Atomically Flat Pt Skin and Striking Enrichment of Co in Underlying Alloy at Pt₃Co(111) Single Crystal with Unprecedented Activity for the Oxygen Reduction Reaction

Shun Kobayashi,‡ Makoto Aoki‡ Mitsuhiro Wakisaka,§ Teppei Kawamoto,‖ Ryo Shirasaka,† Kohei Suda,‖ Donald A. Tryk,‖ Junji Inukai,⁎† Toshihiro Kondo,‡−⊥ and Hiroyuki Uchida*†⊥

†Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu 400-8510, Japan
‡Division of Life, Medical, Natural Sciences and Technology, Organization for Advanced and Integrated Research, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 658-8501, Japan
§Division of Environmental Engineering, Graduate School of Engineering, Toyama Prefectural University, 5180 Kurokawa, Imizu, Toyama 939-0398, Japan
‖Fuel Cell Nanomaterials Center, University of Yamanashi, 6-43 Miyamae-cho, Kofu 400-0021, Japan
⊥Division of Chemistry, Graduate School of Humanities and Sciences, Ochanomizu University, Ohtsuka, Bunkyo-ku, Tokyo 112-8610, Japan

Supporting Information

ABSTRACT: By the use of in situ scanning tunneling microscopy and surface X-ray scattering techniques, we have clarified the surface structure and the layer-by-layer compositions of a Pt skin/Pt₃Co(111) single-crystal electrode, which exhibited extremely high activity for the oxygen reduction reaction. The topmost layer was found to be an atomically flat Pt skin with (1 × 1) structure. Cobalt was enriched in the second layer up to 98 atom %, whereas the Co content in the third and fourth layers was slightly smaller than that in the bulk. By X-ray photoelectron spectroscopy, the Co in the subsurface layers was found to be positively charged, which is consistent with an electronic modification of the Pt skin. The extremely high activity at the Pt skin/Pt₃Co(111) single crystal is correlated with this specific surface structure.

1. INTRODUCTION

The development of highly active and durable cathode catalysts for the oxygen reduction reaction (ORR) is very important for polymer electrolyte fuel cells. Bimetallic alloys of Pt, such as Pt−Co, Pt−Ni, and Pt−Fe, exhibited higher ORR activity than that of pure Pt.1−7 For polycrystalline Pt alloy electrodes, it was found that the kinetically controlled area-specific current densities (jₐ) for the ORR strongly depend on the bulk composition.8 A Pt skin layer forms on Pt alloy surfaces spontaneously in acidic media, and the electronic state of the Pt skin is modified by the underlying alloy.2,3,6,8−11

Very recently, we have demonstrated a distinct composition dependence of jₐ at a series of (111), (110), and (100) faces of Pt₁₀₀−xCoₓ single-crystal rotating disk electrodes, on which well-defined Pt skin layers were intentionally formed by annealing in vacuum (UHV).9 It is essential to analyze the structure, composition, and thickness of the Pt skin layer, together with the composition of the underlying alloy of Pt₁₀₀−xCoₓ single crystal electrodes in the electrolyte solution while controlling the potential. In the present research, we have, for the first time, multilaterally analyzed the Pt skin layer and the underlying alloy of the Pt₇₅Co₂₅(111) electrode, which exhibited very high ORR activity (quite close to the maximum value). We demonstrate a striking enrichment of Co (98 atom %) just under an atomically flat Pt skin layer.

2. RESULTS AND DISCUSSION

First, we observed the microstructure of the Pt₇₅Co₂₅(111) single crystal surface in N₂-purged 0.1 M HClO₄ solution with an in situ scanning tunneling microscope (STM). Details of the measurement are shown in the Experimental Section. All electrode potentials in this article are referred to a RHE. As seen in Figure 1a, the width of the (111) terraces was 30−40 nm and the steps were parallel to each other. A slight influence

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of the shape of the tip apex is seen on the step morphology. It was clearly observed in a high-resolution image (Figure 1b) that the (111) terrace was atomically flat and the distance between the nearest atoms was 0.28 nm, approximately equal to that in Pt(111) (0.277 nm) with steps of monoatomic height of Pt, ca. 0.2 nm. The angles between the atomic rows were 60°. Thus, a Pt skin layer with (1×1) structure was formed on the surface after annealing in H₂. This accords well with our ex situ analysis (Figures S1 and S2 in the Supporting Information).12,13 It is noteworthy that the STM image showed no corrugations in height. In contrast, for Pt−Ni and Pt−Co single crystals annealed in UHV,14,15 corrugations in height (Moiré pattern) have been observed by STM, probably due to a lattice mismatch between the Pt skin layer and the underlying layer. Hence, the annealing of the Pt₅Co(111) single crystal in H₂ played an important role to form a well-defined, atomically flat Pt skin layer.

