

A CO-Tolerant Hydrogen Fuel Cell System Designed by Combining with an Extremely Active Pt/CNT Catalyst

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Abstract Complete oxidation of 2,000 ppm CO in H₂ is attained over 10 wt.% Pt/CNT (carbon nano-tube) catalyst (0.019 g) at room temperature by adding 2,000 ppm O₂ to hydrogen flowing at 100 mL/min. By insetting 5 wt.% Pt/CNT catalyst (0.8 g) in front of a PEFC (polymer electrolyte hydrogen fuel cell), the PEFC generated maximum wattage of 0.45 V × 0.75 A/cm² with no suppression for more than 7 h in a flow of H₂ (400 mL/min) containing 1,000 ppm CO. This result suggests a possibility of the hydrogen fuel cell operating in the shift gas.

Keywords CO-tolerant hydrogen fuel cell ·
Low temperature PROX catalyst · Pt/CNT catalyst ·
Polymer electrolyte hydrogen fuel cell

1 Introduction

From a view of clean and efficient energy source, various types of fuel cell have been proposed [1, 2], and working models using hydrogen or methanol are already in the market. However, one awkward problem is the poisoning of Pt-anode by a trace amount of CO [3]. To avoid the

poisoning by CO, the CO in hydrogen is removed by preferential oxidation (PROX) reaction at 150–170 °C through a reactor. On the other hand, a lot of efforts has been paid to develop CO-tolerant Pt-based anode, but the tolerance is lower than 100 ppm CO. For example, Pt–Ni/C was tolerant for 50 ppm [4] and Pt–Ru on a defect free carbon nano-tube was for 100 ppm CO [5]. If complete oxidation of CO in H₂ is attained at room temperature, we need not the reactor for PROX reaction. That is, the CO in hydrogen can remove by a small amount of catalyst inset in front of the fuel cell, and the fuel cell will operate in hydrogen containing several thousands ppm of CO.

To realize such a CO-tolerant PEFC system, highly active PROX catalyst at room temperature is indispensable. So far, several low temperature PROX catalysts were developed [6–10], but their activity, selectivity, stability and reproducibility, were not fulfill the performance for our aimed CO-tolerant hydrogen fuel cell system. Fortunately, we found extremely active new catalyst, which was prepared by supporting Pt on carbon nano-tube [11]. In this paper, our aimed CO-tolerant hydrogen fuel cell system was realized by using Pt/CNT catalyst, which operated in hydrogen containing 1,000 ppm CO for several hours.

2 Experiment

The support carbon (Carbon nano-tube from Microphase Co., Vulcan carbon, and graphite powder) was degassed for 2 h at room temperature, and then immersed in a nitric acid solution of calculated amount of Pt(NH₃)₂(NO₂)₂ (5, 10, or 15 wt.% in Pt). By stirring the carbon for more than 12 h, and then dried at 40 °C in a flow of N₂. A certain amount of catalyst mounted in a reactor was treated by flowing H₂ at 200 °C. Oxidation reaction of CO in H₂ was performed

