

A study on hydrogen generation from NaBH₄ solution using the high-performance Co-B catalyst

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Received 3 December 2004; accepted 28 December 2004

Available online 11 March 2005

Abstract

For hydrogen generation from an aqueous alkaline NaBH₄ solution, Co-B catalyst was prepared by the chemical reduction method using NaBH₄ as a reduction chemical. To design a hydrogen generator, hydrogen generation rate was measured using the Co-B catalyst as a function of solution temperature, amount of catalyst loading, NaBH₄ concentration, and NaOH (a base-stabilizer) concentration. Activation energy for the hydrogen generation reaction was measured to be 64.87 kJ mol⁻¹. Compared to Ru catalysts previously used, the low-cost Co-B catalyst exhibited comparable activity for the hydrogen generation reaction. Using the hydrogen generation system employing the Co-B catalyst, a 2 W polymer electrolyte membrane fuel cell (PEMFC) stack was operated and successfully powered a cellular phone.

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Keywords: Hydrogen generation; Co-B catalyst; NaBH₄; Polymer electrolyte membrane fuel cell

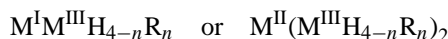
1. Introduction

In response to the ever increasing demand of portable electronic devices with high power density, fuel cells have attracted attention as a power source to replace lithium ion batteries. Among the various types of fuel cell, direct methanol fuel cell (DMFC) has been developed as a strong candidate mainly due to availability of fuel supply. Even though the polymer electrolyte membrane fuel cell (PEMFC) has a higher efficiency and higher power density than DMFC, hydrogen supply has been an obstacle to the application of PEMFC to portable power sources.

Hydrogen has been stored in tanks of compressed or liquefied H₂, in hydrogen-storing alloys, and on activated carbon or carbon nanotubes. However, all the methods are not

suitable for portable applications due to the low volumetric and gravimetric efficiency of hydrogen storage as well as to the safety issue. Instead of those hydrogen storage methods, liquid hydrocarbons (propane, methanol, gasoline, etc.) and chemical hydrides (NaBH₄, KBH₄, LiBH₄, etc.) could be employed as hydrogen sources for portable PEMFC. However, in the case of the liquid hydrocarbons, high-temperature reforming processes are complex in PEMFC operation.

Suda proposed hydrolysis of hydrogen complex compound represented by the general formula [1]:



where M^I is the alkali metal; M^{II} the alkaline earth metal or zinc; M^{III} the boron, aluminum, gallium; R the alkoxy, aryloxy, acyloxy group; n = 0, 1, 2, 3.

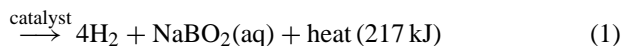
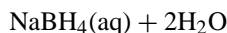
Among the chemical hydrogen complexes, sodium borohydride (NaBH₄) was intensively studied [2–5] as a hydrogen storage material in view of its various advantages: non-flammable and stable in air, easy control of hydrogen generation rate, recycling of the side products, and high H₂ stor-

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age efficiency. A base-stabilized NaBH_4 solution hydrolyzes to hydrogen and sodium metaborate (NaBO_2) only when in contact with selected catalysts [2–5].



The catalysts, Ru, Pt, and Ni have been employed in previous studies [6]. According to the results, low-cost Ni catalyst exhibited low activity to the hydrogen generation reaction, compared with the noble metal catalysts. In this study, the activity of Co, Ni, Mn, Fe, and Cu to hydrogen generation reaction from base-stabilized NaBH_4 solution was examined in comparison with Ru to screen for a low-cost and high-performance catalyst. Using the selected catalyst, the effects of solution temperature, catalyst loading, NaBH_4 concentration, and NaOH concentration on hydrogen generation rate were investigated to design a hydrogen supply system for a 2 W PEMFC stack.

