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## Effect of $\beta$ - $\text{Li}_3\text{N}$ phase, $\text{Li}_2\text{O}$ addition and thermal treatment on the hydrogen sorption behavior of $\text{Li}_3\text{N}$

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## ABSTRACT

The hydriding of  $\text{Li}_3\text{N}$  to  $\text{LiNH}_2$  is investigated to clarify the influence of the  $\beta$ - $\text{Li}_3\text{N}$  phase, the addition of  $\text{Li}_2\text{O}$  and the thermal treatment of  $\text{Li}_3\text{N}$  on the hydrogen storage properties of the Li–N–H system. As-milled  $\text{Li}_3\text{N}$  displays fast initial absorption that is attributed to the formation of  $\beta$ - $\text{Li}_3\text{N}$  nanograins, the increase of the surface area, and the presence of surface defects induced by mechanical milling. However, further hydrogen absorption is retarded in comparison with the as-received sample due to the presence of the  $\beta$ - $\text{Li}_3\text{N}$  phase formed during milling. Thus, commercial  $\text{Li}_3\text{N}$  exhibits the highest hydrogen storage capacity in the first cycle in comparison with as-heated  $\text{Li}_3\text{N}$  and as-milled samples. In the case of  $\text{Li}_2\text{O}$  addition, no interaction with  $\text{Li}_3\text{N}$  was detected. The addition of  $\text{LiH}$  to the commercial  $\text{Li}_3\text{N}$ , as-milled  $\text{Li}_3\text{N}$  and  $\text{Li}_3\text{N}$ - $\text{Li}_2\text{O}$  influences only the stability of the samples under hydrogen cycling. The hydrogen absorption/desorption behavior is mainly controlled by the amount of  $\beta$ - $\text{Li}_3\text{N}$  formed during milling, while at long times the microstructure has a minor effect.

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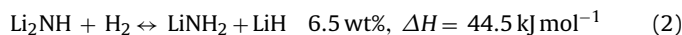
## 1. Introduction

Considering the increasing of both environmental pollution and consumption of fossil energy resources, alternative energy carriers will become essential for the future industrial society. Hydrogen emerges as an excellent candidate mainly for its abundance and nonpolluting nature. However, its utilization as an energy carrier for a sustainable economy requires overcoming several scientific and technological limitations, in particular the development of suitable hydrogen storage media [1].

Storing hydrogen as a solid hydride material is attractive, being both a safe and an efficient strategy. Its volumetric density may be higher than the densities of both compressed and liquid hydrogen. In the last 30 years, substantial progress has been made in optimizing the thermodynamic/kinetic properties of several metal–hydrogen systems. Unfortunately, advances originated in the study of conventional reversible hydrides failed to propose a solution to the problem of hydrogen storage [1–3]. While some materials such as  $\text{MgH}_2$  meet the requirement of gravimetric capacity (7.6 wt% of H), their application is limited due to high thermodynamic stability (for  $\text{MgH}_2$ ,  $\Delta H \cong 70$ – $74 \text{ kJ mol}^{-1} \text{ H}_2$ ), resulting

in high temperatures for hydrogen desorption at atmospheric pressure.

The family of complex hydrides (alanates  $\text{AlH}_4^-$ , amides  $\text{NH}_2^-$  and borohydrides  $\text{BH}_4^-$ ) formed by light metals of groups I–III (Li, Na, Mg) are an alternative to the traditional hydrides. They have excellent gravimetric densities (between 6 and 18 wt% of H) and volumetric densities ( $>100 \text{ kg m}^{-3}$ ) [4,5]. In particular, the Li–N–H system has received special attention in the recent years, starting with the report of Chen et al. [6]. These authors proposed that the  $\text{Li}_3\text{N}$  nitride absorbs hydrogen reversibly according to the following reactions:



Hydriding was accomplished at 0.3 MPa of hydrogen in the temperature range of 170–210 °C for the first step, and about 255 °C for the second step. This last reaction provides a good theoretical hydrogen storage capacity, with a relatively low enthalpy of reaction and a reasonable hydrogen pressure of about 0.1 MPa at 285 °C. Furthermore, additional studies have shown that hydrogen desorption from the  $\text{LiNH}_2$  amide (reverse of reaction (2)) proceeds in two steps [7–11]. First, the amide decomposes to release ammonia ( $\text{NH}_3$ , reaction (3)), which subsequently reacts with the  $\text{LiH}$  hydride to form hydrogen and  $\text{LiNH}_2$  (reaction (4)).



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Ichikawa et al. [8] confirmed the presence of  $\text{NH}_3$  as a gaseous intermediate during decomposition of  $\text{LiNH}_2$ – $\text{LiH}$ . Interestingly, they showed that the quantity of evolved  $\text{NH}_3$  decreases sharply when  $\text{LiNH}_2$  and  $\text{LiH}$  react in a 1:2 ratio or when the  $\text{LiNH}_2$ – $\text{LiH}$  mixture is ball milled. In an independent study [9], it has been demonstrated that reaction (4) is ultrafast and can take place in the order of microseconds,  $\text{LiH}$  being the responsible of the  $\text{NH}_3$  capture.

Several studies have focused on the hydrogen storage properties of the  $\text{LiNH}_2$ – $\text{LiH}$  system, whereas there are fewer works concerning the hydriding process starting from  $\text{Li}_3\text{N}$  [12–15]. Hu and Ruckenstein [12] have reported that partially oxidized  $\text{Li}_3\text{N}$  ( $\text{Li}_2\text{O}$ – $\text{Li}_3\text{N}$ ) is able to absorb reversibly 5 wt% of hydrogen in only 3 min at 180–200 °C. The combination of partial oxidation of  $\text{Li}_3\text{N}$  and the high hydriding/dehydriding temperature was proposed to be the responsible of the improved hydrogen storage observed (fast kinetics and good stability). According to the authors, the presence of  $\text{Li}_2\text{O}$  avoids the generation of hot spots during the hydrogen absorption; the estimated amount of  $\text{Li}_2\text{O}$  was 17 wt%. In another work, the same authors [13] have shown the effect of the heat pretreatment of  $\text{Li}_3\text{N}$  on the hydrogen storage capacity and stability. Despite commercial  $\text{Li}_3\text{N}$  quickly absorbed 5.5 wt% of hydrogen at 230 °C, additional 50 h were required for 2.5 wt% of hydrogen. In contrast,  $\text{Li}_3\text{N}$  preheated at 400 °C in vacuum for 4.5 h absorbed 3 wt% at 230 °C and required only 5 h for extra 6.5 wt% of hydrogen. The same authors [14] demonstrated that the dehydriding of hydrided  $\text{Li}_3\text{N}$  at 400 °C under vacuum induces deactivation of  $\text{Li}_3\text{N}$  as a consequence of sintering. These results are contradictory in relation with the effect of thermal treatment on hydrogen absorption. A recent work has focused on the hydriding of commercial  $\text{Li}_3\text{N}$ , milled  $\text{Li}_3\text{N}$  and  $\text{Li}_3\text{N}$  doped with  $\text{Li}_2\text{O}$  [15]. The as-milled  $\text{Li}_3\text{N}$  material showed the lowest onset temperature for hydrogenation and better cycling properties than the unmilled  $\text{Li}_3\text{N}$ . The addition of  $\text{Li}_2\text{O}$  did not enhance the hydrogen storage performance of commercial  $\text{Li}_3\text{N}$ .  $\text{Li}_2\text{O}$  remains as a separate phase without evidence of interaction with  $\text{Li}_3\text{N}$ .

