

HYDROGEN STORAGE BY REACTION BETWEEN METALLIC AMIDES AND IMIDES

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1- Introduction

As early as 1910, Dafert reported that a reaction between Li_3N and H_2 can occur and generate a compound with a Li_3NH_4 composition [1]. This pioneering study regains a lot of interest in 2002, when Chen claimed that large amounts of hydrogen can be reversibly stored using metallic nitrides like Li_3N or Ca_3N_2 [2]. Lithium nitride is especially promising, since its lightweight leads to hydrogen absorption of 11.4 wt. %, due to the formation of a mixture of one mole of lithium amide (LiNH_2) and two moles of lithium hydride (LiH) [3], which corresponds to the previously reported Li_3NH_4 overall composition. As the demand for highly efficient solid-state hydrogen storage materials for a future hydrogen economy is tremendous, the ability of other metal-N-H systems to store hydrogen has been studied.

This paper details the various metal-N-H systems reported in the literature as possible hydrogen storage materials. In a first part, we discuss the hydrogen storage performances of the Li-N-H system and the desorption mechanism of the LiH-LiNH_2 mixture is especially presented. The possibility of storing hydrogen using two other binary systems (Mg-N-H and Ca-N-H) is described in a second part.

If the above binary systems can store hydrogen, their thermodynamic properties are unfortunately not fully adequate for mobile applications, which require an equilibrium hydrogen pressure of one bar near ambient temperature. To solve this problem, many authors worked on the partial substitution of the metallic cations and, thus, they investigated several ternary systems. In the third part of the paper, we discuss about the performances of the highly promising Li-Mg-N-H system, for which a nice reversibility is obtained at 200°C with an experimental hydrogen capacity of about 5.0 wt. % [4]. Other ternary systems, as Li-B-N-H and Li-Al-N-H, are presented in the last part of this review paper. We especially emphasize the performances obtained in our laboratory at Amiens with a $\text{LiAl}(\text{NH}_2)_4\text{-LiH}$ mixture able to desorb around 6.0 wt. % of hydrogen at only 130°C [5].

2- Hydrogen storage in the Li-N-H system

2.1. Reaction of Li_3N with hydrogen

The pressure-composition isotherms (PCI) of Li_3N at 255°C are presented in figure 1. Upon the first hydrogenation, about 3.6 hydrogen atoms are absorbed per one Li_3N formula unit, which corresponds to 10.3 % of weight uptake. This experimental value is in rather good agreement with the formation of one mole of LiNH_2 and two moles of LiH . The desorption step of the 1st cycle cannot return to the origin, as only two hydrogen atoms are released.

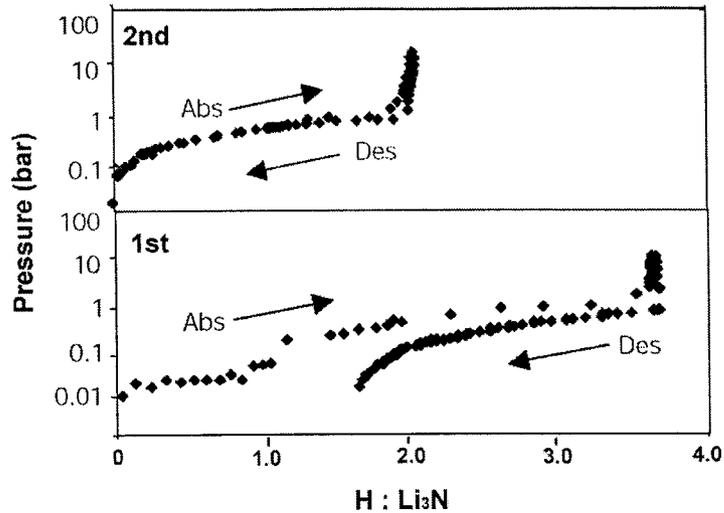


Figure 1. Pressure-Composition isotherms at 255°C for Li_3N : 1st and 2nd absorption-desorption cycles (from ref. [2]).

For the 2nd cycle, the isotherm shows a good reversibility with a hydrogen capacity of about 5.2 wt. %. Through X-ray diffraction, it was shown that the pristine hexagonal Li_3N compound (figure 2a) initially evolves to face-centred cubic Li_2NH and LiH phases (figure 2b). After full hydrogenation, the sample is composed of body-centred tetragonal LiNH_2 and LiH phases (figure 2c) in accordance with the following two-steps reaction path:



Upon desorption, Li_3N cannot be easily formed back, since the dehydrogenated sample remains a mixture of Li_2NH and LiH phases (figure 2d), so that the reversible hydrogen storage is limited to the reaction between lithium imide (Li_2NH) and lithium amide (LiNH_2).

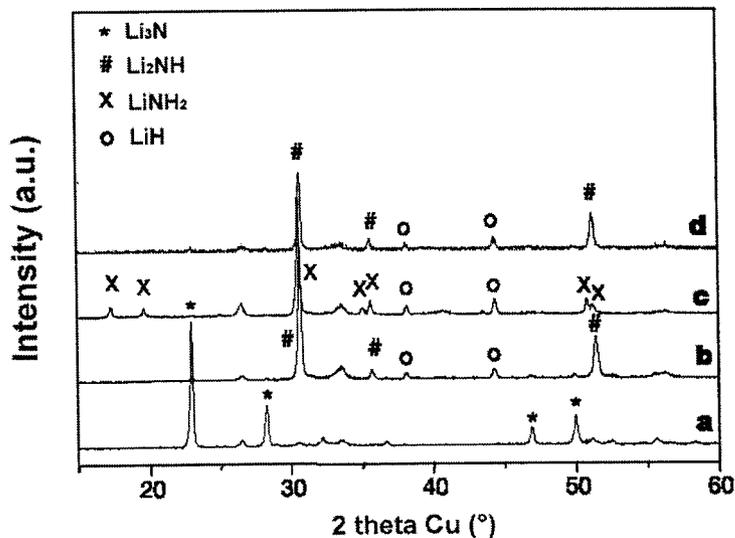


Figure 2. Structural changes during hydrogen absorption-desorption for Li_3N (from ref. [2]). (a) Pristine Li_3N , (b) half-hydrogenated, (c) fully hydrogenated, (d) dehydrogenated.

