Quantity of NH₃ desorption from the Li–N–H hydrogen storage system examined by Fourier transform infrared spectroscopy

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Abstract

A mixture of $LiNH_2$ and LiH is one of the complex hydride systems for hydrogen storage, and desorbs H_2 with a small amount of NH_3 as a contaminant. NH_3 impurity in the H_2 stream for polymer electrolyte membrane fuel cells causes poisoning of the cells, which is severe problem for the application. In this work, NH_3 and H_2 partial pressures in the desorbed gas from $LiH + LiNH_2 + 1$ mol% $TiCl_3$ in a closed system were quantitatively estimated by infrared spectroscopy and gas chromatography analysis. H_2 and NH_3 were significantly desorbed in the high-temperature range of 300–400 °C, and the NH_3/H_2 ratio was on the order of 0.1% in this temperature range.
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1. Introduction

In this paper, ammonia (NH_3) partial pressures in hydrogen (H_2) desorbed from mixture of lithium hydride (LiH) and lithium amide ($LiNH_2$) were estimated by infrared (IR) spectroscopy analysis. The study of hydrogen storage properties of the Li–N–H system, i.e., the hydrogen storage materials consisting of lithium, nitrogen, and hydrogen, originated from the report of Chen et al. [1]. The H_2 desorption reaction of the mixture of LiH and $LiNH_2$ is described by the following reaction:

$$LiH + LiNH_2 \leftrightarrow Li_2NH + H_2. \qquad (1)$$

Further study revealed that the hydrogen desorption kinetics of this reaction was improved by adding Ti compounds (e.g., $TiCl_3$, TiO_2, Ti nano-sized particle) [2]. In addition, the reaction (1) has been experimentally demonstrated to be composed of two elementary steps mediated by NH_3 [3]:

$$2LiNH_2 \leftrightarrow Li_2NH + NH_3, \qquad (2)$$

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$$LiH + NH_3 \leftrightarrow LiNH_2 + H_2. \qquad (3)$$

Therefore, a small amount of NH_3 generated by decomposition of $LiNH_2$ could be emitted from this reaction system. However, it is noted that Ti-catalyzed samples emit drastically smaller amounts of NH_3 than non-catalyzed samples [2].

Knowledge of the emitted NH_3 partial pressure is a crucial issue for developing the metal–N–H system as a hydrogen storage material because contamination with a trace of NH_3 (>10 ppm) in the H_2 feed causes a noticeable decrease in the performance of polymer electrolyte membrane fuel cells [4]. Actually, a small amount of NH_3 emission from the mixture of $LiH + LiNH_2$ can be detected in a thermal desorption mass spectroscopy (TDMS) measurement. However, the TDMS results represent strictly qualitative information.

When the TDMS measurement is performed under non-equilibrium conditions [2,5], thermal gas desorption properties were mainly controlled by reaction kinetics. In this case, unreacted NH_3 with LiH in reaction (3) comes mixed in H_2, and the amount of NH_3 emission may largely depend on the condition of the mixed sample (e.g., the size or surface condition of the particle, grain-boundary structures of the two solid phases, etc.). In contrast, after reaching an equilibrium condition, if a non-

negligible amount of NH_3 exists with any NH_3 partial pressure due to the $LiNH_2$ decomposition reaction (2), NH_3 emission could be explained as thermodynamic in origin, indicating that NH_3 emission is an inevitable issue for this material. In a closed system, partial pressures of the desorbed gases are controlled by initially kinetic and finally thermodynamic properties. Since a practical application of this material in a H_2 storage tank is available for the closed system, NH_3 emission should be considered from both kinetic and thermodynamic viewpoints.

In fact, the NH_3 partial pressure in the desorbed gases from the mixture of $LiH + LiNH_2$ (doped with 1 mol% TiO_2) in the closed system has been quantitatively estimated by Raman spectroscopy [6]. The mixture was heated from room temperature to $400\,°C$, and during this procedure, partial pressures of desorbed H_2 and NH_3 gases were investigated by Raman spectroscopy. H_2 and NH_3 partial pressures calculated from the intensities of the spectra significantly increase with temperature from around $250\,°C$, and $\sim0.1\%$ NH_3/H_2 was emitted in the temperature range of 300–$400\,°C$.

In this work, the NH_3 partial pressures were determined by IR spectroscopy to confirm the previous result. IR absorbance also depends on the concentration of the samples. Therefore, the quantity of the samples can be estimated by IR spectroscopy as well as Raman spectroscopy. Since the NH_3 molecule has an IR active mode, namely the N–H stretching vibration, the quantity of NH_3 can be derived from IR spectra of the sample gas. On the other hand, gas chromatography was used to estimate the quantity of H_2, because H_2 has no IR active mode.

