

IV.A.1e First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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David S. Sholl, Georgia Institute of Technology,
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Project Start Date: March 1, 2005

Project End Date: 2010

- Energy density: 1.5 kWh/L

Accomplishments

- Implemented a method for high-throughput screening of the thermodynamics of metal hydrides using an approach based on calculating the grand potential of the system, coupled with a linear programming method.
- Applied the high-throughput linear program to all 212 compounds in our density functional theory (DFT) database, scanning over 16 million different composition and temperature combinations.
- Identified 34 single-step reactions having apparent favorable thermodynamics and acceptable gravimetric densities.
- Initiated study of including the effects of surface energies on the thermodynamics of hydride nanoparticles.
- Calculated the structure and energy of $\text{Mg}(\text{BH}_4)_2$ based on experimental crystal structure and identified a higher symmetry structure that may be the zero temperature ground state.



Objectives

- Compute thermodynamics of metal hydride systems.
- Compute interfacial properties of hydrides.
- Address fundamental processes in hydrogenation.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

This project is involved with developing new complex metal hydride materials that meet the DOE 2010 hydrogen storage targets:

- Specific energy: 2 kWh/kg

Introduction

Complex metal hydrides such as alanates, amides and borohydrides of period 2 and 3 metals are promising materials for reaching high gravimetric and volumetric hydrogen densities for on-board fuel cell storage. A serious thermodynamic limitation of these materials is that high temperatures are often required to release H_2 . The reaction free energy for decomposition of practical materials must lie in a narrow range of values to allow reversible hydrogenation and dehydrogenation at acceptable temperatures and pressures. In addition, the kinetics of hydrogenation and dehydrogenation must be acceptably.

Research carried out at the University of Pittsburgh and Georgia Tech has focused on using computer modeling to predict the thermodynamics of existing and novel complex hydrides. We have identified several new materials that are predicted to have favorable thermodynamics, some of which are currently being investigated experimentally. We have investigated the thermodynamics of doping as a means of tuning the energies of reaction for hydrides that are too stable or not stable enough. We have also initiated an investigation into the kinetics of selected hydride

materials in an effort to understand the atomic-level phenomena that control the rate of hydrogenation of complex metal hydrides.

Approach

We use quantum mechanical methods for computing the structural, electronic, energetic, and kinetic properties of complex hydrides and related materials. The specific method we use for most of our calculations is periodic plane-wave DFT, which is an approach for computing the approximate solution to the Schrödinger equation for condensed phase (solids) materials. This method requires as input at least an initial guess for the crystal structure of material to be modeled. The DFT method can then be used to optimize the atomic coordinates of each atom in the unit cell, the volume, and the shape of the unit cell. More importantly, we have developed a DFT-based method that can be used to quickly and reliably estimate the enthalpies of reaction for complex hydrides. We have used this method to screen over 300 possible hydrogen storage reactions and have identified several promising materials that have not previously been investigated. We can also calculate the free energies of reaction, including computing the entropic contributions through the phonon density of states. This is a much more computationally demanding approach – we have performed such calculations for a subset of the most promising reaction schemes identified from our screening calculations. We have also used DFT methods to compute kinetics for surface reactions as an initial approach for studying kinetics of reactions involving complex hydrides.

We have used the Vienna Ab initio Simulation Package (VASP) to perform most of the calculations in our work. We have used the gradient corrected approximation with the Perdew-Wang 91 functional [1]. We have used both ultrasoft pseudopotentials and the projector augmented wave method [2].

Results

We performed DFT calculations for the 212 crystal structures containing Al, B, C, Ca, K, Li, Mg, N, Na, Sc, Si, Ti, V, and H. This list includes all relevant compounds from Pearson, Wyckoff, and the Inorganic Crystal Structure Database [3-5]. Importantly, it also includes the recently reported experimental crystal structure of $\text{Mg}(\text{BH}_4)_2$ [6]. The only gaseous compound we considered was H_2 ; we did not include NH_3 or gaseous hydrocarbons as potential products. Using the 13 non-H elements listed above, we examined all 715 element spaces of the form $\text{E}_1\text{-E}_2\text{-E}_3\text{-E}_4\text{-H}$, where E_i is an element from the list above. This approach includes analysis of all 286/98/13 spaces of the form $\text{E}_1\text{-E}_2\text{-E}_3\text{-H}/\text{E}_1\text{-E}_2\text{-H}/\text{E}_1\text{-H}$. In each element space, distinct compositions filling the entire space were defined using

increments in the non-H mole fractions of 0.02. At each composition, the grand potential minimization method using DFT total energy values was applied as the temperature ranged from 0 to 1,000 K in increments of 5 K. In these calculations, the temperature dependence of the grand potential enters only via the chemical potential of H. For every reaction listed below, these calculations were repeated for verification using temperature increments of 0.5 K. In all, these calculations examined >16 million distinct mixtures.

