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Influence of Ammonia on Membrane-Electrode Assemblies in Polymer Electrolyte Fuel Cells

Xiaoyu ZhangDepartment of Mechanical Engineering/
Connecticut Global Fuel Cell Center, University of
Connecticut
Storrs, CT, USA**Joshua Preston**Department of Mechanical Engineering, University
of Connecticut
Storrs, CT, USA**Ugur Pasaogullari**Department of Mechanical Engineering/
Connecticut Global Fuel Cell Center, University of
Connecticut
Storrs, CT, USA**Trent Molter**Connecticut Global Fuel Cell Center, University of
Connecticut
Storrs, CT, USA**Abstract**

An experimental investigation of contamination of polymer electrolyte fuel cell (PEFC) membranes and catalyst layers with ammonia (NH_3) is reported. Cyclic voltammetry (CV) scans and electrochemical impedance spectroscopy (EIS) analyses show that trace amounts of ammonia can significantly contaminate both the polymer electrolyte membrane (PEM) and the catalyst layers. The results show that the catalyst layer contamination can be reversed under certain conditions, while the membrane recovery tends to be much slower, and permanent effects of ammonia contamination is observed. Mechanisms of contamination of the polymer electrolyte and catalyst layers, and performance degradation of the PEFC are also postulated.

Introduction

Ammonia (NH_3) is a potential hydrogen carrier due to its high hydrogen capacity (18% by weight)¹. To generate hydrogen for fuel cell applications, ammonia is reformed, either by cracking²⁻³ or through metal hydride reactions⁴. In either case, residual ammonia will be present in the fuel as a contaminant. Ammonia can also be present in resulting hydrogen during other hydrogen production methods, such as coal gasification⁵. Therefore, understanding the effect of ammonia on the operation, durability and performance of the

polymer electrolyte fuel cells (PEFCs) is of significant importance.

Few studies⁶⁻⁸ analyzed the effect of ammonia in PEFCs. Uribe *et al.*⁶ found that trace ammonia in the anode fuel could severely decrease the fuel cell performance, and the performance does not recover after a long time operation on pure H_2 (clean-up). However, they did not find any evidence of (Pt) catalyst contamination in their cyclic voltammetry (CV) scans. It is postulated that ammonium ion (NH_4^+) forms in the anode catalyst layer by combination of ammonia with proton ($\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$), and the performance degradation is through the occupation of charge sites in the PEM with cationic contaminants, resulting in overall decreased conductivity. Unlike Uribe *et al.*, Soto *et al.*⁷ found that contamination of the membrane-electrode assembly (MEA) by ammonia could be fully recovered, however they did not suggest any different contamination mechanism. Halseid *et al.*⁸ carried out further investigation on the contamination mechanism by ammonia. Their study shows that the hydrogen oxidation reaction (HOR) was significantly affected by ammonia in a H_2/H_2 cell. Halseid⁹ also found that the effect of ammonium on the oxygen reduction reaction (ORR) on Pt in sulfuric acidic solution was significant. However, they have concluded that more work is required to fully understand the poisoning mechanisms of ammonia on PEFCs.

Based on this prior art, we performed an experimental study on the impact of ammonia on the catalyst layers and the PEM of a PEFC. We report the results and our hypotheses for the poisoning mechanisms.

Experimental

The experiments are performed with standard test cells. Commercially available conventional MEAs from Ion Power Inc. (New Castle, DE) based on Nafion® 212 membrane (DuPont, Wilmington, DE, 50.8 μm nominal thickness) with catalyst loadings of 0.4 mg/cm^2 anode and 0.2 mg/cm^2 cathode were used in all the experiments. SIGRACET® 10 BB from SGL Carbon (Meitingen, Germany) is used as the gas diffusion media (GDM) for both the anode and the cathode. All the experiments were conducted with standard single cell hardware with 25 cm^2 active area from Fuel Cell Technologies, Inc (Albuquerque, NM). A fuel cell test station (Scribner Associates 890B) was used to control the fuel cell electronic load (voltage or current), the cell temperature, as well as flow rate, humidity and temperatures of the gases, and for data logging. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) scans were performed with Solartron® SI 1287 and SI 1250, respectively.

