

## IV.G.2 Hydrogen Storage Research – 2007 Annual Report\*

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Contract Number: DE-FG36-04GO14224

Subcontractors:

- University of Florida (UF), Gainesville, FL
- University of Central Florida, Cocoa, FL

Start Date: May 19, 2004

Projected End Date: August 31, 2009

\*Congressionally directed project

### Objectives

- Synthesis and characterization of materials with high H<sub>2</sub> storage potential.
- Catalytic doping and substitution to improve kinetics and reversibility at low temperature (T).
- Employ *ab initio* and density function theory (DFT) calculations to validate the experimental observations.

### Technical Barriers

- Investigate metal hydrides with adequate charge/discharge kinetics, capacity, and cycling characteristics.
- Develop and verify most promising reversible storage materials to meet 2010 and 2015 targets.
- Determine the decomposition products and pathways of materials.
- Perform theoretical modeling to provide guidance for materials development.

- Perform analyses to assess cost effectiveness of materials including scale-up.

### Technical Targets

**TABLE 1.** Technical Targets Achieved with Different Complex Hydrides Compared with the DOE Technical Targets (2007/2010)

Storage Parameters	Zn(BH <sub>4</sub> ) <sub>2</sub>	LiBH <sub>4</sub> /MgH <sub>2</sub>	Li-B-N-H	LiNH <sub>2</sub> /LiH/MgH <sub>2</sub>	DOE Targets
Reversibility	Poor	Reversible at high T	Poor	Reversible at moderate T	Good
Volumetric Capacity	>100 kg/m <sup>3</sup>	>100 kg/m <sup>3</sup>	>100 kg/m <sup>3</sup>	>100 kg/m <sup>3</sup>	>150 kg/m <sup>3</sup>
Gravimetric Capacity	8.4 wt%	>6.0 wt%	>8 wt%	>6 wt%	>6.5 wt%
Gas Analysis	B-H gases with H <sub>2</sub>	H <sub>2</sub>	B-H and N-H with H <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub>
Operating Temperature	85°C	250°C	<200°C	>280°C	-30/85°C
Kinetics	Slow	Medium	Slow	Medium	Fast

### Accomplishments

- Successfully synthesized, purified and characterized Zn(BH<sub>4</sub>)<sub>2</sub> by a mechano-chemical process with different precursors (NaBH<sub>4</sub>/LiBH<sub>4</sub>) + 1/2 ZnCl<sub>2</sub>.
- Identified and quantified desorbing gas from Zn(BH<sub>4</sub>)<sub>2</sub> by gas chromatography mass spectrometry (GC-MS). (Observed diborane and higher borane release with H<sub>2</sub> at the same decomposition temperature.)
- Achieved lower melting and decomposition transition temperatures of Zn(BH<sub>4</sub>)<sub>2</sub>, LiBH<sub>4</sub>+ 1/2 MgH<sub>2</sub> by nanocatalyst doping.
- Synthesized LiNH<sub>2</sub>/LiH/MgH<sub>2</sub> by sonication and catalytic doping with Ti-based additives.
- Synthesized quaternary structure of Li-B-N-H by LiNH<sub>2</sub>/LiBH<sub>4</sub> (2:1) by mechano-chemically milling for 5 hours; it was found that incorporation of a nanocatalyst reduces the desorption temperature.
- Investigated the electronic structure of Zn(BH<sub>4</sub>)<sub>2</sub> including an estimation of lattice parameters.
- Studied effect of substitution of Ni in the Zn(BH<sub>4</sub>)<sub>2</sub> matrix.



## Introduction

Complex hydrides having light weight elements are attractive solutions for on-board hydrogen storage [1,2]. In comparison to the Al-based complex systems such as  $\text{NaAlH}_4$  [3], the B-H [4] and N-H [5]-based hydrides possess high theoretical hydrogen densities that can meet the 2010 DOE and FreedomCAR technical targets. However, in these complex hydrides, the thermal decomposition is associated with not only the release of  $\text{H}_2$  gas, but also with an appreciable amount of either borane or ammonia [6,7]. Destabilization mechanisms [8] and predictive pathway reactions using DFT calculations [9] are the designing tools for the optimized hydrogen storage system for efficient hydrogen storage.

