Enhancing ionic conductivity in lithium amide for improved energy storage materials*

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Abstract
Non-stoichiometry and bulk cation transport have been identified as key factors in the release and uptake of hydrogen in the Li–N–H system. Amide halide phases have been synthesized that have ionic conductivities several orders of magnitude greater than lithium amide, a faster rate of hydrogen release and elimination of the by-product, ammonia. Here we report the effect of both anion- and cation-doping on the hydrogen desorption properties of lithium amide, focusing in particular on how the presence of chloride anions and magnesium cations affects and controls the structure of the amide and imide compounds at the sub-nanometre level. Reducing the chloride content resulted in new low-chloride rhombohedral phases that contain around half of the chloride present in earlier amide chlorides, but maintained the enhancements seen in hydrogen desorption properties when compared to the halide-free system. These materials may also have potential in a range of other energy applications such as all solid state lithium ion batteries, supercapacitors, and CO₂ capture and storage membranes.

Keywords: hydrogen storage, lithium amide, lithium chloride, magnesium chloride, powder x-ray diffraction, temperature-programmed desorption

Mathematics Subject Classification: 2.03

1. Introduction

The transition to a sustainable, environmentally benign, carbon-free energy system that can meet our ever-increasing demands is arguably the defining challenge of our age [1]. A key deficiency is the continuing lack of a convenient, efficient and safe means of storing renewable energy, in particular for mobile applications, with electrochemical—in the form of lithium ion batteries—and chemical storage—in the form of hydrogen gas—considered the most promising solutions.

In automotive transport the move away from fossil fuels towards electric vehicles has already begun [2], but energy density and cost issues severely limit the range of battery-only cars, a problem exacerbated by long recharge times [3]. Fuel cells powered by hydrogen offer much higher energy density and shorter refuel times, and may either act as a range-extender alongside [2]—or replace [3]—batteries in electric vehicles. Hydrogen is an ideal fuel as it has a far higher specific calorific value than any other (2.6 times that of petrol), and is virtually emission/pollution free at the point of use. In addition, the ease of interconversion of electricity and hydrogen as energy carriers potentially provides a solution to the issue of intermittency, in principle rendering the gas a key component of a renewable-energy system [3]. Yet proponents and opponents alike, of the use of hydrogen as a green energy carrier, are agreed that the absence of a low-cost, safe and convenient means of storage represents a serious impediment to its wider use.
Although many complex hydrides can reversibly store large amounts of hydrogen [4], even in those cases where the thermodynamic properties are deemed favourable for reversible hydrogen release under moderate conditions, the kinetics of desorption and rehydrogenation of light metal complex hydrides remain too slow for them to be used as practical hydrogen storage materials. Nanostructuring, in particular through the addition of transition metal catalysts, mechanically milled into the hydride to achieve dispersion and hence accompanied by the benefits of refinement of particle and grain size, is known to improve the hydrogen de/reabsorption kinetics of many hydrides by facilitating splitting of the hydrogen molecule and helping hydrogen to diffuse through passivated surface layers or along grain boundaries in certain cases. Much of the current interest in lightweight complex hydrides was sparked by the discovery of Bogdanović and Schwickardi [5] that the addition of TiCl₃ significantly improved the reversibility of NaAlH₄. This classic example remains a benchmark for complex hydrides, but although the mechanisms of the desorption/hydrogenation processes in this system, and of how the catalysts improve reaction rates, have attracted more scrutiny than most, these studies have struggled to improve on rehydrogenation over many hours, under 160 bar at 200 °C.

One fundamental area that has received comparatively little attention to date is rates of diffusion within the bulk materials themselves. As recent work [6, 7] is now beginning to make clear, this represents a significant oversight. The reaction of lithium amide with lithium hydride (LiH) is known [8, 9] to release 10.4 wt% of hydrogen in two steps:

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

Step 1 has been shown to proceed via the release of ammonia (NH₃), which quickly reacts with lithium hydride to produce hydrogen [10]. A reduction in temperature of H₂ release may be achieved by replacing the lithium amide by its magnesium counterpart [11], which releases ammonia at a lower temperature. Similar lithium magnesium imide products are formed through the reaction of lithium amide and magnesium hydride, but these are found to rehydrogenate preferentially back to magnesium amide and lithium hydride. Step 2, forming lithium nitride, is often discounted as a hydrogen storage reaction, as complete desorption in dynamic vacuum requires temperatures in excess of 320 °C.

