HyMARC: LBNL Technical Activities

2019 DoE Hydrogen and Fuel Cells Program Review
May 1, 2019

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Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Project ID #: ST130

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Overview

Timeline

Project Start: 10/1/2015
Phase 2 Start: 10/1/2018
End: Project continuation determined by DoE. Currently scheduled through 9/30/22

Budget

Federal Share (Prendergast)
- FY18 (Phase 1): $575k
- FY18 (Phase 2): $735k
- FY19 (through 3/31/19): $200k

Federal Share (Long)
- FY18 (Phase 1): $300k
- FY18 (Phase 2): $983k
- FY19 (through 3/31/19): $400k

Barriers Addressed

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

Partners/Collaborators

LBNL – Walter Drisdell
LLNL – Brandon Wood
NIST – Craig Brown, Terry Udovic
NREL – Tom Gennett, Phillip Parilla
PNNL – Tom Autrey, Mark Bowden
SNL – Mark Allendorf, Vitalie Stavila
H_2ST^2 – H_2 Storage Tech Team

Approach: LBNL leads or is Part of Several Focus Area Teams

Focus Areas discussed in this presentation are in red

Task 1: Sorbents

- 1.A Enthalpy/entropy under practical conditions (Lead; NREL, PNNL)
- 1.B Strong-binding sites (theory and synthesis) (Lead)
- 1.C Sorbent packing: MOF monolith synthesis (Lead)
- 1.D Dynamic sorbent materials (Lead)
- 1.E Multiple H_2 binding (Lead)

Task 2: Metal hydrides

- 2.A Non-ideal surfaces and phase nucleation
- 2.C Modulation of B–B and B–H bond strength (Lead)
- 2.D.1 Nanoscale metal hydrides under mechanical stress
- 2.D.2 Non-innocent hosts
- 2.D.3 MgB_2 nanosheets (Lead)
- 2.E Microstructural impacts

Task 3: Hydrogen carriers

- 3.B Aqueous organic carriers
- 3.D.1 Sorbents as hydrogen carriers (Lead)
- 3.D.2 Porous liquids
- 3.F Plasmon interactions for "On-demand" H_2 release

Task 4: Advanced characterization

- 4.C.1 NMR-FTIR-PCT instrument (Lead)
- 4.D.3 XAS/EXAFS
- 4.D.4 Soft X-ray spectroscopies and microscopy (ALS) (Lead)
- 4.D.6 ATR DRIFTS (Lead)

Relevance – FY19 Project Objectives

Sorbents (Task 1)

- Research and development of metal-organic frameworks with high volumetric and gravimetric H_2 storage capacities (Barrier A – C, E).
- Development of metalation procedures for high volumetric and gravimetric H_2 storage capacities (Barrier B)
- *In situ* IR and NMR characterization (Barrier N,O)
- Perform accurate simulations of high-pressure H_2 adsorption in MOFs based upon information from CoRE database

Metal hydrides (Task 2)

- Develop more complete model for metal hydride-graphene interface based upon *in situ* X-ray spectroscopy and theoretical modeling
- Develop synthesis of pure $Mg(BH_4)_2$ NPs wrapped by rGO
- Develop synthesis to enable targeted extrinsic doping using graphene nanoribbon-based systems

Hydrogen carriers (Task 3)

- Set up new flow reactors with GC/MS to probe liquid carrier reactions
- Evaluate sorbents as potential carriers

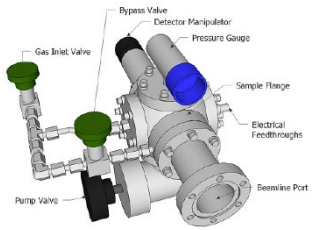
Advanced characterization (Task 4)

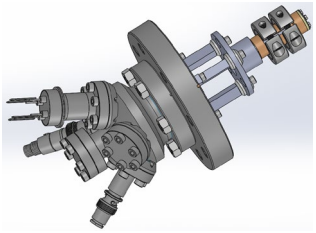
- Develop new methodologies to enable *in-situ* X-ray spectroscopic probing of buried interfaces in metal hydrides under working temperatures

Accomplishment 4.D: Expanded/Enhanced Characterization Capabilities at LBNL. Our Focus is on *in Situ*/Operando Methods

In Situ/Operando Soft X-ray Spectroscopy

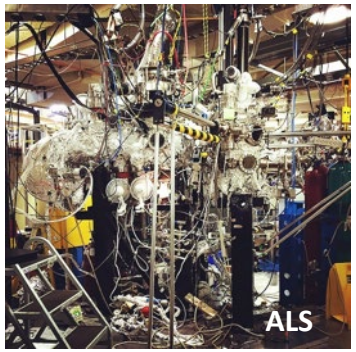
- H_2 adsorption, 1 bar, RT, transmission (bulk)
- H_2 release, RT–500 °C TFY (μm), TEY (nm)
- Hydrogenation, 1 bar, RT–250 °C TFY (μm), TEY (nm)

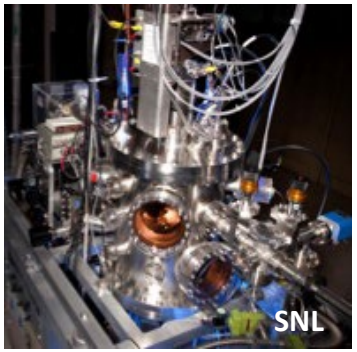




Ambient Pressure XPS (LBNL+SNL)

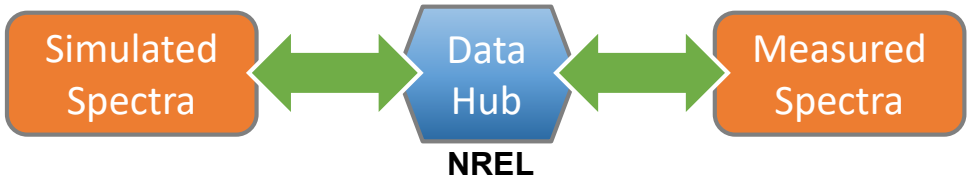
- Synchrotron AP-XPS, ALS BL 11.0.2
- Lab-based AP-XPS, SNL





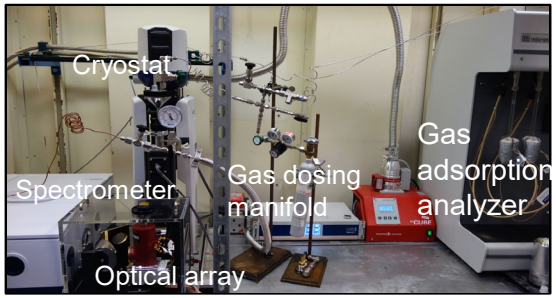
Ex Situ X-ray Spectroscopy

- Multiple ALS BLs for relevant elements (e.g. Mg, B, Li, Na K-edge)
- DFT XANES simulations of "standards" can reveal presence of impurities/ additives



In Situ Infrared Spectroscopy

- Diffuse reflectance system coupled to cryostat (15–373 K) and gas adsorption analyzer (0–100 bar)



