



## Hydrogen release and uptake in the Li–Zn–N system



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### ABSTRACT

Reactions of  $\text{ZnCl}_2 + n\text{LiNH}_2$  at a range of molar ratios and temperatures gave a mixture of  $\text{Zn}_3\text{N}_2$  and  $\text{LiZnN}$  as products; no stable amide chloride, imide chloride or nitride chloride phases were identified. Temperature-programmed desorption with mass spectrometry (TPD–MS) showed that the main gas emitted was ammonia ( $\text{NH}_3$ ). The addition of lithium hydride ( $\text{LiH}$ ) changed the main gaseous product from  $\text{NH}_3$  to  $\text{H}_2$ , which was released at a low temperature beginning around 90 °C. Neither pure  $\text{LiZnN}$  nor  $\text{Zn}_3\text{N}_2$  could be rehydrogenated under the conditions studied. However, mixtures of  $\text{LiZnN}$  and  $\text{Zn}_3\text{N}_2$ , and  $\text{LiZnN}$  and  $\text{LiCl}$  reacted with  $\text{H}_2$  at 300 °C to form  $\text{LiNH}_2$  and zinc metal.

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### 1. Introduction

The Li–N–H system has attracted considerable attention as one of the most promising lightweight systems for reversible hydrogen storage. It involves cycling between  $\text{LiNH}_2$ ,  $\text{Li}_2\text{NH}$  and  $\text{Li}_3\text{N}$  [1–4]. However, the slow absorption kinetics and relatively high operating temperature currently limit its practical application. To improve the system, a variety of ternary Li–M–N–H systems, where M = B, Ca, Al or Mg have also been investigated [5–8]. Amongst them, the Li–Mg–N–H system displays a remarkable improvement in the thermodynamics and kinetics of hydrogen desorption but the rate of reaction is still low below 200 °C [9]. Some ternary systems incorporating transition metals e.g. the Li–Co–N–H system show a considerable improvement in desorption kinetics [10]. To investigate the effect of transition metals on the Li–N–H system, Ti, Fe, Ni or Cr were substituted for one of the Li sites in  $\text{LiNH}_2$ , and Li–Ti–N–H showed a marked reduction in reaction enthalpy with  $\Delta H_{\text{hyd}} = -46.6 \text{ kJ mol}^{-1}$  compared with that of the Li–N–H system ( $-75.67 \text{ kJ mol}^{-1}$ ) [11].

Lithium and magnesium halides were also found to have significant effects on the hydrogen desorption properties of the Li–N–H system [12,13]. Anderson et al. [12] heated  $\text{LiNH}_2$  and  $\text{Li}_2\text{NH}$  with  $\text{LiX}$  and  $\text{MgX}_2$  (X = Cl, Br, I) to form a range of new amide halides. On reaction with  $\text{LiH}$ , in all cases the halide-containing amides and imides released and absorbed hydrogen more rapidly than pure amides/imides.

In this study, we report the results of the reactions between  $\text{ZnCl}_2$  and  $\text{LiNH}_2$ , with and without the presence of  $\text{LiH}$ , under different conditions of stoichiometry and temperature. In contrast to the cases of  $\text{LiCl}$  and  $\text{MgCl}_2$  [12], no stable amide chloride phases were isolated with reactions proceeding to the nitrides  $\text{Zn}_3\text{N}_2$  and  $\text{LiZnN}$  at relatively low temperature. The hydrogen absorption/desorption properties of these products is investigated.

### 2. Experimental

#### 2.1. Sample preparation

The  $\text{LiNH}_2$ ,  $\text{ZnCl}_2$ ,  $\text{LiH}$ , (Sigma–Aldrich, >95%) and  $\text{Zn}_3\text{N}_2$  (Alfa–Aesar, 99%) starting materials were ground together in a pestle and mortar by hand in the desired mole ratio in an argon-atmosphere glovebox. The mixtures were then heated under flowing argon gas at temperatures from 150 to 600 °C and held for up to 24 h.

