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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 Zn_3N_2 and 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 (NH_3). The addition of lithium hydride (LiH) changed the main gaseous product from NH_3 to H_2 , which was released at a low temperature beginning around 90°C . Neither pure LiZnN nor Zn_3N_2 could be rehydrogenated under the conditions studied. However, mixtures of LiZnN and Zn_3N_2 , and LiZnN and LiCl reacted with H_2 at 300°C to form LiNH_2 and zinc metal.

Keywords:

lithium amide, zinc nitride, lithium zinc nitride, hydrogen absorption/desorption, reversible hydrogen storage, temperature-programmed desorption (TPD–MS)

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 LiNH_2 , Li_2NH and Li_3N [1–4]. However, the slow absorption kinetics and relatively high operating temperature currently limit its practical applications. To improve the system, a variety of ternary Li–M–N–H systems, where $M = \text{B}, \text{Ca}, \text{Al}$ 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 LiNH_2 , and Li–Ti–N–H showed a marked reduction in reaction enthalpy with $\Delta H_{\text{hyd}} = -46.6 \text{ kJmol}^{-1}$ compared with that of the Li–N–H system ($-75.67 \text{ kJmol}^{-1}$) [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 LiNH_2 and Li_2NH with LiX and MgX_2 ($X = \text{Cl}, \text{Br}, \text{I}$) to form a range of new amide halides. On reaction with 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 ZnCl_2 and LiNH_2 , with and without the presence of LiH, under different conditions of stoichiometry and temperature. In contrast to the cases of LiCl and MgCl_2 [12], no stable amide chloride phases were isolated with reactions proceeding to the nitrides Zn_3N_2 and LiZnN at relatively low temperature. The hydrogen absorption/desorption properties of these products is investigated.

2. Experimental

2.1 Sample preparation

The LiNH_2 , ZnCl_2 , LiH (Sigma–Aldrich, > 95%) and Zn_3N_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 hours.

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

The sample ($\sim 0.1 \text{ g}$) 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 ml min^{-1} . In this study, all samples were heated at 2°C/minute to 400°C and held at that temperature for 2 hours 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].

2.4 Rehydrogenation

Samples were ground and sealed in a reaction vessel in an argon-atmosphere glovebox and then transferred to the

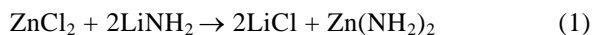
hydrogenation apparatus. Hydrogenation of the samples was attempted at 200 and 300°C under 90 bar H₂ for up to 24 hours.

3. Results and discussion

3.1 Zinc chloride and lithium amide

The reactions between ZnCl₂ and LiNH₂ 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/minute and the reactions were kept at the set temperature for 12 hours.

For samples prepared at 150°C, along with ZnCl₂ and LiNH₂, LiCl was observed in the reaction products. The presence of LiCl is believed to result from a salt metathesis reaction such as that in Equation 1. Although Zn(NH₂)₂ 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 LiNH₂, Li₂NH, LiCl and ZnCl₂ (**Fig. S1**). A substantial proportion of LiNH₂ had decomposed into Li₂NH at 200°C. Previous research [15] reported that at this temperature LiNH₂ decomposed only to a limited extent. This improvement may be caused by the effect of the Cl⁻ ion, which is in agreement with previous work. [12, 16].

At all reactant ratios the products after reaction at 250°C contained small amounts Zn₃N₂ 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 LiNH₂; no remaining ZnCl₂ was observed. The proportion of LiZnN present increased quickly when the temperature was raised to 400°C while that of Zn₃N₂ decreased. Except for the ratio of 1:2, at all other ratios the reactions seemed to be complete at 500°C, as the remaining Zn₃N₂ was converted into LiZnN (**Fig. 1**). At the ratio of 1:2, a considerable amount of Zn₃N₂ (38 wt %) remained at 500°C. It is believed that the 1:2 sample is deficient in Li (*vide infra*) preventing complete transformation of Zn₃N₂ into LiZnN. At 600°C, Zn₃N₂ was not observed. A small amount of LiZnN had been decomposed into LiZn and Zn as reported previously by Toyoura *et al.* [17].

These results suggest the reaction sequence given in Equations 2–4. ZnCl₂ and LiNH₂ may react in a 1:2 ratio to give Zn₃N₂ and LiCl with the release of ammonia (Equation 2). If further LiNH₂ is present a subsequent reaction with Zn₃N₂ is possible yielding LiZnN with the evolution of ammonia (Equation 3). These two reactions can be combined to give Equation 4.



