

## IV.A.8 Tunable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis using Ordered Polymer Templates

Mark D. Allendorf (Primary Contact),  
Eric Majzoub<sup>1</sup>, Jeffery Grossman<sup>2</sup>, Julie Herberg<sup>3</sup>  
Mail Stop 9291  
Sandia National Laboratories  
Livermore, CA 94551-0969  
Phone: (925) 294-2895  
E-mail: mdallen@sandia.gov

DOE Manager  
HQ: Ned Stetson  
Phone: (202) 586-9995  
E-mail: Ned.Stetson@ee.doe.gov

### Subcontractors:

- <sup>1</sup> University of Missouri, St. Louis, St. Louis, MO
- <sup>2</sup> Massachusetts Institute of Technology, Cambridge, MA
- <sup>3</sup> Lawrence Livermore National Laboratory, Livermore, CA

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### Technical Targets

The objective of this project is to achieve tunable thermodynamics and/or kinetics by confining metal hydrides within the chemically and geometrically well-defined pores of templates such as metal-organic frameworks (MOFs) and porous carbons, thus allowing faster H<sub>2</sub> desorption at a lower temperature than bulk. The project addresses the following DOE technical target (Table 1), as outlined in the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

TABLE 1. DOE Targets for Hydrogen Storage

Parameter	DOE 2010 Target	Project Status
Maximum Delivery Temperature	85°C	Tunable kinetics demonstrated for nano-confined NaAlH <sub>4</sub> and LiBH <sub>4</sub> . Size-dependent desorption enthalpy observed for NaAlH <sub>4</sub> .

### Fiscal Year (FY) 2011 Objectives

- Achieve tunable 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 of metal hydride nanoparticles, and develop computational tools to guide synthesis.

### Technical Barriers

This project addresses the following technical barriers from the Storage 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

### FY 2011 Accomplishments

- Demonstrated size-dependent thermodynamics for LiBH<sub>4</sub> infiltrated into porous carbon templates: the bulk orthorhombic-to-hexagonal phase change is not observed, no melting transition occurs, and the material is amorphous.
- Showed that nano-confined NaAlH<sub>4</sub> thermodynamics are tunable: reaction to form the stable intermediate Na<sub>3</sub>AlH<sub>6</sub> is not observed. The enthalpy of H<sub>2</sub> desorption for the one-step decomposition to form NaH, Al, and H<sub>2</sub> is size dependent, consistent with theoretical results.
- Nano-confined NaAlH<sub>4</sub> decomposes more than an order of magnitude faster than bulk hydride.
- Predicted that (MgAlH<sub>5</sub>)<sub>n</sub> clusters are destabilized relative to MgH<sub>2</sub> and that compositional tuning of ΔH° is feasible.



### Introduction

Some of the most attractive hydrogen storage materials, such as MgH<sub>2</sub>, AlH<sub>3</sub>, and LiBH<sub>4</sub>, have unfavorable desorption thermodynamics and are either too stable (e.g. MgH<sub>2</sub> and LiBH<sub>4</sub>) or too unstable (e.g. AlH<sub>3</sub>) in bulk form to be of use 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.

