

# Effect of ammonia on the performance of polymer electrolyte membrane fuel cells

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## Abstract

The effect of ammonia on polymer electrolyte membrane fuel cells (PEMFC) was tested by adding 10 ppm NH<sub>3</sub> to the hydrogen feed to PEMFCs based on GORE™ PRIMEA® membrane electrode assemblies (MEAs). A significant loss in performance was observed. The poisoning process was slow taking 24 h or more to reach a steady state. In some cases no steady state performance was reached during the experiment. The performance loss was reversible in most cases, but only after operation on neat hydrogen for several days. Additions of 1 ppm NH<sub>3</sub> for 1 week also resulted in significant performance loss. An MEA based on carbon supported Pt anode and cathode catalyst did not differ from the GORE™ MEA based on PtRu anode and Pt cathode catalyst. The performance losses were higher than could be explained by the observed increase in ohmic resistance in the cell. There was also a significant decay in performance in a H<sub>2</sub>|H<sub>2</sub> cell, especially at high current density where a reaction limiting current was observed showing that the Hydrogen Oxidation Reaction (HOR) was affected. The Oxygen Reduction Reaction (ORR) on the cathode was also significantly affected by ammonia.

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## 1. Introduction

Ammonia can be used as a hydrogen carrier for fuel cells (FCs). Most studies have evaluated ammonia based hydrogen as fuel for alkaline FCs [1–3], but also phosphoric acid (PA) FCs [4,5] and polymer electrolyte membrane (PEM) FCs [6,7] have been considered. In order to use ammonia in PEMFC, it has to be split to nitrogen and hydrogen upstream the FC. However, traces of ammonia will be present in the hydrogen rich fuel stream [6]. Ammonia is also a likely contaminant in PEMFC operation even if ammonia is not used as the hydrogen carrier. Ammonia may be formed in fuel reforming processes at levels up to 150 ppm [8], especially if the reforming involves homogeneous precombustion with air, or if the fuel itself contains nitrogen containing

species [9]. Ammonia may also be present in ambient air as such. There has also been reports that certain AB<sub>5</sub> metal hydride alloys used for hydrogen storage has a catalytic effect on the formation of ammonia from mixtures of hydrogen and nitrogen [10]. Ammonia may thus be present also in hydrogen from metal hydride storages if there is nitrogen in the hydrogen used to fill these.

To our knowledge, only two different research groups have published papers regarding ammonia contamination of PEMFC [11,12]. The focus of Uribe et al. [11] and Soto et al. [12] was to study poisoning of cells in operation and recovery after exposure to ammonia. The poisoning mechanism was only partly identified.

Uribe et al. [11] found that the cell resistance, as measured by high frequency resistance (HFR), more than doubled when the cell was exposed to 30 ppm ammonia for 15 h. They used MEAs containing 0.15–0.20 mg Pt cm<sup>-2</sup> catalyst on either electrode. The cell resistance started to increase only when the cell had been exposed to ammonia for more than 1 h. Exposure to 30 ppm ammonia for about 1 h resulted in performance losses which were recoverable in about 18 h. Extended exposure to 30 ppm NH<sub>3</sub> for 17 h was not fully recoverable within 4 days of operation

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on neat hydrogen. Cyclic voltammetry (CV) did not indicate any electrochemically active adsorbed contaminants to be present either on the anode or on the cathode. The increase in ohmic cell resistance was not by itself sufficient to explain the observed loss of performance. Uribe et al. suggested that the observed losses also were due to loss of proton conductivity in the anode catalyst layer.

Soto et al. [12] used a GORE™ PRIMEA® series 5621 MEA with 0.45 mg PtRu cm<sup>-2</sup> anode catalyst and 0.6 mg Pt cm<sup>-2</sup> cathode catalyst. The cell resistance was monitored by an automated current interrupt technique. Exposure to 200 ppm NH<sub>3</sub> for 10 h increased the measured cell resistance by about 35%, much less than observed by Uribe et al. who used lower concentration of ammonia. The increase in resistance observed by Soto et al. could only explain about 10% of the performance loss. CVs recorded on the anode did not reveal any electrochemically active species. Soto et al., similarly to Uribe et al., suggested that ammonium interfered primarily with the anode. No detailed hypothesis regarding poisoning mechanism was suggested.

Another relevant study of the effect of ammonia on acidic FCs was made by Szymanski et al. [13]. They studied how PAFC, operating at 191 °C, were affected by ammonia. They found that the ORR occurring at the cathode was the process that was most noticeably affected by ammonia. At 1% conversion of the phosphoric acid to (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>, 84% of the cathode activity was lost. They also found a significant ability of the cell to oxidize ammonium, presumably to nitrogen, especially at high cathode potentials.

## 2. Experimental

MEAs from W.L. Gore & Associates (PRIMEA® 5561 with Pt/Ru anode catalyst (0.45 mg cm<sup>-2</sup>) and a Pt cathode catalyst (0.4 mg cm<sup>-2</sup>)) were used in most experiments. The commercial MEAs were used as received. An MEA with a loading of 0.35 mg Pt cm<sup>-2</sup> on both electrodes was also prepared using a procedure described by Wilson et al. [14] with only minor modifications [7]. Nafion® 112 was used in this MEA.

All gases used were 99.999% pure from AGA including synthetic air (80/20 N<sub>2</sub>/O<sub>2</sub> mix). Hydrogen (99.999%) containing 104 ppm NH<sub>3</sub> (99.95%) by volume was used for additions of ammonia to the system. The conversion was 40% and 80% on the cathode and anode, respectively.

