

## IV.A.4i First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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### Introduction

Researchers at the University of Pittsburgh and Carnegie Mellon University are computing thermodynamic properties of metal hydride alloys, including the heat of reaction ( $\Delta H$ ) for known reactions to test the accuracy of the approach and  $\Delta H$  for new reactions to identify promising destabilized compounds. The heat of reaction is a key indicator of the potential performance of a hydride. If  $\Delta H$  is too large then the temperature required to release hydrogen will be unacceptably high. If  $\Delta H$  is too low, then the hydride will likely not be reversible.

Interfacial properties of hydrides are also computed in this project. Hydrogenation of destabilized hydrides and other systems is studied to assess reversibility, identify common hydrogenation pathways that might be applicable to other materials, and assess the role of interfacial transport. The overall goal of our work is to screen as many possible destabilized hydride systems as possible in order to identify potential candidate systems for experimental exploration.

### Approach

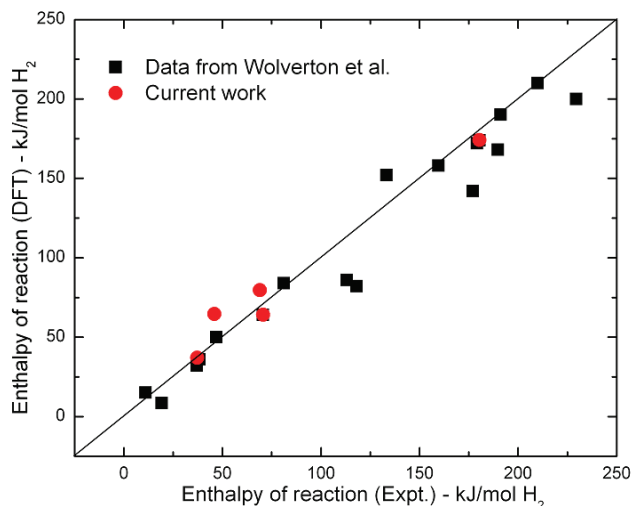
Plane wave density functional theory (DFT) calculations are performed with the Vienna *Ab-initio* Simulation Package (VASP) [1,2]. The calculations examine a spatially infinite material using periodic boundary conditions in all the principal directions. We use both ultrasoft pseudopotentials (USPP) and the projector augmented wave (PAW) method [3] for prediction of reaction enthalpies. Electron exchange and correlation effects are described using the generalized gradient approximation (GGA) with the Perdew-Wang 91 (PW91) functional [4]. We have performed test calculations with the USPP revised Perdew-Burke-Ernzerhof [5] and PAW Perdew-Burke-Ernzerhof [6] functionals, but these resulted in  $\Delta H$  values that were much lower than experimental or PW91 values. The bond energy of  $H_2$  is key to the accuracy of all the  $\Delta H$  calculations. We have therefore computed the bond energy of  $H_2$  from USPP-PW91 and PAW-PW91; both methods give 4.56 eV, which is in good agreement with the experimental value of 4.52 eV [7]. We use a Monkhorst-Pack mesh with a sufficient number of  $k$ -points to converge the energies. Geometry optimizations for bulk structures are performed by allowing all atomic positions and all cell parameters to vary.

The enthalpy of the reaction at 0 K was calculated using,

$$\Delta H = \sum_{\text{products}} E - \sum_{\text{reactants}} E \quad (1)$$

where  $E$  is the total energy of one of the bulk structures of interest as calculated by DFT. We have not accounted for zero point corrections in any of the total energies. The accuracy of our approach has been assessed by comparing our calculated values with experimental values for a number of different hydride materials. The results are shown in Figure 1.