Experiment [12] and theory [13] have highlighted lithium ion mobility as a pivotal factor in both reactions. The close structural relationship between LiNH₂ and Li₂NH may allow ion mobility as a pivotal factor in both reactions. The close

Materials chemists have long used cation and/or anion doping to improve properties in a wide range of different materials. Both were exploited in our preliminary study [6], which found a large range of new amide halide \([\text{Li}_{1+n}\text{m}(\text{NH}_2)X_m]\) and \(\text{LiMg}_{2n}(\text{NH}_2)X_{2m}\), where \(X = \text{Cl}, \text{Br}, \text{I}\) and imide halide \(\text{Li}_2\text{Mg}_{2n}(\text{NH})X_{2m}\) and \(\text{Li}_2\text{Mg}_{2m}(\text{NH})X_{2m}\) phases that released hydrogen reversibly via reactions (2) and (3):

\[
\text{Li}_{1+m}(\text{NH}_2)X_m + \text{LiH} \rightarrow \text{Li}_{2+m}(\text{NH})X_m + \text{H}_2, \tag{2}
\]

\[
\text{LiMg}_{2n}(\text{NH}_2)X_{2m} + \text{LiH} \rightarrow \text{Li}_2\text{Mg}_{2n}(\text{NH})X_{2m} + \text{H}_2. \tag{3}
\]

The most conducting of these, with room temperature ionic conductivities approaching \(10^{-3} \text{ S cm}^{-1}\), were also quickest to release hydrogen on heating and to hydrogenate, and unwanted ammonia release was suppressed. Reductions in the decomposition temperature of lithium amide caused by chlorides have subsequently also been reported by other workers [17, 18]. This marks ionic conductivity as potentially a crucial parameter in optimizing the properties of hydrogen storage materials, whose influence is unlikely to be restricted to nitrogen-containing systems [6, 7].

The key to these improvements lies in the ability of halide anions to affect and control the structure of the amide and imide compounds at the sub-nanometre level. The different phases of the amide chloride have different lithium ion site occupancies and so investigations into their structure may yield important insights into their conductivity and hydrogen storage properties. However, the addition of the relatively heavy halide anions reduces the gravimetric hydrogen capacity of the materials. This study investigates the phase space of lithium amide chlorides with the aim of reducing this gravimetric penalty whilst maintaining the improvements in hydrogen storage properties.

2. Experimental and procedure

Lithium amide (Sigma–Aldrich, 95%) and lithium hydride (Sigma–Aldrich, 95%) were used without further purification. Anhydrous lithium chloride and magnesium chloride (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 in 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 operating in transmission geometry with a Cu-Kα 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-Kα x-ray source. Samples were sealed into polyimide capillaries, allowing for long data collection times without degradation. Powder synchrotron XRD data were collected on beamline I11 at the diamond light source, Oxfordshire [19]. Samples were sealed in borosilicate glass capillaries to prevent degradation during transportation and measurement. Powder XRD data were analysed using the computer programme Topas [20] and structure solution was performed using Rietveld refinement of candidate models.

Temperature-programmed desorption with mass spectrometry (TPD–MS) data were collected using a home-built TPD apparatus described previously [21], 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 h before cooling.

3. Results

3.1. Effect of reaction time on structure

The reaction between lithium amide and lithium chloride was carried out at 400 °C at the molar ratio 3NH₂⁻:1Cl⁻. As observed previously [6], Li₄(NH₂)₃Cl is the product of this reaction and, at this molar ratio, two phases were observed under different conditions: a rhombohedral phase with a hexagonal unit cell was formed after 1 h and a body centred cubic phase was formed after a 12 h reaction time. In the cubic phase, the lithium sites are fully occupied. In the rhombohedral phase, the lithium sites are only partly occupied, potentially providing the opportunity for higher lithium ion mobility. Figure 1 shows the powder XRD patterns of the two phases.

A detailed time dependence study was carried out of reaction times between 1 and 12 h. For reaction times of six or more hours, the cubic I23 phase of Li₄(NH₂)₃Cl was formed, with reaction times shorter than this favouring the formation of the rhombohedral R3 phase. Figure 2 plots the unit cell volumes observed for these phases against reaction time. For a given reaction time, there was considerable variation in observed volume between different experiments, but the overall trend was that increased reaction time resulted in a denser rhombohedral phase and less dense cubic phase.

The transformation from the rhombohedral to the cubic phase was observed in real time using variable temperature powder synchrotron XRD. The rhombohedral phase was heated to 200 °C and then held at this temperature, with diffraction patterns recorded at regular time intervals (figure 3). The patterns show the gradual growth of peaks corresponding to the cubic phase and the corresponding reduction in intensity of those of the rhombohedral phase. The results of these experiments suggest that the cubic phase can be considered to be the thermodynamic product at this reactant ratio, with the rhombohedral phase favoured kinetically.

