Chapter 2

AMIDE-HYDRIDE SYSTEMS FOR HYDROGEN STORAGE

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ABSTRACT

The lack of safe, reliable and efficient hydrogen storage systems remains one of the key obstacles to the hydrogen economy. Amide-hydride systems are a promising class of hydrogen storage materials particularly for vehicular applications. This is because these systems possess relatively high hydrogen storage capacities and release hydrogen under moderate conditions. However, they generally suffer from poor kinetics and their thermodynamic properties still need to be improved, in addition to clearly understanding their reaction mechanisms. A wide range of amide-hydride systems have been studied since the first investigation of the reversible hydrogen uptake of lithium nitride was reported in 2002. Research efforts are being made to enhance the hydrogen storage performances of these amide-hydride systems through various strategies such as addition of catalysts and modifying the composition, amongst others. This chapter will provide an overview of select amide-hydride systems with a focus on the advances made towards improving the hydrogen storage properties of these systems.

Keywords: hydrogen storage, amide-hydride, lithium nitride

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INTRODUCTION

One of the key barriers to the global implementation of the Hydrogen Economy is the lack of suitable hydrogen storage systems, particularly for vehicle applications. The low volumetric density of hydrogen makes it difficult to store large quantities within a small volume. Conventionally, hydrogen is stored as compressed gas in high pressure tanks or liquefied hydrogen in cryogenic tanks. However, tanks are heavy and bulky, and there are associated safety risks with compressed hydrogen. Meanwhile liquefying hydrogen is an energy-intensive process since hydrogen boils at -253°C. Many efforts have been made to store hydrogen in various solid materials. In solid-state storage, hydrogen is either physisorbed into a material with high surface area and suitable pore structure (e.g., metal-organic frameworks) or chemisorbed as a metal, complex or chemical hydride. Physisorption is beneficial in terms of kinetics of hydrogen uptake/release and reversibility of hydrogen uptake. However, chemisorption results in relatively high hydrogen storage capacities.

Key criteria including high volumetric and gravimetric storage capacities, favourable thermodynamics, fast kinetics, good reversibility and long-term cyclability must be fulfilled for a practical hydrogen storage system (US DOE, 2017). Presently, no solid-state material simultaneously satisfies these criteria for on-board applications. In particular, hydrogen storage materials consisting of light elements are advantageous for on-board hydrogen storage applications as they can afford a high gravimetric density. This is the case of metal–N–H systems, which show promise due to their high hydrogen capacities. These systems have received considerable attention following the initial report of the Li-N-H for hydrogen storage in 2002 (Chen et al., 2002). There have been several reviews in this area (Langmi and McGrady, 2007; Cao et al., 2012; Zhang and Wu, 2017), which the reader can refer to for further details. This chapter provides an overview of select amide-hydride systems for hydrogen storage applications. In particular the three systems Li-N-H, Li-Mg-N-H and Li-Ca-N-H are discussed.

LI-N-H SYSTEM

The pioneer work on the Li-N-H system for hydrogen storage was carried out by Chen et al., (2002) over 15 years ago, who investigated the reversible hydrogen uptake of lithium nitride, Li3N. Lithium nitride is typically obtained by reacting Li metal and N2 gas at elevated temperature. Lithium nitride exists in three polymorphic forms namely; α-Li3N, β-Li3N and γ-Li3N. α-Li3N is the stable form at room temperature and pressure and is synthesised from its constituent elements under ambient conditions. The structure of α-Li3N is made up of graphite-like layers of Li hexagons containing a nitride ion in the
middle of each hexagon. The Li₆N hexagons are capped by two further Li ions located above and below the plane, which gives an Li₆N hexagonal bipyramidal configuration (Zintl and Brauer, 1935; Rabenau and Schulz, 1976). β- Li₃N which has a sodium arsenide (Na₃As) structure is produced from α-Li₃N at high pressures of about 4.2 kbar and 300 K (Mali et al., 1987). Meanwhile γ-Li₃N has the structure of Li₃Bi and can be produced from β- Li₃N at extreme pressures of 35-45 GPa, and is stable up to 200 GPa (Lazicki et al., 2005).

