Preparation of Gas Diffusion Electrode
with
Highly-active Catalyst for PEFCs

Minoru MIZUHATA, Kazuaki YASUDA, Keisuke OGURO,
and Hiroyasu TAKENAKA

Osaka National Research Institute, AIST, MITI
1-8-31 Midorigaoka, Ikeda, Osaka 563, Japan

ABSTRACT

The highly-active catalyst for polymer electrolyte fuel cells was prepared by two methods. Trinitro-diammine Pt complex solution was used and directly impregnated onto CB/PTFE electrode sheet. Pt catalyst was loaded by H₂ reduction. Average particle size was ca. 2 nm. The maximum power density was 6.7W/mg-Pt at 0.06 mg/cm² of Pt loading amount. In the other method, an ion-exchange method was applied on the carbon support. Carbon surface were oxidized by ozone gas. Consequently functional groups such as carboxylic group were generated. The acidic species on the functional groups were exchanged by platinum cationic complex such as [Pt(NH₃)₆Cl₂]⁺. The particle size was ave. 2 nm. The cell voltage was 0.5V at 0.4A at 1 atm. These methods were available to prepare the fine active catalyst and avoid a coagulation of platinum particles, comparing with conventional method which is impregnating Pt complex into carbon support, such as H₂PtCl₆ without any pretreatment.

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 lead to intensive studies on platinum supported on gas diffusion electrode. An increase of catalytic activity requires manufacturing an highly-
dispersed Pt loaded carbon electrode(1, 2). The target of lowering Pt amount is assumed at 0.1-0.2g/kW-Pt, i.e., 5-10 W/mg-Pt, because these amounts are comparable with current consumptions in internal combustion engines. However, there are many problems in order to lower loading amount of catalyst. We have been studying a Pt loading technique on carbon powder for PEFC. In previous study, we obtained the cell performance more than 2W/cm²(3). However, we used anionic platinum complex, H₂PtCl₆, as a precursor. Pt loading amount was still high and reducing catalyst amount has been strongly needed.

In this viewpoint, we have been studying on the preparation method of Pt/C electrode using the pretreated carbon having functional groups on its surface (4). According to the study, the carbon support having functional group is available for ion-exchange method between acidic group and platinum complex.

In this study, we present some results concerning new loading methods of Pt catalyst. One of them is the method using platinum complex containing the legand which does not include chlorine species. Another method is using the pretreated carbon with highly active functional group on its surface by means of oxidation by ozone gas flow. The evaluation tests for these electrodes were carried out.

2. Experimental

One of methods for increasing the activity of catalyst is reducing catalyst particle size at the range at a few nanometers. We prepared two types of gas diffusion electrode supporting an highly active catalyst.

Type-I electrode– Using Trinitro-diammine Pt complexes:

We used platinum complex reacting with hydrogen for reducing rapidly. Using platinum complex containing chlorine species, such as H₂PtCl₆, coagulation of the reduced platinum particle occurred. In order to avoid the coagulation, platinum complex which does not include chlorine species, trinitro-diammine platinum complex, was used (5). As an electrode substance, we prepared handmade carbon black(CB)/polytetrafluoro-ethylene (PTFE) composite sheet. CB content was 70 w/o. The thickness was 0.1 mm, which were reduced by hot-pressing to 0.06 mm. The obtained CB/PTFE sheet was cut to the electrode size which was 36.5 mm² (10 cm²). Trinitro-diammine platinum complex solution was used as precursor of platinum catalyst. The Pt solution was dipped and penetrated into CB/PTFE sheet, dried, and reduced in H₂ gas flow. H₂ gas was diluted with N₂ gas less than 50 v/o in order to avoid intensive reaction. Pt loading amount was 0.06-4.0 mg/cm² for each
electrode. For measurement of mass activity, the electrodes with lower platinum loading amount were also used (6). Loading amount is 0.01-0.4 mg/cm². Preparation method is similar as the one for cell performance measurement.

