

IV.A.1m Catalyzed Nano-Framework Stabilized High-Density Reversible Hydrogen Storage Systems

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- Albemarle Corporation, Baton Rouge, LA

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Objectives

Build upon successes previously demonstrated in the community and extend to a wider range of doped, functionalized and catalyzed framework chemistries to:

- Improve material and system gravimetric density, volumetric density and discharge rate of solid state, on-board reversible storage systems.
- Advance the understanding of behavior modification by nano-framework structures (NFS).
- Tune hydride/framework interactions to decrease desorption temperature for highly stable compounds, stabilize high-capacity compounds and influence desorption product formation.
- Activate H₂ dissociation on highly dispersed catalytic sites.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging and Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is intended to advance materials development to close gaps in current media and system approaches and provide a path to reversible high-density H₂ storage systems meeting the DOE 2010 targets:

- System Gravimetric Capacity: 2 kWh/kg
- System Volumetric Capacity: 1.5 kWh/L
- Charging/Discharging Rates (minimum full flow rate): 0.02 (g/s)/kW

Accomplishments

- Atomic and thermodynamic modeling studies show interfacial NFS interactions can alter the relative stability of hydrides and discharged products.
- Preliminary atomic modeling results indicate NFS dopants influence NFS lattice stability and electronic NFS/hydride interfacial interactions.
- Multiple suitable oxide candidates have been evaluated. Ytria-stabilized ZrO₂ NFS were down-selected because of low reducibility and demonstrated compatibility with LiBH₄.
- High surface area NFS have been synthesized with ZrO₂, Al₂O₃, SiO₂, TiO₂ and carbon aerogels.
- Candidate hydride material: Ca(BH₄)₂ has been synthesized at Sandia National Laboratories (SNL).



Introduction

Current complex hydrides have yet to meet the 2010 DOE systems targets, presenting a continuing challenge for the discovery of high-capacity, reversible hydrides. For example, metal borohydrides [M(BH₄)_n] have the potential to meet the targets, but some materials are unstable (such as those containing Ti, Al, or Sc cations) and decompose within minutes or days. Other metal borohydrides (such as those containing Li, Na, K or Ca cations) decompose at temperatures that are higher than what is desired for proton exchange membrane fuel

cell integration and cannot be recharged with gaseous hydrogen at moderate pressures. Thus, there is a need to develop novel techniques that enable high-capacity over numerous absorption/desorption cycles. The current project will address this by incorporating solvated and other forms of complex metal hydrides, with a focus on borohydrides, into nano-scale frameworks of low density, high surface area skeleton material to stabilize, modify thermodynamics, catalyze and control desorption product formation associated with such complex metal hydrides.

Approach

The project at United Technologies Research Center (UTRC) is being conducted in close collaboration with other researchers from the DOE Metal Hydride Center of Excellence (MHCoE). UTRC, SNL, and Albemarle Corporation will team to develop catalyzed framework structures designed for specific advanced hydrogen storage materials (HSM). The team will initially examine the HSMs developed by UTRC/Albemarle under a previous DOE contract, “Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity,” and by SNL under previous MHCoE efforts, these HSMs being borohydrides.

UTRC will use an iterative atomic/thermodynamic modeling and experimental approach to develop NFS materials. Some new high-capacity HSMs are only stable in solvents or with ligands such as amines. Stabilization of these hydrides will be performed instead by the interaction with the NFS cell walls. In addition, nanometer-scale catalytic sites within the NFS cells will activate H_2 , and through hydrogen spillover, facilitate reversibility (rehydrogenation). Containing the HSM constituents after hydrogen discharge within the NFS cells will reduce decrepitation (irreversible phase segregation, separation, or degradation) which can result from reactions such as the formation of refractory metal borides. SNL and Albemarle will provide HSMs or their precursors while UTRC and SNL will incorporate these HSMs into the NFS materials.

