Influence of operation conditions on direct borohydride fuel cell performance

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Abstract

The effects of temperature, concentration of borohydride and supporting electrolyte and oxidant conditions on the performance of direct borohydride fuel cell are reported. Design of flow fields and evaluation of effects of flow conditions were carried out. Durability of the DBFCs was tested over a relatively long period.
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Keywords: Direct borohydride fuel cell; Temperature; Borohydride concentration; NaOH concentration; Flow condition; Oxidant condition

1. Introduction

Significant progress has been made in the development of low temperature fuel cells as alternative power sources to hydrocarbon based energy sources, particularly for vehicles and for stationary power generation [1–3]. Borohydride has been proposed as an alternative fuel for hydrogen, which has concerns in anode poisoning, supply, storage and transportation and cell stack cost [3], and to other organic fuels, which have problems of low activity, low capacity, toxicity and low oxidation efficiency [1,4,5]. Borohydride is easily stored and distributed, chemically stable and non-combustible. The resulting borate is allowed to be recycled back to generate borohydride and no CO_2 is exhausted from the DBFC reactions. A direct borohydride fuel cell (DBFC) has theoretical open circuit voltage of 1.64 V and energy density of 9285 W h (kg $NaBH_4$)$^{-1}$, which are 0.4 V and 3200 W h (kg methanol)$^{-1}$ higher than those of direct methanol fuel cells [3]. The early DBFC, e.g. a KBH_4/O_2 fuel cell, used Ni_2B or Pt anodes, Pt cathodes and an asbestos separator, and delivered maximum peak power densities of up to 95 mW cm^{-2} at 100 mA cm^{-2} and 45 °C [6]. The high resistance of the asbestos made it unsuitable for further use in DBFC.

A recent DBFC using a NiMH anode, a Pt cathode and a Nafion cation exchange membrane [7,8] increased the value to 160 mW cm^{-2} at 300 mA cm^{-2} and 70 °C [8].

The operation parameters have great influence on the DBFC performance. As mentioned in the literature, only dilute fuel, e.g. 2 wt.%, could be used due to use of the asbestos separator [6]. Increase in temperature caused improvement in power density, e.g. 20 and 63 mW cm^{-2} at ambient and 70 °C, respectively [9]. There were concerns for the negative effect of changing the operation parameters on the lifetime and function of materials as well as the cell performance. Overall, more work is required to optimise the operation conditions for a further improvement of DBFC performance.

2. Experimental

2.1. Materials and chemicals

The following materials and chemicals were used as received: $AuCl_3$ (99%, Aldrich), H_2PtCl_6 (99.9%, Janssen), $NaBH_4$ (99%, Fisher), NaOH (99.99%, Aldrich), Nafion solution (5 wt.%, Aldrich), carbon powder (Vulcan XC-72R, Cabot), Ketjen-300J carbon black (Akzo Nobel), carbon paper (Toray, TGPH120, E-TEK), Nafion® 117 membrane (DuPont).

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Deionised water (ELGASTAT B124 Water Purification Unit, The Elga group) and high purity gases (H₂, air and O₂, BOC) were used.

2.2. Preparation of catalysts

Carbon-supported Au and Pt catalysts were prepared following the impregnation method [10]. In a typical run, 200 mg of the Vulcan XC-72R carbon black was dispersed in a 20 ml mixture of isopropanol and deionised water (volume ratio 1:1) at 60 °C under magnetically stirring for 10 min. Then, 185 mg of AuCl₃ was added drop wise and stirred for 1 h. The mixture was then filtered and the resultant slurry was washed with water and dried at room temperature before being transferred into a porcelain boat, which was put in a quartz tube contained in an electric oven. The sample was treated at 400 °C for 2 h in air. A similar procedure was used to fabricate Pt catalysts except that 255 mg of H₂PtCl₆ and a post-treatment temperature of 500 °C were used.

2.3. Fuel cell test

All membrane electrode assemblies (MEAs) were fabricated under comparable conditions, e.g. 2 mg metal catalyst/cm² in the catalytic layers and 1 mg C cm⁻² in the gas diffusion layer. The suspension was spread uniformly over the entire surface with the pipette tip and a hand drier was used to accelerate the drying of the catalysts suspension between each application. Nafion® ionomer (10 wt.% of the catalysts) and iso-propanol was used to prepare the inks for the catalytic layers. Finally, a thin layer of Nafion® solution (1 mg Nafion cm⁻²) was spread on to the surface of each electrode and allowed them dry under atmospheric conditions.

