



Short communication

Experimental factors that influence carbon monoxide tolerance of high-temperature proton-exchange membrane fuel cells

Kyungjung Kwon*, Duck Young Yoo, Jung Ock Park

Energy & Environment Lab, Samsung Advanced Institute of Technology, Nongseo-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-712, Republic of Korea

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ABSTRACT

The poisoning effect of carbon monoxide (CO) on high-temperature proton-exchange membrane fuel cells (PEMFCs) is investigated with respect to CO concentration, operating temperature, fuel feed mode, and anode Pt loading. The loss in cell voltage when CO is added to pure hydrogen anode gas is a function of fuel utilization and anode Pt loading as well as obvious factors such as CO concentration, temperature and current density. The tolerance to CO can be varied significantly using a different experimental design of fuel utilization and anode Pt loading. A difference in cell performance with CO-containing hydrogen is observed when two cells with different flow channel geometries are used, although the two cells show similar cell performance with pure hydrogen. A different combination of fuel utilization, anode Pt loading and flow channel design can cause an order of magnitude difference in CO tolerance under identical experimental conditions of temperature and current density.

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1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) generally use a hydrogen-rich gas mixture at the anode, but impurities such as CO, are detrimental to cell performance. From an economic point of view, CO-free hydrogen is very expensive, and therefore reformat hydrogen is considered for practical usage. The presence of CO in reformat gas is a major problem for the state-of-the-art PEMFC operating at 80 °C because a very small amount (about 10 ppm) of CO can poison the Pt electrocatalyst [1]. To circumvent this problem, CO-tolerant catalysts such as PtRu are used [2–4], and a high-temperature PEMFC in which a higher level of CO can be tolerated is under development [5–9].

Polybenzimidazole (PBI) and poly(2,5-benzimidazole) (ABPBI) are representative membranes for high-temperature PEMFCs, and it has been demonstrated that at temperatures PEMFCs above 150 °C the CO tolerance is 100 times or more greater than in a low-temperature PEMFC [6–8]. The effect of temperature and CO concentration on cell performance has usually been discussed without due consideration of other experimental factors, such as reactant feed mode. For example, ABPBI-based and PBI-based membrane electrode assemblies (MEAs) are operated in the range

of 120–200 °C with fixed flow rates of both anode and cathode gases [6,7]. Korsgaard et al. [8] investigated the influence of cathode gas stoichiometry, which is a reciprocal of gas utilization efficiency, on the performance of a high-temperature PEMFC with CO-containing anode gas. In this study, the CO tolerance of a PBI-based MEA is evaluated by varying the feed mode of CO-containing anode gas, as well as operating temperature and CO concentration. In addition, the effects of anode Pt loading and anode flow channel geometry on CO tolerance are also discussed.

2. Experimental

The cathode of the fuel cell was composed of Tanaka PtCo supported on carbon, polyvinylidene fluoride (PVDF), and SGL carbon paper with a Pt loading of 2 mg cm⁻². Similarly, the anode was composed of Tanaka PtRu supported on carbon, and the same binder and carbon paper as used in the cathode. Two levels (0.5 and 1 mg cm⁻²) of anode Pt loading were employed. Eighty-five percent of phosphoric acid was doped in PBI by immersing a dry PBI membrane in phosphoric acid at 60 °C for 40 min. The phosphoric acid loading is about 90 μmol per unit area (cm²) of the doped membrane.

CO-containing hydrogen and air were used for the anode and cathode gases, respectively, without humidification. The effective dimensions of the electrode were 2.8 cm × 2.8 cm. A single cell com-

* Corresponding author. Tel.: +82 31 280 8162; fax: +82 31 280 9359.
E-mail addresses: k.kwon@samsung.com, kberkeley@dreamwiz.com (K. Kwon).

