

IV.F.1 Hydrogen Storage Research*

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*Congressionally directed project

Objectives

- Synthesis and characterization of materials with high H₂ storage potential.
- New materials and processes discovery.
- Catalytic doping, destabilization and substitution strategies to improve the kinetics and reversibility of hydrides at low temperature.
- Employ ab initio calculations to validate the experimental observations.

Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Accomplishments

- Successfully synthesized, purified, nanocatalyst doped and characterized Zn(BH₄)₂ by a mechano-chemical process with different precursors (NaBH₄/LiBH₄) + 1/2 ZnCl₂.
- Investigated the electronic structure of Zn(BH₄)₂ including estimation of lattice parameters. Studied effect of substitution of Ni in the Zn(BH₄)₂ matrix.
- Synthesized complex borohydrides Mn(BH₄)₂ from different precursors (NaBH₄/LiBH₄). Established thermal desorption and gravimetric weight loss due to hydrogen decomposition.
- Synthesized quaternary structure of Li-B-N-H by LiNH₂/LiBH₄ (2:1) mechano-chemically milling for 5 hours, and found that incorporation of nanocatalyst reduces the desorption temperature; nanoNi seems better catalyst option.
- Prepared Li-Mg-B-N-H complex multinary hydrides by specially designed process; this allows for the greater reversibility of hydrogen sorption at moderate temperatures (150-250°C) and rapid kinetics (5-10 minutes).
- Synthesized polymer samples (special chemical and electrospun processes) and accomplished hydrogen uptake of 10 wt% in initial cycle and reversibility of 3.0 wt% at room temperature.



Introduction

Thermalization and destabilization are the two complimentary strategies employed for the reversible hydrogen storage behavior in complex chemical hydrides [1,2]. In the thermalization process, hydrogen is released from the hydrides [3] (e.g. Zn(BH₄)₂, Mn(BH₄)₂, etc.) by heating to the decomposition temperature. Whereas the destabilization mechanism involves combination and reaction of two or more compounds (e.g. LiNH₂/LiH [4], LiBH₄/MgH₂ [5] pair etc.). Catalytic doping has been proven to enhance the synergistic reaction kinetics and thermodynamics in these thermalized and destabilized hydride systems [6]. In view of the said facts and figures, the current research activity is being conducted to investigate the effects of nanocatalyst doping in the high capacity hydrogen storage materials. Density functional theory (DFT) has been extensively employed to understand the reaction mechanism and thermodynamic stability factors during the hydrogen decomposition process in the new complex hydride systems [7]. Yet another new sorption-based

systems involving polyaniline nanostructures [8] are explored for possible hydrogen storage.

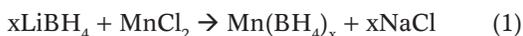
Approach

- 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, 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: Catalyst Doped $\text{Mn}(\text{BH}_4)_x$ ($x=2,3$ & 4)

We have successfully prepared new transition metal based complex borohydrides $\text{Mn}(\text{BH}_4)_x$ ($x=2,3$ & 4) from the stoichiometric reaction (1) by mechano-chemical synthesis route:



$\text{Mn}(\text{BH}_4)_x$ formation is confirmed from the Fourier transform infrared (FTIR) spectrum which indicates the B-H bonding stretch around $2,200 \text{ cm}^{-1}$. Since these borohydrides are amorphous in nature, the X-ray diffraction profiles show no crystalline borohydride reflections. The thermogravimetric analysis (TGA) of the as-synthesized $\text{Mn}(\text{BH}_4)_x$ exhibits gravimetric capacity of 8-10 wt% associated with differential scanning calorimetry endothermic transition at low thermal decomposition temperature of 150°C . The optimized weight loss due to hydrogen decomposition was found to be with ball milling time of 30 minutes. In order to reduce the decomposition temperature further, we have attempted to dope the $\text{Mn}(\text{BH}_4)_x$ with different mole concentrations of nanocatalyst (nanoNi). The thermogravimetric profiles of undoped and nanoNi doped $\text{Mn}(\text{BH}_4)_3$ samples are shown in Figure 1. It is unambiguously observed that nanoNi doping of 1-2 mol% destabilizes the structure with at least 10-20°C reduction in hydrogen thermal decomposition temperature (T_{dec}). Moreover, the nanoNi catalyst