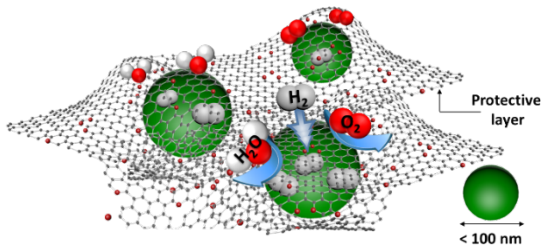
Approach – Hydride Nanoscaling (2.D): Form Nanocomposites with Ultrathin Carbon Nanomaterials as Hosts or Encapsulants

Technical issues for Task 2 (hydrides):

- Bulk materials typically present thick oxidation layer
- Active region buried underneath this
- X-ray probes perhaps too surface sensitive
- Requires cleaning of surface – non-operando

Synergies with Task 4 (Advanced Characterization, 4d3, 4d4):

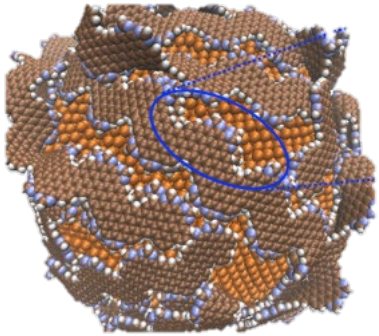
- Nanocomposites exhibit high interface:bulk ratio
- Active region distributed throughout sample
- X-ray probes (and bulk techniques) suitable
- Samples resistant to contamination
- Encapsulation to minimize weight penalty



Functionalized nanoribbons (Felix Fischer)

LBNL nano-hydride Phase 2 2D. approaches:

- Build on Phase 1 material platforms
- 2.A: Thermodynamics modulation to avoid thermodynamic sinks
- 2.D.1, 2.D.2: Nanoencapsulants as non-innocent hosts



Reduced graphene oxide (rGO) (Jeff Urban)

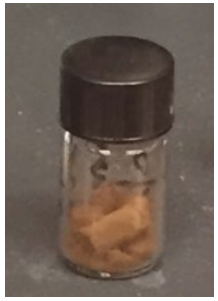
Accomplishment 2.D: rGO Enables Retention of Nanoscale Active Material

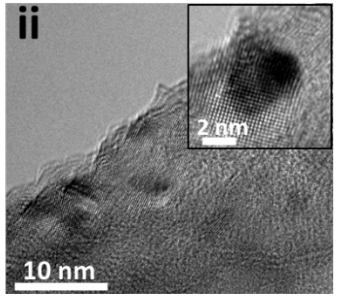
LBNL: Urban, Jeong. SNL: White, Stavila

$Mg(BH_4)_2$@rGO

390 °C
0 bar H_2

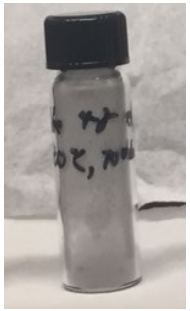
Dehydrogenated (Mg)

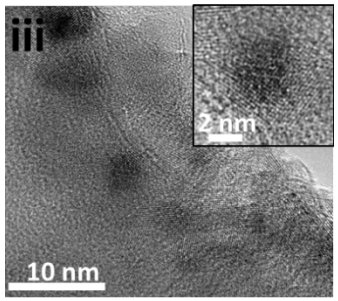




400 °C
700 bar H_2

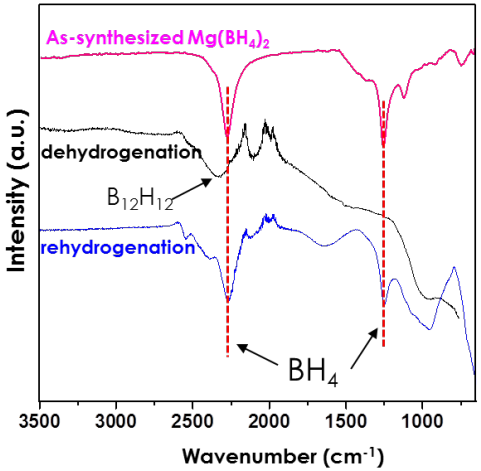
Rehydrogenated (MgH_2)



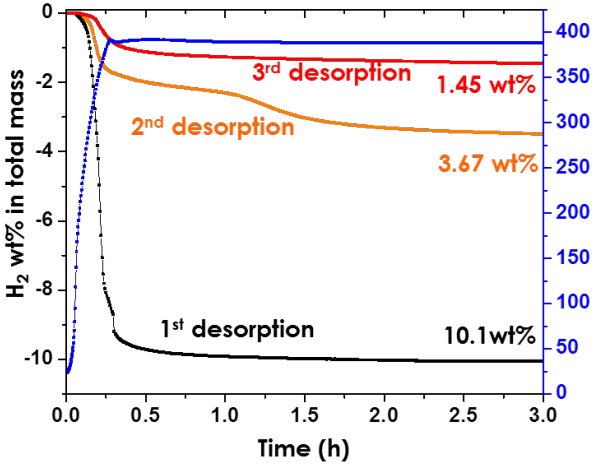


Well-preserved nanostructures after de/rehydrogenation

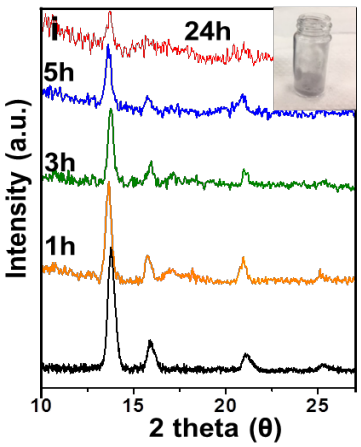
FT-IR: reduced $B_{12}H_{12}$ after rehydrogenation

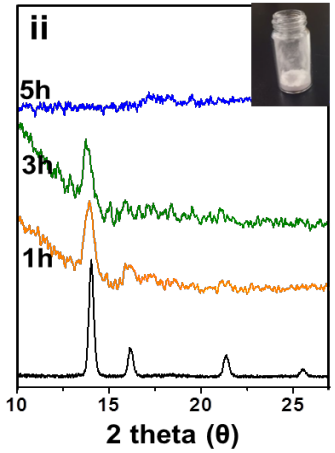


Higher H_2 capacity than bulk γ-MgBH



Increased oxidation stability vs. bulk



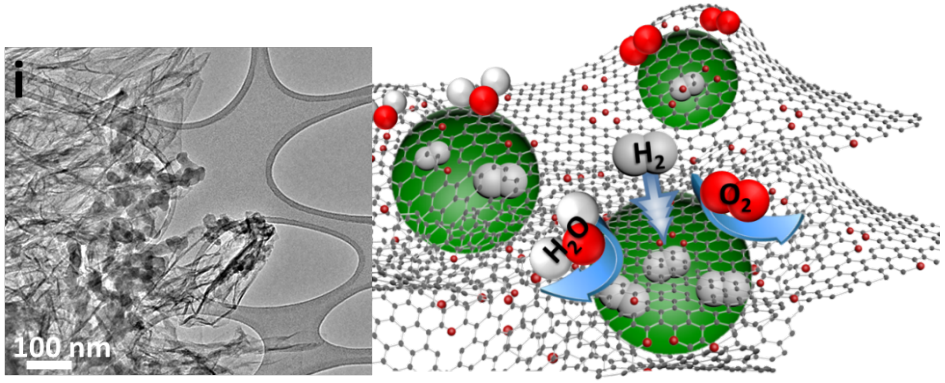


$Mg(BH_4)_2$ @rGO exhibits >10 wt% – a record stable capacity for a complex nanohydride