**Type-II electrode: Using pretreated carbon:**
In this case, pretreated carbon sheet by ozone gas was used, because oxidation process can be carried out in room temperature and without strong oxidant solutions. The surface of CB/PTFE sheet was oxidized by ozone gas flow and acidic functional group was formed, such as carboxyl group. The acidic species on the functional group was ion-exchanged with Pt complex ion such as [Pt (NH₃)₄]²⁺. Pt complex was reduced by H₂ gas flow and loaded on carbon surface. Pt loading amount was ca. 0.09 mg/cm².

**Characterization and measurement of cell performance:**
The loaded Pt catalyst was observed by TEM. Distribution of the particle size of the Pt catalyst was calculated by image analysis (4). For both electrodes, a cell assembly was prepared by hot-pressing with perfluorosulfonic acid membrane. Membrane used was such as Nafion® (Du Pont) 112, mainly. We measured a cell performance using these cell assemblies. Feed gases were H₂ and O₂. Operating pressure ranged from 1.00 to 5.84 atm, temperature ranged from 80 to 100°C. In order to classify resistance and overpotential, IR drop was measured with current interrupter.

For calculating platinum mass activity, the platinum surface area is calculated from the distribution of the platinum particle size and measured by BET method using carbon monoxide adsorption. The mass activity was calculated from current values at 0.9V of cathode potential. The cathode potential which was measured by a single cell with a reference electrode using hydrogen standard electrode. Each value of the cathode potential was determined after subtracting overpotentials assigned to the resistance of membrane, electrode, and so on.

3. Results and discussion

**Type-I electrode**
*cell performance and catalytic activity* — Typical cell performance of PEFC using Type-I gas diffusion electrode is shown in Fig.1. Platinum loading amount is 0.1 mg/cm². Operating feed gases were hydrogen and oxygen.

In this case, operating under the pressure at 1 atm, as feed gas is mostly water vapor, cell
Fig. 1  Cell performance of PEFC using Type-I electrode. Membrane: Nafion®112. Temperature: 100°C. Pt loading amount: 0.1 mg/cm². Feed gas: H₂/O₂.

Fig. 2. Cell performance of PEFC using electrode prepared from trinitro-diammine Pt complex. Feed gas: H₂ and O₂, 5.84 atm. Temperature: 100°C.
performance was not so high. In the case of 5.84 atm, the power density was reaching to 0.85 W/cm². Although this values are still smaller than that of conventional method using platinum catalyst of 4mg/cm², it is necessary to consider the platinum amount. In order to show activity of catalyst, the specific power density is calculated as ; \( \frac{iV}{2w_{Pt}} \); 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. This shows the one of performances of catalyst (7). The specific power density increases as the platinum loading amount decreases as shown in Fig.2.

Power density decreased as the platinum loading amount reduced. In this case, however, the performance did not decrease so much at the platinum amount range below 1.0 mg/cm². Therefore, In the case of 0.06 mg/cm², the power density reached up to 6.7 W/mg-Pt, (0.15g-Pt/kW). In the case of > 0.1 mg/cm², the cell performance increases as the Pt loading amount increases. However, the specific power density decreases. It is shown that the effective amount increases.

Then, we calculated the surface area of platinum surface from the distribution of catalyst particle size with assumption that the platinum particles have spherical form. A typical

![Fig.3. Distribution of platinum particle size on Type-I electrode. Loading amount: 0.06 mg/cm².](image)

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Table I. Variations of average particle size, specific surface area, and surface area in 1 cm² of platinum electrode with platinum loading amount using Type-I electrodes.

| Pt loading amount [mg/cm²] | Average particle size [nm] | Pt specific surface area [m²/g] | Pt surface area in 1 cm² of the electrode [cm²/cm²-electrode] |
|----------------------------|----------------------------|---------------------------------|----------------------------------------------------------|
| 0.06                       | 1.8                        | 64.9                            | 0.389                                                    |
| 0.10                       | 2.1                        | 53.4                            | 0.534                                                    |
| 0.40                       | 2.3                        | 48.7                            | 1.948                                                    |
| 1.00                       | 3.4                        | 40.1                            | 4.01                                                     |
| 4.00                       | 4.8                        | 35.0                            | 14.0                                                     |

example of which loading amount is 0.06mg/cm² is shown in Fig.3. This has very narrow distribution of the particle size.