Keeping these facts in view, the ongoing hydrogen storage research at CERC-USF and UF aims to develop novel complex hydride systems and probe the synergistic effects of nanocatalyst doping and destabilization on reversible hydrogen storage properties. We have used theoretical modeling based on DFT to predict thermodynamic stability and reaction pathways for some of the practical hydrides. Some of the novel complex hydrides designed and developed in the present investigation are: a) undoped and nanocatalyst  $\text{Zn}(\text{BH}_4)_2$ , b) destabilized  $\text{LiBH}_4/\text{MgH}_2$ , c)  $\text{LiNH}_2/\text{LiH}/\text{MgH}_2$  (with and without Ti catalyst), and d) new quaternary hydride Li-B-N-H (cocatalyst doping mechanism, destabilization with  $\text{MgH}_2$ ). Electronic band structure and thermal stabilities of  $\text{Zn}(\text{BH}_4)_2$  with and without additives were correlated with the observed hydrogen decomposition characteristics.

## Approach

- Selection and synthesis of complex hydrides: a) mechano-chemical milling methodology (optimization of milling parameters and precursor concentrations), b) catalytic doping and lattice modification, and c) use of *ab initio* calculations to understand/validate experimental work.
- Structural/microstructural/chemical characterization: phase analysis, grain size analysis, surface morphology.
- Volumetric, gravimetric and thermal analysis: dehydrogenation kinetics, pressure composition temperature (PCT), life cycle kinetics, heat of reaction.
- Gas quantification analysis: gas chromatography of evolving gas using thermal conductivity or mass spec detection, thermal programmed desorption.
- Electronic structure calculations (DFT): establish stable crystal geometry and electronic structure; calculate thermal properties, finite temperature reaction enthalpies.

## Results

**Subtask 1:** Figure 1 represents the simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) profiles of undoped and nanocatalyst doped  $\text{Zn}(\text{BH}_4)_2$ . It is clearly seen that the thermal decomposition temperature of doped hydride is at least 20°C lower than the undoped version. Another interesting feature is that for the undoped  $\text{Zn}(\text{BH}_4)_2$ , a melting (M) endothermic peak is present at around 85°C and another endothermic peak due to gas decomposition (D) occurs at 110°C. Whereas for the doped hydride, both M and D co-exist at 85°C with the onset temperature weight loss (TGA) due to gas decomposition that precedes the melting transition. This feature has not been reported in the literature [10] for the  $\text{Zn}(\text{BH}_4)_2$  system. Again, GC-MS results of the  $\text{Zn}(\text{BH}_4)_2$  as depicted in Figure 2 shows a reduction of