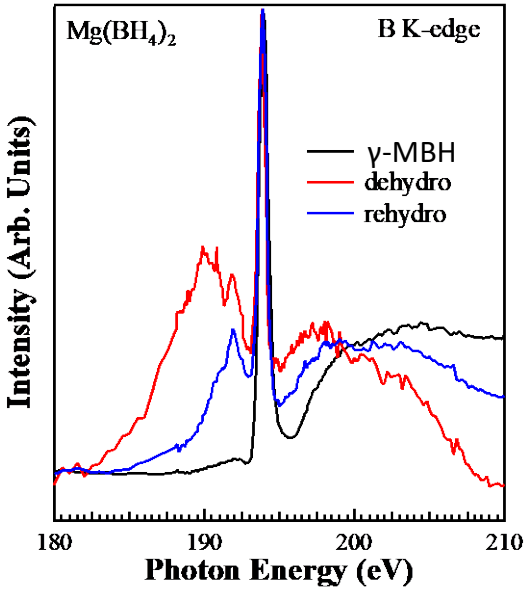
Accomplishment 2.D: Nanoencapsulation Creates Synergy with Task 4 to Enable *in situ* Characterization of Complex Hydrides

Materials synthesized by S. Jeong and J. Urban (MF/LBNL)
SNL: High-P hydrogenations and Sieverts measurements

Sandia National Laboratories



$Mg(BH_4)_2$ nanoparticles (~25 nm) encapsulated in reduced graphene oxide – selective barrier to environmental oxidation



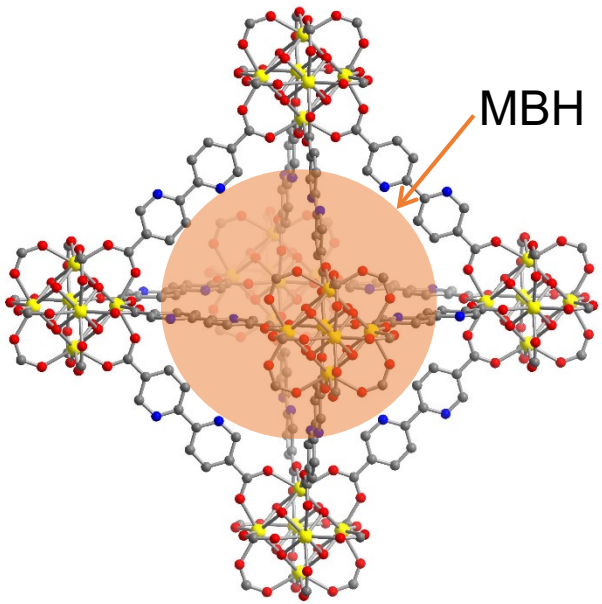
γ-$Mg(BH_4)_2$@rGO :

- H_2 release temperature reduced (<400 °C vs. 500 °C bulk)
- New XANES-accessible T-range (250 °C hydrogenation; 500 °C dehydrogenation) enables operando probing of complex hydrides
- Reduced oxidized content observed at nanoparticle surface
  - Borohydride spectral intensity below 193 eV
  - 194 eV peak from oxidized B
- 1 bar sufficient to rehydrogenate

Accomplishment 2.D: Accelerated H_2 Release from $Mg(BH_4)_2$ Nanoencapsulated in MOF Hosts

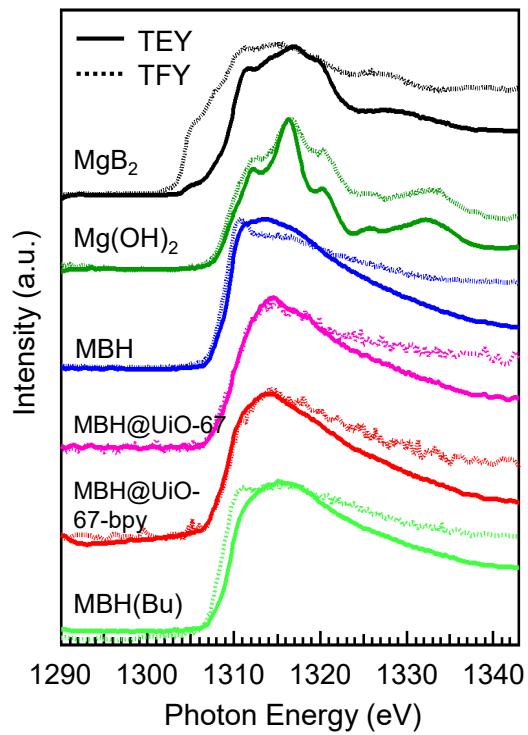
Guo, Liu (LBNL); Stavila (SNL) Sandia National Laboratories

UiO-67-bpy: $Zr_6O_4(OH)_4(bpydc)_6$
UiO-67: $Zr_6O_4(OH)_4(bpdc)_6$

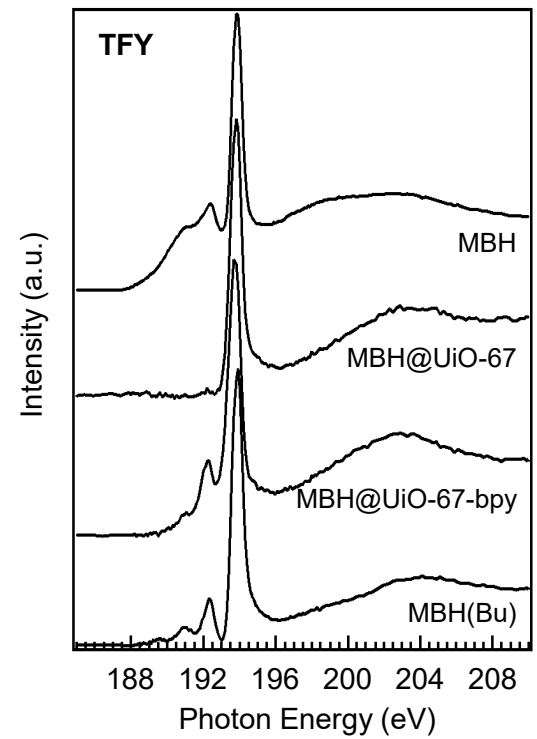


MBH@UiO-67-bpy

Mg K-edge



B K-edge



- TGA suggests range 120–260 °C where MBH is losing mass
- RGA indicates mostly H_2 at 120 °C → record low onset T for MgBH dehydrogenation
- XAS confirms MgBH is present within MOF pores

