

# Carbon monoxide poisoning and recovery on a polymer electrolyte fuel cell with a hydrogen circulation system

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**ABSTRACT:** The impact of carbon monoxide (CO) on fuel cell performance was systematically investigated under varying operating conditions or electrolyte membrane thickness in a single-cell evaluation system equipped with a hydrogen circulation system typically applied in fuel cell vehicles. Among the effects of various parameters, including cell temperature, CO concentration, fuel stoichiometry, and electrolyte membrane thickness, the influence of cell temperature and CO concentration was found to be significant. The voltage in the presence of CO (0.2 ppm) at a constant current of 1.0 A cm<sup>-2</sup> did not decrease at 80 °C of the cell temperature, whereas a large voltage drop was observed at 40 °C, probably due to a decrease in the CO oxidation rate at the anode. Meanwhile, the voltage at 1.0 A cm<sup>-2</sup> significantly recovered even at 40 °C after load cycles between 0.025 and 1.0 A cm<sup>-2</sup>. The voltage recovery was attributed to (i) the accumulation of permeated oxygen from the cathode in the hydrogen circulation system, and (ii) the reduction in the CO supply rate because load cycles were applied to a lower current density. These effects probably led to a smaller CO-to-oxygen ratio and enhanced CO oxidation.

**KEY WORDS:** fuel cell, carbon monoxide poisoning, hydrogen fuel quality, standardization

## 1. INTRODUCTION

Hydrogen quality standards for fuel cell vehicles (FCVs) have been developed to prevent market problems caused by hydrogen fuel. Many discussions have been conducted with automotive manufacturers and infrastructure providers around the world to consider the results of the impurity evaluation tests with single cells and fuel cell stacks/systems, hydrogen quality control, and analytical methods. ISO 14687:2025 provides the hydrogen fuel index and the maximum concentration of each constituent.<sup>(1)</sup>

Among the impurities specified in ISO 14687:2025, carbon monoxide (CO) with an allowable concentration of 0.2 μmol mol<sup>-1</sup> (hereafter ppm) is still a critical component. CO is known as the so-called canary species,<sup>(2,3)</sup> which is likely to contaminate hydrogen fuel when hydrogen is produced by steam reforming of hydrocarbons and purified by a pressure swing adsorption process. In addition, CO is strongly adsorbed on the anode platinum and inhibits the hydrogen oxidation reaction. The presence of CO in hydrogen fuel degrades the performance of the polymer electrolyte fuel cell (PEFC).<sup>(4-13)</sup> Recent fuel cell systems have been designed for use at high power densities to reduce their volume, and the amount of catalyst loading is reduced for lower cost.<sup>(14)</sup> Such higher current densities and lower platinum loadings

should have a greater impact on the degradation in the fuel cell's performance due to the presence of CO.

To mitigate CO poisoning at the anode, the oxygen that permeates through the electrolyte membrane from the cathode should play an important role. Previous studies have shown that increasing the oxygen partial pressure of the cathode or reducing the thickness of the electrolyte membrane increases the degree of oxygen permeation from the cathode and thereby mitigates the negative impact of CO.<sup>(7-9)</sup> Gas chromatography analysis results showed the presence of oxygen at the anode, and its amount was much larger than the concentration of CO specified in the hydrogen quality standard.<sup>(8,9)</sup> The change in the ratio of CO-to-oxygen at the anode with the load cycle also has a significant impact on the mitigation of CO poisoning. According to the literature, the load change from high current density to low current density can mitigate the voltage drop caused by CO.<sup>(12,13)</sup>

Normally, a single-cell evaluation system is a one-way pass where unused hydrogen is directly exhausted out of the system. However, FCVs usually have a hydrogen circulation system that recycles the fuel from the anode outlet to the anode inlet to increase hydrogen utilization. Our previous study revealed that the impact of CO on cell voltage in the hydrogen circulation system is greatly reduced compared with that in the one-way pass

system.<sup>(9)</sup> Oxygen in the hydrogen circulation system should accumulate and lead to the enhancement of CO oxidation. As the previously reported studies were conducted under constant current and limited temperature conditions, a deep understanding of the impact of CO under different operating conditions remains elusive. Therefore, the purpose of this study was to thoroughly investigate CO poisoning and the recovery in the hydrogen circulation system under a wide range of PEFC operating conditions.

