

IV.H.2 Hydrogen Storage Research*

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Contract Number: DE-FG36-04GO14224

Project Start Date: May 19, 2004
Project End Date: August 31, 2009

*Congressionally directed project

- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (K) System Life Cycle Assessment
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorptions
- (Q) Reproducibility of Performance

Technical Targets and Critical Assumptions

This project is conducting to explore and investigate hydrogen storage materials. Insights gained from these studies will be applied toward the design and synthesis of reversible hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Volumetric H₂ density, >45g H₂/L
- Gravimetric H₂ density >6.0 wt%
- Operating temperature, -30/50°C
- Delivery temperature of H₂, -40/80°C
- Cycle life, 1,000 cycles
- Fast absorption/desorption rates

Table 1 represents the critical assumptions the tasks for developing reversible hydrogen storage systems that can meet or exceed the DOE's technical targets.

TABLE 1. Progress towards Meeting Technical Targets and Critical Assumptions for Developing Reversible Hydrogen Storage Materials

Critical Assumptions	TASK 1: Li-Mg-B-N-H	TASK 2: LiMn(BH ₄) ₃ - Xmol%MgH ₂	TASK 4: PANI Nanostructures
Reversibility	Good at lower T ₁ specially processed materials	Reversible at moderate and high temperatures	Good at room temperature, specially processed materials
Volumetric Capacity	> 100 kg m ⁻³	> 100 kg m ⁻³	> 100 kg m ⁻³
Gravimetric Capacity	> 7.0 wt%	> 8.0 wt%	~3-10 wt% uptake
Gas Analysis	H ₂	H ₂	H ₂
Kinetics	Fast	Medium	Fast
DOE Targets Met	YES	YES	YES
Status	80% complete	70% complete	60% complete

TASK 3: Density Functional Theory Calculations to predict, validate and optimize the hydrogen storage properties of complex hydrides and nanostructures [System: Mn(BH₄)₂] – Status: 60% complete

Objectives

- Synthesis and characterization of materials with high H₂ storage potential.
- New materials and processes discovery.
- Catalytic doping, substitution and destabilization to improve the kinetics and reversibility at low temperature.
- Employ ab initio and density functional theory calculations to validate the experimental observations.
- Determine the decomposition products and pathways of materials.
- Perform analyses to assess cost effectiveness of materials including scale up.
- Reduction in the decomposition temperatures, activation energy and overall enthalpy of reaction by nanocatalyst doping, nanocrystalline admixing, etc.

Technical Barriers

This project addresses the following technical barriers from the 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

Accomplishments

- Successfully synthesized multinary complex hydrides involving LiNH_2 , LiBH_4 and MgH_2 using solid-state mechano-chemical process. Unique approach and adopting various processing conditions to prepare these Li-Mg-B-N-H complexes lead to efficient and reversible hydrogen storage capacity >6 wt% at 150 - 175°C . (*Acer Transactions*, 2009; *International Journal of Hydrogen Energy [IJHE]*, 2009)
- Independent validations of pressure-composition-temperature (PCT) characteristics such as H_2 storage capacity, sorption kinetics and gas evolution analysis by Southwest Research Institute[®] (SwRI[®]) of USF-processed Li-Mg-B-N-H complex hydrides. Close match of results were obtained from both SwRI[®] and USF experimental analysis. No evolution of ammonia and di-borane gases has been observed from the mass spectrometry studies by SwRI[®]. (*SwRI[®] Report to DOE and USF*, 2009)
- Accomplished in situ-RAMAN characteristic spectra of $\text{LiBNH}+\text{MgH}_2$ samples at the National Institute of Standards and Technology (NIST). There exists a close match between RAMAN and Fourier transform infrared analyses by both USF and NIST measurements for the identification of B-H and N-H stretches. (*NIST Report to USF*, 2009)
- Successfully synthesized complex borohydrides $\text{LiMn}(\text{BH}_4)_3$ mechanical milling of LiBH_4 and MnCl_2 . Accomplished reversibility of hydrogen sorption cycles in non-reversible hydrides $\text{LiMn}(\text{BH}_4)_3$ by self-catalyzing effects using x mol% MgH_2 . (*IJHE*, 2009)
- Nanomaterials doping and co-doping on the effective hydrogenation and dehydrogenation behavior of multinary complex hydrides (Li-Mg-B-N-H) and Li-Mn-B-H. (*USF-QuantumSphere Inc. Report* 2009)
- Established the structure of new $\text{Mn}(\text{BH}_4)_2$ phase and calculated the thermodynamic stabilities by density functional theory (DFT). (*Journal of Physical Chemistry*, 2009)
- Synthesized polyaniline nanostructures such as nanofibers and nanospheres using chemical and electrospun processes. Accomplished reversible hydrogen storage capacity of 3-10 wt% from room temperature to 100°C (*J. Nanomaterials*, 2008, *J. Nanoscience and Nanotechnology*, *J. Nano Research*, *IJHE*, 2009)



