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## *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  $-253^{\circ}\text{C}$ . 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.

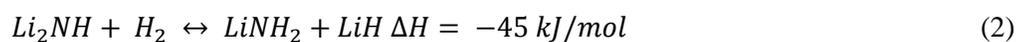
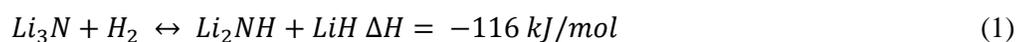
Key criteria including high volumetric and gravimetric storage capacities, favourable thermodynamics, fast kinetics, good reversibility and long-term cyclability must be fulfilled for a practical hydrogen storage system (US DOE, 2017). Presently, no solid-state material simultaneously satisfies these 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,  $\text{Li}_3\text{N}$ . Lithium nitride is typically obtained by reacting Li metal and  $\text{N}_2$  gas at elevated temperature. Lithium nitride exists in three polymorphic forms namely;  $\alpha$ - $\text{Li}_3\text{N}$ ,  $\beta$ - $\text{Li}_3\text{N}$  and  $\gamma$ - $\text{Li}_3\text{N}$ .  $\alpha$ - $\text{Li}_3\text{N}$  is the stable form at room temperature and pressure and is synthesised from its constituent elements under ambient conditions. The structure of  $\alpha$ - $\text{Li}_3\text{N}$  is made up of graphite-like layers of Li hexagons containing a nitride ion in the

middle of each hexagon. The  $\text{Li}_6\text{N}$  hexagons are capped by two further Li ions located above and below the plane, which gives an  $\text{Li}_8\text{N}$  hexagonal bipyramidal configuration (Zintl and Brauer, 1935; Rabenau and Schulz, 1976).  $\beta$ - $\text{Li}_3\text{N}$  which has a sodium arsenide ( $\text{Na}_3\text{As}$ ) structure is produced from  $\alpha$ - $\text{Li}_3\text{N}$  at high pressures of about 4.2 kbar and 300 K (Mali et al., 1987). Meanwhile  $\gamma$ - $\text{Li}_3\text{N}$  has the structure of  $\text{Li}_3\text{Bi}$  and can be produced from  $\beta$ - $\text{Li}_3\text{N}$  at extreme pressures of 35-45 GPa, and is stable up to 200 GPa (Lazicki et al., 2005).

The hydrogenation of  $\text{Li}_3\text{N}$  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):



The above two reactions result in a theoretical hydrogen storage capacity of 5.5 and 6.5 wt.%, respectively. From equation 1,  $\text{Li}_2\text{NH}$  is formed by partial hydrogenation of  $\text{Li}_3\text{N}$ . Upon hydrogenation of  $\text{Li}_3\text{N}$ , Li in the Li layer tend to detach from the  $\text{Li}_3\text{N}$  structure and react with hydrogen to yield  $\text{LiH}$ . Concomitantly, there is substitution of H for Li, which then bonds with N to generate  $\text{Li}_2\text{NH}$ . Juza and Opp (1951a) suggested  $\text{Li}_2\text{NH}$  has a cubic crystal structure with  $Fm-3m$  space group and lattice parameters of  $a = 5.047 \text{ \AA}$ . 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).

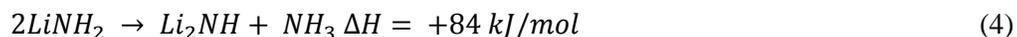
The reverse reaction from equation 2 shows that  $\text{LiNH}_2$  reacts with  $\text{LiH}$  to generate  $\text{Li}_2\text{NH}$  in an amide-hydride reaction. Using powder X-ray diffraction, Juza and Opp (1951b) initially reported the solid-state structure of  $\text{LiNH}_2$  to exist in the space group  $I-4$ . Using powder neutron diffraction, Yang et al., (2006) further confirmed the crystal structure of  $\text{LiNH}_2$  to be tetragonal with  $I-4$  space group and lattice parameters of  $a = 5.03442 \text{ \AA}$  and  $c = 10.25558 \text{ \AA}$ , 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 ( $\text{LiNH}_2$ ) was first prepared by Titherley in 1894 by a direct reaction of metallic Li and  $\text{NH}_3$  (Titherley, 1894). It can also be prepared by reacting  $\text{LiH}$  with  $\text{NH}_3$  at 4 bar and  $100^\circ\text{C}$  or by ball milling pure  $\text{LiH}$  under 4 bar of  $\text{NH}_3$  (Hu and Ruckenstein, 2003a; Leng et al, 2006a). Lithium hydride ( $\text{LiH}$ ) crystallizes in the rock-salt structure and is usually synthesised by reacting Li metal with hydrogen gas at elevated temperatures. At ambient pressure,  $\text{LiH}$  was prepared by contacting liquid Li metal at  $750^\circ\text{C}$  with purified hydrogen for 12 h (Messer et al., 1958). Howie et al., (2012)

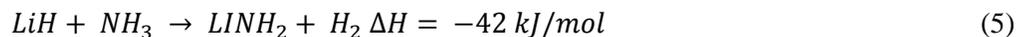
reported the synthesis of LiH from its pure constituents at room temperature and pressures as low as 500 bar. In the presence of catalysts, metallic Li could be quantitatively hydrogenated to LiH at 25–50°C and ambient pressure within 2–5 h (Shih-Tsien et al., 1985).

