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In situ powder neutron diffraction study of non-stoichiometric phase formation during the hydrogenation† of Li₃N

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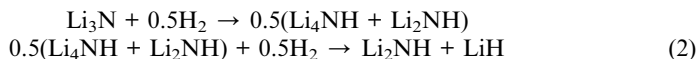
The hydrogenation of Li₃N at low chemical potential has been studied *in situ* by time-of-flight powder neutron diffraction and the formation of a non-stoichiometric Li_{4-2x}NH phase and Li₄NH observed. The results are interpreted in terms of a model for the reaction pathway involving the production of Li₄NH and Li₂NH, which subsequently react together to form Li_{4-2x}NH. Possible mechanisms for the production of Li₄NH from the hydrogenation of Li₃N are discussed.

1. Introduction

Chen *et al.* originally reported the absorption of hydrogen in Li₃N to occur via a reaction of stoichiometric compounds:¹



On the basis of *in situ* neutron diffraction measurements, some of the present authors reported an alternative reaction pathway involving the suppression of LiH in the initial stages of hydrogenation, in addition to the transient formation of Li₄NH and a cubic phase with a variable lattice parameter, related to the stoichiometric imide, Li₂NH.² A possible reaction pathway involving Li₄NH, with the same end-members as in (1) is:



On the basis of Density Functional Theory calculations, Michel *et al.*³ reported that this reaction pathway is marginally energetically favorable compared with reaction (1). The experimentally observed cubic phase has been denoted as quasi-imide,² owing to its similarity with the stoichiometric imide. The quasi-imide phase is believed to be the product of a reaction between Li₄NH and Li₂NH, forming either a non-stoichiometric single phase or an intergrowth phase. Indeed, mechanical

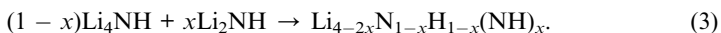
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† We would note that neutron diffraction necessitates the use of the isotope deuterium; the term hydrogen is used in this work in a generic context.

1 mixtures of Li_4NH and Li_2NH have been shown to form single phase components
through solid-state diffusion,^{4,5} according to:



5 The product in (3) has a mixture of the anionic species N^{3-} , H^- and $(\text{NH})^{2-}$, giving
an overall composition $\text{Li}_{4-2x}\text{NH}$. The occurrence of the quasi-imide phase has been
shown to be dependent on the hydrogen chemical potential.⁶ Specifically, at 250 °C,
10 its formation appears to be suppressed for hydrogen pressures in excess of 0.5 bars.
In the present work, the pressure is kept below 0.5 bars at all stages of hydrogenation.

2. Experimental

15 A commercially produced sample of Li_3N (Sigma Aldrich, 99%) was loaded into
a custom designed pressure cell of internal volume 2 cc, with an Al_2O_3 coated vanadium
window, as described in ref. 2. Neutron diffraction patterns were measured on
OSIRIS⁷ at the ISIS neutron facility, UK. The sample is originally observed to be
20 a two-phase mixture of the stable α and the high-pressure β polymorphs of Li_3N ;
annealing the sample under vacuum at 250 °C for 2 h results in a complete conversion
to the α -phase. Loading of hydrogen (deuterium) was effected at 250 °C *via* the
Sieverts method, as described previously,⁶ with a buffer volume of 500 cc, enabling
the required molar up-take in each step to be achieved without the pressure
25 exceeding 0.5 bars. Under these conditions, the formation of the stoichiometric
 Li_2NH will be precluded, at least in the initial stages of the hydrogenation reaction.⁶
Diffraction patterns were collected at molar concentrations $x = \{0.1, 0.15, 0.2, 0.25,$
 $0.3, 0.35, 0.4, 0.5, 0.67, 0.875, 1\}$, where x is the molar ratio of H_2 absorbed to the
original Li_3N . For each step, data collection commenced once the rate-of-change of
30 pressure had reached zero; an indication that the overall hydrogen content was
stable. Each data set was collected for 1 h. The diffraction patterns were analysed
by the Rietveld method using the GSAS software system⁸ to determine the crystal-
line phases present, and their abundance, throughout the hydrogenation process.
Structural models used in the refinement are from Niewa⁹ for Li_4NH , Ohoyama
35 *et al.*¹⁰ for Li_2NH and Bull *et al.*⁵ for $\text{Li}_{4-2x}\text{NH}$.

