

## Electrochemical oxidation of CO over tin oxide supported platinum catalysts

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### Abstract

Tin oxide supported platinum catalysts (Pt/SnO<sub>x</sub>) for use in polymer electrolyte fuel cells were prepared, and their electrochemical oxidation of CO was investigated. From the XPS measurements of Pt/SnO<sub>x</sub> catalysts, it was found that the binding energy of Pt showed no change compared to bulk Pt, regardless of tin oxide addition. In accordance with this result, CO-stripping voltammograms for Pt/SnO<sub>x</sub> catalysts revealed that the peak potential for the pre-adsorbed CO oxidation was almost the same value of Pt/C catalyst. However, the onset potential of CO oxidation shifted negatively compared to PtRu/C catalyst, indicating an enhancement of CO tolerance of Pt/SnO<sub>x</sub> catalysts.

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### 1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted much attention as a clean power source for vehicles and cogeneration systems, because of their high energy conversion efficiency. Conventional PEFCs operate at the temperature lower than 100 °C. Accordingly, electrodes with high electrocatalytic activity for hydrogen oxidation are required, and platinum is widely used. However, the electrocatalytic activity of Pt drastically deteriorates in the presence of carbon monoxide [1]. When hydrogen is produced by the reforming of hydrocarbons such as natural gas, gasoline or methanol, etc., the reformed hydrogen-rich gas contains carbon monoxide. Therefore, reducing the CO concentration in hydrogen-rich gas, such as CO-selective oxidation [2,3], is one way, and developing the new electrodes with high CO tolerance is

another way. With respect to the latter, various kinds of Pt-based alloys have been studied so far, and PtRu alloy (atomic ratio 1:1) showed the highest CO tolerance [4–6]. However, the CO tolerance is insufficient for commercialization, and ruthenium is resourceless in platinum-group metals. Accordingly, it is required to reduce the Ru usage and develop the electrocatalysts without Ru species.

Recently, it was reported that the CO tolerance of Pt was improved by the addition of oxides such as MoO<sub>x</sub>, NbO<sub>x</sub>, and TaO<sub>x</sub> [7–9]. The role of these oxides was proposed to relax the strong CO adsorption on Pt, which originates in the modification of the electronic band structure of Pt and the interaction between Pt and metal oxides. However, the performance of these electrocatalysts is still low compared to PtRu alloys. Then, we focused on tin oxide supported platinum catalysts, which are well known as the catalysts for gas-phase CO oxidation by oxygen with avoiding CO poisoning of Pt [10–13]. The catalytic activity was dependent on the pretreatment conditions (temperature and oxidizing or reducing atmosphere), which was generally attributed to the metal-support interaction. Therefore, it is possible to modify the activity by

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controlling the metal-support interface. In this report, the Pt/SnO<sub>x</sub> catalysts with different pre-heat-treatment were tried to apply to electrocatalysts for CO oxidation.

## 2. Experimental

Platinum catalysts supported on tin oxide were prepared by the impregnation method. An aqueous solution of Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> (Tanaka Kikinzo Kogyo) and SnO<sub>2</sub> (Wako Pure Chemical Industries Ltd.) were used as Pt source and support, respectively. After the calcinations of SnO<sub>2</sub> at 800 °C for 5 h (BET surface area: 5.0 m<sup>2</sup> g<sup>-1</sup>), it was impregnated with Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>. The Pt loading on SnO<sub>2</sub> was 20 wt.%. The mixture was kept on a steam bath at 80 °C until the solution evaporated, and then the resulting powder was heat-treated under different conditions, as summarized in Table 1. One sample, S-1, was pyrolyzed at 400 °C for 0.5 h in air, and then reduced at 90 °C for 2 h under 10% H<sub>2</sub>/N<sub>2</sub> atmosphere. The other sample, S-2, was pyrolyzed at 200 °C for 0.5 h under 10% H<sub>2</sub>/N<sub>2</sub> atmosphere. For comparison, Pt/C (Johnson Matthey, Pt: 40 wt.%) and PtRu/C (Johnson Matthey, Pt: 30 wt.%, Ru: 15 wt.%) were used.

The resulting powders were characterized by X-ray diffraction (Rigaku Rint 1400 x-ray diffractometer, Cu Kα source) and X-ray photoelectron spectroscopy (Shimadzu ESCA-850, Mg Kα source). The crystallite size of Pt was calculated by using the Scherrer's equation.