To use the calculations outlined above, selection criteria must be specified to separate the reactions with useful properties from other reactions. We did this by only retaining single step reactions that release >6.0 wt% H at completion and for which ΔU_0 lies in the range 15-75 kJ/mol H_2 . This enthalpy range is inclusive in the sense that reactions excluded by this criterion will not have desirable reaction thermodynamics even after the uncertainties associated with the DFT calculations are considered. This approach identified 43 distinct reactions, many of which have not previously been studied. All of these reactions are listed in Table 1 and are also shown in Figures 1-3.

Almost all of the reactions we identified involve the combination of either LiBH_4 or $\text{Mg}(\text{BH}_4)_2$ with other materials. For most of the reactions involving LiBH_4 , the reduction in the reaction enthalpy relative to the direct decomposition of LiBH_4 is modest. Mixtures of LiBH_4 with TiN, TiH_2 , ScH_2 , or C, however, yield reactions with substantially lower reaction enthalpies. Some of these reactions involve products that are regarded as refractory, for example TiB_2 ; these may imply the existence of severe kinetic limitations. All of the

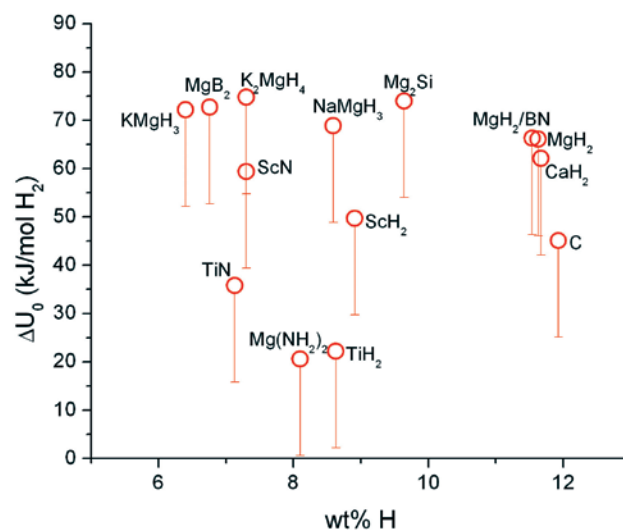


FIGURE 1. Reaction enthalpy as computed from 0 K DFT calculations, ΔU_0 , for all single step reactions involving $\text{Mg}(\text{BH}_4)_2$. The reactants that combine with $\text{Mg}(\text{BH}_4)_2$ in these reactions are indicated in the figure. The error bars for each reaction span the predicted ΔG at 300 K assigned using the methods of Refs [8,12].

TABLE 1. Complete list of single-step reactions identified from a 212 compound database with >6 wt% H₂ released at completion and 15 ≤ ΔU₀ ≤ 75 kJ/mol H₂. All reactions that involve LiBH₄ list ΔU₀ calculated with the low temperature (ortho) crystal structure. Reactions are listed in order of decreasing H₂ capacity.