Recently, experimental evidence and theoretical calculations strongly suggested that the reaction pathways for hydriding/dehydriding  $\text{Li}_3\text{N}$  are more complex than that represented by Eqs. (1) and (2) [16–20]. David et al. [16] have reported a series of non-stoichiometric phases with composition  $\text{Li}_{2-x}\text{NH}_{1+x}$  in the decomposition product of hydrided  $\text{Li}_3\text{N}$ . Indeed, both  $\text{Li}_2\text{NH}$  and  $\text{LiNH}_2$  are the end members of this series with values of  $x=0$  and  $x=1$ , respectively. Weidner et al. [17] have detected the formation of a cubic non-stoichiometric “quasi-imide” phase during deuterium absorption of  $\text{Li}_3\text{N}$  at low pressure, with a composition-dependent lattice parameter. In this last study, the simultaneous formation of  $\text{Li}_4\text{ND}$  was observed as a function of the deuterium content, and the consumption of  $\text{Li}_3\text{N}$  was higher than that suggested by Eq. (1). Chandra et al. [18] have also observed that hydrogenation of  $\text{Li}_3\text{N}$  proceeds along a more complex mechanism than reactions (1) and (2), involving two intermediary phases:  $\text{Li}_4\text{NH}$  and a new solid-solution cubic phase of  $\text{Li}_{2-x}\text{NH}_{1+x}$ , which were observed at hydrogen concentrations between 3.2 wt% H and 8.1 wt%. Moreover, Huq et al. [19] have studied the deuteration of  $\alpha$ - $\text{Li}_3\text{N}$  using in situ neutron diffraction. They observed a change in the unit cell volume of the  $\text{Li}_2\text{NH}$  during absorption and desorption at 250 °C that indicates a possible  $\text{Li}_x\text{ND}_{(3-x)}$  stoichiometry during cycling. Two cubic phases with slightly different lattice parameters were formed after cooling the sample to room temperature. A recent study using neutron diffraction during the in situ deuteration of  $\text{Li}_3\text{N}$  has shown different final phases as a function of pressure [20]. At 0.5 MPa, non-stoichiometric phases were not detected, and the reaction proceeded to the formation of amide

plus  $\text{LiH}$ . However, at lower pressures, a cubic phase with a large variation in lattice parameter was observed. The authors emphasize the relevance of clarifying whether the formed phases have composition  $\text{Li}_{2+y}\text{NH}$  or  $\text{Li}_{2+y}\text{NH}_{1-y}$ . Simultaneously, the stability of the different intermediate phases between  $\text{Li}_2\text{NH}$  and  $\text{LiNH}_2$  has been studied using density functional theory DFT, providing additional insight on the predominant phase in the hydrogenation and dehydrogenation process [21,22].

All above mentioned works were addressed to study the  $\alpha$ - $\text{Li}_3\text{N}$  hydriding/dehydriding reactions. Whereas  $\text{Li}_3\text{N}$  is the only stable binary alkali metal nitride in the  $\text{Li}$ – $\text{N}$  system [23],  $\alpha$ - $\text{Li}_3\text{N}$  is the stable phase at room temperature and ambient pressure. Its hexagonal structure consists of  $\text{Li}_2\text{N}$  layers, widely separated and connected by one lithium atom per unit cell occupying a site between the nitrogen atoms in adjacent layers [24]. At around 0.6 GPa and room temperature,  $\alpha$ - $\text{Li}_3\text{N}$  transforms into a layered hexagonal structure ( $\beta$ - $\text{Li}_3\text{N}$ ) with BN-like honeycomb  $\text{LiN}$  layers [25]. Although the  $\beta$ - $\text{Li}_3\text{N}$  structure retains some key aspects of the  $\alpha$ - $\text{Li}_3\text{N}$ , its  $\text{Li}$ – $\text{N}$  layers switch from a composition [ $\text{Li}_2\text{N}$ ] to [ $\text{LiN}$ ] as nitrogen atoms are shifted from a simple hexagonal packing to hexagonal eutaxy [24]. Huq et al. [26] have presented a detailed structural study of  $\text{Li}_3\text{N}$  in the temperature range of 250–400 °C using neutron powder diffraction. They observed the progressive transformation from  $\beta$  to  $\alpha$ - $\text{Li}_3\text{N}$  above 200 °C. Moreover,  $\beta$ - $\text{Li}_3\text{N}$  presented a high thermal stability, remaining 2.5 wt% untransformed at 400 °C. Considering that commercial  $\text{Li}_3\text{N}$  normally contains both  $\alpha$  and  $\beta$  phases, it is interesting to study the possible effect of  $\beta$ - $\text{Li}_3\text{N}$  presence on the hydrogen storage properties of  $\text{Li}_3\text{N}$ .

In this work, we analyze the role of the  $\beta$ - $\text{Li}_3\text{N}$  phase, the  $\text{Li}_2\text{O}$  presence, and the thermal treatment under vacuum on the hydrogen storage capacity and the hydriding/dehydriding kinetics of  $\text{Li}_3\text{N}$ . We obtain evidence of the formation of a  $\text{Li}_{2-x}\text{NH}_{1+x}$  non-stoichiometric phase under specific experimental conditions, confirming the complex nature of the  $\text{Li}_3\text{N}$  hydriding/dehydriding process. Moreover, the influence of temperature and milling time on the  $\beta$  to  $\alpha$ - $\text{Li}_3\text{N}$  transition is evaluated.

## 2. Experimental

### 2.1. Synthesis of the materials

Powders of  $\text{Li}_3\text{N}$  (>99.9% of purity, Aldrich),  $\text{Li}_2\text{O}$  (>97% of purity, Aldrich) and  $\text{LiH}$  (>95% of purity, Fluka) were used as starting materials. Two sets of samples were prepared to study the effect of different variables on the hydriding/dehydriding behavior of  $\text{Li}_3\text{N}$ . The first group of samples consists of as-received  $\text{Li}_3\text{N}$  powders (commercial, referred as LN), as-milled  $\text{Li}_3\text{N}$  (m-LN), as-heated  $\text{Li}_3\text{N}$  (h-LN) and as-milled mixture of  $\text{Li}_3\text{N}$  with 17 wt% of  $\text{Li}_2\text{O}$  (m-LNO). The time of milling (X) is referred to as m-LNX or m-LNOX, respectively. The second group of samples is formed by LN, m-LN20 and LNO samples which were milled with 27 wt% of  $\text{LiH}$  (1.6 mol%) for 2 h, 2 h and 5 h, respectively. The final samples are hereafter indicated as LN–LH2, m-LN20–LH2 and m-LNO–LH5, respectively. Ball milled samples were prepared using planetary ball milling (Fritsch P-6) with a ball to powder ratio of 40:1 in a hardened steel vial under 0.1 MPa of argon. The as-heated  $\text{Li}_3\text{N}$  sample was obtained after thermal treatment under vacuum at 400 °C for 4 h. All sample handling was done in an MBraun Unilab argon-filled glove box, with oxygen and moisture levels lower than 1 ppm.

### 2.2. Material characterization

The as-prepared and as-cycled samples were characterized by means of powder X-ray diffraction measurements (PXRD, Philips PW 1710/01 Instruments), infrared spectra collection (FTIR Perkin

Elmer Spectrum 400), scanning electron microscopy observations combined with EDS (SEM 515, Philips Electronic Instruments with energy dispersive X-ray spectroscopy),  $N_2$  sorption isotherms (Micromeritics ASAP 2020) and differential scanning calorimetry analysis (DSC TA 2910 calorimeter).

