

Tunable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis Using Ordered Polymer Templates

2010 U.S. DOE HYDROGEN PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

Mark D. Allendorf
Sandia National Laboratories

June 7-11, 2010
Washington, DC

Project ID: ST027



Overview



Timeline

Project start date: September 2008

Project end date: September 2011

Percent complete: 58%

Barriers

- (A) System weight and volume
- (C) Efficiency
- (P) Lack of understanding of hydrogen physisorption and chemisorption

Budget

- Total project funding through FY09:
 - **DOE share: \$520 K**
 - **Contractor share: \$50 K**
- Total funding for FY10: \$720 K

Partners

Mark Allendorf (PI) Sandia. MOFs and related templates

Prof. Eric Majzoub, Univ. MO, St. Louis. BCP templates, ionic hydride modeling

Prof. Jeffery Grossman, MIT. Model benchmarking, non-ionic hydride modeling

Julie Herberg, LLNL. NMR characterization

Terry Udovic, NIST. Neutron spectroscopies

Richard Behrens, Sandia. Desorption kinetics and framework stability

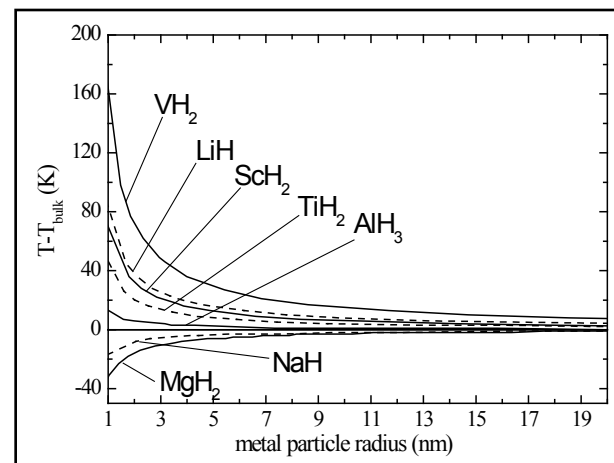
Relevance: Decreasing T(1 bar) would make some metal hydrides much more attractive for hydrogen storage

Theory and experiment suggest nanoscale hydride particles are destabilized relative to bulk, but the origin of this effect is unclear. Both size and local environment may play a role.

Overall Project Objective: Achieve tunable thermodynamics for hydrogen storage materials by controlling nanoparticle size, composition, and environment

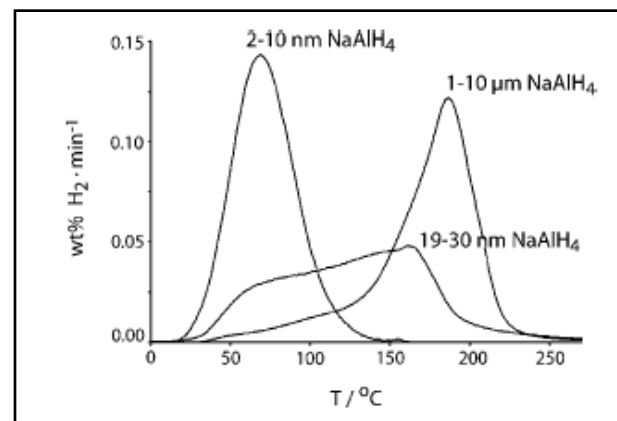
Key Goals for FY09-10

- √ Demonstrate and downselect infiltration methods
- √ Measure desorption kinetics for simple and complex hydride nanoparticles
- √ Benchmark DFT and atomistic nanoparticle models using Quantum Monte Carlo (QMC)
- Quantify effect of nanoparticle size on ΔH°_d
- Develop compositional tuning method



Wulff construction prediction of hydride destabilization as a function of particle size

Kim et al. *Nanotechnology* **20** (2009), 204001



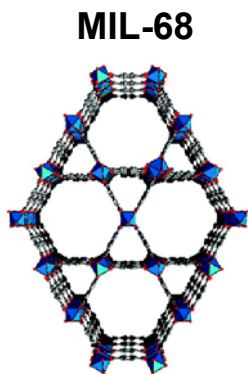
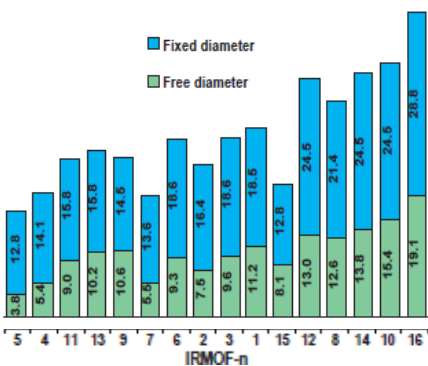
H₂ desorption from NaAlH₄ – infiltrated carbon nanofibers

Wagemans et al. *JACS* 2008

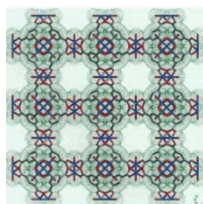
Approach: Use novel *ordered* frameworks to create a suite of templates to *systematically probe* nanoscale effects

MOFs, COFs, ZIFs, and block copolymers can be used to create a suite of templates with micro- to meso-scale pores

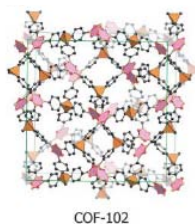
IRMOF entrance (green) and interior (blue) pore diameters



HKUST-1

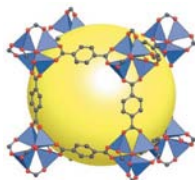


COF-102

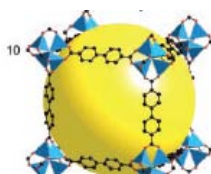


COF-102

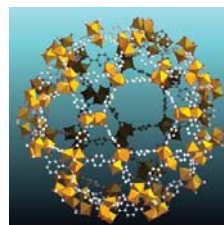
IRMOF-1



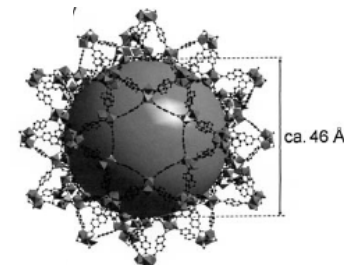
IRMOF-10



MIL-101



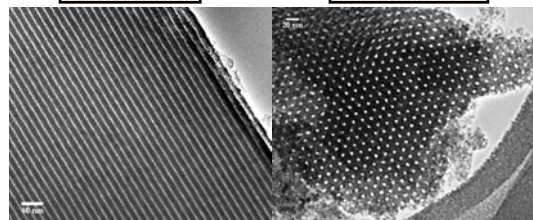
Cr-NDC- MIL-101



BCP and crosslinked phenolic resins

edge-on

top down



Meng, et al., *Chem. Mater.*, **18**, 4447-4464, (2006)

20 Å – 200 Å

10 Å

20 Å

30 Å

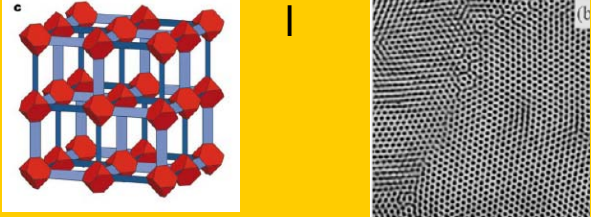
40 Å

50 Å

Approach (cont.) Nanoparticle synthesis is supported by a strong foundation of modeling and characterization

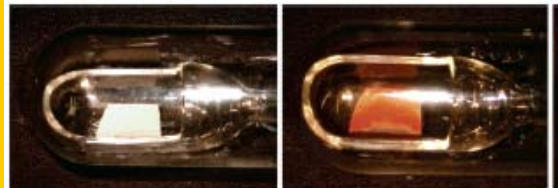
Task 1: Template design, synthesis, activation

MOFs (SNL) | BCP (UMSL)



The image shows two molecular models. On the left is a MOF (SNL) structure, a porous crystalline framework with red and blue spheres. On the right is a BCP (UMSL) structure, a disordered block copolymer with a porous morphology.

