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Author(s)	Wang, Guo-Xiong; Takeguchi, Tatsuya; Yamanaka, Toshiro; Muhamad, Ernee Noryana; Ueda, Wataru
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## Improving CO Tolerance of Pt<sub>2</sub>Ru<sub>3</sub>/C Catalyst by the Addition of Tin Oxide

G. X. Wang, T. Takeguchi, T. Yamanaka, E. N. Muhamad, and W. Ueda

Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

SnO<sub>x</sub>-modified Pt<sub>2</sub>Ru<sub>3</sub>/C catalysts were post-treated in different atmospheres at various temperatures to improve the catalytic activity for H<sub>2</sub>/CO electro-oxidation. The structures of the Pt<sub>2</sub>Ru<sub>3</sub>/C and SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C catalysts were characterized by X-ray diffraction. Electrochemical activities were evaluated by CO stripping voltammetry and single cell test. The SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C catalysts had a lower onset potential for CO electro-oxidation and greater cell voltage than the Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst under high CO concentrations. The SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst treated in 5 % H<sub>2</sub>/Ar at 150°C exhibited the greatest CO tolerance due to that the post-treatment caused the conversion of SnO<sub>2</sub> to SnO<sub>x</sub> (1 ≤ x ≤ 2) without destroying PtRu alloy structure.

### Introduction

In recent years, polymer electrolyte fuel cell (PEFC) has attracted great interest as a promising power source for electric vehicles and residential co-generation systems. However, the CO tolerance of the anode catalyst is still a major challenge for the research and development of PEFC, operating on hydrogen produced by reforming of hydrocarbons (1). Until now, PtRu and PtSnO<sub>x</sub> catalysts are widely-investigated binary catalysts for H<sub>2</sub>/CO electro-oxidation. Compared with that on PtRu catalyst, a lower onset potential of CO electro-oxidation is usually obtained on PtSnO<sub>x</sub> catalyst; however, the CO electro-oxidation rate above the onset potential on PtSnO<sub>x</sub> catalyst is not as sensitive with potential as that on PtRu catalyst. In view of the different catalytic properties of PtRu and PtSnO<sub>x</sub> catalysts toward CO electro-oxidation, it is interesting to investigate their combined effects on CO tolerance by preparing SnO<sub>x</sub>-modified PtRu catalyst.

In this work, nano-sized SnO<sub>2</sub> was prepared by hydrolysis of SnCl<sub>2</sub> in ethylene glycol and then deposited onto a commercial Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst, followed by a post-treatment in different atmospheres at various temperatures. The prepared catalysts were characterized by X-ray diffraction (XRD). CO stripping voltammetry and single cell test were conducted to evaluate the CO tolerance of variously treated catalysts.

### Experimental section

9.4 mg of SnCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in 30 mL ethylene glycol to form a clear solution, and the solution was heated to 190°C at a rate of 10 K min<sup>-1</sup> and kept at that temperature for 0.5 h, and then cooled to room temperature. 500 mg of commercial Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst (Pt: 29.7 wt %, Ru: 23 wt %, TEC61E54, Tanaka Kikinzoku Kogyo K. K., Japan) was added to 80 mL ethylene glycol to form black slurry with mechanical stirring, then the slurry was added into the SnO<sub>2</sub> colloid solution and stirred for about 12 h. Distilled water

was added to the mixture and the pH value was adjusted to about 2 with 0.1 M HCl solution, then the mixture was heated to 90°C and kept at that temperature for 24 h. The obtained catalyst was filtered and washed thoroughly with distilled water. To investigate the effect of treatment atmosphere, the obtained catalysts were treated under N<sub>2</sub> or 5 % H<sub>2</sub>/Ar at 150 °C for 2 h, which were denoted as SnO<sub>2</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150N and SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150H, respectively. To investigate the effect of treatment temperature, the obtained catalysts were treated in 5% H<sub>2</sub>/Ar at 125, 150, 175 or 225°C, respectively, and denoted as SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-125H, SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150H, SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-175H and SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-225H catalyst. The nominal atomic ratio of Pt and SnO<sub>x</sub> is 18:1 in the SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C catalysts.