The above results do not come as a surprise, since the enthalpies for reaction (1) and (2) are -165 and -45 kJ/mol, respectively. Reaction (2) is the only one suitable for a practical hydrogen storage, which limits the capacity to 5.2 wt. %. In order to avoid the presence of inactive LiH formed in reaction (1) and enhance the reversible capacity, it is therefore more suitable to start with lithium imide (Li_2NH) instead of Li_3N . This allows the increase in hydrogen capacity up to 6.5 wt. %.

2.2. Interaction between LiH and LiNH_2

Pure lithium amide (LiNH_2) decomposes to lithium imide (Li_2NH) and ammonia around 380°C [6], whereas lithium hydride liberates hydrogen at temperatures above 500°C [7]. By thoroughly ball-milling LiNH_2 and LiH, hydrogen can be desorbed at a temperature as low as 250°C , with a very low ammonia release [8], as shown in figure 3 with TPD-MS spectra (temperature-programmed-desorption coupled with a mass-spectrometer). This is indicative of a strong interaction between LiNH_2 and LiH in a nano-crystallized ball-milled powder.

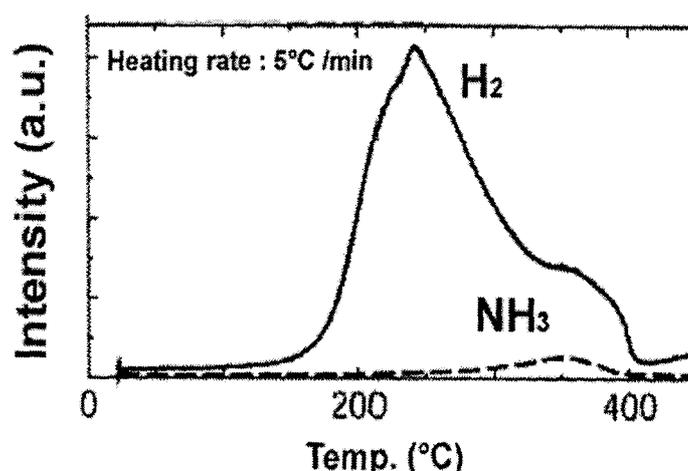


Figure 3. Thermal desorption spectra of hydrogen and ammonia for a ball-milled 1:1 LiH- LiNH_2 mixture (from ref. [8]).

The dehydriding reaction kinetic for 1:1 ball-milled LiH- LiNH_2 mixture was carefully studied [8]. About 5.8 wt. % of hydrogen (90 % of the theoretical capacity) is desorbed within 3 hours at 210°C under vacuum. By adding 1 mol % of TiCl_3 as catalyst, this desorption time can be reduced to 45 min at the same temperature [9]. Interestingly, TiCl_3 is also well-known for its beneficial enhancement of the hydrogen desorption kinetics of sodium alanate (NaAlH_4). The exact mechanism for the kinetics improvement has not yet been identified for both amide and alanate compounds.

The desorption mechanism of the LiH- LiNH_2 mixture was further investigated. A material formed of two pellets stacked onto each other, one being LiH and the other LiNH_2 , was studied by a TPD-MS technique [10-11]. When the vector gas (He) went through the LiNH_2 layer first and then through the LiH layer, only hydrogen was detected in the desorbing gas. In contrast, when the vector gas goes through the LiH layer first and then through the LiNH_2 layer, ammonia was detected in the temperature range between 300 and 400°C . This suggests that ammonia formed by the LiNH_2 decomposition reacts with LiH to form hydrogen. Therefore, it was deduced that hydrogen desorption process for a LiH- LiNH_2 mixture follows a two-steps reaction:



By varying the velocity of the vector gas, the reaction time of NH_3 with LiH has been determined to be of the order of 25 ms [10]. The ultra-fast reaction of LiH and NH_3 prevents an ammonia contamination of the hydrogen desorbing flow. Moreover, this simply means that the kinetic for hydrogen desorption of the LiH-LiNH_2 mixture is controlled by the decomposition rate of LiNH_2 (reaction 3).

Owing to the numerous studies carried out on this system, it is now well recognized that 1:1 LiH-LiNH_2 mixture is a good hydrogen storage material with a hydrogen capacity as high as 6.5 wt. %. Figure 4 gives two pressure-composition isotherms obtained for a 1:1 LiH-LiNH_2 mixture [12]: the values for the plateau pressures are about 2 and 12 bars at 300 and 400°C, respectively. Actually, a temperature of about 280°C is required to obtain a one bar equilibrium hydrogen pressure. This temperature being too high for applications such as polymer electrolyte membrane fuel-cells, many studies have been devoted to the destabilization of the LiH-LiNH_2 system by the partial substitution of Li by other elements, as discussed later with the Li-Mg-N-H system.