2. EXPERIMENTAL

2.1. Membrane-electrode assembly and the single cell

A JARI standard single cell (25 cm<sup>2</sup> electrode area)—whose temperature was controlled by a heating medium—and commercially available membrane-electrode assemblies were used for the single-cell tests. The platinum loadings on the anode and cathode were 0.1 and 0.4 mg cm<sup>-2</sup>, respectively. The electrochemically active surface areas of the anode and cathode, determined by performing cyclic voltammetry measurements at a cell temperature of 40 °C and 100% relative humidity, were 40–45 m<sup>2</sup> g<sup>-1</sup>. The electrolyte membrane was fluorine-based and its thickness was 15 μm. In addition, electrolyte membranes with thicknesses of 20 and 30 μm were also examined to understand the effect of oxygen permeation rate on CO poisoning.

2.2. Experimental apparatus

The tests were conducted by a single-cell evaluation test station equipped with a hydrogen circulation system, which has been described in the literature.<sup>(9)</sup> The anode gas was high-purity hydrogen or hydrogen mixed with 0.2 ppm CO. The anode gas in the hydrogen circulation system was supplied by the amount

consumed in the anode reaction and the amount purged out of the system. The cathode gas was purified air.

2.3. Experimental conditions

The experimental conditions of the single-cell operation test are shown in Table 1. The cell temperature, CO concentration, and fuel stoichiometry were varied as parameters. The definition of gas stoichiometry and the purge rate have been described in the literature.<sup>(9)</sup> As preconditioning before CO addition, the single cell was operated at a current density of 1.0 A cm<sup>-2</sup> using high-purity hydrogen as the fuel over 6 h. After that, CO mixed with hydrogen was fed to the anode over 20 h. Subsequently, the current density was changed in a square wave between 0.025 and 1.0 A cm<sup>-2</sup>. The holding time at each current density was 30 min.

3. RESULTS AND DISCUSSION

3.1. Effect of cell temperature on CO poisoning under constant current conditions

The effect of CO under various operating conditions was evaluated using a single-cell evaluation system equipped with a hydrogen circulation system. Fig. 1 shows the cell voltage change over time due to CO at different temperatures as a representative example. In this figure, the voltage changes with respect to the 0 h when CO began to be supplied to the cell were shown. The voltage began to decrease after 5 h, and the voltage drop after 20 h was –138 mV at 40 °C, –18 mV at 60 °C, and –3 mV at 80 °C, respectively.

The underlying origins of the CO oxidation mechanism at the

Table 1 Single-cell test conditions.

Cell temperature / °C		40	<u>60</u>	80
Humidified temperature / °C	An	Nonhumidified		
	Ca	25 (43% RH)	<u>40</u> (37% RH)	60 (42% RH)
Current density / A cm <sup>-2</sup>		Step 1: Constant current at (a)1.0 Step 2: With load cycle between (b)0.025 and (a)1.0 (each 30 min)		
Gas stoichiometry	An	(a) 1.4, <u>2.0</u> , 2.5 (b) 5.0		
	Ca	(a) 2.5, (b) 10		
Pressure at cell outlet / kPaG	An	5		
	Ca	5		
CO concentration / ppm		0, <u>0.2</u> , 0.4, 1.0		
Purge rate / %		1.0		

\*An: Anode, Ca: Cathode, Underlined: basic conditions

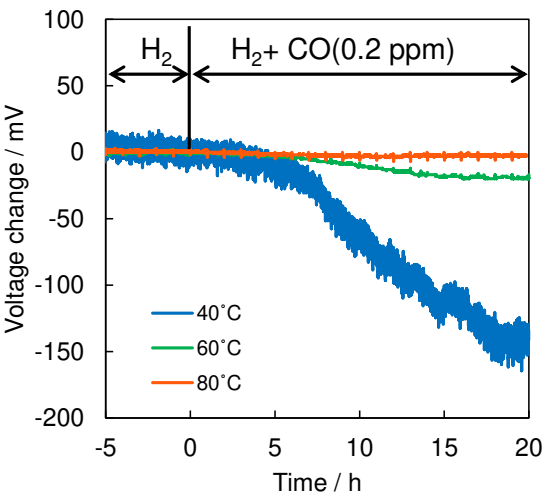
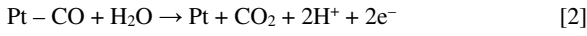


Fig. 1 Change in the cell voltage over time with and without CO addition to the hydrogen circulation system at different temperatures and at a current density of 1.0 A cm<sup>-2</sup>.

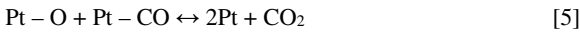
anode electrocatalyst have been widely examined. One of the suggested mechanisms is the electrooxidation of CO by water as the oxygen source, which is shown in Equations 1 and 2.<sup>(10)</sup>



Generally, it is known that the reaction in Equation 2 requires relatively high anode overvoltage. However, the reaction in Equation 2 may be promoted due to the formation of a local mixed potential by the reduction of permeated oxygen from the cathode, which is shown in Equation 3.