Reaction	wt% H ₂	ΔU ₀ (kJ/mol H ₂)
Mg(BH ₄) ₂ → MgB ₂ + 4 H ₂	14.9	54.0
Si + 4 Mg(BH ₄) ₂ → Mg ₂ Si + 2 MgB ₄ + 16 H ₂	13.2	52.7
LiBH ₄ + C → LiBC + 2 H ₂	11.9	45.1
6 LiBH ₄ + CaH ₂ → 6 LiH + CaB ₆ + 10 H ₂	11.7	62.1
8 LiBH ₄ + MgH ₂ + BN → 8 LiH + MgB ₉ N + 13 H ₂	11.6	66.3
2 LiBH ₄ + MgH ₂ → 2LiH + MgB ₂ + 4 H ₂	11.5	66.2
3 Si + MgSiN ₂ + 12 Mg(BH ₄) ₂ → 4 Mg ₂ Si + 2 MgB ₉ N + 36 H ₂	11.2	48.6
BN + 4 Mg(BH ₄) ₂ → 3 MgH ₂ + MgB ₉ N + 13 H ₂	10.9	51.2
NaH + 2 Mg(BH ₄) ₂ → NaMgH ₃ + MgB ₄ + 7 H ₂	10.67	53.2
CaH ₂ + 1.5 Si + 3 Mg(BH ₄) ₂ → CaB ₆ + 1.5 Mg ₂ Si + 13 H ₂	10.6	45.4
2 C + Mg(BH ₄) ₂ → MgB ₂ C ₂ + 4 H ₂	10.3	43.1
CaH ₂ + 3 Mg(BH ₄) ₂ → 3 MgH ₂ + CaB ₆ + 10 H ₂	9.9	47.5
8 LiBH ₄ + Mg ₂ Si → 8 LiH + Si + 2 MgB ₄ + 12 H ₂	9.6	74.0
2 LiBH ₄ + ScH ₂ → 2 LiH + ScB ₂ + 4 H ₂	8.9	49.7
2 LiBH ₄ + TiH ₂ → 2 LiH + TiB ₂ + 4 H ₂	8.6	22.2
2 LiBH ₄ + NaMgH ₃ → 2 LiH + NaH + MgB ₂ + 4 H ₂	8.6	68.9
3 NaH + BN + 4 Mg(BH ₄) ₂ → 3 NaMgH ₃ + MgB ₉ N + 13 H ₂	8.4	48.8
2 LiBH ₄ + Mg(NH ₂) ₂ → MgH ₂ + 2 LiH + 2 BN + 4 H ₂	8.1	20.6
ScH ₂ + Mg(BH ₄) ₂ → MgH ₂ + ScB ₂ + 4 H ₂	8.0	37.5
MgH ₂ → Mg + H ₂	7.7	64.7
5 B + Mg(BH ₄) ₂ → MgB ₇ + 4 H ₂	7.5	41.5
2 MgH ₂ + Mg(NH ₂) ₂ → Mg ₃ N ₂ + 4 H ₂	7.4	26.0
CaH ₂ + 3 NaH + 3 Mg(BH ₄) ₂ → 3 NaMgH ₃ + CaB ₆ + 10 H ₂	7.3	44.3
6 LiBH ₄ + 2 ScN → 6 LiH + 2 ScB ₂ + 2 BN + 9 H ₂	7.3	59.5
3 Si + 8 BN + 5 Mg(BH ₄) ₂ → 2 MgB ₉ N + 3 MgSiN ₂ + 20 H ₂	7.3	47.0
4 LiBH ₄ + K ₂ MgH ₄ → 4 LiH + MgB ₄ + 2 KH + 7 H ₂	7.3	74.8
4 LiH + 3 Mg(NH ₂) ₂ + 2 C → 2 Li ₂ CN ₂ + 2 Mg ₃ N ₂ + 8 H ₂	7.2	47.8
6 LiBH ₄ + 2 TiN → 6 LiH + 2 TiB ₂ + 2 BN + 9 H ₂	7.1	35.9
2 LiNH ₂ + C → Li ₂ CN ₂ + 2 H ₂	7.0	31.4
Al + MgB ₉ N + 2.5 Mg(BH ₄) ₂ → AlN + 3.5 MgB ₄ + 10 H ₂	6.8	53.6
2 LiBH ₄ + MgB ₂ → 2 LiH + MgB ₄ + 3 H ₂	6.8	72.5
MgB ₇ + 1.5 Mg(BH ₄) ₂ → 2.5 MgB ₄ + 6 H ₂	6.7	50.2
12 LiH + 3 Mg(NH ₂) ₂ + 4 BN → 4 Li ₃ BN ₂ + Mg ₃ N ₂ + 12 H ₂	6.7	54.2
K ₂ MgH ₄ + 2 Mg(BH ₄) ₂ → MgB ₄ + 2 KMgH ₃ + 7 H ₂	6.6	51.2
28 LiH + 9 Mg(NH ₂) ₂ + 4 VN → 4 Li ₃ N ₄ V + 3 Mg ₃ N ₂ + 32 H ₂	6.5	47.5
2 ScN + 3 Mg(BH ₄) ₂ → 3 MgH ₂ + 2 ScB ₂ + 2 BN + 9 H ₂	6.5	43.1
NaH + ScH ₂ + Mg(BH ₄) ₂ → NaMgH ₃ + ScB ₂ + 4 H ₂	6.5	34.8
4 LiBH ₄ + 2 KMgH ₃ → 4 LiH + MgB ₄ + K ₂ MgH ₄ + 7 H ₂	6.4	72.2
2 TiN + 3 Mg(BH ₄) ₂ → 3 MgH ₂ + 2 TiB ₂ + 2 BN + 9 H ₂	6.4	19.5
2 LiH + LiNH ₂ + BN → Li ₃ BN ₂ + 2 H ₂	6.3	49.1
2 Li ₃ Na(NH ₂) ₄ + 4 C → 3 Li ₂ CN ₂ + Na ₂ CN ₂ + 8 H ₂	6.1	32.6
4 LiH + 3 LiNH ₂ + VN → Li ₇ N ₄ V + 5 H ₂	6.1	37.4
10 LiH + 5 LiNH ₂ + N ₄ Si ₃ → 3 Li ₅ N ₃ Si + 10 H ₂	6.0	60.1

