

Interaction of hydrogen with metal nitrides and imides

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The pursuit of a clean and healthy environment has stimulated much effort in the development of technologies for the utilization of hydrogen-based energy. A critical issue is the need for practical systems for hydrogen storage, a problem that remains unresolved after several decades of exploration. In this context, the possibility of storing hydrogen in advanced carbon materials has generated considerable interest. But confirmation and a mechanistic understanding of the hydrogen-storage capabilities of these materials still require much work^{1–5}. Our previously published work on hydrogen uptake by alkali-doped carbon nanotubes cannot be reproduced by others^{6–8}. It was realized by us and also demonstrated by Pinkerton *et al.*⁸ that most of the weight gain was due to moisture, which the alkali oxide picked up from the atmosphere. Here we describe a different material system, lithium nitride, which shows potential as a hydrogen storage medium. Lithium nitride is usually employed as an electrode, or as a starting material for the synthesis of binary or ternary nitrides^{9,10}. Using a variety of techniques, we demonstrate that this compound can also reversibly take up large amounts of hydrogen. Although the temperature required to release the hydrogen at usable pressures is too high for practical application of the present material, we suggest that more investigations are needed, as the metal–N–H system could prove to be a promising route to reversible hydrogen storage.

Temperature dependences of hydrogen absorption and desorption in the fresh Li₃N sample were investigated by thermogravimetry (Fig. 1). It can be seen that the absorption of hydrogen begins at a temperature of around 100 °C. In the temperature range 170–210 °C, there is a fast weight gain. A total increase of about 9.3 wt% was achieved after maintaining the sample at 255 °C for half an hour. We noted that if the temperature was kept long enough below 200 °C, the Li₃N sample could also absorb a substantial amount of hydrogen. The hydrogenated sample was cooled down to 50 °C and evacuated to 10^{–5} mbar. The desorption process appeared to be composed of two parts: under high vacuum, a large portion (6.3 wt%) of hydrogen was released at temperatures below 200 °C; the remaining 3 wt% hydrogen could be desorbed only when the temperature was raised above 320 °C. Mass spec-

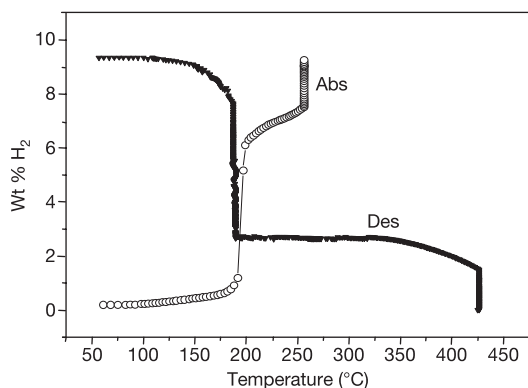


Figure 1 Weight variations during hydrogen absorption and desorption processes over Li₃N samples, details are given in the Methods. Abs, absorption; Des, desorption.

trometry and an ammonia-sensitive reagent were applied to identify the released gas. Only hydrogen was found to be released in the tested temperature range (see Supplementary Information).

Pressure–composition (*P–C*) isotherms of fresh Li₃N samples were measured at several temperatures. Those recorded at 195 °C, 230 °C and 255 °C are presented in Fig. 2. As illustrated in the absorption isotherms, about 3.6 hydrogen atoms can be absorbed by one Li₃N molecule, that is, about 10 wt% of the sample. The hydrogenation degree can be further improved if the starting material Li₃N is free of contamination. Unlike most metal hydrides, which present one plateau in the *P–C* isotherm, Li₃N has two. The first one (in the range 0 < H/Li₃N < 1.1) has rather low equilibrium pressure (below 0.07 bar), so we deduce that hydrogen absorbed in this region might not be easily desorbed, and should correspond to the high-temperature-desorbed portion detected by thermogravimetry. The second plateau is sloped, the overall equilibrium pressure is below 0.2 bar at 195 °C, 0.5 bar at 230 °C and 1.5 bar at 255 °C. The desorption isotherms, as predicted, cannot return to the origin. Under *P–C* isotherm conditions (desorption stopped at 0.04 bar), about 55% hydrogen can be desorbed at temperatures above 230 °C, which is less than that detected by thermogravimetry under high vacuum (10^{–5} mbar). We noticed that after the stop of

