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

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Objectives

- To understand if 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 Metal Hydride Center of Excellence (MHCoE) 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, 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 a system basis of 6% and 0.045 kg/L, respectively.

The systems that we have been concentrating on over the past several years are:

- $ScH_2 + 2LiBH_4 <-> ScB_2 + 2LiH + 4H_2$ 8.9 wt% theoretical, 4 wt% observed (400°C) and
- $Ca(AlH_4)_2 + 2LiBH_4$, 6.6 wt% observed, $Ca(AlH_4)_2 + 6LiBH_4$ 8.5 wt% observed (350°C) and over the past year,
- $AlH_3 - 2LiBH_4$ 7 wt% observed (400°C).

Accomplishments

- NMR analysis of the $ScH_2 + 2LiBH_4 <-> ScB_2 + 2LiH + 4H_2$ (8.9 wt%), predicted by our MHCoE partners at the University of Pittsburgh and Georgia Tech, to have a 34 kJ/mole reaction enthalpy after zero point correction.
- In collaboration with Ewa Ronnebro at Sandia National Laboratories, high-pressure evaluation of the reversibility of this reaction starting with $ScB_2 + 2LiH$.
- Spatially resolved Raman analysis of the reaction products of this system.
- Evaluation of reaction pathways in $Ca(AlH_4)_2 + 2LiBH_4$ and $Ca(AlH_4)_2 + 6LiBH_4$ system the latter which dehydrogenates >8.5 wt% but undergoes partial formation of a $CaB_{12}H_{12}$ salt, a reaction product not previously predicted.
- Transmission electron microscopic examination of phase distributions in Mg incorporated into aerogels.

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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 MHCoE theory group [1] who have calculated formation and reaction enthalpies of systems that fall within the requisite thermodynamic boundaries.

Reaction kinetics are also 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 NMR in collaboration with JPL (see report from Bowman of JPL) and the Caltech NMR facility in order to gain insights into these systems, as they oftentimes show no long-range crystallographic order that could otherwise be studied with our typical approach of X-ray diffraction techniques. We have also been using transmission electron microscopy to better understand phase size and distribution in hydride systems in order to correlate observed isotherm and kinetic behavior with microstructure.

Results

In our previous annual report, we reported on initial results from the $ScH_2 + 2LiBH_4, <\to> ScB_2 + 2LiH + 4H_2$ reaction that was calculated to have a potential gravimetric density of 8.9 wt%, of which we have been able to observe 4 wt% desorption experimentally. A thorough assessment of the reactions in this system conducted over the past year [2] via B, Li and Sc NMR data is shown in Figure 1a-d and reveals that the ScH does not react to form ScB_2 and that the H only appears to desorb from the $LiBH_4$ phase. We have attributed the lack of reactivity to high formation enthalpies of the ScH_2 and ScB_2 phases. Our attempts at rehydrogenating the reaction from right to left, using ScB_2 as a starting material was accomplished to a small extent by the use

of high hydrogen absorption pressure using the facilities of Sandia National Laboratories. The formation of $LiBH_4$ in this reaction can be seen in the 3rd trace of Figure 1a. So while the calculated equilibrium reaction can be discerned to a small extent, the activation barriers to promoting the reactivity of this system appear to be too great for practical applications.

Figure 2a shows an image of reaction products after desorption at 400°C, taken with our micro Raman spectrometer. Of importance is the formation of $Li_2B_{12}H_{12}$ in this reaction [3], shown in Figure 2b, as the rehydrogenation of phases that contain this salt has not yet been demonstrated and thus is an activity that we are pursuing presently. This will be especially important as a number of borohydride-based systems that are being studied by other members of the MHCoE appear to also have the $B_{12}H_{12}$ salt formed during desorption reactions.

Figure 3 shows NMR results of a pure $Ca(AlH_4)_2 : 2LiBH_4$ system, which yields over 6.5% hydrogen. We had previously believed and reported that the use of pure $Ca(AlH_4)_2$ did not demonstrate reversibility but subsequent work this year has shown that some reversibility of the pure alanate system is possible. We have also been attempting to determine the source of the lower percentage of reversibility in the $Ca(AlH_4)_2 : 6LiBH_4$ system and it appears that at least part of this is due to the formation of $B_{12}H_{12}$ during the dehydrogenation reaction. In each of these systems, we believe that aluminum is an important catalytic component and the use of Al in the form of alane appears to also result in some reversibility, an area of research that we have been pursuing.