All experiments reported here were conducted at atmospheric pressure and with a cell temperature of approximately 40 °C. The bubble gas humidifiers, described in more detail in [7], were operated either at room temperature or at approximately 40 °C. Hydrogen containing ammonia was mixed with pure hydrogen downstream of the humidifiers to avoid absorption of ammonia in the water-filled humidifiers. The FC performance increased gradually during the first 2–4 days of operation, and all further experiments were only made after this initial period. Frequent polarization scans shortened the required time to reach stable performance. The performance of symmetrical H<sub>2</sub>|H<sub>2</sub> cells typically stabilized in a few hours.

No reference electrode was included in these experiments. It has been shown that from a theoretical point of view, reference

electrodes in cells with a thin electrolyte film are not reliable [7,15–17]. Since there is no reference electrode in the cell, it is more difficult to separate the different effects of ammonia. For this reason, measurements involving symmetric H<sub>2</sub>|H<sub>2</sub> cell were also made in order to more closely study the effect of ammonium on the anode performance (hydrogen oxidation reaction, HOR).

Gas diffusion layers (GDLs) from E-TEK Inc. (ELAT®, carbon only) were pressed gently onto the active layer of the MEA before it was mounted in the FC housing and tested. Two different cell housings were used in these experiments; one a 6.25 cm<sup>2</sup> cell from ElectroChem Inc.; the other a 10 cm<sup>2</sup> in-house cell design. The 10 cm<sup>2</sup> cell was used in most experiments except were otherwise noted. The applied mechanical pressure on the MEA in the 10 cm<sup>2</sup> housing was controlled using a pneumatic piston [18,19] and set to 1 MPa. The mechanical pressure applied in the 6.25 cm<sup>2</sup> cell housing can only be indirectly controlled by the torque used when assembling the housing. Some of the forces are also absorbed by the gasket material making an exact calculation of pressure applied very difficult. However, the same torque was used each time to improve reproducibility.

The current was controlled using an Agilent 6050A load that may run both galvanostatically and potentiostatically. In order to achieve low cell voltages, a HP 6032A power supply was connected in series with the load. A solid state relay was also connected in series to facilitate current interrupt measurements [7].

## 3. Results

### 3.1. Exposure of PEMFC to NH<sub>3</sub>

A typical cell response to exposure to hydrogen containing 10 ppm NH<sub>3</sub> is shown in Fig. 1. The cell was operated galvanostatically at 0.7 A cm<sup>-2</sup> and allowed to stabilize before 10 ppm NH<sub>3</sub> was added to the fuel gas for 24 h. The ammonia addition was then turned off allowing the cell to recover. Three days after the addition of ammonia was stopped, the gas supply to the cell was stopped for a few hours letting the cell potential fall to 0 V. One day after this, several polarization scans with 2-h interval were performed.

The first thing to notice in Fig. 1 is that the cell resistance increased when ammonia was added. The performance of the cell decreased instantaneously, but it took almost 1 day to reach a seemingly steady state for cell resistance and performance. The increase in cell resistance was only 0.012 Ω cm<sup>2</sup> corresponding to an increase in ohmic losses of about 8 mV. The observed drop in cell potential was about 160 mV, i.e., the increase in ohmic resistance can only explain about 5% of the total potential loss.

Measurements were also performed with other cells running potentiostatically. Typical transients observed during NH<sub>3</sub> poisoning are shown in Fig. 2. The different regions shown in Fig. 2 are: (1) operation on pure hydrogen; (2) poisoning with 10 ppm NH<sub>3</sub> for 4 h; (3) recovery period operating on pure hydrogen recording polarization curves every 4 h; (4) poisoning with 10 ppm NH<sub>3</sub> for 26 h; (5) recovery period operating on pure hydrogen recording polarization curves every 4 h; (6) gas supply to the cell was interrupted in this period so that the cell potential

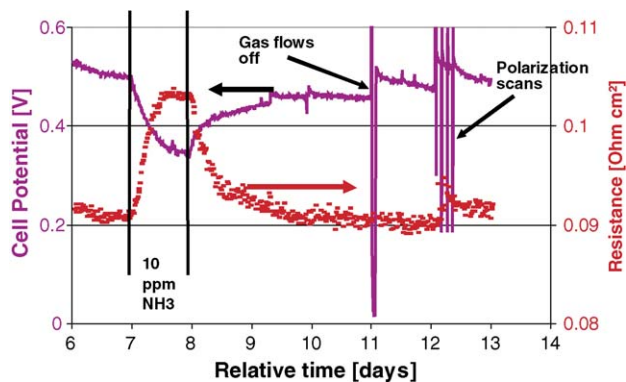


Fig. 1. Performance of 10 cm<sup>2</sup> GORE™ MEA with addition of 10 ppm NH<sub>3</sub> for 24 h. The cell was running galvanostatically at 0.7 A cm<sup>-2</sup> at 40 °C with humidification at 30 °C, 80% conversion on anode, 40% on cathode, 30 and 20 ml N min<sup>-1</sup> minimum flow, respectively. The data are not corrected for ohmic losses.

dropped to 0 V. Note the significant recovery in performance; (7) operation on pure hydrogen.