Ultra high purity (99.999%) hydrogen and nitrogen, and pre-mixed 500 ppm NH_3/H_2 mixture (certified as 514 ppm) were obtained from Airgas. The desired impurity (NH_3) concentration for the anode is obtained by diluting pre-mixed NH_3/H_2 into the humidified hydrogen stream, as shown in Figure 1. By this method, we ensure that only pure hydrogen runs through the humidifiers, therefore potential contamination of the humidifier by adsorption of ammonia into the DI water is eliminated. The humidifier temperature is controlled for the desired final (NH_3/H_2) mixture humidity. The flow rate of NH_3/H_2 mixture is controlled by a mass flow controller (MFC) (Alicat Scientific) for the desired inlet impurity (25 ppm). A 3-way solenoid is installed prior the mixing point to eliminate the contamination of test setup with ammonia. If pure H_2 flow stops for any reason, the controller shuts down the NH_3/H_2 flow and starts a N_2 purge through the mainstream automatically to eliminate back-flow, therefore we assume that there is no residual ammonia in the pure H_2 lines.

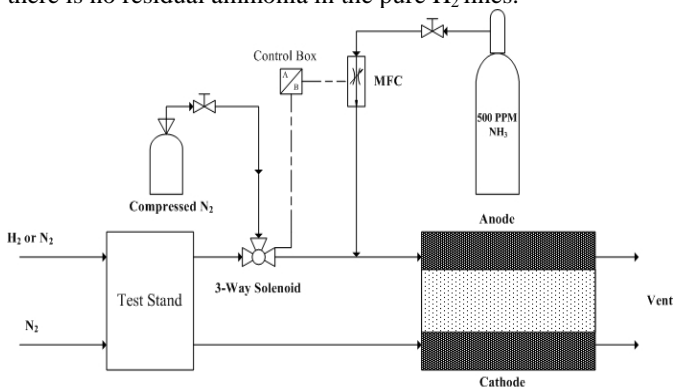


Figure 1. Schematics of ammonia mixing system. Pre-mixed NH_3/H_2 is diluted in the humidified pure hydrogen mainstream to obtain desired concentration.

Our primary objective is to characterize the effect of ammonia and identify the potential mechanisms in our experiments. Note that, the fuel cell is always kept at open circuit except for the periodic electrochemical measurements, and only N_2 is flowed in the cathode. Therefore, the induced migration of cations (e.g. NH_4^+) due to potential field across the MEA is minimized. In addition, there is no oxidation of crossed-over ammonia (or ammonium) in the cathode side. Pure H_2 or H_2 with trace amount ammonia is flowed in the anode, while the cathode was continuously purged with pure N_2 . In this work, we have only characterized non-operating cells to compare with operated cell data collected earlier by us and available in the literature⁶⁻⁸.

Cyclic voltammetry provides a tool for estimating the available catalyst area, and here it is used to study the long term contamination by ammonia, as well as the recovery processes. Four voltammogram cycles were run during each CV while maintaining the cell conditions (e.g. temperature, humidity, pressure). During CV measurements, the original anode (where H_2/NH_3 is supplied) acts as the counter/reference voltammetric electrode, while the original cathode works as the working electrode. Although the anode as a reference electrode is also contaminated, the peaks in CVs do not shift between pure H_2 and H_2/NH_3 CVs, which justifies use of the anode as the reference electrode. Following the CV scans, electrochemical impedance spectroscopy is performed to further characterize the contamination in the membrane. In EIS measurements, AC voltage is applied on the cell. In the results shown here, frequency is swept from 10 kHz to 0.1 Hz. No reference electrodes were used, since EIS is only used to characterize any resistance change of the MEA. The following experiments were carried out.

