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Mixed-metal Li_3N -based systems for hydrogen storage: Li_3AlN_2 and Li_3FeN_2

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ABSTRACT

The hydrogen storage systems Li_3AlN_2 and Li_3FeN_2 were synthesized mechanochemically by two different routes. In each case an intermediate material formed after milling, which transformed into Li_3MN_2 ($M = \text{Al}$ or Fe) upon annealing. The synthesis route had a measurable effect on the hydrogen storage properties of the material: Li_3AlN_2 prepared from hydrogenous starting materials (LiNH_2 and LiAlH_4) performed better than that synthesized from non-hydrogenous materials (Li_3N and AlN). For both Li_3AlN_2 materials, the hydrogen storage capacity and the absorption kinetics improved significantly upon cycling. Ti-doped Li_3AlN_2 synthesized from LiNH_2 and LiAlH_4 showed the best hydrogen storage characteristics of all, with the best kinetics for hydrogen uptake and release, and the highest hydrogen storage capacity of 3.2 wt.%, of which about half was reversible. Meanwhile, Li_3FeN_2 synthesized from Li_3N and Fe displayed similar kinetics to that synthesized from Li_3N and Fe_xN ($2 \leq x \leq 4$), but demonstrated lower gravimetric hydrogen storage capacities. Li_3FeN_2 displayed a hydrogen uptake capacity of 2.7 wt.%, of which about 1.5 wt.% was reversible. For both Li_3AlN_2 and Li_3FeN_2 , doping with TiCl_3 resulted in enhancement of hydrogen absorption kinetics. This represents the first study of a ternary lithium-transition metal nitride system for hydrogen storage.

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1. Introduction

Intensive research efforts worldwide are focused on developing suitable hydrogen storage systems for implementation of a Hydrogen Economy [1,2]. Amongst the most promising candidates for this task are light metal hydrides and their complexes. These possess high volumetric and gravimetric hydrogen densities, but they generally suffer from poor kinetics and are often too stable thermodynamically to release hydrogen at acceptable temperatures [3,4]. Since Chen et al. [5] reported the surprising potential of Li_3N for hydrogen storage in 2002, considerable interest in this and related M–N–H systems has evolved. Most attempts at stoichiometric

inclusion of other materials in the Li–N–H system have produced a Li–Mg–N–H phase [6].

There was also much excitement generated by recent reports of the materials Li_2BNH_6 , $\text{Li}_3\text{BN}_2\text{H}_8$, $\text{Li}_4\text{BN}_3\text{H}_{10}$ [7]. The latter compound releases more than 10 wt.% H above 250 °C [8,9], and the second system dehydrogenates to the known Li_3BN_2 [10]. Likewise, LiAlH_4 and LiNH_2 combine in a 2:1 ratio to give a system with formula $\text{Li}_3\text{Al}_2\text{NH}_{10}$, which releases 6.0 wt.% H at 200 °C [11]. However, all of these systems are irreversible as their exothermic release of H_2 makes them impossible to recharge under practical conditions. Nevertheless, a 2:1 mixture of LiNH_2 and LiAlH_4 was shown to reversibly release 5.2 wt.% H if heated to 500 °C, decomposing to the known

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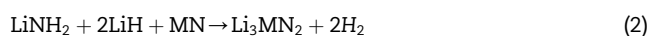
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ternary nitride Li_3AlN_2 [12]. An amorphous metastable phase was observed after milling, which was denoted $[\text{Li}_3\text{AlNH}_4]$, and for which powder XRD and solid-state MAS NMR investigations provided scant clues as to its nature. This latter study by Xiong et al. [12] parallels our own previous independent investigations into the destabilization of Li_3N by Group 13 binary nitrides: we mechanochemically prepared 1:1 mixtures of Li_3N and EN ($E = \text{B}, \text{Al}$ or Ga) [13]. The Al system showed the most promise, absorbing 3.7 wt.% H without doping at 260 °C and 2.4 wt.% at 195 °C. However, powder XRD analysis of the as-prepared or dehydrogenated material showed this to be not the anticipated Li_3AlN_2 , but an as-yet unidentified Li–Al–N intermediate.

The concept of destabilization has been employed by several groups working in the area of hydrogen storage by metal hydrides [14–16], to identify and pursue systems with lower H_2 desorption temperatures. The concept is illustrated for Li_3N in Eqs. (1) and (2) by inclusion of a second metal nitride, MN.