Calculation of vapor pressures requires the free energies, in addition to the enthalpies. The entropies (and hence the free energies) can be computed by calculation of the phonon density of states for the solids, as well as including the free energy of the gas phase  $H_2$ . Calculation of the phonon density of states and the resulting vibrational contributions to the free energy were performed using the PHONON code developed by Parlinski. These calculations used the same exchange-correlation functional and energy cutoff as listed above for our total energy calculations. Force constants were computed using displacements of individual atoms of 0.03-0.07 Å. In order to avoid interaction between



**FIGURE 1.** Comparison of data from experiments or thermodynamic tables for hydride decomposition enthalpies with plane wave DFT predictions. All  $\Delta H$  values are in kJ/mol  $H_2$ . The results shown with black squares are from Wolverton et al. [12] (Comparison of experimental and theoretical  $\Delta H$  values)

images of the displaced atom when defining the phonon density of states, it is necessary to use a relatively large supercell. In most cases we chose a supercell in such a way that it approximates a spherical shape.

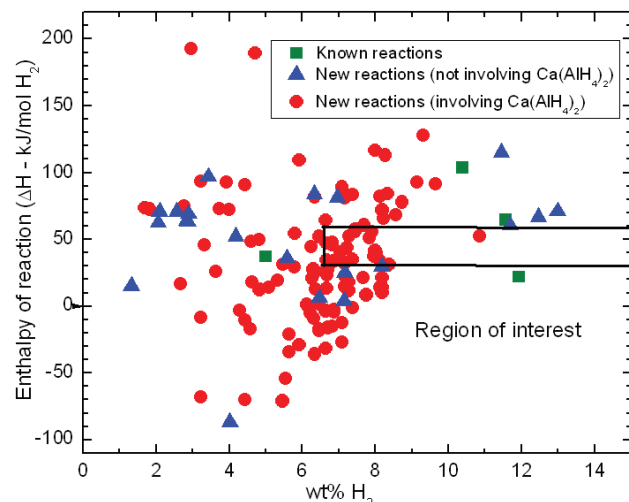
## Results

We have computed  $\Delta H$  for many different possible destabilized hydrides and have plotted  $\Delta H$  vs. the wt% hydrogen uptake in Figure 2. We identify promising candidate reaction schemes by considering each of the reactions shown in Figure 1 that have  $15 \leq \Delta H \leq 75$  kJ/mol  $H_2$  and that yield  $> 6.5$  wt% H storage. We have chosen the value of 6.5 wt% because it is slightly larger than the interim 2010 DOE targets [8]. The range of enthalpies is chosen so that after accounting for the uncertainty associated with our DFT calculations we will capture essentially all reactions that can satisfy the experimental bounds of  $30 \leq \Delta H \leq 60$  kJ/mol  $H_2$ . That is, we identify candidate reactions in an inclusive manner, consistent with our goal of motivating detailed experimental studies of potential candidates.

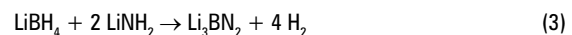
Our inclusive criterion for identifying interesting reaction schemes yields seven reactions. One is the reaction already studied experimentally by Vajo et al. [9]



This reaction can yield a maximum of 11.56 wt% H at completion, and has been demonstrated experimentally to yield  $> 9$  wt% H reversibly. A second reaction is the one suggested recently by Pinkerton et al. [10] and also by Aoki et al. [11]:

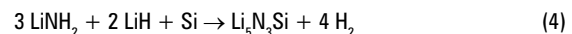


**FIGURE 2.** USPP-DFT predictions of  $\Delta H$  for 129 new destabilized reactions along with 4 known ones. The region of interest includes reactions which have  $> 6.5$  wt%  $H_2$  and reaction enthalpy between 30 – 60 kJ/mol  $H_2$ . (Predicted  $\Delta H$  for destabilized reactions)

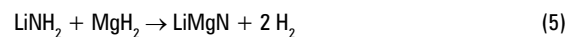


This reaction yields 11.9 wt% H at completion, and is predicted by DFT to have  $\Delta H = 22$  (24) kJ/mol  $H_2$  using the USPP (PAW) approach and the orthorhombic form of  $\text{LiBH}_4$ .

