

Short communication

Evaluation of the hydrogen storage behavior of a $\text{LiNH}_2 + \text{MgH}_2$ system with 1:1 ratio

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Received 30 May 2007; received in revised form 10 July 2007; accepted 11 July 2007

Available online 27 July 2007

Abstract

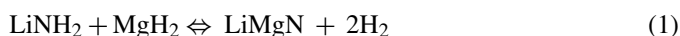
A one-to-one molar ratio of LiNH_2 to MgH_2 was ball milled and characterized to evaluate the proposed hydrogen storage reaction: $\text{LiNH}_2 + \text{MgH}_2 \rightleftharpoons \text{LiMgN} + 2\text{H}_2$. The pressure–composition isotherm shows that less than 3.4 wt.% H_2 is released at a plateau pressure near 20 atm at 210 °C. Furthermore, X-ray diffraction show that the products of the reaction include $\text{Li}_2\text{Mg}_2(\text{NH})_3$ rather than LiMgN . Combined thermogravimetric and residual gas analyses reveal that large quantities of ammonia are released from the system.

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Keywords: MgH_2 ; LiNH_2 ; Dehydrogenation; Ternary imide

1. Introduction

The solid state Li_3N based hydrogen storage system, as described by Chen et al. [1], has been the topic of substantial research; however, the properties desired to develop on-board storage systems have not been obtained. For this reason, the material choices have been broadened to include many other metal–nitride metal–hydride mixtures [2–16]. As experimental characterization of potential materials is time intensive, Density Functional Theory (DFT) calculations offer an attractive option for identifying potential hydrogen storage materials. Recent DFT work by Alapati et al. [17] has shown the following storage mechanism is energetically plausible:



with a calculated 0 K reaction enthalpy of $29.7 \text{ kJ mol}^{-1} \text{ H}_2$.

This reaction is very attractive for on-board hydrogen storage applications for multiple reasons. First, the theoretical storage capacity is higher—8.19 wt.% H_2 compared with 5.35 wt.% for the $(2\text{LiNH}_2 + \text{MgH}_2)$ storage system [11]. Second, the reversible hydriding and dehydriding temperature at 1 atm of hydrogen pressure would be 228 K (−45 °C) if the entropy

change for reaction (1) is taken to be $130 \text{ J K mol}^{-1} \text{ H}_2$ [18]. Furthermore, at room temperature (25 °C) the equilibrium hydrogen pressure would be 4.9 atm. Clearly, this would be ideal for fuel cell applications because the $(\text{LiNH}_2 + \text{MgH}_2)$ mixture would deliver hydrogen at pressures from 1 to 5 atm if a pressure regulator is utilized with the storage system. Last, this system should be less vulnerable to the emission of NH_3 as the concentration of MgH_2 is higher. Previous studies [19–23] have shown that LiNH_2 decomposes to Li_2NH and NH_3 during heating. The latter reacts with LiH very fast – on the order of microseconds – to form LiNH_2 and H_2 , which effectively minimizes the emission of NH_3 [19]. If this fast reaction also occurs between NH_3 and MgH_2 , then the higher concentration of MgH_2 would improve the “capturing” of NH_3 , thus mitigating the NH_3 emission issue.

In spite of the great potentials, the DFT calculation performed in Ref. [17] only addresses the structures and energies of the reactants and products of the reaction. The kinetics of reaction (1) and the identification of other possible phases have not been calculated. These issues, however, can be effectively investigated experimentally. Therefore, the purpose of this work is to experimentally evaluate the storage behavior of this newly proposed reaction.

2. Experimental

Lithium amide (LiNH_2) with 95% purity was purchased from Alfa Aesar, and magnesium hydride (MgH_2) with 95% purity

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was kindly provided by Sandia National Lab. The LiNH_2 and MgH_2 were mixed in a 1:1 molar ratio, and ball milled for 3 h under argon with a Szegvari attritor which had been shown previously to be effective in preventing the formation of the dead zone and producing uniform milling products within the powder charge [24]. Furthermore, a previous study has demonstrated that the seal of the canister of the attritor is air-tight and there is no oxidation during ball milling [25]. The temperature of the milling container was maintained near 18°C by flowing tap water through the cooling jacket. All sample handling was done in an argon glove box to avoid oxidation.