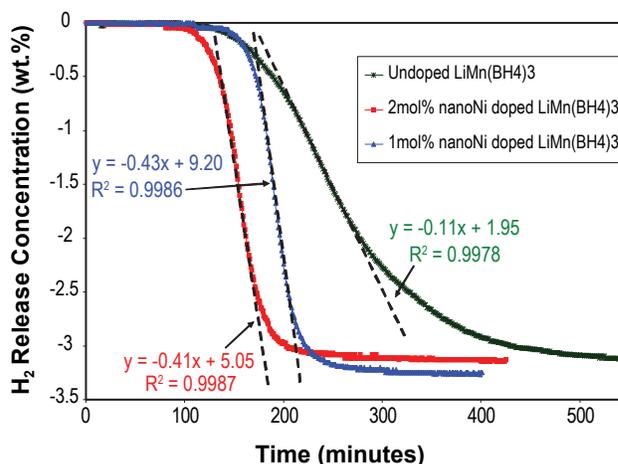


FIGURE 1. Desorption Kinetics Profiles of Undoped and nanoNi Doped $\text{Mn}(\text{BH}_4)_3$

has greater effect on the hydrogen release (desorption kinetics) rate when compared to the undoped $\text{Mn}(\text{BH}_4)_3$, as represented in Figure 1. The optimum concentration of nanoNi was found to be 2 mole.

Overall, the nanocatalyst doped complex borohydrides shows much pronounced effects on the hydrogen release kinetics with lowering the decomposition temperature. These studies indicate the possibilities of developing reversible hydrogen storage material that can operate at low temperature as addressed by DOE targets.

Subtask 2: Complex Borohydrides – Theory

Since the exact $\text{Mn}(\text{BH}_4)_2$ structure is unknown to us, we tried to find the structure based on methodology that we adopted for similar formula unit complex $\text{Zn}(\text{BH}_4)_2$ and then will find out the thermodynamic properties of manganese borohydride. We performed $\text{Mn}(\text{BH}_4)_2$ phonon density of states (DOS) calculations for the space group #13 which corresponds to monoclinic structure and found some soft mode in this phase (see Figure 2(a)). Phonon DOS confirms the stability of $\text{Mn}(\text{BH}_4)_2$ exists at finite temperature. Total density of phonon states $g(w)$ of $\text{Mn}(\text{BH}_4)_2$ in $P-3m1$ symmetry. Total phonon density of states is normalized as:

$$\int g(w)dw=1$$

The electronic band structure calculations of $\text{Mn}(\text{BH}_4)_2$ reveals that these complex borohydrides possesses metallic character as evidenced from the absence of energy band gap. The DOS of pure elemental Mn, B, H and the total $\text{Mn}(\text{BH}_4)_2$ structure is shown in Figure 2(b).

