Storage and Release of Hydrogen as a Fuel of the Fuel Cell with Media of NaBO₂/NaBH₄

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Abstract. The reactions of storage and release of hydrogen as a fuel of the fuel cell with sodium metaborate (NaBO₂) / Sodium borohydride (NaBH₄) media at various pressures and temperatures have been carried out. Hydrogen production is produced from hydrolysis of NaBH₄ and hydrogen storage is carried out with NaBO₂ media which is a by-product of the hydrolysis process of NaBH₄. The process of hydrogen production by hydrolysis of NaBH₄ takes place exotherm so that the highest speed occurs at low temperatures. Furthermore, the resulting NaBO₂ is used as a hydrogen storage material at varying pressures and temperatures. The largest hydrogen storage capacity at 3 bar and 40°C is 35.23% by weight and increases after several repetitions of release and storage. An easy hydrogen storage and release system for fuel cells is needed to anticipate the use of fuel cells as an environmentally friendly energy source for housing and vehicles.

Keywords: Hydrolysis reaction; sodium borohydride; storage of hydrogen; sodium metaborate.

1. Introduction

Hydrogen is an alternative energy carrier that has several advantages, including the energy density to mass is very large, can produce clean energy and can be synthesized from various chemical compounds that contain hydrogen. One of the important uses of hydrogen is as a fuel for fuel cell. Fuel cells are electrochemical equipment that can convert fuel (hydrogen or alcohol) and oxygen into electrical energy and water as a waste [1]. Fuel cell is an equipment that produces adequate energy and environmentally friendly with a wide application, ranging from portable equipments, utilities and vehicles [2]. One of the problems in fuel cells development are hydrogen production and storage. For this reason, efforts to obtain hydrogen production and storage methods are important topics in fuel cell research.

One compound that contains lots of hydrogen is NaBH₄. In early 2000’s, sodium borohydride was the most promising compound as a hydrogen fuel source for Proton Exchane Membrane Fuel Cell (PEMFC) and Direct Borohydride Fuel Cell (DBFC). This is because the hydrogen storage capacity is quite high. However, the use of this compound has problems because the hydrolysis of NaBH₄ takes
place spontaneously so that it is difficult to hold and release hydrogen gas as desired [3].

The use of NaBH₄ as a hydrogen-producing compound is considered to have several advantages including the chemical reaction that occurs is a combination of hydrogen release and storage reactions as can be seen in equations (1) and (2).

\[
\begin{align*}
\text{NaBH}_4 + 2\text{H}_2\text{O} & \rightarrow \text{NaBO}_2 + 4\text{H}_2 + 217 \text{kJ} \quad (1) \\
\text{NaBO}_2 + 4\text{H}_2 & \rightarrow \text{NaBH}_4 + 2\text{H}_2\text{O} \quad (2)
\end{align*}
\]

The reaction (1) above is the hydrogen gas release reaction from NaBH₄ which is also followed by the formation of the NaBO₂ compound, and the reaction (2) is a reaction for hydrogen storage / absorption. This reaction actually takes place irreversibly.

Sodium borohydride is an alkaline hydride that meets the DOE 2015 energy density target for hydrogen storage materials [4]. NaBH₄ is known as a source of hydrogen because of its high hydrogen storage capacity (more than 10.8% by weight) depending on the hydration coefficient [4].

The hydrolysis reaction of NaBH₄ is a reaction of hydrogen gas production, where the reaction takes place exotherm. Furthermore, sodium metaborate that produced from the hydrolysis process can be used as hydrogen storage [4]. Thus, the two reaction can be used as hydrogen production and storage. Formation of NaBO₂ can be controlled by physical reactions, namely by regulating temperature and pressure. Based on previous research [3], the rate of hydrogen production is higher at low temperatures. In addition, the maximum storage/absorption pressure of hydrogen at 2 bars [5]. This research is needed to determine the characteristics of hydrogen gas release and storage test using NaBH₄/NaBO₂ media.

