

Optimization of Polymer Electrolyte Distribution of Ultra-Low Platinum Loading Electrode for PEFC

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Abstract

The optimization of distribution of the solid polymer electrolyte within the catalyst layer for ultra-low platinum loading electrode (ULPLE) has been investigated for higher performance of polymer electrolyte fuel cell. The maximum mass activity at 0.6 V and 80 °C for ULPLE was observed at the concentration of 40 mass% of polymer electrolyte in the catalyst layer in which the platinum catalyst particle is loaded only in the cluster of the polymer on the surface of carbon. The mass activity of catalyst for ULPLE with the catalyst layer having higher polymer electrolyte concentration toward the side of membrane of which layer is composed of three different concentrations of 35, 40 and 50 mass%, was found to be increased by 16% with the additional effect of the increment in ionic conductivity of this layer.

1 Introduction

The development of the polymer electrolyte fuel cell (PEFC) as a power source for automobiles as well as stationary applications has been promoted by the environmental concerns, since PEFC has the advantage of higher energy conversion efficiency compared with the internal combustion engine. There are two technical issues of high durability performance and cost reduction before the practical use of PEFC. We proposed the ultra-low platinum loading electrode (ULPLE) with one-tenth of the platinum loading level of 0.1 mg cm⁻² reported so far.^{1, 2)} 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 electrolyte covered on carbon powder followed by chemical reduction of platinum ion under the hydrogen gas atmosphere. The loading level of platinum catalyst on the carbon depends on the amount of the polymer electrolyte, and particle size tends to increase with its loading level.

In this paper, the effect of polymer electrolyte concentration in the catalyst layer on its catalytic activity has been investigated for the optimization of polymer electrolyte distribution of ULPLE.

2 Experimental

The effect of polymer electrolyte concentration on platinum loading level, electric conductivity and catalytic activity on performance of ULPLE was

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investigated for the optimization of polymer electrolyte distribution of this electrode. The performance of ULPLE with the catalyst layer having higher polymer electrolyte concentration toward the side of electrolyte membrane was also investigated as one sample of ideal cell from the viewpoint of the homogeneous current distribution in the electrode.

2.1 Preparation of single cell

The standard ULPLE was prepared with the following process: the formation process of the layer composed of carbon powders (Cabot, Vulcan XC-72) and polymer electrolyte by applying of the mixture of the powder and 10 mass% polymer electrolyte solution on the FEP sheet; ion-exchange reaction process of platinum ion and proton in the polymer electrolyte using 50 mmol l⁻¹ [Pt(NH₃)₄]²⁺ solution at 60 °C for 6h; washing process with deionized water; and reduction process of 80 °C for 6 h under the hydrogen atmosphere. The catalyst layer with different polymer electrolyte concentrations of 30, 35, 40 and 50 mass% was prepared by changing the composition of carbon powder and polymer electrolyte. The thickness of layer was 12 μm. The catalyst layers with different polymer electrolyte concentrations of 35, 40 and 50 mass% gradated higher toward the side of membrane were also prepared by the process described above. The thickness is 7 μm and its platinum loading level is 0.025, 0.031 and 0.043 mg cm⁻² respectively.

The membrane electrode assembly (MEA) with 25 cm² was then prepared by the hot-pressing of the cathode catalyst layer and the anode one on the both sides of polymer electrolyte membrane (DuPont, Nafion 115) as reported in elsewhere.¹⁾ The single cell was composed of the following serial constitution parts; anode flow plate / gas diffusion backing / MEA / gas diffusion backing / cathode flow plate. The gas diffusion backing was used of carbon paper of 0.24 mm thick. The anode electrode is the same as the cathode one.

2.2 Platinum loading level

Platinum loading level of the catalyst layers was determined by ICP emission spectrometry using an extraction agent of aqua regia.

2.3 Electronic and ionic conductivity of catalyst layer

The obtained value by the measurement of the dried catalyst layer with four probes method was used as the electronic conductivity. The ionic conductivity is the estimated value calculated by the volume fraction ratio of the polymer electrolyte contained in the external volume of catalyst layer to the corresponding ionic conductivity value of the sole polymer electrolyte film composed of the layer.

