New Material Li-Mn-B-H System as Hydrogen Storage Candidate

Pabitra Choudhury[1, 2], Sesha Srinivasan[2], Venkat R. Bhethanabotla[1, 2] and
Elias Stefanakos[2]
[1]Sensors Research Laboratory, Department of Chemical and Biomedical Engineering
[2]Clean Energy Research Center (CERC)
University of South Florida, 4202 E. Fowler Ave., ENB 118, Tampa, FL 33620

Abstract

In this work, we present synthesis and characterization results for Li-Mn-B-H, a new class of complex borohydrides for hydrogen storage materials for vehicles powered by fuel cells. The new complex was prepared with 3:1 ratios of precursor materials, *i.e.*, LiBH4/$MnCl_2$ *via* standard mechano-chemical solid state process. Thermo gravimetric analysis (TGA) of Li-Mn-B-H indicated that a large amount of hydrogen (~8.0 wt %) can be released between 135 ℃ and 155 ℃ under a heating rate of 2 ℃/min in a single dehydrogenation reaction step. An amount of 1.5 mol% nano-Ni was estimated and found to be the optimum concentration for doping of Li-Mn-B-H. It was observed that the decomposition temperature can be lowered by 20 ℃ or more, upon this doping. The nano-Ni doping lowers the melting and thermal decomposition temperature (at least by 20 ℃) of Li-Mn-B-H system as evidenced from calorimetric analysis. The nano-doped Li-Mn-B-H system also exhibits 3-4 time faster dehydrogenation kinetics than the undoped one.

I. Motivation/Background

Suitable means of hydrogen storage are one of the key requirements for hydrogen fuel cell technology. A recent challenge in hydrogen storage is to find light weight complex solid hydrides which have higher gravimetric capacity - larger than 6.0 wt% - and also can exhibit favorable thermodynamics and fast kinetics for hydrogen de-sorption and absorption for on-board vehicular applications. The breakthrough discovery of Ti-catalyzed $NaAlH_4$[1, 2] exhibiting reversible onboard hydrogen storage may not be the ideal system to attain the DOE 2010 and FreedomCAR technical targets. This is due to the maximum achievable hydrogen storage capacity of 5.4 wt% for $NaAlH_4$, which is well below the DOE target of 2010 and also dehydrogenation / re-hydrogenation times are unacceptable. So, borohydride complexes as hydrogen storage materials have recently attracted great interest. The borohydride complexes $NaBH_4$ and $LiBH_4$ possess high hydrogen storage capacity of 13.0 wt% and 19.6 wt%, respectively. However, the release of hydrogen from $NaBH_4$ is possible only by hydrolysis (reaction with H_2O) and this process is irreversible. For the case of $LiBH_4$, the catalytic addition of SiO_2, significantly enhances its thermal desorption[3] at 200 ℃. In general, thermal dehydrogenation and/or re-hydrogenation of $NaBH_4$ or $LiBH_4$ are difficult to achieve because of the thermodynamic stability due to strong B-H interactions[4, 5]. It was found that thermal decomposition of $Zn(BH_4)_2$ comprises of not only the evolution of H_2, but also an appreciable amount of B–H (borane) compounds. Lowering the decomposition temperature by Ni doping may lead to negligible release of boranes[6].

Of the tetrahydridoborates of metals of first transition series, the least studied at the present time are the borohydride complexes of Mn. Almost no information was found in the literature on Li-Mn-B-H systems. We have synthesized and characterized nano-Ni doped and undoped complexes using mechano-chemical, and combined thermal analytical and IR methods, respectively.

II. Experimental Details

Starting materials such as $LiBH_4$ (90% purity) and $MnCl_2$ (99% purity) were obtained from Sigma Aldrich and nano-Ni dopant (99.999%) was obtained from Quantum Sphere Inc.. They were used without further purification. High purity H_2 (99.9999%), N_2 (99.99%) and He (99.99%) were procured from Airgas for the synthesis and analytical measurements. All chemical reactions and operations were performed in a nitrogen filled glove box. $LiBH_4$ and $MnCl_2$ with 3:1 mole ratio was mixed in the stainless steel bowl (80 ml) and the lid sealed with viton O-ring in the glove box. The bowl was then evacuated for sometime to remove the residual oxygen and moisture down to *ppm* levels. A specially designed lid with an inlet and outlet valves weas used for this purpose. The mechano-chemical process employing high energy milling has been carried out by Fritsch pulversette planetary mono mill, P6 in an inert atmosphere. In a similar way, few mole concentrations of nano- dopants were added during the milling process for the synthesis of nano-doped system.

For thermal analysis: The simultaneous DSC and TGA (SDT) analysis pertaining to the weight loss and the heat flow for the reaction enthalpy during thermal decomposition of undoped and nano-doped complex hydride were performed using the TA instruments SDT-Q600 analytical tool. The kinetic measurements were carried out by Hy-Energy PCTPro 2000 sorption equipment.

The B–H bond stretch of the Li-Mn-B-H system was measured *via* Perkin-Elmer Spectrum One FTIR spectrometer. This instrument operates in a single-beam mode and is capable of data collection over a wave number range of 370–7800 cm^{-1} with a resolution of 0.5 cm^{-1}. The complex borohydride samples were palletized and sealed in a specially designed KBr cell for infrared measurements.