In assembling the DBFC, the anode and cathode of the MEA were in contact with high-density graphite blocks (Ralph, Coidan), impregnated with phenolic resin, into which were cut the gas/liquid flow channels. The ridges between the channels provided the electrical contact to the carbon electrodes and the total machined geometrical area of 4 cm² was taken as the active area of the cell. Copper sheets contacted the graphite blocks as current collectors. Electrical heaters were mounted at the rear of the Cu plates to maintain the desired cell temperature which was controlled through a temperature controller and monitored by thermocouples buried in the graphite blocks. Steady-state polarisation measurements were carried out following 10–20 h conditioning, in which the cell was held at 60 °C and fed with the deionised water in order to hydrate the membrane. Once the cell voltage had decayed to a steady value, polarisation curves were recorded using a high precision multimeter and a power supply in galvanostatic mode, starting from open circuit point and moving to higher current densities in varying conditions. For measurements of polarisation curves for individual electrodes in-situ the DBFC, hydrogen gas was purged into the electrode chamber, which formed a combined counter and reference electrode. Cathode polarisation data were derived by subtracting electrode polarisation values from the respective cell polarisation data at various loading current densities [5,11,12]. Other

details for MEA fabrication, fuel cell assembly and operation were reported elsewhere [13].

3. Results and discussion

3.1. Influence of temperature

The DBFC performance was sensitive to cell temperature, as shown in Fig. 1. The peak power density and the sustained current density improved with increasing the temperature due to the increased diffusion coefficients and mass transfer of the reactants and the improved kinetics of borohydride oxidation. The conductivity of the borohydride–sodium hydroxide solution increased with increasing temperature, e.g. the maximum conductivity of NaOH solutions at 85 °C was about three times that at 18 °C [14]. The conductivity of other DBFC components also increased with increasing temperature. On the other hand, crossover and borohydride hydrolysis were enhanced with increasing temperature [9], which caused fuel loss and, more severely, deteriorated the Pt cathode performance. As a result, the decrease in open cell voltages (OCVs) with increasing temperature was observed, e.g. 1.052, 1.045, 0.998 and 0.988 V at 25, 50, 70 and 85 °C, respectively. Another concern was lower stability of borohydride solutions caused by enhanced borohydride hydrolysis with increasing temperature [15], which decreased fuel efficiency. It is worthwhile to consider effect of temperature on the water content of membranes because, at elevated temperatures, partial drying out of the membrane occurred, coupled with poor rehydration and uneven redistribution of water inside the cell, led to the higher resistance and decreased performance [16–18].

The overall improved performance of the DBFCs, e.g. four time increase in power density when the temperature was
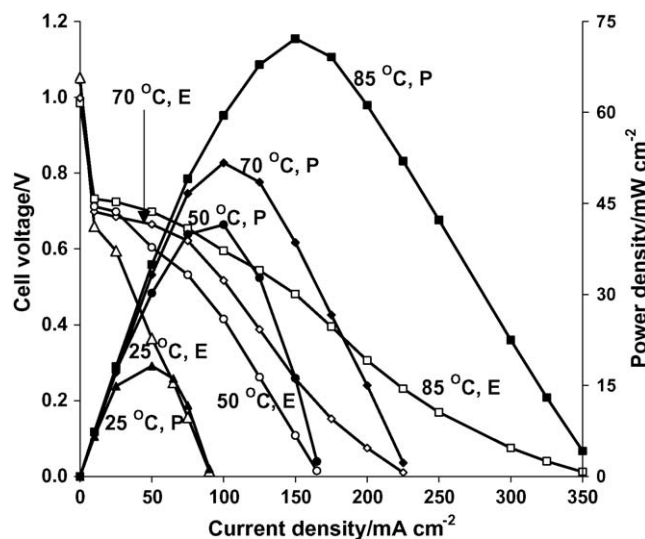

