

IV.A.5n UIUC Progress in MHCoE: Reversible Hydrogen Storage Materials – Structure, Chemistry and Electronic Structure

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Accomplishments

- Showed environmental degradation and poor catalyst mixing in $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ systems (with Sandia National Laboratories [SNL]).
- Identified regions of CaB_6 in possible $\text{Ca}(\text{BH}_4)_2$, supporting limited reversibility (with SNL).
- Determined structure and chemistry of contaminant layers on (de)hydriding cycle (with the University of Nevada).
- Determined structure and energy of combined Mg/boro-hydrides (with GE).
- Proposed a new method to predict accurate reaction enthalpies on molecular-based solids that have substantial contributions from non-harmonic modes. We utilize this method for direct comparison to experiment.
- Predicted the unknown structure in high-temperature (T) LiBH_4 and we are now correlating that with X-ray diffraction (XRD) data (with SNL).

Introduction

Our work at the University of Illinois Urbana-Champaign (UIUC) focuses on resolving issues within current hydrogen storage materials using a combination of electronic structure, structural, and chemical analysis.

We tie together theoretical understanding of electronic, enthalpic, thermodynamic, and surface effects affecting performance of storage materials with microchemical and microstructural experimental analysis, coordinated with other efforts from the Metal Hydride Center of Excellence (MHCoE) partners.

Approach

We employ state-of-the-art characterization tools to investigate the microstructural and microchemical changes that occur in candidate material systems during the uptake and release of hydrogen. This investigation provides fundamental insight to the processes governing hydrogen uptake and release. The characterization is coupled with first-principles, electronic-structure and thermodynamic techniques to predict and assess meta-stable and stable phases, as well as surface effects that can poison or limit kinetics. Electronic-structure and thermodynamic calculations are used to enhance the understanding of MHCoE experimental characterization results on candidate systems. The theoretical work at UIUC is coordinated closely with MHCoE theory partners, as well as experimental efforts.

These coordinated efforts enable a more efficient approach to designing a new system with the required properties.

Results

Experiment

The new vacuum transfer stage has enhanced our ability to observe environmentally sensitive samples in the transmission electron microscope (TEM) in furtherance of the FY goals. Results obtained, in association with several partners, include:

- NaAlH_4 was studied using electron energy loss spectroscopy (EELS) and we found that Ti in small volumes progresses from TiCl_3 to Al_3Ti upon cycling, in agreement with electron paramagnetic resonance (EPR) and other results. However, this examination was carried out at a much smaller scale than previous investigations and so represents a new advance. No material other than Al_3Ti has yet been found. As Al_3Ti is not a catalytic species, this suggests that the Ti catalytic species is a minority species in any operation mechanism. Spectra do not indicate oxidized Ti or Ti metal. Material subjected to 4 wt% cycling yield similar results. Portions of this work were presented at Metal Hydrides

2006 and published in the Journal of Alloys and Compounds.

This work is no longer part of the MHCoe but is now being performed in conjunction with the University of Hawaii, especially to study interrupted cycling tests.