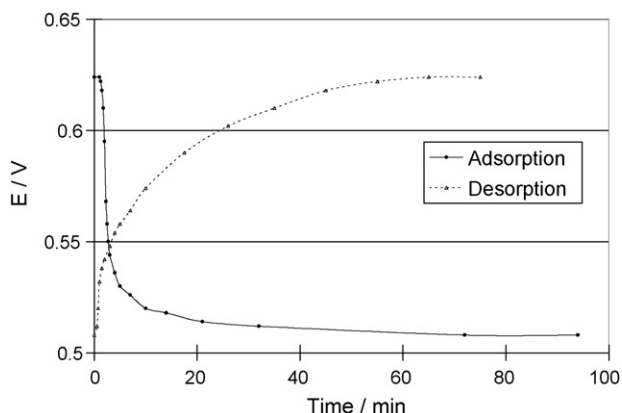


Fig. 1. Voltage response with time for CO adsorption and desorption.

prising the MEA and current-collectors for the anode and cathode was operated over the temperature range of 130–170 °C.

The CO concentration in the anode gas was varied from 0 to 1%. The anode gas was supplied to the MEA through a parallel-serpentine flow channel on the current-collector in two feed modes. For the constant flow rate (cfr) mode, 100 ml min⁻¹ of the anode gas was fed into the MEA. For the constant utilization (cu) mode, the anode was provided with hydrogen at 80% utilization, flow rate of which was a function of the operating current. An air flow of 250 ml min⁻¹ was adopted in the cathode side for both anode gas-feed modes.

Each set of experiments, which involved varying the operating temperature, gas feed mode and CO concentration, was conducted for the two different levels of anode Pt loading. Current–voltage (*I*–*V*) measurements of a single cell were performed by controlling the current density and recording the corresponding voltage. Although more points in the *I*–*V* plot are recorded for the cfr mode, only five corresponding voltage values at 0, 0.1, 0.2, 0.3 and 0.4 A cm⁻² were recorded for the cu mode.

3. Results and discussion

The transient response of cell voltage with the addition and removal of CO in the anode hydrogen gas was examined before a series of CO-tolerance experiments was conducted. Fig. 1 depicts the voltage loss and recovery under conditions of 130 °C, 1% CO concentration, and 0.3 A cm⁻². As soon as 1% CO is introduced into the anode gas, the cell voltage plummets from 0.625 V to about 0.51 V in 10 min. Although there is a gradual decrease in voltage in the following period, the majority of voltage loss occurs within 10 min. However, CO desorption rate is slower than CO adsorption rate. The voltage recovery upon a switch from 1% CO to pure hydrogen starts at a slower rate than that of the initial voltage loss. A slower recovery of voltage from the initial voltage loss of the CO poisoning effect has also been observed for a PBI-based MEA at 125 °C [7]. Meanwhile, stabilization period of about 1 h is required for the full recovery of voltage. This time-frame is similar to that reported by Divisek et al. [3] where a steady-state voltage at 0.4 A cm⁻² was attained after about 100 min for a PtRu anode. Therefore, the above stabilization period of voltage was adopted in the measurement of steady-state values in this study. Incidentally, the whole set of experiments by varying the temperature and CO concentration can be carried out with the same MEA because the full recovery of voltage is confirmed in the least CO-tolerant experimental condition.

Fig. 2 presents the *I*–*V* performance of the MEA employing a PtRu anode with a 0.5 mg cm⁻² Pt loading. The *I*–*V* performance with anode gas of pure hydrogen is compared for various oper-

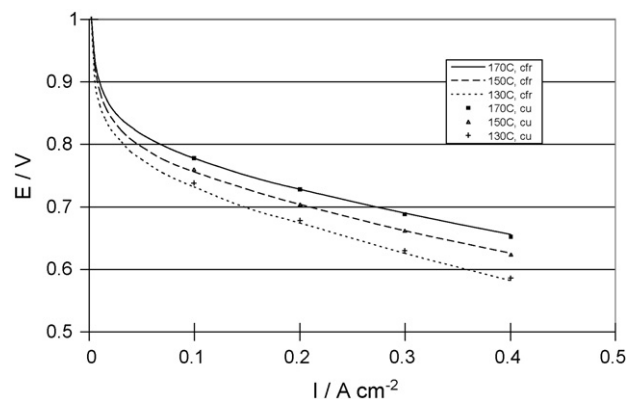


Fig. 2. *I*–*V* performance of 0.5 mg cm⁻² Pt loaded anode with pure hydrogen.