#### 2.2. Temperature-programmed desorption with mass spectrometry (TPD–MS)

The sample (~0.1 g) was placed in a quartz reaction tube (7 mm O/D, 4 mm I/D) inside an argon-filled glovebox and sealed within the reaction chamber. The sealed reaction chamber was then transferred to a home-built temperature-programmed desorption apparatus detailed in previous work [5], connected to a quadrupole mass spectrometer (Hiden Analytical, HPR20), at a constant argon flow of  $100 \text{ ml min}^{-1}$ . In this study, all samples were heated at 2 °C/min to 400 °C and held at that temperature for 2 h before cooling.

#### 2.3. Powder X-ray diffraction (XRD)

Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer, operating in transmission geometry with monochromated  $\text{Cu K}\alpha 1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), and analysed using the Topas computer software [14].

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#### 2.4. Rehydrogenation

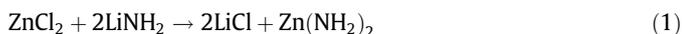
Samples were ground and sealed in a reaction vessel in an argon-atmosphere glovebox and then transferred to the hydrogenation apparatus. Hydrogenation of the samples was attempted at 200 and 300 °C under 90 bar H<sub>2</sub> for up to 24 h.

### 3. Results and discussion

#### 3.1. Zinc chloride and lithium amide

The reactions between ZnCl<sub>2</sub> and LiNH<sub>2</sub> were studied at molar ratios of 1:2, 1:3, 1:4, 1:5, and 1:6 in the temperature range 150–600 °C. The heating rate was 2 °C/min and the reactions were kept at the set temperature for 12 h.

For samples prepared at 150 °C, along with ZnCl<sub>2</sub> and LiNH<sub>2</sub>, LiCl was observed in the reaction products. The presence of LiCl is believed to result from a salt metathesis reaction such as that in Eq. (1). Although Zn(NH<sub>2</sub>)<sub>2</sub> was not observed in the XRD patterns, this may be present in finely divided or amorphous form, or may have reacted further to give another finely divided or amorphous product.



The reaction products from the samples prepared at 200 °C contained a mixture of LiNH<sub>2</sub>, Li<sub>2</sub>NH, LiCl and ZnCl<sub>2</sub> (Fig. S1). A substantial proportion of LiNH<sub>2</sub> had decomposed into Li<sub>2</sub>NH at 200 °C. Previous research [15] reported that at this temperature LiNH<sub>2</sub> decomposed only to a limited extent. This improvement may be caused by the effect of the Cl<sup>-</sup> ion, which is in agreement with previous work [12,16].

At all reactant ratios the products after reaction at 250 °C contained small amounts Zn<sub>3</sub>N<sub>2</sub> and LiZnN. After heating to 300 °C, no lithium amide or imide were observed at the ratio of 1:2, however, some remained at higher ratios of LiNH<sub>2</sub>; no remaining ZnCl<sub>2</sub> was observed. The proportion of LiZnN present increased quickly when the temperature was raised to 400 °C while that of Zn<sub>3</sub>N<sub>2</sub> decreased. Except for the ratio of 1:2, at all other ratios the reactions seemed to be complete at 500 °C, as the remaining Zn<sub>3</sub>N<sub>2</sub> was converted into LiZnN (Fig. 1). At the ratio of 1:2, a considerable amount of Zn<sub>3</sub>N<sub>2</sub> (38 wt%) remained at 500 °C. It is believed that the 1:2 sample is deficient in Li (*vide infra*) preventing complete transformation of Zn<sub>3</sub>N<sub>2</sub> into LiZnN. At 600 °C, Zn<sub>3</sub>N<sub>2</sub> was not observed. A small amount of LiZnN had been decomposed into LiZn and Zn as reported previously by Toyoura et al. [17].

