

# Surface X-Ray Scattering on Pt-skin/Pt<sub>3</sub>Co(111) Single-Crystal Electrode Highly Activity for the Oxygen Reduction Reaction

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The surface structure and the layer-by-layer composition of a Pt-skin/Pt<sub>3</sub>Co(111) single crystal electrode, which exhibited extremely high activity for the oxygen reduction reaction, were analysed by surface X-ray scattering. The topmost layer was found to be an atomically flat Pt-skin layer. In the 2nd layer, cobalt was enriched up to 98 atom %. The extremely high activity at the Pt-skin/Pt<sub>3</sub>Co(111) is correlated with such a specific surface structure.

## 1 Introduction

The development of highly active, highly durable cathode catalysts for the oxygen reduction reaction (ORR) is essential for the development of polymer electrolyte fuel cells. Bimetallic alloys of Pt such as Pt-Co, Pt-Ni, and Pt-Fe exhibited higher activity for the ORR than that of pure Pt [1]. Because the surfaces of Pt-based alloy nanoparticles with Pt-skin layer usually consist of low-index facets such as (111), (100), and (110), the research using well-defined alloy single crystals is important to clarify the mechanism for the enhanced ORR activity. Very recently, we have, for first time, demonstrated a distinct composition dependence of kinetically-controlled area-specific current densities ( $i_c$ ) for the ORR at Pt-skin/Pt<sub>100-x</sub>Co<sub>x</sub>(111), (100), and (110) electrodes. Pt-skin/Pt<sub>75</sub>Co<sub>25</sub>(111) exhibited the highest  $i_c$  value, which was about 27 times higher than that on pure Pt(111)[2]. In the present work, we have analyzed the Pt-skin layer and the underlying alloy of the Pt-skin/Pt<sub>75</sub>Co<sub>25</sub>(111) electrode (with very high ORR activity quite close to the maximum value) by multilateral techniques. In order to understand the layered structure, we carried out in-situ surface X-ray scattering (SXS) measurement under an electrochemical condition.

## 2 Experiment

The Pt<sub>3</sub>Co(111) single crystals were prepared in the same manner as described in our previous work [2]. They were annealed at 1273 K for 1 h in H<sub>2</sub>, resulting in the

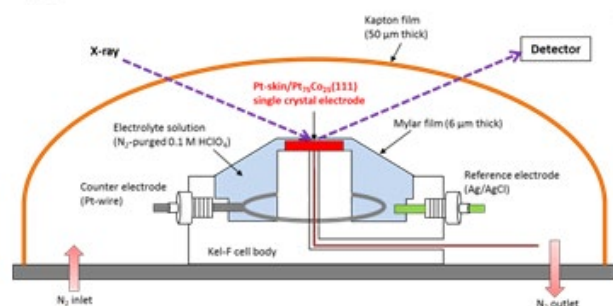


Fig. 1: Schematic illustration of the spectro-electrochemical cell used for in-situ SXS measurement.

formation of a Pt-skin layer on the surface. The layer-by-layer composition of the Pt-skin/Pt<sub>3</sub>Co(111) electrode at 0.4 V vs. reversible hydrogen electrode (RHE) in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> solution was analyzed by in situ SXS at BL-3A and 4C in the PF. The spectro-electrochemical cell for the in situ SXS measurement is shown schematically in Fig. 1. The cell was continuously purged with pure N<sub>2</sub>.

## 3 Results and Discussion

Figure 2 shows the (00) crystal truncation rod (CTR) profile of the Pt-skin/Pt<sub>75</sub>Co<sub>25</sub>(111). Multiple Bragg peaks were observed in an incident X-ray spot with a diameter of ca. 700 μm, suggesting that the Pt<sub>3</sub>Co(111) crystal consists of (111) multiple domains tilted within ±0.1°.

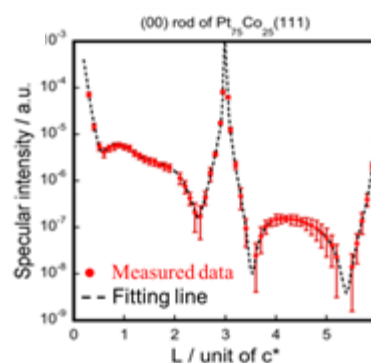


Fig. 2: (00) CTR profile of the Pt-skin/Pt<sub>75</sub>Co<sub>25</sub>(111) single crystal electrode in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> at 0.4 V vs. RHE and 298 K.

By fitting the data (red circles in Fig. 2) with a theoretical equation, the atomic ratios of Pt and Co were calculated [3]. As shown in Fig. 3, the topmost surface layer was found to consist of nearly pure Pt (98 atom % Pt) with one atomic layer thickness. Atomically flat terraces consisting of Pt atoms with (1×1) unit cells and steps with monoatomic height were observed by the use of in situ STM for a Pt-skin/Pt<sub>76</sub>Co<sub>24</sub>(111) single crystal in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> [3]. In contrast, Co atoms were considerably enriched in the second layer to 98 atom %. Such a Co-enriched layer might lead to strain in

the topmost Pt layer, resulting in multiple domains of several hundreds of  $\mu\text{m}$ . The Co contents in the 3rd and 4th layers were 21 and 19 atom %, respectively. These were slightly lower than that of the bulk Co content of 25 atom %, due to the diffusion of Co atoms into the 2nd layer.

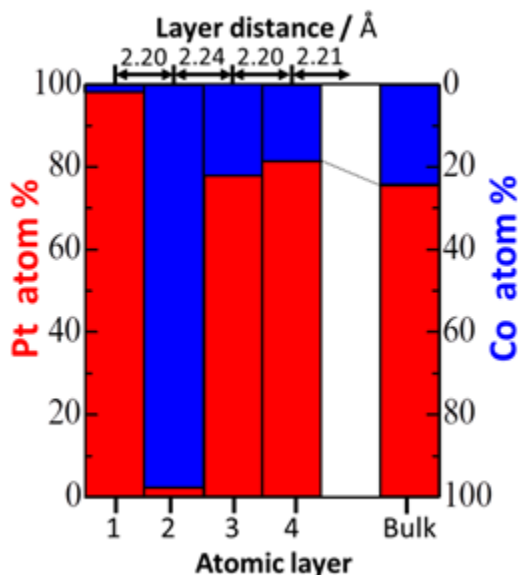


Fig. 3: Alloy composition from the top surface to the bulk of the Pt-skin/Pt<sub>75</sub>Co<sub>25</sub>(111) in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> at 0.4 V vs. RHE and 298 K.

To examine the electronic state of Co in the subsurface layers, X-ray photoelectron spectra (XPS) of Co for the Pt-skin/Pt<sub>75</sub>Co<sub>27</sub>(111) after annealing in H<sub>2</sub> were measured by angle-resolved, grazing-incidence XPS (ARGI-XPS) [3]. The Co in the subsurface layers was found to be positively charged but was not assigned to Co<sup>2+</sup> in CoO. Such an electronically positive state of Co is ascribed to an electron transfer from Co into the Pt-skin layer, i.e., the electronic modification of the Pt-skin layer (d-band center downshift). The extremely high activity for the ORR at the Pt-skin/Pt<sub>3</sub>Co(111) single crystal is correlated with this specific surface structure: atomically flat Pt-skin layer and significant enrichment of Co in the second layer.

#### Acknowledgement

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#### Research Achievements

1. This work was chosen as a PF Highlight in 2017.
2. Reference [3] was chosen as an ACS editors' choice.

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