

First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 100%

Budget

- Requested total: \$1.05M (DOE)
- Cost sharing: \$0.33M
- FY09 \$225K (DOE)
- FY10 \$64K (DOE)

Barriers

- A. System weight and volume
- E. Charging/discharging rates (kinetics)
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Partners

- Caltech, HRL, U. Hawaii, JPL, U. Missouri, NIST, Sandia, Stanford, UIUC, U. Utah
- Coordination of theory work within MHCoe through the theory working group

Objectives-Relevance

Overall Objectives

- Predict new metal hydrides with favorable thermodynamics
- Compute interfacial properties of hydrides
- Address fundamental processes in hydrogenation

Specific Objectives for FY09-FY10

- Complete reaction screening including multistep and metastable reactions and new additions to the database
- Finalize work on thermodynamics of multiple gas-phase species
- Conclude study of thermodynamics of amorphous and crystalline closo-borane structures such as $\text{MgB}_{12}\text{H}_{12}$ and related materials in the screening of candidate reactions
- Finish work on mixed metal hydrides

Milestones

Month/Year	Milestone or Go/No-Go Decision
Feb-07 ✓	Identify single-step reactions having acceptable hydrogen gravimetric densities and thermodynamics using the automated free energy search procedure. Paper has now been published: <i>J. Phys. Chem. C</i> , 112 , 5258-5262 (2008).
Jun-08 ✓	Identify and classify multi-step and metastable reactions having acceptable hydrogen capacities and thermodynamics using the automated free energy search procedure. Interesting multi-step reactions have been identified. More calculations and analysis required.
Sept-08 ✓	Investigate dehydrogenation/hydrogenation pathways for $\text{Mg}(\text{BH}_4\text{H})_2$ in concert with experimental efforts. Experiments have identified $\text{Mg}(\text{B}_{12}\text{H}_{12})$ as a possible amorphous phase intermediate.

Approach

- We use first principles density functional theory to compute structures and energies of solids and gas phase species
- Phonon density of states calculations are performed for finite temperature thermodynamics
- A free energy minimization linear program is used for screening mixtures for promising reactions
- Surface energy calculations are used to assess nanoparticle effects on the thermodynamics
- First principles molecular dynamics is used to generate amorphous phases
- Transition state theory employed for studying surface reactions and diffusion mechanisms

Technical Accomplishments: New Database Entries

We have added 147 new compounds in FY09-FY10 containing
Al-B-C-Ca-K-Li-Mg-N-Na-Sc-Si-Ti-V-H
Structures taken from ICSD and recent literature