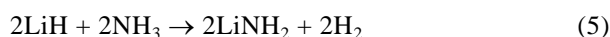
Overall reaction:



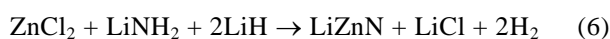
The evolution of ammonia was confirmed by TPD–MS, where a broad peak at 280°C corresponding to ammonia gas was observed. A lesser amount of hydrogen gas was also observed beginning above 300°C and peaking at the higher temperature of about 400°C (**Fig. 2a**). The appearance of a small amount of hydrogen here may be from the decomposition of NH₃ [18]. It should be noted that although the 1:2 ratio should in principle yield Zn₃N₂ stoichiometrically according to Equation 2, both nitrides were observed under virtually all the reaction conditions and ratios studied, indicating that, once formed, Zn₃N₂ competes with ZnCl₂ to react with LiNH₂ *via* Equation 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 (Equation 5) has been demonstrated previously [18]



Lithium hydride was therefore added to the ZnCl₂–*n*LiNH₂ system in an attempt to change the overall reaction pathway to that given in Equation 6, which is the sum of Equations 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 NH₃ to H₂ 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 ZnCl₂ and LiH to form LiCl and, transiently, ZnH₂, which is unstable above 90°C decomposing to form Zn and H₂ [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

Zn₃N₂ (Alfa-Aesar, 99%) and LiNH₂ were mixed in a molar ratio of 1:3, in the temperature range 300–500°C for 1–24 hours, in order to produce pure LiZnN, *via* Equation 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 hours) did not change the remaining Zn₃N₂ into LiZnN with a small amount of Zn₃N₂ (~6 wt.%) remaining.

In order to achieve pure LiZnN, excess LiNH₂ was added to the reactants, which were heated at 500°C for up to 12 hours. Pure LiZnN could be obtained after a 1 hour reaction between Zn₃N₂ and LiNH₂, in a molar ratio of 1:4.2. The hydrogen desorption properties of the reaction between Zn₃N₂ and LiNH₂ were tested using TPD-MS. At about 360°C, ammonia release was observed, indicating the the expected reaction (3) occurred (**Fig. 3a**).

3.4 Zinc nitride and lithium amide with the presense of lithium hydride

LiH was again added in order to chnge the overall reaction pathway in favour of hydrogen production (**Fig. 3b**). A ratio of 1:1:2 for Zn₃N₂, LiNH₂ and LiH, was employed in accordance with the anticipated reaction given by Equation 7 (sum of Equations 3 and 5):



The products of reaction between Zn₃N₂, LiNH₂ and LiH at 500°C for 2 hours were a mixture of LiZnN (~83 wt%) and Zn (~17 wt%). However, the reaction at 400°C for 2 hours achieved pure LiZnN.

Hydrogenation of a mixture of LiZnN + 2LiCl (from the reaction of ZnCl₂ + 3LiNH₂ at 500°C) was attempted at 200–300°C for 12–24 hours under 90 bar H₂. After 20 hours the mixture **Fig. 4a** showed the formation of LiNH₂ (21 wt%), along with Zn (32 wt%) and Li₂O (3 wt%). This indicates that rehydrogenation is possible, however, the presence and stability of LiCl may prevent the formation of ZnCl₂, and therefore full reversibility may not be possible.

A mixture of LiZnN (~86 wt %) and Zn₃N₂ (~14 wt %), (from Zn₃N₂ + 3LiNH₂ at 500°C) was also rehydrogenated to form a mixture of Zn and LiNH₂, in a molar ratio of approximately 1:1 (**Fig. 4b**). This is consistent with hydrogenation of LiZnN in accordance with the following reaction (Equation 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 the pure metal nitrides.

4. Conclusions

Reactions of ZnCl₂ + *n*LiNH₂ at a range of molar ratios and temperatures gave a mixture of Zn₃N₂ and 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 (NH₃), but the addition of lithium hydride (LiH) changed the main gaseous product from NH₃ to H₂, which was released at a low temperature beginning around 90°C. Hydrogenation of LiZnN was shown to occur in the presence of Zn₃N₂ or LiCl forming LiNH₂ and Zn metal.

Acknowledgments

We would like to thank Vietnam International Education Development, Ministry of Education and Training (VIED-MOET) for funding. Equipment used in this research was obtained through *Birmingham Science City (Hydrogen Energy and Advanced Materials 1 projects)* with support from Advantage West Midlands and partly funded by the European Regional Development Fund.