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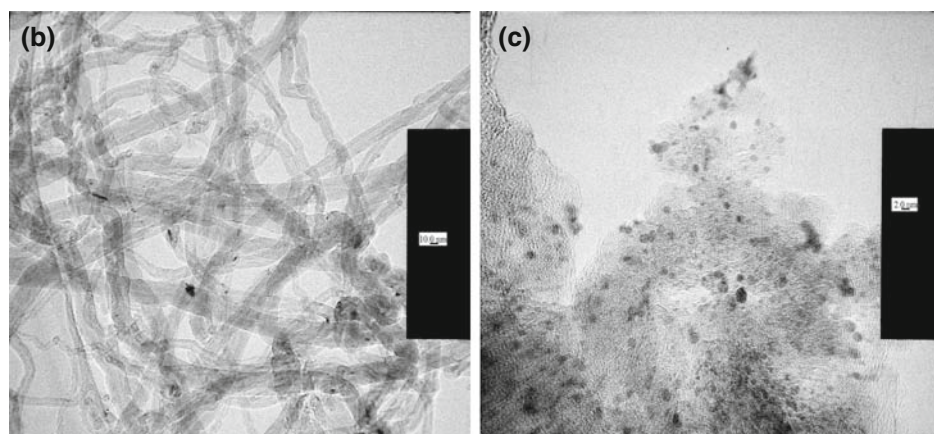
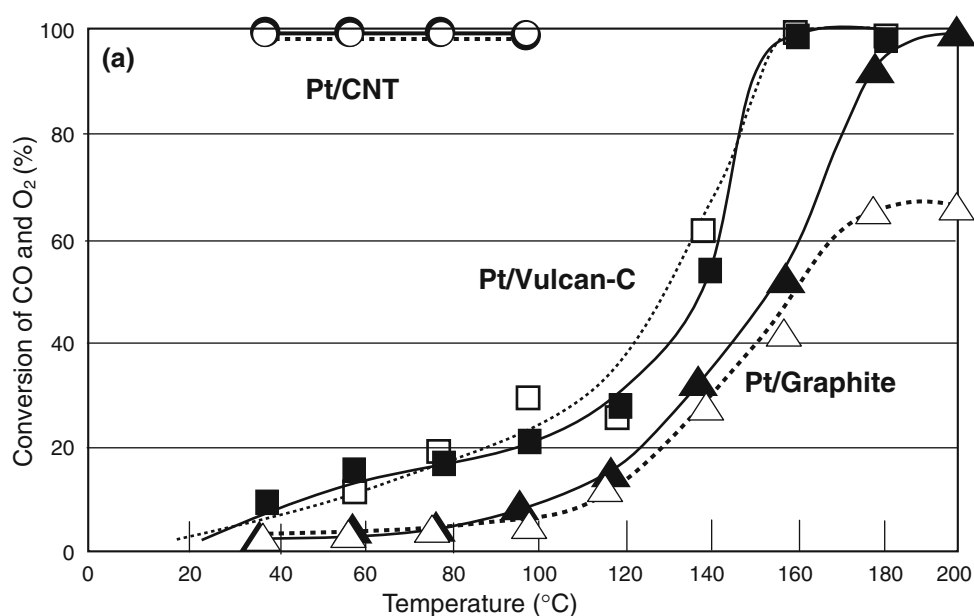
in a flow reactor with an on-line gas chromatography. The complete oxidation of CO in H₂ at room temperature was attained at a value of O₂/CO = 0.75 by increasing the ratio of O₂/CO from 0.5 to 1.0. Complete oxidation of 2,000 ppm CO in H₂ with 2,000 ppm O₂ (O₂/CO = 1) was also confirmed at room temperature over 0.19 g of 10 wt.% Pt/CNT catalyst (the Pt in 10 wt.% Pt/C is equivalent to that in 1.2 wt.% Pt on Al₂O₃) by flowing H₂ at 100 mL/min. The CO in effluent gas measured by an infrared (IR) cell with a 2 m light pass (detectable level is 0.2 ppm CO) proved complete oxidation of CO at room temperature.

Anode of a half cell of PEFC was prepared by hot pressing commercial 35% Pt/C (Tanaka Noble Metal Co.) with a Nafion 115 electrolyte film, and was operated at ca. 80 °C. CO-tolerance of a PEFC system insetting 5 wt.% Pt/CNT catalyst (0.8 g) was monitored by output voltage at 0.75 A/cm², which gave a maximum wattage (0.45 V × with no CO) in a flow of H₂ containing 1,000 ppm of CO and 2.5% O₂ at 400 mL/min.

3 Results and Discussion

In our previous paper [11], we developed an extremely active PROX catalyst, which was prepared by supporting Pt on a carbon nano-tube (Pt/CNT). Interesting fact is that Pt supported on graphite and Vulcan carbon (used for anode) gives not so high activity as Pt/CNT. To realize the difference, performance of 15 wt.% Pt/CNT catalyst (0.39 g), 15 wt.% Pt/Vulcan-C (0.29 g), and 15 wt.% Pt/graphite (0.30 g) are referred in Fig. 1a. The conversion was obtained by flowing a mixture of CO (1.5 mL/min) + H₂ (15 mL/min) + O₂ (1.5 mL/min) + N₂ (38.5 mL/min). It is clear that the activity of Pt/CNT catalyst is exceptionally high at room temperature. It is worthy of note that the activity of precious metal has so often discussed in relation with particle size, and the activity of Au particles is a typical case [12–14]. However, the particle size of Pt evaluated by XRD (not shown here) was 4.0–4.5 nm for Pt/CNT and 3.0–4.5 nm for Pt/Vulcan-C,