reactions we found that contain LiBH₄ involve the combination of LiBH₄ with only one other compound. For the reactions containing Mg(BH₄)₂, however, reactions involving both one and two additional compounds were found. Several reactant mixtures were found for which the DFT-calculated reaction enthalpy is 10-20 kJ/mol lower than that for the direct decomposition of Mg(BH₄)₂. Ten reactions that did not include either LiBH₄ or Mg(BH₄)₂ met the selection criteria above. These include reactions involving Mg(NH₂)₂ from the mixtures 4MgH₂ + Mg(NH₂)₂ and 4LiH + C + 3Mg(NH₂)₂. The outcomes of this screening exercise can be viewed in at least two ways. First, our results provide strong motivation to experimentally test the specific mixtures we have identified from our grand potential approach. At the same time, our calculations predict that *no other combinations* of the 212 compounds we have considered will allow single step reactions to occur at the specified temperature and hydrogen pressure.

After identifying the reactions described above using DFT total energy calculations, it is appropriate to undertake the more time consuming vibrational density of states (VDOS) calculations that allow ΔG(T) to be assessed. To illustrate this, we have performed these calculations for a subset of the reactions listed in Table 1. These calculations did not include a number of materials with relatively complex crystal structures. We did not perform VDOS calculations for Mg(BH₄)₂, for example, because of the complexity of the crystal structure, which contains 330 atoms per unit cell [6,7]. Our calculations accounted for the *ortho* to *hex* phase transition in LiBH₄ as described previously [8]. After computing ΔG(T), we characterized each reaction by finding the temperature at which P_{eq} = 1 bar, T_{eq}, and also the equilibrium pressure at T = 300 K. Our predicted equilibrium pressures at 300 K are shown in Figure 4. The uncertainties shown in this figure result from associating an uncertainty of ±10 kJ/mol H₂ with our DFT-calculated free energies, consistent with the discussion above. This uncertainty corresponds to a large range of pressure (P) and temperature (T) because of the van't Hoff relationship between P, T and free energy [8-10]. The uncertainties that exist in the predicted transition temperatures stem from the inexact nature of the functionals available in current DFT calculations, and no obvious method exists to reduce this uncertainty that can be readily applied to a catalog of hundreds

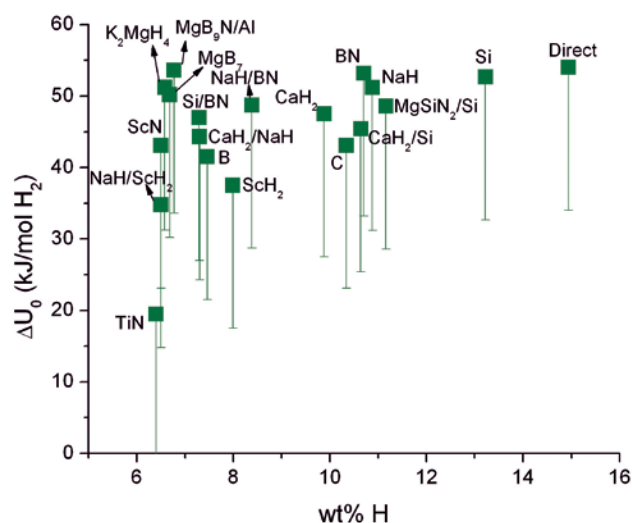


FIGURE 2. Reaction enthalpy as computed from 0 K DFT calculations, ΔU_0 , for all single step reactions involving LiBH_4 . The reactants that combine with LiBH_4 in these reactions are indicated in the figure. The error bars for each reaction span the predicted ΔG at 300 K assigned using the methods of Refs [8,12].

