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Relationship between Degradation of Pt/C and Property of Electrolyte for PEFCs

Shigenori Mitsushima, Kazuki Shinkoda, Fumiya Hiraoka, Koichi Matsuzawa, Ken-ichiro Ota, Yokohama National University(YNU), Japan

1 Introduction

Polymer electrolyte fuel cells (PEFCs) have started commercialization for small size co-generation systems and fuel cell vehicles because of the high power density, capability of start up from ambient temperature and high energy conversion efficiency. In the present technology, platinum electrocatalyst is essential. However toward real commercialization, precious metal loading should be reduced by one tenth or more because of the limit of natural resources. To reduce precious metal loading with high catalytic activity, higher dispersion technology, alloying and core shell technology have been developed [1-3]. These materials were also required high stability during the system lifetime.

Generally, nano-particle is unstable compared to larger particles, and rated load enhances the degradation of electrocatalyst. There are many reports for the degradation of electrocatalyst for PEFCs. For example, the decrease of electrochemical surface area under potential cycling with small size single cells or three – electrode conventional electrochemical cells, platinum consumption under potential cycling, and dissolution of platinum in acidic medium have been reported. The Ostwald ripening and the sintering model have been proposed as degradation mechanism. However, the degradation mechanism has not been clarified, yet [1, 2, 4-6].

In this study, the electrochemical surface area decrease with various pH electrolytes under various potential patterns has been investigated as a fundamental study to clarify the degradation mechanism and improvement of the durability for PEFCs.

2 Experimental

Pt/C (Tanaka K. K., TEC10E50E) water dispersion was painted on a glassy carbon disk (Tokai carbon, GC-20SS) which was polished to mirror surface. Reference and counter electrodes were reversible hydrogen electrode (RHE) and platinum wire, respectively. Electrolyte was in the concentration range from 0.1 to 1 M (=mol dm⁻³) of sulfuric acid (Junsei, Analysis grade) or perchloric acid (Merck, Ultrapur). The potential cycle was applied between 0 to 1.2 V vs. RHE. As shown in Fig. 1, 4 types of potential cycling patterns which were triangle waves with 50 mV s⁻¹ of sweep rate, rectangular waves with 12 s interval, and the combinations of potential step and sweep were applied for 5000-cycle in nitrogen or oxygen atmosphere. The electrochemical surface area was frequently determined by hydrogen desorption wave of the cyclic voltammogram between 0.05 to 1.2 V vs. RHE during potential cycling under nitrogen atmosphere. After potential cycling, the Pt/C was observed by TEM. The particle diameter was determined from a projection area of a particle to the diameter of a circle. The number of the particle was more than 300.

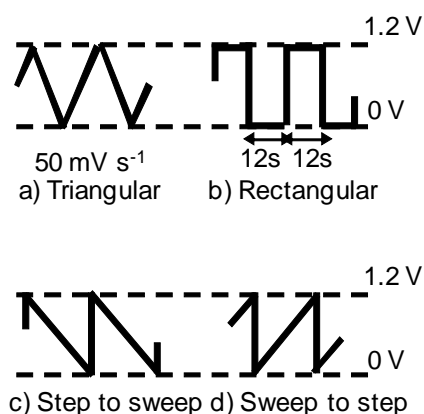


Figure 1: Potential cycling patterns.

3 Results and Discussion

During potential cycling, the shapes of cyclic voltammograms showed normal poly-crystal with small peaks of carbon black support for quinone / hydroquinone, and hydrogen adsorption / desorption and surface oxidation / reduction peaks decreased with potential cycling for all potential patterns. Therefore, the platinum surface did not change to a specific face, and electrochemical surface area was determined by hydrogen desorption charge with $210 \mu\text{C cm}^{-2}$.

