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Effectiveness of Air-Bleeding on the CO Tolerance Improvement of High Temperature Proton Exchange Membrane Fuel Cells

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Keywords： high temperature proton exchange membrane fuel cell, CO poisoning, air-bleeding, fuel cell performance, signal-to-noise ratio.

ABSTRACT

Fuel cell technologies are eco-friendly, and thus they are developed to reach the global goal of net-zero carbon emissions. To increase the fuel cell CO tolerance and simplify purification processes of reformate fuel cell systems, the reformate high-temperature proton exchange membrane fuel cell (HTPEMFC) becomes one of the promising solutions.

In this research, the effectiveness of air-bleeding on the CO tolerance improvement of HTPEMFCs is studied. The voltage signal-to-noise ratio (SNR) and electrochemical impedance spectroscopy analysis indicate that air-bleeding suppresses the CO poisoning reaction, reduces the poisoning intensity, and improves the stability of the HTPEMFC performance. The air-bleeding concentration for the HTPEMFC between 140-180 ℃ with CO of less than 5% is suggested to be 1-1.5%, because excess air does not enhance its effectiveness. The SNR analysis as well indicates that the working temperature and H_2 concentration affect the CO poisoning intensity more significantly than the air-bleeding concentration.

INTRODUCTION

Integration of reformers and fuel cells will be one of the future trends of fuel cell systems. There are other gases in the reformate gas in addition to hydrogen, such as carbon monoxide, nitrogen, and methane (Perng et al., 2021).

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The existence of carbon monoxide has a serious negative impact on the fuel cell performance. Increasing working temperature is one of the effective methods to increase carbon monoxide tolerance of fuel cells. Due to higher carbon monoxide tolerance and other advantages of high temperature (including the more useable recyclable thermal energy, higher possibility of non-precious metal catalysts, and less complex heat and water management), this work takes the high-temperature proton exchange membrane fuel cells (HTPEMFCs) as the main research subject.

Although the HTPEMFC breaks through the working temperature limitation of traditional low temperature proton exchange membrane fuel cells (Chen et al., 2021; Shroti et al.,2022), there is still a minor problem of carbon monoxide poisoning for the HTPEMFCs using CO-containing H_2. In addition to lower cell performance, CO poisoning causes an unstable power output because of the periodic oxidation and adsorption reactions of CO onto the Pt surfaces.

Air-bleeding is a common method to increase the carbon monoxide tolerance of low temperature PEMFCs in a fuel cell system. This method has significant effects on the performance improvement of the fuel cells using reformate gases as fuels. However, there is no literature studying the effects of this method on the HTPEMFCs. As a result, this research aims to study the HTPEMFC behavior under air-bleeding, in order to understand the effectiveness of air-bleeding for the CO poisoning improvement of HTPEMFCs.

As CO-containing hydrogen enters the fuel cell, the adsorption of hydrogen molecules onto the catalyst surface is affected by carbon monoxide molecules, because carbon monoxide molecules occupy the catalyst sites where the hydrogen molecules was originally bonded. This occupancy by CO increases the charge transfer resistance of hydrogen oxidation reaction and thus results in cell performance drop. With the development of fuel cells, researchers have proposed many solutions to CO poisoning, including applying binary alloy catalysts (Pt-Mo, Pt-Ti and Pt-Ru) in the fuel cells, increasing the working temperature of fuel cells, CO filtration, etc. Table 1 shows the comparison of various common methods for increasing CO tolerance.

Table 1. Comparison of various methods to increase CO tolerance

Methods	Working principle of higher CO tolerance	Main disadvantages
Applying Pt-Ru Catalyst	Increase the electrochemical oxidation reaction rates of CO on the catalyst surface (Abdollahzadeh et al., 2018; Vermaak et al., 2021; Molochas et al., 2021; Bashyam et al., 2011; Ehteshami et al., 2013)	1. High cost of binary catalyst 2. The reduced PEMFC durability due to dissolution of Ru (Bashyam et al., 2011; Ehteshami et al., 2013)
Increasing cell temperature	Suppress the bonding reaction of Pt and CO on the catalyst surface (Chen et al., 2014; Devrim et al., 2018)	1. Higher service temperature of material of each component 2. Reduced material life
Adding H_2O_2	Oxidize CO adsorbed on Pt due to dissolved H_2O_2 (Liao et al., 2013)	Reduced membrane life due to the formation of reactive oxygen radicals (• OH and • OOH) (Inaba et al., 2008)
Air-bleeding	Oxidize CO adsorbed on Pt due to existence of O_2 (Scholta et al., 2011; Sun et al., 2013; Zhou et al., 2015; Tullius et al., 2020)	Reduced catalyst life due to catalyst sintering caused by H_2 and O_2 exothermic oxidation reaction (Valdés-López et al., 2020; Inaba et al., 2008)
Appling pulse current	Oxidize CO by controlling the pulse current (Lua et al., 2009)	Only approved in laboratory-scale tests (Adams et al., 2008)

Taccani et al. (2011) tested a HTPEMFC stack using pure hydrogen and a 1% CO/29% CO2/70% H_2 mixture under a wide temperature range, 120-180°C. For pure hydrogen at 160°C, the cell can generate a current density of about 275 mA cm^{-2} at 0.6 V. For the 1% CO-containing mixture, the current density at 0.6 V drops to about 225 mA cm^{-2}.