3. Results and discussion

Two distinct regions can be identified in the neutron diffraction data, marked by the
40 appearance of LiH at around $x = 0.5$ in the measured patterns. Fig. 1 shows repre-
sentative diffraction patterns, along with the refined structural models, in these two
regions, at $x = 0.3$ and $x = 0.875$. The molar phase fractions and quasi-imide lattice
parameter obtained from Rietveld refinement are shown in Fig. 2a and b. Lines in
these figures are calculated from the various reaction pathways, as described below.
45 In the initial stages of hydrogenation, for $x \sim \leq 0.5$, three phases are present in the
sample – Li_3N , Li_4NH and a quasi-imide phase. The lattice parameter of the latter
phase in this region exhibits some variation, shown in Fig. 2b. Above $x = 0.5$, the
phase fraction of Li_4NH is observed to reduce, correlating with the formation of
 LiH and there is a marked change in the refined lattice parameter.

50 In order to interpret these results, they are compared to the reaction pathways in
(1) and (2), where the phase fractions, as a function of x , can be uniquely determined;
details of such a calculation are given in the appendix. From the reaction pathway
in (1),



55 From the reaction pathways in (2):

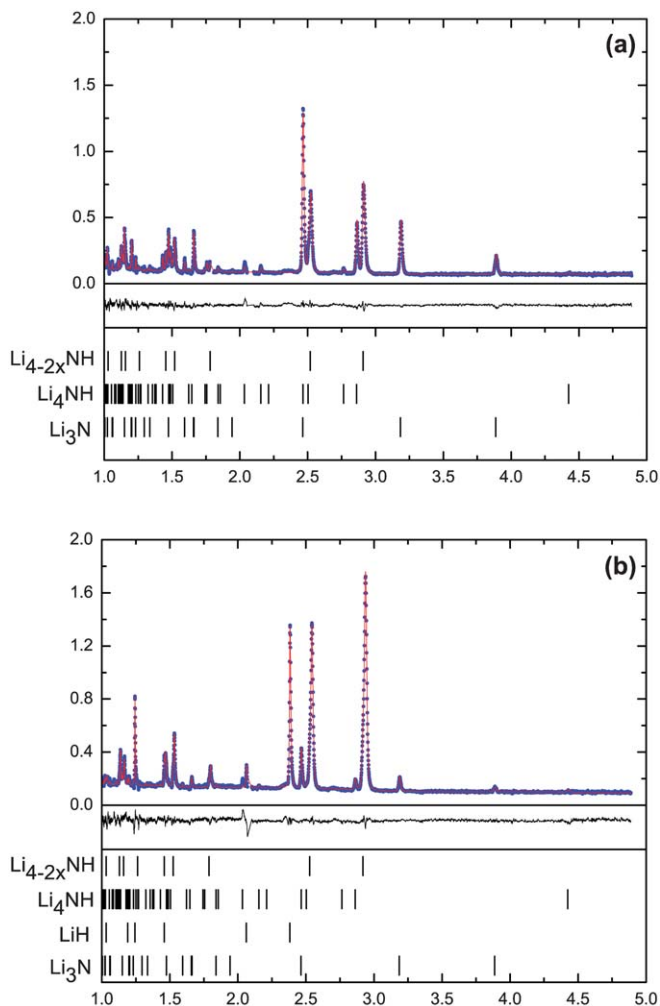
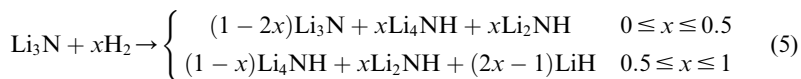
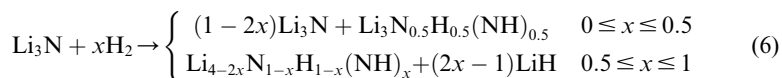


Fig. 1 Neutron powder diffraction patterns and corresponding structural refinement at 250 °C following hydrogen absorption in Li_3N at molar ratios of (a) $x = 0.3$ and (b) $x = 0.875$. The weighted-profile R-factor, R_{wp} , for the two refinements are 0.057 and 0.046, respectively.