XRD patterns of the catalysts were recorded with a powder X-ray diffractometer (RIGAKU, RINT 2000) using Cu K $\alpha$  radiation with a Ni filter. The tube current was 20 mA with a tube voltage of 40 kV.

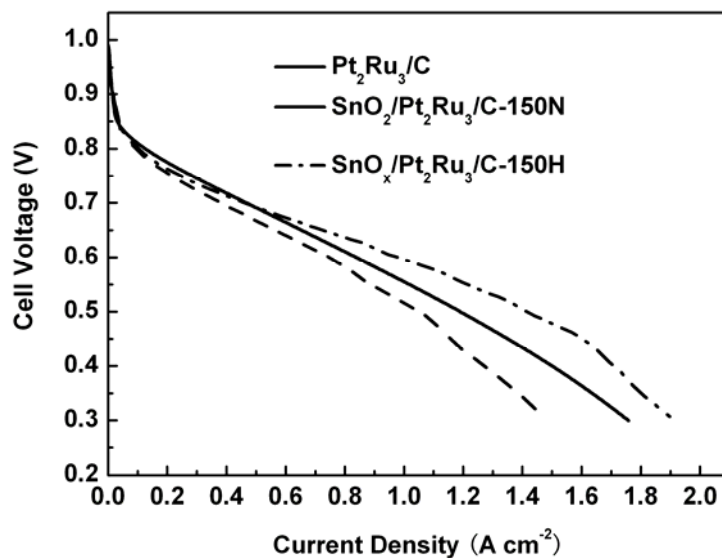
The experimental details regarding CO stripping voltammetry and single cell test were described in previous publication (2). The cathode catalyst (40% Pt/C, Johnson Matthey) loading was 1.2  $\pm$  0.1 mg cm<sup>-2</sup>. Pure H<sub>2</sub> (or CO-contaminated H<sub>2</sub>) and oxygen was fed into the anode and cathode at ambient pressure, respectively. For I-V curve measurement, the cell temperature was 75°C, and the anode and cathode humidifier temperature was 75 and 70°C, respectively. For the constant current discharge measurement, the cell temperature was 70°C, and the anode and cathode humidifier temperature was 70 and 68°C, respectively. The single cell was operated at 0.2 A cm<sup>-2</sup> under pure H<sub>2</sub> for 1 h and H<sub>2</sub>/CO mixture for 2 h to get a stable cell voltage.

## Results and Discussion

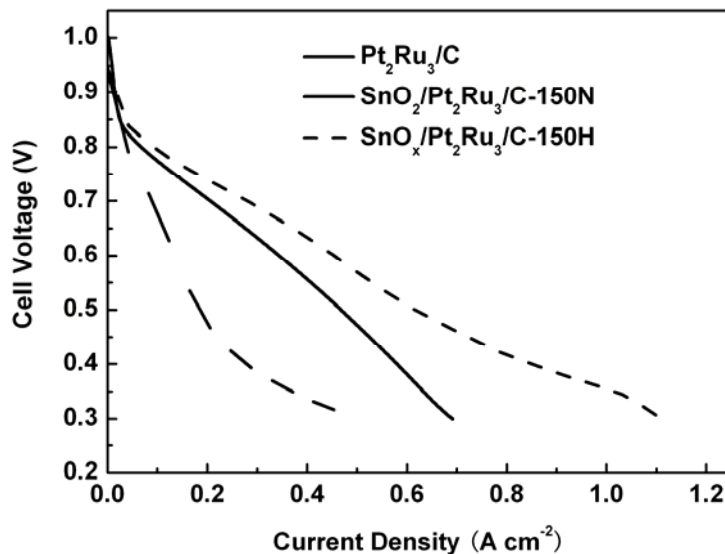
Figure 1 (a) and (b) show the effect of post-treatment atmosphere of SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst on the PEFC performance. The loading of Pt and Ru in the anode was 0.89  $\pm$  0.05 mg cm<sup>-2</sup>. When pure H<sub>2</sub> was fed to anode, the SnO<sub>2</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150N catalyst has a SnO<sub>2</sub> deposition, the particles are randomly distributed on the catalyst surface, the slightly lower performance than the Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst, while the SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150H catalyst has a greater performance at high current densities. This is maybe due to that the reduction treatment in 5% H<sub>2</sub>/Ar made that the SnO<sub>2</sub> in the SnO<sub>2</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst was converted to SnO<sub>x</sub> (1  $\leq$  x  $\leq$  2) and that removed the hydrocarbon species on the catalyst surface. When 500 ppm CO-contaminated H<sub>2</sub> was fed to anode, the SnO<sub>2</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150N catalyst showed the greatest decline, indicating that the addition of SnO<sub>2</sub> into Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst in the SnO<sub>2</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150N catalyst did not improve the CO tolerance. After reduction treatment caused a mass redistribution and the SnO<sub>x</sub> particles combined with Pt<sub>2</sub>Ru<sub>3</sub>/C particles to form SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C composite particles, therefore, the interaction between Pt<sub>2</sub>Ru<sub>3</sub> and SnO<sub>x</sub> particles was strong due to an intact contact, so the SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150H catalyst had a much greater CO tolerance than the Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst.