The hydrogenation of Li₃N is reported to occur via two main steps forming an imide-hydride product in the first step and an amide-hydride product in the second step (Hu et al., 2004):

\[
\text{Li}_3\text{N} + \text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} \quad \Delta H = -116 \text{ kJ/mol} \tag{1}
\]

\[
\text{Li}_2\text{NH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + \text{LiH} \quad \Delta H = -45 \text{ kJ/mol} \tag{2}
\]

The above two reactions result in a theoretical hydrogen storage capacity of 5.5 and 6.5 wt.%, respectively. From equation 1, Li₂NH is formed by partial hydrogenation of Li₃N. Upon hydrogenation of Li₃N, Li in the Li layer tend to detach from the Li₃N structure and react with hydrogen to yield LiH. Concomitantly, there is substitution of H for Li, which then bonds with N to generate Li₂NH. Juza and Opp (1951a) suggested Li₂NH has a cubic crystal structure with \(Fm-3m\) space group and lattice parameters of \(a = 5.047 \, \text{Å}\). However, in another study, powder neutron diffraction revealed the space group of this imide to be \(F-43m\) with almost identical lattice parameters as the former structure (Ohoyama et al., 2005). Even though both studies demonstrated cubic crystal structure with disordered hydrogen atoms, it was later shown theoretically that the \(F-43m\) unit cell was the most stable arrangement (Song and Guo, 2006).

The reverse reaction from equation 2 shows that LiNH₂ reacts with LiH to generate Li₂NH in an amide-hydride reaction. Using powder X-ray diffraction, Juza and Opp (1951b) initially reported the solid-state structure of LiNH₂ to exist in the space group \(I-4\). Using powder neutron diffraction, Yang et al., (2006) further confirmed the crystal structure of LiNH₂ to be tetragonal with \(I-4\) space group and lattice parameters of \(a = 5.03442 \, \text{Å and } c = 10.25558 \, \text{Å}\), and the N-H bonds were shown to be substantially longer in agreement with theoretical predictions (Miwa et al., 2005; Herbst and Hector, 2005). Lithium amide (LiNH₂) was first prepared by Titherley in 1894 by a direct reaction of metallic Li and NH₃ (Titherley, 1894). It can also be prepared by reacting LiH with NH₃ at 4 bar and 100°C or by ball milling pure LiH under 4 bar of NH₃ (Hu and Ruckenstein, 2003a; Leng et al, 2006a). Lithium hydride (LiH) crystallizes in the rock-salt structure and is usually synthesised by reacting Li metal with hydrogen gas at elevated temperatures. At ambient pressure, LiH was prepared by contacting liquid Li metal at 750°C with purified hydrogen for 12 h (Messer et al., 1958). Howie et al., (2012)
Henrietta W. Langmi

reported the synthesis of LiH from its pure constituents at room temperature and pressures as low as 500 bar. In the presence of catalysts, metallic Li could be quantitatively hydrogenated to LiH at 25–50°C and ambient pressure within 2–5 h (Shih-Tsien et al., 1985).

Chen et al., (2002) reported in their initial investigation of Li3N that hydrogen absorption started at around 100°C, and reached 9.3 wt.% after maintaining the sample at 255°C for 30 min. Upon applying high vacuum at temperatures below 200°C, approximately 6.3 wt.% H2 was released. Complete hydrogen desorption was only achieved at temperatures above 320°C. Below 160°C, the reaction between Li3N and H2 is slow (Meisner et al., 2005) but a rapid hydrogen uptake is achieved between 170 and 210°C (Chen et al., 2002). At temperatures up to 280°C, the reversible hydrogen storage capacity of Li3N is about 5.5 wt.% because of the partial dehydrogenation of hydrogenated Li3N (Hu et al., 2005). Complete reversibility of the hydrogenation reaction of Li3N is a difficult task requiring high temperatures over long periods (Chen et al., 2002; Hu and Ruckenstein, 2003a,b). A low rehydrogenation capacity of only 0.4 wt.% was achieved for recovered Li3N material from dehydrogenation at 400°C due to sintering of the material which resulted in deactivation (Hu et al., 2005).

Hu and Ruckenstein (2004) demonstrated Li3N can be partially oxidised forming Li2O/Li3N hybrid material and hydrogenation/dehydrogenation pretreatment of this hybrid leads to faster kinetics, enhanced reversibility and excellent stability relative to pristine Li3N. The reversible capacity of Li2O/Li3N reached 5.0 wt.% in only 3 min at 180°C, and the reversible hydrogen storage capacity and absorption rate remained constant after six cycles at 198°C. The presence of Li2O could also hinder sintering of the material by preventing the large temperature jump that usually occurs during the initial hydrogenation. However, direct doping of Li3N with ca. 5 mol% Li2O followed by annealing revealed that both binary compounds occurred as separate phases with Li2O acting as a spectator in the hydrogen storage reactions with no evidence of enhanced Li+ or H+ mobility (Langmi et al., 2010). Hu et al., (2004) further showed that hydrogen storage stability of Li3N can be enhanced by preheating Li3N in vacuum at 400°C.

