

Hydrogen storage of metal nitrides by a mechanochemical reaction

Yoshitsugu Kojima*, Yasuaki Kawai, Nobuko Ohba

Toyota Central R&D Labs. Inc., Nagakute-cho, Aichi-gun, Aichi 480-1192, Japan

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Abstract

Mechanochemical reaction of metal nitrides (Li_3N , Ca_3N_2 , h-BN, Mg_3N_2 , Si_3N_4 , AlN, TiN, VN, ZrN) was performed in a planetary ball mill. We demonstrated that hydrogen (H_2) can be stored by the ball milling of their respective metal nitrides in a H_2 atmosphere at 1 MPa and room temperature. The H_2 content of ball-milled metal nitrides was 0.2–5.0 wt.%. This reaction did not occur at ambient conditions without a mechanochemical reaction mechanism. Infrared absorption showed that the N–H stretching vibrations of the ball-milled light metal nitrides occurred at $3100\text{--}3500\text{ cm}^{-1}$. The N–H force constant of the metal imides in the ball-milled metal nitrides decreased with the metal ionic radius and the electronegativity. These results indicated that the size of the metal ion and the charge transfer from the metal to nitrogen play important roles for the force constant.

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1. Introduction

A polymer electrolyte fuel cell (PEFC, PEM fuel cell) is the prime power source for fuel cell vehicle (FCV). One of the most widely envisioned sources of fuel for FCV is hydrogen (H_2). Therefore, it is necessary to have a storage system of H_2 and to have H_2 delivered on demand. H_2 can be stored in tanks as compressed or liquefied H_2 or by adsorption on carbon materials [1,2]. It can also be stored in H_2 -absorbing alloys, H_2 -absorbing alloys with high dissociation pressure [3,4] or as a chemical hydride, such as NaBH_4 [5–7], LiBH_4 [8,9], NaAlH_4 [10,11] or MgH_2 [12–14], as well as in an organic hydride, such as methylcyclohexane or decalin [15]. In recent years, attention has been given to metal nitrides [16–21]. Chen et al. reported that metal nitride (Li_3N) absorbed and desorbed hydrogen at high temperature (468–528 K) [16]. It has been reported that the partial substitution of lithium by magnesium in the nitride/imide system (Li–Mg–N–H) destabilizes Li–N–H system [17–21]. For useable H_2 storage, H_2 absorption/desorption at ambient temperature is necessary. Recently, it has been shown that chemical reaction can occur at room temperature during mechanochemical processing [22].

In this paper, we demonstrate that hydrogen can be stored by the process of ball milling metal nitrides in a H_2 atmosphere at a pressure of 1 MPa and at room temperature.

2. Experimental

2.1. Materials

Lithium nitride Li_3N (Kojundo Chemical Laboratory Co. Ltd., Japan, molecular weight: 34.82, density: 1.38 g cm^{-3} , purity: >99%), calcium nitride Ca_3N_2 (Sigma–Aldrich, molecular weight: 148.25, density: 2.63 g cm^{-3} , purity: >99%) hexagonal boron nitride h-BN (Kojundo Chemical Laboratories Co. Ltd., molecular weight: 24.82, density: 2.25 g cm^{-3} , purity: >99%), magnesium nitride Mg_3N_2 (Sigma–Aldrich, molecular weight: 100.95, density: 2.71 g cm^{-3} , purity: >99.5%), aluminum nitride AlN (Kojundo Chemical Laboratories Co. Ltd., molecular weight: 41.0, density: 3.26 g cm^{-3} , purity: 99.9%), silicon nitride Si_3N_4 (Kojundo Chemical Laboratories Co. Ltd., molecular weight: 140.28, density: 3.44 g cm^{-3} , purity: >99.9%), titanium nitride TiN (Kojundo Chemical Laboratories Co. Ltd., molecular weight: 61.91, density: 5.43 g cm^{-3} , purity: 99%), vanadium nitride VN (Sigma–Aldrich, molecular weight: 64.95, density: 6.13 g cm^{-3} , purity: 99%), and zirconium nitride ZrN (Sigma–Aldrich, molecular weight: 105.23, density: 7.09 g cm^{-3}) were used in this experiment. Lithium amide LiNH_2 (Sigma–Aldrich, molecular weight: 22.96,

* Corresponding author. Tel.: +81 561 63 5325; fax: +81 561 63 6137.
E-mail address: kojima@mosk.tytlabs.co.jp (Y. Kojima).

density 1.17 g cm^{-3}) and borane–ammonia complex NH_3BH_3 (Sigma–Aldrich, molecular weight 30.87, purity 90%) were used as reference specimens. High purity H_2 gas (>99.99999%) was used as the reaction atmosphere. Mechanochemical reaction was performed in a planetary ball mill (Fritsch P-5). The mill container (Cr–Mo steel pot with an internal volume of 300 mL) was loaded with 5 g of metal nitride and 40 pieces of steel ball with a diameter of 9.5 mm (ball-to-powder mass ratio of 28:1). The metal nitrides were milled at 400 rpm of rotational speed and 200 rpm of revolutional speed for 20 h in a H_2 gas atmosphere at a pressure of 1 MPa and room temperature (296 K).

