

Article

Studies on the Effects of NH₃ in H₂ and Air on the Performance of PEMFC

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Abstract: The effect of NH₃ in H₂ and in air was investigated at various concentrations ranging from 1.0 ppm to 100 ppm in air and ranging from 0.25 ppm to 10 ppm in fuel. The effect of NH₃ on cathode caused an instantaneous decrease in cell voltage which dropped from 0.734 V to 0.712 V in 30 h and drop rates was 0.73 mV/h for 1 ppm; however, the cell voltage dropped to 0.415 V in 1 h for 100 ppm of NH₃. The voltage could not be recovered after the polarization test (V-I test) but could be recovered to 84.4% after operation with neat air for 1.5 h and 98.4% after cycle voltammogram (CV). It was found that the voltage drop was obvious, and the drop rate increased with the NH₃ concentration in H₂. The voltage drop rates at 500 mA/cm² were 0.54 mV/h for 0.5 ppm of NH₃, 0.8 mV/h for 1 ppm, and 2 mV/h for 10 ppm. The voltage could be recovered from 70.6% to 77.3% after discharged with high purity H₂ for 24 h, to 92.8% after being purged with clean air for 10 h and to 98.4% after CV scan. The tolerance concentration of NH₃ in H₂ for 1000 h was 40 ppb, for 2000 h was 20 ppb, and for 5000 h was 9 ppb.

Keywords: PEMFC; ammonia; performance; effect; tolerance concentration

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) is one of the most suitable candidates for replacing internal combustion engine (ICE) due to its high power density, zero emissions, and low operation temperature [1]. However, if the fuel of fuel cell vehicle (FCV), hydrogen, is produced from fossil fuel or by-products, it will inevitably contain some impurities, such as N₂ [2], CO [2–5], H₂S [5–9], CO₂ [5,7–10], SO₂ [11], and/or NH₃ [5,12–16], etc. These impurities have potential negative influences on the performance of PEMFC.

Among the impurities, ammonia (NH₃) is a common contaminant not only in the hydrogen-rich fuel stream [12] but also in ambient air in some special places, such as heavy traffic tunnels and the livestock industry. At least four different research groups have published papers regarding the ammonia contamination of PEMFC [13–16]. Uribe, F.A et al. [13], Soto, H.J et al. [14], Gomez, Y.A et al. [15], and Halseid, R et al. [16] focused on studying the poisoning of cells in operation and recovery after exposure to ammonia in H₂. The poisoning mechanism was only partly identified.

Uribe, F.A et al. [13] found that the cell resistance measured by high frequency resistance (HFR) was more than doubled when the cell was exposed to 30 ppm NH₃ in H₂ for 15 h. Exposure to 30 ppm ammonia for about 1 h resulted in performance loss, which was recoverable in about 18 h. Extended exposure to 30 ppm NH₃ for 17 h was not fully recoverable within 4 days of operation on pure H₂. Through a cyclic voltammetry (CV) test, no electrochemically active adsorbed contaminant could be identified on either the anode or the cathode. It was suggested that the observed performance loss was due to a loss of proton conductivity in the anode catalyst layer.

In the work of Soto, H.J et al. [14], the cell resistance was monitored by an automated current interrupt technique. Exposure to 200 ppm NH₃ in H₂ for 10 h increased the mea-

sured cell resistance by about 35%, much less than that observed by Uribe, who used a lower concentration of NH_3 . CVs recorded on the anode did not reveal any electrochemically active species. Soto, similarly to Uribe, suggested that ammonium interfered primarily with the anode. Gomez, Y.A et al. [15] also found that 200 ppm NH_3 in H_2 rapidly decreases the voltage of the fuel cell. The cell voltage at a constant current density of 0.1 A/cm^2 decreases from 0.83 V to 0.54 V during a 100 min period, resulting in a total voltage decay of 290 mV.

Halseid, R et al. [16] found that the poisoning of PEMFCs by NH_3 would take 24 h or more to reach a steady state with 10 ppm NH_3 in H_2 . In some cases, no steady state was reached during the experiment. The performance loss was in most cases reversible, but only after operation on high-purity H_2 for several days. The introduction of 1 ppm NH_3 resulted in significant performance loss. The performance loss was higher than could be explained by the observed increase in ohmic resistance in the cell. There is also a significant effect of ammonium on the ORR on the cathode.

In the present work, five different concentrations of NH_3 in air were added to the cathode of a cell, and four different concentrations of NH_3 in H_2 were added to the anode. Effects of NH_3 on both the anode and the cathode were studied over a long period (40 h on cathode and more than 100 h on anode) of durability tests. Uribe, F.A et al. [13], Soto, H.J et al. [14], and Gomez, Y.A et al. [15] studied the effect of relatively high contamination levels (200 ppm, 13–130 ppm, and 200–1000 ppm, respectively). Halseid, R et al. [16] studied FCs contaminated with lower levels of NH_3 in the H_2 (1–20 ppm). In this work, we studied even lower concentrations of NH_3 in H_2 , such as 0.25–10 ppm.

