



## Suppression of CO Adsorption on PtRu/C and Pt/C with RuO<sub>2</sub> Nanosheets

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RuO<sub>2</sub> nanosheets were studied as a promotor for the hydrogen oxidation reaction in the presence of 300 ppm CO/H<sub>2</sub>. The hydrogen oxidation current in 300 ppm CO/H<sub>2</sub> for RuO<sub>2</sub> nanosheet modified PtRu/C catalyst (RuO<sub>2</sub>:Pt:Ru = 0.5:1:1 (molar ratio)) exhibited higher CO tolerance than Pt<sub>1</sub>Ru<sub>1</sub>/C and Pt<sub>2</sub>Ru<sub>3</sub>/C. Based on hydrodynamic voltammetry, chronoamperometry and CO stripping voltammetry, the addition of RuO<sub>2</sub> nanosheets is suggested to suppress CO adsorption on the catalyst surface, resulting in an improvement in CO tolerance.

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Polymer electrolyte fuel cells for stationary applications run on reformed fuel, which is produced through the fuel processing system from raw fuel gas. The United States Department of Energy has set a target cell voltage of over 0.7 V at 0.2 A cm<sup>-2</sup> for 2020,<sup>1</sup> which translates to an anode potential of less than 0.2 V.<sup>2</sup> At this potential, carbon monoxide (CO), which is present in the reformat as a trace impurity, readily adsorbs on the electrocatalyst surface and blocks the hydrogen oxidation reaction (HOR) site.<sup>3</sup> This leads to a decrease in cell voltage and overall performance.<sup>4</sup> CO-tolerant PtRu binary nanoparticles supported on carbon (PtRu/C) are presently used as the anode catalyst.<sup>4–11</sup> However, even with state-of-the-art PtRu/C, the CO concentration must be cut down to 10 ppm, which leads to high system cost. Catalysts with enhanced CO tolerance at low anode potential (<0.2 V vs. RHE) are expected to improve the performance of present residential fuel cells, and may also realize next-generation fuel cells with a simplified fuel processing system running on reformat with higher CO concentration.

In general, CO tolerance can be enhanced either by developing catalysts with higher CO oxidation capability or by suppressing the adsorption of CO. Decreasing the overpotential for adsorbed CO oxidation has been conducted by fine control of the nanostructure and composition, as well as extension to ternary and more complicated alloys.<sup>12,13</sup> Approaches to suppress CO adsorption has also been suggested; for example Rh-porphyrine,<sup>14</sup> organic metal complexes<sup>15</sup> or metal oxides<sup>16–22</sup> have been proposed as additives to Pt-based catalysts.

Metal oxides have been suggested to behave as co-catalysts for CO tolerant catalysts via different mechanisms. TaO<sub>x</sub> and NbO<sub>x</sub> have been reported to weaken the adsorbed CO bond on the Pt surface and enhanced the CO tolerance of Pt/C.<sup>16</sup> The water-gas shift reaction has been suggested to be responsible for the improvement in the CO tolerance of Pt/C modified with MoO<sub>x</sub>.<sup>17,18</sup> The SnO<sub>2</sub> modified PtRu/C<sup>19–22</sup> possessed improved cell performance under a high CO concentration of 500 ppm CO/H<sub>2</sub>, which was attributed to a combination of the promotional effect of SnO<sub>2</sub> and Ru species on CO tolerance. In many cases, the oxide additive partially covers the alloy surface and leads to a decrease in the electrochemically active PtRu surface area and thus the HOR activity. The goal is thus to use an additive that does not block the HOR site but reduces CO adsorption and/or enhances CO oxidation. In this study, we have pursued the use of RuO<sub>2</sub> nanosheets as an additive to commercial Pt<sub>1</sub>Ru<sub>1</sub>/C. It will be shown that RuO<sub>2</sub> nanosheets improves HOR activity and CO tolerance

in 300 ppm CO/H<sub>2</sub> saturated electrolyte, leading to enhanced anode properties.

