Hydrogen storage properties of LiNH₂–LiH system with MgH₂, CaH₂ and TiH₂ added

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ABSTRACT

The addition of different metal hydrides to Li–N–H system offers a possible way to modify its thermodynamic properties and/or the dehydrogenation/hydrogenation kinetics. In this paper we report the hydrogen storage properties of LiNH₂–LiH system with MH₂ added (M = Mg, Ca, Ti) and clarify the chemical interactions occurring during hydrogen cycling. Detailed structural investigations reveal that during heating under hydrogen, MH₂ (M = Mg, Ca) reacts with LiNH₂ to form Li₂Mg(NH)₂ and 2CaNH–Ca(NH₂)₂ solid solution, with simultaneous hydrogen release. Formation of the Li₂NH–CaNH mixture after dehydrogenation of the LiNH₂–LiH with CaH₂ added is proved by XRPD and FTIR, providing a new reversible pathway for hydrogen storage in the Li–Ca–N–H system. Notable improvement in the dehydrogenation temperature and kinetics was observed for LiNH₂–LiH system with CaH₂ and MgH₂ added, without clear effects in the case of TiH₂. The kinetic analysis reveals that dehydrogenation process is diffusion-controlled and the beneficial effect of MgH₂ and CaH₂ is due to the enhancement of Li⁺ mobility.

Introduction

Hydrogen storage remains one of the most challenging technological barriers to the advancement of hydrogen fuel cell technologies for mobile applications. Although there are a variety of ways to store hydrogen, solid-state hydrogen storage provides improved volumetric energy densities in comparison with compressed gas or liquid hydrogen, with a combination of safe and efficient conditions at moderate pressure and temperatures. Recently, much attention has been focused on complex metal hydrides storage systems,

such as borohydrides and amides [1–11]. In particular, the lithium amide (LiNH₂)-lithium hydride (LiH) system has been proposed as a possible candidate [7], because it offers relatively high gravimetric storage capacity (6.5 wt.% of theoretical value) and reversibility in the hydrogen storage:

$$LiNH_{2(s)} + LiH_{(s)} \leftrightarrow Li_2NH_{(s)} + H_{2(g)} \qquad (1)$$
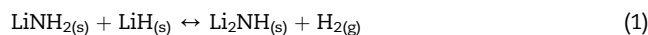
However, the temperatures required for the dehydrogention/rehydrogenation of reaction (1) are still too high for the application of Li–N–H system as commercial hydrogen
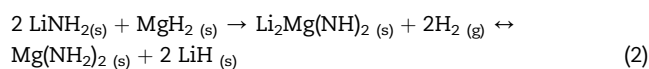
storage material. One strategy to modify the thermodynamic properties with positive effects on the kinetics is the development of new ternary metal–N–H systems, such as Li–Mg–N–H [12–15], Li–Al–N–H [16–18], Li–Ca–N–H [19–22] and others as Li–Ti–N–H [10,23–25], which were investigated on their interaction with hydrogen. In fact, different improvements in the dehydrogenation rates and/or in the thermodynamic parameters were observed by substituting LiH with MgH_2. Luo et al. [12] studied the dehydrogenation of a mixture of $2LiNH_2$–MgH_2 and showed that $LiNH_2$ reacts with MgH_2 to form Li_2NH, $MgNH$, and H_2 as products, with better hydrogen storage performance than Li–N–H system. The decomposition enthalpy for the $2LiNH_2$–MgH_2 mixture was found to be 34 kJ/mol of H_2, which means a relevant reduction compared to 51 kJ/mol for the $LiNH_2$–LiH mixture [13]. Initially, it was thought that Li_2NH and $MgNH$ constitute the products of dehydrogenation of the $2LiNH_2$–MgH_2 mixture. Additional studies demonstrate that the dehydrogenated sample contain $Li_2Mg(NH)_2$ and the rehydrogenated product obtained from $Li_2Mg(NH)_2$ is not $2LiNH_2 + MgH_2$ but $Mg(NH_2)_2 + 2LiH$ [15], as described in:

$$2\ LiNH_{2(s)} + MgH_{2\ (s)} \rightarrow Li_2Mg(NH)_{2\ (s)} + 2H_{2\ (g)} \leftrightarrow$$
$$Mg(NH_2)_{2\ (s)} + 2\ LiH_{\ (s)} \qquad (2)$$

