Short communication

Development of planar, air-breathing, proton exchange membrane fuel cell systems using stabilized sodium borohydride solution

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ABSTRACT

A planar, air-breathing, proton-exchange membrane fuel cell (PEMFC) system using a humidified H_2 gas released from the hydrolysis of a stabilized sodium borohydride ($NaBH_4$) solution with a selected solid catalyst is extensively investigated as a promising energy storage system for mobile power sources. In economic terms, the passive air-breathing PEMFC is quite attractive because can its reliability, fuel utilization, and specific energy can be enhanced by removing auxiliary devices such as the air pump and the humidifier. The rate of hydrogen generation can be manually controlled by adjusting the amount of $NaBH_4$ solution passed through the selected catalyst.

In this study, the rate of hydrogen generation is varied from 0 to $18\,cm^3\,min^{-1}$ by controlling the mass transport of stabilized $NaBH_4$ solution. The open-circuit voltage (OCV) and maximum power density are, respectively, $0.9\,V$ and $128\,mW\,cm^{-2}$ at ambient temperature and pressure. Assuming a fuel conversion efficiency of 100%, the Faradic efficiency and energy efficiency of this system estimated to be 75% and 46%, respectively. In a planar 8-cell series-connected format, the maximum power density and cathode temperature are $3.1\,W$ ($103\,mW\,cm^{-2}$) at $103\,mW\,cm^{-2}$ and $46\,°C$, respectively.

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1. Introduction

The micro proton exchange membrane fuel cell (PEMFC) system has attracted a great interest as an alternative mobile power source for cellular phones, notebook computers, and small robots due to its extraordinary power density and longer operation time. Nevertheless, the practical use of micro PEMFCs is still debated because of the parasitic power consumption caused by sub-systems such as those for cooling, humidification and pressurization devices that lead to complicated operation and rising costs in their present forms.

Much effort has been devoted to overcoming the above drawbacks to the commercial use of PEMFCs. The air-breathing units have been considered as a possible approach with respect to operation and cost. Micro air-breathing PEMFCs can effectively reduce the parasitic power loss induced by auxiliary devices because oxidant can be passively taken from the surrounding air by natural convection and diffusion. Moreover, it allows the design more compact cells to maximize their efficiency in practical operation. In addition, cost-cutting due to the elimination of the auxiliary devices

is also a benefit. These advantages should enhance reliability, fuel utilization and energy density.

On the other hand, given that a compact and inexpensive hydrogen source is essential for the development of micro PEMFCs, attention should be directed to hydrogen generation via the hydrolysis of alkaline or alkaline earth metal hydrides. Sodium borohydride ($NaBH_4$) is one of the most promising candidates for hydrogen production via hydrolysis reactions because it is favourable in terms of specific energy, safety and cost when it is deployed in commercial applications [1–3]. The hydrogen can be effectively generated from stabilized $NaBH_4$ solution with selected catalysts such as Ru [4], Pt/LiCoO [5], Ni-based alloy [6,7] and Co [8,9] based alloy in an alkaline solution as expressed by

$$NaBH_4 + 2H_2O \xrightarrow{(catalyst)} 4H_2 + NaBO_2 + \Delta H \quad \Delta H = 218\,kJ\,mol^{-1}_{NaBH_4} \tag{1}$$
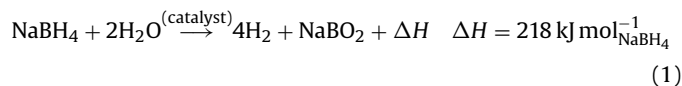
It is difficult to generate a significant amount of hydrogen from the stabilized $NaBH_4$ solution at ambient conditions due to its high pH. In order to increase hydrogen production, there is strong need to add a catalyst to facilitate the reaction of hydrogen generation and that can be removed once the reaction is finished. In practice about $10\,wt.\%$ of the gravimetric yield of hydrogen at more $50\,wt.\%$ of the maximum concentration of stabilized $NaBH_4$ solution can