### Experimental

Pt<sub>1</sub>Ru<sub>1</sub>/C (TEC66E50, 32.4 mass% Pt, 16.8 mass% Ru), Pt<sub>2</sub>Ru<sub>3</sub>/C (TEC61E54, 30.0 mass% Pt, 23.3 mass% Ru), and Pt/C (TEC10E50E, 47.5 mass% Pt) were purchased from Tanaka Kikinzoku Kogyo K.K., and used as-received. The composite catalyst was synthesized following our previous recipe for RuO<sub>2</sub> nanosheet modified Pt/C.<sup>23–25</sup> RuO<sub>2</sub> nanosheet was derived via exfoliation of layered H<sub>0.2</sub>RuO<sub>2.1</sub>·*n*H<sub>2</sub>O through a process reported previously.<sup>26,27</sup> Composite catalysts were prepared by adding the RuO<sub>2</sub> nanosheet colloid to aqueous suspensions of Pt<sub>1</sub>Ru<sub>1</sub>/C or Pt/C with a molar ratio of RuO<sub>2</sub>/Pt/Ru = 0.5/1/1 (RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C) or RuO<sub>2</sub>/Pt = 0.5/1 (RuO<sub>2</sub>ns-Pt/C), respectively.

Electrochemical measurements were conducted with a rotating disk electrode (Nikko Keisoku). Catalyst suspension was prepared by dispersing 18.5 mg of catalyst in 25 ml of 2-propanol/water and 0.1 ml of 5 wt.% Nafion solution. The working electrode was prepared by depositing 5.5 μg-carbon cm<sup>-2</sup> of the catalyst ink on a mirror-polished glassy carbon rod (6 mm in diameter) and vacuum dried at 60°C for 30 min. A carbon fiber (Toho Tenax Co., HTA-3K) 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 HClO<sub>4</sub> at 25°C.

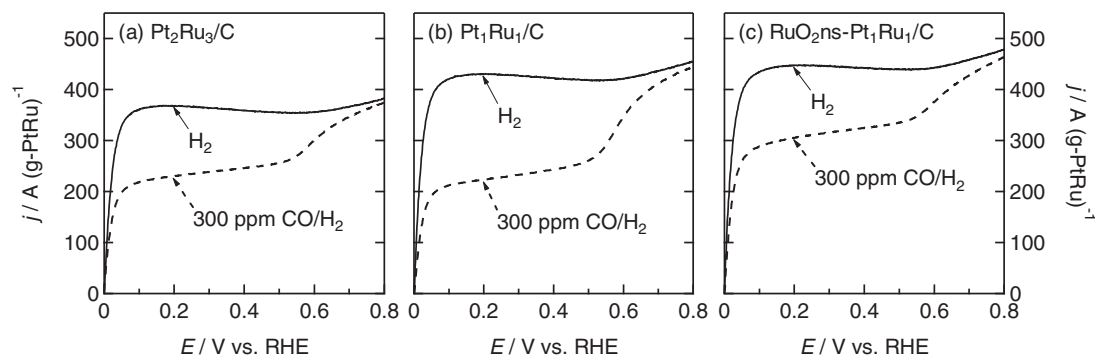
### Results and Discussion

The hydrodynamic linear sweep voltammograms (anodic scan) taken in pure H<sub>2</sub> for Pt<sub>2</sub>Ru<sub>3</sub>/C, Pt<sub>1</sub>Ru<sub>1</sub>/C and RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C are compared in Fig. 1. The RuO<sub>2</sub> nanosheets supported carbon composite has poor hydrogen oxidation reaction activity (Fig. S1). The current due to the hydrogen oxidation reaction (HOR) from RuO<sub>2</sub> nanosheets (which is negligibly small) has been subtracted from the HOR current for RuO<sub>2</sub>ns-PtRu/C. The hydrogen oxidation current of as-received Pt<sub>1</sub>Ru<sub>1</sub>/C is higher than Pt<sub>2</sub>Ru<sub>3</sub>/C. This can be interpreted as Pt<sub>1</sub>Ru<sub>1</sub>/C having a more Pt-rich surface, which is the active component for the hydrogen oxidation reaction. RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C shows comparable HOR current to Pt<sub>1</sub>Ru<sub>1</sub>/C, thus the addition of RuO<sub>2</sub> nanosheets does not obstruct the HOR. The HOR current in the presence of CO (300 ppm CO/H<sub>2</sub>) for Pt<sub>2</sub>Ru<sub>3</sub>/C is comparable with Pt<sub>1</sub>Ru<sub>1</sub>/C. This suggests that Pt<sub>2</sub>Ru<sub>3</sub>/C is more surface-Ru enriched compared to Pt<sub>1</sub>Ru<sub>1</sub>/C, which allows for higher tolerance to CO poisoning. Thus, there is a trade-off between the pure HOR activity and CO tolerance. The RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C combines the advantages of these two catalysts showing high HOR current in both H<sub>2</sub> and CO/H<sub>2</sub>. As summarized in Table I, RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C has high HOR current in