The change in cell impedance was investigated by electrochemical impedance spectroscopy (EIS) tests. To reveal change in electrochemically active species of a cell poisoning with NH_3 , CV tests were carried out. Furthermore, a tolerant limit of NH_3 in H_2 for fuel cells (FCs) was suggested from experimental data of the durability tests.

2. Experimental

2.1. Materials and Equipments

All single fuel cells used in experiments were fabricated from MEAs (membrane electrode assemblies, Shanghai Hesen Electric, Shanghai, China) with a size of 50 cm^2 . The Pt loading was 0.3 mg/cm^2 on each side of the membrane (DuPont, Wilmington, DE, USA). For each contamination experiment, a new MEA was used.

Highly pure H_2 (>99.999%), pure N_2 (>99.999%), and compressed air were used. A low concentration of NH_3 in H_2 and in air was prepared by mixing NH_3 in H_2 or in N_2 in a gas blender to a level of 20 ppm NH_3 in H_2 and 200 ppm NH_3 in N_2 , and then dynamically diluted to a desired concentration.

A fuel cell test bench equipped with an electrochemical station (VMP2/Z, Princeton Applied Research) was developed, which can introduce impurities simultaneously and dynamically into H_2 stream or air (See Figure 1). An electronic load (SUN-FEL200A, SUNRISE POWER) was used for discharging in galvanostatic mode.

2.2. Experiments

2.2.1. Durability (V-t) Test

Durability tests before and after the introduction of NH_3 into the anode and cathode on single cells were carried out to characterize the changes in performance. The performance loss was determined by measuring the voltage drop rate (mV/h) when the cell was discharged at 500 mA/cm^2 . Unless otherwise specified, the cells were operated at $70 \text{ }^\circ\text{C}$ and 101.3 kPa and the anode stream was humidified at $75 \text{ }^\circ\text{C}$. The stoichiometric ratio for H_2 and air were fixed at 1.5 and 3.0, respectively.

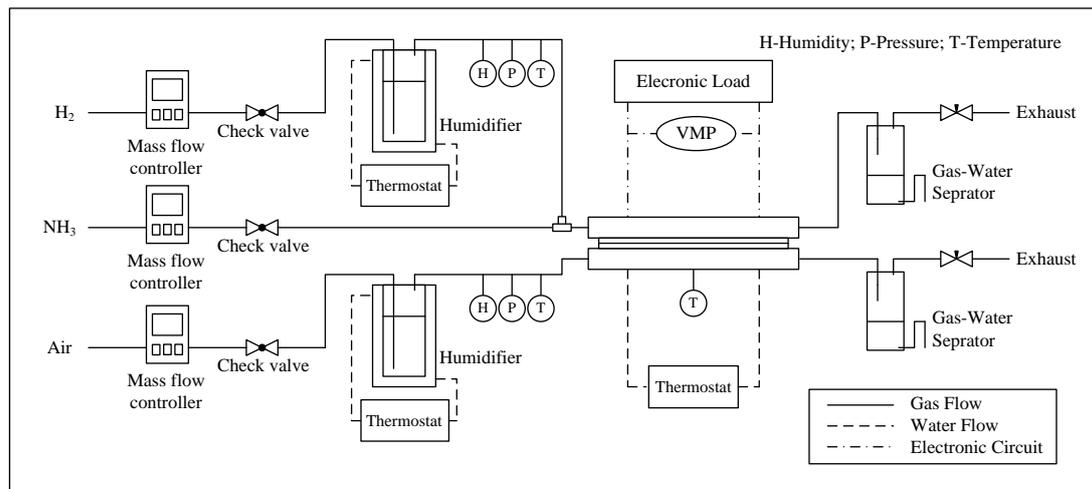


Figure 1. Schematic of PEM fuel cell test bench.

2.2.2. Polarization (V-I) Test

The polarization test is another method used to characterize the change in cell performance. When the V-I test was carried out, the stoichiometries ratio for H_2 and air were kept unchanged. A reference V-I curve was obtained by a measurement with pure H_2 right after the MEA was activated for 30–40 h. Usually, V-I tests were carried out during the V-*t*-tests.

