Selectie Dissolution of Pt–Co Binary Alloys and Surface Enrichment of Platinum in Sulfuric Acid Solution

Azusa Ooi1,*,1, Yoshinao Hoshi2,*,2, Eiji Tada1 and Atsushi Nishikata1

1Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo 152-8550, Japan
2Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Tokyo 152-8550, Japan

The selective dissolution of cobalt and the consequent surface enrichment of platinum in Pt–Co binary alloys immersed in 0.5 mmol·m−3 H2SO4 at 298 K were investigated. Four different Pt–Co alloy thin films with various Pt contents, deposited on glassy carbon sheets by physical vapor deposition, were investigated: 51 at% Pt (Pt51–Co49), 43 at% Pt (Pt43–Co57), 28 at% Pt (Pt28–Co72), and 24 at% Pt (Pt24–Co76). When the thin films were immersed for 24 h in a 0.5 mmol·m−3 H2SO4 solution, a Pt-enriched layer was formed on the surface of all the alloys due to Co-selective dissolution. The enriched layer formed in the higher-Pt alloys (Pt51–Co49 and Pt43–Co57) significantly suppressed further dissolution, whereas the lower-Pt alloys (Pt28–Co72 and Pt24–Co76) exhibited more extensive selective dissolution and roughened surfaces. In this study, the selective dissolution and surface morphology of the Pt-Co alloys are discussed on the basis of these experimental results.

Keywords: selective dissolution, platinum–cobalt binary alloy, proton exchange membrane fuel cell, platinum-enriched layer, inductively coupled plasma mass spectroscopy, electrochemical surface area

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered to be an alternative clean energy conversion device because of their low operating temperature and portability.1) A Pt catalyst is used in the cathode of a PEMFC to enhance the oxygen reduction reaction (ORR); however, Pt is very expensive and its resources are limited. Thus, a mechanism of the enhanced ORR activity is explained by the shift in d-band center in the outermost Pt layers (i.e., the ligand effect)2–9) and by induced strain in the Pt-enriched shell (i.e., the geometric effect).8,9)

However, in PEMFCs, performance loss from the degradation of the catalyst is a major issue.1) The degradation of the catalyst is caused by Ostwald ripening via Pt dissolution and coalescence of Pt nanoparticles in pure Pt catalysts.14–19) In addition, for Pt–M alloy catalysts, selective dissolution of M occurs and the dissolved M ions lead to performance loss.1,2,20,21)

Pickering et al. investigated the dissolution behavior of various binary alloys and classified it into two forms: selective dissolution and simultaneous dissolution. These behaviors were explained on the basis of the difference in the standard electrode potential between two metals and their chemical compositions.22–27) In the case of Pt alloys that contain Co, Ni, or Cu, selective dissolution is expected because of the large potential difference between these elements and Pt. Hoshi et al. focused on the selective dissolution of M from Pt–M alloys and performed immersion tests in 0.5 mmol·m−3 H2SO4 (acid treatment) for equimolar Pt–M alloys (M: Cu, Co, Ni, or Fe) prepared by arc-melting. They showed that a Pt-enriched layer is formed on the surfaces of Pt–M alloys because M selectively dissolves from Pt–M binary alloys.20) They further investigated the compositional effect on selective dissolution behavior using three different Pt–Co alloy compositions (Pt: 50, 40, and 30 at%20) in detail. They concluded that in the case of Pt50–Co50 and Pt40–Co60 alloys, a Pt-enriched layer was formed and suppressed further selective dissolution of Co from the matrix; however, in the case of the Pt30–Co70 alloy, the selective dissolution continued after the Pt-enriched layer formed on the alloy surface. They explained this difference on the basis of the number of Co atoms exposed to the electrolyte. However, the change in surface morphology due to selective dissolution is not well understood, and the detailed mechanism of the selective dissolution and consequent Pt-enrichment was not sufficiently discussed in the previous study.28,29) In this work, we prepared four different Pt–Co binary alloy thin films that varied in Pt content (51, 43, 28, and 24 at%) by PVD. We investigated the selective dissolution of Co and the formation of the Pt-enriched layer on the thin films and compared the results with those for the bulk alloys.29) Furthermore, we proposed a detailed mechanism on the basis of the experimental results.