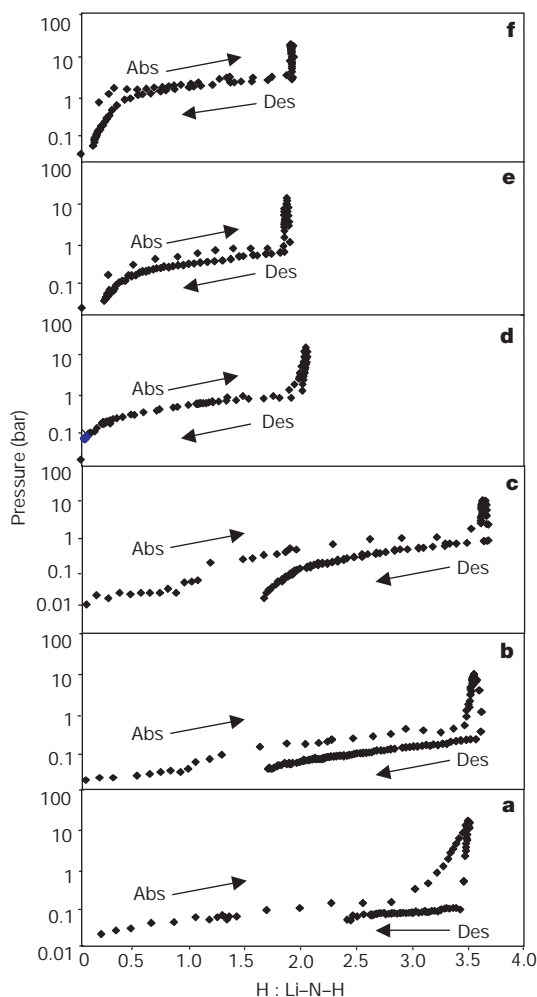
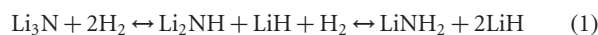


Figure 2 Pressure–composition (*P–C*) isotherms of Li₃N and Li₂NH samples. Pressure was increased step by step to 20 bar then gradually reduced to 0.04 bar, other details are given in the Methods. The x axis represents the molar ratio of H atom to Li–N–H molecule. **a**, Li₃N at 195 °C; **b**, Li₃N at 230 °C; **c**, Li₃N at 255 °C; **d**, Li₃N re-PCI at 255 °C; **e**, Li₂NH at 255 °C and **f**, Li₂NH at 285 °C.

P–*C* isotherm measurements, there was continuous hydrogen desorption from the remaining material under lower pressures, indicating that hydrogen desorption did not complete at that stage. Hysteresis in desorption could be observed; however, after a few cycles of PCIs, it was found to be much improved. As can be seen in Fig. 2d, the repeated absorption–desorption isotherms of the Li₃N sample almost coincide.

To facilitate the understanding of phase and composition changes during hydrogen absorption and desorption in the Li₃N sample, we collected pristine, half-hydrogenated, fully-hydrogenated, half-dehydrogenated and fully-dehydrogenated Li₃N samples for X-ray diffraction measurements. Results (Fig. 3) show that the pristine hexagonal Li₃N phase shifted to face-centred cubic (f.c.c.) lithium imide and hydride phases¹¹ after being half-hydrogenated. The fully-hydrogenated Li₃N sample is composed of body-centred tetragonal lithium amide¹¹, that is, LiNH₂ and the enhanced lithium hydride phase. Phase changes in desorption follow a process almost the reverse of that of absorption. Thus, we deduce that the reversible hydrogen storage in Li₃N sample may take the following reaction path:



The molar ratio of absorbed hydrogen atoms to Li₃N molecule is four: this works out to be 11.5 wt% of Li₃N, corresponding well to that obtained by *P*–*C* isothermal and thermogravimetric measurements. The values of standard enthalpy of formation for Li₃N, Li₂NH, LiNH₂ and LiH from the elements are –197 kJ mol^{–1}, –222 kJ mol^{–1}, –176 kJ mol^{–1} and –91 kJ mol^{–1} (ref. 12), respectively. The overall reaction heat is –161 kJ mol^{–1}.

