Evaluation of alkaline borohydride solutions as the fuel for fuel cell

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Abstract

A fuel cell was assembled using alkaline borohydride solutions as the fuel. The specific gravity, specific viscosity, and melting points of the borohydride solutions were evaluated. With increasing the $NaBH_4$ concentration, the specific gravity was decreased but the viscosity was increased consistently. The effects of $NaBH_4$ and $NaOH$ concentrations on the cell and electrode polarizations were investigated. The increase of $NaBH_4$ concentration improved the anode performance a little but obviously increased the cathode polarization due to the BH_4^- crossover. As a result, the cell polarization increased when using high concentrated borohydride solutions. According to the Nernst's equation, the increase of $NaOH$ concentration is favorable to the anode, but negative to the cathode polarization. In principle, the cell polarization has nothing to do with the $NaOH$ concentration according to the cell reaction $NaBH_4 + O_2 = NaBO_2 + 2H_2O$. However, the experimental results showed that the high concentration of $NaOH$ aggravated the cell polarization at higher current densities.
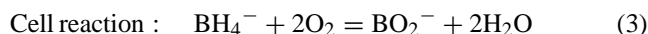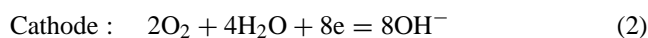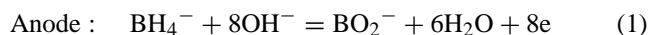© 2003 Elsevier B.V. All rights reserved.

Keywords: Borohydride solution; Specific gravity; Specific viscosity; Melting point; Polarization; Direct borohydride fuel cell

1. Introduction

As a fuel for fuel cell, methanol has attracted much attention due to its high capacity (5.03 Ah/g) in this decade, but the low performances of the direct methanol fuel cell (DMFC) perplex the researchers because of its low open-circuit voltage (OCV), the low electrochemical reactivity of methanol and the methanol crossover. Borohydrides are emerging as potential fuels for fuel cells [1–6] by the reasons of their high capacities, high cell voltage (1.64 V for borohydride and 1.21 V for methanol) and high hydrogen contents. For example, $NaBH_4$ contains 10.6 wt.% hydrogen and its capacity reaches to 5.67 Ah/g that is far more than the value of most hydrogen storage alloys (around 0.3–0.4 Ah/g). Two types of the direct borohydride fuel cell (DBFC) have been reported [4,5,7]. Jasinski [7] used an asbestos membrane to separate the anode and the cathode compartments. The fuel cell using borohydride showed better performance than that using H_2 though there was a decrease in cathode performance due to the presence of fuel in the common electrolyte (asbestos membrane). He suggested this decrease could be offset by use of an electrolyte membrane. Amendola et al. [4,5] constructed a cell with an air cathode and an anode made of highly dispersed

Au/Pt particles supported on high-surface area carbon silk. An anion exchange membrane (AEM) was used as the electrolyte. The number of electrons utilized per molecule of BH_4^- oxidized (about 6.9 out of a possible 8) shows efficient utilization of the BH_4^- oxidation. Specific energy >180 Wh/kg and power densities >20 mW/cm² at room temperature and >60 mW/cm² at 70 °C have been reported. However, they cannot solve the BH_4^- crossover because BH_4^- as an anion is easy to permeate through AEM.

Based on their results, to improve the crossover resistance of the membrane against BH_4^-, we have adapted the fuel cell structure to use a Nafion membrane as the electrolyte to separate the fuel from the cathode. The electrode reactions and cell reaction are the same as those in the suggested model cells [5,7]. BH_4^- reacts with OH^- to form BO_2^-, H_2O and releases electrons at the anode; meanwhile oxygen reacts with H_2O to form OH^- at the cathode. The electrode reactions and cell reaction are described as follows,

$$\text{Anode:} \quad BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e \qquad (1)$$

$$\text{Cathode:} \quad 2O_2 + 4H_2O + 8e = 8OH^- \qquad (2)$$

$$\text{Cell reaction:} \quad BH_4^- + 2O_2 = BO_2^- + 2H_2O \qquad (3)$$

For our cell using a Na^+ form Nafion membrane as the electrolyte, the cation Na^+ acts as the charge carrier in the electrolyte rather than the anion OH^- as the charge carrier, which is different from the Jaskin's and Amendola's cells.