The other suggested CO oxidation reaction pathway involves the permeated oxygen from the cathode, whose reactions are shown in Equations 4 and 5.<sup>(10,11)</sup>



The CO oxidation reaction rate should be slower at lower temperatures. In addition, the oxygen permeation rate from the cathode also decreases at lower temperatures.<sup>(15,16)</sup> For these reasons, the voltage drop due to CO should have been significantly larger at 40 °C.

### 3.2. Effect of cell temperature on CO poisoning under load cycle condition

After 20 h, the current density was changed between 0.025 and 1.0 A cm<sup>-2</sup> while CO was supplied to the anode. Fig. 2 shows the voltage change over time at 1.0 A cm<sup>-2</sup> relative to 0 h when CO addition began. At cell temperatures of 40 and 60 °C, the voltage

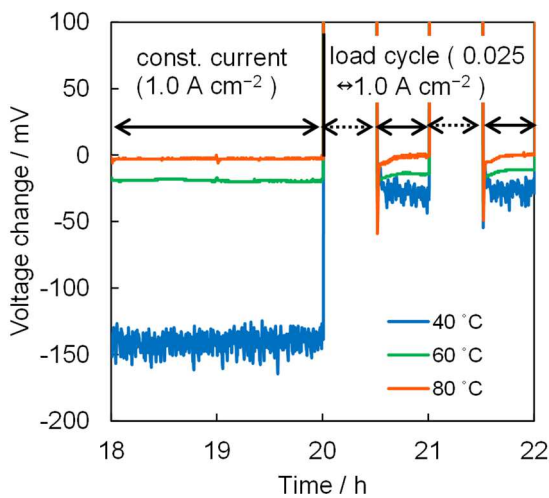


Fig. 2 Voltage change over time at 1.0 A cm<sup>-2</sup> at constant current and load cycle conditions relative to the start of CO addition (solid line: 1.0 A cm<sup>-2</sup>; dashed line: 0.025 A cm<sup>-2</sup>).

drop due to CO was recovered after the load cycles to the low current density. This could be explained by the effect of internal air bleed in the hydrogen circulation system. The CO supply rate decreased to 1/40 because the CO supply rate is proportional to the current density. Meanwhile, the oxygen permeation rate from the cathode, which is thought to promote CO oxidation, depends on the concentration gradient. The oxygen permeation rate should increase at low current densities due to the high air stoichiometry, which increases the oxygen concentration at the boundary between the cathode and the electrolyte membrane. Therefore, the ratio of CO-to-oxygen should be smaller at lower current densities. This should lead to enhanced oxidation of CO, resulting in voltage recovery after the load cycle.

### 3.3. Effects of CO under various conditions

In addition to cell temperature, the effects of CO concentration, fuel stoichiometry, and electrolyte membrane thickness on voltage drop in the presence of CO were investigated. Fig. 3 shows the relationship between those parameters and the voltage change at 1.0 A cm<sup>-2</sup>, which can be ascribed to the presence of CO under constant current conditions and after repeating five cycles of load variation. The voltage dropped drastically at a cell temperature of 40 °C in Fig. 3(a), and at a CO concentration of 1.0 ppm in Fig. 3(b), which exceeded the allowable concentration (0.2 ppm) in ISO 14687:2025. The voltage at 1.0 A cm<sup>-2</sup> recovered after the application of load cycles to a lower load in both conditions. Note that the voltage drop at 1.0 A cm<sup>-2</sup> after the application of load cycles at the allowable concentration of CO in ISO 14687:2025 was slight. For the effect of electrolyte membrane thickness shown in Fig. 3(c), the voltage drop was smaller as the membrane thickness became thinner. This effect could be attributed to the elevated oxygen permeation rate from the cathode as the membrane thickness becomes thinner. For the fuel stoichiometry shown in Fig. 3(d), no significant difference in the effect on voltage was observed.