2.4 Mass activity of catalyst

The mass activity of catalyst was calculated at the IR corrected voltage of 0.6 V under the condition of hydrogen and air of humidified temperature of 80 °C.

3 Results and discussion

The effect of polymer electrolyte concentration on platinum loading level of catalyst layer is shown in Fig. 1. The loading level is found to be increased with increasing the polymer concentration. The loading level is considered to be controlled by the amount of platinum complex ion adsorbed in the polymer electrolyte by ion-exchange reaction with the proton of counter ion.

The effect of the polymer electrolyte concentration on the electronic conductivity of catalyst layer is

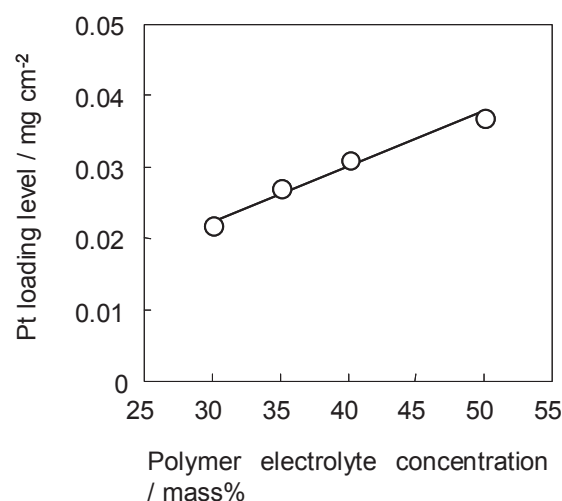


Fig. 1 Effect of polymer electrolyte concentration on Pt loading level of catalyst layer for ultra-low platinum loading electrode.

shown in Fig. 2. The electronic conductivity is found to show the maximum value at the concentration of 35 mass%, and then tends to decrease at higher concentration beyond the value. In the region of the concentration below the value, the distribution of carbon powders in the catalyst layer is not even and the decrease in conductivity is observed with increasing the polymer concentration because of the increase in the insulator materials itself of polymer. The effect of the polymer electrolyte concentration on the ionic conductivity of catalyst layer is also shown in Fig. 3. The ionic conductivity is found to be increased with the polymer electrolyte as expected.

The effect of the polymer electrolyte concentration on the mass activity of catalyst is shown in Fig. 4. The mass activity increases with the increasing polymer electrolyte concentration to reach the maximum at concentration of 40 mass% and tends to decrease at higher concentration. In the region of the concentration below the value, the distribution of carbon powders and polymer electrolyte becomes to be even with the polymer electrolyte resulting in the higher mass activity by the contribution of the more

evenness in the current distribution of catalyst layer. Beyond the value, the mass activity becomes to be lower with the polymer electrolyte. The decrease of

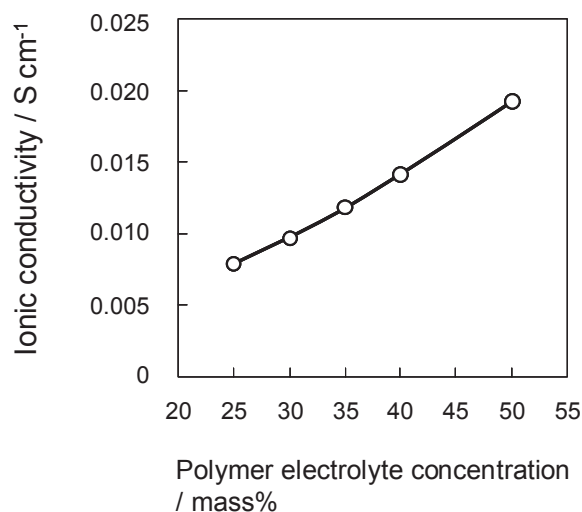


Fig. 3 Effect of polymer electrolyte concentration on ionic conductivity of catalyst layer for ultra-low platinum loading electrode.

