Phase space investigation of the lithium amide halides
Davies, Rosalind A.; Hewett, David R.; Korkiakoski, Emma; Thompson, Stephen P.; Anderson, Paul A.

DOI: 10.1016/j.jallcom.2014.12.130
License: Other (please specify with Rights Statement)

Document Version
Peer reviewed version

Citation for published version (Harvard):

Link to publication on Research at Birmingham portal

Publisher Rights Statement:
NOTICE: this is the author's version of a work that was accepted for publication in Journal of Alloys and Compounds. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Journal of Alloys and Compounds, DOI: 10.1016/j.jallcom.2014.12.130.

Eligibility for repository checked March 2015

General rights
Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

Users may freely distribute the URL that is used to identify this publication.
• Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
• Users may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
• Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.
Phase space investigation of the lithium amide halides.

Rosalind A. Davies, David R. Hewett, Emma Korkiakoski, Stephen P. Thompson, Paul A. Anderson.

Hydrogen Storage Chemistry Group, School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom
Hydrogen and Fuel Cell Group, School of Chemical Engineering, University of Birmingham, Edgbaston, B15 2TT, United Kingdom
Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0QX, United Kingdom.

* p.a.anderson@bham.ac.uk

Abstract
An investigation has been carried out into the lower limits of halide incorporation in lithium amide (LiNH₂). It was found that the lithium amide iodide Li₃(NH₂)₂I was unable to accommodate any variation in stoichiometry. In contrast, some variation in stoichiometry was accommodated in Li₇(NH₂)₆Br, as shown by a decrease in unit cell volume when the bromide content was reduced. The amide chloride Li₆(NH₂)₆Cl was found to adopt either a rhombohedral or a cubic structure depending on the reaction conditions. Reduction in chloride content generally resulted in a mixture of phases, but a new rhombohedral phase with the stoichiometry Li₇(NH₂)₆Cl was observed. In comparison to LiNH₂, this new low-chloride phase exhibited similar improved hydrogen desorption properties as Li₆(NH₂)₆Cl but with a much reduced weight penalty through addition of chloride. Attempts to dope lithium amide with fluoride ions have so far proved unsuccessful.

Keywords: hydrogen storage materials; hydrogen; powder X-ray diffraction; lithium amide halides

1. Introduction
A large range of materials have been shown to store hydrogen reversibly at a higher density than in its gaseous or liquid form. Mobile applications require the material to be light, causing an increasing focus on the complex hydrides of lighter elements such as aluminium (alanates) [1], boron (borohydrides) [2] and, by analogy, nitrogen (amides) [3, 4]. However, despite exhibiting favourable thermodynamics for reversible desorption and absorption of hydrogen, these materials suffer from slow kinetics. Although improvements have been seen on addition of transition metal catalysts [1], this problem is yet to be satisfactorily resolved.

The lithium amide system is one such light metal system that is considered promising for hydrogen storage. Thermal decomposition of LiNH₂ alone evolves ammonia rather than hydrogen, but addition of lithium hydride (LiH) creates a pathway that can experimentally produce up to 9.3 wt% of hydrogen in the two steps shown in Equation 1 [3]. The second of these requires temperatures above 320°C and is not generally considered to be a viable hydrogen storage reaction [4]. However, the first stage alone has been shown to reversibly release up to 6.3 wt% H₂ [3].

Equation 1:  \[ \text{LiNH}_2 + 2\text{LiH} \leftrightarrow 2\text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{Li}_3\text{N} + 2\text{H}_2 \]

Anderson et al. [5] found that the addition of lithium or magnesium halides to lithium amide results in the formation of new amide halide phases that exhibit not only reduced temperatures of hydrogen release, with little or no release of ammonia, on reaction with LiH or MgH₂, but also increased ionic conductivity relative to LiNH₂. However, the addition of heavy halide anions reduces the gravimetric hydrogen capacity of the material.
This study investigates the phase space of lithium amide halides with the aim of reducing the gravimetric penalty as much as possible whilst maintaining the observed improvements in the hydrogen storage properties.