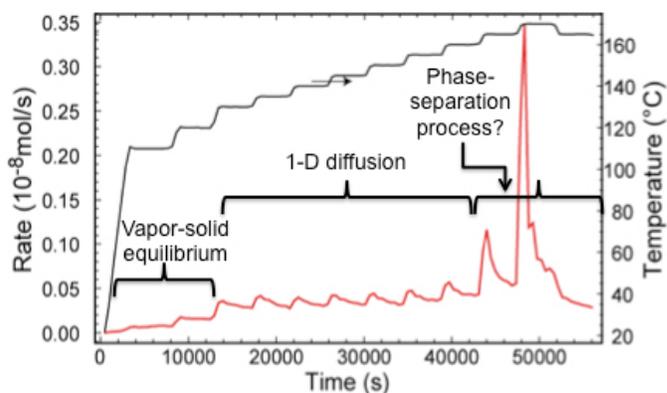
## Results

### Tunable Thermodynamics and Kinetics for Nano-Confined $\text{NaAlH}_4$

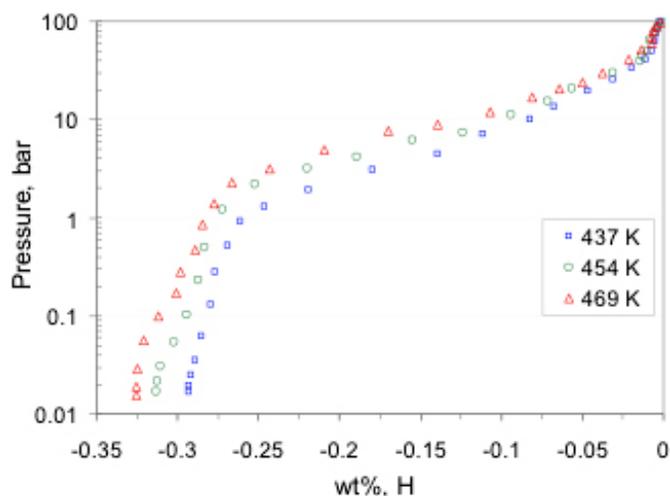
$\text{NaAlH}_4$  is perhaps the most thoroughly characterized hydride in terms of its thermodynamics and kinetics of  $\text{H}_2$  desorption. As such, it is an excellent test case for determining the influence of size and confinement environment on hydride thermodynamics and kinetics. This year, we performed detailed measurements to determine both  $\Delta H^\circ$  and  $E_a$ , using an infiltrated MOF with 1.3-nm pores and a melt-infiltrated porous carbon with uniform 4-nm diameter pores. The results show that both thermodynamics and kinetics are modified and suggest that these properties can be tuned by adjusting pore size.

Our experiments show that confining  $\text{NaAlH}_4$  to  $\leq 4$  nm pores has several effects on the reaction. The  $\text{H}_2$  desorption data for particles in the 1.3-nm MOF template (Figure 1) display evidence of at least two distinct reaction zones: a thermodynamic vapor-solid equilibrium at low reaction extent (<110°C) and a kinetically limited regime at temperatures up to 170°C. We characterized the reactant-product mixture obtained from vapor-solid equilibrium regime, using the 1.3-nm templated hydride, and see no evidence of  $\text{Na}_3\text{AlH}_6$ . This shows that under these conditions the reaction proceeds by a one-step process, which is different from the bulk behavior.

We also measured the temperature dependence of the  $\text{H}_2$  vapor pressure to determine the heat of desorption ( $\Delta H^\circ$ ).



**FIGURE 1.** Hydrogen desorption from  $\text{NaAlH}_4$  infiltrated into the 1.3-nm pores of the MOF Cu-BTC. Light-gray line indicates the temperature profile of the experiment, in which  $\text{H}_2$  was detected using a molecular-beam mass spectrometer.



**FIGURE 2.** Pressure-Concentration-Temperature (PCT) Curves of  $\text{NaAlH}_4$  Confined in 4-nm Nanoporous Carbon

The pressure-composition isotherms of  $\text{NaAlH}_4$  confined in 4-nm nanoporous carbon (Figure 2) are not completely flat and exhibit only one plateau, whereas bulk Ti-catalyzed  $\text{NaAlH}_4$  exhibits two flat plateaus corresponding to a two-step mechanism that forms first  $\text{Na}_3\text{AlH}_6$  followed by  $\text{NaH}$  formation. Hydride confined to 4-nm pores has a lower  $\Delta H^\circ$  than bulk (Table 2), while hydride confined to the 1.3-nm pores of the MOF actually has a higher  $\Delta H^\circ$ . The increased  $\Delta H^\circ$  for small particles agrees with the results of both our nano-prototype electrostatic ground state/density functional theory (DFT) calculations and with a report in the literature for  $\text{NaAlH}_4$  within a porous (0.5–4 nm) carbon template [1]. This is the first quantitative evidence that hydrogen desorption thermodynamics can be tuned by controlling particle size. However, our results below concerning  $\text{LiBH}_4$  show that this behavior is very specific to the particular hydride.

