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Journal of Alloys and Compounds 404–406 (2005) 392–395

Journal of ALLOYS AND COMPOUNDS

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# Towards a viable hydrogen storage system for transportation application

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Received 27 September 2004; received in revised form 12 January 2005; accepted 19 January 2005

**Abstract**

Hydrogen energy may provide the means to an environmentally friendly future. One of the problems related to its application for transportation is "on-board" storage. Hydrogen storage in solids has long been recognized as one of the most practical approaches for this purpose. The H-capacity in interstitial hydrides of most metals and alloys is limited to below 2.5% by weight and this is unsatisfactory for on-board transportation applications. Magnesium hydride is an exception with hydrogen capacity of ~8.2 wt.%, however, its operating temperature, above 350 °C, is too high for practical use. Sodium alanate ($NaAlH_4$) absorbs hydrogen up to 5.6 wt.% theoretically; however, its reaction kinetics and partial reversibility do not completely meet the new target for transportation application. Recently Chen et al. [1] reported that ($Li_3N + 2H_2 \Leftrightarrow LiNH_2 + 2LiH$) provides a storage material with a possible high capacity, up to 11.5 wt.%, although this material is still too stable to meet the operating pressure/temperature requirement. Here we report a new approach to destabilize lithium imide system by partial substitution of lithium by magnesium in the ($LiNH_2 + LiH \Leftrightarrow Li_2NH + H_2$) system with a minimal capacity loss. This Mg-substituted material can reversibly absorb 5.2 wt.% hydrogen at pressure of 30 bar at 200 °C. This is a very promising material for on-board hydrogen storage applications. It is interesting to observe that the starting material ($2LiNH_2 + MgH_2$) converts to ($Mg(NH_2)_2 + 2LiH$) after a desorption/re-absorption cycle.

*Keywords:* Hydrogen storage materials; Gas–solid reaction; Thermodynamic characterization

## 1. Introduction

Chen et al. [1] initially proposed lithium nitride/imide as a hydrogen storage material due to its high hydrogen capacity, up to 11.5 wt.%. The hydrogenation of lithium nitride is a two-step reaction as shown below:

$$Li_3N + H_2 \Leftrightarrow Li_2NH + LiH$$

$$Li_2NH + H_2 \Leftrightarrow LiNH_2 + LiH$$

$Li_3N$ absorbs 5.7 wt.% of hydrogen for the first step and 11.5 wt.% for the two steps in total. Since the hydrogen pressure for the reaction corresponding to the first step is very low, about 0.01 bar at 255 °C [1], only the second step, the reaction of $Li_2NH$ (lithium imide) with $H_2$, will be considered in the current study. Theoretically lithium imide can absorb 6.5 wt.% of hydrogen. According to Chen's results, the plateau pressure for imide hydrogenation is 1 bar at the relatively high temperature of 285 °C; therefore, destabilization is needed before on-board application.

Following the paper by Chen et al. [1], a number of papers were recently published on research on imides as hydrogen storage material. Chen et al. [2,3] further reported the effect of substitution of various elements on the stability of Li imide/amide. It is interesting that Hu et al. [4–6] reported kinetics study on Li imide/amide system and found that the reaction between $NH_3$, released from Li amide, and LiH is an ultra fast reaction. Ichikawa et al. [7,8] reported sorption reversibility and kinetics of Li amide/imide system. Nakamori et al. [9–12] reported the effect of Mg substitu-

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doi:10.1016/j.jallcom.2005.01.131

tion on stability of Li imide/amide systems by means of thermal-gravimetric analysis; powder XRD, Raman and neutron diffraction. Our previous paper [13] reported sorption isotherms of a mixture of ($2LiNH_2 + 1.1MgH_2$), showing desorption hydrogen pressure of 30 bar at 200 °C with hydrogen capacity of 4.5 wt.%.

