Determination of Surface Compositions of Pt-Ru Alloy Thin Films Using Cu Stripping Voltammetry

Hirohisa YAMADA,^{a,*} Toru IKEDA,^b Daisuke SHIMODA,^b Akimasa TASAKA,^b
and Minoru INABA^b

^aDepartment of Chemical Engineering, Nara National College of Technology (22 Yata-cho, Yamatokoriyama, Nara 639-1080, Japan)

^bDepartment of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University (1-3 Tadara-Miyakodani, Kyotanabe, Kyoto 610-0321, Japan)

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Pure Pt, Pure Ru, and Pt-Ru alloy thin films of different compositions (Ru/Pt = 0.5-2.0) were prepared by magnetron sputtering. These thin films were characterized by Cu stripping voltammetry at different deposition potentials. Furthermore, we developed a novel technique to determine the surface Ru/Pt ratio of Pt-Ru alloys using Cu stripping voltammetry. The Ru/Pt ratios calculated from Cu stripping data agreed well with those measured by EDX in the Ru/Pt range of 0.6 to 2.0.

Key Words : Pt-Ru, Alloy, Surface Composition, Under Potential Deposition

1 Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted much attention as power sources to realize low-carbon society in the next generation. Stationary co-generation systems based on PEFCs, called ENEFARM, have been commercialized in Japan since 2009. Durability of PEFCs, which is a big issue for commercialization, has been greatly improved by extensive work by many researchers; however, a longer life over 90,000 h is a big issue for the stacks in 1-kW-class systems. In PEFC-based stationary co-generation systems, Pt-Ru alloy catalyst supported on carbon (Pt-Ru/C), the Ru/Pt ratio of which is typically in the range of 1.0-2.0, is used as an anode catalyst because reformed gas from the city gas as a fuel contains a small amount of CO (~ 1 ppm). It has been reported that the CO tolerance of the Pt-Ru/C catalyst deteriorates gradually in long-term operation, which leads to a significant drop in cell voltage.^{1,2)} This durability issue of the Pt-Ru/C catalyst in PEFCs seems to be common to that in direct methanol fuel cells (DMFCs).³⁾ The major reason for the deterioration of the Pt-Ru/C catalyst is the dissolution of Ru atoms from the catalyst surface during operation, which is especially enhanced at high potentials (typically > 0.8 V). However, many aspects on the stability and durability of the anode Pt-Ru alloy catalyst still remained unclear at present. Recently, we investigated fundamental stability of commercially available Pt-Ru/C catalysts by potential cycling in sulfuric acid, and reported the effects of potential and Ru content on the stability.⁴⁾ In these degradation studies, the surface atomic ratio of Pt-Ru plays an important role in CO tolerance; however, there is no good method to determine the surface atomic ratio in an electrochemical cell during a long-term operation test or an accelerated test at present. In the present study, we report a simple electrochemical method for determining the surface

atomic ratio of the Pt-Ru alloy utilizing Cu stripping voltammetry.^{4,6)}

2 Experimental

Pt-Ru thin films with different compositions prepared by magnetron sputtering were used as samples. Glassy carbon (GC) plates (2×2 cm) were used as substrates. The GC plates were polished to a mirror finish with 1-μm diamond slurry (Maruto Instrument Co., Ltd.) and then cleaned ultrasonically in highly pure water. The Pt-Ru thin films were prepared using a magnetron sputtering equipment (Osaka Vacuum, Ltd., SHK-350) with Pt and Ru targets (diameter: 5 and 2 inch, respectively). While the input power for Ru sputtering was kept at 300 W, that for Pt sputtering was changed in the range of 65-180 W to obtain Pt-Ru thin films of different compositions. Pure Pt and pure Ru thin films were also prepared for comparison. The compositions of the films were determined with an EDX (JEOL Ltd, JED-2300). The surface morphology and the thickness were observed with FE-SEM (JEOL Ltd, JSM-7001FD). The surface was very flat and smooth, and the thickness was ca. 5 μm for each sample. XRD and XPS analyses were conducted using RINT-2500 (Rigaku) with Cu-Kα radiation and using AXIS-165 (Shimadzu) with Mg-Kα radiation (1253.6 eV), respectively.