2. Experimental

2.1 Sample preparation

Pt–Co binary alloy thin films with different compositions and a pure Pt thin film were fabricated on glassy carbon (GC) sheets by physical vapor deposition (PVD, ULVAC, Inc., VPC-1100) and their thicknesses were controlled between 150–200 nm by a quartz crystal microbalance controller (ULVAC, Inc., CRTM-6000G). The chemical composition of the alloys was varied by changing the mass ratio of Pt wire (99.98 mass%) and Co wire (99.998 mass%) used during the deposition process. The deposited thin-film samples were vacuum-encapsulated in a silica glass tube at 2.7 × 10−3 Pa,
homogenized at 873 K for 24 h, and cooled in the furnace. To eliminate oxide layers formed during the heat treatment, the sample surface was dry-polished by sputtering via glow discharge optical emission spectroscopy (GD-OES, HORIBA/Jobin Yvon, JY-5000RF).

The morphologies of the sample surfaces were investigated by field-emission scanning electron microscopy (FE-SEM, JEOL Ltd., JSM-7000F) and the photographs were obtained at a 1.2 kV accelerating voltage. The results are presented in Fig. 1. The polished surface morphology of the PVD sample showed that Pt-Co particles were aggregated on the GC substrate and the average grain size was more than 100 nm, but continuously covered the substrate.

2.2 XRD measurements

The chemical composition of the Pt-Co binary thin films prepared by PVD was determined by X-ray diffraction (XRD, PANalytical B.V., X’pert PRO MRD). First, a standard curve of the lattice constant vs. the chemical composition was constructed from the XRD patterns of the bulk Pt-Co binary alloys, 50 at% Pt (Pt50-Co50), 40 at% Pt (Pt40-Co60), and 30 at% Pt (Pt30-Co70), prepared by arc melting and from the pattern of bulk pure Pt. The relationship between the lattice constant $a$ in nm and the Pt content $x_{Pt}$ in at% is given by eq. (1):

$$a = 0.00032x_{Pt} + 0.36108$$ (1)

Figure 2 shows the XRD profiles of Pt-Co thin films prepared by PVD. These diffraction profiles show only typical face-centered cubic peaks in each sample, which demonstrates that the Pt-Co specimens were single-phase and polycrystalline. On the basis of eq. (1), the chemical compositions of the PVD films were determined to be Pt51-Co49, Pt43-Co57, Pt28-Co72, and Pt24-Co76.

2.3 Electrochemical measurements

 Electrochemical measurements were performed at 298 K in an aerated 0.5 mmol·m$^{-3}$ H$\text{2}$SO$_{4}$ solution, using a two-compartment Teflon cell. The solution was prepared by diluting special-grade sulfuric acid with deionized water (resistance > 18 M$\Omega$). The alloy thin films with a geometric surface area of 0.13 cm$^{2}$ were used as working electrodes. A KCl-saturated silver/silver chloride electrode (SSE) was used as the reference electrode, and was connected in double junction to the test solution to prevent chloride contamination of the electrolyte. A gold wire was used as the counter electrode. In this paper, all the potentials are reported against the standard hydrogen electrode (SHE).

Immersion tests were conducted in 0.5 mmol·m$^{-3}$ H$\text{2}$SO$_{4}$ at 298 K for 24 h. Rest potential was monitored during the immersion tests. After the immersion tests, cyclic voltammetry (CV) was performed for 10 cycles between 0 and 1.4 V at 100 mV/s. The dissolved Co ions in the test solution were quantitatively evaluated by inductively coupled plasma mass spectroscopy (ICP-MS, Agilent Technologies, 7700x).

3. Experimental Results and Discussion

3.1 Effect of Pt content on the selective dissolution of Co

The changes in rest potential, $E_{\text{rest}}$, of the Pt and Pt-Co alloy thin films during the 24 h immersion tests are presented in Fig. 3. The $E_{\text{rest}}$ for pure Pt was very stable at 0.798 V. The $E_{\text{rest}}$ for Pt51-Co49 and Pt43-Co57 were slightly lower than that for pure Pt at the initial stage of immersion and finally became 0.785 and 0.796 V, respectively. Their values are very similar to that of pure Pt, indicating that a Pt-enriched layer is formed during the initial stage and strongly suppresses the selective dissolution of Co, although they are lower than those of the previous bulk samples.29) We cannot explain this difference so far, but they exhibited good reproducibility. On the other hand, the changes in the $E_{\text{rest}}$ for Pt28-Co72 and Pt24-Co76 differed substantially compared to those for Pt51-Co49 and Pt43-Co57. The initial potential for Pt28-Co72 and Pt24-Co76 was very low compared to that for the three other
The resting potential $E_{\text{rest}}$ shifted in the negative direction during the initial stage, followed by a positive shift. The negative shift was not reproducible, probably because the $E_{\text{rest}}$ is very sensitive to the initial surface state of the alloys. A similar potential change was also observed for bulk equimolar Pt–Ni alloy in $0.5 \text{ mmol} \cdot \text{m}^{-3} \text{H}_2\text{SO}_4$. The final potentials for Pt–Co and Pt–Co binary alloys in $0.5 \text{ mmol} \cdot \text{m}^{-3} \text{H}_2\text{SO}_4$ solution for 24 h were 0.677 and 0.617 V, respectively, which implies that the selective dissolution of Co still continued, even though a Pt-enriched layer should have been present on the surface.