Introduction

In this study, we report the on-going hydrogen storage research on physisorption, which is the weak chemical bonding to a material, as well as

chemisorption, which is a strong chemical bond of hydrogen to a host material. Polyaniline (PANI), a conducting polymer, is investigated in both its bulk form as well as in nanostructured forms, more precisely nanofibers and nanospheres, to store hydrogen via physisorption. It is found the bulk form of polyaniline can store only approximately 0.5 wt% hydrogen, which is far short of the 6 wt% required for practical applications. Nanofibers and nanospheres, however, have been developed, which can store between 4 wt% and 10 wt% of hydrogen at room temperature with varying kinetics. A new complex metal hydride comprised of LiBH_4 , LiNH_2 and MgH_2 has been developed to store hydrogen via chemisorption. While the parent compounds require high temperatures and suffer of slow kinetics for hydrogen sorption, the work performed as part of this time period shows that optimized processing conditions reduce the hydrogen release temperature from 250°C to approximately 150°C , while the addition of nano-sized materials has been found to increase the kinetics of hydrogen sorption as well as further decrease the hydrogen release temperature, making this one of the first viable hydrogen storage materials available. We have also successfully studied the hydrogen storage performances in novel complex borohydrides and their destabilized counterparts, $\text{Mn}(\text{BH}_4)_2$, $\text{LiMn}(\text{BH}_4)_3$, and $\text{LiMn}(\text{BH}_4)_{3-x}$ mol% MgH_2 by both theoretical and experimental approaches. It is noteworthy to mention that for the first time that nanostructured polyaniline has been investigated for its reversible hydrogen behavior. Additionally, the thorough investigation of the effects of nano sized additives and processing parameter optimization of the multinary hydride and advanced complex borohydrides are first reported.

Approach

Selection and synthesis of complex hydrides; structural/microstructural/chemical characterization; volumetric, gravimetric and thermal analysis; activation energy by Kissinger's method; gas quantification analysis using gas chromatography (GC) and mass spectrometry (MS); and DFT to study the crystal structure and thermodynamic stability of complex borohydrides and multinary complexes.

Results

Task 1. Destabilized Multinary Complex Hydrides ($\text{LiBH}_4/\text{LiNH}_2/\text{MgH}_2$)

The present work 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 . The parent compounds, LiBH_4

and LiNH_2 , were purchased from Sigma Aldrich with a purity of at least 95%, while MgH_2 was obtained from Alfa Aesar with a purity of 98%. All materials were kept in an inert atmosphere in a glove box and used without further purification. The investigated samples were created in 4 g batches with a constant molar ratio of $2\text{LiNH}_2:\text{LiBH}_4:\text{MgH}_2$, while taking into account the purity of the parent compounds, by employing high energy ball milling (Fritsch Pulverisette 6) for 5 hours at 300 rpm with intermittent hydrogen/argon (5%/95%) purges for 20 minutes before milling and after 2 and 4 hours. This was done to ensure that as little hydrogen as possible was released during the milling process and to reduce the agglomeration of the hydride that occurs when pure hydrogen is used as compared to the hydrogen/argon mixture. The MgH_2 was either added as received or was added as a so-called nano MgH_2 . The nano MgH_2 (nMgH_2) was created by ball milling the commercial MgH_2 (cMgH_2) for 12 hours with intermittent hydrogen/argon purges every 2 hours. This ensured the reduction of particle size as well as the decrease in hydrogen release temperature, as previously reported. Figure 1(a) shows the X-ray diffraction (XRD) pattern comparing the five differently processed complex hydrides. The addition of commercial MgH_2 does not cause the formation of a new complex structure, but instead indicates that the quaternary structure (LiBNH) is preserved, while the MgH_2 simply intermixes with the material.

