

Short communication

The effect of ambient contamination on PEMFC performance

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Abstract

The effect of environmental contamination (NO_x , SO_2) on the performance of proton exchange membrane fuel cells (PEMFC) was studied. The performance of PEMFCs was tested for 100 h with different cathode reactants. According to the *Ambient Air Quality Standard* of PRC, three kinds of cathode gases were applied to operate the fuel cells, which were 1 ppm NO_2 /air, 1 ppm SO_2 /air and a mixture of contaminant gases. The gas mixture contained 0.8 ppm NO_2 , 0.2 ppm NO and 1 ppm SO_2 . Finally, the poisoning behavior and the mechanisms were analyzed by constant-current discharging and cycle voltammetry (CV). During the 100 h test, the potentials of the fuel cell degraded by 65%, 77% and 90% with 1 ppm SO_2 /air, a gas mixture and 1 ppm NO_2 /air, respectively.

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1. Introduction

With the development and application of proton exchange membrane fuel cell (PEMFC) technology, the issues of durability and reliability become great challenges. The environmental effects on fuel cell durability come from the contaminations in the atmosphere. Therefore, the study of the effect of environmental contaminations on the performance of PEMFCs can improve the environmental adaptability of the fuel cell system. Moore et al. [1] pointed out that a low concentration of NO_2 and SO_2 in the air had no obvious effect on the performance of a PEMFC. However, Motadi et al. [2] demonstrated that 2.5 ppm NO_2 in air could cause the cell performance to decline by 50% after running for 25 h, but the cell could be completely recovered after running on pure air for 24 h. But the cell performance decreased by 53% after running with 2.5 ppm SO_2 /air for 45 h and it could not be recovered by running in pure air again for 20 h. The recent research [3,4] on cathode contamination also indicated that 5 and 10 ppm SO_2 in the air can seriously affect the fuel cell performance and the SO_2 poisoned cathode can only be recovered partially.

The concentration of contaminations in practical operational environments of a PEMFC is much lower, so that it is very

meaningful to study the durability of fuel cell in ambient air. To study the PEMFC tolerance to ambient contaminations, the concentrations of NO_x and SO_2 in the test were prepared based on the national code of GB 3095-1996 of *Ambient Air Quality Standard* of PRC [5] (as shown in Table 1). Three kinds of cathode gases containing 1 ppm NO_2 , 1 ppm SO_2 and a gas mixture (1 ppm SO_2 + 0.8 ppm NO_2 + 0.2 ppm NO) were selected to test the PEMFC performance, respectively. The poisoning mechanisms of the cell from different contaminations were analyzed by constant-current discharging and cycle voltammetry (CV) methods. A flow sketch of the test is shown in Fig. 1. The contaminations were fed into the cell entrance after air humidification and the concentrations of the contaminations introduced into the PEMFCs were controlled by a mass flow controller.

2. Experimental

2.1. MEA preparation and fuel cell assemblage

The membrane electrode assembly (MEA) was prepared by hot pressing under 135 °C and 10 MPa for 60 s with Nafion 212 membrane (DuPont, America) and two electrodes. Toray carbon paper (Japan) was used to support the catalyst and gas diffusion layer (GDL). Commercial 50 wt.% Pt/C (Johnson–Matthey) was used as the catalyst on both sides. The platinum loading on the

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Table 1
The upper limit of the main contaminations in ambient air (N mg m^{-3})

Contaminations	Concentration (N mg m^{-3})		
	Annual average	Daily average	1 h average
Sulfur dioxide (SO_2)	0.10	0.25	0.70
Nitrogen oxide (NO_x)	0.10	0.15	0.30
Nitrogen dioxide (NO_2)	0.08	0.12	0.24

Note: Annual average: arithmetic value of daily average concentration in any year; daily average: average concentration of any day; 1 h average: average concentration of any hour.

anode side and the cathode side were 0.3 and 0.5 mg cm^{-2} . Metal end plates and a flexible graphite flow field were used to assemble the single cell. The active area of the fuel cell was 5 cm^2 .