Accomplishment 3.B: New Flow Reactors for Hydrogen Carrier Research

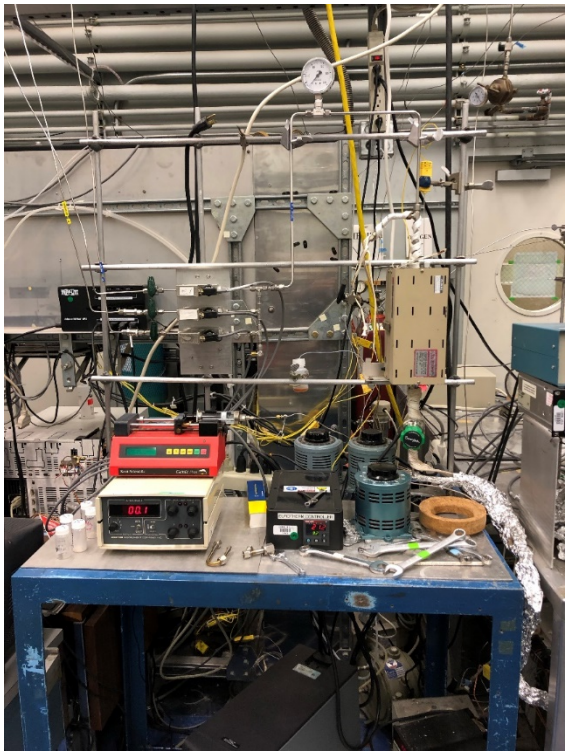
Prof. Gabor Somorjai, Dr. Ji Su

Newly refurbished capabilities in Somorjai lab will be employed to develop catalysts for dehydrogenation/hydrogenation of organic hydrogen carriers. Projects underway:

Methanol Decomposition

900 °C; 300psi; GC;
Liquid- and/or gas-phase reactions

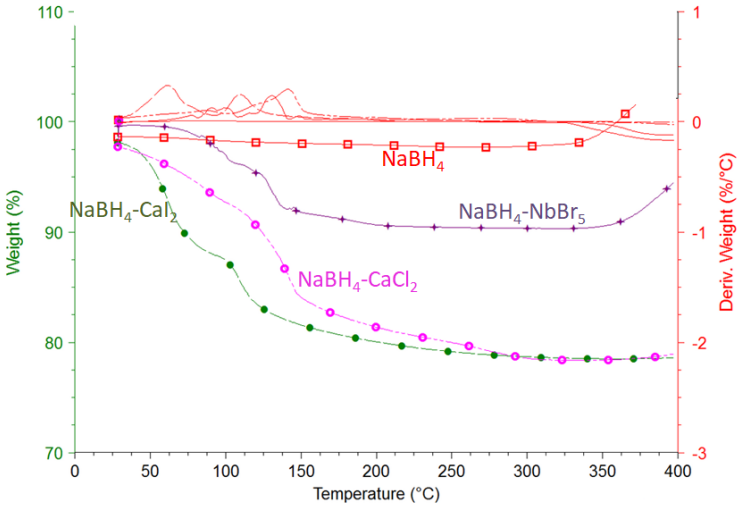
Methane Dehydrogenation



250 °C; GC;
Liquid metal catalyst exploration

Phase-2 Approaches: New Concepts for Boron-based Storage Materials

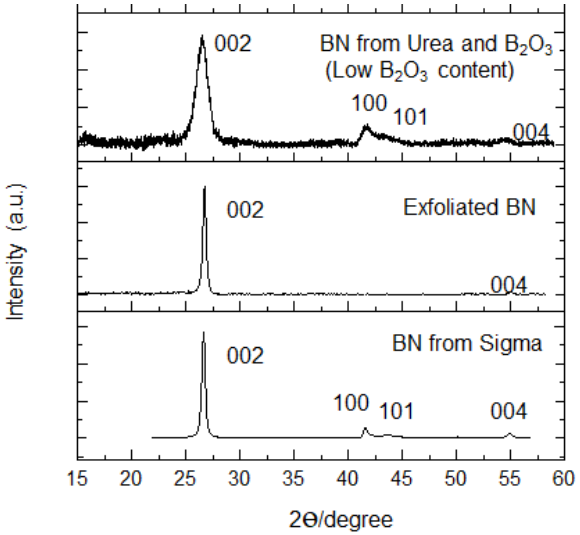
Urban, Jeong, Zhang (LBNL)

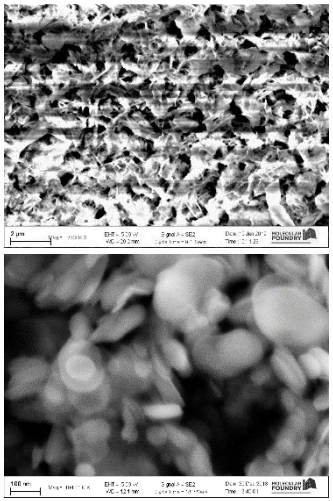


Focus Area 2.C: Borohydrides destabilization by divalent halides

Preliminary data: Thermogravimetric analysis shows that divalent halides enhance decomposition of borohydrides.

Focus Area 1.B.2: porous BN as novel sorbent





Bottom up method

Top down exfoliation method

Recent theory: 8.65 wt% H_2 at 300 K (Zhang et al. *J. Mater. Chem. A*, **2015**, *3*, 9632)

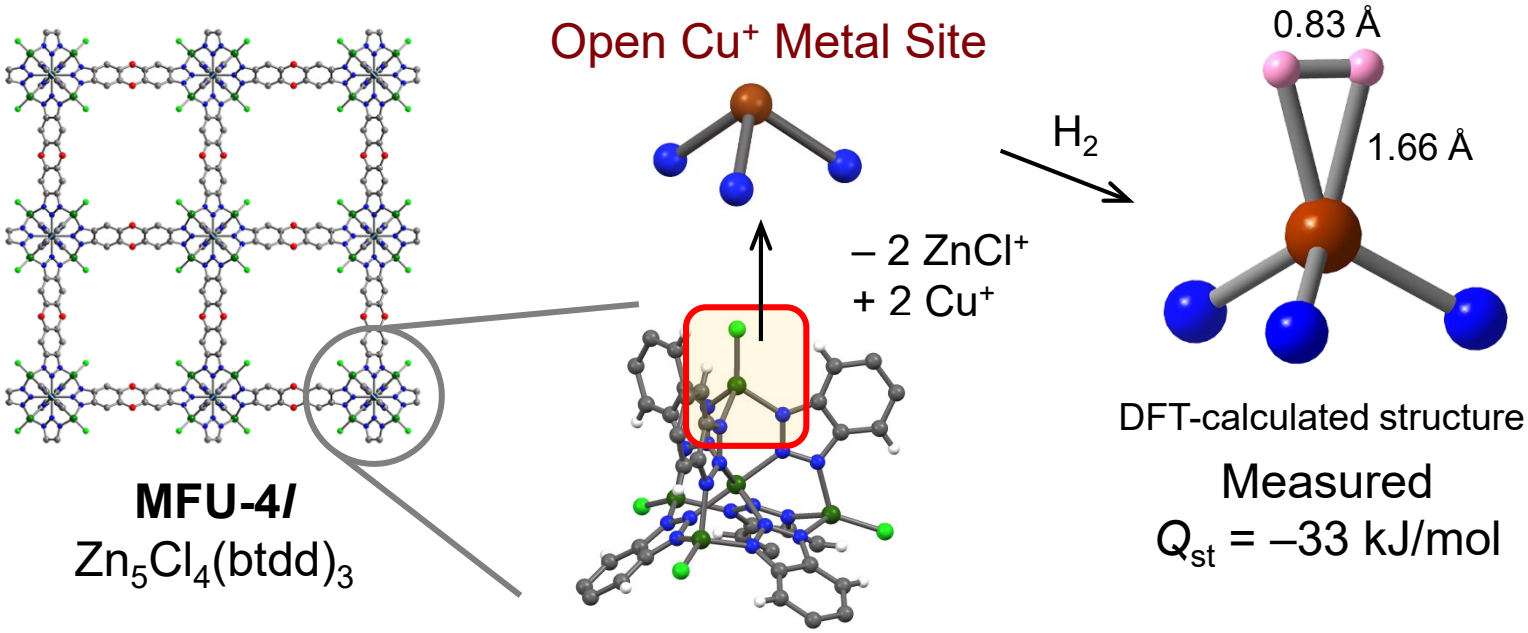
Synthesis of BN sheet materials and further substitutional doping or defects engineering for hydrogen storage

