

Performance of Ultra-Low Platinum Loading Electrode with Electro-Conductive Layer of Hydrophobic Property for PEFC

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Abstract

The ultra-low platinum loading electrode (ULPLE) equipped with the electro-conductive layer of hydrophobic property was turned out to increase the value of mass activity at 0.8 V by 2.85 times higher than that of existing ULPLE under the condition of H₂ and air at 80 °C. The surface area of carbon comprised in the layer was found to be very important to hold the uniformity of current distribution to suppress the polarization of electrochemical reaction. The layer of acetylene black with small surface area of 95 m²g⁻¹ was superior to the case of furnace black with large value of 254 m²g⁻¹ by 1.62 times higher in the value of mass activity. The reason is considered to be the contribution of uniform distribution of acetylene black in the electro-conductive layer of hydrophobic property resulting in higher electron conductivity.

1 Introduction

The development of polymer electrolyte fuel cell (PEFC) has drawn much attention as a clean power source for automobiles as well as stationary applications in the last decade. However, there are two technical issues of cost reduction and high durability performance before its practical use. We have developed ULPLE of which platinum catalyst loading level is extremely low and the deterioration of the catalyst is suppressed.¹⁾ The platinum catalyst is loaded only in the cluster of the polymer on the surface of carbon by special process of ion-exchange reaction of platinum ion and the counter ion of polymer electro-

lyte covered on carbon powder followed by chemical reduction of platinum ion under the hydrogen gas atmosphere. Therefore, the utilization of platinum is very high, and the aggregation of platinum catalyst during continuous operation of PEFC is suppressed.²⁾ However, the diffusibility of reaction gas of oxygen or hydrogen is considered to be decreased by the limitation of reaction site from three phases boundary to two phases zone with no channel of gas phase, since the platinum catalyst particle is fully covered with the polymer. Therefore, the reaction activity for ULPLE will be more sensitive to the current distribution than that of the existing gas diffusion electrode.

In this paper, we will report the effect of carbon powders as a material for the electro-conductive layer equipped with ULPLE on the polarization char-

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acteristics of PEFC and discuss the current distribution and hydrophobic property of the layer affecting the catalyst activity of ULPLE.

2 Experimental

The PEFC with membrane electrode assembly (MEA) using ULPLE equipped with the electro-conductive layer was fabricated by following method.

2.1 Electro-conductive layer

The electro-conductive layer consisting of carbon powder and polytetrafluoro-ethylene (PTFE) by using two types of carbon powder having different surface area (acetylene black ; $95 \text{ m}^2\text{g}^{-1}$, furnace black ; $254 \text{ m}^2\text{g}^{-1}$) was prepared. Table 1 shows the features of these carbon powders. A homogeneous paste for the electro-conductive layer was prepared by mixing the carbon, carboxymethyl cellulose, and deionized water with appropriate amount of PTFE dispersion. The paste was applied on a substrate and dried in air, followed by a heat treatment at $380 \text{ }^\circ\text{C}$ for 30 min. for hydrophobic property.

2.2 ULPLE

The ULPLE equipped with the electro-conductive layer was prepared with the following process : the formation process of the layer composed of carbon (Cabot, Vulcan XC-72) and ionomer by applying the mixture of carbon and ionomer solution on the electro-conductive layer ; ion-exchange reaction process of platinum ion and proton in the ionomer using $50 \text{ mmol l}^{-1} [\text{Pt}(\text{NH}_3)_4]^{2+}$ solution at $60 \text{ }^\circ\text{C}$ for 6 h ; washing process with deionized water ; and reduction process of $180 \text{ }^\circ\text{C}$ for 6 h under the hydrogen atmosphere.

2.3 Membrane electrode assembly (MEA)

The MEA with 25 cm^2 was prepared by hot-pressing of the cathode and anode ULPLEs equipped with electro-conductive layer on the both sides of poly-

mer electrolyte membrane (Dupont, Nafion115). The assembly was rinsed in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ at $80 \text{ }^\circ\text{C}$ and deionized water.

2.4 PEFC

The PEFC was composed of the following serial constitution ; anode gas flow plate / carbon felt / MEA / carbon felt / cathode gas flow plate. The carbon felt as gas diffusion macro layer was treated with PTFE dispersion solution followed by heating at $380 \text{ }^\circ\text{C}$ for 15 min. for hydrophobic property.