- The reaction products produced during the cycling of a TiCl_3 catalyzed $\text{CaH}_2/\text{CaB}_6$ system generated by SNL have been examined via TEM. Unanticipated reaction products (long crystals) were found on a sample that had been through three cycles. These products were not found in the as-milled SNL materials and have not been found on UIUC-generated as-milled or cycled $\text{CaH}_2/\text{CaB}_6$ samples (see next bullet). Microdiffraction indicates tetragonal symmetry ($c/a=0.71$, $c = 7.2 \text{ \AA}$). Energy dispersive X-ray microanalysis and EELS indicate that the particles are comprised of Ca and Cl in a 80/20 at% ratio. In combination with energy dispersive X-ray spectroscopy (EDS) results that show depletion of Cl from the particle, this result indicates that Ca and Cl have been leached. These reaction products are most likely due to environmental exposure.
- Theory has suggested using $\text{Ca}(\text{BH}_4)_2$ which has ~11 wt% capacity. However, we have not observed substantial reversibility in these materials. Electron microscopy, mass spectroscopy, and pressure–composition–temperature (PCT) measurements strongly suggests a kinetic barrier in this material.
- In collaboration with SNL, we have synthesized by ball-milling additional systems of $\text{CaH}_2/\text{CaB}_6$ with various catalysts (Nb_2O_5 , V_2O_5 , TiCl_3 , TiF_3 , and Pt). Uptake and release of these systems (and $\text{Mg}(\text{BH}_4)_2$ systems, see next bullet) were measured on a PCT apparatus (see Figure 1). The samples do not uptake significant amounts of hydrogen. Outgassing of a system was observed with mass spectrometry and found to contain organics in addition to hydrogen, potentially indicating impure starting materials. Using EDS and EELS, we have identified regions of CaB_6 in a material that is hypothesized to be $\text{Ca}(\text{BH}_4)_2$. The trial catalysts used with this system have been located and analyzed and show poor mixing of the catalyst with Ca. No catalyst has been identified that shows significant uptake and release at moderate temperatures and hydrogen pressures. Further modeling is necessary to determine whether any catalyst will work.
- $\text{MgH}_2/\text{MgB}_2$ and catalyst systems synthesized (in collaboration with SNL) by ball milling with catalysts of TiCl_3 , Nb_2O_5 , and Pt have been observed via TEM. Uptake and release were measured on a PCT apparatus (see previous bullet). Samples do not uptake significant amounts of hydrogen. The trial catalysts used with this system have been located and analyzed and also show poor mixing

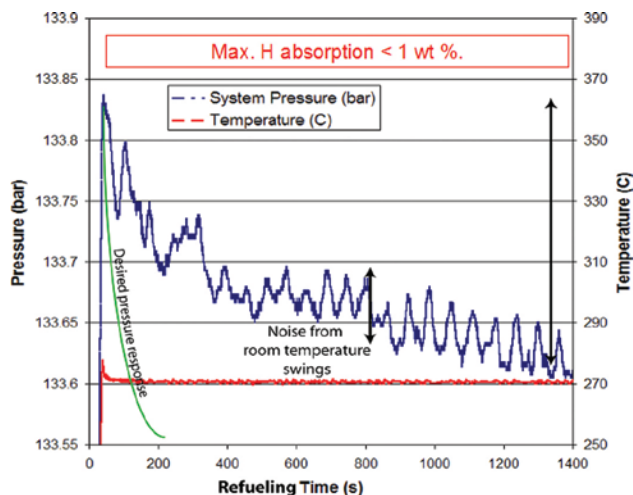


FIGURE 1. Representative pressure–composition–temperature measurement of $\text{Ca}(\text{BH}_4)_2$ materials. Testing of potential $\text{Ca}(\text{BH}_4)_2$ materials on a PCT device reveals little to no reversibility in these materials over a span of approximately 20 minutes. These materials, which are theorized to have nearly 11 wt% storage capacity, are expected to be reversible at approximately 200–250°C. Kinetic hindrance therefore appears to be a problem in these materials; poor mixing of the catalyst may also be at fault (see next figure).

with Mg (see Figure 2). The extent of the reduction of the TiCl_3 catalysts precursor is not yet known; EELS is planned to identify if the Ti is in a reduced Ti^0 metallic state.

Theory

We have addressed structural, enthalpic and thermodynamic issues in several MHCoe metal-hydride systems of interest and their hydrogen-storage reactions. The key to addressing reactions is to know the structures from which reactions occur, since they are often not groundstates. First, the structure of LiBH_4 (18 wt% hydrogen) has been investigated using theoretical and experimental methods. It has two phases, a known low-T orthorhombic phase and an unknown high-T hexagonal phase.

- Using *ab initio* molecular dynamics (MD) (Figure 3), we have developed a new method to predict the enthalpies in molecular-based substances, such as complex metal hydrides, and used it to investigate the structure and phase transformations of LiBH_4 , for which the harmonic approximation (used previously by all other groups) fails due to the importance of non-harmonic modes arising from relative motion of the Li^+ and BH_4^- ions [1,2].
- Predicting New High-Temperature Structures – Using *ab initio* MD versus temperature (Figure 3), we discovered, due to expansion of the LiBH_4 unit cell, a new configuration of the BH_4 units that significantly lowers the absolute energy from