Chen et al. (2014) reported that increasing the working temperature suppresses the adsorption reaction of CO onto the Pt catalyst, and therefore the CO tolerance can be effectively improved. Zhang et al. (2015) studied the effects of the temperature ranging from 120 to 200℃ on HTPEMFCs. They observed that the higher the operating temperature was, the better the cell performance and CO tolerance were. However, at elevated temperatures (above 160℃), the temperature effect became less significant. In the durability test, their experiments showed that membrane aging occurred at 180℃ and it was particularly severe at 200℃. The most suitable working temperature in a compromise between operating life and CO tolerance is in the range of 160-180℃. Devrim et al. (2018) examined and analyzed the temperature influence on the performance of the HTPEMFCs at the temperatures ranging from 140℃ to 200℃. Because deformation of the cell components was observed at high operating temperatures, they suggested 160℃ as a better operating temperature. Babu et al. (2021) proposed a simulation model to study the local spatial effects of CO on the HTPEMFC. Their research indicated that the HTPEMFC can be operated under a CO concentration up to 5% at 180℃. Moreover, they observed an uneven current density distribution over the active area of the MEA due to an uneven CO adsorption on the anode catalyst active sites. Zhang et al. (2021) developed a 3-dimensional model for HTPEMFC stacks. Their paper revealed that the central cells in the stack had better performance due to lower CO coverage on the catalyst caused by internal higher temperature. However, a local hot spot might reduce both H_2 and CO coverage and lead to an elevation of anodic overpotential. Xu et al. (2022) proposed a 3-D numerical model considering elementary reactions of H_2 and CO for HTPEMFCs. Their results indicate that the operating temperature has an obvious effect on the species distribution and elementary reaction rate, leading to a change of CO tolerance.

As the catalyst in the fuel cell is poisoned by CO, flowing a small amount of oxygen or air into the fuel cell anode side can cause a CO oxidation reaction, and lead a drop of CO coverage on the catalyst surface and a recovery of cell performance. This method is called air-bleeding. The air concentration of this method should not be too high, because a high air concentration may cause hydrogen oxidation and local hot spots. Many previous studies have confirmed the effectiveness of air-bleeding approach for low temperature proton exchange membrane fuel cells [14-16, 26-28].

Murthy et al. (2003) studied the effects of air-bleeding on the fuel cell performance with high CO concentrations at different cell temperatures and pressures. They found that an air-bleeding concentration of 5% can completely restore membrane electrode assembly (MEA) performance at 500 ppm CO, and a 15% air-bleeding concentration can partially restore MEA performance at 3000 ppm CO. Additionally, the poisoning effect decreases significantly with increasing the pressure and temperature. Sung et al. (2013) found that an air-bleeding concentration of 5-7% can restore about 90% lost performance of the fuel cell, but the concentration of more than 10% has a negative impact on the cell performance. An air-bleeding concentration of 5% shows a good influence on the cell stability as well under a 300-hour test. Inaba et al. (2008) studied the effects of air-bleeding on membrane aging in the PEMFC with a 5% air-bleeding concentration in a 4600-hour long-term test. The membrane aging rate was negligible before the 2000th hour, but the membrane aging rate became significant after 2000 hours. They found that excessive air on the anode side deteriorated the anodic catalyst, because that enhanced H_2O_2 formation and led to a more serious membrane aging after 2000 hours. The exact cause of anode catalyst aging after introducing air-bleeding is still unclear. In 2020, Delgado et al. (2020) mentioned that adding 1 % air in 10 ppm CO-containing hydrogen fully recovered the cell performance and still maintained a good performance stability.

According to the accessible references, no literature regarding applying the air-bleeding method on the HTPEMFCs was found. As a result, the main objective of this research is to study the HTPEMFC behavior under air-bleeding, in order to understand the effectiveness of air-bleeding on the HTPEMFCs under CO-containing H_2.

