

IV.A.3 Tuneable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis using Ordered Polymer Templates

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Subcontractors:

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- University of California, Berkeley, CA
- Lawrence Livermore National Laboratory, Livermore, CA

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- (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 Hydrogen Storage Multi-Year RD&D 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)

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 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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (A) System Weight and Volume

Accomplishments

- Developed infiltration methods for metal hydrides, e.g. NaAlH₄, MgH₂, LiBH₄, and LiH.
- Demonstrated that H₂ desorption from NaAlH₄ nanoparticles confined within MOF templates is reduced by at least 100°C, a major step toward meeting the DOE Technical Target of 85°C.
- Benchmarked density functional theory (DFT) against Quantum Monte Carlo (QMC), revealing size-dependent nonsystematic errors in H₂ desorption enthalpies. QMC confirms the lowering of temperature (1 bar) for MgH₂ nanoparticles relative to bulk.



Introduction

Some of the most attractive hydrogen storage materials, such as MgH₂, AlH₃, and LiBH₄, have unfavorable desorption thermodynamics and are either too stable (e.g. MgH₂) or too unstable (e.g. AlH₃) 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.

Two classes of nanoporous templates are used to synthesize, stabilize, and store nanoparticles. Crystalline nanoporous materials, which include MOFs, provide the entry point to particles spanning the micro- to low mesoscale (1–5 nm diameters). Block copolymers (BCP) are used to create mesoscale particles (2–30 nm). Importantly, these materials possess very low densities, minimizing the impact on the gravimetric storage capacity. This approach has significant advantages over previous template-based methods: monolithic pore dimensions; access to both micro- and mesoscale particles; and flexibility to modify the template organic component to create chemical or physical stabilization. Furthermore, ordered templates enable the use of the most sophisticated theoretical approaches, including highly accurate QMC methods, to guide materials development.

Results

Template Synthesis and Infiltration – MOF templates having pore diameters ranging from ~1–2 nm (e.g., Figure 1) and BCP templates with diameters ≥ 10 nm (e.g. Figure 2) were synthesized. MOFs were synthesized from published procedures. Porous BCP

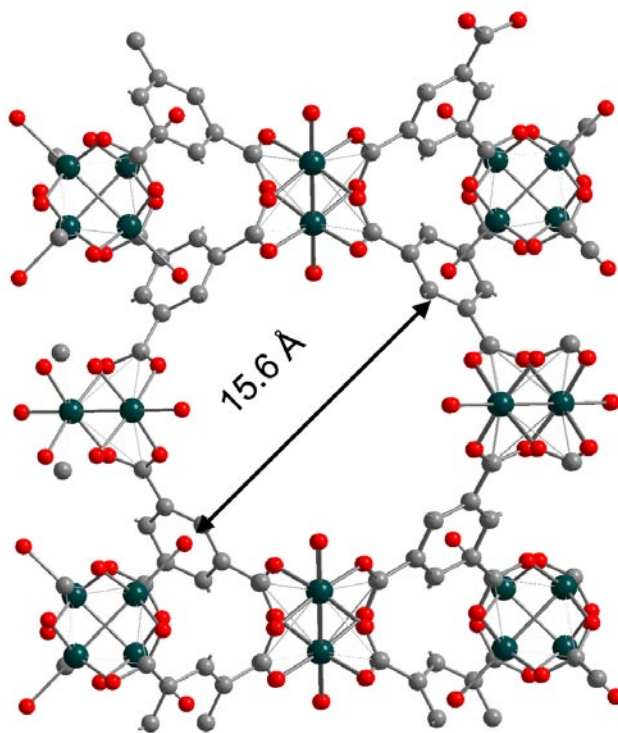


FIGURE 1. Structure of Nanoporous Cubic Copper-Containing MOF Template

templates with pore diameters: ≥ 10 nm were synthesized from polystyrene and polymethylmethacrylate (PS-*b*-PMMA). Figure 2 shows a high-resolution scanning electron microscope (SEM) image of a nanoporous PS film obtained by selectively etching of PS-*b*-PMMA. Vertically oriented columns perpendicular to the substrate are sensitive to the surface preparation. To enable facile characterization of hydride uptake, we prepare these films on gold-coated quartz-crystal microbalance substrates for subsequent hydride infiltration. Other BCP templates are now being grown using spin coating and ultraviolet exposure to crosslink one polymer and degrade the other to create nanopores.

Solution-based infiltration methods for the binary hydrides LiH and MgH₂ were developed, using the organometallic precursors Mg(C₄H₉)₂ and CH₃CH₂Li in organic solvents followed by thermal reduction to the corresponding hydrides. The complex hydrides NaAlH₄, LiBH₄ and LiAlH₄ were infiltrated using hydride solutions in tetrahydrofuran. No template degradation is observed as a result of infiltration with these reactive compounds. Elemental analysis, infrared, and magic-angle spinning nuclear magnetic resonance methods (performed by Dr. Julie Herberg, LLNL) show that the hydride is present throughout the entire template. Loadings are relatively low (4 wt% in the case of NaAlH₄, for example), but are more than sufficient to perform desorption experiments (see following).