Next, we have analyzed the layer-by-layer composition of the Pt skin/Pt₇₅Co₂₅(111) electrode by in situ surface X-ray scattering (SXS), which is one of the most powerful techniques in understanding the structure not only of the topmost surface layer but also of the subsurface layers.16−19 Details of the in situ SXS measurements and analysis procedures are described in the Experimental Section. Figure 2a shows the (00) crystal truncation rod (CTR) profile, which shows the structure along the direction normal to the electrode surface of the Pt skin/Pt₇₅Co₂₅(111) electrode, measured at 0.4 V in N₂-purged 0.1 M HClO₄. It should be noted that multiple Bragg peaks were observed in an incident X-ray spot with a diameter of ca. 700 μm, suggesting that the Pt₇₅Co₂₅(111) crystal consists of (111) multidomains tilted within ±0.1°. From the calculated curve (black dotted line in Figure 2a), by fitting the data (red circles in Figure 2a) with a theoretical equation (see Experimental Section), we obtained the atomic ratios of Pt and Co between the top surface to the bulk of the Pt skin/Pt₇₅Co₂₅(111).

Figure 1. In situ STM images for Pt₅Co₂₅(111) in N₂-purged 0.1 M HClO₄ observed at (a) 0.045 V (50 × 50 nm²) and (b) 0.035 V (high resolution, 5 × 5 nm²) vs RHE. The tip potential and tunneling current were (a) 0.075 V and 5.0 nA and (b) 0.038 V and 35.0 nA, respectively.

Figure 2. (a) (00) CTR profile of the Pt skin/Pt₇₅Co₂₅(111) single-crystal electrode in N₂-purged 0.1 M HClO₄ at 0.4 V vs RHE and 298 K. The circles and dotted line are the experimental data and fitted curve, respectively. (b) The alloy composition from the top surface to the bulk of the Pt skin/Pt₇₅Co₂₅(111).
obtained by the fitting are shown in Table S1. It was confirmed that the topmost surface (Pt skin) layer consists of pure Pt (98 atom % Pt) with one atomic layer thickness. It is striking that Co was considerably enriched in the second layer up to 98 atom %. The Co contents in the third and fourth layers were 21 and 19 atom %, respectively, which were slightly lower than that of the bulk crystal (25 atom % Co). Such a decrease is definitely due to the diffusion of Co atoms into the second layer.9,15,21 As shown in Figure S3, the \(j_\text{k}\) value on the Pt skin/Pt\(_{75}\)Co\(_{25}\)(111) electrode at 0.9 V (−2.97 ± 0.11 mA cm\(^{-2}\)) was ca. 25 times higher than that at pure Pt(111) in the air-saturated 0.1 M HClO\(_4\) solution. On the basis of this SXS result, there is no doubt that such unprecedented activity for the ORR is ascribed to the specific composition gradient of Co. It is also considered that the very high content of Co in the second layer might lead to strain in the topmost Pt layer, resulting in multiple domains of several hundreds of \(\mu\)m.

It has been reported for a Pt skin/Pt\(_{5}\)Ni(111) annealed in UHV that Ni was enriched as high as ca. 50 atom % in the second layer just under the Pt skin monatomic layer.7 Very recently, Kumeda et al. have reported the formation of a Pt skin layer, with the second to fifth layers of the PtNi alloy less than 11 atom % Ni for a PtNi surface alloy formed on a Pt(111) electrode (PtNi/Pt(111) annealed in 5% H\(_2\)).21 It is very atom % Ni for a PtNi surface alloy formed on a Pt(111) layer, with the second to fifth layers of the PtNi alloy less than 11 atom % Ni for a PtNi surface alloy formed on a Pt(111) electrode (PtNi/Pt(111) annealed in 5% H\(_2\)).21 It is very interesting that the enhancement factor for the \(j_\text{k}\) value of the ORR on the surface alloy PtNi/Pt(111) at 0.9 V was nearly identical with that of Pt skin/Pt\(_{3}\)Ni(111), ca. 10 times higher than that on pure Pt(111). Taking these results and the present ones into consideration, the most important factor for a large increase in the ORR activity is the formation of a Pt skin monolayer and the enrichment of the second element (Co or Ni) in the second layer. However, it is still unclear why the concentrations of Co and Ni in the subsurface layers were so different, although one of the factors might be the annealing conditions, i.e., in H\(_2\), 5% H\(_2\) and UHV. Further experiments are necessary to elucidate this effect.