EXPERIMENTAL FACILITIES AND ANALYSIS METHODS

Fuel cell test facility and gas mixer

In this study, a fuel cell test system, as shown in Fig. 1, was used to measure the cell steady and transient performance. The core component of this test station is an electronic load with temperature control and electrochemical impedance spectroscopy (EIS) analysis function. This electronic load is provided by Scribner Associates Inc. and its model number is 890e. This test system can control the experimental parameters, such as gas flow rates, gas concentrations, and cell temperature. It can simultaneously record experimental data, such as fuel cell voltage, current, and power. It can also perform EIS analysis under a constant current. When performing the EIS tests, the working electrode is connected to the cathode side of the fuel cell, which is fed with air. In addition, the counter electrode and reference electrode are connected to the anode side of the fuel cell, which is fed with various hydrogen-containing fuels for different studied cases. The scanning frequency of the EIS tests ranges from 10^4 to 10^{-2} Hz. The amplitude of the EIS alternating current is 5-10% of the direct current, i.e., the tested output current of the fuel cell. In this work, both anodic and cathodic gases were not humidified before being fed into the fuel cell. The gas mixer comprised five calibrated mass flow controllers supplied by Tokyo Keiso Co. Ltd. (model number: NM- 2100DC), and the five types of gas in the experiment were hydrogen, air, nitrogen, carbon monoxide and carbon dioxide. The gas compositions of the CO-containing mixture were regulated by the mass flow rates of the five gases. In this study, CO_2 was the balance gas for the H_2 concentration, and N_2 was the purge gas. In this research, the flow rate of hydrogen was fixed at 300 sccm to avoid an insufficient hydrogen situation under any studied case. For the CO poisoning tests with different CO and hydrogen concentrations, the corresponding CO flow rate and CO_2 flow rate were added into the hydrogen flow of 300 sccm to reach the tested CO and hydrogen concentrations. Moreover, the air flow rate was controlled by the output current with a stoichiometric ratio of 2.0. To maintain the working temperature of the fuel cell, a temperature controller, rod-type heaters and T-type thermocouples were installed.

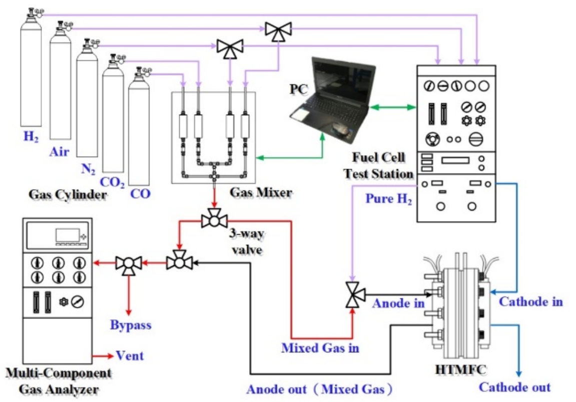

Fig. 1. The schematic diagram of the fuel cell test system

Multi-channel real-time gas analyzer

The mixed gas used in this experiment was to simulate the reformate gas for the study on the HTPEMFC characteristics with CO and air-bleeding on the anode side. To verify the gas compositions of the simulated reformate gases, a multi-channel real-time gas analyzer (Rosemount Analytical NGA 2000) produced by Emerson was applied. Before the test, the zero point and the full-scale of various gases were calibrated to ensure a good accuracy of the real-time gas analysis. Table 2 shows the concentration verification results of various simulated gases from the gas mixer. In this work, the mixed gases of low CO and high CO concentrations under different H_2 concentrations were verified. The verification results demonstrate that the errors for the CO concentration ranging from 0.2% to 5% under different H_2 concentrations are within ±5%, which indicates that the gas mixer in this work can provide the mixed gases with accurate CO concentrations for the HTPEMFC tests.

Table 2 The CO concentration verification of the mixed gases

Setting values of gas mixer	Readings from real-time gas analyzer	CO / H_2 concentration errors
0.21% CO / 70% H_2	0.20% CO / 70.94% H_2	-4.76% / 1.33%
5.00% CO / 70% H_2	4.86% CO / 70.62% H_2	2.80% / 0.88%
0.42% CO / 60% H_2	0.40% CO / 60.44% H_2	-4.76% / 0.73%
5.00% CO / 60% H_2	4.78% CO / 61.32% H_2	4.40% / 2.20%

The single cell

In this study, a single cell with an active area of 25 cm^2 was used to carry out the performance experiments. The end plate material for the single cell was stainless steel, and the material of the current collector plate was copper plated with gold. The bipolar plate was made of graphite, and the flow channel type was a 5-channel serpentine design. The width, depth and spacing of the flow channels were 0.81 mm, 0.80 mm and 0.82 mm, respectively. In this research, the Advent TPS® high temperature MEA (model number : ABM # 25) was adopted. The catalysts for anode and cathode sides are both Pt/C. In order to heat up the single cell in a short time to prevent acid leaching out during the heating period, four high-power heating rods were inserted in the end plates. The input voltage and maximum power of each heating rods was 110 V and 150 W, respectively. In addition, a thermocouple was inserted in the bipolar plate to control the cell temperature. To maintain a uniform temperature distribution inside the cell, the cell was covered by a layer of heat insulation material.

Experimental methods and analysis index

In this paper, the experimental methods, such as the average voltage measurement at a specific current density, transient performance, and the electrochemical impedance spectroscopy were applied to analyze the steady performance, performance stability and the electrochemical losses of the fuel cell under CO poisoning. In addition, the analysis index, signal-to-noise ratio (SNR), was applied to understand the effects of the CO poisoning on the cell behavior and the effects of air-bleeding on the oscillation amplitude of the cell output voltage.