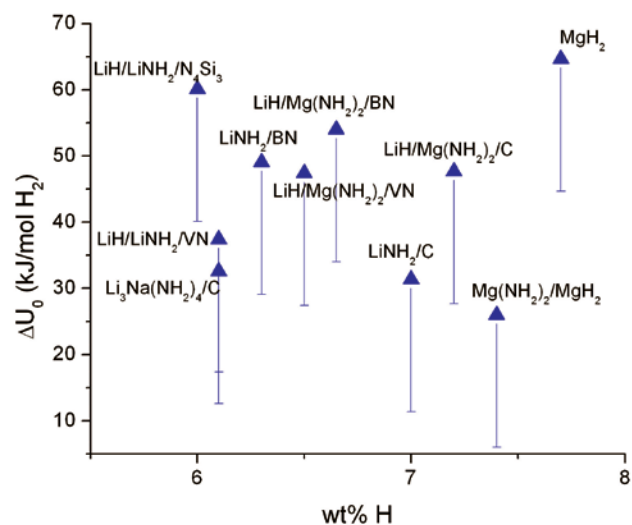


FIGURE 3. Reaction enthalpy as computed from 0 K DFT calculations, ΔU_0 , for all single step reactions that do not include LiBH_4 or $\text{Mg}(\text{BH}_4)_2$. The error bars for each reaction span the predicted ΔG at 300 K assigned using the methods of Refs [8,12].

of crystal structures. It is clear from these uncertainties that precise experimental measurements of the equilibrium properties of the reactions we have identified will be crucial to make better informed decisions about their suitability for practical applications.

The grand potential method we have applied here has several attractive features. As stated above, this method rigorously yields the equilibrium mixture composition with the set of all mixtures of compounds that are included in our database. Moreover, this

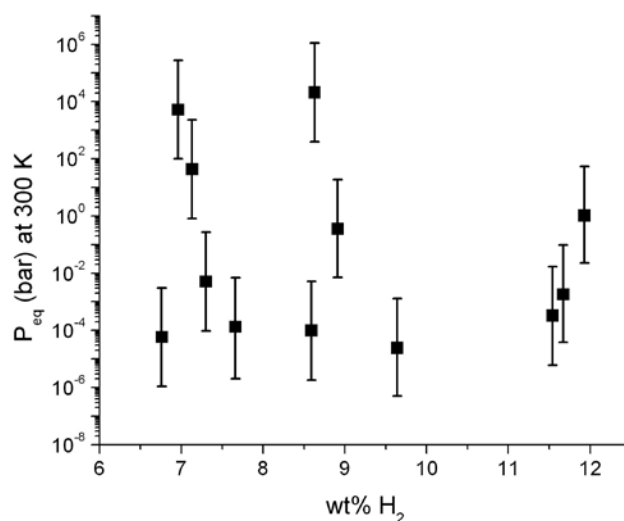


FIGURE 4. Equilibrium pressures at 300 K for 12 single step reactions for which vibrational density of states have been computed. For the 10 reactions involving LiBH_4 only reactants other than LiBH_4 are labeled on the figure. For the other two reactions (labeled by *) all reactants are listed on the figure.

minimization problem defining the method can be specified as a linear program [11], so its unique solution can be found extremely rapidly. The full set of screening calculations described above (>16 million distinct mixture compositions, each treated at 200 distinct temperatures) was performed in several days once the database of DFT total energies was available. This means that it will be possible to routinely repeat this complete screening process whenever the crystal structure of a new compound that is potentially relevant becomes available.

Conclusions and Future Directions

- We will continue work on identifying metastable reactions with the free energy linear program.
- We will identify multistep reactions that cumulatively release an acceptable amount of hydrogen within an acceptable temperature range.
- We will submit a paper on surface reactivities of alkali hydrides in conjunction with the Theory Group.
- We are initiating work on amorphous materials. The immediate aim is to identify the energetics relating the $\text{MgB}_{12}\text{H}_{12}$ amorphous phase observed experimentally in the dehydrogenation of $\text{Mg}(\text{BH}_4)_2$.