III. Results/Discussion

We have successfully prepared new transition metal based complex borohydrides Li-Mn-B-H from the precursors of $LiBH_4$ and $MnCl_2$ in a mechano-chemical process. The DSC, TGA and PCT kinetic profiles of the samples synthesized using the stoicheometric reaction of $LiBH_4$ and $MnCl_2$ in the solid state process are shown in Figures 1-3. It is observed that the endothermic transition due to hydrogen or gaseous decomposition from Li-Mn-B-H precedes the low temperature of phase transition of pure $LiBH_4$ as shown in Figure 1.

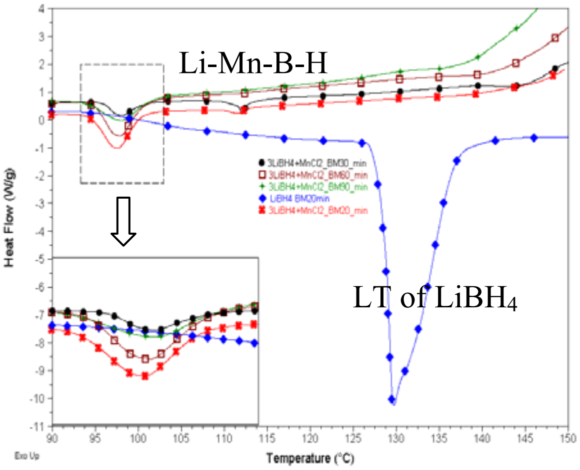

Figure 1. DSC profiles of as-synthesized Li-Mn-B-H and pure $LiBH_4$

The phase transition and decomposition temperatures of Li-Mn-B-H are 95-100 °C and 135 – 155 °C, respectively. The low temperature phase transition of $LiBH_4$ is around 130 °C. In order to reduce the decomposition temperature further, we doped the Li-Mn-B-H system with different mole concentrations of nano-Ni. The thermo gravimetric (TGA) profiles of undoped and doped Li-Mn-B-H samples are shown in Figure 2.

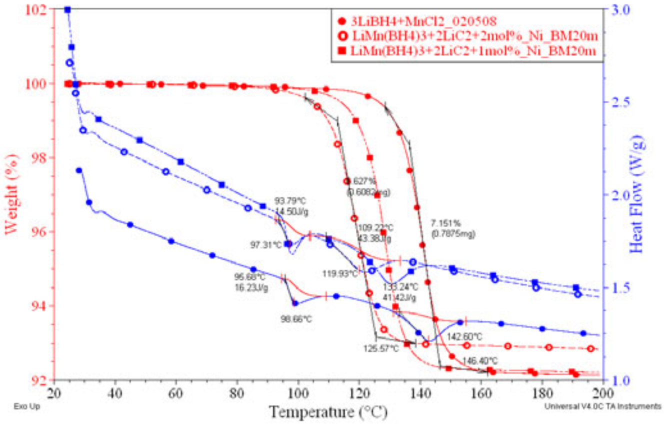

Figure 11. TGA and DSC profiles of the weight loss and heat flow during decomposition of Li-Mn-B-H (only results for 1 and 2 mol% of nano-Ni shown).

It is unambiguously observed that nano-Ni doping of 1 and 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 unoped Li-Mn-B-H as represented in Figure 3.

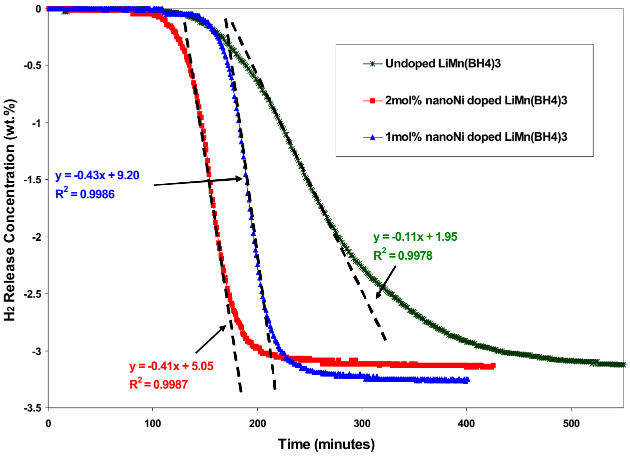

Figure 3. Desorption kinetics profiles of undoped and nanoNi doped Li-Mn-B-H

$[BH_4]^-$ formation is confirmed from the FTIR spectrum which indicates the B-H bonding and stretching band around 2200 - 2400 cm^{-1} and $[BH_4]^-$ ionic movement is around 1130 cm^{-1}.

IV. Conclusion

In this work, the inexpensive mechano-chemical approach of ball milling technique was used to prepare a new class of solvent-free, solid-state complex borohydrides (Li-Mn-B-H) for on-board hydrogen storage by stoicheometrically (1:3) mixing $MnCl_2$ and $LiBH_4$. It is found that the endothermic transition due to hydrogen or gaseous decomposition from the Li-Mn-B-H system precedes the low temperature phase transition of pure $LiBH_4$. The dehydrogenation phase transition and decomposition temperatures of Li-Mn-B-H correspond to 95-100 ^{o}C and 135-155 ^{o}C, whereas, this value for the low temperature phase transition of $LiBH_4$ is around 130 ^{o}C. An optimum nano-Ni doping lowers the decomposition by 20 ℃ or more. Thermo gravimetric (TGA) and desorption kinetic profiles of the undoped and doped Li-Mn-B-H system show that the nano-dopant materials have pronounced effects on the hydrogen release kinetics while lowering the decomposition temperature.

Acknowledgement

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