Crucially, our approach also identifies five interesting reactions that have not previously been proposed or examined. One example is



This reaction yields 7.16 wt% H on completion. Our DFT calculations predict that the reaction enthalpy is 19-30 (23-34) kJ/mol  $H_2$  using the USPP (PAW) approach. The range of values for this reaction reflects the variants in the  $\text{Li}_5\text{N}_3\text{Si}$  crystal structure that were employed in our calculations. A related reaction involves a mixture of  $\text{LiNH}_2$  and  $\text{MgH}_2$ :



This reaction releases 8.19 wt% H on completion, with a DFT-predicted reaction enthalpy of 29.7 (31.9) kJ/mol  $H_2$  using the USPP (PAW) approach. Two other examples identified by our calculations are variants of (2):



These schemes differ from reaction 2 by including larger amounts of  $\text{LiBH}_4$  as a reactant, forming  $\text{MgB}_4$  or  $\text{MgB}_7$  as a product rather than  $\text{MgB}_2$ . Reactions 6 and 7 release 12.5 and 13 wt% H on completion. Our USPP-

DFT calculations predict a reaction enthalpy of 66.8 (69.2-73.1) kJ/mol H<sub>2</sub> using the orthorhombic form of LiBH<sub>4</sub> for the reaction forming MgB<sub>4</sub> (MgB<sub>7</sub>). The range of enthalpies for the latter reaction is due to the different structures of MgB<sub>7</sub>, used to account for the vacancies in the crystal structure. The fifth example involves CaH<sub>2</sub>:

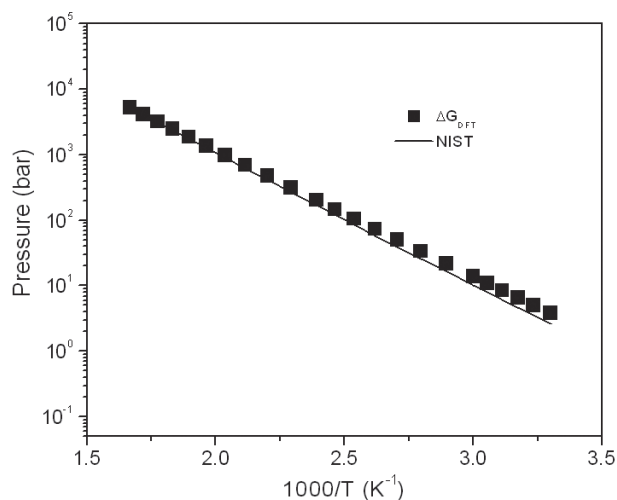


Upon completion, this reaction releases 11.7 wt% H and the DFT-predicted reaction enthalpy is 60 (63) with USPP (PAW).

We have computed the vapor pressures for a select number of reactions from the phonon density of states method. As an example, we show in Figure 3 the vapor pressure curve computed from our DFT calculations compared with the vapor pressure computed from thermodynamic tables from the NIST database. The agreement is remarkably good for this system. However, the agreement for other test systems is not expected to be that good because the accuracy of DFT methods are not good enough to give quantitative agreement with experiments.

## Conclusions and Future Directions

We have demonstrated the utility of using first principles density functional theory to screen candidate reaction schemes for hydrogen storage. We can predict the enthalpy of reaction to within reasonable accuracy to justify further experimental investigations for the most promising candidate materials. Perhaps more importantly, we can quickly discount reaction schemes that have  $\Delta H$  values that are either much too high or



**FIGURE 3.** Vapor pressure of  $2\text{MgH}_2 + \text{Si} = \text{Mg}_2\text{Si} + 2\text{H}_2$  calculated from density functional theory and compared with thermodynamic data from the NIST database. (Calculated vapor pressure curve for the  $\text{MgH}_2 + \text{Si}$  system)

much too low. This is of critical importance because of the challenge posed to experimental groups to synthesize and characterize a large number of different alloys from both a time and financial resources view-point.

We have provided a proof-in-principle that we are able to compute vapor pressures (van't Hoff plots) for hydride reactions, including destabilized hydrides. This should prove useful for estimating the potential usefulness of a given reaction scheme, beyond the simple reaction enthalpy approach.