Figure 2 shows the TEM images Pt/C before and after 5000 triangular potential cycles in various concentration of H_2SO_4 at 25°C . The platinum particle of the initial Pt/C was uniform diameter, and the particle grew during potential cycling. The particle seems larger diameter and distribute for higher concentration. Figure 3 shows the platinum particle diameter distribution in various concentration of H_2SO_4 under nitrogen atmosphere. The particle size distribution was log-normal distribution, and the medium diameters were 2.4, 4.7, 4.7, and 5.6 nm before and after potential cycling in 0.1, 0.5, and 1M, respectively.

Figure 4 shows the medium diameter of platinum particle as a function of pH. The diameter decreased with the increase of pH for all conditions. Figure 4 a) is for triangular pattern in H_2SO_4 and HClO_4 under N_2 or O_2 . The difference between N_2 and O_2 atmosphere was not significant. The particle diameter in H_2SO_4 was larger than that in HClO_4 at the same pH, and this behaviour was same to the dissolution of Pt in acidic media. Therefore, acidity and solubility would be one of important factor in particle growth process. Figure 4 b) is for rectangular and triangular potential cycling pattern in H_2SO_4 under N_2 . The particle diameter of rectangular was ca. 20 % larger than that of triangular, therefore dissolution kinetics would be taken into account for the analysis of the particle growth.

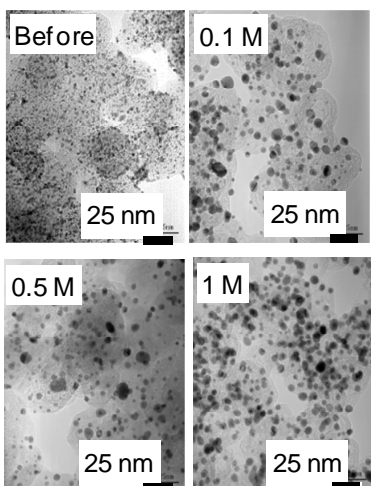


Figure 2: TEM images of Pt/C before and after 5000 triangular potential cycles in various concentration of H₂SO₄ at 25°C.

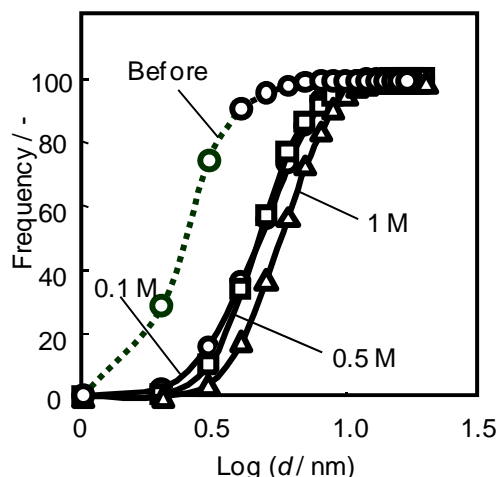
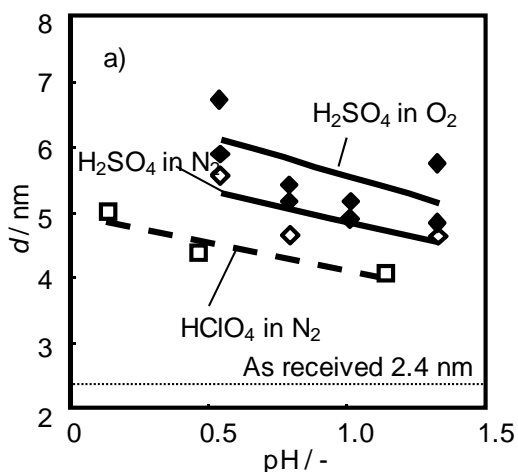
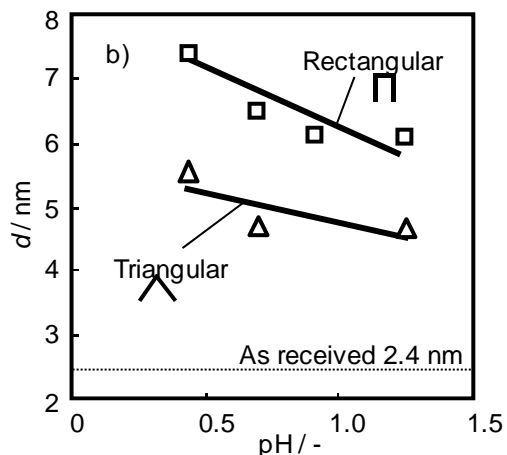