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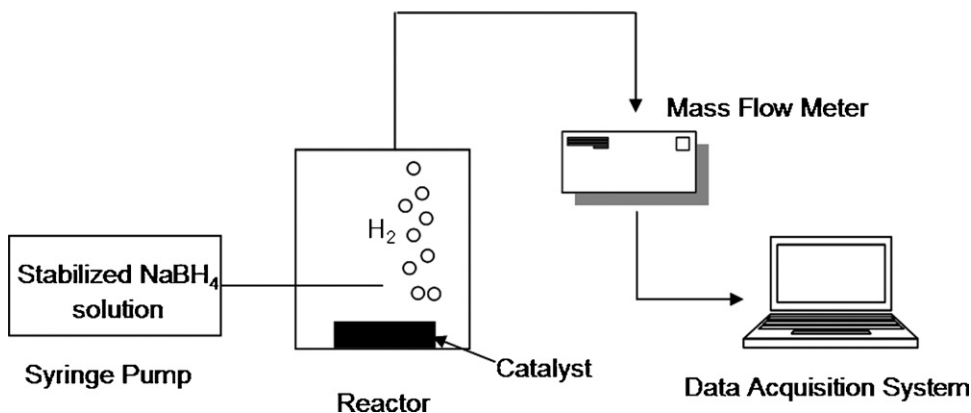*E-mail address:* fighter@kaist.ac.kr (J.-H. Kim).

Fig. 1. Schematic diagram of experimental setup for measuring H_2 generation rate.

be achieved through the addition of a catalyst. Sodium metaborate ($NaBO_2$) solution, which is a remnant of $NaBH_4$ hydrolysis, is drained away from the catalyst and replaced by fresh $NaBH_4$ solution at a filling station. Accordingly, this approach promises a safer and faster response to the hydrogen demand and is an attractive means for hydrogen storage in mobile PEMFCs.

Recently, Gervasio et al. [10] have reported the stable performance of micro PEMFCs with a hydrogen generator using a stabilized $NaBH_4$ solution, even at ambient temperature and pressure. Hilimanen et al. [11] also have discussed the characteristics of a planar free-breathing PEMFC in a dead-end mode with a pressurized anode by humidified hydrogen steam from a hydride tank and a $NaBH_4$ solution.

This investigation examines the feasibility and cell performance of a planar air-breathing PEMFC using a stabilized $NaBH_4$ solution and a selected catalyst. A passive-type PEMFC system without a fuel pump and an air blower is designed and its performance is evaluated systematically at ambient temperature and pressure. An important precaution has been addressed when it is formatted as a planar cell.

2. Experimental

A sodium hydroxide (NaOH) alkaline solution was used as a supporting solution of $NaBH_4$. The self-hydrolysis rate of $NaBH_4$ solutions depends on the pH and solution temperature. Kreevoy and Jacobson [12] reported that this rate is empirically represented by

$$\log t_{1/2} = \text{pH} - (0.034 \times T - 1.92) \tag{2}$$

where $t_{1/2}$ is the time taken (in min) for one-half of a $NaBH_4$ solution to decompose and is dependent on the solution pH and temperature, K.

Sodium borohydride ($NaBH_4$, VenPure AF granules 98+, ALDRICH) and sodium hydroxide (NaOH, 98−, SAMCHUN PURE CHEM.) were used as received. To make a stabilized $NaBH_4$ solution, the desired amount of $NaBH_4$ was added to the alkaline solution (4 wt.% NaOH) with vigorous stirring to enhance the dissolving process. The $NaBH_4$ concentration was 15 wt.%, i.e., an approximately 3.3 wt.% H storage capacity. The catalyst was 60 wt.% Pt–Ru alloy (1:1, a/o) on optimized carbon (E-TEK) and was loaded at 2.5 mg cm^{-2} on carbon cloth. Hydrogen generation through $NaBH_4$ hydrolysis was conducted in a homemade apparatus, its design is shown schematically in Fig. 1. The reaction chamber contained the selected solid catalyst (PtRu on C cloth, E-Tek) for $NaBH_4$ hydrolysis, a syringe pump (KD Scientific Co.) to supply the desired amounts of stabilized $NaBH_4$ solution and a mass flow meter (KOFLOC) to measure the instantaneous mass flow of the produced hydrogen. The mass flow meter signal was recorded by using a PC.

