Short communication

Hydrogen storage behaviour of Li$_3$N doped with Li$_2$O and Na$_2$O

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ABSTRACT

Mixtures of Li$_2$O/Li$_3$N and Na$_2$O/Li$_3$N have been investigated for hydrogen storage. When Li$_3$N is doped with *ca.* 5 mol% Li$_2$O and annealed, both binary compounds exist as separate phases as evident from powder X-ray diffraction. Li$_2$O acts as a spectator in the hydrogen storage reactions and there is no evidence of enhanced Li$^+$ or H$^+$ mobility. Na$_2$O (5 mol%) interacts more strongly with Li$_3$N, leading to the generation of an unidentified phase, which also appears to play no part in the hydrogen storage reactions of the composite system. We conclude that addition of these levels of Li$_2$O or Na$_2$O to Li$_3$N followed by annealing does not improve the hydrogen storage properties of Li$_3$N.

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1. Introduction

There are increasing concerns about the environmental pollution caused by carbon-based fuels, and the depletion of natural reservoirs of these fuels. Hydrogen is an ideal alternative to fossil fuels. However, one of the main challenges concerning the use of hydrogen is the development of a suitable storage medium [1]. Solid-state hydrogen storage materials allow hydrogen to be stored in a compact and safe manner. Many research efforts are focused on solid-state materials such as light metal hydrides and their complexes [2]. Lithium nitride has recently emerged as a promising material for hydrogen storage [3]. It has a theoretical hydrogen storage capacity of 11.5 wt.%, and undergoes hydrogenation/dehydrogenation in two main steps [3,4]:

$$Li_3N + H_2 \leftrightarrow Li_2NH + LiH \qquad \Delta H = -116 \, \text{kJ mol}^{-1} \qquad (1)$$

$$Li_2NH + H_2 \leftrightarrow LiNH_2 + LiH \qquad \Delta H = -45 \, \text{kJ mol}^{-1} \qquad (2)$$

Although in practice, 9.3 wt.% hydrogen is attainable above 250 °C, complete desorption is achieved only at temperatures above 320 °C in dynamic vacuum [3]. In fact, the effective reversible hydrogen storage capacity of Li$_3$N is about 5.5 wt.% at 280 °C or lower [5]. Accordingly, reaction (1) has a much larger negative enthalpy than reaction (2) accounting for the partial desorption of hydrogen under milder conditions.

Considerable research effort has focused on enhancing the hydrogen storage characteristics of the Li–N–H system. For exam-

ple, addition of catalytic amounts of transition metals or metal chlorides [6,7] and partial substitution of Li with Mg [8,9] has been shown to enhance its performance. Furthermore, there has been increasing interest in amide–hydride mixtures, particularly those involving Mg(NH$_2$)$_2$/LiH, LiNH$_2$/MgH$_2$, LiNH$_2$/LiBH$_4$ and LiNH$_2$/LiAlH$_4$ [10–13]. Lithium nitride has an extremely high Li$^+$ ion conductivity ($\sim 10^{-4} \, \Omega^{-1} \, \text{cm}^{-1}$) and could potentially be used in lithium ion batteries [14]. In a recent study, David et al. [15] reported that for the Li–N–H system LiNH$_2$/Li$_2$NH transformation is a bulk reversible reaction that occurs through a non-stoichiometric process, and proposed an ion migration mechanism involving Li$^+$ and H$^+$ ions. It was concluded that Li$^+$ mobility plays a key role in the hydrogenation/dehydrogenation reactions of Li$_3$N.