In 1910, Dafert and Miklauz reported that, when Li₃N reacted with H₂, Li₃NH₄ was formed¹³:



In fact, Li₃NH₄ is the mixture of LiNH₂ and 2LiH. No investigation on the reverse reaction was done. The reason may lie in the known fact that lithium amide will decompose to lithium imide and ammonia at increased temperatures^{14,15}. The existence of LiH seems anomalous (see Supplementary Information).

Inferred from *P*–*C* isothermal and X-ray diffraction results, Li₂NH could reversibly store more hydrogen at temperatures below 300 °C. Figures 2e and f are the *P*–*C* isotherms of the

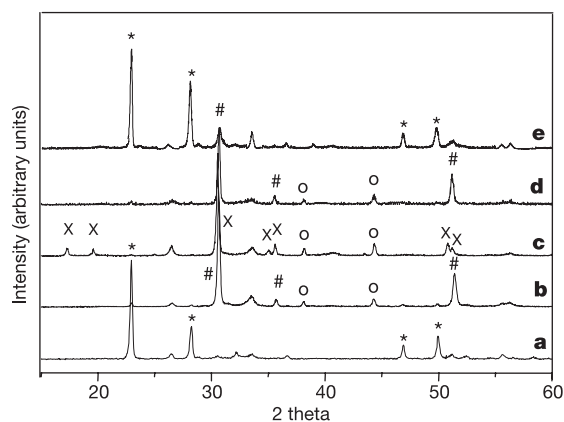


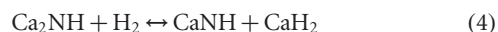
Figure 3 Structure changes during hydrogen absorption and desorption processes. **a**, Pristine Li₃N; **b**, half-hydrogenated sample; **c**, fully hydrogenated sample; **d**, half-dehydrogenated sample and **e**, completely dehydrogenated sample. Peaks marked with an asterisk are the characteristic diffraction of Li₃N, crosses represent LiNH₂, hashes represent Li₂NH and circles represents LiH. Small features around 32–34° and 55–56° are the diffraction peaks of LiOH and Li₂O; the feature at around 26° is carbon. Sample collection and details for measurements are described in the Methods.

Li₂NH sample recorded at 255 °C and 285 °C, respectively. About 1.85 hydrogen atoms, which is equal to about 6.5 wt% of sample, was stored. Almost all hydrogen absorbed can be desorbed. Hydrogen storage leads to the formation of LiNH₂ and LiH, so:



We see that, theoretically, ~7.0 wt% of hydrogen can be reversibly stored in Li₂NH.

A similar hydrogen storage phenomenon was observed in the Ca–N–H system. It was demonstrated that Ca₂NH could reversibly store hydrogen in the temperature range 350–600 °C (see Supplementary Information). *P*–*C* isotherms measured at 500 °C and 550 °C, respectively, are presented in Fig. 4. About 1.8 hydrogen atoms, which is equal to ~1.9 wt% of sample, can be reversibly stored in Ca₂NH. The hydrogenated Ca₂NH sample is composed of CaNH and CaH₂, indicating that hydrogen is stored following the reaction:



Thus, theoretically, about 2.1 wt% of hydrogen can be reversibly stored in Ca₂NH.