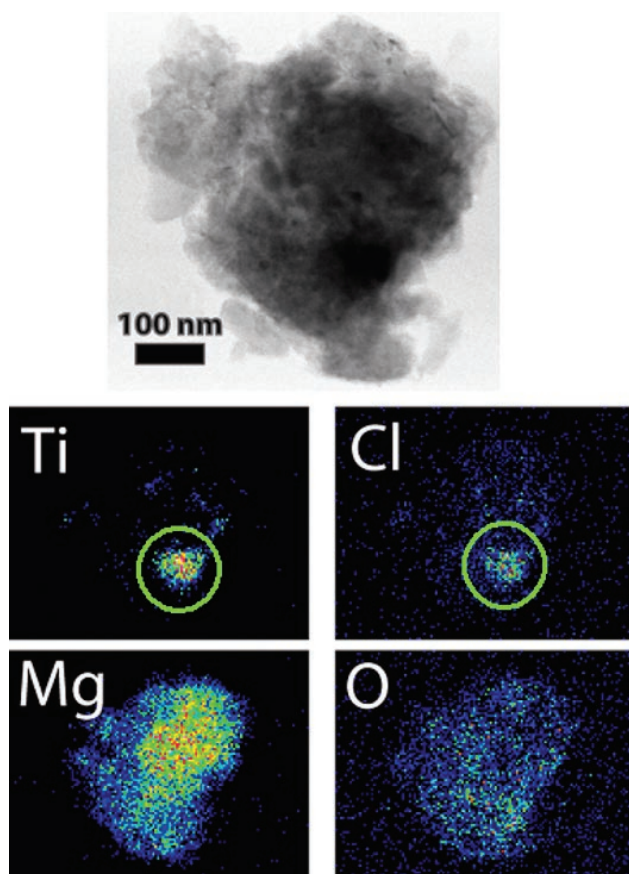


FIGURE 2. Energy dispersive spectroscopy of $\text{Mg}(\text{BH}_4)_2$ materials, indicating poor mixing of catalyst materials. EDS maps of $\text{MgH}_2 + \text{MgB}_2 + 2\text{B} + 0.02\text{TiCl}_3$ utilizing the environmental transfer stage. The maps suggest isolate regions of TiCl_3 , but, due to the nature of electron microscopy, this cannot be proven with this technique. However, electron energy loss spectrometry (planned) can indicate if the Ti is in a Ti^0 metallic form. These materials were fabricated by ball-milling and tested on a PCT device in collaboration with Sandia National Labs. However, the material shows no hydrogen absorption or desorption up to 200°C .

an experimentally suggested $\text{P6}_3\text{mc}$ structure (which is found to be unstable) (Figure 4). Since the reversible capacity of this system occurs at high temperature, it is critical that the correct configuration is identified for experiment. We are also able to predict quantitatively the enthalpy difference due to phase changes (from ortho to hex, and hex to incongruent melt phase); for example, enthalpy for ortho-to-hex (hex-to-melt) transition is calculated as 4.6 kJ/mol at 381 K (as is 6.3 kJ/mol at 553 K), compared to 4.3 kJ/mol (6.9 kJ/mol) from experiment (paper submitted). We have shown that the highest barriers to rotation of the BH_4^- units in the “ideal” $\text{P6}_3\text{mc}$ phase serve as an excellent approximant for the enthalpy of fusion for the hex to incongruent melt, which is directly relevant to the enthalpies determined from the LiBH_4 van’t Hoff plot by Hughes Research Laboratory (HRL).

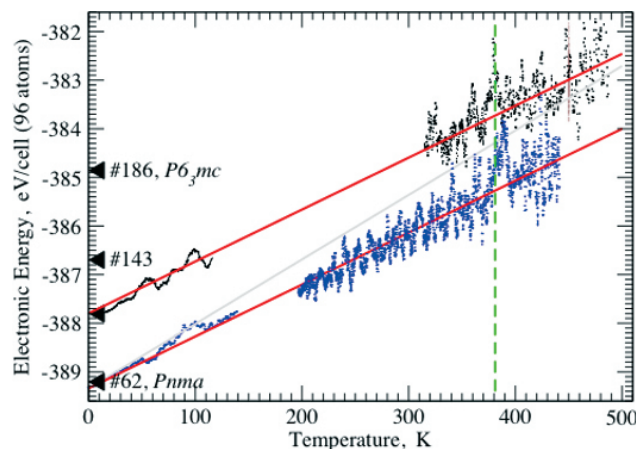


FIGURE 3. *Ab initio* MD electronic energy (in eV) vs. T for solid LiBH_4 phases with fixed B. Solid red lines fitted to MD data have slopes corresponding to average potential energy of $3/2 k_B T$ per moving atom. Thin grey line is fitted to MD data when B atoms are not fixed (MD data not shown for clarity); little change is found for the high-T phase in this case. Experimental T_c is shown by vertical dashed line. The 0 K energies of the structures in Figure 4 are marked.