2.2. The preparation of standard gases

According to the *Ambient Air Quality Standard*, the concentrations of the contaminations applied in this experiment were three times the 1 h average value in Table 1. So the concentration of SO_2 was 2.1 mg m^{-3} (0.74 ppm) and the concentration of NO_2 was 0.72 mg m^{-3} (0.35 ppm). It is well known that the NO_x in the air is mainly composed of NO_2 and NO . According to Table 1, 80% of NO_x is NO_2 and most of the other 20% is NO , so the concentration of NO is 0.18 mg m^{-3} (0.14 ppm). For controlling simplification, the concentrations of SO_2 and NO_x in this experiment were both 1 ppm. A single cell was run with pure air under normal operational conditions to get the baseline, and three other fuel cells were run with 1 ppm NO_2 /air, 1 ppm SO_2 /air and gas mixture (1 ppm SO_2 + 0.8 ppm NO_2 + 0.2 ppm NO /air), respectively. To analyze the degradation phenomena of the cells under different cathode reactive gases the running time of every cell were all over 100 h.

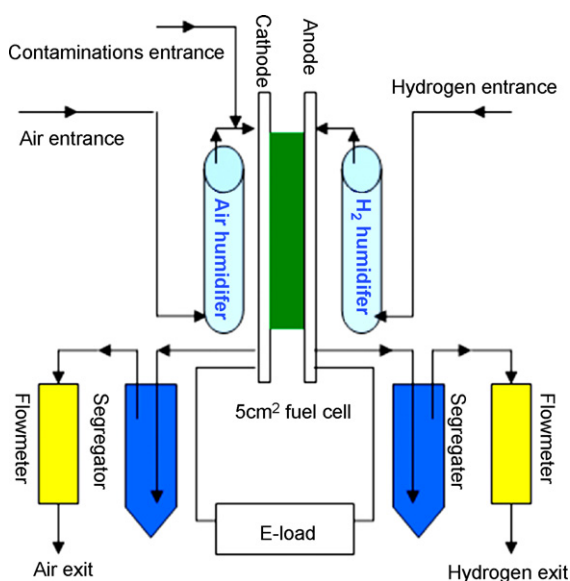


Fig. 1. Sketch of the test setup for the effect of ambient contaminations on fuel cell performance.

2.3. Fuel cell testing

The flow sketch of the test setup is shown in Fig. 1. The humidification temperatures were 65°C at the anode and 68°C at the cathode. The operating temperature of the fuel cell was 70°C . The flux of pure hydrogen was 50 sccm (standard milliliter per minute) and that of the different reactive gas (air containing 1 ppm NO_2 , 1 ppm SO_2 and gas mixture) in cathode side was 600 sccm. The pressures of the reactive gases were 0.1 MPa on both sides.

The fuel cell was tested with constant-current discharge by Arbin BT2000 (America, Arbin instruments) for more than 100 h and the current density was fixed at 500 mA cm^{-2} . The CV measurements were performed by PARSTAT 2273 electrochemical station (America, EG&G Instruments Corp.) after the cell was running for 100 h. The cathode side acted as the working electrode while nitrogen was flowing. In contrast, pure hydrogen was flowing on the anode side to act as the reference and counter electrode. The applied potential range was between 0.05 and 1.4 V and the scanning rate was 20 mV s^{-1} .

3. Results and discussion

3.1. Blank experiment

The constant-current discharging curve of the fuel cell operated in pure air is shown in Fig. 2. It shows that there was not obvious change in the performance of the cell for 100 h. The CV curve after 100 h in Fig. 3 also indicates that the performance of the electrocatalyst was not impaired.

3.2. The effect of NO_2 to PEMFC performance

The performance curve of the fuel cell operated with air containing 1 ppm NO_2 is shown in Fig. 4. The potential of the cell decreased slightly after NO_2 was added and it declined to 0.60 V after running for 100 h. Compared with the initial value of 0.67 V there was 70 mV lost over 100 h. When the cell was operated with pure air, after CV scanning, the potential of the fuel cell was about 0.64 V. These results indicate that the effect of a low concentration NO_2 on the cathode is very slight and the cell performance can be almost recovered totally after CV scanning.