Although Chen et al., (2002; 2003) reported that the first stage in dehydrogenation of the Li-N-H system may proceed according to equation 3 i.e., a direct reaction between LiNH2 and LiH, Hu and Ruckenstein (2003a) demonstrated that this dehydrogenation consists of two primary steps as shown in equations 4 and 5. Chen et al., (2002) had postulated that the interaction of LiNH2 with LiH is likely driven by the reaction between the positively charged hydrogen (Hδ+) in the amide and the negatively charged hydrogen (Hδ−) in the hydride generating H2.

\[
LiNH_2 + LiH \rightarrow Li_2NH + H_2 \quad (3)
\]

\[
2LiNH_2 \rightarrow Li_2NH + NH_3 \: \Delta H = +84 \: kJ/mol \quad (4)
\]
\[ \text{LiH} + \text{NH}_3 \rightarrow \text{LiNH}_2 + \text{H}_2 \quad \Delta H = -42 \text{kJ/mol} \] (5)

Below 400°C, the formation of NH\(_3\) is thermodynamically favourable. Reaction (4) occurs very fast, in as little as 25 ms, which results in suppression of the NH\(_3\) generated during the dehydrogenation reaction (Hu and Ruckenstein, 2003a). It was also revealed from NMR studies that NH\(_3\) is first formed at a low temperature of about 30°C followed by its fast reaction with LiH at 150°C. In another study, it was reported that the dehydrogenation of the amide-hydride system is controlled by NH\(_3\) diffusion through the Li\(_2\)NH product layer on the exterior of the shrinking LiNH\(_2\) core (Shaw et al., 2008). However, Hino et al., (2005a) reported the unavoidable contamination of hydrogen with about 0.1% NH\(_3\) during dehydrogenation of a mixture of LiH and LiNH\(_2\) at temperatures up to 400°C in a closed system. Such release of NH\(_3\) is detrimental to the PEM fuel cell as it can poison the fuel cell catalyst.

Although numerous studies have investigated hydrogenation/dehydrogenation of the Li–N–H system, the underlying reaction pathway is still unclear. More recent investigations have indicated a more complex reaction pathway for the Li–N–H system than initially depicted by Chen et al., (2002). In a subsequent study by Chen et al., (2003), non-stoichiometric phases in the Li–N–H system was inferred. In this case, from the dehydrogenation product of a LiNH\(_2\) + 2LiH mixture, a cubic phase like that of Li\(_2\)NH, but with a ‘shrunken lattice’, was tentatively assigned a composition of Li\(_{2.2}\)NH\(_{0.8}\). From deuteration studies of Li\(_3\)N, Weidner et al., (2007) reported the presence of non-stoichiometric phases with composition-dependent lattice parameters as well as the identification of Li\(_4\)ND and the inhibition of LiD formation at low deuterium content. They therefore postulated that non-stoichiometric phase is intermediate between Li\(_4\)ND and Li\(_2\)ND, with a composition of Li\(_{2+y}\)ND. By employing \textit{in-situ} synchrotron X-ray powder diffraction to investigate the hydrogenation and dehydrogenation reactions of the Li–N–H, Makepeace et al., (2014) reported the formation of non-stoichiometric intermediate species of the form Li\(_{1+x}\)NH\(_{2-x}\). Two models were proposed that demonstrated the possibility of non-stoichiometric phases across the whole range of hydrogen content in the Li–N–H system (Bull et al., 2010). Firstly, the Li\(_{2+y}\)NH\(_{1+y}\) intermediate that forms during the LiNH\(_2\) to Li\(_2\)NH transition and secondly, the Li\(_{2+y}\)NH intermediate that forms during the Li\(_3\)NH to Li\(_2\)NH transition. Non-stoichiometric phases containing N\(^3-\), H\(^-\) and (NH)\(^2-\) anions have been proposed to form between Li\(_3\)NH and Li\(_2\)NH, which react to form a non-stoichiometric solid solution of composition Li\(_{1.5-2x}\)N\(_{1-x}\)H\(_{1.5-x}\)(NH)\(_x\) (Tapia-Ruiz et al, 2013).