Figure 3: Platinum particle diameter distributions before and after 5000 triangular potential cycles in various concentration of H₂SO₄ at 25°C.



a) Triangular wave in H₂SO₄ and HClO₄ under O₂ or N₂.



b) Rectangular and triangular potential pattern in H₂SO₄ under N₂.

Figure 4: Medium platinum particle diameter as a function of pH after 5000 potential cycles.

Figure 5 shows the logarithm of normalized electrochemical surface area as a function of the cycling number with the triangular potential pattern in H₂SO₄ under nitrogen atmosphere. The decreases of the surface area were significantly larger for higher concentration of sulfuric acid. Up to 2000 cycles, the surface area decreased with linear relation in this figure, and after 2000 cycles, the surface area decrease rate decreased, especially lower concentration. This behaviour was the same to all other conditions in this study. Here, we analyzed up to 2000th cycle.

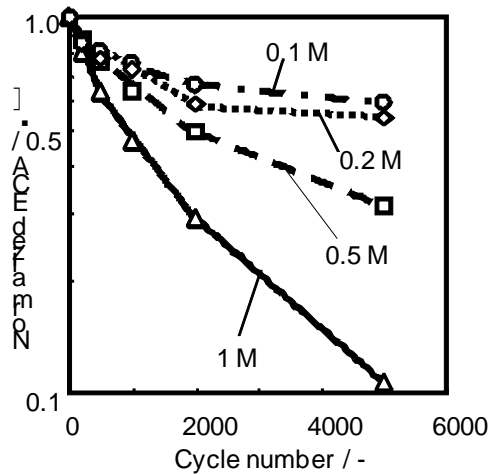
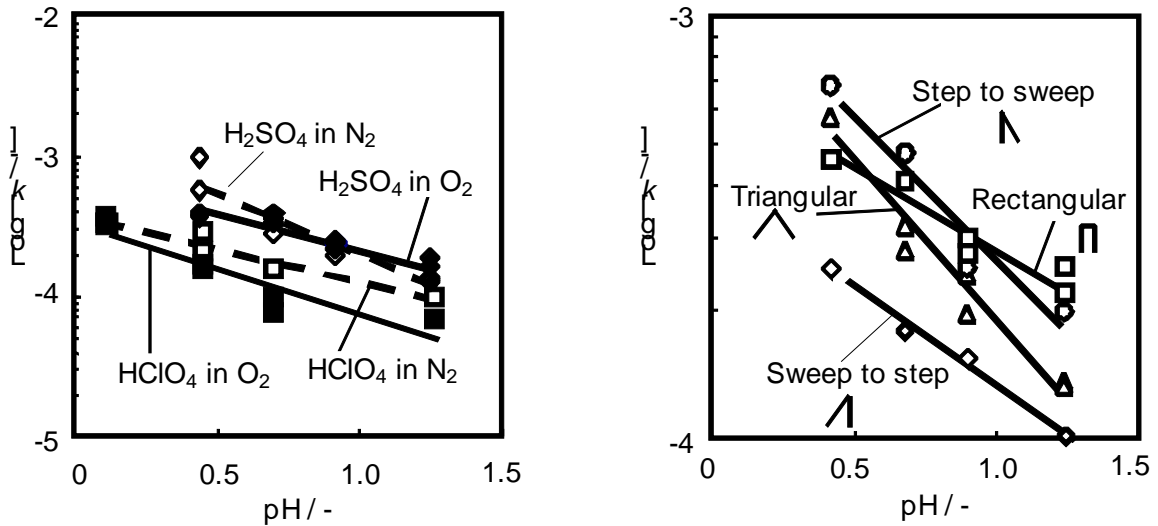


Figure 5: Electrochemical surface area as a function of potential cycling number with triangular potential cycles in various concentration of H₂SO₄ at 25°C



a) Triangular wave in H₂SO₄ and HClO₄ under O₂ or N₂. b) Various potential pattern in H₂SO₄ under N₂.