In Fig. 5 the stripping peak of hydrogen on electrocatalyst in the first cycle is smaller than that in the second cycle. This

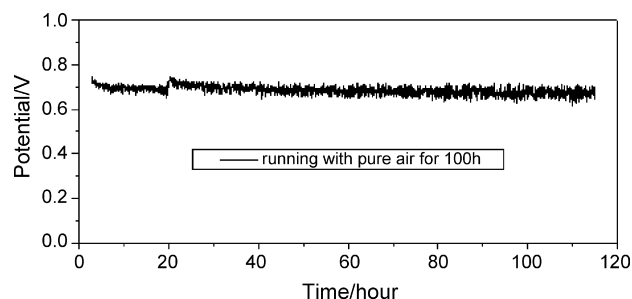


Fig. 2. The constant-current discharging curve of the PEMFC in pure air for 100 h, current density: 500 mA cm^{-2} .

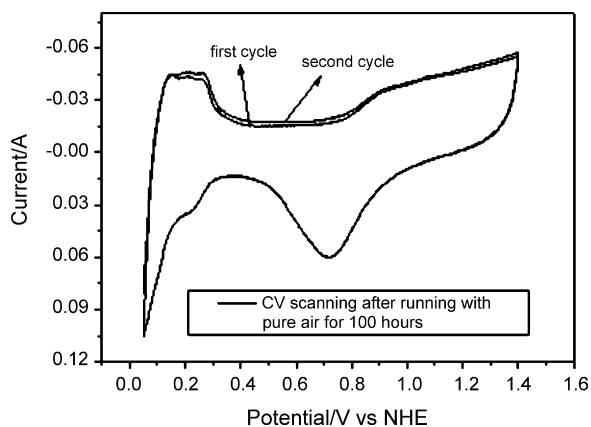


Fig. 3. The CV scanning curve after running with pure air for 100 h, scanning rate: 20 mV s^{-1} .

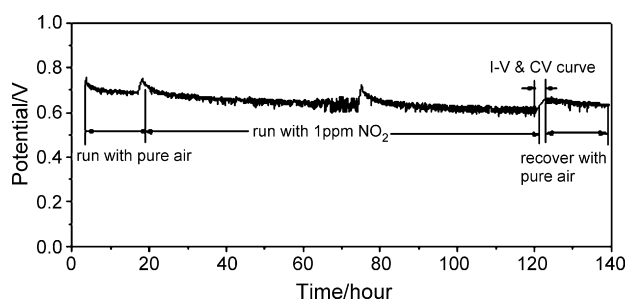
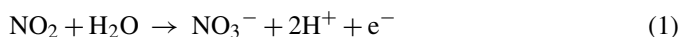


Fig. 4. The constant-current discharging curve of the PEMFC during running with $1 \text{ ppm NO}_2/\text{air}$ for 100 h, current density: 500 mA cm^{-2} .

phenomenon indicates that the degradation of cell performance is related to the adsorption of NO_2 on the catalyst layer. The peak located at 0.75 V is the oxidation peak of the adsorbed NO_2 . The reaction of the adsorbed NO_2 on the electrocatalyst during CV scan can be described by following equation:



The standard electrode potential of Eq. (1) is 0.80 V , which agrees with the CV curves.

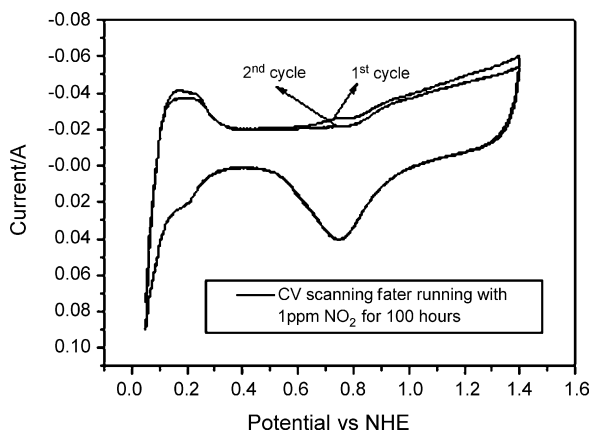


Fig. 5. The CV scanning curve after running with $1 \text{ ppm NO}_2/\text{air}$ for 100 h, scanning rate: 20 mV s^{-1} .

