

Short communication

Influence of anode diffusion layer properties on performance of direct borohydride fuel cell

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Abstract

This study investigates the effect of the anode diffusion layer on the cell performance and stability of a direct borohydride fuel cell (DBFC). Carbon paper with various PTFE contents and thicknesses is used as the anode diffusion layer. In the case of the DBFC, both hydrogen evolution and liquid fuel diffusion have to be considered while selecting an anode diffusion layer. Among the various PTFE-containing diffusion layers, the non-contained diffusion layer yields the best performance. Adding PTFE to the diffusion layer leads to improved gas transport but is unsuitable in the DBFC. In addition, the thinnest (100 μm) diffusion layer gives the best performance among the diffusion layers with various thicknesses. The decrease in the length of the diffusion path is beneficial for both the release of hydrogen gas and the diffusion of liquid fuel. In addition, it is found that the hydrogen evolution rate increases with increasing cell performance. Overall, adequate diffusion of liquid fuel is more important for the performance of a DBFC than the release of hydrogen gas.

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Keywords: Direct borohydride fuel cell; Anode diffusion layer; PTFE contents; Diffusion layer thickness; Hydrogen evolution

1. Introduction

Borohydrides are a group of compounds with high hydrogen contents. For example, NaBH_4 contains 10.6 wt.% hydrogen. Therefore, they are being actively investigated as a source of hydrogen that can be used as the fuel in hydrogen fuel cells such as polymer electrolyte fuel cells (PEFCs) [1–4]. In addition, they can also be used as the anodic fuel in a direct borohydride fuel cell (DBFC) because the direct oxidation of borohydrides takes place at a more negative potential than that of hydrogen gas. The theoretical specific energy is as high as 9.3 Wh g^{-1} if NaBH_4 is used as the fuel. The DBFC uses aqueous alkali borohydride solutions for the anode fuel in a manner similar to that in a direct methanol fuel cell (DMFC). Currently, the DMFC has been widely investigated as a power source for small portable devices [5–8]. It has, however, a low cell voltage and low power density. In addition, it requires a heavy loading of noble metals such as Pt or Pt–Ru alloy as an anode catalyst due

to the low activity of methanol. By contrast, the DBFC has a high cell voltage and a high power density. In addition, non-precious metals such as Ni and Cu are adequate for use as anode catalysts.

Although the DBFC gives a high performance as a power source for small portable devices, there are several problems that need to be solved, e.g., hydrogen evolution at the anode during operation, BH_4^- crossover, NaOH accumulation at the cathode, and NaBO_2 accumulation at the anode [9]. Hydrogen evolution is related to fuel diffusion because it causes a two-phase counter current flow in the anode diffusion layer. The properties of this layer such as the pore size distribution, thickness and hydrophobic content are critical factors in DBFC research.

Paganin et al. [10] have investigated the performance of PEFCs by varying the PTFE content and diffusion layer thickness. A cathode diffusion layer containing 15 wt.% PTFE gave the best performance because PTFE prevented flooding of the electrodes by the product water. The thickness of the diffusion layer was reported to have more influence than the PTFE content. Of the various diffusion layer thicknesses (15, 25, 35, 50, 65 μm), 50 μm was found to give the best performance. Oedegaard et al. [11] investigated the performance of a low-temperature DMFC as a function of the PTFE content of the

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Table 1
Types of diffusion layers tested

Diffusion layer	PTFE content [wt.%]	Thickness [μm]
A20	20	100
B20	20	190
C20	20	280
D20	20	370
B00	0	190
B10	10	190
B30	30	190

anode diffusion layer. The PTFE enhanced the release of carbon dioxide from the diffusion layer and gave a more stable performance. A diffusion layer containing 30 wt.% PTFE gave the most stable behaviour.

This work concerns a study of the influence of anode diffusion layer properties on the performance of a DBFC by differing the PTFE content and the thickness. The significance of the diffusion layer selection and the appropriate properties for DBFCs is also demonstrated.

