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Development of 10 kW-scale hydrogen generator using chemical hydride

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Abstract

We have developed a hydrogen generator that generates high purity hydrogen gas from the aqueous solution of sodium borohydride, $NaBH_4$. This paper discussed the performance testing of the hydrogen generator using a Pt-$LiCoO_2$-coated honeycomb monolith. The $NaBH_4$ solution hydrolyzed to generate H_2 and sodium metaborate when it contacted the monolith. The gravimetric and the volumetric H_2 densities of the system were 2 wt.% and 1.5 kg H_2/100 l, respectively. The volumetric density was similar to that of the compressed H_2 at 25 MPa. The hydrogen generator successfully provided a maximum H_2 generation rate of 120 nl/min. Assuming a standard PEM (polymer electrolyte fuel cell, PEFC) fuel cell operated at 0.7 V, generating 120 nl/min was equivalent to12 kW.

Keywords: Sodium borohydride; Chemical hydride; Hydrogen generator; Catalyst; Hydrogen; Fuel cell

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 such a fuel cell has efficiency much higher than that of conventional combustion engines, a fuel cell vehicle (FCV) is expected as a car having 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). 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.

H_2 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, attention has been given to the hydrolysis of a chemical hydride such as $NaBH_4$ [10–18] because of the large theoretical H_2 content of 10.9 wt.%. $NaBH_4$ is stable compared with other chemical hydrides and is easy to handle. At room temperatures, only a small percentage of the theoretical amount of H_2 was liberated by hydrolysis reaction of $NaBH_4$ and H_2O [14,22], but the hydrolysis is enhanced by using catalysts. Conventionally known catalysts are metal halides, colloidal platinum, activated carbon, Raney nickel [10], fluorinated Mg-based hydride [16] or 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 H_2 by hydrolysis of $NaBH_4$ solution [22]. The catalyst produced 100% of the theoretical amount of H_2 using excess water ($H_2O/NaBH_4 = 210$ mol/mol). Furthermore, it was demonstrated that $NaBO_2$ was recycled back to $NaBH_4$ using coke or methane [23]. In this paper, we have constructed a 10 kW-scale hydrogen generator using $NaBH_4$ as the hydrogen storage material and Pt-$LiCoO_2$ as the catalyst for releasing H_2. The system produced a maximum H_2 generation rate of 120 nl/min.

2. Experimental

2.1. Materials

Sodium borohydride (Rohm and Haas, $NaBH_4$) was used for the reaction with water. The reaction of $NaBH_4$ and H_2O is shown as follows [10]:

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

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The $NaBH_4$ solution hydrolyzes to yield H_2 gas and sodium metaborate ($NaBO_2$). In our system, Pt-$LiCoO_2$ catalyst was selected based on our previous results [22]. We investigated various metal catalysts coated on a metal oxide and found that Pt-$LiCoO_2$ worked as an excellent catalyst for releasing H_2 from the $NaBH_4$ solution. The Pt-$LiCoO_2$ catalyst was synthesized using a conventional impregnation method as described in the previous paper [22]. Dinitrodiammine platinum(II) nitric acid solution ($Pt(NO_2)_2(NH_3)_2$, 33 ml, Pt content of 50 g/l, Tanaka Kikinzoku Kogyo K.K., Japan) and lithium cobaltate powder ($LiCoO_2$, 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-$LiCoO_2$ catalyst contained a Pt content of 1.5 wt.%.

The hydride reactor of our hydrogen generator contains a honeycomb monolith of 150 mm in length and 130 mm in diameter coated with Pt-$LiCoO_2$ (monolith: 808 g; Pt-$LiCoO_2$: 240 g; Al_2O_3: 60 g). The Pt-$LiCoO_2$-coated monolith was prepared by the following method. Pt-$LiCoO_2$ (1000 g), Al_2O_3 sol (620 g, Al_2O_3 20 wt.%) and water (125 g) were mixed with an attritor. A cordierite monolith was dipped into the slurry. After removing the slurry, the monolith was dried at 393 K for 24 h. The dried monolith was calcined for 3 h in air at 723 K. The features of the monolith are Pt-$LiCoO_2$ loading of 0.30 g per 1 g substrate, 400 cells per square inch with 21% blockage resulting in a single channel diameter of approximately 1.2 mm.