Exposure to Ammonia: The contamination tests performed are shown in Table 1. Initially pure H_2 and N_2 were flowed through the anode and the cathode, respectively both with flow rates of 0.25 slpm. After recording baseline electrochemical data (CV and EIS), 25 ppm NH_3 was introduced into the anode. In this study, rather than performance of the PEFC with ammonia in the fuel stream, we focus on electrochemical characteristics of MEA with ammonia present. For these reasons, the cathode is fed with humidified nitrogen, while a small amount of pre-mixed NH_3/H_2 is mixed with humidified H_2 stream to achieve 25 ppm concentration. During exposure to ammonia, CVs were performed periodically to investigate the effect of ammonia on H_2 absorption and Pt oxidation on the cathode catalyst. EIS was also performed after each CV scan. High frequency regions of EIS are used to characterize the changes in the resistance of the membrane.

Table 1. Contamination Tests at Different Relative Humidities. Cells were at Non-running Conditions

RH	Cell (°C)	Dew Points A/C (°C)	Flow Rates A/C (L/min)	NH ₃ in the anode (ppm)
29%	65	40/40	0.25/0.25	25
49%	65	50/50	0.25/0.25	25
80%	65	60/60	0.25/0.25	25

During the tests, the fuel cell temperature was kept constant at 65°C and the inlet gas relative humidity (RH) were varied from 29%, 49% to 80%. The cell is reassembled with virgin MEAs for each test with different RH. Since Nafion properties have significant dependence on the hydration; we hypothesize that the contamination with ammonia will also have significant dependence on hydration.

Recovery after Contamination: Several recovery (clean-up) tests were performed out to investigate the MEA recovery after contamination by ammonia at non-running conditions. Similar to the contamination process, CV and EIS are used to characterize the recovery process. We have performed three recovery processes:

1. The first test was to shut down ammonia flow and keep flowing pure H₂, but everything else (temperature, pressure, relative humidity) was kept at the same conditions.

2. In the second test, following the ammonia shut-down, the relative humidity was kept constant while the temperature of the humidifiers (dew points temperature) and the cell were slowly brought to room temperature (in four hours) and the cell was kept in this condition overnight. Following that, the cell and the humidifiers was brought back to the original temperatures.

3. In the third test, the humidifier temperatures was increased to 65°C (Cell temperature 65°C, anode and cathode RH=100%) and the cell was kept at this condition overnight, and then the humidifiers are brought back to the original condition.

Results and Discussion

Contamination: Figure 2 shows the I-V curves measured by periodical CVs during the contamination processes at three different gas relative humidities. Here, both the anode gas (H₂/NH₃) and the cathode gas (N₂) have the same relative humidity, eliminating the water flux due to concentration gradient. Since the cell is not generating current, there is no water transport across the membrane.

