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Effect of Carbon Monoxide on Polymer Electrolyte Fuel Cell Performance with a Hydrogen Circulation System

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The effect of carbon monoxide (CO) on the performance of polymer electrolyte fuel cells (PEFCs) with either a hydrogen circulation system or a hydrogen one-way pass system is investigated and compared. The voltage drop induced by adding 0.2 ppm of CO to the PEFC with the hydrogen circulation system was less than one-tenth of that observed in the PEFC with the hydrogen one-way pass system at 1000 mA cm$^{-2}$ and a cell temperature of 60 °C. Gas analysis results showed that CO concentration in the hydrogen circulation system was lower than the initially supplied CO concentration. In the hydrogen circulation system, permeated oxygen from the cathode should enhance CO oxidation. This should lead to decrease the CO concentration and mitigate the voltage drop in the hydrogen circulation system.

The current ISO 14687-2 is intended to be initial stage of FCV standards for hydrogen fuel will be issued according to the technical progress of FCVs. The purpose of this study was to understand the effect of CO on the performance degradation of PEFCs with hydrogen circulation systems reflecting actual FCV conditions. The effect of hydrogen circulation on voltage degradation by CO near the upper limit of ISO 14687-2 was evaluated using low platinum loading at the anode and confirmed with a hydrogen one-way pass system. The concentration of CO, carbon dioxide (CO$_2$), and permeated oxygen from the cathode was determined in the hydrogen circulation system.

**Experimental**

**Membrane-electrode assembly and the single cell.**—A JARI standard single cell (25 cm$^2$ 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 loading on the anode and cathode was 0.1 and 0.4 mg cm$^{-2}$, respectively. The electrochemically active surface areas of the anode and cathode were determined using cyclic voltammetry at a cell temperature of 40 °C and 100% relative humidity was 40–45 m$^2$ g$^{-1}$. The thickness of the electrolyte membrane was 15 μm.

**Experimental apparatus.**—Single-cell operation tests were conducted for both a conventional hydrogen one-way pass system and a hydrogen circulation system. The experimental apparatus is shown in Fig. 1. A mixture of high-purity hydrogen (99.99999%) and CO-containing hydrogen was used as the anode gas. The cathode gas was a mixture of nitrogen (79%) and oxygen (21%), and it was used to avoid problems of argon peak separation in the air during oxygen analysis in the hydrogen circulation system. In the hydrogen one-way pass system, anode gas from the cell outlet is exhausted out of the system. In contrast, the anode gas in the hydrogen circulation system that passed through the fuel cell was sent to the condenser, where the water was removed and then returned to the anode inlet using a hydrogen circulation pump. Normally, a FCV fuel cell system has a purge valve to prevent nitrogen accumulation because nitrogen permeates from the cathode into the hydrogen circulation system. The hydrogen circulation system in this experiment was also equipped with a purge valve. CO and CO$_2$ concentrations of the purged gas from the hydrogen circulation system were analyzed.
using a gas chromatograph with a pulsed-discharge helium ion detector (GC-PDHID), and $O_2$ concentration was measured by using a gas chromatograph with a thermal conductivity detector (GC-TCD). The lower detection limits of $CO$, $CO_2$ and $O_2$ are 0.03, 0.04 and 100 ppm, respectively.

**Experimental conditions.** —The experimental conditions of the single-cell operation test in the hydrogen one-way pass and the hydrogen circulation system are shown in Table I. The fuel stoichiometry, $S_f$, in this experiment was defined by Eq. 1:

$$S_f = \frac{F_{in}}{F_{in} - F_{out}},$$  

where $F_{in}$ and $F_{out}$ are the fuel flow rates at the cell inlet and outlet, respectively. The anode gas was not humidified to prevent $CO_2$ contamination from the humidifier’s water, which affects the $CO_2$ analysis in the hydrogen circulation system.

