



## Short communication

## Effect of CO and oxygen on anode degradation in polymer electrolyte fuel cell



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## H I G H L I G H T S

- The CO tolerance of PEFC anode was evaluated by hydrogen pump with supplying CO.
- The CO tolerance was deteriorated by the combination of CO and O<sub>2</sub>.
- Decomposition of ionomer was caused by H<sub>2</sub>O<sub>2</sub> as a by-product of ORR.
- Decomposition of the ionomer was accelerated by CO.
- The CO tolerance is speculated to be caused by the decomposition of the ionomer.

## A R T I C L E I N F O

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## A B S T R A C T

CO tolerance of a polymer electrolyte fuel cell was measured before and after accelerated degradation cell operation in which hydrogen with 200, 500, 1000, and 1500 ppm of CO was supplied to the anode and air was supplied to the cathode in the open-circuit condition. The decrease in CO tolerance was more pronounced when the concentration of CO was increased. However, CO tolerance did not decrease when nitrogen, instead of air, was supplied to the cathode. The amount of fluoride ion in the drain water during the cell operation increased when hydrogen containing 500 ppm CO was supplied to the anode, which indicates the decomposition of perfluorocarbon ionomer. It was found that the combination of CO and oxygen deteriorated the ionomer because H<sub>2</sub>O<sub>2</sub> that was produced as a by-product of the oxygen reduction reaction cannot be completely reduced to water. This is due to the decreased surface area of the Pt–Ru alloy catalyst because of CO adsorption, which results in the degradation of the CO tolerance.

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## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) are now being developed for commercial worldwide production. PEFCs generate electrical power and heat by the hydrogen oxidation reaction (HOR) at the anode and the oxygen reduction reaction (ORR) at the cathode. PEFCs are targeted for use as cogeneration systems for houses and buildings. However, a significant improvement in durability is required before PEFCs can be reliably used worldwide [1]. For residential PEFC systems, hydrocarbon gas such as town gas is often

used as a source of hydrogen. Hydrocarbon gas is reformed to produce a gas mixture containing hydrogen, carbon dioxide, and a trace amount of carbon monoxide (CO) before being supplied to the anode. However, CO in the reformed gas is known to suppress the HOR on the platinum catalyst because it adsorbs on the platinum surface [2–4]. Therefore, platinum–ruthenium alloy on carbon black (Pt–Ru/C) is used as the anode catalyst for residential PEFCs to mitigate the effect of CO adsorption [5–7]. The CO-tolerance of Pt–Ru/C is reported to decay by potential cycling [8]. It is believed that a decrease in CO tolerance of Pt–Ru/C should not occur as long as the potential is kept near the H<sup>+</sup>/H<sub>2</sub> potential in practical operation. Nevertheless, a reduction in CO tolerance is actually observed in long-term operation, the cause of which is still unknown.

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In this study, the effects of CO and oxygen on the anode degradation in PEFCs were investigated by evaluating the CO tolerance. Furthermore, the degradation of the ionomer made of fluorocarbon was evaluated by measuring the fluoride ion content in the drain water of the cell.

## 2. Experimental

### 2.1. CO tolerance measurement

A subscale test cell having 25 cm<sup>2</sup> of electrode area was used to evaluate the CO tolerance of an anode in a membrane electrode assembly (MEA). Both the anode and cathode were composed of catalyst layers and gas-diffusion layers. The anode catalyst layer consisted of Pt–Ru/C catalyst (TEC62E58, Tanaka Kikinzoku Kogyo K.K.) and perfluorocarbon ionomer (Nafion D520, DuPont), while the cathode catalyst layer consisted of Pt/C catalyst and perfluorocarbon ionomer. The gas-diffusion layers for both the electrodes were composed of carbon black and polytetrafluoroethylene (PTFE) pasted on carbon papers. A perfluorocarbon polymer membrane with thickness of 30 μm was used as an electrolyte.