2. Experimental

2.1. Catalyst preparation

To select an alternative catalyst for the hydrogen generation reaction described in Eq. (1), the activities of Ru, Co, Ni, Mn, Fe, and Cu were examined by measuring hydrogen generation rate from base-stabilized aqueous NaBH_4 solutions. All the catalysts were prepared by the chemical reduction method using different starting chemicals. As a representative, to make a Co catalyst, 0.1 M CoCl_2 solution was prepared and then mixed with alkaline NaBH_4 solution as a reducing agent. During the reduction reaction, the solution temperature was maintained below 5°C to prevent a vigorous reaction. The molar ratio of CoCl_2 to NaBH_4 was 1:1.5 to complete the reduction reaction. Then, the precipitates were filtered and washed repeatedly with DI water and dried in a

N_2 chamber at 120°C . Ru, Ni, Mn, Fe, and Cu catalysts were prepared following the above procedure using RuCl_3 , NiCl_2 , MnCl_2 , FeCl_2 , and CuCl_2 as precursors, respectively.

To characterize the selected catalyst, surface morphology was observed by scanning electron microscope (SEM; JEOL, JSM-5200) and the chemical composition was investigated by inductively coupled plasma (ICP; Thermo Jarrellash, Polyscan 61e) analysis. By N_2 adsorption at 77.35 K, the Brunauer–Emmett–Teller (BET) surface area (S_{BET}) of the catalyst was measured. The crystal structure of the catalysts was examined by X-ray diffraction (XRD, Rigaku, D/max-2500 with CuK).

2.2. Hydrogen generation

Fig. 1 depicts the experimental apparatus devised to measure the hydrogen generation rate from base-stabilized aqueous NaBH_4 solution. As a base stabilizer, NaOH was added to the solution. The solution temperature was kept constant within the range of the set value $\pm 0.2^\circ\text{C}$ using a water jacket. The prepared catalyst was put into the solution to start the hydrogen generation reaction and the reactor lid was fastened for gas-tightness. The hydrogen generation rate was measured for gas-tightness. The hydrogen generation rate was measured using a mass flow meter (MFM) and recorded with a personal computer. The volume of the generated hydrogen was calculated by integrating the experimentally measured hydrogen generation rate over time.

3. Results and discussion

3.1. Catalyst screening

To select a catalyst for hydrogen generation from aqueous NaBH_4 solution, the hydrogen generation rate was measured using Ru, Co, Ni, Mn, Fe, or Cu catalysts prepared by the chemical reduction method and 20 wt% NaBH_4 + 5 wt% NaOH solution at 20°C . For comparison, metallic Co powder

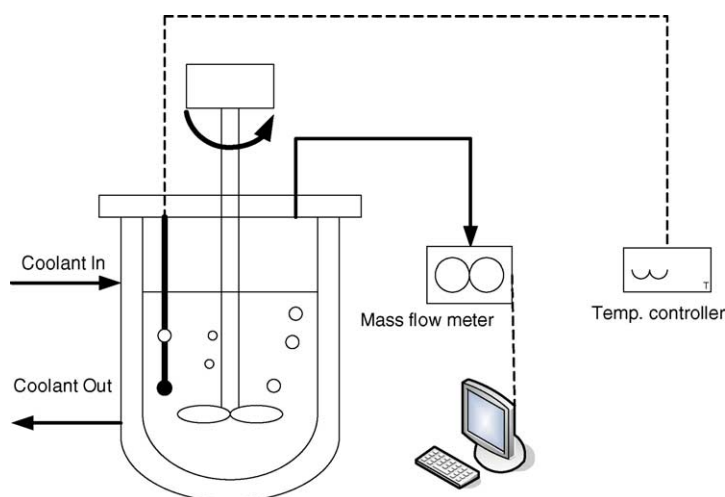


Fig. 1. A schematic diagram of the experimental setup for measuring the hydrogen generation rate.