Task 1: Infiltration, reduction, stabilization (SNL,UMSL)



Two photographs of glass vials. The left vial shows a white solid at the bottom, and the right vial shows a red solid at the bottom, representing the reduction step of the synthesis process.

Particle properties
Template structures

Particle thermodynamics
Optimal compositions

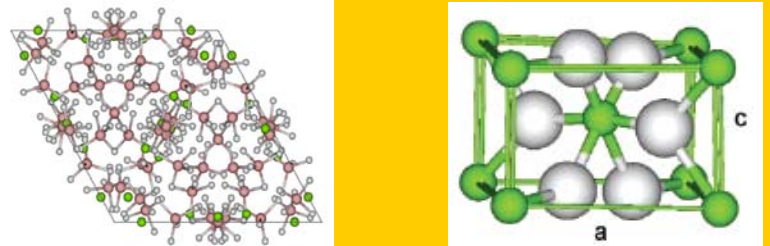
Samples

- Size and composition
- Framework stability
- Desorption kinetics and thermodynamics

Task 3: Theory (MIT, UMSL)

- Tool development: DFT, QMC, NanoPEGS
- Model validation and benchmarking
- Synthetic design

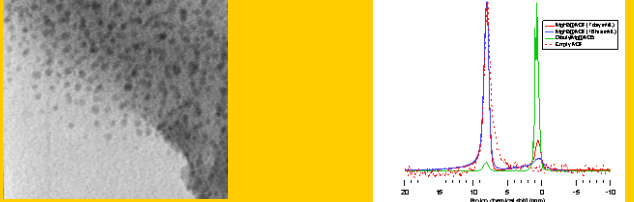
Ionic materials | Covalent materials



The image shows two molecular models. On the left is an ionic material structure with a complex network of red, green, and white spheres. On the right is a covalent material structure with a crystalline lattice of green and white spheres.

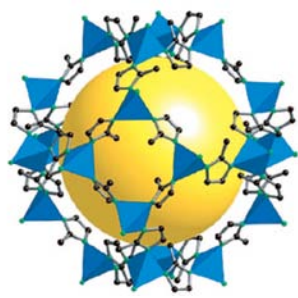
Task 2: Characterization:

- STMBMS (SNL)
- MAS-NMR (LLNL)
- Microporosimetry, XRD, FTIR...
- QENS, IENS, PGA, SANS (NIST)

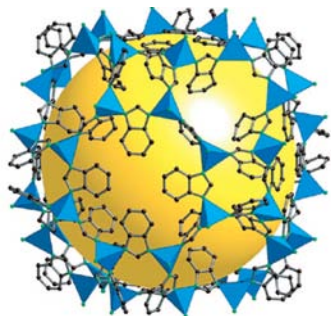


The image contains two plots. On the left is a transmission electron microscopy (TEM) image showing small, dark, spherical nanoparticles. On the right is an X-ray diffraction (XRD) pattern showing a sharp peak at approximately 20 degrees 2-theta, with a legend indicating data for 'Aggregated (SNL)', 'Aggregated (UMSL)', and 'Empty Vial'.

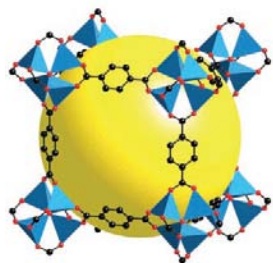
Task 1 Technical accomplishment: MOF Template suite synthesized (1 – 5 nm pores)



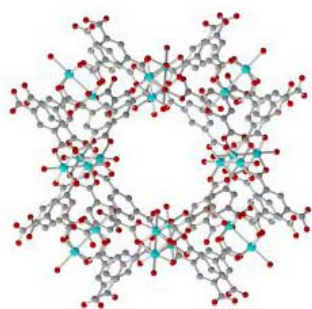
ZIF-8



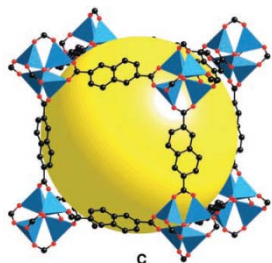
ZIF-11



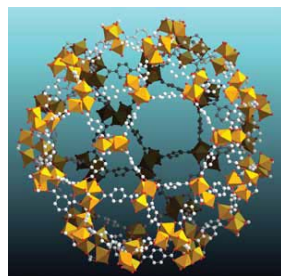
IRMOF-1 (MOF-5)