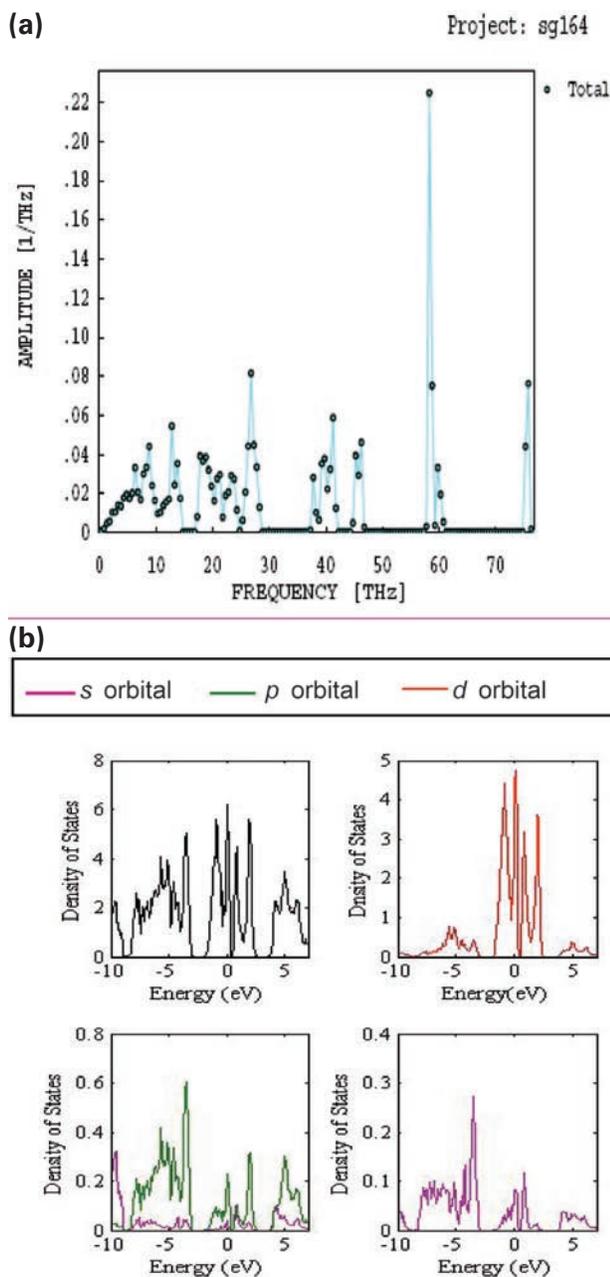


FIGURE 2. (a) Phonon DOS for $\text{Mn}(\text{BH}_4)_2$ (111) supercell considering monoclinic structure (space group #13); (b) total and partial DOS of $\text{Mn}(\text{BH}_4)_2$; zero energy is considered as Fermi energy level.

Subtask 3: Mixed Complex Hydrides (Li-Mg-B-N-H)

The present work also addresses the grand challenge of hydrogen storage by mechano-chemically milling LiBH_4 and LiNH_2 with MgH_2 to produce a new complex quaternary Li-Mg-B-N-H structure. This Li-Mg-B-N-H structure possesses storage capacity of more than 10 wt% at around 150°C . LiBH_4 , LiNH_2 and MgH_2 were mixed in various quantities and synthesized using different conditions such as time of milling, reactive purge gas

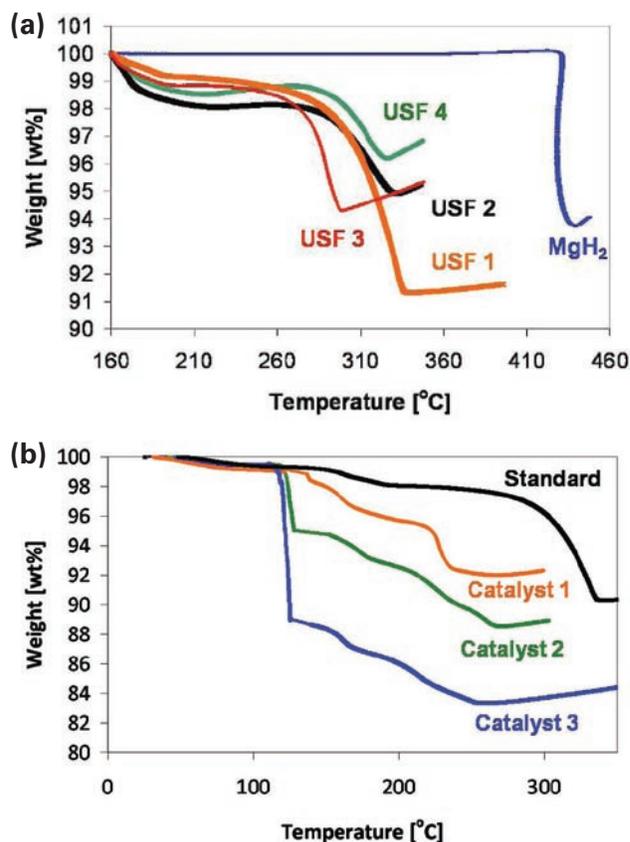


FIGURE 3. TGA comparison of (a) Li-Mg-B-N-H multinary complex hydride showing various synthesis procedures; (b) three catalyst materials added to Li-Mg-B-N-H showing effect of catalyst on complex hydride.

and quantities. Figure 3(a) shows a comparison of four different synthesis procedures. It is found that the capacity of the complex hydride can be increased as well as the desorption temperature decreased based on the specific synthesis technique.

