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## 수소 발생 시스템을 위한 NaHCO<sub>3</sub> Agents를 이용한 고체 NaBH<sub>4</sub> 가수분해 장치

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Solid-state NaBH<sub>4</sub> Hydrolysis Device using NaHCO<sub>3</sub> Agents for Hydrogen Generation System

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## ABSTRACT

## Solid-state NaBH<sub>4</sub> Hydrolysis Device using NaHCO<sub>3</sub> Agents for Hydrogen Generation System

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중탄산나트륨(NaHCO<sub>3</sub>)를 이용하여 고체 상태의 붕소화수소나트륨(NaBH<sub>4</sub>)을 가 수분해를 통해 수소를 생산하는 것과 이것을 통해 시스템을 제작하는 것을 연 구하였다. 온도, 주입되는 용액의 농도와 속도와 같은 다양한 조건을 기준으로 수소가 생성되는 속도를 측정하였다. 수소의 생성 속도와 붕소화수소나트륨의 전환율의 증가는 중탄산나트륨 수용액의 농도의 증가와 관계가 있었다. 그러나 8wt.% 이상의 농도에서는 감소하였다. 이것들을 결과로 하여 프로토 타입의 수 소 발생기를 개발하였다. 시스템은 붕소화수소나트륨이 들어갈 반응기, 중탄산 나트륨을 저장할 탱크, 유체 펌프, 밸브, 냉각 팬 그리고 주입기로 구성되어있 다. 유체 펌프는 붕소화수소나트륨이 들어있는 반응기에 중탄산나트륨 수용액 을 주입기를 이용하여 주입한다. 반응기의 온도와 압력은 관측을 통하여 70도 와 2기압을 유지하도록 한다. 반응기의 압력이 2 기압을 초과하게 되면 유체 펌프의 동작은 정지하며 반응기의 압력이 2 기압 아래에서 시스템이 동작 할 수 있도록 한다. 연료전지가 작동할 수 있는 압력은 2 기압 아래이기 때문에 이와 같은 압력을 정하였고 제작된 수소 발생 시스템을 통해 안정적으로 수소 를 연료전지에 공급할 수 있었다.





#### 1. Research background

Recently, as the necessity of portable and unmanned autonomous systems is emphasized, a power source to activate systems has begun to be important. However, currently available lithium-ion batteries has a low energy density of 200 W/kg, which causes the operating duration to be limited, in spite of their advantages such as easy use and high mobility. If, for example, the lithium-ion battery is used to operate an unmanned aerial vehicle, its energy density is too low to provide the mission duration of 1 hour.

Thus, an energy storage system that is easy to used like a lithium-ion battery and has a high energy density is needed to resolve the above problem. A fuel cell is suitable to meet this requirement. The fuel cell has an energy conversion efficiency higher than 90% because hydrogen is directly converted into electric energy and a high energy density can be realized if hydrogen can be stored in a high storage density as shown in Fig. 1.

However, hydrogen is one of the gas that is very difficult to be stored. That is why it is the lightest and smallest molecule in all of substances. A variety of the hydrogen storage method has been developed as presented in Table 1.

Compressed hydrogen, liquefied hydrogen, metal hydride, and carbon nano-tube have been developed as a hydrogen storage method. However, they are still not suitable due to their low hydrogen storage density and a high cost. therefore, other alternatives are being considered except for the above methods and among them one of the premising method is hydrogen chemical hydride.

The chemical hydride has a high hydrogen storage density compared to other hydrogen storage methods. When compared it with the 2015 DOE target as shown in Fig. 2, the chemical hydride has a superior hydrogen content rather than other hydrogen storage methods.





Among a variety of chemical hydrides, sodium borohydride (NaBH<sub>4</sub>), which has a hydrogen storage density of 10.8 wt.%, is a non-toxic and stable compound, and hydrogen can be simply extracted by a hydrolysis.

Therefore, a hydrogen generation was tried by NaBH<sub>4</sub> hydrolysis to supply hydrogen to a fuel cell in the present study. Aforementioned, hydrogen can be extracted from NaBH<sub>4</sub> hydrolysis. However, when water was reacted only with NaBH<sub>4</sub>, the reaction rate was too slow to generate hydrogen enough to operate a fuel cell. They include catalytic hydrolysis, decomposition by acids, and steam hydrolysis.