Many studies have focussed on the reversible reaction between LiNH\(_2\) and LiH (equation 3) since this reaction has a smaller enthalpy change and can potentially release 6.5 wt.% hydrogen relatively easily. In order to enhance performance of the Li-N-H system various approaches such as modification of the microstructure of the material and employment of catalysts or dopants have been pursued. For enhancement of the kinetics
of the Li-N-H system, ball milling has been employed which reduced the particle sizes of the reactants and improved the kinetics of the reaction (Varin et al., 2010; Yao et al., 2007). Markmaitree et al., (2006) demonstrated that ball milling lowered the onset decomposition temperature of LiNH₂ from 120°C to room temperature. Nevertheless, a temperature of 230°C was needed for complete decomposition. Reduced particle size, increased surface area and decreased activation energy were identified as the principal factors responsible for the enhanced decomposition of LiNH₂. Using a combination of microstructure modification (such as by ball milling) and the addition of a catalyst the desorption temperature and kinetics of hydrogen uptake/release can be improved. The effect of catalysts on the desorption properties of ball-milled mixtures of LiNH₂ and LiH (1:1 molar ratio) with 1 mol% of several catalysts (Fe, Co, or Ni nanoparticles, TiCl₃ and VCl₃) was investigated (Ichikawa et al., 2004; 2005a). In the absence of a catalyst hydrogen was released between 180 and 400°C alongside a considerable amount of NH₃ (Ichikawa et al., 2004). The best hydrogen desorption properties was recorded for the mixture containing 1 mol% TiCl₃. The latter desorbed 5.5–6.0 wt.% hydrogen at 150–250°C and displayed relatively fast kinetics and good reversibility with no NH₃ release (Ichikawa et al., 2005a). The catalytic effect on the hydrogen storage properties of LiNH₂/LiH system can be further affected by the particle size of added catalysts (Isobe et al., 2005). The LiNH₂/LiH mixtures suffer from unfavorable dehydrogenation enthalpy with a minimum temperature of 255°C required to reach an equilibrium pressure of 1 bar during dehydrogenation (Cao et al., 2012). Other research has focussed primarily on the thermodynamic destabilisation of reaction 3 by partial substitution of Li with other elements of higher electronegativity. This is achieved by substituting either LiNH₂ or LiH with the corresponding metal (M)-based compound resulting in Li-M-N-H systems such as the selected systems discussed in the next sections of this chapter.

**Li-Mg-N-H System**

Among the mixed metal amide-hydride systems, Li-Mg-N-H has been most widely studied for hydrogen storage applications. Various combinations of either LiNH₂ and MgH₂ or LiH and Mg(NH₂)₂ can give rise to this mixed metal amide-hydride system. MgH₂ on its own has received attention as a hydrogen storage material due to its high gravimetric and volumetric hydrogen storage capacity (7.6 wt % H₂ and 110 g H₂/L, respectively). However, it suffers from sluggish kinetics. MgH₂ occurs in several forms; α-MgH₂ crystallises in the tetragonal space group (rutile-type structure, P4₂/mmm) at ambient conditions (Zachariasen et al, 1980; Bastide et al., 1963). At high temperatures and pressures, a structural rearrangement occurs causing α-MgH₂ to transform into the orthorhombic γ-MgH₂ with α-PbO₂ type structure. Meanwhile the solid-state structure of Mg(NH₂)₂ consists of a tetragonal unit cell with space group I₄₁/acd (Jacobs et al., 1969),
and this amide can be prepared by reacting MgH$_2$ (or Mg) with NH$_3$ (Serby et al., 2007). Decomposition of Mg(NH$_3$)$_2$ at elevated temperatures of about 200 °C yields the imide (MgNH) and NH$_3$ (Leng et al., 2004a). In the Li-Mg-N-H system, Li is partially substituted with Mg, which has a higher electronegativity. A key factor in the destabilisation of the [NH$_2$]$^-$ anion is charge compensation by the Li$^+$ cation, thus, by substituting with a more electronegative element like Mg, the ionic interaction with this anion is weakened (Orimo et al., 2004).

The reaction between LiNH$_2$ and MgH$_2$ was first reported in 2004. When LiH is replaced with MgH$_2$ in the Li-N-H system the plateau pressure is increased considerably from 0.1 MPa at 250°C for the Li-N-H system to 3 MPa at 200°C for the Li-Mg-N-H system (Luo, 2004a; Xiong et al., 2004). When LiNH$_2$ was partially substituted with 10 mol% Mg, the H$_2$ desorption temperature reduced substantially compared to unsubstituted LiNH$_2$ (Nakamori and Orimo, 2004). Furthermore, the temperature decreased as the Mg content was increased (Orimo et al., 2004). Shahi et al., (2008) investigated a ball-milled mixture of LiNH$_2$ and MgH$_2$, and described the dehydrogenation reaction as follows:

$$2\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{Li}_2\text{NH} + \text{MgNH} + 2\text{H}_2 \leftrightarrow \text{Mg(ND)}_2 + 2\text{LiH} \quad (6)$$

