

Compressed hydrogen generation using chemical hydride

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Received 25 August 2003; accepted 29 March 2004

Available online 17 June 2004

Abstract

In a closed pressure vessel, the reaction of sodium borohydride (NaBH_4) with Pt-LiCoO_2 catalyst and a stoichiometric amount of water drastically increases the pressure owing to the generation of large quantities of hydrogen gas by synergism of hydrogen pressure and the catalyst (gravimetric hydrogen density per unit weight of NaBH_4 and H_2O including the Pt-LiCoO_2 catalyst is 9.0 wt.%, volumetric hydrogen density per unit weight of NaBH_4 and H_2O including the Pt-LiCoO_2 catalyst is $101 \text{ kg H}_2/\text{m}^{-3}$). The hydrogen densities are high enough to reach the US Department of Energy (DOE) targets for use in a fuel cell vehicle (FCV) and also for other applications such as a fuel cell uninterrupted power supply (FCUPS).

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Keywords: Sodium borohydride; Chemical hydride; High pressure; Catalyst; Hydrogen generation

1. Introduction

A fuel cell is a battery, which is actuated with hydrogen (H_2) and oxygen (O_2). The energy obtained by a reaction of H_2 and O_2 is directly converted into electric energy. Since a fuel cell has an efficiency much higher than that of conventional combustion engines, a fuel cell vehicle (FCV) is also expected to have high efficiency [1,2]. A polymer electrolyte fuel cell (PEFC) is the prime power source for a FCV, as well as another application called a fuel cell uninterrupted power supply (FCUPS). The uninterrupted or emergency power system for a FCUPS systems currently combines a battery and a diesel generator. But a PEFC system has the potential to be a future power system for emergency FCUPS. In order to fuel the FCV or FCUPS, a source of proton is required for the electrochemical reaction. One of the most widely envisioned sources of fuel for FCV or FCUPS is H_2 . Therefore, it is necessary to have a storage tank of H_2 to start the system on demand.

Hydrogen can be stored in tanks of compressed [2,3] or liquefied H_2 [3], or by adsorption on activated carbon [4], carbon nanotubes [3,5,6] and graphite nanofiber [7,8] or in

a hydrogen-absorbing alloy [9] or in a chemical hydride such as NaBH_4 [10–18], NaH [19], LiH [20], or NaAlH_4 [21]. Among these methods, much attention has been given to the hydrolysis of a chemical hydride such as NaBH_4 [10–18] because of the large theoretical hydrogen content of 10.9 wt.%. NaBH_4 is stable compared with other chemical hydride and is easy to handle. At room temperatures, only a small percentage of the theoretical amount of hydrogen is liberated by hydrolysis reaction of NaBH_4 and H_2O [14,22], but the hydrolysis is accelerated by the use of catalysts. Conventionally, known catalysts are metal halides, colloidal platinum, active carbon, Raney nickel [10], fluorinated Mg-based hydride [16] and ruthenium supported on anion exchange resin [17,18] as well as cobalt and nickel borides [11,13].

In a previous paper, metal–metal oxide such as Pt-LiCoO_2 was found to work as an excellent catalyst for releasing hydrogen by hydrolysis of NaBH_4 solution [22]. The catalyst produced 100% of the theoretical amount of H_2 using excess water ($\text{H}_2\text{O}/\text{NaBH}_4 = 210 \text{ mol/mol}$). Furthermore, it was demonstrated that NaBO_2 was recycled back to NaBH_4 using coke or methane [23]. Here, we show that by using NaBH_4 , a stoichiometric amount of water, a Pt-LiCoO_2 catalyst and high H_2 pressure, H_2 gas can be generated in large quantities sufficient for use in FCV and FCUPS.

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2. Experimental

2.1. Materials

Sodium borohydride (Rohm and Haas, NaBH_4) was used for the reaction with water. Pt-LiCoO₂ and Pt-TiO₂ catalysts were synthesized using a conventional impregnation techniques [22]. Dinitrodiammine platinum(II) nitric acid solution [$\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$, 33 mL, Pt content of 50 g/L, Tanaka Kikinzoku Kogyo K.K., Japan] and titania powder (TiO₂, 100 g, Sachtleben Chemie GmbH, UV100) or lithium cobaltate powder (LiCoO₂, Nippon Chemical Industries Co. Ltd., product name Cellseed 5) were mixed. The mixture was held at 523 K for 5 h. The dried powder was calcined for 2 h in air at 723 K, thereby coating Pt on the metal oxide. Thus, the Pt-metal oxide catalysts contained a Pt content of 1.5 wt.%. Nickel chloride (NiCl_2 , Wako Pure Chemical Industries Ltd., Japan) was used as a reference catalyst [10].