Figure 3 shows the Co 2p\(_{3/2}\) spectra for the Pt\(_{73}\)Co\(_{27}\)(111) after H\(_2\) annealing by angle-resolved, grazing-incidence X-ray photoelectron spectroscopy (ARGI-XPS).

![Co 2p\(_{3/2}\) spectra for the Pt skin/Pt\(_{75}\)Co\(_{25}\)(111) after H\(_2\) annealing by the ARGI-XPS.](image)

It is striking that the electronic state of Co in the subsurface layers is completely different from that in CoO. An electronically positive state of Co is reasonably explained by an electron transfer from Co into the Pt skin layer, i.e., the electronic modification of the Pt skin layer, which has been linked to a d-band center downshift.8,9,10 Our preliminary density functional theory (DFT) calculations, carried out with a 4 × 4, three-layer model (Figure S5) show clearly that there is such an electron transfer, with the Co underlayer acquiring an average of +0.322 ± 0.039 per atom and the Pt skin layer acquiring an average charge of −0.186 ± 0.006 per atom (Table S2). For Pt(111), the top layer charge was −0.022. The marked electronic effect of the Co underlayer can also be seen in the density of states for the Pt skin layer in comparison with the top layer in Pt(111) (Figure S6). To investigate the electronic modification effect at the Pt skin/Pt\(_{100-x}\)Co\(_x\)(111) single crystals further, we are conducting ARGI-XPS combined with an electrochemical cell, together with further detailed DFT calculations.

3. CONCLUSIONS

We have, for the first time, clarified the surface structure together with the compositions from the surface to the sublayers of a Pt skin/Pt\(_{73}\)Co\(_{27}\)(111) single-crystal electrode by in situ analytical techniques. An atomically flat Pt skin monolayer was formed with a (1 × 1) structure. It was found that Co was enriched in the second layer as high as 98 atom %. The positively charged Co in the subsurface layer strongly indicates an electron transfer from Co into the Pt skin layer, resulting in the unprecedented activity for the ORR. The present results shed light on the structure and electronic characteristics of Pt alloy catalysts, which can help to understand the mechanisms of the ORR and how to improve the ORR activity.

4. EXPERIMENTAL SECTION

The Pt and Pt\(_{75}\)Co\(_{25}\)(111) single-crystal disks were ca. 3.5 mm in diameter and 1.5 mm in thickness, prepared in the same manner as described in our previous work.12,13 The Co composition in bulk was evaluated from photoelectron intensities of the Pt 4f and Co 2p\(_{3/2}\) lines by use of X-ray photoelectron spectroscopy (XPS) after Ar\(^+\) bombardment.12,13

In situ STM observation of the Pt–Co single-crystal surface was performed in N\(_2\)-purged 0.1 M HClO\(_4\) aqueous solution at temperature between 20 and 22 °C by the use of a Nanoscope IIIa (Veeco Instruments Inc.). The detailed procedure of in situ STM observation has been described in our previous work.12,24

The STM images were observed in the constant-current mode with a high-resolution scanner (HD-0.5I). The tunneling tips were prepared by electrochemically etching a tungsten wire in 1 M KOH aqueous solution. The tunneling tips thus prepared were used as the counter electrode, and an RHE was used as the reference electrode.

In situ SXS measurements was performed as follows. After annealing and cooling in H\(_2\), the Pt skin/Pt\(_{75}\)Co\(_{25}\)(111)
electrode was mounted in the spectro-electrochemical cell, which was specially designed for the in situ SXS measurements and was constructed from Kel-F, covered with a N₂-purged Kapton dome, as shown in Figure S4. During the measurements, the electrolyte solution layer thickness between the electrode surface and the 6.0 μm thick Mylar film used as a window was maintained at ca. 100 μm. After filling the electrochemical cell with the N₂-purged 0.1 M HClO₄ potential was applied to the Pt skin/Pt₇₅Co₂₅(111) electrode at 0.4 V vs RHE and this potential was maintained during the measurements. The electrode potential was controlled by a potentiostat equipped with an alternating current impedance analyzer (PGSTAT302N, Metrohm Autolab B.V., The Netherlands). A Pt wire and Ag/AgCl (saturated NaCl) electrode were used as the counter and reference electrodes, respectively.