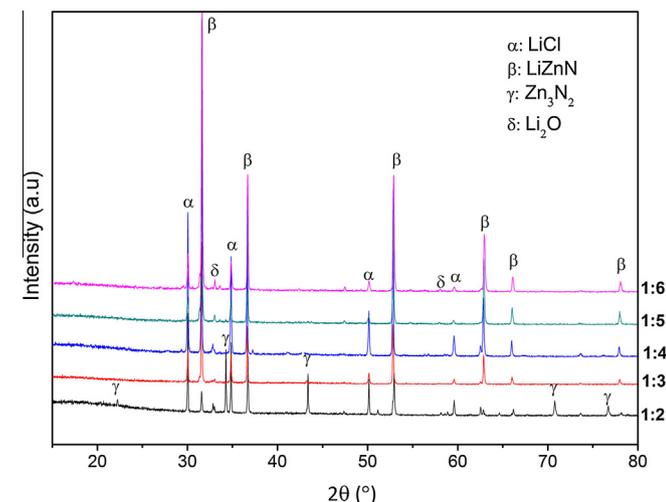


Fig. 1. Powder XRD patterns of the products of reactions between ZnCl<sub>2</sub> and LiNH<sub>2</sub> in a ratio of (a) 1:2, (b) 1:3, (c) 1:4, (d) 1:5, (e) 1:6, at 500 °C for 12 h.

These results suggest the reaction sequence given in Eqs. (2)–(4). ZnCl<sub>2</sub> and LiNH<sub>2</sub> may react in a 1:2 ratio to give Zn<sub>3</sub>N<sub>2</sub> and LiCl with the release of ammonia (Eq. (2)). If further LiNH<sub>2</sub> is present a subsequent reaction with Zn<sub>3</sub>N<sub>2</sub> is possible yielding LiZnN with the evolution of ammonia (Eq. (3)). These two reactions can be combined to give Eq. (4).



Overall reaction:



The evolution of ammonia was confirmed by TPD–MS, where a broad peak at 280 °C corresponding to ammonia gas was observed. A lesser amount of hydrogen gas was also observed beginning above 300 °C and peaking at the higher temperature of about 400 °C (Fig. 2a). The appearance of a small amount of hydrogen here may be from the decomposition of NH<sub>3</sub> [18]. It should be noted that although the 1:2 ratio should in principle yield Zn<sub>3</sub>N<sub>2</sub> stoichiometrically according to Eq. (2), both nitrides were observed under virtually all the reaction conditions and ratios studied, indicating that, once formed, Zn<sub>3</sub>N<sub>2</sub> competes with ZnCl<sub>2</sub> to react with LiNH<sub>2</sub> via Eq. (3).

#### 3.2. Zinc chloride and lithium amide in the presence of lithium hydride

The reaction between ammonia and lithium hydride to yield lithium amide and hydrogen (Eq. (5)) has been demonstrated previously [18]



Lithium hydride was therefore added to the ZnCl<sub>2</sub>–*n*LiNH<sub>2</sub> system in an attempt to change the overall reaction pathway to that given in Eq. (6), which is the sum of Eqs. (4) and (5):



