EFFECT OF AMMONIA AS POSSIBLE FUEL IMPURITY ON PEM FUEL CELL PERFORMANCE

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ABSTRACT

Effects of NH₃ on PEM fuel cell performance are reported. Traces of NH₃ in the anode feedstream cause a decrease in cell current. The extent of the effect depends on NH₃ concentration and time of exposure of the anode to NH₃. We discuss possible mechanisms by which NH₃ affects cell performance.

INTRODUCTION

Polymer electrolyte membrane fuel cells (PEFC) designed for stationary power generation or for transportation applications, will likely operate on reformed fuels. The primary source of H₂ can be methane, methanol or gasoline. Documented reforming processes are used to obtain H₂ from methane [1] or other hydrocarbon fuels. One is the autothermal (ATR) fuel reforming, for which the inlet mixture is CH₄, H₂O, O₂ and N₂ (the last two gases from air) and the outlet major components are H₂, H₂O, N₂, CO₂ and CO. An alternative method, partial oxidation (POX) reforming, requires the same inlet composition except water and produces the same major outlet components as ATR. Both processes produce CO as the most important impurity but also may produce traces of NH₃, estimated in the range of 30 to 90 ppm [1], by the reaction of N₂ and H₂ at high temperatures. With on-board processing of gasoline at relatively early phase of development, outlet NH₃ levels are not well documented and may be a sensitive function of the exact nature of the fuel processor. The report in [1] seems, however, to provide sufficient reason for evaluation of the severity of effects of trace NH₃ on cell performance.

To date, most of the efforts in dealing with impurities in reformates have been centered around the CO catalyst poisoning problem whereas little attention has been given to the effects of trace NH₃ in the fuel feedstream. Szymanski et al. [2] found, for
phosphoric acid fuel cells, that NH$_3$ present as impurity in either fuel or oxidant streams reacts with the electrolyte to form (NH$_4$)$_2$PO$_4$. They concluded that this conversion of protons to ammonium ions lowers the $O_2$ reduction rate at the cathode, leading to cell performance losses. Recently we examined the effect of traces of ammonia in PEM fuel cell anode feed streams [3] and reported that traces of the order of tens of ppm NH$_3$ lead to considerable performance losses. Depending on the length of time that the cell is exposed to ammonia, the losses may become irreversible [3]. Here we report our latest results, including description of our attempts to elucidate the nature of the deleterious effect of NH$_3$ in a PEM fuel cell and to improve NH$_3$ tolerance.

**EXPERIMENTAL**

Figure 1 shows the schematics for testing NH$_3$ tolerance in Nafion™ membrane based H$_2$-Air fuel cells. We prepared membrane and electrode assemblies (MEA) following a reported procedure from our laboratory [4]. The electrode catalyst layers were prepared from carbon-supported 20 % Pt (E-TEK). The catalyst loadings were in the range 0.15 to 0.20 mg Pt/cm$^2$. Both the anode and the cathode catalyst layers were pressed onto a Nafion™ 105 membrane using decals. A carbon cloth backing, not shown in the figure, was used as a gas diffuser. We injected NH$_3$ as an aqueous solution or in the gas phase (diluted in H$_2$ or Ar) into a humidified H$_2$ stream entering the cell. The same port was used for injecting aqueous H$_2$SO$_4$. For injecting the liquid solutions, we used a peristaltic pump. Fuel cells were operated at 80°C, and the anode and cathode humidifier temperatures were 105 °C and 90 °C respectively. We operated the cells with H$_2$ and air flows of 160 and 550 standard cm$^3$ against 30 and 60 psig back pressure respectively. The cell size (electrode geometric active area) was 5 cm$^2$. For cyclic voltammetry (CV) we flowed N$_2$ on the side of the MEA acting as the working electrode and H$_2$ on the other side which we used as counter/reference electrode. We carried out CV scans with a PAR Model 173 Potentiostat coupled with a PAR Model 175 Programmer.

**RESULTS AND DISCUSSION**

Transient effects of NH$_3$. Ammonia was added at the point of fuel injection into the cell. The extent of the effect measured depended on the concentration of NH$_3$ in the fuel inlet stream and the duration of NH$_3$ addition (though the ammonia was added as injected aqueous solution in this experiment, little difference was observed when ammonia was injected as a gas). Fig. 2 shows the cell current density, measured at a cell voltage of 0.5 V, as a function of time following the injection of NH$_3$ at final concentrations in the fuel stream of 13 and 130 ppm. After 1 hour of continuous NH$_3$ injection, the currents were still decreasing. At this point, we recorded polarization curves for each NH$_3$ concentration. These are shown in Fig. 3 along with the polarization curve obtained with
neat H2. The results clearly show the negative effect that the presence of NH3 has on fuel cell performance even at such low levels as 13 ppm.