The amounts of the Co ions dissolved ($\Delta m$) from the Pt–Co alloys during 24 h immersion tests were analyzed by ICP-MS. The results are presented in Fig. 4. The $\Delta m$ decreases with increasing Pt content in the Pt–Co alloys. The amounts of Co dissolved from Pt–Co binary alloys were 0.496, 0.368, 2.51, and 5.77 $\mu$g, respectively. These results agree well with those expected from the $E_{\text{rest}}$ results. A similar tendency has been reported for the bulk Pt–Co alloys.

The selective dissolution behavior of Co dramatically changed between Pt–Co binary thin films with Pt contents of 28 and 43 at%. The relationship between the Pt content in the Pt–Co binary alloys and the amount of Co dissolved is plotted in Fig. 5, together with the data related to bulk Pt–Co alloys. Figure 5 reveals that Pt–Co binary alloy thin films and bulk Pt–Co binary alloys exhibit similar tendencies with respect to the selective dissolution of Co. The Co ions dissolved from Pt–Co alloys ($\Delta m/\mu$g) exponentially increased with decreasing Pt content in the Pt–Co alloys. Recently, a similar trend was reported for the Au–Ag binary alloy system.

### 3.2 Effect of Pt content on ECSA

CV curves of the Pt–Co alloy thin films after the 24 h immersion test were performed to evaluate the electrochemically active surface area (ECSA). The ECSA was calculated on the basis of hydrogen adsorption electric charge ($Q_{\text{H}}$) in the voltammograms, as given by eq. (2):

$$\text{ECSA} = \frac{Q_{\text{H}}}{210}$$

The tenth CV curves for each sample are plotted in Fig. 6. The CV characteristics of all the samples are similar to those of pure Pt, which confirms the formation of a Pt-enriched layer on the surface of the Pt–Co alloys. However, the magnitude of the current density increases as the amount of Pt in the alloys increases. The current density for the Pt–Co binary alloys was approximately seven times greater than that for the Pt–Co alloys.

The average thickness of the Pt-enriched layer ($d$) in monolayers (MLs) for the Pt–Co binary alloy thin films after the 24 h immersion test was approximated from the obtained $\Delta m$ using eqs. (3) and (4) under the assumption that the surface plane is (111):
Selective Dissolution of Pt–Co Binary Alloys and Surface Enrichment of Platinum in Sulfuric Acid Solution

### 3.3 Selective dissolution and surface morphology

Here, we discuss the selective morphology after the selective dissolution. On the basis of the drastic increase in the ECSA for the Pt37–Co63 and Pt34–Co56 alloys, we expected the Pt-enriched layer to be porous. Let us consider that \( n \) pieces of cylindrical pits of radius \( r \) and depth \( d \) are formed and uniformly distributed on the surface as a result of Co selective dissolution and Pt surface diffusion (Fig. 7). The cylinder aspect ratio \( (A_p) \) is represented by eq. (5):

\[
A_p = \frac{d}{2r}
\]

The surface area of a pit \( (S_{pit}) \) is given by the bottom surface \( (S_b) \) and side-wall surface, as shown in eq. (6):

\[
S_{pit} = \pi r^2 + 2\pi rd = S_b(1 + 2d/r)
\]