The catalytic hydrolysis has a rapid ad stable hydrogen generation rate but the borate that is a byproduct can be covered on the surface of catalysts, which leads to the catalyst deactivation. The borate deposition on the catalyst surface as the reaction time elapsed is shown in Fig. 3.

In addition, a high expense and time are necessary to prepare catalysts and its storability is not good in terms of specific volume because the NaBH<sub>4</sub> is stored in a liquid state.

The way using acids is suitable for a good storability because the NaBH<sub>4</sub> is stored in a solid state and used to react with acids as it is itself. In addition, the acids as a reacting agent can be easily prepared and can accelerate the hydrogen generation rate rapidly when acids are injected on the NaBH<sub>4</sub> particles. However, it is difficult to handle due to corrosion caused by its strong acidity and to select components that are resistive to expose to acids.

The steam hydrolysis has a high hydrogen generation rate because the reaction takes place at the high temperature that is a boiling point of water. However, complex device to generate the steam such as a heater, water tank, and other devices makes the system bulky and heavy so that it is not suitable to unmanned aerial vehicle applications as shown in Fig. 4. Therefore, the NaBH<sub>4</sub> hydrolysis using a solution with natural pH as the solid NaBH<sub>4</sub> is used as itself is





proposed in the present study. The advantages of the above NaBH<sub>4</sub> hydrolysis methods are present in Table 2. Amon them, the NaBH<sub>4</sub> hydrolysis using sodium bicarbonate (NaHCO<sub>3</sub>) solution was studied in the present study.





Fig. 1 Energy Efficiency



Fig. 2 Chemical hydride of Density







Fig. 3 NaBO2 deposition (A) Fresh catalyst < (B) < (C) < (D) Used catalyst



Fig. 4 Schematic of the steam hydrolysis reactor system





Tech.	H2 storage densitiy(wt.%)
Compressed	2.5 ~ 4 (300 ~ 700 bar)
Liquefied	5 ~ 7
Metal hydride	2.3 ~ (7.3)
Carbon/MOF	3.3 ~ (7)

Table. 1 hydrogen of storage method





1 a	rable. 2 Companison between method				
	Simplicity	Durability	Safety		
Catalytic hydrolysis	Х	Х	0		
Steam ydrolysis	Х	0	Х		
Acid catalyst	0	0	Х		
NaHCO <sub>3</sub>	0	0	0		

Table. 2 Comparison between method





#### 2. Introduction

Hydrogen has been recognized as an alternative to the existing fossil fuels. First, storage method of hydrogen should be developed to be utilized practical applications. Compressed tank, liquefaction, for and metal hydrides are currently available, which have merits but involve demerits as well. Although it is different in storage density according to the material of the tank, the compressed tank has approximately 13 wt.% storage density of hydrogen, by which hydrogen of 33 kg  $H_2/m^3$  can be stored in maximum[1-4]. However, the high charging pressure of 875 bar is required for the above storage density [3,4]. The liquefaction can store hydrogen without loss but requires the low temperature below 21 K, which makes system bulky due to refrigeration equipment and the energy requirement in the process for the liquefaction [5,6]. In addition, the metal hydride is relatively easier to store and release hydrogen than liquefied and compressed hydrogen but it is too heavy to increase the hydrogen storage density [7]. Compared to the aforementioned methods for the hydrogen storage, chemical hydride is relatively easy to be stored as it has a high hydrogen density and hydrogen can be extracted by a hydrolysis immediately when needed. That is why the chemical hydride has been highlighted as a promising hydrogen storage method [8-10].

Sodium borohydride (NaBH<sub>4</sub>) is used most commonly among the many chemical hydrides. The NaBH<sub>4</sub> can be stored in the liquid and solid state according to the way to extract hydrogen. Generally, catalysts should be used to hydrolyze NaBH<sub>4</sub> in the liquid state, while acid solutions can be used to decompose NaBH<sub>4</sub> in the solid state. First, the NaBH<sub>4</sub> is dissolved in water and the aqueous solution is stored in a fuel tank. Hydrogen can be extracted stably by catalytic hydrolysis when needed. However, it is still problematic in terms of catalyst durability and byproduct disposal. Particularly, sodium metaborate (NaBO<sub>2</sub>) is produced after the hydrolysis, which can be covered on the surface of catalyst, resulting in the serious deactivation of catalyst.