2. Materials and methods

Lithium amide (Sigma–Aldrich, 95%) was used without further purification. Anhydrous lithium halides (Sigma–Aldrich, ≥98%) were dried at 300°C under high vacuum (1 × 10⁻⁶ mbar) for 24 h prior to use. All manipulations were performed in an argon-atmosphere glove box. Amide halides were synthesized by grinding the appropriate halide with LiNH₂ in the desired molar ratio, placing the reaction mixture into a quartz tube, and heating under an argon flow (1 bar) at the required temperature for the specified reaction time.

Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer in transmission geometry with a Cu-Kα₁ X-ray source. Samples were sealed from the atmosphere between two pieces of amorphous tape. Powder XRD data for structural investigations were collected on a Siemens D5000 diffractometer in capillary mode with a Cu-Kα₁ X-ray source. Samples were sealed into polyimide capillaries, allowing for long data collection times without degradation. Powder synchrotron X-ray diffraction data were collected on beamline I11 at the Diamond light source, Oxfordshire [6]. Samples were sealed in borosilicate glass capillaries to prevent degradation during transportation and measurement. Powder XRD data were analysed using the computer program Topas [7], and structure solution was performed using Rietveld refinement of candidate models devised with the help of simulated annealing methods.

Temperature programmed desorption with mass spectrometry (TPD–MS) data were collected using a home-built TPD apparatus described previously [8], coupled to a quadrupole mass spectrometer (HPR-20, Hiden Analytical). Samples were heated at 2°C min⁻¹ to 400°C and held at temperature for 1 hour before cooling.

3. Results and Discussion

3.1 Lithium amide iodide

Lithium amide reacts with lithium iodide at an NH₂⁻ : I⁻ ratio of 2:1 to form the amide iodide Li₃(NH₂)₂I [5,9]. Rietveld refinement against powder synchrotron XRD data confirmed the structure reported previously [9] of a hexagonal unit cell with a = 7.0650(9) Å, c = 11.521(1) Å.

The reaction, shown in Equation 2, between lithium amide and lithium iodide was carried out at 150°C over a range of stoichiometries (0.5 ≤ z ≤ 1) for a reaction time of twelve hours.

Equation 2: (3 − z)LiNH₂ + z LiI → Li₃(NH₂)₂I z

For all the values of z studied, LiNH₂ was observed in the XRD patterns alongside the amide iodide. Figure 1 shows the cell volume of the amide iodide products for values of z between 0.5 and 1. It can be seen that there is, within error, no systematic variation in the cell volume of the amide iodide formed in these reactions.

Analysis of the diffraction patterns of the products showed both Li₃(NH₂)₂I and LiNH₂ present where the value of z was less than one. The consistency in the lattice parameter and the presence of the starting materials in the products indicate that variations in composition cannot readily be accommodated in this structure.

3.2 Lithium amide bromide

Lithium amide reacts with lithium bromide at an NH₂⁻ : Br⁻ ratio of 1:1 to form LiNH₂Br [5,10], whose low temperature hydrogen desorption mechanism has recently been studied in some detail [11]. At a lower bromide
content, it also reacts at a ratio of 6:1 to form Li$_7$(NH$_2$)$_6$Br. Rietveld refinement against powder synchrotron XRD data has confirmed the preliminary structure reported previously for Li$_7$(NH$_2$)$_6$Br [5] of a hexagonal unit cell with $a = 9.84893(3)$ Å, $c = 8.9845(3)$ Å and rhombohedral symmetry. The limits of the bromide content in the structure were investigated. The reaction between lithium amide and lithium bromide, shown in Equation 3, was carried out at 250°C over a range of compositions, between $y = 0.6$ and 2.33, for a reaction time of twelve hours.