2.2. Characterization

The amount of H₂ generated in our experiments were determined as follows. For high pressure systems, weighed amounts of catalysts (1–2.5 g) and NaBH₄ (0.26–5 g) were packed into a pressure vessel having a internal volume of 50–720 mL. H₂O was injected into the vessel via syringe at 296 K. H₂O/NaBH₄ (mol/mol) ratios were 1–6 mol. While the mixture was at room temperature, the pressure and the temperature in the closed pressure vessel increased due to the generation of H₂ gas. The pressure was vented to atmospheric pressure. The vented gas was collected and its volume was measured in a water trap. The gas generated was identified as hydrogen by a gas chromatography. The pressure and the temperature within the reactor vessel were monitored as a function of time. The increase in pressure gave a calculated volume of released gas that was subsequently converted into percent yield after the total amount gas had been collected. Catalyzed tests at atmospheric pressure (0.10 MPa) were conducted with the open pressure vessel using the previous method.

The thermal hydrolysis reaction was carried out using the following method. Sodium borohydride (0.2 g) was loaded into the Erlenmeyer flask (100 mL), followed by a stoichiometric amount of water. The temperature was varied from 296 to 473 K using a oil bath. Blank experiments were carried out in the absence of the reactants.

Crystalline structures of the byproduct by the hydrolysis reaction of NaBH₄ and sodium metaborate (NaBO₂, Kojundo Chemical Laboratory Co. Ltd., Japan) were investigated by wide angle X-ray diffraction. The X-ray diffraction patterns were recorded at room temperature by using a Rigaku Denki Rad-B over a range of diffraction angle (2θ) from 3 to 80° with Cu K α radiation (30 KV, 30 mA) filtered by a monochromator. X-ray photoelectron spectroscopy (XPS) was used to investigate the byproduct and NaBO₂. XPS measurements were performed using a Physical Electronics

PHI-5500MC with a monochromatic Mg K α X-ray source (1253.6 eV) in a ultrahigh vacuum.

3. Results and discussion

The hydrogen yield of NaBH₄ was determined by the following equation

$$\text{Hydrogen Yield} = W_h / (0.213 W_s) \quad (1)$$

where W_h is the mass (g) of generated H₂, W_s is the mass (g) of NaBH₄. The value of 0.213 is the theoretical amount of H₂ per unit weight of NaBH₄ generated. Thermal hydrolysis experiment without using a catalyst provided H₂ yield at 296 K under atmospheric pressure of only 2.4%. However, the H₂ yield increased with temperature and reached a maximum value of 37% at 473 K (temperature: 296–473 K, H₂ yield: 2.4–37%). Thus, without catalyst, the hydrogen generated was not sufficient.

Fig. 1, however, shows the effects of hydrogen generation at 296 K with a catalyst (Pt-LiCoO₂) and a closed pressure vessel over time. When water was injected into the system (NaBH₄ mixed with Pt-LiCoO₂ catalyst) at 296 K, the hydrogen generated gradually increased. After 400 s, the hydrogen yield reached a value of 80% due to the increase of the pressure from 0.10 (1 atm) to 0.68 MPa. Under atmospheric pressure in an open system with the catalyst, H₂ generation reaction took place at 330 s and only 37% was generated. Surprisingly, the hydrolysis reaction of NaBH₄ with the Pt-LiCoO₂ catalyst under high pressure closed system has twice the hydrogen yield in comparison with that of atmospheric pressure and an open system. It is also noted in Fig. 1 that without catalyst in a closed system, the yield is only 2.0% generating only 0.11 MPa. This indicates that the hydrogen generation is not accelerated using only the closed pressure vessel.