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FIGURE CAPTIONS.

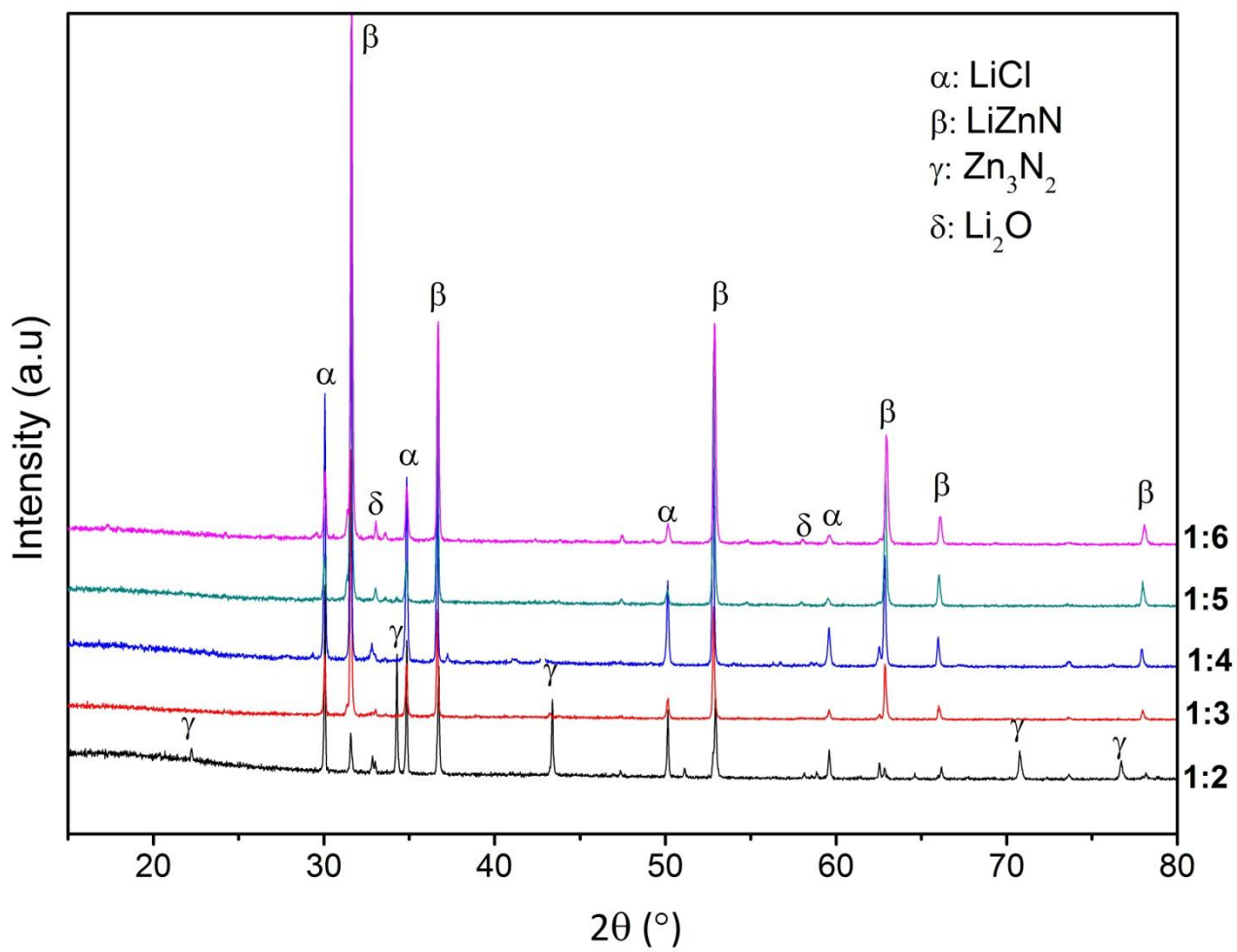
Fig. 1 Powder XRD patterns of the products of reactions between ZnCl₂ and LiNH₂ in a ratio of (a) 1:2, (b) 1:3, (c) 1:4, (d) 1:5, (e) 1:6, at 500°C for 12 hours.

Fig. 2 TPD–MS trace of the reaction of ZnCl₂ and LiNH₂ (a) without and (b) with LiH heated at 2°C min⁻¹ to 400°C, showing traces for hydrogen (blue), ammonia (red) and temperature (green).

