



Short communication

Influences of sodium borohydride concentration on direct borohydride fuel cell performance

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ABSTRACT

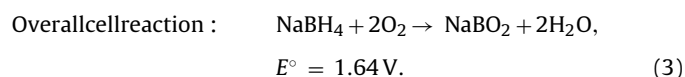
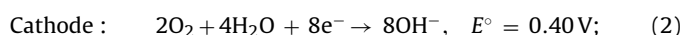
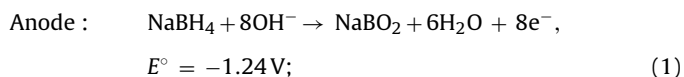
In this work, the effects of sodium borohydride concentration on the performance of direct borohydride fuel cell, which consisted of Pd/C anode, Pt/C cathode and Na⁺ form Nafion[®] membrane as the electrolyte, have been investigated in steady state/steady-flow and uniform state/uniform-flow systems. The experimental results have revealed that the power density increased as the sodium borohydride concentration increased in the SSSF system. Peak power densities of 7.1, 10.1 and 11.7 mW cm⁻² have been obtained at 0.5, 1 and 1.5 M, respectively. However, the performance has decreased when the sodium borohydride concentration has been increased, and the fuel utilization ratios of 29.8%, 21.6% and 20.4% have been obtained at 0.5, 1 and 1.5 M, respectively in the USUF system.

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1. Introduction

The direct borohydride fuel cell has many advantages because it eliminates hydrogen storage problems, safely uses liquid fuel, has a low fuel crossover to the cathode side and has a high theoretical cell voltage (1.64 V) with a high theoretical power density (9.3 kWh kg⁻¹). Due to its many advantages, DBFC has recently been considered as a potential candidate for portable and mobile applications. Moreover, it is especially important to Turkey because the sodium borohydride solution used as the fuel in DBFC is produced from boron mines, and Turkey has 70% of the total World's boron reserves [1].

The anode, cathode and cell reactions in the DBFC are given as the following equations (with using oxygen as oxidant):



Theoretically, one ion of BH₄⁻ can generate eight electrons. However, the numbers of electrons utilized per ion of BH₄⁻ oxidized are fewer than eight due to hydrogen evolution at the anode side and fuel crossover. Hydrogen evolution from the hydrolysis reaction during operation not only decreases fuel utilization but also causes some problems in system designing. In addition to this, BH₄⁻ crossover; NaOH accumulation at the cathode, and NaBO₂ accumulation at the anode are other problems that need to be solved [2].

The direct anodic oxidation of borohydride provides more negative potential than that of hydrogen gas [3]. The only products of the cell chemistry indicated in the reaction (3) are water and borate ion. Borate is both environmentally acceptable and potentially convertible back to borohydride [4].

The operational parameters have great effect on the DBFC performance. Sodium borohydride concentration is one of the important operation parameters. Many studies on the effect of borohydride concentration on its electrochemical oxidation (both fundamental – at small electrodes – and applied – at fuel cells) have been reported [5–9]. In our previous work, we investigated the influences of different operational conditions such as cell tem-

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Nomenclature

| | |
|-----------|------------------------------|
| C_{ex} | experimental charge capacity |
| C_{th} | theoretical charge capacity |
| DBFC | direct borohydride fuel cell |
| E° | standard potential |
| FUR | fuel utilization ratio |
| HCHO | formaldehyde |
| H_2O_2 | hydrogen peroxide |
| MEA | membrane electrode assembly |
| $NaBH_4$ | sodium borohydride |
| $NaBO_2$ | sodium metaborate |
| NaOH | sodium hydroxide |
| PTFE | polytetrafluoroethylene |
| SSSF | steady state/steady-flow |
| USUF | uniform state/uniform-flow |

perature, sodium hydroxide concentration, oxidant conditions and catalyst loading on performance [1]. In this paper, the effects of sodium borohydride concentration on the performance of the 25 cm² DBFC produced in a laboratory environment were examined.