Approach 1.B (Strong Binding Sites): Validation Effort

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

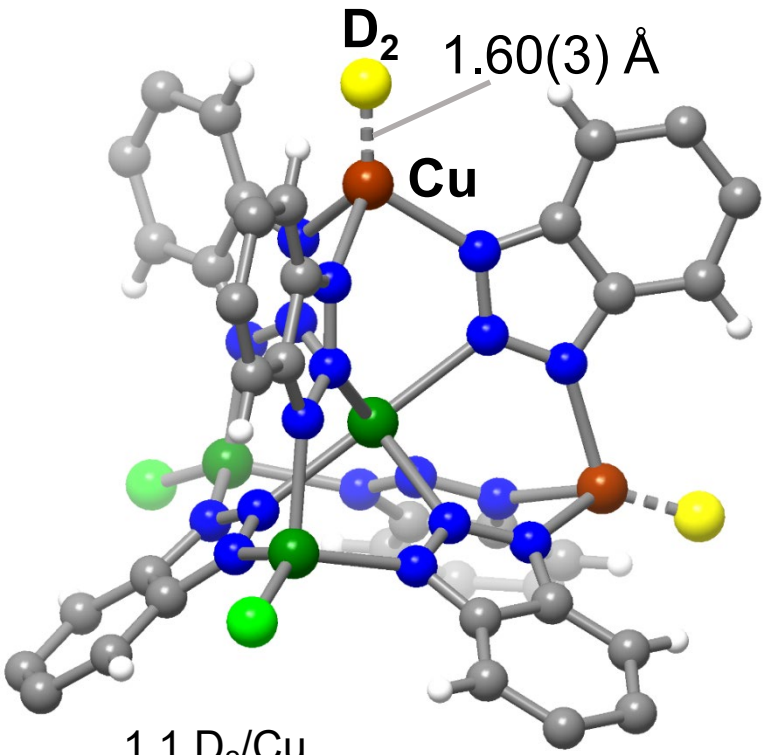
- Values are based upon assumptions about the correlation between adsorption enthalpy and entropy, but these assumptions are not necessarily valid

Bhatia, Myers *Langmuir* **2006**, *22*, 1688
Garrone, Bonelli, Otero Arean *Chem. Phys. Lett.* **2008**, *456*, 68



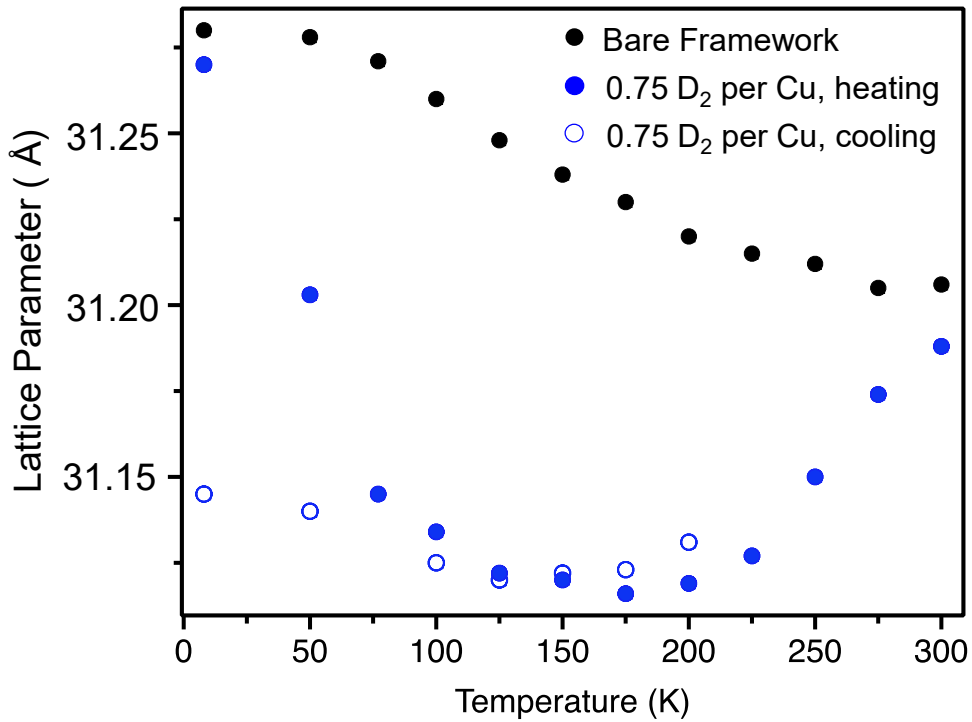
Denysenko, Jelic, Reuter, Volkmer, *Angew. Chem. Int. Ed.* **2014**, *53*, 5832

