Dependence of Catalytic Activity of Gas Diffusion Electrode on the Particle Size of Catalyst for PEFCs

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Dependence of catalytic activity of gas diffusion electrode on the particle size of platinum catalyst was measured using highly-active catalyst for polymer electrolyte fuel cells. The catalyst was prepared using trinitro-diammine Pt complex solution as a precursor. An average particle size of the platinum catalyst ranged in more than 1.2 nm. The catalytic activity of the platinum was evaluated using specific power density, i. e., power density per a unit weight of loaded platinum. At loading amount of Pt catalyst of 0.06 mg/cm², the specific power density reached 6.7 W/mg-Pt. Also, mass activity of platinum catalyst was calculated. At the cathode potential of 0.9 V, the mass activity increased as the particle size decreased down to 1.5 nm. The linear relationship was observed between the mass activity and platinum surface area up to 150 m²/g. The specific activity obtained from the relationship between the mass activity and the surface area of platinum was estimated at 0.95 A/m²-Pt at 90°C and under 5.84 atm. Consequently, the catalytic activity of platinum was kept for the ultra-fine particle such as platinum catalyst particle of 1.5 to 2 nm for PEFCs.

1 INTRODUCTION

Recently, there have been various reports on the development of polymer electrolyte fuel cells (PEFCs) and new materials for the PEFCs have been actively developed. Platinum has been regarded as catalytically the most active metal. Recent development of the solid polymer electrolyte fuel cells has led to intensive studies on platinum and its alloy metal supported on gas diffusion electrode. An increase of catalytic activity requires manufacturing an highly-dispersed Pt loaded carbon electrode^{1,2}. There are many problems in order to lower loading amount of catalyst. We have been studying a Pt loading technique on carbon powder for PEFCs. In the previous study, we obtained the cell performance more than 2 W/cm², where we used anionic platinum complex, H₂PtCl₆, as a precursor³. The platinum loading amount was still high (4.0 mg/cm²) and reducing catalyst amount has been strongly needed. There are two concepts to increase the catalytic activity;

one is a decrease of the particle size and increase of surface area of catalyst. Another is the loading method of highly-dispersed catalyst.

In this viewpoint, we have been studying on the preparation method of Pt/C electrode using the pre-treated carbon having the oxidized functional groups on its surface^{4,5}. According to these studies, the carbon support having functional groups is available for ion-exchange method between acidic group and platinum complex. Also, we have prepared the ultra-fine particle platinum catalyst using trinitro-diammine Pt complex solution as a precursor. Consequently, these methods permitted to control the particle size of the catalyst. On the other hand, it has been said that the catalyst with ultra-fine particle lost its activity because of losing active surface so called as "activity loss"⁶. Although many research groups are using the catalyst with such a small particle in recent works of catalyst, there has been little research for the confirmation of catalyst activity of fine particle for fuel cells and most of them have been carried out with phosphoric acid fuel cells^{6,7}. In the present paper, the dependence of the catalytic activity on the particle size of platinum catalyst was discussed. We focused on a relationship between the mass activity and the specific surface area of the platinum catalyst to clarify the activity loss effect.

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Fig.1 Schematic drawing of the measuring cell with reference electrode.

2 EXPERIMENTAL

One of procedures for increasing the activity of catalyst is reducing catalyst particle size in the range of a few nanometers. We used platinum complex which reacts with hydrogen for reducing rapidly. Using platinum complex containing chlorine, such as H_2PtCl_6 , coagulation of the reduced platinum particle occurred. In order to avoid the coagulation, platinum complex which does not contain chlorine, trinitro-diammine platinum complex, was used⁸⁾. As an electrode substance, we prepared handmade carbon black (CB)/poly-tetrafluoroethylene (PTFE) composite sheet. CBs used in this study are acetylene black, having specific surface area of 50 and 250 m^2/g and furnace black having specific surface area of 560 m^2/g . The CB content was 70 w/o. The thickness of the electrode was 0.1 mm, which were reduced by hot-pressing to 0.06 mm. The CB/PTFE sheet obtained was cut to a circular electrode of a diameter of 36.5 mm (10 cm^2). Trinitro-diammine platinum complex solution was used as a precursor of platinum catalyst. This solution was dipped and penetrated into CB/PTFE sheet, dried, and reduced in H_2 gas flow at 180°C. Then, the H_2 gas was diluted with N_2 gas less than 50 vol% in order to avoid intensive reaction. The Pt loading amount was 0.06–4.0 mg/cm^2 for each electrode.