ating temperatures and the two feed modes. As expected, the cell performance is enhanced at a higher operating temperature. The enhanced reaction kinetics and membrane conductivity with increasing temperature mainly contributes to the improvement of cell performance [6,7]. No substantial difference in cell performance for the different feed modes (cfr and cu) is observed. For the cfr experiment, 100 ml min⁻¹ of anode gas corresponds to 5, 11, 16 and 22% of fuel utilization (U_f) at 0.1, 0.2, 0.3 and 0.4 A cm⁻², respectively. The virtually identical cell performance of the two modes indicates that an excessive fuel for which U_f ranges from 5 to 22 is not necessary for fuel cell operation in the low current density region. In addition, it is confirmed that there is no practical voltage decline up to 80% of the cu mode, and there is a hint of a voltage drop at 90%. Because oxygen reduction at the cathode is a much more sluggish process than hydrogen oxidation at the anode in the absence of CO, the cell voltage should be less sensitive to changes in fuel utilization than in air utilization [10].

The voltage loss of the MEA with a 0.5 mg cm⁻² Pt loading anode in the cfr mode is plotted for various temperatures and CO concentrations in Fig. 3. The voltage loss becomes larger as the temperature is lower and the CO concentration is higher. The voltage loss is magnified as the current density increases because there appears to be a shortage of CO-free catalyst sites to support hydrogen oxidation at high current densities. It has been reported that the voltage loss value of a PBI-based PEMFC for 1% CO at 150 °C and 0.4 A cm⁻² is about 20 mV [7]. This loss is one-third of that for our system measured under the same conditions of temperature, current density and CO concentration.

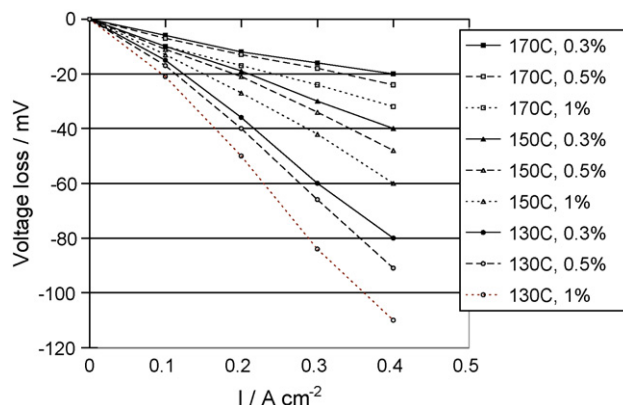


Fig. 3. Voltage loss of 0.5 mg cm⁻² Pt loaded anode for various temperatures and CO concentrations.

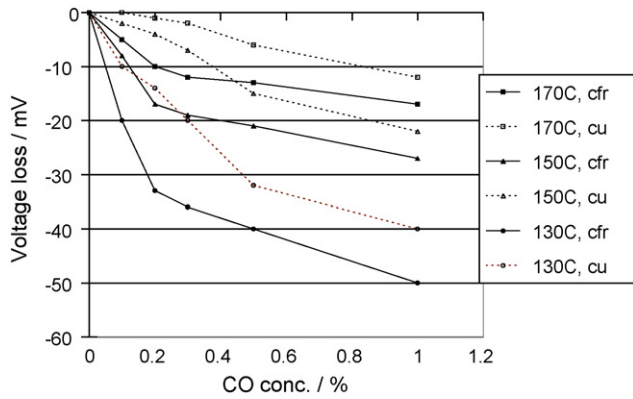


Fig. 4. Voltage loss of 0.5 mg cm^{-2} Pt loaded anode for various temperatures and different fuel feed modes.

The dependence of voltage loss on CO concentration monitored at 0.2 A cm^{-2} is shown in Fig. 4. Although the number of data points is not sufficient for identifying the relationship between voltage loss and CO concentration conclusively, the relationship in the cfr mode is logarithmic and that in the cu mode is fairly close to linear. This tendency holds more clearly for CO concentrations less than 0.5% and gives rise to a superior cell performance with the cu mode. Although the difference in cell voltage depending on the fuel feed mode is not observed in the case of pure hydrogen, the superior cell performance of the cu mode is observed for the whole set of experiments that is conducted with CO in the gas for a 0.5 mg cm^{-2} Pt loading anode.