The electrochemical measurements of the catalysts in 1 M HClO<sub>4</sub> (Wako Pure Chemical Industries) solution were conducted by the following procedure. In the case of tin oxide supported platinum catalysts, a suspension containing the catalyst in water was ultrasonically dispersed for 30 min, and then was dropped onto the glassy carbon disk electrode (0.196 cm<sup>2</sup>) to be 14 μg-Pt cm<sup>-2</sup>. In the case of Pt/C and PtRu/C, a suspension was dropped to be 28 μg-Pt(Ru) cm<sup>-2</sup>. After the water evaporated, the electrode surface was covered with 10 μl of Nafion<sup>®</sup> solution (Aldrich, diluted to 1 wt.% solution with ethanol). The conventional three-electrode cell with reversible hydrogen electrode (RHE) was used, and the cell temperature was maintained at 25 °C. Oxidation of pre-adsorbed CO was measured by CO stripping voltammetry with a scan rate of 20 mV s<sup>-1</sup>. Gaseous CO was purged into the cell for 30 min while maintaining a constant voltage of 0.1 V versus RHE, and then the excess CO in the electrolyte was purged out with Ar for 40 min before the measurement. The potentiodynamic oxidation curves of pure CO were also measured with a scan rate of 20 mV s<sup>-1</sup>. Equilibrium was

achieved by bubbling CO for 30 min at an electrode potential of 0.1 V at an electrode rotation rate of 2000 rpm before the measurement.

## 3. Results and discussion

### 3.1. Characterization

Tin oxide supported platinum catalysts (Pt/SnO<sub>x</sub>) were analyzed by XRD and XPS. X-ray diffraction patterns of resulting catalysts are shown in Fig. 1. Platinum crystallite size calculated by using Scherrer's equation are also summarized in Table 2. Both samples exhibited similar patterns with the peaks assigned to Pt and SnO<sub>2</sub>, and the formation of by-products, such as Pt–Sn alloys and intermetallic compounds, were not observed, regardless of the heat-treatment under the reducing atmosphere.

The XPS spectra of Pt 4f and Sn 3d are shown in Figs. 2 and 3, respectively. The surface atomic ratio estimated by XPS is also summarized in Table 2. It was reported that the positive shift of the binding energy for Pt 4f and Pt 4d led to an increase in d-vacancy and a small contribution of Pt 5d electrons to the CO 2π\* orbital, resulting in the suppression of CO coverage for Pt alloys [14]. In this case, however, the binding energy of Pt 4f for both samples showed almost the same value compared to bulk Pt shown in dotted lines. Accordingly, it is difficult to expect the suppression of CO chemisorption on Pt. On the other hand, for both samples, the

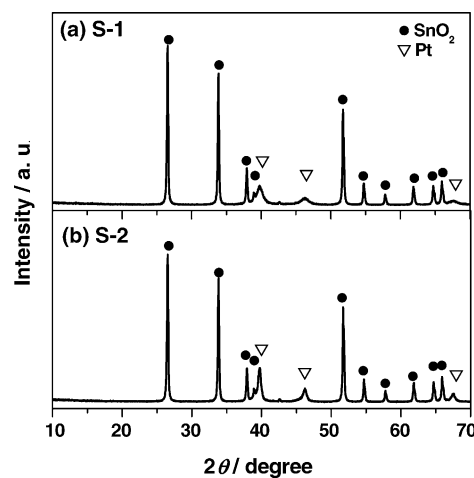


Fig. 1. X-ray diffraction patterns of Pt/SnO<sub>x</sub> catalysts: (a) S-1 and (b) S-2.

Table 2  
Crystallite size of platinum particles and surface atomic ratio for Pt/SnO<sub>x</sub> catalysts

Sample	Crystallite size of platinum particles <sup>a</sup> (nm)	Atomic ratio Sn/Pt <sup>b</sup>
S-1	9	3.2
S-2	17	5.2

<sup>a</sup> Crystallite size of platinum was calculated by using Scherrer's equation.

<sup>b</sup> Surface atomic ratio was determined by XPS analysis.