Fig. 1 a Conversion of CO (open) and O₂ (solid) attained by flowing a mixture of {CO(1.5 mL/min) + O₂(1.5 mL/min) + H₂(15.0 mL/min) + N₂ 38.5 (mL/min)} over 15 wt.% Pt/CNT (0.39 g, ○●), 15 wt.% Pt/graphite (0.30 g, △▲), and 15 wt.% Pt/Vulcan-C (0.29 g, □■) catalysts. **b, c** TEM images of the Pt/CNT and Pt/Vulcan-C catalysts



which were in good agreement with the size evaluated from the TEM image shown in Fig. 1b and c. Therefore, high activity of the Pt on carbon nano-tube is difficult to explain by particle size of Pt. In fact, large Pt particles on carbon nano-tube was far more active than that on the other carbon supports [11]. These facts reveal that physical meaning of the activity and the role of support are not so simple as have been explained by surface area or perimeter length of metal particles. Superior activity of $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ prepared by loading a large amount of FeO_x on a 1 wt.% Pt/TiO_2 also reveals difficulty for the activity and the selectivity for the oxidation of CO in H_2 .

We have to remind that the activity depends on providing rate of reactant molecules to active sites or active component, but the providing is not always direct from gas phase but via diffusion over the support. Under these circumstances, the kinetics and the reaction rate is controlled by the rate determining step on the active component. In the case of selective oxidation of CO on the $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ catalyst, oxidation of CO proceeds via HCOO^- intermediate and the oxidation of HCOO with OH is the rate determining step [15]. This mechanism well explains the enhancement of the oxidation of CO by H_2 and/or H_2O and the hydrogen isotope effect by H_2/D_2 and $\text{H}_2\text{O}/\text{D}_2\text{O}$ [16]. Oxidation of CO on Pt/CNT showed also hydrogen isotope effect by H_2/D_2 [Unpublished data], but the spectroscopic investigation of the Pt/CNT catalyst is difficult.

The experiments on Pt/CNT were performed by flowing H_2 containing rather high concentration of CO ($\text{CO}/\text{H}_2 = 0.10$ in Fig. 1). It was confirmed that the complete oxidation of CO in a flow of (CO (3.0 mL/min) + H_2 (20 mL/min) + O_2 + N_2) at 100 mL/min on 5 wt.% Pt/CNT (0.8 g) at 35–40 °C was attained at $\text{O}_2/\text{CO} = 0.75$ [11]. However, complete oxidation of several thousands ppm CO in H_2 at room temperature should be certified to apply the Pt/CNT catalyst to PEFC. Figure 2 showed the oxidation of 2,000 ppm CO in H_2 with 2,000 ppm O_2 at room temperature by flowing at 100 mL/min on 10 wt.% Pt/CNT (0.19 g) catalyst. Trace amount of CO in the effluent was detected by an IR-cell with 2 m light pass (detectable 0.2 ppm CO), which proved the complete oxidation of CO for 20 h.

Accordingly, the CO in H_2 can remove through the Pt/CNT catalyst inset in front of the PEFC by the oxidation with a certain amount of O_2 . The I–V profile was measured by flowing H_2 containing 2.5% O_2 through a 5 wt.% Pt/CNT catalyst (0.8 g) at 400 mL/min ($\text{SV} = \text{ca. } 2,600 \text{ h}^{-1}$ on the catalyst at room temperature) inset in front of the humidifier of PEFC (ca. 80 °C). The I–V profile was attained in a flow of H_2 (400 mL/min) containing 2.5% of O_2 . The amount of O_2 is ca. 10 times excess for several thousands ppm CO, which is an unavoidable limit of our flow controlling system for the PEFC. Therefore, the PEFC

