

Assessing durability of cathodes exposed to common air impurities

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Abstract

Data are presented to quantify how common air non-condensable impurities such as NO₂, SO₂, and H₂S show a negative effect on the performance of PEMFCs. The severity of the effects of these impurities varies depending on the impurity, concentration, and dosage but in general the impurities containing sulfur showed a stronger effect than NO₂. Complete recovery of the cell performance is obtained after applying neat air following exposure to a total NO₂ dosage of 61.8 μmol. However, to completely recover the cathode exposed to either 118.5 μmol SO₂ or 2160 μmol H₂S, cyclic voltammetry is required to oxidize the sulfur adsorbed on the Pt. The sulfur species formed on the Pt cathode after exposure to these impurities appear to be the same and it appears as strongly and weakly adsorbed sulfur on the Pt.

The data show that the rate of poisoning of PEMFCs by NO₂ does not strongly depend on NO₂ bulk concentration but the rate of SO₂ poisoning of the cathode appear to be strongly dependent on the concentration of SO₂ in the bulk. Relatively high concentrations of impurities were used and the data also show that the cell performance could be totally recovered from NO₂ in neat air after repetitive cycles of exposure/no exposure of 5 ppm NO₂ for 12 h for three cycles (185.4 μmol total dosage). On the other hand, only partial recovery from 5 ppm SO₂ was observed in each cycle and the performance continued to decrease in all the five poisoning cycles (592.5 μmol total dosage).

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1. Introduction

The effects of the air impurities such as SO₂, NO₂, H₂S, and O₃ on the performance of proton exchange membrane fuel cells (PEMFCs) have not been studied extensively in the literature and it is believed that continual exposure to low concentration of these impurities might be detrimental to cell performance. The concentration of SO₂ and NO₂ in the atmosphere should not exceed 0.05 ppm, O₃ concentration should not be higher than 0.20 ppm, and H₂S is limited to less than 1 ppb as specified by the environmental protection agency [1]. Moore et al. [2] studied the effects of common and war zone air impurities on the performance of PEMFCs and reported that low concentrations of SO₂ and NO₂ did not have detrimental effects on cell performance. We hypothesize that this conclusion could be due to the low dosage of these impurities

applied to the cell (i.e. the total dosage was 200 ppb h for NO₂ and 250 ppb h for SO₂). Clearly, tests of the cumulative effect of these species at the EPA levels are not practical and consequently there is a need to establish accelerated durability tests (ADTs) which allow for the development of new materials and proper filtration devices. Here we present data at higher concentrations that should help establish performance baselines as a function of concentration and dosage.

H₂S and SO₂ adsorption on Pt catalysts has been reported in the literature in the aqueous phase. Contractor and Hira [3] reported the end products of SO₂ adsorption on Pt electrode to be linearly and bridge adsorbed sulfur. These two end products formed on the Pt electrode are similar to the products formed from the dissociation of H₂S on the Pt anode on MEA reported by us in a previous study [4]. The poisoning effects of NO₂ on the Pt electrodes have not been reported and therefore require further investigation. Therefore, the aim of the work presented in this paper is to study the long term effects through using higher dosage of these impurities.

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2. Experimental

All experiments were performed using test stations made by Fuel Cell Technology Inc. (Albuquerque, NM) or Scribner Associates Inc. (Southern Pines, NC). The gases used were high purity neat H₂ (99.997%), 200 ppm H₂S in 2% N₂ balanced with air (diluted from 1% H₂S/N₂), high purity neat air premixed with 5 ppm SO₂, high purity neat air premixed with 5 ppm NO₂, bottled industrial grade air, and high purity N₂. The flow rates were set manually according to the measured current for a fixed stoichiometry of 1.2 for the anode and 2.0 for the cathode. A triple path serpentine flow field was used. The anode and the cathode flows were co-current. The temperature of the cell was fixed at 70 °C for all experiments, and the pressures were 101 kPa on each side. Each cell was held at 0.60 V for minimum 60 h before the polarization data were obtained. The humidification temperatures were 85/75 °C.ⁱ The estimated dew points were 80/70 °C, respectively, from the humidity calibration data. No indication of MEA flooding due to excess water was observed at these humidification temperatures during initial experiments in neat hydrogen and air.

Gore MEA, PRIMEA[®] Series 5621 (35 μm nominal membrane thickness), were used for all experiments. This MEA has a Pt–Ru alloy of 0.45 mg cm⁻² Pt–Ru on the anode, and 0.60 mg cm⁻² Pt on the cathode, and our cell used gaskets so that this MEA has an active area of 23.0 cm². The gas diffusion layers were CARBEL[™] CL GDM (16 mils = 0.406 × 10⁻³ m). Silicon coated glass fiber gaskets with a thickness of 10 mils (0.254 × 10⁻³ m) were used for the anode and the cathode sides. Eight lubricated bolts were threaded into taped holes on one of the end plates, and the cell was compressed by applying a torque of 50 in. lb_f/bolt (5.6 N m/bolt).

The current–voltage polarization curves were measured in neat H₂/neat air before the MEA was exposed to the selected contaminant. One set of experiments studied the decay in the current during continual exposure of relatively high concentrations of impurity at a fixed voltage. The exposure occurred at a constant voltage in the range of 0.68–0.70 V because these voltages gave 12 A in neat H₂/neat air prior to exposure to impurity. The flow rate was 101/420 cm³ relative to 0 °C and 101 kPa and this corresponds to a stoichiometry of 1.2/2.0 at 12 A in neat H₂ and neat air. The cathode was then exposed to the impurity and the cell current was monitored with time. When the decrease in current approached a steady state value, additional polarization curves were recorded. The cathode was exposed to 5 and 2.5 ppm SO₂ for a same total dosage of 118.5 μmol, 2.5 and 5 ppm NO₂ for a same total dosage of 61.8 μmol, and to 200 ppm H₂S for a total dosage of 2160 μm. We selected these relatively high concentrations because we are interested in significant signals that will allow us to develop accelerated durability tests (ADTs). The

polarization curves required an additional 4–6 h of exposure to the contaminant. Following the polarization curves, neat air was reintroduced to the cathode and this reintroduction subjected the cathode to neat air for 24 h after the cathode exposure to NO₂ or SO₂ and for 70.5 h after exposure to H₂S. After exposure to neat air, another polarization curve was recorded. If the cell performance did not fully recover in neat air, cyclic voltammetry measurements were made. Following the CV, the impurities were reintroduced to the cathode and the process was repeated including another application of CV. Polarization curves measurements were carried out after the CVs.