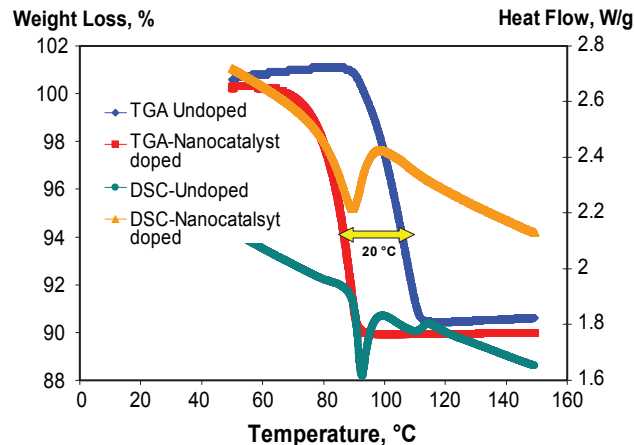


FIGURE 1. TGA/DSC Profiles of Undoped and Doped  $\text{Zn}(\text{BH}_4)_2$

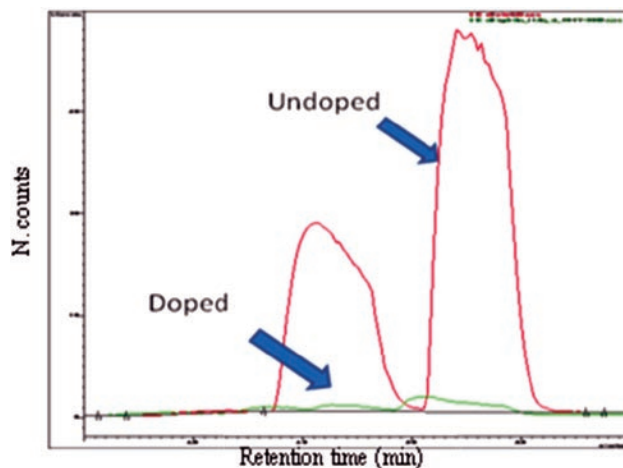


FIGURE 2. GC-MS Profiles of Undoped and Doped  $\text{Zn}(\text{BH}_4)_2$

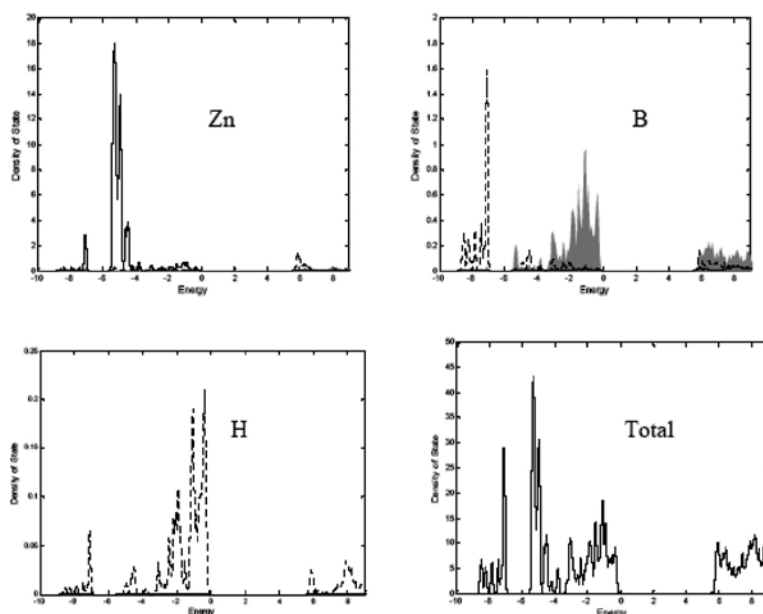
B-H gas evolution by a factor of 20 for the nanocatalyst doped in comparison with the undoped system. This indicates the possibilities of developing reversible hydrogen storage material that can operate at low temperature as addressed by DOE targets.

**Subtask 2:** We have established the most stable crystal structure and ground state electronic properties of  $\text{Zn}(\text{BH}_4)_2$  at 0 K. The total and partial density of states (DOS) of  $\text{Zn}(\text{BH}_4)_2$  obtained from DFT (Figure 3) confirms the following features: a)  $\text{Zn}(\text{BH}_4)_2$  is an insulating material with a band gap of 5.3 eV, b) valence bands of  $\text{Zn}(\text{BH}_4)_2$  are dominated by H's and B's which makes the B-H bond and only small contribution from Zn, c) for boron, the conduction band is dominated by p-orbitals, and d) although H's orbital is dominant in the valence band, a small number of states are found in the conduction band, indicating charge transfer to H-atom. Thermal decomposition temperature ( $T_{dec}$ ) has been calculated based on space group  $p-1$  for the most stable structure is 94.75°C which matches the experimental results (Figure 1).

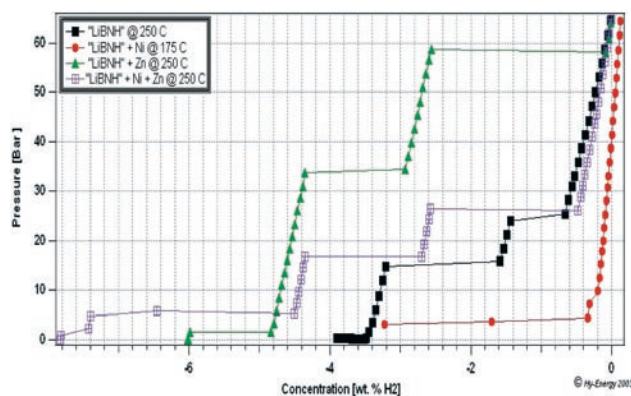
**Subtask 3:** The present work also addresses the grand challenge of hydrogen storage by mechano-chemically milling  $\text{LiBH}_4$  with  $\text{LiNH}_2$  to produce a new complex material. While  $\text{LiBH}_4$  and  $\text{LiNH}_2$  are able to store 18.5 wt% and 8.77 wt% hydrogen, respectively, the temperature required to release the hydrogen is too high for practical applications. Different molar mixtures of  $\text{LiBH}_4$  and  $\text{LiNH}_2$  are prepared by high energy milling under inert ambient. Various catalysts and dopants such as Ti, Ni, Zn-compounds have been investigated to lower the hydrogenation temperature, increase kinetics and tailor the plateau pressure for hydrogen release.