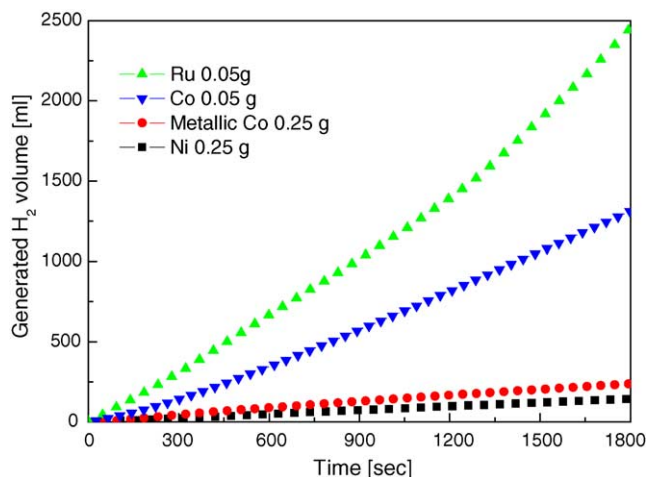


Fig. 2. Hydrogen generation rate measured from 20 wt% NaBH₄ + 5 wt% NaOH solution at 20 °C using 0.05 g of Ru, Co, and 0.25 g of metallic Co and Ni catalyst; Ru, Co, and Ni catalysts were prepared by the chemical reduction method in this study; metallic Co powder was used as received.

was also used as a catalyst. With Mn, Fe, or Cu catalysts, hydrogen generation was negligible and is not shown in Fig. 2. As presented in Fig. 2, for all the Ru, Co, metallic Co, and Ni catalysts, the generated hydrogen volume was almost linearly proportional to the reaction time, implying that the reaction is independent of reactant concentration and 0th order. During 1800 s, the average hydrogen generation rate was calculated to be 1637, 875, 32, and 20 mL min⁻¹ g⁻¹ for Ru, Co, metallic Co, and Ni catalyst, respectively. It should be noted that 0.05 g of Ru and Co and 0.25 g of metallic Co and Ni were used to obtain the data in Fig. 2. Those results clearly show that Co can be a promising alternative non-precious catalyst for the hydrogen generation reaction and that Co catalyst prepared by the chemical reduction method in this study has a much higher activity for the hydrogen generation reaction than metallic Co powder. In this study, the characteristics of the prepared Co catalyst were investigated and the hydrogen generation rate was measured as a function of solution temperature, catalyst loading, NaBH₄ concentration, and NaOH concentration using the prepared Co catalyst.

3.2. Catalyst characterization

Fig. 3 shows a SEM image of the Co catalyst prepared in this study. A plate-like structure was observed. The particle size was several tens to hundreds of nanometers and the specific surface area was measured to be 77 m² g⁻¹. ICP analysis revealed that the prepared catalyst consisted of Co and boron (B) and that atomic ratio of Co to B was 2:1. Boron in the prepared catalyst could be combined with Co during the reduction reaction of CoCl₂ with NaBH₄ used as a reducing agent. XRD analysis showed that the Co-B catalyst had an amorphous structure. Characteristics of the Co-B catalyst made under various conditions will be studied in detail in another article in preparation for publication.

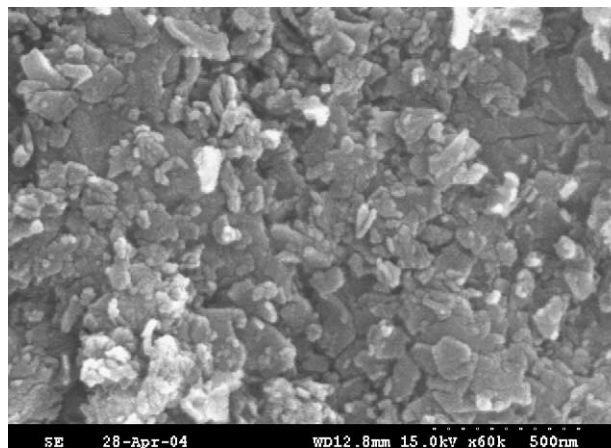


Fig. 3. SEM image of Co-B catalyst prepared by the chemical reduction method.

3.3. Hydrogen generation kinetics

To design a hydrogen generation reactor for a portable PEMFC stack, effects of solution temperature, catalyst loading, NaBH₄ concentration, and NaOH concentration on the hydrogen generation rate should be investigated.

