



Short communication

Effects of operation conditions on direct borohydride fuel cell performance

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ABSTRACT

In this study, the influences of different operational conditions such as cell temperature, sodium hydroxide concentration, oxidant conditions and catalyst loading 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 were investigated. The experimental results showed that the power density increased by increasing the temperature and increasing the flow rate of oxidant. Furthermore, it was found that 20 wt.% of NaOH concentration was optimum for DBFC operation. When oxygen was used as oxidant instead of air, better performance was observed. Experiments also showed that electrochemical performance was not considerably affected by humidification levels. An enhanced power density was found by increasing the loading of anodic catalyst. In the present study, a maximum power density of 27.6 mW cm⁻² at a cell voltage of 0.85 V was achieved at 55 mA cm⁻² at 60 °C when humidified air was used.

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1. Introduction

Fuel cells are electrochemical devices that directly convert chemical energy into electrical energy. They are actively investigated as an attractive alternative to conventional fossil fuel combustion engines for cleaner power generations [1] and usually classified according to the type of electrolyte used in the cells as PEMFC, AFC, MCFC, SOFC and PAFC.

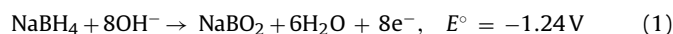
Fuel cells used in portable and mobile applications are expected to operate at ambient conditions with minimum auxiliaries and high power density. These conditions can be provided by using liquid fuels. Because of high capacity (5.03 Ah g⁻¹ [2]) and lower costs, methanol has been widely accepted as a power source for small portable applications. Nevertheless, DMFCs usually show a low theoretical open circuit voltage and small power density due to lower electrochemical activity of methanol and methanol crossover. To increase power density, large amounts of precious metals like Pt or Pt–Ru alloys must be loaded as catalyst [3]. These backgrounds of DMFCs have forced researchers to find alternative fuels such as borohydride and fuel cells especially for portable applications such as DBFC in recent years [4]. DBFC is similar to PEMFC and DMFC according to the usage of membrane electrolyte, similar to AFC because of its alkaline media, and similar to DMFC according to the usage of liquid fuel. Compared with other fuel cells, a DBFC has many advantages because it eliminates hydrogen storage problem,

it uses liquid fuel with safety, low fuel crossover to the cathode side and it has high theoretical cell voltage (1.64 V) and high theoretical power density (9.3 kWh kg⁻¹). Due to the reasons mentioned above, DBFC has recently been considered as a potential candidate for portable and mobile applications. Moreover, DBFC is specifically important for Turkey because 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.

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 anode side and fuel crossover. Hydrogen evolution due to the hydrolysis reaction during operation not only decreases the fuel utilization but also causes some problems in the 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 [5].

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

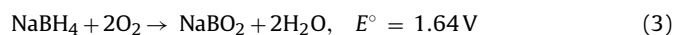
Anode:



Cathode:



Overall cell reaction:



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Nomenclature

AFC	alkaline fuel cell
DMFC	direct methanol fuel cell
DBFC	direct borohydride fuel cell
E°	standard potential
H_2O_2	hydrogen peroxide
HCHO	formaldehyde
MCFC	molten carbonate fuel cell
MEA	membrane electrode assembly
$NaBH_4$	sodium borohydride
$NaBO_2$	sodium metaborate
NaOH	sodium hydroxide
PAFC	phosphoric acid fuel cell
PEMFC	polymer electrolyte membrane fuel cell
PTFE	polytetrafluoroethylene
RH	relative humidity
SOFC	solid oxide fuel cell
TÜBİTAK	The Scientific and Technological Research Council of Turkey

In such a fuel cell, H^- in BH_4^- is oxidized into H^+ directly on the anode. The direct anodic oxidation of borohydride provides a more negative potential than that of hydrogen gas [6]. The only products of the cell chemistry indicated in reaction (3) are water and borate ion. Borate is both environmentally acceptable and potentially convertible back to borohydride [7].

In this paper, the effects of different operation parameters on the performance of the 25 cm² DBFC made in a laboratory environment were examined. As a result, the best cell performance was achieved by using optimum conditions.