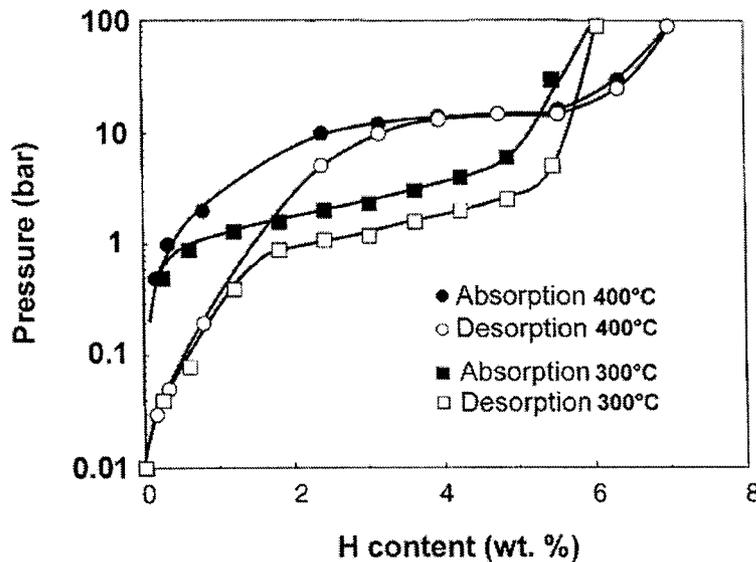
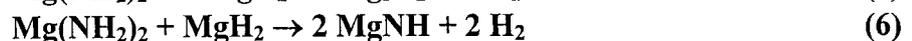
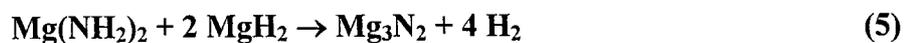


Figure 4. Pressure-compositions isotherms at 300 and 400°C for ball-milled 1:1 LiH-LiNH_2 mixture (from ref. [12]).

3- Other binary metal-N-H systems

3.1. Mg-N-H system

Due to the interesting performances obtained with the LiH-LiNH_2 mixture, several authors have then examined the possibility of storing hydrogen in the Mg-N-H system and they especially focused their efforts on the following reactions having theoretical hydrogen releases of 7.3 and 4.8 wt. %, respectively:



Actually, Nakamori has shown that the weight loss (under one bar of argon) for the 1:2 $\text{Mg}(\text{NH}_2)_2\text{-MgH}_2$ mixture largely exceeds (reaching 16 % at 350°C) the expected value suggesting that not only hydrogen but also ammonia is desorbed upon heating [13]. The intrinsic reason is that, as demonstrated for the Li-N-H system, the desorption occurs via a two-steps process involving first the $\text{Mg}(\text{NH}_2)_2$ decomposition into MgNH and NH_3 , and then the reaction between MgH_2 and NH_3 to form hydrogen. But, the kinetic of this second step is limited: it is much slower than that of LiH with ammonia. Therefore, a significant amount of ammonia contaminates the desorption flow when heating the $\text{Mg}(\text{NH}_2)_2\text{-MgH}_2$ mixture.

More recent papers mention that the ammonia content can be reduced if the $\text{Mg}(\text{NH}_2)_2$ and MgH_2 phases are thoroughly ball-milled. In this case, the experimental hydrogen release at 300°C is close to the expected capacity (7.2 wt. %) and it was confirmed that the desorption product is Mg_3N_2 [14]. Thermodynamic analysis reveals that reaction (5) is mildly endothermic (heat of desorption around 3 kJ/mol H_2), indicating that Mg_3N_2 is hardly converted back to $\text{Mg}(\text{NH}_2)_2$ and MgH_2 under moderate hydrogenation conditions. The Mg-N-H system appears therefore poorly reversible.

3.2. Ca-N-H system

The Li-N-H system has attracted a lot of attention due to its lightweight, but calcium nitride was already reported in the pioneering work of Chen et al. as another compound able to reversibly store hydrogen [2]. The Ca-N-H system was further investigated starting from mixtures of $\text{Ca}(\text{NH}_2)_2$ and CaH_2 [15], for which the hydrogen desorption follows a two-steps process:



Since the first step is exothermic, only the second one (reaction 8) appears suitable for reversible hydrogen storage. The corresponding pressure-composition isotherm at 500°C is presented in figure 5. About 1.8 hydrogen atoms are reversibly stored leading to a low capacity of 1.9 wt. %. Indeed, this Ca-N-H system is very disappointing, because a temperature of at least 400°C is required to achieve a nice reversibility and the theoretical hydrogen capacity is limited to 2.1 wt. %.

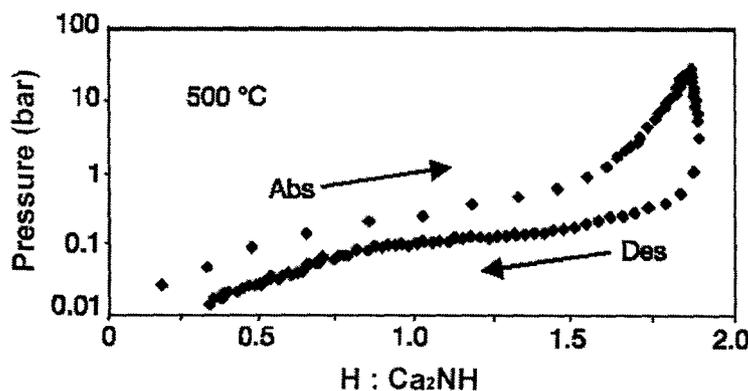


Figure 5. Pressure-composition isotherm at 500°C for Ca_2NH (from ref. [2]).

As a conclusion on the different binary systems, we have to emphasize that, although reversible hydrogen storages in the Mg-N-H and Ca-N-H systems have been demonstrated,

the Li-N-H compounds remain much more promising for the development of highly efficient hydrogen storage materials.

