Electrochemical Evaluation of the Degradation Behavior of Pt/C Cathode Catalyst using Porous Microelectrode

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In order to better understand the cathode catalyst degradation of a polymer electrolyte membrane fuel cell, electrochemical measurements of oxygen reduction reaction (ORR) at a 47 wt\% platinum-loaded carbon (Pt/C) have been conducted using porous microelectrode techniques before and after the polarization for 15 hours. This technique enables an evaluation of the ORR at the Pt/C powder electrocatalyst without any use of binder materials such as Nafion. In the ORR polarization curve at the Pt/C-containing microelectrode, a limiting current is clearly observed in the oxygen saturated 0.5 mol dm\textsuperscript{-3} sulfuric acid. The Tafel plot analysis revealed only a 60 mV/decade slope. After a 15-hour polarization of the Pt/C at +0.7, +0.8, and +0.9 V vs. RHE in an oxygen atmosphere, the following electrochemical measurement demonstrated that (i) the ORR \textit{i}-\textit{E} curve completely shifted in the cathodic direction by about 10 mV, (ii) the electrochemical surface area measured in a nitrogen atmosphere by cyclic voltammetry decreased to 90-94 \%, and (iii) the limiting current density decreased to 85-81 \% at 0.7 V vs. RHE.

\textbf{Key Words} : Cathode Catalyst Degradation, Porous Microelectrode, Pt/C, Oxygen Reduction Reaction

1 Introduction

Polymer electrolyte membrane fuel cells (PEFCs) have attracted much attention in recent years, because of their high power generation efficiency with minimal environmental damages.\textsuperscript{1,2} For the PEFC development, elucidation of its degradation mechanism for each component is required. Especially, clarifying the cathode catalyst degradation mechanism is the central issue for the PEFC development. To evaluate the cathode catalyst degradation, a simple and concise cathode catalyst measurement technique, which can be done before and after the cathodic polarization, is needed. By modifying a porous microelectrode technique,\textsuperscript{3,4} we developed a technique for the powder electrode reaction of hydrogen oxidation and methanol oxidation.\textsuperscript{5,6} Thus far, the cathode reaction at the platinum-loaded carbon (Pt/C) catalyst has been electrochemically measured by employing the Pt/C-Nafion\textsuperscript{7} system.\textsuperscript{7,8}

We focused our attention on the degradation of Pt/C itself by using the porous microelectrode technique. The purpose of this report is to describe the evaluation of the ORR at a practical Pt/C catalyst without using the binder polymer. First, the ORR measurement is conducted at the Pt/C-containing porous microelectrode by measuring the current-potential curve. Next, after a 15-hour polarization in an oxygen atmosphere, the electrocatalytic transformation of the Pt/C is measured.

2 Experimental

Figure 1 shows a schematic illustration of the porous microelectrode, which has a microcavity at the tip of the microelectrode for the Pt/C filling. The porous microelectrode is prepared according to the procedure sited in ref. 6. Briefly, a 50 \textmu m diameter gold wire was inserted into a glass capillary and heat-sealed by shrinking the glass inside and then grinding the tip using emery paper. Subsequently, the tip of the gold electrode was etched in a 1 mol dm\textsuperscript{-3} HCl solution, resulting in a cavity with a depth of 10-20 \mu m. This cavity was filled with the powder catalyst, and the electrocatalyst was evaluated by a conventional electrochemical measurement technique. The Pt/C electrocatalyst was purchased from Tanaka Kikinzoku Kogyo (Pt 46.8 wt\%, abbreviated 47 \% Pt/C).

The electrochemical measurements were carried out in a 0.5 mol dm\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4} solution. Pt foil and Ag/Ag\textsubscript{2}O were used as the counter and reference electrodes, respectively. All potentials reported in this study are with respect to the relative hydrogen electrode (RHE). Measurements of the ORR were conducted using a potentiostat (HZ-5000, Hokuto Denko) at room tempera-
ture. Prior to the ORR measurement, the Pt/C catalyst at the tip of electrode was electrochemically activated in a deaerated 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) solution by potential cycling between +0.05 to +1.38 V versus RHE until the cyclic voltammogram (CV) did not change. After the activation, the electrolytic solution was then saturated with oxygen gas by bubbling for 1 hour. During the O\(_2\) bubbling, the measurement system was left on open circuit. Measurement of the ORR was recorded from at around rest potential in the cathodic direction at the potential sweep rate of 0.5 mV/s.