Generally, the chemical reaction rate increases with the reactor or solution temperature. The hydrogen generation rates were measured using 20 wt% NaBH₄ + 5% NaOH solution and 0.05 g of the prepared Co-B catalyst at various solution temperatures (10–30 °C) and are presented in Fig. 4. The hydrogen generation rate increased for the first few minutes due to activation of the catalyst and then remained almost constant. As the solution temperature increased from 10 to 30 °C, the steady-state hydrogen generation rate increased from 500 to 2750 mL min⁻¹ g⁻¹. The hydrogen generation reaction could be considered 0th order since after a period of activation; the hydrogen generation rate was constant with time in a batch

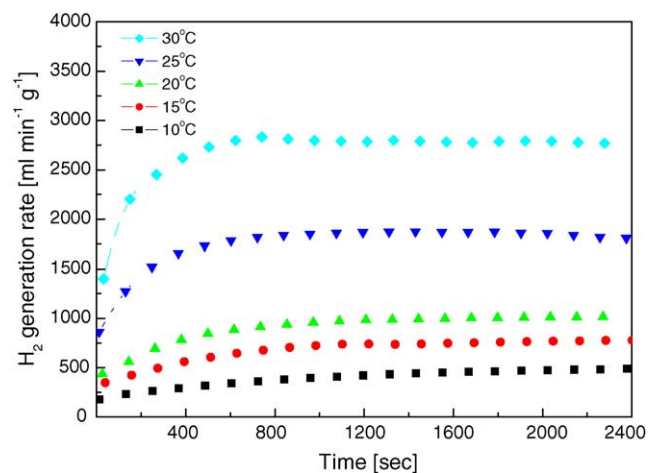


Fig. 4. Effects of solution temperature on the hydrogen generation rate measured from 20 wt% NaBH₄ + 5 wt% NaOH solutions using 0.05 g of Co-B catalyst.

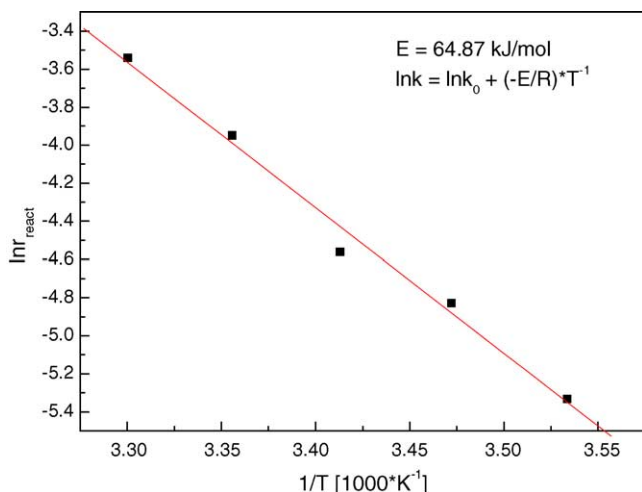


Fig. 5. $\ln r$ vs. $1/T$ plot obtained from the data shown in Fig. 4 for the hydrogen generation reaction using a Co-B catalyst.

reactor. The reaction rate equation can be written as follows:

$$r = k_0 \exp\left(\frac{-E}{RT}\right) \quad (2)$$

where r is the reaction rate ($\text{mol min}^{-1} \text{g}^{-1}$), k_0 the reaction constant ($\text{mol min}^{-1} \text{g}^{-1}$), E the activation energy for the reaction, R the gas constant, and T is the reaction temperature. Following Eq. (2), $\ln r$ versus $1/T$ was plotted in Fig. 5 from the data in Fig. 4. For the hydrogen generation reaction, $\ln r$ was linearly proportional to $-1/T$ in accordance with Eq. (2). Hence, from the slope of Fig. 5, activation energy for the hydrogen generation reaction was calculated to be $68.87 \text{ kJ mol}^{-1}$, which was higher than the previously reported value, 56 kJ mol^{-1} , for Ru catalyst supported on IRA-400 [7].

