

Potential-Dependent Structures and Potential-Induced Structure Changes at Pt(111) Single-Crystal Electrode/Sulfuric and Perchloric Acid Interfaces in the Potential Region between Hydrogen Underpotential Deposition and Surface Oxide Formation by *In Situ* Surface X-ray Scattering

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1 Introduction

Platinum is one of the most important electrode materials not only for basic surface science and electrochemistry but also for various industrial applications such as electrocatalysts for the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) for the polymer electrolyte fuel cells (PEFCs), and the structures and properties of low index surfaces of single-crystal platinum, especially Pt(111), have been extensively studied in electrochemical environments. [1-11] In order to understand the fundamental electrochemical reactions of the Pt(111) electrode and to apply them to industrial applications, we have to clarify the potential-dependent structures, including anion and/or oxygen species adsorptions, at the Pt(111) electrode/electrolyte interfaces over the entire potential range.

In this report, the potential-dependent structures at the Pt(111) single-crystal electrode/sulfuric and perchloric acid solution interfaces were accurately determined over the entire potential region from hydrogen underpotential deposition (H-UPC) to surface oxide formation, and their potential-induced structure change was comprehensively investigated by *in situ* surface x-ray scattering (SXS) measurements. [12]

2 Results and Discussion

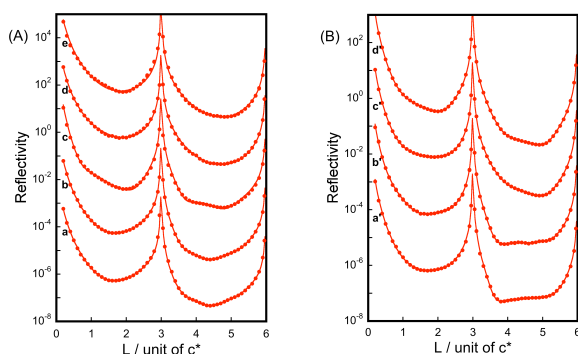


Fig. 1: Reflectivity profiles measured in (A) 0.1 M HClO₄ at **a**: 0.22 V (vs. RHE), **b**: 0.39 V, **c**: 0.57 V, **d**: 0.75 V, and **e**: 0.90 V and in (B) 0.05 M H₂SO₄ at **a'**: 0.22 V, **b'**: 0.39 V, **c'**: 0.59 V, and **d'**: 0.90 V.

Figure 1 shows the reflectivity profiles measured both in 0.1 M HClO₄ and 0.05 M H₂SO₄ electrolyte solutions

at various potentials. We found the potential-dependent interfacial structures both in solutions based on the analyzed data of these profiles. In 0.1 M HClO₄, only the interlayer distance, d_{12} , between the first and second outermost Pt layers is expanded by ca. 2 % not only H-UPD potential region but also electrical double layer potential region. Distance, d_{12} , is mainly relaxed accompanied with the OH adsorption and the structure of the adsorbed 1 ML OH is (1×1) at 0.90 V. In 0.05 M H₂SO₄, compression of d_{12} is relaxed mainly by co-adsorption of OH and sulfate groups with a total coverage of 1 ML and its structure is also (1×1) at 0.90 V.

Acknowledgements

This work was partially supported by Grants-in-Aids for Scientific Research (C) (No. 26410008) and for Scientific Research (KAKENHI) in Priority Area of “3D Active Sites” (No. 15H01045) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan. TK acknowledges an open-lab program at the Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN) in National Institute for Materials Science (NIMS). We wish to thank Dr. Kazuhisa Tamura of the Japan Atomic Energy Agency for his help with the Reflectivity fitting program.

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