Chen et al., (2002) reported in their initial investigation of Li<sub>3</sub>N 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.% H<sub>2</sub> was released. Complete hydrogen desorption was only achieved at temperatures above 320°C. Below 160°C, the reaction between Li<sub>3</sub>N and H<sub>2</sub> 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 Li<sub>3</sub>N is about 5.5 wt.% because of the partial dehydrogenation of hydrogenated Li<sub>3</sub>N (Hu et al., 2005). Complete reversibility of the hydrogenation reaction of Li<sub>3</sub>N 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 Li<sub>3</sub>N 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 Li<sub>3</sub>N can be partially oxidised forming Li<sub>2</sub>O/Li<sub>3</sub>N hybrid material and hydrogenation/dehydrogenation pretreatment of this hybrid leads to faster kinetics, enhanced reversibility and excellent stability relative to pristine Li<sub>3</sub>N. The reversible capacity of Li<sub>2</sub>O/Li<sub>3</sub>N 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 Li<sub>2</sub>O could also hinder sintering of the material by preventing the large temperature jump that usually occurs during the initial hydrogenation. However, direct doping of Li<sub>3</sub>N with ca. 5 mol% Li<sub>2</sub>O followed by annealing revealed that both binary compounds occurred as separate phases with Li<sub>2</sub>O acting as a spectator in the hydrogen storage reactions with no evidence of enhanced Li<sup>+</sup> or H<sup>+</sup> mobility (Langmi et al., 2010). Hu et al., (2004) further showed that hydrogen storage stability of Li<sub>3</sub>N can be enhanced by preheating Li<sub>3</sub>N 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 LiNH<sub>2</sub> 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 LiNH<sub>2</sub> with LiH is likely driven by the reaction between the positively charged hydrogen (H<sup>δ+</sup>) in the amide and the negatively charged hydrogen (H<sup>δ-</sup>) in the hydride generating H<sub>2</sub>.





Below 400°C, the formation of NH<sub>3</sub> is thermodynamically favourable. Reaction (4) occurs very fast, in as little as 25 ms, which results in suppression of the NH<sub>3</sub> generated during the dehydrogenation reaction (Hu and Ruckenstein, 2003a). It was also revealed from NMR studies that NH<sub>3</sub> 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<sub>3</sub> diffusion through the Li<sub>2</sub>NH product layer on the exterior of the shrinking LiNH<sub>2</sub> core (Shaw et al., 2008). However, Hino et al., (2005a) reported the unavoidable contamination of hydrogen with about 0.1% NH<sub>3</sub> during dehydrogenation of a mixture of LiH and LiNH<sub>2</sub> at temperatures up to 400°C in a closed system. Such release of NH<sub>3</sub> 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<sub>2</sub> + 2LiH mixture, a cubic phase like that of Li<sub>2</sub>NH, but with a ‘shrunk lattice’, was tentatively assigned a composition of Li<sub>2.2</sub>NH<sub>0.8</sub>. From deuteration studies of Li<sub>3</sub>N, Weidner et al., (2007) reported the presence of non-stoichiometric phases with composition-dependent lattice parameters as well as the identification of Li<sub>4</sub>ND and the inhibition of LiD formation at low deuterium content. They therefore postulated that non-stoichiometric phase is intermediate between Li<sub>4</sub>ND and Li<sub>2</sub>ND, with a composition of Li<sub>2+y</sub>ND. By employing *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<sub>1+x</sub>NH<sub>2-x</sub>. 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<sub>2-y</sub>NH<sub>1+y</sub> intermediate that forms during the LiNH<sub>2</sub> to Li<sub>2</sub>NH transition and secondly, the Li<sub>2+y</sub>NH intermediate that forms during the Li<sub>4</sub>NH to Li<sub>2</sub>NH transition. Non-stoichiometric phases containing N<sup>3-</sup>, H<sup>-</sup> and (NH)<sup>2-</sup> anions have been proposed to form between Li<sub>4</sub>NH and Li<sub>2</sub>NH, which react to form a non-stoichiometric solid solution of composition Li<sub>4-2x</sub>N<sub>1-x</sub>H<sub>1-x</sub>(NH)<sub>x</sub> (Tapia-Ruiz et al, 2013).

Many studies have focussed on the reversible reaction between LiNH<sub>2</sub> 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

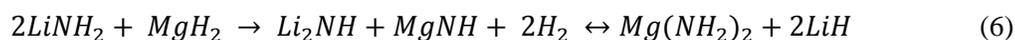
of the Li-N-H system, ball milling has been employed which reduced the particle sizes of the reactants and improved the kinetics of the reaction (Varin et al., 2010; Yao et al., 2007). Markmaitree et al., (2006) demonstrated that ball milling lowered the onset decomposition temperature of  $\text{LiNH}_2$  from  $120^\circ\text{C}$  to room temperature. Nevertheless, a temperature of  $230^\circ\text{C}$  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  $\text{LiNH}_2$ . 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  $\text{LiNH}_2$  and  $\text{LiH}$  (1:1 molar ratio) with 1 mol% of several catalysts (Fe, Co, or Ni nanoparticles,  $\text{TiCl}_3$  and  $\text{VCl}_3$ ) was investigated (Ichikawa et al., 2004; 2005a). In the absence of a catalyst hydrogen was released between 180 and  $400^\circ\text{C}$  alongside a considerable amount of  $\text{NH}_3$  (Ichikawa et al., 2004). The best hydrogen desorption properties was recorded for the mixture containing 1 mol%  $\text{TiCl}_3$ . The latter desorbed 5.5–6.0 wt.% hydrogen at 150– $250^\circ\text{C}$  and displayed relatively fast kinetics and good reversibility with no  $\text{NH}_3$  release (Ichikawa et al., 2005a). The catalytic effect on the hydrogen storage properties of  $\text{LiNH}_2/\text{LiH}$  system can be further affected by the particle size of added catalysts (Isobe et al., 2005). The  $\text{LiNH}_2/\text{LiH}$  mixtures suffer from unfavorable dehydrogenation enthalpy with a minimum temperature of  $255^\circ\text{C}$  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  $\text{LiNH}_2$  or  $\text{LiH}$  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  $\text{LiNH}_2$  and  $\text{MgH}_2$  or  $\text{LiH}$  and  $\text{Mg}(\text{NH}_2)_2$  can give rise to this mixed metal amide-hydride system.  $\text{MgH}_2$  on its own has received attention as a hydrogen storage material due to its high gravimetric and volumetric hydrogen storage capacity (7.6 wt %  $\text{H}_2$  and 110 g  $\text{H}_2/\text{L}$ , respectively). However, it suffers from sluggish kinetics.  $\text{MgH}_2$  occurs in several forms;  $\alpha\text{-MgH}_2$  crystallises in the tetragonal space group (rutile-type structure,  $P4_2/mnm$ ) at ambient conditions (Zachariassen et al, 1980; Bastide et al., 1963). At high temperatures and pressures, a structural rearrangement occurs causing  $\alpha\text{-MgH}_2$  to transform into the orthorhombic  $\gamma\text{-MgH}_2$  with  $\alpha\text{-PbO}_2$  type structure. Meanwhile the solid-state structure of  $\text{Mg}(\text{NH}_2)_2$  consists of a tetragonal unit cell with space group  $I4_1/acd$  (Jacobs et al., 1969),