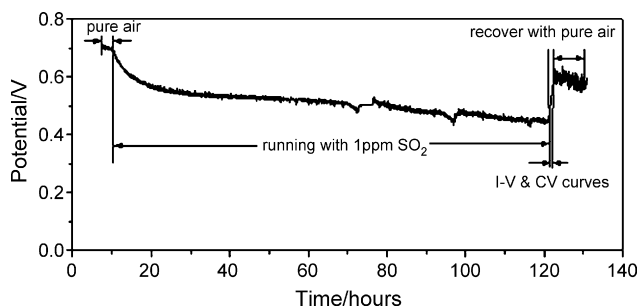


Fig. 6. The constant-current discharging curve of the PEMFC during running with $1 \text{ ppm SO}_2/\text{air}$ for 100 h, current density: 500 mA cm^{-2} .

3.3. The effect of SO_2 on PEMFC performance

Fig. 6 shows the performance curve of the fuel cell operated with $1 \text{ ppm SO}_2/\text{air}$. It can be seen that the cell performance degraded gradually and the potential after 100 h of testing was 0.44 V . Compared with the initial value of 0.68 V , the performance degraded by 35%. Fig. 6 also indicates that the cell performance was partially recovered as the pure air was introduced to the cathode side after CV scanning, and then the cell potential was 0.57 V that is 130 mV lower than the initial potential. This phenomenon indicates that the absorbed SO_2 on the catalyst layer resulted in decreasing the active surface area of the electrocatalyst. The cell performance increased after CV scanning which can be explained by the absorbed SO_2 on the electrocatalyst surface being oxidized and the occupied active sites partly released by the CV scanning.

In Fig. 7, the first cycle of the hydrogen stripping peak is much smaller and the oxidative current increases obviously at a potential of about 1.2 V . This result shows that the absorbed SO_2 on the electrocatalyst occupied the active positions. It can be seen that in the second cycle, the stripping peak of hydrogen increased which means a recovery of cell performance. Jüntgen and Kühl [6] and Mangun and Debar [7] studied the adsorption of SO_2 on activated carbon. They suggested that due to the presence of delocalized electrons at the edge sites of carbons where oxygen can chemisorb, the absorbed SO_2 can react with

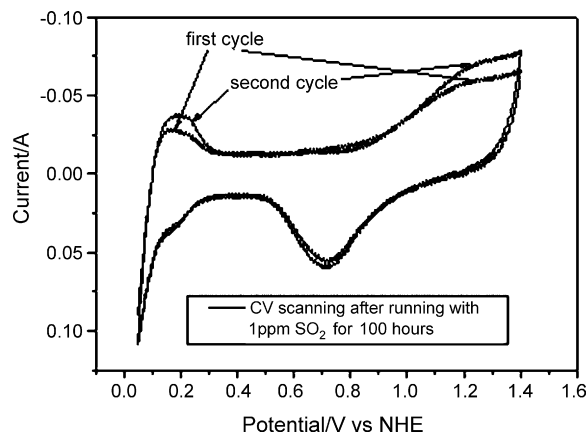
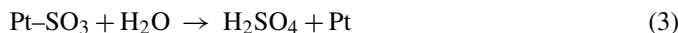


Fig. 7. The CV scanning curve after running with $1 \text{ ppm SO}_2/\text{air}$ for 100 h, scanning rate: 20 mV s^{-1} .

the oxygen to form SO_3 which then reacts with water to form H_2SO_4 . Therefore, the reactions of SO_2 on the Pt/C electrocatalyst surface on the cathode side of the fuel cell can be described by the following equation:



According to the equation, the absorbed SO_2 on the electrocatalyst is oxidized during CV scanning. On the other hand, the performance cannot be completely recovered because the absorbed SO_2 could not be completely desorbed during the electrochemical scanning and was still located on the active sites of the electrocatalyst.