Special Recognitions & Awards/Patents Issued

1. DOE Hydrogen Program R&D Award, "In Recognition of Outstanding Contributions to Hydrogen Storage Technologies", June 2008.

FY 2008 Publications/Presentations

1. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl, "Discovering new metal hydride mixtures for high capacity hydrogen storage using first-principles thermodynamic screening", *Journal of Physical Chemistry C*, **112**, 5258-5262 (2008).
2. Bing Dai, David S. Sholl, and J. Karl Johnson, "First Principles Study of Experimental and Hypothetical $Mg(BH_4)_2$ Crystal Structures", *Journal of Physical Chemistry C*, **112**, 4391-4395 (2008).
3. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl, "First principles screening of destabilized metal hydrides for high capacity H₂ storage using scandium", *Journal of Alloys and Compounds*, **446-447**, 23-27 (2007).
4. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl, "Stability analysis of doped materials for reversible hydrogen storage in destabilized metal hydrides", *Physical Review B*, **76**, 104108 (2007).
5. J. Karl Johnson, "Predicting complex metal hydride thermodynamics with density functional theory", Penn State, Condensed Matter Physics Seminar, University Park, Pennsylvania, April 23, 2008.
6. J. Karl Johnson "Applications of Atomically-detailed Modeling in Chemical Engineering", Clemson University, Department of Chemical Engineering, Clemson, South Carolina, March 27, 2008.
7. J. Karl Johnson, "Predicting Properties of Metal Hydrides from First Principles", West Virginia University, Department of Chemical Engineering, Morgantown West Virginia, March 7, 2008.
8. J. Karl Johnson, "High Throughput Screening of Metal Hydrides from First Principles", *ExxonMobil Metal Hydride Symposium*, Hershey, PA, December 4, 2007.
9. J. Karl Johnson, Sudhakar V. Alapati, Bing Dai, and David S. Sholl, "Thermodynamics of Doped Complex Metal Hydrides", *International Symposium on Materials Issues in a Hydrogen Economy*, Richmond, Virginia, November 12-15, 2007.
10. J. Karl Johnson, Sudhakar V. Alapati, Bing Dai, and David S. Sholl, "The Predictive Power Of Atomically-Detailed Simulations", *AICHE Annual Meeting*, Salt Lake City, UT, 4-9 November 2007.
11. J. Karl Johnson, Sudhakar Alapati, Bing Dai, Ki-Chul Kim, and David Sholl, "Density Functional Screening of Metal Hydride Reactions", *Annual APS March Meeting*, New Orleans, Louisiana, March 10-14, 2008. D. S. Sholl, S.V. Alapati, B. Dai, Ki-Chul Kim, and J. K. Johnson, "Accelerating discovery of high capacity metal hydrides for reversible hydrogen storage using first-principles calculations", *NHA Annual Hydrogen Conference 2008*, Sacramento CA USA March 31–April 4, 2008.
12. D. S. Sholl, S.V. Alapati, Ki-Chul Kim, B. Dai, and J. K. Johnson, "Using thermodynamic properties from first-principles calculations to accelerate the search for metal hydride-based hydrogen storage materials", *ACS and AIChE Joint Spring 2008 National Meeting*, New Orleans, LA USA 6-10 April 6, 2008. Bing Dai, Karl Johnson, Sudhakar V. Alapati, and David S. Sholl, "Prediction of Thermodynamics and Surface Reactions of Complex Metal Hydrides", *AICHE Annual Meeting*, Salt Lake City, UT, 4-9 November 2007.
13. Sudhakar V. Alapati, David S. Sholl, and Karl Johnson, "Stability Analysis Of Doped Materials For Reversible Storage In Destabilized Metal Hydrides", *AICHE Annual Meeting*, Salt Lake City, UT, 4-9 November 2007.
14. D. S. Sholl, S.V. Alapati, B. Dai, and J. K. Johnson, "Discovery of new destabilized hydrides for reversible hydrogen storage using first principles calculations", *Symposium on Hydrogen Storage and Fuel Cell Technology, ACS National Meeting*, Boston, MA, August 2007.
15. Bing Dai, David Sholl, and J. Karl Johnson, "Computational study of surface reaction kinetics and poisoning of metal hydrides", *ACS National Meeting*, Boston, MA, August 2007.

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