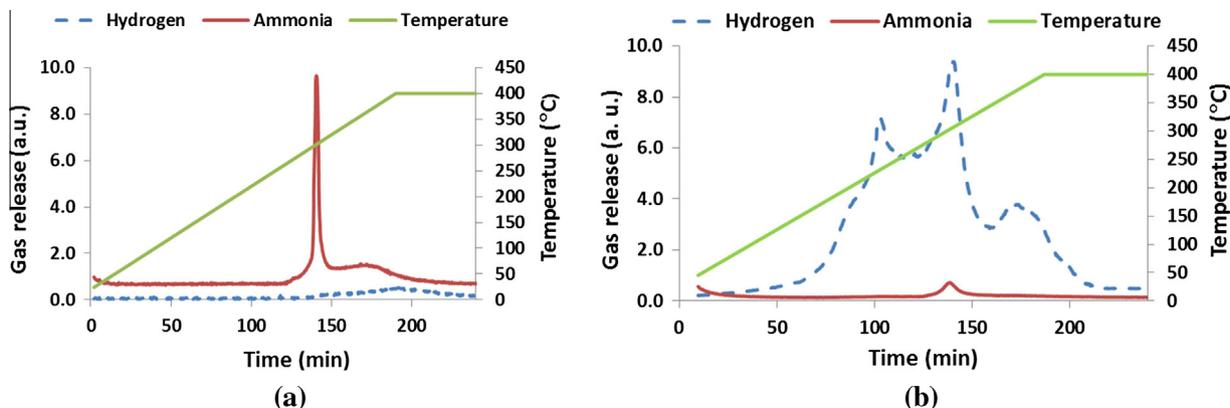
In practice, the addition of LiH resulted in not only the desired products of LiZnN and LiCl but also Zn (from 150 °C) and LiZn (from 500 °C). TPD–MS confirmed the main gaseous product changed from NH<sub>3</sub> to H<sub>2</sub> with an onset temperature of around 90 °C (Fig. 2b). Hydrogen release at such a low temperature could be due to a metathesis reaction between ZnCl<sub>2</sub> and LiH to form LiCl and, transiently, ZnH<sub>2</sub>, which is unstable above 90 °C decomposing to form Zn and H<sub>2</sub> [19]. The decomposition of LiZnN to form LiZn and Zn was observed at the lower temperature of 500 °C.

#### 3.3. Zinc nitride and lithium amide

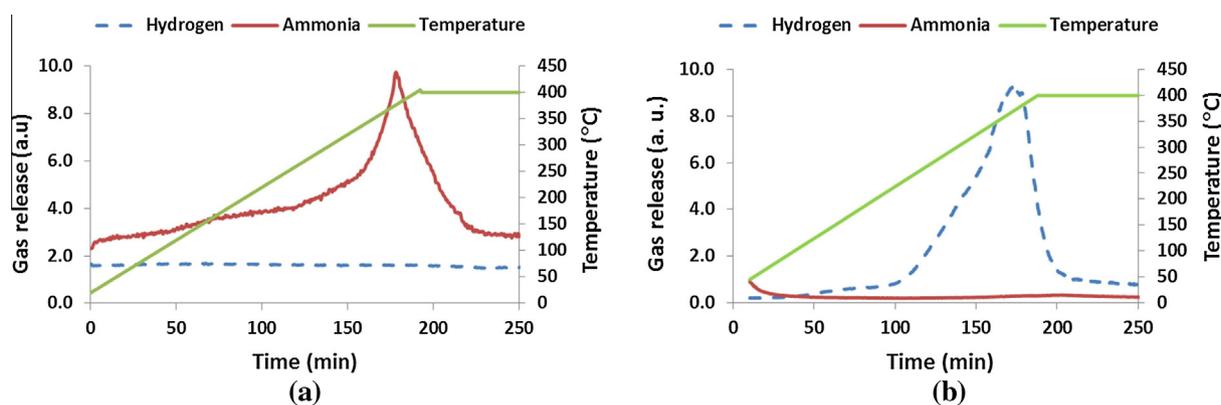
Zn<sub>3</sub>N<sub>2</sub> (Alfa–Aesar, 99%) and LiNH<sub>2</sub> were mixed in a molar ratio of 1:3, in the temperature range 300–500 °C for 1–24 h, in order to produce pure LiZnN, via Eq. (3), without the presence of LiCl. The reaction occurred slowly at 300 °C with a small amount of LiZnN obtained and then faster at 400 °C. At 500 °C LiZnN (~92 wt%) was achieved. A longer reaction time (24 h) did not change the remaining Zn<sub>3</sub>N<sub>2</sub> into LiZnN with a small amount of Zn<sub>3</sub>N<sub>2</sub> (~6 wt%) remaining.

In order to achieve pure LiZnN, excess LiNH<sub>2</sub> was added to the reactants, which were heated at 500 °C for up to 12 h. Pure LiZnN could be obtained after a 1 h reaction between Zn<sub>3</sub>N<sub>2</sub> and LiNH<sub>2</sub>, in a molar ratio of 1:4.2.