2.2. Hydrogen generator

A general schematic diagram for our hydrogen generator is shown in Fig. 1. The hydrogen generator is made up of a fuel tank for a $NaBH_4$ solution, a pump for the solution, the byproduct ($NaBO_2$) solution storage tank, a separator (internal volume 4 l) and a hydride reactor (internal volume 2 l). The material of the fuel tank, the byproduct tank, the separator, the reactor and the piping material were SUS 304 stainless steel. The reactor contained a honeycomb monolith coated with Pt-$LiCoO_2$ catalyst. Fig. 2 shows the overview photograph of our generator. The size of the body is 380 mm × 650 mm × 800 mm.

The amounts of H_2 generated using the generator were determined as follows. For the hydrogen generator, $NaBH_4$ solution (3.8–25 wt.%) entered the bottom of the reactor contained the honeycomb monolith via a pump at 296 K and flowed upward through the channel. The solution flow rate was controlled from 25 to 300 ml/min using the pump. By contacting the honeycomb monolith, the fuel solution generated H_2 gas and $NaBO_2$ (in solution) with a temperature rise. The outlet temperature was measured directly behind the monolith exit of the reactor using a thermocouple. The H_2 gas and the $NaBO_2$ solution were separated by the separator, which also acted as a small storage buffer for H_2 gas. The H_2 generation rate was detected by a Micro Motion flow meter (CMF010) consist of Corioli's sensor and a microprocessor-based transmitter which installed behind the separator.

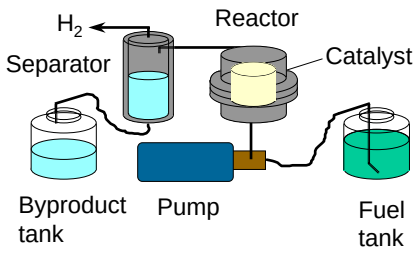

Fig. 1. Schematic diagram of hydrogen generator.

Fig. 2. Overview photograph of hydrogen generator.

2.3. Characterization

Crystalline structure of the byproduct by the hydrolysis reaction of $NaBH_4$ was investigated by wide angle X-ray diffraction. The X-ray diffraction pattern was recorded at room temperature by using a Rigaku Denki Rad-B over a range of diffraction angle (2θ) from 3 to 80° with Cu Kα radiation (30 kV, 30 mA) filtered by a monochrometer.

3. Results and discussion

The H_2 generation rate as a function of time for 3.8 wt.% $NaBH_4$ solution and constant feed of 300 ml/min is shown in Fig. 3. When we start feeding the $NaBH_4$ solution into the Pt-$LiCoO_2$-coated honeycomb monolith of the generator

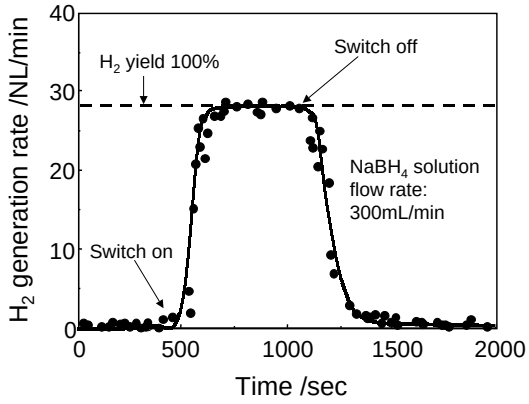

Fig. 3. Response of hydrogen generator.

by switching on the pump, the H_2 gas starts to generate. After 200 s, the H_2 generation rate reaches a constant value of 27 nl/min. By switching off the pump, the H_2 generation ceases in 200 s. The response is stable and independent of the concentration and the feed rate.

The H_2 generation rate (V_h, nl/min) at the H_2 yield of 100% was determined by the following equation:

$$V_h = (0.213 W_s V_s d) \times 11.2 = 2.39 W_s V_s d \quad (2)$$

where W_s (wt.%) is the concentration of $NaBH_4$, V_s (ml/min) is the $NaBH_4$ solution flow rate, and d (g/cm^3) is the density of the $NaBH_4$ solution. The densities of $NaBH_4$, water and NaOH are 1.07 [24], 1.00 [24] and 2.13 g/cm^3 [24], respectively. We calculated the density of the $NaBH_4$ solution by addition relationship of their densities. The values of 0.213 and 11.2 are the theoretical amount of H_2 generated per unit weight of $NaBH_4$ and the volume (nl) occupied by the 1 g of H_2 at STP (273 K, 1 atm), respectively. The dotted line in Fig. 3 is the H_2 generation rate at the H_2 yield of 100%. We found that all $NaBH_4$ is consumed by heterogeneous reactions on the catalytic Pt-$LiCoO_2$ coating. Without the catalyst in the generator, the H_2 generation rate was 0–1 nl/min. The $NaBH_4$ solution is quite stable when maintained at a high pH [17,18]. In our experiment, H_2 did not generate above and including 4 wt.% NaOH (pH 14) at temperatures below 323 K.