$\text{Cu}_3(\text{BTC})_2$ MOF



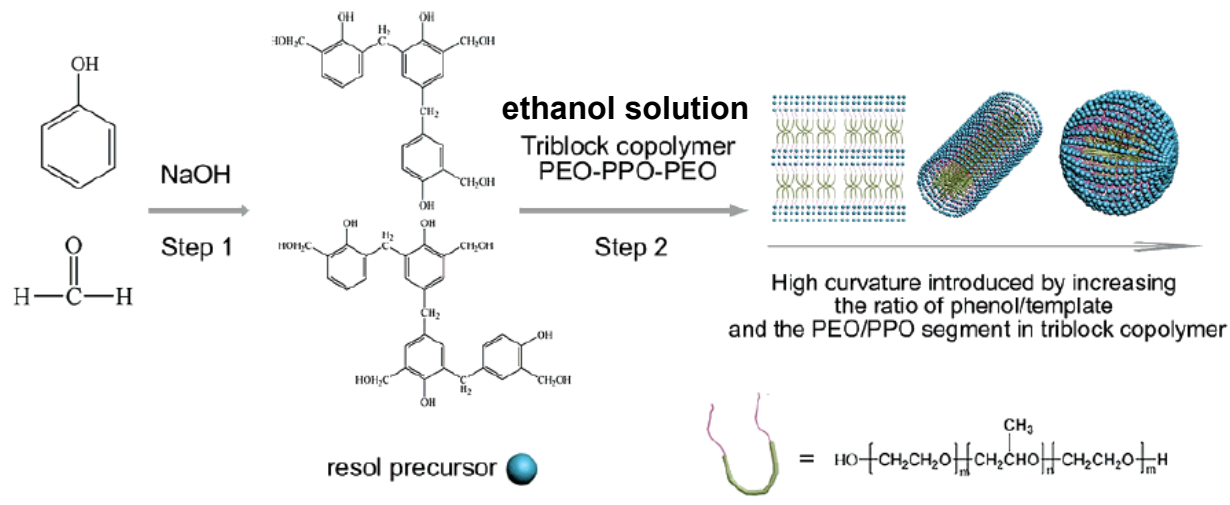
IRMOF-8



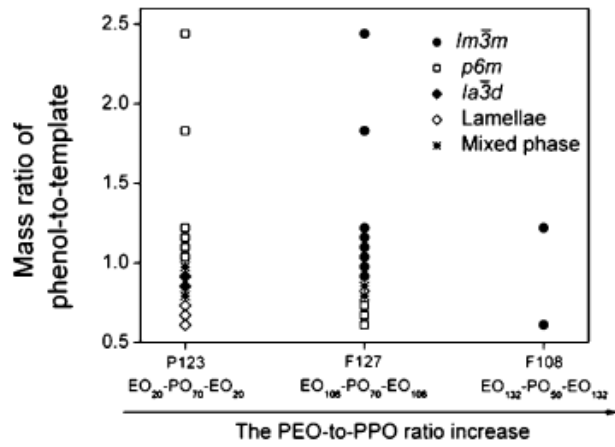
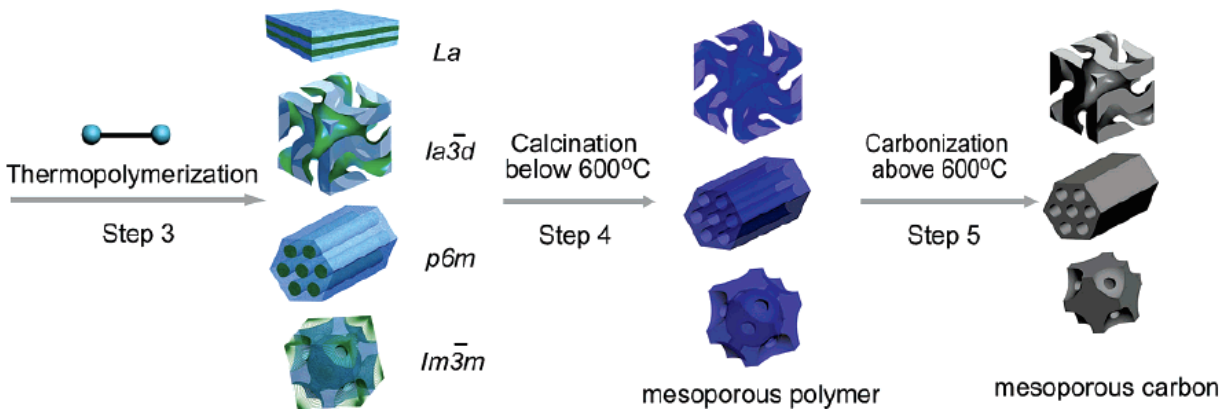
MIL-101

	Pore Opening	Pore Diameter	Surface area m^2/g
ZIF-8	3.4 Å	11.6 Å	1947
Cu_3BTC_2	6.6 Å	13.2 Å	1290
ZIF-11	3 Å	14.6 Å	1676
IRMOF-1	11.2 Å	18.6 Å	2900
IRMOF-8	12.6 Å	21.4 Å	1800
ZIF-95	3.7 Å	24 Å	1240
MIL-101	15 Å	29,34 Å	4100

Task 1 Technical accomplishment: Block-polymer and cross-linked phenolic resins for 2 – 20 nm templates



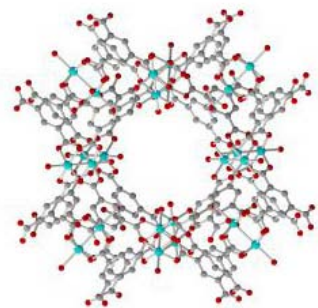
- Advantages:**
- *versatile and easily controlled mesostructure*
 - **narrow pore size distribution**
 - large volumes: 0.8 cc/g
 - tunable pore size: 2-20 nm
 - resol polymer template OR carbon-only template
 - variety of morphologies
 - potentially monolithic



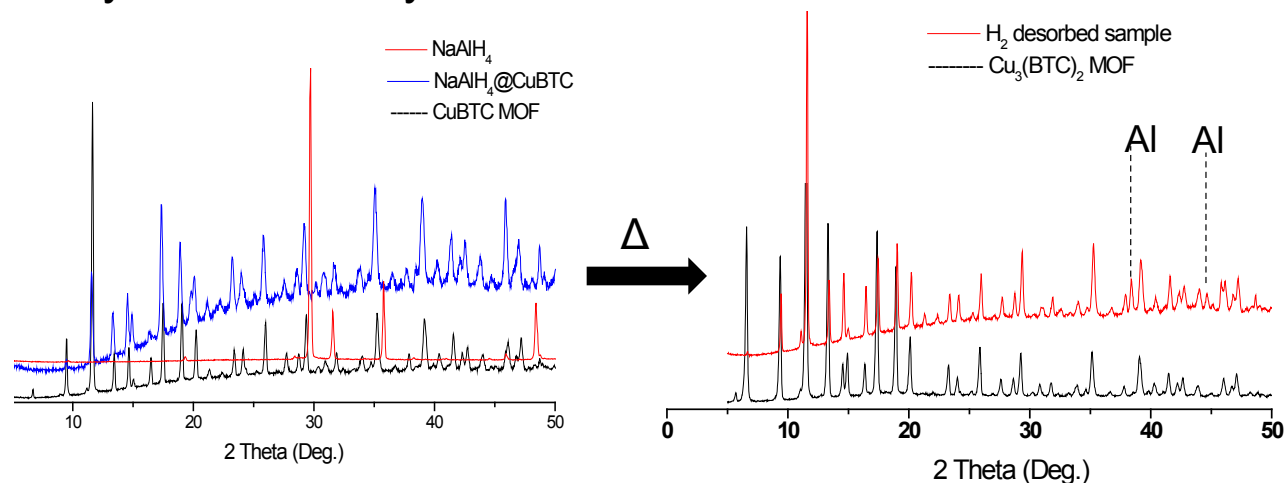
Meng, et al., *Chem. Mater.*, **18**, 4447-4464, (2006)

Task 1 Technical accomplishment: hydride compatibility with MOF templates determined

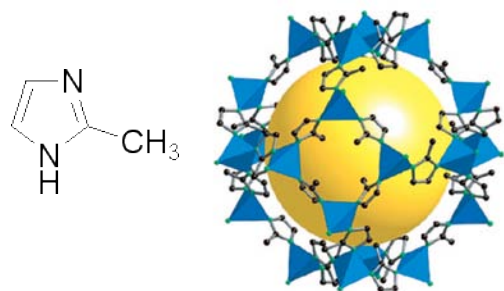
Carboxylate MOFs: chemically and thermally robust



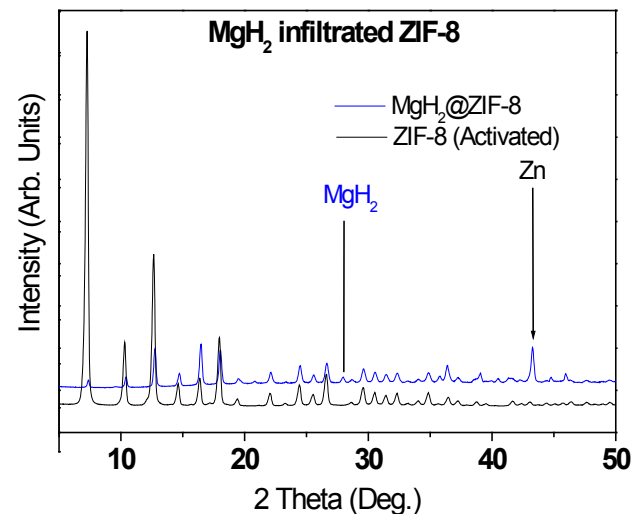
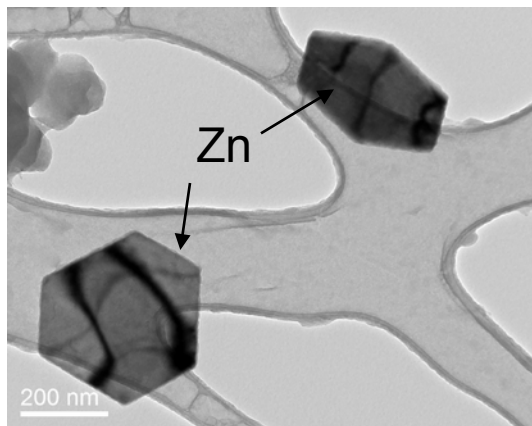
$\text{Cu}_3(\text{BTC})_2$ MOF
(carboxylate linkers)



