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Chemical Hydrogen Compression by MH-NH_3 System

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In order to distribute hydrogen practically, the system of gravimetrically and volumetrically condensed hydrogen has to be developed, which should work under a moderate condition. As one of the candidates of the condensed hydrogen states, we have focused on ammonia (NH_3) because it has a high hydrogen (H_2) density of 18 mass% and is easily liquefied by compression of about 1 MPa at room temperature. Therefore, NH_3 is thought to be one of attractive hydrogen transport media. However, NH_3 is kinetically stable material because high temperature of more than 673 K is required to decompose NH_3 into nitrogen (N_2) and H_2. On the other hand, NH_3 can react with alkali metal hydrides (LiH, NaH and KH) even at room temperature by exothermic reaction, resulting that H_2 is generated. Moreover, the pressure of desorbed hydrogen from the reaction between MH and NH_3 can be increased up to at least 15 MPa because of those exothermic reactions. Here, we would like to propose the new hydrogen compression system by using MH-NH_3 reactions, which could be helpful for the hydrogen distribution.

To overcome the global challenge to the fossil-fuel depletion and the global warming, the energy sources should be distributed to the various kinds of primary energies, such as wind, photovoltaic, solar, geothermal and hydroelectric power generations. An attempt to convert from fossil-fuel to these renewable energies has been underway all over the world [1-5]. However, these fluctuating energy sources are not available anytime and anywhere. Therefore, a suitable energy storage system should be required to deal with the fluctuation and the maldistribution.

Although, the efficient battery system is quite useful and has been utilized in hybrid vehicle, laptop computer, mobile phone, etc., the energy densities of battery are too low to transport a large amount of energy. Consequently, hydrogen has been thought to be suitable energy carrier for a long distance transportation [6-11]. However, the hydrogen energy has a considerable problem to be transported, because the volumetric energy density of hydrogen is quite low whereas the gravimetric energy density of hydrogen is quite high. As shown in Figure 1, the volumetric densities of compressed hydrogen gas at 35 MPa and 70 MPa is only 2.8 and 4.7 kJ/cm^3, which are slightly low compared with liquefied hydrogen (8.4 kJ/cm^3 at 18 K) or compressed natural gas (8.8 kJ/cm^3 at 20 MPa). Although the liquefied or compressed natural gas has been circulated as a clean energy carrier in the world market, the natural gas should be primary and limited energy. Therefore, in order to establish the hydrogen based society, a suitable system to transport hydrogen as secondary energy should be required.

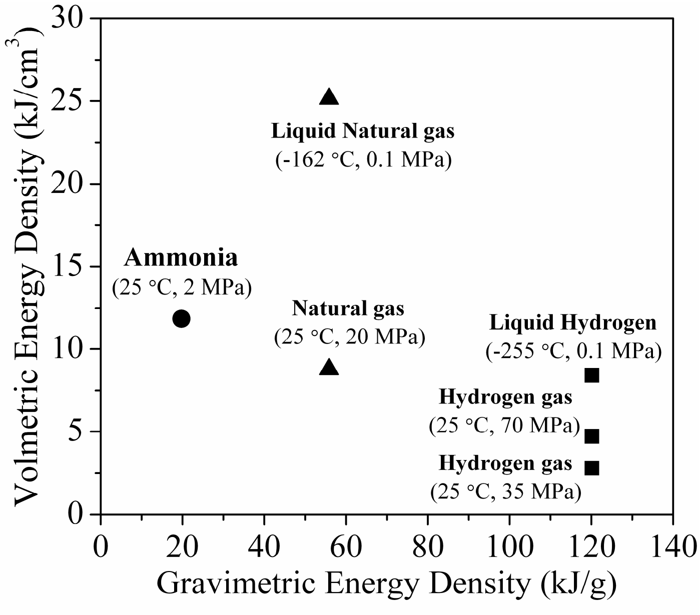

Figure 1: Comparison of various energy carriers in the volumetric viewpoint.

Recently, our group has reported on the efficient conversion from ammonia gas and metal hydride to hydrogen gas and metal amide at a room temperature [12, 13], in which ammonia can be regarded as a hydrogen carrier [14-16]. From the viewpoint as energy carrier, the volumetric energy density of ammonia is 12 kJ/cm^3 at 2 MPa at a room temperature, which is much larger than that of liquefied hydrogen as shown in Fig. 1. Therefore, we have investigated this system from various points of view. Actually, the combination of liquid ammonia and metal hydride MH could be regarded as an interesting hydrogen storage system by following reaction,

$$NH_3 + MH \leftrightarrow H_2 + MNH_2.$$

Since one mole of ammonia generates only one mole of hydrogen, we focus on the liquid state of ammonia as the original system, expecting that the generated hydrogen is high volumetric density. In this paper, we will demonstrate the chemical compression of hydrogen by means of the direct reaction between liquid ammonia and metal hydride.

In this work, commercial lithium hydride (LiH, 99.4 %, Alfa Aesar), sodium hydride (NaH, 95.0 %, Aldrich), and Ammonia NH_3 (99.999 %) were used. The properties of the liquid NH_3 and MH (LiH and NaH) systems were investigated by a following experimental procedure. Figure 2 shows an experimental system. A weighted amount of MH was packed into a reactor made by steel in a glove box (Miwa MFG, MP-P60W) filled with purified Ar gas (> 99.9999%) to avoid oxidation. The sample part of the reactor was soaked into liquid nitrogen after evacuation of the system. Then, gaseous NH_3 was introduced into the reactor, where NH_3 should be solidified in the sample part at -196 °C. Here, the molecular amount of NH_3 was adjusted in relatively lager than that of MH. After closing the VS valve, the reactor was pull out from liquid nitrogen. During an increase in temperature, inside pressure and temperature were monitored by pressure gauge and thermocouple attached to outside of the reactor, respectively.