Fig. 1. Effect of the temperature on the steady cell voltage (E) and power density (P)–current density curves collected from a 2 cm × 2 cm direct borohydride fuel cell with a Nafion® 117 membrane. Anode: Au/C (2 mg Au cm⁻²). Cathode: Pt/C (2 mg Pt cm⁻²). Fuel: 5 wt.% NaBH₄ in 10 wt.% NaOH solution (10 cm³ min⁻¹). Oxidant: O₂ (ambient pressure, 200 cm³ min⁻¹). Flow field: parallel flow field.
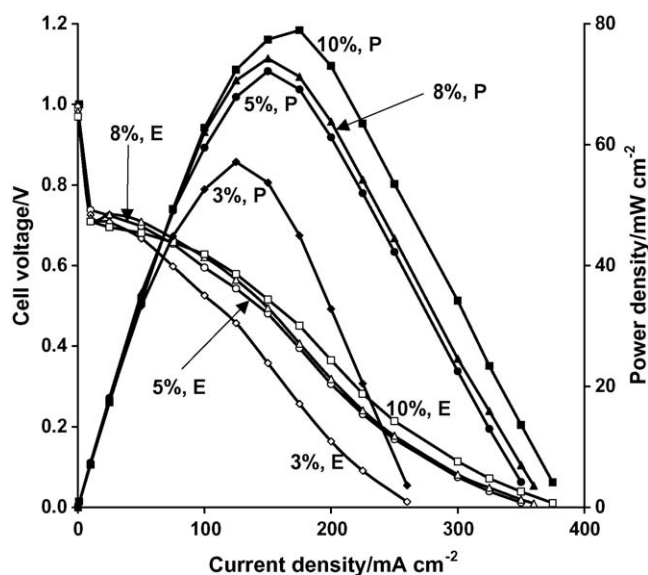
Fig. 2. Effect of borohydride concentration on the steady cell voltage (*E*) and power density (*P*)–current density curves. Concentration of $NaBH_4$ (10 wt.% NaOH solution): 3%, 5%, 8% or 10% in weight. Temperature: 85 °C. Other conditions as in Fig. 1.

Fig. 3. Effect of borohydride concentration on steady-state cell and electrode polarisation curves. Conditions as in Fig. 2.

increased from 25 to 85 °C, indicated that the beneficial effects resulted from increasing temperature outmatched the negative effects. The data also demonstrated that the DBFC could work in a broad range of temperatures and, even at ambient temperature, it was able to deliver reasonably high power densities and energy capacities. These characteristics satisfied the necessary conditions for use as portable power sources.

3.2. Influence of concentrations of borohydride and sodium hydroxide

3.2.1. Borohydride concentration

Fig. 2 and Table 1 show the effect of changing borohydride concentration on the DBFC performance. The OCVs decreased with increasing borohydride concentration due to the effect of borohydride crossover on the cathode performance. The power density and the sustained current density improved with increasing borohydride concentration. For example, the peak power density increased about 30% when the concentration increased from 3% to 5%, but did not increase appreciably for a further increase in the concentration, e.g. only 10% for doubling the borohydride concentration to 10%. There were two opposite effects of increasing borohydride concentration, i.e. improved the mass transfer of the fuel and the kinetics of borohydride oxi-
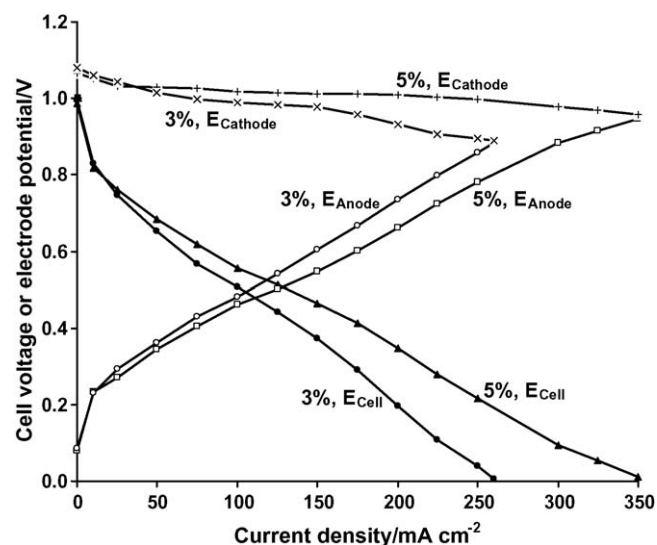
dation, and led to higher power density and higher sustained current density; and, on the other hand, crossover and borohydride hydrolysis were enhanced [9], which deteriorated the Pt cathode performance, caused fuel loss and decreased the OCV. Indeed, as shown in Fig. 3, the DBFC performance was even worse in 5% $NaBH_4$ solution, compared to that in 3% $NaBH_4$ solution, at low current density region where effect of the borohydride crossover was more significant, although the anode performance was similar in both solutions. This indicates that the cathode experienced greater polarisation loss than the anode, with increasing current density, in this region. The inferior performance in the 3% solution than that in the 5% solution, at high current densities, resulted from polarisation losses at both anode and cathode. The better performance in the 5% $NaBH_4$ solution was due to the improved mass transport of borohydride ions, compared to that in the 3% solution. The deterioration in cathode performance was mainly due to the crossover of borohydride, which was significant in the activation overpotential region of polarisation and was enhanced with increasing borohydride concentration. The accumulation of NaOH solution at the cathode was another reason for the deterioration [6,9]. The combined effects of increasing borohydride concentration on the anode and the cathode led to the above observations. Therefore, the borohydride concentration should be optimised in terms of cell performance and cost.

