Suppression of CO Adsorption on PtRu/C Catalysts Modified with Metallic Ruthenium Nanosheets

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PtRu/C catalysts were modified with one-atom-thick metallic Ru nanosheets, and the electrocatalytic activity as well as long term durability were studied for use as an anode catalyst in polymer electrolyte fuel cells. Metallic Ru nanosheet-PtRu/C composite catalysts were obtained by hydrogen reduction of RuO2.1 nanosheet-modified PtRu/C. The hydrogen oxidation reaction activity in 300 ppm CO/H2 saturated 0.1 M HClO4 at 20 mV vs. RHE increased from 89 A (g-PtRu)−1 to 124 A (g-PtRu)−1 for metallic Ru nanosheet modified PtRu/C catalyst. After the accelerated durability test, the hydrogen oxidation reaction activity for the modified catalyst was 1.8 times higher than that of PtRu/C. The results suggest that the CO tolerance and durability of PtRu/C can be easily improved by adding metallic Ru nanosheets.

In this study, we have pursued the use of metallic Ru nanosheets instead of RuO2.1 nanosheets as an additive to enhance the CO tolerance of PtRu/C. By the metallization of RuO2.1 nanosheets to metallic Ru nanosheets, metallic Ru should be in intimate contact with the surface of PtRu nanoparticles, while still maintaining the high surface area of Pt, which we anticipated would lead to an enhancement of CO tolerance.

Experimental

Catalyst preparation.—Commercial PtRu/C (Tanaka Kikinzoku Kogyo K.K., TEC66E50; 32.4 mass% Pt, 16.8 mass% Ru) was used as-received. RuO2.1 nanosheet was derived via exfoliation of layered H2−RuO2.1·nH2O through a process reported previously.25,26 Briefly, 0.1 g of layered H2−RuO2.1·nH2O was added to an aqueous solution of 10% tetrabutylammonium hydroxide (TBA2+·OH−), adjusted to a solid-liquid ratio of 4 g L−1 (TBA2+/H2O = 1.5). The mixture solution was shaken for 10 days and then centrifuged at 2000 rpm for 30 min to remove any non-exfoliated material. The RuO2.1 nanosheet modified PtRu/C (RuO2.1ns-PtRu/C) catalyst was synthesized following our previous recipe.23 RuO2.1 nanosheet colloid was added to an aqueous PtRu/C suspension with a molar ratio of RuO2.1/PtRu = 0.5/1/1. The dispersion was magnetically stirred and ultrasonicated to ensure homogeneous reaction. After sedimentation, the composite was washed with ultrapure water and dried to yield the RuO2.1ns-PtRu/C catalyst as a powder. RuO2.1ns-PtRu/C was reduced under a constant flow of N2(90%) gas at 200 °C for 2 hours to prepare the metallic Ru nanosheet-modified PtRu/C catalyst (Ru(n)s-PtRu/C). Carbon supported metallic Ru nanosheet sample with no PtRu nanoparticles (Ru(n)s/C, 30 mass% Ru supported on Ketjen black (Lion Corp., EC-300J), was prepared by a similar procedure, for sake of comparison. Ru nanoparticles supported on Ketjen black (Ru(np)/C, 30 mass%, average diameter 2.8 ± 0.3 nm) was also synthesized by a conventional impregnation method as a control sample.27

Structural characterization.—The structure was characterized by X-ray diffraction (XRD; Rigaku, RINT-2500 with monochromated Cu Ka radiation at 40 kV and 40 mA). Atomic force microscopy (AFM; Bruker, NanoScope IIIa) was used for morphological characterization. The morphology was also characterized by transmission electron microscopy (TEM; JEOL, JEOL 2010, accelerated voltage of 200 kV) and field-emission scanning electron microscopy (FE-SEM; Hitachi, S-5000, accelerated voltage of 20 kV). X-ray photoelectron spectrometry (XPS; Kratos Analytic Ltd., AXIS-ULTRA DLD,

