

Effect of Nb₂O₅ on the Hydrogen Storage Characteristics of Li-nMg-B-N-H Complex Hydrides

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ABSTRACT

The effect of adding niobium oxide, Nb₂O₅ to a multinary complex hydrides, LiNH₂-nMgH₂-LiBH₄ have been extensively investigated using thermal programmed desorption and pressure-composition isotherms. Two step hydrogen release of ~8wt% at around 165°C and 300°C was obtained for the pristine Li-nMg-B-N-H complex hydride. Addition of 17wt.% Nb₂O₅ causes the reduction of temperature by 10°C in both the decomposition steps. Moreover, the co-additives, 17wt% Nb₂O₅+2mol% nanoNi further reduce the temperature by 27°C, while enhancing the kinetics of hydrogen release.

Keywords: Hydrogen Storage, Complex Hydrides, Hydrogen Sorption, Niobium (V) Oxide, Thermal Programmed Desorption

1. INTRODUCTION

With increase in global warming and depletion of fossil fuels, there is consensus that the search for alternative clean and renewable energy should be a prerogative in the near future [1]. Hydrogen has attracted a great deal of attention as a clean fuel for mobile and stationary applications [2, 3]. Hydrogen, provided it is produced using clean and renewable energy sources, such as solar energy, can either be combusted in an internal combustion engine or used in a fuel cell [4] and to produce energy free of any pollutant by-products, producing solely energy and water. Storage of hydrogen for subsequent use is a contemporary goal in the development of a hydrogen economy [5]. Current options include storing hydrogen in its liquid form or as a compressed gas. Both methods require a large amount of energy and can pose serious safety risks. Current on-board hydrogen storage technologies include 5000- and 10,000-psi compressed gas tanks and cryogenic liquid hydrogen tanks. Volumetric capacity, high pressure and cost are key challenges for compressed hydrogen tanks. The driving range of fuel cell vehicles with compressed hydrogen tanks can be increased by increasing the amount and pressure of hydrogen but at the expense of increased cost and valuable space within the vehicle. Refueling times, compression energy penalties and heat management requirements during compression also need

to be considered as the mass and pressure of on-board hydrogen are increased. Liquid hydrogen (LH₂) tanks can store more hydrogen in a given volume than compressed gas tanks [6]. The issues with liquid hydrogen (LH₂) tanks are hydrogen boil-off, the energy required for hydrogen liquefaction, volume, weight, and tank cost. Hydrogen boil-off must be minimized or eliminated for cost, efficiency and vehicle range considerations, as well as for safety considerations when vehicles are parked in confined spaces. Insulation is required for LH₂ tanks and this reduces system gravimetric and volumetric capacity. Solid-state hydrogen storage in the form of metal hydrides has the potential for reversible on-board hydrogen storage and release at low temperatures and pressures [7]. Compared to high pressure tanks, metal hydride storage requires much lower pressure. Charged with lower purity hydrogen gas, metal hydrides purify the stored gas instantly, and deliver higher purity gas at no additional cost. There are, however, many challenges that these materials must overcome. Specifically, these are to have fast kinetics, a high capacity, e.g. more than 6 wt.% hydrogen, and to be reusable for at least 1000 cycles [8].

Advanced complex hydrides that are lightweight, low cost and have high hydrogen density are essential for on-board vehicular storage [9-16]. Some of the complex hydrides such as alanates [17-22], alanes [23], amides [24, 25], borohydrides [26, 27], magnesium-based hydrides [28, 29] and mixed complex hydrides [30, 31] have been recently reported with improved hydrogen storage characteristics. Solid-state synthesis pertaining to destabilization of LiBH₄ [32], LiNH₂ [33] and LiBH₄/LiNH₂ [34] with MgH₂ has been found to enhance the reversible hydrogen storage characteristics. The multinary complex hydride Li-Mg-B-N-H possesses a theoretical hydrogen capacity of approximately 8-10 wt.%. However, it has been reported that only about 3 wt.% of hydrogen was reversibly released between 160 and 200 °C [35]. It was reported that the MgH₂ acts as a facilitator in self-catalyzing the material to release hydrogen with three main reactions [35, 36].

