Quantitative estimation of NH₃ partial pressure in H₂ desorbed from the Li-N-H system by Raman spectroscopy†

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The partial pressure of NH₃ gas estimated by Raman spectroscopy indicates that ~0.1% NH₃ is inevitably contaminated in H₂ desorbed from the hydrogen storage material composed of LiH and LiNH₂ at any temperatures up to 400 °C in a closed system.

A solid-state hydrogen storage among the various storage methods[1] is now expected as the safest and most effective way of routinely handling hydrogen, and an ideal solid hydrogen-storage material store minimum 6.5 wt.% and at least 65 g/L of hydrogen, and desorbs hydrogen at 60 - 120 °C.[2] Since Chen et al. reported that the Li-N-H system was one of the promising novel hydrogen storage materials,[3] many scientists have focused on this system, because it possesses quite high potentials on the viewpoint of hydrogen capacity and its reversibility. Especially, we have paid attention to a mixed system of lithium hydride LiH and lithium amide LiNH₂, and have found that hydrogen was stored up to 6.5 wt.% according to the following reaction,[4]

$$LiH + LiNH_2 \leftrightarrow Li_2NH + H_2 \qquad (1)$$
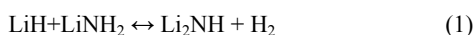
Subsequently, we have clarified that the above hydrogen desorbing reaction proceeds with the following two elementary steps[5];

$$2LiNH_2 \rightarrow Li_2NH + NH_3, \text{ and} \qquad (2)$$

$$LiH + NH_3 \rightarrow LiNH_2 + H_2. \qquad (3)$$
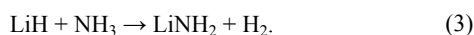
That is to say, at first, LiNH₂ decomposes into lithium imide Li₂NH and NH₃ with an increasing temperature, and then, the generated NH₃ molecule reacts with LiH and transforms into LiNH₂ and H₂ gas. If the reaction completely progress according to the above description (1), we expect that the H₂ gas is only desorbed from the mixture. However, the experimental results[6,7] indicated that a quite small amount of NH₃ were desorbed with the proceeding reaction. From those results, two possibilities can be considered with respect to the NH₃ emission: One is originated in kinetic properties, where a prompt transfer of the NH₃ molecule between two solid phases, from LiNH₂ to LiH, is not completely performed at a finite temperature. Another is originated in thermodynamic properties, where a very low partial pressure of

NH₃ gas should coexist with the main H₂ gas pressure in an equilibrium condition due to the reaction (2).

To clarify which is realized in two possibilities, the equilibrium partial pressures of NH₃ and H₂ emitted from the mixtures with different ratios of LiH to LiNH₂ were simultaneously estimated in a closed system by Raman scattering spectroscopy in this work. The knowledge of the emitted NH₃ partial pressure in the equilibrium condition is quite important for developing the M-N-H system as one of the promising hydrogen storage materials because the contamination with a small amount of NH₃ in desorbed H₂ gas is a serious problem in a practical use for the polymer electrolyte fuel cells (PEFCs). According to Rajalakshmi et al, there was a noticeable decrease in performance of PEFCs with >10 ppm NH₃ concentration, and beyond 20 ppm the poisoning effect was no longer reversible.[8] A possible mechanism by which NH₃ would affect the PEFCs performance could be its reaction with the protons on the membrane, forming NH₄⁺ and decresing membrane conductivity.[9]

It is well-known that some analytical methods, such as thermal desorption mass spectroscopy (TDMS), gas chromatography (GC), infrared spectroscopy (IR) and Raman spectroscopy can be used for determining mixed-gaseous components. However, it is difficult to detect a small amount of NH₃ gas simultaneously with hydrogen gas by the GC experiment due to its strong polarity. Also, the H-H stretching mode in hydrogen gas is infrared inactive for the IR analysis. Therefore, the above two methods are not suitable for simultaneous analysis of NH₃ and H₂ components. The TDMS measurement can be performed for qualitative analysis of the mixed-gaseous components. However, it is to be noted that a quantitative analysis is quite difficult because the NH₃ molecule has many fragment ions like N, NH and NH₂ after ionization. Among some analytical methods, the Raman spectroscopy is the most applicable for simultaneous and quantitative analyses of NH₃ and H₂ mixed gaseous components because both the stretching modes of the N-H in NH₃ and H-H in H₂ are Raman active. In principle, the intensity of Raman-scattered light depends on the densities of scatterers like NH₃ and H₂ molecules. Therefore, the molecular densities can be regarded to directly give the corresponding partial pressures at low pressure range[10]. Thus, we can evaluate their partial pressures from the intensity peak areas for each species in the mixed-gases by the Raman scattering analysis. Indeed, the use of Raman spectroscopy for determining partial pressures of gasses, equilibrium constants, thermodynamic functions and stoichiometric coefficients in gaseous reactions has been established.[11] In this study, the Raman spectra were examined

on the mixed gases of NH_3 and H_2 desorbed from the closed system with the ball milled mixture of LiH and $LiNH_2$ or 2LiH and $LiNH_2$, in which the two kinds of gases are emitted with an increasing temperature.