The SNR is an index for comparing the level of desired signal to the level of noise. The SNR is defined as the ratio of the signal power to the noise power. The formula of SNR is listed as Eq.(1). The SNR can be expressed in decibels (dB), and thus the formula of SNR becomes Eq.(2).

$$\mathrm{SNR} = \frac{P_{signal}}{P_{noise}} = \frac{A_{signal}^2}{A_{noise}^2} \tag{1}$$

$$\mathrm{SNR(dB)} = 10\log_{10}\left(\frac{P_{signal}}{P_{noise}}\right) = 20\log_{10}\left(\frac{A_{signal}}{A_{noise}}\right) \tag{2}$$

where P_{signal}, P_{noise}, A_{signal}, and A_{noise} represent the power of signal, the power of noise, the amplitude of signal, and the amplitude of noise, respectively.

In this work, the effectiveness of air-bleeding on the performance output of the HTPEMFC under CO poisoning is studied. CO poisoning not only reduces the average voltage of the fuel cell, but also increases the amplitude of voltage fluctuation. Thus, one can learn the intensity of CO poisoning by observing the change of average voltage and the amplitude of voltage fluctuation. Thus, to quantify the intensity of CO poisoning with both the average voltage and the amplitude of voltage fluctuation, the SNR is applied in this work. As a result, in this study, the desired signal is the average output voltage of the fuel cell at a constant current density, and the noise is the amplitude of voltage fluctuation under CO poisoning. A smaller SNR represents that the voltage fluctuation caused by CO poisoning compared to the average voltage at a specific current density is less significant, and this indicates that the cell output performance is more stable. A smaller SNR in this paper as well represents a slighter CO poisoning intensity, resulted from a better effectiveness of air-bleeding.

RESULTS AND DISCUSSION

CO poisoning of the HTPEMFC at different temperatures

In this part of test, the influences of the working temperature on the cell performance, voltage fluctuation and the voltage SNR of the HTPEMFC under poisoning were examined.

Fig. 2 shows the influence of working temperature on the HTPEMFC performance under the 1% CO/H_2 mixture. Fig. 3 shows the voltage fluctuation of the HTPEMFC under the 1% CO/H_2 mixture at a current density of 0.2 A cm^{-2}, at various working temperatures. In the tests of Fig. 2, the cell voltage at a specific current density was measured and recorded for 90 min., i.e., the recorded length of Fig. 3, to obtain the average voltage, due to the voltage fluctuation phenomenon. The bars in Fig. 2 represent the average voltages at a specific current density, and the error bars on the average voltages illustrate the standard deviation of the measured voltage values during 90 min.. A larger error bar indicates a larger amplitude of voltage fluctuation. In this work, the voltage fluctuation is caused by CO poisoning. Thus, a larger error bar suggests a stronger CO poisoning effect. As can be seen in Fig. 2, the average voltage at

180oC decreases with increasing the current density due to charge transfer and mass transport polarization. On the other hand, the standard deviation of voltage increases along with the current density. This is because the CO poisoning effect becomes stronger as the current density increases. This phenomenon is due to higher CO coverage on the Pt surface at elevated current densities. This was as well observed and explained in the previous literature (Chen et al., 2013). From Fig. 2, it is found that the average voltage decreases with decreasing the working temperature at the current density ranging from 0.2 to 0.3 A cm^{-2}. For example, the average voltages at 180℃, 160℃ and 140℃ under 0.2 A cm^{-2} are 0.6607 V, 0.6073 V and 0.4669 V, respectively. Compared to the average voltage at 180℃, the performance at 160℃ and 140℃ drop by 8.08% and 29.33%, respectively. This phenomenon shows that the effect of CO poisoning on the performance drop becomes more significant at lower temperatures, and this is because the CO adsorption reaction on the Pt catalyst is exothermic. More Pt active sites are occupied by CO molecules at reduced temperatures, leading to a lower cell performance. It is also observed that the data of 160℃ and 140℃ only appear at some current densities in Fig. 2. This is because the HTPEMFC becomes not operable under some high current densities at 160℃ and 140℃, resulted from the stronger CO poisoning effect at reduced working temperatures. From Fig. 3, it is measured that the voltage fluctuation amplitude at 180oC is 16.72 mV. It increases to 39.63 mV and 154.21 mV as the working temperature decreases to 160℃ and 140℃, respectively. These results lead to an increase in standard deviation of voltage at reduced temperatures in Fig. 2.

Fig. 4 shows the effect of working temperature on the voltage SNR of the HTPEMFC under the 1% CO/H_2 mixture at a current density of 0.2 A cm^{-2}. From Fig. 4, it is found that the SNR values at 180℃, 160℃ and 140℃ are 31.94 dB, 23.75 dB and 9.62 dB, respectively. The SNR of the cell voltage increases with increasing the working temperature. The increase ratio of SNR is 332% as the cell temperature increases from 140℃ to 180℃. As can be found in Fig. 4, the voltage SNR is improved as the working temperature is increased under 1% CO poisoning. This indicates that the noise (voltage fluctuation level caused by CO poisoning) becomes smaller compared to the signal (average voltage), as the temperature increases. In other words, the cell output voltage becomes more stable, and the output voltage has a better quality, as the CO poisoning effect becomes less significant.