Previous studies by authors [37] resulted in developing a high-capacity nanocomposite multinary hydride (LiMgBNH) comprising LiBH₄, LiNH₂ and MgH₂, with a reversible hydrogen storage capacity of ~5-6 wt.% at 150°C. This was achieved by a novel inexpensive

mechano-chemical synthesis procedure. The present study investigates the effect of addition of Niobium oxide (Nb_2O_5) and small fraction nanoNi to the $\text{LiNH}_2/\text{MgH}_2/\text{LiBH}_4$ complex mixture. Niobium (V) oxide acts as a lubricant to allow for easy removal of hydrogen from interstitial sites in metal hydrides [38].

2. EXPERIMENTAL PROCEDURE

Synthesis of the multinary hydride compounds

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 $2\text{LiNH}_2:\text{LiBH}_4$ by employing high-energy ball milling (Fritsch Pulverisette 6) for 5 h at 300 rpm with an intermittent hydrogen/argon (5%/95%) purges for 20 min before milling and after 2 and 4 h. 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 nano MgH_2 (n MgH_2) with 17wt.% Nb_2O_5 was created by ball milling the commercial MgH_2 (c MgH_2) and 17wt.% Nb_2O_5 for 6-12 h with intermittent hydrogen/argon purges every 2 h. This ensured the reduction of particle size as well as the decrease in hydrogen release temperature, as previously reported [40]. An equal amount (1:1 mole ratio) of 17wt% Nb_2O_5 +n MgH_2 and $2\text{LiNH}_2:\text{LiBH}_4$ quaternary compounds were milled to obtain the multinary complex hydride mixture $\text{Li-nMg-B-N-H/Nb}_2\text{O}_5$. Further, co-doping of 2mol% nano Ni was carried out with the above mixture and milled for 30 minutes to obtain $\text{Li-nMg-B-N-H/Nb}_2\text{O}_5$ -nNi.

Structural, Microstructural, chemical, thermal and volumetric characterization

The structural phase identification and average crystallite size determination were characterized using X-ray diffraction (Philips X'Pert diffractometer). All samples were pressed into pellet form in the glove box and sealed with Parafilm® to minimize exposure to the elements. Zero background Silicon disc, 32 mm procured from GEMS Dugout, Pennsylvania, USA, was used for this purpose. The characteristic amide (NH_2) and B–H stretches of the samples were compared via Perkin–Elmer Spectrum One FTIR spectrometer. This instrument operates in a single-beam mode and is capable of data collection over a wavenumber range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 0.5 cm^{-1} . The quaternary and multinary complex hydrides and their doped counterparts were pelletized and sealed in a nitrogen-filled glove box

in a specially designed KBr cell for infrared measurements. Thermal programmed desorption (Quantachrome Autosorb 1C with TCD option) was used to determine the hydrogen release temperature. Hydrogen sorption measurements were carried out on a Sievert's type apparatus (Setaram/HyEnergy PCT Pro 2000) with isothermal conditions, ranging from room temperature up to $250\text{ }^\circ\text{C}$ and with a hydrogen pressure varying from low vacuum to 80 bars (8 MPa). Additionally, the samples were investigated for their kinetics by keeping the sample close to vacuum and ramp the temperature at $1\text{ }^\circ\text{C/min}$ up to $250\text{ }^\circ\text{C}$. Both kinetic- and pressure-dependent hydrogen sorption measurements were performed. The surface morphology of the hydrides was observed using the scanning electron microscope (Hitachi S-800) both in the image and EDS modes.

3. RESULTS AND DISCUSSION

Scanning Electron Microscope (SEM)

Figure 1(a) shows the SEM image of the mixture compound 17wt% Nb_2O_5 + MgH_2 that were milled under inert ambient for 12 hours. It is discernible from the figure that the niobium (V) oxide grains (white spots) are distributed homogeneously throughout the MgH_2 host matrix and are about $2.5\text{ }\mu\text{m}$ in average size. Similarly, the SEM image of the multinary complex hydride $\text{Li-nMg-B-N-H/Nb}_2\text{O}_5$ created by ball milling of LiBNH and 17wt% Nb_2O_5 + MgH_2 exhibits the smooth surface with apparent signatures of Nb_2O_5 grains (see Figure 1(b)).

