



Unprecedented dependence of the oxygen reduction activity on Co content at Pt Skin/Pt–Co(111) single crystal electrodes



M. Wakisaka^a, S. Kobayashi^b, S. Morishima^b, Y. Hyuga^b, D.A. Tryk^a, M. Watanabe^a, A. Iiyama^a, H. Uchida^{a,c,*}

^a Fuel Cell Nanomaterials Center, University of Yamanashi, 6-43 Miyamae, Kofu 400-0021, Japan

^b Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4 Takeda, Kofu 400-8510, Japan

^c Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu 400-8510, Japan

ARTICLE INFO

Article history:

Received 23 March 2016

Accepted 23 March 2016

Available online 31 March 2016

Keywords:

Pt–Co alloy

Single-crystal

Pt-skin layer

Oxygen reduction reaction

Rotating disk electrode

ABSTRACT

The kinetically controlled area-specific activities, j_k , for the oxygen reduction reaction (ORR) were evaluated at well-defined Pt-skin/Pt_{100-x}Co_x(111) single crystal electrodes as a function of Co content by use of the rotating disk electrode method. The Pt-skin layer formed by annealing under a pure H₂ atmosphere was clarified to consist of atomically flat terraces with the same atomic arrangement as the underlying crystal. At 25 atom%–Co, the j_k value reached a maximum as high as 3.0 mA cm⁻² at 0.9 V vs. RHE, which is ca. 25 times larger than that on pure Pt(111). Such an enhanced ORR activity of Pt-skin/Pt–Co(111) electrodes cannot be explained on the basis of decreased OH poisoning, because the surface oxidation charge densities measured at 0.9 V in N₂-purged solution were nearly constant.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Development of highly active cathode catalysts for the oxygen reduction reaction (ORR) is one of the most important subjects to achieve high efficiency with a reduced amount of Pt for polymer electrolyte fuel cells (PEFCs). Pt-based alloy catalysts, Pt–M (M=Fe, Co, Ni, Mn, Cr, V, etc.) have been reported to exhibit higher kinetically controlled current density (area-specific activity) for the ORR, j_k , than that of Pt [1–8]. Based on multi-technique analyses on polycrystalline planar alloy electrodes, we first clearly demonstrated that nonprecious metal elements in Pt–Fe, Pt–Co, and Pt–Ni were dissolved in acidic solution, followed by a spontaneous formation of a Pt-skin layer with a modified electronic structure on the alloy surface, resulting in increases in j_k [9,10]. In practical PEFCs, Pt-based nanoparticles dispersed on carbon supports have been employed in the catalyst layers. The surfaces of the nanoparticles usually consist of low-index crystal facets such as (111) and (100). It has been well recognized that the j_k value for Pt strongly depends on the crystal facet exposed [11]. Stamenkovic et al. have reported that the (111) plane exhibited the highest enhancement of j_k among the low-index crystal facets of the identical composition of Pt₃Ni alloy single crystals [12]. It has also been reported that Pt-enriched M/Pt(111) model electrodes (M=Ni, Co, Cu) exhibited similar enhanced j_k values, by a factor of about ten, compared with that of a pure Pt(111) electrode [13–18].

However, to our knowledge, the dependence of j_k on the alloy composition has not been demonstrated for well-defined alloy single

crystals, most likely due to the difficulty in preparing alloy single crystals with controlled composition. Recently, we have established a facile method for the preparation of Pt–Co alloy single crystals with desired Co content without the use of an ultrahigh vacuum (UHV) system [19]. The present results, which were partially reported in preliminary form [20], include the evaluation of the j_k values for the ORR at Pt-skin layers formed on Pt_{100-x}Co_x(111) single crystal electrodes in air-saturated 0.1 M HClO₄ solution as a function of Co content x by using the rotating disk electrode (RDE) method. It was found that the j_k value at 0.9 V reached a maximum as high as 3.0 mA cm⁻² at $x = 25$ atom%, which is ca. 25 times higher than that on a pure Pt(111) electrode.

