

In situ Monitoring of Structures at Pt(111)/Sulfuric Acid Electrolyte Interface by 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 with an atomic dimension. 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 at an atomic level. 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)/sulfuric acid electrolyte solution interface by using in situ SXS technique.

2 Experimentals

Prior to SXS measurements, Pt(111) disk was annealed 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 0.05 M H₂SO₄ electrolyte solution under electrode potential control. After that, the cell was set to the 6 axes diffractometer, which was installed at the undulator-magnet beamline BL3A, and in situ SXS measurements were carried out at various potentials. An energy of 12 keV was selected. Rods were measured at four potentials. At several scattered points, potential dependence of the scattered intensity was also measured.

3 Results and Discussion

Figure 1 shows the (00) rods measured at four potentials where the characteristic current peaks were observed in the CV. By fitting the data to theoretical three layered model, the interfacial structures were obtained.

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 cyclic voltammogram (CV), layer distance between the outermost and second outermost Pt layers were expanded by ca. 3.5 %. 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 such as water, hydroxyl anion, and sulfonate anion were adsorbed at the atop site of the Pt(111) surface. Detailed structure analyses and potential dependence of the interfacial structures were now under investigation.

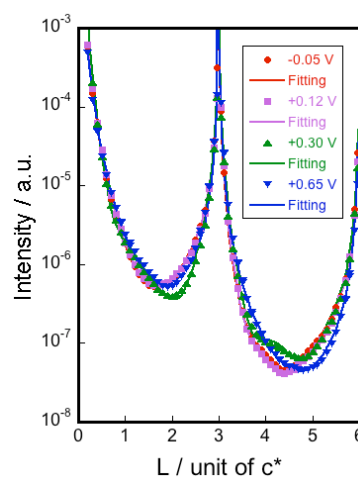


Figure 1. (00) rods from Pt(111)/deaerated 0.05 M H₂SO₄ interface measured at several potentials.

4 Conclusions

We investigated and determined the potential dependent structures at Pt(111)/sulfuric acid interface by in situ SXS technique.

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References

- [1] T. Kondo *et al.*, *J. Phys. Chem. C* **111**, 13197 (2007).
- [2] T. Kondo *et al.*, *Surf. Sci.* in press (2014).
- [3] M. Takahashi *et al.*, *Surf. Sci.* **461**, 213 (2000).
- [4] T. Kondo *et al.*, *J. Electroanal. Chem.* **532**, 201 (2002).
- [5] T. Kondo *et al.*, *Electrochim. Acta* **55**, 8302 (2010).
- [6] M. Takahashi *et al.*, *J. Phys.: Condens. Matter* **22**, 474002 (2010).
- [7] M. Shibata *et al.*, *J. Phys. Chem. C* **116**, 26464 (2012).
- [8] K. Uosaki *et al.*, *J. Phys. Chem. C* **115**, 12471 (2011).