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**Figure 1.** Hydrodynamic linear sweep voltammograms (anodic scan) in 0.1 M HClO<sub>4</sub> saturated with pure H<sub>2</sub> or 300 ppm CO/H<sub>2</sub> for (a) Pt<sub>2</sub>Ru<sub>3</sub>/C, (b) Pt<sub>1</sub>Ru<sub>1</sub>/C and (c) RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C.

**Table I.** HOR current at 0.2 V vs. RHE in 0.1 M HClO<sub>4</sub> saturated with H<sub>2</sub> ( $j_{(H_2)}$ ) or 300 ppm CO/H<sub>2</sub> ( $j_{(CO/H_2)}$ ) acquired from linear sweep voltammograms.

Catalyst	$j / A (g-PtRu)^{-1}$		$\frac{j_{(H_2)} - j_{(CO/H_2)}}{j_{(H_2)}}$
	$j_{(H_2)}$	$j_{(CO/H_2)}$	
Pt <sub>2</sub> Ru <sub>3</sub> /C	367	231	0.37
Pt <sub>1</sub> Ru <sub>1</sub> /C	429	224	0.48
RuO <sub>2</sub> ns-Pt <sub>1</sub> Ru <sub>1</sub> /C	448	304	0.32

**Table II.** Quasi-steady state current obtained from chronoamperometry after 40 min in 0.1 M HClO<sub>4</sub> saturated with 300 ppm CO/H<sub>2</sub> at a polarization potential of 20 mV vs. RHE.

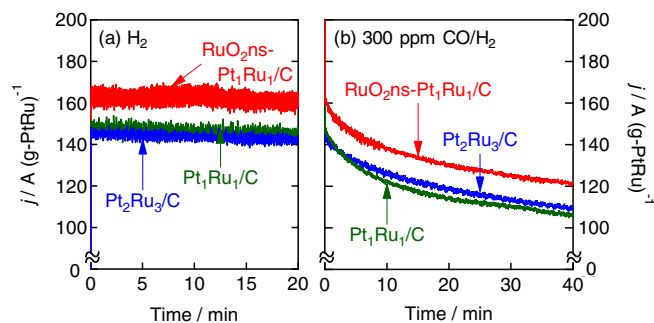
Catalyst	$j / A (g-PtRu)^{-1}$		Decreasing rate (%)
	0 min	40 min	
Pt <sub>2</sub> Ru <sub>3</sub> /C	144	109	24
Pt <sub>1</sub> Ru <sub>1</sub> /C	148	105	28
RuO <sub>2</sub> ns-Pt <sub>1</sub> Ru <sub>1</sub> /C	162	122	25
Pt/C	227	128	44
RuO <sub>2</sub> ns-Pt/C	242	164	32

H<sub>2</sub> ( $j_{(H_2)}$ ) and CO/H<sub>2</sub> ( $j_{(CO/H_2)}$ ) at 0.2 V vs. RHE. The  $j_{(CO/H_2)}$  value for RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C was *c.a.* 1.3 times higher compared to Pt<sub>2</sub>Ru<sub>3</sub>/C and Pt<sub>1</sub>Ru<sub>1</sub>/C. In particular, if one compares the degree of decrease in current between H<sub>2</sub> and CO/H<sub>2</sub>,  $(j_{(H_2)} - j_{(CO/H_2)}) / j_{(H_2)}$ , RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C decreases by only 32%, whereas Pt<sub>2</sub>Ru<sub>3</sub>/C and Pt<sub>1</sub>Ru<sub>1</sub>/C decreases by 37% and 48%, respectively. This shows the high CO tolerance of RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C. Beyond 0.5 V vs. RHE, the oxidation of adsorbed CO (CO<sub>ad</sub>) occurs. The onset of CO<sub>ad</sub> oxidation was similar for the three catalysts, indicating that the CO<sub>ad</sub> oxidation activity was nearly equal.

