

Abstract

The storage and generation of hydrogen is a basic problem for its use in fuel cells. Chemical hydrides such as NaBH₄, LiH and NaH are known as high hydrogen containing materials. NaBH₄, in particular, is stable compared with other chemical hydrides, easy to handle and can be synthesized from common natural resources. However, with mixing of NaBH₄ and H₂O at room temperature, only a small amount of the theoretical yield of hydrogen is liberated. In this work, we show that Pt-LiCoO₂ is an excellent catalyst for releasing hydrogen by hydrolysis of

NaBH₄ solution. Using the catalyst with a stoichiometric amount of water (H₂O/NaBH₄: 2 mol/mol) at a high H₂ pressure above 0.6 MPa produced nearly the theoretical H₂ yield. The 10-kW-scale hydrogen generator comprised a storage vessel of NaBH₄ solution, a solution pump, a byproduct storage tank for the NaBO₂ solution, a separator and a hydride reactor. The reactor contained a honeycomb monolith coated with the Pt-LiCoO₂ catalyst. NaBH₄ was synthesized by annealing NaBO₂ with MgH₂ under high H₂ pressure.

Keywords Sodium borohydride, Catalyst, Chemical hydride, Magnesium hydride, Hydrogen generator

水素貯蔵と発生は燃料電池を利用する場合の重要な問題である。NaBH₄,LiHやNaHなどのケミカルハイドライドは水素貯蔵量の多い化合物として知られている。NaBH₄は他のケミカルハイドライドと比べて安定で扱いやすく,一般的な天然資源から合成ができる。ところが,NaBH₄の加水分解反応による水素発生は、ゆっくり進行するために水素発生を促進するための触媒が必要となる。本報告で筆者らはPt-LiCoO₂がNaBH₄の加水分解

旨

要

触媒として高活性になることを見出した。この触 媒と0.6MPa以上の圧力を組み合わせ、9wt%の水 素発生量を達成した。NaBH₄タンク、ポンプ、副 生成物 (NaBO₂) 貯蔵タンク、セパレータとリアク タ (Pt-LiCoO₂を担持したハニカムモノリス) から 構成される 10kWスケールの水素発生システムを 開発した。また、MgH₂を用いて副生成物である NaBO₂をNaBH₄に変換(再生)できた。

キーワード

水素化ホウ素ナトリウム, 触媒, ケミカルハイドライド, 水素化マグネシウム, 水素発生システム

1. Introduction

A fuel cell is a device that continuously converts the chemical energy of hydrogen (H₂) and oxygen (O_2) into electric energy. Since fuel cells have an efficiency much higher than that of conventional combustion engines, a fuel cell vehicle (FCV) is expected to have a high efficiency.¹⁾ A polymer electrolyte fuel cell (PEFC, PEM fuel cell) is the prime power source for FCVs. One of the most widely envisioned sources of fuel for FCVs is H₂ itself. In such a system, it would be necessary to have a storage tank of H_2 to start the system on demand. The first FCVs were produced on December 2, 2002. These FCVs feature a 35 MPa H₂ storage tank and can travel 300-355 km on a full tank. The driving ranges of the vehicles are obviously small compared to those of gasoline vehicles and this represents the biggest hurdle to FCVs. The improvement of this range depends on a new H₂ storage system.

H₂ can be stored in many different forms including as compressed or liquefied H_2 in tanks,¹⁾ by adsorption on activated carbon¹⁻³⁾ and carbon nanotubes,^{1, 4)} as a hydrogen-absorbing alloy,^{1, 5)} as chemical hydrides including NaBH₄,⁶⁻⁸⁾ NaH,⁹⁾ LiH,¹⁰⁾ NaAlH₄,¹¹⁾ MgH₂,¹²⁾ LiBH₄^{13, 14)} and metal nitrides,^{15, 16)} or as organic hydrides (methylcyclohexane, decalin).¹⁷⁾ Among these methods, much attention has recently been given to the hydrolysis of a chemical hydride, in particular, NaBH₄⁶⁻⁸⁾ because of its stability compared with other chemical hydrides and its easy conversion to H_2 by a catalyst. The reaction of NaBH₄ and H_2O is shown as follows.⁶⁾