Fig. 6 shows the hydrogen generation rate measured using the prepared Co-B catalyst and 20 wt% $\text{NaBH}_4 + 5\% \text{ NaOH}$

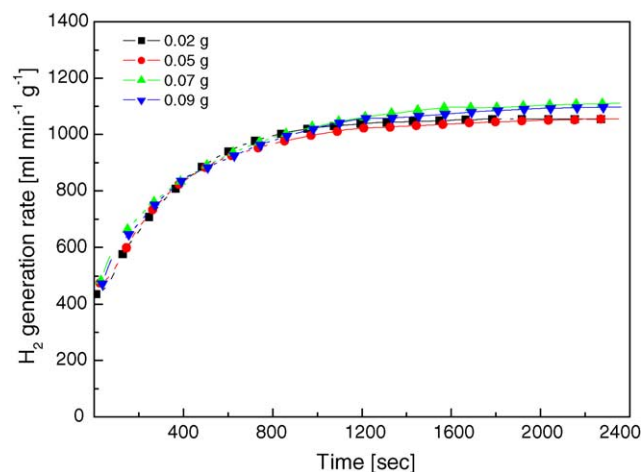


Fig. 6. Hydrogen generation rates from 20 wt% $\text{NaBH}_4 + 5\% \text{ NaOH}$ solutions at 20°C using different weights of Co-B catalyst.

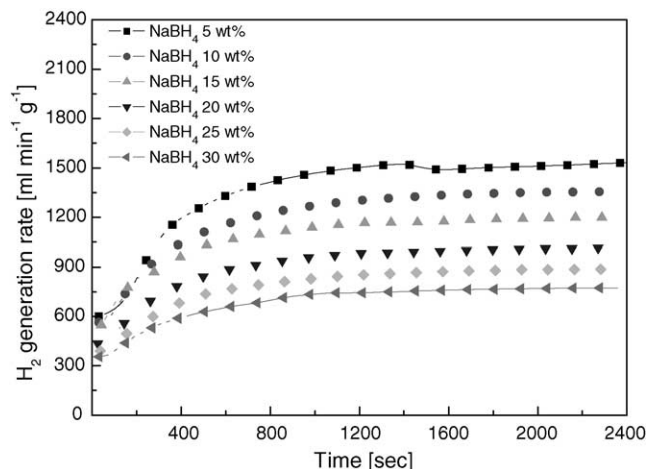


Fig. 7. Effects of NaBH_4 concentration on the hydrogen generation rate measured using x wt% $\text{NaBH}_4 + 5\% \text{ NaOH}$ solutions ($x=5, 10, 15, 20, 25, 30$) at 20°C using 0.05 g of Co-B catalyst.

solution at 20°C . To examine the effects of catalyst loading on the hydrogen generation rate, 0.02, 0.05, 0.07, and 0.09 g of the catalyst were employed. As observed in Fig. 4, the hydrogen generation rate increased for the first a few minutes due to activation of the catalyst and then remained almost constant to be about $1100 \text{ mL min}^{-1} \text{g}^{-1}$. Those results imply that hydrogen generation rate can be determined by controlling the catalyst loading used in the reactor. In Fig. 2, hydrogen generation rate for Co-B catalyst (designated as Co in Fig. 2) was $875 \text{ mL min}^{-1} \text{g}^{-1}$ calculated from the data during 1800 s on average.

Fig. 7 shows the effect of NaBH_4 concentration on the hydrogen generation rate using 0.05 g of Co-B catalyst at 20°C . x wt% $\text{NaBH}_4 + 5\% \text{ NaOH}$ solution was employed ($x=5, 10, 15, 20, 25, 30$). With increasing NaBH_4 concentration in the solution from 5 to 30 wt%, the hydrogen generation rate decreased from 1500 to $600 \text{ mL min}^{-1} \text{g}^{-1}$, Amendola et al. [7,8] reported that, for a Ru catalyst, the hydrogen generation rate from $\text{NaBH}_4 + \text{NaOH}$ solution decreased with increasing NaBH_4 concentration and attributed those results to an increase in solution viscosity.