Figure 2 shows XRD patterns of the Pt<sub>2</sub>Ru<sub>3</sub>/C, SnO<sub>2</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150N and SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150H catalysts. The broad peak at around 26° is associated with the (002) diffraction peak of the carbon support. The diffraction peaks at around 41°, 46°, 69° and 83° are due to diffraction at Pt (111), (200), (220) and (311) planes, respectively. In addition, some other peaks at around 43° and 68° are also observed, which can be related to metallic Ru. However, the diffraction peaks of SnO<sub>x</sub> are absent, which can be due to a small content of tin species or that the SnO<sub>x</sub> exists as amorphous form in the SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C catalysts. The mean crystallite size of the catalysts was also calculated

from the Pt (220) diffraction peak via the Scherrer equation, and the three catalysts have the same mean crystalline size of 3.5 nm. The similar diffraction peaks on the three catalysts indicated that the addition of SnO<sub>2</sub> and subsequent post-treatment under



(a)



(b)

Figure 1 PEFC performance of Pt<sub>2</sub>Ru<sub>3</sub>/C, SnO<sub>2</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150N and SnO<sub>x</sub>/Pt<sub>2</sub>Ru<sub>3</sub>/C-150H catalysts fed with pure H<sub>2</sub> (a) and 500 ppm CO-contaminated H<sub>2</sub> (b).

different atmospheres did not alter the crystalline structure of  $\text{Pt}_2\text{Ru}_3/\text{C}$  catalyst. The performance improvement in the  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H catalysts could be ascribed to the effective interaction between  $\text{SnO}_x$  and  $\text{Pt}_2\text{Ru}_3$  particles.

Figure 3 shows XRD patterns of  $\text{Pt}_2\text{Ru}_3/\text{C}$  and  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$  catalysts treated in 5%  $\text{H}_2/\text{Ar}$  at various temperatures. It can be observed that the intensity of Ru diffraction peak

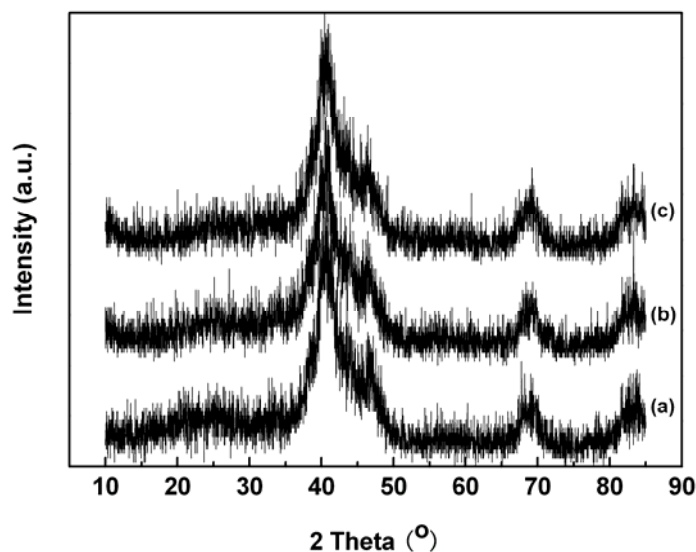


Figure 2 XRD patterns of  $\text{Pt}_2\text{Ru}_3/\text{C}$  (a),  $\text{SnO}_2/\text{Pt}_2\text{Ru}_3/\text{C}$ -150N (b) and  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H (c) catalysts.