Figure 4 represents desorption PCT curves of undoped and catalyst doped Li-B-N-H at 250°C. This quaternary structure exhibits non-reversible hydrogen storage properties (see Figure 5) with a capacity as high as 8 wt% and desorption temperature as low as 175°C with the addition of catalyst materials in optimized concentrations. The destabilization of the structure by adding  $\text{MgH}_2$  destabilizes is presently being carried out for the reversible hydrogen storage at temperatures as low as 125°C.

**Subtask 4:** In our previous FY 2006 annual report, we have demonstrated the synthesis of a pure  $\text{LiNH}_2/\text{LiH}$  system for efficient hydrogen storage by a sonication procedure. Since these complex hydrides exhibit reversible hydrogen storage characteristics at



**FIGURE 3.** DFT/GGA Electronic Local/Total Density of States for the Space Group  $P-1$  (Triclinic)



**FIGURE 4.** Desorption PCT Curves for the Undoped and Catalyst Doped Li-B-N-H System

elevated temperatures, say  $>280^\circ\text{C}$ , doping of different catalysts have been carried out. Again for tailoring the intrinsic property of  $\text{LiNH}_2/\text{LiH}$ , admixing  $\text{MgH}_2$  was found effective to lift the plateau pressure from 0.5-1 bar to 40-50 bars. In this present work, various amounts of  $\text{TiCl}_3$  have been doped into the  $\text{LiNH}_2/\text{LiH}/\text{MgH}_2$  and an increase of desorption kinetics and overall effective hydrogen content was found (Figure 6). The cyclic reversibility for the catalyst doped system is improved two to three times in comparison to the plain hydride (Figure 7).

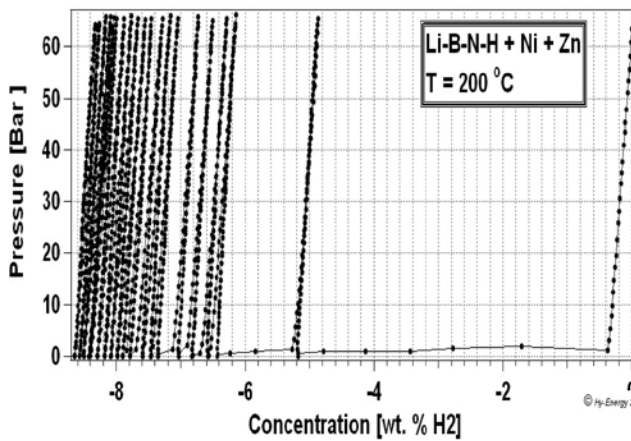


FIGURE 5. Desorption PCT of (Zn/Ni) Co-Doped Li-B-N-H in Various Absorption and Desorption Runs

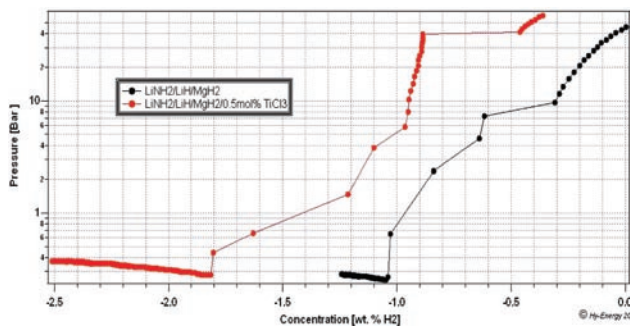


FIGURE 6. Desorption PCT of Undoped and 0.5 mol%  $\text{TiCl}_3$  Doped  $\text{LiNH}_2/\text{LiH}/\text{MgH}_2$