Both in the hydrogen one-way pass system and in the hydrogen circulation system, the single-cell was operated at a current density of 1000 mA cm$^{-2}$ using high-purity hydrogen as the fuel over 6 h. After that, $CO$ mixed with hydrogen was fed to the anode over 20 h. During the operation of the hydrogen circulation system, the purge gas was sampled to analyze $CO$, $CO_2$, and $O_2$ concentrations. The purge rate, $r$, as defined by Eq. 2, was 1%.

$$r = \frac{V_p}{V_p + V_L}$$  

$V_p$ and $V_L$ are the purged amount and the amount of fuel supplied to the hydrogen circulation system between the $n$th and $(n + 1)$th purging, respectively.

**Results and Discussion**

Comparison of voltage change between PEFCs with a hydrogen one-way pass system and a hydrogen circulation system.—The

![Schematic apparatus](image-url)
single-cell tests were conducted using high-purity hydrogen and CO containing hydrogen. The cell voltages during the CO exposure in the hydrogen one-way pass system and in the hydrogen circulation system are shown in Figs. 2a and 2b, respectively. The cell voltage started to drop at 0 h after CO addition, both in the hydrogen one-way pass system and in the hydrogen circulation system. As the CO concentration increased, the voltage drop became larger, and the time until the voltage reached steady state became shorter. As seen in Fig. 2b, when 1 ppm CO was supplied in the hydrogen circulation system, the voltage temporarily dropped to 0.4 V after 4 h and then recovered to 0.46 V after 10 h.

Figure 3 shows a comparison of the voltage change caused by adding CO in the hydrogen one-way pass system and in the hydrogen circulation system. The voltage change, $\Delta V$, is defined in Eq. 3:

$$\Delta V = V_f - V_0,$$

where $V_f$ and $V_0$ are the cell voltages at steady state after CO addition and cell voltage at 0 h, which is the time before CO addition, respectively. The voltage change in the hydrogen circulation system is smaller than that in the hydrogen one-way pass system. At 0.2 ppm CO in the hydrogen circulation system, the voltage change induced by adding CO is less than one-tenth of that observed when the hydrogen one-way pass system is used.

Gas analysis in the hydrogen circulation system.—CO, CO$_2$, and oxygen concentrations in the hydrogen circulation system were analyzed during the single-cell operation to reveal the cause of differences in cell voltage drop between the hydrogen one-way pass system and the hydrogen circulation system. Figure 4 shows the change of CO (a) and CO$_2$ (b) concentration in the hydrogen circulation system over time during the CO exposure test. As shown in Fig. 4a, the CO concentration in the hydrogen circulation system was lower than the supplied CO concentration throughout the CO exposure test. In the case of 1.0 ppm CO in hydrogen, CO concentration in the hydrogen circulation system was temporarily increased to 0.7 ppm and then decreased to below 0.3 ppm.

As shown in Fig. 4b, CO$_2$ concentration in the hydrogen circulation system slightly increased even in the case of using high-purity hydrogen as fuel. Our previous report showed that CO$_2$ was detected in the anode exhaust during the single-cell test with high-purity hydrogen as fuel in the hydrogen one-way pass system. The anode gas was not humidified in this experiment to prevent 

| Table I. Experimental conditions of cell operation test in the hydrogen one-way pass and the hydrogen circulation systems. |
|---|---|
| Cell temperature (°C) | 60 |
| Dew point (anode/cathode)(°C) | Nonhumidified (<−20)/40 |
| Fuel stoichiometry | 2.0 |
| Oxidant stoichiometry | 2.5 |
| Current density (mA cm$^{-2}$) | 1000 |
| Pressure at cell outlet (anode/cathode) (kPa) | 5/5 |
| CO concentration (ppm) | 0.08, 0.15, 0.2, 0.3 (Hydrogen one-way pass) 0, 0.2, 0.4, 1.0 (Hydrogen circulation system) |
contamination with CO₂ from the atmosphere dissolved in the humidifier’s water. The CO₂ generation in the anode exhaust may be attributed to the oxidation of the anode electrocatalyst carbon support by hydrogen peroxide generated from permeated oxygen and hydrogen as shown in Eqs. 4 and 5.23

\[
\begin{align*}
C + H_2O_2 &\rightarrow CO_{ad} + H_2O \quad [4] \\
CO_{ad} + H_2O &\rightarrow CO_2 + H_2O \quad [5]
\end{align*}
\]