The increase in resistance shown in Fig. 2, where the cell was run potentiostatically, is larger than the increase observed running in galvanostatic mode, see Fig. 1. This was also observed in the cell with an MEA based on carbon supported Pt (not PtRu as in the GORE™ MEA), see Fig. 4 which we shall revert to in more detail later. Further, the resistance did not seem to reach a steady state within the period NH<sub>3</sub> was added. The current density (cd) at 500 mV cell potential after 26 h of contamination was 0.25 A cm<sup>-2</sup>. The cell potential at the same cd in the cell before contamination was 0.731 mV. The increased ohmic resistance can explain about 36 mV of the total of 231 mV losses, or about 15%. During the first poisoning, shown as region 2 in Fig. 2, ohmic effects could explain 6 out of 74 mV change, or about 9%. The relative importance of increase in ohmic resistance is consistent with data reported by Soto et al. [12].

Polarization curves were obtained both before and after poisoning of the FC, and after gas supply was temporarily stopped. Typical polarization curves are shown in Fig. 3.

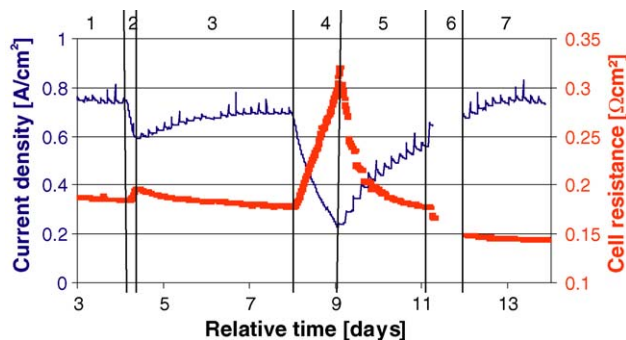


Fig. 2. Performance of 10 cm<sup>2</sup> GORE™ MEA with addition of 10 ppm NH<sub>3</sub> for 4 and 26 h (regions 2 and 4 in the graph). The cell was running potentiostatically at 0.50 V at 40 °C cell temperature, room temperature humidifiers, atmospheric pressure, 80% conversion of H<sub>2</sub>, 40% conversion of O<sub>2</sub> in air, 50 ml N min<sup>-1</sup> minimum flow on either side. The data are not corrected for ohmic losses. See the text for explanation of the different regions.

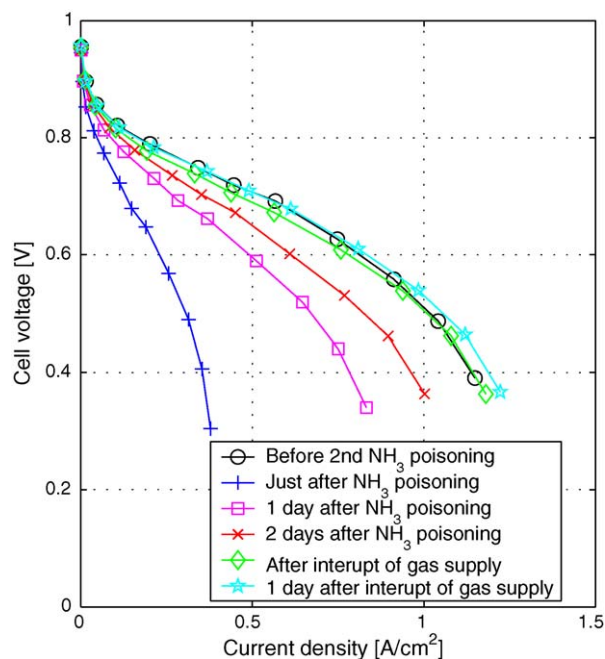


Fig. 3. IR corrected polarization curves obtained before and after addition of 10 ppm NH<sub>3</sub> for 26 h, see region 4 in Fig. 2. Conditions as in Fig. 2. Potential scans were performed on a regular basis every 4 h.

### 3.2. Pt vs. PtRu as anode catalyst

An MEA with carbon supported Pt as anode catalyst, rather than PtRu in the GORE™ MEA, was also tested. The results of the testing are shown in Fig. 4. The different regions of the graph are: (1) operation on pure hydrogen; (2) addition of 10 ppm NH<sub>3</sub>; (3) operation on pure hydrogen; (4) switched from potentiostatic to galvanostatic operation on pure hydrogen; (5) addition of 10 ppm NH<sub>3</sub>; (6) operation on pure hydrogen; (7) operation on pure hydrogen after gas supply had been temporarily stopped.

The cell was run in both potentiostatic and galvanostatic mode, the switch is marked with a thick vertical line in Fig. 4. No large differences between the two modes were observed except that the ohmic resistance increased more in potentiostatic mode than in galvanostatic mode. Recovery was complete after shutting the gas supply off for a while. The effect of ammonia seems to be very similar for both Pt and PtRu based anode catalysts. The loss of cell performance was larger than the effect of increased cell resistance also in this case.

### 3.3. Different contamination levels

Uribe et al. [11] and Soto et al. [12] studied the effect of relatively high contamination levels (13–130 and 200–1000 ppm, respectively). The FCs studied in this work were contaminated with lower levels of NH<sub>3</sub> in the hydrogen (1–20 ppm). In Fig. 5 the result of contamination of a cell for 1 week with 1 ppm NH<sub>3</sub> in the fuel is shown. The influence of even quite low concentrations of ammonia was significant. Recovery of performance was only partial although recovery of membrane conductivity is virtually complete.