Table 1
Effects of concentrations of $NaBH_4$ and NaOH on the DBFC performance[a]

| $C(NaBH_4)$ (%) | 3 | 5 | 8 | 10 | 5 | 5 |
$C(NaOH)$ (%)	10	10	10	10	5	20
OCV/V	0.995	0.988	0.982	0.969	0.985	0.997
P_{Peak} (mW cm^{-2})	57.1	72.2	74.3	78.9	70.5	69.0
j_{max}[b] (mA cm^{-2})	260	350	360	375	320	315

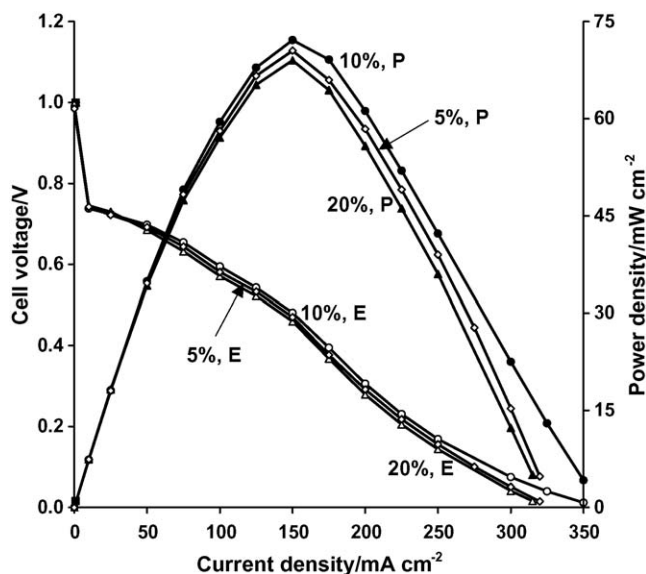[a] 85 °C. Other conditions as in Fig. 1.
[b] Sustained maximum current density.

Fig. 4. Effect of NaOH concentration on the steady cell voltage (E) and power density (P)–current density curves. Concentration of NaOH (5 wt.% NaBH$_4$ solution): shown in the figure. Temperature: 85° C. Other conditions as in Fig. 1.

3.2.2. NaOH concentration

Alkaline concentration is another key factor affecting DBFC performance and Fig. 4 and Table 1 show the related data. The OCVs increased slightly with increasing NaOH, which may be attributed to slight alleviation of the borohydride crossover due to the enhanced blocking paths for borohydride diffusion by the Na$^+$ or OH$^-$ ions or both. The NaOH concentration had a relatively small effect on the DBFC performance, compared to that of the borohydride concentration, e.g. the power density changed only several mW cm^{-2} (Table 1). The power density and sustained current density increased with the NaOH concentration up to 10%, beyond which, they decreased. This can be explained by the following points:

(i) Increase in NaOH concentration was favourable to the anode reaction but had negative effect on the cathode reaction according to the Nernst equation.
(ii) The conductivity of the sodium hydroxide solution increased with increasing NaOH concentration until a maximum value and, at 85 °C, the value is 27% [14]. So the solution conductivity increased with increasing the NaOH concentration and promoted the better performance.
(iii) Increase in NaOH concentration led to increase in viscosity, decrease in availability of the borohydride ions reaching the anode and decrease in the movability of Na$^+$, which was one of the main electrical carriers in the DBFC with the Nafion$^{®}$ 117 membrane, and resulted in the ohmic losses, particularly at high current densities [7].
(iv) Carbonate was formed due to the presence of CO$_2$, if ambient air is used, which affected the electrodes and the electrolyte [19,20].