2. Experimental

2.1. Electrode materials and chemicals

The materials and chemicals used during the tests are listed as follows: $NaBH_4$ (98%, Merck), NaOH (98%, Merck), $PdCl_2$ (99%, Merck), $H_2PtCl_6 \cdot 6H_2O$ (99.95%, Merck), carbon powder (Vulcan, CABOT), Nafion[®] 117 membrane (DuPont), Ni foam (Incofoam), PTFE (Alfa Aesar), isopropyl alcohol (Merck), formaldehyde solution (Merck), Ni net (Precision Ni), carbon paper (Toray, E-TEK), Nafion[®] solution (5 wt.%, Aldrich), H_2O_2 (30%, Merck).

2.2. Preparation of anode catalyst

Pd/C catalyst was prepared by use of the precipitation method. Vulcan XC-72 carbon black was added to deionized water under magnetic stirring for 20 min. Then $PdCl_2$ was added to the solution and stirred for 1 h. Later, 0.5 M NaOH was added to the solution to drop-wise to pH 9–10 and stirred for an additional 30 min. Formaldehyde was then added to the precipitated metal. The mixture was subsequently filtered, and the resultant slurry was washed three times with hot water. Then, the obtained carbon supported palladium was dried for 8 h [10].

2.3. Preparation of anode electrode

Prepared Pd/C powder was mixed with PTFE powder in a weight ratio of 18:1. In addition, water and isopropyl alcohol were added to the mixture to form ink. This ink was stirred for 24 h at room temperature to obtain anodic slurry. The anodic slurry was spread onto a Ni foam substrate. After being wrapped by a nickel net of 100 mesh to prevent the drop of anode catalyst powder, the prepared electrode was pressed at 2 ton cm⁻² and 70 °C for 3 min into a plate to the final form. The size of the prepared electrode was 50 mm × 50 mm and 0.7 mm thick with 3 mg cm⁻² of Pd/C loading [10].

2.4. Preparation of cathode catalyst

A similar procedure was used to fabricate carbon supported Pt as the cathode catalyst. Vulcan XC-72 carbon black was added to the deionized water under magnetically stirring in an ultrasonic bath for 20 min until it became slurry form. Then, H_2PtCl_6 was added to the solution and stirred for 1 h. Later, 0.5 M NaOH was added to the solution drop-wise to pH 9–10 and stirred for an additional 30 min at constant temperature. The solution was stirred for 45 min, and platinized carbon was obtained by the addition of formaldehyde solution. After that, the platinized carbon was filtered, washed with hot distilled water and dried for 2.5 h [10].

2.5. Preparation of cathode electrode

The cathode electrode used in this work consisted of a catalyst layer made of Vulcan XC-72 with 10 wt.% Pt and a gas diffusion layer. The solution that contained the prepared Pt/C catalyst, 75 mg PTFE binder, 3.7 ml water and 3.7 ml isopropyl alcohol was stirred at 60 °C for 1.5 h to produce cathode slurry. Once stirred, it was dried under atmospheric conditions. Then, it was spread onto 0.28-mm-thick PTFE-treated Toray carbon paper with a 0.3 mg cm⁻² Pt loading in the form of a continuous wet film. The prepared electrode was air dried for 24 h, it was heated to 225 °C for 30 min. After that, required quantity of Nafion[®] solution was spread onto the catalyst layer in the form of continuous wet film, and then the electrode was oven dried at 80 °C [10].

2.6. Fabrication of membrane electrode assembly

Before the compression process of MEA, a Nafion[®] 117 membrane was pretreated by boiling in a 10 wt.% H_2O_2 solution and then deionized water. The pretreated membranes were stored separately in deionized water before use at room temperature and were also immersed in 6N NaOH for 30 min before assembly [2,11–14]. The anode, cathode and pretreated Nafion[®] 117 membrane were sandwiched together and hot pressed at 2 ton cm⁻² and 120 °C for 3 min. To humidify and modify the Nafion[®] 117 membrane into the a Na⁺ form, 15 wt.% NaOH solution was circulated for 3 h at 60 °C before every trial of the test fuel cell [11,15].