2.2.3. EIS Test

EIS tests were carried out by a multi-channel potentiostat (VMP2/Z, PAR) in the galvanostatic mode to investigate the impedance change after the introduction of NH_3 . In EIS experiments, the amplitude of the sinusoid disturbance was set at 200 mA, which was 4% of the value of the discharge current, 5 A, i.d. 100 mA/cm^2 . Impedances were measured with 6 steps per decade of frequencies between 10 kHz and 100 MHz. When the EIS tests were carried out to investigate the effect of NH_3 in air, the polarization of the anode could be ignored because of the invariability of pure H_2 stream; therefore, all the changes in EIS could be attributed to the changes at the cathode caused by the poisoning of NH_3 , and vice versa for the anode.

2.2.4. CV Test

Cyclic voltammetry is a sensitive technique for investigating the behaviors of impurities on both the anode and cathode. While CV was carried out to investigate the NH_3 effect on the anode, N_2 at a rate of 300 mL/min was introduced into the anode, which acted as a working electrode. Meanwhile, H_2 at a rate of 300 mL min^{-1} was introduced into the cathode, which acted as a counter electrode and reference electrode. The anode was scanned by the electrochemical station from 0.05 V to 1.4 V vs. RHE and the scan rate was set at 20 mV sec^{-1} (and vice versa when the cathode was used as a working electrode).

3. Results and Discussion

3.1. Effect of NH_3 on the Cathode

A typical cell response to exposure to air containing five different concentrations of NH_3 ranging from 1.0 to 100 ppm is shown in Figure 2. The cell was operated galvanostatically at 500 mA/cm^2 and allowed to stabilize before NH_3 was added to air for 30–40 h. Each concentration of ammonia introduction was continued until the cell voltage dropped to a stable value.

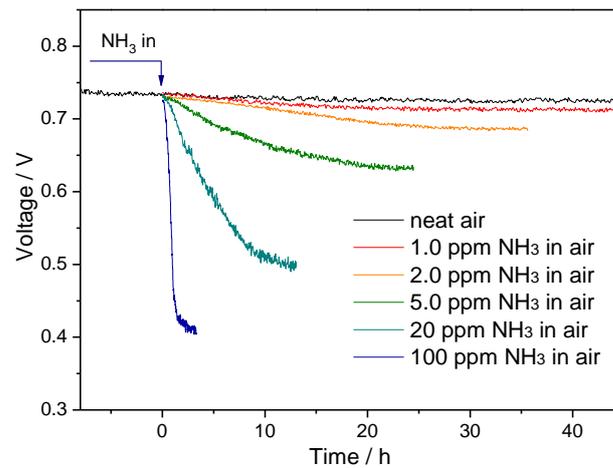


Figure 2. Performance changes of PEMFC after poisoning with NH_3 in air at 500 mA cm^{-2} .

It can be noticed that the cell performance decreased instantaneously when NH_3 was added to the cathode, and the cell voltage drop rate increased with the concentration of NH_3 . It can be also found that the cell voltage decreases operating with neat air as the running time increases because of the unstable and unsuitable operation conditions, unbalanced thermos-water management, slowly but certainly proceeding material aging process. However, in the $V-t$ curve of 1.0 ppm of NH_3 , the cell voltage dropped from 0.734 V to 0.712 V in 30 h, and in that of 100 ppm of NH_3 , the cell voltage dropped to 0.415 V in 1 h.

Figure 3 shows that the cell voltage at the constant current changes with different tests. It can be seen that the cell voltage rapidly decreases after adding the NH_3 . After turning off the NH_3 addition, we carried out the following tests: V-I test, operating with neat air, and CV scan. The cell voltage had little change after the V-I test but recovered to 0.620 V after operating with neat air for 1.5 h. However, through CV scanning, the cell voltage could be recovered to 0.720 V, with a recovery rate of 98.2%.

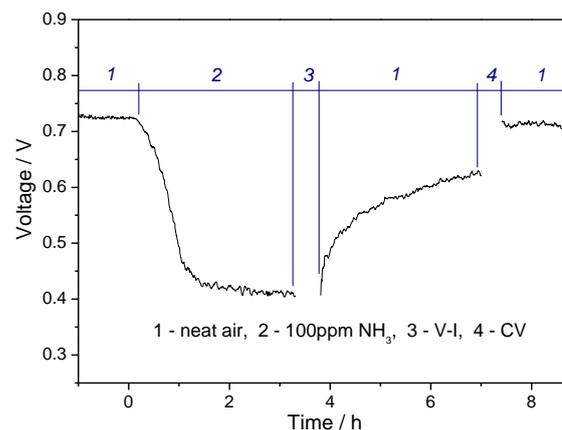


Figure 3. Recovery of cell voltage with discharging with neat air, V-I test, and CV at 500 mA/cm^2 .