In the light of the ion migration mechanism proposed by David et al., we have prepared mixtures of Li$_3$N incorporating small amounts of Li$_2$O. An earlier study demonstrated that Li$_3$N, partially oxidized by exposure to air followed by heat treatment in vacuo, exhibits improved hydrogen storage properties [16]. In the current work, doping of Li$_3$N with Li$_2$O was carried out in an attempt to introduce cation vacancies that may assist Li$^+$ mobility. By using Li$_2$O as our dopant, aliovalent substitution of N^{3-} in Li$_3$N by O^{2-} should occur, creating Li$^+$ vacancies to compensate for the charge imbalance, which should increase Li$^+$ mobility [17]. Aliovalent substitution of N^{3-} in Li$_3$N by NH^{2-} has been reported [18]. In the hydrogenated products of Li$_3$N (i.e. LiNH$_2$ and LiH), the presence of many mobile Li$^+$ ions implies increased likelihood of creating more H$^+$ ions (according to the ion migration model), which should have an impact on the hydrogen storage properties of the Li–O–N–H system. As a follow up to this study, we have prepared analogous mixtures of Li$_3$N and Na$_2$O. Na$_2$O has itself been reported to reversibly absorb hydrogen, forming NaH and NaOH [19]. To the best of our knowledge, no studies of a composite Na$_2$O/Li$_3$N system for hydrogen

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storage have been previously reported. Here we report for the first time an investigation of Na_2O-doped Li_3N for hydrogen storage.

2. Experimental

2.1. Synthesis and manipulation

Commercial powders of Li_3N (STREM, 99.5%), Li_2O (Aldrich, 97%, 60 mesh) and Na_2O (Aldrich, 80%) were used as starting materials. All material and sample manipulations were carried out in a nitrogen-filled glovebox to minimize contamination with atmospheric oxygen and moisture. In the first study Li_3N was mixed with 2 and 5 mol% Li_2O. In the second study it was mixed with 5 mol% Na_2O. The total mass of each mixture was 10 g. These samples were loaded in a 250 mL stainless steel milling vessel containing five stainless steel balls with a diameter of 20 mm, then milled using a Retsch PM100 planetary mill. The ball-to-powder mass ratio was 16:1. Milling was carried out for 3 h at room temperature in a N_2 atmosphere at a rotational speed of 200 rpm. In order to minimize the temperature increase due to milling, the parameters of the mill were set such that after every 5 min of milling in one direction the mill paused for 10 s and then rotated in the reverse direction. The milled sample was then annealed at high temperature. In this procedure, 1.2 g of sample was placed in a monel crucible and loaded in a custom-made quartz tube inside a nitrogen-filled glovebox. The tube was then inserted into a tube furnace and was maintained at either 400 or 620 °C under a flowing stream of nitrogen gas for 12 h. In addition to the doped materials unmilled and milled Li_3N (both undoped) were also investigated in this study.

2.2. Characterization of materials

Samples were characterized by powder X-ray diffraction (XRD), using a Bruker D8 Advance diffractometer or Rigaku Miniflex diffractometer both equipped with a Cu Kα radiation source. Product identification was carried out by reference to the Joint Committee for Powder Diffraction Studies (JCPDS) values in the database of the diffractometer. During XRD analysis, parafilm was used to cover the samples to prevent contact with air during the measurement. Diffraction peaks at ca. 21.6° and 24° arising from parafilm were observed in all the XRD patterns. Differential Scanning Calorimetry (DSC) measurements were performed using a TA Instruments Q20P DSC. In a typical experiment with unhydrogenated samples, 9–10 mg of material was used and the DSC cell was pressurized to an initial pressure of 30 bar with H_2 gas. The sample was heated to 500 °C at 5 °C min^{-1}. Hydrogen absorption/desorption performance was examined using a commercial PCTPro-2000 Sieverts-type instrument manufactured by HyEnergy LLC. High purity hydrogen (Air Liquide, 99.999%) was used in all experiments. For absorption experiments, initial pressure of 30 bar H_2 was employed. For both absorption and desorption, approximately 0.5 g of material was used; this was heated at 2 °C min^{-1} to the desired measurement temperature, where it was held for 12 h. Kinetic curves for both absorption and desorption were obtained. The hydrogen storage capacities reported are expressed as a wt.% of the entire sample.