In an effort to study the impurities on the surface of the PEMFC cathode, the CV was measured while flowing N₂ on the cathode (working electrode) and neat H₂ on the anode (counter and reference electrode). An EG&G Instruments Model 283A potentiostat/galvanostat was used for the CV measurements. The applied potential range was between 0.05 and 1.4 V. The scanning rate was 5 mV/s and four voltammograms were measured in each case. Following the CV, the current–voltage polarization curves were measured in neat H₂/neat air before the cathode was reexposed to the impurities.

In addition to the constant voltage exposure test, we studied the response in the voltage for various square waves of the impurities in air. These were performed by setting the cell current to 12 A at a stoichiometry of 1.2/2.0 while monitoring the cell voltage change with time during the exposure to the impurity and during recovery in neat air. The aim of using a constant cell current is to enable monitoring the change in the cathode overpotential as a function of impurity dosage. A dosage of 118.5 μmol of 5 ppm SO₂ and of 61.8 μmol of 5 ppm NO₂ was applied at each poisoning cycle. The cell performance was recovered in neat air for approximately 24 h.

3. Results and discussions

3.1. Part I: effects of H₂S

The decrease of the cell performance during cathode exposure to 200 ppm H₂S for 10.5 h is shown in Fig. 1. Complete deterioration of the cell performance is observed in this time for this high concentration. Fig. 1 also shows that the cell performance was partially recovered as neat air was introduced to the cathode side for 70.5 h (i.e. the current density increased up to 170 mA/cm²). Fig. 2 shows the polarization curves during poisoning and after recovery of the cathode corresponding to the break at about 10 and 70 h, respectively. The cell performance was severely degraded by 200 ppm H₂S and was partially recovered in neat air. The curves also show that the cell performance was significantly recovered after CV as compared to the performance recovery in neat air. This is due to the oxidation of the sulfur species formed on the Pt that blocks the O₂ from reacting. The CV data shows that the oxidation of two sulfur species occurs during the CV scan as

ⁱ Our convention for specifying operating conditions is to list the anode conditions first followed by the cathode conditions. Thus, the humidification temperatures were 85 °C for the anode and 75 °C for the cathode.

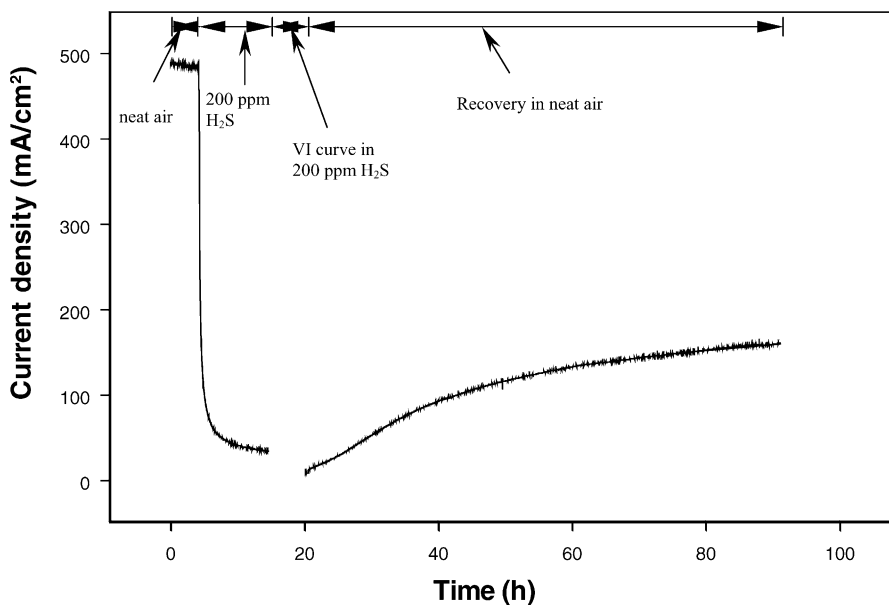


Fig. 1. Transient response in 200 ppm H₂S as it is exposed on the cathode at a cell voltage of 0.68 V.

will be discussed later in details. This oxidation resulted in clearing sulfur occupied Pt sites on the electrode and thus the cell performance recovered.

The poisoning effects are assigned to strong H₂S adsorption on Pt causing the Pt sites to be inaccessible to the oxygen according to the following mechanism proposed by Mathieu and Primet [5].