For the measurement of the Pt/C catalyst degradation, the porous microelectrode containing the Pt/C catalyst was polarized at +0.9, +0.8, and +0.7 V vs. RHE in an oxygen atmosphere for 15 hours. The platinum surface area of the Pt/C catalyst was measured from the adsorption wave of hydrogen in the CV in a nitrogen atmosphere before and after the 15-hour ORR. All the current densities reported in the present study were expressed with respect to the electrochemical surface area, S\(_{Pt}\), determined by CV.\(^{12}\)

### 3 Results and Discussion

Figure 2 shows the current-potential (i-E) curves of the ORR at the 47 % Pt/C-containing porous microelectrode in 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\). From Fig. 2, a Tafel slope of 60 mV/decade and a limiting current were determined. Generally, two slopes of 60 and 120 mV/decade are reported for a conventional Pt electrode.\(^{13,14}\) The result shown in Fig. 2 is considered as a result of three-dimensional packing of Pt/C in the cavity which probably induces a lack of oxygen to cause the diffusion-limiting current that suppresses the 120 mV/decade slope.

Next, the degradation of the 47 % Pt/C catalyst for the ORR before and after the 15-hour polarization at +0.9 V versus RHE were measured in the same way. The results of before and after the polarization are shown in Fig. 3. After the polarization, the ORR i-E curve shifted in the cathodic direction by about 10 mV. The ratio of Pt surface area, S\(_{Pt}\), after the polarization/ before the polarization, is listed in Table 1, which means that the Pt surface area decreases by the polarization. This is probably caused by aggregation, sintering or dissolution of the Pt particle.\(^{15}\) When we compared the limiting current density at 0.7 V vs. RHE using the changed surface area given in Table 1, the current density decreased to 81 % from 9.82 \(\mu\)A cm\(^{-2}\) to 7.94 \(\mu\)A cm\(^{-2}\) due to the 15-hour polarization (Table 1).

In the similar way, the i-E curves of the ORR observed before and after the polarization at +0.8 V vs. RHE and +0.7 V vs. RHE are shown in Figs. 4 and 5, respectively.

![Fig. 2 i-E curve of 47 % Pt/C-containing microelectrode in O\(_2\) saturated 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) solution (left), and its semi-log plot (right).](image1)

![Fig. 3 i-E curve of 47 % Pt/C-containing microelectrode in O\(_2\) saturated 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) solution before and after 15-hour polarization at +0.9 V vs. RHE (left), and its semi-log plot (right).](image2)

![Fig. 4 i-E curve of 47 % Pt/C-containing microelectrode in O\(_2\) saturated 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) solution before and after 15-hour polarization at +0.8 V vs. RHE (left), and its semi-log plot (right).](image3)

**Table 1** Measured Pt surface area, limited current density and Tafel slope measured before and after 15-hour polarization.

<table>
<thead>
<tr>
<th>Pt surface area (cm(^2))</th>
<th>limiting current density at +0.7 V vs RHE ((\mu)A cm(^{-2}))</th>
<th>Tafel slope (mV/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before polarization</td>
<td>after polarization</td>
</tr>
<tr>
<td>+0.9 V</td>
<td>0.0239</td>
<td>0.0219</td>
</tr>
<tr>
<td>+0.8 V</td>
<td>0.0205</td>
<td>0.0193</td>
</tr>
<tr>
<td>+0.7 V</td>
<td>0.0168</td>
<td>0.0152</td>
</tr>
</tbody>
</table>
Since the catalyst was packed in the cavity of the porous microelectrode, a slight difference in the three-dimensional packing of the catalyst might affect a reproducibility of the ORR curves before polarization. In either case, the degradation tendency was almost the same as the result of the +0.9 V vs. RHE polarization (Fig. 3). Also, (i) the cathodic shift of the i-E curve, (ii) the decrease in the electrochemical surface area, and (iii) the decrease in the limiting current density were observed after the +0.8 V and +0.7 V polarizations. Consequently, the porous microelectrode study of the ORR at the Pt/C catalyst revealed that the degradation of the Pt/C catalyst was phenomenologically caused by the 15-hour polarization. The difference in degradation for three potentials is found to be small. For detailed understandings of the degradation mechanism, a wide range polarization will be needed in the future.

4 Conclusion

We have successfully evaluated the Pt/C electrocatalyst degradation by ORR using a porous microelectrode. In the ORR polarization curve at the Pt/C-containing microelectrode, a limiting current was clearly observed in oxygen saturated 0.5 mol dm$^{-3}$ sulfuric acid. The Tafel plot analysis exhibited only a 60 mV/decade slope. After a 15-hour polarization of the Pt/C at +0.7, +0.8, and +0.9 V vs. RHE in an oxygen atmosphere, the subsequent electrochemical measurements demonstrated that (i) the ORR i-E curve totally shifted in the cathodic direction by about 10 mV, (ii) electrochemical surface area of the electrode in a nitrogen atmosphere measured by cyclic voltammetry decreased to 90-94 %, and (iv) the limiting current density decreased to 85-81 %. In the future, we plan to measure the cathode catalyst in combination with ionomer, which represents the cathode of membrane electrode assembly by using the porous microelectrode.

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References