**TABLE 2.** Comparison of Measured  $\Delta H^\circ$  and  $E_a$ 

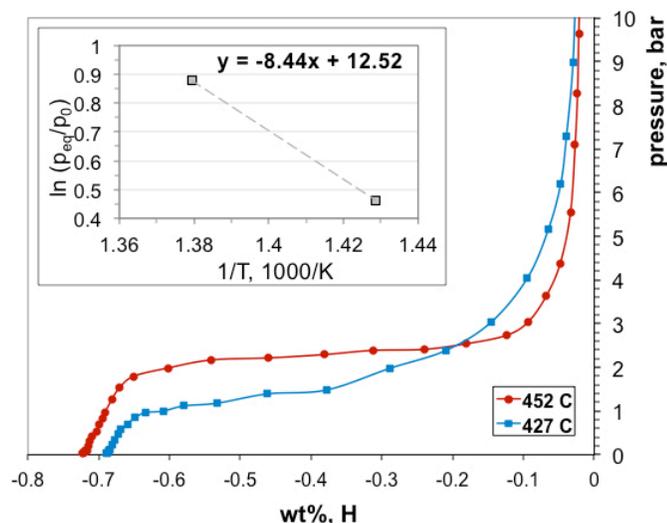
Reaction	1.3 nm <sup>a</sup>		4 nm <sup>b</sup>		Bulk <sup>c</sup>	
	$\Delta H^\circ$	$E_a$	$\Delta H^\circ$	$E_a$	$\Delta H^\circ$	$E_a$
$\text{NaAlH}_4 \rightarrow \text{NaH} + 0.33\text{Al} + 1.5\text{H}_2$	47	47–53	$35 \pm 10$	--	40	121
$\text{NaAlH}_4 \rightarrow 0.33\text{Na}_3\text{AlH}_6 + 0.67\text{Al} + 1.0\text{H}_2$	N/A	N/A	N/A	N/A	37	118

<sup>a</sup>Cu-BTC (MOF) template, solution infiltrated; <sup>b</sup>Porous carbon, melt-infiltrated; <sup>c</sup>Uncatalyzed; N/A – not applicable.

The behavior of the 1.3-nm  $\text{NaAlH}_4$  (Figure 1) nanoparticles in the kinetic regime is consistent with a one-dimensional diffusion model. The measured activation energy (Table 2) is considerably smaller than the uncatalyzed bulk value and somewhat smaller than the value previously reported for 2–10 nm  $\text{NaAlH}_4$  particles on carbon nanofiber [2]. This trend indicates that size has a stronger effect on the desorption kinetics than the chemical environment of the template. The activation energies obtained using the MOF template and the carbon nanofibers are rather similar, although the chemical environments are different; in fact, it is not clear that  $\text{NaAlH}_4$  is actually “confined,” but rather is “supported” on the surface of the carbon nanofibers, differentiating this template even further from the enclosed pores of the MOF.

#### Controlling the Decomposition Pathway of $\text{LiBH}_4$ via Confinement in Highly Ordered Nanoporous Carbon

We find that nanoscale  $\text{LiBH}_4$  melt-infiltrating into 4-nm nanoporous carbon (NPC; 4-nm hexagonally packed cylindrical pores) is kinetically destabilized relative to bulk, but the thermodynamics are unchanged relative to bulk. The PCT for  $\text{LiBH}_4$ @NPC were measured at three different temperatures (Figure 3). The PCT has a clearly identified plateau region, from which we obtain  $\Delta H^\circ$  and entropy  $\Delta S^\circ$

