ROLE OF CARBON DIOXIDE LAYER TO INCREASE ENERGY DENSITY OF A PASSIVE DMFC

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Abstract: The effect of stability of the CO_2 gas layer formed between the anode surface and a porous carbon plate, PCP, was investigated in order to clarify the role of the PCP and the CO_2 gas layer on the electrode performance and mass transfer in a passive DMFC using different types of PCPs with different pore structures. The formation of the CO_2 gas layer was essential for significantly limiting the methanol transport to the anode surface where the gaseous methanol diluted in the CO_2 gas contacted with it. The resistance of the methanol transport across the PCP was affected by the pore structure of the PCP, i.e., the pore size and the bubble point pressure.

Key Words: passive DMFC, porous carbon plate, CO_2 gas layer, methanol crossover

1. INTRODUCTION

A key technology for DMFC with a high energy density is the efficient utilization of a high methanol concentration with a simple and a volume-less system. The authors have proposed a novel electrode structure with a porous carbon plate (PCP) for a small passive DMFC. It was demonstrated that the DMFC with PCP can efficiently use high concentrations of methanol up to neat [1-4], where the electrode structure with PCP largely reduced methanol crossover (MCO) by controlling the rate of methanol supply to the anode. The separation of methanol through this novel electrode structure under open circuit conditions was explained by diffusion control of the methanol by the PCP depending on the properties of the porous material, i.e., thickness, porosity and water absorptivity of the porous material [2]. Under closed circuit conditions, the PCP and the CO_2 gas layer that formed between the anode and the porous plate stably controlled the mass transport of methanol and water from the reservoir to the anode, and increasing the distance between the anode and the porous plate, the power density was decreased suggesting that the CO_2 layer acted as an additional barrier of the mass transport [3, 4]. In this study, the effect of CO_2 discharge from the CO_2 gas layer formed between the anode surface and a porous carbon plate was investigated in order to clarify the role of the PCP and the CO_2 gas layer on the electrode performance and mass transfer in a passive DMFC using different types of PCPs with different pore structures. The relation between the gas discharge through or not through the PCP and the DMFC performance as well as the effect of the gas pressure in the layer were investigated using PCPs with a small pore size, i.e., 1μm average diameter, PCPS, and that with a large pore size, a 42μm average diameter, PCPY. The results were discussed on the basis of the effect of the PCP pore structure on the transport of methanol through the PCP to the anode.

2. EXPERIMENTAL

Two different types of porous carbon plates with different pore structures (PCPY1, PCPS1) were used in this study. The properties and pore structure of these porous carbon plates are listed in Table 1, MEA fabrication procedures were described in our previous reports [3, 4]. MEA with the porous carbon plate was set in a plastic holder as shown in Figure 1.
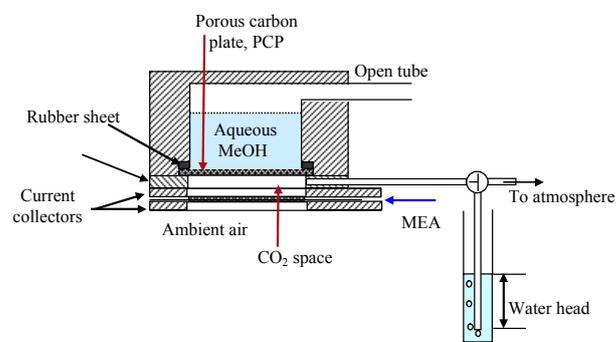

Fig. 1: Schematic diagram of passive DMFC with porous plate and CO_2 control arrangements.

Table 1: Properties of the carbon plates used.

PCP	δ (mm)	α_W (-)	Pore structure measured by the mercury porosimeter			By the Perm-porometer	
			V_P (cm^{3}g^{-1})	$d_{P,ave}$ (μm)	ε (-)	$P_{b.p}$(kPa)	$dp_{,b.p.}$ (μm)
PCPY1	1.0	0.40	0.543	42.3	0.417	3.05	14.8
PCPS1	1.0	0.15	0.556	1.425	0.457	42.76	1.05

δ: Thickness; α_W: Water absorptivity; V_P: Total cumulative volume; d_P: Pore diameter; ε: Total porosity; $P_{b.p}$: Bubble point pressure; $dp_{,b.p}$: Bubble point pore diameter

The cell was horizontally arranged by keeping the reservoir upside down to ensure a consistent contact between the solution and PCP. Under closed circuit conditions, CO_2 gas that produced at the anode was accumulated and a CO_2 gas layer was formed between the porous plate and the anode. This gas layer obstructed methanol transport from the reservoir to the anode [3] To investigate the effect of the PCP pore structure on the formation of the CO_2 layer, the cell performance with the different routes of the CO_2 discharge, i.e., through the PCP or through another additional route, was measured and compared for each type of PCP. To do this, a 5mm thick spacer with a thin tube of 3mm o.d. for the gas discharge was fixed between the anode current collector and the PCP as shown in Figure 1. This tube was connected to a three way valve of which one outlet was opened to the atmosphere and another one was connected to a tube immersed in water with a certain head. When the valve connected the line immersed in water, the pressure of the CO_2 gas layer was controlled by the water head, and CO_2 was discharged through either the PCP or the immersed tube depending on the water head. For the PCPY, CO_2 discharged through the immersed tube when the height of the water head was less than 17cm that was the bubble point head pressure of the plate with the methanol solution. For the PCPS, CO_2 went through the immersed tube at all heights used in this experiment.