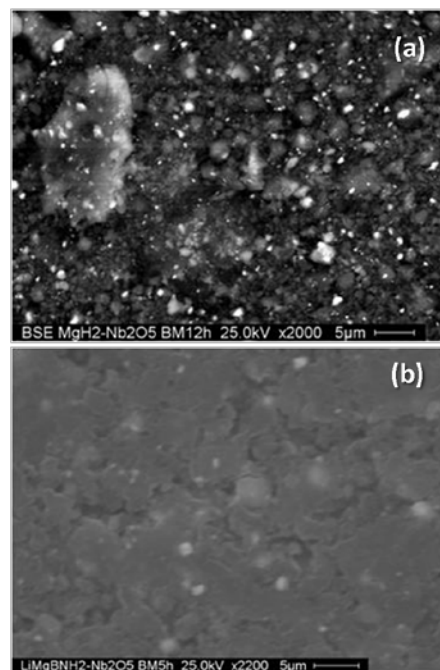


Figure 1. SEM image of (a) 17wt% Nb_2O_5 + MgH_2 and (b) $\text{Li-nMg-B-N-H/Nb}_2\text{O}_5$

X-ray Diffraction (XRD)

Figure 2 represents the XRD profiles comparing the characteristics at different stages of formation of the hydride compound. The lower three results represent the complex of Magnesium hydride and Niobium oxide compound that was hand crushed (0 hours), 6 hours and 12 hours of milling. The relative intensities of the sharp crystalline peaks of MgH_2 decreases for the 6-12 hours of ball milled mixtures. It is also noteworthy to mention that no impurities, such as Fe, which might have been introduced as a result of the ball milling process, were observed from either XRD and/or SEM-EDS measurements. The fourth line from bottom represents the peaks of the LiMgBNH compound and is shown for reference [37]. The top line shows the characteristics of the LiBNH quaternary hydride with $\text{Nb}_2\text{O}_5/\text{MgH}_2$ mixture. It can be observed from the top profile that the presence of $\text{Nb}_2\text{O}_5/\text{MgH}_2$ complex did not induce any additional peaks. This confirms that the addition of $\text{Nb}_2\text{O}_5/\text{MgH}_2$ complex causes the material to intermix and fill voids of the quaternary structure, which results in a nanocrystalline particle distribution, while still preserving the quaternary structure formed by the LiBNH . It can also be observed that for milling time equal to or greater than 5 hours, the phase transformation occurs.

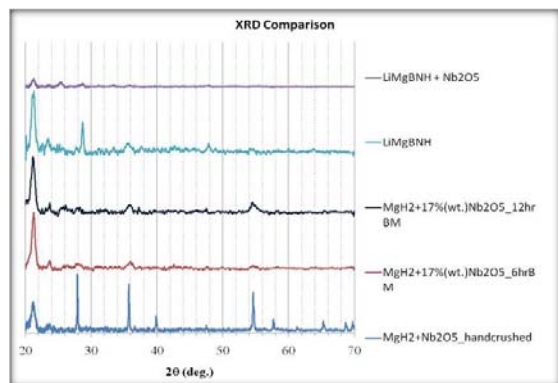


Figure 2. XRD profiles of complex multinary hydride

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3 represents the FTIR spectra of commercial Nb_2O_5 , quaternary hydride (LiBNH) and $\text{LiBNH}+(17\text{wt}\%\text{Nb}_2\text{O}_5+\text{nMgH}_2)$. The chemical information about the B–H, N–H stretches and BH_2 deformation are obtained due to the presence lithium borohydride and lithium amide. The peaks of the symmetric and asymmetric amide anions are shifted from the expected 3312 cm^{-1} and 3259 cm^{-1} to 3302 cm^{-1} and 3244 cm^{-1} , respectively. Furthermore, the peak around 1560 cm^{-1} is characteristic of the amide ion. The B–H stretches, usually found at 2225 cm^{-1} , 2237 cm^{-1} , 2293 cm^{-1} , and 2387 cm^{-1} overlap in the samples to form one

large B–H stretch with a peak around 2320 cm^{-1} . Finally, the BH_2 deformation peaks found at 1120 cm^{-1} and 1092 cm^{-1} in LiBH_4 are observed at 1120 cm^{-1} and 1082 cm^{-1} , respectively, though the peak around 1120 cm^{-1} is extremely weak. However, there is no observable shift in any of the main stretches between the sample with and without Nb_2O_5 , indicating that the chemical composition of the quaternary hydride is kept intact, and there is in fact no formation of a new compound. There is no evidence in the FTIR data indicating the reaction of MgH_2 with either the amide or borohydride, further confirming the XRD data shown in Figure 2.