2.2. Characterization

ThermoNicolet AVATAR 360 E.S.P. FT-IR spectrometer with ATR system was used for IR studies in an inert atmosphere of N_2 . X-ray diffraction intensity curves in an inert atmosphere (Ar) were recorded with $\text{Cu K}\alpha$ radiation (50 kV, 300 mA) filtered by monochromator using Rigaku Rint-TTR. The apertures of the first, second and third slits were 0.5, 0.5 and 0.15 mm, respectively. With the Horiba EMGA-621 Hydrogen Analyzer, H_2 contained in a specimen was extracted by heating at 2273 K in an inert gas (Ar). The decomposed H_2 was released from the specimen and was monitored by a thermal conductivity detector.

Hydrogen absorption properties of the metal nitrides were measured with a commercial pressure–composition–temperature (PCT) automatic measuring system provided by Suzuki Shokan Co. Ltd., Japan (Sievert's type apparatus).

3. Results and discussion

The products after ball milling of Li_3N and Ca_3N_2 were light brown, which are different from the dark brown starting materials [23]. Fig. 1 shows the H_2 contents for various ball-milled metal nitrides. We found that H_2 can be stored by the ball milling of their respective metal nitrides in a H_2 atmosphere at 1 MPa and room temperature. The values differ significantly between the different specimens. It is shown that the ball-milled light metal nitrides such as Li_3N and Ca_3N_2 have the H_2 contents above 3 wt.% while the small amounts of H_2 are stored after the transition metal nitrides have been milled under H_2 pressure

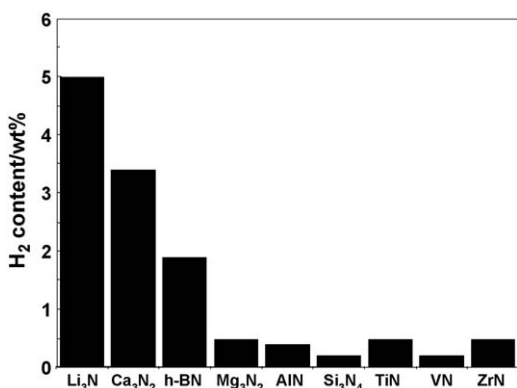


Fig. 1. H_2 content of different ball-milled metal nitrides.

(0.2–0.5 wt.%). The H_2 absorption properties at 9 MPa and room temperature for 20 h were evaluated by the Sievert's apparatus. The H_2 content was also monitored by a hydrogen analyzer. The measurements confirmed that the metal nitrides did not absorb H_2 without a mechanical milling.

The H_2 absorption during milling suggests that the hydrogenation process is a two-step process as follows. H_2 is absorbed on new particle surfaces created by pulverization during initial milling. The absorbed H_2 reacts with metal nitrides such as Li_3N and Ca_3N_2 to form metal imides, metal amides and metal hydrides under further high-energy ball impacts as shown following sections. Local temperature rise, induced by ball impacts, may also contribute to the hydrogenation reaction.

3.1. Ball-milled Li_3N [23]

The total H_2 content in ball-milled Li_3N determined by a hydrogen analyzer was 5.0 wt.% after milling for 20 h. Fig. 2 presents the XRD profiles of the ball-milled Li_3N , Li_3N together with the data of Li_2NH , LiNH_2 , LiH , Li_2O and LiOH . The diffraction peaks of the ball-milled Li_3N at 2θ of 38.3° , 44.5° and 64.8° are raised from (1 1 1), (2 0 0) and (2 2 0) planes of LiH in which its unit cell is cubic in shape [24]. The XRD profiles also show that the ball-milled Li_3N includes unreacted Li_3N . The unit cell of Li_2NH is cubic in shape [24] and the unit cell of LiNH_2 is tetragonal in shape [24]. As the XRD curve of LiNH_2 phase is quite similar to that of Li_2NH phase, it is difficult to characterize the hydrogenating reaction during ball milling only from the XRD curves. The strongest peak of the ball-milled Li_3N in the XRD curve is at about 33° and which comes from either Li_2O or LiOH . The O–H stretching vibration associated with LiOH however, was not observed in the IR spectrum. This contamination might originate from small leaks in the pulverizing system.

The structure of ball-milled Li_3N was investigated by infrared spectroscopy. Fig. 3 shows the infrared absorption spectra of ball-milled Li_3N , Li_3N , LiNH_2 and Li_2NH . Here, Li_2NH was synthesized by decomposing LiNH_2 at 673 K under vacuum

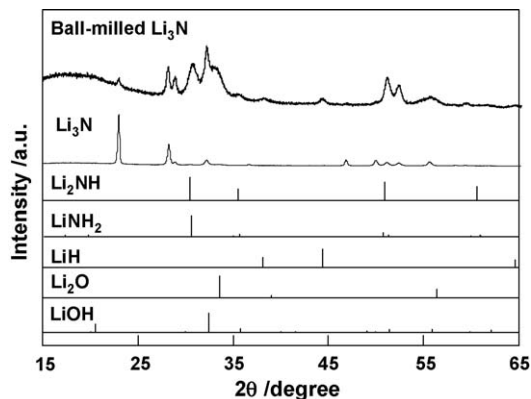


Fig. 2. XRD patterns of ball-milled Li_3N in H_2 and Li_3N together with the data of LiH (JCPDS file No. 09-0189), Li_2NH (JCPDS file No. 06-0417), LiNH_2 (JCPDS file No. 06-0418), Li_2O (JCPDS file No. 12-0254) and LiOH (JCPDS file No. 32-0564). The background broad diffraction in the XRD profiles is due to a polymer film used for shielding from air and H_2O .

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