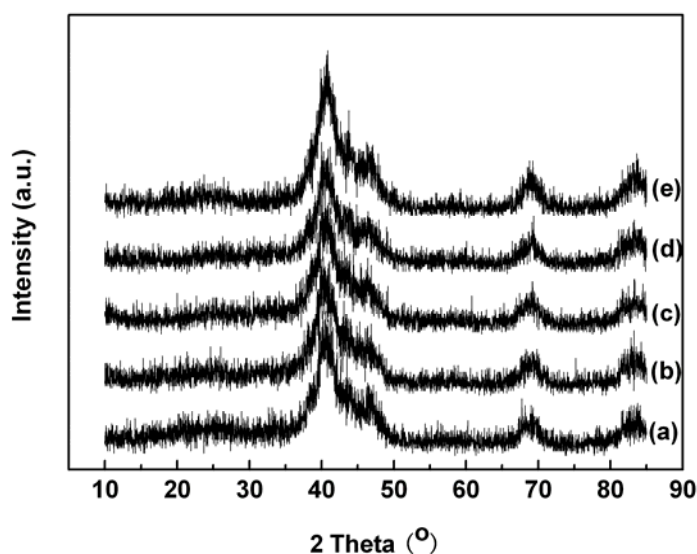


Figure 3 XRD patterns of  $\text{Pt}_2\text{Ru}_3/\text{C}$  (a),  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -125H (b),  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H (c),  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -175H (d) and  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -225H (e) catalysts.

at around 43° on the  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -175H and  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -225H catalysts increases, suggesting that a part of Ru was replaced by Sn from the PtRu alloy.

Figure 4 shows the cell voltage of  $\text{Pt}_2\text{Ru}_3/\text{C}$  and  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$  catalysts under different CO concentrations at a current density of  $0.2 \text{ A cm}^{-2}$ . The loading of Pt and Ru

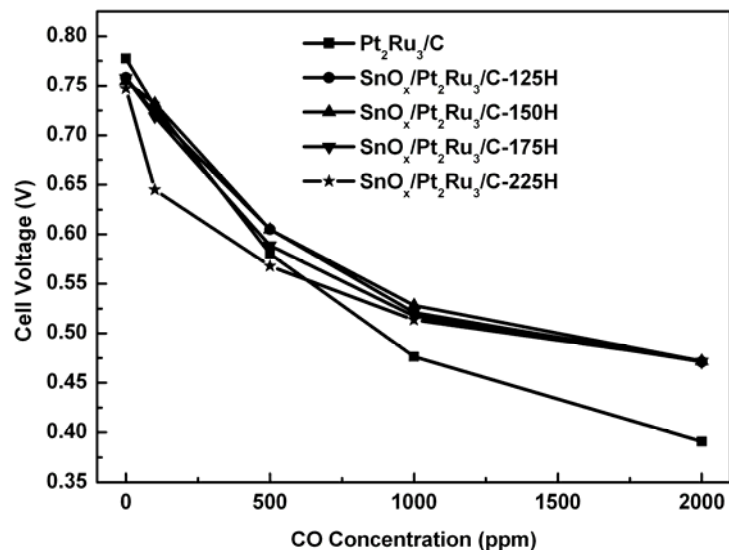


Figure 4 Cell voltages of  $\text{Pt}_2\text{Ru}_3/\text{C}$  and  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$  catalysts at  $0.2 \text{ A cm}^{-2}$  under different CO concentrations.