For measurement of mass activity, the electrodes with lower platinum loading amount were also used⁶⁾. Loading amount was 0.01–0.4 mg/cm^2 . The preparation method was similar as the one for cell per-

mance measurement.

The image of the loaded Pt catalyst was observed by transmission electron microscope (TEM). Distribution of the particle size of the Pt catalyst was measured by image analysis⁴⁾. A cell assembly was prepared by hot-pressing with the electrode sheets and perfluoro-sulfonic acid membrane. Membrane used was mainly Nafion®112 (Du Pont). We tested a cell performance using these cell assemblies. Feed gases were hydrogen, and oxygen or air. Operating pressure ranged from 1.00 to 5.84 atm, and temperature from 80 to 100°C. In order to classify resistance and overpotential, IR drop was determined with the current interrupter method.

For determination of platinum mass activity, a specific surface area of the platinum was measured by chemisorption with carbon monoxide reported in Ref. 9. Also, we estimated the specific surface area from the distribution profile of the platinum particle size. Both results were in agreement with each other within 10%. The mass activity was evaluated from current values at 0.9 V of cathode potential. The cathode potential was measured using hydrogen standard electrode in a single cell, as shown in Fig.1. The measured value of the cathode potential was subtracted by potential drop assigned to the resistance of cell assembly.

3 RESULTS AND DISCUSSION

3.1 Cell performance and catalytic activity

Typical cell performance of PEFC is shown in Fig.2. Platinum loading amount was 0.1 mg/cm^2 . Feed gases were hydrogen and oxygen.

Fig.2 Cell performance of PEFC. Membrane: Nafion®112. Temperature: 90°C. Pt loading amount: 0.1 mg/cm^2 . Feed gas: H_2/O_2

The cell voltage was too low to be measured at atmospheric pressure, since feed gas is mostly water vapor. However, as the operating pressure increased, the maximum output density increased, and it reached 0.85 W/cm^2 at 2.0 A/cm^2 where the cell voltage was 0.43 V in the case at 5.84 atm , although this values are still smaller than that of the conventional method (2.1 W/cm^2) using the platinum catalyst of 4 mg/cm^2 . The cell voltage measured using these type of electrode did not fall down for 240 hours, at least, of intermittent operation; i.e., this cell was operated for 12 hours in every daytime for continuous 20 days.

In order to estimate the catalyst activity, the specific power density, $iV/2w_{\text{Pt}}$, is rather considered; where i , V , and w_{Pt} are current density, cell voltage, and platinum loading amount for each electrode, respectively. This value represents the output power per a unit weight of platinum loaded on the electrode which is one of indexes showing catalytic activity¹⁰⁾. The variations of cell voltage and specific power density with the plati-

num loading amount are shown in Fig.3.

Although there is certain difference between the cell voltage for using catalyst of 4.0 mg/cm^2 and 1.0 mg/cm^2 , the cell voltage did not decrease so much at the platinum amount range below 1.0 mg/cm^2 . In the case of 0.06 mg/cm^2 , the power density reached 6.7 W/mg-Pt , (0.15 g-Pt/kW). The specific power density decreases while the cell voltage increased as the platinum loading amount increased. It is shown that the effective amount of platinum increases with the decrease of the platinum loading amount.

Then, we calculated the surface area of the platinum from the distribution of the catalyst particle size with assumption that the platinum particles have spherical form. As shown in Fig.4, the typical example, loading amount of 0.06 mg/cm^2 , had very narrow distribution of the particle size. The distribution of the catalyst

Fig. 3 Cell performance of PEFC using electrode prepared from trinitro-diammine Pt complex. Feed gas: H_2 and O_2 , 5.84 atm . Temperature: 100°C .

Fig.4 Distribution of platinum particle size on electrode prepared from trinitro-diammine Pt complex. Loading amount: 0.06 mg/cm^2 .

Table 1 Variations of average particle size, specific surface area, and surface area of platinum per a unit area of electrode with platinum loading amount.