3. Results and discussion

3.1. Li_2O-doped Li_3N

Fig. 1 shows the XRD patterns for Li_3N doped with 5 mol% Li_2O. This reveals both materials still to be present as the binary compounds, with no evidence of new peaks corresponding to a mixed Li–N–O phase. The unannealed sample showed the co-existence
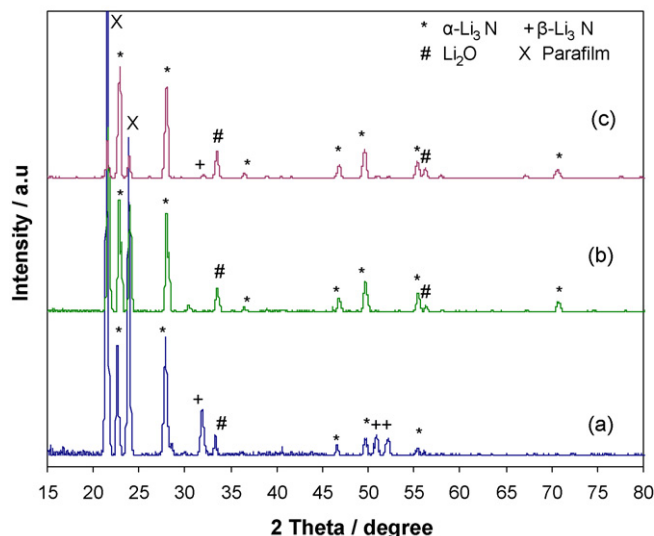

Fig. 1. XRD patterns for 5 mol% Li_2O-doped Li_3N: (a) no heat treatment, (b) annealed at 400 °C, and (c) annealed at 620 °C.

of both α- and β-Li_3N, as well as Li_2O (commercial Li_3N contains both α- and β-phases). After annealing at 400 °C, β-Li_3N was completely transformed to α-Li_3N according to the XRD pattern, which now indicated only α-Li_3N and Li_2O. This is consistent with a literature report that the transformation from β- to α-Li_3N occurs above 200 °C [20]. After heat treatment at 620 °C, the sample was composed predominantly of α-Li_3N and Li_2O, with possibly traces of β-Li_3N. For all three samples, it cannot be ruled out that some substitution of N^{3-} by O^{2-} had occurred, though the presence of remaining Li_2O was clearly evident in the XRD pattern in each case.

DSC experiments in hydrogen showed the profile for Li_2O to be essentially a flat line, indicating as expected that Li_2O did not absorb any hydrogen (Fig. 2). On the other hand, the curve for as-received Li_3N showed both exothermic and endothermic events. The onset of the exothermic event occurred at about 200 °C. This feature is broad, and as the temperature approached 330 °C a second exothermic peak was clearly seen. Both exothermic events are attributed to hydrogen absorption. We note that when the DSC experiments were carried out in nitrogen no thermal events were observed. As described in Eqs. (1) and (2), hydrogenation occurs in
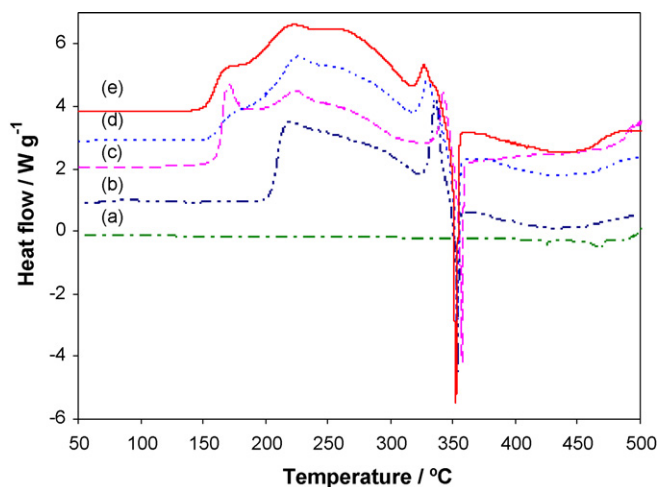

Fig. 2. DSC plots of hydrogen absorption by (a) Li_2O, (b) as-received Li_3N, (c) undoped (milled) Li_3N, (d) Li_3N doped with 2 mol% Li_2O (milled), and (e) Li_3N doped with 5 mol% Li_2O (milled).