

IV.A.2 Tuneable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis using Ordered Polymer Templates

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- Massachusetts Institute of Technology, Cambridge, MA
- Lawrence Livermore National Laboratory, Livermore, CA

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Objectives

- Achieve tuneable thermodynamics for high-gravimetric-capacity metal hydrides by creating and stabilizing nanoparticles with controlled size, composition, and properties.
- Develop synthetic routes for reactive metal nanoparticles within crystalline nanoporous materials and block copolymer templates.

- Systematically probe the effects of size and composition to determine the onset and extent of nanoscale effects on the thermodynamics and kinetics of hydrogen sorption.
- Benchmark theoretical approaches to modeling the thermodynamics metal hydride nanoparticles and develop computational tools to guide synthesis.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is directed toward developing hydrogen storage materials with desorption thermodynamics and kinetics that can be tuned to meet specific system requirements. The project is based on the hypothesis that confinement of metal hydrides within the chemically and geometrically well-defined pores of nanoporous framework materials such as metal-organic frameworks (MOFs) will destabilize the materials, thereby reducing their H₂ desorption temperatures and accelerating the kinetics. If successful, the project will address the following DOE technical targets, as outlined in the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

DOE Targets for Hydrogen Storage

Parameter	DOE 2010 Target	Project Status
Maximum Delivery Temperature	85°C	H ₂ desorption as low as 75°C in vacuum observed for nanoconfined NaAlH ₄ (bulk desorbs at 250°C under the same conditions)

Accomplishments

- Synthesized a suite of MOF and nanoporous carbon templates with <1 nm to 20 nm pore sizes.
- Developed and refined infiltration methods for simple metal hydrides, e.g. LiH, MgH₂ using

organometallic precursor route, achieving loadings of up to 5.8 wt% Li.

- Demonstrated that both the thermodynamics and kinetics of melt-infiltrated LiBH_4 nanoparticles in 2-nm highly porous carbon are greatly improved with respect to bulk LiBH_4 . The onset desorption temperature decreases from 460°C to 220°C (1 bar) and no B_2H_6 impurity is detected.
- Showed that no destabilization of LiH nanoparticles in MOF templates occurs relative to bulk, consistent with quantum Monte Carlo predictions.
- Predicted that $(\text{MgAlH}_5)_n$, where $n = 1-8$, are stable, suggesting that synthesis of this unknown compound in the form of nanoclusters within templates should be feasible.
- Computed the phase diagram of nanocluster NaAlH_4 from first-principles density functional theory (DFT) and nano-PEGS cluster prototypes.
- Predicted that small clusters of AlH_3 increase in stability dramatically, with 1 formula unit of AlH_3 predicted to have a decomposition enthalpy of about 150 kJ/mol H_2 .



Introduction

Some of the most attractive hydrogen storage materials, such as MgH_2 , AlH_3 , and LiBH_4 , have unfavorable desorption thermodynamics and are either too stable (e.g. MgH_2) or too unstable (e.g. AlH_3) in bulk form to be practical, particularly for vehicular transport applications. However, recent theoretical and experimental results indicate that decreasing particle size can substantially reduce the stability of metal hydrides, leading to lower desorption temperatures. The key challenges that must be addressed are to:

1) develop synthetic routes that provide controlled size and composition; 2) stabilize particles over time; and 3) develop computational tools to guide synthesis that can accurately address particle sizes spanning the micro-to-meso length scales. This project addresses all three challenges and, if successful, will create for the first time nanoscale hydrogen storage materials with tailorable composition and size compatible with fuel-cell materials over a wide range of operating temperatures.

Approach

We are using highly ordered, chemically tailorable nanoporous templates to create particles ranging in size from <1 nm to 20 nm, the critical size range at which nanoscale effects are anticipated. These templates are infiltrated with hydride precursors or hydrides themselves, using mild synthetic routes that eliminate template degradation. The resulting template-stabilized

nanoparticles, are characterized to determine particle size, composition, and desorption thermodynamics and kinetics. Validated computational modeling tools guide synthesis. This approach allows nanoparticle dimensions and hydride composition to be systematically varied, enabling the effects of nanoscale dimensions on hydride thermodynamics to be determined.

Results

LiH@MOF Hydrogen Desorption

The H_2 desorption behavior of LiH nanoparticles is not very different from the corresponding bulk-phase materials (Figure 1). Using the simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS), which provides mass data for evolved gas-phase species as a function of time under highly controlled temperature conditions, we obtained a detailed picture of the a series of processes occurring during nanoparticle-composite decomposition.