Pt loading amount [mg/cm^2]	Average particle size [nm]	Pt specific surface area [m^2/g]	Pt surface area in 1 cm^2 of the electrode [$\text{cm}^2/\text{cm}^2\text{-electrode}$]
0.06	1.8	110.9	66.5
0.10	2.1	64.0	64.0
0.25	2.3	53.1	133.5
0.40	2.3	48.7	194.8
1.00	3.4	40.1	401.0
4.00	4.8	35.0	1400

Fig. 5 Variation of mass activity of the Pt catalyst at the cathode potential of 0.9V with Pt particle size. Temperature: 90°C.

particle size depends on the platinum loading amounts. The value of average particle size increased as the loading amount increased. Table 1 shows the calculated platinum surface areas per a unit area of the electrode. The surface area did not increase so much, except the case of 4.0 mg/cm² of the loading amount, even if the loading amount increased. This is a reason for the coagulation effect which appeared with the increase of average particle size in the case of much loading amount of platinum. So we need to estimate the catalytic activity using some parameters related to the surface area of the platinum catalyst.

3.2 Mass activity of platinum catalyst

Platinum mass activity has been used as the index showing the activity loss^{6,7)}. According to studies concerning a relationship between the particle size of the catalyst and its mass activity, it has been suggested that the "activity loss" is observed in the case of using fine particle below ca. 3 - 5 nm^{6,11)}. Since we obtained the fine particle of platinum which dispersed uniformly for catalyst, the relationship between the catalytic activity and the average particle size of catalyst was examined. The variation of the mass activity of the Pt catalyst at 0.9V of the cathode potential with Pt particle size in Fig. 5. The mass activity increased as the particle size decreased down to 1.5 nm with several deviated points around the particle size of ca. 3 nm. If the effect of activity loss caused by the particle size of the catalyst as described in Ref. 6, the mass activity

Fig. 6 Variation of mass activity of the platinum catalyst at 0.9V of the cathode potential with Pt surface area. Pressure: 5.84 atm. Temperature: 90°C.

decreased in the range of the particle size below 3 nm without exception. However, the activity loss by the particle size effect was not observed in the range of the platinum particle size around 2 nm. In some cases of the particle size of 2 - 3 nm, the mass activity was lowered. The reason of the deviation could be caused by the other reasons. Therefore the factors of the activity loss should be discussed.

The mass activity of the platinum catalyst at the cathode potential of 0.9V is shown in Fig. 6. The linear relationship was observed between the mass activity and the platinum surface area. Most of the deviated points in Fig. 5 are relocated below this linear line. The catalytic activity was lost for some case such as the results on the plots deviating from a solid line in Fig. 6. These results were shown in the case using the carbon support with small specific surface area. The specific activity of platinum catalyst represented in the current density per real catalyst area is calculated. The obtained relationship between the specific activity and the average particle size is shown in Fig. 7. This figure reveals that the activity is constant at 0.9 A/m²-Pt in the range of particle size from 1.5 to 5 nm and that in some cases, the decrease of mass activity is observed in the range around 2 nm. In the case where the decrease of the mass activity was observed, the specific surface area of carbon support was less than the other cases. This results suggested that the reduction reaction region between nearest neighbor particles overlapped on the carbon support⁸⁾.

Fig. 7 Variation of the mass activity of the platinum catalyst at the cathode potential of 0.9V with the average particle size of platinum catalyst. Pressure: 5.84 atm. Temperature: 90 °C.

We also tried to obtain the relationship between the mass activity and the specific surface area of the platinum catalyst at lower cathode potential in which the current density increased, for example at 0.85 V. However, as far as we measured, this relationship is not observed so clear because of a lack of the reaction area due to complex micro-pore structure of carbon support, especially, in the case of using carbon support with a large specific surface area for which highly-dispersed platinum catalyst can be loaded. Since it is general that the maximum power density is obtained at the higher current densities, it is necessary for a practical use to increase of the mass activity in the wider range of the current density.

3.3 Pressure dependence of mass activity

In several previous reports ^{6,11}, the mass activity has been measured under atmospheric pressure because of easy operating condition. However, as shown in Fig. 5, the mass activity under various operating pressure showed different profiles from that under the atmospheric pressure. A pressure dependence of the mass activity is shown in Fig. 8. The linear relationships are observed between mass activity and platinum surface area at higher pressures. In the case of operation under the atmospheric pressure, the measured current density depended on the humidification condition. Excessive humidification causes the decrease of mass activity due to decrease of oxygen fraction in the cathode inlet

Fig. 8 Mass activity of the platinum catalyst at the cathode potential of 0.9V. Temperature: 90 °C. Broken line is a result in various sulfuric acid electrolyte solution from Refs. 7 and 12.

gas stream. At 90 °C where the partial pressure of vapor is 0.692 atm, care for humidification was taken the operation at atmospheric pressure. Nevertheless, the current density was unstable, especially using the electrode where much loading amount. Consequently, the value of mass activity was a little unstable and depended on the humidification condition. The mass activity did not increase proportionally above the specific surface area of platinum of 60 m²/g, as shown in Fig. 8. Therefore, it is necessary to confirm the pressure dependence of the mass activity to explain the activity loss for the operation of the PEFCs.