2.7. Performance tests

A schematic test system of DBFC is shown in Fig. 1. After installation of a single cell with an active electrode area of 25 cm² in the test station, performance tests were carried out. In order to determinate the optimal sodium borohydride concentration in the SSSF system, solution was pumped by a peristaltic pump to the anode compartment at a feed rate of 2 ml min⁻¹ while varying the concentration of $NaBH_4$ in 20 wt.% sodium hydroxide solution at 25 °C. Furthermore, the humidified air was fed into the cathode compartment at a rate of 150 ml min⁻¹. Electrical heaters were placed behind each of the graphite blocks to heat the cell to the required temperature. Cell temperature was set at 25 °C. The power density measurements were carried out with an electronic load (Electrochem, Inc. ECL 150). The power densities were calculated from the experimentally measured current densities and potential values.

In addition, discharge capacities were obtained at varying concentrations of $NaBH_4$ in 20 wt.% sodium hydroxide solution at 25 °C in the USUF system. A fuel reservoir of 6 ml was attached to one side of the end plate in which a sodium borohydride solution was kept. The cathode worked by air breathing. Measurements were taken by monitoring cell voltage and current density with working time concurrent with the galvanostatic operation at constant resistance of 1 Ω and at 25 °C [10].

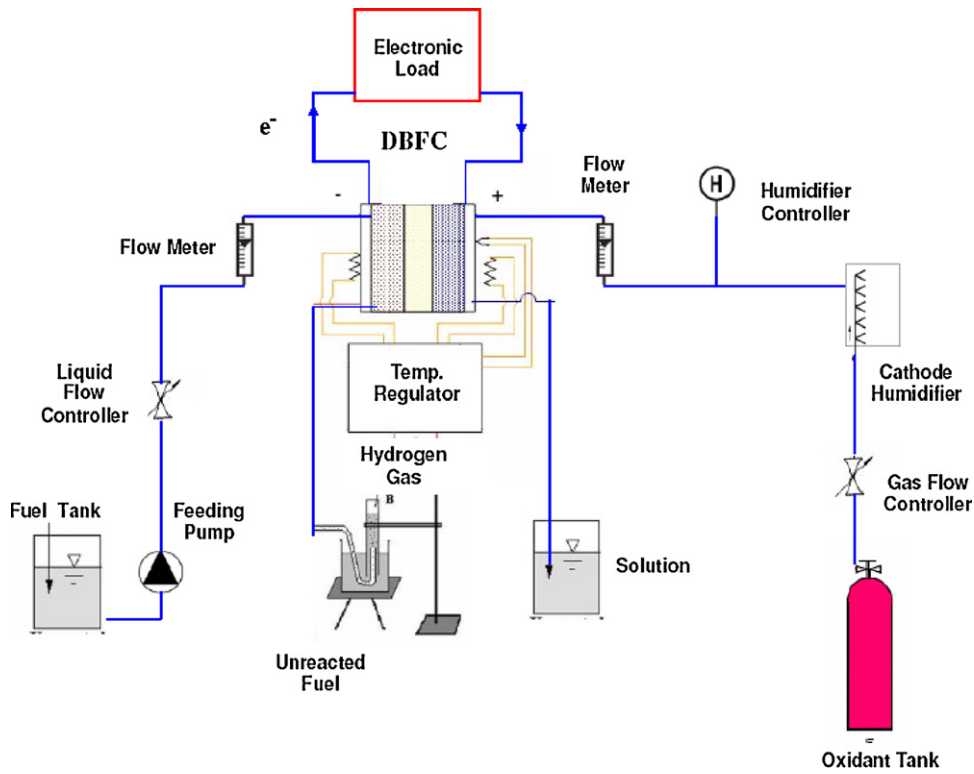


Fig. 1. The schematic test system of the DBFC.