In order to apply the hydrogen generated from $NaBH_4$ hydrolysis, PEFC planar cells were connected. Fig. 2 schematically describes the experimental cell made from polycarbonate of a planar, air-breathing PEFC system using $NaBH_4$. The stabilized $NaBH_4$ solution was quantitatively supplied by a syringe pump (KD Scientific Co.) to the selected solid catalyst (PtRu on C cloth, E-Tek) into the fuel delivery part directly positioned under the membrane–electrode assembly (MEA), and the hydrogen gas was supplied to the anode of the MEA through a gas-permeable membrane (GORE) beneath the MEA.

The MEAs were homemade and prepared using a catalyst-coated-membrane (CCM). The cathode and the anode of the MEA were prepared by spraying a slurry consisting of the catalyst (50 w/o Pt on Vulcan XC-72), Nafion solution (5 w/o, Aldrich), water and glycerol on to a heated Nafion 112 membrane and subsequently removing the solvent by heating to at 150 °C. MEAs with an active area of 10 cm^2 and a catalyst loading of 0.7 ± 0.03 mg$_{Pt}$ cm^{-2} were manufactured by a hot-pressing method. The catalyst slurry was prepared by agitating Pt/C catalyst, ionomer (Nafion solution) and distilled water in an ultrasonic bath until the slurry became viscous an accomplished the desired internal wetting of the catalyst by the ionomer. The CCM was sandwiched between the anode gas-diffusion layer (GDL) and the cathode GDL the polytetrafluoroethylene (PTFE) content was controlled.

In the planar, air-breathing fuel cell design, Au-coated 304 stainless-steel mesh current-collectors were used. The mesh had a thickness of less 0.35 mm, a strand width of less 0.25 mm, and 60% open area. It was desirable to be able to test the air-breathing PEMFC in different electrical cell configurations (single cell and multi-cell
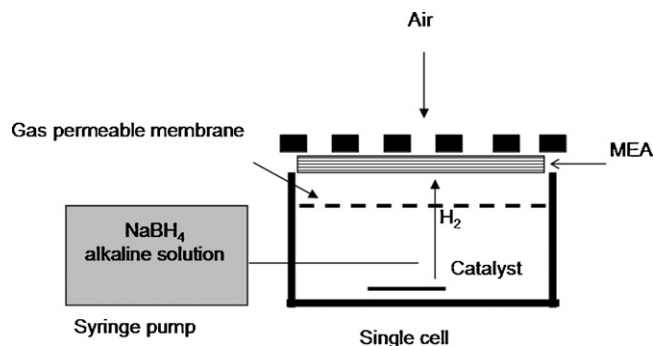

Fig. 2. Schematic diagram of planar air-breathing single cell using aqueous $NaBH_4$ solution with selected solid catalyst.
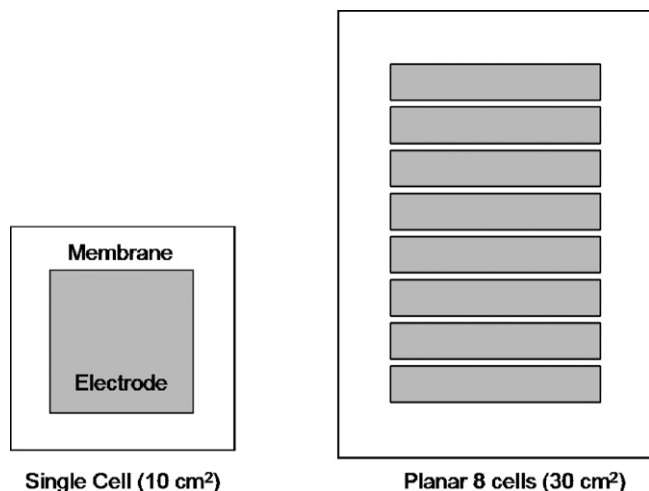
Fig. 3. Configuration of single cell and planar 8-cell MEA.

Fig. 4. H_2 generation rate with stabilized $NaBH_4$ solution and selected solid catalyst.

connected in series). Fig. 3 shows the configurations of a single cell and a series-connected 8 cells planar MEA used in our experiments. As shown in Fig. 3, the single cell has a regular square type and the 8 cells MEA is assembled by a 'banded membrane' concept in which the electrodes overlap such that cathode of one cell straps across the membrane to the anode of the next adjacent cell. The effective areas of the single cell and the planar multi-cell MEA, which consists of 8 cells, were 10 and 30 cm^2, respectively. To bond the metal mesh to the top surface of the GDL, a hot-pressed procedure was applied at 100 °C and 1.5×10^6 Pa for 3 min and then the seven-layered MEA structure was formed. In this work, all experiments for evaluating the performance of MEAs were made at room temperature with air-breathing.