By analogy to observations on CO-poisoned cells, we thought that changing the anode feed back to pure H2 would purge NH3 out allowing complete recovery of the original performance. We thus made a first attempt of recovering cell performances by turning the NH3 off and running on a pure H2 feed. The results, presented in Fig. 2, show that after turning off NH3, the current increased very slowly. In fact, it took about 12 hours for complete recovery to initial cell current (1.2 A/cm²). This behavior is thus quite different from that of CO, which can be purged from the anode with pure H2 resulting in complete performance restoration within a few minutes. This difference suggests either a completely different poisoning mechanism than CO or a much higher energy of adsorption on Pt anode sites.

Long term exposure to NH3. When the fuel cell anode was exposed to NH3 for several hours, the cell performance dropped to impractical low levels. Fig. 4 shows the polarization curve after 15 hours of continued supply of H2 containing 30 ppm of NH3. At that time NH3 injection was turned off and the cell was operated on pure H2 for several days. After 17 hours the cell performance showed some recovery, but beyond this time no further improvement was achieved, as shown by the polarization curve recorded 88 hours after NH3 had been turned off. This result shows that long term exposure to NH3 could degrade the cell performance irreversibly. For comparison, Fig. 4 also shows the initial performance on H2 with no NH3, and the polarization curve after 1 hour of exposure to NH3.

Possible mechanism by which NH3 affects cell performance. Several routes could be suspected as mechanisms by which NH3 affects PEM fuel cell performance. NH3 may react with the protons of the protonic membrane, forming NH4+ and decreasing membrane conductivity. The same effect on ionic conductivity could take place within the catalyst layer, particularly the anode catalyst layer, which contains recast ionomer in protonic form. Anode catalyst poisoning due to NH3 adsorption onto Pt could inhibit hydrogen oxidation. Finally, NH3 may cross over to the cathode, inhibiting the O2 reduction reaction (ORR)[2]. We have examined these alternatives by the following experiments.

To address the possible effect on membrane conductivity, we measured the high frequency resistance (HFR) of the cell. Fig. 5 shows HFR measurements obtained simultaneously with the polarization curves of Fig. 4. After 1 hour of exposure to NH3 the cell performance clearly dropped compared to the original performance on neat H2 (this is best seen in figure 2). However, as shown in Fig.5, the corresponding HFR’s are practically the same. In the short term, as loss of performance is already clearly observed, the presence of NH3 in the anode feedstream appears not to affect the conductivity of the membrane (the conductivity of Nafion membranes in ammonium form is lower by roughly a factor of 4 relative to that in the protonic form).
However, Fig. 5 shows that when NH₃ is kept flowing for longer periods of time, the HFR is affected. After 15 hours of continued H₂/NH₃ flow the HFR more than doubled at higher cell current densities and was significantly higher at low currents. Stopping the flow of NH₃ into the cell and allowing it to run on pure H₂ for several days did not improve the membrane conductivity. Recall (see Fig. 4) that, under these conditions, the cell had irreversibly lost performance.

We used cyclic voltammetry (CV) to investigate the possibility of NH₃ adsorption on the Pt anode catalyst. Once a cell was brought to some performance level in operation on H₂/air or H₂+NH₃/air, operation was interrupted, the H₂ feed into the anode was replaced by N₂ and the air at the cathode was replaced by H₂ (safety note: nitrogen purge should be applied between O₂ and H₂ operation of the same cell electrode). In this two electrode configuration, the MEA was studied by cyclic voltammetry where the cell anode was now the “working electrode” and the original cell cathode became the counter/reference electrode. Cyclic voltammograms were first recorded after operation of the cell with neat H₂ and then after operation with H₂ + 30 ppm NH₃ for 90 minutes. The results are shown in Fig. 6. The two CV’s are practically the same. The H adsorption potential domain (0.1 to 0.4 V) is not affected by the presence of NH₃ in the cell, suggesting that NH₃ does not adsorb significantly on the Pt surface sites. Remember that under similar conditions, i.e., after 90 minutes of exposure to NH₃ at this level, the fuel cell current density at 0.5 V dropped from 1.3 to 0.8 A/cm².