The cyclic voltammetry in Fig. 3 shows the presence of two distinct oxidation peaks at 0.89 V (oxidation peak I) and 1.09 V (oxidation peak II). These peaks give evidence of the presence of two forms of chemisorbed sulfur that are strongly and weakly bound to the Pt. These two peaks have been observed earlier by us at 0.89 and 1.09 V during a potentiodynamic scan measurements on the H₂S poisoned Pt anode

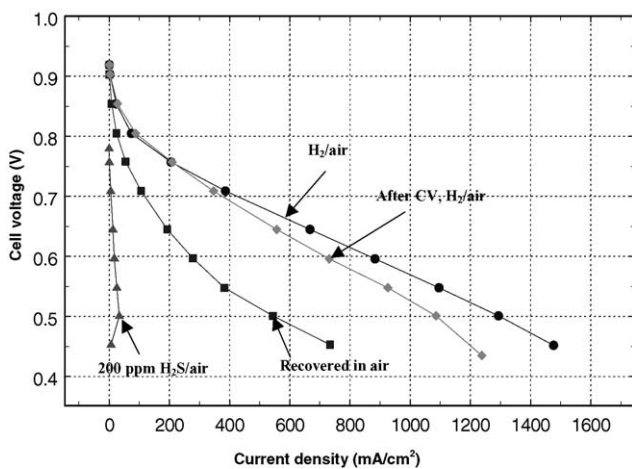
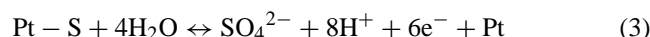


Fig. 2. Polarization curves on the effects of 200 ppm H₂S on the cell performance.

at 70 °C [4]. During the potential sweep, the adsorbed sulfur is oxidized to SO₃ or SO₄²⁻ according to the following reactions proposed by Loučka [6] in the aqueous phase:



It should be noted that based on our previous studies on the effect of H₂S on the cell performance when exposed on the anode side [4], we believe that the sulfur effects we observed after poisoning MEA anode in H₂S are not limited to the anode and extends to the MEA cathode through sulfur cross over from the anode side.

3.2. Part II: effects of NO₂ and SO₂

3.2.1. Effects of NO₂ on cell performance

The polarization curves in Fig. 4 show the effects of 5 ppm NO₂ after a total dosage of 61.8 μmol is applied. Performance loss of the cell occurs, but the reintroduction of neat air on the contaminated cathode recovers the cell performance as shown in Figs. 4 and 5. Fig. 5 shows the percentage of current observed relative to the current in neat air for the clean MEA as function of exposure time to impurity. Approximately 55% loss in current after 12 h exposure to impurity is observed. To further study the effects of 5 ppm NO₂/air, additional poisoning of the cell in 5 ppm NO₂ was made and the data is recorded in the polarization curves shown in Fig. 4. Lower performance is obtained as compared to the first polarization curve in 5 ppm NO₂. Cyclic voltammetry was performed following the second cell exposure to NO₂. This is to investigate the presence of any species adsorbed on the surface of the Pt due to the cathode exposure to NO₂. The CV spectra in Fig. 6 compare the data collected before and after exposure to 5 ppm

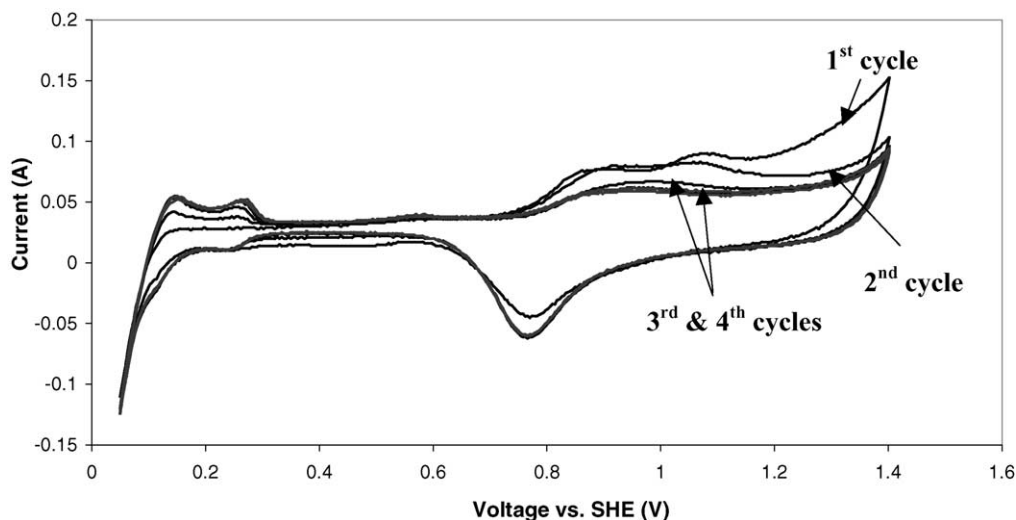


Fig. 3. Cyclic voltammetry spectra obtained after cathode exposure to 200 ppm H₂S/air.

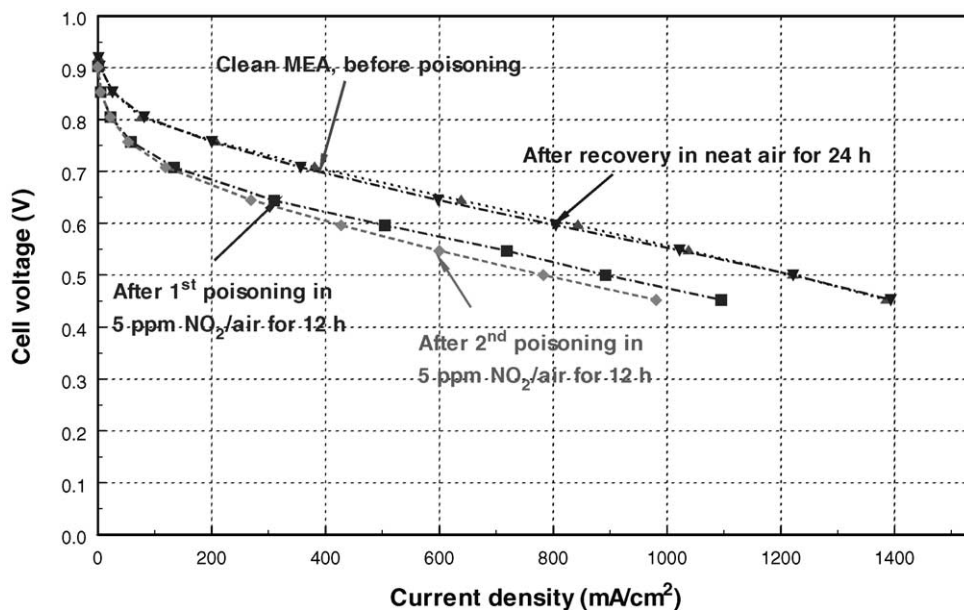
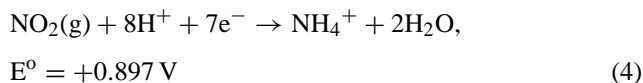


Fig. 4. Polarization for steady state performance showing the effects of 5 ppm NO₂/air.