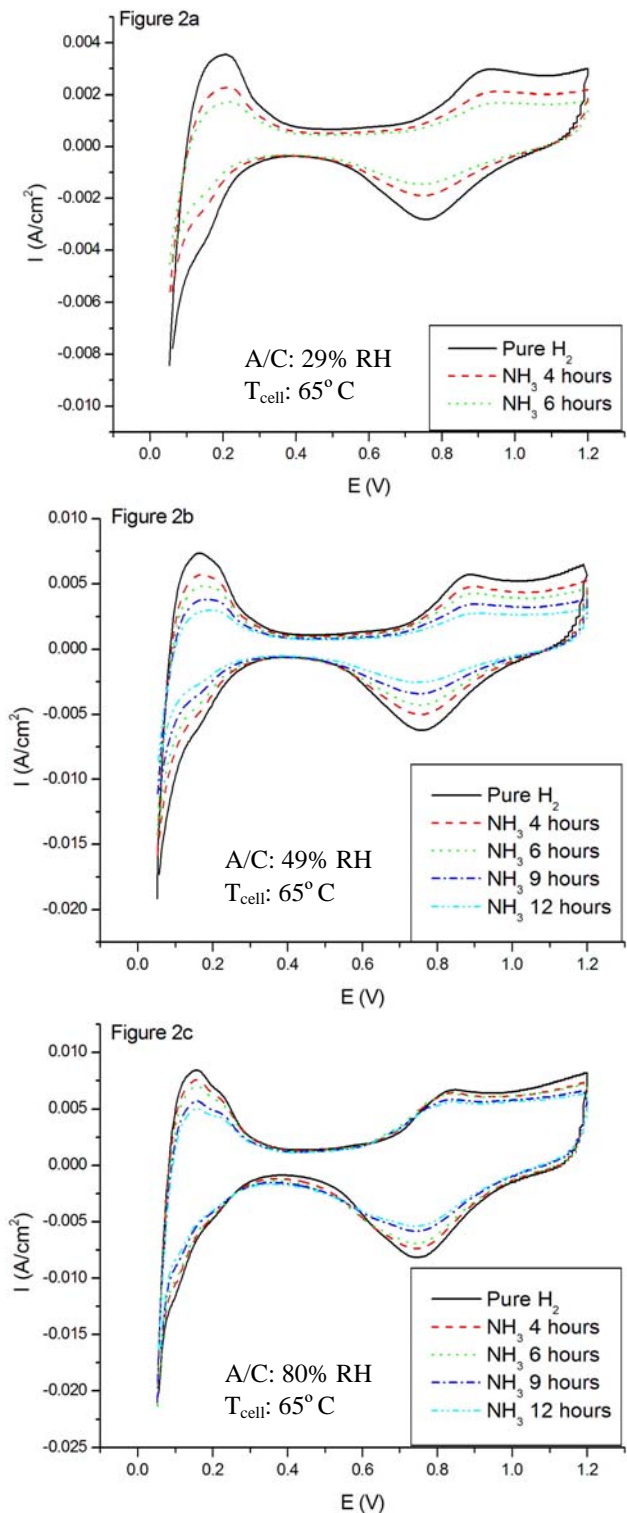


Figure 2. Cyclic voltammograms scans at a) RH 29%, b) RH 49%, c) RH 80%. CVs were obtained with N₂ flowing at the cathode and H₂ or NH₃+H₂ at the anode. Cell was kept at 65°C and scan rate was 20 mV/sec.

The CVs clearly illustrate that the hydrogen absorption peaks and the Pt oxidation peaks decrease monotonously with increasing contamination time. The electrochemical active surface area (ECA) of the cathode significantly decreased, showing a significant impact on the cathode catalyst layer. Figure 3 clearly shows that RH affects the extent of contamination. ECA of the cathode decreases more at low RH than at high RH. Since ammonia is introduced in the anode, the partial pressure difference between the anode and the cathode enables ammonia permeation through the membrane and affects the cathode. A few groups investigated the transport of $\text{NH}_3/\text{NH}_4^+$ in Nafion membranes. Halseid^{8,9} verified that the transport of ammonium in Nafion is rapid. Tricoli and Cussler¹⁰ studied the permeability of ammonia in a 18 μm thick Nafion membrane and found that ammonia permeability at 25 °C and 40 kPa is about $5 \times 10^{-10} \text{ m}^2/\text{s}$ (600 barrers), and it varies weakly with temperature. As a comparison, the permeabilities of H_2 are around $4 \times 10^{-11} \text{ m}^2/\text{s}$ (50 barrers)¹⁰.