where \( m_{Co(111)} \) is the weight of Co atoms in a (111) surface atomic layer, \( S_{initial} \) is the initial surface area before the specimen was immersed in sulfuric acid, \( a \) is the lattice constant of the Pt–Co binary alloy, \( N_A \) is Avogadro’s number, \( M_{Co} \) is the atomic weight of Co, and \( x_{Co} \) is the atom fraction of Co. The initial surface of the thin films was not completely flat, as shown in Fig. 1. The \( S_{initial} \) should be larger than the geometric surface area \( (S_{geo} = 0.13 \text{ cm}^2) \). Unfortunately, the \( S_{initial} \) of the Pt–Co alloys is difficult to determine from the ECSA results because the selective dissolution of Co starts quickly after the specimens are immersed in 0.5 mmol·m\(^{-3}\) H\(_2\)SO\(_4\), leading to an increase in the ECSA. Thus, the ECSA of the pure Pt thin film was used as the \( S_{initial} \) for the Pt–Co alloy thin films because the Pt and Pt–Co alloys were prepared by PVD and dry-polished by GD-OES under the same conditions. The ECSA for the Pt thin film was 0.39 cm\(^2\) and remained unchanged during the 24 h immersion in 0.5 mmol·m\(^{-3}\) H\(_2\)SO\(_4\) solution. The roughness factor, defined as \( (S_{initial}/S_{geo}) \), was calculated to be approximately 3.0. The thicknesses of the Pt-enriched layers were estimated by eq. (3) to be approximately 10, 11, 56, and 121 MLs for Pt37–Co63, Pt43–Co57, Pt28–Co72, and Pt24–Co76, respectively; the results are summarized in Table 1. The thickness of the Pt-enriched layer for Pt37–Co63 is slightly thicker than that of the other work\(^{13} \) where Pt–Co nano particles (4–5 nm) were used. This may be caused by the difference in the particle size because Pt surface diffusion rate is much different between nano particles and thin films due to surface energy.\(^{33} \)

### Table 1 ECSA and thickness of the Pt-enriched layer after 24 h of immersion in 0.5 mmol·m\(^{-3}\) H\(_2\)SO\(_4\) solution.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>ECSA ( (S_{total}, \text{ cm}^2) )</th>
<th>Thickness of Pt-enriched layer ( (d, \text{ MLs}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Pt37–Co63</td>
<td>0.86</td>
<td>10</td>
</tr>
<tr>
<td>Pt43–Co57</td>
<td>0.90</td>
<td>11</td>
</tr>
<tr>
<td>Pt28–Co72</td>
<td>6.71</td>
<td>56</td>
</tr>
<tr>
<td>Pt24–Co76</td>
<td>9.69</td>
<td>121</td>
</tr>
</tbody>
</table>

The surface coverage of pits \( (\theta) \) is defined as the ratio of the sum of the bottom surface area of all the pits to the initial surface area \( (S_{initial}) \), as shown in eq. (7):

\[
\theta = \frac{nS_b}{S_{initial}}
\]

Thus, the total surface area \( (S_{total}) \) after the immersion is calculated according to eq. (8):

\[
S_{total} = S_{initial}(1 - \theta) + nS_{pit}
\]

By substituting eqs. (6) and (7) into eq. (8), eq. (9) is obtained:

\[
S_{total} = S_{initial}(1 - \theta) + \theta S_{initial}(1 + 4A_p)
\]

As the \( \theta \) and/or \( A_p \) increase, the \( S_{total} \) increases. Because the \( \theta \) varies between 0 ≤ \( \theta \) ≤ 1, a large value of \( S_{total} \) will result from an increase in \( A_p \) rather than an increase in \( \theta \). Accordingly, in the cases of Pt37–Co63 and Pt24–Co76, deep pits are predicted to form. Indeed, Chen Y-cK et al. used in situ monitoring via transmission X-ray microscopy images to reveal that pit growth progresses in the depth direction in Au–Ag alloys.\(^{30,34} \)

Let us assume that a pit is formed, as shown in Fig. 7, as a result of Co-selective dissolution and Pt-surface diffusion,\(^{17,18} \) i.e., the pit wall consists of pure Pt and Co atoms are exposed at the pit bottom. Accordingly, the coverage of pits \( (\theta) \) can be given by the fraction of Co atoms in Pt–Co alloys, irrespective of the size and the number of pits. Meanwhile, the \( S_{total} \) is equal to the ECSA given by eq. (2). By substituting the values for \( \theta, S_{initial}, \) and \( S_{total} \) into eq. (9), we obtain the values of the aspect ratio \( (A_p) \). The results are presented in Table 2. If the pit depth \( (d) \) is assumed to be equal to the Pt-enriched layer thickness \( (\delta) \) (Fig. 7), the pit

### Table 2 Pit surface coverage and aspect ratio, and radius after 24 h of immersion in 0.5 mmol·m\(^{-3}\) H\(_2\)SO\(_4\) solution.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Pit surface coverage ( (\theta) )</th>
<th>Aspect ratio ( (A_p) )</th>
<th>Radius ( (\text{r/nm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt37–Co63</td>
<td>0.49</td>
<td>0.61</td>
<td>2.3</td>
</tr>
<tr>
<td>Pt43–Co57</td>
<td>0.57</td>
<td>0.57</td>
<td>2.7</td>
</tr>
<tr>
<td>Pt37–Co63</td>
<td>0.72</td>
<td>5.6</td>
<td>1.4</td>
</tr>
<tr>
<td>Pt24–Co76</td>
<td>0.76</td>
<td>7.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>
radius \((r)\) after 24 h immersion can be approximated to be 2–3 nm in all the samples.  