In this study we report a successful approach to destabilize lithium imide by partial substitution of lithium with magnesium. A mixture of ($2LiNH_2$ + $MgH_2$) can be used to reversibly absorb 5.2 wt.% of hydrogen with hydrogen pressure of approximately 30 bar at 200 °C. This is a very promising hydrogen storage system for on-board transportation application.

## 2. Experimental details

The initial materials, lithium amide ($LiNH_2$) (purity 95%) and magnesium hydride ($MgH_2$) (purity 95%) were purchased from Aldrich and used without pretreatment. The fresh sample was a mixture of $LiNH_2$ and $MgH_2$ in a molar ratio of 2:1. All sample handling was carried out in a glove box under an argon atmosphere. Typically a 6 g mixture was mechanically milled in a SPEX 8000 high-energy mill using six WC milling balls, each weighing 9 g, under an argon atmosphere for 2 h. After ball milling the sample was transferred from milling pot into sample holder in a glove box. Sample preparation is described in detail elsewhere [13].

The sample holder with fresh sample was connected to a Sieverts' system and gradually heated to 240 °C. The amount of hydrogen desorbed was measured by the Sieverts' apparatus described elsewhere [13]. Hydrogen pressures were measured by a Teledyne Taber model 206 piezoelectric transducer, 0–3000 psi, with a resolution of $10^{-2}$ MPa and a Baratron capacitance manometer, 0–3 bar. During sorption the sample temperature and applied pressure were monitored and recorded by a Lab View-based software program.

The amount of hydrogen desorbed from the sample was calculated from the pressure changes in a calibrated volume using the ideal gas law.

High purity hydrogen (Matheson Trigas research purity, 99.999%) was introduced into the sample container upon the completion of a desorption run. Hydrogen contents in the samples are reported as weight percents of the whole sample weight.

Isotherm measurement was carried out after 3-absorption/desorption cycles at 220 °C. In this study desorption isotherms were measured at 200, 220 and 240 °C and an absorption isotherm was measured at 220 °C.

Powder X-ray diffraction (XRD) patterns were collected on a SCINTAG (XDS 2000) powder diffractometer at step increments of 0.02 °, measured during 0.5 s ($\lambda = 1.5406$ Å). The samples were protected from air and moisture by a thin Mylar sheet. Since the Mylar has three peaks in the 2$\theta$ range of 21–28° they were here manually excluded from the XRD-raw data file. Data was collected for fresh and re-absorbed samples. In the following text, fresh sample means the sample after ball milling, i.e. ($2LiNH_2$ + $MgH_2$).

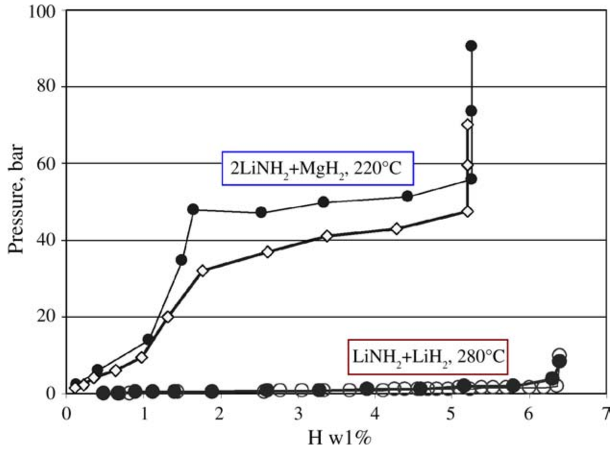

Fig. 1. Pressure-composition isotherms at 220 °C for ($2LiNH_2 + MgH_2$). Isotherms at 285 °C for ($LiNH_2 + LiH$) are included for comparison. Open symbols for desorption and filled symbols for absorption.