2. Experimental

2.1. Electrode materials and chemicals

The materials and chemicals used during the tests were 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 XC-72, CABOT), Nafion® 117 membrane (DuPont), Ni foam (Inco-foam), PTFE (Alfa Aesar), isopropyl alcohol, formaldehyde solution (Merck), Ni net (Precision Ni, PN 45 MN 12% T 88.4), carbon paper (Toray, TGP-H-090, E-TEK), Nafion solution (5 wt.%, Aldrich), H_2O_2 (30%, Merck).

2.2. Preparation of anode catalyst

Pd/C catalyst was prepared by precipitation method. Vulcan XC-72 carbon black was added into deionized water at 90 °C under magnetically stirring for 20 min. Then $PdCl_2$ was added into the solution and stirred for 1 h at 90 °C. Later, 0.5 M NaOH was added into the solution to drop wise until pH 9–10 and stirring continued for an additional 30 min at the same temperature. HCHO was then added to precipitate metal. The solution was left for 12 h to cool at room temperature. After that, the mixture was filtered and the resultant slurry was washed three times with hot water (80–90 °C). Then, carbon supported palladium obtained was dried for 8 h.

2.3. Preparation of anode electrode

Prepared Pd/C powders were mixed with PTFE powders in a weight ratio of 18:1. In addition, water and isopropyl alcohol were added into the mixture to form ink. This ink was stirred for 24 h at

the ambient temperature to obtain anodic slurry. The anodic slurry was spread onto a Ni foam substrate. After being wrapped by a nickel net (liquid diffusion layer) of 100 mesh to prevent the drop of anode catalysts 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.

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 into the deionized water at 90 °C under magnetically stirring in ultrasonic bath for 20 min at 90 °C until it becomes slurry form. Then, H_2PtCl_6 was added into the solution and stirred for 1 h at 90 °C. Later, 0.5 M NaOH was added into the solution to drop wise until pH 9–10 and stirring continued for an additional 30 min at the same temperature. The solution was stirred for 45 min and platinized carbon was obtained by adding formaldehyde solution. After that, platinized carbon obtained was filtered, washed with hot distilled water and dried for 2.5 h.

2.5. Preparation of cathode electrode

The cathode electrode used in this work which consisted of a catalyst layer which was made of Vulcan XC-72 with 10 wt.% Pt and a gas diffusion layer (carbon paper). The solution that was contained 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 a cathodic slurry. After stirring, it was dried under atmospheric conditions. Then, it was spread on 0.28 mm thick PTFE-treated Toray carbon paper with a 0.3 mg cm⁻² Pt loading in the form of continuous wet film. After drying of prepared electrode in the air for 24 h, it was heated to 225 °C for 30 min. After that, required quantity of nafion solution was spread on the catalyst layer in the form of continuous wet film and then the electrode was dried in an oven at 80 °C for 1 h.

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 using at room temperature and were also immersed in 6N NaOH for 30 min before being assembled [5,8–11]. The anode, cathode and pre-treated 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 test in the test fuel cell [8,12].

2.7. Performance tests

A schematic test system of DBFC is shown in Fig. 1. After installing single cell with an active electrode area of 25 cm² in the test station, performance tests were carried out. The sodium borohydride solution was pumped using a peristaltic pump (MasterFlex/LS) to the anode compartment at a feed rate of 2 ml min⁻¹. In order to find an optimum sodium hydroxide concentration, solution was fed to the anode, while varying concentration of NaOH in 1 M sodium borohydride solution at 25 °C. The flow rate of the oxidant was investigated in the range of 10–150 ml min⁻¹ at 1 atm for finding the optimum value of the feeding rate at 25 °C. In addition, the effects of moisture of oxidant were investigated by feeding dry and humidified air (RH: 100%) to the cathode compartment at a