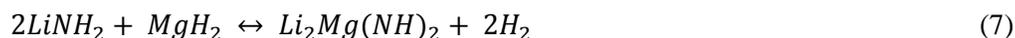
and this amide can be prepared by reacting  $MgH_2$  (or Mg) with  $NH_3$  (Serby et al., 2007). Decomposition of  $Mg(NH_2)_2$  at elevated temperatures of about 200 °C yields the imide ( $MgNH$ ) and  $NH_3$  (Leng et al., 2004a). In the Li-Mg-N-H system, Li is partially substituted with Mg, which 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:

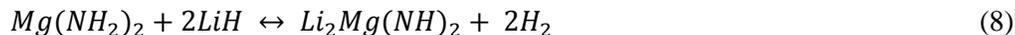


A mixture of  $LiNH_2$  and  $MgH_2$  was found to readily decompose at about 200°C when 30 bar hydrogen gas was applied (Luo, 2004b). A hydrogen storage capacity of 4.5 wt.% was achieved and the enthalpy change was 39 kJ/mol. The PCT isotherms revealed that the decomposition occurred through a two-step process (Luo and Sickafoose, 2006). The sloping part of the PCT plot could be attributed to the formation of an intermediate  $Li_2MgN_2H_3$ , 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  $Li_2Mg(NH)_2$  depicted in equation 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.



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  $\text{Li}_2\text{Mg}(\text{NH})_2$  undergoes two structural transitions from orthorhombic (with space group *Iba2* or *Ibam* and lattice parameters  $a = 9.7837 \text{ \AA}$ ,  $b = 4.9893 \text{ \AA}$ ,  $c = 5.1984 \text{ \AA}$ ) to primitive (with space group *P-43 m* and lattice parameter  $a = 5.0268 \text{ \AA}$ ) at intermediate temperature ( $350^\circ\text{C}$ ) followed by a face-centered cubic crystal structure (with space group *Fm-3 m* and lattice parameter  $a = 5.0988 \text{ \AA}$ ) at high temperature ( $500^\circ\text{C}$ ). 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  $\text{LiNH}_2$  and  $\text{MgH}_2$ , decomposition at  $210^\circ\text{C}$  leads to the formation of  $\text{Li}_2\text{Mg}_2(\text{NH})_3$ ,  $\text{LiH}$  and  $\text{MgH}_2$ . 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  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  in various molar ratios (Ichikawa et al., 2005b; Leng et al., 2005; Leng et al., 2004b; Luo and Sickafoose, 2006; Nakamori et al., 2004). A 3:8 molar mixture of  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  that was initially ball-milled and then dehydrogenated at  $200^\circ\text{C}$  under high vacuum (Ichikawa et al., 2005b) was investigated. From P–C–T measurements at  $200^\circ\text{C}$  two-plateaux-like behaviour was observed and the sample was fully hydrogenated under 9 MPa  $\text{H}_2$ . On the other hand, the P–C–T curve at  $150^\circ\text{C}$  displayed a single-plateau-like behaviour and was only partially hydrogenated under the same  $\text{H}_2$  pressure. Leng et al., (2005) also investigated a 3:8 molar mixture of  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  and reported that hydrogen desorption began at  $140^\circ\text{C}$ , with a peak desorption at  $190^\circ\text{C}$ , and negligible  $\text{NH}_3$  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:



It has been reported that reaction (9) is more complex comprising of multiple intermediate reactions mediated by  $\text{NH}_3$  (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  $\text{NH}_3$ : In the first step,  $3\text{Mg}(\text{NH}_2)_2$  decomposes to  $\text{Mg}_3\text{N}_2$  and  $4\text{NH}_3$  through  $3\text{MgNH}$ ; this is followed by a reaction between  $4\text{NH}_3$  and  $4\text{LiH}$  to form  $4\text{LiNH}_2$  and  $4\text{H}_2$ ; and finally  $4\text{LiNH}_2$  and remaining  $4\text{LiH}$  react and decompose to form  $4\text{Li}_2\text{NH}$  and  $4\text{H}_2$ . Ikeda et al., (2011) studied the cyclic performance

of  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  in a 3:8 molar ratio. Trace amounts of  $\text{NH}_3$  accompanied hydrogen release and the hydrogen storage capacity reduced as  $\text{NH}_3$  concentration increased.

Changing the ratio of  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  in the Li-Mg-N-H system can have negative or positive consequences on the hydrogen storage properties. In a 1:4 mixture of  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  the hydrogen storage capacity is enhanced to 9.1 wt.%, and  $\text{Li}_3\text{N}$  and  $\text{Mg}_3\text{N}_2$  are generated upon decomposition in vacuum at temperatures up to 500°C (Nakamori et al., 2005). As earlier indicated, a 1:2 mixture of  $\text{Mg}(\text{NH}_2)_2$  and LiH releases 5.6 wt.% hydrogen and forms  $\text{Li}_2\text{Mg}(\text{NH})_2$  at 200°C (Luo, 2004a; Xiong et al., 2004; Xiong et al., 2005; Luo and Sickafoose, 2006). Further investigation of the  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  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  $\text{NH}_3$  from the system (Xiong et al., 2006). Cao et al., (2012) pointed out that  $\text{Li}_2\text{Mg}(\text{NH})_2$  is a thermodynamically stable phase, which means that for the  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  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  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  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  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ .

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  $\text{TiCl}_3$ ,  $\text{VCl}_3$ ,  $\text{ScCl}_3$  and  $\text{NiCl}_2$ ) were used as additives on a 1:1  $\text{LiNH}_2/\text{MgH}_2$  system (Price et al., 2012). Hydrogen desorption temperature was lowered in the presence of the additive in the order:  $\text{TiCl}_3 > \text{ScCl}_3 > \text{VCl}_3 > \text{NiCl}_2$ . 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  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  mixture before and after adding V,  $\text{V}_2\text{O}_5$  or  $\text{VCl}_3$  catalysts were compared, the effectiveness of the catalysts was in the order:  $\text{VCl}_3 > \text{V} > \text{V}_2\text{O}_5$  (Shahi et al., 2010). Addition of V,  $\text{V}_2\text{O}_5$  and  $\text{VCl}_3$  reduced the decomposition temperature of the mixture and enhanced the desorption kinetics.