Equation 3: \[(7 - y)\text{LiNH}_2 + y\text{LiBr} \rightarrow \text{Li}_7\text{(NH}_2\text{)}_6\text{Br}_y\]

Increasing the bromide level above $y = 1$ reduced the yield of the amide bromide and large peaks for LiBr were observed in the X-ray diffraction pattern of the product, indicating that the structure cannot accommodate any additional Br$^-$ ions. The product from the reaction at the NH$_2^-$:Br$^-$ ratio 2:1 ($y = 2.33$) contained mainly unreacted starting materials. Reducing the bromide content below $y = 1$ decreased the yield of the amide bromide, with LiNH$_2$ observed in the XRD patterns of the products. A decrease in the cell volume of the amide bromide was observed as $y$ was reduced (Figure 2), with an overall contraction of 1.24%. However, the presence of LiNH$_2$ in the X-ray diffraction patterns of the products means that it is not possible to calculate the exact extent of the non-stoichiometry directly from the reactant ratios.

### 3.3 Lithium amide chloride

Lithium amide reacts with lithium chloride at an NH$_2^-$ : Cl$^-$ ratio of 3:1, forming Li$_4$(NH$_2$)$_3$Cl [5]. After a reaction time of one hour a rhombohedral R$3$ phase is formed and after twelve hours the compound takes a cubic I$2_3$ form [5]. The reaction shown in equation 4 was carried out over a range of compositions between $x = 0.5$ and 1.75 at 400°C for both one and twelve hours to investigate the effect of composition on the structure of amide chlorides under both kinetic and thermodynamic conditions.

Equation 4: \[(4 - x)\text{LiNH}_2 + x\text{LiCl} \rightarrow \text{Li}_4\text{(NH}_2\text{)}_{(4-x)}\text{Cl}_x\]

For both reaction times, increasing $x$ above one caused LiCl to be observed in the reaction products, suggesting that no additional Cl$^-$ ions can be accommodated into the structure. For $x = 1$, as previously observed, reaction for one hour formed a rhombohedral phase. Decreasing the chloride content caused peak splitting in the X-ray diffraction pattern, which could be refined as a mixture of two rhombohedral phases. The presence of two phases in the product prevents accurate determination of the stoichiometry using the reactant ratios. The unit cell volumes of these two phases are shown in Figure 3 and show that the two rhombohedral phases have different cell volumes, with the larger likely to be chloride-rich and the smaller chloride-deficient. Decreasing $x$ below 0.7 caused excess LiNH$_2$ to be observed alongside the rhombohedral phases in the diffraction pattern of the product, suggesting that no further decrease in chloride content can be accommodated. After reaction for 12 hours, as described previously [5], a cubic I$2_3$ phase was observed at $x = 1$. As the chloride content was reduced, the unit cell volume of this cubic phase decreased (Figure 4). Decreasing $x$ below 0.75 caused a rhombohedral phase also to be observed in the X-ray diffraction pattern of the product. This new phase was observed alone at $x = 0.57$, and has been characterized, through Rietveld refinement, as Li$_7$(NH$_2$)$_6$Cl [12]. The unit cell volume of Li$_7$(NH$_2$)$_6$Cl varied slightly in the range $x = 0.5$–0.7 suggesting that some deviation from the ideal stoichiometry may be possible, but much of the chloride excess was
accommodated in the cubic phase for the \( x = 0.7 \) sample, and the chloride deficiency in an additional rhombohedral phase with a smaller unit cell for the \( x = 0.5 \) sample.

Lithium amide, \( \text{Li}_4(\text{NH}_2)_3\text{Cl} \) and \( \text{Li}_7(\text{NH}_2)_6\text{Cl} \) were each heated with \( \text{LiH} \) at 2°C min\(^{-1}\) to 400°C and the gases given off were monitored through mass spectrometry. Figure 5 shows that both chloride-containing samples released hydrogen at a lower temperature than \( \text{LiNH}_2 \), with no deterioration of the properties seen on reduction of the chloride level. This reduction in chloride content increases the theoretical weight percent stored reversibly in the system (through reaction to the corresponding imide chlorides) from 4.4 to 5.4%.