Upon producing the complex hydrides, each sample was characterized for its thermal desorption characteristics using temperature-programmed desorption (TPD) with a heating rate of 1, 5, 10, and $15^\circ\text{C}/\text{min}$. As compared to the quaternary structure, the multinary structure containing MgH_2 showed a 3-step hydrogen release mechanism. Figure 2 represents the PCT isotherms of the multinary complex hydrides created with different processing conditions. The PCT characteristics of USF's complex hydride Li-nMg-B-N-H were also performed at SwRI[®]. Interestingly, these complex hydrides exhibited reversible hydrogen storage behavior and are shown in Figure 2(a). A reversible hydrogen storage capacity of 5-7 wt% was reproducibly obtained for these materials. The cyclic kinetics of Li-nMg-B-N-H reveals a reversible hydrogen storage capacity of 6-8 wt% with fast sorption kinetics around $200\text{-}250^\circ\text{C}$ which matches or exceeds with the set-forth DOE technical targets. With respect to the MS analyses, SwRI[®] reported that the scans did not reveal any evidence for potential parent (or daughter) species (ions); namely, NH_3 , BH_3 , BH_2NH_2 , N_2H_4 .

Task 2. Destabilization of Transition Metal Complex Borohydrides [$\text{LiMn}(\text{BH}_4)_3 + X\text{mol}\%\text{MgH}_2$]

Synthesis of the new complex hydride, $\text{LiMn}(\text{BH}_4)_3$ from the parent compounds LiBH_4 and MnCl_2 (3:1)

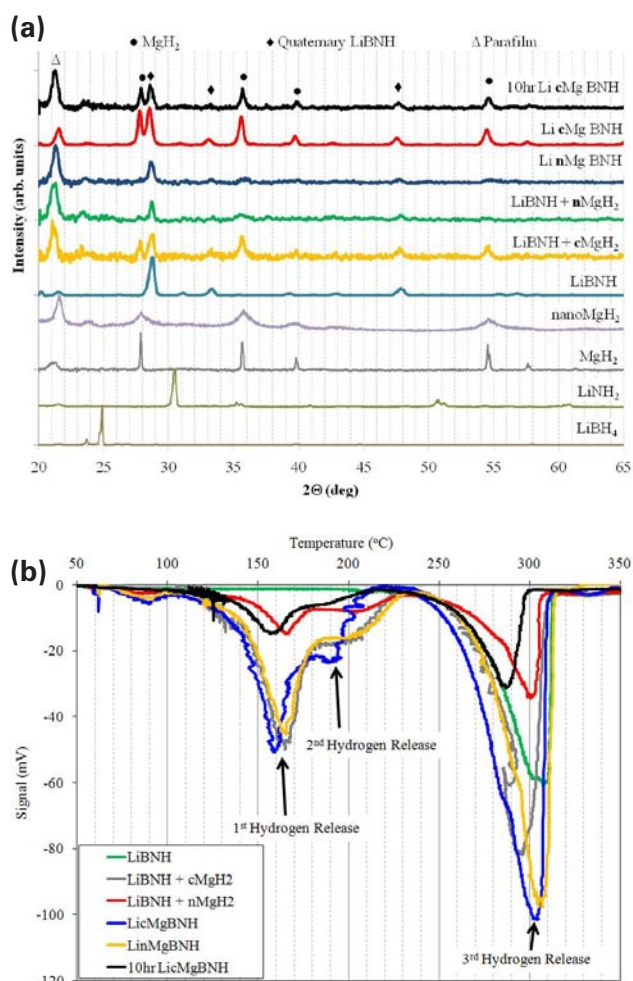
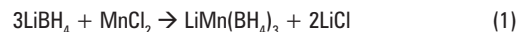


FIGURE 1. (a) XRD (b) TPD Profile of the five differently processed materials as well as the parent compounds, LiBH_4 , LiNH_2 , MgH_2 and nano MgH_2 .

was carried out in solid state employing the mechano-chemical milling process. The reactions proceed based on the stoichiometric ratio given in the equation (1) below,