When the cell voltage dropped to a stable state after poisoning with NH_3 , the addition of NH_3 was turned off, and then a V-I test was carried out. The V-I test results were shown in Figure 4. It can be seen that the polarization loss is closely linked with the NH_3 concentration, and the influence is much more severe when the concentration of NH_3 is above 5.0 ppm. Moreover, the cell could no longer work efficiently at the current density of 900 mA/cm^2 , if the NH_3 concentration was 5.0 ppm. Similarly, the cell would lose its work ability at 700 mA/cm^2 under the effect of 20 ppm of NH_3 , and at 600 mA/cm^2 under the effect of 100 ppm of NH_3 .

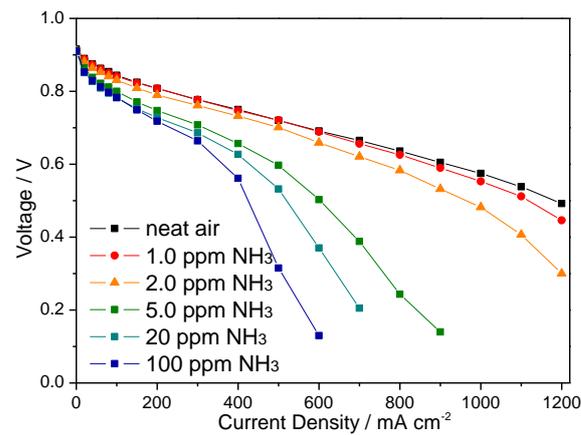


Figure 4. Effects of NH₃ in air on polarization.

3.2. Effect of NH₃ on the Anode

In Figure 5, the results of contamination of a cell with four different concentrations of NH₃ in fuel are shown. The cell was discharged at 500 mA/cm² and the addition of NH₃ was continued for more than 100 h.

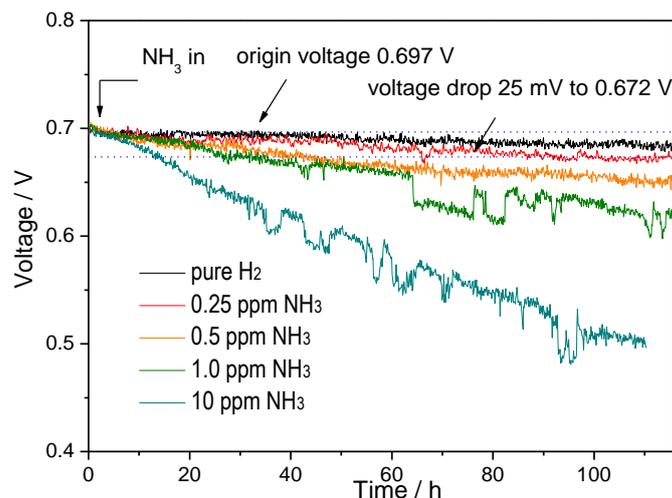


Figure 5. Performance changes of PEMFC after poisoning with NH₃ in fuel.

It can be seen that, in each curve, the voltage drop rate remained approximately constant with the addition of NH₃. For the same reason as operating with neat air, the voltage with pure H₂ also decreases. However, the voltage would fluctuate occasionally, which could be attributed to the adsorption of NH₃ in the membrane. When NH₃ was adsorbed in the membrane, reaction between NH₃ and H⁺ took place (R1), and ammonium would be formed, which would reduce the acidity and proton conductivity of the membrane [17]. In that case, the transfer of proton would be blocked. Simultaneously, NH₃ would be swept by H₂ and H₂O stream intermittently. The adsorption and desorption of NH₃ cost the fluctuation of cell voltage, which is chemisorption.



The voltage drop rate increased with the NH₃ concentration. For example, in the curve of 0.25 ppm of NH₃, the voltage drop from 0.697 V to 0.67 V in 100 h, the voltage drop rate is 0.27 mV/h. In the curve of other concentrations, the voltage drop rates are 0.54 mV/h for 0.5 ppm of NH₃, 0.8 mV/h for 1.0 ppm of NH₃, and 2.0 mV/h for 10 ppm of NH₃.

Serial tests were performed to study the recovery of cell performance after exposed to 10 ppm NH_3/H_2 for more than 100 h. As seen in Figure 6, the cell was recovered through (a) cutting off NH_3 and carrying out the polarization curve test and EIS test, (b) running with pure H_2 , (c) purging the anode with clean air, (d) and testing with CV. It was found that after the NH_3 poisoning, the cell voltage dropped to ca. 0.492 V, and even discharged with high-purity H_2 for as long as 24 h, the cell voltage was lightly recovered. It merely rose from 0.492 V to 0.539 V, i.e., 77.3% of the original value. After being purged with clean air for 10 h, the cell voltage was further recovered to 0.647 V, i.e., 92.8% of the original value. After CV scan, the cell voltage could be recovered to 0.686 V, i.e., 98.4% of the original value. During the composite processes treatment, the anode surface was cleaned with moist H_2 at first; meanwhile, some NH_4^+ cations could be washed out. When clean air was introduced, with CV scan in higher potential, the substance adsorbed on the surface was removed. Therefore, cell performance was mostly, if not completely, recovered.

