THE EFFECT OF RELATIVELY HIGH AMMONIA CONCENTRATIONS IN REFORMATTE ON PEMFC PERFORMANCE

Herie J. Soto, W-k. Lee and J. W. Van Zee
Fuel Cell Research Laboratory
Department of Chemical Engineering
University of South Carolina, Columbia, SC 29208

Mahesh Murthy
W. L. Gore & Associates, Inc.
201 Airport Road, Elkton, MD 21922-1488

ABSTRACT

Data are reported for Gore’s advanced PRIMEA® Membrane Electrode Assembly (Series 5621) with reformate at 101 kPa and at 70°C. The steady state polarizations curves for different NH3 concentrations (i.e., 80 and 200 ppm NH3) in neat reformate (40% H2, 17% CO2, and 43% N2) were measured and compared with a polarization curve for 500 ppm NH3 in neat H2. The polarization losses from neat hydrogen and neat reformate are discussed. The results show that cell performance was decreased when ammonia was introduced in the reformate (for example, the current density dropped from 825 to 200 mA/cm2 at 0.6 V). A cyclic transient test for 80 ppm NH3 was performed to determine rates of poisoning and recovery.

INTRODUCTION

As the PEMFC industry approaches commercialization, fuel cell stack and systems suppliers are performing field testing and are consequently being confronted with operating their systems in more demanding environments than those utilized in well controlled laboratory testing. Thus, it is imperative that studies be conducted relating to the effect of contaminants in the fuel on the fuel cell performance. In the use of PEMFC, reforming methanol, natural gas, gasoline, or other types of hydrocarbon fuels can produce a hydrogen rich gas (30-40% H2). This hydrogen rich gas may contain traces of impurities such as the well-known carbon monoxide, hydrogen sulfide and ammonia. These poisons or impurities affect the performance of PEMFC.

The literature contains a number of references reporting the effect of impurities on the performance of perfluorosulfonic acid membranes in chloralkali electrolyzers. Some work has been carried out on the effect of impurities such as ammonia. Uribe et al.2 reported that traces of NH3 in neat H2 degrade the PEMFC performance. They showed that the performance could be fully recovered by neat H2 after short times of NH3 exposure (1 to 3 hours). However, the longer times NH3 exposure decreased the cell performance to levels that can not be recovered even several days of neat H2 operation.

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Recently, we studied the response of Gore’s advanced PRIMEA® Series 56 Membrane Electrode Assemblies (MEAs) exposed to levels up to 1,000 ppm NH3 in neat hydrogen for a PEMFC. These data provide a baseline to compare data obtained on simulated reformate mixtures of hydrogen, carbon dioxide, and nitrogen containing various levels of NH3. In this study, we added ammonia in the neat reformate as an anode gaseous impurity. Though data on fuel cell performance utilizing hydrogen/NH3 and reformate mixtures is separately available, a detailed analysis of the individual components in the reformate mixtures and their effect on cell performance is lacking. In an effort to begin this analysis, the study reported here will show the effects of NH3 in reformate on the cell performance and compare these effects with hydrogen/NH3 mixture data.

EXPERIMENTAL

The experiment focused on the performance of PEM fuel cells in the presence of NH3 in reformate at the anode side. At the beginning, polarization performances were measured for neat hydrogen (100 % H2) and a “standard” neat reformate (RMS) consisting of, 40 % H2, 17 % CO2, and 43 % N2. After obtaining polarization curves with neat hydrogen and neat reformate, polarizations for reformate containing NH3 were measured. In the experiments, two different levels of NH3 in the reformate were examined to study the interaction of ammonia with diluted H2. The concentration of NH3 was 80 ppm in the reformate and 200 ppm in the neat H2 fuel. Thus if we operate at the same dew point or partial pressure of water vapor, the ratio of ammonia to hydrogen will be constant. Polarization curves were obtained by randomly setting the cell voltage from 0.45 V to open circuit voltage and measuring the resulting steady state currents. The randomization gave reproducible results and accounted for any hysteresis in the reported current densities. While recording the polarization curve, the flow rates were adjusted to maintain the desired stoichiometry as discussed below. Also, cyclic voltammetry (CV) studies were performed for the different NH3 concentrations. A scan rate of 5 mV/s was used and the voltage range between 50 mV and 800 mV was used. During these CVs, nitrogen gas was added at a flow rate of 200 cm3/min on the anode, while in the cathode, hydrogen was used at a flow rate of 200 cm3/min.

After establishing steady state behavior, the transient experiment was conducted for 80 ppm NH3 at a fixed current density of 600 mA cm⁻². These transient conditions corresponded to repetitive introductions of NH3 concentration (10 hrs) followed by periods with reformate (10 hrs) for 3 cycles. The objective of this experiment was to determine the relative rates of poisoning and recovery for NH3 in reformate. The procedures used to obtain the rates of poisoning and recovery are discussed in detail by Murthy et al.