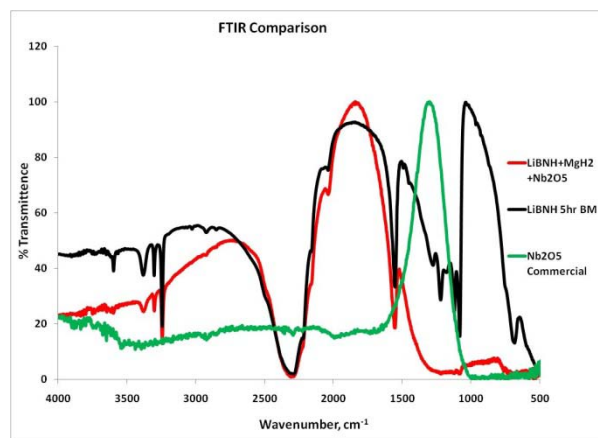


Figure 3. FTIR spectra of complex multinary hydride with and without addition of Nb_2O_5

Thermal Programmed Desorption (TPD)

The thermal decomposition characteristics of the $17\text{wt}\%\text{Nb}_2\text{O}_5+\text{MgH}_2$ samples at different stages of milling were measured using TPD with a heating rate of $1^\circ\text{C}/\text{min}$. The hydrogen release temperatures for the $\text{Nb}_2\text{O}_5/\text{MgH}_2$ complex for different durations of milling are shown in Figure 4. It can be observed that the peaks representing the temperature of desorption decrease with increase in milling time. The temperatures of desorption for MgH_2 with niobium oxide with milling times of 0 hours and 6 hours are 410.4°C and 364.3°C respectively. Whereas for the 12 hours milled samples, the temperature of desorption was further lowered to 346.2°C . We have used the optimized 12 hours milled $17\text{wt}\%\text{Nb}_2\text{O}_5+\text{MgH}_2$ samples for rest of the measurements given below.

Figure 5 shows the TPD curves of Li-nMg-B-N-H multinary hydride with and without Nb_2O_5 additive. It can be observed that the addition of niobium oxide decreased the desorption temperature from 163°C to 155°C for the first peak and from 299°C to 289°C for the second desorption peak. Niobium oxide interacts with the quaternary structure and destabilizes it, thereby releasing hydrogen at lower temperatures. This implies that the

addition of niobium oxide helps in enhancing the decomposition kinetics of the Li-nMg-B-N-H compound.