2. Experimental

$LiNH_2$, LiH (95% purity each) and 1 mol% $TiCl_3$ (99.999% purity) as an additive were purchased from Sigma–Aldrich Co., and mechanically milled for 2 h under 1 MPa H_2 atmosphere using a planetary ball mill apparatus (Fritsch, P7). The thermal gas desorption properties were examined by TDMS (ANELVA Co., M-QA200TS) combined with thermogravimetry (Rigaku Co., TG8120) in a purified helium flow with $300\,cm^3$/min at a heating rate of $10\,°C$/min.

A schematic diagram of the apparatus is shown in Fig. 1. First, $\sim1\,g$ of the mixed powder was loaded into the sample cell ($19.6\,cm^3$) without exposing the sample to air, and the system was evacuated by opening V_5. Second, after closing all valves except V_1, the sample cell was heated to some measurement
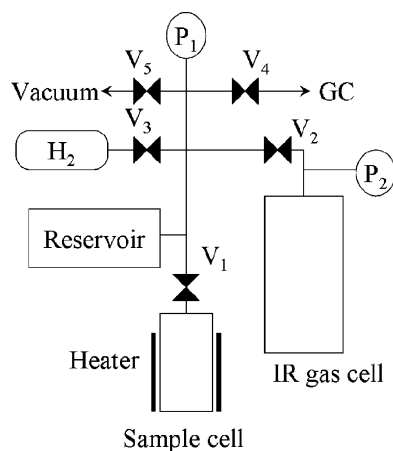
temperatures at a heating rate of $5\,°C$/min, and the system was maintained at each temperature for 30 min. Third, the value of the total pressure was recorded by the pressure gauge P_1 with V_1 closed; then, desorbed gas in the reservoir ($89.9\,cm^3$) was introduced into the IR gas cell ($7736\,cm^3$) by opening V_2. IR spectra were collected by Fourier transform IR spectrometer (FTIR, JASCO Co., FT-IR-6100) with accumulation of 128 scans. Limit of NH_3 detection in this system is higher than 0.1 Pa. Next, V_4 was opened and the desorbed gas was fed into the gas sampler to determine the quantity of H_2 by the GC apparatus (Shimadzu Co., GC-9A). After these measurements, V_2 and V_4 were closed, and V_3 was opened to introduce the hydrogen from the gas cylinder into the reservoir up to the same pressure value as before opening V_2 at the third step. Then, the process went back to the second step and continued to investigate at $100\,°C$ intervals up to the temperature of $400\,°C$.

The quantities of desorbed NH_3 and H_2 were estimated by integration of IR ($\sim3334\,cm^{-1}$) and GC peak intensities, respectively. The calibration curves, which correlate peak area with gas pressure were obtained by using 1060 ppm NH_3 in He, or 99.99999% pure H_2 gases. Following this, the calibration curves enable us to quantitatively calculate the partial pressures of NH_3 and H_2.

3. Results and discussion

Fig. 2 shows the results of TDMS measurement of the mixture of $LiH + LiNH_2 + 1$ mol% $TiCl_3$ in He flow at the heating rate of $10\,°C$/min. Hydrogen desorption started from about $150\,°C$ and peaked around $240\,°C$. Quite small amounts of NH_3 were detected at only high temperatures ($>\sim280\,°C$). It seems to be difficult to determine the quantity of the gas species by means of TDMS, because fragment ions can be generated by ionization of NH_3 gas.

Gas desorption properties of the mixture of $LiH + LiNH_2$ in a closed system were examined by the IR and GC methods. The IR spectra of NH_3 (totally symmetric N–H stretching vibration) are shown in Fig. 3. The IR absorption peaks are found only when the mixture was heated above $300\,°C$. The quantity of desorbed H_2 was revealed by the GC measurement (GC spectrum not shown). From these results, the NH_3 and H_2 partial pressures were calculated by means of each calibration curve.

