

Surface observation of Pt / HOPG electrode in acid solution contained hydrogen peroxide

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Polymer electrolyte fuel cells (PEFCs) are expected for use as a power source in the next generation because of their high performance. The durability is one of the most important issues in commercialization of PEFCs. Various mechanisms have been considered for the gradual degradation of the cell stacks through the long-term operation. Hydrogen peroxide produced by the operation of PEFCs likely affects on electrode / electrolyte interfaces in PEFCs and impairs the performance. However, the detail degradation mechanism has not been well-understood.

In this study, a model electrode was prepared by electrodeposition of Pt on highly oriented pyrolytic graphite (HOPG), and then surface observation of the Pt / HOPG electrode was made in the presence of hydrogen peroxide. Then, the effect of the hydrogen peroxide on the activity of Pt / C was discussed.

For the preparation of Pt / HOPG electrode, 0.01 mol dm⁻³ H₂PtCl₆ contained 0.02 mol dm⁻³ HClO₄ aqueous solution was used as an electrolyte. A large surface area of Pt wire was employed for a counter electrode. Ar gas was bubbling through the electrolyte during the electrodeposition process. The current density was kept at 1.8 mA cm⁻² and the deposition time was 5 s.

Electrochemical measurements were carried out in O₂-saturated 1.0 mol dm⁻³ H₂SO₄ containing various molar ratio of H₂O₂. Ag / AgCl electrode was used as a reference electrode, and Pt wire as a counter electrode. The surface observation was carried out by scanning electron microscope (SEM).

Figure 1 a) shows the SEM image of prepared Pt / HOPG electrode. The sizes of Pt particles were ca. 100 nm and Pt particles were distributed uniformly.

Figure 1 b) and c) show the SEM images of model electrode surface kept under the open circuit condition for 15 h in 1.0 mol dm⁻³ H₂SO₄ without H₂O₂ and with 0.1 mol dm⁻³ H₂O₂, respectively. No surface changes were observed irrespective with the presence of H₂O₂. When concentration of H₂O₂ increased up to 1.0 mol dm⁻³, Pt particles were aggregated on HOPG without increasing the particle size and the scar on HOPG surface caused by oxidation was observed as given in Fig. 1 d). Based on these results, the presence of hydrogen peroxide is clarified to influence on the aggregation of Pt and enhance the rate of etching on HOPG surface.

The SEM image of Pt / HOPG electrode applied at 0 V vs. RHE for 15 h was shown in Fig. 1 e). The aggregation of Pt particles and the scar on HOPG was also observed.

By applying the voltage, Pt particles moved on HOPG surface and aggregated with the Pt particle size remained unchanged even under the low H₂O₂ concentration.

Figure 2 shows the cyclic voltamograms of Pt / HOPG electrode in 1.0 M H₂SO₄. Hydrogen absorption current of the electrode immersed in 1.0 mol dm⁻³ contained 0.1 mol dm⁻³ H₂O₂ for 15 h decreased due to the aggregation of Pt particles. Therefore, it is suggested that the presence of hydrogen peroxide in PEFCs may impair the activity of Pt / C electrode.

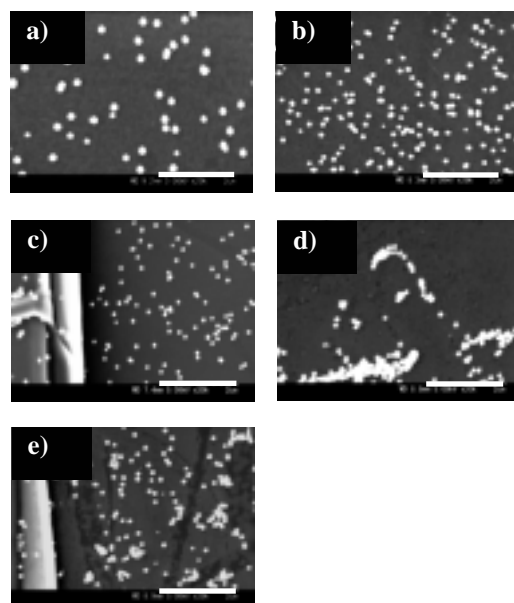


Figure 1 SEM images of Pt / HOPG electrode, a) as prepared, b) after kept at open-circuit potential in O₂-sat-1.0 M H₂SO₄, and c) after kept at open-circuit potential in the solution contained 0.1 M H₂O₂, d) after kept at open-circuit potential in the solution contained 1.0 M H₂O₂ and e) after applied at 0 V vs. RHE in O₂-sat-1.0 M H₂SO₄ containing 0.1 M H₂O₂ at room temperature for 15 h. The bar indicated 2 μm.

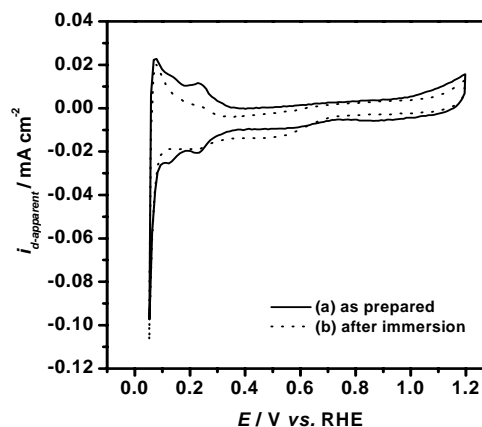


Figure 2 Cyclic voltamograms of Pt/HOPG electrode at the sweep rate of 0.1 V/s for: (a) as prepared and (b) after immersion in O₂-sat-1.0 M H₂SO₄ containing 1.0 M H₂O₂ at room temperature for 15 h.

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