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PEMFC System for Utilization of Exhaust Gas from Bright Heat Treatment furnace

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ABSTRACT

Exhaust gas from bright heat treatment furnaces can be used as a fuel for fuel cells because it is rich in hydrogen. However, it contains carbon monoxide (CO); when a CO-containing gas is used as a fuel gas in a proton-exchange membrane fuel cell (PEMFC), cell performance decreases. Therefore, it is necessary to remove contaminants from hydrogen-rich exhaust gas. In this study, the effect of CO contaminants in hydrogen gas on the PEMFC stack performance was firstly evaluated. The experimental results showed a correlation between CO concentration and fuel cell stack performance, wherein performance degraded quickly because of CO poisoning. Furthermore, for improving the performance of the PEMFC stack using the CO-containing hydrogen gas, three methods were evaluated: molecular sieve adsorption, methanation reaction, and air bleeding. These methods were effective against CO poisoning and delayed performance deterioration. In particular, methanation refining was observed to be the most effective method for reducing CO poisoning.

Keywords: PEM fuel cell, carbon monoxide, bright heat treatment furnace, refining process

1. INTRODUCTION

A wide range of technologies that utilize hydrogen is available, with a specific use as an atmosphere gas in bright heat treatment furnaces. Atmospheric gas is filled into the furnace during heat treatment. A schematic of an atmosphere furnace is shown in Fig. 1. The heat treatment of metal parts and components under an atmosphere that does not contain oxygen or carbon dioxide prevents oxidation and decarburization of the workpieces. Furthermore, hydrogen creates a reduction atmosphere, enabling bright heat treatment wherein some oxides on the metal surface are reduced[1]. The exhaust gas from bright heat treatment furnaces contains impurities from metal parts. Although the exhaust gas is hydrogen-rich, it is combusted generally because of the contamination. Thus, effective utilization of the exhaust gas is strongly required in terms of energy loss. The exhaust hydrogen could potentially be used as a fuel for fuel cells. However, it contains CO which can cause poisoning and can significantly degrade the fuel cell performance. It is also known that CO reduces not only the performance but also the lifetime of the fuel cell[2]. Therefore, it is necessary to treat impurities in the exhaust hydrogen to achieve effective utilization. However, current CO-poisoning mitigation measures are difficult to apply in small-scale facilities because of their high cost and high energy consumption. Thus, a simple refining method is required. In this study, the effect of CO-containing hydrogen gas on the performance of a PEMFC stack and the CO tolerance of the system have been evaluated using a simple refining method with the aim of developing a system with high impurity tolerance.

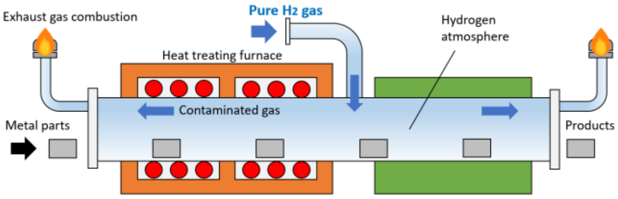

Fig. 1 Schematic illustration of bright heat treatment furnace

2. EXPERIMENTAL

A schematic diagram of the experimental apparatus used in this study is shown in Fig. 2. The fuel cell stack was a 1 kW PEMFC stack consisting of 48 cells, with a 5 N hydrogen cylinder and a 1000 ppm CO-containing hydrogen cylinder mixed with CO-containing gas at a predetermined concentration at the anode. The stack was dead-ended, with 0.1 s of purging once in every 10 s. The cathode was supplied with indoor air; the operating conditions of the constant voltage test are listed in Table 1. Herein, molecular sieve adsorption,