## 4. CONCLUSION

The effect of CO was evaluated under various operating conditions using a single-cell evaluation system with a hydrogen circulation system employed in typical FCVs. Among the parameters of cell temperature, CO concentration, fuel stoichiometry, and electrolyte membrane thickness, the effects of cell temperature and CO concentration were found to be significant. The voltage in the presence of CO (0.2 ppm) at a constant current condition of 1.0 A cm<sup>-2</sup> was not affected at 80 °C,

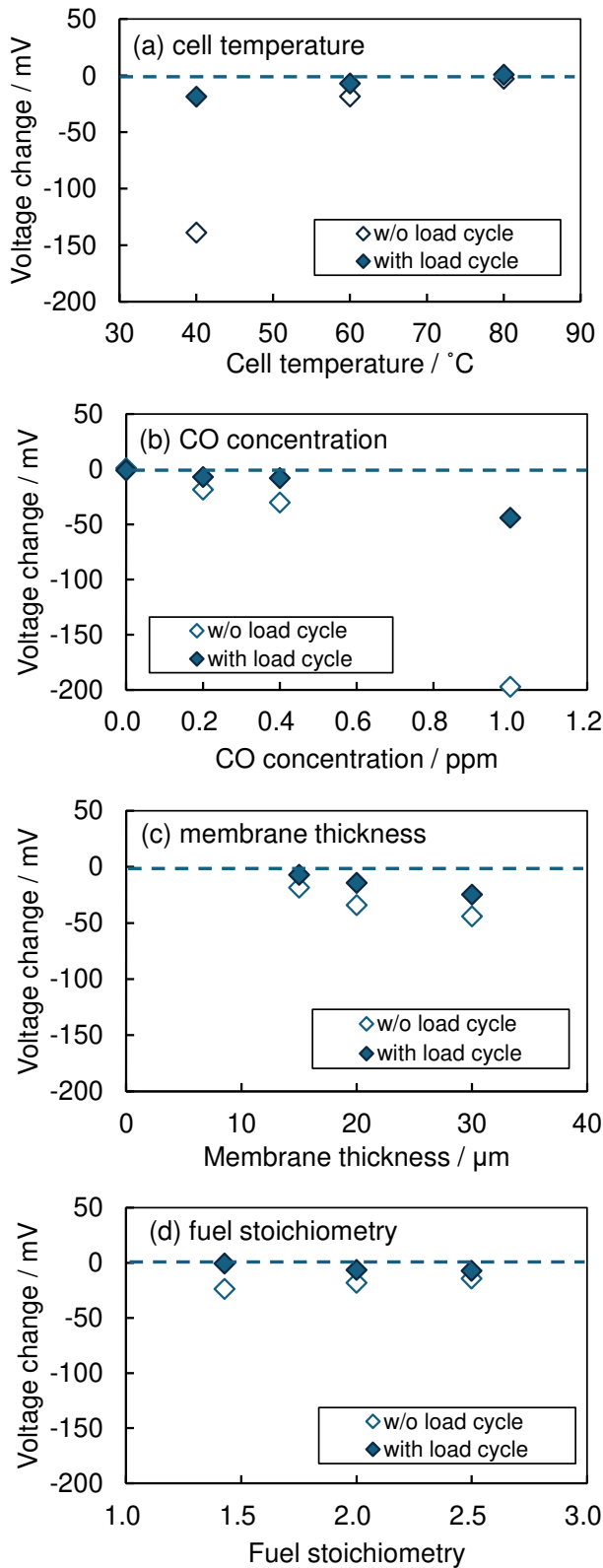


Fig. 3 Voltage changes at  $1.0 \text{ A cm}^{-2}$  due to CO in hydrogen at constant current and after repeating five cycles of load variation under various operating conditions or membrane thicknesses.

whereas a large voltage drop was observed at  $40^\circ\text{C}$ , probably due to a decrease in the CO oxidation rate at the anode. Meanwhile, the voltage at  $1.0 \text{ A cm}^{-2}$  significantly recovered, even at  $40^\circ\text{C}$ , after load cycles between  $0.025$  and  $1.0 \text{ A cm}^{-2}$  were applied. These behaviors should be related to oxygen permeation from the cathode. The factors that had a larger effect on voltage at low temperatures were the lower CO oxidation rate and the lower oxygen permeation rate. The recovery of the effect of CO on the voltage after the load cycle to lower current density was ascribed to (i) the accumulation of permeated oxygen from the cathode in the hydrogen circulation system, and (ii) the reduction in the CO supply rate due to the application of load cycles at a lower current density, resulting in a smaller CO-to-oxygen ratio. The CO concentration also had a large effect, but no significant voltage drop was observed unless the CO concentration exceeded  $0.2 \text{ ppm}$  as defined by ISO 14687:2025.

Future automotive fuel cell systems are expected to have higher loads with lower platinum loadings. On the other hand, thinner electrolyte membranes that are more permeable to oxygen and higher operating temperatures are also expected. The suitability of allowable concentration of impurities in the hydrogen quality standards for fuel cell applications should be discussed while considering the fuel cell operating conditions and membrane-electrode assembly specifications.

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