Effect of metal type and loading on hydrogen storage on NaAlH₄

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Abstract

Although hydrogen has a great potential as clean energy, safe practical storage of hydrogen for applications such as fuel cells has been a major challenge. NaAlH₄ is one of the metal hydrides, which are candidates for hydrogen storage in vehicles. However, the rather slow absorption/desorption kinetics is still a significant drawback. To alleviate this problem, purified NaAlH₄ was ground with TiCl₃, ZrCl₄, or HfCl₄. Desorption kinetics and capacities were observed under TPD-like operation. Absorption efficiency was determined by raising the temperature up to 125 °C. Of the three doped metals investigated for the positive effect on facilitating NaAlH₄ decomposition, TiCl₃ assists the best on the first reaction while ZrCl₄ and HfCl₄ do for the second one. Despite the kinetics enhancement directly involves with the ZrCl₄ amount, there is a threshold of ZrCl₄-content which affects. 6% ZrCl₄ is considered as an appropriate amount to improve the hydrogen release because it simultaneously decreases the desorption temperature and gives the outstanding rate. In hydrogen desorption, ZrCl₄ provides the most amount of released hydrogen, but for hydrogen absorption TiCl₃-doped NaAlH₄ possesses the highest capacity. It is believed that the metal size is one of the key factors resulting in such the behavior.

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1. Introduction

Hydrogen is a promising fuel to replace the existing fossil fuels. It can be cleanly converted to electricity in fuel cell. However, storing hydrogen effectively and economically is still a challenge since, hydrogen is the lightest gas. For application in vehicles, high-pressure storage tank is impractical due to the weight and safety concerns, while the cryogenic hydrogen storage has volumetric constraints and economic cost. Hydrogen storage in metal hydrides is one of the potential means to meet the requirements of onboard hydrogen storage.

For decades, many scientific and engineering studies involving chemical absorption/desorption of hydrogen from metal hydrides and development of such storage devices have been carried out. Unfortunately, no material has been identified that has the combination of a high gravimetric hydrogen density, adequate hydrogen dissociation energetic, and low cost required for commercial vehicular application [1].

Among several potential hydrides, sodium aluminum hydride, NaAlH₄, seems to be a candidate for practical onboard hydrogen storage material. It can store high weight percent hydrogen with the low price per unit of stored hydrogen. Unlike the interstitial intermetallic hydrides, NaAlH₄ releases hydrogen through a series of decomposition reactions e.g.:

\[
\text{NaAlH}_4 \rightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \rightarrow \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2
\]  

(1)

Theoretically, the first and second steps consist of 3.7 and 1.9 wt% of H₂ released, respectively, for a net reaction of 5.6 wt% gravimetric H-storage. In 2001, Jensen and Gross [2] reported that, the first decomposition occurs at 210–220 °C for a relative short time (≤3 h) but the decomposition reactions of NaAlH₄ and Na₃AlH₆ can only be
reversed under severe conditions and these reaction kinetics are very slow at low temperature.

In 1997, Bogdanović and Schwickardi [3] studied the wet doping of β-TiCl3 or Ti(OBu)4 on NaAlH4. They concluded that a few mole percents of titanium compounds show superior kinetics for hydrogen absorption and desorption. Both alkoxide and chloride compounds have been used by different methods (wet doping, semi-doping and dry doping) to improve hydrogen storage of NaAlH4 [4,5].

However, chlorides such as TiCl3, ZrCl4, VCl5 or other transition metals perform better on dehydrogenation reaction than alkoxides since, they do not leave any hydrocarbon impurities during H2 discharge that can cause fuel cell less efficiency [4,6,7]. In addition, in 1999, Zidan et al. [8] found some effects of two doped metals on different steps of decomposition by using temperature-programmed measurements. They showed that zirconium is inferior to titanium as a catalyst for the dehydridding of NaAlH4 to Na3AlH and Al but a superior one for the dehydriding of Na3AlH to NaH and Al. The significant keys for improvement of absorption/desorption kinetics are the amount of doping [9], milling time [4,7,10] and particle size [6,7].

In this work, effects of ZrCl4, TiCl3, and HfCl4 on the NaAlH4 hydrogen absorption/desorption kinetics and capacity were investigated.

2. Experimental procedure

NaAlH4, TiCl3 (99.5%), HfCl4 (99.5%) and ZrCl4 (99.5%) were purchased from Aldrich Chemical. Hydrogen gas (99.99%) and helium gas (99.99%) were used in sorption kinetics. THF (99.5%) and n-pentane (98%) were obtained from Aldrich Chemical. NaAlH4 was purified by THF and re-crystallized by n-pentane, following the previously reported procedures [11]. To prepare modified NaAlH4, 1 g of purified NaAlH4 was ground with one of three catalysts (TiCl3, ZrCl4 or HfCl4) by mortar and pestle under nitrogen atmosphere for 25 min to obtain fine mixtures, following the previous study [9].

To study the effect of added catalyst, the amount of metals chloride (TiCl3, ZrCl4, HfCl4) was varied between 0 and 9 mol%. After grinding, about 1.3 g of powder mixture was put under evacuum (1.013 kPa) for 2 h and was then immediately placed into stainless steel sealed vessel (20 cm3). To observe the released amount of hydrogen in the desorption process, the known volume vessel was subjected to pressurization to 356.368 kPa (37 psig) and heated with the 20 °C/min heating rate until 125 °C. Hereafter, the hydrogen uptake began and further extended for the next 12 h. Hydrogen capacities were calculated by the equation of state with the compressibility factor at different temperature. The above experimental set-up was shown schematically in Fig. 1.