 $NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \cdots \cdots \cdots (1)$

Under appropriate conditions, 0.213 g of H_2 is liberated per 1 g of NaBH₄, or alternatively, 0.109 g of hydrogen per 1 g of NaBH₄ and 2H₂O. Conventional catalysts are metal halides (NiCl₂, CoCl₂), colloidal platinum, activated carbon, Raney nickel,⁶⁾ Ru supported on ion exchange resin beads⁷⁾ and fluorinated particles of a Mg-based material.⁸⁾

In this review, we first describe in Section 2, hydrogen generation using a catalyst that can achieve a sufficient rate and quantity of H_2 generation in a fuel cell. It is shown that by using

NaBH₄, a stoichiometric amount of water, Pt-LiCoO₂ and a high H₂ pressure, H₂ can be generated in large quantities. In **Section 3**, we describe the development of a 10-kW-scale hydrogen generator using NaBH₄ as the hydrogen storage material and Pt-LiCoO₂ as the catalyst for releasing H₂. In **Section 4**, we demonstrate that NaBO₂ can be recycled back to NaBH₄ using coke.

2. Hydrogen generation using catalysts¹⁸⁾

The H₂ production profiles of reaction of NaBH₄ and water (H₂O/NaBH₄: 210 mol/mol) with or without a catalyst are shown in **Fig. 1**. Without using a catalyst, the amount of H₂ increases with time and approaches a constant conversion value of 7 % because of the increased solution pH. The amount of H₂ generated is increased by using a catalyst. The H₂ generation rates using Pt-LiCoO₂ and Pt-CoO are constant and do not change over time. The stoichiometric amount of H₂ is generated in 15 minutes using the Pt-LiCoO₂ catalyst. The catalysts are not consumed during the hydrolysis and are reusable. Sodium borohydride reacts more than 10 times faster using Pt-LiCoO₂ than the Ru catalyst.⁷⁾

Figure 2 shows a transmission electron micrograph of Pt-LiCoO₂. The dark areas are nano-Pt particles of about 2 nm diameter. The nano-Pt particles are dispersed on the LiCoO₂ substrate. The H_2 generation rate is higher using Pt on LiCoO₂ than on other metal oxide substrates. It is supposed that the high surface area of the nano-Pt particles and the LiCoO₂ surface results in the highest H_2 generation



Fig. 1 H_2 production profiles for reaction of NaBH₄ with water.

rate. The reaction model shows an electron is released through catalyzed oxidation of the BH_4 ion. This electron reduces the H^+ in water and for two such reactions H_2 gas is liberated.

The H_2 yield using the Pt-LiCoO₂ catalyst increases with an increase in water content and is 89 % at a $H_2O/NaBH_4$ molar ratio of 4. An X-ray diffraction intensity curve of the byproduct indicates that the diffraction peaks of the byproduct are from NaBO₂·2H₂O. As such, the reaction is approximated as follows.

 $NaBH_4 + 4H_2O \rightarrow NaBO_2 \cdot 2H_2O + 4H_2 \cdots$ (2) The gravimetric and volumetric H_2 densities of this reaction are 5.3 wt% and 5.4 kg/100 L, respectively, when the weight of water is taken into account.

In a closed pressure vessel, the reaction of NaBH₄ with the Pt-LiCoO₂ catalyst and a stoichiometric amount of water drastically increases the pressure owing to generation of large quantities of H₂ gas due to a synergism of the high H₂ pressure above 0.6 MPa and the catalyst.¹⁹⁾ The gravimetric H₂ density has a maximum value of 9.0 wt% at a catalyst content of 0.2 g/g and a unit weight of NaBH₄. This indicates that the H₂ generation is described by Eq. (1).

Table 1 shows the gravimetric H_2 density of various H_2 storage materials. MgH₂ contains 7.6 wt% of H_2 ,¹⁾ but the dissociation pressure of 1 bar is not at room temperature but at 573 K. The decomposition temperature of NaAlH₄ could be lowered by doping the hydride with a catalyst such as Ti clusters.²⁰⁾ NaAlH₄ requires 373 K to absorb 3.4 wt% H₂ within 7 min at 10 MPa. To date, the highest H₂ absorption and desorption reported for any hydrogen-absorbing alloy is 2.5 wt%.⁵⁾ The best value of H₂ adsorption for carbon materials is 5.1



Fig. 2 TEM of Pt-LiCoO₂ catalyst.