2. **Method**

2.1. *The Production of Hydrogen Through Hydrolysis of NaBH₄ dan the Characterization*
A certain amount of NaBH₄ is put into the prepared reactor, DI water is added little by little to the reactor and the solution is shaken vigorously. Hydrogen gas will flow immediately and the volume of hydrogen produced is measured in volume. Production tests were carried out at various temperatures (0°C, 15°C, 25°C, 35°C, and 40°C) and the volume/time was measured. NaBH₄ compounds and the results of hydrolysis reactions (NaBO₂) were characterized using XRD and FT-IR.

2.2. *Storage of Hydrogen Gas at Various Pressure and Temperature*
The test of hydrogen storage/absorption by NaBO₂ is carried out by entering a certain amount of NaBO₂ powder into a stainless steel vial that is known for it’s mass, then propagated. Vials containing NaBO₂ are weighed, then hydrogen gas is flowed into a vial with 1 bar at a various temperature (25°C, 30°C, 40°C) for 30 minutes. After the hydrogen flowing process, the remaining gas is removed and the vial is weighed again. The procedure is also carried out for 2, and 3 bar pressure variations and at temperatures of 25°C, 30°C, 40°C. The powder products were analyzed by FT-IR. The structure of compounds and functional groups can be seen by FT-IR test.

2.3. *The Effectiveness of Capacity of Storage Hydrogen*
The amount of hydrogen absorbed is used to calculate the capacity and effectiveness of hydrogen absorption. Hydrogen storage and release is tested 4 times to determine the effectiveness of sodium metaborate in hydrogen storage.
3. Discussion

3.1. Characterization of Sodium borohydride and Sodium Borohydride Hydrolysis Product

3.1.1. X-Ray Diffraction (XRD) Characterization
Identification using XRD is useful to determine the crystallinity of sodium borohydride compounds. The XRD characterization results from NaBH₄ and NaBO₂ compounds as a result of hydrolysis from NaBH₄ are presented in Figures 1 and 2.

![XRD diffractogram from NaBH₄](image)

**Figure 1.** XRD diffractogram from NaBH₄

XRD characterization results from Figure 1 shows the diffraction pattern of NaBH₄ at position 2θ = 29.118° and 2θ = 41.621°. This data corresponds to the results of previous studies where the peak of NaBH₄ were seen at 2θ = 29° [6]; 28.9° and 41.360° [7] and 30° [8]. Characterization data that corresponds to the characterization data in previous studies indicate that the compound used contains sodium borohydride. The high intensity and sharp diffraction pattern is the crystallinity of sodium borohydride, while the diffraction pattern which tends to be short or wide is caused by amorphicity of sodium borohydride.
XRD characterization results from Figure 2 shows the diffraction pattern at $2\Theta = 28.76^\circ, 32.47^\circ, 33.96^\circ$ dan $40.44^\circ$ in hydrolysis product of $\text{NaBH}_4$. This data corresponds to the results of previous studies which showed the presence of sodium metaborate peak ($\text{NaBO}_2$) as a result of hydrolysis of $\text{NaBH}_4$ at $2\Theta = 24^\circ, 32^\circ, 40^\circ$ [7] dan $2\Theta = 28^\circ$ [8].

3.1.2. **FTIR Characterization**

Identification and characterization using FT-IR is useful to determine the functional groups contained in sodium borohydride and sodium metaborate. FTIR characterization results of sodium borohydride and sodium metaborate are presented in Figures 3 and 4.
From figure 3 it can be seen that at wave numbers of 1,103.59 cm\(^{-1}\) and 2,270.09 cm\(^{-1}\) indicate the presence of group B-H. This data corresponds to the results of previous studies where the vibration bonding B-H group at a wavelength of 1,110 cm\(^{-1}\) and stretching vibration B-H at a wave number of 2,010 cm\(^{-1}\) to 2,516 cm\(^{-1}\) \cite{6}; B-H groups are reported also in wave numbers of 2,200 cm\(^{-1}\), 2,400 cm\(^{-1}\) dan 1,125 cm\(^{-1}\) \cite{7}.