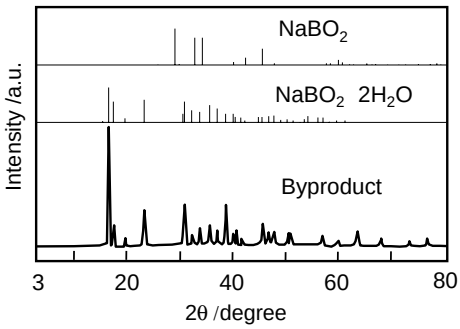

Fig. 5. X-ray diffraction intensity curve of byproduct.

The H_2 generation rate was measured in 4 wt.% NaOH and 8.6–25 wt.% $NaBH_4$ water solution. The steady-state H_2 generation rates as a function of the $NaBH_4$ concentration are shown in Fig. 4. As the $NaBH_4$ concentration is increased, the H_2 generation rate linearly increases and reaches a value of 120 nl/min at 25 wt.%. Amendola et al. reported that as weight percent NaOH increased, H_2 generation rate decreased [18]. But, the H_2 generation rate using our generator is independent of the NaOH concentration as shown in Fig. 4. This may be due to the fact that the Pt-$LiCoO_2$ catalyst has high activity. It is also noted in Fig. 4 that 100% of the stoichmetric amount of H_2 was generated by the reactor as long as the concentration is below 25 wt.% and the H_2 generation rate is below 120 nl/min. X-ray diffraction was used to estimate the structure of the byproduct obtained from the solution ($NaBH_4$ concentration: 25 wt.%). Fig. 5 illustrates the X-ray diffraction intensity curve of the byproduct together with those of $NaBO_2$ [25] and $NaBO_2 \cdot 2H_2O$ [26]. The diffraction peaks of the byproduct are from $NaBO_2 \cdot 2H_2O$, as shown in the figure.

Fig. 6 shows the effect of the $NaBH_4$ solution flow rate on the steady-state H_2 generation rate and the outlet temperature at the 25 wt.% $NaBH_4$ and 4 wt.% NaOH solution.

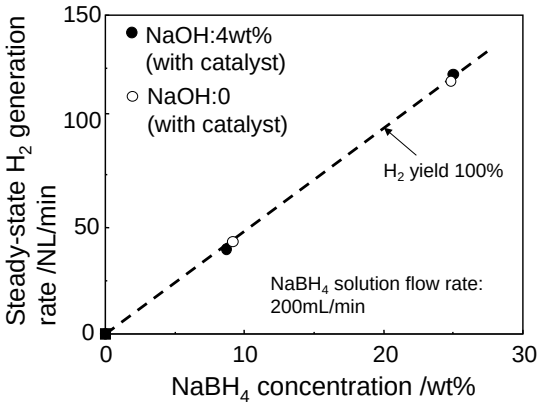

Fig. 4. Influence of $NaBH_4$ solution concentration on steady-state H_2 generation rate.

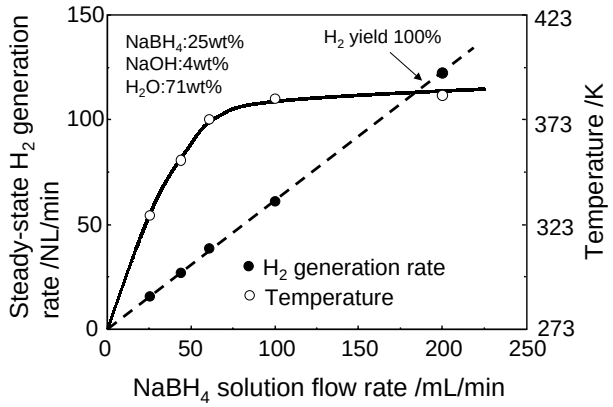

Fig. 6. Influence of $NaBH_4$ solution flow rate on steady-state H_2 generation rate.

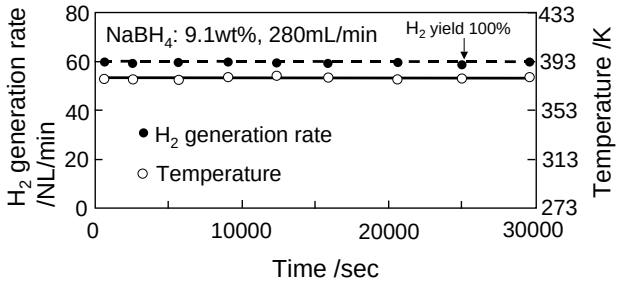

Fig. 7. Durability of hydrogen generator.