Hydrogen can be extracted directly from solid-state NaBH<sub>4</sub> without the catalyst to avoid above problems of the catalytic hydrolysis. It has been reported that acid solutions such as HCI and H2SO4 could be used to hydrolyze the solid NaBH<sub>4</sub> [11,12]. However, these strong acids have difficulties in storage and handling. Particularly, HCl solution is quickly vaporized so the HCI vapor causes leakage and corrosion. In addition, hydrogen can contain sodium (Na) produced after the reaction, resulting in contaminating fuel cell electrocatalysts [13]. The NaBH<sub>4</sub> hydrolysis is possible to be activated by adding water on the solid NaBH<sub>4</sub> instead of acids but the reaction will be too slow to produce hydrogen quickly when needed. Steam can be used to accelerate the reaction but the steam generator is bulky and energy consuming, which makes the system less effective [14,15]. Hence, a new hydrolysis agent is required, which should be safe and easy enough to carry, not storing acids. In the present study, a hydrogen generation from solid-state NaBH<sub>4</sub> particles using sodium bicarbonate (NaHCO<sub>3</sub>) solution was proposed The NaHCO<sub>3</sub> solution has a neutral pH so that it is more stable in storage and handling, harmless on a human body and environmentally friendly compared to methods using acids. In addition, the NaBH<sub>4</sub> hydrolysis reaction can be accelerated by using the NaHCO<sub>3</sub> solution instead of water and steam.

In the present study, NaHCO<sub>3</sub> was used as a catalytic solution and the NaBH<sub>4</sub> solid particles were stored in a reacting chamber. The effect of the temperature, NaHCO<sub>3</sub> concentration and injection speed on the rate of hydrogen production was investigated. In addition, a prototype of hydrogen generation system based on the hydrolysis of the solid-state NaBH<sub>4</sub> using the NaHCO<sub>3</sub> solution was developed and the operation stability was evaluated.





Table. 3 Composition of gas product of the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> agent.

	Concentration (mol %)
$H_2$	99.9512
СО	0.0017
$CO_2$	0.0471





## 3. Experiment

#### 3.1 Methods

NaBH₄ (97%, DAE JUNG, Korea) and NaHCO3 (99%, SAM CHUN, Korea) were purchased. The NaHCO<sub>3</sub> solution was used as the agent to accelerate the hydrolysis of the solid NaBH<sub>4</sub>. Reaction setup was prepared to investigate the reaction characteristics of the solid NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> solution as shown in Fig. 5. The reaction was performed in a water bath to control the reaction temperature due to the exothermic nature of NaBH4 hydrolysis. The NaHCO<sub>3</sub> solution was precisely injected on the solid NaBH<sub>4</sub> particles using a syringe pump. After the reaction, water vapor was separated through a moisture trap and the hydrogen flow rate was measured by a volumetric flow meter (VFM, TSM-110). The saturation solubility of NaHCO<sub>3</sub> solution is 8.8 wt.% at 25°C. When the solubility higher than 8.8 wt.%, NaHCO<sub>3</sub> precipitates can be extracted as the temperature decreased down to  $25^{\circ}$  C. Therefore, the concentration of NaHCO<sub>3</sub> solution was selected below its solubility such as 4, 5, 6, 7, and 8 wt.%. In addition, the reaction temperature range of 50-80°C was selected as control parameters for the reaction test. Furthermore, the optimal NaBH<sub>4</sub>/NaHCO<sub>3</sub> reaction ratio and the reaction rate constant were found.







Fig. 5 Schematic of experimental setup





#### 3.2. Analysis of hydrolysis products

The NaBH<sub>4</sub> hydrolysis generates hydrogen only as a gaseous product and NaBO<sub>2</sub> as a byproduct in the liquid state after being dissolved by the excessive water (x) as shown in Eq. 1.

$$NaBH_4 + (2+x)H_2O \rightarrow NaBO_2 + 4H_2 + xH_2O \tag{1}$$

When NaHCO<sub>3</sub> is reacted with NaBH<sub>4</sub>, however, the reaction mechanism would be different with the catalytic hydrolysis. Thus, the gas composition of products should be analyzed because CO and CO<sub>2</sub> can be formed from NaHCO<sub>3</sub>. The gaseous product was analyzed using gas chromatography (YL6100 GC). The analysis was repeated five times for accuracy. Nitrogen was used as a carrier gas of gas products.