3.4. The effect of gas mixture to PEMFC performance

Based on the above testing results, low concentrations of NO_2 and SO_2 in air all can affect the performance of the fuel cell. However, the contaminations in the ambient usually exist together so that the effect of a gas mixture on the fuel cell performance must be tested. According to the *Ambient Air Quality Standard*, the gas mixture contained 1 ppm SO_2 , 0.8 ppm NO_2 and 0.2 ppm NO.

Fig. 8 shows the performance curve of the fuel cell running with this gas mixture for 100 h. It can be seen that the cell performance decreases step by step and the potential of the cell is 0.53 V after running for 100 h. Compared with the initial value of 0.69 V the potential degraded by 23%. However, when the fuel cell was operated with pure air after CV scanning the potential recovered to 0.65 V. This phenomenon indicated that the effect of the ambient contaminations on the fuel cell did not overlap and the degradation of the cell caused by the interaction effects for every composition.

Fig. 9 shows the CV curves of the cell after running with the gas mixture for 100 h, in the first cycle, there are two peaks at the potentials of 0.83 and 1.2 V. The peak located at 0.83 V agreed with that at 0.75 V in Fig. 5. It shifted to more positive values due to the small quality of NO in the gas mixture. The oxidized peak of NO usually located at much more positive potentials [8]. The peak located at 1.2 V is the oxidation peak of SO_2 which is smaller than that in Fig. 7. This phenomenon indicates that the adsorption of the contaminants on the electrocatalyst is

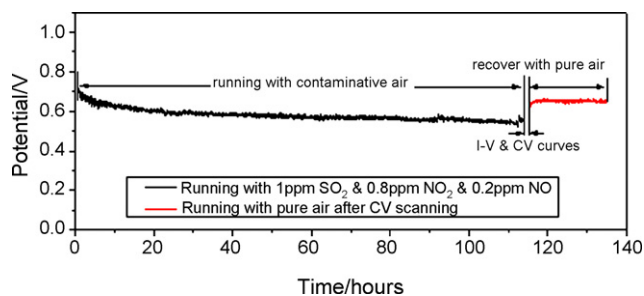


Fig. 8. The constant-current discharging curve of the PEMFC during running with the gas mixture of 1 ppm SO_2 + 0.8 ppm NO_2 + 0.2 ppm NO for 100 h, current density: 500 mA cm^{-2} .

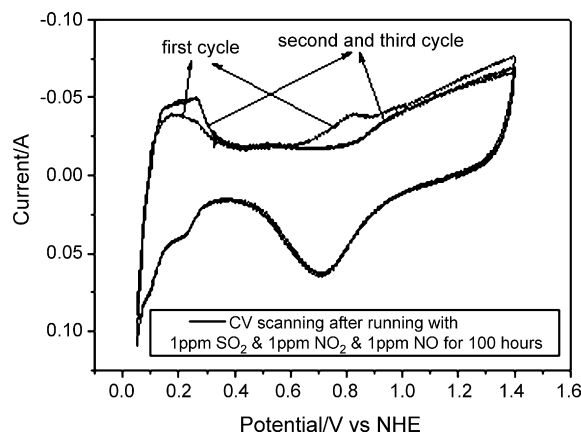


Fig. 9. The CV scanning curve after running with gas mixture of 1 ppm SO_2 + 0.8 ppm NO_2 + 0.2 ppm NO for 100 h, scanning rate: 20 mV s^{-1} .

much more complicated when different contaminations simultaneously exist. The adsorption is a competitive reaction and the contamination that easily adsorbs on the electrocatalyst has the priority. Therefore, we can conclude that compared with SO_2 , the adsorptive reaction of NO_2 on the catalyst surface is much easier. The slow decrease of fuel cell performance in the gas mixture can be explained from that the adsorptive quantity of SO_2 in gas mixture experiment is less than that of 1 ppm SO_2/air .