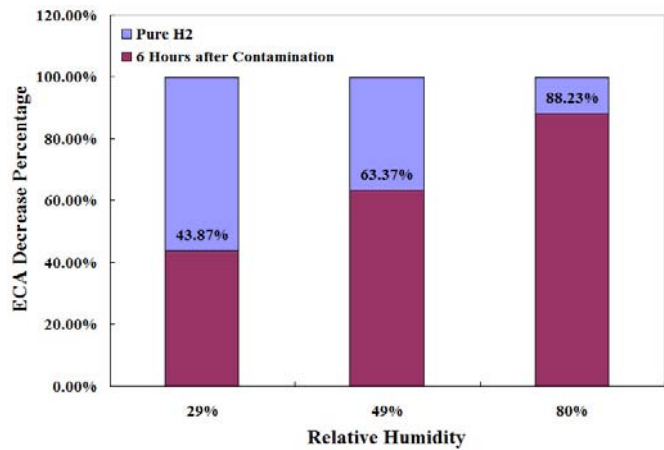


Figure 3. Comparison of ECA decrease percentage after 6 hours contamination at different RH (29%, 49%, 80%)

Figure 4 shows the EIS results at RH 49%. It shows that high frequency response increases gradually, which shows that the membrane resistance increased during contamination. The membrane resistance increased by 60 m Ω ($1.5 \Omega \cdot \text{cm}^2$).

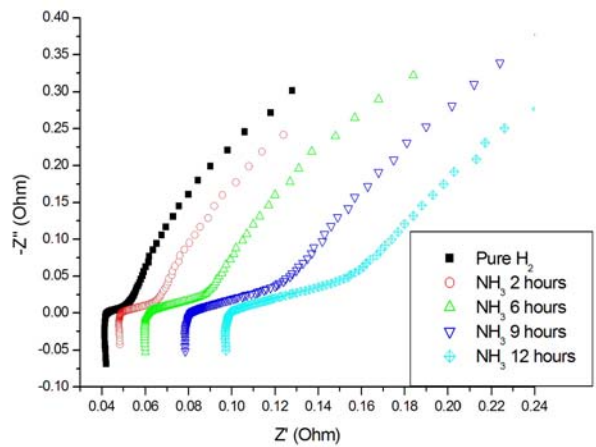


Figure 4. EIS recorded during the contamination processes at RH 49%. Sweep frequency 10000 – 0.1 Hz, amplitude 10 mV.

Recovery: Figure 5 shows the results of the CVs recorded during recovery at RH 49% by the first test described in experimental section. In this test, only the gas in the anode changed, where the gas is switched to pure H_2 . Very little recovery is observed in the H_2 adsorption and Pt oxidation peaks. The CV obtained prior to any contamination is shown as a reference. In particular, there is minimal improvement after 84 hours of pure H_2 flow.

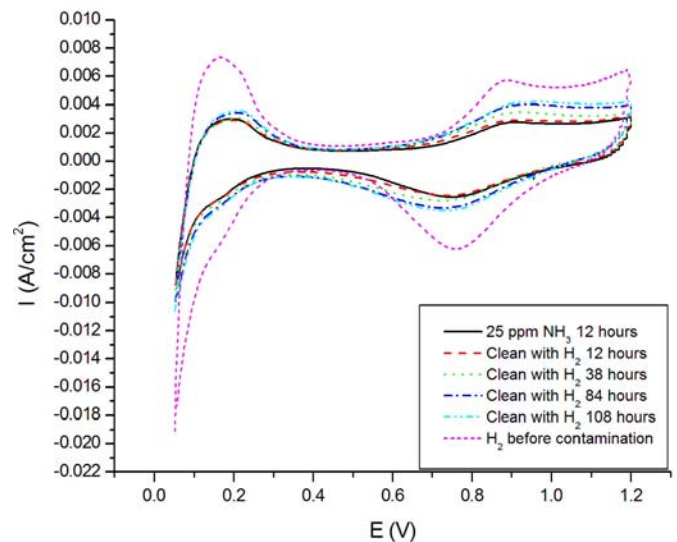


Figure 5. First recovery process at RH 49% by feeding pure H_2 at the anode. Both hydrogen absorption and Pt oxidation peaks can not be recovered fully.

Then the 2nd effort was carried out (shown in Figure 6) but the peaks still showed limited improvement. In this case, the cell temperature was decreased to room temperature at constant RH.