Permeated oxygen also has the possibility to oxidize carbon as shown in Eq. 6.

\[
C + O_2 \rightarrow CO_2 \quad [6]
\]

In the case of CO-containing hydrogen, the CO₂ concentration obviously increased after 0 h. The CO₂ concentration in the hydrogen circulation system became higher as the supplied CO concentration increased. CO in the hydrogen fuel can be oxidized and accumulates as CO₂ in the hydrogen circulation system.

It has been reported that CO in the hydrogen fuel is oxidized to CO₂ during the PEFC operation,2,8,11,20 and many discussions have been made on the CO oxidation mechanism at the anode electrocatalyst. One of the suggested mechanism is the electrooxidation of CO by water as the oxygen source, which are shown in Eqs. 7 and 8.24

\[
\begin{align*}
Pt + CO &\leftrightarrow Pt - CO \quad [7] \\
Pt - CO + H_2O &\leftrightarrow Pt + CO_2 + 2H^+ + 2e^- \quad [8]
\end{align*}
\]

Generally, it is known that the reaction in Eq. 8 requires relatively high anode overvoltage. But the reaction in Eq. 8 may be promoted due to the formation of a local mixed potential by reduction of permeated oxygen from the cathode, which is shown in Eq. 9.

\[
1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad [9]
\]

The other suggested CO oxidation reaction pathway is permeated oxygen from the cathode. The degree of cell voltage drop due to CO during the PEFC operation became small when the cathode oxygen pressure was high25 or electrolyte membrane thickness was thin.26

Figure 4. Change of (a) CO and (b) CO₂ concentration over time during the CO addition in the hydrogen circulation system at a cell temperature of 60 °C and 1000 mA cm⁻² current density.

Figure 5. Relationship between originally supplied CO concentration and CO concentration measured in the hydrogen circulation system at a cell temperature of 60 °C and 1000 mA cm⁻² current density.

Figure 6. Change in oxygen concentration over time during CO addition in the hydrogen circulation system at a cell temperature of 60 °C and 1000 mA cm⁻² current density.
Our previous results also showed that the existence of permeated oxygen in the anode has been experimentally confirmed during the fuel cell operation. The reactions are shown in Eqs. 10 and 11.

\[
\begin{align*}
\text{O}_2 + 2\text{Pt} & \leftrightarrow 2\text{Pt} - \text{O} & [10] \\
\text{Pt} - \text{O} + \text{Pt} - \text{CO} & \leftrightarrow 2\text{Pt} + \text{CO}_2 & [11]
\end{align*}
\]

Figure 5 shows the maximum and steady state CO concentrations in the hydrogen circulation system with respect to the supplied CO concentrations shown in Fig. 4. In the case of 1.0 ppm CO in hydrogen, the maximum CO concentration in the hydrogen circulation system was 0.7 ppm. Generally, the CO concentration in the hydrogen circulation system is lower than the supplied CO concentration, which indicates that CO is not accumulated in the hydrogen circulation system.

The oxygen concentration change over time in the hydrogen circulation system during CO exposure is shown in Fig. 6. In the case of high-purity hydrogen as fuel, the oxygen concentration increased monotonically, and the oxygen concentration at 30 h was 40 ppm. The result showed that oxygen is present in the hydrogen circulation system as well as in the hydrogen one-way pass system. Most of the permeated oxygen should react with hydrogen to form water, but some remained in the anode and circulated in the hydrogen circulation system.