Structural information of the different samples was obtained by PXRD analysis (CuK $\alpha$  radiation, graphite monochromator) and FTIR analysis. During the PXRD data collection all the samples were maintained under Ar atmosphere using a tightly sealed sample holder to prevent the reaction between samples and air. The formation degree of  $\beta$ -Li $_3$ N from  $\alpha$ -Li $_3$ N phase,  $A$  (in %), was calculated from XRD measurements using the equation

$$A_{\beta\text{-Li}_3\text{N}} = \frac{I_{\beta\text{-Li}_3\text{N}}}{I_{\beta\text{-Li}_3\text{N}} + I_{\alpha\text{-Li}_3\text{N}}} \times 100 \quad (5)$$

where  $I$  represents the intensity of the most intense reflections of  $\alpha$ -Li $_3$ N or  $\beta$ -Li $_3$ N. Crystallite size of the  $\alpha$  and  $\beta$ -Li $_3$ N phases were estimated from the most intense diffraction peaks by the Scherrer equation. For IR spectroscopy measurements, the selected samples were grounded with dry KBr under purified argon atmosphere and pressed to pellets. Solid-state IR spectra were obtained in the range of 450–4000  $\text{cm}^{-1}$  using a specially designed cell. Handling was done inside the glove box to avoid contact with air.

Morphological and textural characterizations were performed via SEM observations and  $N_2$  sorption measurements. For the SEM, the samples were dispersed on stick-mounted holders and introduced into hermetic plastic recipients in the argon-filled glove box to minimize the material's surface exposure to oxygen and humidity. Textural measurements were performed at liquid nitrogen temperature to determine the specific surface area (SSA) based on the Brunauer–Emmett–Teller (BET) method, pore volume and size distribution. Before measurements, the samples were evacuated at 150 °C overnight.

The thermal behavior of the samples was studied by DSC using a heating rate of 5 °C  $\text{min}^{-1}$  and an argon flow rate of 122  $\text{ml min}^{-1}$ . About 10 mg of sample was loaded into aluminum capsules hermetically closed in a glove box under a purified argon atmosphere. The heat associated with the  $\alpha$  to  $\beta$ -Li $_3$ N phase transition was estimated from DSC curves using the peak area and the mass of each sample.

Isothermal hydrogen sorption curves were obtained using modified Sieverts-type equipment, coupled with a mass flow controller. Isothermal hydrogen absorption curves were measured at 200 °C with a hydrogen pressure of only 0.7 MPa (2 h) and then switched to 3.0 MPa (additional 5 h). In some cases the first stage at 0.7 MPa is not performed. Isothermal hydrogen desorption curves were obtained at 250 °C under vacuum (0.025 MPa). Each sample was heated up to the reaction temperature under vacuum and kept at this temperature for 30 min before measuring the hydrogen absorption/desorption reaction. For non-isothermal absorption measurements, the sample was heated at 5 °C  $\text{min}^{-1}$  from room temperature to 200 °C at 3.0 MPa of hydrogen pressure. The reported values of hydrogen uptake/release are expressed as wt% with respect to the amount of Li $_3$ N in the starting sample, to facilitate the comparison between the sorption curves.

### 3. Results and discussion

#### 3.1. Structural and microstructural characteristics of the Li $_3$ N samples

Fig. 1 shows the XRD patterns of as-received Li $_3$ N (LN), as-milled Li $_3$ N (m-LN20), as-heated Li $_3$ N (h-LN) and as-milled Li $_3$ N–Li $_2$ O mixture (m-LNO5). The commercial LN exhibits the coexistence of both  $\alpha$ -Li $_3$ N (main phase, stable) and  $\beta$ -Li $_3$ N (metastable), with the

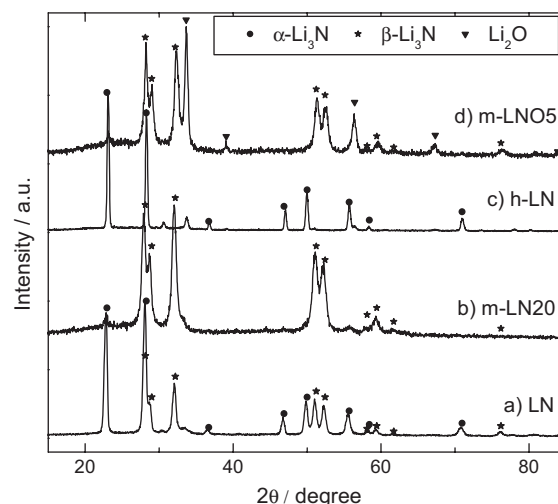


Fig. 1. PXRD patterns of: a) LN; b) m-LN20; c) h-LN; d) m-LNO5.

simultaneous presence of minor amounts of Li $_2$ O. The sample m-LN20 shows mainly the peaks attributable to  $\beta$ -Li $_3$ N. This indicates the almost complete  $\alpha$  to  $\beta$ -Li $_3$ N transition after milling for 20 h. In contrast, the complete transition of  $\beta$  to  $\alpha$ -Li $_3$ N phase as well as the crystallization of Li $_2$ O is observed after a thermal treatment at 400 °C for 4 h (h-LN). Moreover, milling of the Li $_3$ N–Li $_2$ O mixture for 5 h also induces the transition of  $\alpha$  to  $\beta$ -Li $_3$ N phase (m-LNO5 sample). The peaks of Li $_2$ O are clearly identified and no evidence of interaction between Li $_3$ N and Li $_2$ O is detected.

The SEM examinations of the different samples reveal that the commercial Li $_3$ N is formed by agglomerates (assemblages of particles) with a wide size distribution: ~6% of the agglomerates between 100 and 200  $\mu\text{m}$ , 21% between 20 and 50  $\mu\text{m}$  and 62% being <20  $\mu\text{m}$ . A detail of the surface of these agglomerates shows several particles of 1–2  $\mu\text{m}$  (Fig. 2a), which are aggregated in secondary particles of 10  $\mu\text{m}$ . After ball milling for 20 h, the agglomerate size distribution is modified: ~12% of the agglomerates between 100 and 200  $\mu\text{m}$ , 23% between 50 and 100  $\mu\text{m}$  and 54% between 20 and 50  $\mu\text{m}$ . These results suggest that additional large agglomerates form due to cold welding after a prolonged milling time. The surface of these agglomerates (Fig. 2) shows particles of different sizes. In comparison with as-purchased Li $_3$ N (Fig. 2a), the as-milled Li $_3$ N consists of smaller particles (<0.5  $\mu\text{m}$ , Fig. 2b) that are relatively homogeneous in shape and size. Moreover, the h-LN sample presents a lower fraction of small size agglomerates than the LN sample: 5% of the agglomerates between 100 and 200  $\mu\text{m}$ , 27% between 20 and 50  $\mu\text{m}$  and 48% being <20  $\mu\text{m}$ . The surface of the agglomerates shows large pores (Fig. 2c) in comparison with the commercial Li $_3$ N (Fig. 2a).

Table 1 summarizes the crystallite sizes, the SSA and the equivalent particle size of the different Li $_3$ N samples. It can be seen that the crystallite size of both  $\alpha$  and  $\beta$ -Li $_3$ N has been reduced to less than

Table 1  
Microstructural characteristics of as-received and as-prepared Li $_3$ N samples.