(K(NH₂))(NH₃)₂, (Li(NH₃)₄)₂(B₆H₆)(NH₃)₂, (NH₂)CN, (NH₄)₂B₁₂H₁₂, (NH₄)B(CN)₄, Al(BH₄)₃, Al₁₄Mg₁₃, Al₁₈Mg₃Ti₂, Al₂₃V₄, Al₂MgC₂, Al₃₀Mg₂₃, Al₄₅V₇, Al₄C₃, Al₄Ca, AlB₁₂, AlNC₃H₁₀, B₁₀C₆H₃₀N₂, B₁₃C₂, B₁₃N₂, B₂₀C₃H₃₀N₂, B₄C, BC₂N, BC₄KN₄, BCH₅N₂, C₁₂N₆, C₂Ca, C₂H₁₈N₁₈, C₂H₄N₄, C₂N₂, C₂N₂(NH), C₃N₄, C₅N₄, Ca(BH₄)₂, Ca(NH₂BH₃)₂, Ca₁₁N₆(CN₂)₂, Ca₂Si, Ca₂Si₅N₈, Ca₄Al₃Mg, Ca₄N₂(CN₂), Ca₄TiN₄, Ca₅(Si₂N₆), CaAlSi, CaB₁₂H₁₂, CaB₄, CaC₄N₆, CaSiN₂, CH₃NH₂BH₃, H₉CN₉, K(HCN₂), K₂(B₁₀H₁₀), K₂B₁₂H₁₂, K₂B₆H₆, K₂Li(NH₂)₃, K₂LiAlH₆, K₂Mg(NH₂)₄, K₂Na(NH₂)₃, K₂NaAlH₆, K₃Si₆N₁₁H₆, K₅C₂HN₄, K₈Si₄₆, KAl(NH₂)₄, KB₂₁H₁₈, KBH₄, KC₄N₃, KC₈, KCaN₃H₆, KLi₃(NH₂)₄, KLi₇N₈H₁₆, KNH₂, KSi, Li(B(CN)₄), Li(NH₂BH₃), Li₁₂Si₇, Li₁₃Si₄, Li₁₅Si₄, Li₂B₁₂C₂, Li₂B₁₂H₁₂, Li₂B₁₂Si₂, Li₂Ca(NH)₂, Li₂MgSi, Li₂Na₄N₂, Li₂NaN, Li₃(BH₆), Li₃Na₃N₂, Li₃NaSi₆, Li₄Na₂N₂, Li₅NaN₂, LiAlB₁₄, LiAlC₄H₁₆N₄, LiAlMg₁₀H₂₄, LiB, LiB₁₃C₂, LiBH, LiBH₂, LiK(BH₄)₂, LiMg, LiMgH₃, LiN₃Si₂, LiNa₂(NH₂)₃, LiNa₂AlH₆, LiNa₂N, LiNa₅N₂, LiSc(BH₄)₄, LiSi₃C₉H₂₇N₂, Mg(BH₄)₂(NH₃)₂, Mg₂B₂₄C, Mg₇TiH₁₆, MgAl₂Si₂, MgB₁₂C₂, MgB₁₂H₁₂, MgB₁₂Si₂, MgC₄N₆, N₂B₁₀H₁₈, N₂BH₇, N₃B₃H₁₂, N₃B₃H₆, N₄B₁₀H₂₂, N₄B₁₀H₈, N₄B₉H₁₁, Na₂(B₁₀H₁₀), Na₂B₂₉, Na₃(BN₂), Na₃B₂₀, Na₃C₆N₉, Na₄Si₄, Na₅Al₃H₁₄, Na₈Si₄₆, NaAl(NH₂)₄, NaB(CN)₄, NaB₁₅, NaBH₄, NH₃BH₃, NH₄HCN₂, Sc₁₅C₁₉, Sc₂AlC, Si₂B₂C₁₂H₃₇N₅, Si₂C₇H₁₈N₂, SiB₃, SiC, Ti₂AlC, Ti₆Si₂B, TiV, V₁₂Al₃C₈, V₂N, V₅Si₃, V₅SiB₂, VC₈H₂₄N₄