The incident X-ray energy of 12.27 keV (wavelength: 1.100 Å) was selected to avoid fluorescence from the Pt substrate. Reflectivity measurements, i.e., (0 0) crystal truncation rod (CTR) measurements, were carried out along the direction normal to the surface, and each reflectivity was a rocking-curve integrated intensity, which was normalized with the incident X-ray intensity. Structure parameters, such as the element type (ClO₄⁻, Pt, and Co), coverage of ClO₄⁻ in the adsorbate layer, and ratio of Pt and Co from the topmost to fourth layers, and layer distance between these layers along the direction normal to the electrode surface, were quantitatively determined from the least-squares fitting to the reflectivity data with a kinematical calculation based on a specific interfacial model. Fittings with all possible structure models were carried out, and the fitting result, which gave the lowest χ² value among all of the fitting results, was taken as a best-fit result. In the adsorbate layer, the best fit showed that the element type was not an oxygen species but ClO₄⁻ and therefore ClO₄⁻ was employed as an adsorbate in the present study. The amount of ClO₄⁻ in the adsorbed layer was estimated by considering that one monolayer corresponds to 7.88 × 10⁻¹⁴ cm⁻², which was calculated from the bulk crystal.

Angle-resolved, grazing-incidence XPS (ARGI-XPS) measurements were performed in a UHV chamber. A hemispherical electron spectrometer (model 10-360, ULVAC-PHI), an X-ray source (model 10-610, ULVAC-PHI), and a toroidal monochromator (model 10-420, ULVAC-PHI) were attached to a CTR electron spectrometer (model 10-360, ULVAC-PHI), an X-ray source (model 10-610, ULVAC-PHI), and a toroidal monochromator (model 10-420, ULVAC-PHI) were attached to the UHV chamber. All of the XP spectra were obtained with monochromatic Al Kα radiation (hv = 1486.58 eV) at 200 W. The incident angle of the X-rays was between 1 and 2°, whereas the detection angles of the photoelectrons were adjusted to 75 and 0°. Binding energies were calibrated by the use of Ag 3d₅/₂ (368.26 eV), Pt 4f₇/₂ (71.2 eV), and the Fermi energy EF of Pt (0 eV). The pass energy and resolution of the electron spectrometer were 23.50 and 0.66 eV (full width at half-maximum of Ag 3d₅/₂), respectively.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01793.

Details of low energy electron diffraction pattern, low energy ion scattering spectra, the j₁ value, and the structural parameters of in situ SXS (PDF)

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**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: jinukai@yamanashi.ac.jp (J.I.).
*E-mail: kondo.toshihiro@ocha.ac.jp (T.K.).
*E-mail: h-uchida@yamanashi.ac.jp (H.U.).

**ORCID**

Toshihiro Kondo: 0000-0002-5235-7648
Hiroiyuki Uchida: 0000-0001-6718-5431

**Author Contributions**

S. Kobayashi prepared all Pt–Co(111) single-crystal electrodes and performed the electrochemical measurements. He also prepared the original draft of the manuscript. M. Aoki and K. Suda performed the in situ SXS measurements. M. Aoki also analyzed the SXS results with T. Kondo. M. Wakisaka analyzed the composition of the Pt₇₅Co₂₅(111) single crystal by XPS and supervised the ARGI-XPS. R. Shirasaka performed the ARGI-XPS measurement of the Pt₇₅Co₂₅(111) single crystal. T. Kawamoto performed the in situ STM observation of the Pt₇₅Co₂₅(111) single-crystal electrode and analyzed the results. He also carried out the in situ SXS measurements. D. A. Tryk carried out DFT calculations. He also discussed all of the results and revised the final version of manuscript. J. Inukai supervised the in situ STM and in situ SXS measurements. T. Kondo supervised the measurement and analysis of the in situ SXS of the Pt₇₅Co₂₅(111) single crystal. H. Uchida coordinated this work and revised the manuscript thoroughly.

**Notes**

The authors declare no competing financial interest.

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