Further, including the solid-state reaction in (3):



The molar phase fractions calculated from reaction pathways in (4), (5) and (6) are shown in Fig. 3. The experimentally observed molar phase fractions for Li_3N up to $x \sim 0.3$, and for LiH correlate well with the calculated values in (5) and (6), with those for $\text{Li}_{4-2x}\text{NH}$ and Li_4NH falling somewhere between the two models, suggesting that reaction (3) is only partially completed. We would note that, since this is

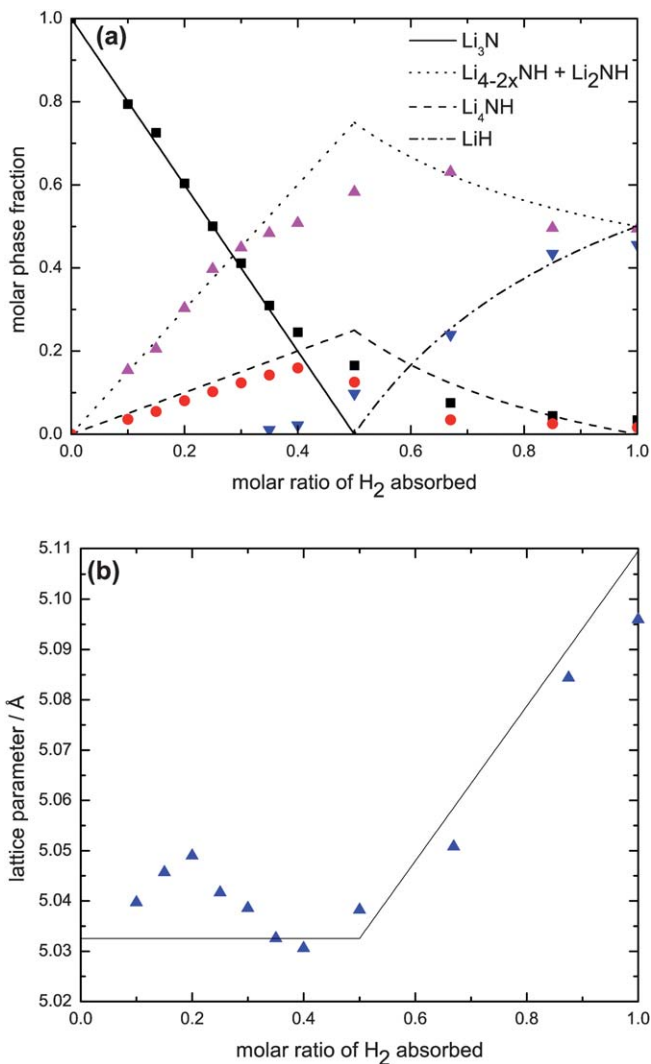
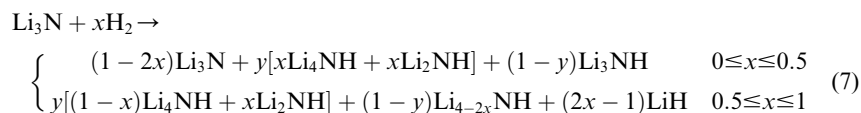


Fig. 2 Parameters determined from Rietveld refinement of neutron diffraction data from hydrogen absorption in Li₃N. (a) Molar phase fractions lines calculated from the hypothetical reaction pathway in (7), as described in the main text, and symbols representing experimentally determined values (squares – Li₃N, circles – Li₄NH, up-triangles – Li_{4-2x}NH and down-triangles – LiH). (b) Lattice parameter of the cubic quasi-imide phase (symbols), Li_{4-2x}NH, with corresponding calculated values from (6), as described in the main text (solid line).

a solid state reaction, it does not have an effect on the hydrogen pressure. If a fraction, y , remains unreacted, the pathway can be written as:



The phase fractions from (7) with $y = 0.5$ are shown in Fig. 2a compared with the experimental data. No Li₂NH is discernable in the neutron diffraction data, hence the calculated fractions for Li₂NH have been added to that of the quasi-imide

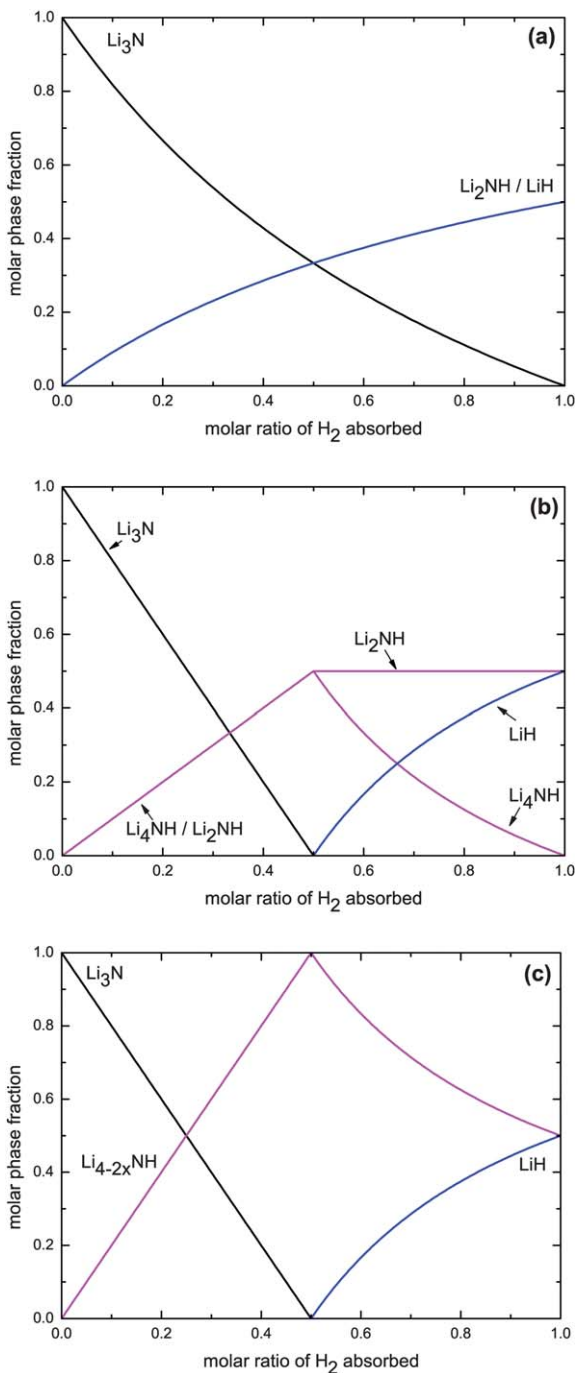


Fig. 3 Calculated molar phase fractions from (a) reaction pathway (4), (b) reaction pathways (5) and (c) reaction pathways (5) followed by the solid-state reaction (6).

phase to enable a direct comparison. The refined phase fractions are represented reasonably well across the range of x , with the exception of the proximity of $x = 0.5$. In this region, a new phase is forming, and the quasi-imide is changing

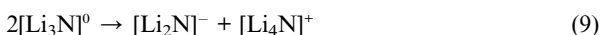
1 its stoichiometry, so the relaxation time of the phase transitions might be
expected to be large. Hence, the value of y might be expected to vary across the
range of x .

5 The quasi-imide phase as expressed in (6) is suggestive of non-stoichiometry
on the Li lattice, which is not the case in this structural model. Rather, the
non-stoichiometry arises from the interchange of the anionic species, which
can be made clearer by expressing the composition in relation to the stoichiometric
imide as:

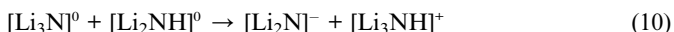


15 The variation of the quasi-imide lattice parameter with x is estimated by inter-
polation of data at $x = 1$ and 0.6 , taken from Bull *et al.*,⁵ from which a linear
variation, $a = 4.9555 + 0.1541x$, is obtained. Using this in conjunction with (6)
enables the variation in the lattice parameter along the reaction pathway to be
determined. Up to $x = 0.5$ is compositionally invariant, and so the lattice
parameter is constant. Above $x = 0.5$, there is a linear increase in the lattice
parameter. As can be seen in Fig. 2b, there is a good level of agreement with
the calculated and empirical values.