The MEAs used in the experiment were PRIMEA® MEA Series 5621 (W.L Gore & Associates, Inc., Elkton, MD), consisting of GORE-SELECT® membranes (35 μm nominal membrane thickness) and catalyst loadings 0.45 mg/cm² Pt-Ru alloy on the anode and 0.6 mg/cm² Pt on the cathode. The active area of the membrane was 25 cm² and the triple-serpentine flow fields consisted of 30 equally spaced channels of height 0.1 cm and width 0.08 cm. The gas diffusion media (GDM) used in the experiment were CARBEL™ CL GDM (16 mils = 0.406 x10⁻³ m) for both the anode and the cathode sides of the MEA. A compressible material (silicone coated fiberglass) with a measured...
thickness of 0.254 x 10^-3 m (10 mils) was used as a gasket. Another thin gasket (1.2 mils = 0.305 x 10^-5 m), referred to as the sub-gasket, was placed between the MEA and the gas diffusion media for maintaining the right compression inside the fuel cell and also ensures a robust alignment of the GDM on the active area during cell assembly. This sub-gasket reduced the active area from the nominal 25 cm^2 of flow field to 22 cm^2 of active MEA. Eight bolts were lubricated and threaded into tapped holes on one of the end plates, and the cell was compressed by applying a torque of 5.65 J/bolt (50 in-lbf /bolt).

All experiments were performed using test stations with a reformate unit made by Scribner Associates. This reformate unit controls the mixture of the gases by adjusting mass flow controllers. These mass flow controllers were calibrated with a bubble flow meter. Ultra High Purity (UHP) hydrogen (99.999 %), premixed high purity NH3/H2, bottled air (industrial grade), high purity N2 (99.998 %), and instrument grade carbon dioxide (99.99 %) were used. Note that this CO2 contains traces of CO less than 5 ppm. The stoichiometry corresponded to flow rates that were 1.2 times greater than that required (by the measured current) for hydrogen (i.e., 20 % excess hydrogen) and 2.0 times greater than that required for air (i.e., 100 % excess air). In the experiment, dry NH3 was added through mass flow controller at the anode inlet (i.e., NH3 was injected between the humidity bottle and the fuel cell). The gas temperature and its humidity were controlled by sparging the gases through water in a humidity tank. The temperature of the cell was fixed at 70 °C for all of the experiments. Also, the pressures of the anode and the cathode sides were both 101 kPa (0 psig). The temperatures of humidification bottles were set at 85 °C for the anode and 75 °C for the cathode streams and these temperatures correspond to measured dew points of 80 °C and 70 °C for the anode and cathode respectively. Multiple MEAs were used for different levels of NH3 in reformate. The MEAs typically were operated continuously for 250 to 350 hours, and therefore, the data reported here can be considered beginning-of-life data.

RESULTS AND DISCUSSION

Figure 1 shows the polarization curves for neat hydrogen and neat reformate. The cell performance was decreased when the neat reformate was introduced (i.e., the current density dropped from 1.05 to 0.825 A/cm^2 at 0.6 V). This performance difference between neat H2 and neat reformate is associated with dilution of hydrogen in the anode stream as reported by Murthy et al. It is noted that the composition of the neat reformate was 40 % H2 and 17 % CO2 balanced with N2. The effects of NH3 in the reformate are also shown in this figure for two levels of concentration: 80 ppm NH3 and 200 ppm NH3. The cell performance decreased as the NH3 concentration in the reformate increased. Also shown in Fig.1, cell performance for 200 ppm and 500 ppm NH3 in neat hydrogen was compared with the performance of 80 ppm and 200 ppm NH3 in reformate. Note that the ratios of NH3 to H2 for the 200 ppm and 500 ppm NH3/H2 mixtures are the same as the 200 ppm NH3 in reformate (i.e. the ratio of 500 ppm NH3 with 100 % H2 is same as the ratio of 200 ppm NH3 with 40 % H2). The result shows that the performances of 500 ppm NH3 in neat H2 and 200 ppm NH3 in reformate are comparable and that at these high concentrations of ammonia, substantial poisoning of the surface controls the polarization. At lower concentrations, such as with the 80 ppm NH3 in RMS, the concentration of ammonia appears not to be sufficient to cover all of the sites and the
performance in reformate is better than with 200 ppm in H₂ at higher current densities. The difference in exposure time is not thought to be a reason for the better performance by 80 ppm in RMS at current densities greater than 0.4 A/cm² but additional experiments with the same exposure or dosage are being performed to verify this conclusion.