These results indicate that the hydrogen generation is remarkably improved using Pt-LiCoO₂ catalyst under high pressure above 0.6 MPa owing to their synergistic effect. One explanation of the catalysis function is that electrons

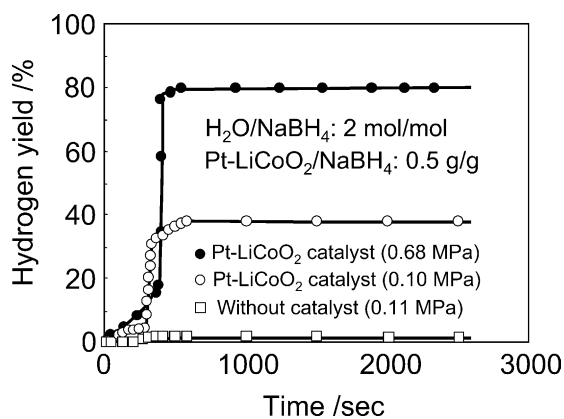


Fig. 1. Hydrogen yield as a function of time by different pressure at 296 K.

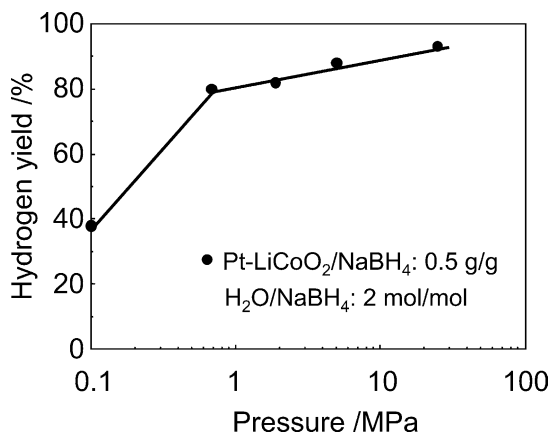


Fig. 2. Influence of pressure on hydrogen yield at 296 K ($\text{H}_2\text{O}/\text{NaBH}_4$: 2 mol/mol, Pt-LiCoO₂/NaBH₄: 0.5 g/g).

are discharged through the Pt-LiCoO₂ catalyst from BH₄⁻ ion. H⁻ ion from BH₄⁻ ion is then oxidized to give molecular H₂. On the other hand, this electron can reduce the H⁺ in water and hydrogen gas is generated. It is considered that the activity of the catalyst increases under high pressure. Pt-TiO₂ and NiCl₂ were also used as catalysts for hydrogen generation from NaBH₄ solution at the stoichiometric amount of water using a closed pressure vessel. In these experiments, catalyst/NaBH₄ was 0.2 g/g. The hydrogen yields using Pt-TiO₂ and NiCl₂ were 4.4 and 4.5%, respectively and low compared with that of Pt-LiCoO₂ (hydrogen yield: 89%). Therefore, our key finding is that the use of a Pt-metal oxide catalyst having high activity under high pressure results in a significant increase in the amount of hydrogen generated.

Fig. 2 shows the hydrogen yield versus the pressure at the stoichiometric amount of water using Pt-LiCoO₂ catalysts. Under high pressures (0.7–25 MPa), H₂ yields up to 80–93% are obtained. The hydrogen yield as a function of added water ($\text{H}_2\text{O}/\text{NaBH}_4$) is shown in Fig. 3. The yield increases with increasing $\text{H}_2\text{O}/\text{NaBH}_4$ ratio. As the $\text{H}_2\text{O}/\text{NaBH}_4$ ratio approaches 2, there is a strikingly sharp increase in the hy-

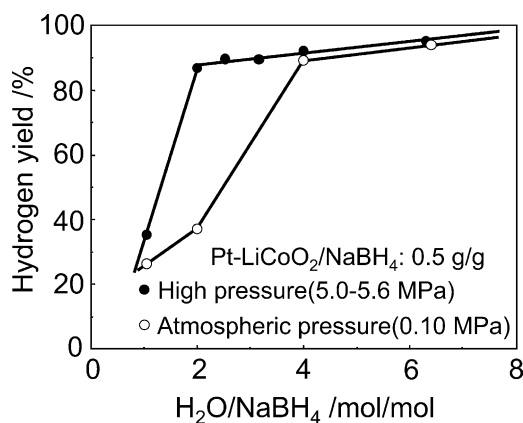


Fig. 3. Influence of water added, $\text{H}_2\text{O}/\text{NaBH}_4$, on hydrogen yield at 296 K (Pt-LiCoO₂/NaBH₄: 0.5 g/g).