Starting materials, LiH (Sigma-Aldrich Co.) and $LiNH_2$ (Strem Chemicals Inc.) with 95% purity each and 1 mol % TiO_2 (Millennium Chemicals Inc., 82.8%) as a catalyst were mixed by mechanical milling method. The ratios of LiH to $LiNH_2$ were fixed at two different values of 1 : 1 and 2 : 1. The ratio in the former sample is an ideal ratio of the reaction (1), while the latter system contains twice excess LiH compared to $LiNH_2$ in molar ratio. The reason is because excess LiH might prevent the NH_3 emission, assuming a slow kinetics of the reaction between LiH and NH_3. However, if the amount of NH_3 emission is independent of the amount of LiH, we can judge that the NH_3 emission would originate in the thermodynamic equilibrium state of the Li-N-H hydrogen storage system.

Before heating the ball milled mixtures for proceeding of the H_2 desorption reaction (1), the sample cell was evacuated down to a few Pa order. As the optical cell is located far from the heater, the Raman-scattered light is derived from gas molecules at room temperature. The light source is an Ar ion laser (Spectra-physics Inc., Stabilite 2017) operated at 488.0 nm with the output power of 300 mW, and Raman spectra were analyzed by a triple monochromator (JASCO, TRS-600) with a liquid-N_2 cooled charge coupled device (CCD) detector (Princeton Instruments Inc. model LN/CCD-1100-PB). Accumulation time and number were, respectively, 200s and 5 times for N-H totally symmetric stretching mode region, and those were 50s and 1 time for H-H stretching mode one.

Prior to the measurement of Li-N-H system, we confirmed that it is possible to quantitatively estimate the partial pressure of NH_3 and H_2 in an artificial gas mixture of the 1:1 molar ratio. First, the Raman spectrum from each pure gas of NH_3 or H_2 was monitored to determine the each relation between the integrated peak intensity and the pressure obtained from the pressure sensor. Next, the Raman spectroscopic intensities of N-H and H-H stretching modes in the gas mixture were derived, and then, the partial pressures of NH_3 and H_2 were calculated by use of above relation. As shown in Fig. 1, the partial pressure ratio of NH_3 and H_2 could indicate almost 1:1. Furthermore, the calculated total pressure, that is the
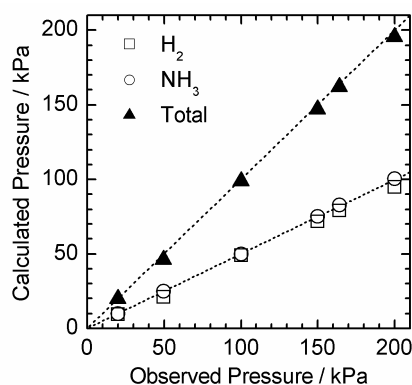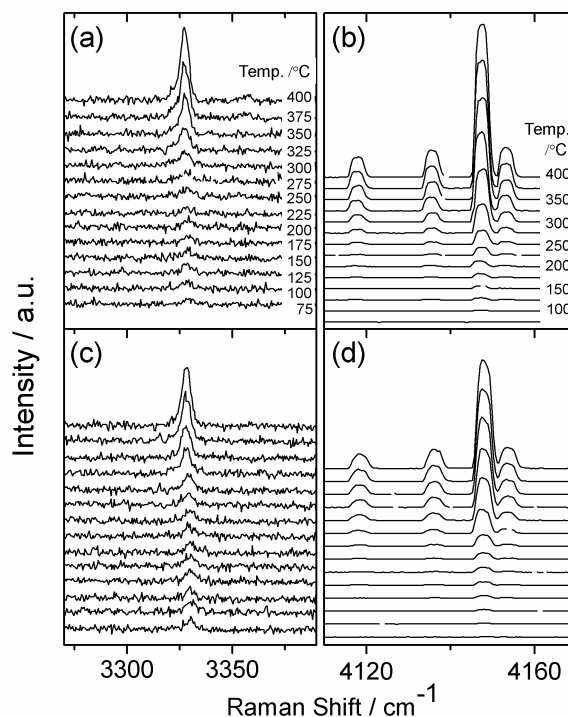
Fig. 2 Collected Raman spectra of the desorbed gas from the mixture of 1:1 LiH and $LiNH_2$ (a:NH_3, b:H_2) and 2:1 LiH and $LiNH_2$ (c:NH_3, d:H_2). Observed peaks are originated in totally symmetric stretching mode of NH_3 (a and c), and stretching mode of H_2. (b and d) Extra peaks at ~4118, 4135, 4153 in (b) and (d) are originated in the rotation of the H_2 molecule. In those four figures, the Raman spectrum at the highest temperature is shown at the top and the others are drawn in the order of the decreasing temperature from the upper side.

sum of the partial pressures, was confirmed to be consistent with

the pressure measured by the pressure sensor (see also Fig. 1). Therefore, it was clear that the quantitative analysis of partial pressures of Raman active mixed gases method can be easily performed by Raman spectroscopy.