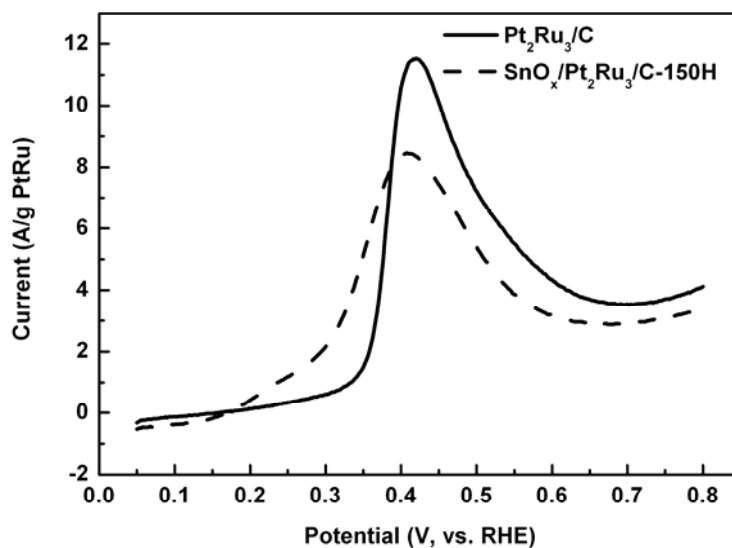


Figure 5 CO stripping voltammetry on  $\text{Pt}_2\text{Ru}_3/\text{C}$  and  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H catalysts in  $0.1 \text{ M HClO}_4$  at  $25^\circ\text{C}$ , scan rate:  $5 \text{ mV s}^{-1}$ .

in the anode was  $0.53 \pm 0.05 \text{ mg cm}^{-2}$ . The  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H catalyst has a slightly greater performance than the  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -125H catalyst, while the  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -175H catalyst has a slightly lower performance than the  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H catalysts. For the  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -225H catalyst, the cell voltage under 100 ppm and 500 ppm CO-contaminated  $\text{H}_2$  decreases greatly, indicating that the PtSn alloy formation by displacing Ru decreases the CO tolerance under low CO concentrations. Under 1000 ppm and 2000 ppm CO-contaminated  $\text{H}_2$ , the performance of different  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$  catalysts is similar and greater than that of the  $\text{Pt}_2\text{Ru}_3/\text{C}$  catalyst. The  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H catalyst showed the greatest CO tolerance among the  $\text{Pt}_2\text{Ru}_3/\text{C}$  and different  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$  catalysts, CO stripping voltammeteries were conducted to investigate the difference between the  $\text{Pt}_2\text{Ru}_3/\text{C}$  and  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H catalysts, as shown in Figure 5. On the  $\text{Pt}_2\text{Ru}_3/\text{C}$  catalyst,  $\text{CO}_{\text{ads}}$  is electro-oxidized in a relatively sharp stripping peak centered at 0.420 V, while the  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H catalyst has a peak potential of 0.408 V, and the onset potential for  $\text{CO}_{\text{ads}}$  electro-oxidation on the  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$ -150H catalyst is greatly shifted negatively, indicating that the addition of  $\text{SnO}_x$  promotes  $\text{CO}_{\text{ads}}$  electro-oxidation at low potentials.

## Conclusions

$\text{SnO}_2$  nanoparticles were prepared by hydrolysis of  $\text{SnCl}_2$  in ethylene glycol and deposited onto the commercial  $\text{Pt}_2\text{Ru}_3/\text{C}$  catalyst, followed by a post-treatment in different atmospheres at various temperatures to form  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$  composite catalysts. XRD results indicated that the treatment atmosphere did not alter the crystalline structure of  $\text{Pt}_2\text{Ru}_3/\text{C}$  catalyst; however, the reduction treatment caused a great improvement in CO tolerance due to a strong interaction between  $\text{SnO}_x$  and  $\text{Pt}_2\text{Ru}_3$  particles. The treatment temperature also had a pronounced effect on the CO tolerance of  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$  catalyst. The  $\text{SnO}_x/\text{Pt}_2\text{Ru}_3/\text{C}$  catalyst treated in 5%  $\text{H}_2/\text{Ar}$  at  $150^\circ\text{C}$  showed the greatest CO tolerance due to a mild reduction treatment, while the high-temperature reduction treatment at  $175^\circ\text{C}$  and  $225^\circ\text{C}$  destroyed the PtRu alloy structure and decreased the cell voltage under low CO concentrations. The CO stripping voltammetry result verified that the addition of  $\text{SnO}_x$  promoted the CO electro-oxidation at low potentials.

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