X-ray diffractometer (XRD, D/MAX-3C, Rigaku) and mid-infrared spectroscopy (MID-IR, Nicolet6700, Sinco) were used to reveal the role of NaHCO<sub>3</sub> in the NaBH<sub>4</sub> hydrolysis. For comparisons, six samples were prepared: i) pure NaBH<sub>4</sub>, ii) pure NaHCO<sub>3</sub>, iii) products after the NaBH<sub>4</sub> hydrolysis without NaHCO<sub>3</sub>, iv) products after the NaBH<sub>4</sub> hydrolysis with NaHCO<sub>3</sub>, v) products after the NaHCO<sub>3</sub> solution is dried, and iv) products after the NaHCO<sub>3</sub> hydrolysis by heating at 90° C.

#### 3.3. Hydrogen generation system

Based on the parametric study on the characteristic of solid NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> agent, a prototype of the hydrogen generation system was developed to verify possibility to be utilized for practical applications such as portable generators. The solid NaBH<sub>4</sub> hydrolysis was relatively difficult to control the hydrogen generation rate compared to the catalytic hydrolysis from the NaBH<sub>4</sub> solution. For example, if a fixed-bed reactor is used for this reaction, the excessive reaction will take place because the NaHCO<sub>3</sub> solution is supplied continuously on the NaBH<sub>4</sub> that is fixed in the







reactor. Thus, the excessive reaction causes the NaHCO<sub>3</sub> solution to be evaporated due to the heat of reaction, which makes it difficult to control the hydrogen generation rate. Thus, the hydrogen generation system should be developed considering how to control stably the hydrogen generation rate. The conceptual schematic of the hydrogen generation system is shown in Fig. 6. The NaHCO<sub>3</sub> solution was injected into the reactor in which the NaBH<sub>4</sub> particles were placed. The NaHCO<sub>3</sub> injection rate was controlled to control the reaction. The generated hydrogen was pressurized temporarily in the reactor and the pressure was released using a solenoid valve to supply hydrogen when needed. The controller was programmed to control the on-off time of the pump and the valve to be open or closed according to the reactor pressure. The NaHCO<sub>3</sub> solution was injected again to generate hydrogen until the pressure reaches the predetermined value. Finally, the hydrogen pressure was regulated to be supplied to the fuel cell.







Fig. 6 Schematic of the hydrogen generation system





### 4. Results and discussion

#### 4.1. Effect of NaHCO<sub>3</sub> concentration

The hydrogen generation rate and hydrogen yield of the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> solution according to the performance parameter as shown in Fig. 7. The effect of the NaHCO<sub>3</sub> concentration of the hydrogen generation rate and hydrogen yield is shown in Fig. 7(a). The NaHCO<sub>3</sub> solution was injected on the solid NaBH<sub>4</sub> particles at different concentrations of 4, 5, 6, 7, and 8 wt.%. The injection rate of NaHCO<sub>3</sub> and the amount of NaBH<sub>4</sub> were fixed to 20 ml/h and 1 g at all reactions.

The hydrogen yield indicates the percentage ratio of the actual amount of hydrogen generation to the theoretical one. The theoretical amount of hydrogen possible to be generated from the stoichiometric hydrolysis is 2588 ml per NaBH<sub>4</sub> of 1 g at 25° C. The hydrogen generation rate and hydrogen yield increased in linearly proportional to the NaHCO<sub>3</sub> concentration. It means that the HCO<sub>3</sub><sup>-</sup> and OH<sup>-</sup> ions in the NaHCO<sub>3</sub> solution could accelerate the hydrolysis rate of NaBH<sub>4</sub>. At the high concentration of NaHCO<sub>3</sub>, more ions would be working for the NaBH<sub>4</sub> hydrolysis. The effect of the ions on the NaBH<sub>4</sub> hydrolysis is discussed in the section of 3.5. Even though the highest NaHCO<sub>3</sub> concentration was used, the hydrogen yield was approximately 74% for a single injection of NaHCO<sub>3</sub> solution. The remaining NaBH<sub>4</sub> can be used for the next injection so that 100% of NaBH<sub>4</sub> is utilized.







