications”, Department of Chemistry, Colorado School of Mines, February 22nd, 2019.
- K.E. Hurst. “Hydrogen Storage: Measurements Protocols and Reproducibility” Invited Talk Electrochemical Society Fall Meeting Atlanta, GA. Oct. 17, 2019
- K.E. Hurst. “Plasmonic Mediated Hydrogen Desorption for Metal Hydrides” ALD 2019. Seattle, WA July 22, 2019
- K.E. Hurst. “Measurements and Materials for Hydrogen Storage” Colorado School of Mines Metallurgical and Materials Engineering Department Seminar. Golden, CO. April 11, 2019
- K.E. Hurst. “Plasmon interactions for on-demand hydrogen release in hydrogen carriers Pacific Northwest National Laboratory June 16, 2019

Presentations

- Fitzgerald, M. A.; Leick, N.; Gross, K.; Christensen, S.T.; Gennett, T.; Pylypenko, S. "Transmission Electron Microscopy of Novel Nano-structured Metal Hydrides", Colorado School of Mines, November 15, 2019.
- N. Leick “Mg(BH4)2*0.3 THF from University of Hawaii”, borohydride workshop, Whitefish, October 2019
- N. Leick “A Glimpse Into NREL’s Hydrogen Storage Efforts“ NREL seminar, Golden, September, 2019
- N. Leick, V. Stavila, K. Gross, M. Bowden, T. Gennett, S. Christensen “Role of additives on the H2 storage properties of Mg(BH4)2” ACS spring meeting, Orlando, April 2019
- N. Leick, V. Stavila, N. Strange, M. Martinez, M. Toney, T. Gennett, S. Christensen “Atomic Layer Deposition on Mg(BH4)2: A Route to Improved Automotive H2 storage” ALD conference, Seattle, July 2019
- N. Leick, T. Mattox, T. Gennett, J. Urban “Focus Area 2c: Modulation of B-H Bond Strength in Borohydrides” HyMARC Face-to-Face Meeting, Richland, July 2019
- S. Christensen and N. Leick, K. Gross, S. Pypylenko, M. Fitzgerald “ALD (Atomic Layer Deposition) Synthesis of Novel Nanostructured Metal Borohydrides” Hydrogen Storage Tech Team, Southfield, September 2019
- Pailing, C. and Wunder N. “HyMARC Data Hub” Data Analysis and Visualization Group, Computational Sciences Center, National Renewable Energy Laboratory, July 17, 2019.
- Barnett, B. R. “Coordination-driven approaches to gas separations and fuel storage in metal–organic frameworks” Department of Chemistry, University of Texas at Austin, December 9, 2019
- Shulda, S., Strange, N., Parilla, P, and Gennett, T. “Multi-Technique Characterization of Hydrogen Storage Materials for Improved Material Development” Gordon Research Conference, Barcelona, Spain, July, 2019.
- Shulda, S., Parilla, P,and Gennett, T. “New Instrument Summary” Site Visit, Colorado School of Mines, Golden, CO, November 15, 2019
- Robert Bell, Glory Russell-Parks, Amelia Huffer, Sarah Shulda, Madison Martinez, Noemi Leick, Philip Parilla, Brian Trewyn, Thomas Gennett, “Ionic Liquid Additives for Lowering the Decomposition Temperature of Magnesium Borohydride”, 2019/04 ACS Spring Meeting, location: Orlando FL
- Supplemental slides in Tom G.’s talk at 2019/04 Annual Merit Review, Supplemental slides, location: DC
- Robert Bell, NREL, PNNL, UH, “Improving Mg(BH4)2 Cyclability with Borohydride Salt Additives”, 2019/07 Face to Face, location: PNNL
- Robert Bell, “Organic Borohydride Salts and Interactions with Ethers & Mg(BH4)2”, 2019/10 Hydrides Meeting, location: Whitefish
- Robert Bell, “Understanding Cyclability and Additive Pathways in Hydrides: Task 3C”, 2019/11 Site Visit,

Task 5: Collaboration & Coordination: Seedling Projects

The HyMARC team assists individual projects by providing:

- **Designated HyMARC point-of-contact**
- **Technical expertise concerning specific scientific problems**
- **Access to HyMARC capabilities**

Ongoing Seedling projects

- *Development of Magnesium Boride Etherates as Hydrogen Storage Materials* (U. Hawaii)
- *Electrolyte Assisted Hydrogen Storage Reactions* (Liox Power)
- *ALD Synthesis of Novel Nanostructured Metal Borohydrides* (NREL)
- *Optimized Hydrogen Adsorbents via Machine Learning & Crystal Engineering* (U. MI)

New Seedling projects

- *Optimal Adsorbents for Low-Cost Storage of Natural Gas and Hydrogen: Computational Identification, Experimental Demonstration, and System-Level Projection,* U. Michigan
- *Developing A New Natural Gas Super-Absorbent Polymer (NG-SAP) for A Practical NG Storage System with Low Pressure, Ambient Temperature, and High Energy Density,* Penn State U.
- *Heteroatom-Modified and Compacted Zeolite-Templated Carbons for Gas Storage,* Montana State U.
- *Theory-Guided Design and Discovery of Materials for Reversible Methane and Hydrogen Storage,* Northwestern U.
- *Methane and Hydrogen Storage with Porous Cage-Based Composite Materials,* Univ. Delaware
- *Uniting Theory and Experiment to Deliver Flexible MOFs for Superior Methane or Hydrogen Storage,* U. South FL
- *Metal-Organic Frameworks Containing Frustrated Lewis Pairs for Hydrogen Storage at Ambient Temperature* U. South FL
- *Hydrogen Release from Concentrated Media with Reusable Catalysts,* U. Southern California
- *A Reversible Liquid Hydrogen Carrier System Based on Ammonium Formate and Captured CO_2,* Washington State U.
- *High Capacity Step-Shaped Hydrogen Adsorption in Robust, Pore-Gating Zeolitic Imidazolate Frameworks,* Mines
- *Development of Magnesium Borane Containing Solutions of Furans and Pyrroles as Reversible Liquid Hydrogen Carriers,* U. Hawaii