Current–voltage curves were measured galvanostatically with an electronic load, A KIKUSUI electronic load (PLZ7OUA) was interfaced to a computer, and an electronic load was also employed to control the constant voltage (CV) and constant current (CC) mode. For recording the power–time curves, an interval of more than 3 min was used to obtain stable voltage and the cathode temperature was measured by a miniature (0.0005-in. thick) thermocouple (CO-1T, OMEGA), that was installed between the cathode of the MEA and the cover plate with an air hole.

3. Results and discussion

Considering the fact that a stable and steady hydrogen generation has been regarded as a key feature of mobile PEMFC systems for high-power applications, a systematic investigation has been made of the correlation between the mass transport of a stabilized $NaBH_4$ solution and the rate of hydrogen generation, as reported in Fig. 4. The flow rate of $NaBH_4$ solution (15 wt.%, 1 M alkaline solution) was varied from 2.0 to 5.0 $cm^3 h^{-1}$ and area of carbon cloth (PtRu) for a $NaBH_4$ hydrolysis was fixed at 1 cm^2. It is noted that the rate of hydrogen generation is highly dependant on the flow rate of $NaBH_4$ solution provided to a catalytic reactor; there is a proportional relationship as shown in Fig. 4. When the $NaBH_4$ solution is provided at 3.0 $cm^3 h^{-1}$, the maximum and nominal hydrogen generation rates are approximately 18 and 14 ml min^{-1}, respectively. Both results are higher than 10 ml min^{-1}, which is that required in a conventional PEMFC system to sustain 1.0 W of the electrical power. On increasing the flow rate of $NaBH_4$ solution, hydrogen generation becomes saturated, as shown in Fig. 4. This observation can be explained by a reduction in the catalytic activity of the PtRu catalyst or by precipitation of sodium borate ($NaBO_2$) as a by-product on the catalytic
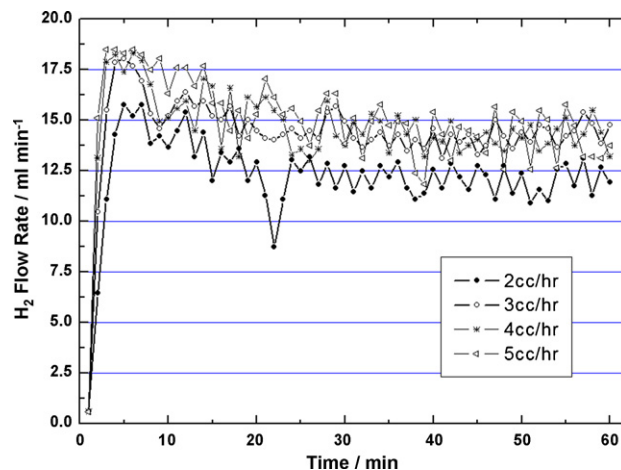
sites because the $NaBO_2$ formed on these sites can reduce the solubility of $NaBH_4$ and result in a low specific energy of the system [9]. Nevertheless, effective control of hydrogen generation is still considered as a strong advantage of the stabilized $NaBH_4$ solution.