PtRu binary alloy nanoparticles supported on carbon (PtRu/C) is presently used as the anode catalyst for polymer electrolyte fuel cells in residential fuel cell systems.1–4 Carbon monoxide, which is present in the reformate as a trace impurity, rapidly and strongly adsorbs on the Pt surface, blocking the hydrogen oxidation reaction (HOR) sites.9 The onset potential for the oxidation of adsorbed CO on PtRu is about 200 mV lower than Pt.11 However, the onset potential is higher than the typical anode potential when operated at low current density,12 which means that adsorption of CO on the PtRu surface will lead to gradual loss of cell performance. Therefore, catalysts with enhanced CO tolerance at a potential near the H+/H2 potential are necessary to improve the performance of present residential fuel cells.

CO tolerance can be enhanced either by developing catalysts with higher CO oxidation capability at low potential or by suppressing the adsorption of CO on the catalyst surface. Decreasing the overpotential for the oxidation of adsorbed CO has been conducted by fine control of the nanostructure and composition, as well as extension to ternary and more complicated alloys.12,13 For example, decoration of Pt nanoparticles with Ru atoms was shown to give rise to high CO tolerance.14–18 PtRu nanoplatelets synthesized by galvanostatic replacement of Pb0 supported on carbon by Pt and Ru was reported to show high methanol oxidation activity.19 The high CO tolerance has been attributed to the synergistic effect between Pt and Ru atoms, i.e., the CO mobility on the catalyst surface from Pt to Ru was increased by the intimate contact of the atoms. Despite such improved performance, the Ru decoration simultaneously decreases the amount of Pt on the surface and contact of the atoms. Despite such improved performance, the Ru decoration simultaneously decreases the amount of Pt on the surface and contact of the atoms. Despite such improved performance, the Ru decoration simultaneously decreases the amount of Pt on the surface and contact of the atoms. Despite such improved performance, the Ru decoration simultaneously decreases the amount of Pt on the surface and contact of the atoms. Thus, the design of CO tolerant catalysts should be considered by an additive that does not block HOR sites, while reducing CO adsorption, and/or enhancing the CO oxidation activity.

We recently reported a concept that is different to conventional alloys or composites, which is based on the addition of RuO2.1 nanosheets to commercial PtRu/C. The composite catalyst effectively improves the HOR activity and CO tolerance in 300 ppm CO containing H2 gas.21 The enhanced catalytic behavior was attributed to the suppression of CO adsorption to active sites for HOR.

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15 kV and 10 mA, Mg Kα standard) was conducted for analysis of the chemical state of Pt and Ru.

**Electrochemical characterization.**—Electrochemical measurements were conducted with a rotating disk electrode (Nikko Keisoku, SC-5) connected to an automatic polarization system (Hokuto Denko, HSV-100). Catalyst suspensions were prepared by dispersing 18.5 mg of the catalyst in 25 mL of 2-propanol/water solution (75/25 volume ratio). A 5 wt% Nafion solution (100 μL) was added to the catalyst suspension as a proton conducting binder to ensure adhesion. The working electrode was prepared by depositing 5.5 μg-carbon cm⁻² on a mirror-polished glassy carbon rod (6 mm diameter), which corresponds to approximately a monolayer in height of the carbon black particles, and vacuum dried at 60°C for 30 min. A carbon fiber (Toho Tenax Co., HTA40 E13 K 200tex) was used as a counter electrode, and a reversible hydrogen electrode (RHE) was used as a reference electrode. All electrochemical measurements were performed in 0.1 M HClO₄ at 25°C.