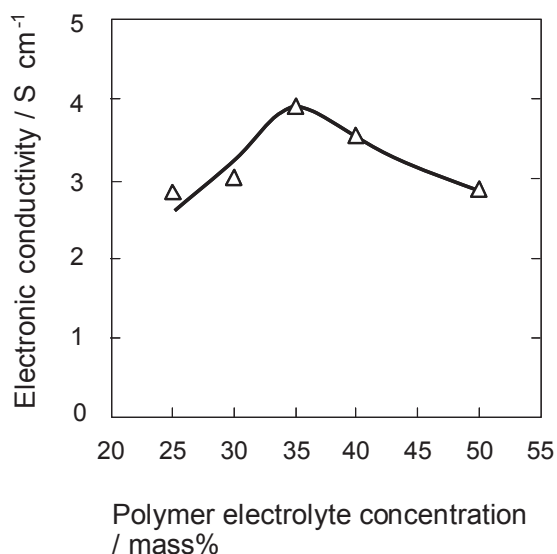


Fig. 2 Effect of polymer electrolyte concentration on electronic conductivity of catalyst layer for ultra-low platinum loading electrode.

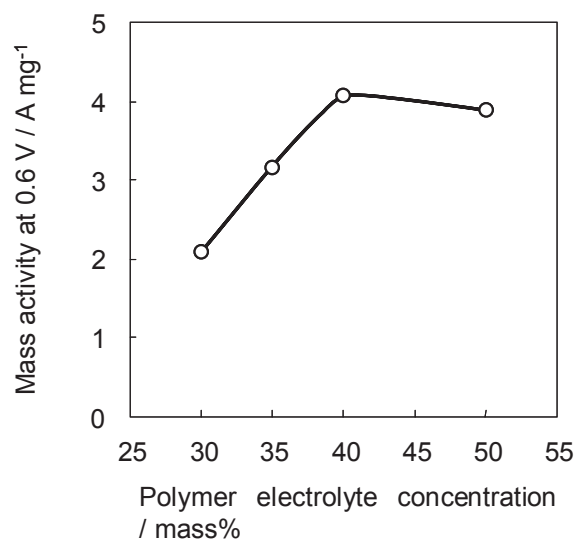


Fig. 4 Effect of polymer electrolyte concentration of catalyst layer on mass activity of ultra-low platinum loading electrode at 0.6 V and 80 °C under humidified gas of H₂ (U_f = 60%) / air (U_o = 40%). Thicknesses of catalyst layer : 12 μm.

mass activity seems to be caused by the decrease of active surface area of platinum particle with the crystal growth of platinum particle at higher concentration.³⁾

The platinum loading level was found to be increased with increment of polymer electrolyte concentration, and electronic conductivity and ionic conductivity were also found to be affected by the concentration and to be maximum value at 35 and 50 mass% respectively. Furthermore, mass activity of catalyst of platinum catalyst was also depend on the concentration and took maximum value at 40 mass%. In other words, the catalytic activity and electric conductivity of ULPLE as well as the size and amount of platinum catalyst were turned out to be strongly dependent on the concentration. Therefore, the optimization of distribution of polymer electrolyte concentration has been carried out based on the deduction that catalytic activity can be further improved.

The effect of the gradation of the concentration was investigated using ULPLE with the catalyst layer having higher polymer electrolyte concentration toward the side of membrane of which layer is composed of three different concentrations of 35 mass% with the maximum electronic conduction at the layer of side of gas diffusion backing, 40 mass% with maximum mass activity at intermediate one, and 50 mass% with maximum ionic conductivity at the one of side of membrane respectively. The ULPLE having single catalyst layer with the concentration of 40 mass%, thickness of 21 μm and platinum loading level of 0.095 mg cm^{-2} was also prepared for the comparison. The schematic diagram of the ULPLE with gradation of polymer electrolyte concentration is shown in Fig. 5. As shown in the figure, this electrode has the structure of which polymer electrolyte concentration and platinum loading level increase toward the side of membrane. The mass activity of platinum of this electrode is shown in Fig. 6 with the case of single layer with the concentration of 40 mass% indicating the maximum activity. Mass activity of this electrode is improved than that of single layer at the high load area below the 0.7 V. The mass activity of

