

IV.A.1q Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

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- J. Reiter, Jet Propulsion Laboratory (JPL), Pasadena, CA

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Objectives

- To understand as to whether thermodynamically tractable reactions based on hydride destabilization that should be reversible but appear not to be, are kinetically limited.
- To address short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths.
- To address the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization. Systems of interest determined through “theoretical screening” by Center partner members.
- To understand issues related to grain growth and surface/interface energies, vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions.
- To follow up on previously studied reactions with phase identification via X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and transmission electron microscopy.

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 Plan:

- (A) System Weight and Volume
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

Data are typically reported as gravimetric densities on a materials basis only. The contribution to the system weights from the tank walls and tubing are not considered in our values whereas the 2010 targets for gravimetric and volumetric capacity are targeted on system’s basis of 6% and 0.045 kg/L, respectively.

Accomplishments

Motivated by the more recent work of Alapati, Johnson and Sholl, the systems that we have synthesized and analyzed over the past year are:

- $\text{TiH}_2 + 2\text{LiBH}_4 \rightarrow \text{TiB}_2 + 2\text{LiH} + 4\text{H}_2$ 8.6 wt% and 22 kJ/mole H_2 theoretical, and
- $\text{CaH}_2 + 6\text{LiBH}_4 \rightarrow \text{CaB}_6 + 6\text{LiH} + 10\text{H}_2$, analogues where Sr (9.1 wt%) and Ba have been substituted for Ca.
- X-ray and NMR analysis of the destabilization systems above.
- Wetting analysis of reactants of prospective use with scaffolds that minimize diffusion path lengths.
- Evaluation of reaction pathways where closo-borane intermediate phases are formed.
- Continuation of transmission electron microscopic examination of phase distributions in Mg incorporated into aerogels.



Introduction

Candidate hydride destabilization systems of technological interest must meet the requirements of generating high gravimetric densities of hydrogen and do so at reaction enthalpy values of between 30 and 40 kJ/mole for tractable thermal management of storage systems. While thermochemical databases have been of

use in exploring initial candidate systems, we have relied on the efforts of the Metal Hydride Center of Excellence theory group [1] who have calculated formation and reaction enthalpies of systems that fall within the requisite thermodynamic boundaries.

Reaction kinetics also represent a critical gauge of engineering utility and our approach is to work with the most promising candidates as determined by thermodynamics, and to study the kinetics of hydrogen release. Kinetics will be dominated by solid-state diffusion rates in hydride destabilization systems and both volumetric and analytical techniques are required in order to understand reaction pathways.

Approach

We have been evaluating the most promising hydride destabilization systems using Sieverts volumetric techniques to determine actual gravimetric hydrogen release and the associated kinetics aided by standard catalysts. We have been working with spectroscopic analyses like XRD diffraction and NMR in collaboration with JPL (see report from J. Reiter of JPL) and Sonjong Hwang of the Caltech NMR facility in order to gain insights into these systems.

Results

In Figure 1 we show the results of the reaction $\text{TiH}_2 + 2\text{LiBH}_4 \rightarrow \text{TiB}_2 + 2\text{LiH} + 4\text{H}_2$, where: $\Delta U_{\text{OK}} = 22.2 \text{ kJ/mol H}_2$ (8.6 wt% capacity). In spite of the compelling thermodynamics of this reaction which made this a system of promise, our desorption measurements of ball milled powders taken over a 95-hour run showed no reaction. The lack of reactivity was confirmed by powder XRD and by NMR. Apparently, the stability of TiH_2 and TiB_2 do not allow activation under these conditions or kinetics are very slow for desired reaction.