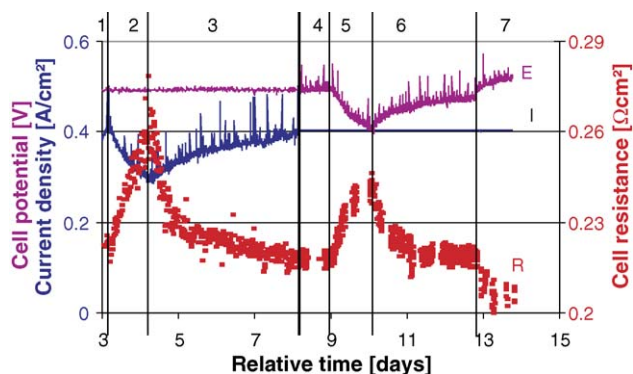


Fig. 4. Performance of a 10 cm<sup>2</sup> *in-house* prepared MEA with carbon supported Pt catalyst on either electrode with addition of 10 ppm NH<sub>3</sub> for about 26 h (region 2 and 4 in the graph). The cell was first run potentiostatically at 0.50 V then galvanostatically at 0.40 A cm<sup>-2</sup>. Operational parameters are the same as given in Fig. 2 except minimum flow of hydrogen was 30 ml N min<sup>-1</sup>. The data are not corrected for ohmic losses. See the text for explanation of the different regions.

### 3.4. Symmetric H<sub>2</sub>|H<sub>2</sub> cell

An MEA was tested with hydrogen on both electrodes to better isolate the effect of ammonium on the anode reaction (HOR). The different regions indicated in Fig. 6 are: (1) initial operation on pure hydrogen; (2) addition of 10 ppm NH<sub>3</sub>; (3) operation on pure hydrogen with polarization scans recorded every day; (4) operation on pure hydrogen with polarization scans every 2.5 h; (5) operation on pure hydrogen after gases had been temporarily stopped.

Ammonia containing hydrogen has to be added downstream of the humidifiers so that the anode feed gas is not fully humidified. Hence, when ammonia was not added to the cell, the same flow rate of pure, dry hydrogen was added downstream of the anode humidifier.

We notice from Fig. 6 that the cell resistance did not decrease when operating on pure hydrogen after exposure to ammonia in contrast to the H<sub>2</sub>/O<sub>2</sub> cells presented above. Further, potential scanning and interruption of gas supply to the cell did not affect

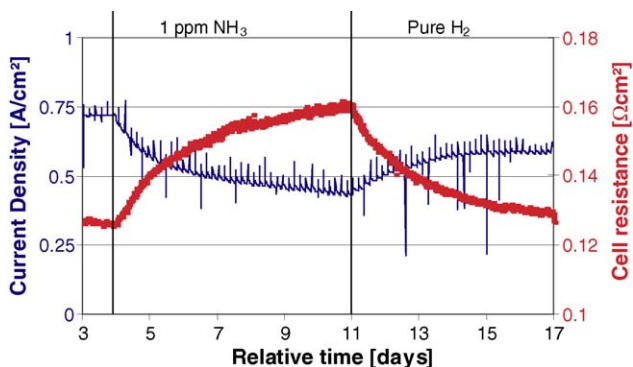


Fig. 5. Performance of 10 cm<sup>2</sup> GORE™ MEA with addition of 1 ppm NH<sub>3</sub> for 1 week. The cell was running potentiostatically at 0.50 V at 40 °C cell temperature, room temperature humidifiers, atmospheric pressure, 80% conversion of H<sub>2</sub>, 40% conversion of O<sub>2</sub> in air, 10 and 20 ml N min<sup>-1</sup> minimum flow on anode and cathode respectively applying potential scanning every 4 h. The data are not corrected for ohmic losses.

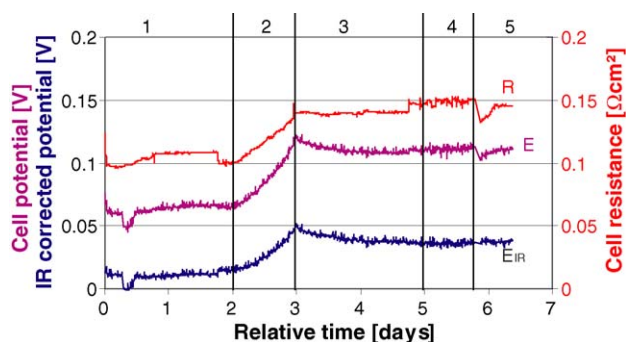


Fig. 6. Performance of 6.25 cm<sup>2</sup> GORE™ MEA running in symmetric mode with addition of 10 ppm NH<sub>3</sub> for 1 day. The cell was running galvanostatically at 0.50 A cm<sup>-2</sup> at 41 °C cell temperature, humidifiers at 39 °C, atmospheric pressure, 50 ml N min<sup>-1</sup> humidified hydrogen on each side with addition of 5.3 ml N min<sup>-1</sup> dry hydrogen or hydrogen contaminated with ammonia downstream of the humidifiers on the anode side.

the cell resistance. There was a slight recovery of performance when the addition of ammonia was stopped.