The electrochemical characterization of the Pt-Ru thin films were conducted using a three-compartment electrochemical cell and a potentiostat (ALS, Model 600C). Sulfuric acid (98 %, Tama Chemical Co., Inc., analytical grade) was diluted with highly pure water to prepare 0.5 M H₂SO₄, which was used as an electrolyte solution. The counter and reference electrodes were a Pt mesh and a reversible hydrogen electrode (RHE), respectively. Argon gas was of ultra-high purity (Taiyo Nissan), and hydrogen gas was obtained from a hydrogen generator

(Round Science, RHG-1000).

The Pt-Ru thin film electrodes were characterized by cyclic voltammetry and Cu stripping voltammetry.^{4,6)} Cyclic voltammetry was performed between 0.05 and 0.6 V at 20 mV s⁻¹ under Ar atmosphere, and a steady-state voltammogram was recorded. For Cu stripping voltammetry, the test electrode was immersed in 2 mM CuSO₄ dissolved in 0.5 M H₂SO₄, and the potential was polarized at 0.30, 0.4, 0.45 and 0.5 V (vs. RHE), at which the underpotential deposition (UPD) of Cu occurs, for 30 min. The potential was then swept from each potential to 0.9 V at 20 mV s⁻¹ to obtain a stripping voltammogram.

Fig. 1 XRD patterns (A), and Ru 3d (B) and Pt 4f (C) XPS spectra on Pt-Ru thin films with Pt:Ru = (a) 5:3, (b) 1:1 and (c) 1:2.

3 Results and Discussion

The compositions of Pt-Ru thin films determined by EDX are shown in Table 1. By changing the input power for Pt, we obtained Pt-Ru thin films with different compositions in the range of Pt:Ru = 2:1 to 1:3. XRD patterns of the Pt-Ru thin films with Pt:Ru ratios of 5:3, 1:1, and 1:2 are shown in Fig. 1 (A). The 5:3 and the 1:1 Pt-Ru thin films gave typical diffraction patterns assigned to the face-centered cubic (fcc) phase of Pt, and any diffraction peaks assigned to the hexagonal closed packing (hcp) phase of Ru were not observed. In contrast, the 1:2 Pt-Ru thin film showed diffraction pattern assigned to the hcp structure, though the peaks were broad and weak and hence the crystallinity was poorer than the 5:3 and 1:1 thin films. In the phase diagram of Pt-Ru,⁷⁾ the hcp phase is not thermodynamically stable at Pt:Ru = 1:2 and therefore it is a meta-stable phase prepared at room temperature. Figures 1 (B) and (C) show XPS Pt_{4f} and Ru_{3d} spectra,^{8,9)} respectively, of the thin films. The peak area of the Pt peaks decreased, while the Ru peaks increased with increasing the Ru content in the film. These changes were in agreement with the results determined by EDX in Table 1.

Figure 2 shows Cu stripping voltammograms (CuSVs) with different deposition potentials for pure Ru, pure Pt and Pt-Ru (1:1) thin films superposing on the respective cyclic voltammograms obtained in 0.5 M H₂SO₄ without

Table 1 Compositions of Pt-Ru thin films obtained by magnetron sputtering.

Input power for Pt (W) ^{a)}	50	65	110	130	160	180
Ru/Pt ^{b)}	2.87	2.05	0.97	0.79	0.62	0.53
Pt:Ru ^{c)}	1:3	1:2	1:1	5:4	5:3	2:1

a) Input power for Ru was 300 W. b) Estimated by EDX.

c) Approximate ratio.

Fig. 2 Cu stripping voltammograms with different deposition potentials for Cu_{UPD} on (a) pure Ru, (b) pure Pt and (c) Pt-Ru (1:1) alloy thin films. Scan rate: 20 mV s⁻¹. Each CuSV is superposed on a cyclic voltammogram measured under Ar atmosphere.