STMBMS data for EtLi infiltrated sample reveal that desorption of C_2H_4 occurs at temperatures between 50-200°C, indicating formation of LiH (Figure 1,

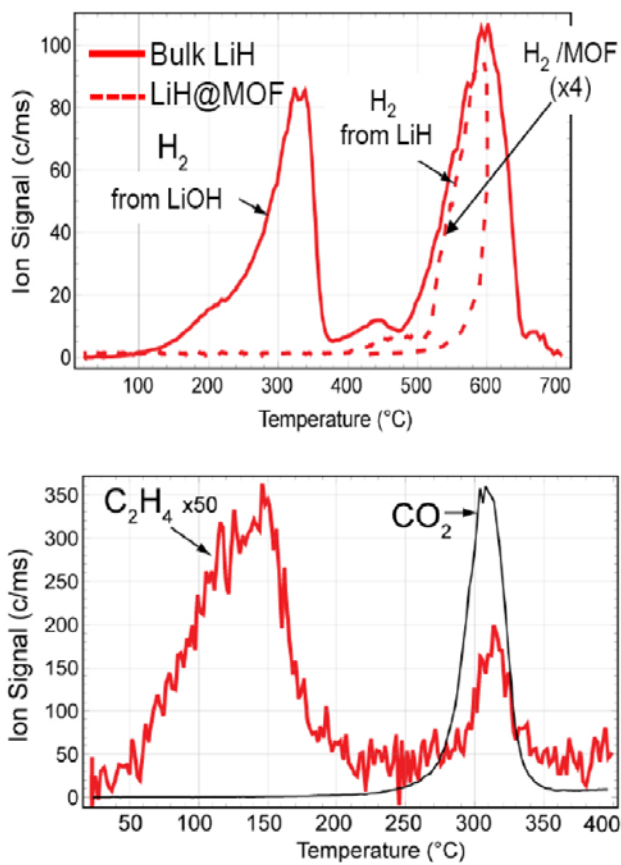


FIGURE 1. Top: Hydrogen desorption from bulk LiH in comparison with LiH@CuBTC MOF. Bottom: Reduction of EtLi and MOF decomposition.

top). The MOF template decomposes at $\sim 260\text{--}350^\circ\text{C}$. Hydrogen desorption from bulk LiH peaks at $\sim 580^\circ\text{C}$ in this experiment (Figure 1, bottom). Similarly, H_2 desorption from MOF-confined LiH occurs at approximately the same temperature. This indicates that neither the thermodynamics nor the kinetics of nano-LiH are significantly altered by nanoconfinement. These observations are consistent with our quantum Monte Carlo calculations (see below), which suggest that only clusters as small as $(\text{LiH})_n$, $n=1,2$ are destabilized. Moreover, these results indicate that, contrary to predictions based on a Wulff construction model [1] (see following), nanoscale LiH is not significantly stabilized by nanoscale confinement. Experiments to quantify the thermodynamic properties of the LiH@MOF are currently underway.

Controlling the Decomposition Pathway of LiBH_4 via Confinement in Highly Ordered Nanoporous Carbon

The decomposition behavior of LiBH_4 has been investigated in the presence of highly ordered nanoporous carbon (NPC) with columnar pores of average pore diameter 2.0 nm and a narrow size distribution with surface area and pore volume of about $594\text{ m}^2/\text{g}$ and $0.35\text{ cm}^3/\text{g}$, respectively. The columnar pores are packed in a hexagonal geometry. X-ray diffraction and infrared spectroscopy measurements confirm that infiltrated samples result in non-crystalline LiBH_4 within the pore structure of the carbon. In contrast to previous studies of LiBH_4 confined in 12 nm and larger carbon aerogel pores, the non-crystalline LiBH_4 embedded in 2.0 nm pores not only results in the disappearance of the structural phase transition at around 100°C , and the melting transition, but also the significant decrease of the onset desorption temperature from 460°C to 220°C . Diborane release is suppressed or eliminated in the decomposition of non-crystalline LiBH_4 in the 2.0 nm pores, and only forms during the infiltration process.