2. Experimental

2.1. Types of diffusion layer

Different types of diffusion layer were used for the anode but only one type of diffusion layer was used for the cathode throughout the experimental programme. Toray carbon paper TGP-H 060 with 20 wt.% PTFE was used as the cathode diffusion layer. Toray carbon paper with different PTFE contents and thicknesses was served as the diffusion layer for the anode. Details of diffusion layers tested are given. In Table 1, the notations A, B, C and D indicate a carbon paper thickness of 100, 190, 280 and 370 μm , respectively, and the numbers 00, 10, 20 and 30 indicate a PTFE content 0, 10, 20 and 30 wt.%, respectively.

2.2. Preparation of membrane electrode assembly

A commercial Nafion[®] 115 (DuPont) membrane was used for the electrolyte. The membrane was pretreated with a 5 wt.% H_2O_2 solution at 80 °C for 1 h to remove the remaining organic and inorganic contaminants, immersed in a 1 M NaOH solution, and then heated to 80 °C for 1 h to allow sodium ions to substitute for cations in the sulfon groups of the Nafion membrane. Catalyst slurries were prepared by mixing 40 wt.% Pt/C catalyst (Johnson Matthey) with isopropyl alcohol (HPLC grade) and the mixture was then ultrasonicated for 30 min. Finally, a 5 wt.% Nafion[®] solution (DuPont) was added to the mixture, which was ultrasonicated again for 30 min. These catalyst slurries were spray-coated on the prepared carbon paper using an automated spraying machine. The Pt loading was 0.4 mg Pt cm^{-2} on both electrodes. The prepared electrodes and membrane were hot pressed at 140 °C for 90 s to fabricate a membrane electrode assembly (MEA) with an active area of 25 cm^2 .

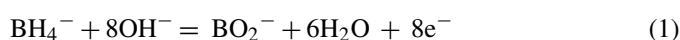
2.3. Operating conditions and electrochemical measurement

A single cell consists of a MEA sandwiched between two flow-field plates made from graphite blocks. The channels in the graphite blocks form a semi-serpentine flow field with a width and a depth of 1 mm each. All the cells were tested at a cell temperature of 70 °C. The anode fuel was 800 ml of an alkali borohydride solution containing 10 wt.% NaBH_4 and 10 wt.% NaOH. The solution was pumped into the anode side of cell at a flow rate of 10 ml min^{-1} . Oxygen, the oxidant, was humidified at 70 °C and supplied to the cathode at a flow rate of 200 ml min^{-1} . The amount of hydrogen produced during operation was measured using a mass flow controller calibrated for hydrogen (Bronkhorst Hi-Tech). The current–voltage (I – V) curves were measured using an electronic loader (EP-1000, Deagil Electronics). The open-circuit voltage (OCV) was measured when the cell voltages were stable. The I – V measurements were performed by applying a constant current for 3 min at each point. The power densities were calculated from the steady-state voltages and applied currents.

3. Results and discussion

3.1. Hydrogen evolution

Eq. (1) represents the reaction for the anodic oxidation of borohydride. This reaction competes with the hydrolysis reaction shown in Eq. (2).



Hydrogen gas, which is produced by the hydrolysis reaction at the anode, causes some problems. The hydrolysis reaction depletes BH_4^- ions, which are needed as the anodic fuel. If all the BH_4^- ions are used for anodic oxidation, each BH_4^- ion will release eight electrons, as shown in Eq. (1). In practice, however, the actual number of electrons released by BH_4^- is less than eight due to the hydrolysis reaction. Therefore, hydrogen evolution reduces the utilization efficiency of the fuel. Suda and coworkers [12] reported that the actual number of electrons released by each BH_4^- ion was approximately 6. This was determined using a three-electrodes system at 30 °C on a Pt catalyst. In addition, hydrogen evolution decreases the rate of the anode reaction because hydrogen bubbles hinder the active sites of the catalysts. Above all, hydrogen evolution has an adverse effect on fuel diffusion. Hydrogen bubbles form dead zones by occupying some of the space in the channel, as shown in Fig. 1. If not removed easily by the fuel flow, these dead zones hinder the diffusion paths. This is particularly a problem at a slow flow rate. Fig. 2 shows the dead zones at a different fuel flow rates of 20 and 100 ml min^{-1} . The dead zones are effectively removed at a fast flow rate. These dead zones were observed by a high-resolution digital camera using transparent flow-field plates made from poly(bisphenol-A carbonate). Fig. 3 shows the effect of the fuel flow rate on cell performance. The cell per-