NO₂. Absence of any oxidation peaks corresponding to adsorbed surface species and overlapping of the CV spectra for the clean and poisoned MEA reveals that the poisoning of NO₂ is not catalyst surface poisoning and suggests that the ionomer and/or the catalyst–ionomer interface could be affected by the exposure to NO₂. We hypothesize that NO₂ gets electrochemically reduced on the cathode thus competes with O₂ for Pt sites. The product of this reduction is the formation of NH₄⁺ according to reaction 4 [7]. NH₄⁺ is an ionomer poison as reported in previous studies on the effects of ammonia on PEMFCs anodes [8].



To study the effects of NO₂ applied with the same total dosage at lower bulk concentrations on the cell performance, the MEA cathode was exposed to 2.5 ppm NO₂/air for 24 h (same total dosage as for 5 ppm NO₂ exposure, that is a total dosage of 61.8 μmol), the percentage current as the MEA is exposed to NO₂ is presented in Fig. 5 in terms of the ratio of the current recorded to the current obtained in neat H₂/neat air prior to cell poisoning. It also compares the effects of 2.5 ppm NO₂ with the 5 ppm NO₂. From comparing these two curves, it appears that the rate of poisoning is not a strong function of the NO₂ concentration in the bulk (i.e. the rate of poisoning is not linearly dependent on the concentration of the NO₂ in the bulk). The polarization curves in Fig. 7 show the effects of 2.5 ppm NO₂ on the cell performance.

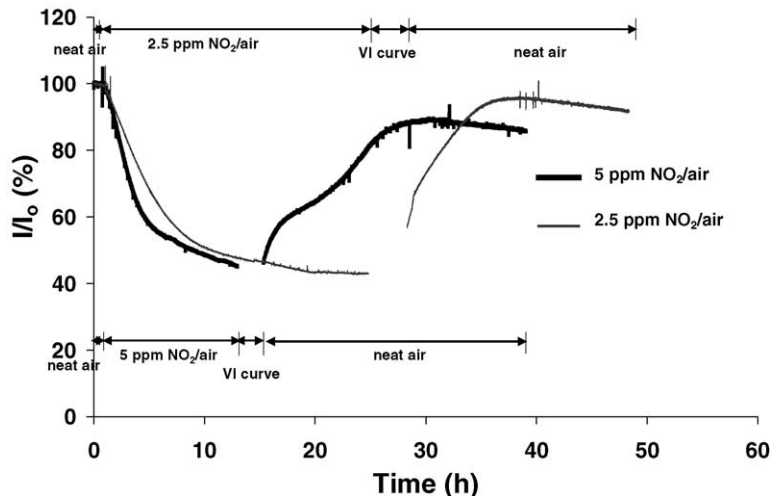


Fig. 5. Transient response comparing the cell performance during and after exposure to same dosage of 2.5 and 5 ppm NO₂/air.

A comparison of the effects of the two concentrations is aided by a graph of cathode overpotential such as that shown in Fig. 8. That is, it is difficult to compare the poisoning effects since the baseline performances with neat hydrogen/neat air could vary from one MEA to the other. These overpotentials are calculated from the difference between the cell potential with neat hydrogen/neat air and the cell potential of interest at the same current density. Therefore, to call this an overpotential, it is assumed that the hydrogen overpotential with neat hydrogen is negligible, and that the ohmic contribution to the cell voltage and the cathodic overpotential depend only on the current density. Fig. 8 shows that the overpotentials obtained are slightly higher (i.e. less than 38%) for the cath-

ode exposed to same dosage of 5 ppm as compared to 2.5 ppm NO₂. This suggests some concentration gradient effect since the same dosage is applied of the contaminant as discussed before. However, these differences appear not to be linearly dependent on the NO₂ concentration in the bulk as mentioned earlier.

3.2.2. Effects of SO₂ on cell performance

Fig. 9 shows cell current percent of original current in neat air as function of SO₂ dosage. During the 23 h exposure to 5 ppm SO₂/air (total dosage of 118.5 μmol SO₂), the current decreased by approximately 78%, however, after exposure to the same dosage of 2.5 ppm SO₂/air, the current decreased

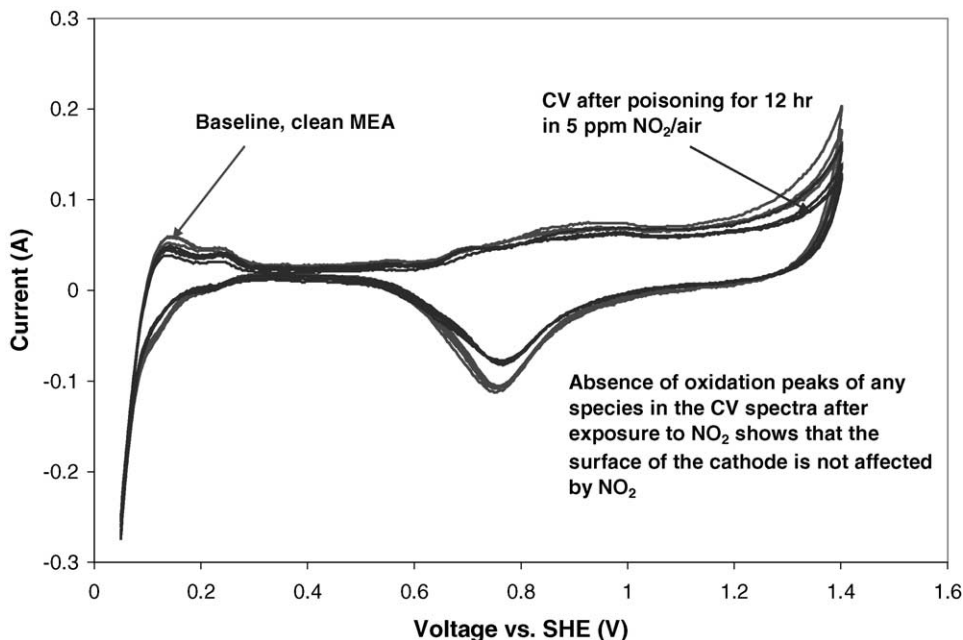


Fig. 6. Cyclic voltammety spectra obtained after cathode exposure to 5 ppm NO₂/air.