CO tolerance is usually defined as the maximum CO concentration that produces a voltage loss within a certain value [7]. When the voltage loss limit is set at 20 mV, the CO tolerance of each experimental condition is plotted in Fig. 5. A different value of 10 mV was chosen for CO tolerance at 170°C because a loss of less than 20 mV is observed with CO concentrations up to 1%. The CO tolerance with a 10 or 20 mV voltage loss limit is evaluated by linear interpolation between adjacent data points if corresponding CO concentration data to the voltage limit is absent. It should be noted that there is a difference in CO tolerance depending on the fuel feed mode. A lower CO tolerance for the cfr mode is observed over the whole temperature range. The dependence of CO tolerance on the fuel feed mode, which is eventually related to U_f , suggests that U_f is an important factor in the evaluation of CO tolerance, as well as other apparent fac-

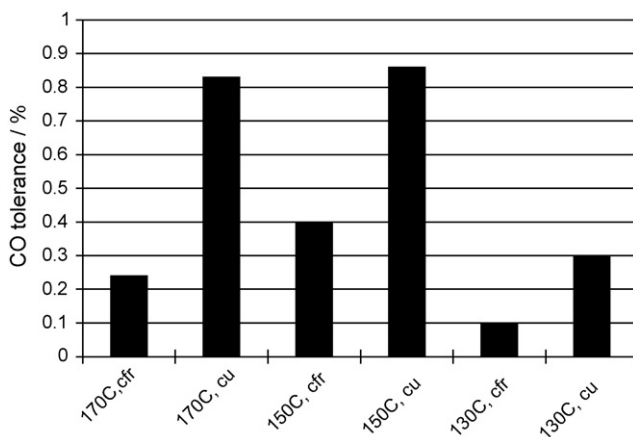


Fig. 5. CO tolerance of 0.5 mg cm^{-2} Pt loaded anode for various temperatures and different fuel feed modes.

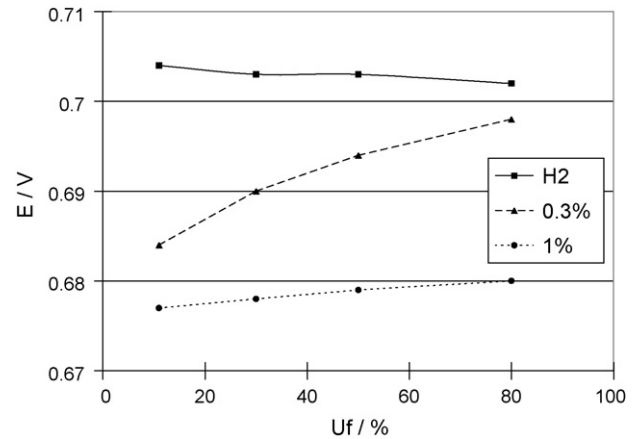


Fig. 6. Dependence of cell voltage at 0.2 A cm^{-2} on fuel utilization for various CO concentrations.

tors, such as temperature, current density, and the type of anode catalyst.

To elucidate the effect of U_f on cell performance, the cell voltage at 0.2 A cm^{-2} is plotted versus U_f in Fig. 6 for a 0.5 mg cm^{-2} Pt loading anode at 150°C . As shown in Fig. 2, hydrogen fuel in which U_f is lower than 80% is redundant from the viewpoint of practical PEMFC operation. Although there is a negligible increase in cell voltage with decreasing U_f of pure hydrogen from 80 to 11%, the tendency with CO-containing hydrogen is the opposite. The cell voltage with 0.3% CO concentration decreases by 15 mV with decreasing U_f from 80 to 11%. The difference in cell voltage with variation in U_f is less conspicuous at a higher CO concentration. The dependence of cell voltage on U_f with CO-containing hydrogen can be explained by means of the concept of 'critical' CO coverage, which is similar to the 'critical' current. Springer et al. [1] used the critical current as an indication of the CO poisoning effect at a catalyst by the limited rate of hydrogen oxidation occurring on a reduced number of CO-free catalyst surface sites. When CO starts to adsorb on catalyst surface sites beyond the critical CO coverage at an applied current density, a voltage loss will appear.