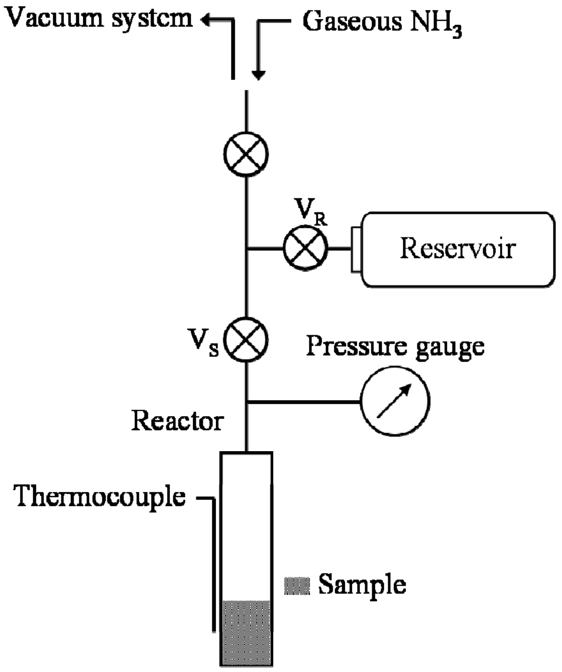

Figure 2: Experimental system.

Figure 3 shows variations of inside pressure and outside temperature of the reactor during the reaction between liquid NH_3 and LiH as a function of time. Here, since the thermocouple was attached to the outside of the reactor, the measuring temperature would be slightly different from the inside temperature. While the reactor was soaked into liquid nitrogen, the pressure was stable because the reaction between solid NH_3 and hydrides should be quite slow due to solid-solid reaction at such a low temperature. With the return of temperature to room temperature, inside pressure drastically increases. An NH_3 vapour pressure should also increase after melting. The pressure change observed during increasing temperature was compared with the variation of NH_3 vapour pressure referred from a database in NIST [17], to understand a starting temperature of the reaction. The results are shown in inset of Fig. 3. It was noteworthy that the increase in the pressure started at around -20 °C. In the case of LiH, the pressure was reached up to more than 12 MPa within 1 hour, assuming that a NH_3 vapour pressure at 25 °C is about 1 MPa [17]. Continuously, 20 MPa was obtained after 4 hours, and the maximum pressure was about 26 MPa after a month. This value was higher than the estimated maximum pressure at 25 °C, 23 MPa, obtained by the amount of liquid NH_3 (2.4 g), LiH (0.7 g), and a system volume (10 cc), which was discussed later. A similar phenomenon was confirmed for the reaction of liquid NH_3 with NaH by using the same experimental system, where the results were omitted in this paper. In this case, the pressure gain was saturated after reaching to about 12 MPa within 4 hours. This is because that the maximum pressure of this system was estimated to be about 13 MPa by a rough calculation at 25 °C from the amount of liquid NH_3 (2.4 g), NaH (1.3 g), and the system volume (10 cc).

Anyway, from these results, the reaction kinetics of NaH with liquid ammonia was thought to be much greater than LiH.

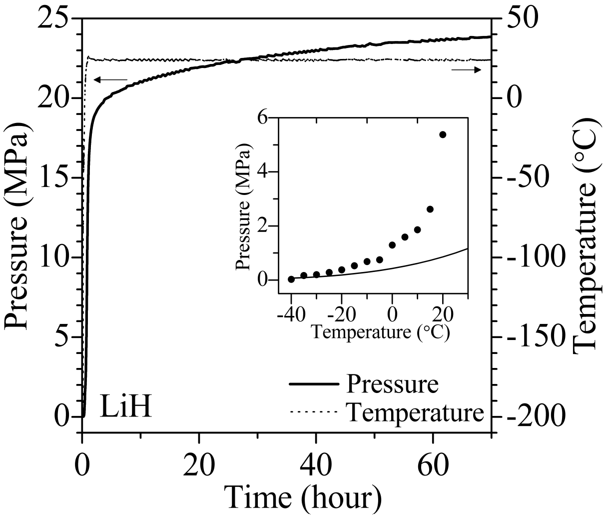

Figure 3: Variations of inside pressure and outside temperature of the reactor. Inset: Experimental pressure change and a vapour pressure of NH_3 in NIST.

In this work, we have demonstrated the production of compressed hydrogen via the direct reaction between liquid NH_3 and MH. Even below room temperature, the reaction started and more than 15 MPa of H_2 was generated within 1 hour. For the systems, the existence of NH_3 would be an essential problem for an application to a fuel cell. However, H_2 and NH_3 can be separated by using a suitable membrane. In addition, it had already clarified that metal amides as the reaction products was easily recycled back to hydrides below 300 °C under 0.5 MPa of H_2 flow condition [15], [16], [18]. Therefore, the reaction of NH_3 and MH would be a potential method as a chemical compressor of H_2 for practical use.

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