Fig. 7 Hydrogen generation rate and hydrogen yield of the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> solution according to the performance parameter : (a) Effect of the NaHCO<sub>3</sub> concentration, (b) Effect of the NaBH<sub>4</sub>/NaHCO<sub>3</sub> reaction ratio, (c) Effect of the NaHCO<sub>3</sub> injection rate, and (d) Effect of the temperature.





#### 4.2. The effect of $NaHCO_3/NaBH_4$ reaction ratio

The greater than 2 moles of  $H_{20}$  (x+2) is required to hydrolyze completely 1 mole of NaBH4 as shown in Eq. 1. The excessive water (x) does not participate in the hydrolysis and causes the hydrogen storage density to decrease. Thus, the reaction ratio of the NaHCO<sub>3</sub> solution to unit mass of NaBH<sub>4</sub> is an important parameter to determine the hydrogen storage density. The reaction ratio was varied by increasing the amount of NaHCO3 solution but the amount of NaBH<sub>4</sub> and the NaHCO<sub>3</sub> concentration were fixed to 1 g and 6 wt.%, respectively. The hydrogen generation rate and hydrogen yield as a function according to the NaHCO<sub>3</sub>/NaBH<sub>4</sub> reaction ratio is shown in Fig 7(b). When the reaction ratio was less than 1, the hydrogen was not generated properly and the reaction stopped after a few minutes. At the reaction ratio greater than 1, the hydrogen yield increased with increasing the reaction ratio. The hydrogen generation rate also increased in proportion to the reaction ratio of 1-4 but maintained its value at the reaction ratio higher than 5. The hydrogen generation rate reached maximum when 6 wt.% NaHCO<sub>3</sub> was used. At that time, the hydrogen generation rate per unit weight of  $NaHCO_3$  was 1750 ml/min-g. This value is comparable with those obtained with solid state catalysts (220-1170 ml/min-gcatalyst) [16-17].

#### 4.3. The effect of NaHCO<sub>3</sub> injection rate

The hydrogen generation rate and hydrogen yield according to the NaHCO<sub>3</sub> injection rate is shown in Fig 7(c). The injection rate of NaHCO<sub>3</sub> solution was varied into 10, 20, 30, 40 ml/h. The amount of NaBH<sub>4</sub> and the NaHCO<sub>3</sub> concentration were fixed to 1 g and 6 wt.%, respectively. The hydrogen generation rate at 30 ml/h was six times faster than that at 10 ml/h. At the injection rate of 40 ml/h, however, the hydrogen generation rate decreased even if the NaHCO<sub>3</sub> solution was injected faster. The hydrogen yield increased with the NaHCO<sub>3</sub> injection rate. At 40 ml/h, the hydrogen yield increased, although the hydrogen generation rate at 30







ml/h. That was because at 40 ml/h the hydrolysis was sustained for longer. The NaHCO<sub>3</sub> injection rate should be minimized to improve the fuel efficiency so that the optimal injection rate would be a range of 20–30 ml/h.

#### 4.4. The effect of the temperature and activation energy

The hydrogen generation rate and hydrogen yield according to the temperature is shown in Fig. 7(d). The hydrogen generation rate was measured at the different reaction temperature of 50, 60, 70, and 80° C. Basically, the hydrogen generation rate and hydrogen yield increased with the temperature. It seems that the NaHCO3 behaves as a catalyst of which the reaction rate has a function of temperature.

With the result of Fig. 7(d), the activation energy was calculated by Arrhenius plot as shown in Fig. 8. The Arrhenius plot was obtained from the reaction rate according to the reaction temperature. The activation energy of 300 kJ/mol was required to hydrolyze the NaBH<sub>4</sub> without the catalyst. When the catalyst was used, it could be reduced by 50 kJ/mol [17-26]. On the other hand, the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> solution had the activation energy of 8.85 kJ/mol, which is very low compared to the catalytic hydrolysis. It means that the efficiency of hydrogen generation from NaBH<sub>4</sub> can be improved by using NaHCO<sub>3</sub> as an agent.