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methanation modification, and air bleeding were evaluated as simple refining methods. These methods are low in cost and energy consumption and can be adapted to small-scale facilities. Molecular sieve adsorption and methanation reforming are external purification methods. In each application, the CO-containing hydrogen gas was supplied to the FC stack using a molecular sieve adsorber or a methanation reactor. The molecular sieve absorber was filled with zeolite, which selectively absorbs CO, and the CO molecules passing through the adsorption apparatus were selectively removed. The methanation reactor was used for methanation reforming. In the methanation reaction, a nickel catalyst is used to reduce CO to methane (CH_4) on the catalyst; the formation of CH_4 in the reactor can be described using Eqs. (1) and (2). Air bleeding, an internal reforming method, involves the addition of a small amount of air into the feed gas. Subsequently, CO is oxidized by oxygen in the added air on the anode electrocatalyst to form CO_2 [3]. However, excessive air injection should be avoided because it may produce hydrogen peroxide (H_2O_2), which can chemically degrade fuel cells [4]. Herein, air was added during the mixing of the CO-containing hydrogen gas to adjust its concentration and move it to the FC stack. The CO_2 formation reaction by air bleeding is described in Eq. (3).

$$\mathrm{CO+3H_2 \rightarrow CH_4+H_2O} \tag{1}$$

$$\mathrm{2CO+2H_2 \rightarrow CH_4+CO_2} \tag{2}$$

$$\mathrm{CO+\frac{1}{2}O_2 \rightarrow CO_2} \tag{3}$$

Table 1 Operating condition for constant voltage test

Stack voltage [V]	31.2 (0.65/cell)
Operating temperature [°C]	65 (max.)
Anode gas pressure [MPa]	0.06

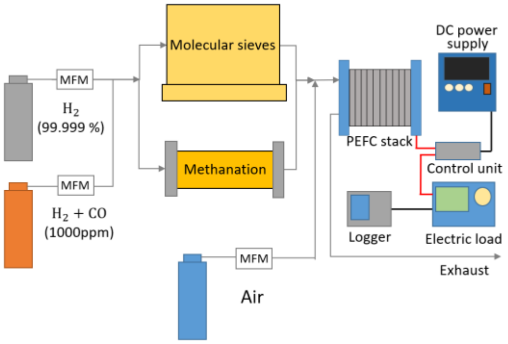

Fig. 2 Schematic diagram of experimental system

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Effect of CO-containing hydrogen supply on PEMFCs

To evaluate the effect of CO-containing hydrogen on the stack performance, constant voltage tests were performed with different CO concentrations at the anode (5, 10, and 20 ppm CO). All tests were run with pure hydrogen for 30 min to achieve a steady-state operation before the CO-containing hydrogen gas was supplied. The output current of the constant voltage test at 31.2 V for each CO concentration is shown in Figure 3. The current decreased gradually after CO injection, and the current drop gradually increased. The severe performance degradation at higher CO concentrations is attributed to the high amount of CO adsorbed on the catalyst surface with high CO dosages. The slope of the decrease in current slowed as the current value approached 5 A, suggesting that the CO adsorption and desorption rates on the catalyst surface reached an equilibrium because the amount of CO mixed with the supplied hydrogen gas decreased with decrease in current.

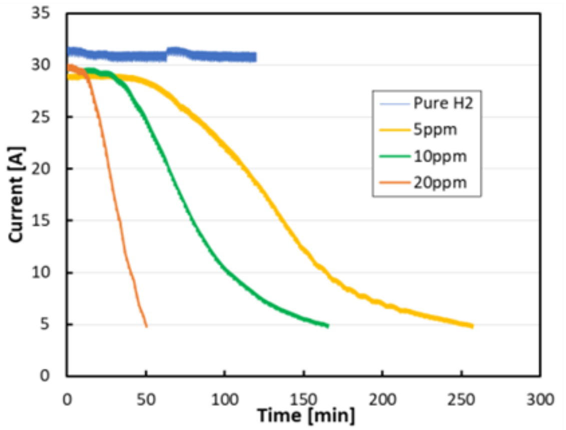

Fig. 3 Output currents in the case of CO-containing hydrogen supply

3.2 Evaluation of the PEMFC performance in the simple refining method

The simple refining method was applied on 5 ppm CO feed. For the molecular sieve technique, the current was maintained for 79 min after the injection of CO-containing hydrogen, with the current decreasing gradually afterward. In methanation modification, the current was maintained for 6 h until the end of the test, and no decrease in performance was observed. The CO concentration decreased because of the CO to methane conversion in the methanation reactor. To evaluate the air bleeding method, a constant voltage was applied upon adding 1% air to the 5 ppm CO hydrogen feed gas.