A mixture of LiNH$_2$ and MgH$_2$ was found to readily decompose at about 200°C when 30 bar hydrogen gas was applied (Luo, 2004b). A hydrogen storage capacity of 4.5 wt.% was achieved and the enthalpy change was 39 kJ/mol. The PCT isotherms revealed that the decomposition occurred through a two-step process (Luo and Sickafouse, 2006). The sloping part of the PCT plot could attributed to the formation of an intermediate Li$_2$MgN$_2$H$_3$, and the plateau could be ascribed to the uptake of three hydrogen atoms leading to the formation of Mg(NH$_2$)$_2$ and LiH.

An investigation was conducted on the reaction of 2:1 molar ratio of LiNH$_2$ and MgH$_2$ at 50-350 °C (Xiong et al., 2004). It was shown that hydrogen was released at 166°C compared to 272°C for the ternary Li-N-H system. Analysis of the dehydrogenated material by XRD revealed that it was the mixed imide Li$_2$Mg(NH)$_2$ depicted in equation 7.

$$2\text{LiNH}_2 + \text{MgH}_2 \leftrightarrow \text{Li}_2\text{Mg(NH)}_2 + 2\text{H}_2 \quad (7)$$

However, upon rehydrogenation, XRD analysis revealed that the rehydrogenated material consisted of Mg(NH$_2$)$_2$ and LiH and not the initial components i.e., LiNH$_2$ and MgH$_2$, suggesting that it is thermodynamically favourable for the -NH$_2$ group to bond with Mg instead of Li. Xiong et al. (2004) thus suggested that the following chemical reaction (equation 8) is responsible for reversible hydrogen storage in the Li-Mg-N-H system.

$$2\text{LiNH}_2 + \text{MgH}_2 \leftrightarrow \text{Li}_2\text{Mg(NH)}_2 + 2\text{H}_2$$
\[ Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2 \]

(8)

Equation 7 gives a theoretical hydrogen storage capacity of 5.6 wt.%. Further analysis indicated a more complex reaction mechanism than the single-step reaction depicted in equation 7 (Xiong et al., 2006).

Rijssenbeek et al., (2008) reported that the crystal structure of Li₂Mg(NH)₂ undergoes two structural transitions from orthorhombic (with space group \( Iba2 \) or \( Ibam \) and lattice parameters \( a = 9.7837 \text{ Å}, b = 4.9893 \text{ Å}, c = 5.1984 \text{ Å} \)) to primitive (with space group \( P-43 \text{ m} \) and lattice parameter \( a = 5.0268 \text{ Å} \)) at intermediate temperature (350°C) followed by a face-centered cubic crystal structure (with space group \( Fm-3 \text{ m} \) and lattice parameter \( a = 5.0988 \text{ Å} \)) at high temperature (500°C). The structural changes arise as a result of disordering of the Li, Mg and cation vacancies as a function of temperature. Osborn et al., (2007) found that for a 1:1 mixture of LiNH₂ and MgH₂, decomposition at 210°C leads to the formation of Li₂Mg₂(NH)₃, LiH and MgH₂. The hydrogen desorption capacity for such a system reached 6.1 wt.% and an endothermic enthalpy value of 45.9 kJ/mol was achieved (Liu et al., 2008).

There has been many efforts towards combining Mg(NH₂)₂ and LiH in various molar ratios (Ichikawa et al., 2005b; Leng et al., 2005; Leng et al., 2004b; Luo and Sickafouse, 2006; Nakamori et al., 2004). A 3:8 molar mixture of Mg(NH₂)₂ and LiH that was initially ball-milled and then dehydrogenated at 200°C under high vacuum (Ichikawa et al., 2005b) was investigated. From P–C–T measurements at 200 °C two-plateaux-like behaviour was observed and the sample was fully hydrogenated under 9 MPa H₂. On the other hand, the P–C–T curve at 150°C displayed a single-plateau-like behaviour and was only partially hydrogenated under the same H₂ pressure. Leng et al., (2005) also investigated a 3:8 molar mixture of Mg(NH₂)₂ and LiH and reported that hydrogen desorption began at 140°C, with a peak desorption at 190°C, and negligible NH₃ emission. This Li-Mg-N-H system exhibited enhanced properties over that of Li-N-H system with a reversible hydrogen storage capacity of approximately 7.0 wt.% at moderate temperature and pressure according to the following reaction:

\[ 3Mg(NH_2)_2 + 8LiH \leftrightarrow Mg_3N_2 + 4Li_2NH + 8H_2 \]