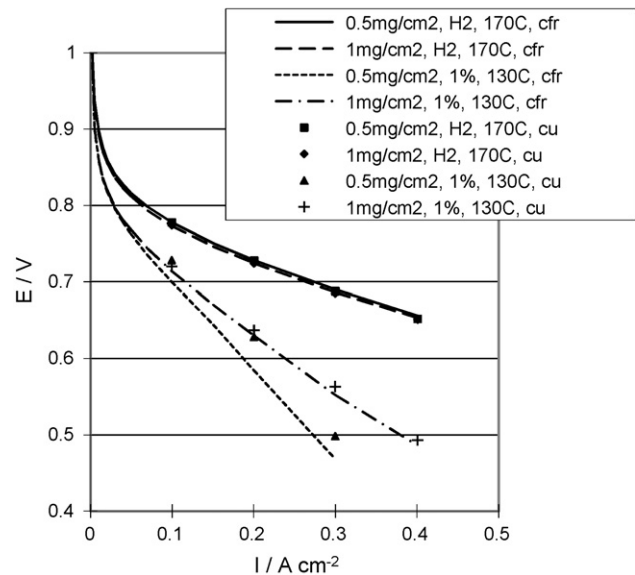


Fig. 7. I - V performance of 0.5 and 1 mg cm^{-2} Pt loaded anodes under various experimental conditions.

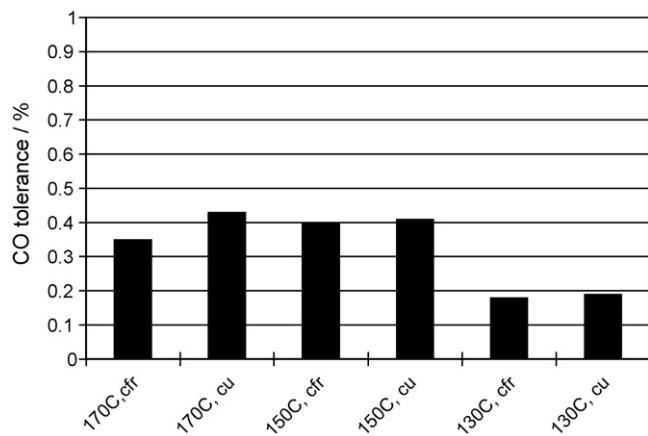


Fig. 8. CO tolerance of 1 mg cm⁻² Pt loaded anode for various temperatures and different fuel feed modes.

The same set of experiments with varying temperature, CO concentration and fuel feed mode was conducted for a PtRu anode with a 1 mg cm⁻² Pt loading. The *I*-*V* performances of certain selected experiments are compared in Fig. 7 for anodes with different Pt loading. The eight *I*-*V* experiments in Fig. 7 can be classified into two categories, that is, the most (1% CO and 130 °C) and the least (pure hydrogen and 170 °C) capable condition of CO adsorption. If the cell performance does not depend on the two variables of anode Pt loading and fuel feed mode, the *I*-*V* curve should be the same regardless of the anode Pt loading and the fuel feed mode. This situation applies to the least capable condition of CO adsorption. The four *I*-*V* curves with pure hydrogen at 170 °C follow the same trend. By contrast, the anode Pt loading and the fuel feed mode affect the cell performance in the most capable condition of CO adsorption. First, a superior cell performance is found with the higher Pt loading anode, and second, a superior cell performance of the cu mode compared with the cfr mode occurs with a 0.5 mg cm⁻² Pt loading anode. Although there is no difference in cell performance between 0.5 and 1 mg cm⁻² Pt loading with pure hydrogen in the temperature range of 130–170 °C, the choice of anode Pt loading and fuel feed mode influences the cell performance in a situation where a large amount of CO is expected to adsorb on catalyst. Therefore, the discrepancy in CO tolerance depending on the fuel feed mode shown in Fig. 5 can be alleviated by using an anode with higher Pt loading. The CO tolerance between the cfr and cu modes is compared for a PtRu anode with a 1 mg cm⁻² Pt loading in Fig. 8. Unlike the case of a 0.5 mg cm⁻² Pt loading anode, a similar level of CO tolerance is obtained regardless of the fuel feed mode. In a situation where high CO adsorption is expected, such as a combination of high CO concentration and low temperature, an experimental choice of a low anode Pt loading and a low *U_f* leads to an ambiguity in determining the CO tolerance of a system. Because a higher *U_f* means a more economical usage of fuel, the choice of the maximum value of *U_f* with no decline in cell voltage with pure hydrogen would be appropriate in the determination of CO tolerance. For the determination of anode Pt loading, it would be desirable to reduce the Pt loading as low as possible without sacrificing of cell performance. On the other hand, this optimization of anode Pt loading with pure hydrogen could incur some uncertainty about CO tolerance by reaching the critical CO coverage more easily.