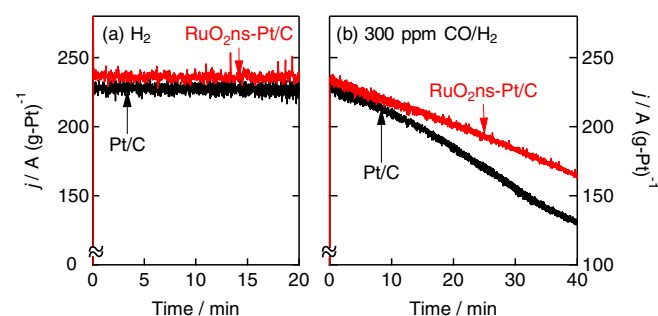
Chronoamperograms for Pt<sub>2</sub>Ru<sub>3</sub>/C, Pt<sub>1</sub>Ru<sub>1</sub>/C and RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C in pure H<sub>2</sub> and 300 ppm CO/H<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> are shown in Fig. 2. The HOR activity in H<sub>2</sub> (steady-state current after 20 min) follows the general trend observed by linear sweep voltammetry; *i.e.* Pt<sub>2</sub>Ru<sub>3</sub>/C  $\approx$  Pt<sub>1</sub>Ru<sub>1</sub>/C < RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C (Table II). Upon introducing 300 ppm CO, the HOR current gradually decreases due to poisoning of the surface with CO. The HOR activity in CO/H<sub>2</sub> at

20 mV vs. RHE (quasi-steady state current after 40 min) was Pt<sub>1</sub>Ru<sub>1</sub>/C  $\approx$  Pt<sub>2</sub>Ru<sub>3</sub>/C < RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C (Table II). Pt<sub>1</sub>Ru<sub>1</sub>/C is easily poisoned by CO, which can be seen as the quick decrease in current in the first 10 min. The decline in HOR current for RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C was similar to Pt<sub>2</sub>Ru<sub>3</sub>/C, suggesting that the tolerance against CO<sub>ad</sub> is similar.

In order to understand the enhanced CO tolerance by the addition of RuO<sub>2</sub> nanosheets, a simplified electrocatalyst with no metallic Ru was prepared (RuO<sub>2</sub>ns-Pt/C). Chronoamperograms for Pt/C and RuO<sub>2</sub>ns-Pt/C in pure H<sub>2</sub> and 300 ppm CO/H<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> are shown in Fig. 3. The decline in the HOR current for RuO<sub>2</sub>ns-Pt/C is milder compared to Pt/C, indicating that RuO<sub>2</sub> nanosheets slows down the CO poisoning. The oxidation of CO<sub>ad</sub> occurs at potentials much higher than 20 mV vs. RHE (above 0.5 V vs. RHE for Pt-Ru/C and 0.7 V vs. RHE for Pt/C (Fig. S2)). Thus, the improved CO tolerance by the addition of RuO<sub>2</sub> nanosheets should not be due to enhanced CO<sub>ad</sub> oxidation ability, but the suppression of CO adsorption on the catalyst surface.



**Figure 2.** Chronoamperograms at 20 mV vs. RHE in 0.1 M HClO<sub>4</sub> saturated with (a) H<sub>2</sub> or (b) 300 ppm CO/H<sub>2</sub> for Pt<sub>2</sub>Ru<sub>3</sub>/C (blue), Pt<sub>1</sub>Ru<sub>1</sub>/C (green) and RuO<sub>2</sub>ns-Pt<sub>1</sub>Ru<sub>1</sub>/C (red).



**Figure 3.** Chronoamperograms at 20 mV vs. RHE in 0.1 M HClO<sub>4</sub> saturated with (a) H<sub>2</sub> or (b) 300 ppm CO/H<sub>2</sub> for Pt/C (black) and RuO<sub>2</sub>ns-Pt/C (red).

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