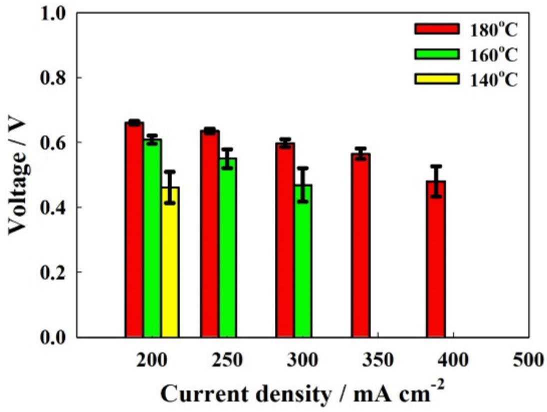

Fig. 2. Influences of working temperature on cell performance under the 1% CO/H_2 mixture

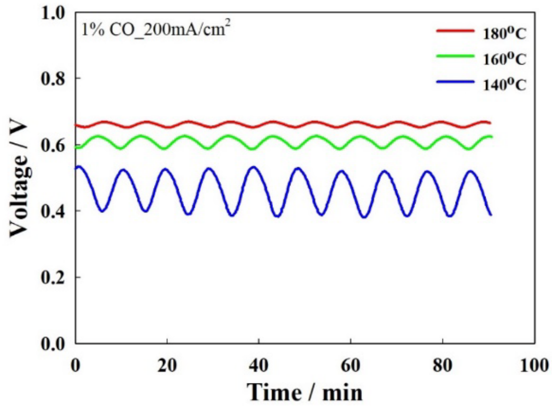

Fig. 3. Influences of working temperature on the voltage fluctuation of the HTPEMFC under the 1% CO/H_2 mixture at a current density of 0.2 A cm^{-2}

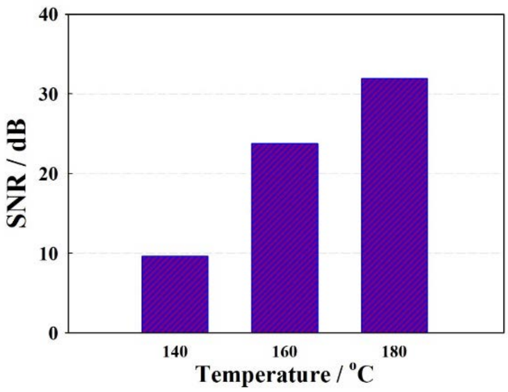

Fig. 4. Influences of working temperature on the voltage SNR of the HTPEMFC under the 1% CO / H_2 mixture at a current density of 0.2 A cm^{-2}

CO poisoning of the HTPEMFC at different H2 concentrations

In this part of experiment, the influences of the hydrogen concentration on the cell performance, voltage fluctuation, and the voltage SNR of the HTPEMFC under poisoning were studied. Fig. 5 shows the average voltage and the standard deviation of the fluctuating voltage of the HTPEMFC at 160℃

and different current densities under 5% CO/CO2/ H2 mixtures of various H_2 concentrations. Fig. 6 shows the voltage fluctuation of the HTPEMFC at a current density of 0.2 A cm^{-2} under 5% $CO/CO_2/H_2$ mixtures of various H_2 concentrations. As can be seen in Figs. 5-6, the cell average voltage decreases as the H_2 concentration decreases. At the current density of 0.2 A cm^{-2}, the average voltage decreases by about 21.2% as the H_2 concentration decreases from 95% to 40%. In addition, the standard deviation of voltage increases along with the H_2 concentration. According to previous papers (Chen et al., 2014; Zhao et al., 2020), the CO poisoning effect becomes more obvious if the H_2 concentration decreases, because a reduced H_2 concentration enhances the Pt-CO bonding reaction. Thus, the reduced average voltage and elevated voltage fluctuation amplitude are resulted from the enhanced CO poisoning effect at reduced H_2 concentrations.

Fig. 7 shows the effect of hydrogen concentration on the voltage SNR of the HTPEMFC at 160℃ and 0.2 A cm^{-2} current density under 5% $CO/CO_2/H_2$ mixtures of various H_2 concentrations. From the results of SNR, it is observed that the SNR value increases from 7.33 dB to 21.93 dB, an increase ratio of 299%, as the H_2 concentration increases from 40% to 95%. The quality of output voltage becomes better as the H_2 concentration increases. This is as well due to the reduced CO poisoning intensity at elevated H_2 concentrations.

From the results of Figs. 2-4 and Figs. 5-7, one can understand that an elevated CO poisoning intensity reduces the average cell performance, increases the voltage fluctuation, and decreases the voltage SNR. Thus, one can determine the CO poisoning intensity by the average cell voltage, voltage fluctuation amplitude and the voltage SNR at a constant current density. As a result, in the next part of this paper, the SNR is used to quantify the effectiveness of air-bleeding on the CO tolerance improvement.