ZIFs :degrade upon infiltration with metal hydrides

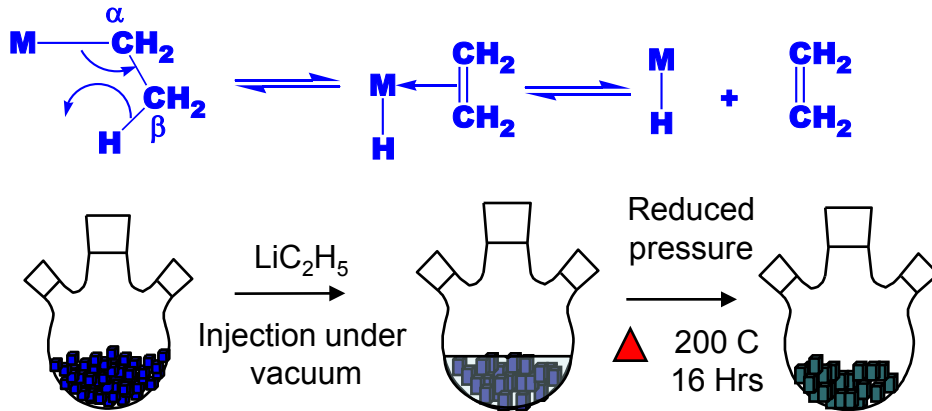


ZIF-8
(imidizolate linkers)

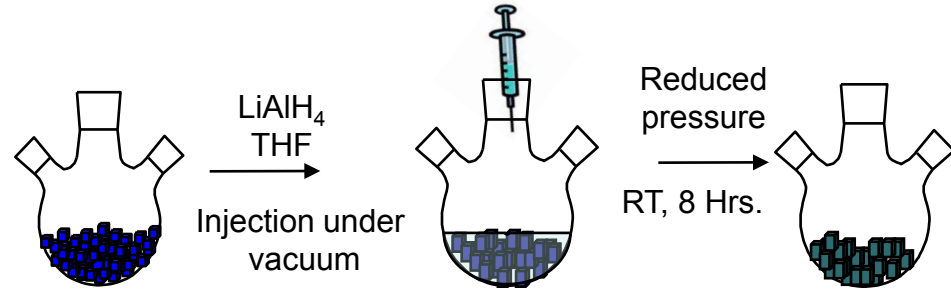


Task 1 Technical accomplishment: Hydride infiltration methods for MOFs and carbon templates developed

Simple hydrides (LiH, MgH₂)

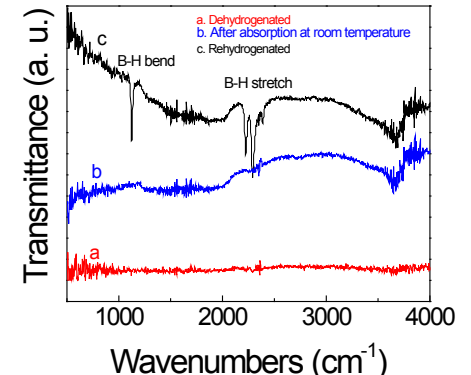
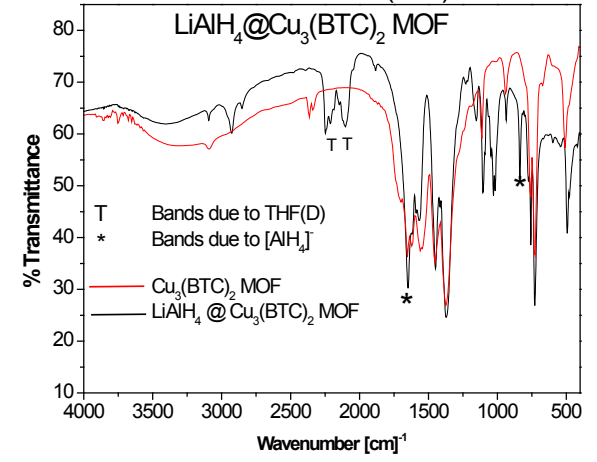
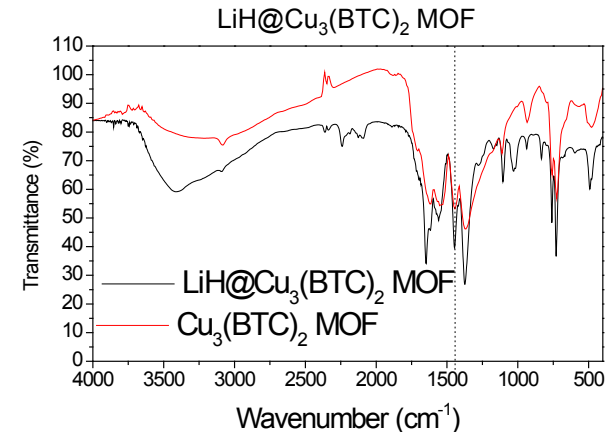
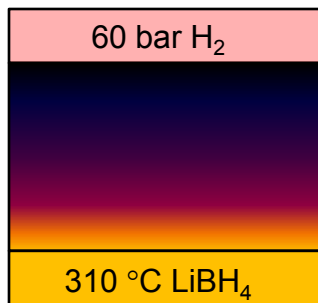


Complex hydrides (LiAlH₄, NaAlH₄)

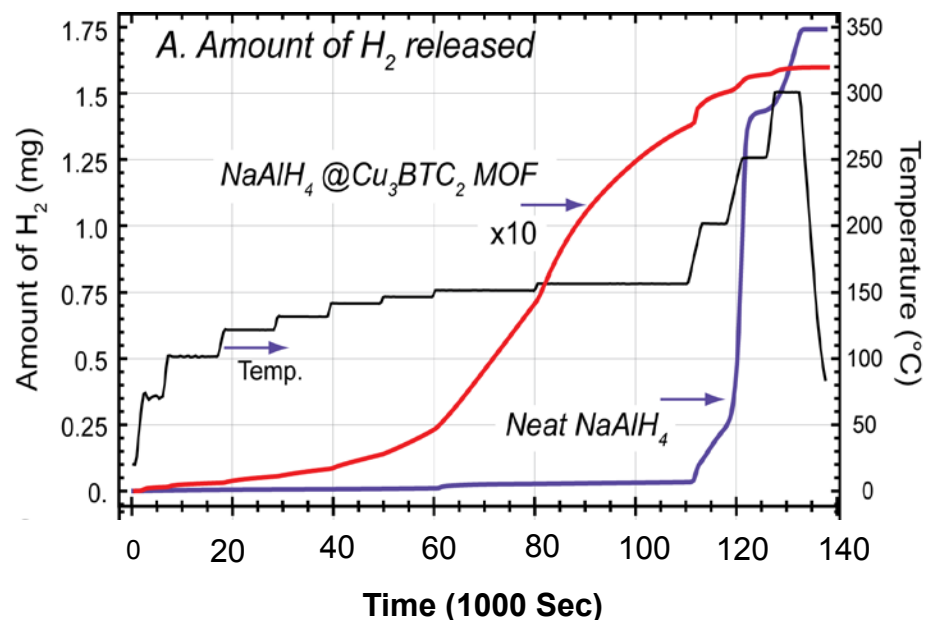


Activated MOF

Melt infiltration/porous C (LiBH₄)