NaBH_4 hydrolyzes to generate hydrogen without catalysts unless it is base-stabilized. Therefore, to control the hydrogen generation rate, NaOH was added to NaBH_4 solution to make the solution basic. Fig. 8 demonstrates hydrogen generation rate measured from 20 wt% $\text{NaBH}_4 + x\% \text{ NaOH}$ ($x=1, 3, 5, 10, 15, 20$) solution at 20°C using 0.05 g of Co-B catalyst. With increasing NaOH concentration to 10 wt%, the steady-state hydrogen generation rate increased from 500 to $1200 \text{ mL min}^{-1} \text{g}^{-1}$ and then, at higher concentrations, remained almost constant to be $1200 \text{ mL min}^{-1} \text{g}^{-1}$. These results are opposite to those obtained using Ru catalyst. In previous studies using Ru catalyst [6], hydrogen generation from NaBH_4 solution decreased with increasing NaOH concentration, probably due to suppression of hydrogen formation by hydroxide ions. Fig. 8 demonstrates that the increase in

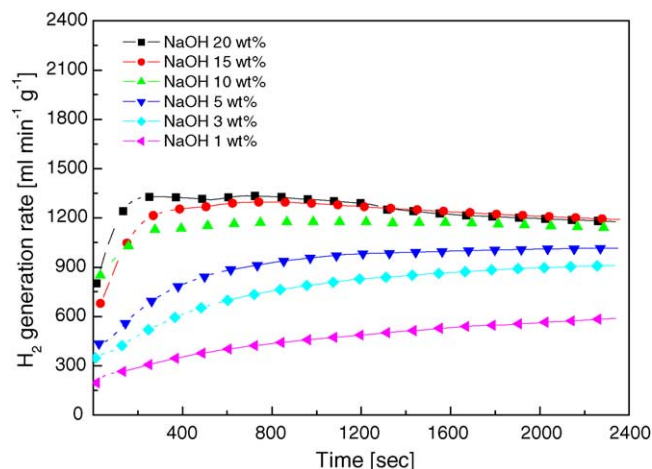


Fig. 8. Effects of NaBH_4 concentration on the hydrogen generation rate measured from 20 wt% $\text{NaBH}_4 + x$ wt% NaOH solutions ($x = 1, 3, 5, 10, 15, 20$) at 20°C using 0.05 g of Co-B catalyst.

hydrogen generation rate with increasing NaOH concentration is more significant during the first few minutes than at steady-state, reflecting that the hydroxides ions affected activation of the Co-B catalyst. Hua et al. [9] reported that using Ni catalyst, a NaBH_4 solution containing a higher concentration of NaOH produced hydrogen at a higher rate. Those results demonstrate that the NaBH_4 hydrolysis mechanism is dependent on catalyst and is different for Co-B or Ni catalysts from a Ru catalyst. To elucidate the reaction mechanism, hydrogen generation kinetics is under further investigation using various catalysts.

3.4. Hydrogen supply to a PEMFC stack

Based on the results shown in Figs. 4–8, a hydrogen supply system was designed and applied to a 2 W PEMFC stack. The six-cell PEMFC stack was fabricated as a miniaturized

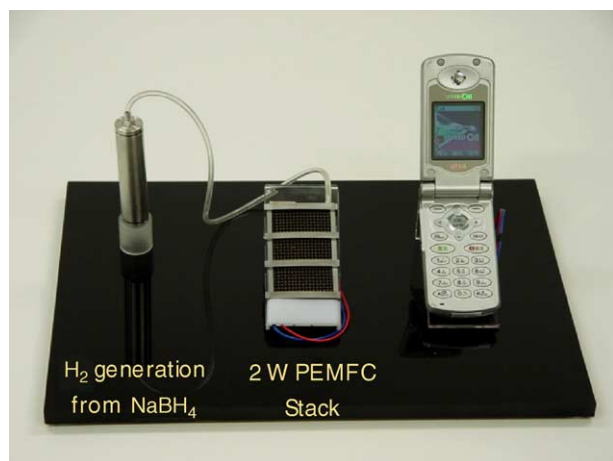


Fig. 9. A cellular phone powered by a miniaturized passive air-breathing PEMFC stack operating on hydrogen generated from NaBH_4 solution.