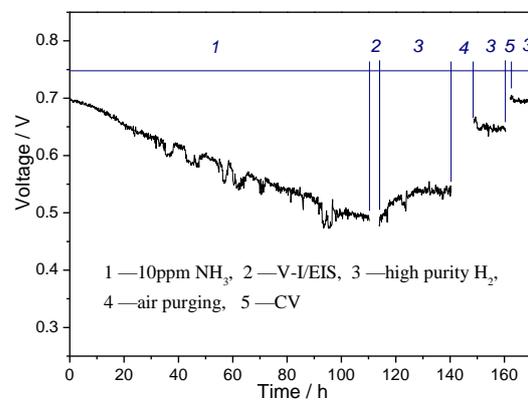


Figure 6. Recovery of cell voltage with discharging with pure H_2 , air purging, and CV.

Figure 7 shows the polarization curves after poisoning with different concentrations of NH_3/H_2 . Each polarization test was carried out 100 h after the addition of NH_3 . It seems that the polarization losses did not strengthen too much in the curves of 0.25 ppm and 0.5 ppm of NH_3 . However, it was much more severe when 1 ppm or higher concentrations of NH_3 were introduced into the anode. Compared to the effect of NH_3 in air, it was found that the polarization losses were much more severe with the same concentration levels in H_2 .

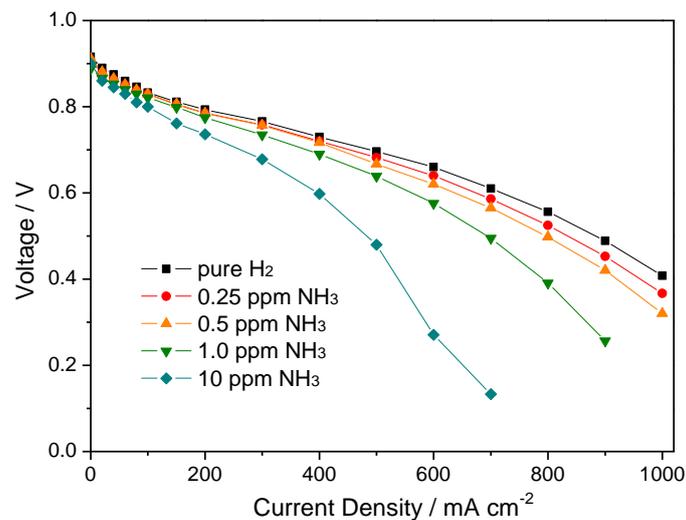


Figure 7. Effects of NH_3 in H_2 on polarization.

3.3. Recovery Mechanism Study

3.3.1. Impedance Study

In order to clarify the effect of NH_3 in air and H_2 on the impedance of PEMFC, EIS tests were carried out to study the impedance changes during the durability tests. Nyquist plots drawn in EIS tests show the same pattern as shown in Figure 8a,b: an inductive line at a high frequency range and a depressed capacitive semicircle at intermediate and low frequency ranges [18,19]. The inductive lines intersecting with the real axis correspond to the total ohmic resistance of the cell. This single semicircle loop, often called the “kinetic loop”, occurs when the electrode process is dominated only by the interfacial kinetics of the ORR process. The radii of the semicircle show the polarization resistance of the cell. The electrochemical parameters (Table 1) of the MEAs were analyzed via an equivalent circuit (EC) method (Figure 8c). R_{ct} represents the charge transfer resistance of the ORR; R_s represents the total ohmic resistance of the cell, which can be expressed as the sum of the contributions from contact resistances between components and ohmic resistances of the cell components; R_m represents the mass transfer impedance.