All the experiments were conducted in a totally passive mode with the surrounding air at ambient conditions (293K and 1atm). The time progress of the current density, i-t characteristics, at 0.1V was measured. Steady current density, methanol flux, and water flux were determined by measuring current density as well as changes in concentration and weight of methanol solution [3, 4]. The methanol converted to current at the anode was not included in the methanol flux across the PCP in this study. This flux denotes the methanol crossover itself when the valve is closed. However, it also denotes the sum of the methanol crossover and the methanol that went out through the tube when the valve is opened to atmosphere.

3. RESULTS and DISCUSSION

Figure 2 shows the effect of the valve operation, closed and opened to the atmosphere, for the passive DMFC with the porous plate, PCPS1, on the current density at 0.1V and 16mol/L. Initially, the valve was closed. The current density was initially high at 140mA/cm^2, decreased to 100mA/cm^2 within a few minutes, and then slightly decreased within 2.7h to 90mA/cm^2. During this time, the cell temperature was almost constant at 305K. The initial decrease in current density was due to the controlled rate of the methanol transfer by the CO_2 gas layer formed between the PCP and the anode surface [3]. For this same condition with the PCPS1, the current density was controlled by the rate of methanol supplied to the anode [4]. When the valve was opened to the atmosphere at 2.7h, the current density increased up about 200mA/cm^2 and the cell temperature increased to 318K. These increases were caused by the higher methanol supply caused by the valve opening to the atmosphere, thus, the gas accumulated in the CO_2 gas layer was discharged to the atmosphere through the tube. Therefore, the resistance to the methanol transport through the PCP decreased and
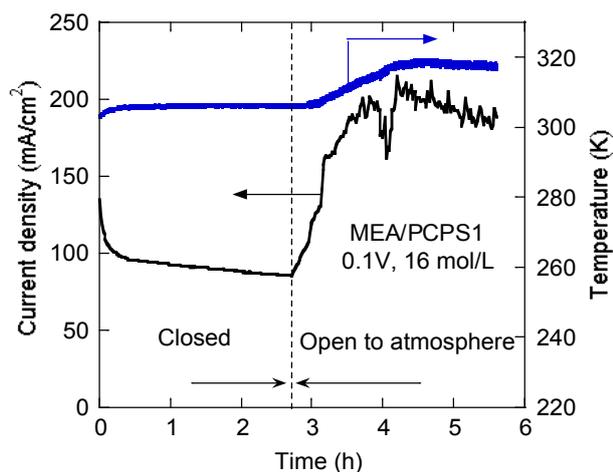
Fig. 2: Current profile during continuous operation of passive DMFC with PCPS1, MEA/PCPS1, at cell voltage of 0.1V and 16mol/L with different valve operations, closed and open to the atmosphere.
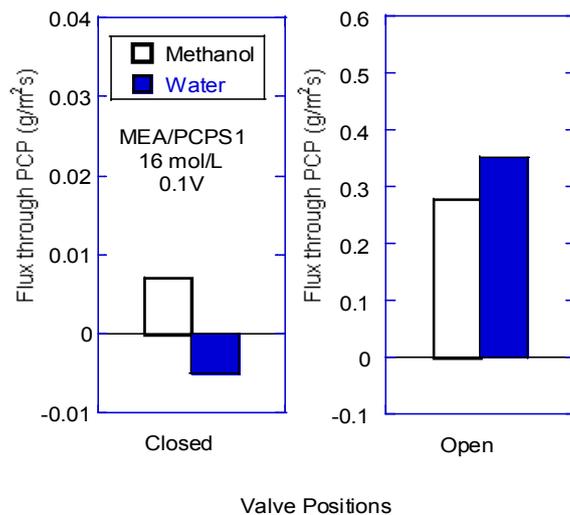

Fig. 3: The effect of the valve operation on the methanol and water fluxes across PCPS1, at cell voltage of 0.1V and 16 mol/L.
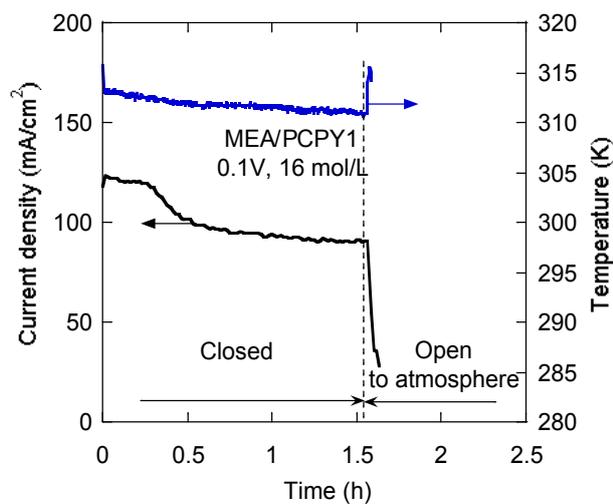