Overall, the NaOH concentration should be optimised in terms of the requirements to stabilise borohydride, the DBFC performance and cost.
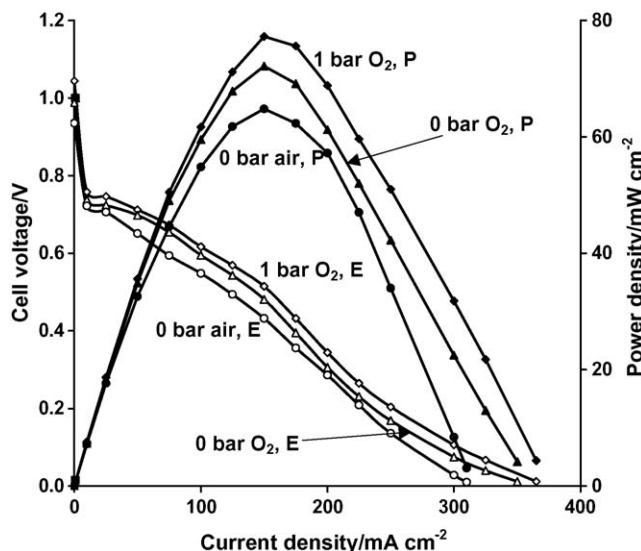

Fig. 5. Effect of oxidant conditions on steady cell voltage (E) and power density (P)–current density curves. Oxidant: air or O$_2$ (0 and 1 bar). Other conditions as in Fig. 1.

3.3. Influence of oxidant condition

Better performance was achieved using O$_2$ rather than air and a further improvement was realised under pressurised conditions, as shown in Fig. 5 and Table 2. For example, the OCVs and the sustained current densities were higher at 1 bar than those at ambient pressure for all of the MEAs. The peak power density increased with increasing pressure and a peak power density of 77.3 mW cm^{-2} was achieved using the MEA with the Pt/C cathode at 1 bar oxygen.

The effect of oxidant conditions mainly attributed to the improved cathode kinetics due to the increased oxidant supply.

3.4. Influence of flow conditions

3.4.1. Flow field

Two types of flow patterns, i.e. parallel (PFF) or single-serpentine (SFF) channels (Fig. 6) were compared based on the same channel depth and the same ratio of the channel area to the total MEA area. The DBFC with the SFF was slightly better than that with the PFF, i.e. an increase of 3.5% in the peak power density at ambient pressure. At the 1 bar pressure, the difference became smaller (Table 3). The flow field design is related to

Table 2
Effects of oxidant conditions on the DBFC performance[a]

Oxidant	OCV/V	P_{Peak} (mW cm^{-2})	j_{max}[b] (mA cm^{-2})
0 bar O$_2$	0.988	72.2	350
1 bar O$_2$	1.044	77.3	365
0 bar air	0.935	64.8	310
1 bar air	0.964	67.8	315

[a] The MEAs were operated under the conditions of 5% NaBH$_4$ + 10% NaOH and 85 °C unless otherwise stated. Other conditions as in Fig. 1.
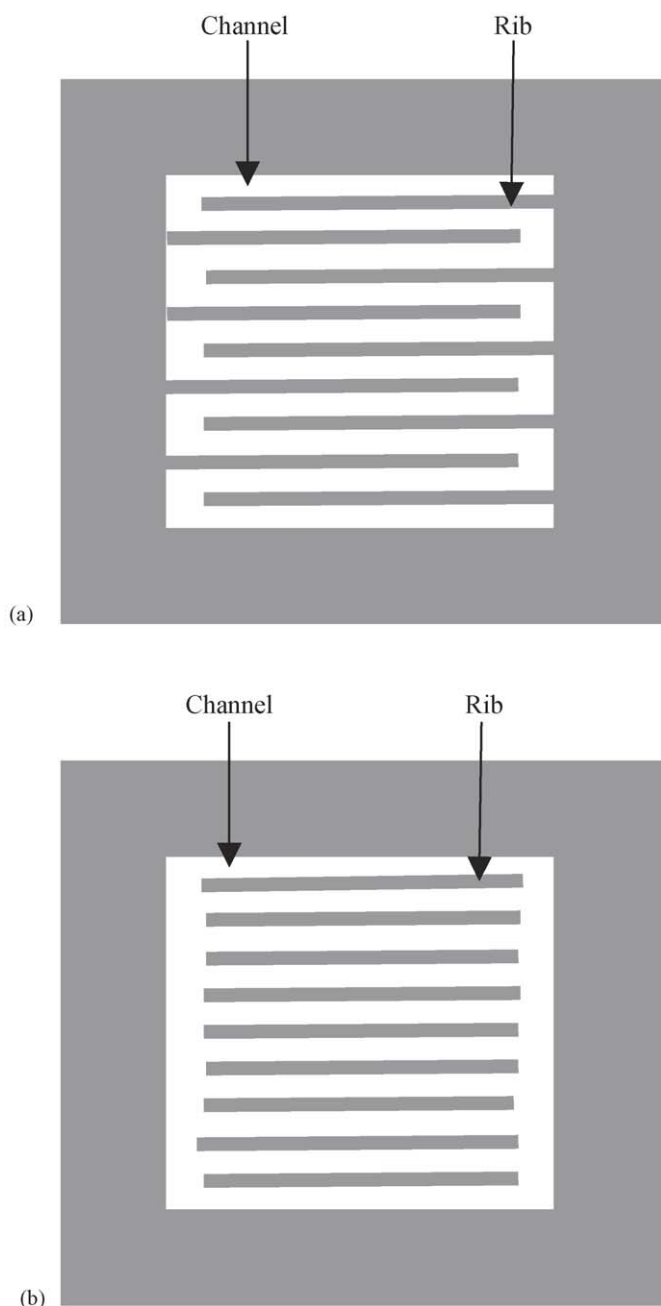[b] Sustained maximum current density.