Fig. 4 shows the NH_3 and H_2 partial pressures calculated from the IR and GC measurements, respectively, in the desorbed gases from the as-milled sample. The partial pressures of desorbed NH_3 and H_2 were increased above the temperature of $300\,°C$, and the ratio of NH_3 to H_2 is on the order of 0.1% in
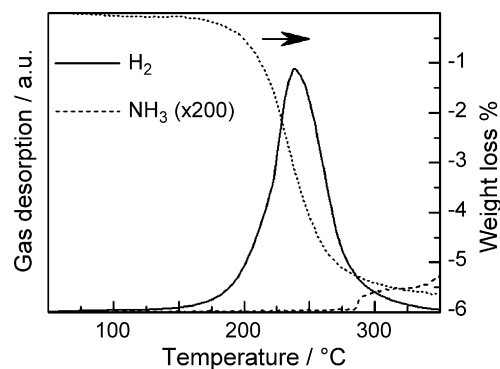

Fig. 1. Schematic diagram of the apparatus. V and P denote valves and pressure gauges, respectively.

Fig. 2. Thermal desorption mass spectra and thermogravimetry for the as-milled sample of $LiH + LiNH_2 + 1$ mol% $TiCl_3$. The measurement was performed in the heating process up to $350\,°C$ under a He gas flow atmosphere at a heating rate of $10\,°C$/min. Here, the solid and dashed lines indicate H_2 and NH_3 (enlarged scale) desorption, respectively. The dotted line denotes weight loss percent.
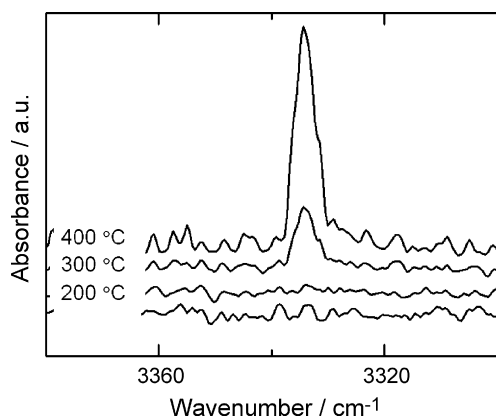
Fig. 3. Collected IR spectra of the desorbed NH_3 from the mixture of $LiH + LiNH_2 + 1$ mol% $TiCl_3$. Observed peaks originate from the totally symmetric stretching mode of N–H.

this temperature range. These results are approximately consistent with previous results obtained from Raman spectroscopy as reported in [6].

In this experimental method, a part of the desorbed gas content was removed from the gas handling system at every measurement, and only pure hydrogen was dosed into the system from the gas cylinder. This process artificially lowered the NH_3/H_2 ratio, and estimated NH_3 loss at any measurement
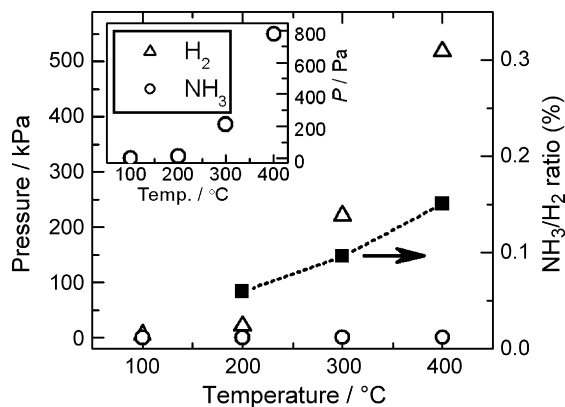

Fig. 4. Calculated pressures of the emitted gases from the mixtures of $LiH + LiNH_2 + 1$ mol% $TiCl_3$ in heating process up to 400 °C. The NH_3/H_2 ratios are also represented. Inset shows NH_3 emission in an enlarged scale.

temperature was less than 20% of desorbed NH_3 pressure at the next measurement temperature. If desorbed gas content could reach an equilibrium state, NH_3 pressure would be constant in spite of the initial NH_3 pressure. However, since these measuring procedures would not achieve a complete equilibrium state, the NH_3/H_2 ratio derived in this work might slightly underestimate the equilibrium value. Although we cannot discuss thermodynamics and kinetics of gas desorption in this study, from both the Raman and IR results, the contamination with 0.1 mol% NH_3 in H_2 seems to be intrinsic for this material in the closed system. In addition, it should be clarified in further studies whether NH_3 desorption is a kinetic or thermodynamic property.

4. Summary

The NH_3 and H_2 partial pressures in the desorbed gas from $LiH + LiNH_2 + 1$ mol% $TiCl_3$ in the closed system were quantitatively estimated by FTIR and GC analyses. The amount of desorbed H_2 and NH_3 were drastically increased at high temperatures of 300 °C, and the NH_3/H_2 ratio was on the order of 0.1% at 300–400 °C.

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