Figure 4 shows some of our results from our transmission electron microscopy (TEM) work that we have been doing in collaboration with HRL Laboratories and the University of Hawaii. This work has emphasized the incorporation of Mg and other reactants into carbon aerogel scaffolds. The behavior of these materials has been shown by some investigators to result in improve kinetics with possible changes to thermodynamic behavior. We have been interested in seeing the compositional distribution of reactants through the use of energy filtered imaging and X-ray microanalysis in order to be sure that the Mg that is incorporated into the aerogel structure gets incorporated into the nanopores. From the results of Figure 4 we can see that the majority of Mg is essentially in bulk form. The limited incorporation of Mg into the aerogel, in the results shown here indicate little evidence of Mg in nanoscale form. The isotherm behavior of these materials is bulk like. Subsequent microstructural work on material from the University of Hawaii shows that Mg at the nanoscale can be incorporated into the aerogel with higher Mg concentrations than we've seen from material from HRL Laboratories, although complete cycling behavior studies are underway only just now underway.
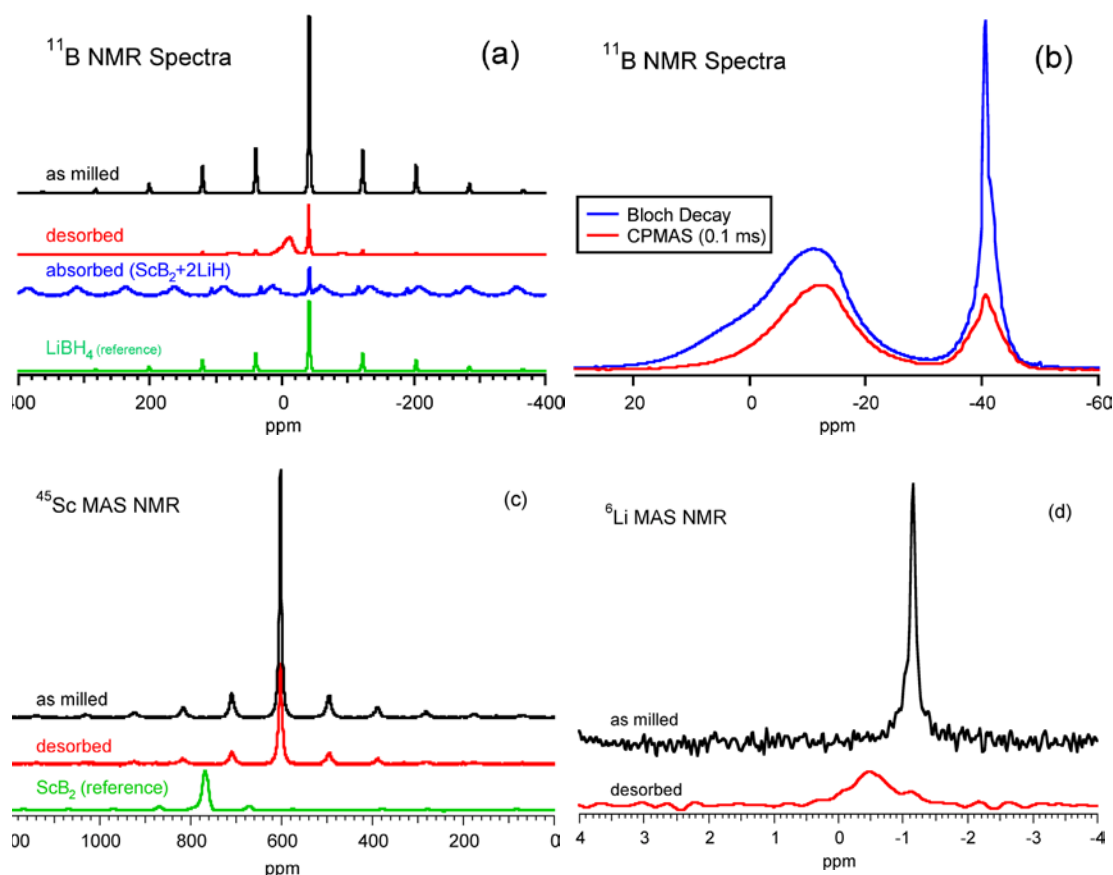
FIGURE 1. (a) Bloch decay [11]B magic angle spinning (MAS) NMR spectra with neat $LiBH_4$ (Sigma-Aldrich) added as a reference. No change of $LiBH_4$ peak observed after ball milling. (b) The [11]B MAS (blue) and cross polarization MAS (CPMAS) spectra (red) show formation of elemental boron in the amorphous phase (broad shoulder at ~5 ppm) and formation of intermediate phase (with peak at -12 ppm), recently identified [2] as the $[B_{12}H_{12}]^{2-}$ species. Note that a ^{11}B MAS NMR spectrum of ScB_2+2LiH system after absorption treatment at high H_2 pressure (896 bar, and 460°C for 48 hr) also included where the broader spinning sidebands in this spectrum are due to un-reacted ScB_2. The small peak at -41 ppm, indicates very limited $LiBH_4$ formation (~3%) in the reaction product. So the reverse reaction is seen but under technologically challenging conditions. (c) Shows un-reacted ScH_2 still present in desorption product, ScB_2/other Sc compounds not detectable in [45]Sc MAS NMR spectra. (d) [6]Li MAS NMR spectra also show distinctive signature of phase changes from $LiBH_4$ (-1.1 ppm) to $Li_2B_{12}H_{12}$ (-0.5 ppm). Presence of LiH confirmed by independent [6]Li CPMAS NMR measurements (not shown) because extremely long spin lattice relaxation behavior inhibits observation during recording of MAS spectra. As with X-ray diffraction data, NMR results identify decomposition products of $LiBH_4$, but show no evidence of ScH_2 reacting to form the ScB_2 product destabilization phase.