## 3. Results

### 3.1. Absorption/desorption isotherms

After 3-sorption cycles at 220 °C the absorption/desorption isotherms for this sample were measured at 220 °C and they are shown in Fig. 1. The isotherms for a sample of ($LiNH_2 + LiH$) at 280 °C [13] were included for comparison. It can be seen that Mg-substituted material can deliver 41 bar of hydrogen at 220 °C. It can also be seen

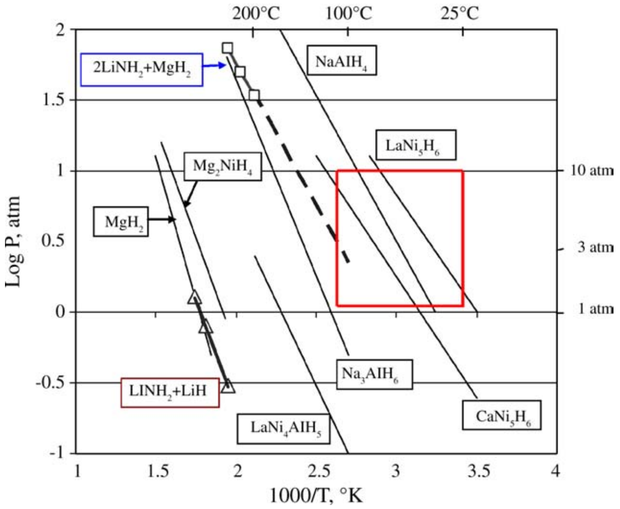

Fig. 2. Van't Hoff plots for ($2LiNH_2 + MgH_2$). Van't Hoff plots for some classical metal hydrides and sodium aluminium hydrides are included for comparison. The red box indicates the ideal operating pressure and temperature range for on-board application. Dashed line is the extrapolation of Van't Hoff plot for ($2LiNH_2 + MgH_2$). For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.

that substitution of LiH in ($LiNH_2 + LiH$) by (1/2 $MgH_2$) significantly destabilizes this system, which makes it a more practical hydrogen storage system.

### 3.2. *Van't Hoff plot*

Van't Hoff plot for this material is shown in Fig. 2 and those for some classical metal hydrides and sodium aluminium hydrides [14] are included for comparison. The red box in this plot indicates the ideal operating pressure and temperature range for hydrogen storage on-board application. This material ($2LiNH_2 + MgH_2$) may fall in the red box range according to the extrapolated line (the dashed line in Fig. 2) of the Van't Hoff plot. Desorption enthalpy was calculated from the Van't Hoff plot for ($2LiNH_2 + MgH_2$) to be approximately 39 kJ/mol-$H_2$.

## 4. Discussion

In order to understand the reactions in hydrogen sorption process for our new sample ($2LiNH_2 + MgH_2$) identifying the re-absorbed species is very important for future research on performance optimization. In this section we report the results on identification of the re-hydrogenated sample by the comparison of desorption profiles and powder XRD patterns of fresh and re-hydrogenated samples.

### 4.1. *Desorption profiles*

Since the fresh sample ($2LiNH_2 + MgH_2$) was in its hydrogenated-form, the 1st run was desorption. The sample was then re-hydrided at 220 °C and the 2nd desorption followed. Desorption profiles and the sample temperatures for 1st (fresh sample, $2LiNH_2 + MgH_2$) and 2nd (re-hydrogenated) runs are shown in Fig. 3.

It can be seen from this figure that at 220 °C the desorption of the re-hydrogenated sample completed within approximately half an hour, however, it lasted much longer for fresh sample, more than 15 h, even though the desorption temperature was 240 °C, which is higher than for re-hydrided samples (220 °C).

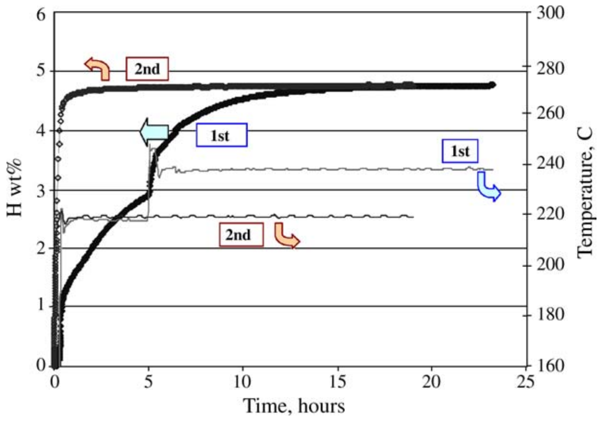

Fig. 3. Desorption profiles for ($2LiNH_2 + MgH_2$) for 1st and 2nd desorption runs at indicated temperatures. Symbols are for hydrogen weight percents, lines are for desorption temperatures.

