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Effect of Diffusion Layer for Cell Performance in DMFC
직접메탄올 연료전지에서 전지 성능에 대한 확산층의 영향

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Abstract

The diffusion layer within MEA(membrane electrode assembly) has been evaluated important factor for improvement of cell performance in DMFC. The diffusion layer in MEA structure leads to the reduction of catalyst loss in active catalysts layer as well as prevention of water-flooding in cathode. Cell performance is directly affected by interior properties of diffusion layer materials. Acetylene Black and RuO_2 with large pore size and low porosity compared to Vulcan XC-72R gave better performance caused by vigorous methanol diffusion and water removal. And RuO_2 as diffusion layer materials showed different behavior in anode and cathode compartment, that is, diffusion layers in anode and cathode side make methanol diffusion and water removal facilitate, respectively.

1. Introduction

MEA(membrane electrode assembly) structure in PEFC consists of a membrane, a electrode and a backing(diffusion) layer which is used for reduction of mass transport limitation to the polarization characteristics. The diffusion layer in PEFC consists of a thin layer of carbon black mixed with poltetrafluoroethylene(PTFE) that is laid on a macro-porous carbon paper and provides a physical micro-porous support for the catalyst layer allowing liquid / gas transport to / from the catalyst layer. Although the diffusion layer is a relatively minor component in a fuel cell, it is certain that optimal choice of the diffusion layer can lead to substantial improvements in the performance of the cell. From this point of view, some studies have been progressed by improving the characteristics of the diffusion layer in terms of compositions, thickness and materials.

2. Experimental

For structural analyses of diffusion layer materials, we measured the surface area, mesopore area, micropore ratio and average pore radius by using Porosimeter. And the resistances of diffusion layer were measured vertically or horizontally in each side of MEA and indicated values are the average. The cell polarization curves were obtained in potentiometer(WMPG-1000).

Carbon powder(Vulcan XC-72R and Acetylene black) and RuO_2 ink solution for the formation of diffusion layer were synthesized by using 40wt % PTFE and IPA(Isopropyl Alcohol). Diffusive layers were prepared by pasting the carbon and RuO_2 on Teflonized carbon paper(TGPH-090) substrate using the above synthesized solution. Manufactured composites of carbon paper and diffusion layer were heat-treated for formation of porous structure in air condition and at 350°C for 1 hour. Then catalyst layer was pasted on the diffusion layer using 5 wt % Nafion® solution as a binder. And the anode(PtRu black, Johnson-Matthey Co.) and cathode(Pt black, Johnson-Matthey Co.) catalysts contain 15 wt % and 7 wt % Nafion®, respectively. In order to prevent performance discrepancy as amount of catalysts, catalysts loadings at both sides were controlled almost constantly, ~5 mg/cm^2. Hot pressing(110°C, 800 psi for 3min) of MEA was performed for unit cell test.

3. Results and Discussion

3.1 Structural analysis of diffusion layer and used catalysts

The properties of diffusion layer materials were indicated in Table 1. From Porosimeter measurements, multi-point BET(m^2/g), mesopore area(m^2/g) micropore ratio(%) and average pore radius(Å) for each components were investigated. The morphology of diffusion layer materials differed in surface area and pore size distribution. Acetylene Black and RuO_2 have a smaller surface area and larger pore radius compared with Vulcan XC-72R. And Vulcan XC-72R has large mircopore(<2nm) ratio of ~47 % while Acetylene Black and RuO_2 have no micropore. RuO_2 has a very small surface area of ~15 m^2/g

and the largest average pore radius of ~155 Å. And RuO_2 has very low resistance along horizontal and vertical direction compared with other materials.

3.2 Comparisons of the unit cell performance according to diffusion layer.

The effect of diffusion layer(DL) morphology on unit cell performance was investigated. Figure 1 shows the cell potential - current density plots in DMFC unit cell that involves or not diffusion layer under oxygen flow. The cell performances tested by using Acetylene black and RuO_2 diffusion layer were much better than other cases. Although large difference in open circuit voltage(OCV) wasn't observed in Figure 1(a), the apparent feature in these plots was the large difference of ohmic polarization region. The polarization curves of the cell using Acetylene Black or RuO_2 diffusion layer were located relatively high, therefore the cell performances were good.

The pore size of diffusion layer will obviously affect the cell performance through the control of fuels(methanol and oxygen) and products(CO_2 and H_2O) flow. Acetylene Black and RuO_2 with large pore size compared with Vulcan XC-72R gave better performance in the diffusion-limited region where maximum power density is obtained. It means that the pore size of diffusion layer is required to be large for amicable diffusion of fuels and products and many micropores in Vulcan XC-72R make diffusion of fuels and products difficult. Another fact known from figure 1 is that the polarization slope of the cell using RuO_2 diffusion layer in ohmic controlled region is relatively flat. It resulted from low resistance of RuO_2 diffusion layer.

Due to the low electrocatalytic activity at low temperature, the properties of catalysts and ohmic characteristics of diffusion layer become very important. Since the diffusion layer prevents catalysts from moving into the carbon paper, the cell performances with diffusion layer are much better than that of without diffusion layer.

3.3 Effect of the RuO_2 diffusion layer for cell performance

For the evident analysis of diffusion layer properties that affect cell

performance, the effect of diffusion layer in regard to each electrode was investigated. For these studies, RuO_2 as diffusion layer was used because it showed the best cell performance in previous research.