**FIGURE 3.** PCT Curves of  $\text{LiBH}_4$ @NPC Measured at Three Different Temperatures

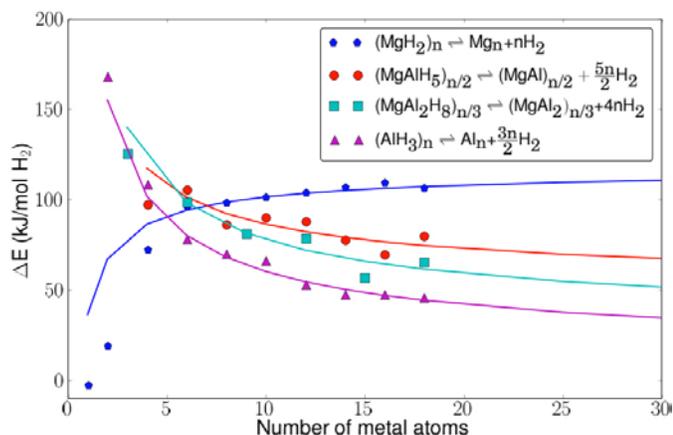
of  $70 \text{ kJ mol}^{-1} \text{ H}_2$  and  $104 \text{ J K}^{-1} \text{ mol-H}_2^{-1}$ , respectively. This strongly suggests that in contrast to  $\text{NaAlH}_4$ , confinement, or particle size alone, has no effect on the thermodynamics of  $\text{LiBH}_4$  decomposition. This result may be somewhat surprising in light of the many theoretical studies on nanoscale materials such as  $\text{MgH}_2$  and other simple saline hydrides. It suggests, therefore, that decomposition of this hydride is thermodynamically limited by the strength of the B-H bonds in the  $\text{BH}_4$  anion, which Fourier transform infrared data (not shown) indicate are similar to those of the bulk.

The benefits of incorporating  $\text{LiBH}_4$  into ordered 4-nm pore frameworks are twofold. First, the desorption behavior up to six cycles is clearly reversible [3]. Second, the release of diborane per gram of infiltrated  $\text{LiBH}_4$  can be dramatically reduced compared with both bulk hydride and hydride confined in 15 nm or 9 nm NPC. These observations clearly show that confining hydrides within a nanoporous material can change a material that is unusable in bulk form to one that could have practical utility in some applications. Importantly, the differences between the behavior of  $\text{NaAlH}_4$  described above and  $\text{LiBH}_4$  in these hard-carbon frameworks indicate that the interactions with the framework are hydride dependent, suggesting that a proper choice of hydride and framework chemistry can lead to a storage material having the desired properties.

#### Computational Modeling of Hydride Nanoparticles

The narrow range that  $\Delta H^\circ$  can assume for a successful vehicular hydrogen storage material ( $20\text{--}50 \text{ kJ mol}^{-1}$ ) lies roughly between two physical bounds: chemical bonds that are usually too strong, and hydrogen bonds that are usually too weak. One strategy for modulating  $\Delta H^\circ$  is to use compositional tuning in conjunction with nanoscale confinement. Our prior work demonstrated that  $\text{MgH}_2$  nanoclusters are destabilized, but only at extremely small sizes ( $<5$  formula units). Here, we describe high-accuracy fixed-node diffusion quantum Monte Carlo (DMC) calculations to evaluate the change in energy for the removal of  $\text{H}_2$  from mixed Mg-Al clusters, which we hypothesized would have stability intermediate between  $\text{MgH}_2$  and  $\text{AlH}_3$ . Our results show that this is indeed the case and show that  $\Delta H^\circ$  values between  $20\text{--}50 \text{ kJ mol}^{-1}$  can be obtained.

The DMC calculations confirm our hypothesis. First, they indicate that mixed Mg-Al nanoclusters are stable, i.e.,  $\Delta E$  is greater than zero (Figure 4). Second, the desorption



**FIGURE 4.** Alloying Mg and Al at the nanoscale results in particles with intermediate hydrogen desorption energy and enhanced stability over bulk. The hydrogen desorption energy is a function of size. All data are from DMC calculations.

energy of these clusters is intermediate between the pure materials. For example, the  $\text{MgAl}_2/\text{MgAl}_2\text{H}_8$  stoichiometry in addition to the  $\text{MgAl}/\text{MgAlH}_5$  stoichiometry, as is evident in Figure 4. This can be understood from the fact that the hydrides are ionic and the pure metallic clusters have metallic bonding. As a result, there are no bond networks to create nonlinear effects as a function of size. There are only magic numbers in the binding energy of the metals for small sizes, but this effect diminishes with increasing size and does not change the overall trend.