3.2. Effect of chloride content on structure

The reaction shown in (4) was carried out over a range of Cl⁻ compositions between x = 0.5 and 1.75 at 400 °C for reaction times of 1 and 12 h to investigate the effect of composition on the amide chloride under both kinetic and thermodynamic conditions

\[
(4 - x) \text{LiNH}_2 + x \text{LiCl} \rightarrow \text{Li}_4(\text{NH}_2)_3\text{Cl}_x.
\]

The phases observed across the range of x values are shown in figure 4. For x = 1, reaction for 1 h formed a rhombohedral R3 phase. Increasing the chloride content formed a cubic I23 phase, suggesting that the rhombohedral structure is unable to accommodate any additional Cl⁻ ions into the structure beyond the NH₂Cl⁻ ratio of 3:1. It is likely to be because the structure of the rhombohedral phase requires Cl⁻ ions to be located on the NH₂ sites, which becomes disfavoured as the chloride content increases. When x was made more positive than 1.14, excess LiCl was observed in the XRD pattern in addition to the cubic phase; therefore additional Cl⁻ ions cannot be accommodated into the cubic structure beyond the NH₂Cl⁻ ratio of 2.5:1.

Decreasing the chloride content below x = 1 initially caused peak splitting in the XRD pattern, which can be
refined as a mixture of two rhombohedral phases. Due to the presence of two phases, it is not possible to calculate the stoichiometries directly from the reactant ratios. Decreasing $x$ below 0.7 caused excess LiNH$_2$ also to be observed alongside the rhombohedral phases in the diffraction pattern of the reaction products.

The investigation into the 12 h reactions found that, as described previously [6], a cubic I$_{213}$ phase is observed at $x = 1$. Increasing the Cl$^-$ content caused excess LiCl to be observed in addition to the cubic phase, suggesting no additional Cl$^-$ ions can be accommodated into the structure. As $x$ was decreased below 1, a mixture of the cubic phase and an additional phase was observed until the new phase was observed alone at $x = 0.57$. This new phase can be refined to a hexagonal unit cell with rhombohedral symmetry, similar to the rhombohedral phases of both Li$_4$(NH$_2$)$_3$Cl and Li$_7$(NH$_2$)$_6$Br [6]. This $x$ value corresponds to an NH$_2^-$:Cl$^-$ ratio of 6:1, which is in agreement with the structural refinement, implying a formula of Li$_7$(NH$_2$)$_6$Cl for the new compound. At chloride contents lower than $x = 0.57$, excess lithium amide was observed, indicating that the lowest level of chloride that can be accommodated into the structure is a NH$_2^-$:Cl$^-$ ratio of 6:1.

### 3.3. Effect of chloride content on hydrogen desorption properties

As discussed previously, the amide chloride Li$_4$(NH$_2$)$_3$Cl can accommodate a range of stoichiometry. However, this is not useful unless the improved hydrogen release properties are maintained, relative to LiNH$_2$ + LiH. Reaction (5) was carried out for $x$ values from 0.6 to 1 on samples formed after a 1 h reaction time

$$\text{Li}_4(\text{NH}_2)_3\text{Cl}_x + (4 - x)\text{LiH} \rightarrow \text{Li}_{8-x} \times (\text{NH}_2)_x\text{Cl}_x + (4 - x)\text{H}_2 \uparrow.$$  

(5)

Temperature-programmed desorption measurements (figure 5) show that the onset and peak of hydrogen release remained constant for the $x$ values where 0.6 $\leq x \leq 1$.

The structures of the imide chlorides formed as a product of reaction (5) were also investigated, to determine whether

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**Figure 3.** Powder synchrotron XRD patterns of Li$_4$(NH$_2$)$_3$Cl after heating under different time and temperature conditions, showing the reduction in height of the peaks corresponding to the rhombohedral R3 phase (red, top right) and the appearance and growth of peaks representing the cubic I$_{213}$ phase (black, bottom right).
the non-stoichiometry was maintained in the dehydrogenated product. There was a decrease in the lattice parameter in the cubic cell of Li$_{8-x}$(NH)$_{4-x}$Cl$_x$ as $x$ was decreased in the range 1 $\geq x \geq$ 0.7, before it increased again between 0.7 $\geq x \geq$ 0.6. This contraction of the unit cell, consistent with lower content of the larger chloride anion, can also be seen clearly on examination of the position of the (111) peak in the XRD patterns of these products. Figure 6 shows the shift of the (111) peak to a higher position as the value of $x$ decreased, consistent with the decrease in unit cell size.