platinum at 0.6 V, internal resistance of single cell measured by 1 kHz impedance analyze and platinum loading level are summarized in Table 1. From the table, mass activity of ULPLE with gradation of the concentration is found out to be enhanced 16% from the case of single layer. This result means the catalytic activity of ULPLE with the advantage of high utilization of platinum catalyst is able to further improve by the application of the catalyst layer with gradation of concentration. This result is assumed to be caused by the optimization of distribution of properties for platinum particles, such as its amount and its size in the catalyst layer with gradation of the concentration. Furthermore, this table shows the decrease of internal resistance of PEFC applied ULPLE with the gradation of concentration. This decrease seems to be caused by the improvement of ionic conductivity by 1.7% increase of average concentration of polymer electrolyte in catalyst layer and by the optimization of the distribution of the electrolyte as the ionic conductor.

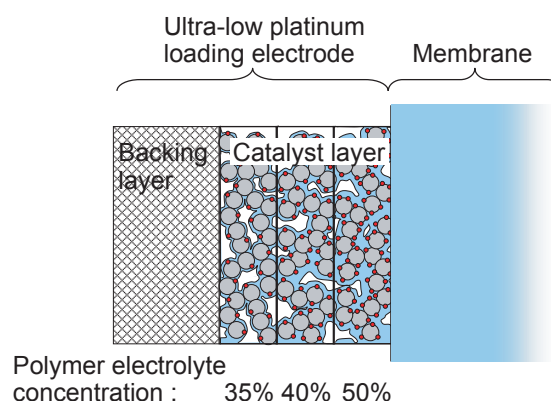


Fig. 5 Schematic diagram of ultra-low platinum loading electrode with catalyst layer having higher polymer electrolyte concentration toward the side of electrolyte membrane of which layer is composed of three different concentrations of 35, 40 and 50 mass%.

Table 1 Mass activity of platinum loaded in ultra-low platinum loading electrode with the catalyst layer having gradation of polymer electrolyte concentration at 0.6 V and 80 °C under humidified gas of H₂ (U_f = 60%) / air (U_o = 40%).

Catalyst layer for ULPLE	Mass activity at 0.6 V / A mg ⁻¹	Internal resistance of single cell at 0.6 V / mΩ cm ²	Total Pt loading level / mg cm ⁻²
Catalyst layer with gradation of concentration	4.09	285	0.099
Catalyst layer with 40 mass% of concentration	3.53	335	0.095

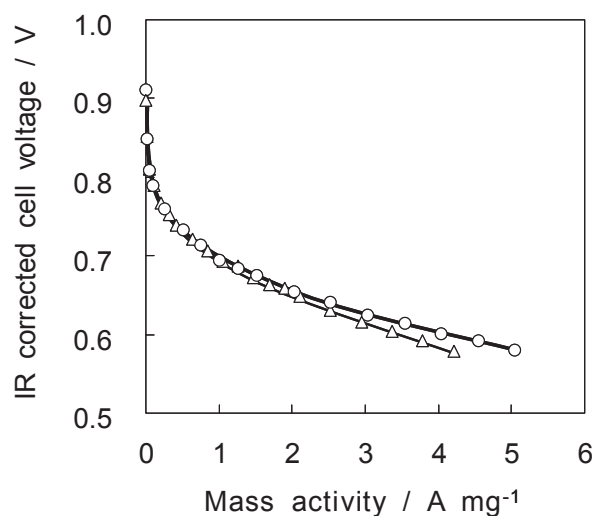


Fig. 6 Mass activity of ultra-low platinum loading electrode with the catalyst layer having gradation of polymer electrolyte concentration (○) and the layer with 40 mass% of the concentration (△) at 80 °C under humidified gas of H₂ (U_f = 60%) / air (U_o = 40%).

4 Conclusions

The results of this paper are summarized as

described below.

- 1) The mass activity of platinum loaded in catalyst layer of ULPLE depends on polymer electrolyte concentration and takes the maximum value at the concentration of 40 mass %.
- 2) The mass activity of platinum for ULPLE with higher polymer electrolyte concentration toward the side of membrane was to be increased by 16%.

Acknowledgement

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