

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

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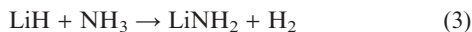
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The partial pressure of NH₃ gas estimated by Raman spectroscopy indicates that ~0.1% NH₃ inevitably contaminates the H₂ desorbed from a hydrogen storage material composed of LiH and LiNH₂ at any temperature up to 400 °C in a closed system.

Solid-state hydrogen storage among the various storage methods¹ is now expected to be the safest and most effective way of routinely handling hydrogen, and an ideal solid hydrogen-storage material would store a minimum 6.5 wt% and at least 65 g L⁻¹ of hydrogen, and desorb hydrogen at 60–120 °C.² Since Chen *et al.* reported that the Li–N–H system was one of the most promising novel hydrogen storage materials,³ many scientists have focused on this system, because it possesses quite high potential 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



Subsequently, we have clarified that the above hydrogen desorption reaction proceeds with the following two elementary steps:⁵



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 progresses according to the above description, reaction (1), we would expect that only H₂ gas is desorbed from the mixture. However, the experimental results^{6,7} indicated that quite a small amount of NH₃ was desorbed as the reaction proceeded. From these results, two possibilities can be considered with respect to the NH₃ emission: One is originated in kinetic properties, where 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 equilibrium conditions due to reaction (2).

To clarify which of the two possibilities is realized, 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. 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 contamination with a small amount of NH₃ in desorbed H₂ gas is a serious problem in the practical use of the polymer electrolyte fuel cells (PEFCs). According to Rajalakshmi *et al.*, there was a noticeable decrease in the 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 decreasing 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 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 these analytical methods, Raman spectroscopy is the most applicable for simultaneous and quantitative analyses of NH₃ and H₂ mixed gaseous components because the stretching modes of both 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 peak intensity 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 NH₃ and H₂ desorbed from the

† Electronic supplementary information (ESI) available: schematic diagram of the apparatus and desorption mass profile of the 1 : 1 mixture of LiH and LiNH₂ with/without TiO₂ as a catalyst. See <http://www.rsc.org/suppdata/cc/b5/b503356j>

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closed system with a ball milled mixture of LiH and LiNH₂ or 2LiH and LiNH₂, in which the two kinds of gases are emitted with an increasing temperature.

Starting materials, LiH (Sigma-Aldrich Co.) and LiNH₂ (Strem Chemicals Inc.) with 95% purity each and 1 mol% TiO₂ (Millennium Chemicals Inc., 82.8%) as a catalyst were mixed by the mechanical milling method. The ratios of LiH to LiNH₂ were fixed at two different values of 1 : 1 and 2 : 1. The ratio in the former sample is the ideal ratio of reaction (1), while the latter system contains twice as much LiH compared to LiNH₂ in molar ratio. The reason is because excess LiH might prevent NH₃ emission, assuming slow kinetics of the reaction between LiH and NH₃. However, if the amount of NH₃ emission is independent of the amount of LiH, we can judge that the NH₃ emission would originate in the thermodynamic equilibrium state of the Li–N–H hydrogen storage system.

Before heating the ball milled mixtures for proceeding with the H₂ desorption reaction (1), the sample cell was evacuated down to the order of a few Pa. 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 was an Ar ion laser (Spectra-physics Inc., Stablite 2017) operated at 488.0 nm with an output power of 300 mW, and Raman spectra were analyzed by a triple monochromator (JASCO, TRS-600) with a liquid-N₂ cooled charge coupled device (CCD) detector (Princeton Instruments Inc. model LN/CCD-1100-PB). Accumulation time and number were, respectively, 200 s and 5 times for the N–H totally symmetric stretching mode region, and were 50 s and 1 time for the H–H stretching mode.

Prior to measurement of the Li–N–H system, we confirmed that it is possible to quantitatively estimate the partial pressure of NH₃ and H₂ in an artificial gas mixture of 1 : 1 molar ratio. Firstly, the Raman spectrum from each pure gas, NH₃ or H₂, was monitored to determine the relation between the integrated peak intensity and the pressure obtained from the pressure sensor. Next, the Raman spectroscopic intensities of the N–H and H–H stretching modes in the gas mixture were derived, and then, the partial pressures of NH₃ and H₂ were calculated by use of the above relation. As shown in Fig. 1, the ratio of the partial pressure of NH₃ and H₂ is indicated to be almost 1 : 1. Furthermore, the calculated total pressure, that is the sum of the partial pressures, was confirmed to be consistent with the pressure measured by the pressure sensor

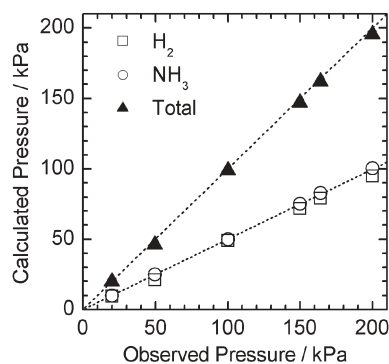


Fig. 1 The relations between calculated pressure and observed pressure of a 1 : 1 gas mixture of NH₃ and H₂. Dotted lines indicate ideal total or partial pressures (calculated pressure) corresponding to real pressure (observed pressure).