	Crystallite size (nm)		SSA ( $\text{m}^2 \text{gr}^{-1}$ )	Equivalent particle size ( $\mu\text{m}$ ) <sup>a</sup>
	$\alpha$ -Li $_3$ N	$\beta$ -Li $_3$ N		
LN	21	18	4	1.15
m-LN20	14	14	5	0.92
m-LNO5	14	14	3	1.53
h-LN	33	–	4	1.15

<sup>a</sup> The equivalent particle size was calculated from SSA assuming spherical particles.

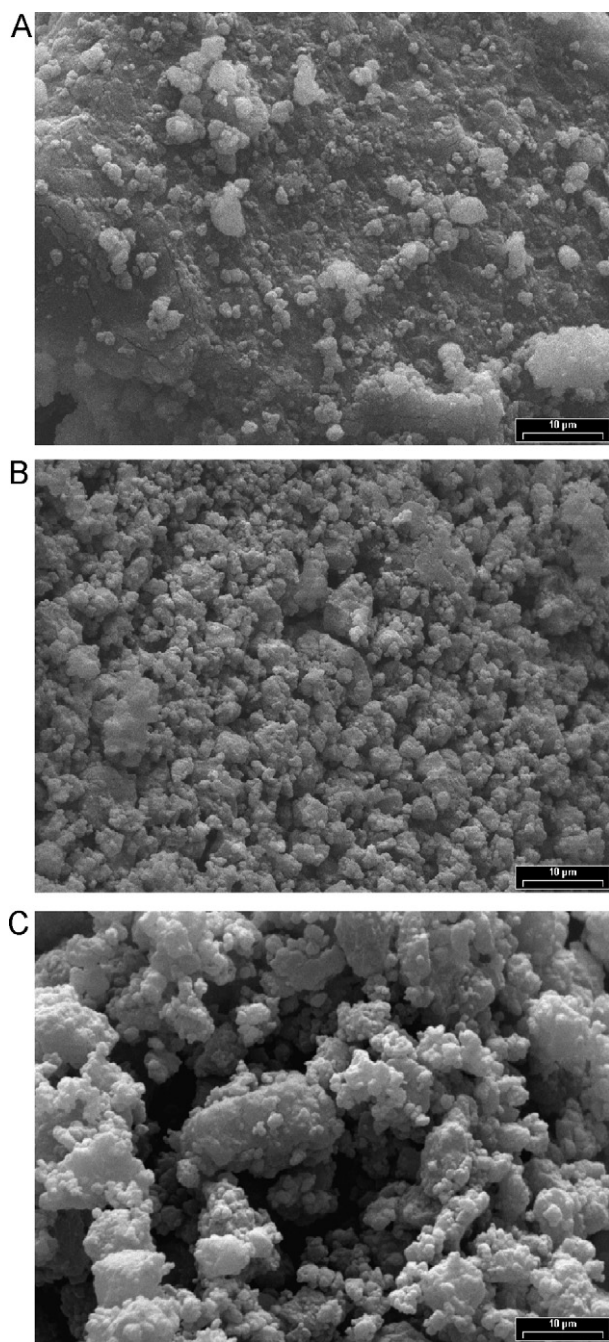


Fig. 2. SEM images of the as-prepared samples: a) LN; b) m-LN20; c) m-LN.

15 nm after 20 h of milling. In contrast, thermal treatment notably increases the crystallite size to 33 nm. It must be remarked that the SSA of  $\text{Li}_3\text{N}$  increases slightly after milling. The equivalent particle size calculated for the LN and m-LN samples is in agreement with the SEM examination. In addition, the equivalent particle size calculated from the SSA is much larger than the crystallite size estimated from XRD peak broadening. This indicates that each  $\text{Li}_3\text{N}$  particle identified by SEM contains several crystallites.

Thermal stability of the LN, m-LN and m-LNO samples was investigated using DSC measurements (Fig. 3). All samples display a similar thermal behavior, characterized by the presence of an exothermic peak that presents two interesting features. First of all, the peak temperature increases as milling time progresses from the LN sample (250 °C, which contains the  $\beta\text{-Li}_3\text{N}$  phase) to the m-LN20 sample (344 °C, which consists mainly of  $\beta\text{-Li}_3\text{N}$ ). Secondly,

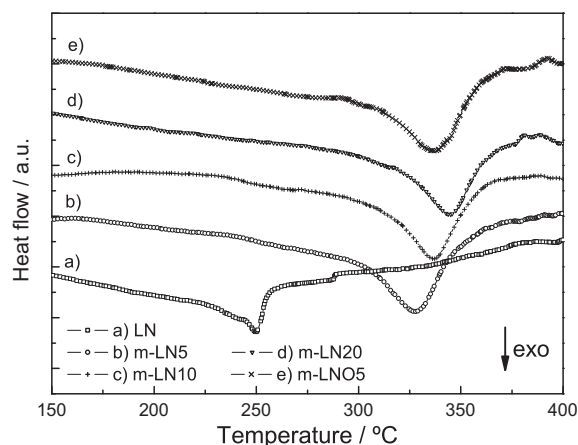


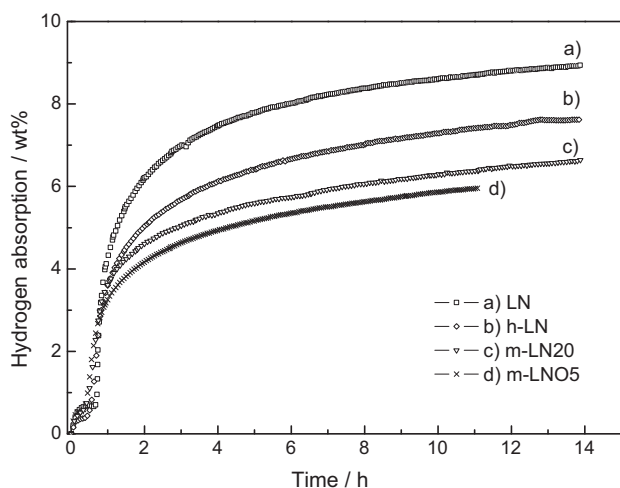
Fig. 3. DSC curves of: a) LN; b) m-LN5; c) m-LN10; d) m-LN20; e) m-LNO5.

the peak area increases with respect to the LN sample due to milling, but it seems to become constant after 5 h of milling. On the basis of Fig. 1, the exothermic peak observed for the different samples can be associated with the  $\beta$  to  $\alpha\text{-Li}_3\text{N}$  phase transition. Considering that the endothermic peak area is directly correlated with the proportion of the  $\beta\text{-Li}_3\text{N}$  phase in the sample, an estimation of the heat flow as a function of milling time was done (see Table 2). The peak area increases from about  $55 \text{ J g}^{-1}$  for LN to  $154 \text{ J g}^{-1}$  for the m-LN20 sample, being about  $155 \text{ J g}^{-1}$  after 5 h of milling. Moreover, the DSC curve for the m-LNO5 sample also presents the exothermic peak due to the  $\text{Li}_3\text{N}$  phase transformation but at a lower temperature, similar to that corresponding to m-LN10. These values reveal that the proportion of the  $\beta\text{-Li}_3\text{N}$  metastable phase increases respect to the  $\alpha\text{-Li}_3\text{N}$  due to milling, but it remains practically constant after 5 h of milling.