Conclusions and Future Directions

- The ScH_2-$2LiBH_4$ is of particular interest as a 34 kJ/mole system when zero point energy correction is taken into account. Predicted dehydrogenation reaction products are not discernable via X-ray or NMR. We attribute this to high formation enthalpies of ScH_2 and ScB_2. However, hydrogenation at high pressures has resulted in formation of some $LiBH_4$.

- $Ca(AlH_4)_2$:$2LiBH_4$ and $Ca(AlH_4)_2$:$6LiBH_4$ systems are of interest in dehydrogenation/hydrogenation reactions but the latter reaction during dehydrogenation results in $B_{12}H_{12}$ formation. The reversibility of the $B_{12}H_{12}$ phase is the subject of intense study in order to determine possible hydrogenation pathways.

- NMR analysis is used to identify near neighbor species that are not distinguishable via X-ray diffraction in all of our work.

- Continued collaboration with T. Baumann (Lawrence Livermore National Laboratory) in synthesis of aerogels with pore size range down to 1 to 2 nm. Surface/interface effects will play a dominant role in reaction enthalpy behavior at these size dimensions, where plan to use aerogels as scaffolds that will maintain short diffusion distances and perhaps highlight the role of hydride size/stability.

- Use of surface treatments/additives to enhance wetting of hydrides in aerogel pores. Continued analysis of size and size dependent behavior using TEM and Sieverts analysis.
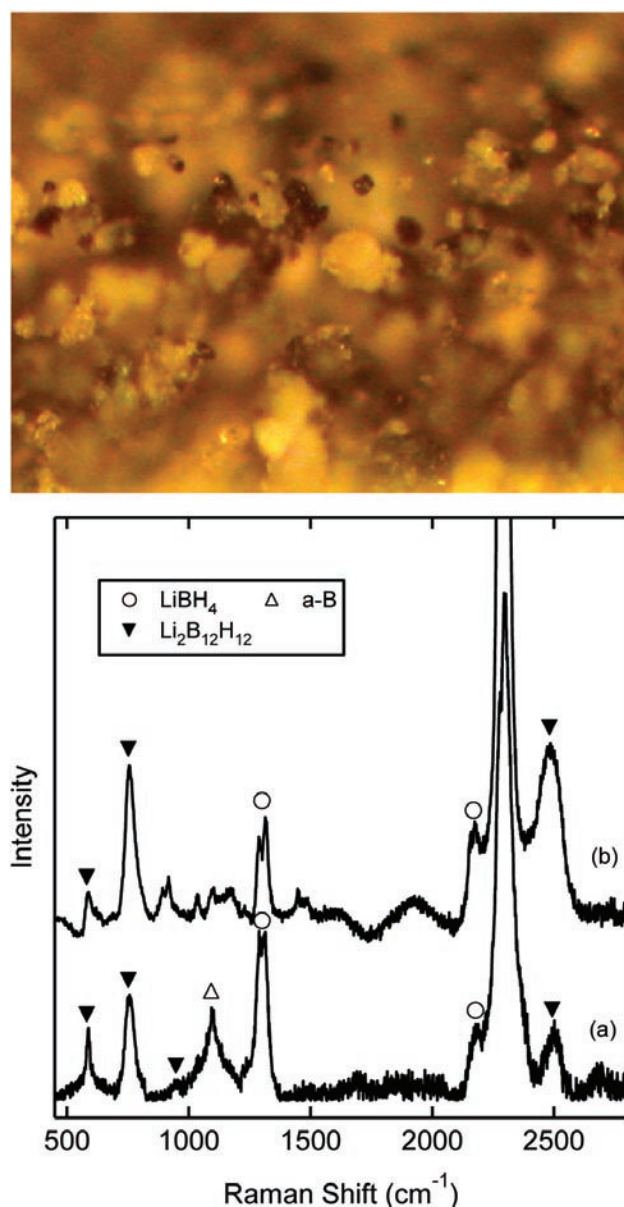
