Surface Structure and Layer-by-Layer Composition of Pt-Skin/Pt_3Co(111) Electrode with Very High Activity for the Oxygen Reduction Reaction

The surface structure and the layer-by-layer composition of a Pt-skin/Pt_3Co(111) single crystal electrode, which exhibited extremely high activity for the oxygen reduction reaction, were analyzed by multilateral techniques. The topmost layer was found to be an atomically flat Pt-skin layer with (1×1) structure. In the second layer, cobalt was enriched up to 98 at.%. The positively charged Co in the subsurface layer suggests an electronic state of the Pt-skin layer modified by Co. The extremely high activity at the Pt-skin/Pt_3Co(111) is correlated with such a specific surface structure.

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 a Pt-skin layer usually consist of low-index facets such as (111), (100), and (110), research using well-defined alloy single crystals is important to clarify the mechanism of the enhanced ORR activity. Very recently, we demonstrated for the first time a distinct composition dependence of kinetically-controlled area-specific current densities (j_k) for the ORR at Pt-skin/$Pt_{100-x}Co_x$(111), (100), and (110) electrodes. Pt-skin/$Pt_{73}Co_{27}$(111) exhibited the highest j_k value, which was about 27 times higher than that on pure Pt(111) [2]. In the present work, we analyzed the Pt-skin layer and the underlying alloy of the Pt-skin/Pt_3Co(111) electrode (with very high ORR activity quite close to the maximum value) by multilateral techniques.

The Pt_3Co(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_2, resulting in the formation of a Pt-skin layer on the surface.

The layer-by-layer composition of the Pt-skin/Pt_3Co(111) electrode at 0.4 V vs. reversible hydrogen electrode (RHE) in N_2-purged 0.1 M $HClO_4$ solution was analyzed by in situ surface X-ray scattering (SXS). The

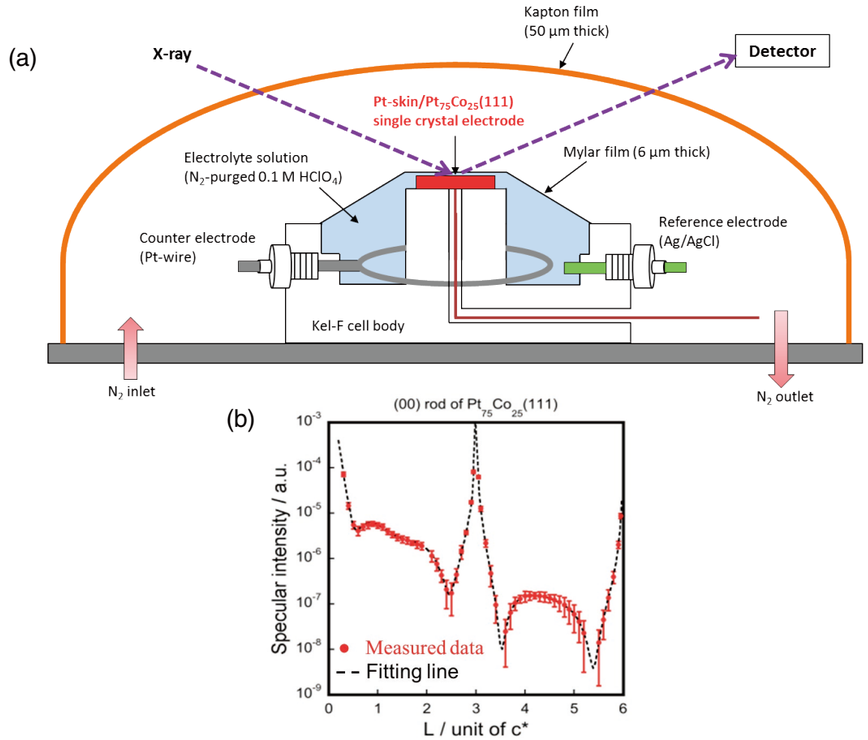

Figure 1: (a) Schematic illustration of the spectro-electrochemical cell used for in-situ SXS measurement. **(b)** (00) CTR profile of the Pt-skin/$Pt_{75}Co_{25}$(111) single crystal electrode in N_2-purged 0.1 M $HClO_4$ at 0.4 V vs. RHE and 298 K. Reproduced from Ref. 3 with permission of the American Chemical Society.