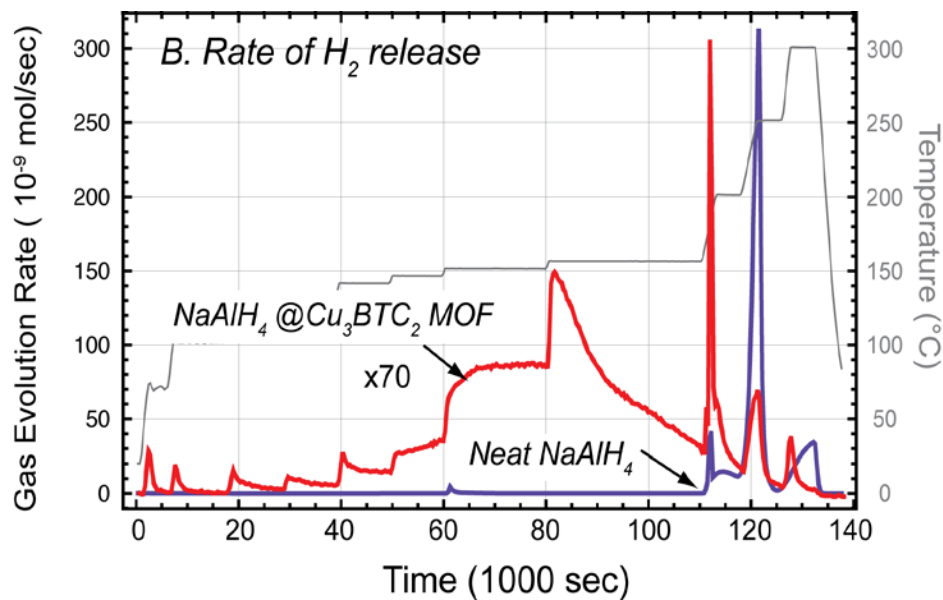
Task 2 Technical accomplishment: Thermal desorption of H₂ from NaAlH₄@Cu(BTC)



Size: 8 formula units/pore (< 1.3 nm)

Desorption behavior

- Bulk : H₂ desorbs at T ≥ 160 °C
- NaAlH₄@MOF: 80% H₂ desorption at T < 160 °C
- H₂ at T ≥ 300 °C: NaH



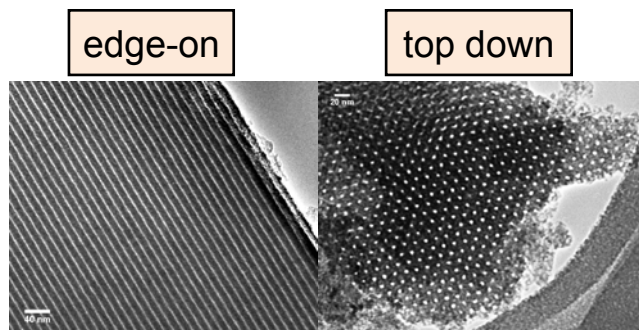
Rate of release

- Deuterated solvent (TDF) used
 - MOF stable to T ≥ 250 °C
 - 130 – 155 °C H₂ must be from NaAlH₄, not solvent or template decomposition
- ☞ **NaAlH₄ nanoparticles are destabilized relative to bulk**

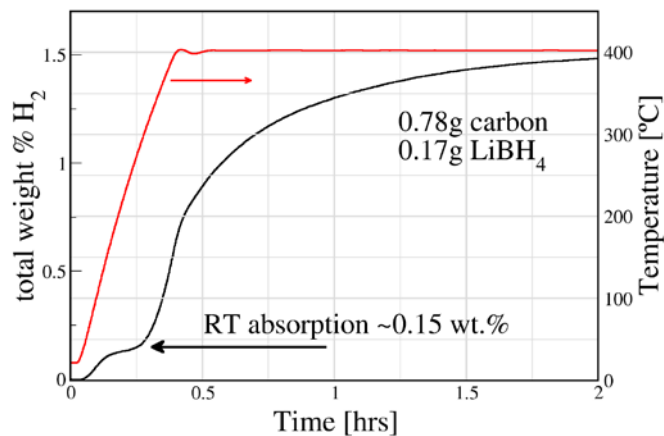
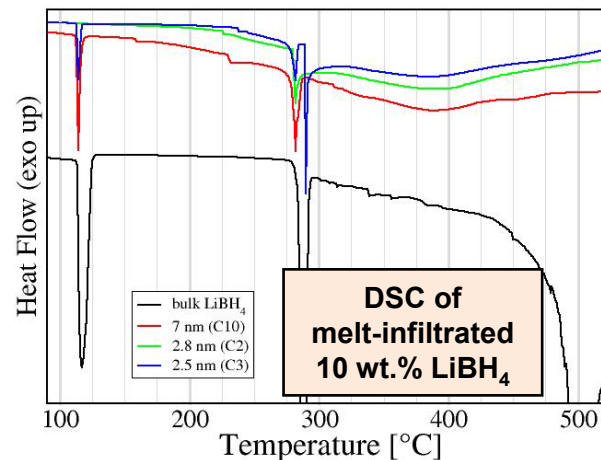
Bhakta et al. *J. Amer. Chem. Soc.* **131** (2009), 13198

Task 2 Technical accomplishment: LiBH_4 infiltration of carbons show reduced melting and decomposition temperatures

Highly-ordered hard with hexagonally packed cylindrical pore structure

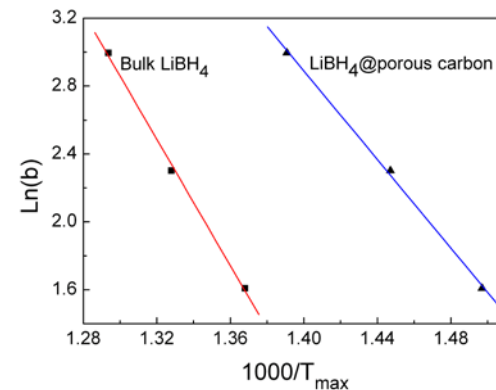


Meng, et al., *Chem. Mater.*, **18**, 4447-4464, (2006)