3. Results and discussion

3.1. Effect of sodium borohydride concentration in the SSSF system

The effects of sodium borohydride concentration on the cell performance were investigated at 0.5, 1 and 1.5 M. The power density

increased in correlation to increased sodium borohydride concentration in the SSSF system due to the increase of mass transfer of the fuel and the kinetics of borohydride oxidation. Peak power densities of 7.1, 10.1 and 11.7 mW cm^{-2} were obtained at 0.5, 1 and 1.5 M, respectively (Fig. 2). The results of the present study remain consistent with the results reported for the change of sodium borohydride concentration by Cheng and Scott [16].

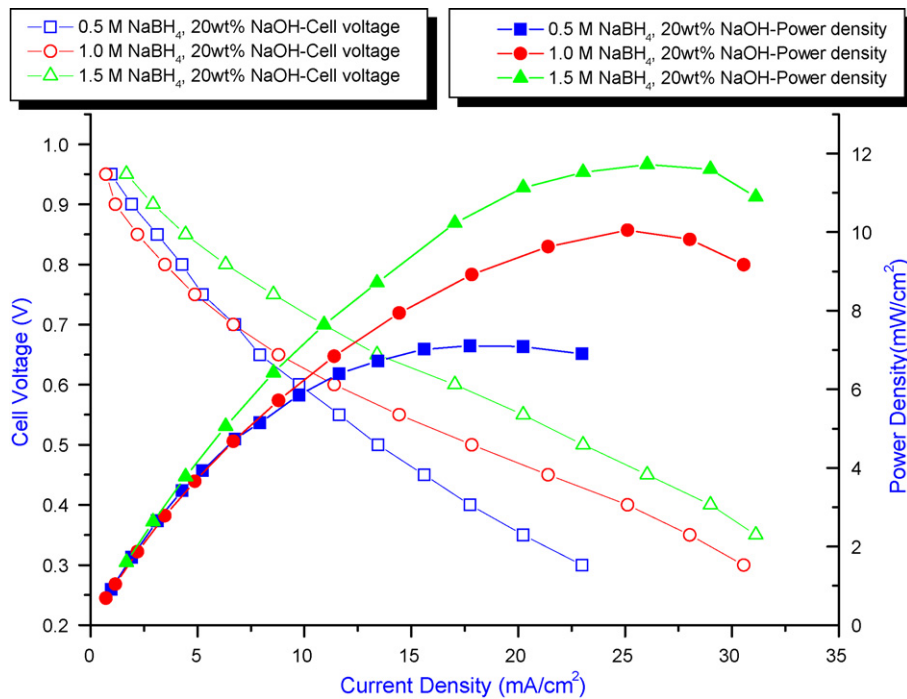


Fig. 2. Curves of cell polarization and power density for DBFC at different NaBH_4 concentrations. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion® N117. Temperature: 25 °C. Flow rate of humidified air: 150 ml min^{-1} (1 atm, RH: 65%). Flow rate of fuel: 2 ml min^{-1} .

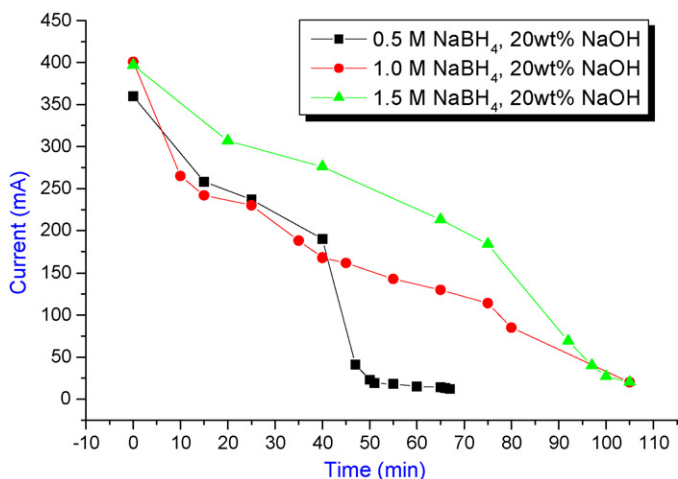


Fig. 3. The change of current with working time at different NaBH_4 concentrations. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion® N117. Temperature: 25°C . Resistance: 1Ω .