In situ Powder Neutron Diffraction Results



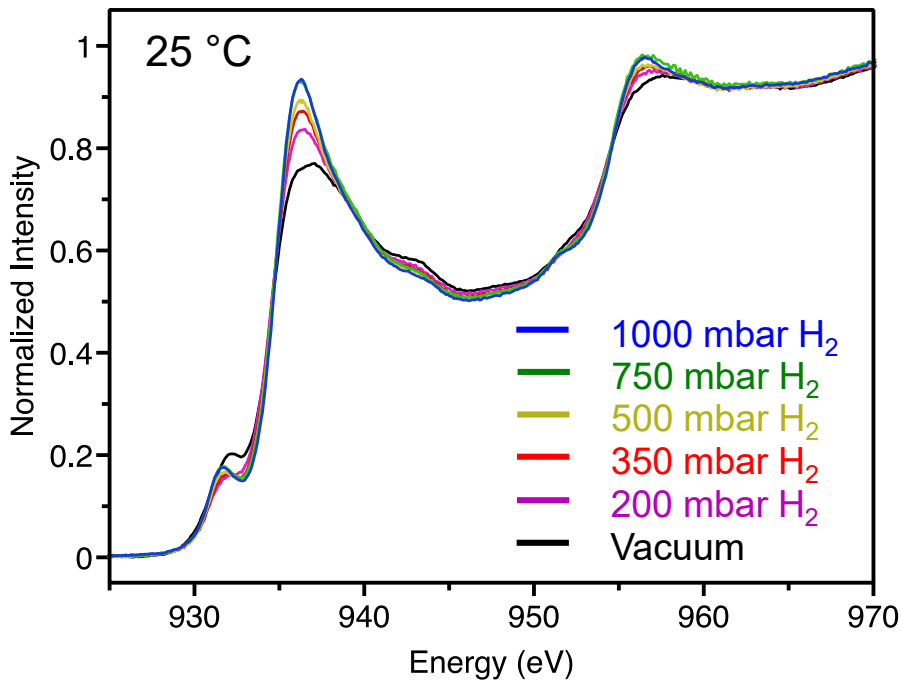
1.1 D_2/Cu
dosed at 100 K

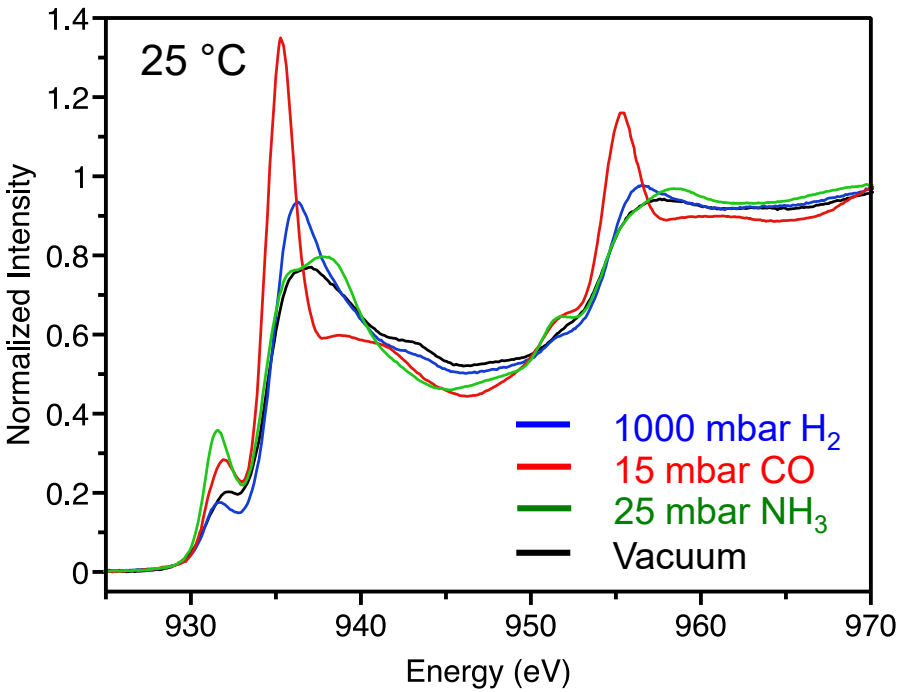
with Craig Brown and Jacob Tarver (NIST)



- Cu-bound D_2 can be resolved despite disorder with Zn–Cl at these sites
- Dosing below 80 K leads to a metastable structure with d(Cu–D_2) ~ 1.9 Å
- Significant lattice contraction with strong D_2 binding
- Kinetics data will allow us to measure the activation energy for D_2 binding

In Situ X-ray Absorption Spectra of Cu^{I}-MFU-4*l*





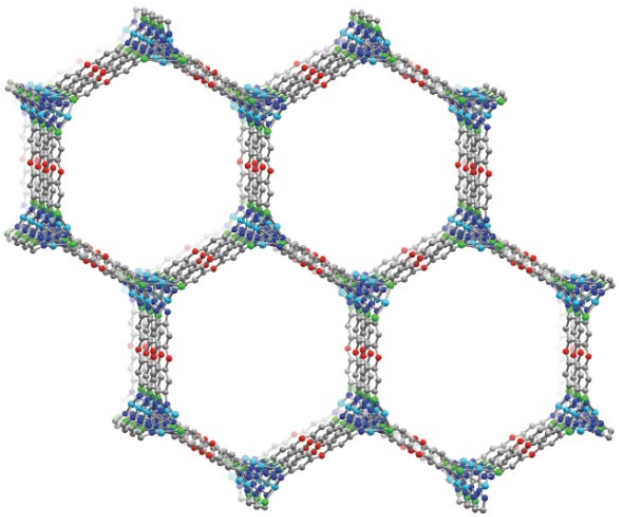
- Cu L-edge data probe how 3*d* manifold is affected by interaction with adsorbate
- Increase in edge intensities indicate increased 3*d* hole character on H_2 binding
- CO produces a similar response to H_2 while NH_3 shifts the edges to higher energy
- Calculations to map spectral changes to adsorbate electronic character in progress

with Greg Su, Walter Drisdell, and David Prendergast (LBNL)

Accomplishment 1.B: Synthesis of MOF with Validated Adsorption Energy in Optimal Range

Hypothesis:
Open V^{2+} coordination sites will place us in this range

- No such MOFs were known, but we've finally made one

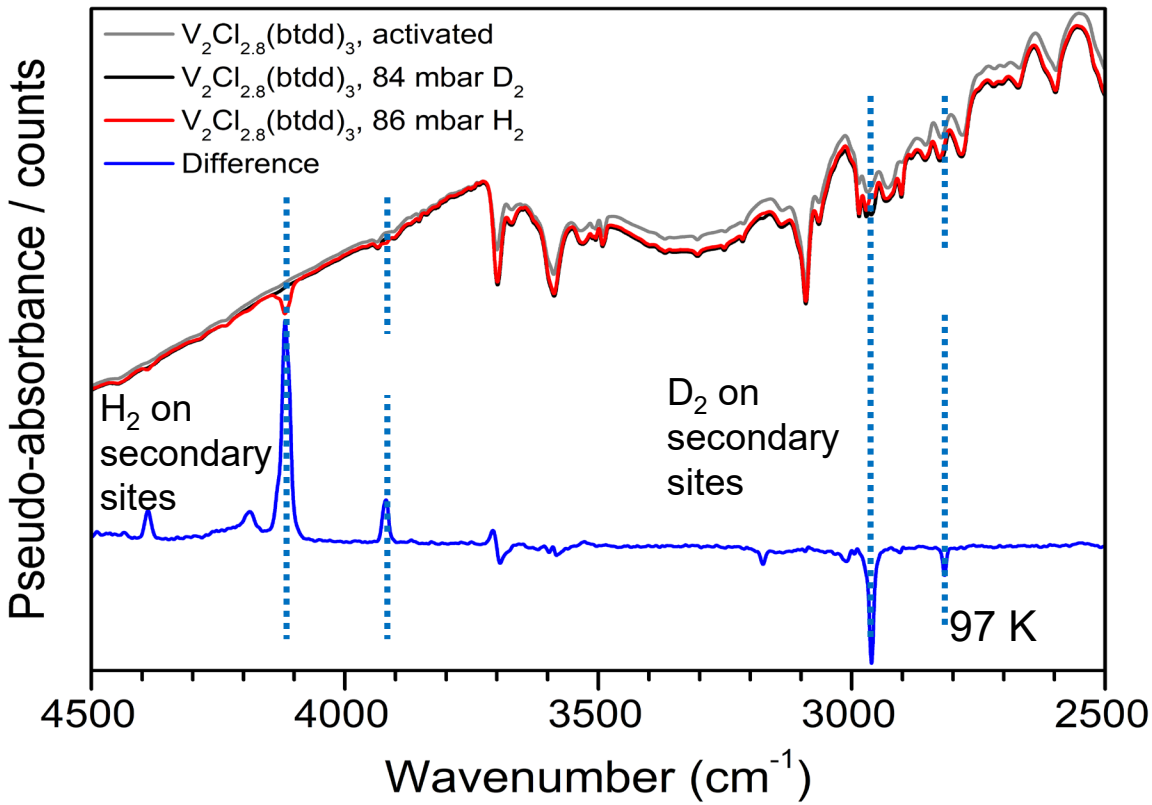


$V_2Cl_{2.8}$(btdd)