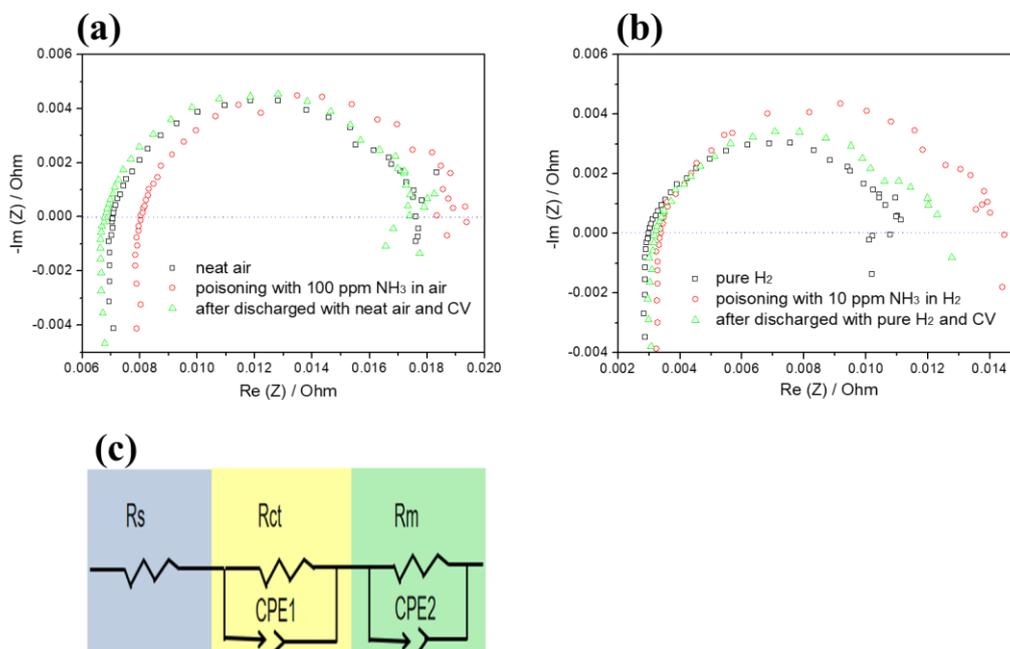


Figure 8. Nyquist plots of the impedance spectra measured before and after a cell poisoning with NH_3 in air (a) and fuel (b); (c) the equivalent circuit.

Table 1. The electrochemical parameters of the MEAs under different conditions.

	R_s (ohm)	R_{ct} (ohm)	R_m (ohm)
Neat air	0.00050102	0.0010346	0.00033082
Poisoning with 100 ppm NH_3	0.0005323	0.0011421	0.0003605
After neat air purging for 3 h	0.0004884	0.00099123	0.00028034
Pure H_2	0.00055808	0.00042653	0.00043754
Poisoning with 10 ppm NH_3 in H_2	0.00055964	0.00045434	0.00051119
After operating with pure H_2 for 24 h	0.00055835	0.00043846	0.00046464

In Figure 8a, three Nyquist plots of the cathode under different states are shown: in clean air, after being poisoned by 100 ppm of NH_3 , and after being discharged with clean air and CV scanned.

Under the effect of NH_3 , the R_s increases; however, the capacitive semicircle varies slightly. This means the impedance change is mainly attributable to the increase of ohmic resistance, which is due to the NH_4^+ absorption on the surface of catalyst and its transfer into the membrane. After the addition of NH_3 was shut down, the cell was discharged with neat air for 3 h, and the cathode was scanned by CV; the impedance spectra were greatly recovered. The immovability in polarization resistance showed that the Pt/C catalyst was not affected by NH_3 . However, in the catalysis of Pt/C, NH_3 could be oxidized to N_2 or nitrogen oxides, and then be swept out of the cathode by air flow and water. The Reactions are proposed as follows:

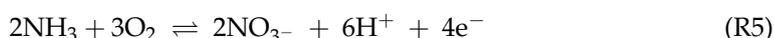
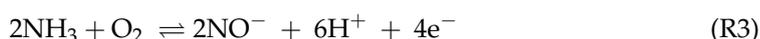


Figure 8b shows the impedance test results of cell poisoning with 10 ppm NH_3 in H_2 recovered by certain methods, such as purging with pure H_2 and CV scanning.

It can be seen that both the ohmic and polarization resistance increased with the addition of NH_3 . After the methods mentioned above were taken to recover the cell, the polarization resistance decreased but could not return to the original level, as well as the ohmic resistance. This means that some of the NH_3 added to the anode was absorbed in the membrane. Ammonium formed by reaction (R1) could not be easily swept out of the membrane, which caused the increase in ohmic resistance. Other NH_3 might be adsorbed by Pt/C catalyst [20], which caused the increase in polarization resistance. Under the oxidation circumstance of the anode and the absence of oxygen, the adsorbed NH_3 molecule can be oxidized by losing one or two proton(s):



3.3.2. Cyclic Voltammetry Study

CV was employed to investigate the adsorption and desorption of NH_3 on the surface of Pt, because it is a sensitive tool for the diagnostic of the surface state change, including the determination of the electrochemical active surface (EAS) of an electrode [21,22].