Fig. 4: Current profile during continuous operation of passive DMFC with PCPY1, MEA/PCPY1, at cell voltage of 0.1V and 16 mol/L with different valve operations, closed and open to the atmosphere.
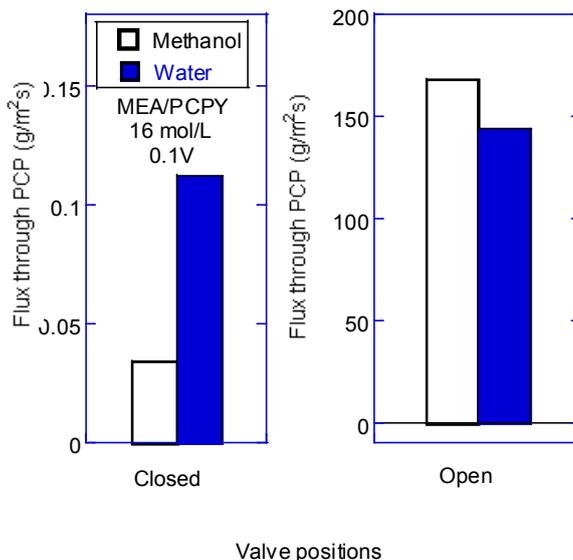

Fig. 5: The effect of the valve operation on the methanol and water fluxes across PCPY1, at cell voltage of 0.1V and 16 mol/L.

a larger amount of methanol reached the anode surface resulting in the higher current density. However, at the same time, the cell temperature increased, flooding appeared at the cathode surface and fluctuations were seen in the current density suggesting that a high methanol crossover

occurred. Figure 3 shows the methanol and water fluxes through the PCP for the i-t experiments shown in Figure 2. As clear from the figure, the methanol flux increased after the valve opening from 0.007 g/m^2s to 0.277 g/m^2s, while, the back diffusion of water, i.e., the negative flux of water

[3] appeared only for the strong restriction of the methanol transport through the PCP. This clearly showed that the blocking of the CO_2 gas generated at the anode from escaping from the space between the PCP and the anode to the outside significantly controlled the methanol flux through the PCP. Although the methanol flux at the valve opening was relatively high, the methanol solution in the reservoir remained for a couple of hours after the opening suggesting that the resistance of PCPS1 to the flow of the methanol solution was relatively high.

Figure 4 shows the effect of the valve operation on the performance for the passive DMFC using PCPY1 at 0.1V and 16 mol/L. When the valve was closed, the current density became stable at $100mA/cm^2$ after 1.5h. It rapidly decreased to less than $20mA/cm^2$ within a few minutes when the valve was opened to the atmosphere. Under this condition, the methanol solution in the reservoir flowed out through the PCP and then through the open tube within a few minutes showing that the resistance of the PCPY1 for the fluid flow was relatively small. The calculated fluxes in the case of Fig. 4 are shown in Figure 5. The very large fluxes of methanol and water through the PCPY1 after the valve opening resulted in the very rapid reduction in the current density due to the high methanol cross over and the flooding at the cathode. The sudden increase in the cell temperature just after the valve opening as shown in Fig. 4 also supported the occurrence of the large methanol crossover. PCPY1, which had the large pore diameter of 42μm, could not resist the methanol transport due to permeation when the CO_2 escaped to the atmosphere.

In case of PCPS1, with small pore diameter, changing CO_2 pressure did not affect cell performance, where, within the measured range of pressure, CO_2 escaped through the water head not through the PCP and the fluxes of methanol and water was not affected. On the other hand in case of PCPY1 with large pore diameter, performance was not affected by increasing CO_2 pressure from 5 to 10 cm-$_{H2O}$ while it increased when the CO_2 pressure was further increased to 20 cm. This could be related to the reduction in MCO in case of 20 cm-$_{H2O}$ than that in case of 5 or 10 cm-$_{H2O}$ where CO_2 at 20 cm-$_{H2O}$ pushes part of methanol solution from the pores of the PCP and evolved through it in contrast to 5 and 10 cm-$_{H2O}$ where CO_2 evolved through the water head

It was found that PCPS1 with the small pores could control the methanol transfer irrespective of the pressure variation in this experiment and the methanol concentration, while PCPY1 with the large pores could not strictly control it thus showing a higher methanol transport through the PCP. The quantitative mechanism for the acceleration of the methanol transport for the PCPY1 is complicated. Based on these view points, PCPS1 would be preferred in the design of a high energy density DMFC for small power sources.

4. CONCLUSION

The formation of the CO_2 gas layer was very important for significantly restricting the methanol transport to the anode surface where the gaseous methanol diluted in the CO_2 gas came in contacted. The resistance to the methanol transport across the PCP was affected by the pore structure of the PCP, i.e., the pore size and the bubble point pressure.

When the pore size was large, i.e., 42μm, the bubbles through the PCP accelerated the methanol transport.

The changes in the CO_2 pressure affect the performance only when they affected the methanol and water fluxes through the PCP within the measured pressure range.

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