(9)

It has been reported that reaction (9) is more complex comprising of multiple intermediate reactions mediated by NH₃ (Leng et al., 2004b; 2006b; Shigehito et al., 2008). Leng et al., (2004b) indicated that the reaction proceeded by the following three types of elementary reactions mediated by NH₃: In the first step, 3Mg(NH₂)₂ decomposes to Mg₃N₂ and 4NH₃ through 3MgNH; this is followed by a reaction between 4NH₃ and 4LiH to form 4LiNH₂ and 4H₂; and finally 4LiNH₂ and remaining 4LiH react and decompose to form 4Li₂NH and 4H₂. Ikeda et al., (2011) studied the cyclic performance
of Mg(NH$_2$)$_2$/LiH in a 3:8 molar ratio. Trace amounts of NH$_3$ accompanied hydrogen release and the hydrogen storage capacity reduced as NH$_3$ concentration increased.

Changing the ratio of Mg(NH$_2$)$_2$/LiH in the Li-Mg-N-H system can have negative or positive consequences on the hydrogen storage properties. In a 1:4 mixture of Mg(NH$_2$)$_2$/LiH the hydrogen storage capacity is enhanced to 9.1 wt.%, and Li$_3$N and Mg$_3$N$_2$ are generated upon decomposition in vacuum at temperatures up to 500°C (Nakamori et al., 2005). As earlier indicated, a 1:2 mixture of Mg(NH$_2$)$_2$ and LiH releases 5.6 wt.% hydrogen and forms Li$_2$Mg(NH)$_2$ at 200°C (Luo, 2004a; Xiong et al., 2004; Xiong et al., 2005; Luo and Sickafoose, 2006). Further investigation of the Mg(NH$_2$)$_2$/LiH system in 1:1, 1:2 and 1:3 ratios indicated that reducing the amount of LiH in the mixture leads to an increase in the release of NH$_3$ from the system (Xiong et al., 2006). Cao et al., (2012) pointed out that Li$_2$Mg(NH)$_2$ is a thermodynamically stable phase, which means that for the Mg(NH$_2$)$_2$/LiH system the most promising composition with the highest hydrogen capacity and the lowest operating temperature has a molar ratio of 1:2. Furthermore, similar features of the PCT isotherms in terms of the dehydrogenation plateau pressures for the Mg(NH$_2$)$_2$/LiH system in 1:2, 1:4 and 3:8 molar ratios indicates that these systems are thermodynamically similar in that respect (Aoki et al., 2007; Cao et al., 2012). Cao et al., (2012) concluded that the key dehydrogenation reaction in the lower temperature range can hardly be modified by changing the molar ratio of Mg(NH$_2$)$_2$/LiH.

Apart from understanding the mechanisms various investigations involving addition of dopants have been conducted to enhance the hydrogenation/dehydrogenation kinetics of the Li-Mg-N-H system. Transition metal halides (including TiCl$_3$, VCl$_3$, ScCl$_3$ and NiCl$_2$) were used as additives on a 1:1 LiNH$_2$/MgH$_2$ system (Price et al., 2012). Hydrogen desorption temperature was lowered in the presence of the additive in the order: TiCl$_3$ > ScCl$_3$ > VCl$_3$ > NiCl$_2$. The isothermal sorption kinetics of the modified systems were only slightly improved after the first dehydrogenation cycle relative to the unmodified system but were considerably improved in rehydrogenation cycles. When the dehydrogenation characteristics of 1:2 Mg(NH$_2$)$_2$/LiH mixture before and after adding V, V$_2$O$_5$ or VCl$_3$ catalysts were compared, the effectiveness of the catalysts was in the order: VCl$_3$ > V > V$_2$O$_5$ (Shahi et al., 2010). Addition of V, V$_2$O$_5$ and VCl$_3$ reduced the decomposition temperature of the mixture and enhanced the desorption kinetics.

Inclusion of LiBH$_4$ in the LiNH$_2$-MgH$_2$ system led to an improvement in sorption kinetics via reduction of the onset temperature (Yang et al., 2008). In this case, LiNH$_2$ first reacted with LiBH$_4$ to yield Li$_4$BN$_3$H$_{10}$, which then reacted with MgH$_2$ to pre-form Li$_2$Mg(NH)$_2$ nuclei for the subsequent reaction between Mg(NH$_2$)$_2$ and LiH, and thus improved the overall kinetics of the reaction. Meanwhile KH has been demonstrated to remarkably improve hydrogen desorption properties of the Mg(NH$_2$)$_2$/LiH system (Wang et al., 2009). Hydrogen desorption began at ca. 80°C. Approximately 5 wt % of hydrogen could be reversibly stored at about 107°C compared to 186°C for the system without
additive. The enhanced reaction kinetics was attributed to the presence of potassium in the reacting system, which weakened the amide N-H and imide Li-N bonds. It has been shown that addition of NaOH to a 1:2 Mg(NH$_2$)$_2$/LiH system leads to enhanced dehydrogenation/hydrogenation kinetics (Liang et al., 2011).