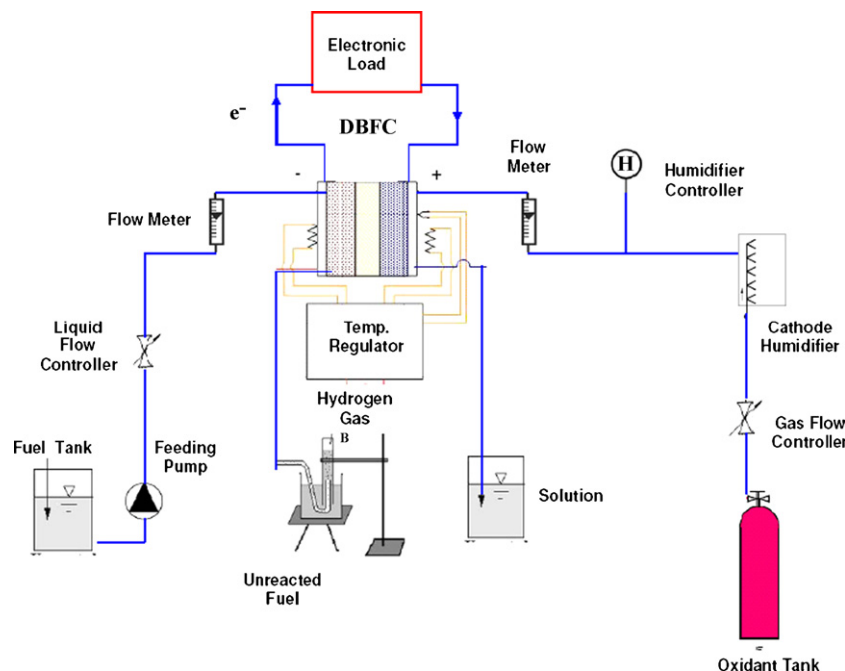


Fig. 1. The schematic test system of the DBFC.

feed rate of 90 ml min^{-1} at 25°C . Electrical heaters were placed behind each of the graphite blocks to heat the cell to the required temperature. Cell temperature was set at $25\text{--}60^\circ\text{C}$ to evaluate the effect of temperature on the cell performance. Air and oxygen were used as oxidant to evaluate the effect of oxidant type on the cell performance at 25°C at a feed rate of 90 ml min^{-1} (1 atm, RH: 65%). The power density measurements were carried out using an electronic load (Electrochem, Inc. ECL 150). The power densities were calculated from the experimentally measured current densities and potential values.

3. Results and discussion

3.1. Effect of temperature

The variation of the power density, current density and cell voltage at different temperature is presented in Fig. 2. The power density increased by increasing the temperature because of reducing activation polarization in the cell. Peak power density of 11.7, 16.4, 21.8 and 27.6 mW cm^{-2} were obtained at 25, 40, 50 and 60°C , respectively. These results are consistent with the literature information given for the changing of the temperature [10,13,14].

The reduction kinetics of oxygen is slower in fuel cells that work at low temperatures than those that work at high temperatures. Reduction kinetic and oxidation kinetic of borohydride increases by increasing the temperature due to the reduced polarization. Moreover, anolyte viscosity decreases since movability of ions is increased. Thus, diffusion coefficient increases with decreasing of mass transfer losses. As a result, electrolyte conductivity increases, ohmic losses decrease. However, some disadvantages, which are caused of decreasing of productivity, like borohydride crossover and hydrolysis occur at elevated temperature. In addition, cell resistance increases by increasing the temperature because it causes partial drying of the membrane.

3.2. Effect of sodium hydroxide concentration

As shown in Fig. 3, the cell performance was improved with increasing sodium hydroxide concentration from 10 wt.% to 20 wt.%

because of increasing the conductivity of the solution and decreasing hydrolysis; however, further increase in sodium hydroxide concentration to 30 wt.% caused a decrease in the power density owing to increasing of solution viscosity and decreasing of movement capability of Na^+ ions. The best cell performance was achieved at 20 wt.% of NaOH concentration in our studies; nevertheless, this value has been found as 10 wt.% of NaOH concentration in the Cheng and Scott's reported work [14].

Furthermore, melting point of sodium borohydride solution is affected from sodium hydroxide concentration [8]. In addition, Borate (BO_2^-) production resulting from borohydride oxidation could potentially be problematic since it has a low solubility and could limit the permitted level of discharge after which precipitation of borate might occur [15] and its solubility limit is not only