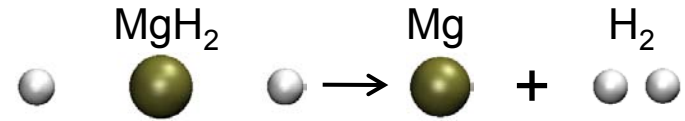
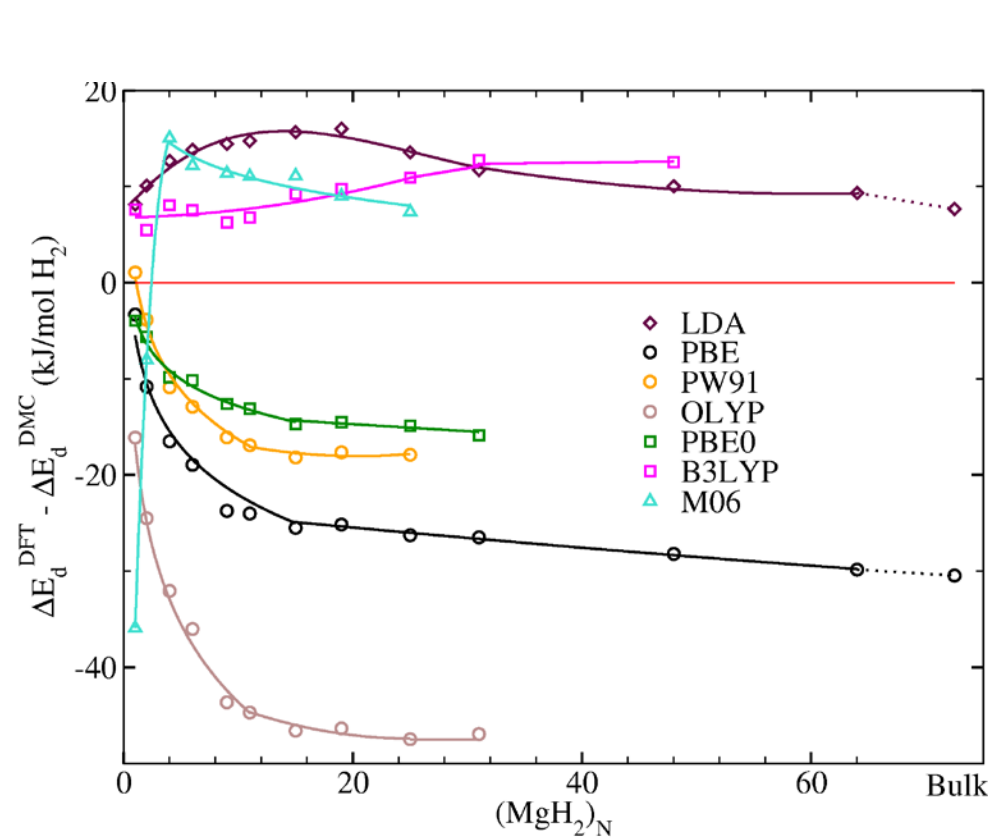
Gram-quantity Kinetics Measured

- 1st absorption 400°C, 60 bar H_2
- 2nd desorption
- 7.5 wt.% w.r.t. starting LiBH_4
- 1.6 wt.% w.r.t. carbon



- LiBH_4 confined in cylindrical pore carbon rapidly decomposes following melting
- The activation energy is reduced from 155 kJ/mol to 108 kJ/mol
- 2-5 nm diameter pores show identical behavior: surface chemistry important

Task 3 Technical accomplishment: Benchmarking of DFT by Quantum Monte Carlo reveals non-systematic errors

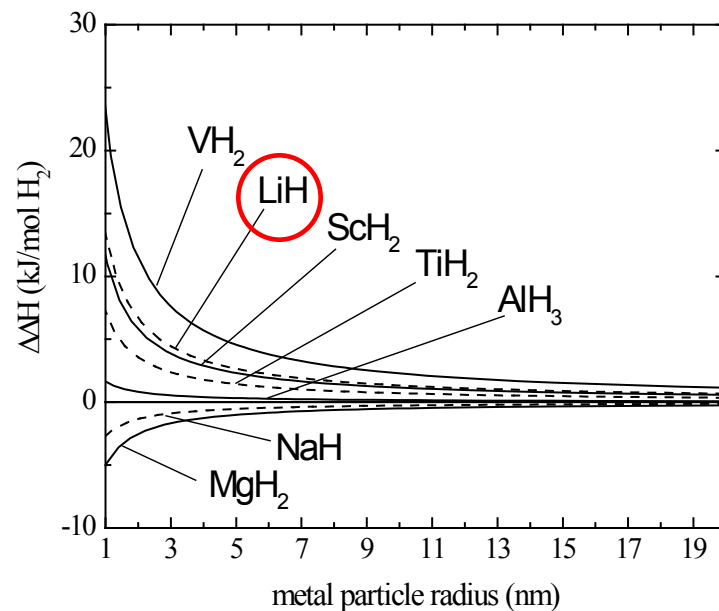
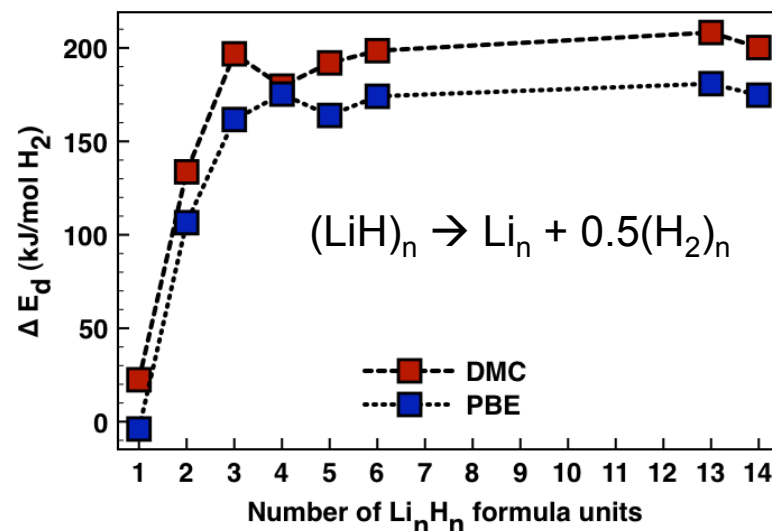


- Computed the difference between QMC and other methods as a function of size
- QMC benchmarked by:
 - CCSD(T)/QZ at small size
 - Experiment at bulk
- Error has strong size-dependence
- Size dependence is method dependent

Predicted $(\text{MgH}_2)_n$ dehydrogenation energies

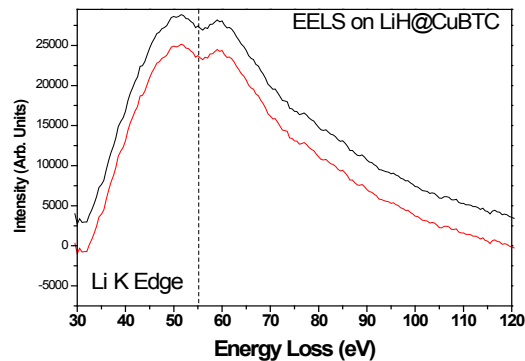
Task 3 Technical accomplishment: QMC modeling reveals minimal destabilization in $(\text{LiH})_n$ clusters

- Nonsystematic DMC-DFT difference
 - No zero-point energy included (yet)
- Clusters destabilized only at $n < 3$
- Slope of Li_nH_n binding is higher than $(\text{Li})_n$, so energy binding increases with cluster size
- Wulff construction predicts LiH is stabilized as size decreases
 - Opposite of DMC trend
 - Validity of Wulff construction for $r < 3$ nm is questionable