- Crystal structure determined from powder X-ray diffraction of activated sample

  (*R*-3*m*, *a* = 38.943(3) Å, *c* = 8.259(1) Å, *V* = 10842(2) Å^3)
- Langmuir SA = 3290 m^2/g, BET SA = 1930 m^2/g
- ΔH from DRIFTS = –21.0 kJ/mol

IR Spectra for $V_2Cl_{2.8}$(btdd) Dosed with H_2 and D_2



	***v*(H–H)** (cm^{-1})
free H_2	4161
Ni_2(*m*-dobdc)	4025
$V_2Cl_{2.8}$(btdd)	3919
Cu^I-MFU-4*l*	3252

- Subtraction of D_2 spectrum from H_2 spectrum unambiguously resolves peaks
- Largest bathochromic shift yet observed for M^{2+} in a porous material
- Energy decomposition analysis exhibits that V^{2+} has the most favorable energetics in $M^{II}_2Cl_2$(btdd) (M = Ti, V, Mn, Co, and Ni)

Challenges to Address Moving Forward

MOF	Metal ion	ΔH from DRIFTS (kJ/mol)	Q_{st} from isotherms (kJ/mol)	ΔH from theory (kJ/mol)	Total H_2 uptake at 298 K, 100 bar (g/L of crystal)
Ni_2(*m*-dobdc)	Ni^{2+}	–13.7	–12.3	–18.6	11.9
Cu^I-MFU-4*l*	Cu^+	–33.6	–32.7	–44.8	11.0
Cu^I-CFA-1*	Cu^+	in progress	in progress	in progress	in progress
$V_2Cl_{2.8}$(btdd)	V^{2+}	–21.0	–21	–25.4	in progress

*See the reviewer-only slides section for details

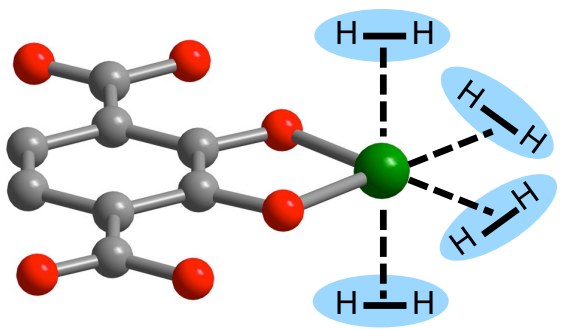
- Gain a complete understanding of H_2 adsorption in these V^{II} and Cu^I systems:
  - High-pressure adsorption isotherms and *in situ* spectroscopy
  - Neutron diffraction studies
  - Computational studies to understand strong temperature dependence of ΔH
- Increase the density of the available metal binding sites

Approach 1.E: 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" challenge 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

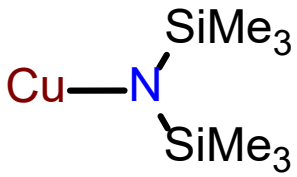
Next-Generation



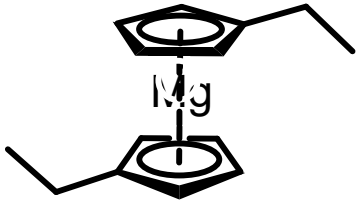
4 or 5 H_2 per metal cation

Gas phase reaction*

- Established ALD materials
- No solvent
- Good pore accessibility
- No counter-ions remain



CuHMDS



$Mg(Cp^{Et})_2$

* Summary table is in the backup slides section

Future Directions (Sorbents)

- Synthesize smaller pore analogues of Cu^{I}-MFU-4*l* and $V_2Cl_{2.8}$(btdd) to increase volumetric H_2 capacities
- Develop further sampling and data processing methods (e.g. H_2/D_2 subtraction) to measure accurate ΔH_{ads} and ΔS_{ads} in frameworks with open metal sites
- Continue metalation of frameworks with functionalized linkers to access low-coordinate metal sites
- Pursue flexible MOFs that can maximize H_2 usable capacity through step-shaped adsorption isotherms
- Characterize molecular H_2 binding free energies across three families of sorbent materials
- Complete and upload the H_2 storage benchmark database

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

Collaborations

- **LBNL/UC Berkeley (adsorbents)** **Jeffrey Long:** synthesis & characterization, *in situ* IR-NMR spectroscopy; **Martin Head-Gordon:** computation
- **LBNL/UC Berkeley (hydrides)** **David Prendergast:** theory, simulated spectroscopy; **Jeffrey Urban:** nanomaterials synthesis; **Jinghua Guo:** soft X-ray characterization; **Felix Fischer:** molecular synthesis; **Gabor Somorjai:** heterogeneous catalysis; **Stephen Whitelam:** theory, kinetics of porous materials
- **LBNL/UC Berkeley (H_2 carriers)** **Jeffrey Long:** synthesis & characterization; **Hanna Breunig:** techno-economic analysis
- **LBNL (advanced characterization)** **David Prendergast:** theory, simulated spectroscopy; **Jeffrey Long:** *in situ* IR-NMR spectroscopy
- **LLNL** **Brandon Wood:** multi-scale modeling and computational spectroscopy
- **NREL** **Thomas Gennett, Phillip Parilla:** characterization
- **PNNL** **Thomas Autrey, Mark Bowden:** carriers, NMR
- **SNL** **Mark Allendorf, Vitalie Stavila:** synthesis & characterization
- **NIST** **Craig Brown:** neutron diffraction and neutron spectroscopy
- **Additional collaborations** **Walter Drisdell** (LBNL); **Stephen FitzGerald** (Oberlin College); **Jeffrey Grossman** (MIT); **Agiltron, Inc.**

Summary (FY19 Internal LBNL Milestones)

Task	Milestone	Due	Status
1.B.1	**Electronic structure computations:** Generate a benchmark database tailored towards H_2 with the goal of providing inexpensive predictive analytics.	9/2019	50%
1.B.2	**Synthesis of adsorbents with optimal binding energies:** Determine the enthalpy of H_2 binding in V_2Cl_2(btdd) using both low-P isotherms and variable-temperature DRIFTS.	9/2019	100%
1.C.1	**MOF monolith synthesis:** Demonstrate monolith HKUST-1 takes up 50% greater volumetric H_2 uptake compared to the corresponding powder MOF.	9/2019	50%
1.D.1	**Flexible MOFs:** Synthesize 4 derivatives of Co(bdp) derivatives. Measure isotherms at 77 K to observe how step pressure changes with substitution pattern.	9/2019	20%
1.E	**Multiple H_2s per metal:** Demonstrate metalation of both Mg and Ca in two different frameworks and measure H_2 heat of adsorption.	9/2019	20%
2.C	**B–B bond activation:** Synthesize halide-substituted MgB_2 and/or organic compounds incorporated into the MgB_2 matrix.	6/2019	5%
3.D.1	**Analysis of adsorbents as carriers:** TEA to establish metrics for H_2 delivery.	9/2019	30%
4.C.1	**NMR-FTIR-PCT instrument:** Set up a benchtop NMR magnet with a high-pressure gas adsorption analyzer.	9/2019	20%
4.D	**Advanced synchrotron and ATR DRIFTS characterization techniques:**		

Acknowledgements

This work was supported by the U.S. Department of Energy (US DOE), Office of Energy Efficiency and Renewable Energy (EERE), Fuel Cell Technologies Office (FCTO), under Contract No. DE-AC02-05CH11231.