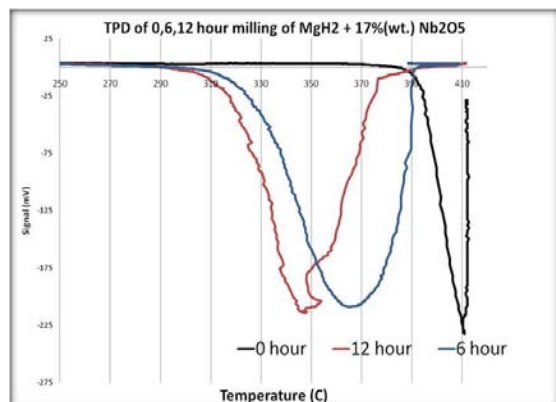


Figure 4. TPD profiles of 17wt% Nb₂O₅+MgH₂ compound at various milling durations

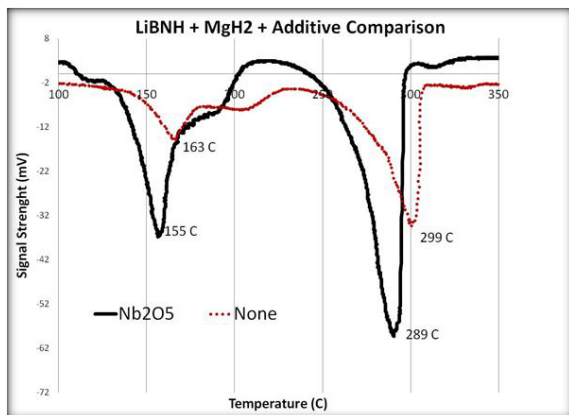


Figure 5. TPD comparison of Li-nMg-B-N-H with and without Nb₂O₅ additive

Figure 6 demonstrates the TPD spectra for LiMgBNH with plain Nb₂O₅, plain nanoNi and the combination of Nb₂O₅+nanoNi. From this figure, it is apparent that co-doping of nanoNi along with Nb₂O₅ further lowered the decomposition temperatures significantly. It can be observed from the second desorption peak, the hydrogen release temperature is 205°C for LiMgBNH sample with niobium and nano-nickel whereas, it is 232°C with plain nanoNi and 289 °C, with plain Niobium Oxide.

Pressure-Composition Isotherms (PCI)

The PCI studies of the complex hydride, Li-nMg-B-N-H+17wt% Nb₂O₅ was carried out under the following conditions: temperature, T = 150–175 °C; pressure difference between aliquots, ΔP = 3 bars (0.3 MPa); absorption pressure limit, P_a = 80 bars (8 MPa); desorption pressure limit, P_d = 0 bar (0 MPa); and reservoir volume, V_r = 160 cm³. The dehydrogenation

experiment was followed by the rehydrogenation for at least 10 h. Figure 7 shows the PCI curve overlaid with the TPD results for the sample. The stepwise weight loss due to hydrogen release at the decomposition temperatures has been observed. The total percent weight loss from the complex hydride after the two desorption peaks was ~8 wt.% with a ~3 wt.% loss at 150.7°C in the first peak and ~4wt.% loss at 287.5°C in second peak.

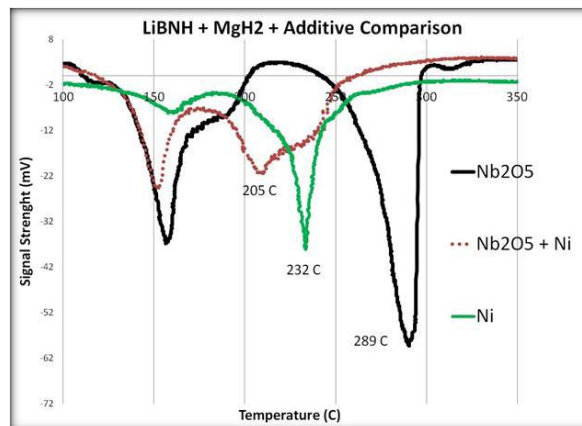


Figure 6. TPD spectra of LiMgBNH with different additives

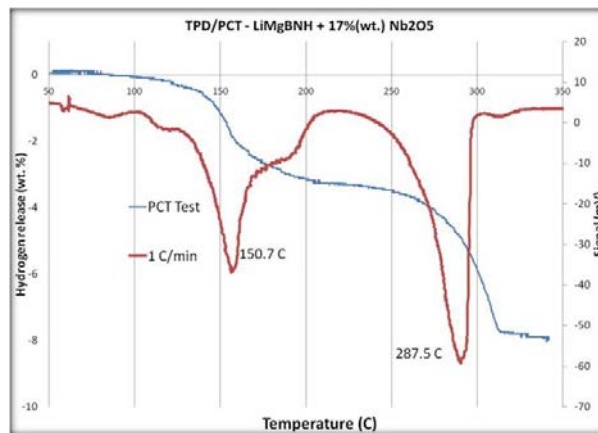


Figure 7. TPD/PCI of Li-nMg-B-N-H with Nb₂O₅

4. CONCLUSION

Addition of Niobium Oxide (Nb₂O₅) to a complex hydride consisting of LiBH₄, LiNH₂, and MgH₂ enhances the hydrogen sorption kinetics at low temperatures. When niobium oxide was added to Li-nMg-B-N-H, the desorption temperature decreased by 10 °C. Further reduction to 27°C was obtained for the samples co-doped with Nb₂O₅ and 2mol% nanoNi. An optimization of co-doping concentrations and their hydrogen storage behavior are currently being carried out and will be reported in the subsequent publications.

5. ACKNOWLEDGEMENTS

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