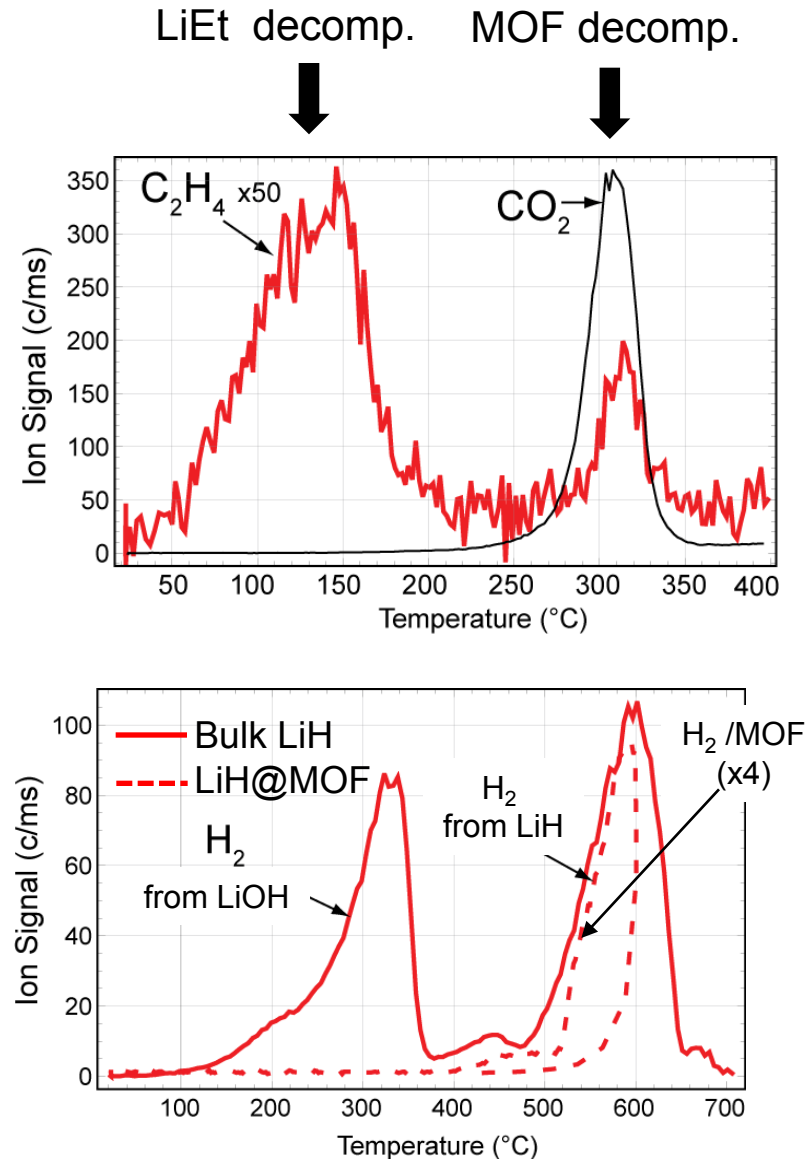


Task 2 Technical accomplishment: LiH@MOF infiltration and desorption behavior

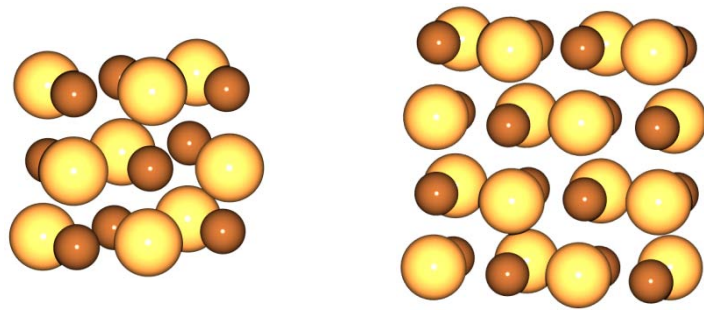
- Solution infiltration using LiC_2H_5
- $\text{LiC}_2\text{H}_5 \xrightarrow{\Delta} \text{LiH} + \text{C}_2\text{H}_4$
 - Elemental analysis: 0.92 wt% Li (1.5 Li atoms per large pore)
- TEM/EELS confirms Li in the pores



- No H_2 desorption below MOF T_{decomp}
- **Consistent with theory**
 - QMC: no destabilization except $(\text{LiH})_n$ ($n=1,2$)
 - Wulff construction mode: nano LiH is stabilized relative to bulk



Task 3 Technical accomplishment: Nano-PEGS finds high-symmetry large ionic clusters for computational studies



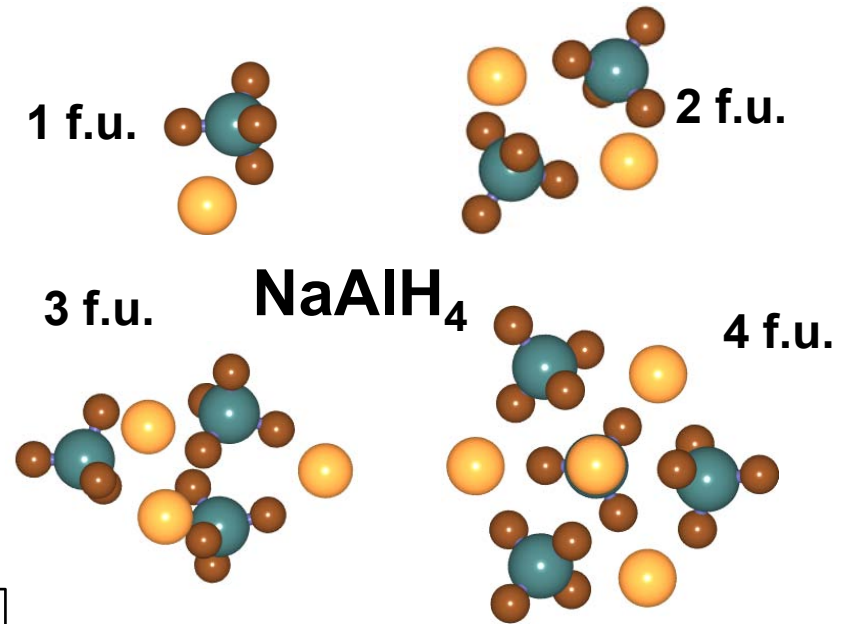
9 f.u.

16 f.u.

Lithium hydride sheets [100]

acceptance criterion

$$p(E_1 \rightarrow E_2) = \min \left[\frac{g(E_1)}{g(E_2)}, 1 \right]$$



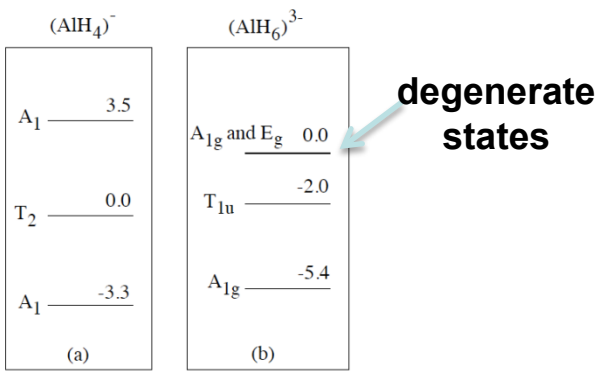
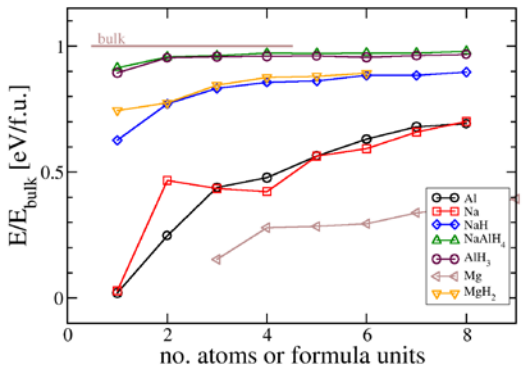
Wang & Landau, PRE, **64**, 056101, (2001)

Advantages of Energy-Space Random Walk:

- Monte Carlo minimization does **NOT** get stuck in local minima
- finds all high symmetry (low energy) cluster polymorphs **in one run**

Task 3 Technical accomplishment: NaAlH_4 nanoclusters decompose without going through Na_3AlH_6 intermediate

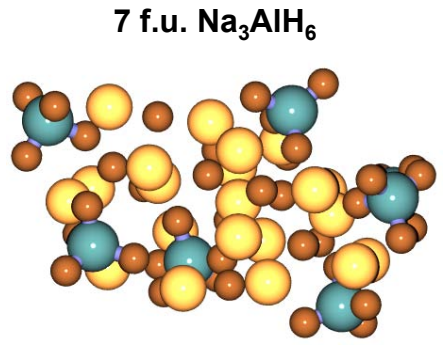
Ionic Clusters Rapidly Approach Bulk Cohesive Energy