Inclusion of  $\text{LiBH}_4$  in the  $\text{LiNH}_2\text{-MgH}_2$  system led to an improvement in sorption kinetics via reduction of the onset temperature (Yang et al., 2008). In this case,  $\text{LiNH}_2$  first reacted with  $\text{LiBH}_4$  to yield  $\text{Li}_4\text{BN}_3\text{H}_{10}$ , which then reacted with  $\text{MgH}_2$  to pre-form  $\text{Li}_2\text{Mg}(\text{NH})_2$  nuclei for the subsequent reaction between  $\text{Mg}(\text{NH}_2)_2$  and LiH, and thus improved the overall kinetics of the reaction. Meanwhile KH has been demonstrated to remarkably improve hydrogen desorption properties of the  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  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<sub>2</sub>)<sub>2</sub>/LiH system leads to enhanced dehydrogenation/hydrogenation kinetics (Liang et al., 2011).

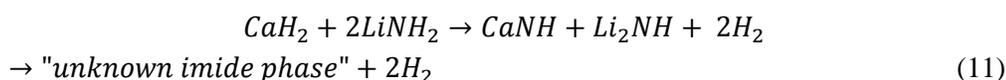
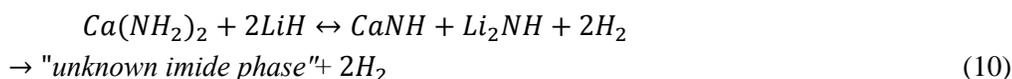
More recently, Cao et al., (2017) studied the effect of dopant Sr(OH)<sub>2</sub> on the 1:2 Mg(NH<sub>2</sub>)<sub>2</sub>/LiH system. The work showed that both the thermodynamic and kinetic properties of this amide-hydride system was affected by the presence of Sr(OH)<sub>2</sub>. When 0.1 mol Sr(OH)<sub>2</sub> 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<sub>2</sub>)<sub>2</sub>/LiH system. The overall reaction enthalpy of the 0.1 Sr(OH)<sub>2</sub>-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<sub>2</sub>O<sub>5</sub>, TiCl<sub>3</sub> and graphite) on the hydrogen absorption/desorption kinetics of 2:1.1 LiNH<sub>2</sub>/MgH<sub>2</sub> 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

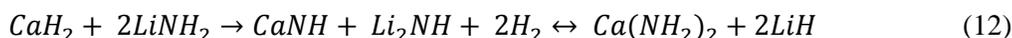
Similarly, to LiNH<sub>2</sub>-LiH reactions, amide-hydride reactions involving Ca(NH<sub>2</sub>)<sub>2</sub> and CaH<sub>2</sub> have been reported with CaNH formed upon heating to 300°C and Ca<sub>2</sub>NH formed after heating to 500°C (Hino et al., 2005b; Wu, 2008). The synthesis of Ca(NH<sub>2</sub>)<sub>2</sub> can be carried out mechano-chemically by ball milling of calcium hydride (CaH<sub>2</sub>) in NH<sub>3</sub> 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.

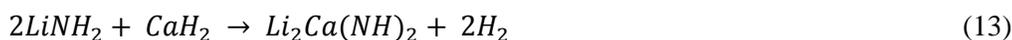
Further work on the Li-Ca-N-H system was carried out by Tokoyoda et al., (2007) on two kinds of ball-milled mixtures: 1:2 Ca(NH<sub>2</sub>)<sub>2</sub>/LiH and 1:2 CaH<sub>2</sub>/LiNH<sub>2</sub>. About 4.5 wt.% hydrogen was desorbed starting at about 100 °C, peaking at around 200 and 220°C for the composites of CaH<sub>2</sub>/LiNH<sub>2</sub> and Ca(NH<sub>2</sub>)<sub>2</sub>/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<sub>2</sub>NH and CaNH. The hydrogen desorption reactions from both systems were expressed as follows:



Upon rehydrogenation the unknown imide phases transformed into the composite of Ca(NH<sub>2</sub>)<sub>2</sub> and LiH. Therefore, the reversible reaction in the Li-Ca-N-H systems is given by equation 12:



Chu et al., (2010) investigated the dehydrogenation/rehydrogenation behaviour of three LiNH<sub>2</sub>/CaH<sub>2</sub> samples with molar ratio of 2:1, 3:1 and 4:1. It was found that 2:1 LiNH<sub>2</sub>/CaH<sub>2</sub> transforms to ternary imide Li<sub>2</sub>Ca(NH)<sub>2</sub> after desorption of about 4.5 wt.% H<sub>2</sub> 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<sub>2</sub>Ca(NH)<sub>2</sub> is formed via equation 13:



The crystal structure of Li<sub>2</sub>Ca(NH)<sub>2</sub> 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]<sub>6</sub> octahedra separated by Li cations. The mobile Li<sup>+</sup> ions within the two-dimensional channels defined by Ca[NH]<sub>6</sub> octahedra layers were found to influence the hydrogenation properties of the ternary imide.

For the 4:1 LiNH<sub>2</sub>/CaH<sub>2</sub> mixture, after dehydrogenation at 350°C, it transformed to a new compound with composition, Li<sub>4</sub>CaN<sub>4</sub>H<sub>6</sub> (equation 14). However, rehydrogenation

of both  $\text{LiCa}(\text{NH})_2$  and  $\text{Li}_4\text{CaN}_4\text{H}_6$  yielded  $\text{LiNH}_2$ ,  $\text{LiH}$  and the solid solution of  $2\text{CaNH}-\text{Ca}(\text{NH}_2)_2$ .



