In-situ vibrational spectroscopy of Pt oxides formation on the low index planes of Pt

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Introduction

The activity of oxygen reduction reaction (ORR) must be enhanced for reduction of Pt loading in electrocatalysts of fuel cells. In previous reports, it was shown that Pt oxides inhibit the ORR.[1,2] It is important to study the nature of Pt oxides in electrochemical environments in order to improve the ORR activity of electrocatalysts. As observation of Pt oxide, XPS study under the UHV condition has found PtOH and PtO in the Pt oxides formation region.[3] However there has been no spectroscopic study on Pt oxides using *in-situ* observation.

We have studied the correlation between Pt oxides formation and the ORR activity on the low index planes of Pt using *in-situ* infrared reflection absorption spectroscopy (IRAS) and nanoparticle surface enhanced Raman spectroscopy (NPSERS).

Experimental

Single crystal beads of Pt were prepared in reference to previous reports.[4,5] The ORR activity was measured in 0.1 M $HClO_4$ using hanging meniscus rotating disk electrode with a rotation rate of 1600 rpm.

IRAS

All IRAS spectra were measured using subtractively normalized interfacial FT-IR (SNIFTIRS) in 0.1 M HF.[6] Reference spectra were collected at 0.1 V (RHE). Infrared light was incident to the electrode surface through a BaF_2 prism covered with polypropylene film that prevents dissolution of the prism.

NPSERS

Au nanoparticles (60 nm in diameter) were supported on Pt(100) and Pt(110), enhancing Raman signals of the adsorbates even on an atomically flat surface.[7,8] All Raman spectra were measured in 0.1 M HF with the excitation light of the Raman signals was He/Ne (632.8 nm).

Results and Discussion

IRAS spectra gave a band around 1050 cm^{-1} and NPSERS spectra gave a band around 500 cm^{-1} in the Pt oxide formation region. The IRAS band was shifted to higher wavenumber at higher potentials; the band is due to the adsorbate. The bands around 1050 cm^{-1} and 500 cm^{-1} are assigned to OH bending vibration of PtOH and PtO stretching vibration based on EELS study.[9]

The integrated band intensities of PtOH and PtO are increased with the increase of the applied potential, showing that the coverage of Pt oxides is increased. The correlations between the band intensity and the applied potential are shown in Fig. 1. The onset potential of PtOH formation is lower than that of PtO, and depends on the surface structure strongly: Pt(110) < Pt(100) < Pt(111). PtOH is produced at the onset potential of the Pt oxide formation on Pt(111) which was estimated from cyclic voltammogram. On Pt(100) and Pt(110), however, PtOH is formed in the adsorbed hydrogen region.

The NPSERS band of PtO appears above 0.7 V on both Pt(100) and Pt(110). The onset potential agrees with those at which voltammetric peaks of Pt oxides appear. The order of band intensity of PtOH at 0.9 V is Pt(110) < Pt(111) < Pt(100), whereas that of PtO is Pt(110) < Pt(100). The order of the ORR activity at 0.9 V was Pt(100) < Pt(111) < Pt(110) regardless of the scanning direction, consequently PtOH and PtO are one of the factors for the deactivation of the ORR.

As mentioned above, we have established monitoring PtOH and PtO formation process by using in-situ vibrational spectroscopy techniques.

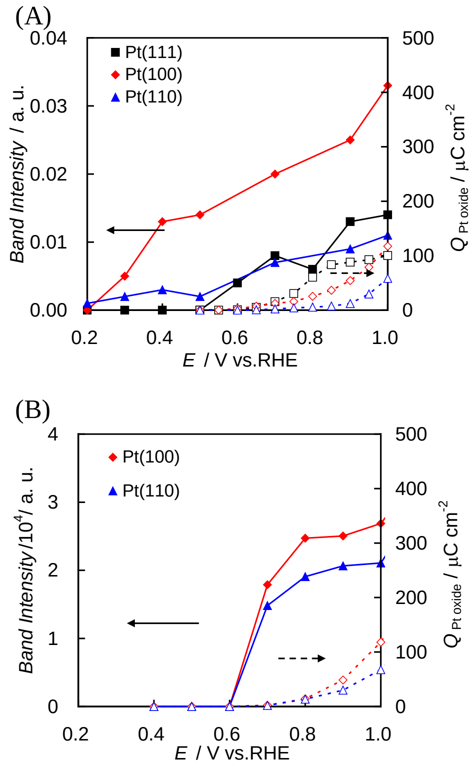

Fig. 1 Potential dependence of the integrated band intensity of PtOH (A) and PtO (B). Solid and open marks show the band intensity and anodic charge of Pt oxides, respectively.

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