Furthermore, we can also evaluate the  $\alpha$  to  $\beta\text{-Li}_3\text{N}$  phase transformation by estimation of the formation degree of  $\beta\text{-Li}_3\text{N}$  (see Eq. (5)) from XRD measurements. To complete the analysis, additional samples were prepared by milling during different times, or milling followed by heating. Table 2 summarizes the formation degree of  $\beta\text{-Li}_3\text{N}$  calculated for several samples. Commercial  $\text{Li}_3\text{N}$  possesses about 30% of  $\beta\text{-Li}_3\text{N}$  phase. After milling for 5 h the fraction of  $\beta\text{-Li}_3\text{N}$  phase is 90% and it remains practically constant after 20 h of milling. Total transformation from  $\alpha$  to  $\beta\text{-Li}_3\text{N}$  phase is not reached under the experimental milling conditions, probably due to the powders sticking in the milling chamber. The m-LN20 heated at 225 °C for 5 h shows about 68% of  $\beta\text{-Li}_3\text{N}$  phase, indicating that partial transition from  $\beta$  to  $\alpha\text{-Li}_3\text{N}$  phase occurs slowly at this temperature. Analyses performed using EDS on m-LN5 and m-LN20 demonstrate that the Fe amount is lower than 1 at%. This result indicates that Fe contamination is not a necessary factor to induce the  $\alpha$  to  $\beta\text{-Li}_3\text{N}$  phase transition during milling, as it was previously suggested [27]. Finally, the values of heat flow obtained from DSC measurements are in agreement with the trends found by XRD (Table 2).

Table 2  
Summary of the DSC results and formation degree of  $\beta\text{-Li}_3\text{N}$  obtained from XRD.

Samples	Peak temperature (°C)	Peak area ( $\text{J g}^{-1}$ )	$A_{\beta\text{-Li}_3\text{N}}$
LN	250	55	30
m-LN1	–	–	76
m-LN5	328	155	90
m-LN10	337	152	92
m-LN20	344	154	93
m-LNO5	337	144	90
m-LN20 heated at 225 °C, 5 h	–	–	68



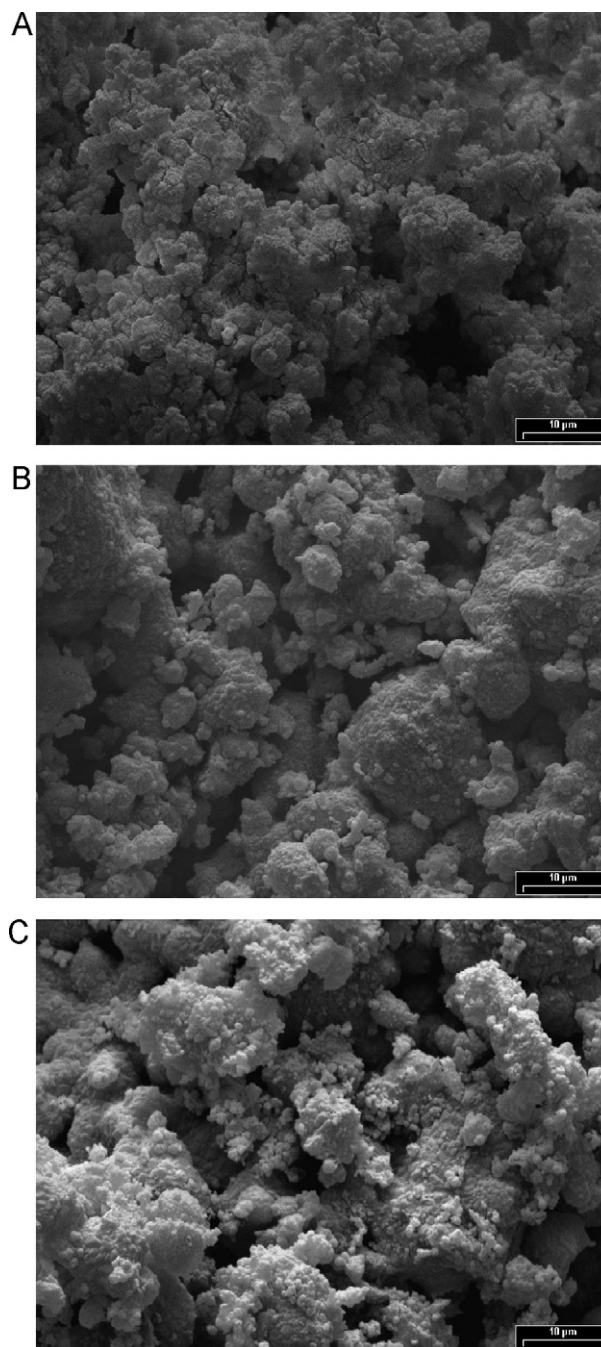
**Fig. 4.** Hydrogen absorption kinetics of: a) LN; b) h-LN; c) m-LN20; d) m-LNO5. Non-isothermal absorption from room temperature to 200 °C under 3.0 MPa of hydrogen pressure.

### 3.2. Hydriding/dehydriding behavior of $\text{Li}_3\text{N}$ samples

The hydrogen absorption behavior of the different  $\text{Li}_3\text{N}$  samples was investigated under non-isothermal conditions (3.0 MPa of hydrogen pressure, final temperature 200 °C). All samples absorb about 3 wt% in the first hour, while additional hydrogen uptakes involve longer times, of about 12 h (Fig. 4). In previous works, it was experimentally observed that  $\text{LiNH}_2$  and  $\text{Li}_2\text{NH}$  were formed at similar rates, which suggests that both phases were produced from the reaction between  $\text{Li}_3\text{N}$  and  $\text{H}_2$  gas in addition to the conversion of  $\text{Li}_2\text{NH}$  to  $\text{LiNH}_2$  (reaction (2)) [19]. We believe that a similar situation occurs during our  $\text{Li}_3\text{N}$  hydriding experiments and thus it is not possible to correlate each stage with reaction (1) or (2). After 12 h of hydriding, the best kinetics was observed for commercial LN, which displays the highest hydrogen content of 8.9 wt%. The final hydrogen storage capacity for m-LNO5, m-LN20 and h-LN was about 6.0, 6.5 and 7.5 wt%, respectively. Thus, for milled- and commercial-LN materials there is a correlation between the  $\beta\text{-Li}_3\text{N}$  fraction in the starting sample (Table 2) and the final hydrogen storage capacity obtained (Fig. 4). In the case of h-LN sample, the absence of  $\beta\text{-Li}_3\text{N}$  might suggest superior hydrogen storage capacity. However, the thermal treatment increases both the crystallite size of  $\text{Li}_3\text{N}$  and the agglomerate size distribution respect to commercial LN, negatively influencing its hydrogen reactivity [16].

Accordingly, hydrogen absorption/desorption cycling was performed for the best two samples after the first absorption cycle (Fig. 4), i.e. LN and h-LN. The amount desorbed from these samples at 250 °C was 3 and 1.3 wt%, respectively, after 3 h under vacuum. Successive hydrogen absorption (200 °C) and desorption (250 °C) cycling leads to a progressive reduction in the reversible hydrogen storage capacity for the LN sample, with 2.7 wt% of hydrogen absorbed after the 5th cycle. The loss of reversibility observed may be partially associated with the formation of  $\text{NH}_3$ , in agreement with previous works [7,8,10,11].