More recently, Cao et al., (2017) studied the effect of dopant Sr(OH)$_2$ on the 1:2 Mg(NH$_2$)$_2$/LiH system. The work showed that both the thermodynamic and kinetic properties of this amide-hydride system was affected by the presence of Sr(OH)$_2$. When 0.1 mol Sr(OH)$_2$ was added both the dehydrogenation onset and peak temperatures decreased by ca. 70 and 13°C, respectively. Furthermore, the de/re-hydrogenation rates of one time at 150°C accelerated compared to the pristine Mg(NH$_2$)$_2$/LiH system. The overall reaction enthalpy of the 0.1 Sr(OH)$_2$-doped sample was calculated to be 44 kJ/mol. The aforementioned studies thus illustrate the potential of additives in the enhancement of hydrogen storage properties of the Li-Mg-N-H system. Furthermore, decreasing the particle size of the reactants provides effective means of enhancement of the dehydrogenation/hydrogenation kinetics of the Li-Mg-N-H system. For instance, the effect of different high energy milling times as well as the addition of catalysts (Nb$_2$O$_5$, TiCl$_3$ and graphite) on the hydrogen absorption/desorption kinetics of 2:1.1 LiNH$_2$/MgH$_2$ mixture was studied (Barison et al., 2008). It was found that a prolonged milling time effectively enhanced the dehydrogenation/hydrogenation kinetics, irrespective of the presence or absence of any type of catalyst. The improvement in kinetics was attributed to the reduced average crystallite size, which led to increased surface to bulk ratio, thereby improving the solid–solid reactivity and shortening the hydrogen diffusion paths.

**LI-Ca-N-H SYSTEM**

Similarly, to LiNH$_2$-LiH reactions, amide-hydride reactions involving Ca(NH$_2$)$_2$ and CaH$_2$ have been reported with CaNH formed upon heating to 300°C and Ca$_2$NH formed after heating to 500°C (Hino et al., 2005b; Wu, 2008). The synthesis of Ca(NH$_2$)$_2$ can be carried out mechano-chemically by ball milling of calcium hydride (CaH$_2$) in NH$_3$ atmosphere at room temperature (Wu, 2008). The pioneer work on the Li-Ca-N-H system was reported by Xiong et al., (2004) in their investigation of on ternary imides for hydrogen storage. It was demonstrated that the operation temperature of the Li–Ca–N–H system is significantly lower than that of the Li–N–H and Li-Mg-N-H systems, which makes it attractive for hydrogen storage applications. However, the reversible hydrogen storage capacity for Li-Ca-N-H is also lower than that of the latter two systems. It was shown that Li-Ca-N-H starts to absorb hydrogen at about 70°C peaking at 132°C, which were lower than the values for Li-Mg-N-H (100 and 157°C, respectively). Hydrogenated Li-Ca-N-H releases hydrogen at about 100°C with two desorption peaks observed at
approximately 140°C and 206°C. Meanwhile, Li-Mg-N-H, displays a major desorption peak at 166°C.

Further work on the Li–Ca–N–H system was carried out by Tokoyoda et al., (2007) on two kinds of ball-milled mixtures: 1:2 Ca(NH$_2$)$_2$/LiH and 1:2 CaH$_2$/LiNH$_2$. About 4.5 wt.% hydrogen was desorbed starting at about 100 °C, peaking at around 200 and 220°C for the composites of CaH$_2$/LiNH$_2$ and Ca(NH$_2$)$_2$/LiH, respectively. After heating up to 400°C the dehydrogenated states of both systems formed “an unknown imide phase.” Meanwhile after heating up to 200°C in vacuum the dehydrogenated states composed of the mixed phases of Li$_2$NH and CaNH. The hydrogen desorption reactions from both systems were expressed as follows:

$$\text{Ca(NH}_2\text{)}_2 + 2\text{LiH} \leftrightarrow \text{CaNH} + \text{Li}_2\text{NH} + 2\text{H}_2$$

→ "unknown imide phase" + 2H$_2$ \hspace{1cm} (10)

$$\text{CaH}_2 + 2\text{LiNH}_2 \rightarrow \text{CaNH} + \text{Li}_2\text{NH} + 2\text{H}_2$$