We have demonstrated the successful preparation of new alkali-transition metal-based complex borohydrides, $\text{LiMn}(\text{BH}_4)_3$ from the precursors of LiBH_4 and MnCl_2 by the mechano-chemical process. To reduce the decomposition temperature further, we have attempted to dope the $\text{LiMn}(\text{BH}_4)_3$ with different mole concentrations of nanomaterials (nano-Ni). It was clearly noticed that doping with nanoNi lowers the decomposition temperature and at the same time enhances the kinetics of the reaction. It is unambiguously seen from the thermogravimetric analysis and TPD analyses that nano-Ni doping of

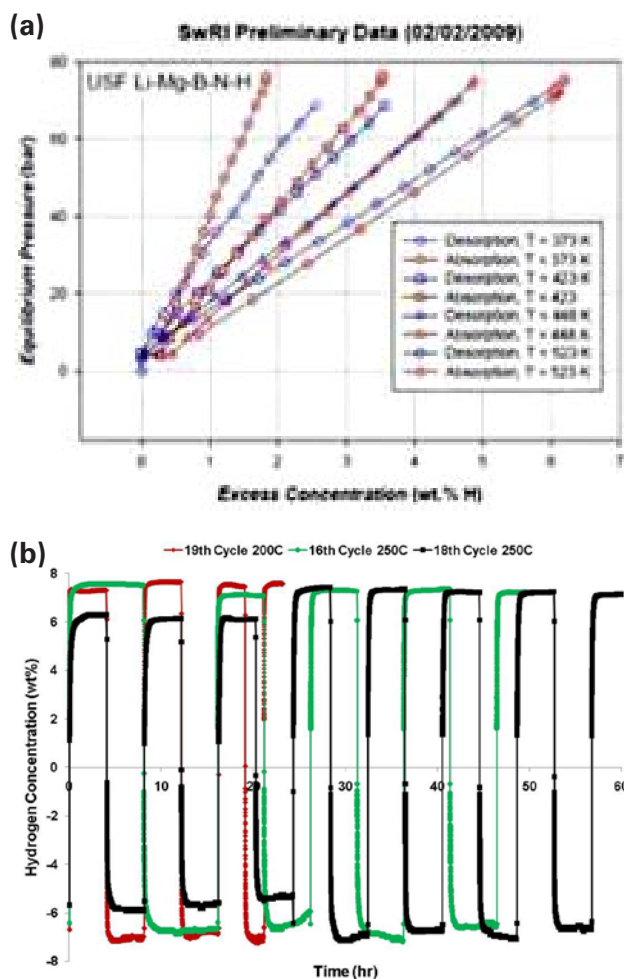


FIGURE 2. (a) PCT and (b) Hydrogen Cycling Kinetics of Li-nMg-B-N-H Complex Hydrides at Different Temperatures

1-2 mol% destabilizes the structure with at least 10-20°C reduction in hydrogen thermal decomposition temperature (T_{dec}). Moreover, the nano-Ni has greater effect on the hydrogen release (desorption kinetics) rate when compared to the undoped $\text{LiMn}(\text{BH}_4)_3$ as observed in Figure 3(a). The optimum concentration of nano-Ni was found to be 1-2 mol% which can speed up the initial decomposition reaction at least 2 to 3 times when compared to the undoped counterpart. In order to further confirm the reversible hydrogen storage behavior of this MgH_2 admixed LiMnBH , we have systematically executed PCT measurements at constant temperatures of 100°C. Figure 3(b) demonstrates the reversible hydrogen sorption behavior at 100°C with total capacity of 3.5 wt%.

Task 3. Polyaniline (PANI) Nanofibers (Chemical and Electrospun Methods)

Conducting polyaniline nanofibers were synthesized using chemical templating method followed by