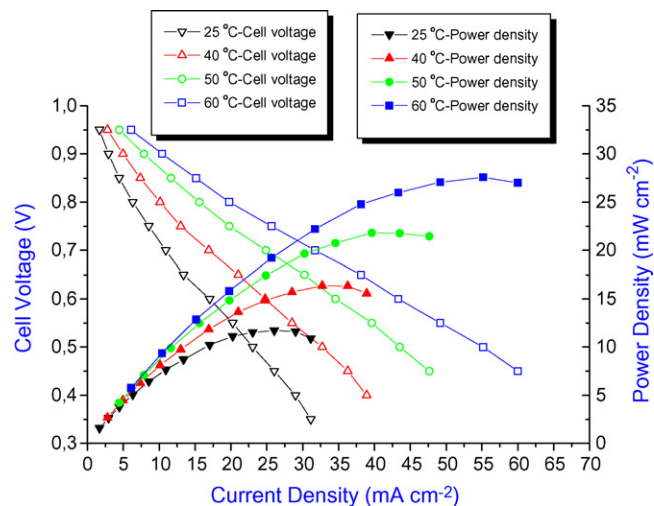


Fig. 2. Cell polarization and power density curves for DBFC at different temperatures. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion N117. Flow rate of the humidified air: 150 ml min^{-1} (1 atm, RH: 65%). Fuel: 500 ml, 1.5 M NaBH_4 in 20 wt.% NaOH solution. Flow rate of the fuel: 2 ml min^{-1} .

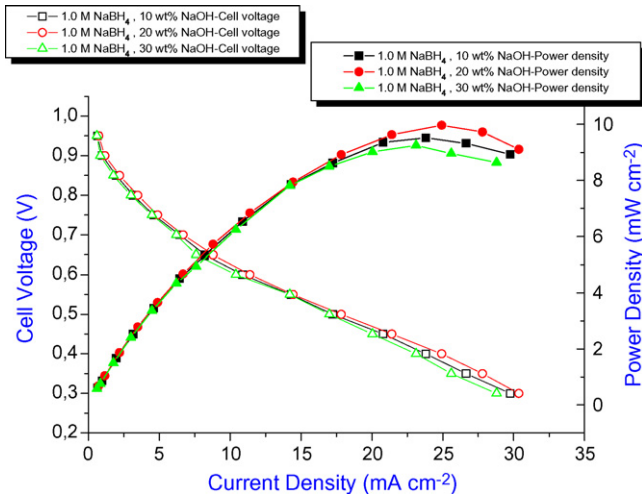


Fig. 3. Curves of cell polarization and power density for DBFC at different NaOH concentrations. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion N117. Temperature: 25°C . Flow rate the of the humidified air: 150 ml min^{-1} (1 atm, RH: 65%). Flow rate of the fuel: 2 ml min^{-1} .

a function of temperature but also a function of NaOH concentration [16]. Therefore, the sodium hydroxide concentration should be optimised in terms of cell performance for portable applications, in particular.

3.3. Effect of oxidation conditions

Air and oxygen were used as oxidant to evaluate the effect of oxidant type on the cell performance. Better performance was obtained by using oxygen, compared to air under the same conditions (Fig. 4). It can be explained that cathode kinetics are better when using oxygen instead of air [17]. A maximum power density of 11.7 mW cm^{-2} was obtained at 26 mA cm^{-2} by using oxygen; however, when air was used as oxidant, a maximum power density of 7.3 mW cm^{-2} at 14.6 mA cm^{-2} was obtained. Furthermore, it has been demonstrated by Cheng and Scott [14] when air is used as oxidant instead of oxygen, carbonate is formed due to the presence of CO_2 . Thus, electrode and electrolyte are negatively affected. The

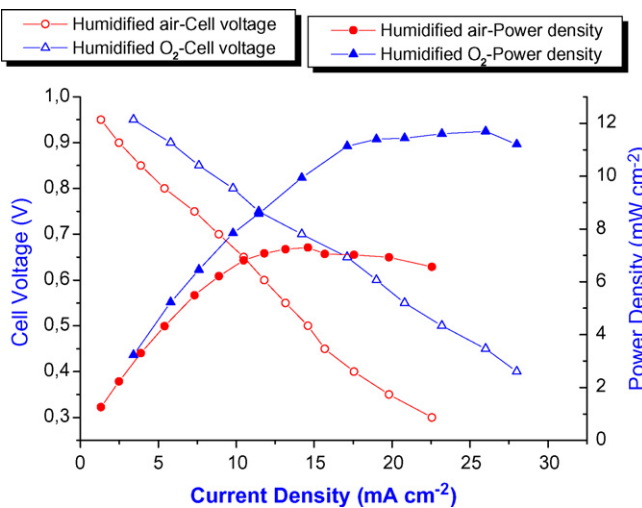


Fig. 4. Curves of cell polarization and power density for DBFC at different kinds of oxidants. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion N117. Temperature: 25°C . Flow rate of the humidified oxidant: 90 ml min^{-1} (1 atm, RH: 65%). Fuel: 0.5 M NaBH_4 in 20 wt.% NaOH solution. Flow rate of the fuel: 2 ml min^{-1} .