Results

In Fiscal Year 2008, much effort was devoted to down-selection of suitable NFS candidates and their synthesis and evaluation. These efforts included the following:

- Atomic and Thermodynamic Modeling (A&TM).** The A&TM examined various oxide supports and their influence on hydride stability, hydride dehydrogenation intermediates and product formation. In addition, the effect of doping was explored to change the electronic character of hydride adsorption and dehydrogenation reactions.
- NFS Development and Synthesis.** The initial focus of the NFS development and synthesis has been on the oxide candidates identified through A&TM and confirmed through compatibility experiments. In addition to the down-selected ZrO_2 NFS, carbon aerogels were prepared as they have the potential to be suitable NFS for non-ligand stabilized hydride materials.
- Compatibility Studies with $LiBH_4$.** The compatibility of various oxide and non-oxide support structures with $LiBH_4$ was investigated. These studies were used, in part, to verify the predictions of the A&TM effort and identify appropriate analytical techniques for evaluation. Hydrogen desorption via a Sievert’s apparatus, differential scanning calorimetry (DSC) and X-ray diffraction (XRD) were the primary techniques utilized in determining the compatibility of the support and hydride.

Atomic and Thermodynamic Modeling

The first modeling phase investigated the influence of oxide nano-frameworks on hydride stability, hydride dehydrogenation intermediates and product formation. Thermochemical and Gibb’s energy minimization calculations were conducted with Outokumpu HSC Chemistry to assess the stability and identify potential decomposition mechanisms between a selected model hydride, $LiBH_4$, and the most stable known phases of oxide framework candidate materials. $LiBH_4$ was used for initial compatibility screening because of high reactivity and existing atomic and thermodynamic data. Atomic simulations were made of the interfacial interactions of oxide nano-framework slabs with clusters formed from $LiBH_4$. The purpose of A&TM modeling was to pre-screen possible oxide substrates for reducibility (or hydrogen extraction of NFS oxygen to form water) and the interaction of the hydride on the surface of the NFS. Reducibility is undesirable as it is critical to retain the NFS intact for long-term performance. Figure 1 shows the $LiBH_4$ physisorption interactions were in order of decreasing significance: $SiO_2 > Al_2O_3 > ZrO_2$, where the $LiBH_4$ interfacial Li atoms strongly bonded with surface O atoms, and very weak secondary interactions occurred of proximal B and H with oxide surface cations. The ZrO_2 framework was predicted to have low reducibility in the H_2 atmosphere and in contact with hydride. The weaker $ZrO_2/LiBH_4$ interactions provided a good starting point for designing NFS that facilitate dehydrogenation of the very stable $LiBH_4$. Lithium was the only product that showed significant adsorption on the oxide surfaces upon dehydrogenation. In fact, since the Li-oxide bonding interactions were simulated to be equally strong in the fully hydrided state as in the discharged state, the dehydrogenation thermodynamics were not predicted to change by the presence of the interface.

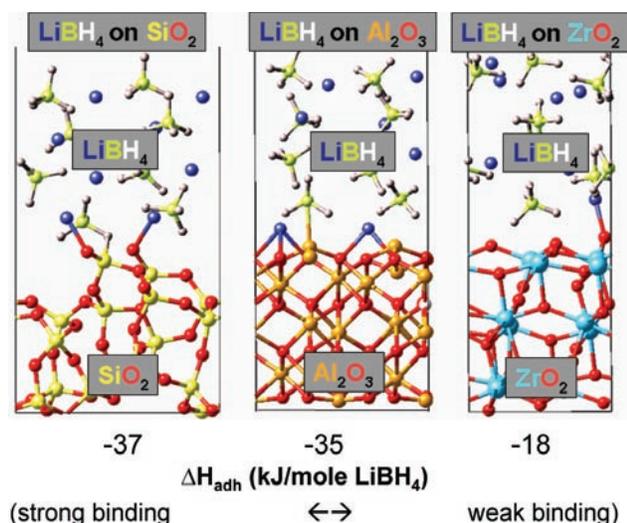


FIGURE 1. Model predictions of LiBH_4 adhesion to selected NFS. ZrO_2 structure is predicted to have low reducibility in an H_2 atmosphere and weaker tunable interfacial associative interactions with LiBH_4 .