Moreover, it is clearly discernible from this figure that the thermal decomposition temperature of the mixed complex hydrides is much lower than the pure MgH_2 . The addition of various catalytic dopants to the multinary complex hydride shows promise in reducing the hydrogen desorption temperature as compared to the unmodified complex hydride. The gravimetric weight loss of the complex hydride with optimized concentrations of the catalyst materials are shown in Figure 3(b). The weight loss was improved from 10 wt% H_2 to as much as 18 wt%, while reducing desorption temperature, although gas analysis is required to determine the quantity of hydrogen and other gases evolved during desorption. We have also found the reversible hydrogen absorption-desorption behavior (~3-4 wt%) of the new complex hydride Li-Mg-B-N-H as shown in Figure 4. This could be possible by the destabilization of the structure and catalytic doping

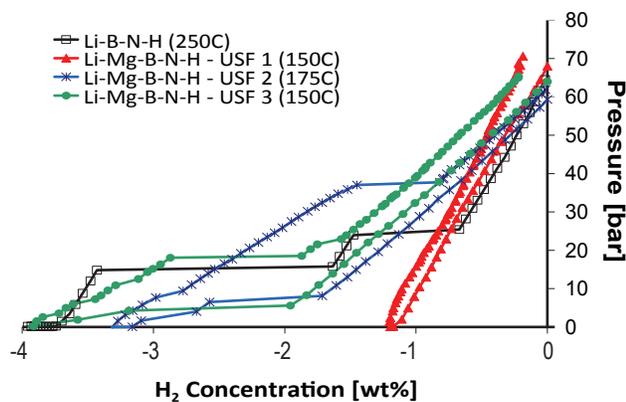


FIGURE 4. Pressure-concentration-temperature curves of absorption and desorption cyclings at temperatures 150-175°C for Li-Mg-B-N-H.

strategies involved in the development of multinary complex hydride phases.

Subtask 4: Polyaniline (PANI) Nanostructures

Conducting polymer nanostructures combine the advantages of organic conductors and low dimensional systems and therefore should yield many interesting physicochemical properties and useful applications [9,10]. It was recently reported that polyaniline could store as much as 6 to 8 wt% hydrogen [11], which was later refuted by team of researchers [12]. Though many controversial results were reported in terms of hydrogen uptake [13] in polymer nanocomposites, there are still number of parameters, tailor made properties and surface morphologies to be investigated before these materials are commercially employed for on-board hydrogen storage. In this subtask, we collaborate with University of L'Aquila, Italy for developing and demonstrating polyaniline nanostructures which are prepared by chemical templating techniques. The as-prepared polyaniline nanostructures are subjected to FTIR analysis and found the well defined benzenoid and quinoid rings at 1,500 and 1,600 cm^{-1} (see Figure 5).

We are currently in the process of exploring hydrogen absorption and desorption characteristics of these polyaniline nanostructures and their structural, microstructural, chemical, surface and optical property correlations.

