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Potential Dependent Structures at Pt(111)/Electrolyte Solution Interfaces Using *In situ* Surface X-ray Scattering

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1 Introduction

To fully understand the mechanisms of electrochemical reactions and to apply these reactions to modern nanotechnology such as fuel cells, sensors, and molecular devices, it is essential to know the structures at the electrode/electrolyte interfaces *in situ* in real time at an atomic level. Surface X-ray scattering (SXS) technique using synchrotron radiation is one of the most promising methods to investigate the three-dimensional interfacial structures *in situ* with an atomic dimension. Using this technique, we have investigated various interfacial structures such as Au single crystal electrode/sulfuric acid interface [1,2], electrodeposited Pd, Ag, and Pt on Au(111) electrode [3-7], and underpotentially deposited Ag bilayer on Au(111) during Ag/AgCl reaction [8].

Pt is one of the most useful electrocatalytic materials and then it is of great importance to investigate the structure at Pt single crystal electrode/electrolyte interface under electrode potential control *in situ*. Here we reported to investigate the potential dependent structures at Pt(111)/electrolyte solution interfaces by using *in situ* SXS technique.

2 Experiment

Prior to SXS measurements, Pt(111) disk was annealed at 1600 °C for more than 2 h under argon/hydrogen atmosphere using an induction heater and quenched with an ultrapure water under an argon/hydrogen atmosphere. The electrochemical cell for the SXS measurements was filled with a deaerated 0.1 M $HClO_4$ or 0.05 M H_2SO_4 electrolyte solution under electrode potential control. After that, the cell was set to the 6 axes diffractomator, which was installed at the undulator-magnet beamline BL3A, and *in situ* SXS measurements were carried out at various potentials, where distinguishing current waves were measured in the cyclic voltammograms (CVs). An energy of 12 keV was selected.

3 Results and Discussion

By fitting the (00) rod data to theoretical three-layered model, the interfacial structures were determined.

In 0.1 M $HClO_4$ solution, at -0.05 V (vs. Ag/AgCl) and +0.12 V, where hydrogen underpotential deposition (UPD) current continued to flow and just finished to flow, respectively, in the CV, a layer distance between the outermost and second outermost Pt layers was expanded by ca. 3.5 %. At +0.30 V just more negative than the potential where oxidation current started to flow, several oxygen species such as water and/or perchlorate anion were randomly adsorbed on the Pt(111) surface. The layer distance between the outermost and second outermost Pt layers was relaxed to that of the same distance as bulk Pt. At +0.55 V, where the oxidation spike was observed in the CV, oxygen species which maybe hydroxide anion were adsorbed on the Pt(111)-(1×1) surface with a *p*(2×2)_3O structure. At +0.65 V, where the pre-oxidation current peak just finished to flow in the CV, oxygen species which maybe hydroxide anion were adsorbed at an atop site of the Pt(111)-(1×1) surface with a (1×1) structure. Potential dependent dynamics of the interfacial structures were now under investigation.

In 0.05 M H_2SO_4, on the other hand, at -0.05 V (vs. Ag/AgCl) and +0.12 V, where hydrogen UPD current continued to flow and just finished to flow, respectively, in the CV, the layer distance between the outermost and second outermost Pt layers were expanded by ca. 3.5 %, as well as in the case in 0.1 M $HClO_4$. At +0.30 V in the double layer potential region, several oxygen species such as water and sulfonate anion were adsorbed on the Pt(111) surface. At +0.65 V, where the pre-oxidation current peak just finished to flow in the CV, oxygen species which maybe hydroxyl anion were adsorbed at the atop site of the Pt(111) surface with the (1×1) structure. Potential dependent dynamics of the interfacial structures were now under investigation.

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