Thermogravimetric analysis (TGA) was done using a TA Instruments Q500 TGA purged with argon. During loading, the sample was exposed to the atmosphere for less than a minute before being closed in the furnace and purged for 90 min at room temperature. The effluent gas from the TGA chamber was constantly monitored using a quadrupole Residual Gas Analyzer (RGA). To quantify the composition of the effluent gas, RGA was calibrated with two calibration gases. The detail of calibration can be found in Ref. [25].

An Advanced Materials Corporation Gas Reaction Controller device was used to collect pressure–composition isotherm (PCI) data. A sample size of 0.5 g was used, and samples were loaded and removed in an argon glove box. X-ray diffraction (XRD) was done using a Bruker D8 Advance diffractometer with 0.02° step size with a $\text{Cu K}\alpha$ source. The X-ray samples were prepared with 10 wt.% silicon and loaded into quartz capillary tubes in an argon glove box. The capillaries were sealed with wax, allowing for XRD patterns to be taken without exposure to the atmosphere.

3. Results and discussion

The combination of TGA and RGA allows for simultaneous evaluation of the weight loss and the emitted gaseous species. A weight loss of 8.73% is shown in Fig. 1, which is slightly (0.54%) larger than the predicted value [17]. However, the composition analysis of the effluent gas reveals emission of NH_3 . Using an approach established in a previous study [26], the NH_3 concentration in the effluent gas is calculated via the following

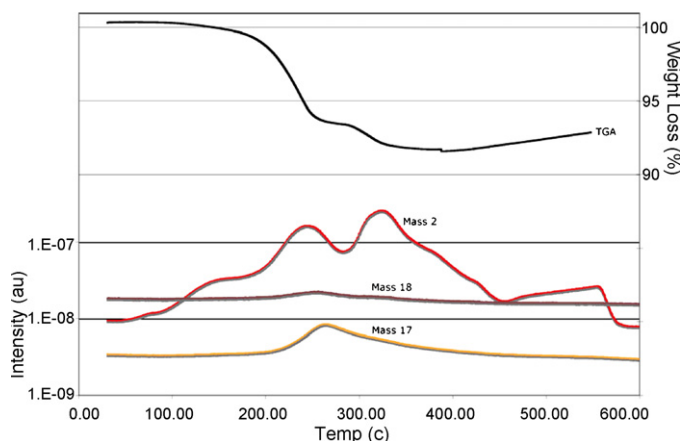


Fig. 1. Thermogravimetric analysis and the composition profile of the effluent gas from the ball-milled $\text{LiNH}_2 + \text{MgH}_2$ sample heated at 5°C min^{-1} to 550°C .

equation:

$$I_{\text{Mass 17}}^{\text{NH}_3} = I_{\text{Mass 17}} - 0.212 I_{\text{Mass 18}} \quad (2)$$

