The effects of ruthenium-oxidation states on Ru dissolution in PtRu thin-film electrodes

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The effects of ruthenium (Ru)-oxidation states were investigated on Ru dissolution from PtRu thin-film electrodes, with the 200 cycles between 0.4 and 1.05 V (versus normal hydrogen electrode). The Ru-oxidation states of the PtRu thin films were systematically modified by an anodic (oxidation) treatment. The anodic-treated PtRu electrodes, whose methanol-oxidation activity was similar to untreated electrodes before the 200 cycles, showed a remarkable decrease in methanol oxidation after the cycles, because of the Ru dissolution from the PtRu surface. The results suggest that the Ru-oxide species are the origin of Ru dissolution in the PtRu alloy.

I. INTRODUCTION

Direct-methanol fuel cells (DMFCs) have attracted considerable attention as power sources for portable electronic devices because of their high energy density, easy handling of liquid, low operating temperatures, etc.^{1–3} In general, the platinum-ruthenium (PtRu) alloy is currently considered to be the most promising DMFC anode catalyst for methanol oxidation.^{4–7}

Recently, the stability of electrocatalysts has received a great deal of attention, because the electrode performance can degrade after the long-term operation of fuel cells, due to the dissolution of the noble metal-based catalysts and the aggregation of catalyst nanoparticles.⁸ In particular, Piela et al.⁹ reported on DMFCs that Ru from the PtRu anode can cross through the proton exchange membrane (Nafion) and settle on the Pt cathode. This Ru crossover, which originates in Ru dissolution from the PtRu anode, can degrade the performance of all the major components of the fuel cell. It has been reported that the anode potential of a DMFC can vary from ~0.4 to ~1.0 V [versus normal hydrogen electrode (NHE)] during on-off operations, and the Ru dissolution is caused by cycling between the reduced and oxidized states of Ru [thermodynamically, metallic Ru oxidizing to Ru(OH)₃, and RuO₂·2H₂O, respectively, at 0.74 and 0.94 V versus NHE].¹⁰ Accordingly, our group has recently investigated the effects of a metal-phosphate coating layer on the block of Ru crossover.¹¹ However, the origin of Ru dissolution from the PtRu alloy is not completely elucidated. Therefore, it is important to identify the mechanisms of Ru dissolution from PtRu-alloy anodes.

The oxophilic Ru metals as pair sites of Pt metals allow the water dissociation for the promotion of methanol activation, and the adsorption of OH species on the Ru sites facilitates the oxidation of CO on adjacent Pt sites.¹² The oxophilic properties of Ru also allow the easy formation of oxide species, and Ru oxides are present on the PtRu alloy surface at a significant fraction.¹³ Enhanced proton transport in the hydrous Ru oxides (RuO₂·H₂O or RuO_xH_y) in Pt–RuO₂ has been reported.¹⁴ Recently, it was also reported that the mixture of Pt metal and hydrous Ru oxide phase shows better performance than a bimetallic alloy.¹⁵ In this letter, the effects of ruthenium-oxidation states were studied on Ru dissolution from PtRu thin-film electrodes.

II. EXPERIMENTAL

The PtRu thin-film alloy was deposited on indium tin oxide (ITO)-coated glass (Samsung Corning, Cheonan, Korea) by radio frequency magnetron sputtering using Pt and Ru targets. The sputtering was performed under an Ar atmosphere with a flow rate of 30 standard cubic centimeters per minute (sccm) at an operating pressure of 10 mTorr and room temperature (RT). The Ru-oxidation states of the PtRu thin films were modified with an anodic treatment in a 0.5 M H₂SO₄ solution at 1.1 V (versus NHE) for 15 or 30 min at 50 °C. The Ru dissolution from the untreated and anodic-treated PtRu thin-film electrodes was examined with a repeated potential cycling in a 0.5 M H₂SO₄ solution between 0.4 and 1.05 V at RT and a scan rate of 500 mV/s for 200 cycles.

