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음극 확산층의 물성에 따른 직접보로하이드라이드 연료전지 성능평가

박기태, 정운호, 이향미, 천국, 최동웅, 김성현*
고려대학교 화공생명공학과

Influence of Anode Diffusion Layer Properties on the Performance of Direct Borohydride Fuel Cell

Ki Tae Park, Un Ho Jung, Hyang Mee Lee, Kook Chun, Dong Woong Choi, Sung Hyun Kim*
Department of Chemical and Biological Engineering, Korea University

1. Introduction

Borohydrides are actively investigated as a source of hydrogen which can be used as the fuel of hydrogen fuel cells like polymer electrolyte fuel cells (PEFC). They are not only the source of hydrogen but also the anodic fuel of direct borohydride fuel cell (DBFC), because direct anodic oxidation of borohydrides provides more negative potentials than that of hydrogen gas. The theoretical energy density can reach as high as 9.3 Wh/g of $NaBH_4$ if the sodium borohydride is used as the fuel.

Although DBFC shows high performance as a power source of the small portable devices, there are several problems to be solved such as hydrogen evolution at the anode during operation, BH_4^- crossover, NaOH accumulation at the cathode, and $NaBO_2$ accumulation at the anode. In particular, hydrogen evolution is related to the fuel diffusion, because it causes a two-phase counter current flow in the anode diffusion layer. In this case, the properties of anode diffusion layer like pore size distribution, thickness, and hydrophobic contents are critical factors in DBFC research.

In this work, we studied the influence of the anode diffusion layer properties on the performance of DBFC by differing PTFE content and thickness. We also demonstrated the significance of diffusion layer selection and the appropriate properties for DBFC.

2. Theory and experimental

The anodic oxidation of borohydrides is postulated as Eq. (1). However, this reaction competes with the hydrolysis reaction described as Eq. (2).

$$BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e \qquad (1)$$

$$BH_4^- + 2H_2O = BO_2^- + 4H_2 \qquad (2)$$

Therefore, the actual anodic reaction is described as Eq. (3).

$$BH_4^- + x\,OH^- \rightarrow BO_2^- + (x-2)H_2O + (4 - \frac{1}{2}x)H_2 + x\,e \qquad (3)$$

The x is called as columbic number which means the actual number of electrons released by BH_4^- ion. Hydrogen gas which is produced by hydrolysis reaction at the anode induces some problems. The hydrolysis reaction of Eq. (2) depletes BH_4^- ions which have to be used as the anodic fuel. Thus, the hydrogen evolution diminishes the efficiency of fuel utilization. Above all, hydrogen evolution is negative for fuel diffusion, because hydrogen release flow disturbs fuel diffusion and the hydrogen bubbles form dead zones by occupying some space of channel as shown in Fig. 1. These dead zones hindered the diffusion paths and those were not removed easily by fuel flow.

In this study, different types of diffusion layers were used for anode, but only one diffusion layer was used for cathode throughout the experimental. Toray carbon paper TGP-H 060 of 20wt% PTFE contents was used for the cathode diffusion layer. The diffusion layers for the anode used Toray carbon paper with different PTFE contents and thickness. Types of diffusion layers tested are shown in Table 1.

Single cells consist of MEA sandwiched between two flow field plates of graphite blocks. The channels in the graphite blocks formed a semi-serpentine flow field with width and depth of 1 mm, respectively. All the cells were tested at a cell temperature of 70 ℃. The anode fuel was 800 ml alkali borohydride solution containing 10 wt% $NaBH_4$ and 10 wt% NaOH. It was pumped into the cell at a flow rate of about 10 ml/min. The oxygen, the oxidant, was humidified at 70 ℃ and supplied by 200ml/min. The amount of hydrogen gas produced during operation was measured by mass flow controller for the use of hydrogen (Bronkhorst Hi-Tech). Polarization curves were measured by an electronic loader (EP-1000, Deagil Electronics). Polarization curve measurements were conducted by applying constant currents for 3 min at each point. Power densities were calculated from the steady-state voltages and applied currents.

3. Results and discussion

Polarization curves for cells of varying PTFE contents are shown in Fig. 2. When the different PTFE-contained carbon papers were used as the anode diffusion layer, single cells showed much different patterns of performance. On the whole, the performances of single cells were decreased drastically with increase of PTFE contents. The maximum power density of 152 mW/cm^2 for B00 was about 2.5 times higher than 62 mW/cm^2 for B30 as shown in Table 2.

This result can be explained by two major factors such as hydrogen release and fuel diffusion. According to theory, adding PTFE to the diffusion layer leads to better gas transport, as gas and liquid transport takes place in different paths. In the case of DBFC, the paths of gas transportation were not so important as DMFC. Because, even if the paths of gas transportation were not formed by PTFE coating, hydrogen gas was spontaneously released from diffusion layer, because quite a few amount of hydrogen gas was produced.

Figure 3 shows contact angles between carbon papers and fuel drops with various PTFE contents. The contact angles between fuel drops and carbon papers with different PTFE contents were measured by sessile drop method at 25 ℃. From B00 to B30 the contact angles were increased with increasing PTFE contents. The contact angles indicate the wet-abilities of carbon papers for liquid fuel. The high contact angle means low wet-ability. The more wetable diffusion layer was the more favorable for fuel diffusion, because diffusion layer with high wet-ability showed large contact surface between diffusion layer and fuel drop. Therefore, PTFE coating to the diffusion layer is undesirable for liquid diffusion.