Technical Accomplishments: Promising New Single Step Reactions

Interesting reactions (2 reactions)	wt.%	ΔU_0 (kJ/mol H ₂)
$2\text{MgH}_2 + \text{Mg}(\text{NH}_2)_2 \rightarrow \text{Mg}_3\text{N}_2 + 4\text{H}_2$	7.4	26
$\text{LiH} + 2\text{LiNH}_2 + \text{KBH}_4 \rightarrow \text{Li}_3\text{BN}_2 + \text{KH} + 4\text{H}_2$	7.48	43.61
Reactions involving B ₁₂ H ₁₂ species (10 reactions)	wt.%	ΔU_0 (kJ/mol H ₂)
$5\text{Si} + 10\text{Mg}(\text{BH}_4)_2 + 4\text{KBH}_4 \rightarrow 5\text{Mg}_2\text{Si} + 2\text{K}_2\text{B}_{12}\text{H}_{12} + 36\text{H}_2$	8.1	37.3
$5\text{Mg}(\text{BH}_4)_2 + 2\text{KBH}_4 \rightarrow 5\text{MgH}_2 + \text{K}_2\text{B}_{12}\text{H}_{12} + 13\text{H}_2$	6.94	38.04
$4\text{LiBH}_4 + 5\text{Si} + 10\text{Mg}(\text{BH}_4)_2 \rightarrow 5\text{Mg}_2\text{Si} + 2\text{Li}_2\text{B}_{12}\text{H}_{12} + 36\text{H}_2$	9.46	40.96
$5\text{Si} + 10\text{Mg}(\text{BH}_4)_2 + 2\text{Ca}(\text{BH}_4)_2 \rightarrow 5\text{Mg}_2\text{Si} + 2\text{CaB}_{12}\text{H}_{12} + 36\text{H}_2$	8.85	41.18
$5\text{Mg}(\text{BH}_4)_2 + \text{Ca}(\text{BH}_4)_2 \rightarrow 5\text{MgH}_2 + \text{CaB}_{12}\text{H}_{12} + 13\text{H}_2$	7.72	43.09
$2\text{LiBH}_4 + 5\text{Mg}(\text{BH}_4)_2 \rightarrow 5\text{MgH}_2 + \text{Li}_2\text{B}_{12}\text{H}_{12} + 13\text{H}_2$	8.36	43.1
$5\text{Si} + 12\text{Mg}(\text{BH}_4)_2 \rightarrow 5\text{Mg}_2\text{Si} + 2\text{MgB}_{12}\text{H}_{12} + 36\text{H}_2$	9.21	43.62
$\text{Mg}(\text{BH}_4)_2 \rightarrow (5/6)\text{MgH}_2 + (1/6)\text{MgB}_{12}\text{H}_{12} + (13/6)\text{H}_2$	8.09	47.06
$\text{LiH} + 3\text{Ca}(\text{BH}_4)_2 \rightarrow 3\text{CaH}_2 + (1/2)\text{Li}_2\text{B}_{12}\text{H}_{12} + (13/2)\text{H}_2$	6.03	56.53
$\text{Ca}(\text{BH}_4)_2 \rightarrow (5/6)\text{CaH}_2 + (1/6)\text{CaB}_{12}\text{H}_{12} + (13/6)\text{H}_2$	6.26	57.41

- Many of the single step reactions identified involved refractory materials, e.g., BN, TiB₂, etc.
- We have excluded reactions that involve C because of the possibility of forming alkanes in the product stream.

Technical Accomplishments: Metastable Reactions

- The accuracy of the DFT calculations is estimated to be about ± 10 kJ/mol H₂
- It is therefore possible that reactions with DFT free energies ~ 10 kJ/mol H₂ higher than the reaction identified in the linear program may actually be lower in energy experimentally
- It is also possible that kinetic pathways will favor reactions with slightly larger free energies
- To account for these possibilities we have developed a method of identifying metastable reactions:
 - The linear program identifies the equilibrium reaction
 - Each one of the possible solid products is excluded in turn from the database and the linear program is run again
 - If the new run identifies a reaction with a free energy within 10 kJ/mol H₂ then the reaction is added to the metastable list
 - The process is repeated for excluding pairs, triples, etc. of compounds