Figure 2 shows the differential scanning calorimetry (DSC) plots of bulk LiBH_4 , a physical mixture of LiBH_4/NPC , and $\text{LiBH}_4@\text{NPC}$. In agreement with bulk LiBH_4 , the DSC plot of the physical mixture of LiBH_4/NPC shows the orthorhombic to hexagonal structure transition at a temperature of 115°C and melting at 284°C . The decomposition peak of bulk LiBH_4 appears around 495°C . Rapid dehydrogenation after the melting was observed for LiBH_4/NPC , and the decomposition peak appeared around 345°C . In contrast, the pre-melted sample of $\text{LiBH}_4@\text{NPC}$ did not show the structure transition from orthorhombic to hexagonal and no distinct melting point was observed, indicating that LiBH_4 confined in NPC becomes amorphous. $\text{LiBH}_4@\text{carbon aerogel}$ has a lower, but distinct melting point. We can

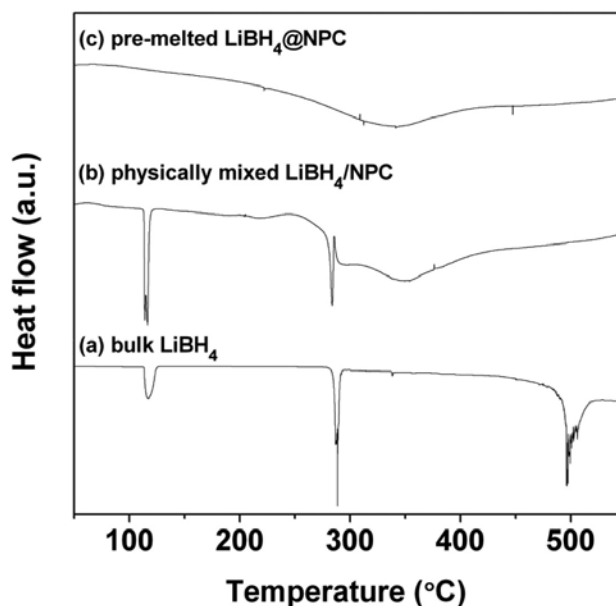


FIGURE 2. DSC traces of (a) bulk LiBH_4 , (b) physically mixed LiBH_4/NPC , and (c) pre-melted $\text{LiBH}_4@\text{NPC}$. The heating rate was $10^\circ\text{C}/\text{min}$.

see that LiBH_4 confined in NPC begins to decompose *below* the normal melting point.

Theoretical Modeling of Hydride Nanoparticles

Quantum Monte Carlo Modeling: Computational modeling of Li and $(\text{LiH})_n$ clusters ($n = 1\text{--}20$) clusters was completed, in which quantum Monte Carlo calculations were compared with the results of DFT obtained from a variety of functionals and the literature. These results enabled us to conceptually test the predictions of a Wulff construction model of hydride destabilization [2]. Comparing the diffusion Monte Carlo (DMC) predictions to the Wulff construction (Figure 3), we find that DMC predicts very little change in the hydrogen absorption energy over most values of n , with only LiH and $(\text{LiH})_2$ destabilized relative to bulk. In contrast, the Wulff construction predicts that LiH is *stabilized* as its particle radius decreases below $\sim 9\text{ nm}$. In fact, of the hydrides examined by Kim et al., only MgH_2 and NaH are predicted to be destabilized at the nanoscale. Our previous DMC results for MgH_2 are consistent with this, although the destabilization occurs at much small particle sizes ($<1\text{ nm}$ diameter). Unfortunately, we cannot perform comparable simulations for NaH clusters because of the lack of high-quality effective core potentials for sodium. Nevertheless, these results suggest that size affects the energetics of hydride nanoparticles only at extremely small sizes. The corollary, however, is that altered chemistry of hydrides, in particular a change in the thermodynamics observed by the group of de Jongh et al. [3], as well as changes in kinetics observed by several

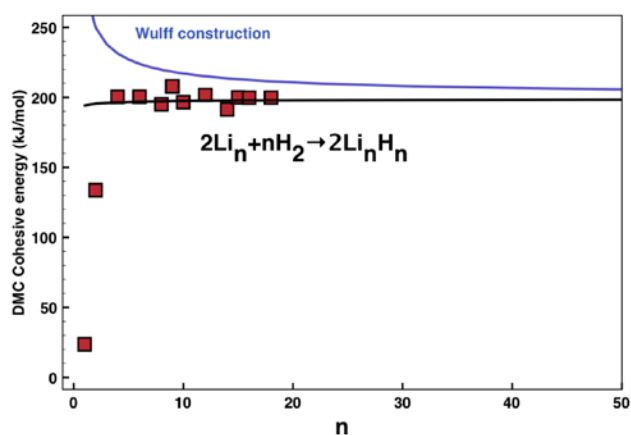


FIGURE 3. Energy per H_2 molecule gained by transforming Li metal to the hydride, along with the same calculated from the $n^{-1/3}$ extrapolation. The results from the Wulff construction are shown as well and are referenced to the value for bulk predicted by DMC.

groups, are connected in some way to the local chemical environment of the scaffold pores.