* Corresponding author. Tel.: +81-426-20-0154; fax: +81-426-20-0150.
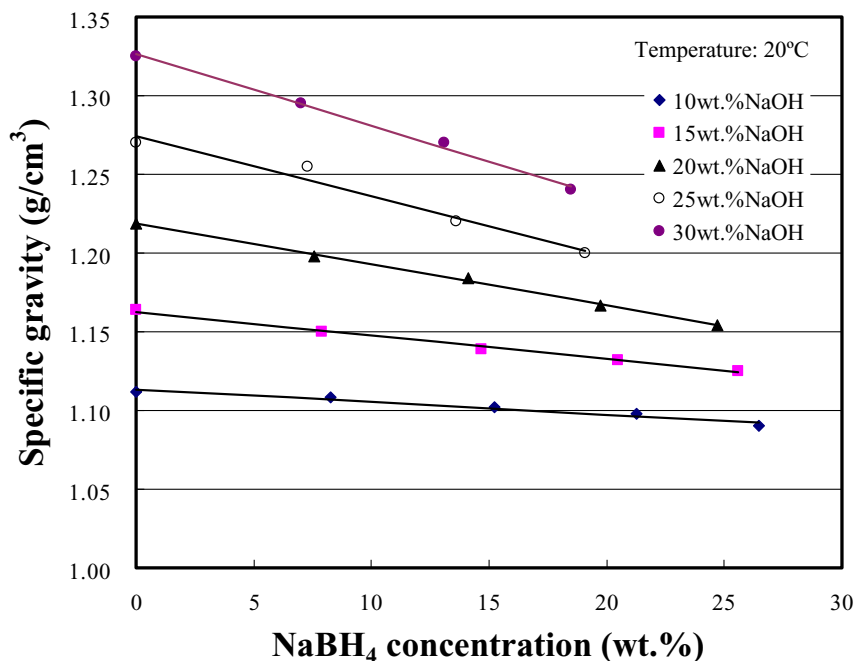*E-mail address:* bq96001@ns.kogakuin.ac.jp (Z.P. Li).

Fig. 1. Relationship between the specific gravity and the NaBH$_4$ concentration.

Our cell configuration and electricity generation mechanism have been reported in our previous research [8]. In this paper, we investigated effects of NaBH$_4$ and NaOH concentrations on cell performances. In addition, it is considered that the mechanical properties and temperature property of the fuels are important for the fuel cell system design and determination of the auxiliary machine specifications. We evaluated some fundamental properties of borohydride solutions, such as specific gravity, specific viscosity and melting points.

2. Experimental details

The borohydride solutions were prepared by dissolving sodium borohydride (purity: 98%) in alkaline solutions (NaOH purity: 95%). The specific gravity was determined with the precious specific gravity bottles. The specific viscosity was measured with a calibrating viscometer. Melting points were determined by the method of differential scanning calorimetry (DSC).

A surface treated Zr–Ni alloy [9] was used as the anode catalyst. The Pt-black with carbon black substrate was used as the cathode catalyst. The preparation methods of MEA and the fuel cell assembling were described in our previous report [8]. A Na$^+$ form Nafion 117 was used as the electrolyte. An Hg/HgO 6.1 M NaOH (20 wt.% NaOH) was applied as the reference electrode. The cell and electrode polarizations were measured at 0.5 l/min of fuel flow rate, 5 l/min of humidified oxygen flow rate at operation temperature 60 °C. Oxygen humidification was conducted by bubbling method at the same temperature.