2.5 Electron conductivity

The measurement of electron conductivity of the electro-conductive layer was conducted by the four points probe method. (Mitsubishi Chemical Co., Loresta-EP).

2.6 Contact angle

The contact angle was measured to evaluate the hydrophobicity of electro-conductive layer. After $4 \text{ } \mu\text{l}$ water was dropped on the layer, the height (h) of the drop and width (2r) of contact surface between the drop and the layer were measured. The contact angle θ was calculated by using the equation (1).

$$\theta = 2 \tan^{-1}(h/r) \quad \dots \dots (1)$$

3 Results and discussion

The SEM photograph of surface of the electro-conductive layer is shown in Fig. 1. The surface of the layer of acetylene black is found to be smooth and homogeneous. On the other hand, the surface in the case of furnace black is rough by the agglomeration of carbon powders. The dispersion of the carbon powders in the case of the former was more homogeneous in the carboxymethyl cellulose aqueous solution than the case of the latter resulting in the smooth surface of the layer.

The effect of PTFE content in the electro-conductive layer on the electron conductivity of the layer is shown in Fig. 2. The electron conductivity of the layer with furnace black is found to be decreased with increasing PTFE content, but the conductivity in the case of acetylene black is increased with increasing PTFE content to reach the maximum at around 35%. This tendency shows that the dispersibility of carbon and PTFE particles in the paste for electro-conduc-

Table 1 Features of carbon powder for electro-conductive layer.

	Surface area / $\text{m}^2 \text{g}^{-1}$	Particle size / nm	Oil absorption / $\text{ml } 100 \text{ g}^{-1}$
Acetylene black	95	35	170
Furnace black	254	30	174

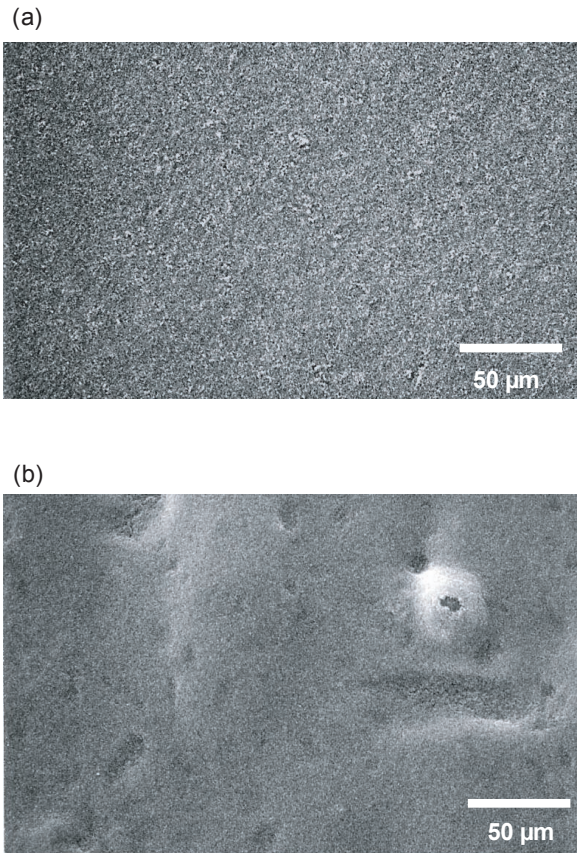


Fig. 1 SEM images of the surface on electro-conductive layer with a different type of carbon powder of acetylene black (a) and furnace black (b).

tive layer of acetylene black powder having smaller surface area is superior to that of furnace black powder. This is derived from the fact that the surface of acetylene black carbon is more smooth than that of furnace black resulting in higher affinity with PTFE particles.³⁾ In the case of furnace black of low dispersibility, PTFE particles seem to be unevenly distributed as insulator. In the case of acetylene black, PTFE particles serve as the binder between carbon particles resulting in high electron conductivity. The dispersibility of carbon and PTFE particles seems to affect on hydrophobicity of the layer. The effect of PTFE content in the layer on the contact angle of the layer is shown in Fig. 3. It is found that the contact angle is increased with increasing PTFE content and the contact angle of acetylene black is larger than that of furnace black. For better analysis on the relationship between electron conductivity and