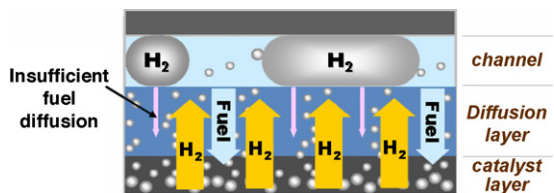


Fig. 1. Schematic diagram of two-phase transport in anode diffusion layer in DBFC.

Table 2
Cell performance for anode diffusion layers with various PTFE contents

	B00	B10	B20	B30
Open-circuit voltage (V)	1.04	1.05	1.05	1.05
Current density at 0.6 V (mA cm^{-2})	230	150	140	100
Maximum power density (mW cm^{-2})	152	94	88	62

formance increases with increasing flow rate because hydrogen bubbles are removed from the channel.

The rate of the hydrogen evolution during operation is related with PTFE content and anode diffusion layer thickness. When 10 ml min^{-1} of the fuel solution is supplied to the anode, the outlet flows are $120\text{--}285 \text{ ml min}^{-1}$ under different diffusion layer conditions. These results show that a large amount of hydrogen gas is generated and occupies 92–96% of the outlet flow. The relationship between the amount of hydrogen evolved and the cell performance is explained in Section 3.4.

3.2. Effect of PTFE content

The current–voltage curves for the anode diffusion layer with different PTFE contents are given in Fig. 4. When different PTFE-containing carbon papers are used as the anode diffusion layer, single cells exhibit different performances. Overall, the performance decreases drastically with increasing PTFE content. A maximum power density of 152 mW cm^{-2} is obtained for B00. This is about 2.5 times higher than the 62 mW cm^{-2} delivered by B30, as shown in Table 2. The stability of the cell voltage also decreases with increasing PTFE content, as shown

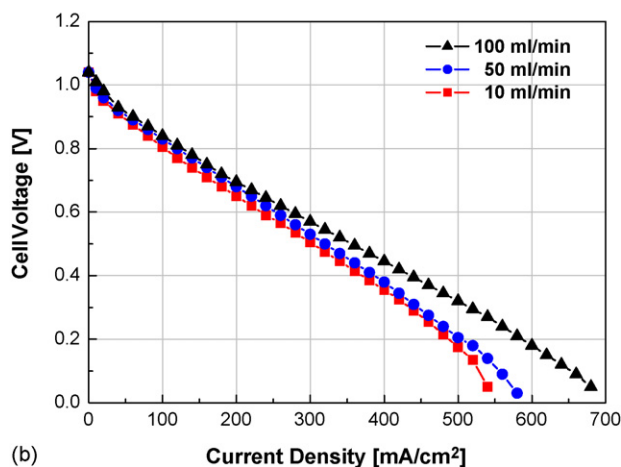
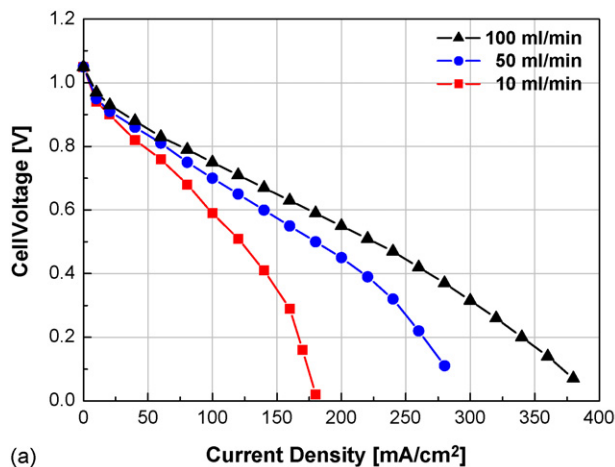


Fig. 3. Current–voltage curves for cells with: (a) B30 and (b) B00 at various fuel flow rates.

in Fig. 5. The stability was measured using a multi-meter (Fluke MB45) at a constant current density of 180 mA cm^{-2} for 10 min.