In Figure 9a combined with the Table 2, the CV results of a cell poisoning with 100 ppm NH_3 in air for 2 h (curve b) and then discharged with neat air for 3 h (curve c) are shown, as well as the one tested with pure H_2 (reference curve a). With the contamination of 100 ppm NH_3 , the CV curve changed significantly. The broader oxidation curve in ca. 0.8 V can be attributed to the oxidation of adsorbed ammonia molecules. On the other hand, the double layer region became smaller after contamination, changing from 0.28 V~0.68 V to 0.35 V~0.68 V, because of the weakened capacity of the catalyst layers due to the adsorption of ammonia. However, the H-desorption peaks in the range of 0.1 to 0.3 V showed little variation. After air purging for 3 h, curve b was close but not similar to the original one (curve a), which clarified the irreversibility of the cell performance after the cell was poisoned by NH_3 in the cathode. The reason to explain why the CV curve changes so much needs to be found through deeper research.

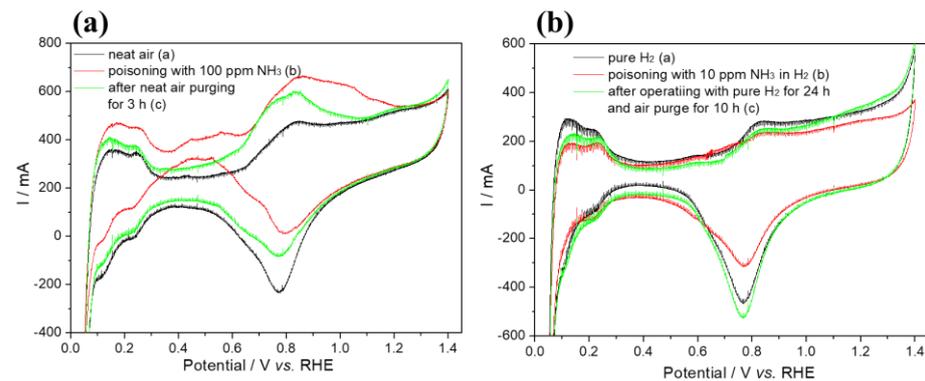


Figure 9. CV curves before and after poisoning with NH₃ in air (a) and in fuel (b).

Table 2. The ECSAs before and after poisoning with NH₃ in air and fuel.

	ECSA ($\text{m}^2\text{g}_{\text{Pt}}^{-1}$)
Neat air	53.95
Poisoning with 100 ppm NH ₃	50.775
After neat air purging for 3 h	59.395
Pure H ₂	79.97
Poisoning with 10 ppm NH ₃ in H ₂	61.175
After operating with pure H ₂ for 24 h	67.415

The CV results poisoning with 10 ppm NH₃ in H₂ for 100 h (curve b) and then discharging with pure H₂ for 24 h and purging with air for 10 h (curve c) are shown in Figure 9b, as well as the one tested with pure H₂ (reference curve a). It can be seen in curve b that the H-desorption peaks in the range of 0.1 to 0.3 V decrease after the introduction of NH₃, and due to the strong adsorption of NH₃ on Pt, the EAS of Pt is blocked by NH₃, which in turn suppresses the HOR, leading to a decrease in cell performance. Furthermore, there exists a reduced oxidation peak of Pt at 0.85 V in curve b. This peak could be caused by the reduction of the EAS of Pt. Indeed, the reduction peak for PtO or PtO₂ at 0.7 V during the cathodic scan became weaker, because less Pt oxides were generated during the previous anodic scan. After being discharged with pure H₂ and purged with neat air, curve c recovered almost completely, but the H-desorption peaks in the range of 0.1 to 0.3 V became smaller than that of the reference one (curve a), implying that the surface properties (EAS, particle size, etc.) of Pt/C might be changed. Therefore, the poisoning effect of NH₃ cannot be completely recovered by CV oxidation.

3.4. Determination of Tolerant Limit of NH₃ in H₂

Compared with air, the lower concentration of NH₃ in H₂ has a more severe performance degradation. Therefore, it is important to set a tolerance limit of NH₃ in H₂ for automotive applications, under which the fuel cell should not be impacted to lose too much work efficiency in a certain period and the cell should be able to perform under rather low degradation rates. In automotive application, the ideal lifetime should be 5000 h or more [23]. However, nowadays, the technologies for the lifespan of FC do not reach that high a level. If the level of 5000 h is set, the tolerance limit would be set extremely low, and the cost of hydrogen would be impractically high. Therefore, it could be considered that the tolerance limit of NH₃ can be set in three phases. The running time of FC must reach 1000 h in the first phase, 2000 h in the second phase, and 5000 h in the third phase. Additionally, the limitation of the decrease in cell voltage at 500 mA/cm² was set at 25 mV.