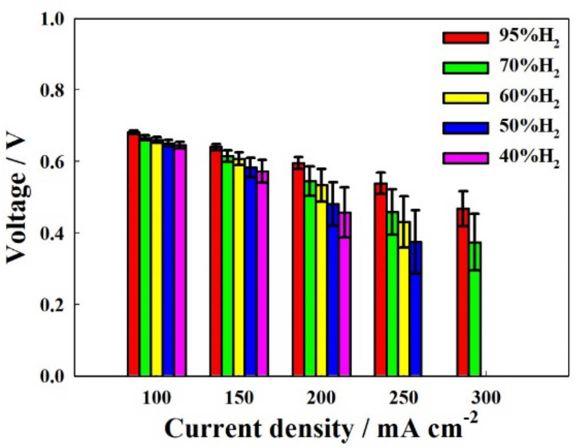

Fig. 5. Influences of hydrogen concentration on fuel cell performance under 160℃ with 5% $CO/CO_2/H_2$ mixtures

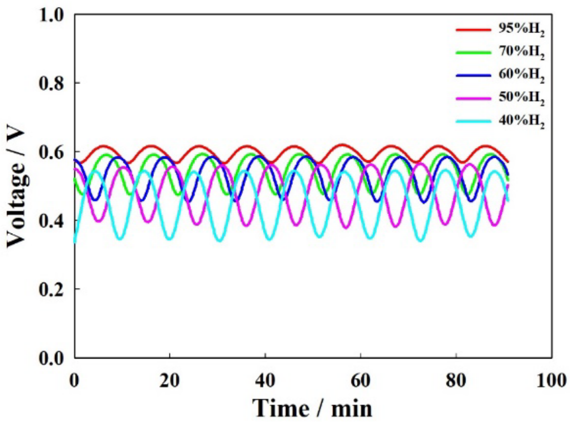

Fig. 6. Influences of hydrogen concentration on the voltage fluctuation of the HTPEMFC under 160℃ and 0.2 A cm^{-2} current density with 5% $CO/CO_2/H_2$ mixtures

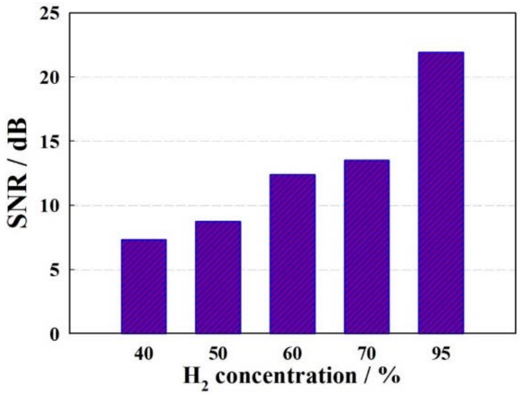

Fig. 7. Influences of hydrogen concentration on the voltage SNR of the HTPEMFC under 160℃ and 0.2 A cm^{-2} current density with 5% $CO/CO_2/H_2$ mixtures

Effect of air-bleeding on the HTPEMFC

In the third part of our experiment, the effectiveness of air-bleeding was examined by evaluating the voltage SNR of the HTPEMFC at a constant current density. To understand the effectiveness of air-bleeding on the HTPEMFC under different conditions, the voltage SNRs of the fuel cell at intermediate temperatures under low CO concentrations, and those at high temperatures under high CO concentrations are presented and discussed. Fig. 8(a) shows the voltage SNRs under140℃ and 500 mA cm-2 with 0.7% CO/H_2 mixtures of various air-bleeding concentrations. In addition, Fig. 8(b) discloses the voltage SNRs under 180℃ and 400 mA cm^{-2} with 5% CO/H_2 mixtures of various air-bleeding concentrations. As seen in Fig. 8(a), the voltage SNR at 500 mA cm^{-2} increases from 7.74 dB to 9.78 dB, an increase ratio of 126%, as 1.5% air is added into the anode gas of the HTPEMFC at 140℃ under the 0.7% CO/H_2 mixture. Moreover, the voltage SNR increases with increasing the air-bleeding concentration within the tested air concentration range. From Fig. 8(b), the voltage SNR at 400 mA cm^{-2} increases from 9.96 dB to11.64 dB, an increase ratio of 117%, as 1% air-bleeding is applied to the HTPEMFC at 180℃ under the 5% CO/H_2 mixture. It is as well observed that the voltage SNR does not change significantly as the air concentration becomes higher than 1%. This indicates that excess air does not enhance the effectiveness of air-bleeding on the CO poisoning tolerance improvement of the HTPEMFC. Compared to Fig. 4 and Fig. 7, the change of voltage SNR along with the air concentration in Fig. 8 is less obvious. This is because the effect of working temperature and H2 concentration on the CO poisoning intensity is more significant than the effect of air bleeding concentration. Additionally, the results in Fig. 8 as well indicate that the SNR index can quantify the intensity of CO poisoning even if the effect of a specific parameter on the CO poisoning is not very significant.