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  $\text{NH}_3$  during hydrogen desorption as  $\text{NH}_3$  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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## REFERENCES

- Aoki, M., Noritake, T., Nakamori, Y., Towata, S. and Orimo, S. 2007. “Dehydriding and Rehydriding Properties of  $\text{Mg}(\text{NH}_2)_2\text{-LiH}$  Systems.” *Journal of Alloys and Compounds* 446:328–31. doi: 10.1016/j.jallcom.2006.11.141.
- Barison, S., Agresti, F., Russo, S. L., Maddalena, A., Palade, P., Principi, G. and Torzo, G. 2008. “A Study of the  $\text{LiNH}_2\text{-MgH}_2$  System for Solid State Hydrogen Storage.” *Journal of Alloys and Compounds* 459:343–7. doi: 10.1016/j.jallcom.2007.04.278.
- Bastide, J. P., Bonnetot, B., Létoffé, J. M. and Claudy, P. 1980. “Polymorphism of Magnesium Hydride under High Pressure.” *Materials Research Bulletin* 15:1215–24. doi: 10.1016/0025-5408(80)90023-9.
- Bull, D. J., Weidner, E., Shabalin, I. L., Telling, M. T. F., Jewell, C. M., Gregory D. H. and Ross, D. K. 2010. “Pressure-dependent Deuterium Reaction Pathways in the Li–N–D System.” *Physical Chemistry Chemical Physics* 12:2089–97. doi: 10.1039/B903821N.
- Cao, H., Zhang, Y., Wang, J., Xiong, Z., Wu, G. and Chen, P. 2012. “Materials Design and Modification on Amide-Based Composites for Hydrogen Storage.” *Progress in Natural Science: Materials International* 22:550–60. doi: 10.1016/j.pnsc.2012.11.013.
- Cao, H., Wang, H., Pistidda, C., Milanese, C., Zhang, W., Chaudhary, A. L., Santoru, A., Garroni, S., Bednarcik, J., Liermann, H. P., Chen, P., Klassena, T. and Dornheim, M. 2017. “The Effect of  $\text{Sr}(\text{OH})_2$  on the Hydrogen Storage Properties of the  $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$  System.” *Physical Chemistry Chemical Physics* 19:8457–64 doi: 10.1039/C7CP00748E.
- Chen, P., Xiong, Z., Luo, J., Lin, J. and Tan, K. L. 2002. “Interaction of Hydrogen with Metal Nitrides and Imides” *Nature* 420 (2002) 302–4. doi: 10.1038/nature01210.
- Chen, P., Xiong, Z., Luo, J., Lin, J. and Tan, K. L. 2003. “Interaction between Lithium Amide and Lithium Hydride.” *The Journal of Physical Chemistry B* 107:10967–70. doi: 10.1021/jp034149j.
- Chu, H., Xiong, Z., Wu, G., He, T., Wu, C. and Chen, P. 2010. “Hydrogen storage Properties of Li–Ca–N–H System with Different Molar Ratios of  $\text{LiNH}_2/\text{CaH}_2$ .”

- International Journal of Hydrogen Energy* 35:8317-21. doi: 10.1016/j.ijhydene.2009.12.009.
- Herbst J. F. and Hector, L. G. 2005. "Energetics of the Li amide/Li imide Hydrogen Storage Reaction." *Physical Review B* 72:125120. doi: 10.1103/PhysRevB.72.125120.
- Hino, S., Ichikawa, T., Ogita, N., Udagawa, M. and Fujii, H. 2005a. "Quantitative Estimation of NH<sub>3</sub> Partial Pressure in H<sub>2</sub> Desorbed from the Li-N-H System by Raman spectroscopy." *Chemical Communications* 24:3038-40. doi: 10.1039/B503356J.
- Hino, S., Ichikawa, T., Leng H. and Fujii, H. 2005b. "Hydrogen Desorption Properties of the Ca-N-H system." *Journal of Alloys and Compounds* 398: 62-6. doi.org/10.1016/j.jallcom.2005.01.052.
- Howie, R. T., Narygina, O., Guillaume, C. L., Evans, S. and Gregoryanz, E. 2012. "High-pressure Synthesis of Lithium Hydride." *Physical Review B* 86:064108. doi: 10.1103/PhysRevB.86.064108.
- Hu, H. Y. and Ruckenstein, E. 2003a. "Ultrafast Reaction between LiH and NH<sub>3</sub> during H<sub>2</sub> Storage in Li<sub>3</sub>N." *Journal of Physical Chemistry A* 107:9737-9. doi: 10.1021/jp036257b.
- Hu, H. Y. and Ruckenstein, E. 2003b. "H<sub>2</sub> Storage in Li<sub>3</sub>N. Temperature-Programmed Hydrogenation and Dehydrogenation." *Industrial & Engineering Chemistry Research* 42:5135-9. doi: 10.1021/ie030498o
- Hu, H. Y. and Ruckenstein, E. 2004. "Highly Effective Li<sub>2</sub>O/Li<sub>3</sub>N with Ultrafast Kinetics for H<sub>2</sub> Storage." *Industrial & Engineering Chemistry Research* 43:2464-7. doi: 10.1021/ie049947q.
- Hu, H. Y., Yu, N. Y. and Ruckenstein, E. 2004. "Effect of the Heat Pretreatment of Li<sub>3</sub>N on Its H<sub>2</sub> Storage Performance." *Industrial & Engineering Chemistry Research* 43:4174-7. doi: 10.1021/ie0498394.
- Hu, H. Y., Yu, N. Y. and Ruckenstein, E. 2005. "Hydrogen Storage in Li<sub>3</sub>N: Deactivation caused by a High Dehydrogenation Temperature." *Industrial & Engineering Chemistry Research* 44: 4304-9. doi: 10.1021/ie0501834.
- Ichikawa, T., Hanada, N., Isobe, S., Leng, H. Y., and Fujii, H. 2005a. "Hydrogen Storage Properties in Ti Catalyzed Li-N-H system." *Journal of Alloys and Compounds* 404-406:435-8. doi: 10.1016/j.jallcom.2004.11.110.
- Ichikawa, T., Isobe, S., Hanada, N. and Fujii, H. 2004. "Lithium Nitride for Reversible Hydrogen Storage." *Journal of Alloys and Compounds* 365:271-6. 10.1016/S0925-8388(03)00637-6.
- Ichikawa, T., Tokoyoda, K., Leng, H. and Fujii, H. 2005b. "Hydrogen Absorption Properties of Li-Mg-N-H system." *Journal of Alloys and Compounds* 400:245-8. doi: 10.1016/j.jallcom.2005.03.068.