The electrochemical measurements were made with a conventional three-electrode electrochemical system at RT. The PtRu thin-film electrodes, the Pt wire, and the saturated calomel electrode served as the working, counter, and reference electrodes, respectively. All the

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potentials have been converted and are presented versus NHE in this article. The electrochemical properties of the PtRu thin-film electrodes were determined by cyclic voltammetry at potentials ranging from 0.06 to 0.47 V, at a scan rate of 50 mV/s in 0.5 M H₂SO₄. The methanol-oxidation activities on these electrodes were investigated in a solution of 0.5 M H₂SO₄ and 2 M CH₃OH at a scan rate of 50 mV/s. All the solutions were purged with N₂ gas for 30 min before each electrochemical measurement. The chemical bonding states and approximate surface compositions of the Pt and Ru were analyzed by x-ray photoelectron spectroscopy (XPS). The nanostructures of the PtRu thin films were determined by x-ray diffraction, and the surface morphologies were observed with atomic force microscopy (AFM). Before each surface analysis, the electrochemically treated samples were washed with deionized water and dried under vacuum.

III. RESULTS AND DISCUSSION

Figure 1 shows the XPS spectra of the Ru 3p_{3/2} core levels of the PtRu thin films. The spectra show that the Ru-oxidation states were modified significantly by the anodic treatment in the H₂SO₄ solution at 1.1 V. The peaks located at 461.1, 462.2, 463.8, and 466.9 eV can be identified with metallic Ru, RuO₂, hydrous RuO₂, and RuO₃, respectively.^{16,17} As shown in Fig. 1(a), the Ru-oxidation states of the untreated PtRu electrodes con-

sist of metallic Ru (~50%), RuO₂ (~29%), hydrous RuO₂ (~12%), and RuO₃ (~9%). [These values were estimated by XPS fitting to provide a qualitative estimate of the distribution of the Ru-oxidation states. The peaks were fitted using a Doniach-Sunjic line shape (intensity and width),¹⁸ with the four oxidation-state peak positions fixed and with the fitting procedure performed with an XPS curve simulator.^{19,20}] After the anodic treatment for 30 min, the relative amount of metallic Ru decreased to ~28%, while the amounts of RuO₂ and hydrous RuO₂ increased to ~38% and ~26%, respectively. The increase in the concentration of Ru-oxide species was attributed to the formation and accumulation of irreversible Ru oxides with bridged oxygen, OH, and water, during the anodic treatment.²¹ It should be noted, however, that the oxidation states of Pt were not significantly altered by the anodic treatment, as shown in Fig. S1.

Table I shows the active surface areas of the untreated PtRu and the anodic-treated PtRu, as determined with the hydrogen-desorption (Pt-H) method from the cyclic voltammograms in the H₂SO₄ solution before 200 cycles (Fig. S2).²² The increase in the active surface area following the anodic treatments may be due to an increase in surface roughness that resulted from the formation of irreversible Ru-oxide species. It should be noted that the anodic treatment of the PtRu alloy for 30 min at 1.1 V does not considerably alter the surface composition.

The efficiency of the untreated PtRu and the anodic-treated PtRu electrodes for methanol oxidation was evaluated before and after the 200 cycles, as shown in Fig. 2. The current densities in the methanol oxidation were

FIG. 1. XPS spectra of Ru 3p_{3/2} for (a) the untreated PtRu, and anodic-treated PtRu thin films for (b) 15 min and (c) 30 min at 1.1 V.

FIG. S1. XPS spectra of Pt 4f for the untreated and anodic-treated PtRu thin films on the ITO-coated glass. The marked peak positions are from the standard samples of metallic Pt.

TABLE I. The active surface areas were determined using the hydrogen-desorption (Pt–H) method (as shown in Fig. S2), and the approximate surface compositions were estimated by XPS to serve as a qualitative comparison.

Anodic treatment	Before 200 cycles		After 200 cycles	
	Active surface area (per 1 cm ² sample)	Surface composition Pt: Ru (at.%)	Active surface area (per 1 cm ² sample)	Surface composition Pt: Ru (at.%)
Untreated	1.21 cm ²	65: 35	1.41 cm ²	68: 32
15 min at 1.1 V	1.37 cm ²	65: 35	1.58 cm ²	70: 30
30 min at 1.1 V	1.45 cm ²	66: 34	1.99 cm ²	72: 28

FIG. S2. Cyclic voltammograms of thin-film electrodes in the 0.5 M H₂SO₄ solution at a scan rate of 50 mV/s: (a) before and (b) after 200 cycles. (color online)

normalized to the active surface area. The insets in Fig. 2 show the same oxidation data, normalized to the 1 cm² sample area. Before the cycles, the anodic-treated PtRu electrodes and the untreated PtRu electrodes have similar methanol-oxidation activities. It appears that the Ru-oxide species formed as a result of the anodic treatments can contribute to methanol-oxidation activities.^{15,23}