Potential cycling between 5 and 800 mV vs RHE at a scan rate of 100 mV s⁻¹ was conducted for 20 cycles to clean the catalyst surface. The electrochemically active surface area (ECSA) of the catalyst was characterized by CO stripping voltammetry. Gaseous CO was purged into the electrolyte for 40 min while maintaining a constant potential of 100 mV vs. RHE. Excess CO in the electrolyte was purged out by bubbling N₂ gas for 40 min. Pre-adsorbed CO (COad) was electro-oxidized by voltammetry at a scan rate of 10 mV s⁻¹. The amount of COad was estimated by integration of the COad stripping peak, corrected for the electrical double-layer capacitance, assuming a monolayer of linearly adsorbed CO on the metal surface and the Columbic charge necessary for oxidation as 420 μC cm⁻². The HOR activity in pure H₂ was measured by chronoamperometry at 20 mV vs. RHE at a rotation rate of 400 rpm. After characterization in 0.5 M H₂SO₄ solution to estimate the surface Ru composition of the catalysts. The potential was kept at 300 mV vs. RHE for 120 sec, and then the potential was swept up to 800 mV vs. RHE at a scan rate of 100 mV s⁻¹. Surface Ru composition was determined from the ratio of the charge from the first and second peak, which are associated with the Cu oxidation charge on Ru and Pt, respectively.

![Figure 1](image1.png)

**Figure 1.** Typical (a) HR-SEM, (b) TEM images and (c) corresponding PtRu particle size distribution derived from (b) for Ru(ns)-PtRu/C.

**Results and Discussion**

**Structural characterization of PtRu/C catalysts modified with metallic Ru nanosheets.**—Figure 1 shows typical HR-SEM and TEM images of metallic Ru nanosheet-modified PtRu/C and the corresponding histogram of the PtRu nanoparticle size distribution obtained from TEM. The average diameter of PtRu nanoparticles for Ru(ns)-PtRu/C was 4.3 ± 0.4 nm, comparable to that of as-received PtRu/C (4.2 ± 0.3 nm) (Fig. S1). This shows that the PtRu nanoparticles do not grow by the metallization process. The XRD patterns for all catalyst give the typical diffraction peaks of the face-centered cubic phase of PtRu (Fig. S2). The fcc(220) diffraction peak at 2θ = 68.5° (d = 0.1369 nm) in Ru(ns)-PtRu/C was identical in peak position and width to PtRu/C and RuO₂₁₁₇-PtRu/C (Fig. 2), indicating the alloying state of PtRu nanoparticles is the same for all catalysts. Peaks associated with metallic Ru nanosheets (2D-hcp) are not observed due to the low content. Figure 3 shows the Ru 3p½ XPS data for PtRu/C, RuO₂₁₁₇-PtRu/C and Ru(ns)-PtRu/C. The Ru 3p½ spectra could be deconvoluted into two components for metallic Ru and ruthenium in a higher oxidation state (hydrous ruthenium oxide) (Table I). XPS analysis of RuO₂₁₁₇-PtRu/C (Fig. S3) reveals that all of Ru⁺⁺⁺ is reduced to Ru⁰⁺ by the H₂ treatment. Thus, Ru⁺⁺⁺ is assigned to partially oxidized ruthenium in the pristine PtRu/C that cannot be reduced with H₂ at 200°C. XPS data shows that 45 at.% of Ru in PtRu/C is oxidized due to atmospheric exposure, in agreement with other studies. The ratio of Ru⁺⁺⁺ is naturally higher for RuO₂₁₁₇-PtRu/C (53 at.%) than that of PtRu/C (45 at.%), owing to the addition of RuO₂₁₁₇ nanosheet. After H₂ reduction, the Ru⁰⁺ content for RuO₂₁₁₇-PtRu/C increased to 61 at.% from 47 at.% for RuO₂₁₁₇-PtRu/C. No change in the Pt 4f spectra is evident (Fig. S4).

![Figure 2](image2.png)

**Figure 2.** XRD patterns of PtRu/C, RuO₂₁₁₇-PtRu/C and Ru(ns)-PtRu/C.

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The ECSA of RuO2.1ns-PtRu/C is estimated as 15.3% and 84.7%, respectively (Fig. S5). This is in excellent agreement with the nominal atomic ratio of 15.6% for Ru(ns)-PtRu/C.