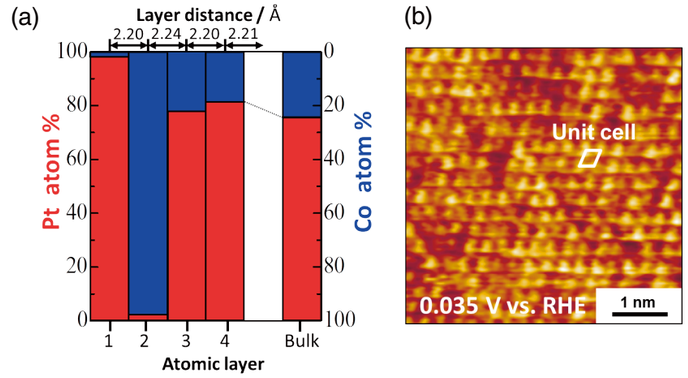

Figure 2: (a) Alloy composition from the top surface to the bulk of the Pt-skin/$Pt_{75}Co_{25}$(111) in N_2-purged 0.1 M $HClO_4$ at 0.4 V vs. RHE and 298 K. **(b)** In-situ STM images for $Pt_{76}Co_{24}$(111) in N_2-purged 0.1 M $HClO_4$, observed at 0.035 V vs. RHE. The tip potential and tunneling current were 0.038 V and 35.0 nA. Reproduced from Ref. 3 with permission of the American Chemical Society.

spectro-electrochemical cell for the in situ SXS measurement is shown schematically in **Fig. 1 (a)**. **Figure 1 (b)** shows the (00) crystal truncation rod (CTR) profile of the Pt-skin/Pt_3Co(111). Multiple Bragg peaks were observed in an incident X-ray spot with a diameter of ca. 700 μm, suggesting that the Pt_3Co(111) crystal consists of (111) multiple domains tilted within ±0.1°.

By fitting the data (red circles in **Fig. 1(b)**) with a theoretical equation, the atomic ratios of Pt and Co were calculated [3]. As shown in **Fig. 2 (a)**, the topmost surface layer was found to consist of nearly pure Pt (98 at.% Pt) with a layer thickness of one atom. Atomically flat terraces (**Fig. 2(b)**, 30–40 nm in width) consisting of Pt atoms with (1×1) unit cells and steps with monoatomic height were observed by using in situ STM for a Pt-skin/$Pt_{76}Co_{24}$(111) single crystal in N_2-purged 0.1 M $HClO_4$ [3]. In contrast, Co atoms were considerably enriched in the second layer to 98 at.%. Such a Co-enriched layer might lead to strain in the topmost Pt layer, resulting in multiple domains of several hundreds of μm. The Co contents in the third and fourth layers were 21 and 19 at.%, respectively. These were slightly lower than that of the bulk Co content of 25 at.%, due to the diffusion of Co atoms into the second layer.

It has been reported for a Pt-skin/Pt_3Ni(111) after annealing in UHV that the Ni content of the second layer was 50 at.% with one monolayer Pt-skin [4]. The ORR activity on the Pt-skin/Pt_3Ni(111) was ca. 10 times higher than that of Pt(111). Thus, the most important factor for significantly high ORR activity is the formation of a monoatomic Pt-skin layer and the enrichment of the second element (Co or Ni) in the second layer. However, further experiments are necessary to clarify why the contents of Co and Ni in the second layers were so different.

To examine the electronic state of Co in the subsurface layers, X-ray photoelectron spectra (XPS) of Co for the Pt-skin/$Pt_{73}Co_{27}$(111) after annealing in H_2 were measured by angle-resolved, grazing-incidence XPS (ARGI-XPS) [3]. It was found that the Co $2p_{3/2}$ spectrum at the surface (detection angle = 75°) was significantly different from that for the bulk (detection angle = 0°). The Co in the subsurface layers was found to be positively charged but was not assigned to Co^{2+} in CoO, since the satellite peak observed for CoO was not observed. Such an electronically positive state of Co is ascribed to an electron transfer from Co into the Pt-skin layer, i.e., electronic modification of the Pt-skin layer (d-band center downshift). The extremely high activity for the ORR at the Pt-skin/Pt_3Co(111) single crystal is correlated with this specific surface structure: atomically flat Pt-skin layer and significant enrichment of Co in the second layer.

This work was supported by funds for the "Superlative, Stable, and Scalable Performance Fuel Cell" (SPer-FC) project from the New Energy and Industrial Technology Development Organization (NEDO) and a Grant-in-Aid (No. 25410007) for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan.

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BEAMLINES

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