In situ Monitoring of Structures at Pt(111)/Perchloric Acid Electrolyte Interface by Surface X-ray Scattering

Toshihiro KONDO1,2,*, Takuya MASUDA2, Tong SHONGFU2, Nana AOKI1,2, and Kohei UOSAKI2
1Ochanomizu University, 2-1-1, Ohtsuka, Bunkyo-ku, Tokyo 112-8610, Japan
2National Institute for Materials Science (NIMS), 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan

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 in situ technique, we have investigated various interfacial structures such as Au single crystal electrode/sulfuric acid interface [1], electrodeposited Pd, Ag, and Pt on Au(111) electrode [2-6], and underpotentially deposited (UPD) Ag bilayer on Au(111) during Ag/AgCl reaction [7].

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)/perchloric acid electrolyte solution interface by using in situ SXS technique.

2 Experiments
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 0.1 M HClO₄ 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 at Photon Factory, 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 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/or perchlorate anion were randomly adsorbed on the Pt(111) surface. At +0.65 V, where the pre-oxidation current peak just finished to flow in the cyclic voltamogram (CV), oxygen species which maybe hydroxide 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.

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

Acknowledgement
This work was supported by and conducted at the Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN) in NIMS.

References