After the ZrO_2 framework was down-selected, we wanted to look at the effect of changing the ZrO_2 electronic character with dopants on ZrO_2 reducibility, hydride adsorption and dehydrogenation reactions. Of particular interest were the first row transition metal dopants Sc, Ti, and V, each with differing valence states. Calculations were made to identify the most stable lattice substitution sites for 8 atomic % of these dopants in the ZrO_2 $P12_1/c_1$ framework slab (111) surfaces. The Sc and Ti dopants were more stable substituted in the subsurface and V was more stable at the surface. Then calculations were made to evaluate the doped framework reducibility. Doped slab interfaces were created with LiBH_4 clusters and then relaxed as shown in Figure 2. Increased hydride interactions occurred with increasing dopant electronegativity ($\text{Sc} < \text{Ti} < \text{V}$), where electronegativity is the measure of electron affinity in bonding interactions. Simulations were then made for elevated temperatures using molecular dynamics to determine which species remain after LiBH_4 decomposition on the doped surfaces. The most favorable adsorbed species were confirmed separately by a series of adsorption calculations. The dehydrogenation enthalpies were then determined by the difference in stability between the fully hydrided interface and the hydride decomposition products, taking the interfacial adsorbates remaining after dehydrogenation into account. The interfacial interactions were determined for the range of NFS dopant compositions given in Table 1. The most significant result showed that LiBH_4 adsorption strength was unaltered and Li adsorption was weakened on the Sc-doped ZrO_2 surface. Thus, the simulations showed that the substitution of Sc effectively lowered the endothermicity of LiBH_4 decomposition compared to the undoped $\text{LiBH}_4/\text{ZrO}_2$ interface. These results show that framework doping can have a

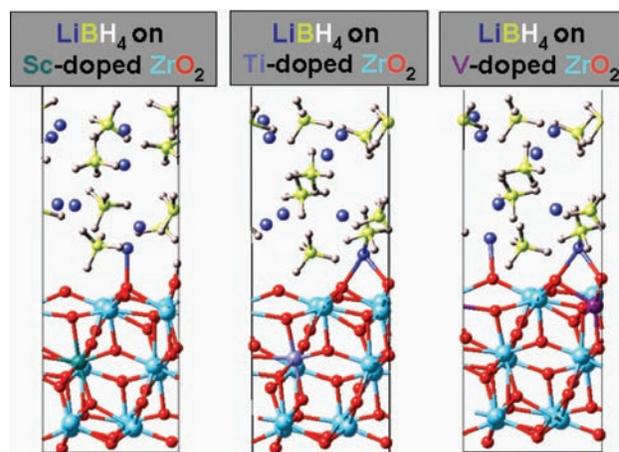


FIGURE 2. Dopants in the NFS are introduced in the most favorable position to balance lattice stability. Modeling of the electronic interfacial interactions with the hydride predicts Sc will enhance LiBH_4 dehydrogenation.

significant effect on hydride behavior, and can be used to tune desired characteristics.

TABLE 1. Modeling of the Electronic Interfacial Interactions with the Hydride Predicts Sc will Enhance LiBH_4 Dehydrogenation

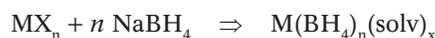
Ground State LiBH_4 Dehydrogenation Reaction Predictions on NFS ¹	ΔH_{deh} kJ/mole LiBH_4
ZrO_2	+112
$\text{Zr}_{0.92}\text{Sc}_{0.08}\text{O}_2$	+85
$\text{Zr}_{0.92}\text{Ti}_{0.08}\text{O}_2$	+125
$\text{Zr}_{0.92}\text{V}_{0.08}\text{O}_2$	+120

¹Calculated for favorable discharge to single adsorbed *Li on surface.

Hydride and NFS Synthesis

SNL has produced $\text{Ca}(\text{BH}_4)_2$ through desolvating material obtained from Sigma-Aldrich Co., resulting in high-purity materials composed of 70:30 of the alpha:beta phases. No detectable solvent remained according to XRD and thermo-gravimetric analyses. This material is being used in preliminary NFS-HSM compatibility testing at UTRC which will continue through FY 2009.

In addition, SNL is pursuing alternate $\text{Ca}(\text{BH}_4)_2$ synthesis using solvent based methods, which will facilitate subsequent solution oriented nano-framework incorporation tasks.



Preliminary solution deposition of the borohydride onto silica substrates indicates that this method has promise.