An H-cell was applied to measure the amount of NaBH$_4$ crossover through Nafion membrane at 60 °C. Two compartments of the H-cell were separated with a Nafion membrane. Hundred milliliter of fuel containing 10 wt.% NaBH$_4$ and 20 wt.% NaOH was in one compartment and 100 ml of 20 wt.% NaOH solutions was in another compartment. The amount of NaBH$_4$ crossover was determined by measuring the NaBH$_4$ concentration in the compartment where only 20 wt.% of NaOH solution was poured at the beginning. The NaBH$_4$ content was quantitatively determined by iodimetric analysis [10].
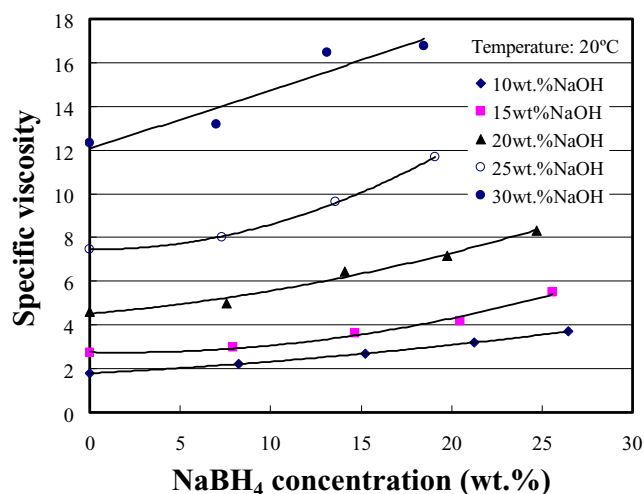

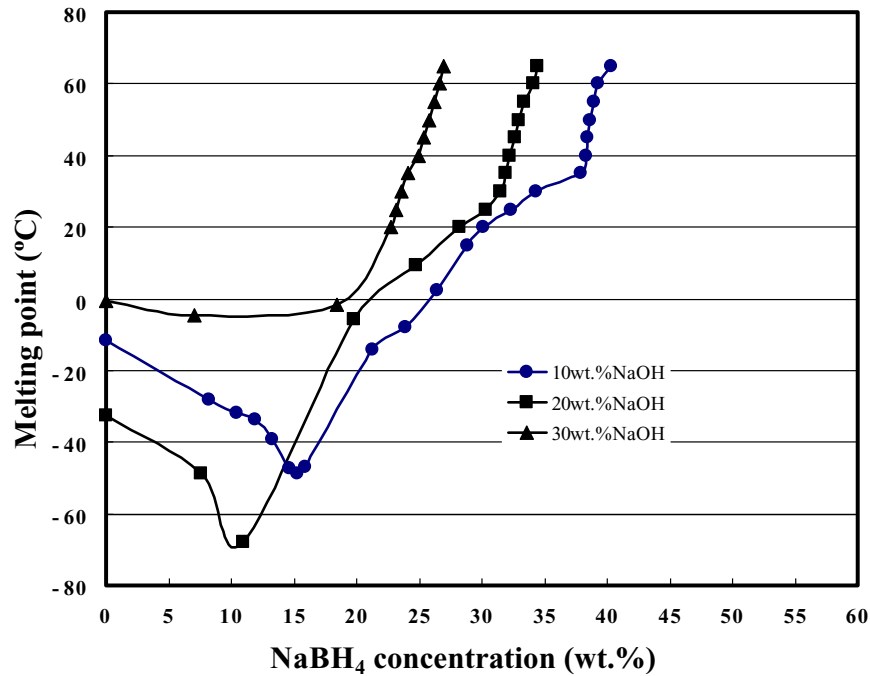Fig. 2. Relationship between the specific viscosity and the NaBH$_4$ concentration.

Fig. 3. Relationship between the melting points between the NaBH$_4$ and NaOH concentration.

3. Results and discussion

3.1. Mechanical properties and melting points of the alkaline borohydride solutions

Increase of the NaBH$_4$ concentration in the alkaline borohydride solutions resulted in decrease of the specific gravity. It decreased more quickly when the alkaline borohydride solutions contained more NaOH as shown in Fig. 1. With increasing the NaBH$_4$ concentration, the specific viscosity increased as shown in Fig. 2. It demonstrates a quick increase when the alkaline borohydride solutions contain higher concentrations of NaOH. It implies that Na$^+$ movability will decrease with increasing the viscosity, which results in increasing the ohmic loss of the cell performance.