As the $NaBH_4$ flow rate increases, the H_2 generation rate increases and reaches 120 nl/min at the rate of 200 ml/min. The temperature of the byproduct solution increased rapidly inside the reactor due to the high exothermic reaction [22]. This temperature was measured directly behind the monolith. After the $NaBH_4$ solution was fed, the temperature increased and had a constant value when the flow rate was constant. The temperature increases with the $NaBH_4$ flow rate and shows a value of 384 K at 200 ml/min.

Temperature dependencies of the solubility of $NaBH_4$ and $NaBO_2$ were determined by visual observation. In our experiment, the solubility of $NaBO_2$ and $NaBH_4$ is shown as follows:

$$\text{solubility of } NaBH_4\ (\text{g}/100\,\text{g water}) = -261 + 1.05T \quad (3)$$

$$\text{solubility of } NaBO_2\ (\text{g}/100\,\text{g water}) = -245 + 0.915T \quad (4)$$

where T is the temperature (K).

Eqs. (3) and (4) indicate that the solubility of $NaBO_2$ decreases compared with that of $NaBH_4$ and the concentration of $NaBH_4$ should be below 26 wt.% at 333 K in order to keep the byproduct ($NaBO_2$) a solution state.

Durability is one of the major criteria for the generator. Fig. 7 shows the outlet temperature of the byproduct solution and the steady-state H_2 generation rate as a function of time. The generator shows during 30,000 s no decrease of the H_2 generation rate. At the steady-state, the temperature of the byproduct solution is 373 K for the following conditions: $NaBH_4$ solution feed 280 ml/min, $NaBH_4$ concentration 9.1 wt.%.

Table 1 shows the specification of our hydrogen generator. The gravimetric and the 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. Assuming that the ratio of weight/volume of the tanks is constant (12 kg/25 l), those densities increase with the size of the fuel tank and the byproduct tank (gravimetric H_2 density: 2 wt.%; volumetric H_2 density: 1.5 kg H_2/100 l; fuel tank: 60 kg, 125 l; byproduct: 60 kg, 125 l). The volumetric H_2 density is similar to that of a compressed H_2 system at 25 MPa, because to store 1.3 kg of H_2 requires a volume of 100 l at 25 MPa.

Table 1
Specification of hydrogen generator

Hydrogen (nl/min)	120
Fuel flow (nl/min)	200
Body size	380 mm × 650 mm × 800 mm 197.6 l
Weight (kg)	80
Tank size	Fuel tank (25 l, 12 kg) Byproduct tank (25 l, 12 kg)
Gravimetric hydrogen density (wt.%)	1.3–2.0
Volumetric hydrogen density (kg/100 l)	0.5–1.5
Fuel content: $NaBH_4$ (wt.%)	25
Catalyst: Pt-$LiCoO_2$ (g)	240

The volumetric H_2 density was calculated by assuming that a ratio of outer/inner volume is 1.2 [3,27].

We can estimate power levels using our system. Assuming a standard PEM (PEFC) fuel cell operating at 0.7 V, generating 120 nl/min (0.18 g H_2/s) is equivalent to 12 kW ($0.18\,\text{mol/s} \times 96{,}500\,\text{C/mol} \times 0.7\,\text{V} = 17\,\text{kA} \times 0.7\,\text{V}$). Our hydrogen generator is used to power a specially designed 10 kW H_2/air PEM fuel cell. The fuel cell consumes $NaBH_4$ and generates $NaBO_2$ solution. The high gravimetric and volumetric H_2 densities in our chemical hydride system without using high H_2 pressure may be highly effective as a H_2 storage system for FCV, FCUPS or for any emergency power source.

4. Conclusions

We have developed a 10 kW-scale hydrogen generator that generates high purity H_2 gas from aqueous solutions of $NaBH_4$. The generator was made up of a fuel tank for the $NaBH_4$ solution, a pump for the solution, the byproduct ($NaBO_2$) solution storage tank, a separator and a hydride reactor. The reactor contained a honeycomb monolith coated with Pt-$LiCoO_2$ catalyst. The maximum H_2 generation rate was 120 nl/min. The gravimetric and the volumetric H_2 densities of the system were 2 wt.% and 1.5 kg/100 l, respectively.

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