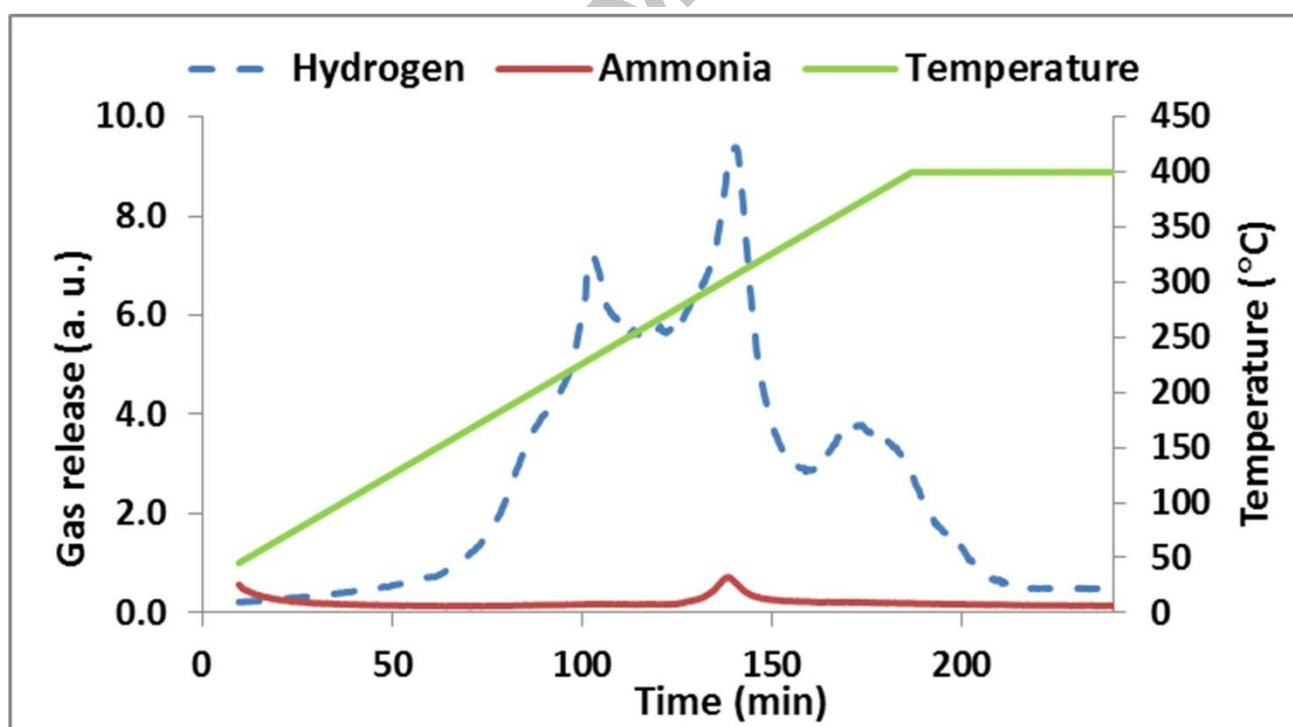
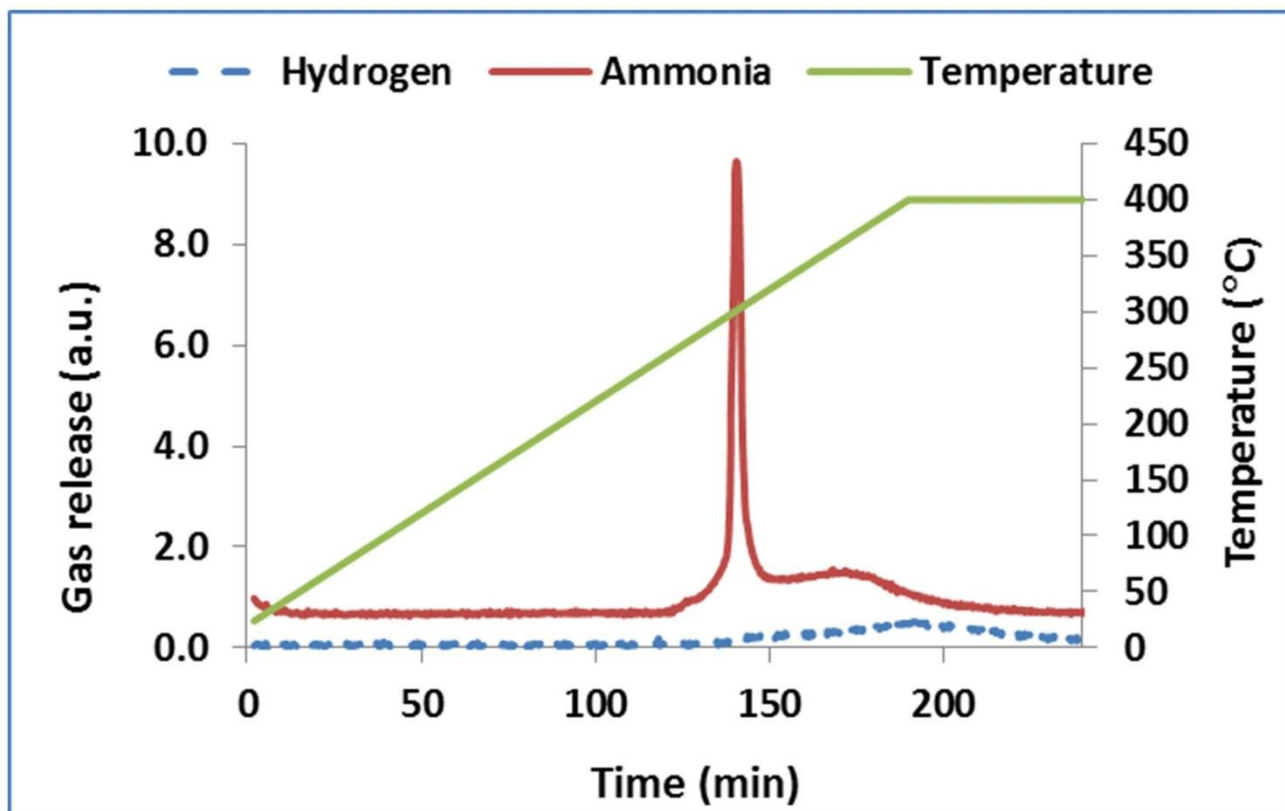
Fig. 3 TPD–MS trace of the reaction of Zn₃N₂ and LiNH₂ (a) without and (b) with LiH heated at 2°C min⁻¹ to 400°C, showing traces for hydrogen (blue), ammonia (red) and temperature (green).