Conclusions and Future Directions

Subtasks 1 & 2: $\text{Mn}(\text{BH}_4)_2$ (Experiment and Theory)

- New transition metal complex borohydrides have been explored for the hydrogen storage.
- We have established the crystal structure and electronic band structure of complex hydrides such

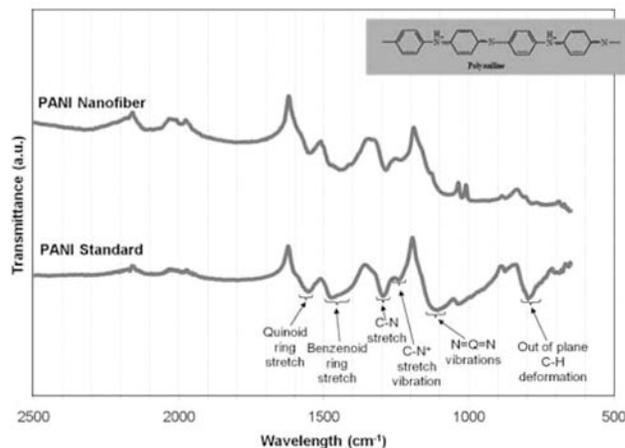


FIGURE 5. FTIR spectra of PANI nanofibers and nanospheres prepared by chemical templating technique.

as $\text{Mn}(\text{BH}_4)_2$ and its doped version based on DFT calculations.

- Analysis of the residual gas after thermal decomposition of $\text{Mn}(\text{BH}_4)_2$ by gas chromatograph/mass spectrometer (GC/MS) is underway.
- Kinetic and thermodynamic characteristics optimization of $\text{Mn}(\text{BH}_4)_2$ by catalytic doping and lattice substitution.

Subtask 3: Li-Mg-B-N-H

- USF prepared and processed Li-Mg-B-N-H materials exhibited new multinary structure having hydrogen storage reversibility of 4-8 wt% at temperature range of 150-250°C.
- Initial catalysts studies indicate significant temperature reduction for hydrogen decomposition.
- GC/MS of the desorbed gases is underway.

Subtask 4: PANI Nanostructures

- Hydrogen absorption is feasible in PANI nanonetworks.
- Different PANI nanostructures such as nanofibers and nanospheres were synthesized and explored the possible hydrogen sorption measurements.
- Future works to decorate PANI nanonetworks with carbon nanotubes and transition metals such as Ni.

Special Recognitions & Awards/Patents Issued

1. Methods and Processes for producing complex hydrides exhibiting higher hydrogen storage capacity and fast sorption kinetics at moderate temperatures, S.S. Srinivasan, M. Jurczyk, Y. Goswami, E. Stefanakos, Provisional Patent filed on 19 March 2008, University of South Florida, Tampa, FL.

2. Won a Grant Proposal competition from the California based Nanomaterials Manufacturing Company QuantumSphere Inc. for the Hydrogen Storage Project.

FY 2008 Publications/Presentations

1. Room temperature hydrogen storage behavior in PANI nanofibers, M.U. Jurczyk, S.S. Srinivasan, A.R. Phani, S. Santucci, A. Kumar, Y.D. Goswami, E.K. Stefanakos, 2008 Manuscript Submitted to Journal of Nanoscience and Nanotechnology.

2. Effect of catalyst doping on the thermal decomposition behavior of $Zn(BH_4)_2$, S. Srinivasan, D. Escobar, Y. Goswami, E. Stefanakos, *Int. J. Hydrogen Energy*, Article in Press.

3. Nanocatalyst doping of $Zn(BH_4)_2$ for on-board hydrogen storage, S. Srinivasan, D. Escobar, M. Jurczyk, Y. Goswami, E. Stefanakos, *J. Alloys and Compounds*, Article in Press.

4. Identification of a new stable phase for high capacity hydrogen storage material $Zn(BH_4)_2$ from density functional theory and lattice dynamics, P. Choudhury, V.R. Bhethanabotla, E. Stefanakos, *Phys. Rev. B*, 77, 2008, 134302.

5. Ni-induced destabilization dynamics of crystalline zinc borohydride, P. Choudhury, V.R. Bhethanabotla, E. Stefanakos, *APL*, 92, 2008, 134101.

6. Nanocrystalline effects on the Reversible H_2 storage of complex hydrides, S. Srinivasan, M. Jurczyk, A. Kumar, Y. Goswami, E. Stefanakos, American Ceramic Society Meeting: Materials Innovation in an Emerging Hydrogen Economy, Feb. 24-27, 2008, Cocoa Beach, FL.

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