Figure 2(a) shows the cell potential - current density plots at 70°C under oxygen flow. The low cell performance without diffusion layer is originated from catalysts infiltration into carbon paper. It resulted in substantial catalysts loss and - especially at high current region - diffusion limitation caused by methanol flow obstruction which arose from permeation of PtRu nanoparticles into macropore of carbon paper. Therefore, the role of anode diffusion layer becomes important in high current density region, that is, the RuO_2 diffusion layer in methanol supplying part made methanol flow facilitate to anode catalyst layer.

The cells with RuO_2 diffusion layer at only cathode also gave better cell performance than that of without diffusion layer. It is believed that water-flooding phenomena of cathode catalyst was diminished by hydrophobic diffusion layer which facilitated the water removal from the catalysts layer.

The cell performance under air flux is shown in Figure 2(b) and, in this case, the role of diffusion layer is more obvious. The difference between oxygen and air is related to the lower partial pressure of oxygen in air and the diffusive blanketing effect of nitrogen in air. Thereby, diffusion layer in cathode side becomes more important than that of anode side. As predicted in Figure 1, diffusion layers in anode and cathode side made methanol diffusion and water removal facilitate, respectively. The contribution of cathode diffusion layer for cell performance is much larger than that of anode diffusion layer. And combined effect was shown in the cell performance with diffusion layers at both electrodes.

4. Conclusions

The diffusion layer in liquid feed DMFC is the flow channel for fuels (methanol and oxygen) and products (CO_2, H_2O). The optimal diffusion layer in MEA structure leads to the reduction of catalyst loss in active catalysts layer, caused by the formation of dense layer between carbon paper and catalyst layer.

Acetylene Black and RuO_2 with large pore size and low porosity compared to Vulcan XC-72R gave better performance caused by vigorous methanol diffusion and water removal. Especially, the unit cell of the RuO_2 diffusion layer with the lowest resistance brought the highest cell power density due to low ohmic polarization.

RuO_2 as diffusion layer materials showed different behavior in anode and cathode compartment. When it was used as anode diffusion layer, the cell performance increased due to minimization of catalyst loss and facile methanol diffusion. As a result, the role of anode diffusion layer is important in high current density region, which is diffusion limited region. And when it was used in cathode diffusion layer, the cell performance increased remarkably due to reduction of water flooding of cathode catalysts. In conclusion, the effect of diffusion layer on cell performance became dominant at low temperature and especially in air operation.

5. References

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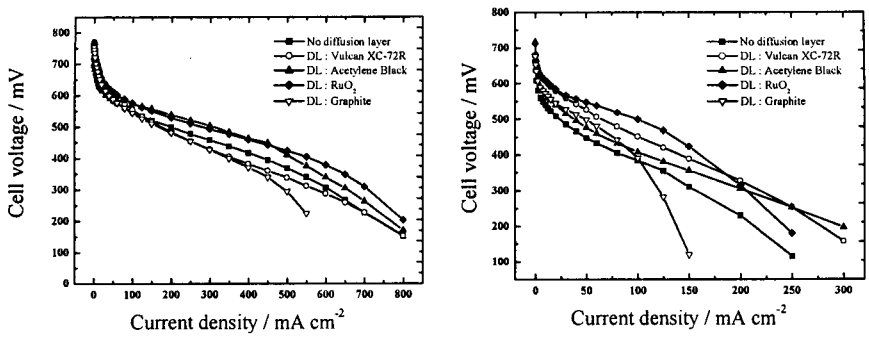
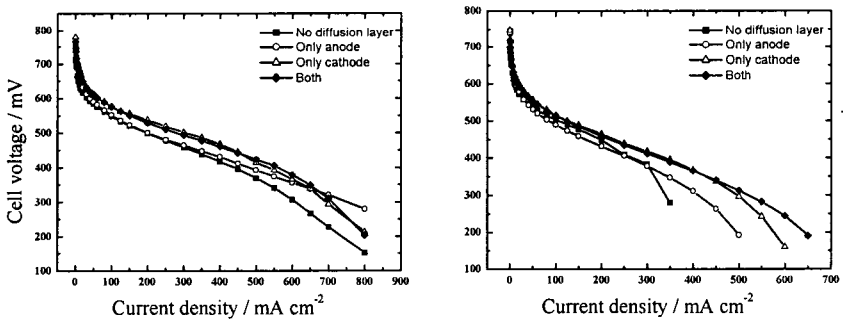
Table 1. The properties of diffusion layer materials

Classification		Vulcan XC-72R	Acetylene Black	RuO_2	Graphite	No DL
Porosimetry	Multi-Point BET(m^2/g)	229.3	127.9	15.4	25.1	
	Mesopore area (2-50nm)(m^2/g)	121.5	127.9	15.4	21.7	
	Micropore ratio (%)(<2nm)	47.1	0	0	13.6	
	Average pore radius(Å)	70.5	89.5	155.2	113.5	
Resistance	Vertical(Ω/thickness)	6.0-9.5	4.5-6.0	1.4-1.8		1.7-2.1
	Horizontal(Ω/cm)	6.9-8.7	5.9-6.3	1.1-1.3		3.1-4.0



(a) (b)

Figure 1. Cell potential vs. current density plots according to diffusion layer at (a) 70°C (b) 30°C. ; anode feed : 2 M methanol solution at 1cc/min, cathode feed : dry O_2 at 500cc/min, (membrane : Nafion® 117)



(a) (b)

Figure 2. Influence of RuO_2 diffusion layer for cell potential vs. current density plots at 70°C under (a) oxygen and (b) air flow ; anode feed : 2 M methanol solution at 1cc/min.
(membrane : Nafion® 117)