Thus, if the dehydrogenation product in Eq. (2) (Li_3MN_2) is more thermodynamically stable than that in Eq. (1) (Li_3N), then the left hand side of Eq. (2) is destabilized, and LiNH_2/LiH should desorb H_2 at lower temperatures than is the case for Eq. (1), although the inclusion of MN results in a lower overall wt.% hydrogen capacity for the system. Solid-state DFT calculations using the WIEN2k software package indicate that inclusion of AlN and FeN as described in Eq. (2) stabilizes the right hand side of Eq. (2) by 39 and 29 kJ mol^{-1} , respectively [17]. These numbers can be compared with the value of 30.4 kJ mol^{-1} reported in the literature for the stabilization of Li_3AlN_2 with respect to Li_3N [12]. Hence, inclusion of the foreign nitride should destabilize the hydrogenated LiNH_2/LiH state by offering a thermodynamically preferable alternative to Li_3N ; viz. Li_3MN_2 , as exemplified by Eq. (2). Among the transition metal nitrides obvious candidates for incorporation with Li_3N are the light metal nitrides TiN, VN and FeN, which form the stable ternary systems Li_5TiN_3 [18], Li_7VN_4 [19] and Li_3FeN_2 [20] respectively. In order for the destabilization strategy to work as exemplified in Eq. (2), a stable nitride containing the metal in its (III) oxidation state is needed. The most amenable of these systems is Li_3FeN_2 , which has been known for a long time [20]; rather surprisingly it does not appear to have been investigated as a hydrogen storage material. The electrochemical [21] and deintercalation [22] properties of Li_3FeN_2 have been studied; however the focus of such studies has typically been on lithium ion battery applications [23]. In this work we report: (i) further exploration of the Li–Al–N system; and (ii) the first investigation, to our knowledge, of Li_3FeN_2 for hydrogen storage.

2. Experimental

2.1. Synthesis of Li_3AlN_2

All storage and manipulation of materials was carried out in a nitrogen-filled glovebox to minimize the possibility of sample contamination from atmospheric oxygen and

moisture. A 1:1 molar ratio of Li_3N (STREM, 99.5%) and AlN (Aldrich, 98+%) was loaded into a 250 mL stainless steel vessel containing five stainless steel balls of diameter 20 mm. The ball-to-powder mass ratio was 54:1. The materials were milled for 48 h at a rotational speed of 200 rpm using a Retsch PM100 ball mill. The parameters of the mill were set such that after every 5 min of milling the mill paused for 10 s and the direction of rotation was automatically reversed. A fresh $\text{Li}_3\text{N}/\text{AlN}$ sample was doped with 2 mol% TiCl_3 and milled in a similar manner. The milled materials were loaded into a monel crucible, which was placed inside a custom-made quartz tube; this was subsequently placed inside a tube furnace and annealed at 620 °C for 16 h under a flowing stream of N_2 gas. Annealing caused the sample to sinter, and it required grinding with a pestle and mortar before subsequent analysis.

In the second synthesis route the starting materials were LiNH_2 (Aldrich, 95%) and LiAlH_4 (Aldrich, 95%). Milling parameters were similar to those reported in a previous study by Xiong et al. [12]. A 2:1 molar mixture of LiNH_2 and LiAlH_4 was milled for 12 h at a rotational speed of 200 rpm. The ball-to-powder mass ratio was 30:1. The parameters of the mill were set such that after every 60 s of milling the mill paused for 30 s and the direction of rotation was reversed. Another $\text{LiNH}_2/\text{LiAlH}_4$ mixture was doped with 2 mol% TiCl_3 and also milled. The undoped and doped mixtures were annealed at 500 °C for 16 h in a flowing stream of N_2 .

2.2. Synthesis of Li_3FeN_2

The starting materials Li_3N (STREM, 99.5%), Fe (Fisher, 99%) and Fe_xN ($2 \leq x \leq 4$) (All-Chemie, 99.9%) were used as received, without further purification. Li_3N was combined with Fe and Fe_xN , both with and without an additional 2 mol% TiCl_3 catalyst, such that the total mass of the mixture was approximately 5 g and the molar ratio Li:Fe was 3.5:1. The samples prepared from Fe were placed in a 250 mL stainless steel milling vessel containing five stainless steel balls of diameter 20 mm. The ball-to-powder mass ratio was 32:1. The samples prepared from Fe_xN were placed into a 50 mL tungsten carbide milling vessel containing 10 tungsten carbide balls of diameter 10 mm. The ball-to-powder mass ratio was 16:1. Milling was carried out under a nitrogen atmosphere using a Retsch PM100 planetary mill at 200 rpm for 10 h at a time. Milling was performed in 5 min intervals, followed by a 10 s pause and the direction of rotation was alternated for each consecutive segment. The milled samples were annealed for 17 h at 720 °C. Similarly to Li_3AlN_2 , annealing produced a mass of sintered powder. Nishijima et al. [22] reported a similar method for making Li_3FeN_2 using Li_3N and Fe_4N as starting materials; however, they were unsuccessful in isolating a single phase using Li_3N and Fe as starting materials.

2.3. Sample characterization

Powder XRD patterns were measured using a Bruker D8 Advance diffractometer ($\text{CuK}\alpha$ radiation). The samples were mounted in a PVC holder and covered with parafilm to protect them from contact with air during the measurements. The parafilm resulted in additional diffraction peaks at ca. 21.6 and

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