(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 Raman spectra collected from NH₃ or H₂ gas emitted from the ball milled mixture of LiH and LiNH₂ with 1 : 1 and 2 : 1 molar ratios at various temperatures. We can see that the integrated peak intensities corresponding to NH₃ and H₂ increase with 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 LiNH₂ mixture in the 1 : 1 molar ratio as a function of reaction temperature. The amount of emitted H₂ slightly increases with the increasing temperature up to 250 °C and drastically increases from 275 °C. The total pressure monitored by the pressure sensor was almost equal to the deduced partial pressure of H₂ gas, indicating that almost all the emitted gas is H₂. The partial pressure of emitted NH₃ (shown in the inset) is ~0.1% of that of desorbed H₂ at more than 275 °C, and increases with increasing H₂ desorption. For the ball milled mixture of 2LiH and LiNH₂, as is seen in Fig. 3b, both the NH₃ and H₂ partial pressures were almost the same as in the 1 : 1 mixture.† Actually, the NH₃ and H₂ desorption profiles in the TDMS measurements, which were obtained in previous works, were similar to the behaviours of the partial pressures.⁶ This suggests that the quite small amount of NH₃ emission does not originate 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% NH₃ should be poor,¹² some countermeasures like an NH₃ trapping filter must be considered in use of this kind of H-storage material.

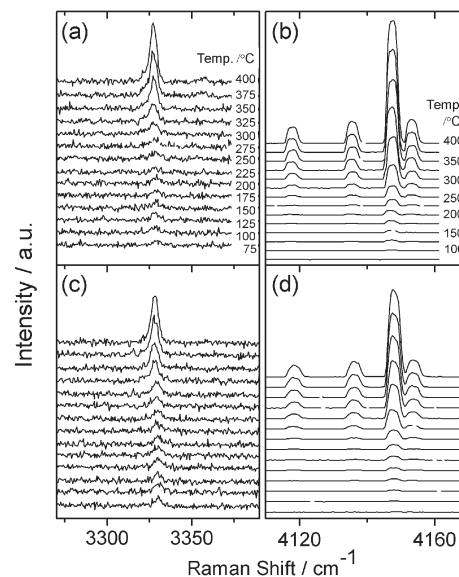


Fig. 2 Collected Raman spectra of the desorbed gas from the mixture of 1 : 1 LiH and LiNH₂ (a: NH₃, b: H₂) and 2 : 1 LiH and LiNH₂ (c: NH₃, d: H₂). Observed peaks originate from the totally symmetric stretching mode of NH₃ (a and c), and the stretching mode of H₂ (b and d). Extra peaks at ~4118, 4135, 4153 in (b) and (d) originate from rotation of the H₂ molecule. In these 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.

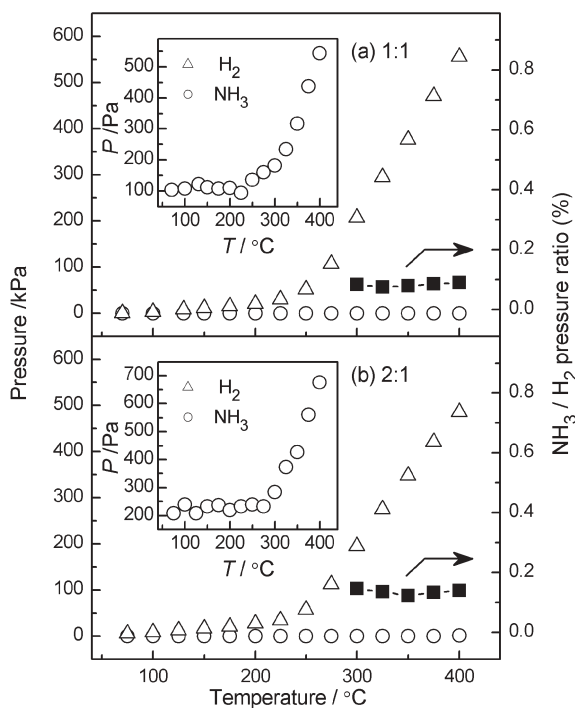


Fig. 3 Calculated pressures of the emitted gases from the mixtures of LiH and LiNH₂ (a: 1 : 1, b: 2 : 1) in the process of heating up to 400 °C. The NH₃ : H₂ ratios are also shown. Inset shows NH₃ emission in an enlarged scale.

In conclusion, we performed an evaluation of the simultaneous partial pressures of the mixed gases of NH₃ and H₂ by means of Raman spectroscopic analysis. The gases emitted from the mixtures of LiH and LiNH₂ with 1 : 1 and 2 : 1 molar ratios in the closed system at any temperature up to 400 °C were estimated to be composed of 0.1% NH₃ and 99.9% H₂. The 0.1% NH₃ impurity is inevitable in the closed system, because the NH₃ emission properties might be originated in the thermodynamic character of 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 in the background lines for both the NH₃ partial pressures should not be essential properties because the relation between the peak intensity area and the NH₃ pressure was derived from measurements in the order of a few kPa of NH₃ by use of a pressure sensor which covers a pressure range from 0 to 500 kPa in an absolute value.

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