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A new synthesis route of ammonia production through hydrolysis of metal – Nitrides

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ABSTRACT

Recently ammonia has emerged as a potential hydrogen storage material because it contains 17.8 wt% hydrogen. Here, we propose a new synthesis route of ammonia production using hydrolysis of nitrides, which is based on the conversion technique using thermal energy, solar heat or exhaust heat to form NH_3 directly. Lithium metal has been tested as a starting material for the above purpose. We present the detailed results on room temperature nitridation of lithium metal, it is found that the nitridation properties are strongly affected by the surface state of lithium metal. The ammonia synthesis via hydrolysis of lithium nitride succeeds and it is strongly dependent on the reaction rate and temperature.

Introduction

Hydrogen has been considered as an energy carrier capable of replacing current energy infrastructure based on fossil fuels [1]. However, being the lightest element of the periodic table and availability in gaseous form at ambient temperature and pressure conditions, i.e. very low density, it requires efficient storage method. Among all the current storage methods, bonded hydrogen to metal in solid form can be used for the onboard applications more effectively. Several storage materials, e.g. $LaNi_5$ [2], Ti-Cr-V body-centered cubic (bcc) alloys [3], Mg [4], complex hydrides [5], borohydride ammonia borane complexes [6], C or BN nanostructures [7] have shown their merits for hydrogen storage in terms of their capacity, however, still have several deficiencies on other targeted fronts. Recently ammonia has emerged as a potential off board hydrogen storage material owing to its high hydrogen content (17.8 wt%) [8,9]. As it needs a high temperature (~300 °C) to be decomposed catalytically into nitrogen and hydrogen [10] thus making it unsuitable for low-temperature PEM fuel cells. Ammonia has an advantage in terms of its direct use to high-temperature SOFC with very similar or even better performance to hydrogen [11,12]. Since it can also be used for on-board applications by using high-temperature SOFC/DAFC, according to the present state of the art, it is being considered

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as hydrogen delivery media more than a storage medium. Ammonia is being synthesized directly from nitrogen in the air and hydrogen using well established the Haber-Bosch process [13–16]. In this case, splitting of nitrogen molecule into active nitrogen atom is the rate limiting step to allow the formation of ammonia due to strong N≡N bond (945 kJ mol^{-1}) [17]. Thus the reaction may proceed only at high temperatures (500–600 °C) and high pressures (20–40 MPa) with effective catalysts. Extensive studies have been devoted to the catalytic ammonia synthesis over last decade [18–21]. The search for alternative routes for ammonia production is now a days in demand due to large number of applications in particular, recent interest as energy storage media. Several methods have been proposed in last decade including ammonia production using integrated biomass gasification [22], electrochemical synthesis of ammonia using conventional techniques [23,24] or by non-conventional i.e. solar hydrogen system [25], Nuclear based ammonia production [26] etc. It is suggested that the use of renewable energy sources for the production of ammonia can reduce the environmental footprint and can enhance the overall ammonia production efficiencies [27]. Here we propose a direct synthesis route of ammonia using hydrolysis of nitrides as follows, where we do not need high temperature.

$$6Li + N_2 \rightarrow 2Li_3N \quad (1)$$

$$2Li_3N + 6H_2O \rightarrow 6LiOH + 2NH_3 \quad (2)$$

Both the reactions were performed below 100 °C, which allows us to design the whole production plant using renewable energy sources e.g. solar and waste heat. Moreover, we do not need a direct supply of even hydrogen gas in contrast to the Haber-Bosch process, which eliminate the gasification process for hydrogen production. In this work, we used lithium as starting material and examined its nitridation properties as well as the hydrolysis process to achieve ammonia synthesis.

Experimental

The starting material Lithium metal (99%) and Li_3N (≥99. 5%) were purchased from Sigma-Aldrich. The nitridation of lithium metal was carried out in a differential scanning calorimetry (DSC, TA Instruments Q10 PDSC) under N_2 (≥99.9999%) atmosphere. Hydrolysis reaction was performed in a homemade reactor system as shown in Fig. 1. The lower part of the reactor is filled with water and heated to 100 °C to generate water vapor. The solubility of NH_3 in liquid water is more than water vapor as can be seen in Table 1 [28], the hydrolysis reaction was performed with water vapor instead of liquid water to avoid the formation of hydrous ammonia. The nitride sample was kept at the metallic filtered (2 μm) plate, which allows water vapor to pass through it. The sample part was maintained at different temperatures to see the effect of reaction temperature. A water absorbing filter was placed at the above sample part to stop excess water vapor and allow anhydrous NH_3 only. The reactor was connected to Gas chromatography system (GC-14B, Shimadzu) to observe the gaseous species generated during hydrolysis. The XRD analysis was performed using Rigaku-RINT 2500 equipped with CuKα radiation. To avoid any oxygen and moisture contamination to samples, polyimide sheet (Dupont-Toray Co. Ltd., Kapton) was used to cover the samples on a glass plate.

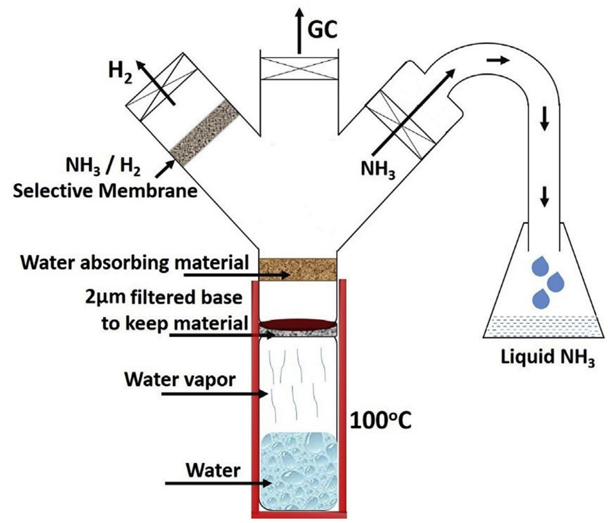

Fig. 1 – Schematic of the experimental set-up used for NH_3 generation.

Table 1 – Solubility of Ammonia in water at different temperatures.

S. No.	Temperature (°C)	Ammonia solubility (wt%)
1.	0	47.3
2.	10	40.6
3.	20	34.1
4.	30	29.0
5.	40	25.3
6.	50	22.1
7.	60	19.2
8.	70	16.2
9.	80	13.3
10.	90	10.2
11.	100	6.9

Results & discussion

The nitridation of lithium metal has been reported to take place at more than 200 °C at 1.0 MPa N_2 pressure in the literature [29–34]. However, the negative Gibbs free energy change (ΔG) value from thermodynamic calculation [HSC Chemistry 6.0 software (Outotec, Oberursel, Germany)], suggest the feasibility of this reaction at room temperature also. The room temperature reaction of lithium with nitrogen has been claimed by Besson et al. [35] and Markowitz et al. [36], which is later mentioned by Rhein et al. [37] and Schiemann et al. [38]. According to above reports, this reaction proceed at high temperature (~200 °C) with dry nitrogen, while the