Based on these data and our previous work,24 it is concluded that H2 treatment of RuO2.1ns-PtRu/C at 200 ◦C successfully converted the RuO2 nanosheets to metallic Ru nanosheets, as evidenced from the higher ECSA of Ru(ns)-PtRu/C, which is attributed to the modification with metallic Ru nanosheets and PtRu nanoparticles.

The onset and peak potential of the COad oxidation for Ru(ns)-PtRu/C were observed at 300 and 520 mV vs. RHE, respectively. These potentials are shifted 30 mV negative compared to PtRu/C (onset potential at 330 mV vs. RHE and peak potential at 550 mV vs. RHE). The results suggest that the modification of metallic Ru nanosheet effectively enhanced the oxidation of COad for PtRu/C. It is well known that Ru promotes the oxidation of COad by supplying an oxygen source to adjacent Pt sites via the so-called bi-functional mechanism.36 The lower onset potential may be a signature of a bi-functional effect between metallic Ru nanosheet and PtRu alloy nanoparticles. The lower peak potential and the sharper peak suggests improved kinetics of the COad oxidation for Ru(ns)-PtRu/C. As shown in Fig. 4d, the peak potential for Ru(ns)/C and Ru(np)/C was 520 and 530 mV vs. RHE; Ru/ns)/C exhibits slightly faster reaction kinetics for oxidation of COad than Ru(np)/C. From the result, the negative shift of onset and peak potential for Ru(ns)-PtRu/C in comparison with PtRu/C is attributed to the modification with metallic Ru nanosheet, which acts as a promoter for COad oxidation.

**HOR activity and CO tolerance.—**Hydrodynamic voltammograms of HOR in pure H2 for PtRu/C, RuO2.1ns-PtRu/C and Ru(ns)-PtRu/C are compared in Fig. 5a. Diffusion limited current (jlim) is obtained above 100 mV vs. RHE. The voltammograms of RuO2.1ns-PtRu/C show comparable behavior to PtRu/C, indicating that the addition of RuO2 nanosheets does not obstruct the HOR activity. The jlim for Ru(ns)-PtRu/C was also similar to that of PtRu/C. Thus, the modification with metallic Ru nanosheet does not interfere with HOR sites on PtRu surface.

Hydrodynamic voltammograms of HOR in the presence of trace CO (300 ppm CO/H2) are compared in Fig. 5b. The HOR current for all of the catalysts were smaller than that in pure H2, which is attributed to adjacent Pt sites via the so-called bi-functional mechanism.36 The lower peak potential and the sharper peak suggests improved kinetics of the COad oxidation for Ru(ns)-PtRu/C. As shown in Fig. 4d, the peak potential for Ru(ns)/C and Ru(np)/C was 520 and 530 mV vs. RHE; Ru/ns)/C exhibits slightly faster reaction kinetics for oxidation of COad than Ru(np)/C. From the result, the negative shift of onset and peak potential for Ru(ns)-PtRu/C in comparison with PtRu/C is attributed to the modification with metallic Ru nanosheet, which acts as a promoter for COad oxidation.

![Figure 3. X-ray photoelectron spectra of the Ru 3p3/2 region for (a) PtRu/C, (b) RuO2.1ns-PtRu/C, and (c) Ru(ns)-PtRu/C. Red and blue lines are the deconvoluted fitted lines assigned to Ru0 and Ru+1, respectively.](image)

![Figure 4. COad stripping voltammograms for (a) PtRu/C, (b) RuO2.1ns-PtRu/C, (c) Ru(ns)-PtRu/C, (d) Ru(ns)/C, and (e) Ru(np)/C in 0.1 M HClO4 at a scan rate of 10 mV s−1. Solid line: 1st cycle after CO adsorption; broken line: 2nd cycle.](image)
to CO poisoning of the catalyst surface. In the case of PtRu/C, the HOR current below the onset of CO oxidation was less than half of that in pure H₂. Upon polarization above 300 mV vs. RHE, the current increases due to the oxidation of weakly adsorbed CO on the catalyst surface.\(^{37}\) CO\(_{ad}\) oxidation in 300 ppm CO/H₂ is observed at a lower potential than the CO\(_{ad}\) oxidation onset potential from CO\(_{ad}\) stripping voltammetry (Fig. 4), due to the low CO coverage.\(^{37}\)