4. Hydrogen storage in the Li-Mg-N-H system

As shortly discussed previously, substitution of Li by other elements in the Li-N-H system could lead to materials more adequate from a thermodynamic point of view, which means having a one bar equilibrium hydrogen pressure at a temperature lower than 280°C. This hypothesis was confirmed by first-principle calculations predicting that an effective method for destabilizing LiNH₂ is to partially substitute Li by other elements with larger electronegativity [16-18]. In parallel to these theoretical approaches, Luo has experimentally studied the desorption behaviour of a ball-milled 1:2 MgH₂-LiNH₂ mixture [19], for which the corresponding pressure-composition isotherms at 200, 220 and 240°C are presented in figure 6. The plateau pressures are high: the Li-Mg-N-H system has an equilibrium pressure of 34 bars at 200°C, whereas it is largely below one bar at the same temperature for the 1:1 LiH-LiNH₂ mixture.

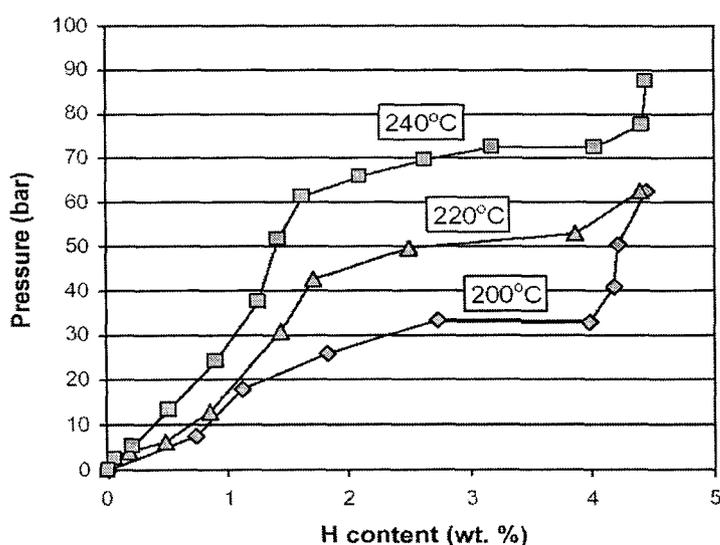


Figure 6. Pressure-composition isotherms at 200, 220 and 240°C for ball-milled 1:2 MgH₂-LiNH₂ mixture (from ref. [19]).

The desorption enthalpy was calculated from these isotherms using the Van't Hoff law: its value is about 39 kJ/mol H₂ for the 1:2 MgH₂-LiNH₂ mixture [19], while it ranges from 45 [2] to 65 kJ/mol H₂ [12] for 1:1 LiH-LiNH₂. Therefore, it can be seen that the substitution of LiH by the less stable MgH₂ hydride significantly reduces the system stability. If the hydrogen equilibrium pressures are high at temperatures required for reversibility, the extrapolation of the Van't Hoff plot reveals that a pressure around one bar is expected at 90°C [20-21], which would satisfy the pressure-temperature conditions required for mobile fuel-cells applications. The enhancement of the reactivity, at low temperatures, of the 1:2 MgH₂-LiNH₂ mixture by adding adequate catalysts should be therefore a promising way to make a good material for on-board hydrogen storage.

Actually, we have shown later in our laboratory that the desorption of the 1:2 MgH₂-LiNH₂ mixture leads to a never reported Li₂Mg(NH)₂ imide and that, upon rehydrogenation, this compound does not go back to the starting phases, but rather to a mixture of Mg(NH₂)₂ and

LiH [4]. This transformation can be easily observed from the X-ray diagrams exhibited in figure 7. The following reaction is therefore responsible for reversible hydrogen storage:



The structure of the new ternary $\text{Li}_2\text{Mg}(\text{NH})_2$ imide was recently determined by combined synchrotron X-ray diffraction and neutron diffraction studies [22]. This phase crystallizes in an orthorhombic unit cell with Ibam or Iba2 space group. It remains difficult to distinguish Ibam from Iba2 based on systematic absences of the experimental diffractograms. This structure can be described as a supercell of cubic Li_2NH , with a doubling of the a axis, due to the ordering of the cation vacancy introduced by the substitution of two Li atoms by a single Mg atom. Moreover, at elevated temperatures, $\text{Li}_2\text{Mg}(\text{NH})_2$ undergoes two structural transitions from orthorhombic to primitive cubic at 350°C and, then, from primitive cubic to face-centred-cubic at 500°C . The disordering of the Li, Mg and cation vacancies as a function of temperature drives the structural transitions.

The experimental hydrogen absorption of $\text{Li}_2\text{Mg}(\text{NH})_2$ is about 5.0 wt. % at 200°C in good agreement with reaction (9) (theoretical capacity of 5.6 wt. %). In addition, we have to emphasize that, in spite of the low density of the 1:2 $\text{Mg}(\text{NH}_2)_2$ -LiH mixture (1.1 as measured by liquid pycnometry), the volumetric capacity is rather high: close to $60 \text{ g}/\text{dm}^3$ vs. $70 \text{ g}/\text{dm}^3$ for pure liquid hydrogen.