We also examined the OH coverages for the various Pt-skin-covered alloy surfaces, finding near constancy of the coverage at 0.9 V vs. RHE with increasing Co content, which suggests that the conventional view of the ORR catalysis must be modified.

2. Experimental

The preparation method of Pt–Co single crystal beads (solid solution) with desired Co contents (within an error of ± 2 atom%) has been described in our previous work [19]. The crystal quality was checked by the appearance of (111) facets on the crystal bead surface in proper positions and conventional X-ray diffraction. The alloy crystals, as well as pure Pt crystal, were shaped into disk electrodes of ca. 3.5 mm in diameter and 1 mm in thickness for the RDE measurements. Prior to each electrochemical measurement, the alloy single crystal surface was freshly prepared by heating to 1223 K and subsequently cooling to room temperature under an atmosphere of pure H₂ (ZERO-A, Sumitomo

* Corresponding author. Tel.: +81 55 220 8619; fax: +81 55 220 8618.
E-mail address: h-uchida@yamanashi.ac.jp (H. Uchida).

Seika, Japan) with an infrared lamp (MILA-5000PN, ULVAC, Japan). As described in Section 3.1, this heat treatment resulted in the formation of an atomically flat Pt-skin layer on each of the Pt–Co alloy single crystals. Then, the disk electrode was embedded in a Teflon sleeve and subjected to the RDE measurement in 0.1 M HClO₄ solution saturated with synthetic ultrahigh-purity air (ZERO-U, Sumitomo Seika, Japan). The 0.1 M HClO₄ electrolyte solution was prepared from HClO₄ (Suprapur, Kanto Chemicals, Japan) and Millipore-Q water. A reversible hydrogen electrode (RHE) was employed as the reference electrode. All the electrode potentials in the present paper referred to the RHE.

The low-energy electron diffraction (LEED, ErLEED100, SPECS, Germany) and low-energy ion scattering (LEIS, Model 1800C, ULVAC-PHI, Japan) measurements were performed in a UHV analysis chamber. Prior to the measurements, the Pt–Co alloy single crystal electrode was annealed in the same manner as described above under a H₂ atmosphere in a separate stainless steel chamber. The Pt–Co single crystal was then transferred to the UHV analysis chamber via a transfer vessel without exposing the electrode surface to air in order to maintain the surface structure and composition. In situ scanning tunneling microscopy (STM) observation of the surface was performed by use of a Nanoscope E (Veeco). The procedure of in situ STM observation has been described in the literature [21].

3. Results and discussion

3.1. Characterization of Pt-skin layer on Pt–Co(111)

Figure 1a shows LEIS spectra for a Pt₈₀Co₂₀(111) surface before and after the heat treatment in H₂. The Co signal around 280 eV disappeared

after the heat treatment, indicating the formation of a Pt-skin layer on the Pt–Co(111). The LEED pattern (Fig. 1b) demonstrated a hexagonal (1 × 1) structure of the Pt-skin layer. Furthermore, we have observed atomically flat terraces of the Pt-skin layer in N₂-purged 0.1 M HClO₄, as shown by an in situ STM image in Figure 1c. It should be emphasized that the STM image exhibits no corrugations in height caused by a lattice mismatch between the Pt-skin layer and the underlying Pt–Co(111) alloy. On the basis of these results, we conclude that the Pt-skin layer formed consists of atomically flat terraces with the same atomic arrangement as the underlying crystal.

3.2. Electrochemical behavior of the Pt-skin layer on Pt–Co(111) surfaces

Figure 2a shows cyclic voltammograms (CVs) of Pt-skin/Pt_{100–x}Co_x(111) single crystal electrodes at various Co atom%, *x*, in N₂-purged 0.1 M HClO₄ solution. We have conducted the CV measurements in a hanging-meniscus configuration with careful attention to exposing only the (111) plane to the solution. The CVs demonstrate the atomically flat (111) terrace of Pt-skin layers with a smaller peak, ascribed to (110) steps, at 0.13 V than those previously reported in Refs. 19 and 20. As compared to the CV of pure Pt(111), dramatic changes were observed in both the hydrogen underpotential deposition (H_{UPD}) and surface oxidation of the Pt-skin/Pt–Co(111) electrodes. The H_{UPD} wave shifted to less positive potentials, and the H_{UPD} charge, *Q*_{HUPD} decreased almost linearly with increasing *x* [22]. Similar phenomena have also been reported for the Pt₃Ni(111) single crystal and Pt-enriched M/Pt(111) model electrodes [12–18]. Because the number of surface Pt sites on the Pt-skin was unchanged, such a decrease in *Q*_{HUPD} can be ascribed to the modified electronic structure of the