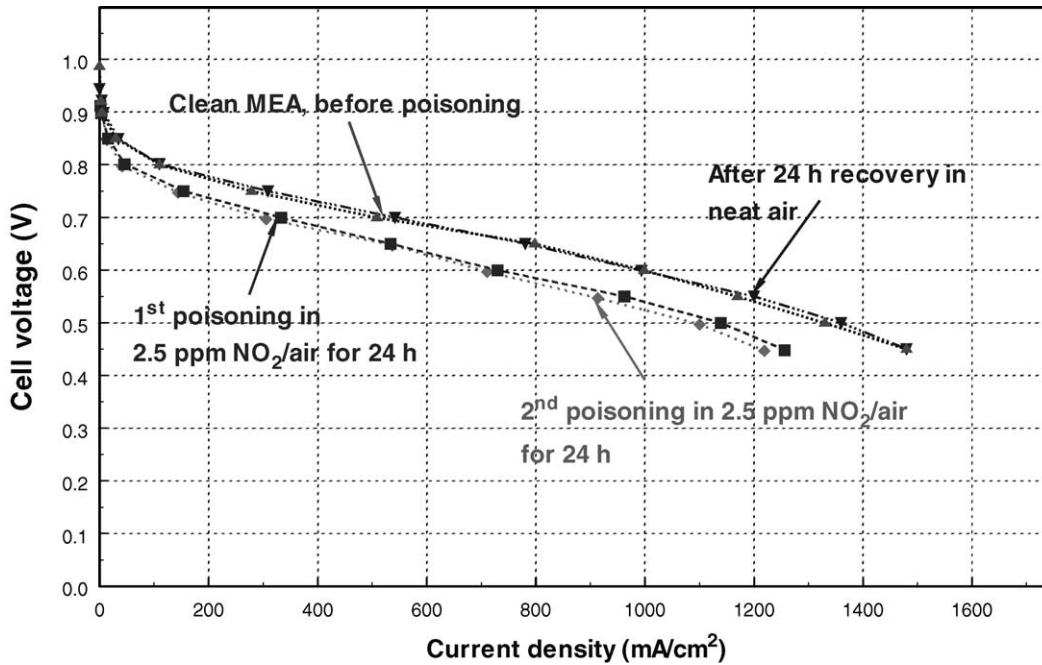


Fig. 7. Polarization for steady state performance showing the effects of 2.5 ppm NO₂/air.

by approximately 53%. From comparing the transient data during cathode exposure to 5 and 2.5 ppm of SO₂, it appears that the rate of poisoning is a strong function of the SO₂ concentration in the bulk and that higher poisoning rate is observed during the exposure to 5 ppm SO₂. The poisoning effects of SO₂ appear to be severe as seen in the polarization curve data in Figs. 10 and 11. However, recovery of the cell

performance is obtained after applying CV on the poisoned cathode. It should also be noted that the cell recovery after applying 2.5 ppm SO₂ is lower compared to 5 ppm SO₂. These comparisons are discussed below in details.

A comparison of the effects of the two concentrations is aided by a graph of cathode overpotential such as that shown in Fig. 12. Fig. 12 shows that the overpotentials obtained

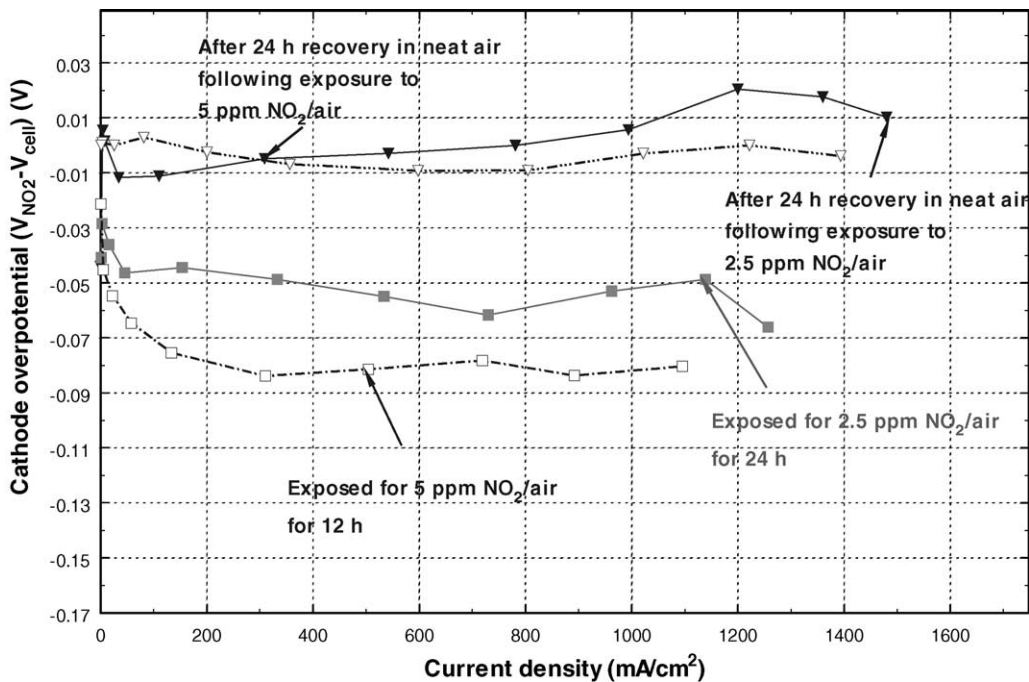


Fig. 8. Cathode overpotential (calculated by difference) comparing the cell response after exposure to 2.5 and 5 ppm NO₂/air.