Figure 2 shows the results of the destabilization reaction $\text{SrH}_2 + 6\text{LiBH}_4 \rightarrow \text{SrB}_6 + 6\text{LiH} + 10\text{H}_2$, a 9 wt% system. This reaction was not calculated specifically by Alapati, Sholl and Johnson but the use of higher Z alkaline earth elements was motivated by the possibility that larger electron densities might translate to weaker bonds and better thermodynamics and/or kinetics. Our initial work shows that after desorption at 350°C , sample changes to strong green colored powder. Powder XRD of desorption product shows unanticipated reaction paths producing phases, including: a LiSrH_3 trivalent, SrB_6 as noted by very broad peaks meaning a small sized reaction phase, unreacted LiBH_4 and LiH . This reaction

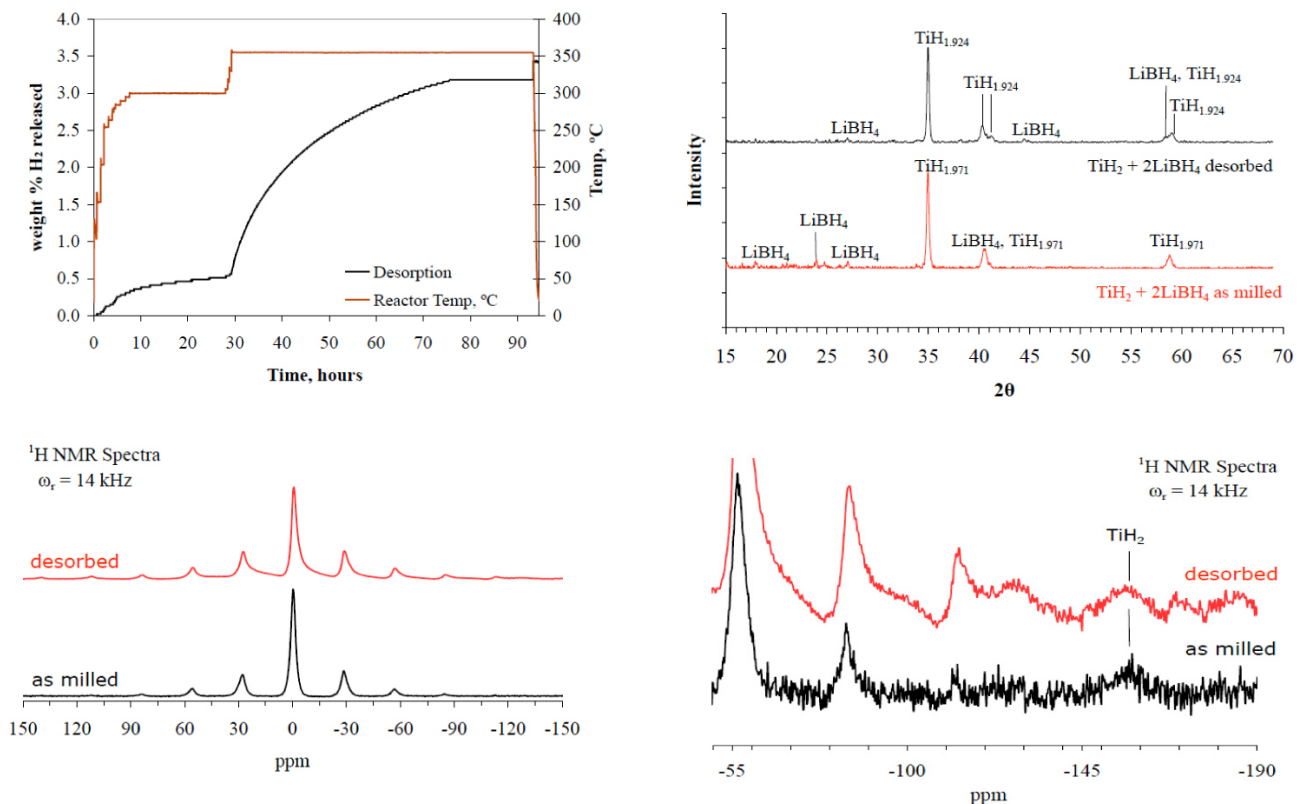


FIGURE 1. Kinetic desorption measurement from the $\text{TiH}_2 + 2\text{LiBH}_4 \rightarrow \text{TiB}_2 + 2\text{LiH} + 4\text{H}_2$ up to 350°C shown in upper left. XRD data from as milled and reacted sample shown in upper right. ^1H MAS NMR spectra shown at lower left and the same ^1H MAS NMR spectra as, blown up to show the TiH_2 peaks at -159 ppm in lower right.