The above findings can be explained in terms of two major factors, namely, the release of hydrogen gas and the diffusion of liquid fuel. According to theory, addition of PTFE to the diffusion layer leads to better gas transport because gas and

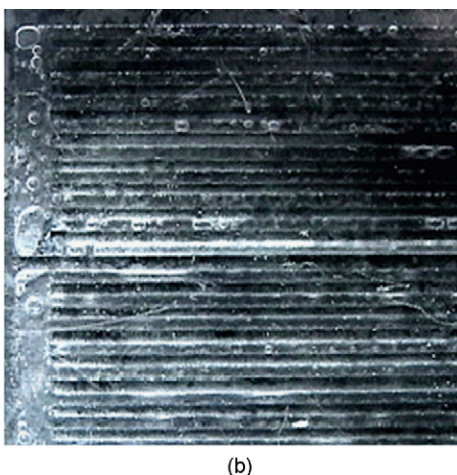
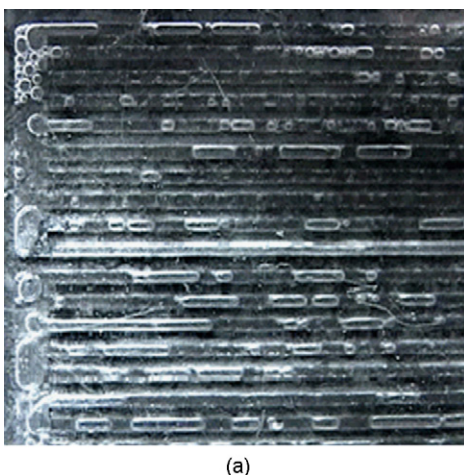


Fig. 2. Dead zones formed by hydrogen bubbles at a different fuel flow rate of: (a) 20 ml min^{-1} and (b) 100 ml min^{-1} .

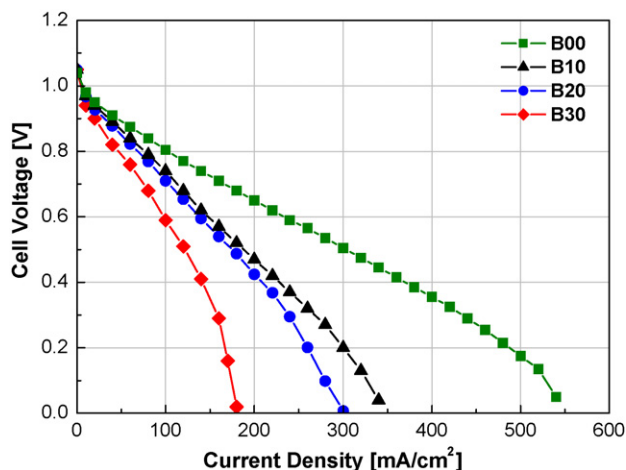


Fig. 4. Current–voltage curves for anode diffusion layer with various PTFE contents.

liquid transport occur through different pathways [11]. Therefore, there are optimum values for the PTFE content for DMFCs and PEFCs, even though PTFE has an undesirable influence on some of the properties of the diffusion layer, e.g., it decreases the porosity and increases the electrical resistance [13,14]. In particular, the DMFC is similar to the DBFC because the anode reaction of DMFC generates CO_2 gas. Although a small amount of CO_2 gas is produced, the process for the generation, growth and release of CO_2 bubbles from the anode diffusion layer affects the performance and stability of the DMFC [11]. In the case of the DBFC, however, the pathways for gas transportation are not as important. This is because, even if the pathways for gas transportation are not formed by the PTFE coating, hydrogen is released spontaneously from the diffusion layer due to the large amount of hydrogen gas produced.