Figure 2 shows the anode overpotential for the various NH₃ concentrations in reformate and in neat H₂. The anode overpotential was obtained from the data shown in Fig. 1. These overpotentials are calculated from the difference between the cell potential with neat hydrogen and the cell potential with different NH₃ concentrations at the same current density. This calculation removes the cathode overpotential and the IR losses from the data if we assume that both of these losses are a function of current density only. Again the lower coverage at 80 ppm NH₃ in RMS is shown at current densities greater than 0.3 A/cm². Additional experiments at lower concentrations should be performed to determine if there is a lack of interaction between H₂ and NH₃ adsorption. This lack of competitive adsorption may simplify the understanding of the poisoning mechanism.

Figure 3 shows an example of the transient performance at a constant current density 600 mA/cm² for 200 ppm NH₃ in reformate. It shows how the cell voltage changes when 200 ppm NH₃ was added for 19.5 hours followed by a neat reformate for 20 hours. The cell voltage substantially decreased (from 0.64 V to 0.34 V) when the 200 ppm NH₃ was added at the anode side. The polarization curve was measured with 200 ppm NH₃ after introducing 200 ppm NH₃ for 9.0 hours (i.e., the V-I curve for 6.5 hours shown by the label on Fig. 3). After finishing the polarization measurement, the cell voltage was measured in the presence of 200 ppm NH₃ at 600 mA/cm² for four more hours. Then the neat reformate was introduced for 20 hours. The cell voltage was almost recovered by 20 hours of neat reformate. Thus the poisoning/recovery rates are slow but the decrease in the number of active sites appears to be reversible in neat reformate. Also, Figure 3 shows that the membrane resistance (obtained by a current interrupt technique) was increased when the cell voltage was decreased. However, this resistance (i.e., 5x10⁻³ Ω during NH₃ exposure) does not account for the 0.3 V of loss. This accounts only for 0.066 V loss. The fact that the resistance cannot account for all of the voltage loss may indicate the presence of adsorption on the catalysts as well as a reversible complexation reaction of the ammonia with the ionomer in the electrode. The current interrupt measurement typically does not include ionic resistance changes in the electrode. The gradual increase in resistance may be related to the part of the poisoning mechanism related to the complexation with the ionomer in the membrane. Clearly more studies are required for a better and more complete explanation. Figure 4 shows the polarization curve with 200 ppm NH₃ after 9 hours of exposure. The cell performance was completely recovered, compared to the baseline of neat reformate, by 20 hours of neat reformate after 19.5 hours exposure of 200 ppm NH₃.

Figure 5 shows the cyclic transient test with 80 ppm NH₃ in reformate. The cell performance decreased from 0.65 V to 0.45 V for the first cycle as the 80 ppm of NH₃ were introduced. After exposing the fuel cell to neat reformate for 10 hours the performance increased to 0.63 V. For the second and third cycle the recovery is almost constant, reaching a performance of 0.60 V. Poisoning rates were measured for each cycle and, these rates were 0.23 mV/min for the first cycle, 0.20 mV/min for the second cycle, and 0.24 mV/min for the third cycle. Recovery rates were also measured, these rates were 0.64 mV/min for the first cycle and 0.46 mV/min for the second cycle. Table
1 shows a comparison of these rates for 80 ppm NH₃ in reformate and 200 ppm NH₃ in H₂. The rates of poisoning decreased when the ammonia is in reformate but at the same time the recovery step is almost four times slower in reformate.

Figure 6 shows the CV performed after exposing the anode to 200 ppm NH₃ in reformate for 19.5 hrs. The resulting peak from 0.28 V to 0.5 V is a CO peak. This CO is resulting due to the reverse water gas shift reaction as discussed by de Bruijin et al. That is, one would expect an equilibrium reaction to occur on the Pt sites of the anode:

\[ CO₂ + H₂ = CO + H₂O \]  \[ \text{[1]} \]

Electrochemically the reactions are:

anode: \[ CO + H₂O = CO₂ + 2H^+ + 2e^- \]  \[ \text{[2]} \]

cathode: \[ 2H^+ + 2e^- = H₂ \]  \[ \text{[3]} \]

For reaction \[ \text{[1]} \], \( \Delta H^{o}_{343} K = 41.16 \text{ KJ/mol} \), \( \Delta S^{o}_{343} K = 42.03 \text{ J/mol} \), and \( \Delta G^{o}_{343} K = 26.7 \text{ KJ/mol} \). The equilibrium potential of electrochemical reaction \[ \text{[2]} \] is \( E^o = -138 \text{ mV vs. SHE} \). Using thermodynamic data for the involved species, the equilibrium concentration of CO was calculated. This was calculated for inlet and outlet conditions assuming saturation of water vapor at 343 K. For our case, these equilibrium concentrations were 19.2 ppm CO for inlet and 3.5 ppm CO for the outlet. To prove that the peak was CO, a voltammogram was measured after the anode was exposed to 500 ppm NH₃ in neat H₂ shown in Figure 7. No peak was observed, leading one to conclude that the peak in Fig. 6 is a CO oxidation peak. Another voltammogram was recorded after exposing the anode with reformate free of NH₃ for just five minutes and the same peak as in Fig. 6 was observed. This tells us that the CO in the anode is due to the reverse water gas shift reaction. Future work will study the interaction of CO and NH₃.