Reviewers: Thank you for the constructive feedback.

Technical Backup Slides

Accomplishment 1.B: Benchmarking Density Functionals

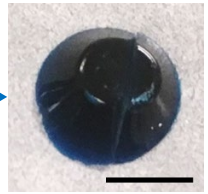
- **Objective:** To identify inexpensive density functionals which can predict hydrogen binding energies accurately
- Dataset consists of wide variety of binding motifs commonly encountered in hydrogen adsorption frameworks:
  - Organic linkers, main group and transition metal open binding sites
- 40 density functionals including LDAs, GGAs, metaGGAs and hybrids, with and without empirical dispersion correction (-D3) assessed

	Density functional	Rank	Root Mean Square Error*
Best performing functionals	ωB97M-V	1	1.55 kJ/mol
	ωB97X-V	2	1.80 kJ/mol
	B97-D3(BJ)	4	1.91 kJ/mol
Commonly used functionals	PBE	18	2.99 kJ/mol
	B3LYP-D3	16	2.64 kJ/mol

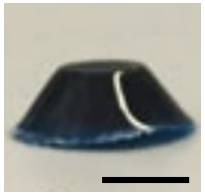
- ωB97M-V is a range-separated, hybrid metaGGA with VV10 non-local correlation offers the best performance
- B97-D3(BJ), a GGA functional with empirical dispersion correction represents the best tradeoff between accuracy and cost

Accomplishment 1.C: HKUST-1 Monolith Synthesis is Reproducible

	Density (g/cm^3)	Cu:BTC ratio[1]	Langmuir SA (m^2/g)	Pore volume (cm^3/g)	H_2 uptake at 77 K, 1 bar (g/L)
Monolith	1.01[2]	1.43	1750	0.63	22.5
Reported monolith[3]	1.10[2] (1.04)[4]		1470	0.52	
Powder	0.43[5]	1.37	2150	0.77	11.2
.cif data	0.881	1.50	2240[6]	0.80[6]	n.a.



0.5 cm



0.5 cm

[1]Determined from TGA data. [2]Archimedean immersion method. [3]Tian, Zeng, Vulpe, Casco, Divitini, Midgley, Silvestre-Albero, Tan, Moghadam, Fairen-Jimenez *Nat. Mater.* **2018**, *17*, 174. [4]Mercury porosimetry. [5]Hand packing density: Peng, Krungleviciute, Eryazici, Hupp, Farha *J. Am. Chem. Soc.* **2013**, *135*, 11887. [6]Calculated using *Materials Studio*.

- HKUST-1 monolith density is greater than HKUST-1 powder density
- At 77 K and 1 bar, volumetric H_2 uptake of the monolith is twice as high as observed for the packed powder
- High-pressure H_2 and CH_4 isotherms will be collected

Accomplishment 1.E: Summary of Zr-Based MOF Metalations

Metal Site	Metalating Reagent	Metalation yield (%)	Langmuir SA (m^2/g)	H_2 Uptake* (mmol/g)
UiO-67-PhOpydc system				
UiO-67-PhOpydc		n/a	2880	9.2
Cu	$Li[Cu(CH_3)_2]$	86	70	0.78
Cu	$Cu(CH_3CO_2)$	72	2370	8.4
Cu	$Cu(N(SiMe_3)_2$	22	2000	9.4
Cu	$[Cu(Mes)]_n$	9	2640	9.4
$Mn(CO)_x$	$Mn(CO)_5Br$	40	1500**	5.3
$Re(CO)_x$	$Re(CO)_5Cl$	26	1510**	6.2
Li	*n*-BuLi	33	n.d.	5.3
UiO-68-cat system				
UiO-68-cat		n/a	3470	6.7
Ni	$Ni(C_3H_5)_2$	17	1870	3.4
Mg	$Mg(Cp^{Et})_2$	108	3220	7.0

*Excess uptake at 77 K and 1 bar. **Measured before photolysis.

Remaining Challenges and Barriers

- Complete insertion of metal cations into *O*,*O*-, *N*,*O*- or *N*,*N*-chelating groups within MOFs is a key synthetic challenge
- Can we demonstrate adsorption of 3 or more H_2 molecules per metal?
- Establishing a valid correlation between ΔH and ΔS for H_2 adsorption under target operating conditions: 5-100 bar and –40 to 60 °C
- Can we manipulate ΔS with synthetic chemistry?
- While accurate computational tools are available for calculating binding energies, the optimal trade-off point between accuracy and expense is still under investigation
- Achieve size control in synthesis and reversibility of encapsulated $Mg(BH_4)_2$ materials
- Incorporate theoretical insights on graphene-hydride interface into advanced synthesis of these materials
- Performing *in situ* soft X-ray spectroscopies achieving realistic hydrogen storage (i.e. UHV requirement)
- Understanding coordination/reactivity of $Mg(BH_4)_2$ with oxide and graphene interfaces
- The relations between the strength and number of open metal sites, overall pore morphology and the adsorbent performance in H_2 storage are not fully understood

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

Responses to Previous Year Reviewers' Comments

FY18 Reviewer Comment	FY19 Response to Comment
ANL (ST-001, Ahluwalia) showed that even in the most optimistic case of 4 H_2 molecules per metal, the theoretical uptake (at 25 °C, 100 bar) is still a factor of two lower than the value needed to reach the system target.	Our current focus is the development of (gas-phase) metalation procedures for the multiple H_2 adsorption per metal site. Once experimental protocols are established, metalation of open metal site MOFs with f-block elements (higher coordination number) and optimization of framework dead space will be considered. In addition, we initiated a new task for the monolith formation, whose volumetric uptake can be twice as large as powder samples.
The theory effort has not supported the experimental work closely. Much of the work on predicting candidates and variations could use a more HT DFT. Also, it remains to be seen whether this functional has such a good performance across the board. More effort needs to be devoted to multiple H_2s and understanding bonding, polarization, and dynamics.	The Density Functional benchmarking effort assesses the performance of dispersion-corrected density functionals (e.g. PBE-D3) across a range of chemically diverse binding motifs, containing one or multiple H_2s bound to a single metal site. Quantifying anharmonic effects and polarization of gas binding are the subject of current research, but slightly outside the scope of this particular database endeavor. We will be reporting progress on both these topics shortly.
A stronger integration of theory in the design of experiments is recommended. This connection needs to be more direct.	HyMARC is structured to leverage capabilities and investments at individual labs. Regarding theory/modeling, these capabilities are largely centered at LLNL (although computational spectroscopy is a strong capability of the Molecular Foundry). Five 2017-18 hydride-related HyMARC publications involve close theory-experimental collaborations. In addition, two review articles were published coauthored by theorist with experimentalists.