Two carbon aerogels have been specified by UTRC and synthesized by Aspen Aerogels using different precursor routes to produce desired non-carbon elements; one has nominally 8 wt% nitrogen and the other has residual oxygen. These will be used to examine the effectiveness in stabilizing candidate borohydride compositions which previously have required ligand stabilization. Brunauer-Emmett-Teller (BET) porosimetry analysis on these materials measured surface areas between 600 and 800 m²/g, pore diameters between 16 and 24 nm and a density of 0.26 g/cm³. In addition, a nominally 9 mol% yttria stabilized zirconia aerogel has been prepared by Aspen Aerogels. After the standard calcination at 550°C for 1 hr, this material had a measured surface area of 138 m²/g and a pore diameter of approximately 12 nm. As the NFS material does not contribute directly to the storage of hydrogen, but rather exists to retain the hydrogen storage material itself, it is necessary to minimize the weight and volume of the NFS. High surface area combined with low density is preferred in the NFS, as well as a tailored pore size distribution, in order to optimize gravimetric and volumetric capacities.

Experimental Studies

The first experimental screening step was to evaluate whether candidate hydrides could cause nano-framework degradation. This screening was conducted in conjunction with thermodynamic/atomistic modeling. LiBH₄ was used as the base case hydride for initial compatibility screening because of its high reactivity, availability, and existing thermodynamic data. The experiments involved ball milling of LiBH₄ with potential NFS materials, which included various low and high surface area oxides, carbides, nitrides and carbon aerogels. Analysis of both the initial and dehydrated states was conducted using DSC, Sievert's device gas desorption and XRD.

The ZrO₂ nano-framework material was down-selected based on atomistic simulations, thermodynamic modeling, as well as preliminary DSC and hydrogen desorption experiments on zirconia powder combined with LiBH₄. The energetic states of the LiBH₄ combined with ZrO₂ were probed by DSC, as shown in Figure 3. As a comparison, the results for pure LiBH₄ are shown. The 50 wt% LiBH₄ combined with ZrO₂ has a similar endothermic profile as pure LiBH₄, suggesting that ZrO₂ is stable and non-reactive in the presence of this strongly reducing hydride in agreement with A&TM predictions.

In 2003, silica was reported as a catalyst for LiBH₄ dehydrogenation by Züttel *et al.* [1]. However, in contrast with the ZrO₂ support structure, A&TM predicts SiO₂ to be thermodynamically unstable. After the combination of a SiO₂ aerogel and 50 wt% LiBH₄ via ball milling, only XRD peaks for the starting

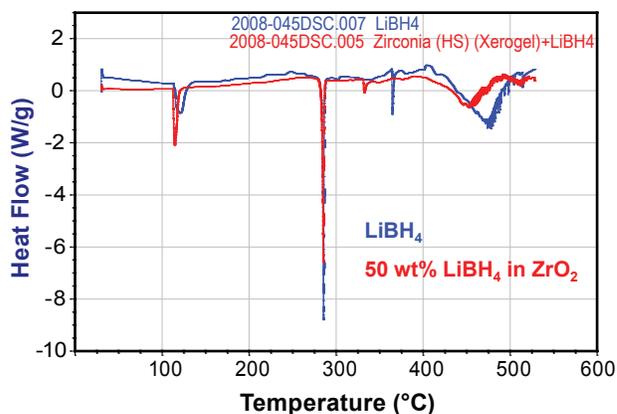


FIGURE 3. DSC of 50 wt% LiBH₄ + ZrO₂ powder (138 m²/g) presents a similar endothermic profile as pure LiBH₄. This suggests that ZrO₂ is stable and non-reactive in the presence of this strongly reducing hydride.

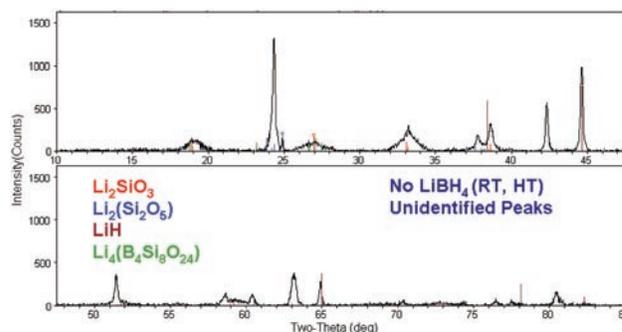


FIGURE 4. Commercial SiO₂ aerogel + LiBH₄ after hydrogen discharge and attempted hydrogen adsorption. The SiO₂ structure has been irreversibly reacted to form lithium silicate species. This reactivity supports thermodynamic modeling showing instability of SiO₂ in the presence of the strongly reducing LiBH₄.