**Figure 4.** FTIR spectra of NaBO\(_2\)

Figure 4 shows the peak at wave numbers of 700.43 cm\(^{-1}\); 719.92 cm\(^{-1}\); 955.13 cm\(^{-1}\); 1,224.32 cm\(^{-1}\) dan 1,423.32 cm\(^{-1}\) which shows the presence of B-O groups. This data corresponds to the results of previous studies where B-O groups are present at wave numbers of 100 cm\(^{-1}\) – 600 cm\(^{-1}\)\cite{7}, and 1,000 cm\(^{-1}\) - 1,500 cm\(^{-1}\) \cite{8}. At the above spectrum there are also a B-O-H group which indicates the presence of sodium metaborate hydrated, so that to remove the hydrate it is heated at 120\(^{\circ}\)C with the aim of evaporating the water contained in the product reaction.

### 3.2. The Production and Storage of Hydrogen

#### 3.2.1. The Production of Hydrogen Gas from the Hydrolysis of NaBH\(_4\)

Hydrogen gas production from hydrolysis of NaBH\(_4\) in this study was carried out at various temperatures and time. Hydrogen production data as a function of time and temperature are shown in Figure 5.

**Figure 5.** The volume of Hydrogen Gas production at various temperature
Based on Figure 5 above it can be seen that at 0°C 61 mL of hydrogen gas is produced with a relatively faster time compared to 25°C with a volume of 63 mL of hydrogen gas. Hydrogen production at low temperatures are more and faster. This is because the hydrolysis reaction is exothermic, so the hydrogen release process will take place more quickly at low temperatures. This can be seen also from previous research [3] which shows that the effect of reaction temperature on hydrogen production rates is more pronounced at the initial temperature.

3.2.2. Hydrogen Storage by Using NaBO$_2$

The most important feature of hydrogen is its ability to be stored. There are many methods used for hydrogen storage, such as in the form of compressed gases, in liquid or physical storage in nano carbon tubes and in the form of metal hydrides. Among storage methods, effective storage methods are metal hydride storage due to high storage capacity and operating conditions in environmental conditions. The amount of gas that can be stored in a hydrogen storage system is determined by the nature of the adsorbent material and the operating conditions of the storage system namely pressure and temperature.

In this study, NaBO$_2$ which is a by-product of NaBH$_4$ hydrolysis is used as a material for storing hydrogen. The hydrogen storage capacity of NaBO$_2$ at varying pressures and temperatures is shown in Table 1.

| No | Pressure (bar) | Temperature (°C) | Capacity of Hydrogen storage (% w/w) |
|----|----------------|------------------|-------------------------------------|
| 1  | 1              | 25               | 13                                  |
| 2  | 1              | 30               | 12.5                                |
| 3  | 2              | 30               | 31                                  |
| 4  | 3              | 40               | 35.23                               |
| 5  | 3              | 30               | 13.89                               |
| 6  | 3              | 25               | 27.15                               |
| 7  | 2              | 25               | 16                                  |
| 8  | 1              | 40               | 12.67                               |
| 9  | 2              | 40               | 29.38                               |

Based on Table 1 above it can be seen the hydrogen storage capacity of the NaBO$_2$ material at various pressure and temperature. The most absorbed hydrogen using sodium metaborate is at 3 bar and 40°C as much as 35.23% by weight. Previous studies have shown that hydrogen storage capacity in sodium metaborate is 10.8 wt% [9].

The relationship between pressure and temperature on hydrogen storage capacity using the design of experiment (DOE) application is presented in Figure 6.
Based on Figure 6 it can be seen that temperature and pressure have an influence on hydrogen absorption capacity, but the pressure has a greater influence than temperature. Hydrogen absorption capacity is quite significant in the range of 30°C to 40°C. At a pressure of 1 bar to 2 bars, a very significant increase in hydrogen absorption occurs, while at a pressure of 2 bar to 3 bar the increase in percent of absorbed hydrogen produced is not too significant.