wt% at a temperature of 77 K.²⁾ The hydrolysis of sodium hydride produces H₂ at 4 wt%.⁹⁾ LiH produces a H₂ yield of 34 % upon addition of stoichiometric amounts of water,²¹⁾ which corresponds to a gravimetric H_2 density of 2.6 wt%. In comparison, the gravimetric H₂ density of NaBH₄ is 5.3 wt% by hydrolysis with water.¹⁸⁾ Using the Pt-LiCoO₂ catalyst, hydrolysis of NaBH₄ with a stoichiometric amount of water in a pressure vessel yields more than 2 times the H₂ than the H₂ storage materials mentioned above that are utilized at around room temperature. This table does not include carbon nanotubes because conflicting results have been published concerning the reversible storage of H_2 in carbon nanotubes.^{4, 22)} At an operating pressure of 70 MPa and 298 K, gaseous H₂ can be stored at a volumetric density of 39 kgH₂/m.²³⁾ The volumetric H₂ density of the system including NaBH₄, H₂O and the Pt-LiCoO₂ catalyst is 101 kgH₂/m³, providing 160 % more capacity than compressed H₂ at 70 MPa.

3. Hydrogen generator²⁴⁾

Figure 3 shows a photograph of our generator system. The size of the body is $380 \times 650 \times 800$ mm³. The hydrogen generator is made up of a fuel tank of NaBH₄ solution, a solution pump, a byproduct storage tank for the NaBO₂ solution, a separator (internal volume 4 L) and a hydride reactor (internal volume 2 L). The reactor contains a honeycomb monolith coated with Pt-LiCoO₂ catalyst, as shown in Fig. 3. For the hydrogen

Table 1Gravimetric H_2 densities of various H_2 storage
materials.

Materials	Temperature/K	Gravimetric H ₂ density/wt% (references)
NaBH ₄ +2H ₂ O+Pt -LiCoO ₂ catalyst+high pressure	296	9.0(19)
NaBH ₄ +4H ₂ O	296	5.3(18)
$LiH+H_2O(H_2 \text{ yield: } 34\%)$	Ordinary temperature	2.6(21)
NaH+1.5H ₂ O	Ordinary temperature	4.0(9)
MgH ₂	573	7.6(1)
NaAlH₄	373	3.4(20)
Ti-xV-Cr-Mn		
(x=45 and 55; Ti/Cr/Mn=24:31:10,	313	2.5 (5)
H ₂ pressure: 7-0.01MPa)		
Super activated carbon		
(AX-21, 5 MPa)	298	0.9(2)
(AX-21, 3 MPa)	77	5.1(2)

generator, NaBH₄ solution enters the bottom of the reactor via a pump at 296 K and flows upward through the channel. The solution flow rate is controlled from 25 to 300 mL/min using the pump. Upon contact with the honeycomb monolith, the fuel solution generated H₂ gas and NaBO₂ (in solution) corresponding with a temperature rise. The H₂ gas and the NaBO₂ solution are separated by the separator, which also acts as a small storage buffer for H₂ gas.

When we start pumping the NaBH₄ solution into the Pt-LiCoO₂-coated honeycomb monolith (Pt- $LiCoO_2$: 240 g) in the generator, H_2 gas is generated. After 200 seconds, the H₂ generation rate reaches a constant value. By switching off the pump, the H_2 generation ceases, also in 200 seconds. The response is stable and independent of the concentration and the feed rate. The steady-state H₂ generation rates are shown as a function of the $NaBH_4$ concentration in Fig. 4. As the $NaBH_4$ concentration is increased, the H₂ generation rate linearly increases and reaches a value of 120 NL/min (12 kW) at 25 wt%. Without catalyst in the generator, the H₂ generation rate is 0-1 NL/min. The NaBH₄ solution is quite stable when maintained at a high pH.^{7, 24)} As the NaBH₄ flow rate increases, the H₂ generation rate increases and reaches 120 NL/min at the feed rate of 200 ml/min. The temperature of the byproduct solution increases rapidly inside the reactor due to the highly exothermic reaction.

The gravimetric and volumetric H_2 densities of the generator containing the fuel tank and the byproduct tank are 1.3 wt% and 0.5 kg/100 L, respectively.



Fig. 3 Overview photographs of honeycomb monolith and hydrogen generator.

Assuming that the ratio of weight/volume of the tanks is constant (12 kg/25 L), these densities increase with the size of the fuel tank and the byproduct tank (gravimetric H₂ density: 2 wt%, volumetric H₂ density: 1.5 kgH₂/100 L, fuel tank: 60 kg, 125 L, byproduct tank: 60 kg, 125 L). The volumetric H₂ density is similar to that of a compressed H₂ system at 30 MPa, because storing 1.5 kg of H₂ requires a volume of 100 L at 30 MPa.²³⁾ The volumetric H₂ density was calculated by assuming that the ratio of outer/inner volume is 1.3.