Polarization curves were recorded before and just after ammonia exposure. Such curves were also recorded with regular intervals thereafter. The polarization curves are shown in Fig. 7. A slight recovery after stopping ammonia additions was also observed in the polarization scans. However, the most striking observation was that there seems to be a limiting current in the system. This is not a mass transfer limiting current as the polarization curve obtained for pure hydrogen does not show any sign of a limiting current. It is rather a reaction limiting current, possibly the Tafel step in the Tafel-Volmer HOR mechanism [7,20]. The increase in ohmic resistance was responsible for about 20 mV of the total increase in overpotential of the cell of 55 mV in Fig. 6 where the cell was running galvanostatically at 0.50 A cm<sup>-2</sup>. The total losses in the symmetric cell were moderate at relatively low currents.

It should also be noted that the sum of the overpotential of the HOR and HER (hydrogen evolution reaction) were measured in this cell because there is no reference electrode. It is thus possible that ammonia affects both reactions, and that the effect on HOR alone is smaller than indicated by these results.

## 4. Discussion

### 4.1. Adsorption of NH<sub>3</sub> in the membrane

Typically the increase in cell resistance when exposed to ammonia is about 20% in most cases presented here. We have previously reported that there is a linear relationship between ammonium content in the membrane phase and conductivity of Nafion® 117 in aqueous solutions [21]. Further, the conductivity of proton form Nafion® is about 3.8–4.2 times higher than ammonium form [11,21]. Based on this, and assuming that the physical properties of the ionomer in the GORE™ PRIMEA® are the same as for Nafion® 117, the cation fraction of ammonium in the membrane phase,  $y_{\text{NH}_4^+}$ , is estimated from the observed resistance in pure proton form and after poisoning as given in

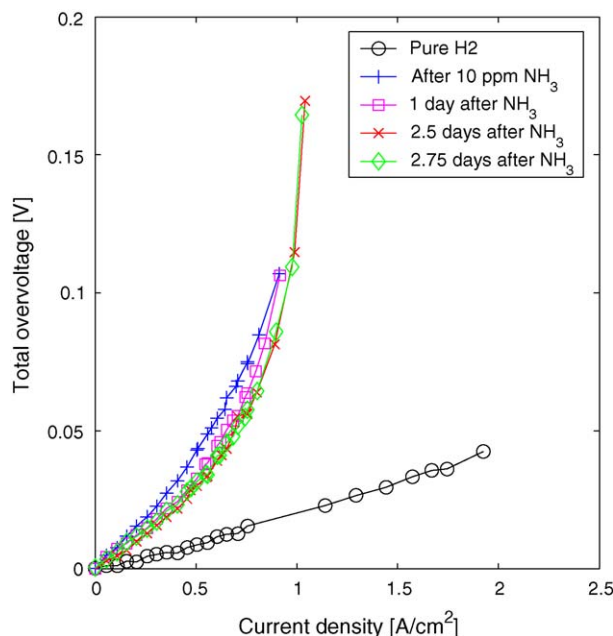


Fig. 7. IR corrected polarization curves for 6.25 cm<sup>2</sup> GORE™ MEA running in symmetric mode with addition of 10 ppm NH<sub>3</sub> for 1 day. Operating conditions as in Fig. 6. The total overvoltage, i.e. including both HOR and HER, is shown.

Eq. (1) and presented in Table 1.

$$y_{\text{NH}_4^+} = \frac{R_{\text{contam}} - R_{\text{H}^+}}{R_{\text{NH}_4^+} - R_{\text{H}^+}} \approx \frac{1}{3} \left( \frac{R_{\text{contam}}}{R_{\text{H}^+} - 1} \right) \quad (1)$$

The amount of sulfonic acid groups in the membrane can also be estimated, but several assumptions must be made. (1) The dry thickness  $l$  of the membrane in the GORE™ MEA is about 25 μm [22] and that of Nafion® 112 about 50 μm. (2) The total area of the membrane, which is assumed to be accessible to ammonium, is approximately twice as large as the active area. (3) The density of dry Nafion®  $\rho$  is 2.05 g cm<sup>-3</sup> [23]. (4) The equivalent weight of the ionomer  $M$  is 1100 g mol<sup>-1</sup>. (5) The membrane used in the GORE™ MEA is reinforced with inert ePTFE (expanded PolyTetraFluoroEthylene) fabric, but the volume of this phase is not subtracted from the total membrane volume. The number

of sulfonic acid groups can then be estimated:

$$n_{\text{SO}_3^-} = \frac{2Al\rho}{M} \quad (2)$$

The results of these calculations are given in Table 1. Only some of the NH<sub>3</sub> added is absorbed in the membrane. Different factors affecting the mass balance for ammonia/ammonium in the fuel cell are discussed in the following sections.

#### 4.1.1. Volatility of ammonia over PFSA membranes

The equilibrium between ammonium in the membrane and ammonia in the gas phase can be described by the two reactions:



Based on Le Châteliers principle, one would expect Eq. (3) to be shifted to the left because the strong acid found in perfluorosulfonic acid (PFSA) ionomers stabilizes the ammonium ion in the membrane phase. Further, the Henry's law constant,  $k_{\text{H,NH}_3} = p_{\text{NH}_3}/c_{\text{NH}_3}$ , see Eq. (4), for ammonia dissolved in water is very small so that the solubility of ammonia in water is high. Since the PFSA ionomer contains a large fraction of water, also in the ammonium form of the ionomer [21], it would be expected that ammonia also has a high solubility in the PFSA ionomer. We would thus expect both Eqs. (3) and (4) to be shifted to the left so that the vapor pressure of ammonia over an PFSA membrane would be very low indeed.

Data from the symmetrical cell in Fig. 6 show that the cell resistance did not fall after the addition of ammonia was stopped. This shows that the ammonium stays in the membrane phase confirming the low volatility of ammonium in PFSA ionomers.