Xiong et al. [8] and Wu [21] reported that hydrogenation/dehydrogenation behavior and final products of the interaction in Li–Ca–N–H and Li–Mg–N–H systems are comparable. For example, $Li_2Ca(NH)_2$ was synthesized by dehydrogenation of $LiNH_2$–$2CaH_2$, in similar way than $Li_2Mg(NH)_2$ is obtained by the reaction (2). However, dehydrogenation from the $2LiNH_2$–CaH_2 mixture starts at about 70 °C, while for $LiNH_2$–MgH_2 and $LiNH_2$–LiH composites hydrogen release was observed over 100 °C and 150 °C, respectively [8]. Although $2LiNH_2$–CaH_2 mixture (~4.5 wt.%) has lower hydrogen capacity than $LiNH_2$–MgH_2 (~5.5 wt.%), it was demonstrated that the mechanism of the reversibility involves the formation of $CaNH + Li_2NH$ in the hydrogenated state [21]:

$$2\ LiNH_{2(s)} + CaH_{2\ (s)} \rightarrow CaNH_{(s)} + Li_2NH_{(s)} + 2H_{2(g)} \leftrightarrow$$
$$Ca(NH_2)_{2\ (s)} + 2LiH_{(s)} \qquad (3)$$
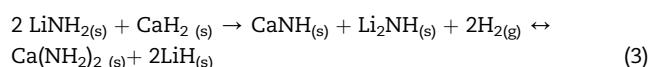
The appearance of $Li_2Ca(NH)_2$ is only possible after the previous formation of $CaNH$ and Li_2NH during dehydrogenation at high temperature (>300 °C). Further work using different $LiNH_2$–CaH_2 molar ratios (2:1, 3:1 and 4:1) [22] demonstrates that reaction involved in the reversibility depends on the starting molar ratio. In the case of 4:1 molar ratio, the $LiNH_2$–CaH_2 mixture transforms to a new compound with a composition of $Li_4CaN_4H_6$ during dehydrogenation, while rehydrogenation gives $LiNH_2$, LiH and the solid solution $CaNH$–$Ca(NH_2)_2$ [22]. So far, the hydrogen storage reversibility pathway for Li–Ca–N–H system shows different compounds depending on local composition changes and temperature/pressure conditions [19,20,22].

In the case of Ti metal as possible doping of $LiNH_2$, diverse Ti-containing additives were reported as the effective catalysts in the Li–N–H system [23–25]. Excellent reversibility was shown in the presence of $TiCl_3$, but the hydrogen storage

capacity was reduced [23]. In addition, the effect of Ti compounds with different sizes was also examined [24]. The studies revealed that nanoparticles of Ti or TiO_2 were effective in reducing the desorption temperature. However, micronsized Ti and TiO_2 did not show a good catalytic effect. Therefore, it was suggested that the particle size of the precursor may be an important factor to act as an effective catalyst. Studies using X-ray absorption spectroscopy measurements [26] indicate that the Ti atoms in the Ti compounds have a common electronic state, in particular suggests the formation of $TiCl_3.5NH_3$. Nevertheless, any of these studies includes the use of TiH_2 in enough amounts to form the $LiNH_2$–$2TiH_2$ mixture. A possible reaction between $LiNH_2$–$2TiH_2$ involves the formation of Ti_2N and LiH as solid products during dehydrogenation [27]. Using density functional theory calculations, the enthalpy of this reaction was estimated to be low, but this needs to be investigated experimentally.

Motivated by these previous investigations, a comparative study of the hydrogen storage properties of $LiNH_2$–LiH system with MH_2 added (M = Mg, Ca and Ti) was performed using constant amount of additive and same experimental conditions. In this work, different interactions between MH_2 and $LiNH_2$ were identified, which determine the nature of the reversible reaction. The analysis was extended in order to examine the effect of additive on the thermodynamics and kinetics of the Li–N–H system. A proposal of the reaction pathway for each system is further discussed.

Experimental

Synthesis of the composites

The starting materials were commercial $LiNH_2$ (Aldrich, 95%), LiH (Fluka, 95%), TiH_2 (Aldrich, 98%), CaH_2 (Merck, 95%) and MgH_2 (Aldrich, 98%), which are referred as LN, L, Ti, Ca and Mg, respectively. All samples were handled in an MBraun Unilab glove argon-filled glove box, with oxygen and moisture levels lower than 1 ppm. For all studies, high purity hydrogen (Linde, 99.999%) and argon (Linde, 99.999%) were used.

The sample preparation was carried out by mechanical milling of the following mixtures: $LiNH_2$-1.6LiH (LNL), $LiNH_2$-1.6LiH-0.2TiH_2 (LNLTi), $LiNH_2$-1.6LiH-0.2CaH_2 (LNLCa) and $LiNH_2$-1.6LiH-0.2MgH_2 (LNLMg). The amount of LiH was added in excess to minimize the emission of NH_3 [18]. The mechanical milling was performed using a sequence of 15 min milling and 10 min pause in a planetary ball mill at 500 rpm (Fritsch Pulverisette 6) under 0.1 MPa of argon. About 1.5 g of mixture was placed in an 80 mL stainless steel mill chamber with 5 stainless steel balls of 14.5 mm of diameter. To avoid NH_3 emission, the mill chamber was opened after 1 h, 2 h and 3 h to mix the powders and eliminate possible dead zones. All samples were ball milled for 5 h with a ball to powder ratio of 53:1.

Characterization of the composites

Structural, textural, thermal and hydrogen storage properties of the as-milled and as-cycled samples were studied using differential scanning calorimetry (DSC, TA 2910 calorimeter), powder X-ray diffraction (XRPD, Philips PW 1710/01