In Figure 5, the original voltage and the dropped voltage poisoning with NH₃ were indicated by two straight lines. The line at 0.697 V indicated the original voltage and the

one at 0.672 V as the voltage drop tolerance limit. Based on the experimental results given in Figure 5, the time spent for 25 mV of cell voltage decrease, and for the four corresponding concentrations of NH₃, the time spent to reach 25 mV voltage decrease under the effect of certain concentration of NH₃ can be obtained. In Figure 10, C_{NH_3} , the concentration of NH₃, is plotted against $1/t$. A polynomial relationship between the two variables can be drawn out:

$$C_{NH_3} = 44888 \left(\frac{1}{t}\right)^3 - 2170.3 \left(\frac{1}{t}\right)^2 + 45.251 \left(\frac{1}{t}\right) \quad (1)$$

where t is time of fuel cell running, h, and C_{NH_3} is NH₃ concentration, ppm.

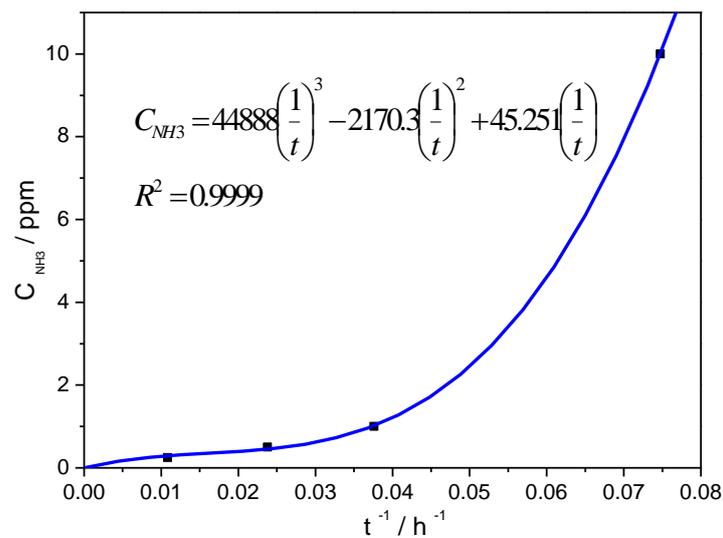


Figure 10. Relationship between the concentration of NH₃ and the maintained time allowed for a cell voltage drop of 25 mV.

From Equation (1), the tolerance limit for a 25 mV voltage drop can be calculated. For example, to reach a running time of 1000 h, the concentration of NH₃ in H₂ should be controlled at a level of 40 ppb. For 2000 h of operation time, the concentration of NH₃ should be decreased to 20 ppb. For 5000 h of operation time, the concentration of NH₃ should be controlled at 9 ppb, which is very close to the level set by the national standard [24].

In this work, the determination of the tolerance limit was discussed based on the durability test results. However, the influence factors on the behavior of NH₃ effect may be multiple. Therefore, more experiments should be carried out in various operation conditions, such as Pt loading, the operating current density, or voltage and cell temperature, etc. Nevertheless, the method in this paper can be applied in the same way; furthermore, the effects of other hydrogen impurities, such as CO and H₂S, etc., can also be investigated as well.

4. Conclusions

The present work investigated the poisoning effect of a low concentration of NH₃ in air and in fuel on PEMFC. From the experimental results, the following conclusions can be drawn:

- (1) The effect of NH₃ on the cathode in the concentration range from 1.0 to 100 ppm was investigated. The cell voltage would drop to a stable value when the NH₃ was added to the cathode, and the value decreased with NH₃ concentration. Through discharging with neat air and then CV, the cell voltage could be recovered to 98.2% of the original level. NH₃ addition in air caused the increase in polarization resistance, which could be recovered through discharging with neat air. However, the CV curve

changed significantly under the effect of NH_3 , which could not be recovered by neat air purging.

- (2) The effect of NH_3 on the anode in the concentration range from 0.25 to 10 ppm was investigated. The cell voltage drop rate remained approximately constant with the addition of NH_3 ; however, the voltage would fluctuate occasionally. The cell voltage could be recovered to 98.4% of the original level through discharging with pure H_2 , neat air purging, and CV scan. NH_3 in fuel would cause the ohmic and polarization resistance to increase, which was irreversible when the methods mentioned above were taken to recover the cell. The irreversibility was also shown in the CV curves. The H-adsorption peaks in the range of 0.1–0.3 V after poisoning with NH_3 could not be recovered to the original one.
- (3) The tolerance limits of NH_3 concentration in H_2 were determined and a polynomial relationship between the concentration of NH_3 for a cell voltage drop of 25 mV and the corresponding time of operation was established. The allowable concentration of NH_3 in H_2 for a fuel cell operation time of 1000 h is 40 ppb, while for 2000 h, the limit should be lowered to 20 ppb. For 5000 h, the limit should be controlled at 9 ppb.

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