Table 1  
Pre-heat-treatments for Pt/SnO<sub>x</sub> catalysts

Sample	Heat-treatment
S-1	Pyrolysis at 400 °C for 0.5 h in air → reduction at 90 °C for 2 h in 10% H <sub>2</sub> /N <sub>2</sub>
S-2	Pyrolysis at 200 °C for 0.5 h in 10% H <sub>2</sub> /N <sub>2</sub>

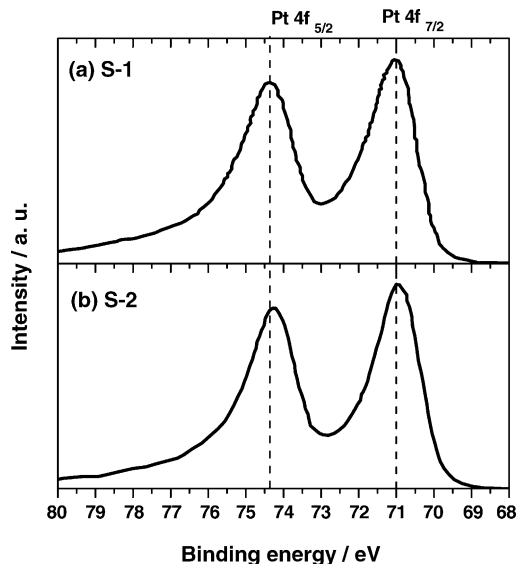


Fig. 2. XPS spectra of Pt 4f for: (a) S-1 and (b) S-2. Dotted lines show peak positions of the corresponding binding energies of bulk Pt.

spectra of Sn 3d showed asymmetric shape and the binding energy at the peak slightly shifted to negative side compared to bulk  $\text{SnO}_2$ . These results indicate the presence of SnO at the surface, because of the partial reduction of  $\text{SnO}_2$  support during heat-treatments under the reducing atmosphere. The surface atomic ratio of Sn/Pt for S-2 was about 1.6 times larger than that of S-1, regardless of the same amount of platinum loading. This difference would be caused by the aggregation of platinum.

### 3.2. Electrochemical properties

Cyclic voltammograms (CVs) of the Pt/ $\text{SnO}_x$  catalysts in 1 M  $\text{HClO}_4$  solution are shown in Fig. 4. For comparison, the

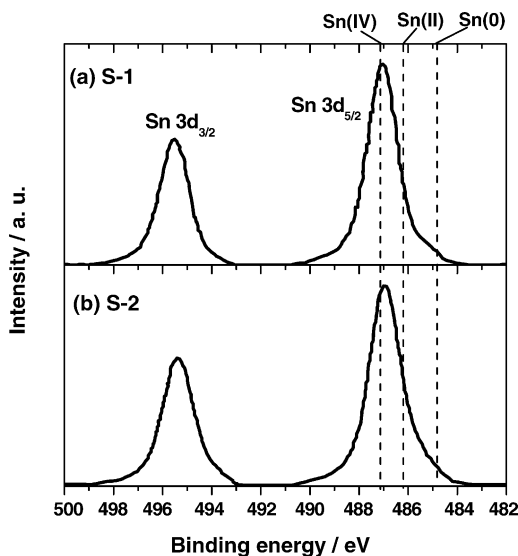


Fig. 3. XPS spectra of Sn 3d for: (a) S-1 and (b) S-2.

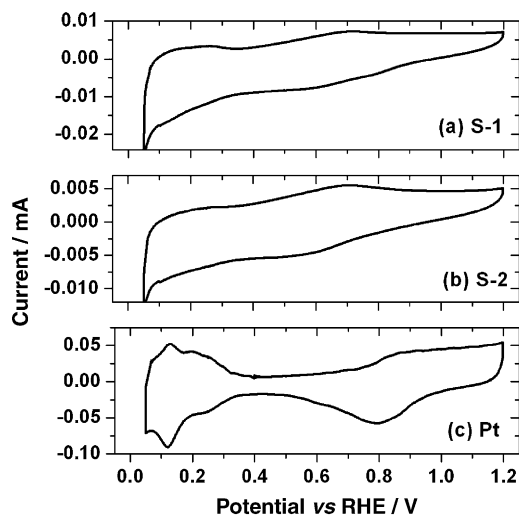


Fig. 4. Cyclic voltammograms of: (a) S-1, (b) S-2, and (c) Pt/C in 1 M  $\text{HClO}_4$  solution. Sweep rate:  $20 \text{ mV s}^{-1}$ , temperature:  $25^\circ\text{C}$ .