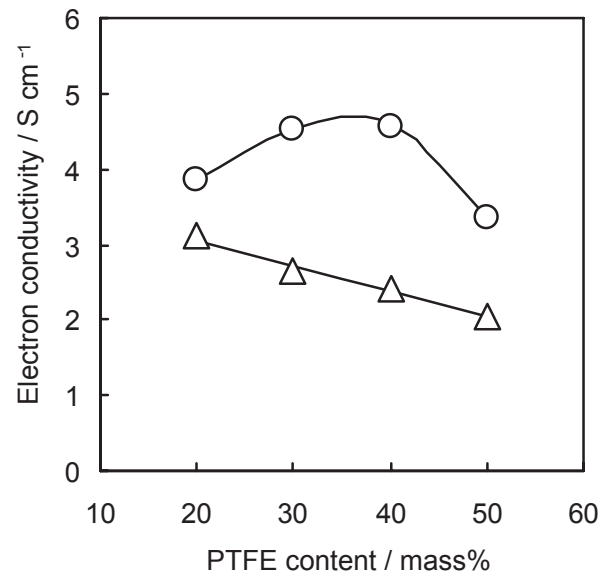


Fig. 2 Effect of PTFE content on electron conductivity of electro-conductive layer with a different type of carbon powder of acetylene black (○) and furnace black (Δ).

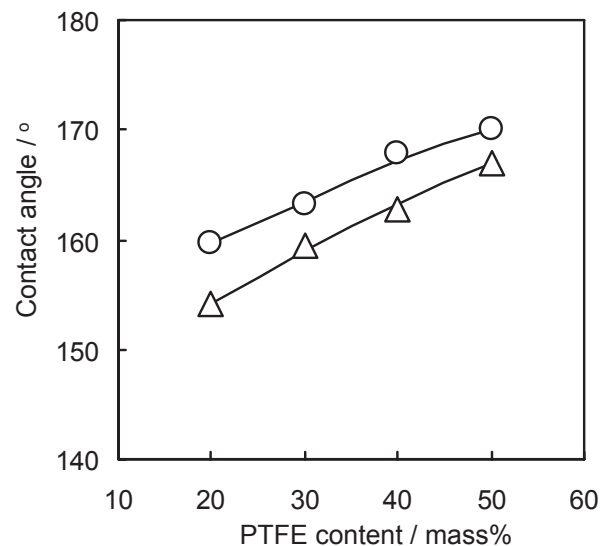


Fig. 3 Effect of PTFE content on contact angle of electro-conductive layer with a different type of carbon powder of acetylene black (○) and furnace black (Δ).

hydrophobicity, the electron conductivity re-plotted with the contact angle is shown in Fig. 4. It is found that the layer of acetylene black is to improve hydrophobicity with maintaining high electron conductivity.

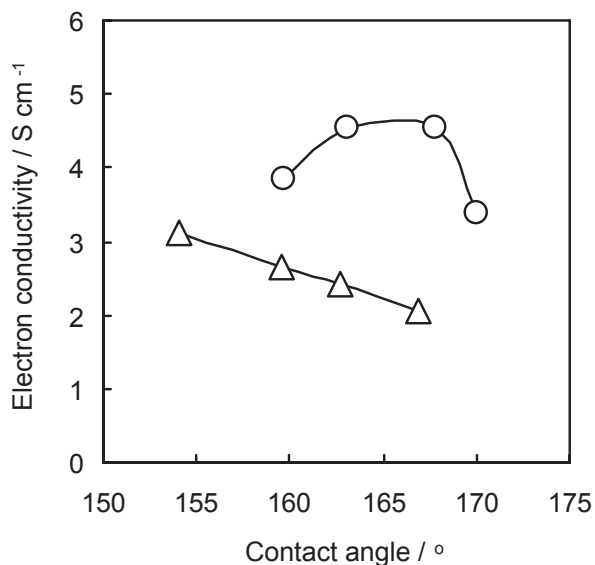


Fig. 4 Relationship between contact angle and electron conductivity for electro-conductive layer with a different type of carbon powder of acetylene black (O) and furnace black (Δ).