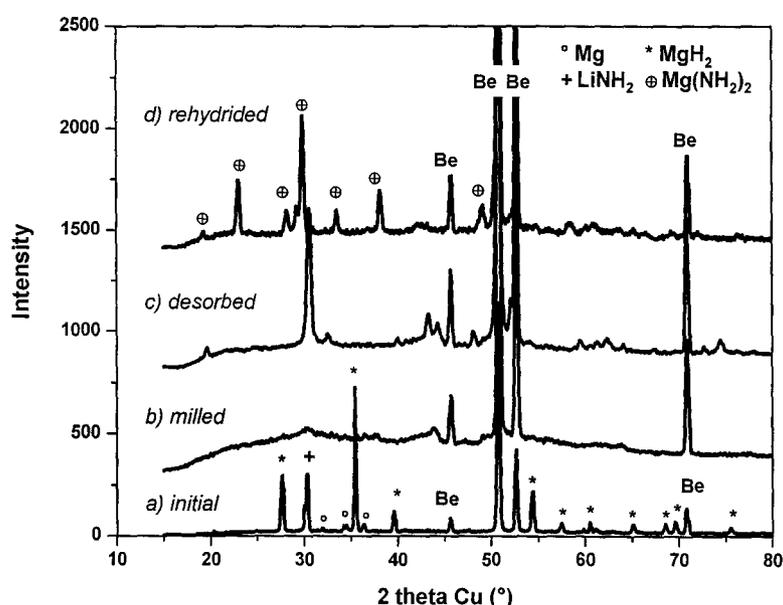


Figure 7. X-ray diagrams of 1:2 MgH_2 - LiNH_2 : initial mixture (a), 12 h ball-milled (b), desorbed at 200°C (c), rehydrogenated under 100 bars at 200°C (d)

To get a better knowledge of the reaction mechanism, we undertook a direct comparison of the first hydrogen desorption processes of the 1:2 $\text{Mg}(\text{NH}_2)_2$ -LiH and 1:2 MgH_2 - LiNH_2 mixtures. Indeed, a slight ammonia release occurs when heating 1:2 MgH_2 - LiNH_2 under vacuum. This can be explained if we assume that the hydrogen release proceeds via the classical two-steps reaction encountered with the amide-hydride systems. The following two reactions can be written for the 1:2 MgH_2 - LiNH_2 mixture:



As the reaction of MgH_2 with NH_3 (reaction 11) is slow, a slight amount of ammonia can be released when the 1:2 MgH_2 - LiNH_2 mixture is desorbed under dynamic vacuum. Conversely, for 1:2 $\text{Mg}(\text{NH}_2)_2$ - LiH , the presence of LiH in the initial mixture avoids the ammonia release (as shown by mass spectrometry in figure 8) as LiH reacts very quickly with NH_3 [10] issued from the $\text{Mg}(\text{NH}_2)_2$ decomposition. LiH acts as an ammonia getter and therefore enables to keep the integrity of the starting material and to have a better cyclability upon the following hydrogen absorption-desorption cycles.

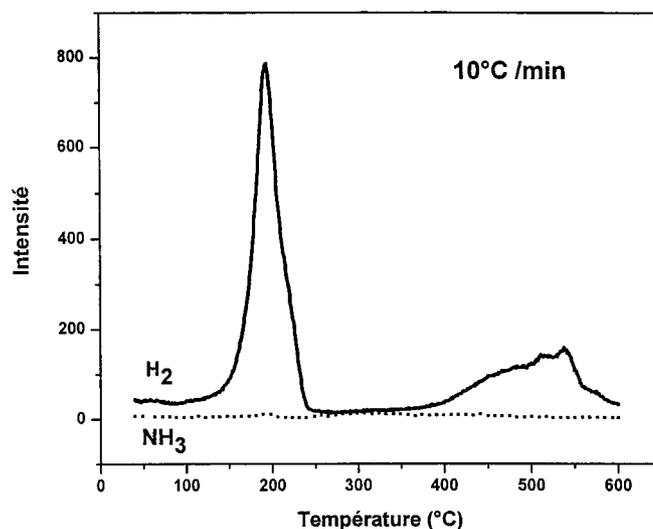


Figure 8. Thermal desorption spectra of hydrogen and ammonia for 1:2 $\text{Mg}(\text{NH}_2)_2$ - LiH

Figure 9 shows the desorption kinetics under primary vacuum, for the 1:2 $\text{Mg}(\text{NH}_2)_2$ - LiH mixture, at different temperatures (180, 200 and 220°C). At 180°C, the full desorption (around 5.1 % of weight loss) occurs in 180 min. The desorption rates are much faster at 200 and 220°C, since 60 and 25 min are sufficient for the achievement of the desorption process, making the 1:2 $\text{Mg}(\text{NH}_2)_2$ - LiH system as one of the most performing materials with high storage capacities at these temperatures. The activation energy of desorption process was calculated using the Arrhenius law; a value of 107 kJ/mol was found, which is in very good agreement with that reported by Xiong (102 kJ/mol) [20]. This high kinetic barrier puts at the present a restriction onto the low temperature applications of 1:2 $\text{Mg}(\text{NH}_2)_2$ - LiH without the help of catalysts addition.

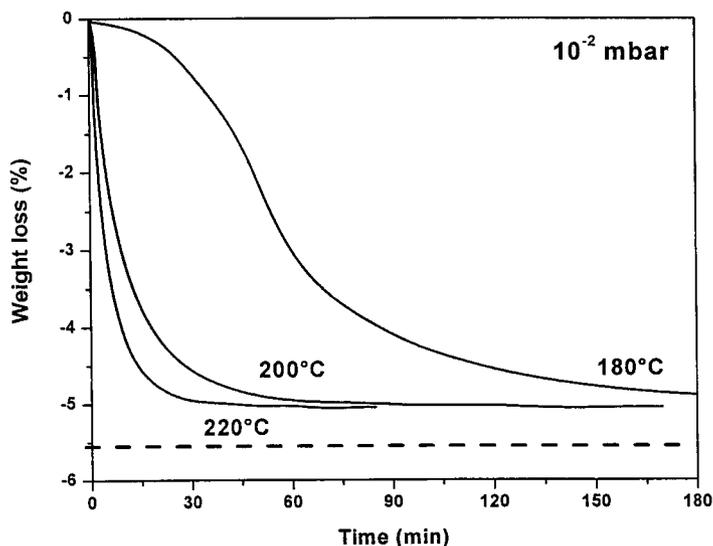
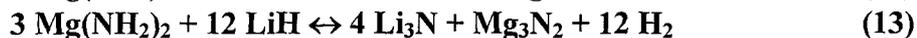
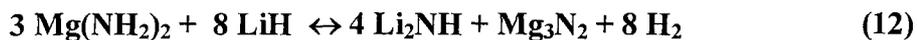