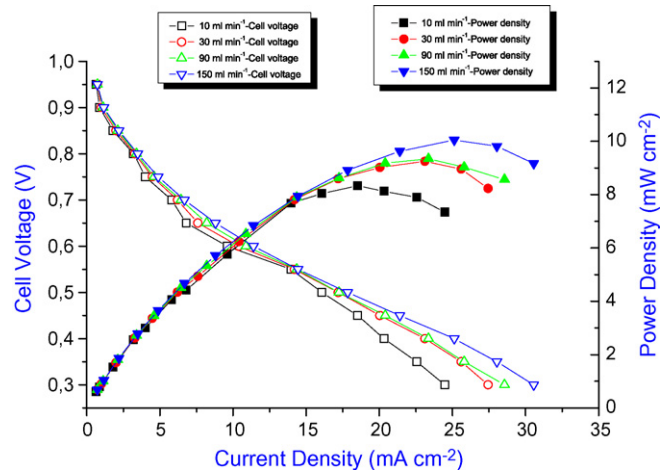


Fig. 5. Curves of cell polarization and power density for DBFC at different flow rates of oxidant. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion N117. Temperature: 25°C . Oxidant: Humidified air (1 atm, RH: 65%). Fuel: 1.0 M NaBH_4 in 20 wt.% NaOH solution. Flow rate of the fuel: 2 ml min^{-1} .

results of the present study are consistent with the results reported for the changing of oxidant by Cheng and Scott [14].

The flow rate of oxidant is another key factor effecting cell performance. Polarization curves were obtained at 10, 20, 90 and 150 ml min^{-1} (Fig. 5). By increasing the flow rate of oxidant, a small increase in power density was observed because of increasing mass transfer, e.g. 8.5 and 10.1 mW cm^{-2} at 10 and 150 ml min^{-1} , respectively. The tendency of the increasing power density is in good agreement with results obtained by Cheng and Scott [14].

In addition, the effect of moisture of oxidant was investigated by sending dry and humidified air to the DBFC. A maximum power density of 7.3 mW cm^{-2} was obtained at 14.6 mA cm^{-2} by using humidified air as oxidant. In the same way, a maximum power density of 7 mW cm^{-2} was obtained at 14 mA cm^{-2} by using dry air as oxidant. The results showed that the electrochemical performance is not considerably affected by humidification levels; a small increment of power density was observed (Fig. 6). Since water is produced at the cathode and the solution is fed to the anode, humidification effect is not observed.

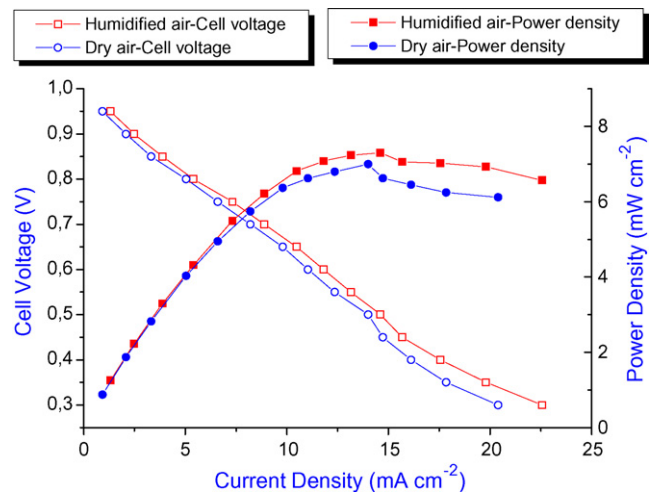


Fig. 6. Curves of cell polarization and power density for DBFC at different oxidant moist. Anode: 10 wt.% Pd/C, 0.30 mg cm^{-2} . Cathode: 10 wt.% Pt/C, 0.30 mg cm^{-2} . Membrane: Nafion N117. Temperature: 25°C . Flow rate of air: 90 ml min^{-1} (1 atm). Fuel: 1.0 M NaBH_4 in 20 wt.% NaOH solution. Flow rate of the fuel: 2 ml min^{-1} . RH: 100%.

