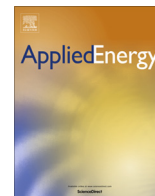




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Accelerated hydrolysis of solid-state NaBH_4 by injecting NaHCO_3 solution for hydrogen generation [☆]

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HIGHLIGHTS

- NaHCO_3 was used as a catalytic solution to hydrolyze NaBH_4 in the solid-state.
- NaHCO_3 solution was injected and immediately the hydrogen is generated.
- Effect of reaction conditions on hydrogen generation rate was investigated.
- Prototype hydrogen generator was developed and the performance was evaluated.

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ABSTRACT

Sodium bicarbonate (NaHCO_3) was used as a catalytic solution and the solid-state sodium borohydride (NaBH_4) were stored in a reacting chamber. The NaHCO_3 solution was injected when the hydrogen is needed. The hydrogen generation rate was measured as various conditions such as the temperature, and the concentration and injection speed of NaHCO_3 solution. The hydrogen generation was initiated immediately when the NaHCO_3 solution was injected. The hydrogen generation rate and NaBH_4 conversion increased with increasing the NaHCO_3 concentration but decreased with increasing the injection speed of NaHCO_3 solution. Based on above results, a prototype of hydrogen generation system was developed. The system consisted of a chamber containing solid NaBH_4 particles, an aqueous NaHCO_3 tank, a liquid pump, valves, cooling fans and sensors. The liquid pump supplied the NaHCO_3 solution to the NaBH_4 chamber through an injector. The temperature and pressure of the NaBH_4 chamber were monitored during the reaction and maintained into 70 °C and 2 bar, respectively. The liquid pump was stopped when the pressure reached 2 bar, while it was restarted to generate hydrogen when the pressure was less than 2 bar because the fuel cell consumed hydrogen during the operation. The hydrogen generation system can provide the stable hydrogen to operate the fuel cell.

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1. Introduction

Hydrogen has been recognized as an alternative to the existing fossil fuels. First, storage method of hydrogen should be developed to be utilized for practical applications. Compressed tank, liquefaction, 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].

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Sodium borohydride (NaBH_4) is used most commonly among the many chemical hydrides. The NaBH_4 can be stored in the liquid and solid state according to the way to extract hydrogen. Generally, catalysts should be used to hydrolyze NaBH_4 in the liquid state, while acid solutions can be used to decompose NaBH_4 in the solid state. First, the NaBH_4 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_2) 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_4 without the catalyst to avoid above problems of the catalytic hydrolysis. It has been reported that acid solutions such as HCl and H_2SO_4 could be used to hydrolyze the solid NaBH_4 [11,12]. However, these strong acids have difficulties in storage and handling. Particularly, HCl solution is quickly vaporized so the HCl 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_4 hydrolysis is possible to be activated by adding water on the solid NaBH_4 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_4 particles using sodium bicarbonate (NaHCO_3) solution was proposed. The NaHCO_3 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_4 hydrolysis reaction can be accelerated by using the NaHCO_3 solution instead of water and steam.

In the present study, NaHCO_3 was used as a catalytic solution and the NaBH_4 solid particles were stored in a reacting chamber. The effect of the temperature, NaHCO_3 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_4 using the NaHCO_3 solution was developed and the operation stability was evaluated.

2. Experiment

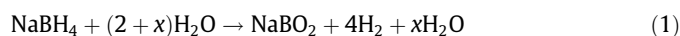
2.1. Methods

NaBH_4 (97%, DAE JUNG, Korea) and NaHCO_3 (99%, SAM CHUN, Korea) were purchased. The NaHCO_3 solution was used as the agent to accelerate the hydrolysis of the solid NaBH_4 . Reaction setup was prepared to investigate the reaction characteristics of the solid NaBH_4 hydrolysis using the NaHCO_3 solution as shown in Fig. 1. The reaction was performed in a water bath to control the reaction temperature due to the exothermic nature of NaBH_4 hydrolysis. The NaHCO_3 solution was precisely injected on the solid NaBH_4 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_3 solution is 8.8 wt.% at 25 °C. When the solubility higher than 8.8 wt.%, NaHCO_3 precipitates can be extracted as the temperature decreased down to 25 °C. Therefore, the concentration of NaHCO_3 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 $\text{NaBH}_4/\text{NaHCO}_3$ reaction ratio and the reaction rate constant were found.

2.2. Analysis of hydrolysis products

The NaBH_4 hydrolysis generates hydrogen only as a gaseous product and NaBO_2 as a byproduct in the liquid state after being dissolved by the excessive water (x) as shown in Eq. (1).



When NaHCO_3 is reacted with NaBH_4 , however, the reaction mechanism would be different with the catalytic hydrolysis. Thus, the gas composition of products should be analyzed because CO and CO_2 can be formed from NaHCO_3 . 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, Sincro) were used to reveal the role of NaHCO_3 in the NaBH_4 hydrolysis. For comparisons, six samples were prepared: (i) pure NaBH_4 , (ii) pure NaHCO_3 , (iii) products after the NaBH_4 hydrolysis without NaHCO_3 , (iv) products after the NaBH_4 hydrolysis with NaHCO_3 , (v) products after the NaHCO_3 solution is dried, and (iv) products after the NaHCO_3 hydrolysis by heating at 90 °C.

2.3. Hydrogen generation system

Based on the parametric study on the characteristic of solid NaBH_4 hydrolysis using the NaHCO_3 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_4 hydrolysis was relatively difficult to control the hydrogen generation rate compared to the catalytic hydrolysis from the NaBH_4 solution. For example, if a fixed-bed reactor is used for this reaction, the excessive reaction will take place because the NaHCO_3 solution is supplied continuously on the NaBH_4 that is fixed in the reactor. Thus, the excessive reaction causes the NaHCO_3 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. 2. The NaHCO_3 solution was injected into the reactor in which the NaBH_4 particles were placed. The NaHCO_3 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_3 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.

3. Results and discussion

3.1. Effect of NaHCO_3 concentration

The hydrogen generation rate and hydrogen yield of the NaBH_4 hydrolysis using the NaHCO_3 solution according to the performance parameter as shown in Fig. 3. The effect of the NaHCO_3 concentration of the hydrogen generation rate and hydrogen yield is shown in Fig. 3(a). The NaHCO_3 solution was injected on the solid NaBH_4 particles at different concentrations of 4, 5, 6, 7, and 8 wt.%.

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