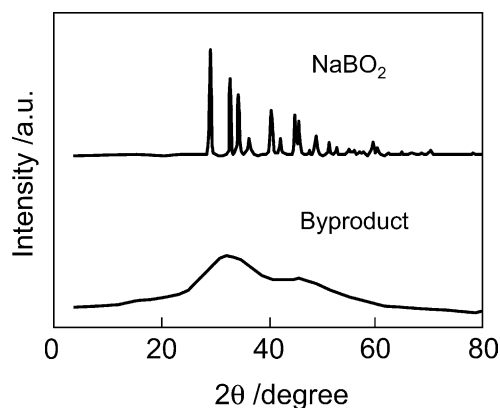


Fig. 4. Wide-angle X-ray diffraction intensity curves of byproduct and NaBO₂.

drogen yield from 35 up to 87%. The hydrogen yield above $\text{H}_2\text{O}/\text{NaBH}_4 = 2$ tapers off reaching 95% at ratio = 6. However, in an open system, the $\text{H}_2\text{O}/\text{NaBH}_4$ ratio must be significantly increased (4 mol/mol) to obtain similar results.

To determine what remaining species exists after the hydrogen generation at $\text{H}_2\text{O}/\text{NaBH}_4 = 2$, the mixture of the byproduct and the catalyst was dissolved in water. The filtrate was evaporated at 323 K, subsequently vacuum drying was carried out at room temperature to give the byproduct. X-ray diffraction intensity curve of the byproduct is shown in Fig. 4. The byproduct shows broad XRD peaks. The broad peak positions (2θ , 32.5°; d -spacing, 0.275 nm; 2θ , 44.8°; d -spacing, 0.202 nm) correspond to those of NaBO₂ as shown in the same figure. XPS of the B(1s), O(1s), and Na(1s) core levels were determined for the byproduct and NaBO₂. The B(1s), O(1s), and Na(1s) peaks (XPS binding energies) from the byproduct were 192.0, 531.6 and 1071.4 eV, respectively. The binding energies are in close agreement with those from NaBO₂ [B(1s) peak: 192.0 eV, O(1s) peak: 531.6 eV, Na(1s) peak: 1071.5 eV]. We found that the byproduct is an amorphous sodium metaborate. Thus, the reaction of NaBH₄ and water at the stoichiometric amount of water using the Pt-LiCoO₂ catalyst under high pressure is shown as follows



the time required for an increased generation of hydrogen was defined as the induction period. The induction period was approximately independent of the pressure as shown in Fig. 1. As the temperature increased (296 → 313 K), the induction period decreased [induction period: 400 → 50 s (Pt-LiCoO₂/NaBH₄: 0.5 g/g, $\text{H}_2\text{O}/\text{NaBH}_4$: 2 mol/mol)], but the hydrogen generated was constant and independent of temperature. Increasing the amount of the catalyst also decreased the induction period [induction period: 700 → 2 sec (Pt-LiCoO₂/NaBH₄ 0.2 g/g–7.6 g/g, $\text{H}_2\text{O}/\text{NaBH}_4$: 2 mol/mol)]. These results indicate the presence of the critical temperature for the reaction of NaBH₄ with water.

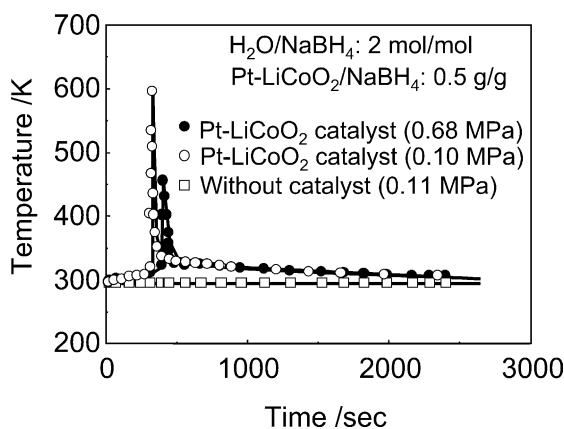
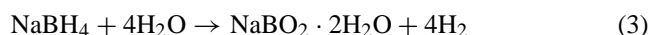


Fig. 5. Temperature of hydrolyzed NaBH_4 as a function of time by different pressure.