The general features of isotherms for Li₂NH and the recyclable portion of Li₃N at temperatures below 300 °C resemble each other closely, indicating similar thermodynamic properties. Thermodynamic analysis was performed over the Li₂NH and the Ca₂NH systems. As all the absorption/desorption isotherms are slightly sloped, we chose the middle points for calculation. Using van't Hoff plots (see Supplementary Information), it is revealed that the standard enthalpy of absorption (ΔH_{ab}) is about –66.1 kJ mol^{–1} for Li₂NH and –88.7 kJ mol^{–1} for Ca₂NH. In Li–N–H systems, the absorption and desorption isotherms coincide after a few cycles, so the calculated ΔH_{abs} should be equal to ΔH_{des} . To raise the plateau pressure up to 1.0 bar, a temperature above 275 °C is required. This temperature is on the high side for the immediate applications of the system. The hydrogenation temperature ranges for Li₂NH, Li₃N and Mg₂NiH₄ ($\Delta H = -64.4 \text{ kJ mol}^{-1}$) are close to each other¹⁶, while Li₃N and Li₂NH possess much higher storage capacity than Mg₂Ni (~11.5 wt% and 7.0 wt% versus ~3.8 wt%).

Li₃N, Li₂NH and Ca₂NH have fast kinetics in hydrogen storage. For a 500 mg sample, almost all hydrogen (for Li₂NH and Ca₂NH) or a substantial amount of hydrogen (for Li₃N) can be absorbed within 10 min under 30 bar of hydrogen and at 255 °C (for Li₃N and Li₂NH) and 500 °C (Ca₂NH), respectively (see Supplementary Information). Desorption rate strongly depends on temperature and hydrogen pressure. All these three systems can be recycled: after

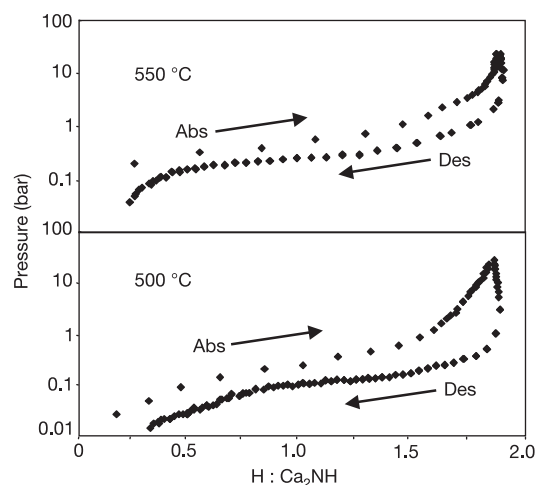


Figure 4 *P*–*C* isotherms of the Ca₂NH sample measured at 500 °C and 550 °C, respectively. For details of measurement, please refer to the Methods.

cycles of absorption/desorption, the overall capacity fluctuates within 10% (see Supplementary Information).

Elements, especially those in groups I–IV and some transition metals, have their nitride, hydride and amide/imide forms. There is, therefore, still plenty of scope for further exploring metal–N–H systems for hydrogen storage. In the present work, we have found that Li–N–H and Ca–N–H systems provide interesting methods of reversible hydrogen storage. However, to meet practical applications at more moderate temperatures and with improved chemical stability, further work is needed for better material design, engineering and mechanistic understanding. □

Methods

Lithium nitride was synthesized by heating commercial lithium metal under a purified nitrogen atmosphere at 100 °C overnight. Owing to the contamination introduced in loading and transferring of the sample, the degree of nitrogenation is less than 95%. The Li₂NH sample was synthesized by decomposing commercial LiNH₂ (95% purity) at temperatures above 350 °C overnight. The Ca₂NH sample was prepared by hydrogenation followed by dehydrogenation of Ca₃N₂ + CaH₂ (1:1) mixture at temperature around 550 °C.