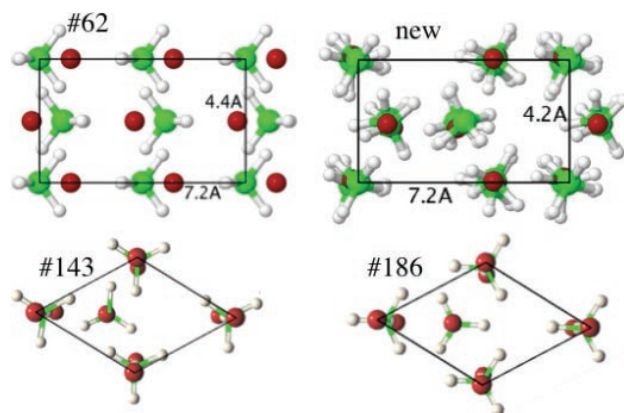


FIGURE 4. Structures of LiBH_4 molecular solids. Upper: (left) low-T orthorhombic (24-atom) Pnma [#62] and (right) the predicted high-T phase. Lower: hexagonal 12-atom cell for (left) structure #143 having concerted BH_4 rotations, and (right) ideal $\text{P6}_3\text{mc}$ [#186] in the [0001] projection. Comparing upper and lower right structures reveals the hexagonal nature of the predicted high-T LiBH_4 solid phase if H positions are averaged over their disorder.

- Predicting van’t Hoff Plots - From the above findings, we can predict accurately the T-dependent enthalpies and van’t Hoff plots (P-T phase diagram). We have applied the new methods to LiBH_4 destabilized with MgH_2 and find agreement with experiment within 1 kJ/mol-H_2 . We are finalizing a paper related to the van’t Hoff calculation. The initial work was presented at Metal Hydrides 2006 (paper in preparation).

- Verifying Structural Data - We are currently comparing predicted, high-T LiBH_4 phase against that obtained experimentally with XRD in a windowed Be holder. Although the holder was found to not be appropriate for distinguishing between the two different high-temperature hexagonal phases, large decreases in peak amplitudes are noted in the room temperature orthorhombic phase, consistent with the onset of large amplitude vibrations in the positions of the hydrogen atoms. The anisotropy of this low-T LiBH_4 phase has been measured and compared against experiment. The shift of position of the diffraction peaks and the decrease in intensity are consistent with theory. Moreover, the modulus for each direction in orthorhombic LiBH_4 calculated via DFT, with the a -axis the softest direction and the c -axis hardest, agrees with that found in experiment.
- Surface Poisoning Effects – Although it is known that the bi-alkali complex $\text{Na}_2\text{LiAlH}_6$ is reversible, the corresponding Li_3AlH_6 complex is not, mainly due to issues with LiH. The difference in reaction energy between LiH, NaH, and KH with H_2O and O_2 (including OH^- and O^{2-}) has been investigated. We find that LiH is strongly poisoned by H_2O in comparison with NaH and KH. We suggested that the presence of NaH or MgH_2 will prevent the poisoning of LiH and its complexes, which is now being tested at SNL. This assessment agrees with experimental data from the National Institute of Standards and Technology's (NIST's) Chembook. Additionally, in collaboration with the SNL and Carnegie Mellon University (CMU)/Pitt theory, results are being validated with surface calculations and obtain relevant enthalpies.
- Data Accumulation and Sharing – All the electronic-structure energetics, structures, etc., are stored in our ORACLE® database, developed mainly from a separate DOE/Basic Energy Sciences grant. The *Structural Database* (<http://data.mse.uiuc.edu>) underwent an upgrade to make uploads of data more reliable (too many additions at one time crashed the server). The coordinated theory effort will add more metal-hydride systems as the calculations are completed. Currently, the database contains:
 - 4,500 binary systems, including some metal-hydrides, loaded by UIUC.
 - ~158 hydrides that yield ~220 reactions, loaded by Pitt/CMU.