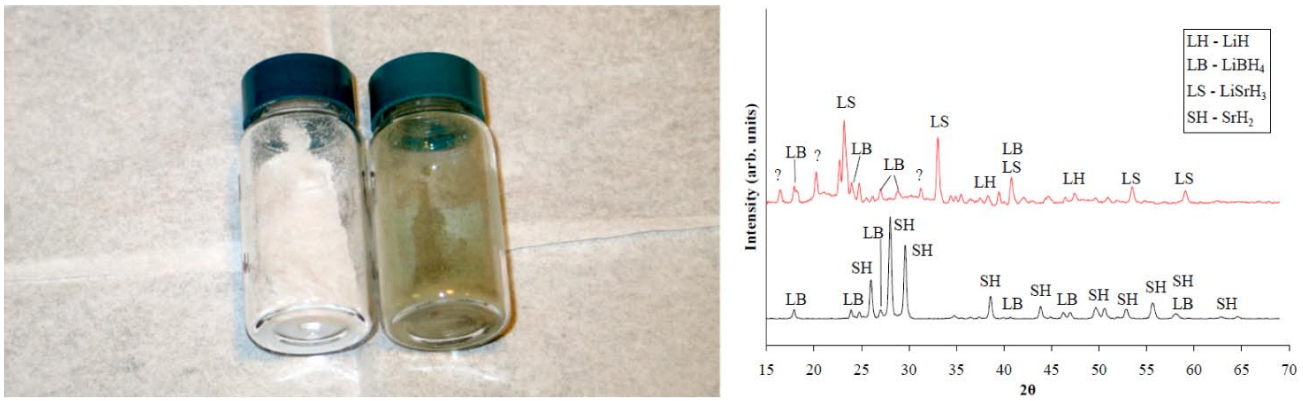


FIGURE 2. The $\text{SrH}_2 + 6\text{LiBH}_4 \rightarrow \text{SrB}_6 + 6\text{LiH} + 10\text{H}_2$ system has reacted at 350°C as shown by the color change in the upper left. X-ray data in the upper right shows intermediate reaction product phases that were formed.

yielded 3.5 wt% H_2 initially but further assessment of reaction pathway kinetics is still needed.

Figure 3 shows an example of some of the wetting experiments that we have been performing in assessing the extent of wet-ability/reactivity for the purposes of setting up destabilization reactions in carbon aerogel scaffolds. Assessing surface reactivity will be crucial in promoting destabilization reactions in carbon aerogel scaffolds. In an effort to determine the intrinsic reactivity of constituents that might affect the ability to incorporate hydrides into scaffolds and ultimately, the kinetics of destabilization, wetting experiments of LiBH_4 were performed over compressed disks of MgH_2 and TiH_2 . In the case of LiBH_4 over MgH_2 , we can see the poor reactivity between these phases as evidenced by the “beading” of the LiBH_4 on the surface of the MgH_2 .

Figure 4 shows our efforts at improving the spatial resolution of MgH_2 that has been infiltrated into an aerogel. We have employed energy filtered imaging, using an energy filter located on our TF20 transmission electron microscope and using the $\text{Mg } L_{2,3}$ edge as an image source. The zero loss images of the microstructure are shown in the upper set and the corresponding Mg images are shown in the lower set. The Mg images (bright features) suggest that Mg is fairly uniformly distributed in the aerogel structure. There is though, possibility that the images are dominated by thickness effects. In the future we plan avoid this by the use plasmon imaging to better resolve the differences in electron density of the hydride phase (14 eV) and that are distinct from the metal (10 eV), oxide (22 eV) and carbon (25 eV) signatures.