At 298 K, the standard-state enthalpy change (ΔH°) for the reaction of NaBH_4 with H_2O can be calculated from the standard enthalpies -188.6 KJ (NaBH_4), -571.6 KJ ($2\text{H}_2\text{O}$), -977.0 KJ (NaBO_2) and 0 KJ (4H_2), respectively [24]. Therefore, the standard-state enthalpy change is -217 KJ and such a reaction is exothermic. Fig. 5 shows the temperature of the hydrolyzed NaBH_4 in the vessel as a function of time. It is shown that the temperature at the beginning of the steep increasing is about 323 K and we believe that this corresponds to the critical temperature for the reaction of NaBH_4 with water. The temperature in the vessel at 0.68 MPa shows the maximum value of 453 K after the induction period, and decreases rapidly with time. The maximum temperature is 140 K lower than that under atmospheric pressure. This may be due to the influence of water. Under atmospheric pressure, the H_2 yield increased with an increase in water [89% at $\text{H}_2\text{O}/\text{NaBH}_4$ (mol/mol) of 4], as shown in Fig. 3. The water added is two times compared with that under high pressure. After the H_2 generation at $\text{H}_2\text{O}/\text{NaBH}_4=4$, the byproduct was prepared and characterized using the same method described before. It was shown by the X-ray diffraction and the XPS that the byproduct is also amorphous NaBO_2 . We consider that the hydrated NaBO_2 ($\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$) changes into NaBO_2 , when the byproduct is prepared by vacuum drying. Then, the reaction of NaBH_4 and water using the Pt-LiCoO₂ catalyst under atmospheric pressure is shown as follows



reaction Eqs. (2) and (3) indicate that the stable structure of the byproduct depends on pressure.

The structure of the byproduct at 0.1 MPa is $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$, while that at high pressure, it is NaBO_2 . The temperature rise shown in Fig. 5 is 140 K higher for the catalyzed reaction at 0.10 MPa compared to 0.68 MPa which corresponds to the addition of two water molecules in the heat of formation of $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$. Fig. 1 also clearly indicates that

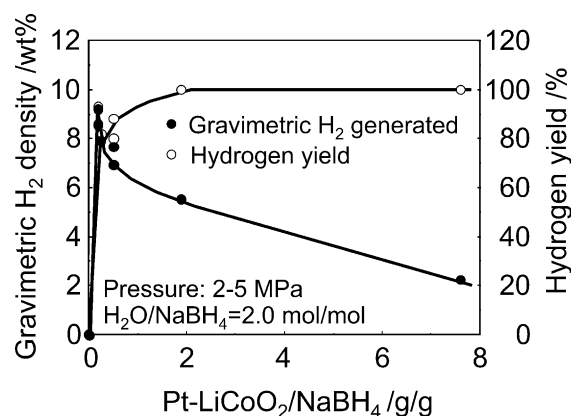


Fig. 6. Influence of Pt-LiCoO₂/NaBH₄ on gravimetric hydrogen density and hydrogen yield ($\text{H}_2\text{O}/\text{NaBH}_4$: 2 mol/mol).

the lower temperature exothermic reaction produced twice the yield of H_2 presumably since the H_2 is not consumed to hydrated NaBO_2 .

Fig. 6 shows the hydrogen yield and the gravimetric hydrogen density versus Pt-LiCoO₂/NaBH₄ (mol/mol) at 296 K. The hydrogen yield increases with increasing catalyst, approaching 100%, but the gravimetric hydrogen density per unit weight of NaBH₄ and H₂O including the catalyst decreases with the catalyst. As seen in Fig. 6, the gravimetric hydrogen density has a maximum value of 9.0 wt.% at the catalyst content of 0.2 g/g to unit weight of NaBH₄.