Figure 6: Rate constant of the electrochemical surface area decrease as a function of pH.

If the electrochemical surface area decrease rate is proportional to the electrochemical surface area: *S*, the following equation is obtained.

$$\delta S / \delta n = - k S \tag{1}$$

The *n* and *k* were the cycling number and the rate constant of the surface area decrease, respectively. The rate constants were determined by the slope of Figure 5. Figure 6 shows the rate constant as a function of pH. The rate constants decreased with the increase of pH, which were expected from the particle diameter. Figure 6 a) is the rate for triangular pattern in H₂SO₄ and HClO₄ under N₂ or O₂. The difference between N₂ and O₂ was not significant,

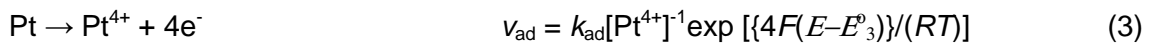
and the rate constant in H₂SO₄ was larger than that in HClO₄, which would correspond to the particle growth. Figure 6 b) is the rate for various potential cycling pattern in H₂SO₄ under N₂. In the 4 potential cycling patterns, the combination with the sweep oxidation and the step reduction showed the smallest rate constant in all pH. The combination with the step oxidation and the sweep reduction showed the largest rate constant in lower pH region. The dependence of the rate of the triangular pattern on pH was larger than others. Therefore, the kinetics of the simultaneously reactions of oxidation and reduction would affect to these behaviours.

The dissolution reaction follows the acidic dissolution in acid solution under oxidizing atmosphere [5].

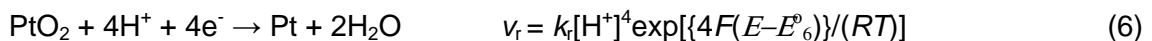


However, the rate determining reaction under potential cycling would not same to the equilibrium. At least, there are 2 kinds of dissolution reactions which are anodic and cathodic processes [4]. Here, we consider the simplest simultaneously reactions of dissolution and protection during anodic and cathodic processes. The reactions and the reaction rate equation might be as follows:

(Anodic)



(Cathodic)



Here, v , E , and E_i^0 were the reaction rate, the potential, and the equilibrium potential for each reaction, respectively. The dissolution reactions are equations (3) and (5), and the protection reactions are equations (4) and (6). The protection reaction rates would be lower than that of dissolution reaction, because the protection reactions were more complex than the dissolution reactions. At that time, the step oxidation would enhance the dissolution, because the dissolution amount before the oxidation layer formation would be larger than that of sweep oxidation, and the sweep reduction would enhance the dissolution, because the oxide which was the reactant of the dissolution would be maintained longer time than step reduction during reduction process.

4 Conclusion

In order to clarify degradation mechanism of Pt/C, the electrochemical surface area under potential cycling has been investigated in various conditions. The electrochemical surface area decrease seems to be proportional to the surface area up to 2000 potential cycles, and the rate constant of electrochemical surface area decrease increased with the decrease of pH. The rate constant in H₂SO₄ was larger than that in HClO₄. These behaviours were same to the solubility of platinum bulk metal in acidic medium. The rate constant was affected by potential cycling pattern. The rate constant of the combination of sweep oxidation and step reduction was smaller than that of rectangular, triangular, and the combination of step oxidation and sweep reduction. These behaviours could be explained by the kinetics of simultaneously reactions of anodic dissolution and oxide formation, and cathodic dissolution and surface reduction.

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