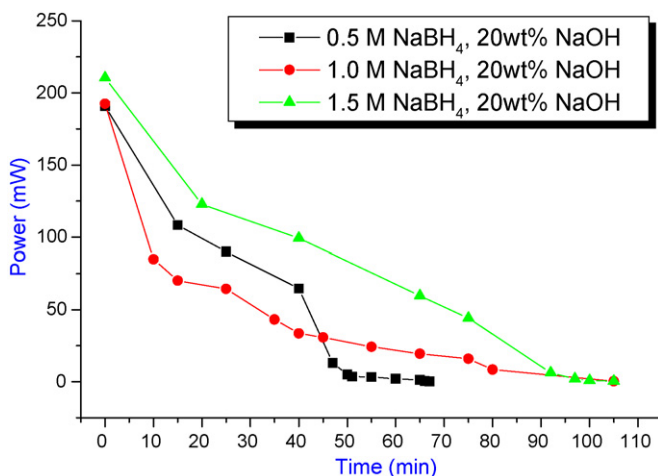


Fig. 4. The change of power with working time at different NaBH_4 concentrations. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion® N117. Temperature: 25°C . Resistance: 1Ω .

Furthermore, the melting point of sodium borohydride solution is affected by sodium borohydride concentration [11]. In addition, borate (BO_2^-) production that occurred from borohydride oxidation can potentially be problematic since it has a low solubility [17], and its solubility limit is not only a function of temperature but also a function of sodium borohydride concentration [18]. Therefore, the sodium borohydride concentration should be optimized particularly in terms of cell performance for portable applications.

3.2. Effect of sodium borohydride concentration in the USUF system

3.2.1. Discharge capacity, fuel utilization ratio and number of electrons

Discharge capacities were obtained at varying concentrations of NaBH_4 in 20 wt.% sodium hydroxide solution at 25°C (Figs. 3 and 4 and Table 1) in the USUF system.

Fig. 5 shows the fuel utilization ratio and Fig. 6 illustrates the number of electrons utilized during BH_4^- oxidation obtained as a function of sodium borohydride concentration at room temperature. For NaBH_4 , the theoretical specific energy charge capacity

Table 1

Discharge capacities at different sodium borohydride concentrations.

| Concentration (M) | Current-time (mAh) | Power-time (mWh) |
|-------------------|--------------------|------------------|
| 0.5 | 191.55 | 78.935 |
| 1.0 | 278.042 | 69.703 |
| 1.5 | 393.475 | 141.94 |

was accepted as 9293 Wh kg^{-1} and 5667 Ah kg^{-1} , respectively [17]. Fuel utilization ratio was calculated by comparison of theoretical ampere-hour capacity and experimental ampere-hour capacity. The latter was calculated by the multiplication of experimentally obtained current and time values (Eq. (4)). The FURs of 29.78%, 21.62% and 20.4% were obtained at 0.5, 1 and 1.5 M, respectively.

$$\text{FUR (\%)} = \frac{C_{ex}}{C_{th}} \times 100 \quad (4)$$

Even though performance improved with the increase in sodium borohydride concentration in the SSSF system, it decreased by an increase in concentration in the USUF system for two main reasons. One of them is an increase in hydrogen gas, and the other is an increase in the fuel crossover.