Conclusions and Future Directions

For FY 2008, we will continue experimental studies of the microchemical and microstructural changes occurring in different candidate systems that are supplied by the various MHCoe partners. In addition to

diffraction and EDS analysis, EELS will continue to be used to identify electronic states within the materials.

Finalizing study on the electronic-structure calculations on the bulk phase of LiBH_4 in the hexagonal high-T phase, along with H_2 , hexagonal MgB_2 , MgH_2 and LiH will be conducted with input from the HRL group. Current work on kinetics and poisoning issues in borohydride and alanates will be continue to try to ameliorate the problems with, for example, secondary reactions within the Li-alanate to increase H_2 yield. Our suggested use of, for example, MgH_2 as a getter for OH^- is now being tested experimentally. Calcium-borohydride system is not showing reversibility experimentally. We will collaborate with partners as appropriate to help understand the issues.

Additional calculations will be performed with input from experimental partners regarding key issues affecting their programs:

- The *Structural Database* will continue to be updated and used by partners. Currently, the database has 4,500 binary systems and ~158 hydrides that yield ~220 reactions. We will add modifications to expand use, scope, and vetting reliability (current care-and-feeding at the National Center for Supercomputing Applications).
- We will continue to address kinetics and poisoning issues, as we have done with Mg/Li alanate storage system reactions (with SNL, HRL, Pitt/CMU). We will finalize theory and publications for structural changes and thermodynamics in LiBH_4 (with SNL and Pitt/CMU).
- We will develop (with NIST) the use of the calculations of phase diagrams method to make thermodynamic prediction of reversible reactions via linear programming using the enthalpies in the *Structural Database*. Recently, thermodynamics via linear programming was used to show that previous predicted reactions were not thermodynamically stable. This would be a useful and general tool for the MHCoe.
- We will complete results on NaAlH_4 systems to identify Al_3Ti and minority constituents (with the University of Hawaii).

FY 2007 Publications/Presentations

1. D.D. Johnson, "Calculating enthalpies of hydrogen storage complex-metal hydrides," presentation at Metal Hydrides, Hawaii, October 2006.
2. D. D. Graham, I.M. Robertson, L. F. Culnane, C. Jensen, M. Sulic, "Combining Electron Energy Loss Spectroscopy and Energy Dispersive Spectroscopy for Identification of Catalytic Species in Hydrogen Storage Materials," presentation at Metal Hydrides, Hawaii, October 2006.

3. N.A. Zarkevich and D.D. Johnson (UIUC), Comment on “Structural Stability of Complex Hydrides: LiBH₄ Revisited,” *Physical Review Letters*, **97(11)** (2006) 119601-4.
4. N.A. Zarkevich, Teck L. Tan, and D.D. Johnson, “First-principles prediction of phase-segregating alloy phase diagrams and a rapid design estimates of their transition temperatures,” *Physical Review B* **75(10)** (2007) 104203-12.
5. D. D. Graham, I.M. Robertson, L. F. Culnane, C. Jensen, M. Sulic, “Ti EELS Standards for Identification of Catalytic Species in NaAlH₄ Hydrogen Storage Materials,” *Journal of Alloys and Compounds*, accepted.
6. Nikolai Zarkevich and D.D. Johnson, “Predicting Enthalpies of Molecular Substances at Finite Temperatures,” submitted to *Physical Review Letters*.

7. E. Majzoub (Sandia), N. Zarkevich and D.D. Johnson (UIUC) “Temperature-dependent XRD of Orthorhombic LiBH₄: Theory and Experiment,” in preparation.

8. N.A. Zarkevich, S. Alapati, and D.D. Johnson, “First-principles Prediction of Enthalpies and Van’t Hoff plots for Complex Metal-hydride Hydrogen-storage Reactions,” in preparation.

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1. Lodziana, Z.; T. Vegge. Structural stability of complex hydrides: LiBH₄ revisited. *Physical Review Letters*, **93 (14)** (2004) 1.
2. Zarkevich, N. A.; D. D. Johnson, “Comment on ‘Structural Stability of Complex Hydrides: LiBH₄ Revisited,’ ” *Physical Review Letters*, **97 (11)** (2006) 119601-4.