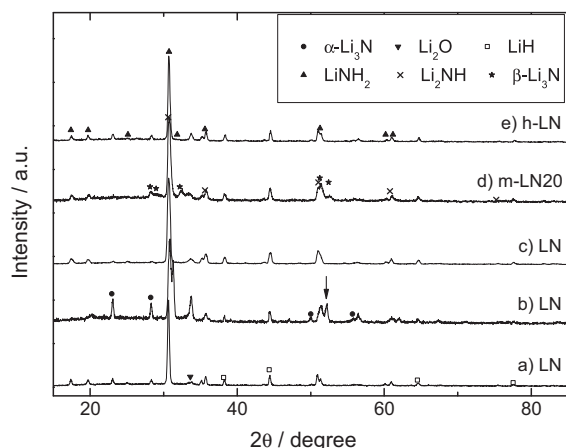
To compare the morphological and microstructural changes of the samples as consequence of cycling, SEM observations and surface area determinations were carried out. Fig. 5 shows the surface morphology of the as-cycled LN (Fig. 5a, 5th absorption cycle), m-LN20 (Fig. 5b, first absorption cycle) and h-LN (Fig. 5c, 5th absorption cycle) samples. The surface of these agglomerates displays several particles between 1 and 2  $\mu\text{m}$ , which are aggregated in secondary particles of different sizes. A comparison with the morphology of the powders presented in the Fig. 2 shows that the surface roughness has clearly changed for the LN and m-LN



**Fig. 5.** SEM images of as-cycled samples: a) LN; b) m-LN20; c) h-LN.

samples, while it looks similar for the h-LN material after cycling. However, these modifications are not reflected in the values of the specific surface area: the three samples have BET areas of about of  $2 \text{ m}^2 \text{ g}^{-1}$  after successive hydrogen cycling.

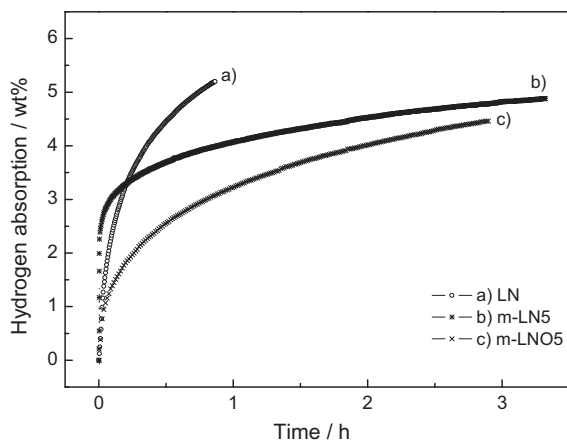
To obtain additional insight on the hydriding/dehydriding process, Fig. 6 shows PXRD patterns of the samples after cycling. During the first absorption for the LN and m-LN samples, both  $\text{LiNH}_2$  and  $\text{Li}_2\text{NH}$  phases are formed, whereas  $\alpha\text{-Li}_3\text{N}$  (curve a) and  $\beta\text{-Li}_3\text{N}$  (curve d) phases remain unhydrided. Note that the  $\beta\text{-Li}_3\text{N}$  phase is still present after 12 h of heating at 200 °C. Moreover, after the 5th hydrogen absorption cycle, PXRD patterns for the LN and h-LN samples show the formation of  $\text{LiNH}_2$ , minor amounts of  $\text{Li}_2\text{NH}$  and remnant  $\alpha\text{-Li}_3\text{N}$  (curve c and e, respectively), without clear differences between both samples after cycling.  $\text{Li}_2\text{O}$  is also detected, probably due to the crystallization of  $\text{Li}_2\text{O}$  present in the



**Fig. 6.** PXRD patterns of: a) first absorption of LN; b) first desorption after absorption (a) of LN; c) 5th cycle of absorption of LN; d) first absorption of m-LN20; e) 5th cycle of absorption of h-LN. Non-isothermal absorptions were performed from room temperature to 200 °C, under 3.0 MPa of hydrogen pressure. Isothermal desorption was performed at 250 °C, under 0.02 MPa of hydrogen pressure.

commercial  $\text{Li}_3\text{N}$  (Fig. 1, curve a) as a consequence of the prolonged thermal treatment. Moreover, the formation of a  $\text{Li}_{2-x}\text{NH}_{1+x}$  phase [18] is identified from PXRD for LN after the first hydrogen desorption (indicated by an arrow in curve b, Fig. 6). Probably, minor amounts of  $\text{Li}_4\text{NH}$  are also formed, as it is inferred from the incipient peak at about  $2\theta = 20.2^\circ$  [28]. Our results are in agreement with recent works, which show that the  $\text{Li}_3\text{N}$  hydriding/dehydriding mechanism is a more complex process than that represented by Eqs. (1) and (2) [16–20].

The hydrogen storage capacity as well as the hydrogen absorption rate of the  $\text{Li}_3\text{N}$  samples presented in Fig. 4 differ of those obtained by Langmi et al. [15]. They showed that milled  $\text{Li}_3\text{N}$  has better hydrogen cycling properties than unmilled  $\text{Li}_3\text{N}$ , whereas the addition of  $\text{Li}_2\text{O}$  does not modify the absorption behavior. However, no mention was made to the presence of  $\beta\text{-Li}_3\text{N}$  in the milled  $\text{Li}_3\text{N}$ . In order to analyze the different performance of commercial and milled  $\text{Li}_3\text{N}$  samples during the first hour of hydrogen absorption and to relate it with the presence of the  $\beta\text{-Li}_3\text{N}$  phase, isothermal measurements at 200 °C under 0.7 MPa of hydrogen pressure (Fig. 7) were carried out. As-purchased LN displays superior hydrogen storage, while m-LN5 and m-LNO samples absorb less hydrogen under the same experimental conditions. Moreover, the highest hydriding rate is obtained for the m-LN5 sample after the first 10 min. Then, two opposite factors seem to con-



**Fig. 7.** Hydrogen absorption kinetics of: a) LN; b) m-LN5; c) m-LNO5. Isothermal absorption at 200 °C and 0.7 MPa of hydrogen pressure.

trol the hydriding process at different times. At the beginning of hydrogen absorption, the kinetic behavior is strongly influenced by the microstructural modifications introduced by milling. The milling process produces significant internal, structural changes such as defects, micro-stresses and local imperfections in  $\text{Li}_3\text{N}$ , which induce the  $\alpha\text{-}\beta$  phase transition. In addition, ball milling reduces the crystallite size of  $\text{Li}_3\text{N}$  and increases the specific surface area (Table 1). All these characteristics make the milled  $\text{Li}_3\text{N}$  grains more reactive to hydrogen. However, this situation is reverted after prolonged hydriding, since the final hydrogen storage capacity of the m-LN sample does not reach the same value of commercial LN. This suggests that other mechanisms influence the absorption reaction at long times, which could be associated with the  $\beta\text{-Li}_3\text{N}$  fraction in the starting sample (Table 2).