Fig. 8 Arrhenius plot for the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> agent.





#### 4.5. Product analysis

When NaHCO<sub>3</sub> is dissolved in water, first it is ionized into Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> by hydrolysis as expressed in Eq. 2-3.

$$2NaHCO_3 + 2H_2O \rightarrow 2Na^+ + 2HCO_3^- + 2H_2O$$
<sup>(2)</sup>

 $2Na^{+} + 2HCO_{3}^{-} + 2H_{2}O \rightarrow 2Na^{+} + 2H_{2}CO_{3} + 2OH^{-}$ (3)

At the temperature higher than  $65^{\circ}$  C, the ions are combined into Na<sub>2</sub>CO<sub>3</sub>, then generating CO<sub>2</sub> as Eq. 5-6.

$$2Na^{+} + 2H_2CO_3 + 2OH^{-} \xrightarrow[heating>65^{\circ}C]{} 2Na_2CO_3 + 3H_2O + CO_2$$
(5)

$$Na_2CO_3 + 3H_2O \rightarrow NaOH + NaHCO_3 + H_2O \tag{6}$$

Generally, the temperature increased to  $90-100^{\circ}$  C due to the heat of reaction of the NaBH<sub>4</sub> hydrolysis. Thus, gaseous products other than H<sub>2</sub>, such as CO and CO<sub>2</sub>, could be generated by the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> agent. The composition of gas products was analyzed and the result is presented in Table 1. The H<sub>2</sub> occupied 99.9512% of gas products and the trace of CO and CO<sub>2</sub> was included with 0.0017% and 0.0417%, respectively. Rattana Muangrat et al. [27] reported that CO and CO<sub>2</sub> could be generated by the hydrothermal reaction of burnt sugars on an alkali catalyst such as NaHCO<sub>3</sub>. In the simple hydrolysis of NaBH<sub>4</sub>, however, CO and CO<sub>2</sub> were not generated. Thus, the products of the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> agent were compared with those of the catalytic hydrolysis by using XRD analysis and MID-IR spectroscopy.









Fig. 9 Results of XRD analysis of sample: (a) NaBH<sub>4</sub>, (b) NaBH<sub>4</sub> hydrolysis, (c) NaBH<sub>4</sub> hydrolysis using NaHCO<sub>3</sub> agent[30-35], (d) NaHCO<sub>3</sub>, (e) Dried after NaHCO<sub>3</sub> hydrolysis, and (f) NaHCO<sub>3</sub> hydrolysis by heating[36-39]





#### 4.6. XRD analysis and MID-IR spectroscopy

The NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> solution had the activation energy lower than the catalytic hydrolysis but after the reaction, CO and CO<sub>2</sub> was detected even if the amount was very low. The effect of NaHCO<sub>3</sub> on the NaBH<sub>4</sub> hydrolysis was investigated by XRD analysis of three samples: (a) NaBH<sub>4</sub>, (b) NaBH<sub>4</sub> + H<sub>2</sub>O, and (c) NaBH<sub>4</sub> + NaHCO<sub>3</sub> + H<sub>2</sub>O. It can be seen that CO<sub>2</sub> is generated by the hydrolysis of NaHCO<sub>3</sub> as Eq. 5. However, mechanism of CO generation is not clear. Thus, three samples, (d) NaHCO<sub>3</sub>, (e) Na<sub>2</sub>CO<sub>3</sub>, and (f) H<sub>2</sub>CO<sub>3</sub>, were also analyzed to confirm possibility of additional reactions and a role of NaHCO<sub>3</sub> for the hydrolysis of NaBH<sub>4</sub>.

The results of XRD analysis are shown in Fig. 9 [28-37]. When the NaBH<sub>4</sub> is hydrolyzed, the NaBO<sub>2</sub> remains as a byproduct in the liquid state. For the XRD analysis, the samples were perfectly dried at room temperature for 24 hours. The sample (c) that is the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> as an agent was much different with the sample (b). If the NaHCO<sub>3</sub> was used as the catalyst for the hydrolysis of NaBH<sub>4</sub>, the peaks corresponding to the NaBO<sub>2</sub> (sample (b)) should be detected at the sample (c) because the NaBO<sub>2</sub> is the main byproduct of the hydrolysis of NaBH<sub>4</sub>. However, almost peaks were not matched between the sample (b) and (c) except for peaks of Na BH<sub>4</sub> and caused different reactions.