We are currently investigating kinetics of hydrogenation reactions and the effect of oxide formation. We are working closely with experimental groups and providing information on interfacial energies in order to estimate finite-size effects on the thermodynamics of hydrogen storage for nanoparticles. Future work also includes the following planned activities:

- Contribute data to the UIUC toolbox data base
- Collaborate with Ursula Kattner, NIST by computing thermodynamic properties of LiB4 and other materials
- Continue work on computing P-T diagrams for metal hydrides
- Continue work on interfacial energies
- Continue work on destabilized hydride reversibility
- Investigate new reaction schemes for destabilized hydrides including other light elements

## Special Recognitions & Awards/Patents Issued

1. Invited talk at the International Symposium on Materials Issues in Hydrogen Production and Storage, Santa Barbara, CA, August 20-25, 2006.
2. Invited talk at the Fall MRS meeting, special session on hydrogen storage.

## FY 2006 Publications/Presentations

1. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl "Identification of Destabilized Metal Hydrides for Hydrogen Storage Using First Principles Calculations", *Journal of Physical Chemistry B*, **110**, 8769-8776 (2006).

## Invited Talks

1. J. Karl Johnson, Sudhakar V. Alapati, Bing Dai, David S. Sholl "Computational Study of Metal Hydride Destabilization" *American Physical Society March Meeting*, Baltimore, MD, 13-17 March, 2006.
2. J. Karl Johnson, "Atomistic Simulations of Novel Hydrogen Storage Materials", *Pittsburgh-Cleveland Catalysis Society*, Pittsburgh, PA, 9 December, 2005.

3. J. Karl Johnson, "Atomistic Simulations of Novel Hydrogen Storage Materials", *Department of Chemical Engineering, Brigham Young University*, Provo, Utah, 1 December, 2005.
4. J. Karl Johnson, Sudhakar V. Alapati, Bing Dai, Giovanni Garberoglio, David S. Sholl, "Computational Studies of Hydrogen Storage: Metal Organic Frameworks and Destabilized Metal Hydrides", *W. E. Heraeus Seminar on Hydrogen Storage with Novel Nanomaterials*, Bad Honnef, Germany, 23-27 October, 2005.

#### Contributed Talks

1. Giovanni Garberoglio, Anastasios Skoulidas, Karl Johnson, "Mechanisms of Hydrogen Adsorption in Metal Organic Frameworks", *AIChE Annual Meeting*, Cincinnati, Ohio, 31 October to 4 November, 2005.
2. Karl Johnson, Giovanni Garberoglio "Hydrogen Storage in Metal Organic Frameworks: Predictions from Computer Simulations", *Symposium on Materials for the Hydrogen Economy, Materials Science & Technology 2005* Pittsburgh, Pennsylvania, September 25-28, 2005.
3. Sudhakar V. Alapati, David S. Sholl and J. Karl. Johnson, "Screening Destabilized Alloys for Hydrogen Storage Applications and Prediction of Thermodynamic Properties using First Principles", *2006 Midwest Thermodynamics and Statistical Mechanics Conference*, Akron, OH, May 25-26, 2006.
4. Bing Dai, David S. Sholl and J. Karl. Johnson, "First Principles Investigation of Adsorption and Dissociation of Hydrogen on the Mg<sub>2</sub>Si Surface", *2006 Midwest Thermodynamics and Statistical Mechanics Conference*, Akron, OH, May 25-26, 2006.
5. Bing Dai, Sudhakar V. Alapati, David S. Sholl and J. Karl. Johnson, "First Principles Investigation of Adsorption and Dissociation of Hydrogen on the Mg<sub>2</sub>Si Surface" *231<sup>st</sup> American Chemical Society National Meeting*, Atlanta, Georgia, 26-30 March 2006.
6. Sudhakar V. Alapati, Bing Dai, J. Karl. Johnson and David S. Sholl, "First Principles Calculations of Destabilized Alloys for Hydrogen Storage Applications" *2006 TMS Annual Meeting*, San Antonio, TX, 12-16 March, 2006.

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