- Ikeda, S., Tokoyoda, K., Kiyobayashi, T. and Kuriyama, N. "Cyclic Properties and Ammonia By-Product Emission of Li/Mg–N–H Hydrogen Storage Material." *International Journal of Hydrogen Energy* 36 (2011) 8373–80. doi: 10.1016/j.ijhydene.2011.04.086.
- Isobe, S., Ichikawa, T., Hanada, N., Leng, H. Y., Fichtner, M., Fuhr, O. and Fujii, H. 2005. "Effect of Ti catalyst with Different Chemical Form on Li–N–H Hydrogen Storage Properties." *Journal of Alloys and Compounds* 404–406:439–42. doi.org/10.1016/j.jallcom.2004.09.081.
- Jacobs, V. H. and Juza, R. 1969. "Preparation and Properties of Magnesium Amide and Imide." *Zeitschrift fuer Anorganische und Allgemeine Chemie* 370:254–61. doi: 10.1002/zaac.19693700508. [*Journal of Electrochemistry and Applied Physical Chemistry*]
- Juza, R. and Opp, K. 1951a. "Metallamide und Metallnitride, 24. Mitteilung. Die Kristallstruktur des Lithiumamides." *Zeitschrift fuer Anorganische und Allgemeine Chemie* 266:325–30. doi: 10.1002/zaac. 19512660606. [Metallamides and Metal Nitrides, 24th Comm-unication. The Crystal Structure of the Lithium Amide. *Journal of Inorganic and General Chemistry*]
- Juza, R. and Opp, K. 1951b. "Metallamide und Metallnitride, 25. Mitteilung. Zur Kenntnis des Lithiumimides." *Zeitschrift fuer Anorganische und Allgemeine Chemie* 266:313–24. doi: 10.1002/zaac. 19512660607. [Metallamides and Metal Nitrides, 25th Comm-unication. To the knowledge of Lithiumimides. *Journal of Inorganic and General Chemistry*]
- Langmi, H. W. and McGrady, G. S. 2007. "Non-hydride Systems of the Main Group Elements as Hydrogen Storage Materials." *Coordination Chemistry Reviews* 251:925–35. doi: 10.1016/j.ccr.2006.09.009.
- Langmi, H. W., Culligan, S. D. and McGrady, G. S. 2010. "Hydrogen storage Behaviour of Li<sub>3</sub>N Doped with Li<sub>2</sub>O and Na<sub>2</sub>O." *Journal of Power Sources* 195: 2003–7. doi:10.1016/j.jpowsour.2009.10.008.
- Lazicki, A., Maddox, B., Evans, W. J., Yoo, C. S., McMahan, A. K., Pickett, W. E., Scalettar, R. T., Hu, M. Y. and Chow, P. 2005. "New Cubic Phase of Li<sub>3</sub>N: Stability of the N<sup>3-</sup> Ion to 200 GPa." *Physical Review Letters* 95:165503. doi: 10.1103/PhysRevLett.95.165503.
- Leng, H. Y., Ichikawa, T., Hino, S., Hanada, N., Isobe, S. and Fujii, H. 2004a. "New Metal–N–H System Composed of Mg(NH<sub>2</sub>)<sub>2</sub> and LiH for Hydrogen Storage." *The Journal of Physical Chemistry B* 108:8763–5. doi: 10.1021/jp048002j.
- Leng, H., Ichikawa, T., Hino, S., Nakagawa, T. and Fujii, H. 2004b. "Mechanism of Hydrogenation Reaction in the Li–Mg–N–H System." *The Journal of Physical Chemistry B* 109:10744–48. doi: 10.1021/jp0504571.
- Leng, H. Y., Ichikawa, T., Isobe, S., Hino, S., Hanada, N. and Fujii, H. 2005. "Desorption Behaviours from Metal–N–H Systems Synthesized by Ball Milling."

- Journal of Alloys and Compounds* 404–406:443–7. doi: 10.1016/j.jallcom.2004.09.082.
- Leng, H. Y., Ichikawa, T., Hino, S., Hanada, N., Isobe, S. and Fujii, H. 2006. “Synthesis and Decomposition Reactions of Metal Amides In Metal–N–H Hydrogen Storage System.” *Journal of Power Sources* 156:166–70. doi: 10.1016/j.jpowsour.2005.03.228.
- Leng, H., Ichikawa, T., Fujii, H. 2006b. Hydrogen Storage Properties of Li–Mg–N–H Systems with Different Ratios of LiH/Mg(NH<sub>2</sub>)<sub>2</sub>.” *The Journal of Physical Chemistry B* 110:12964–68. doi: 10.1021/jp061120h.
- Liang, C., Liu, Y., Wei, Z., Jiang, Y., Wu, F., Gao, M. and Pan, H. 2011. “Enhanced Dehydrogenation/Hydrogenation Kinetics of the Mg(NH<sub>2</sub>)<sub>2</sub>–2LiH System with NaOH Additive.” *International Journal of Hydrogen Energy* 36:2137–44. doi: 10.1016/j.ijhydene.2010.11.068.
- Liu, Y., Zhong, K., Gao, M., Wang, J., Pan, H. and Wang, Q. 2008. “Hydrogen Storage in a LiNH<sub>2</sub>–MgH<sub>2</sub> (1:1) System.” *Chemistry of Materials* 20:3521–7. doi: 10.1021/cm800271a.
- Luo, W. 2004a.”(LiNH<sub>2</sub>–MgH<sub>2</sub>): A Viable Hydrogen Storage System.” *Journal of Alloys and Compounds* 284–287. doi: 10.1016/j.jallcom.2004.03.119.
- Luo, W. 2004b. “Corrigendum to “(LiNH<sub>2</sub>–MgH<sub>2</sub>): A Viable Hydrogen Storage System”: [J. Alloys Comp. 381 (2004) 284–287].” *Journal of Alloys and Compounds* 385:316. doi: 10.1016/j.jallcom.2004.10.017.
- Luo, W. F. and Sickafoose, S. 2006. “Thermodynamic and Structural Characterization of the Mg–Li–N–H Hydrogen Storage System.” *Journal of Alloys and Compounds* 407:274–81. doi: 10.1016/j.jallcom.2005.06.046.
- Makepeace, J. W., Jones, M. O., Callear, S. K., Edwards, P. P. and David, W. I. F. 2014. “*In situ* X-Ray Powder Diffraction Studies of Hydrogen Storage and Release in the Li–N–H System.” *Physical Chemistry Chemical Physics* 16:4061–70.
- Mali, M., Roos, J. and Brinkmann, D. 1987. “Nuclear-Magnetic-Resonance Evidence for a New Phase Induced by Pressure in the Superionic Conductor Li<sub>3</sub>N.” *Physical Review B* 36:3888–90. doi: 10.1103/PhysRevB.36.3888.
- Markmaitree, T., Ren, R. and Shaw, L. L. 2006. “Enhancement of Lithium Amide to Lithium Imide Transition via Mechanical Activation.” *The Journal of Physical Chemistry B* 110:20710–18. doi: 10.1021/jp060181c.
- Meisner, G. P., Pinkerton, F. E., Meyer, M. S., Balogh, M. P. and Kundrat, M. D. 2005. “Study of the Lithium–Nitrogen–Hydrogen System.” *Journal of Alloys and Compounds* 404–406:24–6. doi: 10.1016/j.jallcom.2004.11.103.
- Messer, C., Damon, E., Maybury, P., Mellor, J. and Seales, R. 1958. “Solid–Liquid Equilibrium in the Lithium Lithium Hydride System.” *The Journal of Physical Chemistry* 62:220–2. doi: 10.1021/j150560a018.