It was found that there were extreme values in melting points corresponding to NaBH$_4$ and NaOH concentrations. The alkaline borohydride solution consisting 20 wt.% of NaOH and 11 wt.% of NaBH$_4$ showed the melting point of $-68\,^\circ$C. Though the NaBH$_4$ concentration was decreased to a very low level, the melting points can keep under $-30\,^\circ$C if the alkaline borohydride solution contained 20 wt.% of NaOH. Considering the properties of the fuel fluid at low temperature as shown in Fig. 3, the fuel fluid containing 20 wt.% of NaOH and 10 wt.% of NaBH$_4$ is favorable for DBFC.
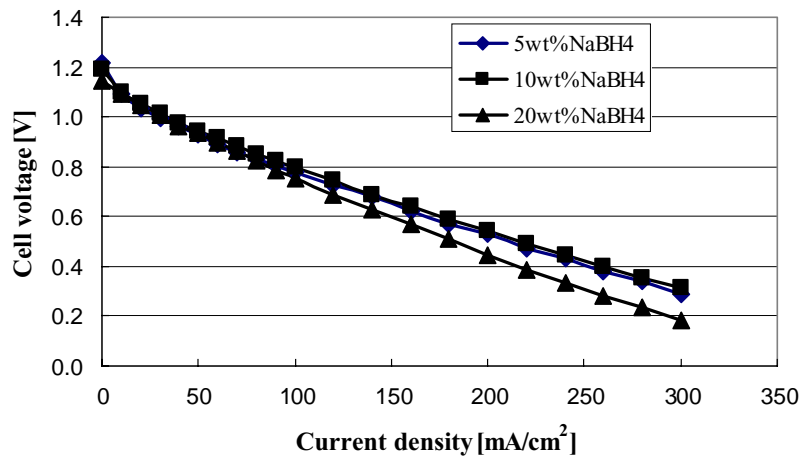

Fig. 4. Polarization curves for 60 $^\circ$C oxygen-cathode DBFC on Na$^+$ form Nafion 117. Anode: 200 mg/cm^2 fluorinated MH, fuel flow rate 0.5 l/min. Cathode: 1 mg/cm^2 Pt-black, humidified O$_2$ at 5 l/min.
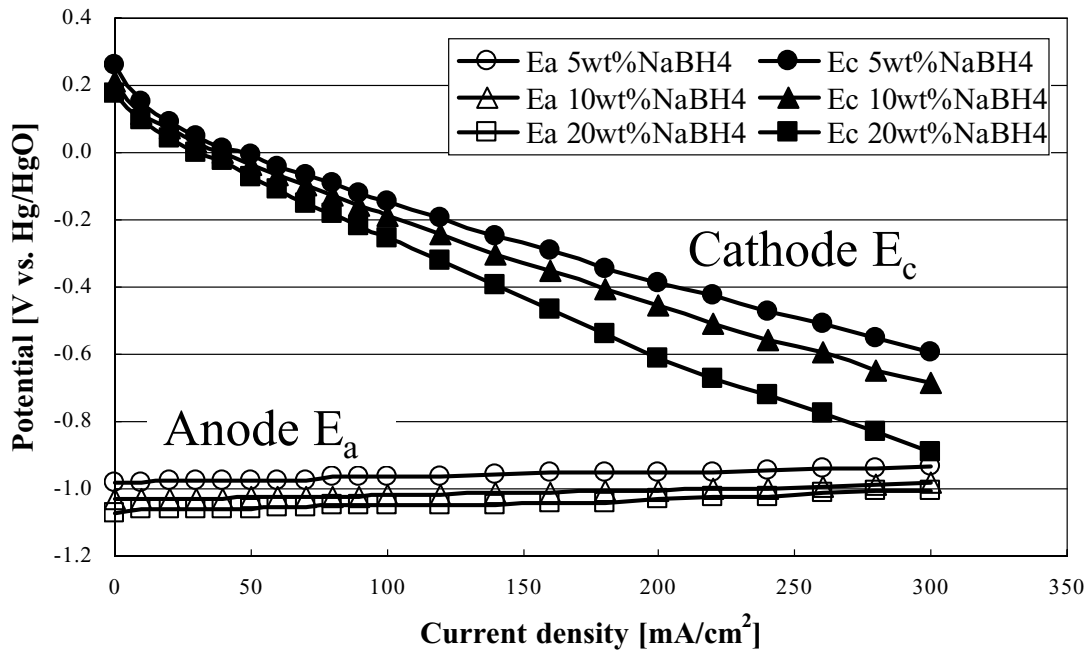
Fig. 5. Polarization curves for 60 °C anode and cathode. Anode: 200 mg/cm² fluorinated MH, fuel flow rate 0.5 l/min. Cathode: 1 mg/cm² Pt-black, humidified O₂ at 5 l/min. NaOH concentration: 20 wt.%.