Figure 4 shows the effect of diffusion layer thickness on the cell performance. When diffusion layers of various thicknesses were investigated, A20 was found to give the best performance of 144 mA/cm^2 corresponding to 2.6 times increase in maximum power density compared with the worst-performing of 55 mA/cm^2 for D20 as shown in Table 3. The effect of diffusion layer thickness was attributed to increase in the length of diffusion paths, because the long diffusion paths decrease both the rate of fuel diffusion and the rate of hydrogen release.

4. Conclusions

The diffusion layer can substantially affect the performance of DBFC. Parameters that are critical to cell performance include the PTFE content of the diffusion layer and the diffusion layer thickness. In the case of DBFC, to investigate the effects of diffusion layer properties, both fuel diffusion and hydrogen evolution should be considered. The B00 which contained 0 wt% PTFE gave the most stable and highest performance among the various PTFE-contained diffusion layers. Although adding PTFE to the anode diffusion layer is favorable for hydrogen gas release, it is invalid for DBFC and PTFE in the diffusion layer disturbs the diffusion of liquid fuel. This result shows that the primary diffusion layer property which determines the performance of DBFC is not release of hydrogen gas from the diffusion layer but the diffusion of liquid fuel. The A20, the thinnest diffusion layer, gave the best performance, because the thinner thickness was better for both diffusion of liquid fuel and hydrogen gas release. Consequently, although the hydrogen evolution negatively affected on the fuel diffusion and the amount of hydrogen evolution was increased with increasing wet-ability and decreasing thickness, sufficient fuel diffusion by using appropriate diffusion layer was more important than hydrogen gas release for the DBFC performance. For the selection of diffusion layer, the thinner thickness and the more wetable diffusion layer is better for DBFC performance.

Acknowledgements

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5. References

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Table 1. Types of diffusion layers tested

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

Table 2. Cell performances for anode diffusion layers with variable PTFE contents

	B00	B10	B20	B30
OCV	1.04 V	1.05 V	1.05 V	1.05 V
Current Density at 0.6 V	230 mA/cm^2	150 mA/cm^2	140 mA/cm^2	100 mA/cm^2
Maximum Power Density	152 mW/cm^2	94 mW/cm^2	88 mW/cm^2	62 mW/cm^2

Table 3. Cell performances for anode diffusion layers with variable PTFE contents

	A20	B20	C20	D20
OCV	1.05 V	1.05 V	1.04 V	1.05 V
Current Density at 0.6 V	220 mA/cm^2	140 mA/cm^2	125 mA/cm^2	90 mA/cm^2
Maximum Power Density	144 mW/cm^2	88 mW/cm^2	77 mW/cm^2	55 mW/cm^2

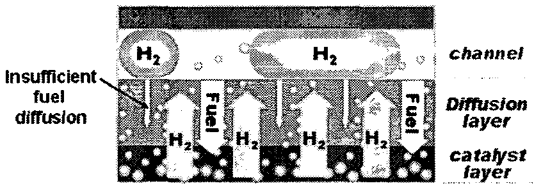

Fig. 1. Schematics of the two-phase transport in the anode diffusion layer in DBFC

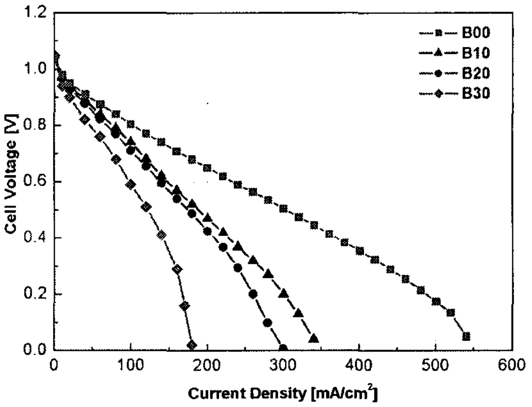

Fig. 2. Polarization curves for anode diffusion layers with various PTFE contents

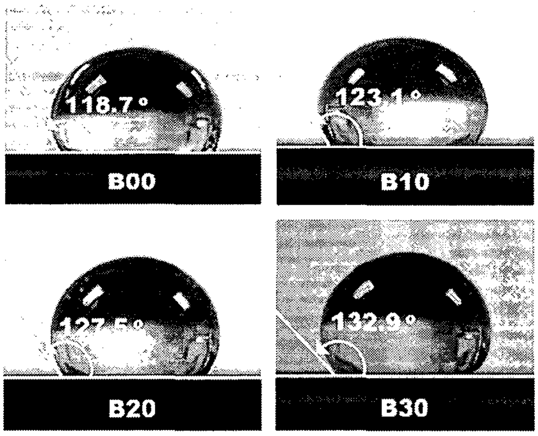

Fig. 3. Contact angles between fuel drops and carbon papers with various PTFE contents

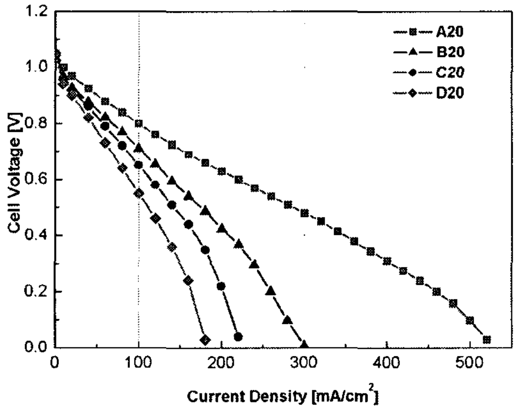

Fig. 4. Polarization curves for anode diffusion layers with various thicknesses