The current fluctuated significantly because of purging, but the current decreased gradually with a constant slope from the initiation of the CO-containing hydrogen supply. A steady-state value at approximately 24 A was maintained after 5 h. Finally, after 6 h of operation, the performance reduced by approximately 22% compared to that measured before the CO-containing hydrogen gas was introduced in the system. The accumulation of nitrogen in air in the dead-end stack may have caused a decrease in hydrogen partial pressure and a decrease in current.

After 250 minutes of supplying CO-containing hydrogen, the power retention rate for each method was 17% when CO was supplied directly to the stack, 43% when molecular sieve adsorption was applied, 78% when air bleeding was applied, and 100% when methanation reforming was applied (no power loss observed). Compared with the cases where CO was directly supplied, the power retention rates of the simple purification methods were higher. The effects of methanation modification, air bleeding, and molecular sieve adsorption on the reduction of CO poisoning was confirmed in that order. The effectiveness of methanation modification for preventing CO poisoning was clearly demonstrated.

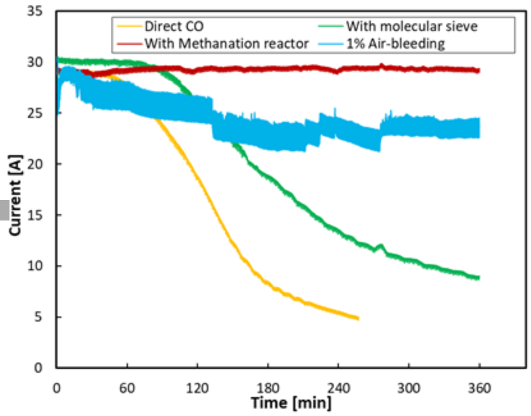

Fig. 4 Current behavior for each method with 5ppm CO concentration

3.3 *Evaluation of the PEMFC performance in terms of methanation reaction methods at different CO concentrations*

To evaluate the effect of methanation reforming on the PEMFC stack performance, constant voltage tests were conducted for 6 h at different concentrations of CO (5, 20, and 50 ppm). The concentration of 20 ppm was chosen as it is typically observed in the bright heat treatment furnace exhaust air. The current in the methanation reactor under various CO concentrations is shown in Fig. 5. At 20 ppm CO, the current was maintained over the 6 h test period when CO-containing hydrogen was supplied. Even at a concentration of 20 ppm, CO in the fuel stream was methanated; the CO concentration was reduced to a level that did not affect performance. At 50 ppm CO, the current was approximately 29.5 A when pure hydrogen was supplied, but a slight decrease was observed 200 min after the test was started. At the end of the 6 h test, the current decreased to approximately 28.5 A. Slight performance degradation of 3% was observed at 6 h, which can be attributed to the increased voltage because of methane accumulation in the stack. First, 50 ppm methane produced by the methanization of CO was fed into the stack. This methane was not discharged because of the dead-end design, and it was accumulated in the stack. Over time, the methane concentrated and the overvoltage increased due to the partial pressure decrease of hydrogen.

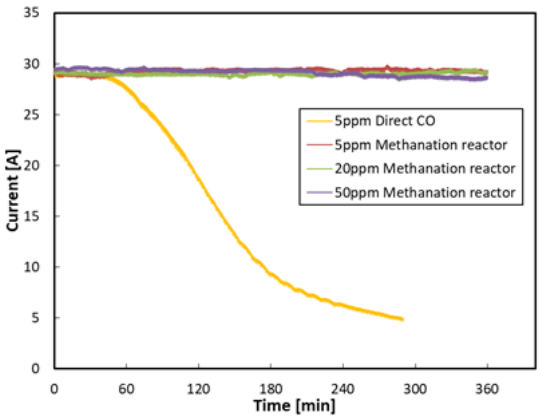

Fig. 5 Output currents when using Methanation refining with different CO concentration