The hydrogen generated by $NaBH_4$ hydrolysis between a quantitatively supplied $NaBH_4$ solution (15 wt.%) and the PtRu catalyst can be passively supplied to the planar air-breathing PEMFC, as shown in Fig. 2. The fuel utilization can be improved by a dead-end design of cell and the anode can be pressurized [11]. Fig. 5 shows open-circuit voltage (OCV) profiles and cathode temperature values of a planar air-breathing PEMFC cell operated with stabilized $NaBH_4$ solution (15 wt.%) as a hydrogen source. The flow rate of $NaBH_4$ solution and the area of the PtRu catalyst for hydrolysis are 4.0 $cm^3 h^{-1}$ and 1.0 cm^2, respectively. The planar air-breathing PEMFC cell shows a higher OCV and a lower cathode temperature compared with the conventional passive air-breathing DMFC. The OCV of planar air-breathing PEMFC cell reaches over 0.9 V and then stabilizes within 1 min after providing $NaBH_4$ solution and the cathode temperature is 28 °C at OCV, while the OCV and the cathode temperature of the conventional passive air-breathing DMFC are less than 0.6 V and 45 °C, respectively. Therefore, a strong advantage of $NaBH_4$ as a hydrogen source is that the hydrogen can be released without energy consumption at ambient temperature and pressure. Unlike the conventional passive air-breathing DMFC, the voltage drop and combustion reaction with oxygen at the cathode can be effectively diminished in this system.
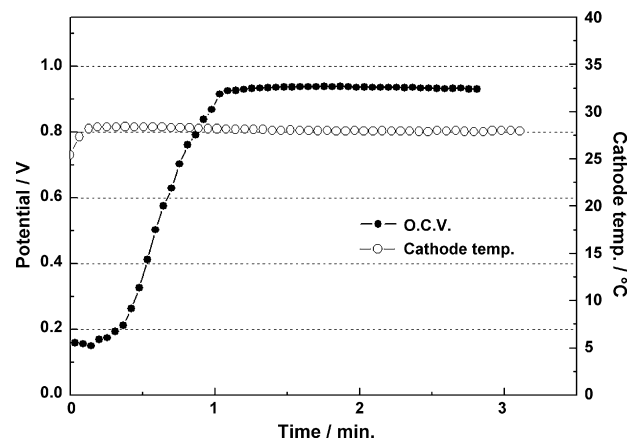

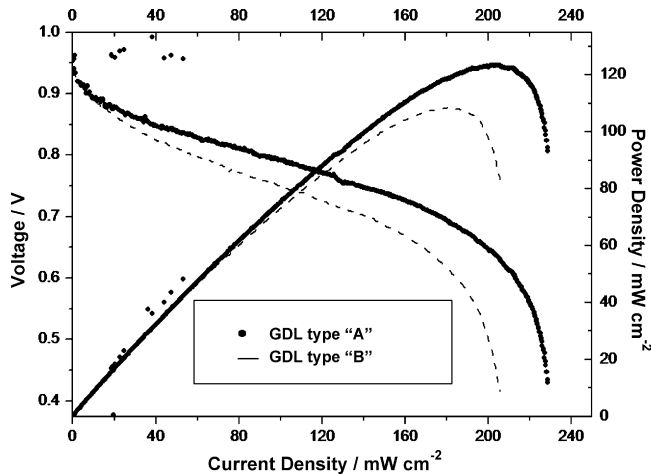Fig. 5. Open-circuit voltage (OCV) and cathode temperature of $NaBH_4$ air-breathing PEMFC.

Fig. 6. Polarization curves with different GDLs (A: high air permeability with high PTFE content, B: low air permeability with low PTFE content) for NaBH$_4$ air-breathing PEMFC.

In general, the performance of an air-breathing PEMFC using only natural convection of oxidant (air) significantly depends on the cathode GDL. For comparative purposes, different cathode GDLs (A: high air permeability with high PTFE content, B: low air permeability with low PTFE content) were employed to obtain polarization curves, as given in Fig. 6. Under ambient temperature and pressure, the PEMFC system with the cathode GDL (A) shows better cell performance. In practice, the maximum power output with cathode GDL (A) is 128 mW cm^{-2}, but only 110 mW cm^{-2} with cathode GDL (B). This is attributed to the fact that the cathode GDL (A), which has higher air permeability and higher PTFE content, can strongly enhance mass transport of oxidant into the cathode catalyst layer and improve water flooding from the electrochemical reaction. More interestingly, it can be seen clearly that the concentration limit in the high drain current region occurred in the polarization curves and therefore further decrease of the concentration loss and development of the GDL of both electrodes has to be conducted.