#### 4.1.2. Mass transfer limitations in the GDL

The diffusion rate of ammonia through the mainly hydrogen filled GDL can be estimated to find if there are any mass transfer limitations for absorption of ammonia. The mass transfer coefficient was found to be high [7,20]. According to evaluations of the mass transfer rate, more than 98% of the added ammonia was absorbed.

Table 1  
Mass balance for NH<sub>3</sub> added to the fuel cell through the fuel gas

| Experiment   | Figure              | $n_{\text{SO}_3^-}$ (μmol) | $y_{\text{NH}_4^+}$ (-) | $n_{\text{NH}_3}$ (μmol) | Ads. NH <sub>3</sub> (%) |
|--|---------------------|----------------------------|-------------------------|--------------------------|--------------------------|
| PtRu   Pt galvanostatic 10 ppm NH <sub>3</sub>                             | Fig. 1              | 93                         | 0.05                    | 39                       | 12                       |
| PtRu   Pt potentiostatic 10 ppm NH <sub>3</sub>                            | Fig. 2 <sup>a</sup> | 93                         | 0.28                    | 39                       | 67                       |
| Pt   Pt potentiostatic 10 ppm NH <sub>3</sub>                              | Fig. 4 <sup>b</sup> | 186                        | 0.07                    | 24                       | 54                       |
| Pt   Pt galvanostatic 10 ppm NH <sub>3</sub>                               | Fig. 4 <sup>c</sup> | 186                        | 0.03                    | 25                       | 22                       |
| PtRu   Pt potentiostatic 1 ppm NH <sub>3</sub>                             | Fig. 5              | 93                         | 0.07                    | 24                       | 27                       |
| H <sub>2</sub>  H <sub>2</sub> cell PtRu   Pt Galv. 10 ppm NH <sub>3</sub> | Fig. 6              | 58                         | 0.12                    | 35                       | 20                       |

The data given are moles of sulfonic acid groups in the membrane ( $n_{\text{SO}_3^-}$ , Eq. (2)), cation fraction of ammonium in the membrane ( $y_{\text{NH}_4^+}$ , Eq. (1)), total moles of NH<sub>3</sub> added to the cell through the fuel gas ( $n_{\text{NH}_3}$ ), and how much of this NH<sub>3</sub> that was absorbed in the membrane ( $n_{\text{NH}_3}^{\text{abs}} = n_{\text{SO}_3^-} * y_{\text{NH}_4^+} / n_{\text{NH}_3}$ ). All MEAs were based on carbon supported PtRu anode catalyst except as noted.

<sup>a</sup> Data for second addition of NH<sub>3</sub> only.

<sup>b</sup> Operating in potentiostatic mode (first part of Fig. 4).

<sup>c</sup> Operating in galvanostatic mode (second part of Fig. 4).

Performance degradation of the cells seems to follow a first order response as does recovery. This indicates that there is no significant adsorption of ammonia on carbon in the GDLs. If adsorption of ammonia was significant, one would expect a second order response because the GDL would only gradually become saturated with ammonia. The change in ammonia concentration at the surface of the active electrode would thus not be instantaneous. Soto et al. [12] found recovery of performance to follow a second order response, but this can not be explained by adsorption effects because the initial degradation followed a first order response.

#### 4.1.3. Oxidation of ammonium

Oxidation of ammonium on platinum in acidic solutions to form nitrogen and/or nitric oxides have been observed [7,24]. However, the oxidation rates are modest and much lower than in alkaline solutions. The potential at which this electrochemical oxidation occurs is relatively high, typically  $>700 \text{ mV}_{\text{RHE}}$ . Nitrogen is one of the oxidation products of this process. Oxidation of ammonium to nitrogen may be one way by which ammonium is removed from the cell. Szymanski et al. [13] assumed that this was the primary “sink” of ammonium in their PAFC study. We have also detected nitric oxide as a possible oxidation product, but only at higher potentials.

The polarization of the FC anode is small in normal operation, see Fig. 7. Therefore, it is not likely that oxidation of ammonium to nitrogen or other volatile species takes place at the anode. This is also supported by the observation that the cell resistance of the symmetrical cell, typically operating at low potentials, did not recover when operating on pure hydrogen gas after a one day exposure to ammonia. The cathode of an FC typically operates at potentials in a range where we have observed oxidation of ammonium to form nitrogen. One should also note that the oxidation current from these processes will normally not be detectable in an FC because of the large reduction current due to the ORR.

## 4.2. Effects of ammonia on PEMFC

There are several effects of ammonia on PEMFC performance that are conceivable which will be discussed in the following.

#### 4.2.1. Distribution of ammonium throughout the MEA

Uribe et al. [11] and Soto et al. [12] found that effects of ammonium on conductivity or complexation of the ionomer by ammonium in the anode catalyst layer were the primary reason for loss of performance. These conclusions were based on the fact that ammonia enters the FC on the anode side, and that CVs of the cathode did not show any signs of electrochemically active species (nor did the anode). However, the membrane in a PEMFC is typically 10–100  $\mu\text{m}$  thick. The time constant for diffusion of ammonium from the anode to the cathode is of the order  $l^2/D_{\text{NH}_3}$  or typically 10–100 s. Migration of ammonium is then not included, but would only lead to even shorter time constants if included. The rapid transport of ammonium in Nafion<sup>®</sup> was verified experimentally by using pH and ion selective electrodes for ammonium to monitor the exchange of protons and

ammonium between the membrane phase and an aqueous phase. The exchange process was complete within minutes. Fast ion exchange for alkali metal ions has also been observed by Samec et al. [25]. The argument that the anode is necessarily more affected because ammonia enters on the anode side is thus not valid. Diffusion is fast enough for the cathode to be significantly affected by ammonium.