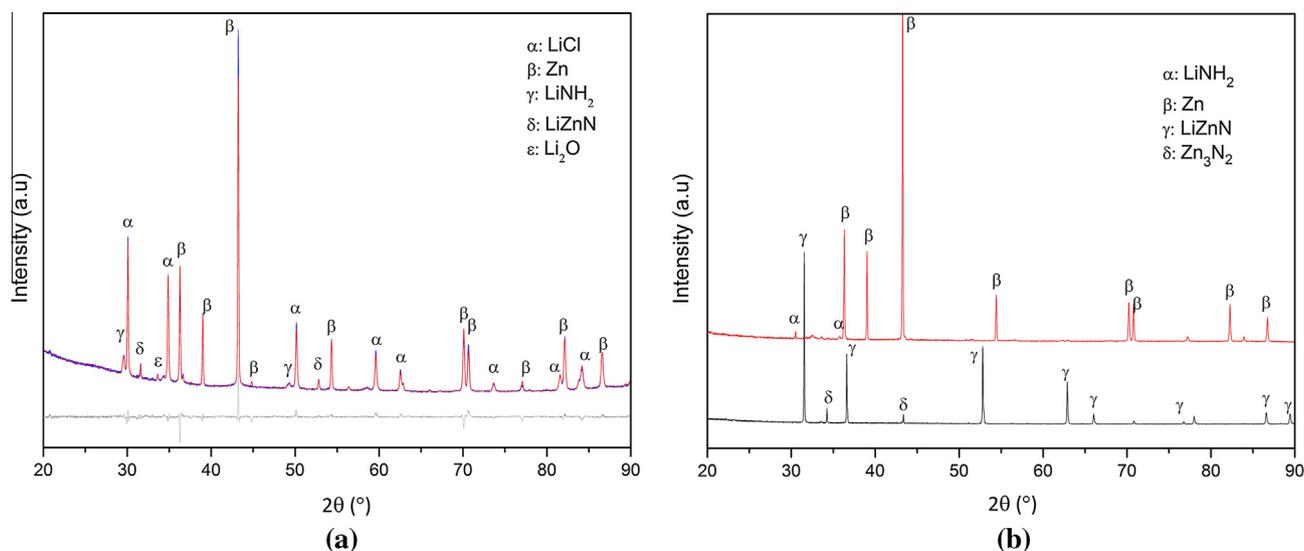
The hydrogen desorption properties of the reaction between Zn<sub>3</sub>N<sub>2</sub> and LiNH<sub>2</sub> were tested using TPD–MS. At about 360 °C, ammonia release was observed, indicating the expected reaction (3) occurred (Fig. 3a).



**Fig. 2.** TPD-MS trace of the reaction of  $\text{ZnCl}_2$  and  $\text{LiNH}_2$  (a) without and (b) with  $\text{LiH}$  heated at  $2\text{ }^\circ\text{C min}^{-1}$  to  $400\text{ }^\circ\text{C}$ , showing traces for hydrogen (blue dashed traces), ammonia (red solid traces) and temperature (green straight lines).



**Fig. 3.** TPD-MS trace of the reaction of  $\text{Zn}_3\text{N}_2$  and  $\text{LiNH}_2$  (a) without and (b) with  $\text{LiH}$  heated at  $2\text{ }^\circ\text{C min}^{-1}$  to  $400\text{ }^\circ\text{C}$ , showing traces for hydrogen (blue dashed traces), ammonia (red solid traces) and temperature (green straight lines).