According to a comparison of the power density at different operating modes in Fig. 7, the power density of the air-breathing PEMFC single cell could be immediately achieved to over 90% of the maximum and then gradually increased to 100 mW cm^{-2} under a CV mode (0.7 V). Moreover, the power density is maintained at more than 100 mW cm^{-2} with a stable supply of hydrogen from NaBH$_4$
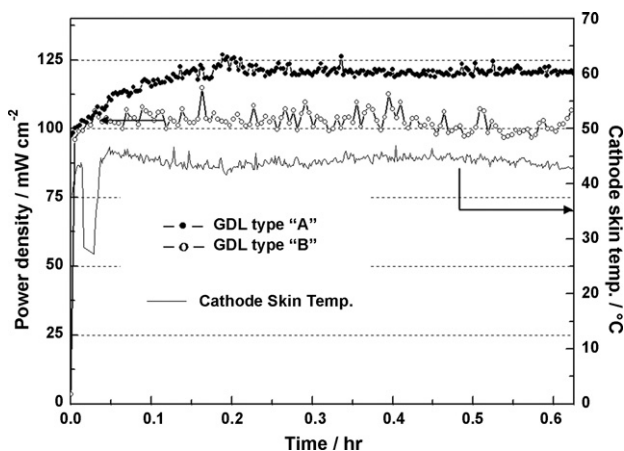

Fig. 7. Effect of cathode GDL on power densities and cathode temperature (flow rate of stabilized NaBH$_4$ solution (15 wt.%): 4 cm^3 h^{-1}).
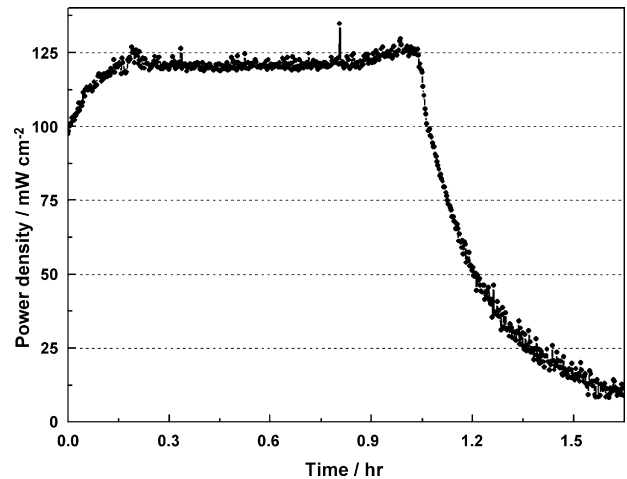

Fig. 8. Power density as function of time for NaBH$_4$ air-breathing PEMFC single cell using cathode GDL (A) (flow rate of stabilized NaBH$_4$ solution (15 wt.%): 4 cm^3 h^{-1}).

hydrolysis and reaches more than 123 mW cm^{-2} due to the GDL (A) with higher air permeability and the increased MEA performance under a CV mode. In addition, it is also found that the cathode temperature is kept below 45 °C during operation. These results reveal that a planar air-breathing PEMFC using NaBH$_4$ can be remarkably improved by MEA development and that it can be considered to be very suitable for mobile applications because there is less BOP (balance of plant) such as a humidifier, air pump and recycler.

The power density profiles of a planar air-breathing PEM single cell with a cathode GDL (A) as a function of time are presented in Fig. 8. It should be noted that the power density is steadily more that 120 mW cm^{-2} with continuous supply of the stabilized NaBH$_4$ solution, but dramatically falls to almost zero when the supply is stopped. The fast response of cell power to the flow rate of stabilized NaBH$_4$ solution results in a high fuel conversion efficiency of NaBH$_4$ and a high Faradic efficiency of the NaBH$_4$-passive PEMFC. The fuel conversion efficiency (Eq. (3)) of NaBH$_4$ and the Faradic efficiency (Eq. (4)) are defined as

$$\eta_{\text{fuel conversion}} = \frac{\text{Measured H}_2 \text{ amount(cm}^3)}{\text{Theoretical H}_2 \text{ amount of NaBH}_4\text{(cm}^3)} \tag{3}$$

$$\eta_{\text{Faradic}} = \frac{\text{Measured discharging capacity(Ah)}}{\text{Theoretical discharging capacity(Ah)}} \tag{4}$$

In addition, the efficiency of fuel cell can also be assessed on the basis of energy (Wh) by taking into account both the voltage and current. If follows that the energy efficiency can be expressed as

$$\eta_{\text{Energy}} = \frac{\text{Measured discharging capacity(Wh)}}{\text{Theoretical discharging capacity(Wh)}} \tag{4}$$

Assuming the fuel conversion efficiency to be 100%, the Faradic efficiency is calculated to be 75% and, especially, the energy efficiency is 46% in this system, which is much higher than that of the conventional passive DMFC, namely 16% [13]. The significant increase of energy efficiency of the planar air-breathing PEMFC using NaBH$_4$ could result from a higher operating voltage (passive DMFC: less than 0.4 V) and a lower fuel crossover.