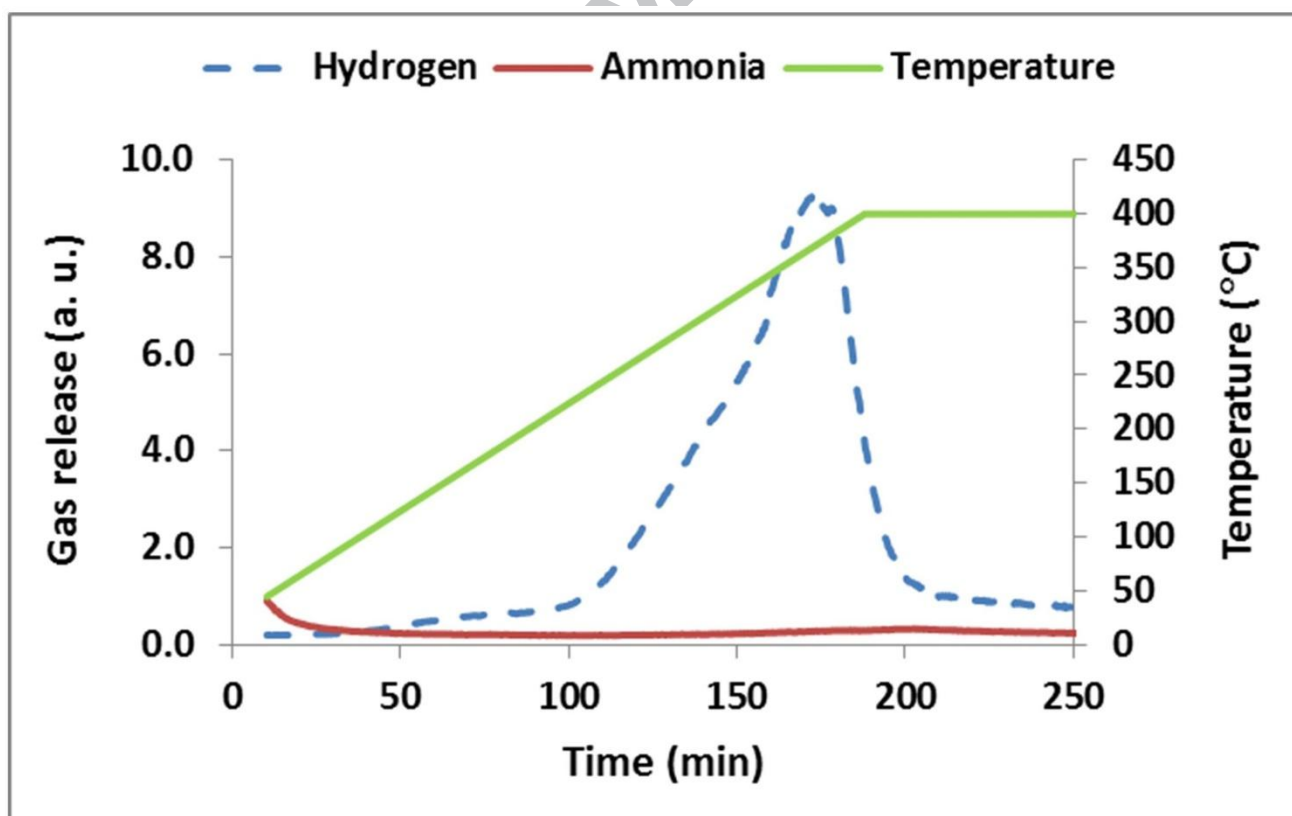
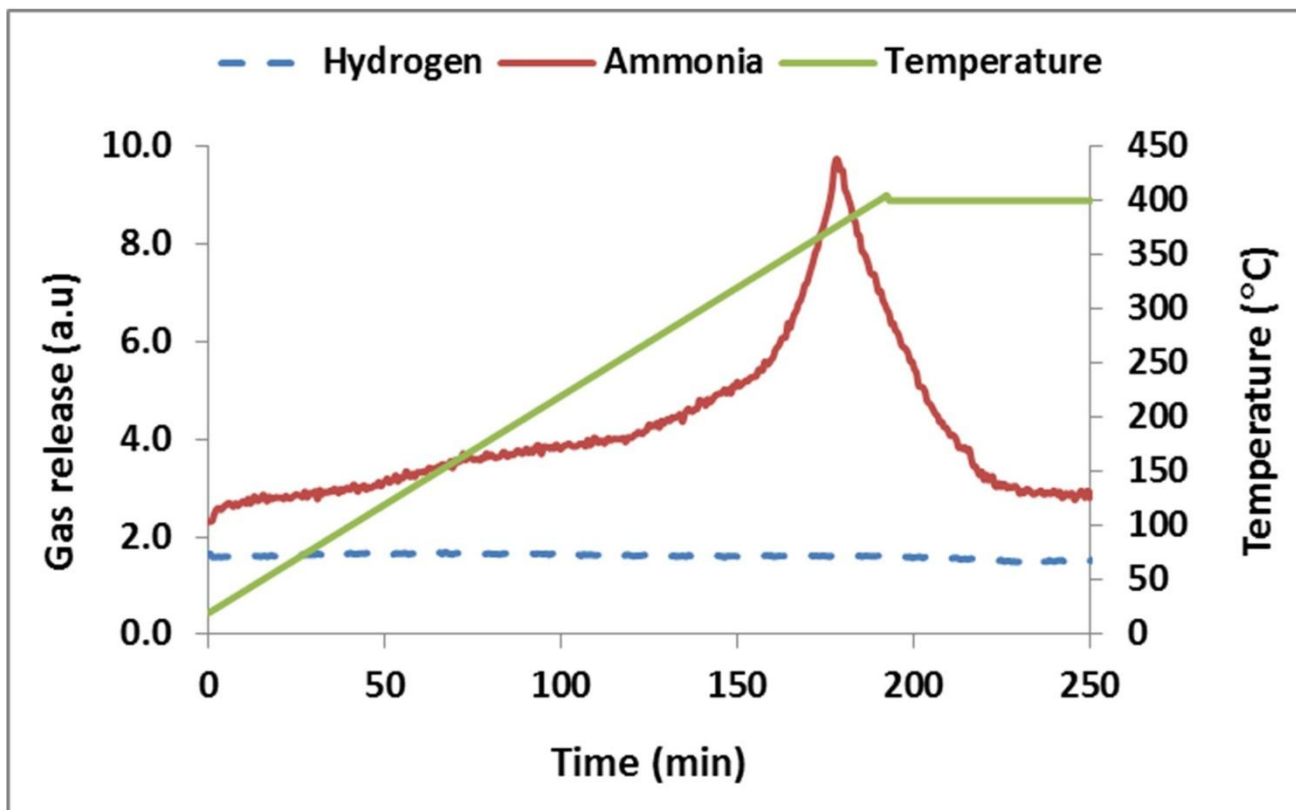
Fig. 4 (a) Powder XRD pattern of the products of the hydrogenation of a mixture of LiZnN and LiCl under 90 bar H₂, at 300°C for 20 hours showing observed (blue), Rietveld fit (red) and difference (grey) plots. (b) Powder XRD pattern of a mixture of LiZnN (86 wt%) and Zn₃N₂ (14 wt%) before (lower trace) and after (upper trace) hydrogenation at 300°C for 20 hours.