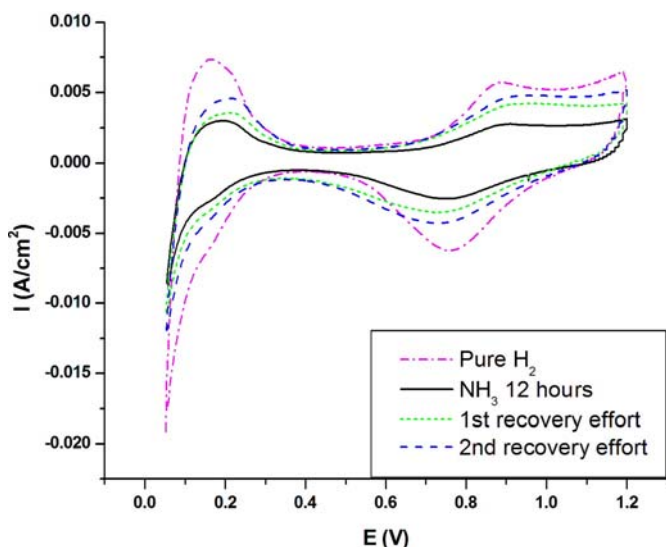


Figure 6. Comparison of different recovery efforts at RH 49%.

Figure 6 shows the recovery attempt with the third test as described in experimental section. In this case, the humidifier temperatures were increased to provide 100% RH gases. It is seen that both the H_2 adsorption peaks and the Pt oxidation peaks recover greatly, although the measured electrochemical active area is not as high as the uncontaminated catalyst layer.

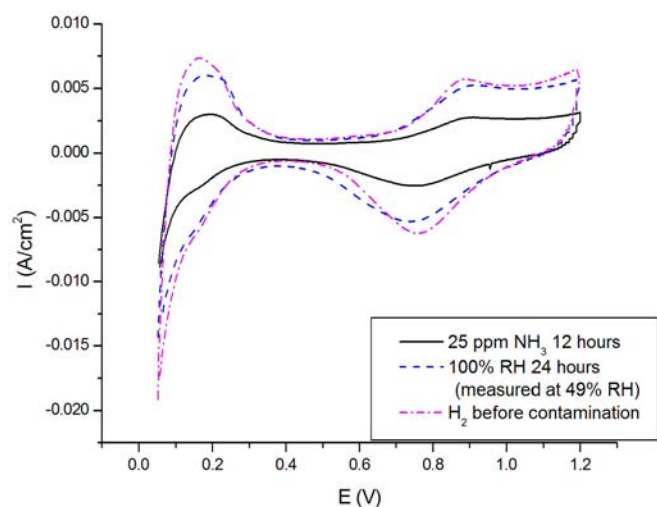


Figure 6. Third recovery process. After staying at RH 100% for 24 hours, the hydrogen absorption and Pt oxidation peaks recovered significantly.

Similar experiments were also carried out on RH 29% and 80%. The results again show that fully saturated gas streams are helpful for recovery from ammonia contamination. For the RH=80% case, just switching to pure H_2 enabled recovery, however increasing RH to 100% didn't help much further. The overall conclusion is that higher RH is required to enable recovery of cathode catalyst layer.

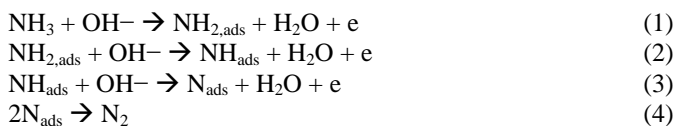
Uribe *et al.*⁶ proposed that ammonia can affect PEM fuel cell performance in several ways. Firstly, ammonia may adsorb protons at the anode and form NH_4^+ ($NH_3+H^+ \rightarrow NH_4^+$), which in turn decreases the conductivity of the membrane. Secondly, ammonia absorption onto Pt may block H_2 oxidation at the anode. Finally, by crossing over to the cathode, ammonia can further affect the oxygen reduction reaction (ORR).