In sharp contrast, high HOR current is observed in the case of RuO\(_2\)-ns-PtRu/C and Ru(ns)-PtRu/C even at low potential. The HOR current at 200 mV vs. RHE for Ru(ns)-PtRu/C was higher than that of PtRu/C and RuO\(_2\)-ns-PtRu/C. The results indicate that the modification with metallic Ru nanosheets effectively improves the CO tolerance.

Figure 6a shows chronoamperograms in pure H₂ at 20 mV vs. RHE (\(\omega = 400 \text{ rpm}\)) for PtRu/C, RuO\(_2\)-ns-PtRu/C, and Ru(ns)-PtRu/C. The HOR activity is normalized to the total mass of metal. The HOR activity in pure H₂ (steady-state current after 20 min) for RuO\(_2\)-ns-PtRu/C and Ru(ns)-PtRu/C was similar to or slightly higher than PtRu/C. Chronoamperograms in 300 ppm CO/H₂ are shown in Fig. 6b. The HOR activity of all catalysts decreased sharply in the first 60 min due to accumulation of CO on the catalyst surface, and then leveled off to a quasi-steady current (notice that the potential applied for 20 mV vs. RHE is much lower than the onset potential of CO\(_{ad}\) oxidation). Taking the quasi-steady state HOR current at 5 hours as a measure of HOR activity, Ru(ns)-PtRu/C has 1.3 times higher activity (124 A (g-PtRu)\(^{-1}\)) than that of PtRu/C (93 A (g-PtRu)\(^{-1}\)). Excluding the mass of metallic Ru nanosheets (which contributes marginally to HOR), the HOR activity is 132 A (g-PtRu)\(^{-1}\). The decreasing rate of HOR activity, estimated from the change in the HOR current divided by the time from 3 to 5 hours was 1.7 A (g-PtRu)\(^{-1}\) hour\(^{-1}\) for PtRu/C. In the case of Ru(ns)-PtRu/C, a steady-state is obtained after 3 hours (decreasing rate is negligible, 0 A (g-PtRu)\(^{-1}\) hour\(^{-1}\)). Fig. 6c shows the ratio of current decay normalized by the current at 0 sec. It can be seen that the CO poisoning in the initial 60 min is impeded for Ru(ns)-PtRu/C. More importantly, steady-state current was obtained after 3 hours for Ru(ns)-PtRu/C, while for PtRu/C, a continuous decrease in current was observed even after 5 hours of polarization. Since the onset of CO\(_{ad}\) oxidation occurs above 200 mV vs. RHE (Figs. 4 and 5), electronic and bi-functional effects cannot explain the enhanced HOR activity at 20 mV vs. RHE in 300 ppm CO/H₂. Conversely, the enhancement in CO tolerance by the modification with metallic Ru nanosheets is most likely due to the suppression of CO adsorption on the Pt surface.

**Durability of the catalysts.—** The HOR activity (measured at \(E = 20 \text{ mV}\) vs. RHE with \(\omega = 400 \text{ rpm}\) after 60 min) after accelerated durability test (ADT) at 1000 and 3000 steps are compared with the initial activity in Table II. The retention in HOR activity is more pronounced for the Ru(ns)-PtRu/C. After the 3000 potential step ADT test, the HOR current of Ru(ns)-PtRu/C was 97 A (g-PtRu)\(^{-1}\), 1.8 and 1.3 times higher than PtRu/C (55 A (g-PtRu)\(^{-1}\)) and RuO\(_2\)-ns-PtRu/C (75 A (g-PtRu)\(^{-1}\)), respectively. Based on Cu-stripping voltammetry, the surface Ru composition of PtRu/C decreased from 16 to

Figure 5. Hydrodynamic voltammograms (anodic scan, 20 mV s\(^{-1}\)) with a rotation rate of 400 rpm in 0.1 M HClO\(_4\) saturated with (a) pure H₂ or (b) 300 ppm CO/H₂ for PtRu/C (black line), RuO\(_2\)-ns-PtRu/C (blue line) and Ru(ns)-PtRu/C (red line).