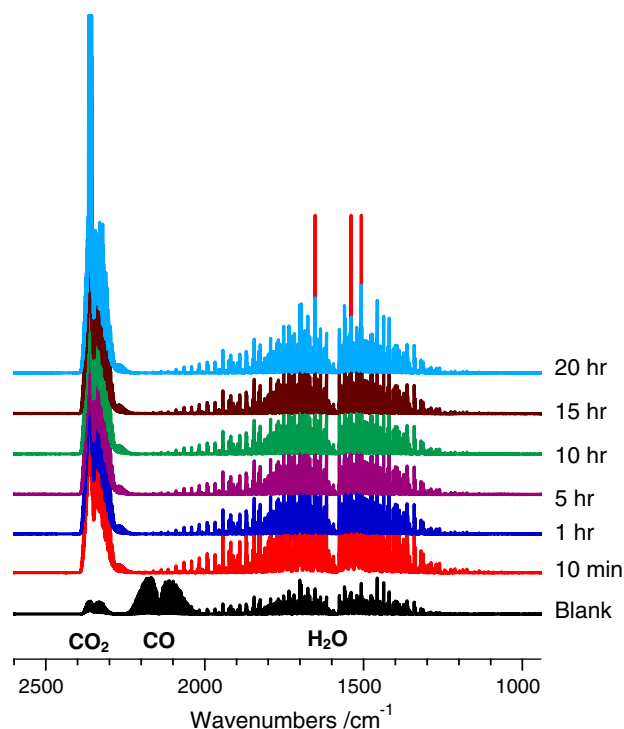


Fig. 2 I.R. spectrum of outlet gas proves complete oxidation of 2,000 ppm CO in H_2 to CO_2 with 2,000 ppm O_2 over the 10% Pt/CNT catalyst (0.19 g) at room temperature. Flow rate was 100 mL/min

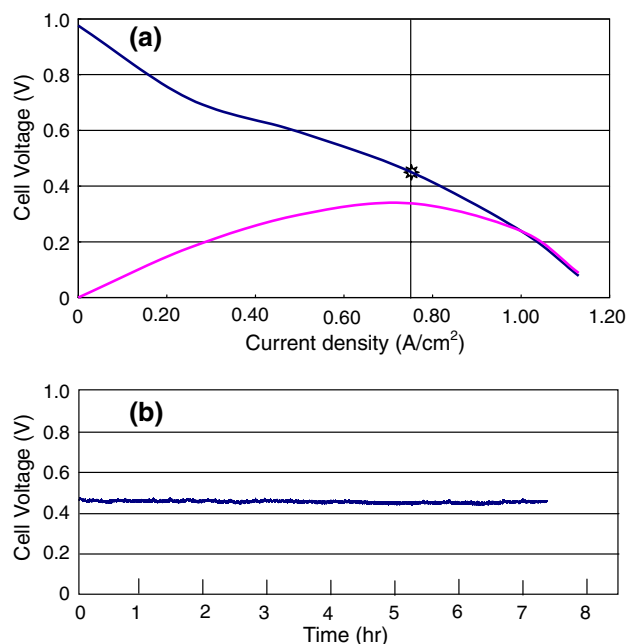


Fig. 3 a An I–V curve of a half cell with an anode of 35% Pt/C attained by flowing H_2 with 25,000 ppm O_2 and no CO at 400 mL/min. **b** Performance of the PEFC setting 5 wt.% Pt/CNT catalyst (0.8 g). A steady output voltage at 0.75 A was monitored by flowing H_2 containing 1,000 ppm CO and 25,000 ppm O_2 through at 400 mL/min ($\text{SV} = 2,600 \text{ h}^{-1}$)

may lose ca. 4% of output power by reacting H₂ with O₂, but it is not an important problem for our purpose because O₂ gives no influence on the I–V profile as the blank I–V profile with no CO shows in Fig. 3a. The maximum wattage of the PEFC attained in the blank I–V profile was 0.75 A/cm² × 0.45 V. If the Pt-anode of PEFC will be poisoned by CO, the output voltage at 0.75 A/cm² is sensitively suppressed. After the blank test of the PEFC, about 1,000 ppm of CO was added to H₂ flow, and the output voltage at 0.75 A/cm² was monitored with time. As shown in Fig. 3b, the output voltage at 0.75 A/cm² took no suppression in H₂ containing 1,000 ppm of CO, that is, the PEFC system is tolerant for 1,000 ppm CO. We could conclude that development of CO-tolerant anode for several thousands ppm CO is impractical, but the development of hydrogen fuel cell system being tolerant for CO of several thousands ppm is practical as demonstrated in this paper. Taking these results into account, we conclude that developing of active PROX catalyst such as Pt/CNT will make realize the PEFC system operating in the shift gas.

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