3.2. Cell performances

Regard to the cell reaction (3), the electromotive force (emf) is determined by the Nernst's equation,

$$E = E^0 + \frac{RT}{8F} \ln \frac{a_{\mathrm{BH_4^-}} \, p_{\mathrm{O_2}}^2}{a_{\mathrm{BO_2^-}} \, a_{\mathrm{H_2O}}^2} \tag{4}$$

It is expected that the open-circuit potential of the anode and the cell performance would be improved by using highly concentrated NaBH₄ solutions. However, the experimental results showed that anode potentials were less negative than the standard potential of tetrahydridoborate ion (−1.34 V versus Hg/HgO) as shown in Fig. 4. From our previous experimental results, we believe that the observed potential was established among BH₄⁻ and other partially
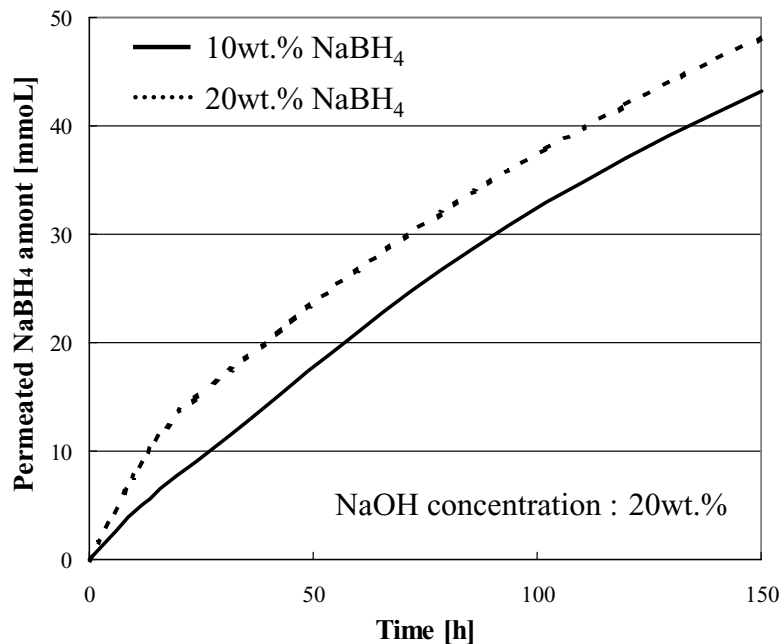