CONCLUSION

In our preliminary experiments, the polarization curves for various levels of NH₃ concentration in reformate and in hydrogen were measured. The results show that at high concentrations of NH₃ (i.e., 500 ppm NH₃ in H₂ and 200 ppm NH₃ in reformate), substantial poisoning of the surface controls the polarization and at lower concentrations (i.e., 80 ppm NH₃ in reformate) ammonia does not cover all the reaction sites. Note that the data reported here cannot differentiate between NH₃ adsorption on Pt or the ionomer. This difference should be determined in future experiments. Poisoning and recovery rates are much slower in reformate than in hydrogen but the decrease in the number of active sites appears to be reversible in reformate. It appears that NH₃ and CO is both at the surface and there are some interactions between them.

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REFERENCES

1. S.G. Chalk, J.M. Miller, and F.W. Wagner, *J. Power Sources*, 86, 45 (2000).
2. F.A. Uribe, S. Gottesfeld, T.A. Zawodzinski, *J. Electrochem. Soc.*, 149 (3), A293-A296 (2002).
3. H.J. Soto, W-k. Lee, J.W. Van Zee, and M. Murthy, submitted *Electrochemical and Solid-State Letters*, August 2002.
4. M. Murthy, M. Esayian, A. Hobson, S. MacKenzie, W-k. Lee and J.W. Van Zee, *J. of the Electrochemical Society*, 148 (10), A1147 (2001).
5. W-k. Lee, Ph.D. dissertation, Department of Chemical Engineering, University of South Carolina, Columbia, SC, 29208 (2000).
6. W-k. Lee and J.W. Van Zee, S. Shimpalee, S. Dutta, ASME IMECE Conference Proceedings, HTD-Vol. 364-1, 359, Nashville, TN, Nov. 1999.
7. M. Murthy, W-k. Lee, and J.W. Van Zee, *AIChE Spring National Meeting*, Paper T9 #83i, New Orleans, LA, March 10 – 14, 2002.
8. A.F. de Bruijin, D.C. Papageorgopoulos, G.J.M. Janssen, *J. Power Sources*, 110, 117 (2002).

Figure 1. Performance comparisons for 80 and 200 ppm NH₃ in reformate; and 200 and 500 ppm NH₃ in H₂ (T_{cell} = 70 °C, T(A/C) = 85/75 °C, P(A/C) = 101/101 kPa).
Figure 2. Comparison of anode overpotential for 80 and 200 ppm NH$_3$ in reformate; and 200 and 500 ppm NH$_3$ in H$_2$ (T$_{cell}$ = 70 °C, T(A/C) = 85/75 °C, P(A/C) = 101/101 kPa).

Figure 3. Transient performance for 200 ppm NH$_3$ in neat reformate at 600mA/cm$^2$ (T$_{cell}$ = 70°C, T(A/C) = 85/75 °C, P(A/C) = 101/101 kPa).
Figure 4. Effects on the cell performance with 200 ppm NH₃ in reformate 
(T_{cell} = 70°C, T(A/C) = 85/75 °C, P(A/C) = 101/101 kPa).

Figure 5. Cyclic transient performance of 80 ppm NH₃ in reformate at 600 mA/cm² 
(T_{cell} = 70 °C, T(A/C) = 85/75 °C, P(A/C) = 101/101 kPa).
Figure 6. Cyclic voltammogram with 200 ppm NH$_3$ in reformate to show the CO oxidation ($T_{\text{cell}} = 70$ °C, $T(A/C) = 85/75$ °C, $P(A/C) = 101/101$ kPa).

Figure 7. Cyclic voltammogram with 500 ppm NH$_3$ in neat H$_2$ ($T_{\text{cell}} = 70$ °C, $T(A/C) = 85/75$ °C, $P(A/C) = 101/101$ kPa).
| NH$_3$ concentration          | Poisoning rate (mV/min) | Recovery rate (mV/min) |
|-------------------------------|-------------------------|------------------------|
| 200 ppm NH$_3$ in H$_2$       | -0.96*                  | 2.12*                  |
| 80 ppm NH$_3$ in reformate    | -0.22                   | 0.55                   |

Table 1. Comparisons of the poisoning and recovery rates for NH$_3$ in neat H$_2$ and in reformate.

* Quoted from paper T9 #76d in *AIChE Spring National Meeting*, New Orleans, LA, March 10 – 14, 2002.