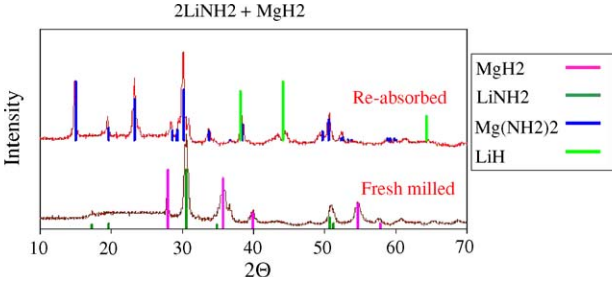

Fig. 4. Powder XRD patterns for fresh ($2LiNH_2 + MgH_2$) and re-hydrogenated samples.

### 4.2. *Comparison of powder XRD patterns of fresh and re-hydrided samples*

Fig. 4 shows powder XRD patterns of fresh and re-hydrided samples. The fresh sample contains mainly $LiNH_2$ and $MgH_2$, while the re-hydrided sample contains mainly LiH and $Mg(NH_2)_2$. This observation indicates that, upon re-hydrogenation, the de-hydrogenated sample converts to new compounds, $Mg(NH_2)_2$ and LiH. The following equation describes the reactions in the sorption process:

$$\begin{aligned} &MgH_2 + 2LiNH_2 \Rightarrow Li_2Mg(NH)_2 + 2H_2 \\ &\quad \Leftrightarrow Mg(NH_2)_2 + 2LiH \end{aligned}$$

Here we propose that the fresh sample, i.e. ($2LiNH_2 + MgH_2$), most likely transforms into a mixed ternary imide during the first dehydrogenation process since neither $Li_2NH$ nor MgNH, $Mg_3N_2$ were observed [13], however, more work on determination of its structure is ongoing, here we use $Li_2Mg(NH)_2$ only as a notation of the desorbed material. A new material, $Mg(NH_2)_2 + 2LiH$, was formed upon the completion of re-hydrogenation process. Therefore, the reversible sorption process is between ($Li_2Mg(NH)_2 + 2H_2$) and ($Mg(NH_2)_2 + 2LiH$), as described in the above equation. The isotherms reported above, indeed, represent this reaction and ($2LiNH_2 + MgH_2$) is not included in the reversible process. In this paper, however, ($2LiNH_2 + MgH_2$) is used as a symbol to denote the starting material we used.

## 5. Conclusion

Half substitution of Li by Mg in ($LiNH_2 + LiH$) can destabilize lithium imide/amide storage system significantly. The Mg-substituted material in this study can absorb 5.2 wt.% of hydrogen reversibly and delivers hydrogen at approximately 30 bar at 200 °C. The isotherms for ($2LiNH_2 + MgH_2$) at 200, 220 and 240 °C, and Van't Hoff plot as well, were generated. The enthalpy of desorption for this material was calculated to be 39 kJ/mol-$H_2$ from Van't Hoff plot. It is interesting to observe that the mixture of ($MgH_2 + 2LiNH_2$) converts to ($Mg(NH_2)_2 + 2LiH$) after a desorption/re-absorption cycle. This is a very promising on-board hydrogen storage material for transportation applications.

## Acknowledgements

W. Luo thanks Prof. T. Flanagan for kind advises and valuable suggestions. The authors also thank S. Spangler and K. Stewart for preparing sample, equipments and XRD tests. Also thanks to Jim Wang, Karl Gross for support and discussions. The authors thank Sandia LDRD Office for financial support to initiate this project. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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