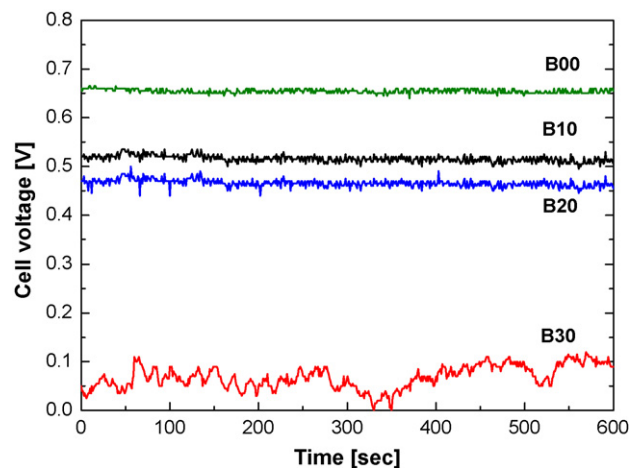


Fig. 5. Stability of cell voltage for various PTFE-containing anode diffusion layers.

The contact angle between the carbon paper and a drop of the fuel at various PTFE contents is shown in Fig. 6. The contact angles were measured at 25°C by means of the sessile drop method. The volume of the fuel drop was $10\ \mu\text{l}$, and it contains 10 wt.% NaBH_4 and 10 wt.% NaOH . From B00 to B30, the contact angle increases with increasing PTFE content. A high contact angle implies low wettability. A highly wettable diffusion layer is favourable for the diffusion of liquid fuel because a diffusion layer with a good wettability gives a large contact surface between the diffusion layer and the fuel drop. Therefore, a PTFE coating on the diffusion layer is undesirable for liquid diffusion. In particular, alkali borohydride solutions are so viscous and dense [15] compared with methanol that fuel diffusion is strongly dependent on the wettability of the diffusion layer.

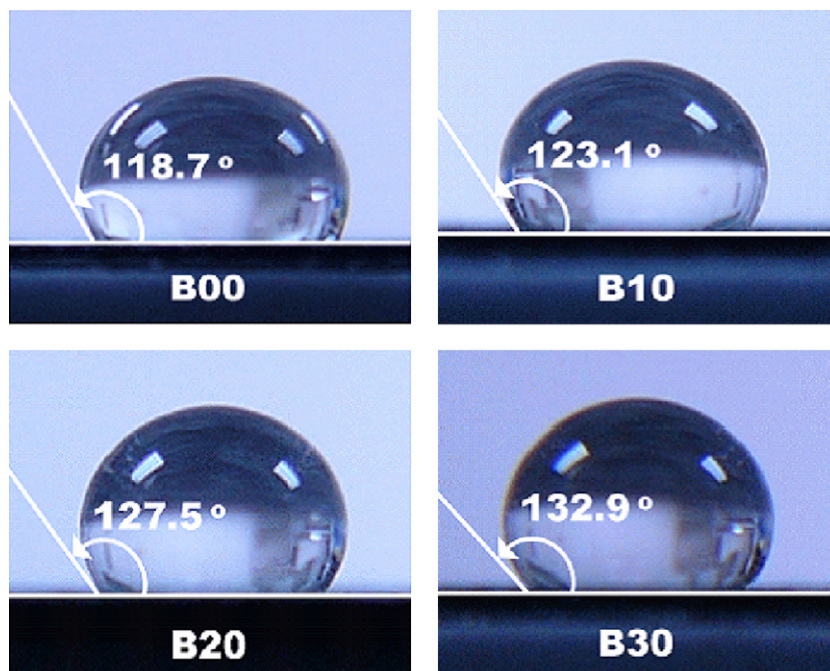


Fig. 6. Contact angles between fuel drops and carbon paper with various PTFE contents.