3. Results and discussion

3.1. Hydrogen desorption

3.1.1. Purified NaAlH4

The amount of desorbed hydrogen in term of weight percent of as-received and purified NaAlH4 are plotted as a function of temperature as shown in Fig. 2, comparing with the previous study [5]. The purified NaAlH4 has higher hydrogen storage capacity than the as-received one, but the hydrogen desorption occurs at temperature higher than the unpurified one, probably because the purified NaAlH4 composes crystalline phase, which is more difficult to decompose. However, the hydrogen storage capacity is less than the theoretical value (5.6 wt%) [2,4,5] and that reported by Jensen et al. [5]. In this experiment, the technique is similar to that of Jensen et al. [5] but less moisture and oxygen control. Thus, the contamination of water and oxygen on NaAlH4, may cause surface damages of NaAlH4 and obstruct the desorption/absorption of hydrogen.
3.1.2. Effect of metal loading types

Even though the doped metallic compounds belong to the same group in the periodic table, the metals act differently to the hydrogen absorption/desorption as shown in Fig. 3. Doping TiCl3, ZrCl4 and HfCl4 on NaAlH4 can lower the first hydrogen desorption temperature to around 170 °C. The second decomposition reaction takes place at around 190 °C for TiCl3, around 210 °C for ZrCl4 and HfCl4. Moreover, among the three doping catalysts, ZrCl4 shows the best kinetic performance and the highest amount of released hydrogen.

3.1.3. Effect of metal loading amount

Fig. 4 shows the hydrogen desorption capacity in different amounts of ZrCl4 doped in NaAlH4. Both desorption temperature and rate were dependent on the amount of doped ZrCl4 on NaAlH4 (Fig. 5). It was found that 6 mol% ZrCl4 doped NaAlH4 results in hydrogen desorption at the lowest temperature among the samples. The maximum rate of hydrogen released corresponds to ZrCl4 level, which starts to converse beyond 6 mol%. It can be hypothesized that this may be caused by the lattice distortion (atomic substitution in formation of Zr2+ and Zr3+ instead of Zr4+) [12]. In the low metal adding, the distortion causes the increase in the lattice of NaAlH4 therefore hydrogen can desorb easily.

3.2. Hydrogen absorption

The dependency of amount of absorbed hydrogen in doped NaAlH4 with various halide compounds is shown in Fig. 6. TiCl3 doped NaAlH4 has the highest hydrogen absorption rate in the first hour. This is due to the ionic radius of Ti ion [10]. It was expected that the low rate of hydrogen
discharge be observed for doped metals with radii significantly larger or smaller than 7.4 nm, the midpoint between Na⁺ (9.7 nm) and Al³⁺ (5.1 nm). Likewise, there is a range of ionic radius (7.3–8 nm) that holds the highest potential to enhance hydrogen charge rate. Because Ti³⁺ (7.6 nm) has smaller ionic radius than that of Zr⁴⁺ (8.6 nm) and Hf⁴⁺ (8.5 nm) [10,13], this Ti³⁺ can easily substitute into the lattice on the surface of material. A reason why the hydrogen uptake rate of HfCl₄-doped material is lower than that of the ZrCl₄-doped one is possibly concerned with symmetry of orbital. Among the three species, Hf⁴⁺ has an electron configuration in the f orbital whereas those of others are in the p orbital, synchronizing with Al³⁺. With this configuration, it is unlikely to cause the atomic overlap between Al³⁺ and Hf⁴⁺. The sample rendered by ZrCl₄ sustains hydrogen at higher capacity so it can be interpreted that the activity of HfCl₄ to facilitate absorption reaction is considerably lower than that of ZrCl₄.

In the first cycle, H₂ contained in the metal hydride is desorbed for use, and then H₂ is absorbed for storage. Because of irreversibility of the desorption–absorption cycle, the desorbed amount is significantly larger than the absorbed amount. In the second and third cycle, the desorption and absorption capacity are found to become nearly constant and essentially equal the first cycle absorption capacity. Hence, the degree of rehydrogenation [11] or the cyclic ability of the doped materials is calculated as the ratio of absorption to desorption capacity in the first cycle and summarized in Table 1. Obviously, all doped samples are not entirely reversible and show significantly lower absorption capacity than the first desorption capacity. A major reason of the incomplete absorption may be the formation of large metallic aluminum particles from NaAlH₄ decomposition in Eq. (1), thereby hampering the diffusion mechanism necessary for recombination [14,15].

4. Conclusions

Doping TiCl₃, ZrCl₄, and HfCl₄ on NaAlH₄ enhances the kinetics and decreases the reaction temperature in both hydrogen absorption and desorption. TiCl₃ renders the best on the first decomposition reaction, while ZrCl₄ and HfCl₄ do for the 4 one. A small amount of ZrCl₄ on NaAlH₄ is sufficient for catalyzing the discharge of hydrogen. However, 6 mol% ZrCl₄ was found to be an appropriate amount because it simultaneously decreases the desorption temperature and gives the outstanding rate. Of all the three doped metals, TiCl₃ provides the highest absorption capacity. It is believed that the ionic radius of the doped metal is one of the key factors resulting in such the behavior.

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Table 1

| Type of metal loadings | Desorption | Absorption | Degree of rehydrogenation |
|-----------------------|------------|------------|--------------------------|
| TiCl₃                 | 3.05       | 1.93       | 63.3                     |
| ZrCl₄                 | 3.17       | 1.78       | 55.7                     |
| HfCl₄                 | 2.88       | 1.42       | 49.3                     |

* These numbers were measured after reaching an equilibrium state.