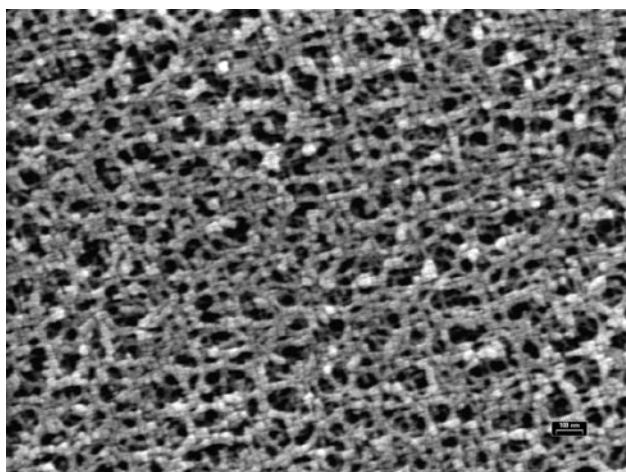


FIGURE 2. SEM Image of Preliminary Nanoporous PS Film from the Selective Etching of PS-b-PMMA

Hydrogen Desorption Kinetics – The H_2 desorption kinetics of metal-hydride nanoparticles are very different from the corresponding bulk-phase materials (Figure 3). Using a unique Sandia instrument known as 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 complex chemistry occurring during nanoparticle decomposition.

The desorption of H_2 by MOF-confined $NaAlH_4$ occurs at much lower temperatures than the bulk-phase material. STMBMS data for a series of temperature steps (Figure 3) reveals that complex desorption behavior by both bulk and MOF-confined $NaAlH_4$. Pure $NaAlH_4$ desorbs most of its H_2 (~70 wt%) at ~250°C (Figure 3A). H_2 from MOF-confined $NaAlH_4$ begins to desorb at 70°C, followed by a series of desorption events that culminate in steady-state release at 150°C (Figure 3B). Thus, the nanoscale hydride decomposes at temperatures $\geq 100^\circ C$ lower than bulk $NaAlH_4$. Simultaneous H_2 and solvent desorption at ~70°C also suggests that nanoscale effects may result from a combination of reduced size and the local chemical environment confining the clusters. These observations confirm the key hypothesis of this project, namely, that confinement within ordered nanoporous frameworks destabilizes metal hydrides.

Theoretical Modeling of Hydride Nanoparticles

– The group of Dr. Jeffery Grossman at University of California, Berkeley (UCB) completed computational modeling of Mg and $(MgH_2)_n$ clusters ($n = 1-40$) clusters, comparing QMC calculations with the results of DFT obtained from a variety of functionals and the literature (Figure 4). This computational benchmarking of popular computational methods reveals several important points. First, all methods indicate that the desorption energy decreases as the cluster size reaches very small

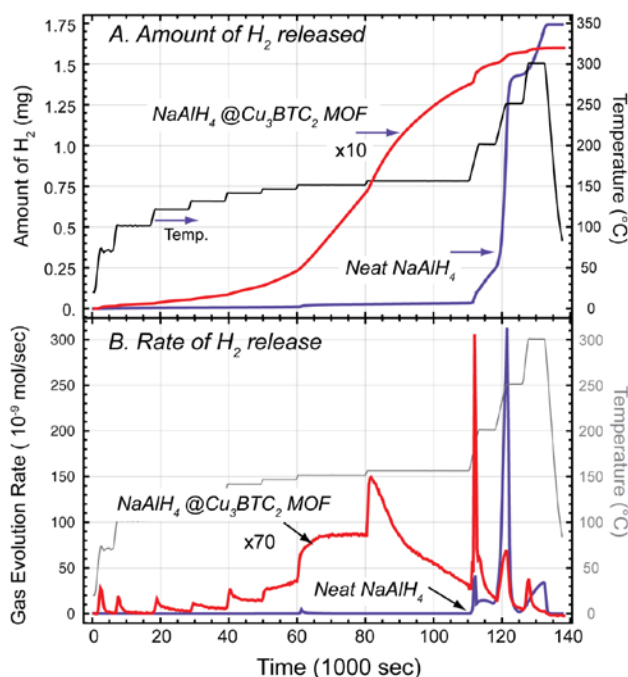


FIGURE 3. A. Amount of H_2 Released from $NaAlH_4$ -Infiltrated MOF Compared with Pure $NaAlH_4$. B. Rate of H_2 Released from $NaAlH_4$ @ Cu_3BTC_2 MOF Compared with Neat $NaAlH_4$