Springer et al. [1] pointed out the locally different anode overpotential along the anode flow field, where the local reactant concentrations in the flow channel were determined by the inlet flow conditions and the cell current because the local critical current of CO poisoning is different along the flow channel. A difference

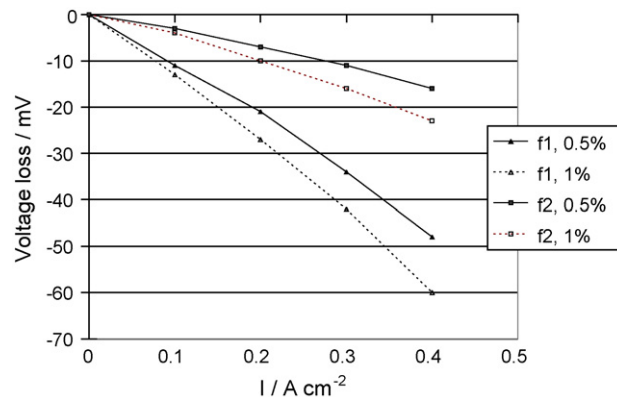


Fig. 9. Voltage loss of 0.5 mg cm⁻² Pt loaded anode for different CO concentrations and flow channel geometries.

in cell performance could appear in the presence of CO in the anode gas between flow channel geometries where the same cell performance is obtained with pure hydrogen. Fig. 9 depicts the difference in voltage loss of two different flow channel geometries at 150 °C. Although the cell performance of the two geometries is practically identical with pure hydrogen, the voltage losses with 0.5 and 1% CO vary by a factor of three. The cell with an improved flow channel design (f2: parallel-serpentine design with a different aspect ratio of flow channel from that of f1) shows better performance than the cell with a parallel-serpentine design (f1) in the presence of CO in the anode gas, and 20 mV voltage loss is observed that agrees with a reported value [7] for 1% CO and 0.4 A cm⁻². A difference in CO tolerance depending on the fuel feed mode by a factor of three is seen in Fig. 5. Therefore, an order of magnitude difference in CO tolerance can be evaluated by a different combination of fuel utilization, anode Pt loading and flow channel design under identical experimental conditions of temperature and current density. The current level of our research on the effect of flow field geometry is such that flow field geometry is proved to be one of the important factors in determining the CO tolerance of a fuel cell. The optimization of flow channel design for maximizing CO tolerance is in progress.

4. Conclusions

The performance of a high-temperature PEMFC with CO-containing hydrogen anode gas is investigated with varying CO concentration, operating temperature, fuel feed mode, and anode Pt loading. The loss in cell voltage is a function of fuel utilization and anode Pt loading, as well as obvious factors such as CO concentration, temperature, and current density. A difference in cell performance with CO-containing hydrogen is observed between cells with different fuel feed modes and flow channel geometries, whereas the cells exhibit the same cell performance with pure hydrogen. A different combination of fuel utilization, anode Pt loading and flow channel design can cause an order of magnitude difference in CO tolerance under identical experimental conditions of temperature and current density.

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