3.4 Fluoride doping

With fluorne being the lightest of the halides, attempts were made to dope \( \text{LiNH}_2 \) with \( \text{F}^- \). Reactions between \( \text{LiNH}_2 \) and \( \text{LiF} \) were carried out over a range of \( \text{NH}_2^- : \text{F}^- \) ratios from 4:1 to 2:1, at temperatures up to 500°C, for reaction times of up to 3 days. Under these conditions, no change was observed in the diffraction patterns of the products when compared to those of the starting materials. It is thought that this was due to the high stability of \( \text{LiF} \), making reaction with \( \text{LiNH}_2 \) thermodynamically disfavoured.

Potassium fluoride has a lower heat of formation than lithium fluoride, and so reactions between lithium amide and potassium fluoride were carried out for 12 hours at 400°C. The diffraction pattern of the products showed that a metathesis reaction had occurred, as described by equation 5 below.

\[
\text{Equation 5:} \quad 6 \text{LiNH}_2 + \text{KF} \rightarrow \text{KLi}_2(\text{NH}_2)_4 + \text{LiF} + 2 \text{LiNH}_2
\]

Again, the stability of \( \text{LiF} \) appears to dictate the result of the reaction, preventing uptake of fluoride ions into the lithium amide structure.

4. Conclusion

The lower halide doping limits of lithium amide were investigated for the series of amide halides. It was found that no stoichiometry other than \( \text{Li}_3(\text{NH}_2)_2\text{I} \) was observed in the iodide system and that an amide fluoride system was not obtained on reaction of \( \text{LiNH}_2 \) with \( \text{LiF} \) or \( \text{KF} \). Lowering the bromide content in \( \text{Li}_7(\text{NH}_2)_6\text{Br} \) led to a reduction in the unit cell volume, suggesting the accommodation of amide ions on some bromide sites in the structure. For the amide chloride system, \( \text{Li}_4(\text{NH}_2)_3\text{Cl} \), a mixture of rhombohedral and cubic phases was observed except at the stoichiometry \( \text{Li}_7(\text{NH}_2)_6\text{Cl} \), where a new phase was observed. This new low-chloride phase exhibited similar improved hydrogen desorption properties when compared to lithium amide as \( \text{Li}_4(\text{NH}_2)_3\text{Cl} \), but with a much reduced weight penalty through addition of chloride.

5. Acknowledgments

We thank the EPSRC for the studentship of Rosalind Davies via the Hydrogen, Fuel Cells and their Applications Centre for Doctoral Training, the RCUK Energy Programme (Supergen UKSHEC2) and Advantage West Midlands (Science City Hydrogen Energy Project) for funding. The Bruker D8 system used in this research was obtained, through the Science City Advanced Materials Project: Creating and Characterising Next Generation Advanced Materials, with support from AWM and part funded by the European Regional Development Fund (ERDF). The authors would like to acknowledge Dan Reed for his help in the preparation and running of the TPD-MS, Diamond light source for the provision of beamtime (proposal number EE3909), and Paul Adamson for help in using beamline I11.
References


Figure Captions

FIG1: Unit cell volumes and errors (3σ) for Li₃(NH₂)₃−zIₖ.

FIG2: Unit cell volumes and errors (3σ) for Li₃(NH₂)₇−yBrₙ.

FIG3: Unit cell volumes and errors (3σ) for the two rhombohedral Li₄(NH₂)₄−xClₓ phases observed after a one hour reaction time.

FIG4: Unit cell volumes and errors (3σ) for the different phases of Li₄(NH₂)₄−xClₓ after a twelve hour reaction time; the red points and axis correspond to the cubic phase that is formed, with the black and blue points and the black axis representing the two rhombohedral phases.

FIG5: TPD–MS traces for the lithium amide chlorides and lithium amide on reaction with lithium hydride.
Highlights

- The lower limits of halide incorporation in lithium amide have been investigated.
- The only amide iodide stoichiometry observed was Li₃(NH₂)₂I.
- Solid solutions were observed in both the amide chloride and amide bromide systems.
- A 46% reduction in chloride content resulted in a new phase: Li₇(NH₂)₆Cl.
- New low-chloride phase maintained improved H₂ desorption properties of Li₄(NH₂)₃Cl.