- Miwa, K., Ohba, N., Towata, S., Nakamori, Y., Oriimo, S. 2005. "First-principles Study on Lithium Amide for Hydrogen Storage." *Physical Review B* 71:195109 doi: 10.1103/PhysRevB.71.195109.
- Nakamori, Y. and Orimo, S. 2004. "Li-N Based Hydrogen Storage Materials." *Materials Science and Engineering: B* 108:48-50. doi: 10.1016/j.mseb.2003.10.044.
- Nakamori, Y., Kitahara G. and Orimo, S. 2004b. "Synthesis and Dehydrogenating Studies of Mg-N-H Systems." *Journal of Power Sources* 138:309-312. Doi: 10.1016/j.jpowsour.2004.06.026.
- Nakamori, Y., Kitahara, G., Miwa, K., Ohba, N., Noritake, T., Towata, S., Orimo, S. 2005. Hydrogen Storage Properties of Li-Mg-N-H Systems, *Journal of Alloys and Compounds* 404:96-8. doi: 10.1016/j.jallcom.2004.10.089.
- Ohoyama, K., Nakamori, Y., Orimo, S. and Yamada, K. 2005. "Revised Crystal Structure Model of Li<sub>2</sub>NH by Neutron Powder Diffraction." *Journal of the Physical Society of Japan* 74:483-7. doi: 10.1143/JPSJ.74.483.
- Orimo, S., Nakamori, Y., Kitahara, G., Miwa, K., Ohba, N., Noritake, T. and Towata, S. 2004. "Destabilization and Enhanced Dehydrogenating Reaction of LiNH<sub>2</sub>: an Electronic Structure Viewpoint." *Applied Physics A* 79:1765-7. doi: 10.1007/s00339-004-2927-0.
- Osborn W., Markmaitree T. and Shaw, L. L. 2007. "Evaluation of the Hydrogen Storage Behavior of a LiNH<sub>2</sub> + MgH<sub>2</sub> System with 1:1 ratio." *Journal of Power Sources* 172:376-8. doi: 10.1016/j.jpowsour.2007.07.037.
- Price, C., Gray, J., Lascola Jr, R. and Anton, D. L. 2012. "The Effects of Halide Modifiers on the Sorption Kinetics of the Li-Mg-N-H System." *International Journal of Hydrogen Energy* 37:2742-9. doi: 10.1016/j.ijhydene.2011.07.046.
- Rabenau, A. and Schulz, H. 1976. "Re-evaluation of the Lithium Nitride Structure." *Journal of the Less Common Metals* 50:155-9. doi: 10.1016/0022-5088(76)90263-0.
- Rijssenbeek, J., Gao, Y., Hanson, J., Huang, Q., Jones, C. and Toby, B. 2008. "Crystal Structure Determination and Reaction Pathway of Amide-Hydride Mixtures" *Journal of Alloys and Compounds* 454:233-44. doi: 10.1016/j.jallcom.2006.12.008.
- Shahi, R. R., Yadav, T. P., Shaz, M. A. and Srivastava, O. N. 2008. "Effects of Mechanical Milling on Desorption Kinetics and Phase Transformation of LiNH<sub>2</sub>/MgH<sub>2</sub> Mixture." *International Journal of Hydrogen Energy* 33:6188-94. doi: 10.1016/j.ijhydene.2008.07.029.
- Shahi, R. R., Yadav, T. P., Shaz, M. A. and Srivastava, O. N. 2010. "Studies on Dehydrogenation Characteristic of Mg(NH<sub>2</sub>)<sub>2</sub>/LiH Mixture Admixed with Vanadium And Vanadium Based Catalysts (V, V<sub>2</sub>O<sub>5</sub> and VCl<sub>3</sub>)." *International Journal of Hydrogen Energy* 35:238-46. doi: 10.1016/j.ijhydene.2009.10.029.
- Shaw, L. L., Osborn, W., Markmaitree, T. and Wan, X. 2008. "The Reaction Pathway and Rate-Limiting Step of Dehydrogenation of the LiNH<sub>2</sub> + LiH mixture." *Journal of Power Sources* 177: 500-5. doi: 10.1016/j.jpowsour.2007.11.029.