Technical Accomplishments: Example of Metastable Reaction

Original reaction		wt.%	ΔU_0 (kJ/mol H ₂)	T _{est} (K)
$\text{LiH} + 2\text{LiNH}_2 + \text{KBH}_4 \rightarrow \text{Li}_3\text{BN}_2 + \text{KH} + 4\text{H}_2$		7.48	43.61	508
Removed materials	Products of metastable paths	wt.%	ΔU_0 (kJ/mol H ₂)	T _{est} (K)
-Li ₃ BN ₂	$2\text{LiH} + \text{LiNH}_2 + \text{BN} + \text{KH} + 2\text{H}_2$	3.74	38.15	529
-KH	$\text{LiH} + \frac{4}{5}\text{KBH}_4 + \frac{1}{5}\text{Li}_3\text{BN}_2 + \frac{1}{5}\text{KLi}_7\text{N}_8\text{H}_{16} + \frac{4}{5}\text{H}_2$	1.5	46.64	541
-KH & KLi ₇ N ₈ H ₁₆	$\frac{69}{100}\text{LiH} + \frac{23}{100}\text{KBH}_4 + \frac{31}{100}\text{K} + \frac{77}{100}\text{Li}_3\text{BN}_2 + \frac{23}{50}\text{KNH}_2 + \frac{323}{100}\text{H}_2$	6.04	47.66	549
-KH & KLi ₇ N ₈ H ₁₆ & K	$\text{LiH} + \frac{1}{3}\text{KBH}_4 + \frac{2}{3}\text{Li}_3\text{BN}_2 + \frac{2}{3}\text{KNH}_2 + \frac{8}{3}\text{H}_2$	4.99	47.44	550
-KH & KLi ₇ N ₈ H ₁₆ & KNH ₂	$\text{K} + \text{Li}_3\text{BN}_2 + \frac{9}{2}\text{H}_2$	8.42	48.31	550
-KH & KLi ₇ N ₈ H ₁₆ & K & KNH ₂	$\text{LiH} + \frac{3}{7}\text{KBH}_4 + \frac{4}{7}\text{Li}_3\text{BN}_2 + \frac{2}{7}\text{K}_2\text{Li}(\text{NH}_2)_3 + \frac{16}{7}\text{H}_2$	4.27	48.8	565
-Li ₃ BN ₂ & KH	$\frac{13}{9}\text{LiH} + \frac{7}{9}\text{KBH}_4 + \frac{2}{9}\text{BN} + \frac{2}{9}\text{KLi}_7\text{N}_8\text{H}_{16} + \frac{4}{9}\text{H}_2$	0.83	44.2	600
-KH & Li ₃ BN ₂ & KLi ₇ N ₈ H ₁₆ & KH & KLi ₇ N ₈ H ₁₆ & Li ₃ BN ₂ KNH ₂	$2\text{LiH} + \text{LiNH}_2 + \text{K} + \text{BN} + \frac{5}{2}\text{H}_2$	4.68	47.82	606

Collaborations: Experimental

- Rebecca Newhouse, Sandia and Ewa Ronnebro (formerly Sandia)
 - We are computing the thermodynamics of the doped materials: $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ and $\text{Mg}(\text{B}_{(1-x)}\text{C}_x)_2$
- Y. Filinchuk, R. Černý, Grenoble, Geneva
 - Experimental powder XRD gave $\text{Mg}(\text{BH}_4)_2$ structure of $P6_1$, Our DFT calculations gave $P6_122$ as the ground state, which prompted Filinchuk et al. to obtain single crystal XRD, which confirmed our predicted $P6_122$ structure as the correct ground state. *Chem. Mater.*, **2009**, *21*, 925.
- Channing Ahn, CalTech
 - Testing several systems we predicted to have favorable thermodynamics, including $\text{LiBH}_4/\text{TiH}_2$ and $\text{LiBH}_4/\text{CaH}_2$
- Zak Fang, Utah
 - We are providing calculations for the LiMgN system
- Andrew Goudy, DSU / Fred Pinkerton, GM
 - Independently both working on $\text{CaH}_2 + 6 \text{LiBH}_4$
- John Vajo, HRL
 - Testing several systems for which we have made predictions, including LiBC and $\text{Mg}(\text{BC})_2$

Collaborations: Theory

We are working closely with many other computational people within the MHCoE:

- Mark Allendorf (Sandia, leader of Theory Group)
- Bruce Clemens (Stanford)
- Duane Johnson (Illinois)
- Ursula Kattner (NIST)
- Eric Majzoub (Missouri)

Future Work

- **Finish and submit paper on multistep reactions**
- **Finish and submit paper on metastable reactions and additional database entries**
- **Revised and resubmit paper on $B_{12}H_{12}$**