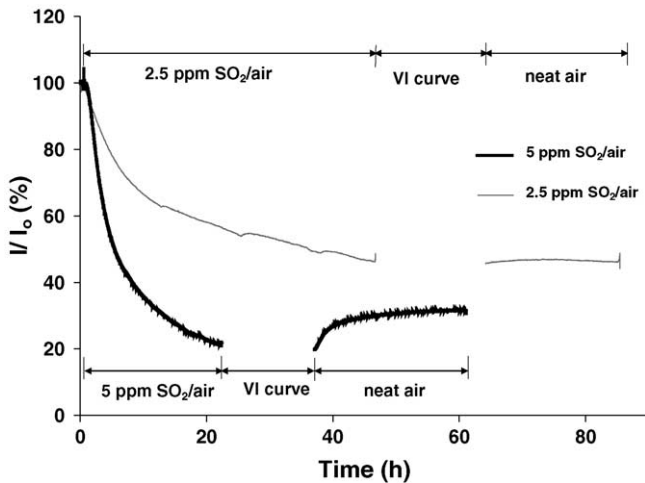
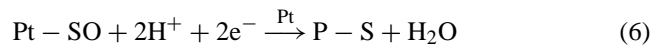
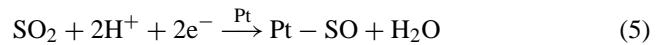


Fig. 9. Transient behavior and comparison of the cell response after exposure to 2.5 and 5 ppm SO₂/air.

are higher after cathode exposure to 5 ppm as compared to 2.5 ppm SO₂. This suggests a concentration gradient effect since the same total dosage is applied as discussed before. Partial recovery is obtained after applying neat air for 24 h after the cathode exposure to 5 ppm SO₂, however, the recovery in neat air after 2.5 ppm SO₂ is very small. Performance recovery is obtained after applying cyclic voltammetry according to the procedure described before. The cyclic voltammetry spectra in Fig. 13 shows the presence of two ox-

idation peaks at approximately 0.89 and 1.05 V. These peaks correspond for the presence of two sulfur species adsorbed on the surface of the Pt catalyst. Similar peaks were observed after subjecting the Pt on both the anode and cathode to H₂S as discussed before. SO₂ adsorption on Pt was studied in the aqueous phase by Contractor and Hira [9]. They showed that SO₂ gets reduced on the Pt electrochemically to sulfur with formation of SO intermediate as shown in the following reactions:



3.3. Part III: initial durability tests

Fig. 14 shows five cycles representing the voltage decrease and recovery as 5 ppm SO₂ is applied followed by recovery in neat air. In Fig. 15, a comparison of the steady state performance is presented in terms of the polarization curve before and after applying the poisoning and recovery cycles. It can be seen that almost total cell performance recovery was achievable after applying CV though the cathode was exposed to five cycles of poisoning in 5 ppm SO₂/air (592.5 μmol total applied dosage).

The results obtained after applying 5 ppm NO₂/air on the cathode are shown in Fig. 16 where sustained complete recovery of the performance is achieved after applying three cycles of the contaminant (185.4 μmol total applied dosage).

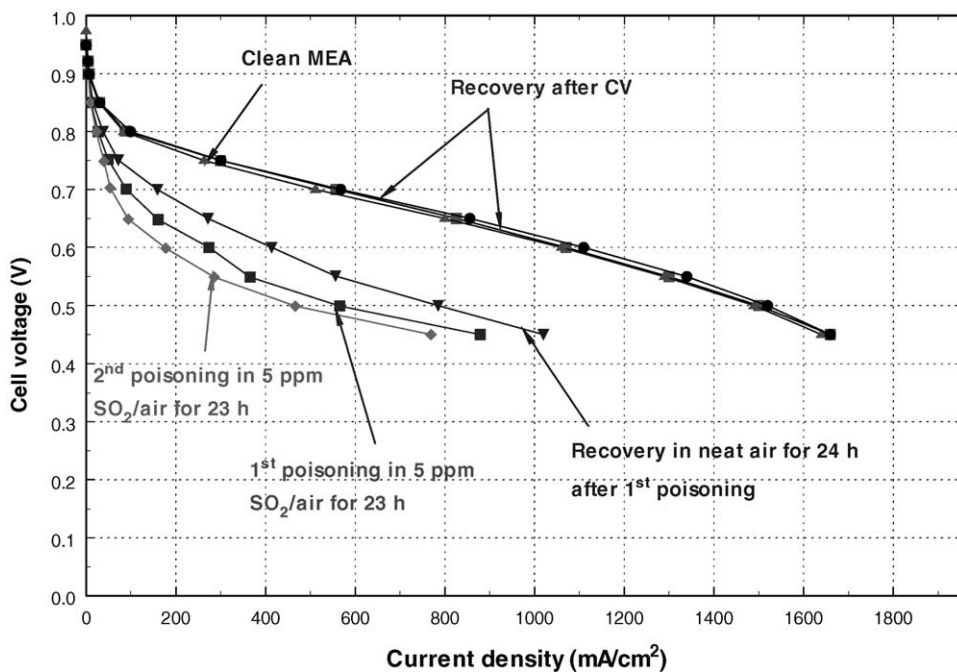


Fig. 10. Polarization for steady state performance showing the effects of 5 ppm SO₂/air.