3.5. The comparison of different impurities on fuel cell performance

Fig. 10 shows the overlaid curves of the PEMFC performance during 100 h. It shows that the order of the different contamination effects on the fuel cell performance is SO_2 , mixture gas and NO_2 , and the effect of the SO_2 is the greatest. When the 1 ppm NO_2 was added, no obvious changes occurred in the cell performance in the first 20 h. But the fuel cell potential dropped rapidly when 1 ppm SO_2 was introduced and there was 120 mV lost in the cell performance during the first 20 h. In the following 80 h, the potential of the fuel cell dropped 70 mV in the NO_2 testing and 120 mV in the SO_2 testing. As shown in Table 2, the potential drops of the PEMFCs with different cathode gases were: 70, 240 and 160 mV for 1 ppm NO_2/air , 1 ppm SO_2/air and gas mixture, respectively. The effect of gas mixture on fuel cells is between that of 1 ppm NO_2/air and 1 ppm SO_2/air .

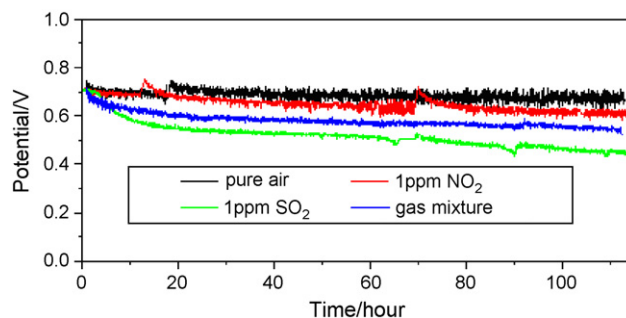


Fig. 10. The constant-current discharging curves of the PEMFC during running with different cathode gas for 100 h, current density: 500 mA cm^{-2} .

Table 2

The performance of a PEMFC at different times when running with various cathode gases

Contaminations	Nitrogen oxide (NO ₂)	Sulfur dioxide (SO ₂)	Mixture gas
Initial value (V)	0.67	0.68	0.69
Potential after 100 h V ⁻¹	0.60	0.44	0.53
Potential lost after 100 h V ⁻¹	0.07	0.24	0.16
Attenuation (%)	10	35	23
Potential after CV scanning (V)	0.60	0.57	0.65
Recovery (%)	94	84	94

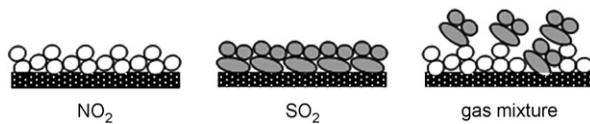


Fig. 11. Schematic of air contaminations adsorbing on the catalyst layer.

From the potential and the recovery percent of the fuel cell running with pure air after CV scanning in Table 2, the data for NO₂ is almost same as that of the gas mixture. This phenomenon suggested that as the gas mixture was added, the adsorption reaction of NO₂ took place first. Jüntgen and Kühn [6] also stated that the presence of nitrogen-containing groups should suppress the adsorption of SO₂ on activated carbon. Therefore, the adsorption of NO₂ on the catalyst layer resulted in less area remaining for the adsorbing of SO₂. As shown in Fig. 11 the effect of SO₂ on fuel cell performance in the gas mixture was due to the competitive adsorption between NO₂ and SO₂, which caused the quantity of SO₂ that directly touched with electrocatalyst to be reduced greatly. Thus, the contribution of SO₂ to the degradation of fuel cell performance in the gas mixture was lower than that of the same concentration of SO₂ in air only.

4. Conclusions

Low-level concentration of contaminations in the ambient air can all affect the fuel cell performance to some degree. The effect of SO₂ in this work is the most serious of the three different cathode reactive gases: NO₂, SO₂ and a mixture of these contaminants. The potential of the fuel cell dropped by 240 mV with 1 ppm SO₂ over 100 h and 84% of the cell performance can be recovered after CV scanning. On the other hand when the fuel cell operated with 1 ppm NO₂ the performance only decreased 70 mV and the potential could be almost completely recovered after CV scanning. However, the decrease of the cell potential running with the gas mixture was 160 mV and after the CV scanning the potential recovered 94%, which was same as that of NO₂.

Acknowledgements

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