3.4. Lithium magnesium amide chloride

An equivalent phase space investigation was carried out on the mixed lithium magnesium system to see what effect reducing the chloride level had on the structure of the product.
Li₃Mg₀.₅(NH₂)₃Cl with LiH was indexed to a cubic unit cell where vacancies are already present as the lithium ions causing vacancies to be created, compared to the 6:1 occupied in the 3:1 structure, with the addition of magnesium decreases the desorption temperature for Li₃Mg₀.₅(NH₂)₃Cl but not for Li₆Mg₀.₅(NH₂)₆Cl.

Reducing the chloride level below this ratio caused excess LiNH₂ to be observed in the XRD patterns of the products, indicating that this is the lowest level of chloride that the structure can accommodate. Temperature-programmed desorption measurements show that the onset and peak of hydrogen desorption were increased to a higher temperature as \( x \) was reduced from 1 to 0.57 for the lithium magnesium system (figure 7). Addition of magnesium reduced the temperature of desorption for the 3:1 NH₂:Cl⁻ ratio of 6:1, a new phase was observed, with a structure the similar to that of the lithium-only rhombohedral phase observed at the same ratio but with a disordered replacement of one seventh of the Li⁺ ions with Mg²⁺ (reaction 7).

\[
(4 - x)\text{LiNH}_2 + \frac{1}{2} \text{MgCl}_2 \rightarrow \text{Li}_{4-x}\text{Mg}_{x/2}(\text{NH}_2)_{4-x}\text{Cl}_x. \tag{6}
\]

As with the lithium only system, reducing the chloride level in the system caused a rhombohedral phase to be formed in preference to a cubic phase (figure 7). On reducing the chloride level to the NH₂ to Cl⁻ ratio of 6:1, a new phase was observed, with a structure similar to that of the lithium-only rhombohedral phase observed at the same ratio but with a disordered replacement of one seventh of the Li⁺ ions with half as many Mg²⁺ (reaction 7)

\[
6\text{LiNH}_2 + \frac{1}{2} \text{MgCl}_2 \rightarrow \text{Li}_6\text{Mg}_{0.5}(\text{NH}_2)_6\text{Cl}. \tag{7}
\]

4. Conclusion

Non-stoichiometry and bulk cation transport have been identified as key factors in the release and uptake of hydrogen in the Li–N–H system [12]. Previously, we have reported that the addition of halides to lithium amide results in the formation of amide halide phases that have ionic conductivities several orders of magnitude greater than lithium amide, a faster rate of hydrogen release and elimination of the by-product, ammonia [6]. Here we have investigated further the effect of both anion- and cation-incorporation on the structural and hydrogen desorption properties of lithium amide, focusing in particular on how the presence of chloride anions and magnesium cations affects and controls the structure of the amide and imide compounds at the sub-nanometre level.

The reaction between lithium amide and lithium chloride at 400 °C in the molar ratio 3NH₂:1Cl⁻ resulted in the formation of a new low-chloride rhombohedral phase and cubic phases except at the stoichiometry Li₂(NH₂)₆Cl, where a single phase was observed. This new low-chloride rhombohedral phase contained little more than half of the halide present in Li₆(NH₂)₆Cl but, importantly, maintained the enhancements seen in hydrogen desorption properties when compared to the halide-free system. The reaction between lithium amide and magnesium chloride at 400 °C in the molar ratio 3NH₂:1Cl⁻ resulted in the formation of a new low-chloride rhombohedral phase, Li₆Mg₀.₅(NH₂)₆Cl. The presence of magnesium was found to reduce the desorption temperature for Li₆Mg₀.₅(NH₂)₆Cl but not for Li₆Mg₀.₅(NH₂)₆Cl.

The deliberate engineering at the nanoscale of compounds with much improved bulk diffusion is likely to be complementary, rather than an alternative, to current methods of kinetic enhancement, and thus affords a very high probability of producing materials whose performance is markedly superior to the current generation. These results point the way to a radical new approach for optimizing the hydrogen desorption and reabsorption kinetics that recent analysis suggests is capable of delivering a step-change in these key properties [7]. We also note that, though developed for light-weight hydrogen storage, some of these materials may have potential in a range of other energy applications such as solid state lithium ion batteries, supercapacitors, and CO₂ capture and storage membranes.
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