Fig. 2 shows collected Raman spectra from NH_3 or H_2 gas emitted from the ball milled mixture of LiH and $LiNH_2$ with the 1:1 and 2:1 molar ratios at various temperatures. We can see that the integrated peak intensities corresponding to NH_3 and H_2 increase with the increasing temperature. From these results, the partial pressures of the mixed gases were estimated from the integrated peak intensities in the collected spectra. Fig. 3a shows the partial pressures of the emitted gases from the LiH and $LiNH_2$ mixture in the 1:1 molar ratio as a function of reaction temperature. The amount of emitted H_2 slightly increases with the increasing temperature up to 250 °C and drastically increases from 275 °C. The total pressure monitored by pressure sensor was almost equal to the deduced partial pressure of H_2 gas, indicating that almost all the emitted gas is H_2. The partial pressure of emitted NH_3 (shown in the inset) is ~0.1% of that of desorbed H_2 at more than 275 °C, and increases with that of H_2 desorption. For the ball milled mixture of 2LiH and $LiNH_2$, as is seen in Fig. 3b, both the NH_3 and H_2 partial pressures were almost the same as in the 1:1 mixture.[‡] Actually, the NH_3 and H_2 desorption profiles in the TDMS measurements, which were obtained in previous works, were

Fig.1 The relations between calculated pressures and observed pressure of the 1:1 gas mixture of NH_3 and H_2. Dotted lines indicate ideal total or partial pressures (calculated pressure) corresponding to real pressure (observed pressure).
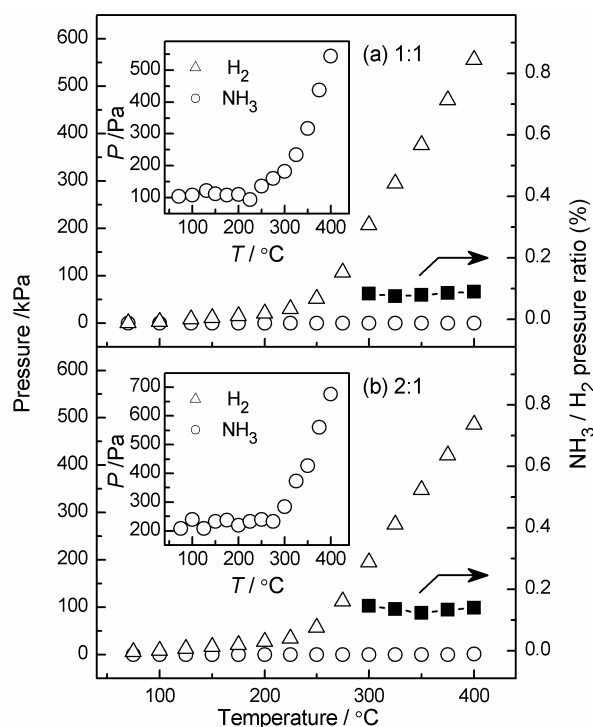
Fig.3 Calculated pressures of the emitted gases from the mixtures of LiH and LiNH$_2$ (a; 1:1 , b; 2:1) in heating process up to 400 °C. The NH$_3$ / H$_2$ ratios are also shown. Inset shows NH$_3$ emission in an enlarged scale.

similar to the behaviours of the partial pressures.[6] This suggests that the quite small amount of NH$_3$ emission is not originated in the lack of LiH in the mixture, and is essential for the reaction (1) in the closed system as one of the equilibrium characters. As the PEFCs performance with 0.1% NH$_3$ should be poor,[12] some countermeasures like an NH$_3$ trapping filter must be considered in use of this kind of H-storage materials.

In conclusion, we performed the evaluation of the simultaneous partial pressures of the mixed gases of NH$_3$ and H$_2$ by means of Raman spectroscopic analysis. The emitted gases from the mixtures of LiH and LiNH$_2$ with 1 : 1 and 2 : 1 molar ratios in the closed system at any temperatures up to 400 °C were estimated to be composed of 0.1% NH$_3$ and 99.9% H$_2$, The 0.1% NH$_3$ impurity is inevitable in the closed system, because the NH$_3$ emission properties might be originated in the thermodynamic characters in the Li-N-H hydrogen storage system.

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Notes and references

‡The data below 1 kPa mainly have errors of ~ 100 Pa at each point, and the difference of the background lines for both the NH$_3$ partial pressures should not be essential properties. Because, the relation between the peak intensity area and the NH$_3$ pressure was derived from the mesurements in a few kPa order of NH$_3$ by use of the pressure sensor which covers a pressure range from 0 to 500 kPa in an absolute value.

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