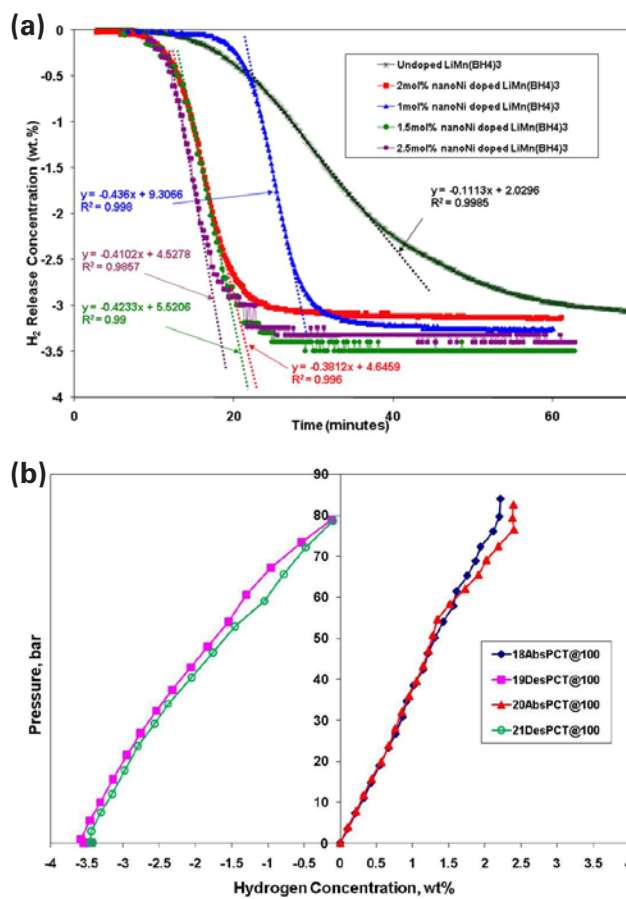


FIGURE 3. (a) Dehydrogenation Kinetics and (b) PCT of $\text{LiMn}(\text{BH}_4)_2$ and $\text{LiMnBH-Xmol}\%\text{MgH}_2$

electrospun process. Figure 4(a) shows the cycle life kinetics of the electrospun PANI nanofibers. No hydrogen uptake was observed until the sample was heated to 100°C. The initial high capacity of 11 wt% is not fully observed when desorbing the hydrogen, as only 8 wt% is released. This occurs in a two-step process characterized by a fast (physisorption) hydrogen release and a slower (chemisorption) hydrogen release step. This hydrogen behavior is due to hydrogen bonding with both unterminated bonds as well as with the surface of the nanofibers. The PANI nanofiber chemical method, however, absorbed hydrogen at 30°C and did so reversibly with a capacity of approximately 3wt%, as seen in Figure 4. Unlike the electrospun nanofibers, the hydrogen was absorbed and released in a one-step process with very rapid kinetics of less than 10 min. This fast hydrogen sorption is most likely due to the higher surface area of the chemically grown nanofibers as opposed to the electrospun nanofibers that exhibit a much smoother surface. The surface morphologies before and after hydrogen sorption of these PANI nanofibers encompass significant changes in the microstructure (nanofibrillar swelling effect) which clearly suggest effective hydrogen uptake and release.

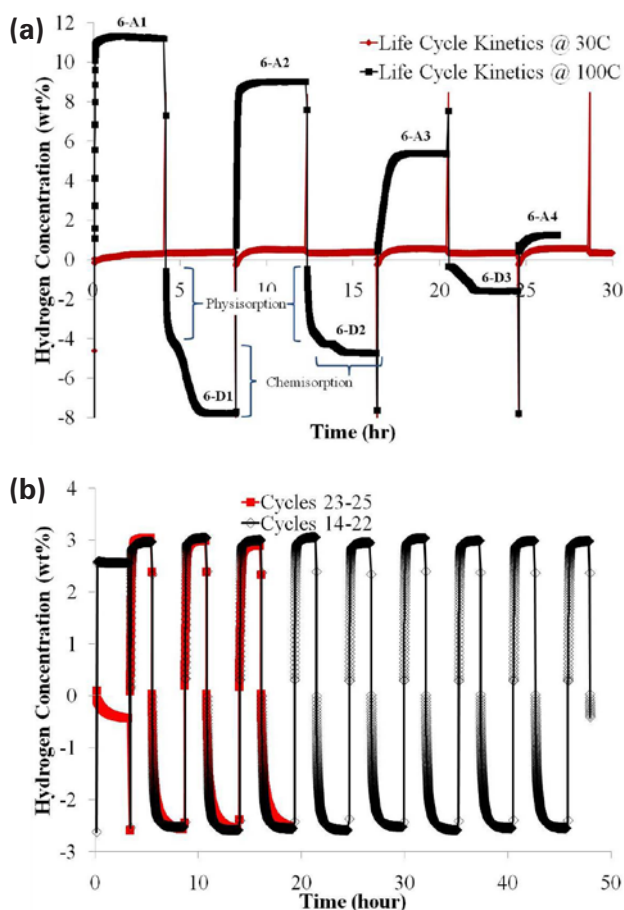


FIGURE 4. Hydrogen Cycling Kinetics in Polyaniline Nanofibers Prepared by (a) Electrospun (b) Chemical Methods