Table 1 shows the gravimetric hydrogen density of various hydrogen storage materials. MgH₂ contains 7.6 wt.% of hydrogen [25]. But the dissociation pressure of 1 bar is not at room temperature but at 573 K. Bogdanovič et al. showed that the decomposition temperature of NaAlH₄ can be lowered by doping the hydride with a catalyst such as Ti(OBu)₄ [21]. It requires 393 K for generating 3.4 wt.% hydrogen. Furthermore, the kinetics is poor, which may be due to the ionic nature of the crystal. The highest hydrogen absorption and desorption reported for any hydrogen-absorbing alloy is 2.5 wt.% [9]. The best value of hydrogen adsorption in carbon materials has been 5.1 wt.% at a temperature of 77 K [4]. Hydrolysis reaction of sodium hydride produces hydrogen of 4 wt.% [19]. The hydrogen yield of lithium hydride upon addition of stoichiometric amounts of water is 34% [26]. This corresponds to the gravimetric hydrogen density of 2.6 wt.%. The gravimetric hydrogen density of NaBH₄ is 4.3 wt.% by the conventional excess water method [17]. Our results indicate that hydrolysis reaction of NaBH₄ and a stoichiometric amount of water with the Pt-LiCoO₂ catalyst using the pressure vessel yields hydrogen over two times compared with hydrogen storage materials mentioned above, which are utilized around room temperature. This table does not include carbon nanotube and graphite nanofiber because conflicting results have been published concerning the reversible storage of hydrogen in carbon nanotubes [3,5,6] and graphite nanofibers [7,8].

Table 1
Comparison of gravimetric hydrogen density of various hydrogen storage materials

Materials	Temperature (K)	Gravimetric hydrogen density (wt.%) (references)
NaBH ₄ + 2H ₂ O + LiCoO ₂ -based catalyst + high pressure (Pt-LiCoO ₂ /NaBH ₄ = 0.2 g/g)	296	9.0 (this work)
NaBH ₄ 20 wt.%, NaOH 10 wt.%, H ₂ O 70 wt.%	298	4.3 [17]
LiH + H ₂ O (hydrogen yield: 34%)	Ordinary temperature	2.6 [26]
NaH + 1.5H ₂ O	Ordinary temperature	4.0 [19]
MgH ₂	573	7.6 [25]
NaAlH ₄	393	3.4 [21]
Ti-xV-Cr-Mn(x = 45 and 55; Ti/Cr/Mn = 24:31:10, H ₂ pressure: 7–0.01 MPa)	313	2.5 [9]
Superactivated carbon (AX-21, 5 MPa)	298	0.9 [4]
Superactivated carbon (AX-21, 3 MPa)	77	5.1 [4]

At an operating pressure of 70 MPa at 298 K, The volume of tanks for gaseous hydrogen allows storage density of 39 kg H₂/m³ [27]. The densities of NaBH₄, water and LiCoO₂ is 1.08 g/cm³ [12], 1.00 g/cm³ and 5.06 g/cm³ [28], respectively. We assumed that the averaged value of our materials (H₂O/NaBH₄: 2 mol/mol, Pt-LiCoO₂ catalyst /NaBH₄: 0.2 g/g) is 1.12 g/cm³ by addition relationship of their densities. This is the value we used to calculate the volumetric hydrogen density. The volumetric hydrogen density of NaBH₄ and H₂O including the catalyst is 101 kg H₂/m³, provides 160% more capacity than compressed hydrogen at 70 MPa.

A vehicle powered by FCV requires 5 kg of H₂ for a 500 Km range [25]. The US Department of Energy hydrogen density goals for vehicular hydrogen storage call for systems with 6.5 wt.%, 62 kg H₂/m³ [3]. Our system of compressed hydrogen generation using the chemical hydride is currently only capable of meeting this goal. Although the generation of hydrogen is irreversible, the byproduct, NaBO₂ can be recycled back to NaBH₄ using coke or methane [23]. The very high gravimetric and volumetric hydrogen densities in our chemical hydride system may also be highly effective as a hydrogen storage system for FCUPS or for any emergency power source.

4. Conclusion

The Pt-LiCoO₂ catalyst and high H₂ pressure above 0.6 MPa produced nearly theoretically H₂ yield using stoichiometric amount of water (H₂O/NaBH₄ = 2 mol/mol). The compressed hydrogen generation using chemical hydride may lead to a new H₂ storage technology for FCV and FCUPS.

Acknowledgements

We are greatly indebted to Mr. K. Suzuki and Mr. H. Hayashi and Mr. Y. Isogai for their help and Mr. M. Kimbara, Dr. T. Hioki and Dr. G. J. Shafer for discussions.

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