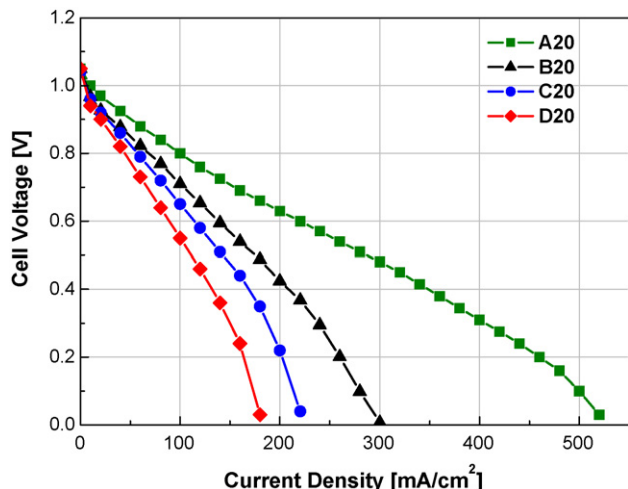


Fig. 7. Current–voltage curves for anode diffusion layers with various thicknesses.

High wettability of the diffusion layer is also beneficial for the stability of the DBFC. In the high current density region, the cell performance will become very unstable if the fuel supply rate is irregular or insufficient for an appropriate reaction rate. In the case of a diffusion layer with high wettability, liquid fuel can transfer not only through the pores but also through the surface of the carbon fibres because the contact surface between the carbon fibre and the liquid fuel increases with increasing wettability of the carbon paper. Therefore, as the wettability of the diffusion layer increases, the rate of fuel diffusion in the anode diffusion layer is enhanced and becomes more uniform through the whole area of the layer. Therefore, adding PTFE to the layer is undesirable for the performance and stability of the DBFC.

3.3. Effect of diffusion layer thickness

The effect of the anode diffusion layer thickness on cell performance is presented in Fig. 7. A diffusion layer thickness of 100 μm (A20) is found to give the best current density of 144 mA cm⁻², which corresponds to a 2.6-fold increase compared with the worst-performance of 55 mA cm⁻² for the 370 μm diffusion layer (D20), as shown in Table 3. The effect of the anode diffusion layer thickness is attributed to increase in the length of the diffusion path because a long diffusion path decreases the rates of both fuel diffusion and hydrogen release. The fuel concentration in the catalyst layer decreases with increasing path length. The stability of the cell voltage also decreases with increasing diffusion layer thickness, as shown in Fig. 8, because the supply of fuel to the catalyst layer is

Table 3
Cell performance for anode diffusion layers with various thicknesses

	A20	B20	C20	D20
Open-circuit voltage (V)	1.05	1.05	1.04	1.05
Current density at 0.6 V (mA cm ⁻²)	220	140	125	90
Maximum power density (mW cm ⁻²)	144	88	77	55

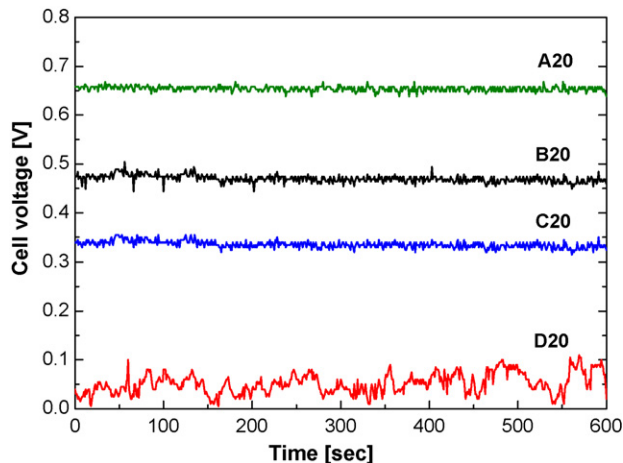


Fig. 8. Stability of cell voltage for various anode diffusion layer thicknesses.

inadequate. Although A20 gives the most stable and high performance, there are some problems. A20 easily cracked and a significant amount of the catalyst slurry was washed away by the fuel flow. Therefore, it is believed that using a diffusion layer that is too thin is inadequate for long-term operation.