**Fig. 4.** (a) Powder XRD pattern of the products of the hydrogenation of a mixture of  $\text{LiZnN}$  and  $\text{LiCl}$  under  $90\text{ bar H}_2$ , at  $300\text{ }^\circ\text{C}$  for  $20\text{ h}$  showing observed (blue), Rietveld fit (red) and difference (grey) plots. (b) Powder XRD pattern of a mixture of  $\text{LiZnN}$  ( $86\text{ wt}\%$ ) and  $\text{Zn}_3\text{N}_2$  ( $14\text{ wt}\%$ ) before (lower trace) and after (upper trace) hydrogenation at  $300\text{ }^\circ\text{C}$  for  $20\text{ h}$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 3.4. Zinc nitride and lithium amide in the presence of lithium hydride

$\text{LiH}$  was again added in order to change the overall reaction pathway in favour of hydrogen production (Fig. 3b). A ratio of

1:1:2 for  $\text{Zn}_3\text{N}_2$ ,  $\text{LiNH}_2$  and  $\text{LiH}$ , was employed in accordance with the anticipated reaction given by Eq. (7) (sum of Eqs. (3) and (5)):



The products of reaction between  $\text{Zn}_3\text{N}_2$ ,  $\text{LiNH}_2$  and  $\text{LiH}$  at  $500\text{ }^\circ\text{C}$  for 2 h were a mixture of  $\text{LiZnN}$  (~83 wt%) and  $\text{Zn}$  (~17 wt%). However, the reaction at  $400\text{ }^\circ\text{C}$  for 2 h achieved pure  $\text{LiZnN}$ .

### 3.5. Rehydrogenation

Hydrogenation of a mixture of  $\text{LiZnN} + 2\text{LiCl}$  (from the reaction of  $\text{ZnCl}_2 + 3\text{LiNH}_2$  at  $500\text{ }^\circ\text{C}$ ) was attempted at  $200\text{--}300\text{ }^\circ\text{C}$  for 12–24 h under 90 bar  $\text{H}_2$ . After 20 h the mixture Fig. 4a showed the formation of  $\text{LiNH}_2$  (21 wt%), along with  $\text{Zn}$  (32 wt%) and  $\text{Li}_2\text{O}$  (3 wt%). This indicates that rehydrogenation can occur, however, the presence and stability of  $\text{LiCl}$  may prevent the formation of  $\text{ZnCl}_2$ , and therefore full reversibility may not be possible.

A mixture of  $\text{LiZnN}$  (~86 wt%) and  $\text{Zn}_3\text{N}_2$  (~14 wt%), (from  $\text{Zn}_3\text{N}_2 + 3\text{LiNH}_2$  at  $500\text{ }^\circ\text{C}$ ) was also rehydrogenated to form a mixture of  $\text{Zn}$  and  $\text{LiNH}_2$ , in a molar ratio of approximately 1:1 (Fig. 4b). This is consistent with hydrogenation of  $\text{LiZnN}$  in accordance with the following reaction (Eq. (8)):



This result is potentially interesting as it shows that hydrogenation is not dependent on the presence of chloride and that higher gravimetric hydrogen contents may be obtained through investigation of metal nitrides. In this case, however, neither pure  $\text{LiZnN}$  nor  $\text{Zn}_3\text{N}_2$  were rehydrogenated under the conditions studied.

## 4. Conclusions

Reactions of  $\text{ZnCl}_2 + n\text{LiNH}_2$  at a range of molar ratios and temperatures gave a mixture of  $\text{Zn}_3\text{N}_2$  and  $\text{LiZnN}$  as products. No stable amide chloride, imide chloride or nitride chloride phases were identified. Temperature-programmed desorption with mass spectrometry (TPD–MS) showed that the main gas emitted during these reactions was ammonia ( $\text{NH}_3$ ), but the addition of lithium hydride ( $\text{LiH}$ ) changed the main gaseous product from  $\text{NH}_3$  to  $\text{H}_2$ , which was released at a low temperature beginning around  $90\text{ }^\circ\text{C}$ . Hydrogenation of  $\text{LiZnN}$  was shown to occur in the presence of  $\text{Zn}_3\text{N}_2$  or  $\text{LiCl}$  forming  $\text{LiNH}_2$  and  $\text{Zn}$  metal.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jallcom.2014.12.190>.

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