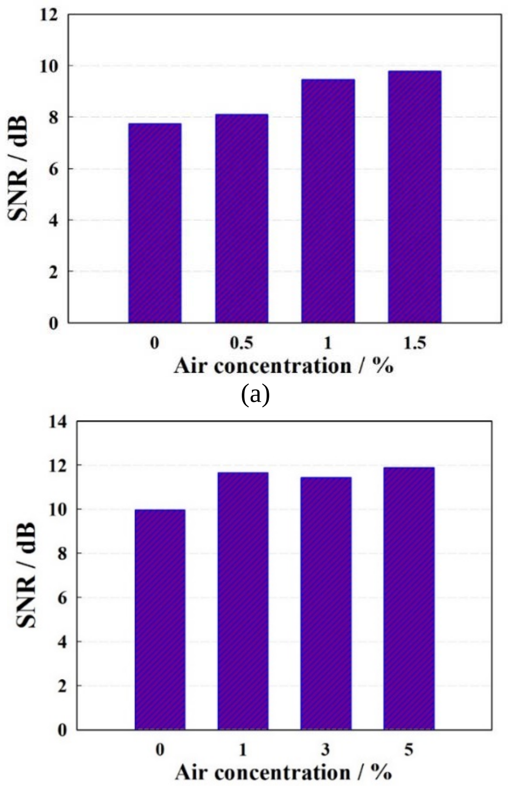

Fig. 8. (a) The voltage SNRs under 140℃ and 500 mA cm^{-2} with 0.7% CO/H_2 mixtures of various air-bleeding concentrations ; (b) The voltage SNRs under 180℃ and 400 mA cm^{-2} with 5% CO/H_2 mixtures of various air-bleeding concentrations

To further verify the effect of air-bleeding on the CO tolerance of the HTPEMFC, the electrochemical impedance spectroscopies of the HTPEMFC under CO poisoning with and without air-bleeding were measured and analyzed. Fig. 9 shows the electrochemical impedance spectroscopies of the HTPEMFC operated at 0.2 A cm^{-2} with and without air-bleeding under the three different conditions, 140℃ and the 0.7% CO/H_2 mixture, 180℃ and the 1% CO/H_2 mixture, and 180℃ and the 5% CO/H_2 mixture. From this figure, one can observe a slight change in the fuel cell EIS after applying air-bleeding to the fuel cell anode side under the three different conditions. The ohmic resistance (R_{ohm}), and the charge transfer and mass transport resistance (R_{ct} +R_{mt}) of the EIS in Fig. 9 are further analyzed and illustrated in Fig. 10. It is seen that air-bleeding has a negligible effect on the ohmic resistance. Nevertheless, a decrease in the charge transfer and mass transport resistance can be observed as air-bleeding is applied. At 140℃ and the 0.7% CO/H_2 mixture, the charge transfer and mass transport resistance reduces from 1273.9 ohm-cm^2 to 1221.1 ohm-cm^2. At 180℃ and the 1% CO/H_2 mixture, the charge transfer and mass transport resistance reduces from 1060.7 ohm-cm^2 to 1021.1 ohm-cm^2. At 180℃ and the 5% CO/H_2 mixture, the charge transfer and mass transport resistance reduces from 1125.3 ohm-cm^2 to 1059.1 ohm-cm^2. The decreased charge transfer and mass transport resistance is due to a decrease in the CO poisoning intensity, resulted from the CO oxidation reaction by air existing in the anode. These results verify the discussion about Fig. 8. Both the voltage SNR and EIS results indicate that air-bleeding suppresses the CO poisoning reaction, and reduces the CO poisoning intensity in the HTPEMFC

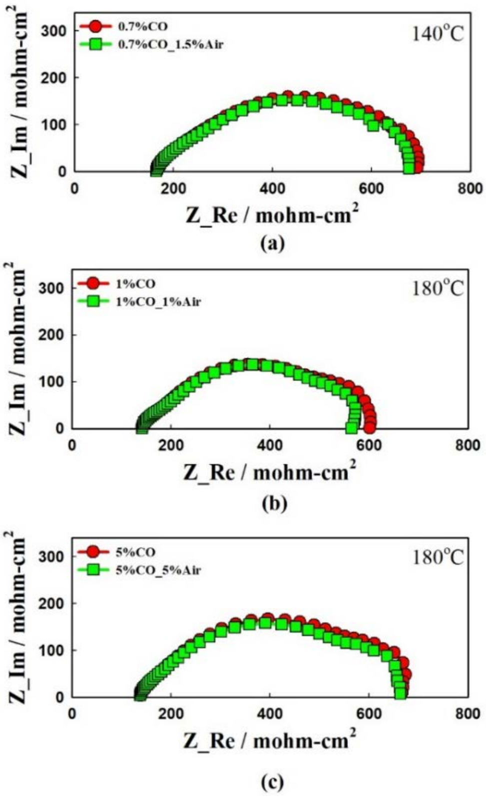

Fig. 9. The electrochemical impedance spectroscopies of the HTPEMFC at 0.2 A cm^{-2} with and without air-bleeding at (a) 140℃ and the 0.7% CO/H_2 mixture; (b) 180℃ and the 1% CO/ H_2 mixture; (c) 180℃ and the 5% CO/H_2 mixture