Electronic structure of isolated anions (charge compensated)*

*Ozolins, V.; Udovic, T.; Majzoub, E.H.; J. Al. Comp, (2004) 375, 1-10

Small Clusters of Na_3AlH_6 Are Unstable Due to Jahn-Teller Distortions And Do Not Appear To Be Decomposition Intermediates



Relaxes to $\text{NaH} + \text{NaAlH}_4$

Each cluster energy calculated separately

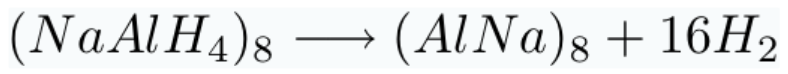
$(\text{NaAlH}_4)_1, (\text{NaAlH}_4)_2, (\text{NaAlH}_4)_3, (\text{NaAlH}_4)_4, (\text{NaAlH}_4)_5, (\text{NaAlH}_4)_6, \dots$
 $(\text{NaH})_1, (\text{NaH})_2, (\text{NaH})_3, (\text{NaH})_4, (\text{NaH})_5, (\text{NaH})_6, (\text{NaH})_7, (\text{NaH})_8, \dots$
 $\text{Al}_1, \text{Al}_2, \text{Al}_3, \text{Al}_4, \text{Al}_5, \text{Al}_6, \text{Al}_7, \text{Al}_8, \text{Na}_1, \text{Na}_2, \text{Na}_3, \text{Na}_4, \text{Na}_5, \text{Na}_6, \text{Na}_7, \text{Na}_8, \dots$
 $(\text{NaAl})_1, (\text{NaAl})_2, (\text{NaAl})_3, (\text{NaAl})_4, (\text{NaAl})_5, (\text{NaAl})_6, (\text{NaAl})_7, (\text{NaAl})_8, \dots$
 $(\text{AlH}_3)_1, (\text{AlH}_3)_2, (\text{AlH}_3)_3, (\text{AlH}_3)_4, (\text{AlH}_3)_5, (\text{AlH}_3)_6, (\text{AlH}_3)_7, (\text{AlH}_3)_8, \dots$
 $(\text{Na}_3\text{AlH}_6)_1, (\text{Na}_3\text{AlH}_6)_2, (\text{Na}_3\text{AlH}_6)_3, (\text{Na}_3\text{AlH}_6)_4, (\text{Na}_3\text{AlH}_6)_5, \dots$

$$G(T, p) = \sum_i x_i F_i(T) - \frac{\mu_{\text{H}_2}(T, p)}{2} \sum_i x_i n_i^H$$

$$f_s = \sum_i x_i n_i^s = \text{constant}$$

Phase diagram determined via free energy minimization following A. Akbarzadeh, V. Ozolinš, C. Wolverton, Adv. Mater. 2007, 19, 3233–3239

Decomposition pathway for clusters up to 8 formula units appears to be a single step decomposition



Future Plans

Remainder of FY10 (Project year 2)

- **Nanoparticle synthesis**

- MOFs: test size effect in 1 – 3 nm size range for NaAlH_4 and MgH_2
- Develop synthetic method to make hydride combinations
 - **Go/No-Go (9/2010)**: Continue compositional tuning effort?
- Complete infiltration of carbon templates with complex hydrides
- Complete investigation of size effects (2 -- 15 nm)

- **Dehydrogenation thermodynamics and kinetics**

- NaAlH_4 , MgH_2 , and mixed-hydride nanoparticle desorption kinetics
- LiBH_4 -infiltrated carbon templates: bulk kinetics as a function of pore size

- **Theory**

- Compute properties of $(\text{NaH})_n$ and $(\text{LiH})_n$ nanoparticles
- Model cluster thermodynamics in mixed-metal Mg-Al-H system

FY11 (Project year 3)

- Measure rehydrogenation kinetics of nanoscale hydrides
- Synthesize compositionally tuned nanoclusters, using QMC modeling as guide
- Complete investigation of pore chemistry effects
 - Evaluate size vs. template interaction effects in carbon templates



Collaborations



Project Team:

- **Prof. Jeffery Grossman, MIT Mater. Sci. Eng.** (subcontract to Sandia). Lead investigator, non-ionic hydrides and code validation (project funds 1 postdoc)
- **Prof. Eric Majzoub, Univ. of Missouri St. Louis Dept. of Physics** (subcontract to Sandia). Lead investigator, BCP templates, and complex hydride modeling (project funds 1 postdoc) (2 grad students other funds)
- **Dr. Julie Herberg, Lawrence Livermore National Laboratory** (Sandia subcontract). Lead investigator, NMR analysis of metal hydride nanoparticles
- **Dr. Terry Udovic, NIST** (funding from DOE to NIST). Lead investigator, neutron analytical probes.
- **Other collaborations:**
- **Prof. Ian Robertson, Univ. Illinois U-C (UIUC).** TEM tomographic imaging of infiltrated templates
- **Prof. Roland Fischer, Ruhr Univ. Bochum (Germany).** Leading group worldwide developing MOF infiltration methods. Visited Sandia March 2009; visits by Sandia staff and postdoc in May and June 2009



Summary of Key Results

Relevance: Many attractive hydrides are too stable for practical use; nanoconfinement could mitigate this problem

Approach: Use highly ordered nanoporous materials such as MOFs and BCP to systematically probe the origins of nanohydride destabilization

Technical accomplishments and progress:

- Synthesized templates covering 1 – 15 nm size range
- Infiltrated with LiH, MgH₂, LiBH₄, LiAlH₄, NaAlH₄, yielding particles as small as 1.5 nm diameter
- Observed 50-100°C drop in NaAlH₄@MOF vs. bulk and decrease in m.p. of LiBH₄@hex-C
- Benchmarked DFT against QMC; found significant nonsystematic errors in DFT
- New NanoPEGS code developed and tested for simple and complex hydrides

Collaborations: Interdisciplinary team effectively integrates experiment and theory



Proposed future research: 1) modulate thermodynamics of simple hydrides through compositional tuning; 2) separate effects of size and pore₉ chemical environment to determine relative magnitudes

Supplemental Slides

Approach Summary: Task Structure and Project Deliverables

Task 1	Nanoparticle synthesis and characterization (SNL, UMSL, LLNL, NIST) <ul style="list-style-type: none">• 1 -5 nm: Sandia• 5 – 20 nm: UMSL• NIST: x-ray, neutron, gamma methods• LLNL: MAS-NMR
Task 2	Sorption measurements and kinetics (UMSL, SNL)
Task 3	Theoretical Modeling for Rational Design of Particles (MIT, UMSL) <ul style="list-style-type: none">• Benchmarking, validation, simple hydrides: MIT• Strongly ionic materials: UMSL
Task 4	Project management (SNL)

Technical objectives

- **Task 1:** Optimized nanoparticle synthetic procedures, suitable for further development and scale up, for one simple hydride (e.g. MgH_2) and one complex hydride (e.g. NaAlH_4)
- **Task 2:** Quantified size and composition dependencies of nanoparticle dehydrogenation thermodynamics and kinetics
- **Task 3:** Validated computational modeling approaches predicting to the properties of hydride nanoparticles

Our approach compliments ongoing work in the DOE Office of Fuel Cell Technologies and elsewhere by developing highly ordered platforms for nanoparticle synthesis and validated theoretical approaches that enable systematic tuning of nanoparticle thermodynamics and kinetics