Fig. 6. Flow fields: (a) serpentine (SFF) and (b) parallel (PFF). Channel width: 2 mm; channel depth: 2 mm; channel length: 20 mm; rib width: 2 mm; rib length: 18 and 16 mm for the SFF and the PFF, respectively.

distributions of fuel and oxidant and transport of the reaction products. In principle, the SFF has better mass transport environment and less channel blocking than the PFF [21]. Hence, better performance can be expected for the DBFC with the SPP, compared that with the PFF, especially at high current densities, where the performance was under mass transport control and the requirement for a higher rate of the fuel supply was predominated. The relatively small effect of the flow field on the DBFC performance indicated that, presumably, the mass transport limitation in the DBFC was less severe than that in the other types of FCs [21].

Table 3
Effects of flow conditions on the DBFC performance[a]

Flow field and rate	OCV/V	P_{Peak} (mW cm^{-2})	j_{max}[b] (mA cm^{-2})
PFF, 5 ml min^{-1}	0.979	60.3	285
PFF, 10 ml min^{-1}	0.985	63.1	300
PFF, 20 ml min^{-1}	0.990	63.9	310
PFF, 50 ml min^{-1}	0.991	64.5	315
PFF, 100 ml min^{-1}	0.992	65.3	320
PFF, 1 bar O$_2$	1.035	66.5	315
SFF, 10 ml min^{-1}	0.996	65.3	305
SFF, 1 bar O$_2$	1.037	67.3	330

[a] The MEA with the Au/C anode (1 mg Au cm^{-2}) and was operated at ambient pressure and 85 °C unless otherwise stated. Other conditions as in Fig. 1.
[b] Sustained maximum current density.

3.4.2. Flow rate of the fuel

Fig. 7 and Table 3 compare the performance of the DBFC with the PFF at different flow rates of the fuel. The greater increase in the performance was observed in the flow rate range of 5–10 ml min^{-1}, i.e. ca. 5% increase in the power density for a doubling flow rate. The further increase in the flow rate to 100 ml min^{-1} only led to the 3.5% increase in the power density. The higher fuel velocity promoted better mass transport of the fuel and alleviated possible channel blocking and product accumulation and, thus, improved the performance. Under the conditions, the influence of flow rate was relatively small and it was economic to use low flow rates.