The oxygen concentration in the hydrogen circulation system increased after CO injection to the anode. The oxygen concentration became high when the CO concentration was high. This tendency was similar to that previously reported in the hydrogen one-way pass system. It appears to be due to the difference in the oxygen consumption rate and to depend on whether CO is adsorbed at the anode electrocatalyst or not. If there is no CO at the anode electrocatalyst, permeated oxygen reacts with hydrogen. On the other hand, if CO is adsorbed at the anode electrocatalyst, permeated oxygen reacts with hydrogen and CO. The CO oxidation rate seems to be slower than that of hydrogen. When the CO coverage is high, the oxygen consumption rate may be low. Therefore, the oxygen exhaust rate should increase during the CO feeding.

In the case of 0.2 ppm CO in hydrogen (Fig. 6), the oxygen concentration after 30 h was 72 ppm. In contrast, CO concentration in the hydrogen circulation system after 30 h was 0.02 ppm when 0.2 ppm CO were present in the hydrogen (Fig. 4a). These results show that the oxygen concentration was excessively high compared with the CO concentration in the hydrogen circulation system.

Discussion of the difference of voltage change between the hydrogen one-way pass system and the hydrogen circulation system.—As seen in Fig. 3, the voltage change by adding CO in the hydrogen circulation system is smaller than that in the hydrogen one-way pass system. The reason for the mitigation of the voltage drop in the hydrogen circulation system should be the internal air bleed by oxygen permeated from the cathode. Oxygen should play an important role in the CO oxidation. The existence of permeated oxygen in the anode has been experimentally confirmed both in the hydrogen one-way pass system and the hydrogen circulation system (Fig. 6). Oxygen in the hydrogen circulation system should accumulate, whereas oxygen in the hydrogen one-way pass system is exhausted from the system. Therefore, the oxygen concentration in the hydrogen circulation system should be larger than that in the hydrogen one-way pass system. The increase of oxygen concentration in the hydrogen circulation system should lead to enhancement of CO oxidation. Figure 5 shows that when the supplied CO concentration was 0.2 ppm in the hydrogen fuel, the CO concentration in the hydrogen circulation system was 0.02 ppm. Fuel stoichiometry in the experiment was 2.0, which means the fuel supply rate from the gas cylinder is equal to the gas supply rate from the hydrogen circulation system. Consequently, the CO concentration at the anode inlet should decrease to 0.1 ppm because the gas from the cylinder, which contains CO, is diluted by the gas from the hydrogen circulation system. Such CO dilution in the hydrogen circulation system should also result in the mitigation of the voltage drop.

Conclusions

The effect of CO on PEFC performance degradation was investigated using a hydrogen circulation system, and it was compared with a hydrogen one-way pass system under the conditions of low platinum loading at the anode and of low CO concentration. At 0.2 ppm CO in the hydrogen circulation system, the voltage change induced by adding CO is less than one-tenth of that observed when the hydrogen one-way pass system is used. In the hydrogen circulation system, permeated oxygen from the cathode should enhance CO oxidation. This should lead to decrease the CO concentration and mitigate the voltage drop in the hydrogen circulation system. The impact of impurities on PEFC performance has been discussed mainly on the result of one-way pass system. The evaluation in the hydrogen circulation system is also important to discuss the allowable concentration limit of impurities in the hydrogen fuel for the FCVs. These results should be considered for revision of ISO 14687-2 as well as for the fuel cell component development and the operating condition which assumed the actual FCVs such as the load cycles.

The hydrogen circulation system used in our experiments was designed in consideration of the actual system configuration, but there are some differences from the actual system. Representative example of the condition is water management in the system. The anode humidification condition in this experiment was dry, whereas commercial systems are thought to be humidified by water circulation via hydrogen circulation system and water exchange from cathode gas outlet by using membrane humidifier. In particular, above considerations are important when evaluating water-soluble impurities. Future work is to evaluate the behavior of impurities in the hydrogen circulation system which is closer to commercial system.

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