#### 4.2.2. Ohmic effects

The increase in bulk membrane resistance can only explain parts of the total performance loss in the cell, typically 5–15%. However, as suggested by Uribe et al. [11] and Soto et al. [12], the ionic conductivity in the active catalyst layers is also affected. Lower ionic conductivity in either of the active layers may also affect FC performance.

#### 4.2.3. Effect on the HOR

The HOR in the symmetrical  $\text{H}_2|\text{H}_2$  cell is affected, especially at high  $cd$  where a limiting current became apparent, see Fig. 7. The reason for the limiting current could be that adsorbed species partially blocks the anode catalyst surface. Uribe et al. [11] and Soto et al. [12] did not observe any electrochemically active species by CV on the FC anode. We have found that the presence of ammonium shifts the potentials of the hydrogen adsorption process on Pt in aqueous solutions, but hydrogen desorption is not affected [7,24]. Clearly, more work is needed to gain a better understanding of the effect of ammonium on the HOR.

#### 4.2.4. Effects on the ORR

The effect of ammonium on the ORR on Pt in sulfuric acidic solution has been found to be significant [7,26]. The mol fraction of ammonium in the ionomer is relatively low as shown in Table 1, but even at quite low concentrations of ammonium in sulfuric acid (about 10%  $\text{NH}_4^+$ ), we observed an increase of more than 100 mV in overpotential required to drive the ORR at a given  $cd$  [7,26]. The effect of ammonium on the ORR seems to be the most important effect at moderate  $cd$ . At high  $cd$  the reaction limiting current of the HOR becomes more important so that the ammonium effect on the anode is also important.

The mechanism by which ammonium affects the ORR is not clear. The effect could be caused by formation of adsorbed species originating from electrochemical oxidation of ammonium that blocks active sites on the cathode. It could also be caused by a mixed potential on the cathode due to ORR and simultaneous oxidation of ammonium. Further, in the Damjanovic mechanism for oxygen reduction [27], protons occurs in the rate determining step for the ORR on both reduced and oxidized Pt. Ammonium reduces the proton activity in the active cathode layer and may thus affect the ORR. This effect has been observed by Antoine et al. [28]. Okada et al. [29] have also suggested that the field gradient in the double layer may be influenced by ammonium absorption in the PFSA ionomer (the Frumkin effect). The Tafel slope of the ORR, particularly at low  $cd$ , can also be affected by adsorption of species due to effects on the symmetry factor for oxygen adsorption at high potentials where the Temkin isotherm is valid [26].

### 4.3. Recovery after exposure to $\text{NH}_3$

#### 4.3.1. Timescale of performance recovery

Both poisoning and recovery after ammonia exposure are slow processes taking hours if not days to reach a steady state. This is very different from for example, CO poisoning which has a pure surface poisoning effect. There is a significant volume of ionomer not contained between the active electrodes because the membrane must be cut to a larger diameter to enable sealing of the gas compartments using gaskets. This membrane volume may act as a buffer volume for ammonium in the MEA. During poisoning, ammonium diffuses *in-plane* along the membrane out to the electrochemically inactive part of the membrane. During recovery this ammonium can diffuse back to the active MEA reducing the recovery rate. The time constant for this process, where the characteristic distance is 1 cm, is several days. Another reason for the slow response may be that processes contributing to “sinks” in the mass balance for ammonia in the cell are slow like the oxidation of ammonium.

#### 4.3.2. Potential scanning of the fuel cell

Potential scanning of the cell also seems to at least speed up recovery if not also make recovery more complete, see Fig. 1 where potential scanning seemingly has a positive effect on cell performance. However, it was also observed that the stability of cells running on neat hydrogen without  $\text{NH}_3$  seemed to be better if regular potential scanning was applied [7]. This is believed to be due to removal of oxides forming on the cathode over time, see also Section 4.3.3. It is thus not clear if potential scanning has a positive effect on recovery from  $\text{NH}_3$  exposure in particular. However, it is conceivable that changing the potential of primarily the cathode through a potential scan may be beneficial because (adsorbed) species on the cathode then may be reduced or oxidized. Also oxidation of ammonium as such is likely to proceed at a higher rate at higher cathode potentials.

#### 4.3.3. Formation of Pt oxides on the catalyst

Recovery of the FC after exposure to ammonia seems to be improved by turning off the gas supply to the cell letting the cell voltage drop to zero, see Figs. 1 and 2. Increased cell performance after shutting off the cell for a while has also been observed by Jarvi et al. [30]. They found this to be caused by removal of a relatively stable oxide layer that had formed on the Pt catalyst over time, especially at high cathode potentials. Uribe and Zawodzinski [31] found that operation of the FC at low potentials at regular intervals improved stability. Applying CV techniques, they showed that a stable oxide was formed on the cathode over time.

In our experiment with a symmetrical cell, there was only a temporary decrease in cell resistance after interrupting the gas supply, see Fig. 6. The IR corrected overpotential of the cell was not affected by the interruption of gas supply. The reason is believed to be that in this cell the electrodes operate at a low potential so that the Pt catalyst is not oxidized.