FIGURE 2. (a) Optical micrograph of a $ScH_2 + 2LiBH_4$ mixture after desorption at 400ºC for 20 hours. Desorption product segregates into two phases that are distinguished by their white and dark colors, respectively. The dark phase in the as-milled mixture is not Raman active as determined by our spatially resolved analysis. (b) B-H bending and stretching modes of $LiBH_4$ around 1,300 and 2,300 cm^{-1} present in both samples, and not affected by decomposition at temperatures below 400ºC. The broad peak at 1,100 cm^{-1} corresponds to Raman modes from B-B bonding in amorphous boron. The additional B-H bending and stretching modes around 500-1,000 cm^{-1} and 2,500 cm^{-1} consistent with calculated and measured [2] B-H vibrational modes in $Li_2B_{12}H_{12}$. These results suggest that the ball-milled $ScH_2 + 2LiBH_4$ mixture segregates back into its initial components upon melting and solidifying of $LiBH_4$. The dark phase contains ScH_2 while the white phase contains $LiBH_4$ and its thermal decomposition products. The solid triangles, open circles, and open triangles identify modes from $Li_2B_{12}H_{12}$, $LiBH_4$, and amorphous boron, respectively.
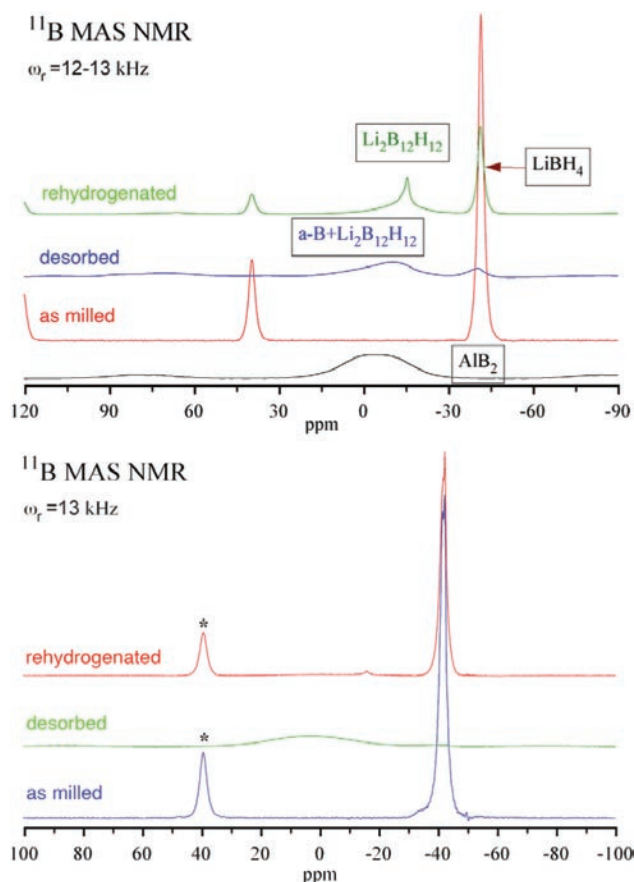

FIGURE 3. (a) ^{11}B MAS NMR, showing reversible formation of $LiBH_4$ using pure AlH_3 mixed with $LiBH_4$. (b) Reformation of $LiBH_4$ when a pure $Ca(AlH_4)_2$ is used in the destabilization reaction. Formation of $Li_2B_{12}H_{12}$ is also observed in all alanate reaction systems resulting in a competing reaction that limits reversibility of $LiBH_4$ formation during rehydrogenation.