3.4 *0.8% O_2 supply test*

The heat-treatment reactor exhaust gas contains oxygen. Therefore, stack performance was evaluated by supplying oxygen during the methanation reaction. The formation CH_4 in the reactor is described by Eqs. (1) and (2), while Eq. (4) was also considered. The reaction described in Eq. (5) was also observed under the oxygen-supply condition.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{4}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + \ 58\mathrm{Kcal} \tag{5}$$

Herein, the concentration of O_2 supplied with CO-containing hydrogen was 0.8%, which is assumed to be the concentration in the exhaust gas of the bright heat treatment furnace. The CO concentration was 20 ppm and the O_2 concentration in the methanation reactor was also measured after passing through the methanation reactor. The stack current and O_2 concentration in the gas after it passes through the methanation reactor are listed in Fig. 6 when hydrogen gas containing 0.8% O_2 was supplied. The current was maintained for 6 h from the initial CO injection to the end of the experiment, and no decrease in performance was observed. Even at 0.8% O_2 supply, the oxygen concentration was reduced to the ppm level for 6 h until the end of the experiment, confirming that the reaction between hydrogen and O_2 occurred in the methanation reactor. The highest O_2 concentration of 9.87 ppm was measured at 173 min. Water droplets were observed on the tubes of the methanation reactor from the time when the test was initiated until 30 min after the CO supply test. The water droplets originated from the reaction between the remaining oxygen and hydrogen in the methanation reactor, and the current during the early stages of the test was low because of flooding. From Eq. (5), approximately 161 mL/min of water vapor was generated in the methanation reactor. Because no water droplets were observed 30 min after supplying CO, water condensation in the reactor was not significant and water vapor was removed from the reactor. The methanation reactor can remove CO and O_2 and supply hydrogen-rich gas of 20 ppm CH_4 to the PEMFC without affecting the power-generation performance.

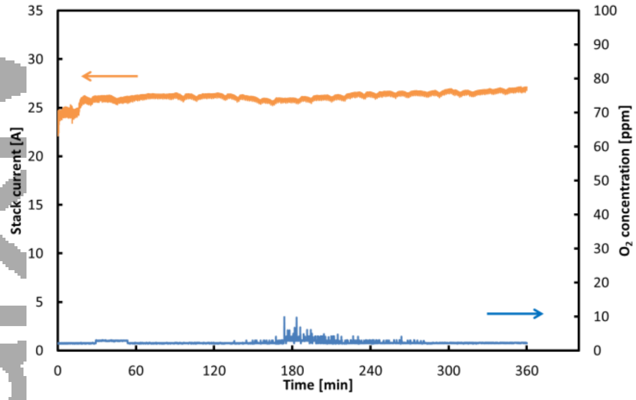

Fig. 6 Output current in methanation reactor and O_2 concentration after passing through the reactor（H_2/CO 20ppm/ O_2 0.8%）

4. CONCLUSION

In this study, the effect of CO-containing hydrogen gas on the PEMFC stack performance and the CO tolerance of the fuel cell system with simple refining methods were evaluated. The main aim was to realize a fuel cell system that possesses high impurity tolerance and utilizes exhaust hydrogen gas. In the constant voltage test with CO-containing hydrogen supply, the current decreased gradually after CO injection and severe degradation in performance was observed. To use exhaust gases as fuel for PEMFCs, a CO-removal device is necessary before feeding the exhaust gases to the PEMFCs to reduce the CO concentration to a level that does not affect performance. As a simple refining method, molecular sieve adsorption mitigated the decrease in performance, but it did not achieve long-term mitigation because of the upper limit of CO adsorption. Air bleeding showed a gradual decrease in current of approximately 22% over 6 h, but a certain level of performance was maintained. For the methanation modification method, the current remained constant for 6 h without any decrease in performance These results indicate that simple refining by methanation modification is useful for reducing CO poisoning. In addition, methanation reforming was effective for CO- and O_2-containing exhaust gases because H_2O, a product of the O_2 reaction in the methanation catalyst, maintained the PEMFC electrolyte membrane performance. In the future, the effective use of exhaust hydrogen can be achieved by applying the methanation reforming method in small-scale PEMFC systems that can be equipped with simple hydrogen-refining equipment such as a bright heat treatment furnace.

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