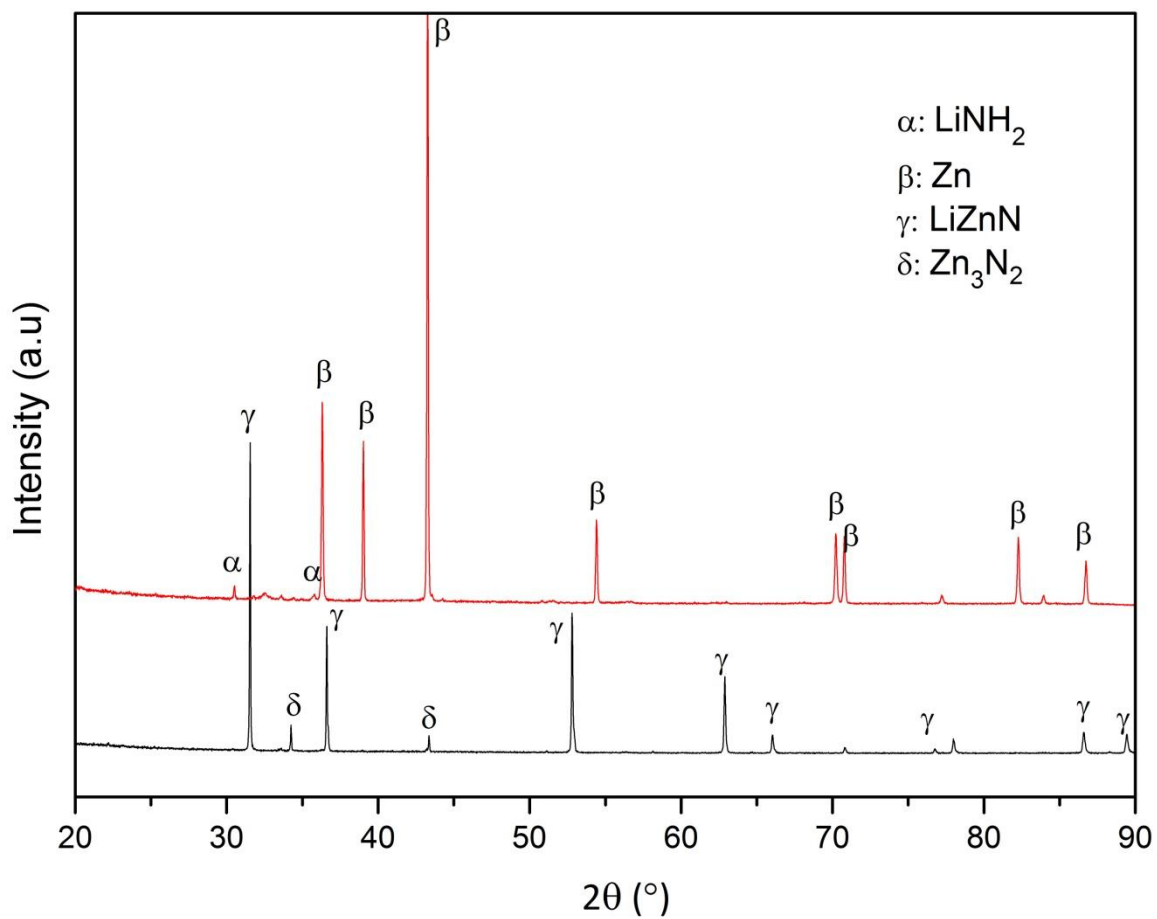
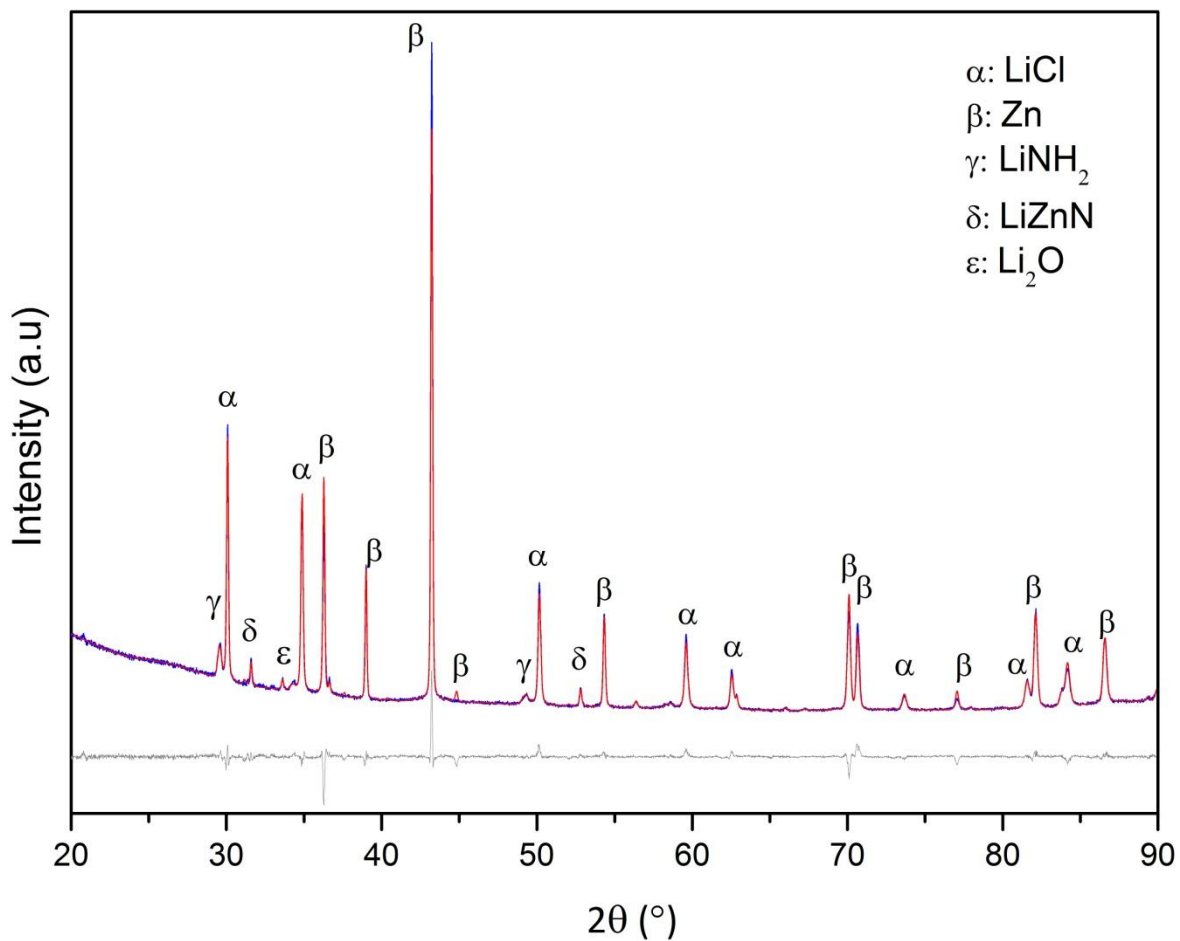
Fig. S1 Powder XRD patterns of the products of reactions between ZnCl₂ and LiNH₂ in a ratio of (a) 1:2, (b) 1:3, (c) 1:4, (d) 1:5, (e) 1:6, at 200°C for 12 hours.



ACCEPTED







Highlights

- Reactions of $\text{ZnCl}_2 + n\text{LiNH}_2$ gave a mixture of Zn_3N_2 and LiZnN as products.
- No stable amide chloride, imide chloride or nitride chloride phases were identified.
- The addition of lithium hydride (LiH) changed the main gaseous product from NH_3 to H_2 .
- Neither pure LiZnN nor Zn_3N_2 could be rehydrogenated under the conditions studied.
- $\text{LiZnN}/\text{Zn}_3\text{N}_2$, and LiZnN/LiCl mixtures hydrogenated at 300°C to form LiNH_2 and Zn metal.

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