3.2.3 Hydrogen Storage Effectiveness from NaBO$_2$

Hydrogen storage effectiveness in NaBO$_2$ express how much hydrogen can be stored on storage media using sodium metaborate. Figure 7 present the hydrogen storage capacity for 4 repetitions. After the experiment, it turned out that sodium metaborate used could be reused as a production and storage of hydrogen 4 times. One of the effects of repetition of the reaction is the reduced mass of NaBO$_2$ but the increasing storage capacity.

Based on Figure 7 above can be seen the effect of repetition of storage and release of hydrogen from sodium metaborate. The increase in hydrogen storage capacity can be caused by the sodium metaborate that is used still contains a lot of water so that when the absorption process of hydrogen is blocked by water molecules. In addition, an increase in hydrogen storage capacity can also be caused
because when hydrogen production is first produced, not all sodium borohydride is completely hydrolyzed. Repetition of the use of sodium metaborate as hydrogen storage will increase the effectiveness of hydrogen storage.

Sodium borohydride (NaBH₄) which results from absorption of hydrogen by sodium metaborate (hydrogenation of NaBO₂) was analyzed using FTIR as shown in figure 8.

![Figure 8. FT-IR spectra of NaBO₂ hydrogenation](image)

In Figure 8, from the FT-IR spectra can be seen that at wave numbers 1,103.59 cm⁻¹ and 2,270.09 indicate the presence of B-H group from NaBH₄.

4. Conclusion
Hydrogen gas can be produced from the NaBH₄ hydrolysis reaction which takes place exothermic. Besides hydrogen gas, the product of NaBH₄ hydrolysis also produces sodium metaborate (NaBO₂) which can function as a hydrogen storage. Pressure and temperature have a large influence on hydrogen storage capacity, but pressure has a greater influence on hydrogen storage than temperature.

5. References
[1] Rohendi D, Majlan EH, Mohamad AB, Daud WRW, Kadhum AAH and Shyuan LK 2015 Effects of temperature and backpressure on the performance degradation of MEA in PEMFC. *Int J Hydrogen Energy* **40** 34.
[2] Rohendi D, Majlan EH, Mohamad AB, Daud WRW, Kadhum AAH and Shyuan LK 2014 Effect of PTFE content and sintering temperature on the properties of a fuel cell electrode backing layer. *J Fuel Cell Sci Technol.* **11** 4.
[3] Li Q and Kim H 2012 Hydrogen production from NaBH₄ hydrolysis via Co-ZIF-9 catalyst. *Fuel Process Technol.* **100** 43–8.
[4] Santos DMF and Sequeira CAC 2015 On the electrosynthesis of sodium borohydride. *Int J Hydrogen Energy* **35** 18 9851–61.
[5] Ou T, Panizza M and Barbucci A 2013 Thermochemical recycling of hydrolyzed NaBH₄. Part II: Systematical study of parameters dependencies. *Int J Hydrogen Energy* **38** 36 15940–5.
[6] Mao J, Gu Q, Guo Z and Liu HK 2015 Sodium borohydride hydrazinates: synthesis, crystal structures, and thermal decomposition behavior. *J Mater Chem A Mater energy Sustain.* **00** 1–8.
[7] Chen W, Ouyang LZ, Liu JW, Yao XD, Wang H and Liu ZW 2017 Hydrolysis and regeneration
of sodium borohydride (NaBH₄) A combination of hydrogen production and storage J Power Sources 359 400–7.

[8] Lang C, Jia Y, Liu J and Wang H 2017 NaBH₄ regeneration from NaBO2 by high-energy ball milling and its plausible mechanism Int J Hydrogen Energy 42 18 13127-135.

[9] Nunes HX, Ferreira MJF, Rangel CM and Pinto AMFR 2016 Hydrogen generation and storage by aqueous sodium borohydride (NaBH₄) hydrolysis for small portable fuel cells (H₂-PEMFC) Int J Hydrogen Energy 41 34 15426–32.

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