#### 4.3.4. Extent of FC performance recovery

As shown in Figs. 1 and 2, the observed recovery was complete in some cases and in others not. Both complete and in-

complete recovery have been observed in both galvanostatic and potentiostatic mode in this work. It could also be noted that cells run in potentiostatic mode absorbs a somewhat higher fraction of the ammonia fed to the cell, see Table 1. The effect of operational mode, if any, is not clarified. It is interesting to note that Uribe et al. [11], who ran the cell potentiostatically, observed incomplete recovery whereas Soto et al., running the cell galvanostatically, observed complete recovery.

#### 4.3.5. Effect of operating temperature

Soto et al. [12] observed a quicker recovery of the cell after exposure to 200 and 1000 ppm  $\text{NH}_3$  than we do here. In only 10 h they had complete recovery after exposure to 200 ppm  $\text{NH}_3$  for 10 h. Our experiments, with 10 ppm  $\text{NH}_3$ , typically required 3–4 days for complete recovery. One possible explanation may be that Soto et al. ran their experiments at 70 °C whereas 40 °C was used in our experiments. Higher temperature may increase the rate of oxidation of ammonium possibly explaining the large difference in recovery rates. On the other hand, Uribe et al., operated their cell at 80 °C [11]. When their cell was exposed to 30 ppm  $\text{NH}_3$  for 1 h, complete recovery was only found after 12 h of operation on pure hydrogen. This is in line with our findings. At longer exposure times, Uribe et al. found recovery to be incomplete in contrast to our findings. It is thus not possible to make firm conclusions as to the effect of temperature on recovery rate, but we would generally expect higher recovery rates at higher temperatures.

### 4.4. Tolerance towards ammonia

As was shown in Section 3.3, the poisoning effect of ammonia is severe even in the case where the cell is exposed to only 1 ppm  $\text{NH}_3$ . The performance loss observed is not acceptable for practical applications. This has several implications:

- (1) If ammonia is to be used as hydrogen carrier for PEMFC, virtually all traces of ammonia must be removed. This can be accomplished by absorption of ammonia in an acid trap before entering the FC [11].
- (2) Traces of ammonia in hydrogen fuel based on reforming of liquid fuels may be detrimental to FC performance.
- (3) The content of nitrogen in the hydrogen may have to be closely monitored to prevent back-reaction to ammonia catalyzed by metal-hydride alloys [10].
- (4) It is not clear what the effect of ammonia in the oxidant (air) stream is. If ammonia can be absorbed on the cathode as well, equally large problems with ammonia poisoning may be experienced.

Recovery after exposure to ammonia is relatively slow. Therefore, even short exposure of PEMFC to high levels of ammonia may be detrimental to performance. Clearly, more work is needed in order to understand the mechanisms of ammonia poisoning, and the consequence of this poison for PEMFC performance and durability. Tolerance levels towards ammonia need to be more firmly established.

There may also be ways to improve the tolerance of the PEMFC to ammonia through design and choice of materials. Different cathode catalyst materials is one option. The purpose of these catalysts would be either to enhance the oxidation rate of ammonium on the cathode so that the “sink” for ammonia in the mass balance would be larger. Alternatively, the catalyst could possibly be formulated, by using other noble metals in combinations with Pt, so that the ORR is less affected by the presence of ammonium on the cathode. In alkaline systems, iridium and Pt–Ir alloys have been found to have a better activity for oxidation of ammonia than pure Pt [32,33]. Onset of oxidation at a lower potential compared to pure Pt is of particular interest. These catalysts could have a potential for increased oxidation of ammonium also in PEMFC making the PEMFC more tolerant to ammonia. Okada et al. demonstrated that the ORR kinetics of a Nafion® covered Pt disk in sulfuric acid can be recovered by addition of D- $\alpha$ -alanine when exposed to Na<sup>+</sup> or Ca<sup>2+</sup> ions [34]. Other additives were also tried, but no details were reported. Durability and stability of these additives would have to be assessed.

Also the anode seems to be affected by ammonium. At high cd a limiting current is observed which is not due to mass transfer limitations. It is most probably a reaction limiting current due to the Tafel step in the Tafel–Volmer mechanism for HOR [7,20]. Active sites on the anode are blocked by a species rendering them inaccessible to HOR. The nature of these species has not been identified. It is not clear if it is possible to reduce the effect of ammonium on HOR directly by choosing other anode catalyst materials.

## 5. Conclusions

Poisoning of PEMFCs by ammonia is severe. It is also slow taking 24 h or more to reach a steady state. In some cases no steady state was reached during the experiment. The performance loss was in most cases reversible, but only after operation on neat hydrogen for several days. Additions of 1 ppm NH<sub>3</sub> resulted in significant performance losses. An MEA based on carbon supported Pt catalyst did not differ from the GORE™ MEA which uses a PtRu based anode catalyst. The performance losses were higher than could be explained by the observed increase in ohmic resistance in the cell. There was also a significant decay in performance in a symmetrical H<sub>2</sub>|H<sub>2</sub> cell, especially at high cd where a reaction limiting current was observed. There is also a significant effect of ammonium on the ORR on the cathode. The effect on the ORR is dominant at lower cd, but at higher cd the reaction limiting current of the HOR becomes a more important limitation of the cell. Clearly more work, both experimental and modelling, is required to better understand the different poisoning mechanisms of PEMFC induced by ammonia.

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