The possibility of NH₃ crossover to the cathode catalyst was also investigated with CV in a similar fashion as described above. In this experiment, the gases flowing to the electrodes were exchanged such that pure hydrogen was fed to the original anode and nitrogen was fed to the original cathode, the latter becoming the working electrode for CV experiments. After operating the cell with H₂ contaminated with NH₃, the CV recorded for the cathode catalyst was similar to those in Fig. 6, showing no sign of catalyst poisoning by NH₃ adsorption.

The remaining alternative explanation for the observed performance loss is that the ionic conductivity of the catalyst layer is the first to be adversely affected by neutralization of protons with ammonia, leading to an ammonium-form Nafion ionomer in the catalyst layer. Such loss of protonic conductivity in the anode catalyst layer may be detrimental to cell performance as the protonic flux required to maintain a current of the order of 1 A/cm² throughout the anode cannot be sustained after protons in the anode have been significantly replaced by NH₄⁺ ions. If the anode is first to be affected, as expected because NH₃ is a component of the anode feed stream, the high frequency resistance may still show no rise as cell performance starts to drop. One may ask why then is the effect seen on the CV of the anode catalyst so small after prolonged exposure to NH₃ (Fig. 6). One could expect some effect on the process: Pt + H⁺ + e⁻ → Pt-H_ads as proton population diminishes by neutralization with NH₃. However, such effect on the CV may be relatively much smaller than that observed on cell current at given level of proton replacement because CV current densities are 3 orders of magnitude lower than cell current densities. It is interesting to point out that the CV results are very different from

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those obtained in the presence of CO impurity at similar anodes. For instance, 100 ppm of CO introduced in the anode fuel stream brings about strong performance loss after 2 minutes [5]. Concurrently, the H adsorption peaks in the CV completely disappear [6].

We attempted to accelerate the recovery of performance of the cell described in Fig.2 (lower curve) by injecting a 10 mM solution of H$_2$SO$_4$ into the anode. Equivalents of acid injected were more than 10 times the original amount of base (NH$_3$) introduced into the cell. The recovery rate was, however, unaffected. We also briefly attempted to chemically oxidize NH$_3$ with O$_2$ at the anode catalyst layer, by bleeding 6% of air along with a fuel stream containing 30 ppm NH$_3$. However, the presence of air in the fuel feed stream under these conditions had no beneficial effect.

CONCLUSIONS

The presence of trace NH$_3$ in the anode fuel feedstream clearly degrades the PEM cell performance. The extent of performance deterioration depends on NH$_3$ impurity level and the time of cell exposure to it. With short times of exposure (1 to 3 hours) the original performance can be fully recovered (the mechanism of recovery probably involves proton generation by anodic hydrogen oxidation current). Longer times of exposure (e.g. 15 hours) decrease the cell performance to impractical levels and the cell does not recover even after several days of operation on pure H$_2$.

Cyclic voltammetry shows that Pt catalyst surfaces both in anode and cathode are not directly poisoned by NH$_3$. The conductivity of the membrane is affected after longer times of exposure, whereas cell performance starts dropping as soon NH$_3$ is brought to the cell. It thus seems that replacement of H$^+$ by NH$_4^+$ ions within the anode catalyst layer is a primary reason for cell current drop, with drop in membrane conductivity adding to the problem at longer times.

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**Figure 1:** Scheme for testing NH$_3$ tolerance in H$_2$-Air PEM fuel cells
Figure 2: Effect of two concentrations of NH₃ on cell current at 0.5 V cell voltage. The impurity was injected as an aqueous solution into the anode feedstream. Catalyst loadings: 0.17 mg Pt/cm² in both anode and cathode. Cell temperature was 80 °C. Initial currents (t=0) were obtained on neat H₂. The uppermost point on the right indicates the current density after 12 hours of operation on neat H₂, following the 1 hour exposure to NH₃.

Figure 3: Effect of NH₃ on H₂-Air fuel cell performance at 80 °C. Same cell as in Fig. 2, one hour after NH₃ injection had started.
Figure 4: Effects of long term NH₃ exposure on H₂-air fuel cell performance at 80 °C. 30 ppm NH₃(g) were injected into the anode feedstream.

Figure 5: Effects of long term NH₃ exposure on H₂-air fuel cell high frequency resistance at 80 °C. 30 ppm NH₃(g) were injected into the anode feedstream. These curves were simultaneously recorded with polarization curves in Fig. 4.
Figure 6: Cyclic voltammetry at the electrode used as the anode in a 5 cm$^2$ fuel cell after operation with neat H$_2$ and with H$_2$ + 30 ppm NH$_3$ injected at the anode feedstream for 1.5 hour. CV's were obtained with N$_2$ flowing at this electrode and H$_2$ at the other side of the MEA. Cell temperature: 80 °C.