FY 2008 Publications/Presentations

1. J. Purewal, S.-J. Hwang, R.C. Bowman, Jr., E. Rönnebro, B. Fultz and C.C. Ahn, "Hydrogen Sorption Behavior of the ScH_2-$LiBH_4$ System: Experimental Assessment of Chemical Destabilization Effects," J. Phys. Chem. C, 112, 8481-8485 (2008).

2. S.-J. Hwang, R.C. Bowman, J.W. Reiter, J. Rijssenbeek, G.L. Soloveichik, J.-C. Zhao, H. Kabbour and C.C. Ahn, "NMR Confirmation for Formation of $[B_{12}H_{12}]^2$ Complexes during Hydrogen Desorption from Metal Borohydrides," J. Phys. Chem. C, 112 (9), 3164-3169 (2008).

3. H. Kabbour, C.C. Ahn, S.-J. Hwang, R.C. Bowman Jr., J. Graetz, "Direct synthesis and NMR characterization of calcium alanate," J. Alloys Compounds, 446, 264-266 (2007).
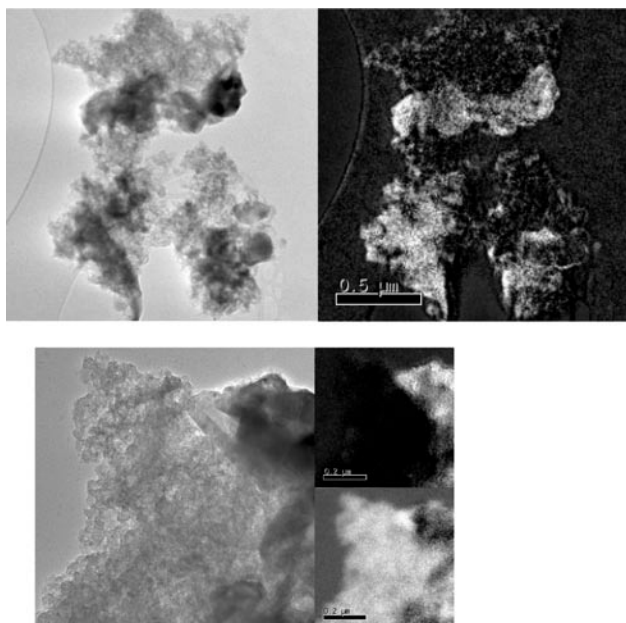
FIGURE 4. As part of an effort in looking into the possible effects of size on the thermodynamic properties of hydrogenation/dehydrogenation, and in conjunction with HRL Laboratories and Univ. Hawaii, we have been looking at elemental distributions of Mg in carbon aerogels. Because of the lack of "wettability" of Mg on typical carbon surfaces, schemes that promote the incorporation of Mg, especially into the small pore dimensions of aerogels needs to be verified. Sample 50559-60-1-c shows aerogel clusters in bright field image at left. Mg image on right formed by using Mg $L_{2,3}$ edge. The "white specular" regions are results of artifacts from difficulties with background subtraction. Region in upper right of these images shown in images below (and rotated 90° anti-clockwise). Mg $L_{2,3}$ image at 1/2 scale in upper right. Carbon K image at 1/2 scale in lower right.

Presentations

1. R.C. Bowman, Jr., S.-J. Hwang, J.W. Reiter, C. Kim, H. Kabbour, J. Purewal, C. C. Ahn, "Evaluations of Formation and Reversibility of Metal Borohydrides via Volumetric and Nuclear Magnetic Resonance Methods" Invited presentation at Materials Innovations in an Emerging Hydrogen Economy, Cocoa Beach, FL, February 24-27, 2008.

References

1. S.V. Alapati, J.K., Johnson and D.S. Sholl, "Large-scale screening of metal hydride mixtures for high-capacity hydrogen storage from first-principles calculations," J. Phys. Chem. C, 112 (14), 5258-5262 (2008).

2. J. Purewal, S.-J. Hwang, R.C. Bowman, Jr., E. Rönnebro, B. Fultz and C.C. Ahn, "Hydrogen Sorption Behavior of the ScH_2-$LiBH_4$ System: Experimental Assesment of Chemical Destabilization Effects," J. Phys. Chem. C, 112, 8481-8485 (2008).

3. S.-J. Hwang, R.C. Bowman, J.W. Reiter, J. Rijssenbeek, G.L. Soloveichik, J.-C. Zhao, H. Kabbour and C.C. Ahn, "NMR Confirmation for Formation of $[B_{12}H_{12}]^2$ Complexes during Hydrogen Desorption from Metal Borohydrides," J. Phys. Chem. C, 112 (9), 3164-3169 (2008).