3.4. Fuel supply at the anode diffusion layer

The relationship between the hydrogen evolution rate and maximum power density for various PTFE contents and thick-

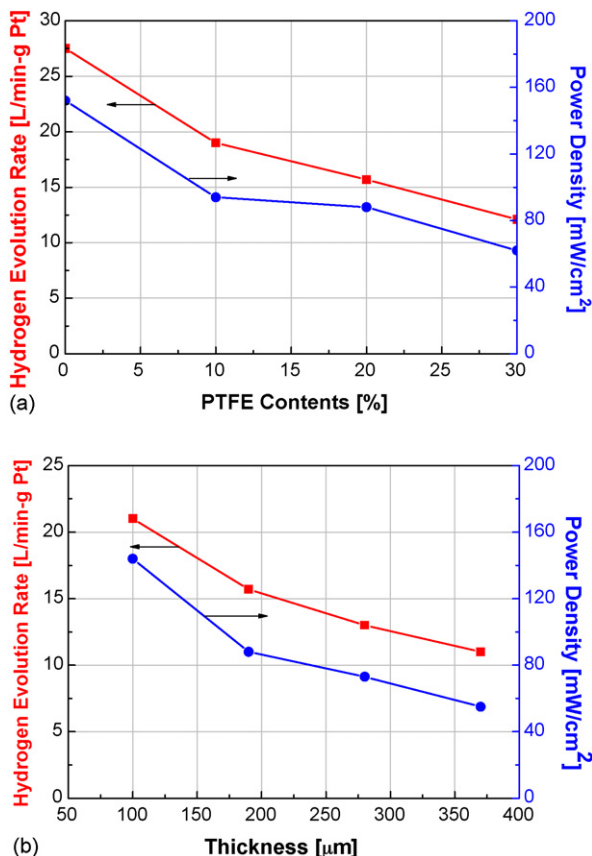


Fig. 9. Hydrogen evolution rate and power density as function of: (a) PTFE content and (b) thickness of anode diffusion layer.

nesses is given in Fig. 9. The reason why the maximum power densities increase with increasing hydrogen evolution rate is due to the effect of the diffusion layer properties, which increase the rate of fuel diffusion. The increasing diffusion rate of fuel not only enhances the cell performance but also increases of the degree of hydrogen evolution. This is because it increases the rates of both the anodic oxidation reaction and the hydrolysis reaction. This phenomenon suggests that adequate fuel diffusion is a more important determinant of DBFC performance than the release of hydrogen gas from the anode diffusion layer. Therefore, those properties of the diffusion layer that increase the rate of fuel diffusion are favourable for DBFC. A comparison of B30 with B00 in Fig. 3 shows that there is less deviation in cell performance with flow rate in B00 than in B30. Although the dead zones are not easily removed at a slow flow rate, in the case of B00, the dependence of the cell performance on the flow rate decreases because the rate of fuel diffusion in the diffusion layer is sufficient.

4. Conclusions

The anode diffusion layer can affect the performance of the DBFC considerably. The parameters critical to the cell performance include the PTFE content of the diffusion layer and the diffusion layer thickness. In the case of DBFC, both fuel diffusion and hydrogen evolution should be considered when examining the effects of the diffusion layer properties. The B00 layer, which contains 0 wt.% PTFE, gives the most stable and highest performance among the various PTFE-containing diffusion layers. Although adding PTFE to the anode diffusion layer is favourable for the release of hydrogen gas, it is detrimental to the performance of the DBFC because it disturbs the diffusion of liquid fuel. This shows that the diffusion of liquid fuel has a larger effect on determining the performance of the DBFC than the release of hydrogen gas from the diffusion layer. The A20 layer, which is the thinnest of those studied, gives the best performance because a thinner layer is better for both the diffusion

of liquid fuel and the release of hydrogen gas. In addition, the DBFC performance is enhanced even though there is an increase in the rate of hydrogen evolution. Therefore, although hydrogen evolution adversely affects fuel diffusion and the amount of hydrogen increases with increasing wettability and decreasing thickness, adequate fuel diffusion using an appropriate diffusion layer is more important for DBFC performance than the release of hydrogen gas. For the selection of a diffusion layer, a thin layer with a high wettability is desirable.

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