result of Pt/C catalyst is also shown. In Ar saturated solution, anodic desorption and cathodic adsorption of hydrogen on Pt were observed in the potential region of 0–0.3 V versus RHE for both catalysts. However, the double layer region (at around 0.3–0.7 V) and the peaks attributed to Pt-oxide layer formation/reduction (at over 0.8 V) were not observed. Alternatively, the anodic current gradually increased from 0.35 up to ca. 0.7 V, and a corresponding cathodic current peak was observed at ca. 0.5–0.6 V. Similar redox peaks were reported for the Sn-modified Pt electrodes [15,16], which was attributed to the Sn(II)/Sn(IV) redox couple for tin oxide/hydroxide species immobilized onto Pt. Considering that there was tin monoxide on the catalysts surface, the similar redox reaction should be promoted.

The CO-stripping voltammograms of Pt/ $\text{SnO}_x$ , Pt/C, and PtRu/C are shown in Fig. 5. The anodic peak potentials of CO oxidation and the electrochemical surface area for each catalyst are summarized in Table 3. The electrochemical surface area of precious metal determined by the  $\text{CO}_{\text{ad}}$  oxidation assuming a monolayer of linearly adsorbed CO, because the H-adsorption/desorption peak for the Pt/ $\text{SnO}_x$  and PtRu/C were not well defined. For the sample of S-1, the peak potential of the CO oxidation showed a negative shift of 0.04 V compared to Pt/C catalyst and evaluated to be 0.70 V, although the S-2 exhibited almost the same value of 0.74 V. However, this peak potential for S-1 was much larger than that

Table 3

Peak potential of CO oxidation and electrochemical surface area for each catalyst

Sample	Peak potential of CO oxidation vs. RHE (V)	Electrochemical surface area <sup>a</sup> ( $\text{m}^2 \text{g}^{-1}$ -Pt(Ru))
S-1	0.70	11.2
S-2	0.74	6.11
Pt/C	0.74	36.4
PtRu/C	0.51	91.4

<sup>a</sup> Electrochemical surface area was determined by  $\text{CO}_{\text{ad}}$  oxidation.

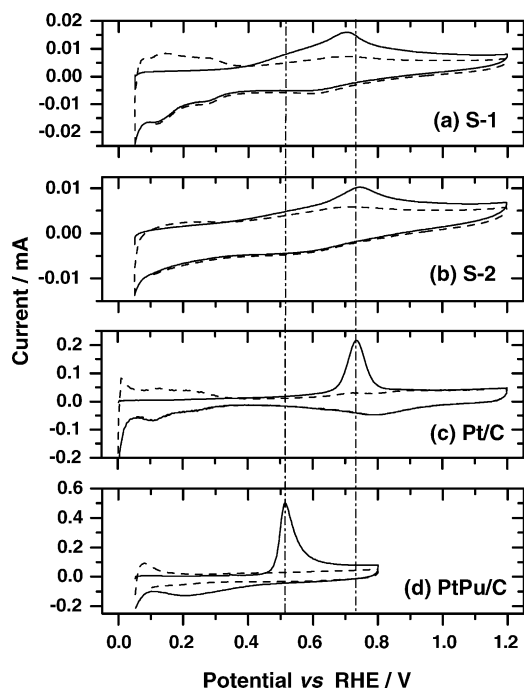


Fig. 5. CO-stripping voltammograms of the catalysts in 1 M HClO<sub>4</sub> solution: (a) S-1, (b) S-2, (c) Pt/C, and (d) PtRu/C. Sweep rate: 20 mV s<sup>-1</sup>, temperature: 25 °C. Solid lines show first scan and dotted lines show second scan.

for PtRu/C (0.51 V). On the other hand, for both Pt/SnO<sub>x</sub> catalysts, the onset potential of CO oxidation was below 0.4 V, indicating the possibility of the improvement in CO tolerance. Considering that the Sn(II)/Sn(IV) redox couple was observed for each Pt/SnO<sub>x</sub> catalyst in Ar saturated solution, this might promote the stripping removal of adsorbed CO on Pt. In this measurement, however, it was difficult to compare the catalytic activity of each electrocatalyst to the others.