Figure 6. Chronoamperograms at 20 mV vs. RHE with a rotation rate of 400 rpm in 0.1 M HClO\(_4\) saturated with (a) pure H₂ and (b) 300 ppm H₂/CO for PtRu/C (black line), RuO\(_2\)-ns-PtRu/C (blue line) and Ru(ns)-PtRu/C (red line). (c) Chronoamperograms from (b) shown in normalized current.
The CO tolerance of commercial PtRu/C was improved by the modification with metallic Ru nanosheets, which was obtained by the metallization of RuO₂ nanosheets derived from layered K₂RuO₂. In the presence of trace CO (300 ppm CO/H₂), the HOR current at 20 mV vs. RHE of PtRu/C increased to 124 A (g-PtRu)⁻¹ from 89 A (g-PtRu)⁻¹ by the modification with metallic Ru nanosheets. The durability of the catalyst was also improved by the modification with metallic Ru nanosheets. The HOR activity of Ru(ns)-PtRu/C after accelerated durability test was 97 A (g-PtRu) with metallic Ru nanosheets. The HOR current of Ru(ns)-PtRu/C after 300 potential step ADT testing increased to 124 A (g-PtRu) at 20 mV vs. RHE before and after durability test.

The CO tolerance of commercial PtRu/C was improved by the modification with metallic Ru nanosheets, which was obtained by the metallization of RuO₂ nanosheets derived from layered K₂RuO₂. In the presence of trace CO (300 ppm CO/H₂), the HOR current at 20 mV vs. RHE of PtRu/C increased to 124 A (g-PtRu)⁻¹ from 89 A (g-PtRu)⁻¹ by the modification with metallic Ru nanosheets. The durability of the catalyst was also improved by the modification with metallic Ru nanosheets. The HOR current of Ru(ns)-PtRu/C after accelerated durability test was 97 A (g-PtRu)⁻¹, which is 1.8 times higher than PtRu/C (55 A (g-PtRu)⁻¹). The enhancement in HOR activity and durability in the presence of CO by the modification with metallic Ru nanosheets most likely suggests suppression of CO adsorption on the catalyst surface.

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### Table II. HOR activity acquired by chronoamperometry at 20 mV vs. RHE before and after durability test* of catalysts.

| Catalyst        | Initial | After 1000 cycles | After 3000 cycles |
|-----------------|---------|-------------------|-------------------|
| PtRu/C          | 89      | 64                | 55                |
| RuO₂₁₃ns-PtRu/C | 111     | 86                | 75                |
| Ru(ns)-PtRu/C   | 124     | 112               | 97                |

*Accelerated durability test (ADT) in 300 ppm CO/H₂ was conducted by square-wave potential stepping between 5 and 400 mV vs. RHE with a holding time of 3 seconds at each potential.

### Conclusions

The CO tolerance of commercial PtRu/C was improved by the modification with metallic Ru nanosheets, which was obtained by the metallization of RuO₂ nanosheets derived from layered K₂RuO₂. In the presence of trace CO (300 ppm CO/H₂), the HOR current at 20 mV vs. RHE of PtRu/C increased to 124 A (g-PtRu)⁻¹ from 89 A (g-PtRu)⁻¹ by the modification with metallic Ru nanosheets. The durability of the catalyst was also improved by the modification with metallic Ru nanosheets. The HOR current of Ru(ns)-PtRu/C after accelerated durability test was 97 A (g-PtRu)⁻¹, which is 1.8 times higher than PtRu/C (55 A (g-PtRu)⁻¹). The enhancement in HOR activity and durability in the presence of CO by the modification with metallic Ru nanosheets most likely suggests suppression of CO adsorption on the catalyst surface.

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