Fig. 6. Migration of sodium borohydride through Nafion membrane (N-117) when changing the NaBH₄ concentration at 60 °C.
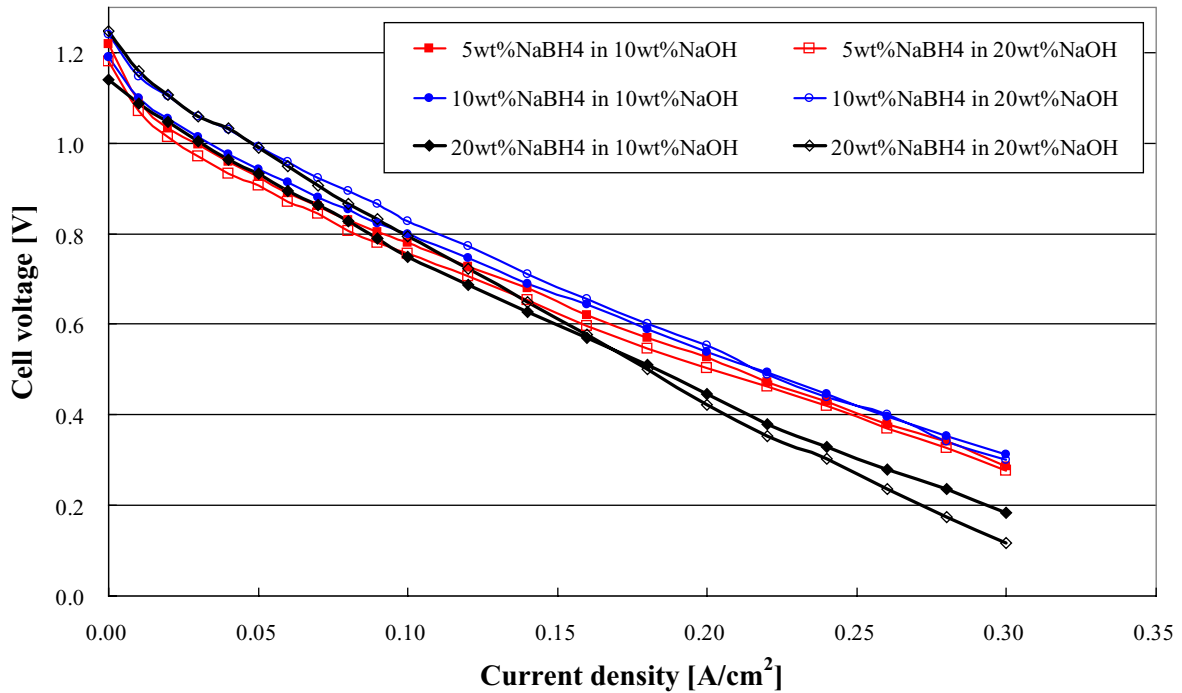
Fig. 7. Cell polarization curves for 60 °C oxygen-cathode DBFC on Na$^+$ form Nafion 117 membrane. Anode: 200 mg/cm^2 fluorinated MH, fuel flow rate 0.5 l/min. Cathode: 1 mg/cm^2 Pt-black, humidified O$_2$ at 5 l/min.

oxidized intermediates, especially molecular hydrogen caused by the hydrolysis reaction of BH$_4$$^-$ [11], so that the observed potentials were less negative than the theoretical value.

It is found that the increase of the borohydride concentration in the anolyte decreased the cell performance, which violated the Nernst's equation. In order to find the reasons for this phenomenon, we measured the anode and the
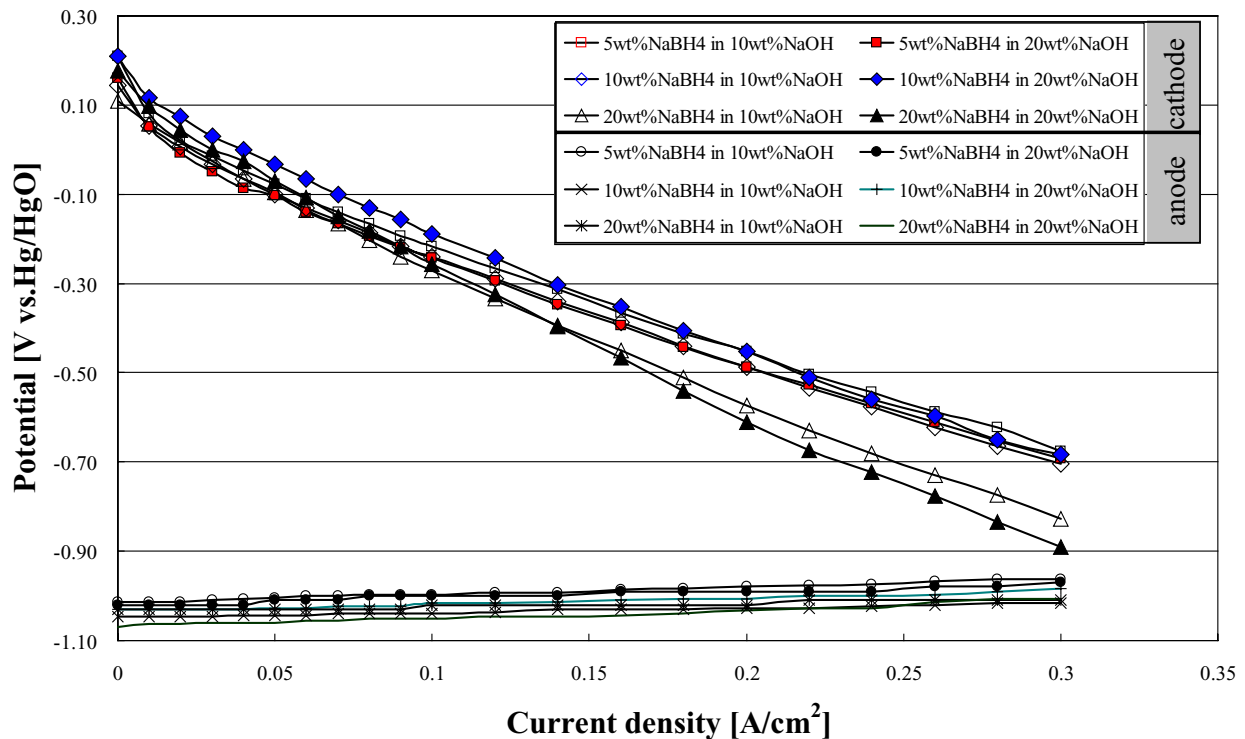