Conclusions

- Complex borohydrides $\text{LiMn}(\text{BH}_4)_3$ has been successfully synthesized from the solid state mechano-chemical process of $\text{Na}(\text{Li})\text{BH}_4$ and MnCl_3 .
- The thermal decomposition of $\text{LiMn}(\text{BH}_4)_3$ exhibits weight loss due to hydrogen desorption of around 9.0 wt% at $\sim 150^\circ\text{C}$ (same or exceeds the DOE and FreedomCAR targets).
- Destabilization of the complex hydride mixture $\text{LiBH}_4/\text{LiNH}_2/\text{MgH}_2$ produces multinary hydride structure for reversible hydrogen storage behavior at moderate temperatures.
- Among the various methodologies, nano- MgH_2 mixed with quaternary LiBNH structure showed relatively enhanced hydrogen decomposition characteristics as observed from TPD.
- PANI nanofibers and nanospheres have been prepared from chemical and electrospun synthesis route. Hydrogen cycling kinetics measurements demonstrate promising reversibility.

Future Directions

- NanoPd and NanoAg doping on the hydrogen decomposition characteristics of $\text{LiMn}(\text{BH}_4)_3$.
- Analysis of the residual gas after thermal decomposition of $\text{LiMn}(\text{BH}_4)_3$ by GC/MS.
- Hydrogen sorption measurements (full cycle life kinetics, PCT, etc.) of nanocatalysts doped with LiAlH_4 +nano MgH_2 complex mixture.
- Estimation of enthalpy of reaction from the van't Hoff equation from the PCT data.
- GC/MS of the desorbed gases during dehydrogenation process.
- Thermodynamic characterization of the USF developed Li-Mg-B-N-H complex materials.
- New discovery of materials with nanocatalyst doping.
- Reproducibility and repeatability of optimized materials for the high reversible hydrogen sorption behavior.
- Activation energy calculations with different processing conditions to estimate and understand the effects of nanocatalyst dopants.
- Synthesis of polyaniline nanofibers by chemical and electrospun method to increase the surface area and hydrogen reaction sites.

Special Recognitions & Awards/Patents Issued

- S.S. Srinivasan, M.U. Jurczyk, E.K. Stefanakos and D.Y. Goswami, Methods and processes for producing complex hydrides exhibiting high hydrogen storage capacity and fast sorption kinetics at moderate temperatures, *Non Provisional patent (Electronic file application number: 61037869)*, University of South Florida, Tampa, FL, USA, 2007.
- Won a *Grant Proposal competition* from the California-based Nanomaterials Manufacturing Company QuantumSphere Inc., 2008-2009.

FY 2009 Publications/Presentations

- 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, 2009 *Journal of Nanoscience and Nanotechnology* (In Print).
- M.U. Niemann, S.S. Srinivasan, A.R. Phani, A. Kumar, D.Y. Goswami, E.K. Stefanakos, Electrospun polyaniline nanofibers for hydrogen storage, *J. Nano Research*, 2009, In Press.
- Niemann, M.U., Srinivasan, S.S., McGrath, K., Kumar A., Goswami, D.Y., Stefanakos, "Tailoring the Activation Energy by different processing conditions and nanocatalyst doping of Li-Mg-B-N-H systems", *Int. J. Hydrogen Energy*, 2009 (Manuscript under preparation).

4. Nano-Ni Doped Li-Mn-B-H System as a New Hydrogen Storage Candidate, P. Choudhury, S. Srinivasan, V.R. Bhethanabotla, E.K.Stefanakos, Y. Goswami, K. McGrath, *Int. J. Hydrogen Energy*, 2009 (Submitted).
5. Andrew Vittetoe, Michael Niemann, Sessa Srinivasan, Ashok Kumar, Lee Stefanakos, Yogi Goswami, Sylvia Thomas, Destabilizing Lithium Aluminum Hydrides for Hydrogen Storage, *Int. J. Hydrogen Energy*, 2009.
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9. Choudhury, P., Bhethanabotla, V.R. and Stefanakos, E. (2008) “Identification of a New Stable Phase for High Capacity Hydrogen Storage Material Zn(BH₄)₂ fFrom Density Functional Theory and Lattice Dynamics,” *Phys. Rev. B*, 77, 134302.