After 200 cycles (0.4–1.05 V at 500 mV/s), the untreated PtRu electrodes showed a small decrease in methanol-oxidation activity. However, the anodic-treated PtRu electrodes, whose activity was similar to that of the untreated electrodes before the 200 cycles, show a remarkable decrease in methanol oxidation. The surface

FIG. 2. Current densities versus applied potentials, which were normalized to the active surface area (Table I), for the untreated and anodic-treated PtRu thin-film electrodes in 0.5 M H₂SO₄ + 2 M CH₃OH: (a) before and (b) after 200 cycles. The insets show methanol oxidation normalized to the 1 cm² sample area. (color online)

areas of the electrodes increased because of the exposure of the Pt centers that resulted from the Ru having been depleted from the PtRu alloy after 200 cycles (Table I and Fig. S2). This Ru depletion is also confirmed by XPS estimates of the composition of Pt and Ru in the PtRu surface. Therefore, the decrease in methanol-oxidation activity [Fig. 2(b)] appears to be attributable to the Ru dissolution from the PtRu surface after 200 cycles.

Figure 3 shows the Ru 3p_{3/2} peak in the XPS spectrum for the PtRu electrodes that were anodic-treated for 30 min, both before and after 200 cycles. The relative amounts of RuO₂ and hydrous RuO₂ decreased after the 200 cycles, which implies that the Ru dissolution from the PtRu alloy is caused by the Ru-oxide species, namely, the non-alloyed and segregated Ru oxides in the PtRu surface (see Fig. S3). For a homogeneous (solid-solution) metallic PtRu alloy, the dissolution potential is expected

FIG. 3. XPS spectra of the Ru $3p_{3/2}$ for the anodic-treated PtRu electrodes at 1.1 V for 30 min: (a) before [same as Fig. 1(c)] and (b) after 200 cycles.

FIG. S3. Schematic illustration of the proposed mechanism of Ru dissolution from the PtRu surface. (color online)

to increase more than the Ru redox potential because of the increase in the critical potential for the dissolution in alloy.^{24,25} Ru dissolution from the PtRu alloy during fuel-cell operation may be caused by the Ru-oxide species

FIG. 4. AFM images of (a) the untreated, (b) anodic-treated PtRu for 30 min at 1.1 V, and (c) after 200 cycles of sample (b).

rather than by the metallic Ru. Therefore, the segregated Ru-oxide species in the PtRu surface have disadvantages in enhancing the long-term stability of the PtRu anode for methanol oxidation.

The surface morphology of the untreated PtRu thin films is shown in Fig. 4(a) by AFM. The surface of the as-deposited PtRu thin films was relatively smooth, with a lateral roughness (root-mean-square peak-to-peak distance) of ~50 nm, and a vertical roughness (root-mean-square peak-to-valley height) of ~2 nm. After the anodic treatments, the formation of segregated Ru-oxide species on the PtRu surface caused the surface to become rough, with a lateral roughness of ~10 nm and a

vertical roughness of ~ 3 nm [Fig. 4(b)]. After the 200 cycles, the surface lateral roughness and vertical roughness remained almost the same [Fig. 4(c)] despite the dissolution of segregated Ru-oxide species on the PtRu surface.

Ru oxidation can occur on the PtRu surface, and these oxide precipitates make the surface rougher than before. The decreased peak-to-peak distance from ~ 50 to ~ 10 nm can be attributed to the existence of sites with Ru-oxide precipitates. Because of the dissolution of Ru oxides, the surface roughness looks the same after 200 cycles. This rough estimation indicates that the size of the segregated Ru-oxide species is on a nanometer scale. These are illustrated in Fig. S3.

IV. CONCLUSIONS

The effects of Ru-oxidation states were investigated on the Ru dissolution from PtRu thin-film electrodes to compare the alloyed Ru metal with several Ru-oxide species. The Ru-oxidation states in the PtRu thin-film electrodes were modified systematically by the anodic treatment. The surface of PtRu thin-film electrodes was altered and Ru-oxide species were formed. However, these oxide species were more easily dissolved than the alloyed Ru metal. Therefore, we suggest that the Ru dissolution in the PtRu alloy is attributable to the segregated Ru-oxide species in the PtRu surface. For the long-term stability of Ru-based catalysts, further studies of various Ru oxides should be pursued, on specific comparison between hydrous and anhydrous Ru oxide.

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