We also explored the possibility of alloying magnesium and aluminum to tune the hydrogen desorption energy. MgAlH_5 is a hypothetical compound, capable of storing up to 8.5% hydrogen by weight. However, DFT studies by Akbarzadeh et al. indicate that the bulk material is unstable relative to $\text{MgH}_2 + \text{Al} + 1.5\text{H}_2$ [4]. We hypothesize that the stability of Mg-Al clusters will be intermediate between that of AlH_3 and MgH_2 , assuming that a stable cluster can form. In our initial DMC calculations, shown in Figure 4 for MgAlH_5 clusters with up to eight formula units, we find that the desorption energy scales quite differently from that of the Li clusters. This energy is highest for MgAl and progressively decreases until it reaches values near the appropriate range for hydrogen storage ($\sim 20\text{--}60 \text{ kJ mol}^{-1}$) for an eight formula-unit cluster. These clusters are also of the correct size to be made within a MOF, having diameters around 1 nm. We are currently exploring different alloying concentrations to further enhance the tunability of these clusters and are initiating an experimental plan to determine if such clusters can be formed.

Phase Diagram of Nano-Cluster NaAlH_4 from First-Principles DFT and Nano-PEGS Cluster Prototypes: We have calculated the phase diagram of small clusters of atoms in the Na-Al-H ternary system using first-principles and determine the decomposition pathway of NaAlH_4 as a function of Na:Al ratio and cluster size up to 8 formula units. We included as decomposition products clusters of Na, Al, mixed NaAl, and ionic clusters AlH_3 , NaH, and NaAlH_4 . Cluster geometries for ionic clusters were obtained by relaxing prototype electrostatic ground state (PEGS) structures using density-functional theory calculations;

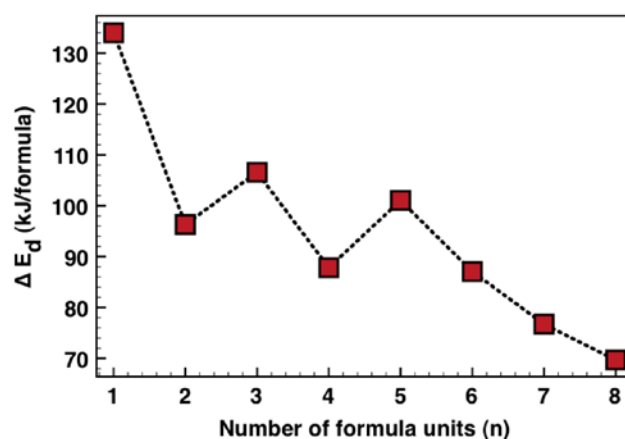


FIGURE 4. DMC predictions of the H_2 desorption energy from $(\text{MgAlH}_5)_n$, where $n = 1 - 8$.

vibrational free energy was also calculated for each of the clusters. We find that small clusters of AlH_3 increase in stability with smaller cluster size from enthalpies of around 51 to 160 kJ/mol H_2 for 8 and 1 formula units, respectively. In contrast, small clusters of NaH have an enthalpy of decomposition of about 70 kJ/mol H_2 , and show no destabilization with size until the cluster is two formula units or smaller when they spontaneously decompose. Clusters of NaAlH_4 also show increasing stability with decreasing cluster size with an enthalpy of decomposition that increases from 80 kJ/mol H_2 for 8 f.u. clusters) to 150 kJ/mol H_2 for 1 f.u. clusters. Most interestingly, NaAlH_4 clusters are found to decompose directly into mixed metal AlNa clusters in one step. The lack of intermediate Na_3AlH_6 in the decomposition path is in agreement with recent experimental work on nanoconfined NaAlH_4 in nanoporous carbons.