materials were present, indicating that no crystalline products from undesirable reactions had occurred during ball milling. Following hydrogen desorption of the SiO₂ + LiBH₄ mixture and subsequent attempts to re-hydrogenate, XRD indicated significant irreversible decomposition to various lithium silicates, as shown in Figure 4. Additional DSC analysis confirmed that the endothermic profile of the SiO₂ + LiBH₄ combination was significantly different than that of pure LiBH₄.

Nine possible framework materials were combined with LiBH₄ for the initial compatibility screening experiments. In addition to ZrO₂, Al₂O₃ was identified as a favorable framework candidate due to high chemical stability and low reducibility.

Samples of Ca(BH₄)₂ prepared at SNL combined with the ZrO₂ NFS and the two aforementioned carbon aerogels have also been produced for testing. Further studies involving XRD, DSC and hydrogen desorption for the Ca(BH₄)₂ are currently underway.

Conclusions and Future Directions

Conclusions

- Atomic and thermodynamic modeling studies show interfacial NFS interactions can alter stability of hydride and discharged products.
- Preliminary results from modeling indicate dopants balance both NFS lattice stability and electronic NFS/hydride interfacial interactions.
- Compatibility screening has been conducted on a combination of LiBH_4 and nine different candidate framework materials including SiO_2 , Al_2O_3 and ZrO_2 .
- Zirconia has been down-selected based on initial modeling results: low reducibility, chemical stability and weak interfacial interactions.

Future Direction

Atomic Modeling

- The simulations have been expanded to include oxide interfaces with $\text{Ca}(\text{BH}_4)_2$ clusters.
- Virtually tune doped NFS to balance hydride stability and dehydrogenation.
- Virtually develop doped, functionalized, catalyzed NFS to enhance reversibility.

Framework and Hydride

- In FY 2009, Albemarle Corporation will synthesize ligand-stabilized $\text{NaTi}(\text{BH}_4)_4$ for incorporation into the NFS materials.
- Continue to assess oxide, modified carbon and other alternative framework materials.
- Examine support interactions with selected $\text{NaTi}(\text{BH}_4)_4$ ligand and $\text{Ca}(\text{BH}_4)_2$.
- Evaluate doped, heterogeneously catalyzed and functionalized nano-frameworks.

FY 2008 Publications/Presentations

1. D. Mosher, S. Arsenault, S. Opalka, X. Tang, T. Vanderspurt, B. Laube and R. Brown, "Catalyzed Nano-Framework Stabilized High-Density Reversible Hydrogen Storage Systems," IEA Task 22 Meeting, Quebec, Canada, March 2-5, 2008.
2. D. Mosher, S. Opalka, X. Tang, S. Arsenault, T. Vanderspurt, B. Laube and R. Brown, "Development and Application of New High-Capacity Hydrogen Storage Materials," IEA Task 22 Meeting, Petten, Netherlands, September 3-7, 2007.
3. S. Arsenault, D. Mosher, S. Opalka, X. Tang, T. Vanderspurt, B. Laube, R. Brown, E. Rönnebro, T. Boyle, F.-J. Wu, and J. Strickler, "Catalyzed Nano-Framework Stabilized High-Density Reversible Hydrogen Storage Systems", 2008 DOE Hydrogen Program Annual Merit Review – Washington DC, June 9-13, 2008. Presentation #STP16.
4. D. Mosher, S. Arsenault, S. Opalka, T. Vanderspurt, X. Tang, B. Laube, E. Rönnebro, and T. Boyle, "Development of Nano-Framework / Hydride Composites for Improved Hydrogen Storage", International Symposium on Metal-Hydrogen Systems, Reykjavik, Iceland, June 24-28, 2008.

References

1. A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, Ph. Mauron, Ch. Emmenegger, "Hydrogen Storage Properties of LiBH_4 ", J. Alloys and Compounds 356 (2003).