After the hydrolysis of NaHCO<sub>3</sub>, the part of product was dried (sample (e)) and the other was heated by 90° C (sample (f)). The samples of NaHCO<sub>3</sub> were analyzed by XRD but it was difficult to find the specimen corresponding to the sample (d) and (f) in XRD database. Na<sub>3</sub>H(CO)<sub>3</sub> was the most similar with them but not accurate. Particularly, it was not clear that the formation of  $H_2CO_3$  that is present as an aqueous solution. In addition, interference between XRD patterns could take place because they are a compound that is similar with the sample (b) and (c).

The molecular combination of the product obtained by the hydrolysis of  $NaBH_4$ 





using the NaHCO3 as an agent was analyzed by MID-IR as shown in Fig. 6. As a result, CO and CO<sub>2</sub> (2200-2500/cm) were detected, and Na and combinations of O-H, C-O, and C=O were also detected. The NaHCO<sub>3</sub> is ionized in an aqueous solution as Eq. 2, and then  $H_2CO_3$  is formed.

The H<sub>2</sub>CO<sub>3</sub> solution has pKa = 3.6 ( $K_a = [H^+][HCO_3^-]/[H_2CO_3]$ ). When CO<sub>2</sub> is dissolved, the solution has pKa = 6.3 ( $K_a = [H^+][HCO_3^-]/[[H_2CO_3]+[CO_2(aq)]]$ ) that is weak acidy. However, if the  $CO_2$  escapes from the above, the solution has pKa = 10.33 ( $K_a = [H^+][CO_3^{2-}]/[HCO_3^{-}]$ ) that is strong alkali. When the NaHCO<sub>3</sub> solution is injected on the NaBH<sub>4</sub>, the solution would be acidic because the  $CO_2$  is not released as the NaHCO<sub>3</sub> solution does not increase in temperature  $(<65^{\circ}C)$  [45]. Thus, the acidic solution can accelerate the NaBH<sub>4</sub> hydrolysis. However, when the temperature increases by the heat of reaction (>65°C), the solution is alkali because  $CO_2$  is released. The alkali solution tends to stabilize the NaBH4 hydrolysis so that the hydrogen generation is also stabilized. In the catalytic hydrolysis of NaBH<sub>4</sub>, the hydrogen generation rate can increase dramatically because the NaBH<sub>4</sub> solution can boil off by the heat of reaction. However, the hydrogen generation rate did not increase dramatically at 80°C because the reaction was stabilized properly by using NaHCO<sub>3</sub> solution as shown in Fig. 7(d). The above statement was supported by the IR analysis of products after the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> solution. Furthermore, it was certain that the  $Na_2CO_3$  was formed by the heat generated by NaBH<sub>4</sub> hydrolysis. Thus, the NaOH was generated during the reaction, which could affect the NaBH<sub>4</sub> hydrolysis. In addition, the CO and  $CO_2$  were detected by the IR analysis. It means that the CO was generated from NaHCO<sub>3</sub>. Therefore, it is assumed that the CO was formed when intermediates of the reaction was not converted into  $CO_2$ . From the MID-IR spectroscopy, we disclosed that CO can be generated in the middle of the hydrolysis reaction of NaBH<sub>4</sub> with ions of NaHCO<sub>3</sub> dissolved in the water. Although a minute amount was detected, the CO should be removed perfectly to prevent the catalyst of the fuel cell from being deactivated [46,47]. The CO generation in the





reaction can be controlled by making  $H_2CO_3$  to be converted perfectly into  $Na_2CO_3$ , thereby generating  $CO_2$  only as shown in Eq. 5. The concentration of  $CO_2$  was 0.0417%, which is too low to deactivate the catalyst of the fuel cell.

After the hydrolysis of NaBH<sub>4</sub> using the NaHCO<sub>3</sub> solution, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (borax) can be produced. The borax can be reacted with Na<sub>2</sub>CO<sub>3</sub>, being converted into NaBO<sub>2</sub> as Eq. 7 [48].

$$Na_2B_4O_7 + 2Na_2CO_3 + H_2O \rightarrow 4NaBO_2 + 2NaHCO_3 \tag{7}$$

The NaBO<sub>2</sub> can be recycled into NaBH<sub>4</sub> through a catalytic process using MgH<sub>2</sub> or Mg<sub>2</sub>Si [49].