Figure 9. Desorption kinetics of ball-milled 1:2 $\text{Mg}(\text{NH}_2)_2$ - LiH

The performances of mixtures with higher LiH / Mg(NH₂)₂ molar ratio were also studied in order to increase the hydrogen storage capacity. The reactions (12) and (13) with theoretical hydrogen capacities of 7.0 and 9.2 wt. % have been successfully achieved by Leng [23] and Nakamori [24], respectively:



Although the hydrogen capacity increases with the molar ratio of LiH to Mg(NH₂)₂, the temperature for complete hydrogen desorption is strongly increased from 200°C for reaction (8) to more than 500°C for reaction (12). Indeed, the high stabilities of the transitory imide phases formed upon desorption make difficult the achievement of the formation of Li and Mg nitrides. It seems that the ball-milled 1:2 Mg(NH₂)₂-LiH mixture remains the best material among the Li-Mg-N-H system, due to both a high hydrogen storage capacity (5.6 wt. %) and a relatively low operating temperature (200°C).

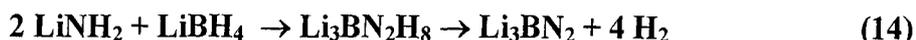
Aiming at further decreasing the desorption temperature, preliminary results have been reported on the Na-Mg-N-H system [25]. The ball-milled 1:1.5 Mg(NH₂)₂-NaH mixture can reversibly store hydrogen at a temperature as low as 160°C. However, the capacity is limited to about two hydrogen atoms, that means 2.1 wt. % of the starting material. The structural changes occurring upon hydrogen absorption-desorption are still unknown.

5. Other ternary systems

5.1. Li-B-N-H system

Combination of LiBH₄ and LiNH₂ by ball-milling has recently become the subjects of increasing research activities, due to the possibility of forming various Li-B-N-H phases. Meisner has even published an experimental binary LiBH₄-LiNH₂ phase diagram [26] revealing the possible existence of at least three different defined compounds: Li₂BNH₆, Li₃BN₂H₈ and Li₄BN₃H₁₀. Actually, these compounds cannot be considered as pure amides as their structure is formed by the coexistence in the same crystallographic unit cell of the two complex BH₄⁻ and NH₂⁻ anions [27].

As possible hydrogen storage materials, it appears that Li₃BN₂H₈ is the most promising phase with a hydrogen release exceeding 10.0 wt. % around 350°C (cf. Figure 10) and a limited ammonia contamination (2-3 mole % of the generated gas) [28]. Further experiments have shown that the Li₃BN₂H₈ compound melts at 190°C and therefore that the hydrogen release occurs from the liquid state leading after full desorption to a mixture of various solid Li₃BN₂ polymorphs [29]. The theoretical hydrogen release is 11.8 wt. % according to the following reaction:



Calorimetric investigations indicate that the desorption process of Li₃BN₂H₈ is exothermic, implying that the reverse reaction is not thermodynamically favoured and is not feasible under moderate conditions.

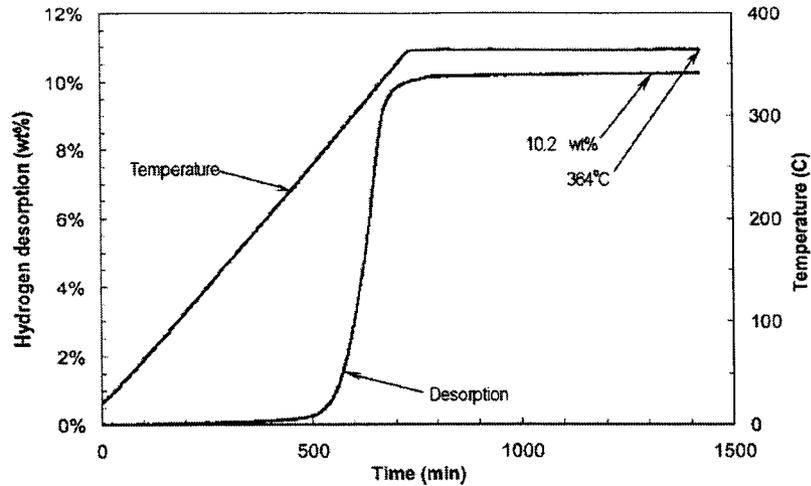


Figure 10. Hydrogen desorption of $\text{Li}_3\text{BN}_2\text{H}_8$ (from ref. [28])

5.2. Li-Al-N-H system

Several groups [30-32] have shown that LiAlH_4 can be strongly destabilized by mixing with LiNH_2 . For the 1:2 LiNH_2 - LiAlH_4 mixture, a large amount of hydrogen is already desorbed upon ball-milling with decomposition of LiAlH_4 into Li_3AlH_6 and Al. Heating under vacuum at 300°C of this ball-milled powder leads to an additional hydrogen release. The overall hydrogen desorption reaches almost 8.0 wt. %, which is in very good agreement with the following reaction:



Unfortunately, most of the desorbed hydrogen cannot be loaded back, probably due to thermodynamic reasons, which are still not clearly identified.