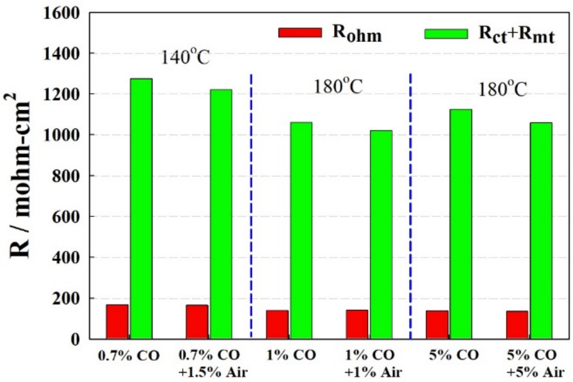

Fig. 10. The Rohm and $R_{ct}+R_{mt}$ of the HTPEMFC at 0.2 A cm^{-2} with and without air-bleeding at different working temperatures and CO/H_2 mixtures

CONCLUSIONS

This study discusses the characteristics of the HTPEMFC under the CO poisoning conditions, and the effectiveness of air-bleeding on the CO tolerance improvement of the high-temperature proton exchange membrane fuel cell. To analyze the experimental results, the average cell voltage, voltage fluctuation and the voltage SNR of the fuel cell at specific current densities are examined. The conclusions of this research are as follows,

1. Both the voltage SNR and EIS results indicate that air-bleeding suppresses the CO poisoning reaction, and reduces the CO poisoning intensity in an HTPEMFC. Moreover, the SNR index can quantify the intensity of CO poisoning even if the effect of a specific parameter on the CO poisoning is not very significant.
2. Air-bleeding improves the stability and quality of the output performance of the HTPEMFCs under CO poisoning, because the SNR of the output voltage is improved by air-bleeding. In addition, the optimal air-bleeding concentration for the HTPEMFC at between 140-180℃ under H_2 blended with CO of less than 5% is suggested to be 1%~1.5%. Excess air does not enhance the effectiveness of air-bleeding on the CO poisoning tolerance improvement of the HTPEMFC.
3. The increase ratio of SNR is 332% as the cell temperature increases from 140℃ to 180℃. The increase ratio of SNR is 299%, as the H_2 concentration increases from 40% to 95%. The increase ratio of SNR is only 126%, as the air-bleeding concentration increases from 0% to 1.5%, for the HTPEMFC at 140℃ under the 0.7% CO/ H_2 mixture. The effects of working temperature and H_2 concentration on the CO poisoning intensity are more significant than that of air bleeding concentration. However, the air-bleeding is the most economically friendly method for improving the CO tolerance of fuel cell when the operating temperature and hydrogen concentration are limited. As a result, applying air-bleeding is a practical method for CO tolerance improvement of HTPEMFCs.

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NOMENCLATURE

A_{signal}	amplitude of signal
A_{noise}	amplitude of noise
EIS	electrochemical Impedance Spectroscopy
MEA	membrane electrode assembly
P_{signal}	power of signal
P_{noise}	power of noise
R_{ohm}	ohmic resistance
R_{ct}	charge transfer resistance
R_{mt}	mass transport resistance
SNR	signal to noise ratio
V	voltage
$Z_{\_Im}$	imaginary part of EIS diagram
$Z_{\_Re}$	real part of EIS diagram

空氣溢入法對改善高溫型質子交換膜燃料電池一氧化碳容忍度之有效性研究

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摘 要

氫能燃料電池屬於潔淨能源科技，因此燃料電池在現今全球淨零碳排的發展趨勢下倍受重視。近年來由重組器提供富氫之混合氣體成為提供燃料電池燃料的解決方案之一。此種富氫氣體須經過純化處理降低其一氧化碳濃度以避免過高的一氧化碳毒化反應降低燃料電池性能，為使燃料電池對於一氧化碳容忍程度能夠提升，並且簡化純化過程，開發重組式高溫型質子交換膜燃料電池成為未來趨勢之一。

本研究以高溫型質子交換膜燃料電池做為研究主題，探討空氣溢入法對改善高溫型質子交換膜燃料電池一氧化碳容忍度之有效性研究。由電壓訊雜比以及電化學阻抗得知，空氣溢入法可抑制高溫型質子交換膜燃料電池內一氧化碳之毒化反應，減少毒化之強度，同時可增加電池性能穩定性。對操作溫度在 140-180 ℃、CO 濃度 5%以下的高溫型質子交換膜燃料電池而言，1-1.5%乃建議的較佳陽極溢入空氣濃度，過高的空氣濃度可能降低空氣溢入法之有效性。由電壓雜訊比之分析結果亦得知電池溫度與陽極氫氣濃度對一氧化碳毒化強度之影響高於溢入空氣濃度。