passive air-breathing type as a power source for a cellular phone [10]. To feed the 2 W PEMFC stack, the hydrogen generation rate should be higher than 24 mL min^{-1} with a fuel stoichiometry of 1.5. The temperature of the fabricated hydrogen generator was not controlled and was exposed to ambient conditions. Thus, the hydrogen generation rate was not kept constant as shown in Figs. 4–8. Instead, the hydrogen generation rate was controlled by the contact time of the catalyst with the solution using a specially designed device. As presented in Fig. 9, the PEMFC stack was successfully operated on hydrogen from NaBH_4 solution and powered a cellular phone with power consumption of 2 W.

4. Conclusions

To develop a low-cost high-performance catalyst for hydrogen generation from base-stabilized NaBH_4 solution, Co, Ni, Fe, Mn, and Cu catalysts were prepared by chemical reduction method and their activity to the hydrogen generation reaction was measured in comparison with previously used precious Ru catalyst. Among the non-noble catalysts, the prepared Co catalyst exhibited the highest hydrogen generation rate of $875 \text{ mL min}^{-1} \text{ g}^{-1}$ from 20 wt% $\text{NaBH}_4 + 5$ wt% NaOH solution at 20°C ; Ru catalyst showed $1637 \text{ mL min}^{-1} \text{ g}^{-1}$ under the same condition. Based on the results, the prepared Co catalyst was selected as an alternative catalyst. SEM, ICP, and XRD analysis revealed that the prepared Co catalyst consisted of amorphous Co-B compound with plate-like structure. With increasing solution temperature, hydrogen generation rates increased and activation energy of for the NaBH_4 hydrolysis reaction was calculated to be $68.87 \text{ kJ mol}^{-1}$. With increasing NaBH_4 concentration from 5 to 30 wt% in $\text{NaBH}_4 + 5$ wt% NaOH solution at 20°C , hydrogen generation rate decreased from 1500 to $600 \text{ mL min}^{-1} \text{ g}^{-1}$ while it increased from 500 to $1200 \text{ mL min}^{-1} \text{ g}^{-1}$ with increasing NaOH concentration from 1 to 10 wt% in 20 wt% $\text{NaBH}_4 + \text{NaOH}$ solution at 20°C . From those experimental results, a 2 W hydrogen supply system was designed employing the prepared Co-B catalyst. Using the hydrogen generated from the fabricated reactor, a passive air-breathing 2 W PEMFC stack was successfully operated and powered a cellular phone.

References

- [1] Suda, U.S. Patent, US 6,358,488 B1 (2002).
- [2] H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hockstra, E.K. Hyde, J. Am. Chem. Soc. 75 (1953) 215.
- [3] H.C. Brown, C.A. Brown, J. Am. Chem. Soc. 84 (1962) 1493.
- [4] A. Leby, J.B. Brown, C.J. Lyons, Ind. Eng. Chem. 52 (1960) 211.
- [5] Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai, H. Hayashi, Int. J. Hydrogen Energy 27 (2002) 1029.
- [6] S.U. Jeong, R.K. Kim, E.A. Cho, H.-Y. Ha, S.-A. Hong, I.-H. Oh, S.H. Kim, Development of a hydrogen generator using NaBH_4 so-

- lution for feeding a miniaturized PEMFC, in: Proceedings of the 6th International Conference on New Energy Systems and Conversions, Nov. 9–13, Busan, 2003, pp. 275–279.
- [7] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, M. Binder, *Int. J. Hydrogen Energy* 25 (2000) 969.
- [8] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder, *J. Power Sources* 85 (2000) 186.
- [9] D. Hua, Y. Hanxi, A. Xingping, C. Chuansin, *Int. J. Hydrogen Energy* 28 (2003) 1095.
- [10] I.-H. Oh, S.K. Park, E.A. Cho, H.Y. Ha, S.-A. Hong, Characteristics of the monopolar type small polymer electrolyte membrane fuel cell for portable sources, in: Proceedings of the First International Conference on Polymer Batteries and Fuel Cells, 2003.