

Micro-Electrochemical Study on the electrochemical property of Pt : Effect of Crystal Orientation and Grain Boundary

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Pt is used as the cathode catalyst of Polymer Electrolyte Fuel Cell (PEFC). Pt catalyst with high catalytic activation and durability has been required for reduction of Pt usage. One of the solutions to improve the oxygen reduction reaction (ORR) activity is a surface structural control of Pt nanoparticles^[1]. However, the effect of surface structures on the degradation process of Pt has remained unclear. In this study, a micro-electrochemical system for electrochemical measurements on a small area with the size of $2.0 \times 10^{-4} \text{ cm}^2$ was applied to examine the effect of surface structures, such as a crystal orientation and a grain boundary, on the electrochemical behavior of Pt.

Polycrystalline Pt (Nilaco, Japan) was used as a specimen. Polycrystalline Pt was heat-treated for grain coarsening at 1823 K for 8 h. The average grain size was approximately 300 – 400 μm . Crystal orientations were investigated by electron backscatter diffraction (JEOL, JSM-6500F working at 25 kV). The specimen were polished with finer grade diamond pastes down to 0.25 μm , and finally cleaned ultrasonically with ethanol.

We fabricated a micro-electrochemical cell similar to that developed by Suter et al.^[2]. Figure 1 shows the image of the micro-electrochemical cell. A gold wire is used as a counter electrode. A W wire with W oxide, W/WO_x , is used as a pseudo reference electrode. All potential values are referred to the SHE. A micro-capillary is a glass tube (inner diameter is 140 μm , outer diameter is 570 μm). The micro-electrochemical cell was fixed instead of a revolving nosepiece of an optical microscope. This system allows the micro-electrochemical measurement at the small desired regions by switching between the objective lens and the micro-electrochemical cell.

Cyclic voltammetry (CV) measurements were performed in 0.5 M H_2SO_4 solution at 298 K by using the micro-electrochemical cell. Potential scan was started from 0.6 V in the anodic direction and was cycled at 10 mV s^{-1} in the range of 0.6 – 1.5 V.

Figure 2(a) shows the EBSD pattern of polycrystalline Pt surface. Region (A), (B) and (C) represent the polarization areas in this study: (A) is Pt(3 2 30), (B) is Pt(405) and (C) is the multi-plane surface including grain boundary. Here, Pt(3 2 30) is regarded as Pt(100), and Pt(405) as Pt(110). The CVs in the region (A), (B), and (C) are shown in Fig. 2(b). The anodic current observed in Fig. 2(b) means Pt oxide formation^[3]. The oxidation rate depended on the crystal orientation; the amount of charge passed during oxidation was large for Pt(110) compared

to Pt(100). This micro-electrochemical system allowed capture of the effect of the crystal orientation on the electrochemical property of Pt without Pt single crystals. In addition, the anodic current in the region (C) including mainly Pt(100) and a grain boundary was larger than that in the region (A) including only Pt(100). This result suggests that the grain boundary undergoes fast oxidation.

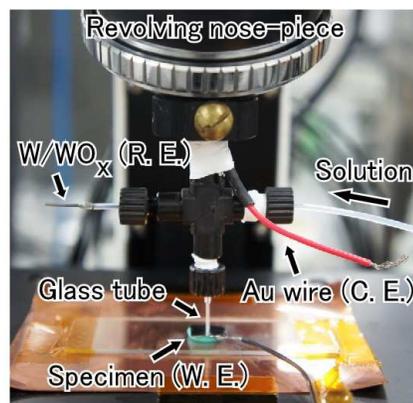


Fig. 1 Appearance of the micro-electrochemical cell used in this study.

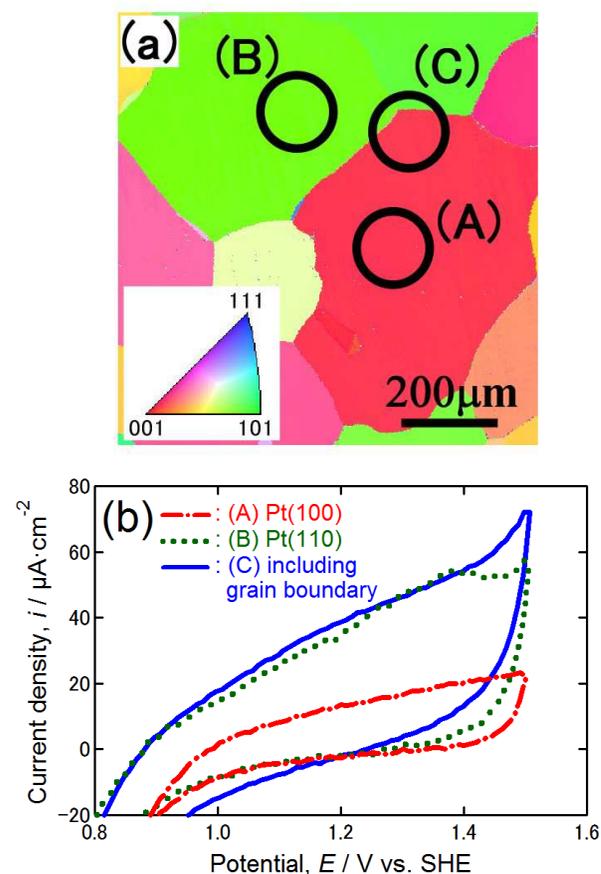


Fig. 2(a) EBSD pattern of polycrystalline Pt surface. Region (A), (B) and (C) represent the polarization areas in this study. (b) 2nd sweep of microscopic voltammetric curves of regions (A), (B) and (C) in 0.5 M H_2SO_4 solution at 298 K.

- [1] M. Inaba et al., *Electrochim. Acta*, **52**, 1632 (2006).
[2] T. Suter et al., *Electrochim. Acta*, **47**, 191(2001).
[3] B. E. Conway, *Prog. Surf. Sci.*, **49**, 331(1995).