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Feasibility and performance of the mixture of MgH_2 and $LiNH_2$ (1:1) as a hydrogen-storage material

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Abstract

A 1:1 molar ratio mixture of MgH_2 and $LiNH_2$ was predicted to release 8.1 wt.% H under moderate conditions. This binary mixture of MgH_2–$LiNH_2$ was found to be a multinary complex system induced by mechanical ball milling, due to the metathesis reaction between the initial components. It was found that dehydrogenation from this system was initialized by the formation of LiH and $Mg(NH_2)_2$ via such metathesis. The hydrogen sorption performance studied in this work shows a strong influence of the ball-milling parameters which determine the subsequent dehydrogenation pathways. An adequate ball milling facilitates hydrogen release, whereas insufficient milling results in a sluggish hydrogen desorption and severe NH_3 emission. A maximum amount of 7.3% was obtained with formation of the ternary nitride LiMgN; however, desorption temperatures of up to 600 °C had to be applied.

Keywords: Hydrogen storage; Thermodynamics; Metal amides; Hydrogen desorption

1. Introduction

Reversible hydrogen storage systems with high H-capacity are crucial to onboard vehicle applications. Although the US Deparment of Energy's 2015 performance target was revised down to a system gravimetric density of 5.5 wt.% instead of 9.0 wt.%, this still poses a great challenge for materials investigators: a chemical hydrogen storage material has to contain more than 7 mass% hydrogen which can be endothermically released at temperatures lower than 200 °C [1].

A Li–Mg–N–H system comprising a 1:1 molar ratio of $LiNH_2$–MgH_2 has been selected for further investigation [2]. Using first-principles calculations, Alapati et al. [3] predicted that the amide–hydride combination of $LiNH_2$ and MgH_2 at a 1:1 molar ratio would desorb 8.1 wt.% H via the following reaction:

$$LiNH_2 + MgH_2 \rightarrow LiMgN + 2H_2 \quad (1)$$

An enthalpy change of 29 kJ/mol H_2 was also calculated by means of density functional theory (DFT); this change falls in the range of ideal thermodynamics for a hydrogen-storage material. Following this prediction, Lu et al. [4] demonstrated experimentally an excellent agreement with the above prediction. A capacity of 8.1 wt.% was measured in the temperature range of 160–220 °C with LiMgN as dehydrogenation product. The desorbed product LiMgN doped with $TiCl_3$ could fully be rehydrogenated. In a report by Osborn et al. [5], however, only 3.4 mass% hydrogen release was measured at 210 °C. Moreover, a large amount of NH_3 emission was detected by thermogravimetry and no or little LiMgN was formed. In another attempt by Liu et al. [6], a total of 6.1 wt.% H_2 was obtained from the $LiNH_2$–MgH_2 system in two steps at 222 and 390 °C, respectively. The enthalpy change of dehydrogenation was found to be 45.9 kJ/mol H_2, which is much higher than the predicted value. Moreover, Mg_3N_2 was identified as the desorbed product instead of LiMgN. Different pathways and reaction products resulted due to various sample preparation conditions [7], reported by Liang et al. in a supplementary work to Ref. [6]. In a recent follow-up

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communication by Lu et al. [8], the authors also found that the reaction pathway of the $LiNH_2$–MgH_2 mixture was dependent on the mechanochemical processing conditions. Mild ball-milling conditions would favor the formation of LiMgN, i.e. the predicted dehydrogenation product.

The diverse performances of $LiNH_2$–MgH_2 found by different investigators indicate the complexity of this hydrogen-storage system. In order to investigate the feasibility and performance in relation to the sample processing, different ball-milling parameters, such as revolutions per minute (rpm) and duration, were tested with or without $TiCl_3$ as additive. Sampling at different desorption stages was performed to trace the phase and structure development during dehydrogenation.

2. Experimental

2.1. Sample preparation

$LiNH_2$ (Sigma Aldrich, >95%), MgH_2 (Alfa Aesar, 98%) and $TiCl_3$ (Acros Organics, 99%) were stored in a glovebox under Ar as a protecting atmosphere and used as received. For the ball-milling process, the starting chemicals were loaded into a milling vessel inside the glovebox, at a 1:1 molar ratio of $LiNH_2$:MgH_2, with varying amounts of $TiCl_3$. Ball milling was performed using a Retsch PM 400E. While keeping the powder to ball weight ratio constant at 1:90, revolution rates of 100, 150, 200 and 400 rpm were employed. Milling periods were varied from 2.5 to 96 h. $TiCl_3$ was used to investigate its effect on hydrogen sorption. Detailed ball-milling conditions are listed in Table 1, which covers various combinations of milling energy and duration.