According to studies concerning a relationship between particle size of catalyst and the catalytic activity, it has been suggested that the loss activity exists in the case of using fine particle below ca. 3 nm (8). However, in this case, the activity of the catalyst is obviously increased. The distribution of catalyst depends on the platinum loading amounts. The value of average particle size increases as the loading amount. Table I shows the calculated surface areas. Surface area does not increase so much, except the case of 4.0 mg/cm² of the loading amount, even the loading amount increases. This is because the coagulation effect appeared with increase of an average particle size and particle size increased, when much platinum was loaded. Therefore the activity loss by the particle size effect was not observed in this range of the platinum particle size.

**Mass activity of platinum catalyst** —— Platinum mass activity has been used as the index showing the activity loss (6, 8). Results of measurement of the surface area by BET method is not so different as that from TEM measurement in Table I (within 5%). In Fig.4, mass activity of the platinum catalyst at 0.9V of the cathode potential. The pressure dependence is also shown. The linear relationships are observed between mass activity and platinum surface area at each pressure. The mass activity did not decrease at the lower range of platinum loading amount, although, in the lower pressure, mass activity decreases at more
Platinum surface area [m²/g]

Fig. 4. Mass activity of the platinum catalyst at 0.9V of the cathode potential. Broken line is a result in various sulfuric acid electrolytes solution from Ref.(6, 9).

than 80 m²/g of platinum surface area because of decrease of fraction of oxygen in cathode inlet gases by humidification.

However, in this case, comparing with the result in various sulfuric acid electrolytes solution, these values are much lower than the results for the liquid solutions (9). It is suggested that the reaction area consisting of three phase; gas, electrolyte, and platinum active surface was not completely constructed. This time, we have not finished optimizing the loading method yet. Then further studies are going to be continued for this optimization of loading method.

Type-II electrode

According to our previous work (4), the deposition of platinum on various carbon blacks was carried out by forming active functional groups on the surface of carbon support, and exchanging these active groups with ammonium platinum chloride. An exchange between cationic platinum complexes and surface functional groups takes place. Platinum particles
Fig. 5. Distribution of platinum particle size on Type-II electrode. Loading amount: 0.09 mg/cm².

Fig. 6. Cell performance of PEFC using electrode prepared by ion-exchange method. Feed gas: H₂ and O₂, 1.00 atm. Temperature: 80°C. a; ion-exchange method (Pt: 0.09 mg/cm²), b; H₂PtCl₆ impregnation (Pt: 0.1 mg/cm²).

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are extremely small (0.75-1.7 nm) and highly dispersed on the surface of carbon black. The catalytic activity mainly depends on the particle size rather than the loading amount of catalyst. In this case, also, highly-dispersed Pt catalyst was obtained. An average Pt particle size was ca. 2 nm and a S.D. of the distribution is 0.487 nm as shown in Fig.5. These results show that the Pt catalyst prepared from ion-exchange method is highly-dispersed and has narrow distribution. The cell performance of the cell assembly is shown in Fig.6. The performance of cell prepared by ion-exchange method is superior to that prepared by conventional method.

4. Conclusion

The highly-active catalyst for polymer electrolyte fuel cells were prepared. One method was that newly Pt complex was used and directly impregnated onto a CB/PTFE electrode sheet. Catalyst was reduced by H₂ and highly-dispersed Pt catalyst was loaded on untreated carbon surface. The power density reached up to 6.7 W/mg-Pt, which was obtained in the case that 0.06 mg/cm² of Pt was loaded on each electrode. For another case, an ion-exchange method was applied to preparing the electrode. The particle size was av. 2 nm, and had a narrow distribution. The cell voltage was 0.5 V at 0.4 A/cm² at 1 atm. Although the cell performance was improved from conventional method, it is necessary to increase the activity more than the present state. However, a possibility of lowering Pt loading amount was shown for various application of PEFCs.

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