→ "unknown imide phase" + 2H$_2$ \hspace{1cm} (11)

Upon rehydrogenation the unknown imide phases transformed into the composite of Ca(NH$_2$)$_2$ and LiH. Therefore, the reversible reaction in the Li–Ca–N–H systems is given by equation 12:

$$\text{CaH}_2 + 2\text{LiNH}_2 \rightarrow \text{CaNH} + \text{Li}_2\text{NH} + 2\text{H}_2 \leftrightarrow \text{Ca(NH}_2\text{)}_2 + 2\text{LiH}$$

(12)

Chu et al., (2010) investigated the dehydrogenation/rehydrogenation behaviour of three LiNH$_2$/CaH$_2$ samples with molar ratio of 2:1, 3:1 and 4:1. It was found that 2:1 LiNH$_2$/CaH$_2$ transforms to ternary imide Li$_2$Ca(NH)$_2$ after desorption of about 4.5 wt.% H$_2$ at 350°C. Its reversible hydrogen storage capacity was 2.7 wt.% at 200°C. This ternary imide likely corresponds to the unknown imide phase in equation 11, which Wu et al., (2007) had also previously identified through XRD and Rietveld refinement. Therefore the ternary imide Li$_2$Ca(NH)$_2$ is formed via equation 13:

$$2\text{LiNH}_2 + \text{CaH}_2 \rightarrow \text{Li}_2\text{Ca(NH}_2\text{)} + 2\text{H}_2$$

(13)

The crystal structure of Li$_2$Ca(NH)$_2$ was determined using neutron powder diffraction data by Wu (2008). The structure was reported to be composed of infinite layers of edge-shared Ca[NH]$_6$ octahedra separated by Li cations. The mobile Li$^+$ ions within the two-dimensional channels defined by Ca[NH]$_6$ octahedra layers were found to influence the hydrogenation properties of the ternary imide.

For the 4:1 LiNH$_2$/CaH$_2$ mixture, after dehydrogenation at 350°C, it transformed to a new compound with composition, Li$_4$CaN$_4$H$_6$ (equation 14). However, rehydrogenation
of both LiCa(NH)$_2$ and Li$_4$CaN$_4$H$_6$ yielded LiNH$_2$, LiH and the solid solution of 2CaNH-Ca(NH)$_2$.

$$2\text{LiNH}_2 + \text{CaH}_2 \rightarrow \text{Li}_4\text{CaN}_4\text{H}_6 + 2\text{H}_2 \quad (14)$$

Despite the relatively lower operating temperature of the Li–Ca–N–H system, its reversible hydrogen storage capacity is limited, and further investigations are warranted to fully understand and optimise the hydrogen storage performance of the system.

**CONCLUSION**

Since the first investigation of the Li-N-H system for hydrogen storage over 15 years ago several other amide-hydride systems have been studied. In order to meet the requirements for a viable hydrogen storage system it is crucial for these systems to possess high hydrogen storage capacities, fast kinetics, favourable thermodynamics and good reversibility. It is also key to inhibit the release of NH$_3$ during hydrogen desorption as NH$_3$ can easily poison the fuel cell during operations. None of the amide-hydride systems studied so far meets all the aforementioned requirements. Although the Li-N-H system has high hydrogen storage capacity with good reversibility, the hydrogen desorption/absorption temperature is high. Several approaches have been undertaken to improve the hydrogen storage properties of this system, most notably, the substitution of Li with an element of higher electronegativity such as Mg. Such thermodynamic modification helps reduce the operating temperature. Thus the Li-Mg-N-H system has been widely studied and shows more promise for hydrogen storage applications due to its high hydrogen storage capacity and relatively moderate operating temperature. Efforts such as addition of catalysts and decrease of particle size have proven effective in enhancing dehydrogenation/hydrogenation kinetics. The Li–Ca–N–H system operates at a relatively lower temperature but its reversible hydrogen storage capacity is inadequate for practical applications. Despite the progress made on amide-hydride systems for hydrogen storage there are still uncertainties regarding the mechanisms of dehydrogenation/hydrogenation of these ternary systems. The structures of intermediates arising from the reactions need to be clearly defined as they can provide vital information in elucidating the reaction pathways. A better understanding of the amide-hydride interactions will undoubtedly be beneficial in tuning the systems already studied as well as in the search for novel metal–N–H storage systems that can meet the requirements for practical applications. Further modifications of the amide-hydride systems to improve their hydrogen storage properties is therefore warranted.
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