Fourier transform infrared spectroscopy (FTIR) measurements were conducted using a Perkin Elmer Spectrum GX FTIR system. The powdery samples were mixed with KBr and pressed into pellets and measured at a resolution of 4 cm^{-1}.

Table 1
Sample preparation conditions.

Sample name	Milling conditions	$TiCl_3$ addition
S100 rpm-2.5 h	100 rpm, 2.5 h	–
S100 rpm-2.5 h-Ti	100 rpm, 2.5 h	5 wt.% $TiCl_3$
S100 rpm-48 h	100 rpm, 48 h	–
S100 rpm-48 h-Ti	100 rpm, 48 h	10 wt.% $TiCl_3$
S100 rpm-96 h	100 rpm, 96 h	–
S100 rpm-96 h-Ti	100 rpm, 96 h	10 wt.% $TiCl_3$
S150 rpm-10 h	150 rpm, 10 h	–
S150 rpm-15 h	150 rpm, 15 h	–
S150 rpm-20 h	150 rpm, 20 h	–
S150 rpm-25 h	150 rpm, 25 h	–
S150 rpm-30 h	150 rpm, 30 h	–
S200 rpm-5 h	200 rpm, 5 h	–
S200 rpm-10 h	200 rpm, 10 h	–
S200 rpm-10 h-Ti	200 rpm, 10 h	5 wt.% $TiCl_3$
S200 rpm-20 h	200 rpm, 20 h	–
S400 rpm-20 h-Ti	400 rpm, 20 h	16 wt.% $TiCl_3$

Phase identification was performed by X-ray diffractometry (XRD) on a Philips X'PERT diffractometer (Cu Kα radiation). In order to protect samples against air, a sample-holder consisting of a Kapton foil hood and a silicon single-crystal base was used. The powdery samples were spread evenly onto the silicon crystal and then sealed with the Kapton foil hood inside the glovebox. The measurement was conducted in the 2θ range of 10–80° at a step length of 0.02°.

Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204 HP housed inside the glovebox to detect heat effects accompanying hydrogen desorption. Samples were heated at 5 °C min^{-1} under 3 bar He.

For the quantification of H desorption, a carefully calibrated homemade Sieverts system was used to measure the H_2 volume evolved in a temperature programmed desorption (TPD) mode or isothermal desorption mode. The TPD mode was run at a temperature ramping of 5 °C min^{-1} from 30 to 600 °C and held at 600 °C for 1 h, whereas for the desorption isotherms the temperature was first raised to 225 °C at 5 K min^{-1} and held at this temperature for at least 20 h.

The N and H contents were determined by elemental analysis using an instrument from Elementar Analysensysteme GmbH.

3. Results and discussion

3.1. Metathesis reaction through ball milling

The amide–hydride combination of $LiNH_2$–MgH_2 at 2:1 molar ratio was first investigated by Luo [9] as a hydrogen-storage system. A considerable improvement in hydrogen-sorption properties was achieved compared to its predecessor $LiNH_2$–LiH system [10]. Interestingly, after cycling of the system, $Mg(NH_2)_2$ and LiH were formed, instead of $LiNH_2$ and MgH_2. It was later recognized that there exists a metathesis conversion from $LiNH_2$ and MgH_2 to $Mg(NH_2)_2$ and LiH that could be achieved by heating $LiNH_2$ and MgH_2 at 200 °C under H_2 pressure [11].

$$2LiNH_2 + MgH_2 \rightarrow Mg(NH_2)_2 + 2LiH \quad (2)$$

In the presence of $LiBH_4$, this conversion takes place at lower temperature [12].

FTIR spectra are shown in Fig. 1 after milling at 100 rpm for various durations. For the shortest milling time of 2.5 h, the characteristic N–H vibrations of the primary component $LiNH_2$ at 3312 and 3258 cm^{-1} were clearly detected for the samples with and without $TiCl_3$ addition. Differences appear as milling was extended to 48 h. While the doublet of 3312 and 3258 cm^{-1} persists in the pure $LiNH_2$–MgH_2 sample (S100 rpm-48 h), broadening and shifting of the absorbance become obvious with the $TiCl_3$-doped sample (S100 rpm-48 h-Ti), indicating the formation of $Mg(NH_2)_2$ at 3272 and 3326 cm^{-1}. With