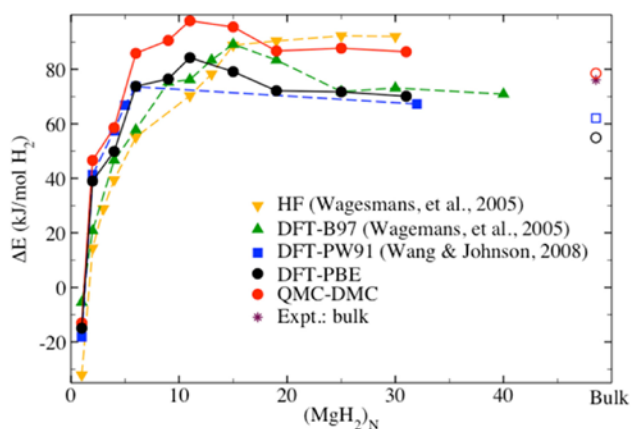


FIGURE 4. Comparison of H_2 Desorption Energies for $(MgH_2)_n$ Clusters Predicted by QMC vs. Various DFT Functionals

dimensions. However, there is enormous variation in the *quantitative* trends. For example, the results of Wagemans et al. [1] predict that the desorption energy drops below the bulk value at $n = 12$, while QMC predicts that the desorption energy is actually *higher* than the bulk value at this size. Differences between DFT and QMC at this size are as high as 25 kJ/mol. We are confident of the accuracy of QMC, based on excellent agreement with the bulk value and the overall convergence behavior of the code. These results suggest that size may not be the only factor at work, since

various investigators report accelerated kinetics for both MgH_2 and NaAlH_4 at sizes considerably larger than this (≥ 2 nm for NaAlH_4 supported on carbon nanofibers and ~ 5 nm for MgH_2 colloids).

Extension of the NanoPEGS Model to Nanoclusters – The Prototype Electrostatic Ground State (PEGS) code, a highly successful model that identifies the correct ground-state structure for charged materials, was extended to nanoscale clusters by its developer, Prof. Eric Mazjoub. NanoPEGS was first applied to MgH_2 clusters and provided prototype structures for DFT and quantum-chemistry calculations performed at UCB. Nano-PEGS clusters of NaAlH_4 , $\text{Ca}(\text{BH}_4)_2$, and $\text{Mg}(\text{BH}_4)_2$ are currently being explored. The results show that electrostatics are a useful simplification of the interatomic potential in the ionic as well as complex hydrides, allowing a rapid investigation of cluster geometries for nanoscale as well as bulk materials.

Conclusions and Future Directions

- MOFs are well-defined, chemically stable templates for metal-hydride nanoparticles.
- Hydride confinement shifts H_2 desorption to lower temperatures, but both the size and chemical environment of the templates pores.
- H_2 desorption energies predicted by DFT methods may contain significant nonsystematic errors and should be checked against high-level methods to assess their accuracy.
- Next year we will systematically vary both pore dimensions and chemical environment to identify the factors controlling nanoscale hydride stability, and develop synthetic methods to enable compositional tuning of hydride properties. Computational modeling using QMC, DFT, and NanoPEGS will continue to guide synthetic efforts. We also will down-select to specific hydrides and optimize the infiltration methods to maximize loading.

FY 2009 Publications/Presentations

1. R.K. Bhakta, J.L. Herberg, B. Jacobs, A. Highley, R. Behrens, Jr., M.D. Allendorf “Metal organic frameworks as templates for nanoscale NaAlH_4 ,” communication submitted to *J. Amer. Chem. Soc.*, May 2009.
2. Z. Wu, M.D. Allendorf, J.C. Grossman “Nanoscale effects on metal hydride thermodynamics: quantum Monte Carlo benchmarking of density functional theory,” communication submitted to *J. Amer. Chem. Soc.*, July 2009.
3. R.K. Bhakta, J.L. Herberg, R. Behrens, and M.D. Allendorf “Metal-organic frameworks as templates for nanoscale metal hydrides,” Spring meeting, American Chemical Society, Salt Lake City, March 22–26, 2009.
4. M. D. Allendorf, Tech Team briefing, Sept. 12, 2008, Livermore, CA.
5. M.D. Allendorf, Metal Hydride Center of Excellence Face-to-face meeting, Dec. 19, 2008.
6. E.H. Majzoub “A computational tool for complex ionic hydrides: global optimization using prototype electrostatic ground states,” invited presentation, Purdue Hydrogen Symposium 2009, Purdue University, Lafayette, Indiana, 22 April, 2009.
7. E.H. Majzoub “Computational approach to the structure and thermodynamics of metal borohydrides,” American Physical Society March Meeting, March 2009.
8. E.H. Majzoub “Prototype electrostatic ground state approach to predicting crystal structures of ionic compounds: Applications to hydrogen storage materials,” Hydride Materials Theory Workshop, Materials Research Society Meeting, San Francisco, California, 24 March, 2008.

References

1. Wagemans et al. (2005)