Conclusions and Future Directions

Conclusions

- Both thermodynamic and kinetic effects are observed when metal hydrides are confined within nanoporous templates.
- Simple hydrides (e.g. LiH and MgH_2) are not destabilized until very small cluster sizes (≤ 5 formula units). This is confirmed by both theory and experiment, invalidating the Wulff construction model for at least these two materials.
- Two complex hydrides we examined, NaAlH_4 and LiBH_4 , are kinetically destabilized by nanoconfinement. In addition, thermodynamic destabilization is either observed (LiBH_4 at $\sim 2 \text{ nm}$) or predicted (NaAlH_4 , at 8 formula units, or $\sim 1 \text{ nm}$), suggesting that both size and pore environment influence hydride stability.

Future Directions

- Complete an investigation of nanoscale LiBH_4 , using both MOF and NPC templates with overlapping pore sizes so that the effects of size and pore chemistry can be systematically evaluated.
- Investigate LiBH_4 decomposition on graphene sheets for comparison with hard carbon framework experimental results.
- Complete Mg-Al-H cluster phase diagram (collaboration with MIT).
- Complete investigation of compositional tuning within the Mg-Al-H system.
- Complete and submit journal articles on:
 - 1) nanocluster thermodynamics of complex hydrides using nanoPEGS+DFT computational framework;
 - 2) experimental and theoretical tests of the Wulff construction model, using simple hydrides; and
 - 3) the influence of size and pore environment on complex hydride stability, using LiBH_4 as a model material.
- Complete infiltration of nanoporous hard carbons with $\text{Ca}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2$, and LiAlH_4 .

FY 2010 Publications/Presentations

1. X. Liu, D. Peaslee, C.Z. Jost, and E.H. Majzoub “Controlling the Decomposition Pathway of LiBH_4 via Confinement in Highly Ordered Nanoporous Carbon,” accepted *J. Phys. Chem. C*, July 2010.
2. Z.G. Wu, M.D. Allendorf, J.C. Grossman “Quantum Monte Carlo Simulation of Nanoscale MgH_2 Cluster Thermodynamics,” *J. Amer. Chem. Soc.* **131** (2009), 13918.
3. R.K. Bhakta, J.L. Herberg, B. Jacobs, A. Highley, R. Behrens, Jr., N.W. Ockwig, J.A. Greathouse, and M.D. Allendorf “Metal-Organic Frameworks As Templates for Nanoscale NaAlH_4 ,” *J. Amer. Chem. Soc.* **131** (2009), 13198.
4. R.K. Bhakta, J.L. Herberg, R. Behrens, J. Grossman, Z. Wu, and M.D. Allendorf “Experimental and computational investigation of MOF-templated metal hydride nanoparticles,” Fall ACS meeting, Washington, D.C. August 17–20, 2009.

5. R.K. Bhakta, J.L. Herberg, A. Highley, R. Behrens, and M.D. Allendorf; “Investigation of Metal Hydride Nanoparticles Templated in Metal Organic Frameworks,” Fall MRS meeting, Nov. 30 – Dec. 3, 2009, Boston, MA.
6. R.K. Bhakta, J.L. Herberg, A. Highley, R. Behrens, and M.D. Allendorf; “Investigation of Metal Hydride Nanoparticles Templated in Metal Organic Frameworks,” ACS Spring 2010 ACS meeting; SF, CA March 21–25, 2010.
7. M.D. Allendorf, R. Bhakta, R. Behrens, Jr., E.H. Majzoub, X. Liu, D. Peaslee, J.L. Herberg, L.K. Wagner, J.C. Grossman “Effects of confinement on the thermodynamics and kinetics of metal hydrides templated in ordered nanoporous frameworks,” 1st International Conference on Materials for Energy, Karlsruhe, Germany, July 5–8, 2010.
8. E.H. Majzoub “Thermodynamics of Nanocluster Complex Hydrides: Theory and Experiment”, invited keynote lecture at MH2010, Moscow, Russia, July 2010.
9. E.H. Majzoub “Thermodynamics of nanocluster complex hydrides”, Materials Research Society, Boston, Fall 2009.
10. X. Liu, C.Z. Jost, David Peaslee, E.H. Majzoub “Ordered Block Copolymer Templates for the Preparation of Nanoscale Metal Hydrides”, Poster MRS Fall 2009, Boston.
11. E. Majzoub, “Tunable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis Using Ordered Polymer Templates,” Tech Team presentation, Detroit, 09/2009.

References

1. B. Dai et al.
2. Kim et al., *Nanotechnology*, **20** (2009), 204001.
3. J.B. Gao et al. *J. Phys. Chem. C* **114** (2010), 4675.
4. Akbarzadeh et al. *Physical Review B* **79**, 184102, 2009.