- Shigehito, I., Takayuki, I., Haiyan, L., Hironobu, F. and Yoshitsugu, K. 2008. "Hydrogen Desorption Processes in Li–Mg–N–H systems." *Journal of Physics and Chemistry of Solids* 69:2234–2236. doi: 10.1016/j.jpcs.2008.04.002.
- Shih-Tsien, L., Wei, K., He-Zhong, L., Jing-Kui, L. and Yun, X. 1985. "Catalytic Synthesis Of Lithium Hydride under Mild Conditions." *Acta Chimica Sinica* 3: 201-9. doi: 10.1002/cjoc.19850030304.
- Song Y. and Guo, Z. X. 2006." Electronic Structure, Stability and Bonding of the Li-N-H Hydrogen Storage System." *Physical Review B* 74:195120. doi: 10.1103/PhysRevB.74.195120.
- Sørby, M. H., Nakamura, Y., Brinks, H. W., Ichikawa, T., Hino, S., Fujii H. and Hauback, B. C. 2007. "The Crystal Structure of LiND<sub>2</sub> and Mg(ND<sub>2</sub>)<sub>2</sub>." *Journal of Alloys and Compounds* 428:97-301. doi: 10.1016/j.jallcom.2006.03.037.
- Tapia-Ruiz, N., Sorbie, N., Vaché, N., Hoang, T. and Gregory, D. 2013. "Rapid Microwave Synthesis, Characterization and Reactivity of Lithium Nitride Hydride, Li<sub>4</sub>NH, Materials." 6:5410-26. doi: 10.3390/ma6115410.
- Titherley, A. W. 1894. "Sodium, Potassium, and Lithium Amides." *Journal of the Chemical Society, Transactions* 65:504-22. doi: 10.1039/CT8946500504.
- Tokoyoda, K., Hino, S., Ichikawa, T., Okamoto, K. and Fujii, H. 2007. "Hydrogen Desorption/Absorption Properties of Li–Ca–N–H System." *Journal of Alloys and Compounds* 439:337–41. doi: 10.1016/j.jallcom.2006.08.234.
- US DOE. 2017. "Targets for Onboard Hydrogen Storage Systems for Light Duty Vehicles." Accessed 12 January 2018. [https://energy.gov/sites/prod/files/2017/05/f34/fcto\\_myrrdd\\_table\\_onboard\\_h2\\_storage\\_systems\\_doe\\_targets\\_ldv\\_1.pdf](https://energy.gov/sites/prod/files/2017/05/f34/fcto_myrrdd_table_onboard_h2_storage_systems_doe_targets_ldv_1.pdf).
- Varin, R. A., Jang, M. and Polanski, M. 2010. "The Effects of Ball Milling and Molar Ratio of LiH on the Hydrogen Storage Properties of Nanocrystalline Lithium Amide and Lithium Hydride (LiNH<sub>2</sub>+LiH) System." *Journal of Alloys and Compounds* 491:658–667. doi: 10.1016/j.jallcom.2009.11.035.
- Wang, J., Liu, T., Wu, G., Li, W., Liu, Y., Araujo, C., Scheicher, R. H., Blomqvist, A., Ahuja, R., Xiong, Z., Yang, P., Gao, M., Pan, H. and Chen, P. 2009. "Potassium-Modified Mg(NH<sub>2</sub>)<sub>2</sub>/2LiH System for Hydrogen Storage." *Angewandte Chemie International Edition* 48: 5828–32. doi: 10.1002/anie.200805264.
- Weidner, E., Bull, D. J., Shabalin, I. L., Keens, S. G., Telling, M. T. F. and Ross, D. K. 2007. "Observation of Novel Phases during Deuteration of Lithium Nitride from in situ Neutron Diffraction." *Chemical Physics Letters* 444:76–9. doi: 10.1016/j.cplett.2007.07.010.
- Wu, F. 2008. "Structure of Ternary Imide Li<sub>2</sub>Ca(NH)<sub>2</sub> and Hydrogen Storage Mechanisms in Amide-Hydride System." *Journal of the American Chemical Society* 130:6512-22. doi: 10.1021/ja800300e.

- Wu G., Xiong, Z., Liu, T., Liu, Y., Hu, J., Chen, O., Feng, Y. and Wee, A. T. S. 2007. "Synthesis and Characterisation of a New Ternary Imide –  $\text{Li}_2\text{Ca}(\text{NH})_2$ ." *Inorganic Chemistry* 46:517-21. doi: 10.1021/ic060769y.
- Xiong, Z., Wu, G., Hu, J. and Chen, P. 2004. "Ternary Imides for Hydrogen Storage." *Advanced Materials* 16:1522–5. doi: 10.1002/adma.200400571.
- Xiong Z. T., Hu, J. J., Wu, G. T., Chen, P., Luo, W. F., Gross, K. and Wang, J. 2005. "Thermodynamic and Kinetic Investigations of the Hydrogen Storage in the Li–Mg–N–H System." *Journal of Alloys and Compounds* 398: 235-9. doi: 10.1016/j.jallcom.2005.02.010.
- Xiong, Z., Wu, G., Hu, J., Chen, P., Luo, W. and Wang, J. 2006. "Investigations on Hydrogen Storage over Li–Mg–N–H Complex—the Effect of Compositional Changes." *Journal of Alloys and Compounds* 417:190–4. doi: 10.1016/j.jallcom.2005.07.072.
- Yang, J. B., Zhou, X. D., Cai, Q., James, W. J. and Yelon, W. B. 2006. "Crystal and Electronic Structures of  $\text{LiNH}_2$ ." *Applied Physics Letters* 88: 41914. doi: 10.1063/1.2163258.
- Yang, J., Sudik, A., Siegel, D., Halliday, D., Drews, A. and Carter, E. A. R. 2008. "A Self-Catalyzing Hydrogen-Storage Material." *Angewandte Chemie International Edition* 47:882–7. doi: 10.1002/anie.200703756.
- Yao, J. H., Shang, C., Aguey-Zinsou, K. F. and Guo, Z. X. 2007. "Desorption Characteristics of Mechanically and Chemically Modified  $\text{LiNH}_2$  and  $(\text{LiNH}_2+\text{LiH})$ ." *Journal of Alloys and Compounds* 432:277–82. doi: 10.1016/j.jallcom.2006.05.113.
- Zachariasen, W. H., Holley, Jr., C. E. and Stamper, Jr., J. F. 1963. "Neutron Diffraction Study of Magnesium Deuteride." *Acta Crystallographica A*, 16:352-3. doi: 10.1107/S0365110X63000967.
- Zhang, B. and Wu, Y. 2017. "Recent Advances in Improving Performances of the Lightweight Complex Hydrides Li-Mg-N-H System." *Progress in Natural Science: Materials International* 27:21–33. doi: 10.1016/j.pnsc.2017.01.005.
- Zintl, E. and Brauer, G. 1935. "Constitution of Lithium Nitride." *Zeitschrift fuer Elektrochemie und Angewandte Physikalische Chemie* 41:102. [Journal of Electrochemistry and Applied Physical Chemistry]