The intercepts of EIS curves (e.g. Figure 4) with the real axis represent the total internal resistance of the cell¹¹. Increase of the internal resistance shows that the conductivity of the membrane decreases upon introduction of ammonia, since everything else that contributes the cell resistance is kept constant, these EIS results support the first hypothesis of Uribe *et al.*. However, we find that conductivity loss is not that significant to cause the cell performance degradation seen in Uribe *et al.*'s data, since the increase of the internal resistance is relatively small compared to the overall decrease in cell performance.⁷⁻⁸

During CV scans, H_2 crosses over to the cathode and get oxidized on Pt. Then it forms protons and is driven back to the anode by the electric field. Inside the MEA, ions actually move in an opposite way as they do in a running cell. Any effect ammonia has on the cathode catalyst layer will be visible from CV curves. Also, conclusions can be drawn that ammonia can cross over the membrane and contaminate the cathode catalyst layer. The results were shown in Figure 2. Hydrogen absorption and Pt oxidation peaks dramatically decreased, as more and more ammonia cross-over the membrane. That means ammonia actually can adsorb on the Pt surface and decrease the available reaction surface.

Uribe *et al.*⁶ and Soto *et al.*⁷ also performed CVs but didn't find any obvious difference before and after contamination. It is of importance to describe why our results differ. There are two possible reasons that can cause these totally different findings. Firstly, their cells were in operation when introducing ammonia, and then purged with pure gases to measure CVs. However, after shutting down the cell, CV can not be measured until the cell potential drops below 0.14V¹², which usually takes long time. All the contaminants could have been removed by pure gases before any CV measurement. Second, as indicated in previous sections, high RHs accelerate the recovery, which also helps to clean the contaminants before any measurement. In our experimental set up, ammonia is continuously supplied to the anode during CV measurements, which enable continuous supply of ammonia.

When the cell is not in operation and oxygen does not exist, ammonia may only accumulate gradually and adsorb on the Pt surface occupying reaction sites. That in turn decreases the active area of the catalyst layer, which can be seen from Figure 2. However, in a running cell ammonia will gain protons at the anode to form NH_4^+ , crossover the membrane under potential field, and finally affect the catalyst layer at the cathode. A few studies¹³⁻¹⁴ exist regarding the oxidation of ammonia on platinum. Gootzen¹³ mentioned four possible reactions that could happen on Pt surface:



where different potentials triggers different reactions. During contamination in operation, adsorbates could accumulate on Pt surface at the cathode, which greatly reduces the possibility of oxygen reduction. Recently, Halseid *et. al.*¹⁵ found that ammonium has a significant impact on the ORR activity on Pt electrode in sulfate solutions. Adsorbates were found at potentials above 0.4 V in the solution.

Although the experiments showed that a trace amount of ammonia can contaminate MEAs, the cell performance can be mostly recovered. Some NH_4^+ can stay absorbed in the membrane, and it is not easily removed.

Conclusion

An experimental study of the effect of trace amount of ammonia in hydrogen stream is performed using cyclic voltammetry and electrochemical impedance spectroscopy. It is found that small concentrations of ammonia can impact the cell performance. We have found significant evidence that ammonia contaminates both the Pt electrode and the membrane. Cyclic voltammetry shows that ammonia affects the hydrogen absorption and Pt oxidation reaction at the cathode. NH_3 or NH_4^+ adsorbs onto the Pt surface, which in turn decreases the active area of the catalyst. EIS shows that ammonia in the H_2 stream also affects the conductivity of the membrane. The former can be fully recovered, while the latter one is not easily removed.

Our future work on ammonia contamination includes similar detailed characterizations on operating PEFCs, in order to identify the absorption characteristics, and to verify the impact of ammonia both on catalyst layers as well as in membranes under potential gradient.

Acknowledgments

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