Conclusions and Future Directions

- The destabilization reactions that we have concentrated on so far have limited hydrogen release, due to either to the poor reactivity of the species (in spite of favorable thermodynamics),

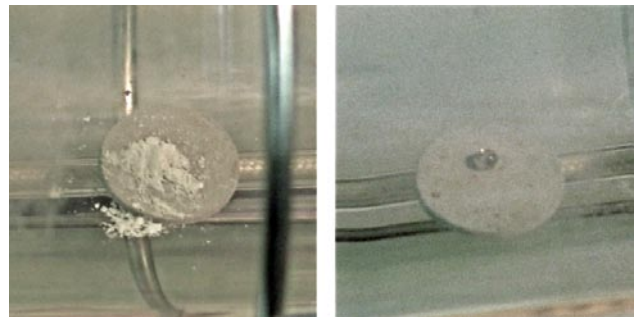


FIGURE 3. Images above show melting behavior of LiBH_4 over a milled and compacted MgH_2 powder. The initial LiBH_4 before heating is shown on the left and upon heating, forms a bead with a large contact angle, indicating a poor reactivity between these two phases.

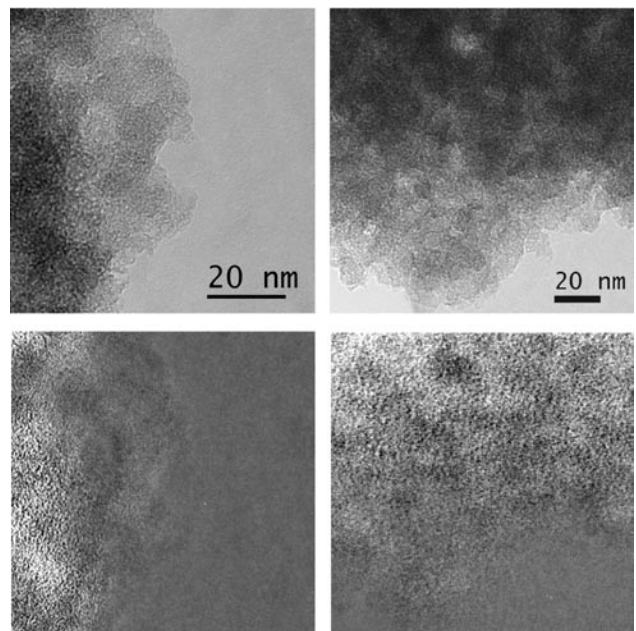


FIGURE 4. Energy filtered images of Mg incorporation into carbon aerogel. Zero loss images of the microstructure are shown in the upper set and the corresponding Mg images are shown in the lower set.

which can be due to high formation enthalpies of one or more of the reacting species. Promoting reactivity through careful control of wetting behavior will better enable us to promote constituent reactivity.

- Formation of intermediate compounds, not predicted by has also been a problem that we have been attempting to work around. The stable closo-borane structures have appeared as intermediate phases when borohydrides have been used as a reactant. Using conditions that suppress the formation of these stable phases will be vital in our continuing work in this area.
- Basic wetting behavior studies have been an instrumental first step in determining the viability of destabilization reactions.
- We plan to explore schemes for promoting surface reactivity as we work to complete our effort in this area.

FY 2009 Publications/Presentations

1. "Fabrication and hydrogen sorption behaviour of nanoparticulate MgH_2 incorporated in a porous carbon host," Adam F Gross, Channing C Ahn, Sky L Van Atta, Ping Liu and John J Vajo, *Nanotechnology* (2009).
2. "Synthesis and hydrogen storage properties of MgH_2 incorporated carbon aerogel scaffold," Shu Zhang, Adam F Gross, Sky L Van Atta, Maribel Lopez, Ping Liu, Channing C Ahn, John J Vajo and Craig M Jensen, *Nanotechnology* (2009).
3. " $LiSc(BH_4)_4$ as a Hydrogen Storage Material: Multinuclear High Resolution Solid State NMR and First-Principles Density Functional Theory Studies" Kim, C. et al. submitted to *J. Phys. Chem. C*. (Feb 2009).

Presentations

1. "Vehicular Hydrogen Storage with Ad(b)sorbent Materials," C. Ahn, APS Energy Research Workshop Program and Hydrogen Focus Topic Symposium chair, *American Physical Society, March 2009, Natl. Meeting, Pittsburgh*.

References

1. Alapati, S. V.; Johnson, J. K.; Sholl, D. S., *J. Phys. Chem. C* 2008, **112**, 5258-5262.