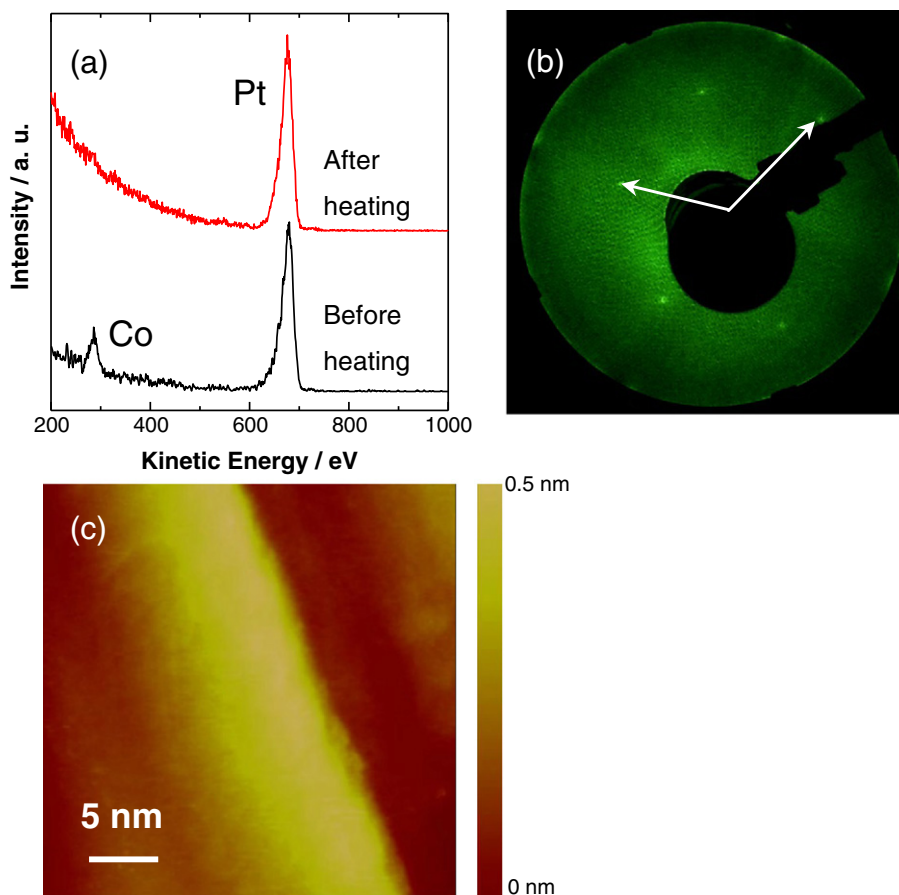


Fig. 1. (a) LEIS spectra for a Pt₈₀Co₂₀(111) electrode before and after the heating under H₂ atmosphere. Incident Ne⁺ ion energy and scattering angle were 1000 eV and 136°. (b) A LEED pattern for the Pt₈₀Co₂₀(111) electrode after the H₂-heating. Incident electron beam energy was 133 eV. (c) An in-situ STM image of a Pt₇₈Co₂₂(111) electrode surface prepared by the H₂-heating at 0.1 V in N₂-purged 0.1 M HClO₄. The set point current and tip potential were 1.6 nA and 0.2 V, respectively.

Download English Version:

<https://daneshyari.com/en/article/178640>

Download Persian Version:

<https://daneshyari.com/article/178640>

[Daneshyari.com](https://daneshyari.com)