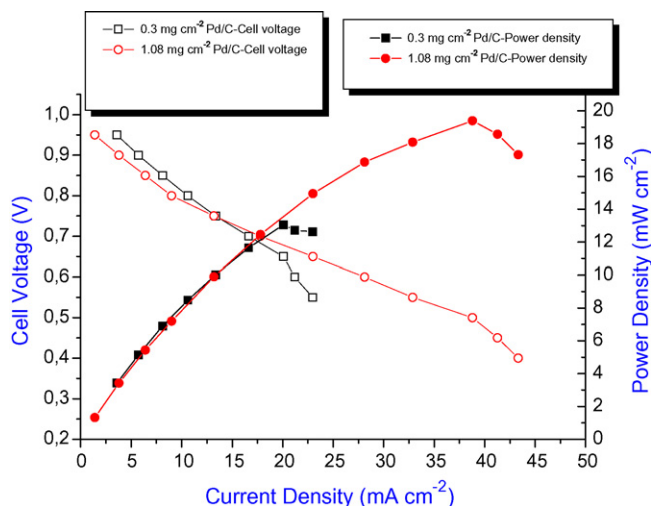


Fig. 7. Curves of cell polarization and power density for DBFC at different anode catalyst loading. Cathode: 10 wt.% Pt/C, 0.30 mg cm⁻². Membrane: Nafion N117. Temperature: 25 °C. Flow rate of the humidified air: 30 ml min⁻¹ (1 atm, RH: 65%). Fuel: 1.0 M NaBH₄ in 20 wt.% NaOH solution. Flow rate of the fuel: 2 ml min⁻¹.

3.4. Effect of catalyst metal loading

Fig. 7 shows the polarization curve obtained as a function of catalyst loading at room temperature. Cell performance by using the anode loaded with 0.3 mg cm⁻² of anodic Pd catalyst supported on carbon is compared with that by using the anode loaded with 1.08 mg cm⁻² of anodic Pd catalyst supported on carbon. An enhanced power density was found by increasing the loading of anodic catalyst. A maximum power density of 12.7 mW cm⁻² was obtained at 21.2 mA cm⁻² by using 0.3 mg cm⁻² Pd/C; however, when 1.08 mg cm⁻² was used as anode catalyst, a maximum power density of 19.4 mW cm⁻² was obtained at 38.8 mA cm⁻². It is similar to the behavior of the Jin-Ho Kim et al.'s work [17].

4. Conclusions

The effects of different operation parameters on the performance of the DBFC were investigated in this work. The DBFC performance was improved by increasing the operative temperature. For example, the peak power density increased to 127% when the temperature increased from 25 °C to 60 °C. The increasing of power density indicated that the DBFC performance was sensitive to the cell temperature.

Nevertheless, the performance first increased and then decreased slightly with increasing sodium hydroxide concentration because of decreasing of movement capability of Na⁺ since solution viscosity increases. The best cell performance was achieved at 20 wt.% of NaOH concentration in the present study.

When oxygen was used as oxidant instead of air, better performance was observed. The maximum power density of 11.7 mW cm⁻² was obtained at 26 mA cm⁻² by using oxygen; however, when air was used as oxidant, maximum power density of

7.3 mW cm⁻² at 14.6 mA cm⁻² was obtained. This is due to a higher mass transfer.

Increase in the flow rate of oxidant caused a small improvement in power density, e.g. 8.5 and 10.1 mW cm⁻² at 10 and 150 ml min⁻¹, respectively, because of increasing mass transfer and decreasing cathode kinetics.

The oxidant moisture had a small effect on the cell performance. A maximum power density of 7.3 mW cm⁻² was obtained at 14.6 mA cm⁻² by using humidified air as oxidant. On the other hand, a maximum power density of 7 mW cm⁻² was obtained at 14 mA cm⁻² by using dry air as oxidant. The cell performance was found to not be very sensitive to feed with humidified oxidant compared to that of the other operation parameters.

It was observed that power density improved with increasing loading of anode catalyst. The maximum power density of 12.7 mW cm⁻² was obtained at 21.2 mA cm⁻² by using 0.3 mg cm⁻² Pd/C; however, when 1.08 mg cm⁻² was used as an anode catalyst, maximum power density of 19.4 mW cm⁻² was obtained at 38.8 mA cm⁻².

The experimental results show that the effects of the operation parameters on the cell performance are different and it is believed that these parameters show different effect on the performance of the cell assembled with different MEAs. Therefore, operation parameters should be optimized for different MEAs to ensure the best cell performance.

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