Surface Structure and Layer-by-Layer Composition of Pt-Skin/Pt₇₅Co₂₅(111) Electrode with Very High Activity for the Oxygen Reduction Reaction

The surface structure and the layer-by-layer composition of a Pt-skin/Pt₇₅Co₂₅(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 〈111〉 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/Pt₇₅Co₂₅(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 nanoparticules 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 (jₖ) for the ORR at Pt-skin/Pt₇₅Co₂₅(111), (100), and (110) electrodes. Pt-skin/Pt₇₅Co₂₅(111) exhibited the highest jₖ 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/Pt₇₅Co₂₅(111) electrode (with very high ORR activity quite close to the maximum value) by multilateral techniques. The Pt₇₅Co₂₅(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 H₂, resulting in the formation of a Pt-skin layer on the surface. The layer-by-layer composition of the Pt-skin/Pt₇₅Co₂₅(111) electrode at 0.4 V vs. reversible hydrogen electrode (RHE) in N₂-purged 0.1 M HClO₄ solution was analyzed by in situ surface X-ray scattering (SXS). The 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 〈111〉 units and steps with monatomic height were observed by using in situ STM for the ORR at the Pt-skin/Pt₇₅Co₂₅(111) single crystal is correlated with this specific surface structure: atomically flat Pt-skin layer and significant enrichment of Co in the second layer.

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REFERENCES


BEAMLINES

BL-3A and BL-4C