where $I_{\text{Mass 17}}$ and $I_{\text{Mass 18}}$ are the intensities of the species with the mass-to-charge ratio of 17 (hereafter called Mass 17) and 18 (Mass 18), respectively, and can be measured directly from the experiment. $I_{\text{Mass 17}}^{\text{NH}_3}$ is the intensity of NH_3^+ species which is part of the total intensity of Mass 17. $I_{\text{Mass 18}}$ in the present study is due to H_2O^+ species which are formed through the reaction between a trace amount of O_2 and a large amount of H_2 . $I_{\text{Mass 18}}$ affects $I_{\text{Mass 17}}$ through OH^+ species whose intensity is 21.2% of the H_2O^+ intensity. With the aid of Eq. (2) it is found that the intensity of NH_3 , $I_{\text{Mass 17}}^{\text{NH}_3}$, at the peak position (260°C) is $1.14 \times 10^{-10} \text{ Torr mg}^{-1}$ (Fig. 1), which can be converted to the NH_3 concentration of 16.4 ppm mg^{-1} . The normalization of the ammonia concentration by the sample mass allows for fair comparisons between samples. Comparing this NH_3 concentration to the level found in the $\text{LiNH}_2 + \text{LiH}$ system with a 1:1.1 molar ratio [26], the present system has an ammonia concentration that is two orders of magnitude higher. This high NH_3 concentration, which may be a result of the slow kinetics of MgH_2 's conversion of NH_3 to H_2 , also means that the weight loss larger than the theoretical prediction in the TG analysis (Fig. 1) is due to the NH_3 emission.

Fig. 2 shows the desorption curve of the ball-milled $\text{LiNH}_2 + \text{MgH}_2$ sample at 210°C . The PCI data indicates that the released hydrogen is at most only 3.4 wt.%, which is substantially lower than the 8.19 wt.% H_2 predicted from reaction (1). This result is consistent with the finding that the weight loss in the TG analysis is not just from hydrogen release, but also from NH_3 emission as well.

The deviations between the observed phenomena and the predictions from reaction (1) can be explained by examining the XRD patterns of the reactants and products of the reaction. As shown in Fig. 3, the ball-milled sample (Fig. 3B) has LiNH_2 , MgH_2 , and the Si used to align the pattern. The sample dehydrogenated at 210°C in the PCI unit (Fig. 3A) shows remaining MgH_2 , newly formed $\text{Li}_2\text{Mg}_2(\text{NH})_3$ and LiH in addition to

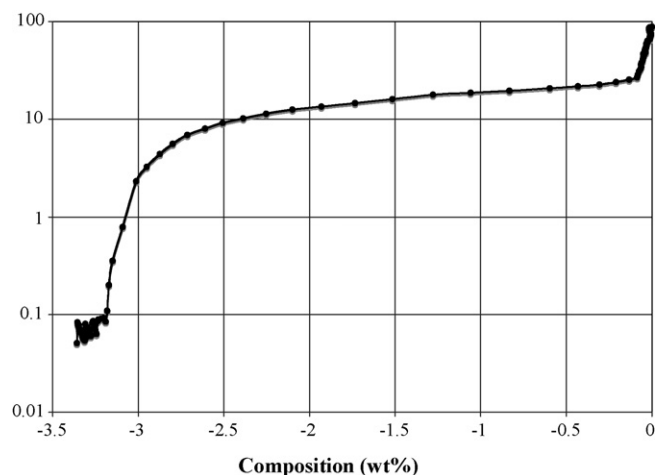


Fig. 2. The desorption pressure–composition isotherm for the ball-milled $\text{LiNH}_2 + \text{MgH}_2$ mixture at 210°C .

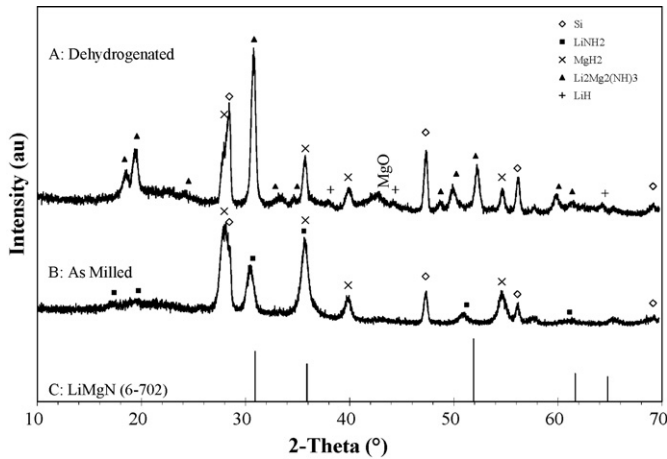
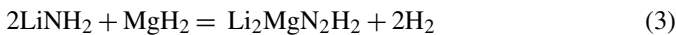
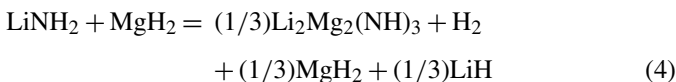