Fig. 10 Results of MID-IR analysis of sample: (a) NaBH<sub>4</sub> hydrolysis using NaHCO<sub>3</sub> agent, (b) NaHCO<sub>3</sub>, (c) Dried after NaHCO<sub>3</sub> hydrolysis, and (d) NaHCO<sub>3</sub> hydrolysis by heating[45-51]





### 5. Operating characteristics of system

The prototype of hydrogen generator based on the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> agent was developed as shown in Fig. 11. The system consists of the reactor and the pump for injecting NaHCO<sub>3</sub> solution, and the reactor pressure was measured by the pressure sensor. The operation procedure is shown in Fig. 12. After the system was initiated, the pump was started to inject the NaHCO<sub>3</sub> solution and was stopped when the pressure reached the limited value that was fixed to 2 bar. The pump was operated again when the pressure was less than the limit as hydrogen was consumed. When the  $NaHCO_3$  solution was injected so excessively that the pressure was raised rapidly, the value was open to maintain the stable pressure with a range of 1.3-2 bar. The change of hydrogen pressure during the operation is shown in Fig. 13. The concentration and injection rate of the NaHCO<sub>3</sub> solution were fixed to 6 wt.% and 20 ml/h. The maximum pressure was controlled to be 2 bar. The pressure decreased with time because hydrogen was released to operate the fuel cell stack. When the pressure reached down to 1.6 bar, the pump was restarted to inject the NaHCO<sub>3</sub> solution, and the reactor was pressurized again. It was verified that the hydrogen generator based on the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> agent can supply hydrogen stably to the fuel cell.

The system using the NaHCO<sub>3</sub> is not much heavier than those using the catalyst. The NaOH additive, which stabilizes the NaBH<sub>4</sub> solution, is not used because the NaBH<sub>4</sub> is reacted in the solid-state. In addition, the weight of water can be reduced by reducing the excessive water to dissolve the NaBH<sub>4</sub> considering its solubility. When the NaHCO<sub>3</sub> solution is injected, the water in the solution is reacted with the NaBH<sub>4</sub>; thus, the addition water is not required. If the system uses the amount of water as near as the stoichiometry, a high H<sub>2</sub> storage capability can be realized.







Fig. 11 Prototype of hydrogen generator based on the  $NaBH_4$  hydrolysis using the  $NaHCO_3$  agent



Fig. 12 Operation algorithm of the hydrogen generator







Fig. 13 Pressure change of the hydrogen generator





## 6. Conclusion

In the present study, the hydrogen generation from solid-state NaBH<sub>4</sub> particles using NaHCO<sub>3</sub> agents was proposed, because the NaHCO<sub>3</sub> is not strong acid and is harmless on a human body and environmentally friendly. The effect of the NaHCO<sub>3</sub> concentration, NaHCO<sub>3</sub> injection rate, NaBH<sub>4</sub>/NaHCO<sub>3</sub> reaction ratio and temperature on the hydrogen generation rate and hydrogen yield was investigated. The hydrogen generation rate and hydrogen yield increased with increasing the  $NaHCO_3$  concentration and injection rate. In addition, the hydrogen generation rate with the temperature because the NaHCO<sub>3</sub> behaves as a catalyst of which the reaction rate has a function of temperature. The Arrhenius plot was obtained from the reaction rate according to the temperature. The NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> solution had the activation energy of 8.85 kJ/mol, which is very low compared to the catalytic hydrolysis. After the reaction, CO and CO<sub>2</sub> were detected even if the amount was very low. Thus, products of the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> agent were compared with those of the catalytic hydrolysis by using XRD analysis and MID-IR spectroscopy. The prototype of hydrogen generator based on the NaBH<sub>4</sub> hydrolysis using the NaHCO<sub>3</sub> agent was developed and the performance on the hydrogen generation was evaluated.





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#### Patent

"METHOD	0F	HYDROGEN	GENERATION	USING	SOLID-STATE	CHEMICAL
HYDRIDE"	10-20	14-0089001				