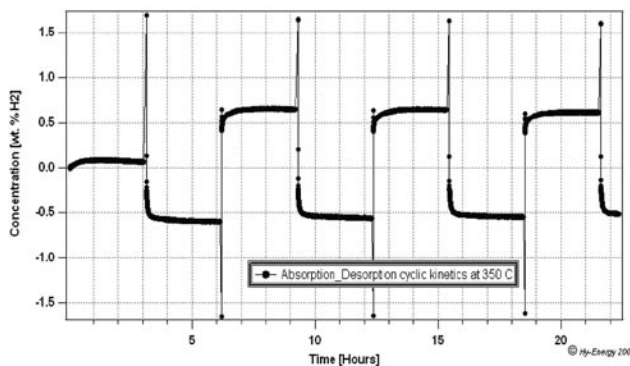


FIGURE 7. Absorption and Desorption Cycling Kinetic Curves of 0.5 mol%  $\text{TiCl}_3$  Doped  $\text{LiNH}_2/\text{LiH}/\text{MgH}_2$

## Conclusions

### Subtask 1

- An optimum milling duration of 15-30 minutes was sufficient to complete the reaction  $2\text{NaBH}_4 + \text{ZnCl}_2 = \text{Zn}(\text{BH}_4)_2 + 2\text{NaCl}$ .

- GC-MS analysis demonstrated the release of B-H (borane) gas with  $\text{H}_2$  at the same decomposition temperature.
- Catalytic doping of the new  $\text{Zn}(\text{BH}_4)_2$  mixture shows a reduction of decomposition temperature. The nanocatalyst was found to be better than Ti compounds.

### Subtask 2

- Stability analysis of  $\text{Zn}(\text{BH}_4)_2$  by DFT.
- Thermal properties (entropy, internal energy and heat capacity etc.) of  $\text{Zn}(\text{BH}_4)_2$  using lattice dynamics.
- Possible substitution of Zn by Ni in  $\text{Zn}(\text{BH}_4)_2$  to become a more stable structure.

### Subtask 3

- New quaternary Li-B-N-H was successfully synthesized and characterized.
- Zn and nanocatalyst doping of Li-B-N-H proved to lower the desorption temperature.

## Future Directions

### Subtask 1

- Analysis of the residual gas after thermal decomposition of  $\text{Zn}(\text{BH}_4)_2$  by GC-MS.
- Kinetic and thermodynamic characteristics optimization of  $\text{Zn}(\text{BH}_4)_2$  by catalytic doping and lattice substitution.
- Develop the new transition metal complex borohydrides,  $\text{Zr}(\text{BH}_4)_4$ ,  $\text{Mn}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ .

### Subtask 2

- Finite temperature reaction enthalpy of complex pure zinc borohydride calculated with a combination of DFT and lattice dynamics methods.
- Effect of additives on decomposition reaction equilibria for these systems from DFT, lattice dynamics and thermodynamics.

### Subtask 3

- Li amides structural modification and catalyst doping to enhance the kinetics and reduce the dehydrogenation temperature.
- Long-term cycling studies of Li amides, borohydrides and mixed complex hydrides.
- Explore different transition metal nanocatalysts for the lowering the decomposition temperature of borohydrides/amides and their mixtures.



**Subtask 4**

- Nanoengineering and nanocatalyst doping based on the conceptual model.
- Validation of pathway mechanisms of nanoengineering methodology.

**Special Recognitions & Awards/Patents Issued**

1. Dr. Sesha Srinivasan was awarded with a memento for his invited talk at the 94<sup>th</sup> Indian Science Congress, Annamalai University, Chidambaram, India, March 2007.
2. DOE Office of Basic Energy Sciences approved the whitepaper based on the ongoing hydrogen storage research and encouraged the principle investigator (PI) to submit a full proposal.
3. Two book chapters on hydrogen energy published by the PI, and the researchers involved in the project.
4. Two Masters students graduated (Diego Escobar, Luis Rivera) and their thesis dissertation submitted to University of South Florida in 2007.