The value of electron conductivity and the contact angle at 30% PTFE content are shown in Table 2. The value of electron conductivity for the acetylene black is found to be 1.71 times higher than that of furnace black. The contact angle of acetylene black and furnace black is 163.1° and 159.5° respectively. In this condition, V-I characteristics of the PEFC using ULPLE equipped with the layer are shown in Fig. 5 together with in the case of no layer. It is found that the polarization in the case of electro-conductive layer is smaller than that of the ULPLE with no layer and the performance of PEFC with the acetylene black type electro-conductive layer is superior to that of the furnace black type. The cell voltage of the PEFC using the ULPLE equipped with electro-conductive layer containing acetylene black is 100 mV, and the voltage of the case of furnace black is 50 mV higher than that of the case of no layer. This improvement is assumed to be caused by the electro-conductive layer having high hydrophobicity and

Table 2 Electron conductivity and contact angle of electro-conductive layer.

	Electron conductivity / S cm ⁻¹	Contact angle / °
Acetylene black	4.52	163.1
Furnace black	2.64	159.5

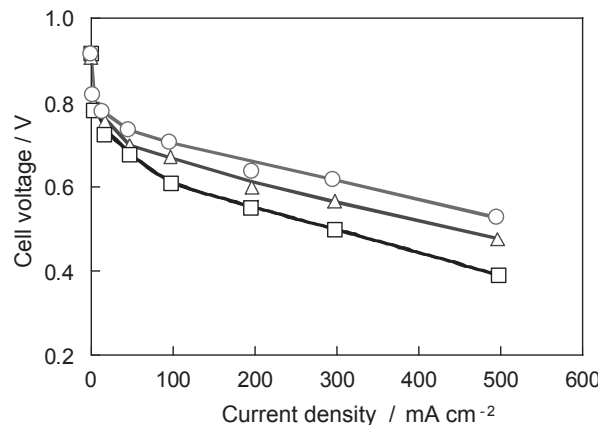


Fig. 5 Polarization curves for PEFC using electro-conductive layer with a different type of carbon powder of acetylene black (O) and furnace black (Δ) under condition of H₂ / air at 80°C. □: No electro-conductive layer. Pt loading: O, Δ 0.036 mg cm⁻², □ 0.037 mg cm⁻².

high electron conductivity resulting in high water repellency and high current collectivity. The difference in cell voltage at a given current density when the PEFC is operated successively on oxygen and air is plotted in Fig. 6. The difference in theoretical electromotive force on oxygen and air for cathode gas is 12 mV calculated from the equation (2).

$$E = E^0 - (RT/nF) \ln[(P_{H_2}) \cdot (P_{O_2})^{1/2} / P_{H_2O}] \quad \dots \dots (2)$$

E^0 : Standard electromotive force, R : Gas constant, n : Number of charge transfer, F : Faraday constant, P_{H_2} , P_{O_2} : Partial pressure of hydrogen and oxygen, P_{H_2O} : Partial pressure of water vapor

However, the diffusibility of air becomes low when water generated from the electrode reaction in the fuel cell operation remains in the electrode, resulting in the increase of difference in cell voltage on oxygen and air. The difference at 300 mA cm⁻² of ULPLE with layer is 40 mV smaller than that of ULPLE with no layer. This result means that the layer suppress water flooding in the electrode resulting in the improvement of gas diffusibility. Furthermore, the difference in cell voltage on oxygen and air in the case of acetylene black is found to be smaller than that of furnace black. This is derived from the fact that the pore size of the acetylene black is larger than that

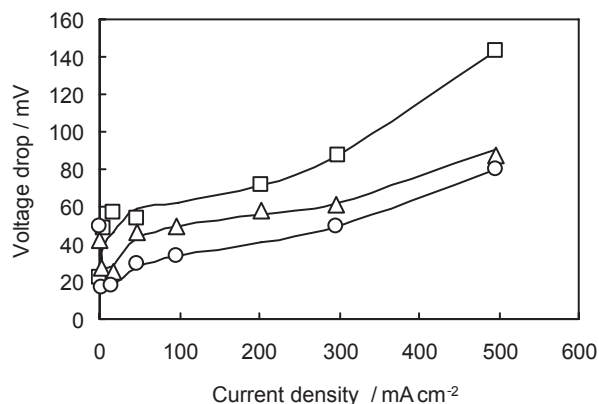


Fig. 6 Voltage drop for PEFC using electro-conductive layer with a different type of carbon powder of acetylene black (O) and furnace black (Δ) after change of condition from H₂/O₂ to H₂/air. □: No electro-conductive layer.

of the furnace black as shown in Fig. 7 for pore size distribution of electro-conductive layer, resulting in the high diffusibility of air.