Fig. 1 shows a schematic diagram of the test cell to evaluate CO tolerance of the anode. All the tests were performed at 70 °C and under full humidification. First, the voltage between the anode and cathode in the hydrogen pump operation was measured at current densities of 0 to 500 mA cm<sup>-2</sup> when pure hydrogen gas was supplied to both the anode and cathode. HOR occurs on the Pt–Ru/C catalyst in the anode (Eq. (1)) and a proton reduction reaction occurs on the Pt/C catalyst in the cathode (Eq. (2)). The cell voltage ( $V(H_2)$ ) comprises the overpotential of HOR ( $\eta_a(H_2)$ ), the overpotential of the proton reduction reaction ( $\eta_c(H^+)$ ), and an ohmic loss (IR) in the membrane (Eq. (3)).



$$V(H_2) = \eta_a(H_2) + \eta_c(H^+) + IR \quad (3)$$

Subsequently, hydrogen containing 200 ppm of CO was supplied to the anode, and pure hydrogen was supplied to the cathode in the open-circuit condition for 3 h. Then, the cell voltage ( $V(H_2 + 200 \text{ ppm CO})$ ) was measured again at current densities of 0 to 500 mA cm<sup>-2</sup> (Eq. (4)). The voltage increase observed for the CO-added hydrogen was more pronounced than that observed when pure hydrogen was used. This was because the HOR overpotential at the Pt–Ru/C catalyst increased due to CO adsorption and decrease in active surface area for the electrochemical reaction.

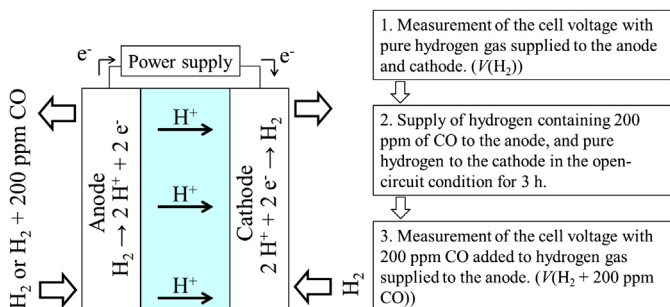


Fig. 1. A schematic diagram of the test cell for evaluation of CO tolerance of the anode.

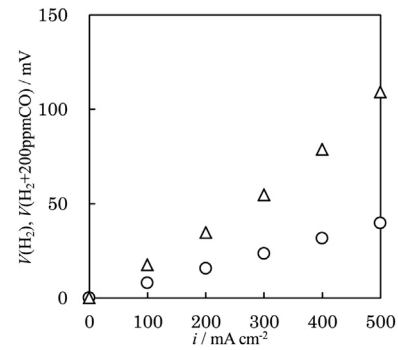


Fig. 2. The voltage required for the hydrogen pump operation. (○): H<sub>2</sub> was supplied to both the anode and cathode. (△): (H<sub>2</sub> + 200 ppm CO) was supplied to the anode and H<sub>2</sub> to the cathode.

The difference ( $\Delta\eta_a$ ) in the voltages between the pure hydrogen supply and the CO-added hydrogen supply is used as an indicator for the CO tolerance of the anode (Eq. (5)). The CO tolerance is low when  $\Delta\eta_a$  is large.

$$V(H_2 + 200 \text{ ppm CO}) = \eta_a(H_2 + 200 \text{ ppm CO}) + \eta_c(H^+) + IR \quad (4)$$

$$\Delta\eta_a = V(H_2 + 200 \text{ ppm CO}) - V(H_2) = \eta_a(H_2 + 200 \text{ ppm CO}) - \eta_a(H_2) \quad (5)$$

### 2.2. Accelerated tests for anode degradation

Hydrogen with high CO content was supplied to the anode to investigate the effect of CO and oxygen on the anode degradation under the accelerated conditions. All the tests were performed at 70 °C under full humidification. First, the CO tolerance was measured in the same manner as described above. Then, hydrogen with a high concentration of CO was supplied to the anode and air was supplied to the cathode in the open-circuit condition for 110 h. The open-circuit voltage fell by a value in the range of 0.9 to 1 V during the accelerated tests. After that, the adsorbed CO on the anode catalyst was removed by an anodic potential sweep. The potential sweeps were performed twice at a scan rate of 0.1 V s<sup>-1</sup> between 0 and 1 V vs. RHE, while supplying hydrogen to the cathode and nitrogen to the anode. Finally, the CO tolerance of the anode was measured again by the method described above. Then, the difference between the initial CO tolerance and that after the accelerated test was evaluated.

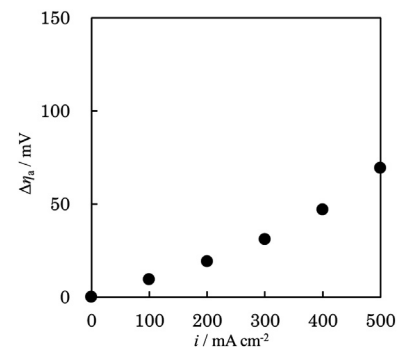


Fig. 3.  $\Delta\eta_a$  obtained by Eq. (5) and the data in Fig. 2.

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