

Adsorbed Structures of Oxygen Species on Pt(111) during Oxygen Reduction Reaction

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1 Introduction

It is very important to clarify the adsorbed structure of oxygen species on the platinum electrode surface during oxygen reduction reaction (ORR), which is a key reaction at the cathode of the polymer electrolyte membrane fuel cell (PEMFC) and then, the potential-dependent structures at the Pt single-crystal electrode/electrolyte solution interfaces has been extensively studied as a model system using various surface analysis techniques [1-6]. Because adsorbed oxygen species reacts immediately, however, the adsorbed structure of oxygen species has not been elucidated yet, so the ORR mechanism is still unknown.

Using *in situ* surface x-ray scattering (SXS) technique with a spectro-electrochemical cell in the thin layer configuration, we can control the electrolyte solution thickness and therefore, *i.e.*, we can control the reaction rate by the cell configuration [7-9]. Using such configuration, in this study, we tried to find the adsorbed structure of oxygen species on Pt(111) single-crystal electrode surface during ORR.

2 Experiment

After annealing and quenching, the Pt(111) single-crystal disk was set to the spectro-electrochemical cell [7] and the SXS measurements were carried out in the electrolyte solution, which was saturated by air bubbling. The Pt(111) electrode made contact with the solution while keeping the potential at 0.2 V (vs. RHE), where the electrode surface was covered with underpotentially deposited hydrogen. The electrode potential was scanned in the positive or negative direction from 0.2 V, then stopped at a certain potential at which the SXS measurement was going to be carried out. After holding the potential for more than 10 minutes, the SXS measurement was carried out with the electrolyte thickness of ca. 30 μm . *In situ* measurement was carried out under an open air environment, which means oxygen is induced to the solution through the Mylar@ window. All the data fitting with a theoretical equation was carried out using a three-layered model.

3 Results and Discussion

Figure 1 shows a typical rod result. Based on the potential dependent rod fitting with a theoretical equation, ca. 0.2 ML oxygen species exists on the Pt(111) surface during ORR. In ultra-high vacuum (UHV), the (2 \times 2) adsorbed structure was observed on the Pt(111)-(1 \times 1) surface and this adsorbed amount was similar to one

observed in UHV. The detailed potential-dependent adsorbed structure of oxygen species are now under investigation.

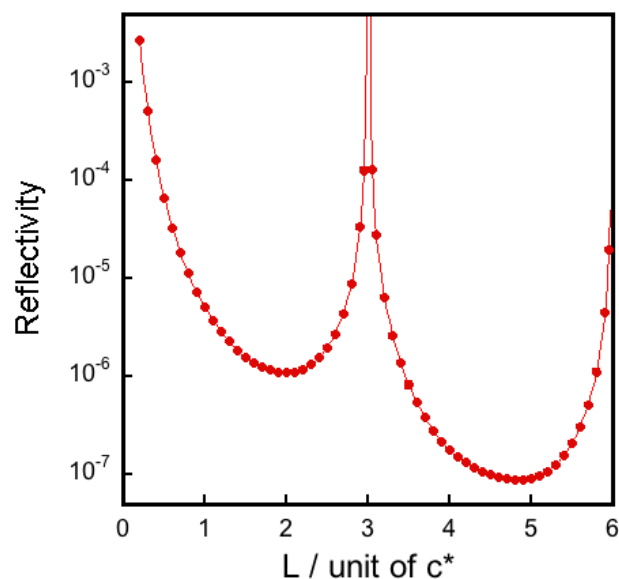


Fig. 1: The (00) rod measured at 0.4 V vs. RHE. Circles and solid line represent the data points and best fitting curve, respectively.

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