Recently, it has been demonstrated that the hydrogenation of  $\text{Li}_3\text{N}$  is a more complex mechanism than that represented by reaction (1) and (2), involving non-stoichiometric phases [16–20]. In this context, the hydrogenation process of  $\alpha\text{-Li}_3\text{N}$  occurs because of  $\text{Li}^+$  ions migrate cooperatively through the cation vacancies within the lithium deficient  $\text{Li}_2\text{N}$  layers and interact with the hydrogen gas [16]. However, first-principles calculations have revealed that  $\alpha\text{-Li}_3\text{N}$  and  $\beta\text{-Li}_3\text{N}$  have distinct  $\text{Li}^+$  ion diffusion mechanisms: in  $\alpha\text{-Li}_3\text{N}$  it occurs within the  $\text{Li}_2\text{N}$  plane, while in  $\beta\text{-Li}_3\text{N}$  it happens within the pure Li plane [29]. In addition, lower migration energy barriers for the  $\text{Li}^+$  ion diffusion in  $\alpha\text{-Li}_3\text{N}$  respect to  $\beta\text{-Li}_3\text{N}$  were reported. Therefore, increasing the  $\text{Li}^+$  mobility is the basis of the mechanism of hydrogenation of  $\text{Li}_3\text{N}$ . The different crystallographic structure of  $\alpha\text{-Li}_3\text{N}$  and  $\beta\text{-Li}_3\text{N}$  and the dissimilar  $\text{Li}^+$  diffusion mobility could be responsible for the detrimental absorption behavior observed in milled-LN samples, which contain about 90% of  $\beta\text{-Li}_3\text{N}$ , respect to commercial LN that possesses 30% of  $\beta\text{-Li}_3\text{N}$ . In this sense, although the h-LN sample contains only  $\alpha\text{-Li}_3\text{N}$  phase, hydrogen absorption behavior is affected by the microstructural modifications introduced as a consequence of the thermal treatment. Considering that these modifications affect Li diffusion, heating of commercial  $\text{Li}_3\text{N}$  under vacuum for 4 h has a negative effect on hydriding performance.

Combination of hydrogen absorption/desorption measurements and structural/microstructural characterizations by XRD, DSC, SEM and SSA suggest that ball milling induces both  $\alpha$  to  $\beta\text{-Li}_3\text{N}$  phase transition and the modification of the  $\text{Li}_3\text{N}$  microstructure. The amount of  $\beta\text{-Li}_3\text{N}$  phase determines the kinetics of the hydrogenation at 200 °C and the hydrogen storage capacity in the milled  $\text{Li}_3\text{N}$ . The addition of  $\text{Li}_2\text{O}$  does not have any effect on the extension of the  $\alpha$  to  $\beta\text{-Li}_3\text{N}$  phase transition and it acts as an inert component in the  $\text{Li}_3\text{N}\text{-Li}_2\text{O}$  starting mixture, with a hydrogen absorption kinetics that correlates with the amount of  $\beta\text{-Li}_3\text{N}$  phase in the sample as consequence of milling time. On the other hand, the thermal treatment favors the crystallite growth, influencing its reactivity with hydrogen. However, the microstructural changes in the starting samples showed a weaker effect on the hydrogen storage properties respect to the amount of  $\beta\text{-Li}_3\text{N}$  phase.

### 3.3. Hydriding/dehydriding behavior of $\text{Li}_3\text{N}\text{-LiH}$ mixtures

From the above results, the as-received LN showed the higher hydrogen storage capacity with a gradual degradation of the hydrogen storage capacity under hydrogen cycling. The formation of  $\text{NH}_3$  during dehydriding of  $\text{LiNH}_2$  has been suggested to be the main reason for this depletion in the hydrogen storage properties [8–11]. For this reason, powders of LiH were added to  $\text{Li}_3\text{N}$  by milling to produce m-LN-LH2, m-LN20-LH2 and m-LNO-LH5 samples. Fig. 8 displays the XRD patterns of the different milled  $\text{Li}_3\text{N}\text{-LiH}$  mixtures. Minor changes are observed in the LN-LH mixtures respect to the starting LN samples (Fig. 1). The  $\alpha\text{-Li}_3\text{N}$  and  $\beta\text{-Li}_3\text{N}$  (74%, Eq. (5)) phases are identified in the LN-LH2 mixture, while an almost

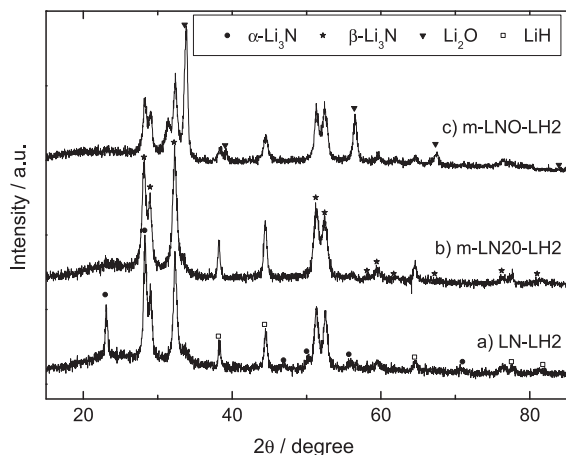


Fig. 8. PXRD patterns of: a) LN-LH2; b) m-LN20-LH2; c) m-LNO-LH5.

complete transition to the  $\beta$ - $\text{Li}_3\text{N}$  phase is obtained in the LN20-LH2 sample. In contrast, after milling of the LNO-LH5 mixture the peak at  $2\theta = 31.4^\circ$  is clearly identified, indicating an interaction between  $\text{Li}_2\text{O}$  and LiH. FTIR measurement performed on the commercial  $\text{Li}_2\text{O}$  detect the presence of a band at  $3677\text{ cm}^{-1}$ , that can be associated with  $\text{Li}(\text{OH})$  (results not shown) [30]. This band is also clearly identified in the FTIR spectra of LNO-LH5, without the observation of the bands at  $3180$  and  $3250\text{ cm}^{-1}$  or  $3260$  and  $3315\text{ cm}^{-1}$  due to the presence of  $\text{Li}_2\text{NH}$  or  $\text{LiNH}_2$ , respectively [31]. Then, the diffraction peak observed at  $2\theta = 31.4^\circ$  originates in the interaction between of  $\text{Li}_2\text{O}$  containing LiOH with LiH.

Hydrogen absorption curves were measured for the different milled  $\text{Li}_3\text{N}$ -LiH mixtures (Fig. 9) under isothermal conditions ( $200^\circ\text{C}$ , pressure of  $\text{H}_2 = 0.7\text{ MPa}$ ). The LN-LH2 sample absorbed 7.5 wt% of hydrogen in 2 h, whereas 4.5 and 2.7 wt% of hydrogen are incorporated in m-LN20-LH2 and m-LNO-LH5 samples, respectively. After this absorption step of 2 h, the hydrogen pressure was switched to 3.0 MPa to increase the hydrogen uptake (not shown). Final hydrogen storage capacities were 9.6, 7.0 and 4.2 wt% after 7 h for LN-LH, m-LN20-LH2 and m-LNO-LH5, respectively. After this first absorption, the samples were submitted to three successive cycles of desorption ( $250^\circ\text{C}$ , pressure of  $\text{H}_2 = 0.025\text{ MPa}$ )/absorption ( $200^\circ\text{C}$ , pressure of  $\text{H}_2 = 0.7\text{ MPa}$  for 2 h followed by 3.0 MPa for 7 h). All samples reached practically the same final reversible hydrogen uptake of about 3.5 wt% for LN-LH

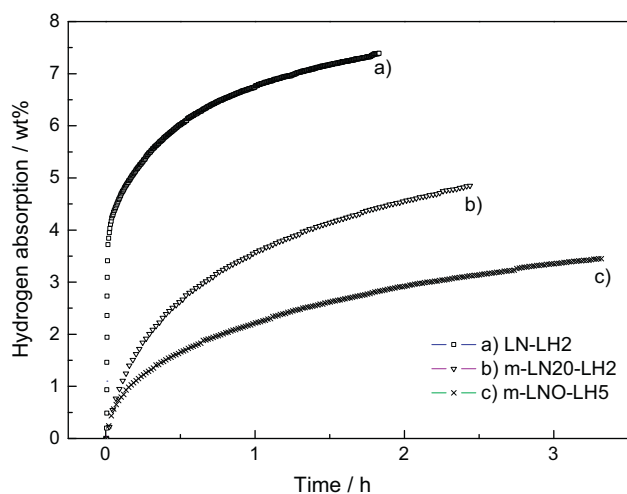


Fig. 9. Hydrogen absorption kinetics of: a) LN-LH2; b) m-LN20-LH2; c) m-LNO-LH5. Isothermal absorption at  $200^\circ\text{C}$  and 0.7 MPa of hydrogen pressure.