Hydrogen is generated from both hydrolysis reaction and oxidation reaction of borohydride. Hydrogen evolution not only reduces

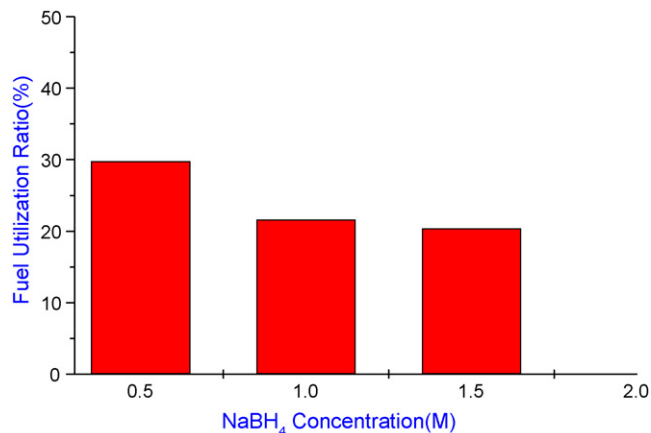


Fig. 5. The effect of concentration of NaBH_4 on fuel utilization ratio. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion® N117. Temperature: 25°C . Resistance: 1Ω .

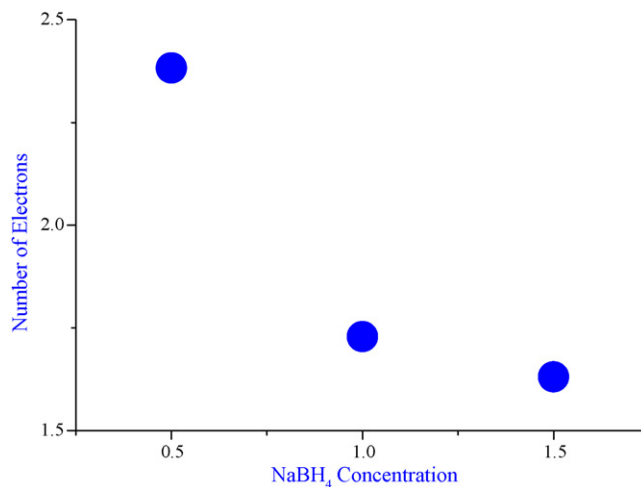


Fig. 6. The number of electrons utilized during BH_4^- oxidation as a function of NaBH_4 concentration. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion® N117. Temperature: 25°C .

fuel efficiency but also causes other problems such as fuel safety [5]. Moreover, hydrogen bubbles aggregated easily between the anode electrode and membrane, thus, due to reduced fuel contact, productivity of borohydride oxidation falls. In addition, it causes increased ohmic resistance by blocking ion transfer from the membrane. The rate of hydrolysis reaction can be decreased through optimization of the operation temperature and the fuel concentration.

Furthermore, fuel crossover improved by the increase in sodium borohydride concentration. With increased the fuel crossover, cathode activation polarization increased because of the increase in mixed potential and ohmic polarization enhanced due to solution viscosity. Mobility of the carrier ions (Na^+) decreased as the solution viscosity increased [5]. Although the decrease in mobility of the ions can be compensated in the SSSF systems by energy gain to ions by usage of a pump, it cannot be prevented in the USUF systems.

4. Conclusions

The effect of sodium borohydride concentration on the performance of the DBFC was investigated in this work. It was found that the DBFC performance improved with the increase of sodium borohydride concentration due to the increase of mass transfer of fuel and the kinetics of borohydride oxidation in the SSSF system; nevertheless, the increase in sodium borohydride concentration caused a decrease in the performance from borohydride crossover and hydrogen gas in the USUF system. Furthermore, the number of electrons used was found as 2.4 out of a total of 8 electrons and the FURs of 29.8%, 21.6% and 20.4% were obtained at 0.5, 1 and 1.5 M, respectively in the USUF system.

In addition, it is believed that the parameters used in this work may reveal different effect on the performance of a cell assembled with different MEAs. Therefore, sodium borohydride concentra-

tion should be optimized for different MEAs to ensure the best cell performance.

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