The size range at which  $\Delta E$  is predicted to reach a value between  $20 \text{ kJ mol}^{-1}$  and  $50 \text{ kJ mol}^{-1}$  range is given in Table 3. From the DMC results, the estimated size range for the MgAl alloy is from  $\sim 74$  metal atoms up to the bulk, whereas Al alone has only a very small range between 10 and 40 atoms. This confirms that alloying can significantly alter the size range in which nanoparticles have the desired desorption energies. However, the effects of errors in DFT predictions are very evident here. The estimated size ranges are dramatically different for the various functionals. It is thus clear that the accuracy of the method used to obtain  $\Delta E$  is critical.

**TABLE 3.** Estimated Size Range with  $\Delta E$  in the Range  $20\text{--}50 \text{ kJ mol}^{-1}$

	DMC	B3LYP	LDA	M06	PBE
MgAl	74 – ∞	Never	44 – ∞	Never	16 – ∞
Al	10 – 40	17 – 2,000	13 – 100	15 – 80	7 – 20

## Conclusions and Future Directions

- We demonstrated that size-dependent effects on both the thermodynamics and kinetics of hydrogen desorption from metal hydrides are possible as a result of nanoconfinement.

- Our results show that 1–4 nm  $\text{NaAlH}_4$  nanoclusters undergo single-step decomposition with fast kinetics, effectively increasing the storage capacity by 50% under fuel cell conditions.
- We predict that  $\text{MgH}_2/\text{H}_2$  desorption thermodynamics can be shifted to a more favorable thermodynamic regime by creating Mg-Al-H nanoclusters.
- During the remainder of the project, we will develop a synthetic method to make mixed Mg-Al-H nanoclusters, and will complete  $\text{H}_2$  desorption measurements for  $\text{NaAlH}_4$ ,  $\text{MgH}_2$ ,  $\text{LiBH}_4$ ,  $\text{LiNH}_2$ , and  $\text{Ca}(\text{BH}_4)_2$  in MOFs and nanoporous carbons.

## FY 2011 Publications/Presentations

- Xiangfeng Liu, David Peaslee, Christopher Z. Jost, Eric H. Majzoub, Theodore F. Baumann “First-Principles Calculated Phase Diagram for Nanoclusters in the Na-Al-H System: A Single-Step Decomposition Pathway for  $\text{NaAlH}_4$ ,” *J. Phys. Chem. C* 115 (2011), 2636.
- Liu X.F., Peaslee D., Jost C.Z., E.H. Majzoub et al. “Systematic Pore-Size Effects of Nanoconfinement of  $\text{LiBH}_4$ : Elimination of Diborane Release and Tunable Behavior for Hydrogen Storage Applications,” *Chem. Mater.* 23 (2011), 1331.
- R.K. Bhakta, V. Stavila, A. Highley, B. Jacobs, S. Maharrey, T. Alam, R. Behrens, E.H. Majzoub, M.D. Allendorf “Modified  $\text{NaAlH}_4$  hydrogen desorption thermodynamics and kinetics by nanoconfinement in MOFs,” submitted to *J. Phys. Chem. C*.
- Lucas K. Wagner, Eric Majzoub, Mark Allendorf, and Jeffrey C. Grossman “Using size and composition to tune the metal-hydride desorption energy: benchmark calculations,” submitted to *J. Amer. Chem. Soc.*
- Raghu Bhakta, Richard Behrens, Aaron Highley, Sean Maharrey, Deneille Wiese-Smith, Benjamin Jacobs, Mark Allendorf, Eric Majzoub, X. Liu, D. Peaslee, Lucas Wagner, Jeffrey Grossman “Investigation of metal hydride nanoparticles templated in metal-organic frameworks,” presented at *Nano and Surface Science Approaches to Production and Storage of Hydrogen*, 14–19 November 2010, Noordwijkerhout, The Netherlands.
- 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.
- E.H. Majzoub “Thermodynamics of Nanocluster Complex Hydrides: Theory and Experiment”, invited keynote lecture at MH2010, Moscow, Russia, July 2010.

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- X. Liu et al. *Chem. Mater.*, 23, 1331, 2011.