Cu^{2+} ions. It was shown that the CuSVs were quite sensitive to the surface composition. On pure Pt, two stripping peaks at 0.4 and 0.65 V were observed when Cu atoms were deposited at 0.3 V, at which the surface of the Pt thin film was completely covered with a monolayer of Cu_{UPD} . When the deposition potential increased to 0.4 and 0.45 V, at which the surface was covered with an incomplete monolayer of Cu_{UPD} , the area of the 0.4 V peak decreased, while that of the 0.65 V peak did not change appreciably. In contrast to these, only a single stripping peak appeared at 0.4 V on pure Ru. The peak area significantly decreased when the deposition potential increased to 0.4 V, and disappeared when deposited at 0.45 V. This is because oxygen containing species were formed at potentials above 0.4 V on Ru,¹⁰⁾ which prevented the UPD of Cu^{2+} on the Ru surface when deposited at 0.4 and 0.45 V.^{5,11)}

The surface Ru/Pt ratio of Pt-Ru alloy can be correlated with the charges for Cu stripping from Ru atoms and Pt atoms from the full coverage at 0.3 V as:

$$\text{Ru/Pt} = Q_{\text{Ru},0.3}/Q_{\text{Pt},0.3} = (Q_{\text{total},0.3} - Q_{\text{Pt},0.3})/Q_{\text{Pt},0.3} \quad (1)$$

Here $Q_{\text{Ru},0.3}$, $Q_{\text{Pt},0.3}$, and $Q_{\text{total},0.3}$ are the charges for Cu strip-

ping from the Ru, Pt, and the total (Ru + Pt) atoms, respectively, on the Pt-Ru thin film surface when Cu atoms were deposited at 0.3 V. Unfortunately $Q_{\text{Pt},0.3}$ cannot be directly obtained from the CuSV of Pt-Ru alloy thin films. However, because Cu atoms are not deposited on Ru atoms at 0.45 V as shown in Fig. 1 (A), we can obtain the following equation:

$$Q_{\text{total},0.45} = Q_{\text{Pt},0.45} \quad (2)$$

where $Q_{\text{total},0.45}$ and $Q_{\text{Pt},0.45}$ are the charges for Cu stripping from the total (Pt + Ru) and the Pt atoms, respectively, when Cu atoms were deposited at 0.45 V. Furthermore, if we assume the shape of the stripping peaks from Pt atoms is not changed by the Ru/Pt ratio on the surface, $Q_{\text{Pt},0.3}$ can be obtained by the following equation:

$$Q_{\text{Pt},0.3} = RQ_{\text{Pt},0.45} = RQ_{\text{total},0.45} \quad (3)$$

where R is the proportional constant for $Q_{\text{Pt},0.3}/Q_{\text{Pt},0.45}$. Consequently, we can estimate the Ru/Pt surface atomic ratio using the following equation and the values of $Q_{\text{total},0.3}$, $Q_{\text{total},0.45}$, and R :

$$\text{Ru/Pt} = (Q_{\text{total},0.3} - RQ_{\text{total},0.45})/RQ_{\text{total},0.45} \quad (4)$$

Fig. 3 Variation of R in Eq. (4) with the Ru/Pt ratio estimated by EDX.

Fig. 4 Ru/Pt ratios calculated from CuSV data with $R = 1.20$ plotted against those measured by EDX.

The R values of the Pt-Ru thin films with different Ru/Pt ratios, which were obtained using Eq. (4) are plotted against the Ru/Pt ratios estimated by EDX in Fig. 3. The R value was constant in the range of Ru/Pt = 0.6 to 2.0, which confirmed the validity of Eq. (4). Beyond this range (*i.e.* Ru/Pt = 0.5 and 3.0), the R values were slightly lower and higher, respectively, the reason of which is not clear at present. The average value in the range of Ru/Pt = 0.6 to 2.0 was estimated to be 1.20 from Fig. 3. Figure 4 shows the Ru/Pt ratios calculated from CuSV data using Eq. (4) with $R = 1.20$ plotted against those measured by EDX. The Ru/Pt ratios calculated from CuSV data were in good agreement with those measured by EDX in the range of Ru/Pt = 0.6 to 2.0. It should be noted that the CuSV gives the information of the outermost surface of the Pt-Ru alloy, and hence the technique developed in the present study is very useful in the evaluation of the surface Ru/Pt ratio, especially in degradation studies.

4 Conclusion

Pt-Ru thin films of different compositions were prepared by magnetron sputtering. CuSVs were obtained at different deposition potentials. We developed a novel method for the estimation of the surface Ru/Pt ratio using CuSV. The Ru/Pt ratios calculated from CuSV data agreed well with those measured by EDX in the Ru/Pt range of 0.6 to 2.0. It is concluded that the technique developed in the present study is successfully applicable to the analysis of the surface composition of Pt-Ru alloy catalysts.

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