P–C Isotherm measurements

Hydrogen uptake by Li–N–H and Ca–N–H systems was measured with a commercial pressure–composition isotherm (PCI) unit provided by Advanced Materials (<http://www.advanced-material.com>). Static P–C isotherms were determined at temperatures of 195 °C, 230 °C, 255 °C, 285 °C for Li–N–H samples and 500 °C and 550 °C for Ca₂NH samples. The delay time was extended to 200 s, that is, data was recorded only when there was no pressure change within 200 s. The dimensions of the sample cell are about 1.0 cm in diameter and about 3.0 cm in height. A sample of approximately 500 mg was tested each time. A tube furnace with accuracy of 0.1 °C was used as the heater. A thermocouple was closely contacted to the outer surface of the hydrogenation chamber. The possible uncertainties of P–C isothermal measurements may originate from the following three aspects: (1) a temperature difference between sample and thermocouple, estimated to be in the range of ±5.0 °C; (2) the variation in sample density during absorption and desorption; and (3) contamination introduced in the sample loading and gaseous phase.

Thermogravimetric measurements

Weight variation within hydrogenation and dehydrogenation processes was monitored with an intelligent gravimetric analyzer (IGA) from Hiden (<http://www.hiden.co.uk>). Temperature was measured with a thermocouple placed slightly above the sample. A sample of about 200 mg was tested. In the hydrogenation process, about 3.0 bar of purified hydrogen was introduced into sample chamber; the temperature was gradually increased from 50 °C to 255 °C at 2 °C min^{−1} intervals and was maintained at 255 °C for 30 min. In the dehydrogenation process, the hydrogenated sample was cooled to 50 °C. The sample chamber was evacuated to 10^{−5} mbar, and the sample temperature was gradually increased to 195 °C and kept constant until weight loss was almost undetectable. After this, sample temperature was further increased to 430 °C. The uncertainties in thermogravimetric measurements mainly come from the contamination of the sample during loading when exposure to air is unavoidable. The temperature difference between sample and thermocouple was around ±5.0 °C.

Desorption and structural measurements

Temperature-programmed desorption (TPD, with purified Ar as carrier gas) was conducted on a home-made Reactor-MS-GC combined system. Around 300 mg of sample was tested each time. Mass spectrometry (MS) and gas chromatography (GC) were applied to detect the outlet gases. Because ammonia is probably formed during desorption, the outlet gas was conducted into Nessler's reagent to identify any trace of NH₃. A Bruker D8-advance X-ray diffractometer with CuK α radiation was used to identify structural/compositional changes. Except for the complete dehydrogenated Li₃N sample, which was collected by heating the pre-hydrogenated sample to 430 °C under high vacuum, other samples at different degrees of hydrogenation and dehydrogenation were obtained after various stages of PCI measurements (at 255 °C).

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Evidence for recycled Archaean oceanic mantle lithosphere in the Azores plume

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The compositional differences between mid-ocean-ridge and ocean-island basalts place important constraints on the form of mantle convection^{1,2}. Also, it is thought that the scale and nature of heterogeneities within plumes and the degree to which heterogeneous material endures within the mantle might be reflected in spatial variations of basalt composition observed at the Earth's surface. Here we report osmium isotope data on lavas from a transect across the Azores archipelago which vary in a symmetrical pattern across what is thought to be a mantle plume. Many of the lavas from the centre of the plume have lower ¹⁸⁷Os/¹⁸⁸Os ratios than most ocean-island basalts and some extend to subchondritic ¹⁸⁷Os/¹⁸⁸Os ratios—lower than any yet reported from ocean-island basalts. These low ratios require derivation from a depleted, harzburgitic mantle, consistent with the low-iron signature of the Azores plume. Rhenium-depletion model ages extend to 2.5 Gyr, and we infer that the osmium isotope signature is unlikely to be derived from Iberian subcontinental lithospheric mantle. Instead, we interpret the osmium isotope signature as having a deep origin and infer that it may be recycled, Archaean oceanic mantle lithosphere that has delaminated from its overlying oceanic crust. If correct, our data provide evidence for deep mantle subduction and storage of oceanic mantle lithosphere during the Archaean era.