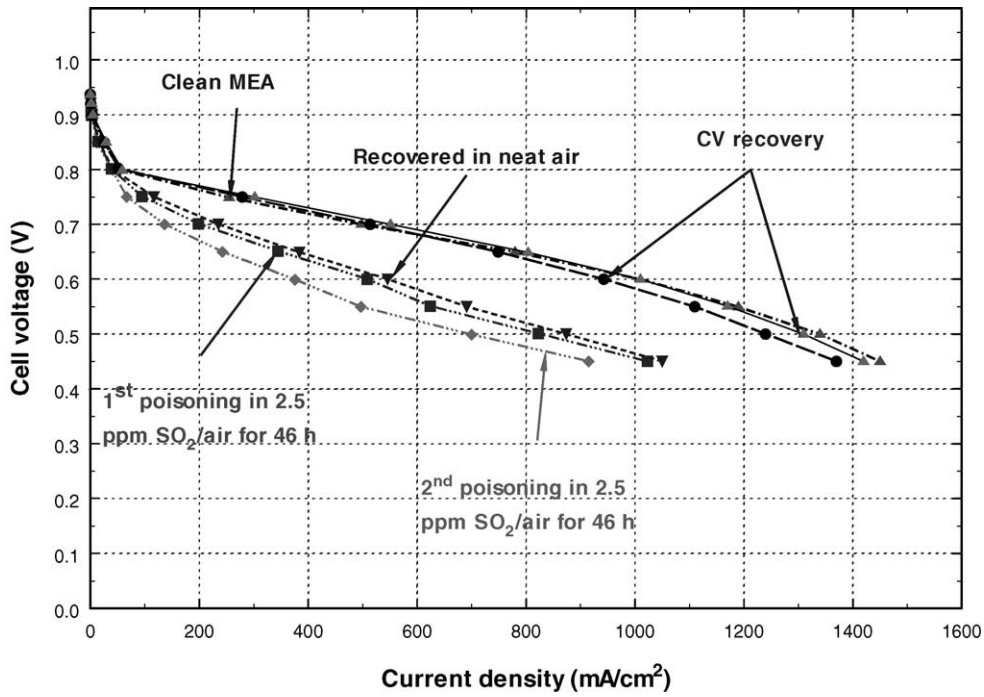


Fig. 11. Polarization for steady state performance showing the effects of 2.5 ppm SO₂/air.

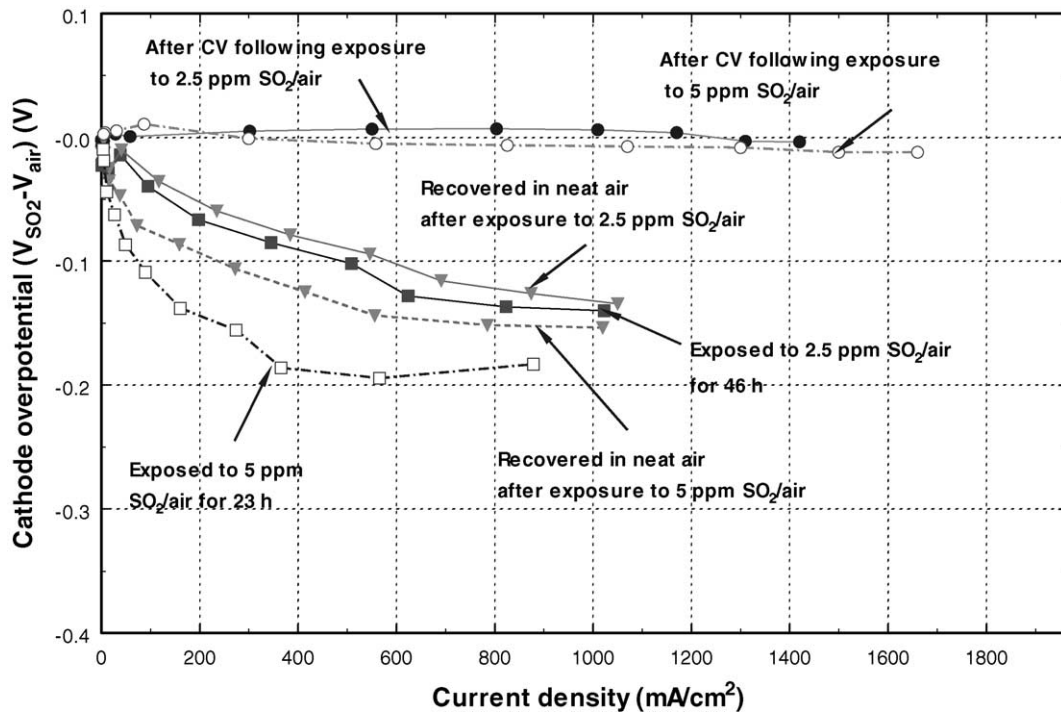


Fig. 12. Cathode overpotential (calculated by difference) comparing the cell response after exposure to 2.5 and 5 ppm SO₂/air.

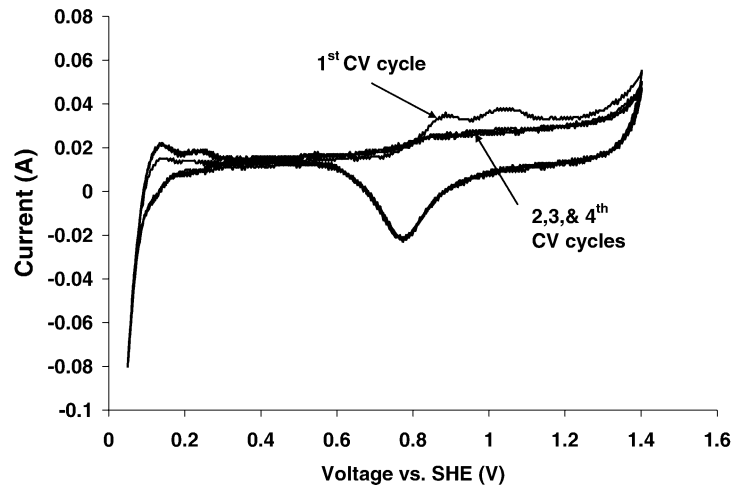


Fig. 13. Cyclic voltammetry spectra obtained after cathode exposure to 2.5 ppm SO₂/air.