The catalyst activities were evaluated from the mass activity of ULPLE with the electro-conductive layer. This value is expressed by the current per mass of platinum catalyst at IR corrected 0.8 V. This result is summarized in Table 3. It is found that the value of mass activity of acetylene black and furnace black is 2.85 and 1.76 times higher than that of the no layer, and the acetylene black is 1.62 times higher than that of the furnace black. In the case of the

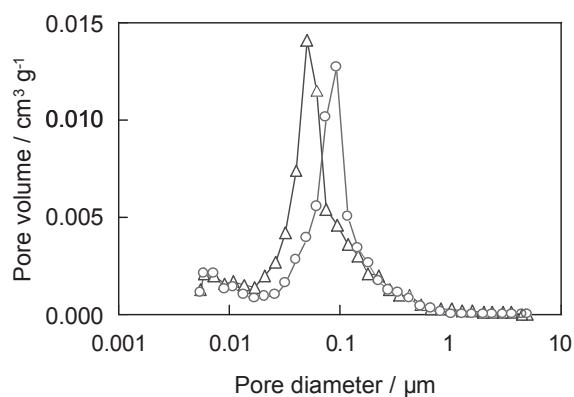


Fig. 7 Pore size distribution for electro-conductive layer with a different type of carbon powder of acetylene black (O) and furnace black (Δ).

ULPLE with no layer, the carbon felt as gas diffusion macro layer contacts with catalyst layer of ULPLE directly, therefore current collecting place is limited at only contact point between carbon fiber and ULPLE, resulting in unhomogeneous current distribution in the electrode. On the other hand, the ULPLE equipped with the layer yields homogeneous current distribution. Therefore, the value of mass activity is increased with the reaction zone of catalyst. For further consideration of these phenomena, the impedance measurement for PEFC using ULPLE with the layer has been conducted. The impedance spectra for the PEFC using ULPLE with the electro-conductive layer is shown in Fig. 8. It is found that the diameter of the first arc of acetylene black is smaller than that of furnace black. This means that the charge transfer resistance of the former is smaller than that of the latter. The second arc as showing mass transfer resistance is also smaller in the case of the acetylene black. This is derived from the fact that the gas diffusibility of acetylene black is higher than that of furnace black resulting in the increase of the active site of electrochemical reaction. These results mean that

Table 3 Mass activity at 0.8 V for PEFC using electro-conductive layer.

	Acetylene black type	Furnace black type	No layer
Mass activity / A g ⁻¹	371.1	229.5	130.1

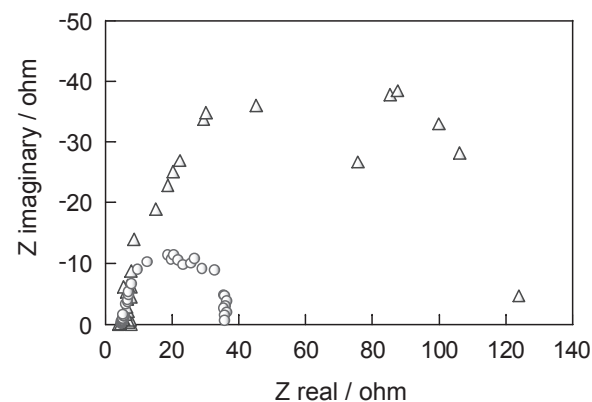


Fig. 8 Impedance spectra for PEFC using electro-conductive layer with a different type of carbon powder of acetylene black (O) and furnace black (Δ).

the high electron conductivity and hydrophobicity of the layer improve the current distribution and suppress water flooding in the electrode resulting in the good oxygen diffusibility.

4 Conclusions

The results of this paper are summarized as described below.

- 1) The cell voltage of the PEFC using the ULPLE equipped with the electro-conductive layer including acetylene black and furnace black at 30% PTFE content is 100 mV and 50 mV higher than that of the case of no layer respectively.
- 2) The value of mass activity at IR corrected 0.8 V of the PEFC with the acetylene black layer is 1.62 times higher than that of furnace black layer.

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