20 Whilst the exact mechanisms of hydrogenation in this system are still not
clear, both the refined phase fractions and the variation in the quasi-imide lattice
parameter lend weight to the reaction pathways in (2) and (3). In particular, the
suppression of LiH in the initial stages of hydrogenation provides an excess of
Li, which is accommodated in either the Li_4NH or $\text{Li}_{4-2x}\text{NH}$ phase. It is, there-
fore, of interest to consider how these phases might form. There is a wealth of
literature concerning superionic conductivity in Li_3N , in particular the beneficial
role of small amounts of hydrogen on ionic conductivity.¹¹⁻¹⁴ In the pure material,
vacancies play a vital role in determining the ionic conductivity,¹⁵ and so it
might be expected that they are also important in the hydrogenation process.
30 Li_3N has a layered structure comprising alternate planes of Li_2N and of Li.¹⁶
An intrinsic Frenkel-pair defect can be introduced by the transport of a Li
atom from the Li_2N layer to the Li layer:¹⁵



This type of mechanism would allow, in principle, the addition of heterolytically
dissociated hydrogen to produce Li_2NH and Li_4NH . Wahl discusses the substitution
of Li with H,¹⁷ leading to the formation of NH^{2-} anions. The negative charge can
be stabilised by the addition of Li^+ from a neighbouring cell, resulting in a vacancy in
the Li_2N plane:



45 Of particular relevance in this mechanism is the production of the compound
 Li_3NH .

4. Conclusion

50 *In situ* powder neutron diffraction data from the hydrogenation of Li_3N have been
presented. Rietveld profile refinement of a structural model to the data has been used
to determine the relative phase fractions along the reaction pathway. The appear-
ance of a non-stoichiometric phase, $\text{Li}_{4-2x}\text{NH}$, exhibiting a variation in lattice
parameter with overall hydrogen content, has been observed. The analysis has
55 been interpreted in terms of a reaction pathway with the transient formation of
 Li_4NH and Li_2NH , and the subsequent solid-state reaction to $\text{Li}_{4-2x}\text{NH}$.

A. Calculation of reaction pathways

The reaction pathway associated with (1) can be expressed in terms of x , the ratio of moles of H_2 absorbed to moles of Li_3N :



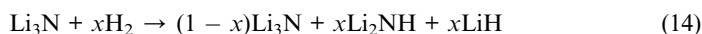
where n_{Li_3N} , n_{Li_2NH} and n_{LiH} are the molar amounts of Li_3N , Li_2NH and LiH . It is possible to relate the molar amounts and the number of each component in a matrix formalism:

$$\begin{pmatrix} 3 \\ 1 \\ 2x \end{pmatrix} = \begin{pmatrix} 3 & 2 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 1 \end{pmatrix} \begin{pmatrix} n_{Li_3N} \\ n_{Li_2NH} \\ n_{LiH} \end{pmatrix} \quad (12)$$

where the column matrix on the LHS represents the amount of Li, N and H in the reactants, and the 3×3 matrix represents the amount of Li, N and H in each of the products. The molar amounts can be obtained by inversion of the 3×3 matrix:

$$\begin{pmatrix} n_{Li_3N} \\ n_{Li_2NH} \\ n_{LiH} \end{pmatrix} = \begin{pmatrix} 3 \\ 1 \\ 2x \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ -\frac{1}{2} & \frac{3}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{3}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1-x \\ x \\ x \end{pmatrix} \quad (13)$$

Yielding the reaction:



The phase fractions are then:

$$f_{Li_3N} = \frac{1-x}{1+x} \quad (15)$$

$$f_{Li_2NH} = \frac{x}{1+x} \quad (16)$$

$$f_{LiH} = \frac{x}{1+x} \quad (17)$$

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