**FY 2007 Publications/Presentations**

1. Metal/complex hydrides for hydrogen storage, Diego Escobar, *Masters Thesis, 2007, University of South Florida, USA*.
2. Synthesis and characterization and hydrogenation behavior of  $\text{LiBH}_4/\text{MgH}_2$ , *Masters Thesis, 2007, University of South Florida, USA*.
3. Nanocatalyst doping of  $\text{Zn}(\text{BH}_4)_2$  for on-board hydrogen storage, Sesha Srinivasan, Diego Escobar, Michael Jurczyk, Yogi Goswami, Elias Stefanakos, *J. Alloys and Compounds*, 2007, Submitted.
4. Structural, microstructural and thermal characteristics of  $\text{Zn}(\text{BH}_4)_2$ , D. Escoba, S. Srinivasan, Y. Goswami and E. Stefanakos, *Int. J. Hydrogen Energy*, 2007, Under preparation.
5. Hydrogen storage behavior of ZrNi 70/30 and ZrNi 30/70 composites, D. Escobar, S. Srinivasan, Y. Goswami and E. Stefanakos, *J. Alloys and Compounds*, 2007, Article in Press.
6. Polyaniline based nanocomposite materials for hydrogen storage, M. Jurczyk, S. Srinivasan, A. Kumar, E. Stefanakos, *Int. J. Hydrogen Energy*, 2007, Article in Press.
7. Investigation of  $\text{LiBH}_4/\text{LiNH}_2$  system for hydrogen storage, M. Jurczyk, S. Srinivasan, A. Kumar, E. Stefanakos, 2007, *TMS Annual Meeting and Exhibition*, Orlando, FL.
8. Conventional metal hydrides and Advanced Complex hydrides for hydrogen storage, Presentation by Sesha Srinivasan at the Hydrogen Energy Center, *Banaras Hindu University, Varanasi, India*, March 15, 2007.

9. Hydrogen storage in nanocatalyzed  $\text{Zn}(\text{BH}_4)_2$ , Abstract accepted and full manuscript submitted IHEC'2007, Istanbul, Turkey, (*Int. J. Hydrogen Energy* [proceedings]).
10. Nanoclusters and nanocatalysts for environmental and energy applications, Presentation by Sesha Srinivasan at the National catalysis research center, *Indian Institute of Technology, Chennai, India*, March 19, 2007.
11. Effect of nanocatalyst doping on the hydrogen storage behavior of new complex borohydrides, Sesha Srinivasan, Diego Escobar, Luis Rivera, Michael Jurczyk, Pabitra Choudhury, Yogi Goswami and Elias Stefanakos, *WHTC 2007-ZERO REGIO Workshop, Italy*.
12. Nanomaterials for Energy Storage and Environmental Detoxification Applications, Sesha Srinivasan, Nikolai Kislov, Diego Escobar, Pabitra Choudhury, Yogi Goswami, Elias Stefanakos and Yusuf Emirov, *Recent Developments in Nanomaterials*, Accepted and Published, March 13–14, 2007, *Banaras Hindu University, Varanasi, India*.
13. FreedomCAR Tech Review Meeting, Detroit, MI, October 19, 2006.
14. Reversible hydrogen storage behavior in  $\text{ZnCl}_2$  catalyzed  $\text{LiBH}_4/\text{MgH}_2$ , L. Rivera, S. Srinivasan, J. Wolan, E. Stefanakos, 2006, *MRS Fall Meeting*, Boston, MA.
15. Destabilized  $\text{LiBH}_4/\text{MgH}_2$  for reversible hydrogen storage, L. Rivera, S. Srinivasan, J. Wolan, M. Smith, E. Stefanakos, 2006, *AICHE Fall National Meeting*, San Francisco, CA.
16. Hydrogen production and storage, E. Stefanakos, Aug. 7, 2006, Energy Science Center, *Swiss Federal Institute of Technology (ETH), Switzerland*.
17. Hydrogen production and storage by  $\text{TiO}_2$  photocatalysts and advanced complex hydrides, Poster Presentation, Sesha Srinivasan, International symposium on material issues in Hydrogen production and storage, *University of California, Santa Barbara, CA*, August 20-25, 2006.

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