The ability of Li_3AlN_2 to reversibly store hydrogen has been also discussed in a recent paper by Chen [33]. As shown in figure 11, about 5.1 wt. % of hydrogen can be absorbed and desorbed by Li_3AlN_2 . If the absorption is achieved at temperature below 350°C , the hydrogen release is much more difficult, since a temperature of 500°C is required to complete the hydrogen recovery. The fully hydrogenated sample consists of a mixture of LiNH_2 , LiH and AlN :



Indeed, it is amazing to notice that this reaction is closely related to the first one described in the paper about the hydrogenation of Li_3N [2]. Here, Li_3AlN_2 can be simply considered as $\text{Li}_3\text{N} + \text{AlN}$, the latter nitride being inert during the hydrogenation process!!

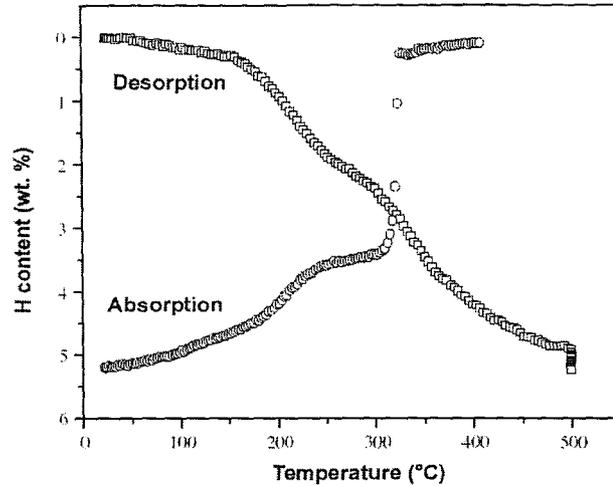
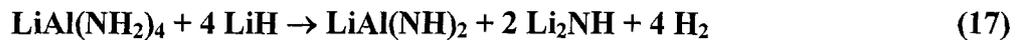


Figure 11. Hydrogen absorption and desorption of Li_3AlN_2 (from Ref. [33])

The investigation of the Li-Al-N-H system has been carried out in our laboratory through an original approach consisting, first, in the preparation of the $\text{LiAl}(\text{NH}_2)_4$ compound and, then, its mixture with LiH [5]. The thermal decomposition of $\text{LiAl}(\text{NH}_2)_4$ under primary vacuum leads to a strong ammonia release at 138°C related to the formation of the $\text{LiAl}(\text{NH})_2$ imide. Following a similar process as that demonstrated for the Li-N-H system, four moles of LiH have been successfully added to one mole of $\text{LiAl}(\text{NH}_2)_4$ to trap ammonia, due to the very fast reaction of LiH with NH_3 . The following reaction, with a theoretical hydrogen release of 6.2 wt. %, is expected:



The 1:4 $\text{LiAl}(\text{NH}_2)_4$ -LiH mixture desorbs a large amount of hydrogen around 130°C , whereas no ammonia release is observed at the same temperature, as shown by mass spectrometry in figure 12. The experimental desorption capacity, obtained by both gravimetric and volumetric measurements, exceeds 5.5 wt. % (cf. figure 13). This material is therefore highly promising as it desorbs hydrogen at a temperature about 60°C lower than the 1:2 $\text{Mg}(\text{NH}_2)_2$ -LiH mixture.

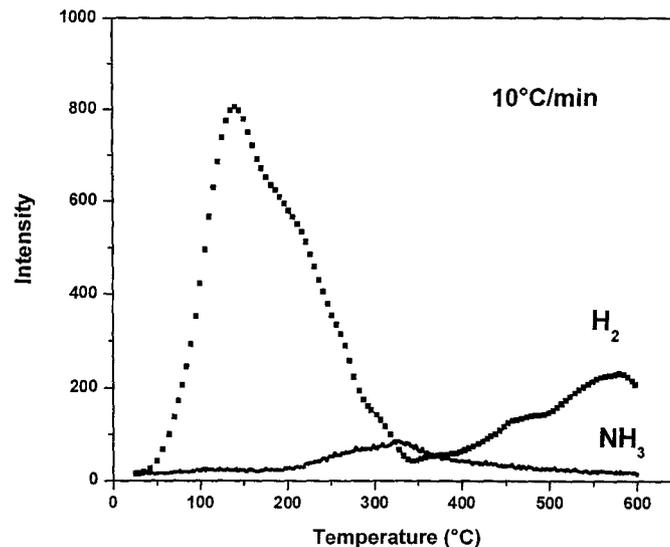


Figure 12. Thermal desorption spectra of hydrogen and ammonia of 1:4 $\text{LiAl}(\text{NH}_2)_4$ -LiH

Unfortunately, the attempts of rehydrogenation at 130°C are not successful. It seems that these poor performances are due to the low stability of $\text{LiAl}(\text{NH}_2)_2$ formed upon desorption. This $\text{LiAl}(\text{NH}_2)_2$ compound is rapidly decomposed into a mixture of LiNH_2 and AlN [5], the latter phase being inert towards hydrogen at 130°C. Due to the lack of reactivity of AlN , the Li-Al-N-H system does not therefore present a good reversibility for the hydrogen storage process.