In order to achieve higher power output and operating voltage for use in mobile applications such as cellular phones and MP3 and PDA units, it is necessary to connect several cells in series and formulate larger active areas. Fig. 9 gives the results from CC tests (CC mode) of a planar air-breathing PEMFC, in which 8 single cells are series connected and use the stabilized NaBH$_4$ solution. The overall active areas of the system and the selected solid catalyst are 30 and 1.5 cm^2, respectively, and the flow rate of NaBH$_4$ solution
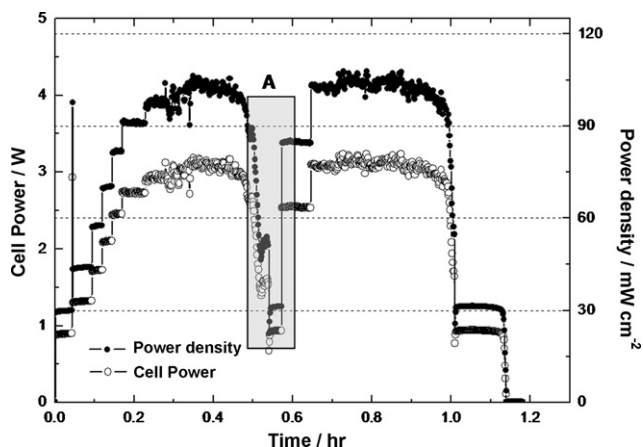
Fig. 9. Constant current test of passive, planar 8-cell PEMFC using stabilized $NaBH_4$ solution (flow rate of $NaBH_4$ solution: 5.5–6.5 cm^3 h^{-1}).

is in the range of 5.5–6.5 cm^3 h^{-1}. The applied drain current gradually increases in the stabilized voltage mode, and the maximum power and the cathode temperature are 3.1 W (103 mW cm^{-2}) at 175 mA cm^{-2} and 46 °C, respectively. As can be seen in Fig. 9 that even though the $NaBH_4$ solution is constantly provided, the cell power dramatically falls due to the voltage-drop of one single cell positioned at the edge during the measuring time of 30 min, marked as A, and is then restored to normal by a load-off for 1 min. It is likely that the sudden power-drop can be caused by an imbalance of fuel throughout the overall cell or a serial connection for high operating voltage. Therefore there is strong need for further investigation in order to identify the factors involved in the undesirable sudden decrease in power.

4. Conclusions

A planar air-breathing PEMFC, single cell (10 cm^2) and 8 cells (30 cm^2) series connected, using a humidified H_2 gas released from the hydrolysis of a stabilized $NaBH_4$ solution with a selected solid catalyst has been extensively investigated. The OCV of the single cell reaches over 0.9 V and then stabilizes within 1 min after providing the $NaBH_4$ solution. The cathode temperature is 28 °C under the OCV mode, whereas the OCV and cathode temperature for the conventional passive air-breathing DMFC are less than 0.6 V and 45 °C, respectively. This behaviour can be mainly explained in terms of a voltage drop and a combustion reaction with oxygen at the cathode by methanol crossover. The power density of the air-breathing PEMFC single cell immediately reaches over 90% of the maximum and then gradually increases to 100 mW cm^{-2} under a CV mode (0.7 V). Moreover, the power density is more than 100 mW cm^{-2} with a stable supply of hydrogen from $NaBH_4$ hydrolysis and is more 123 mW cm^{-2} due to the GDL (A) with higher air permeability and increased MEA performance under a CV mode. In a CV test, it is shown that, assuming a fuel conversion efficiency of 100%, the Faradic efficiency is 75% and the energy efficiency is 46%, which is much higher than that (16%) of the conventional passive DMFC. The significant increase in energy efficiency of the planar air-breathing PEMFC using $NaBH_4$ probably results from a higher operating voltage (passive DMFC: less 0.4 V) and a lower fuel crossover. In order to achieve higher power output and operating voltage for use in mobile applications, a CC test (CC mode) of the planar air-breathing 8-cell PEMFC has been conducted. The maximum power and the cathode temperature are 3.1 W (103 mW cm^{-2}) at 175 mA cm^{-2} and 46 °C, respectively.

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