Fig. 3. XRD patterns of the $\text{LiNH}_2 + \text{MgH}_2$ mixture at the as-milled condition and after dehydrogenation at 210°C using the desorption procedure of measuring the pressure–composition isotherm. Note that ternary imide, $\text{Li}_2\text{Mg}_2(\text{NH})_3$, is formed during dehydrogenation. This phase has been indexed as a tetragonal structure with approximate lattice parameters of $a = 5.154 \text{ \AA}$ and $c = 9.596 \text{ \AA}$.

the silicon. No or little LiMgN (Fig. 3C), if any, is formed. Many studies [8,11–14] have demonstrated that when LiNH_2 and MgH_2 are mixed in a 2:1 ratio, the following reaction takes place at temperatures between 180 and 220°C .



It is shown that this reaction can release $5.2 \text{ wt.}\%$ H_2 at 210°C [12,13]. In the present study LiNH_2 and MgH_2 are mixed in a 1:1 ratio, with a much higher MgH_2 concentration than the previous studies [8,11–14]. However, the high MgH_2 concentration does not lead to the formation of LiMgN as predicted by reaction (1). Instead, part of the MgH_2 does not participate in the reaction at 210°C , while other MgH_2 reacts with LiNH_2 to form the ternary imide $\text{Li}_2\text{Mg}_2(\text{NH})_3$. Formation of this ternary imide has also been reported previously, but using the $\text{LiH} + \text{Mg}(\text{NH}_2)_2$ mixture in a 1:1 molar ratio as the reactant [10]. Based on the present XRD analysis, the overall dehydrogenation reaction of the $\text{LiNH}_2 + \text{MgH}_2$ mixture at 210°C taking place near the equilibrium condition (i.e., using the desorption procedure of measuring the pressure–composition isotherm) is proposed to be



The proposed reaction can theoretically release $4.06 \text{ wt.}\%$ H_2 , which is close to $3.4 \text{ wt.}\%$ H_2 measured from the PCI experiment (Fig. 2) if the presence of some oxides in the starting powders is considered. In addition, it is found that the ratio of the integrated areas of the de-convoluted MgH_2 (200) peak to LiH (200) peak after dehydrogenation at 210°C (Fig. 3) is 6.31. This ratio is close to the ratio of 5.64 (i.e., 89% of 6.31) obtained from a known mixture of $\text{MgH}_2 + \text{LiH}$ in a 1.00:0.53 volume ratio (i.e., 1:1 molar ratio), suggesting that the MgH_2 and LiH in the reaction product at 210°C are close to the 1:1 molar ratio.

In short, the present study unambiguously reveals that reaction (1), although having favorable thermodynamic driving force

[17], does not occur; instead, $\text{Li}_2\text{Mg}_2(\text{NH})_3$ is formed, either because of its fast reaction kinetics or its more favorable thermodynamic driving force than LiMgN . Furthermore, the high MgH_2 concentration does not mitigate the issue of NH_3 emission effectively, and the hydrogen storage capacity is lower than the $(2\text{LiNH}_2 + \text{MgH}_2)$ system because of the presence of un-reacted MgH_2 in the $(\text{LiNH}_2 + \text{MgH}_2)$ system.

Acknowledgements

This work was supported under the U.S. Department of Energy (DOE) Contract No. DE-FC36-05GO15008. The vision and support of Dr. Carole Read, DOE Technology Manager, is greatly appreciated. The authors are also indebted to Dr. Weifang Luo, Sandia National Laboratory, for kindly providing the MgH_2 powder used in this study.

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