Then, to investigate the intrinsic CO tolerance of catalysts, the potentiodynamic oxidation of CO was conducted in CO saturated solution. The current density was normalized by the amount of loaded precious metal and electrochemical surface area, and results are shown in Fig. 6(a) and (b), respectively. In this experiment, nonfaradaic effects should be small because all catalysts exhibited small and identical background current in Ar saturated solution. As shown in Fig. 6(a), for both Pt/SnO<sub>x</sub> catalysts, the onset potential of CO oxidation shifted negatively compared to Pt/C and PtRu/C, and the anodic current increased at two regions, 0.35–0.9 V and over 0.9 V. Generally, for Pt/C catalysts, the anodic current at below 0.9 V is attributed to the pre-oxidation of CO which is weakly adsorbed on Pt. In this case, however, the both Pt/SnO<sub>x</sub> catalysts exhibited higher current density compare to Pt/C at the former region of 0.35–0.9 V, regardless of the extremely small electrochemical surface area. Taking into account that the electronic band structure of Pt showed no change, these results also indicate that the Sn(II)/Sn(IV) redox couple should promote the CO oxidation. The latter region of over 0.9 V should be attributed to the CO oxidation

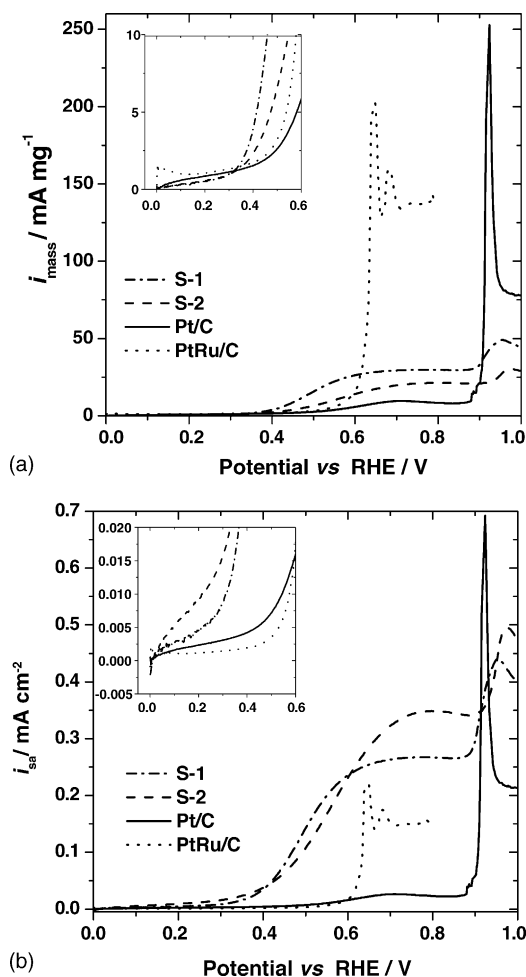


Fig. 6. Potentiodynamic oxidation curves of CO on Pt/SnO<sub>x</sub>, Pt/C, and PtRu/C by rotating disk electrode at 2000 rpm (1 M HClO<sub>4</sub>, 25 °C, 20 mV s<sup>-1</sup>). The current density was normalized by: (a) the amount of loaded precious metal and (b) electrochemical surface area. The inset represents a magnification of the low potential region.

on Pt, which is not affected by tin oxide. Moreover, as shown in Fig. 6(b), both Pt/SnO<sub>x</sub> catalysts showed extremely high electrocatalytic activity for CO oxidation with lower onset potential. Consequently, these results suggest that the highly homogeneous dispersion of platinum on tin oxide would improve the CO tolerance drastically. In this stage, however, it was difficult to elucidate what mechanism made the electrocatalytic difference between S-1 and S-2, although S-1 exhibited the lowest onset potential. The location relationship between Pt and Sn(II) might affect the electrocatalytic activity.

#### 4. Conclusions

Tin oxide supported platinum catalysts were prepared, and their electrochemical CO oxidation was investigated. The Pt/SnO<sub>x</sub> catalysts showed higher electrocatalytic activity for CO oxidation with lower onset potential compared to Pt/C,

although the binding energy of Pt 4f showed no change. This result indicated that the Sn(II)/Sn(IV) redox couple should promote the CO oxidation. Furthermore, it was also suggested that the highly homogeneous dispersion of platinum on tin oxide would improve the CO tolerance drastically.

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