Here we compared these results with that for aqueous sulfuric acid solution shown by broken line in Fig. 8 ¹² as a reference, because the liquid solution can penetrate into the micro pores of carbon black and large reaction area is obtained. The value of the mass activity are much lower than those in the liquid solutions. It is suggested that the reaction area consisting of three phase; gas, electrolyte, and platinum active surface was not completely constructed. In this work, we could have not finished optimizing the loading method yet. Then further studies are going to be continued for the optimization of loading method.

Fig.9 Cell voltage and specific power density of PEFC. Membrane: Nafion®112. Temperature: 70°C. Pt loading amount: 0.1mg/cm². Feed gas: H₂/Air.

3.4 The mass activity for the system using air as cathode inlet gas

In the case of using air as oxidant, the partial pressure of oxygen is much less than that of oxygen gas under the same operating pressure. Hence, the cell voltage is not so high as the results for the operation using H₂ and O₂, as shown in Fig. 9. For example, under operating pressure of 2.94 atm, the specific power density reaches to ca. 2.2 W/mg-Pt. However, at higher current densities, where the maximum power density obtained, the cathode potential is considerably influenced by the mass transport of cathode gas. Thus, this result does not reflect the catalytic activity directly.

The relationship between the mass activity and the specific surface area of platinum in the H₂/air PEFCs' system is shown in Fig. 10. Although the gradient of line for H₂/air system is less than that for H₂/O₂, the linear relationship was obtained for both systems. The mass activity was kept up to specific surface area of platinum of 150 m²/g and activity loss was not observed. In the case of H₂/air system, the catalytic activity is also kept, though the fraction of oxidant gas is low because of the decrease in the oxygen gas around catalyst due to the consumption through reaction.

3.5 Relationship between specific activity and platinum particle distance

The activity loss for PEFCs' catalyst was observed in the case of using carbon support with small surface area and/or operating under lower (atmospheric) pressure. The reaction area for each platinum particle depends on these factors. Using the carbon support with

Fig.10 Mass activity of the platinum catalyst at the cathode potential of 0.9V. Temperature: 70°C, Pressure: 2.94 atm.

small surface area, the distance between nearest neighbor particles was short. Watanabe et al. introduced the parameter of the distance for phosphoric acid solution and described the relationship between the particle distance of catalyst and mass activity quantitatively⁷⁾. Based on his concept, the decrease of the catalytic activity was observed in the case of the particle distance of less than ca. 15 nm as shown in Fig.11. The derivative points in Fig. 7 were relocated onto the broken line

Fig.11 Relationship between specific activity and platinum particle distance based on Watanabe's equation⁷⁾. Temperature: 90°C, Pressure 5.84 atm, Feed gas: H₂ and O₂.

tive points in Fig. 7 were relocated onto the broken line in this figure. It is suggested that the catalytic activity was lowered by the overlapping of the reaction area between the nearest neighbor particles.

As described above, the decrease of mass activity was explained by the humidification condition around the platinum particles from the pressure dependence and the influence of neighboring particles from the specific activity of the platinum in this work. Although conventional explanation of activity loss is based on the crystallographic assumption, such as a distortion or transformation of the crystal structure, these factors was not observed. It is necessary to clarify the reason of the 'activity loss' for the PEFC's operation because of importance of the evaluation of the materials for the cells.

4 CONCLUSION

Dependence of catalytic activity of gas diffusion electrode on the particle size of platinum was measured using highly-active platinum catalyst for polymer electrolyte fuel cells. The catalyst particle size ranged from 1.5 to 5 nm. The power density reached up to 6.7W/mg-Pt obtained in the case that 0.06 mg/cm² of Pt was loaded on each electrode. The mass activity measured at 0.9 V of cathode potential increases as the Pt particle size decreased down to 1.5 nm. The mass activity linearly increased as the specific surface area of platinum increased. The specific activity of the platinum catalyst was estimated at 0.95 A/m²-Pt at 90°C and under 5.84 atm. The activity loss for PEFCs' catalyst was observed in the case of using carbon support with small surface area and/or operating in a lower (atmospheric) pressure. These factors cause overlapping of the reaction area between neighboring particles and covering the reaction area with excess water.

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