3.5. Durability test

Stability of the DBFC was tested by monitoring cell voltage change with the working time during the galvanostatic operation at 20 mA cm^{-2} and 25 °C. An example is shown in Fig. 8, where the fluctuation in the cell voltage was due to addition of the
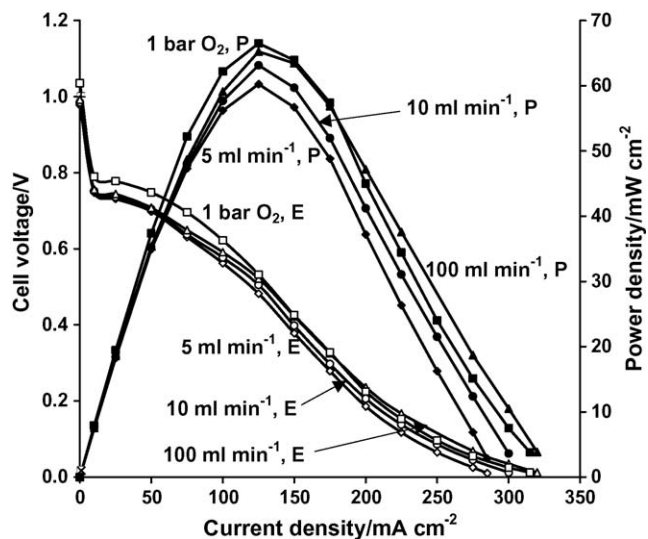

Fig. 7. Effect of flow conditions on steady cell voltage (*E*) and power density (*P*)–current density curves. Flow rate: 5, 10 and 100 ml min^{-1}. Anode: Au/C (1 mg Au cm^{-2}). Oxidant: O$_2$ (0 and 1 bar). Other conditions as in Fig. 1.
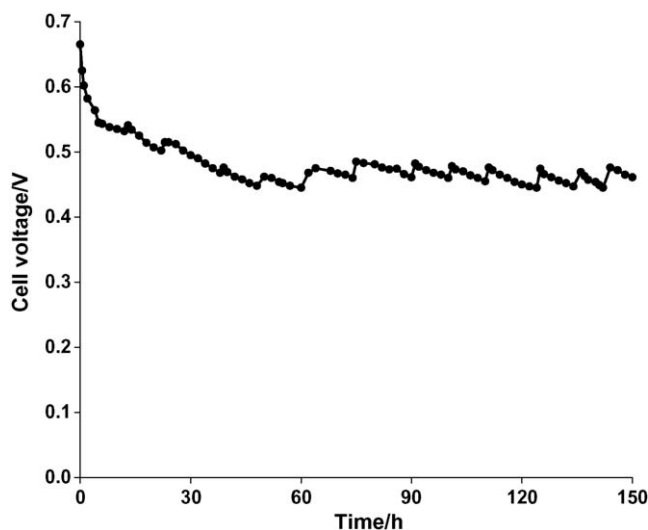
Fig. 8. Durability of the DBFC. Applied current density: 20 mA cm^{-2}. Temperature: 25 °C. Other conditions as in Fig. 1.

new solutions or restarting the experiments after an overnight break. The DBFC showed initial high performance even at low temperature and maintained a relatively stable performance for a period of up to 150 h.

The DBFC experienced a gradual deterioration with time, suggesting that the stability of the DBFC over an extended period was still a matter of concern. The reasons for the deterioration was presumably due to changes in the catalyst states (e.g. surface area and porosity), the membrane function, supplies of the fuel and the oxidant as well as the removal of the products (e.g. H_2O and the gas bubbles), etc. It is worthwhile to point out that Nafion® 117 membrane is not ideal in terms of anion crossover, which prevent transports of both borohydride and hydroxyl ions, although it is the most stable one in alkaline media among the tested membranes in this work. The problem regarding OH^- conduction will be addressed in a parallel work. Overall, optimisations in the components of the DBFC and the operation conditions are required.

4. Conclusions

The DBFC performance was greatly determined by operation conditions, especially the cell temperature and the fuel concentration. The reaction kinetics at the anode and cathode were improved with increasing temperature. Increase in borohydride concentration increased the anode reaction rate and the cell conductivity. However, higher temperature and higher borohydride concentration promoted higher degrees of crossover and hydrolysis of borohydride and thus, polarised the cathode. Increase in NaOH concentration was favourable for the anode reaction and increased the conductivity, but had negative effects on the cath-

ode reaction and the transport of charge-carrying ions and the availability of the borohydride ions reaching the anode. Therefore, an optimisation of these parameters is required.

Better DBFC performance was achieved using O_2 rather than air and a further improvement was realised under higher pressures due to the improved cathode kinetics.

The DBFCs with the serpentine flow field showed better performance than those with the parallel flow field. The DBFC performance was improved with increasing flow rate, although the improvement was relatively small.

The DBFC showed a relatively stable performance for a period of up to 150 h even at low temperature, although a further improvement in the DBFC stability is required.

Acknowledgements

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