Fig. 8. Polarization curves for 60 °C anode and cathode when changing concentrations of NaBH$_4$ and NaOH.

cathode polarizations. It was found that the anode performance was improved a little when increasing the $NaBH_4$ concentration in the anolyte, but the cathode performance was significantly deteriorated as shown in Fig. 5. It means that the $NaBH_4$ concentration in the anolyte influenced the cathode potentials. According to experiment results of permeability of $NaBH_4$ through Nafion membranes as shown in Fig. 6, the fuel crossover was confirmed. It was believed that the performance decrease of the cathode when increasing $NaBH_4$ concentration of the anolyte was related to the borohydride crossover that shifted the cathode potential.

Fig. 7 shows that the fuel cell using 10 wt.% $NaBH_4$ and 20 wt.% NaOH solution demonstrated a better performance than that using other compositions in our test solutions. The cell using the fuel containing 20 wt.% of $NaBH_4$ and 20 wt.% of NaOH showed a higher over-potential than that using the fuel containing 10 wt.% of NaOH at high current densities. Fig. 8 shows the anode and cathode polarizations when changing the $NaBH_4$ and NaOH concentration. The anode showed a small change in polarization. However, cathode showed a quicker linear decrease in potential at high current densities when the NaOH concentration of the anolyte containing 20 wt.% $NaBH_4$ was increased from 10 to 20 wt.%.

It is understandable that the increase of NaOH concentration is favorable to the anode but will cause a negative effect to the cathode according to the Nernst's equation based on electrode reaction (1) and (2). In principle, the NaOH concentration has nothing to do with the cell polarization. The cathode potential decrease in linear fashion was mostly due to the ohmic losses. The movability of charge carrier (Na^+) is probably decreased due to the increase of the solution viscosity when increasing the NaOH concentration as shown in Fig. 2. In the small current range, the Na^+ flux was small so that the influence was not significant. However, in the large current range, the large Na^+ flux was required so that the influence of the Na^+ movability was amplified. As a result, the cell performance was dominated by the Na^+ movability in the large current range. Therefore, the high concentration of NaOH aggravated the cell polarization at higher current densities.

4. Conclusions

Increase of the $NaBH_4$ concentration in the borohydride solutions resulted in decrease of the specific gravity but increase of the viscosity consistently. The borohydride solution consisting 11 wt.% of $NaBH_4$, 20 wt.% of NaOH showed the lowest melting point of $-68\,^\circ$C in the test range. It was found that the increase of $NaBH_4$ concentration improved the anode performance a little but resulted in an obvious increase in cathode polarization when using highly concentrated sodium borohydride solutions as the fuel. Generally, the cell voltage has nothing to do with the NaOH concentration. However experimental results showed that cell polarization was increased because the high concentration of NaOH decreased the movability of the charge carrier (Na^+) due to the increase of the viscosity.

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