Figure 8 presents the changes in \(\Delta m\) and ECSA as a function of time for bulk Pt\(_{50}\)–Co\(_{50}\) and Pt\(_{30}\)–Co\(_{70}\) alloys, as reported in a previous study.\(^{29}\) As evident in Fig. 8(a), the \(\Delta m\) and ECSA for Pt\(_{50}\)–Co\(_{50}\) remained unchanged with time, which means that the surface of the high-Pt-content thin films (Pt\(_{51}\)–Co\(_{49}\) and Pt\(_{43}\)–Co\(_{57}\)) employed in the present study will be completely covered with a Pt-enriched layer. A schematic drawing of the cross-section of the Pt\(_{51}\)–Co\(_{49}\) specimen is shown in Fig. 9(a). The pit radius was estimated to be 2–3 nm. This value may be overestimated because the Pt-enriched layer (\(\delta\)) may be thicker than the pit depth (\(d\)) as the pit bottom may be covered with the Pt-enriched layer. Accordingly, the actual pit radius for Pt\(_{51}\)–Co\(_{49}\) and Pt\(_{43}\)–Co\(_{57}\) may be even smaller than the estimated values (2–3 nm). In addition, because the \(A_p\) for the Pt\(_{51}\)–Co\(_{49}\) is less than 1 (0.61), the surface of the Pt\(_{51}\)–Co\(_{49}\) appears to not be substantially roughened by the selective dissolution process. However, as indicated in Fig. 8(b), the \(\Delta m\) and ECSA of the bulk Pt\(_{30}\)–Co\(_{70}\) alloy continues to increase linearly with time. Accordingly, in the case of the low-Pt-content alloys (Pt\(_{12}\)–Co\(_{72}\) and Pt\(_{13}\)–Co\(_{76}\), the selective dissolution will likely continue from the bottom of the pits. The pit radius \(r\) was estimated to be 2–3 nm, and the aspect ratio \(A_p\) was estimated to be 5–8 (pit depth: 10–20 nm) after 24 h of immersion. If the dissolution primarily occurs through the Pt-enriched layer, the dissolution rate should decrease with increasing time, and the ECSA should not change substantially. Accordingly, the selective dissolution should primarily occur from the bottom of the pit. A schematic drawing of the cross-section of the Pt\(_{24}\)–Co\(_{76}\) is shown in Fig. 9(b). In the future, we will observe the nanoscale surface morphology to confirm the validity of the proposed mechanism.

4. Conclusion

The selective dissolution behavior of Co from Pt–Co binary alloy thin films, under immersion in 0.5 mmol·m\(^{-3}\) H\(_2\)SO\(_4\), was investigated. The amount of Pt in the Pt–Co binary alloy thin films drastically changed the selective dissolution behavior of Co. At Pt concentrations greater than 40 at% Pt, the surface was completely covered with a Pt-enriched layer (approximately 10 monolayers thick) and further selective dissolution was suppressed. However, at Pt concentrations less than 30 at% Pt, the amount of Co selectively dissolved and the ECSA exponentially increased with decreasing Pt content. These results were successfully described by a model of numerous pits being induced by selective dissolution. In these calculations, the radius of the pits was estimated to be 2–3 nm and the pit aspect ratio \(A_p\) was determined to be 7.8 and 5.6 for Pt\(_{28}\)–Co\(_{72}\) and Pt\(_{28}\)–Co\(_{76}\), respectively, after 24 h of immersion in 0.5 mmol·m\(^{-3}\) H\(_2\)SO\(_4\) solution. The pit growth appeared to progress along the depth direction, which led to a further increase in the ECSA.

Acknowledgments

The authors acknowledge the Center for Advanced Material Analysis, Tokyo Institute of Technology, for assistance with the ICP-MS, GD-OES, and XRD analyses.

REFERENCES

Selective Dissolution of Pt–Co Binary Alloys and Surface Enrichment of Platinum in Sulfuric Acid Solution

1355