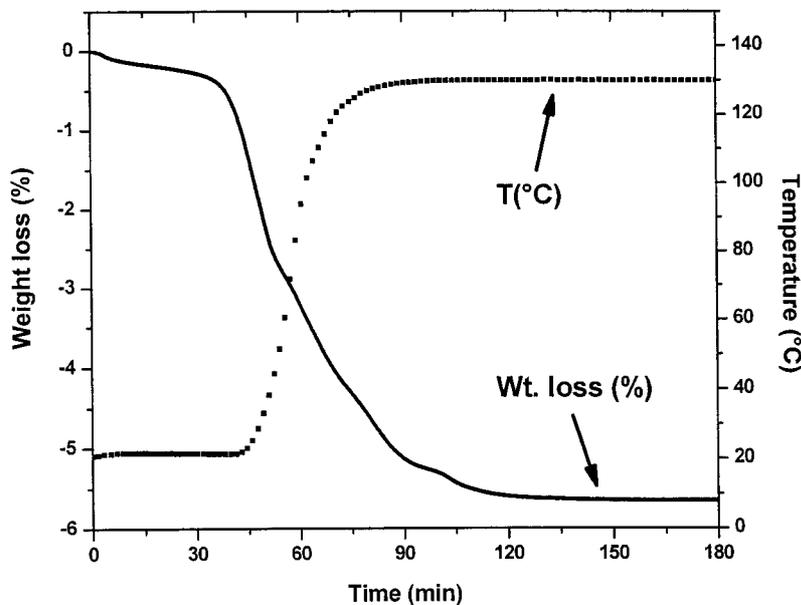


Figure 13. Hydrogen desorption of ball-milled 1:4 $\text{LiAl}(\text{NH}_2)_4\text{-LiH}$

Additional experiments are presently being pursued to try to stabilize the $\text{LiAl}(\text{NH}_2)_2$ phase and other materials able to desorb large amounts of ammonia at low temperatures are studied in the hope that their mixtures with appropriate amounts of LiH can give new materials able to store large amounts of hydrogen at temperatures around 100°C.

6. Conclusions

Metal-N-H systems provide interesting materials for reversible hydrogen storage. Table I summarizes the systems that have been investigated and their main hydrogen storage properties. The mixtures with hydrogen capacities reaching 10.0 wt. % (as 1:2 $\text{LiNH}_2\text{-LiH}$ and 1:4 $\text{Mg}(\text{NH}_2)_2\text{-LiH}$) unfortunately need a high temperature (more than 500°C), and often a secondary vacuum, to achieve metallic nitrides formation and therefore a full hydrogen desorption. Conversely, the Li-B-N-H and Li-Al-N-H systems exhibit very nice desorption curves, especially the 1:4 $\text{LiAl}(\text{NH}_2)_4\text{-LiH}$ mixture able to desorb about 6.0 wt. % of hydrogen at only 130°C. But, these materials suffer from a poor reversibility, due to the lack of reactivity of Li_3BN_2 or AlN towards hydrogen under moderate conditions.

Another important point concerns the possible ammonia contamination of the desorbing flow. This phenomenon is especially encountered for the Mg-N-H system, due to the slow reaction kinetic between MgH_2 and ammonia. To solve this problem, the positive effect of LiH as ammonia getter, when present in the starting mixture, is demonstrated by many studies. This

is a key issue and has led to the preparation of Li-Mg-N-H materials with very nice performances.

Indeed, among the various amide-imide systems of Table I, the 1:2 $\text{Mg}(\text{NH}_2)_2\text{-LiH}$ mixture presently appears as the best hydrogen storage material, with a high capacity (5.6 wt. %), a relatively low operating temperature (about 190°C) and only traces of ammonia contamination. Efforts have still to be made to increase its reactivity at lower temperatures, since this material could lead to an equilibrium hydrogen pressure of about one bar at 90°C , which is the pressure-temperature couple required for mobile applications.

Table I. Hydrogen storage properties for various metallic amide-imide systems.

| Starting materials | Desorption products | wt. % H | Temp. desorption | Reversibility | Ref. |
|--|---------------------------------------|---------|--------------------------|---------------|------------|
| 1:1 $\text{LiNH}_2\text{-LiH}$ | Li_2NH | 6.5 | 280°C | + | [8-9] |
| 1:2 $\text{LiNH}_2\text{-LiH}$ | Li_3N | 10.3 | $\sim 500^\circ\text{C}$ | - | [2-3] |
| 1:1 $\text{Mg}(\text{NH}_2)_2\text{-MgH}_2$ | MgNH | 4.8 | 300°C | - | [14] |
| 1:2 $\text{Mg}(\text{NH}_2)_2\text{-MgH}_2$ | Mg_3N_2 | 7.3 | 350°C | -- | [13] |
| 1:1 CaNH-CaH_2 | Ca_2NH | 2.1 | 500°C | - | [15] |
| 1:2 $\text{Mg}(\text{NH}_2)_2\text{-LiH}$ | $\text{Li}_2\text{Mg}(\text{NH})_2$ | 5.6 | 190°C | ++ | [4, 19-21] |
| 3:8 $\text{Mg}(\text{NH}_2)_2\text{-LiH}$ | $\text{Li}_2\text{NH-Mg}_3\text{N}_2$ | 7.0 | $\sim 400^\circ\text{C}$ | + | [23] |
| 1:4 $\text{Mg}(\text{NH}_2)_2\text{-LiH}$ | $\text{Li}_3\text{N-Mg}_3\text{N}_2$ | 9.2 | $\sim 500^\circ\text{C}$ | - | [24] |
| 2:1 $\text{LiNH}_2\text{-LiBH}_4$ | Li_3BN_2 | 11.8 | 350°C | -- | [28] |
| 1:2 $\text{LiNH}_2\text{-LiAlH}_4$ | $\text{Al-Li}_2\text{NH-LiH}$ | 8.1 | 300°C | -- | [30-32] |
| 1:4 $\text{LiAl}(\text{NH}_2)_4\text{-LiH}$ | $\text{AlN-Li}_2\text{NH}$ | 6.2 | 130°C | -- | [5] |

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