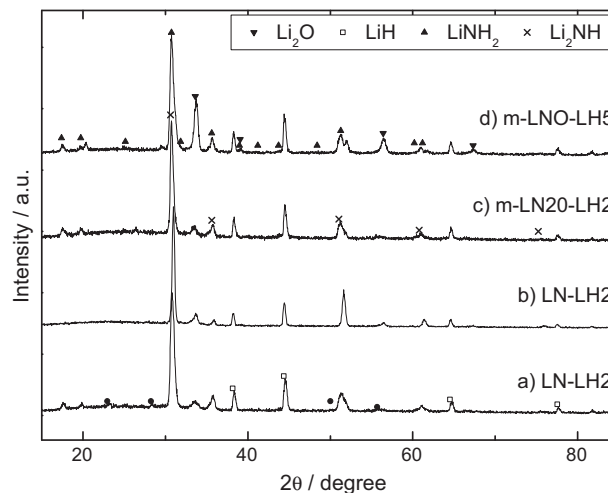


Fig. 10. PXRD patterns of: a) first absorption of LN-LH2; b) first desorption after absorption (a) of LN-LH2; c) 2nd cycle of absorption of m-LN20-LH2; d) 2nd cycle of absorption of m-LNO-LH5. Isothermal absorption at  $200^\circ\text{C}$  (initial 0.7 MPa of hydrogen pressure for 2 h followed by 3.0 MPa of hydrogen for 7 h). Isothermal desorption at  $250^\circ\text{C}$  (0.02 MPa of hydrogen pressure).

and 3.0 wt% for m-LN20-LH2 and m-LNO-LH5 samples, in spite of the dissimilar first absorption cycle.

PXRD patterns from Fig. 10 were used to identify the phases present in the samples after the first absorption cycle (LN-LH sample, curve a), third absorption cycle (LN-LH and LN20-LH2 samples, curves c and d) and first desorption cycle (LN-LH sample, curve b). The diffraction patterns reveal that for the three samples the main product of the hydriding is  $\text{LiNH}_2$  and LiH, with minor amounts of  $\text{Li}_2\text{NH}$ . On the other hand,  $\text{Li}_2\text{O}$  is clearly identified in the samples LN-LH and LN20-LH2, probably due to both the crystallization of  $\text{Li}_2\text{O}$  present in the starting samples and the progressive oxidation of the samples during cycling/handling. In the case of m-LNO-LH5, minor amounts of  $\text{Li}_4\text{NH}$  seem to be formed during cycling [28]. The PXRD of the first desorption cycle (Fig. 10, curve b) shows only the presence of  $\text{Li}_2\text{NH}$ , LiH and  $\text{Li}_2\text{O}$ . These results were unequivocally corroborated by FTIR measurements.

By comparison of the hydriding/dehydriding behavior of the  $\text{Li}_3\text{N}$  samples with those where LiH was intentionally added, we can conclude that the main difference is associated with the stability of these samples under hydrogen cycling. This result demonstrates that the degradation of the  $\text{Li}_3\text{N}$  sample during hydrogen cycling due to the formation of  $\text{NH}_3$  was reduced/eliminated by LiH addition, as was expected in accordance with previous works [8–11]. The differences observed in the first cycle in the presence of LiH manifest two factors that influence the hydriding kinetics: the presence of the  $\beta$ - $\text{Li}_3\text{N}$  phase, which transforms during desorption cycling at  $250^\circ\text{C}$ , and the microstructural modifications introduced by milling. For example, in the LN sample the content of  $\beta$ - $\text{Li}_3\text{N}$  phase is 30%, while in the LN-LH sample is about 74%. In addition, the LN-LH sample was submitted to milling for 2 h to improve the mixing with LiH. Both factors affect the absorption rate in opposite ways, as it was analyzed for the Fig. 4. In the case of the m-LNO-LH5 sample, its low hydrogen storage capacity in the first cycle is also due to the presence of contamination in the starting  $\text{Li}_2\text{O}$ .

#### 4. Conclusions

Different samples obtained from as-purchased  $\text{Li}_3\text{N}$  were analyzed to determine the role of the  $\beta$ - $\text{Li}_3\text{N}$  phase,  $\text{Li}_2\text{O}$  and the thermal treatment of  $\text{Li}_3\text{N}$  on the hydrogen sorption properties. Combination of XRD, DSC, SEM and SSA studies were used to



understand the influence of the microstructure and structural changes on the hydrogen sorption kinetics.

The results of the present study demonstrate that as-received  $\text{Li}_3\text{N}$  displays the best behavior during the hydrogen absorption/desorption cycling. The milling procedure promotes the  $\alpha$  to  $\beta$  structural transition in the commercial  $\text{Li}_3\text{N}$  and  $\text{Li}_3\text{N-Li}_2\text{O}$  samples, with the simultaneous refinement of the microstructure and local/surface modifications. These microstructural changes improve the absorption rate at short times under 0.7 MPa of hydrogen and 200 °C. However, the predominant factor during additional hydriding is the amount of  $\beta$ - $\text{Li}_3\text{N}$  present in the sample. In comparison with  $\alpha$ - $\text{Li}_3\text{N}$ , the  $\beta$ - $\text{Li}_3\text{N}$  phase retards the absorption rate with a detrimental effect on the total hydrogen storage capacity. No interaction between  $\text{Li}_2\text{O}$  and  $\text{Li}_3\text{N}$  was observed during milling and the hydrogen absorption behavior is dominated by the presence of the  $\beta$ - $\text{Li}_3\text{N}$  phase. The  $\text{Li}_3\text{N}$  thermally treated at 400 °C exhibits an intermediate performance between as-received  $\text{Li}_3\text{N}$  and as-milled samples, without a clear beneficial effect of the annealing on the hydrogen sorption.

The addition of LiH to the commercial  $\text{Li}_3\text{N}$ , as-milled  $\text{Li}_3\text{N}$  and  $\text{Li}_3\text{N-Li}_2\text{O}$  mainly affects the hydrogen storage capacity in the first cycle and then the stability of the samples under cycling, with reversible hydrogen storage capacities of 3.0–3.5 wt% after three cycles. The hydrogen absorption/desorption behavior is mainly controlled by the amount of  $\beta$ - $\text{Li}_3\text{N}$  formed during milling with an unappreciable effect of the microstructure at long times, both in the samples with and without LiH. The hydriding/dehydriding reaction was shown to be a complex process, as suggested by the identification of  $\text{Li}_4\text{NH}$  and a non-stoichiometric  $\text{Li}_{2-x}\text{NH}_{1+x}$  phase under different experimental conditions.

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