4. Recycling process ²⁵⁾

 $NaBH_4$ can be formed by a reaction of $NaBO_2$ with $CaH_2^{26)}$ or with MgH_2 .^{25, 27)} As CaH_2 vigorously reacts with water and is difficult to handle, attention has focused on MgH_2 . The reaction of $NaBO_2$ and MgH_2 is represented as follows.

 $NaBO_2 + 2MgH_2 \rightarrow NaBH_4 + 2MgO \cdots (3)$ As the standard-free-energy change ΔG° for the reaction is -270 kJ,²⁸⁾ the reaction can proceed spontaneously. $NaBH_4$ is synthesized by annealing a mixture of the byproduct $NaBO_2$ and MgH_2 under high H₂ pressure. Temperature desorption scans, infrared absorption²⁹⁾ and X-ray diffraction measurements indicate that annealing of the substrate mixture under a high H₂ pressure produces $NaBH_4$ and MgO.

Figure 5 shows the NaBH₄ yield as a function of temperature. As the temperature increases, the yield increases and has a maximum value of 97 % at 823 K (pressure; 7 MPa). Figure 5 also shows the



Fig. 4 Influence of NaBH₄ solution concentration on steady-state H₂ generation rate.

hydrogen desorption curve of MgH₂. There is prominent desorption centered at 733 K. The observed decrease of the yield above 823 K is attributed to the melting of NaBH₄ (778 K).²⁹⁾ The yield increases with pressure and approaches a constant value of 97 % at 7 MPa and 823 K. When NaBO₂ is mixed with magnesium, the yield is only 10 % and is much lower than that using MgH₂ as shown in Fig. 5. The low reactivity is probably due to agglomeration of Mg particles at 823 K.

The recycling of NaBH₄ is shown in **Fig. 6**. This process uses coke and NaBO₂ and can be described by a combination of Eq. (3) and the following general reactions.^{30, 31)}

$NaBO_2 \cdot 2H_2O \rightarrow NaBO_2 + 2H_2O \ (>550 \text{ K}) \cdot \cdot (4)$
$2CO + 2H_2O \rightarrow 2CO_2 + 2H_2 \text{ (Fe}_2O_3\text{-}Al_2O_3$
catalyst, 473-773 K)(5)
$2Mg + 2H_2 \rightarrow 2MgH_2$ (H ₂ pressure, 523-673 K)
(6)
$2MgO + Si \rightarrow 2Mg + SiO_2$ (pressure < 0.1 Pa,
1473 K) · · · · · · · · · · · · · · · · · ·
100



Fig. 5 Influence of temperature on NaBH₄ yield (7MPa, 2h) and temperature desorption scan of MgH₂.



Fig. 6 Recycling process of NaBH₄.

 $SiO_2 + 2C \rightarrow Si + 2CO \text{ (arc furnace >1800 K)}$(8)

Reactions (3)-(8) combine to produce

 $NaBO_2 \cdot 2H_2O + 2C \rightarrow NaBH_4 + 2CO_2 \cdots (9)$ If this is combined with the onboard hydrogen generation reaction (Eq. (2)), the overall reaction is

 $2C + 4H_2O \rightarrow 2CO_2 + 4H_2 \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (10)$

Thus, $NaBO_2$ can be recycled back to $NaBH_4$ using coke at a high temperature above 1800 K. This corresponds to a low energy efficiency.

5. Conclusions

We have developed H₂ storage and generation using a chemical hydride. Pt-LiCoO₂ synthesized using the conventional impregnation method was an excellent catalyst for releasing H₂ from the stabilized NaBH₄ solution, and a 10-kW-scale hydrogen generator that generates high purity H₂ gas from aqueous solutions of NaBH₄ was developed. NaBH₄ was synthesized by annealing a mixture of $NaBO_2$ with MgH₂ under high H₂ pressure. NaBO₂ could be recycled back to NaBH₄ using coke at high temperature. As the energy efficiency of the recycling process is low, the very high gravimetric and volumetric H_2 densities in the chemical hydride system may be highly effective as a H₂ storage system for a fuel cell uninterrupted power supply (FCUPS) or for any emergency power source.

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