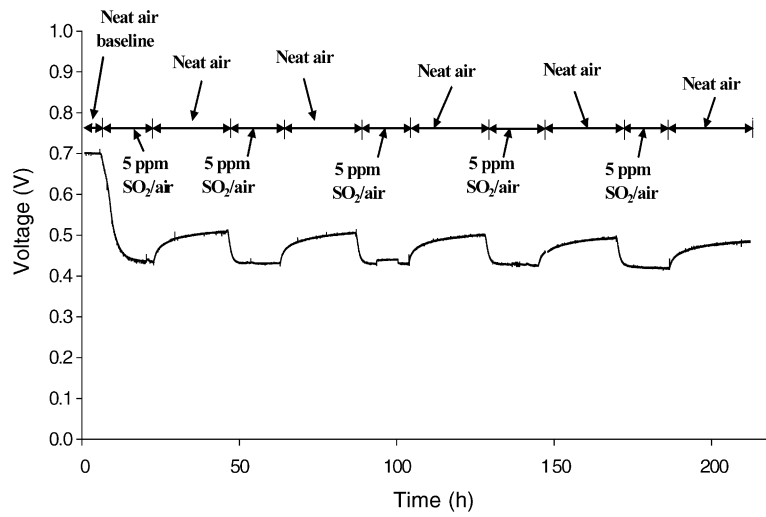


Fig. 14. Initial durability tests in 5 ppm SO₂/air.

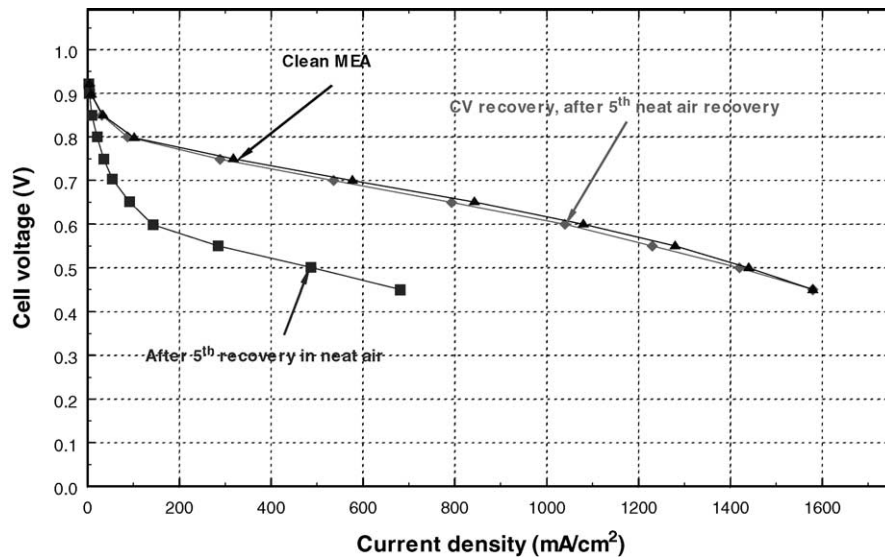


Fig. 15. Performance recovery in neat air and CV after applying five cycles of poisoning and recovery in 5 ppm SO₂/air and neat air.

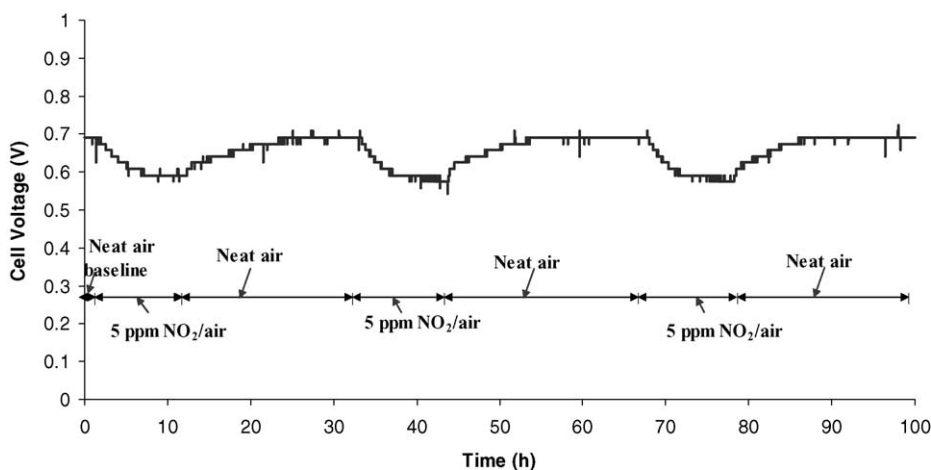


Fig. 16. Initial durability tests in 5 ppm NO₂/air.

4. Conclusions

NO₂ in air applied on the cathode with a total dosage of 61.8 μmol degrades the performance of the fuel cell by approximately 50%, however the cell performance completely recovers after applying neat air for 24 h. The poisoning effects of NO₂ do not appear to be a catalyst poisoning issue since no surface species were detected during the CV scan. On the other hand, the effects of a total dosage of 118.5 μmol of SO₂ in air degrades the performance of the cell as function of SO₂ concentration in the bulk, i.e. the performance decreased by 53% at 2.5 ppm SO₂ as compared to 78% decrease at 5 ppm SO₂ for the same applied dosage. Preliminary tests on H₂S effects show a strong negative impact on the performance on the MEA. Two sulfur species are formed on the Pt cathode after exposure to either SO₂ or H₂S. These species are identified as strongly and weakly adsorbed sulfur on the Pt cathode. To recover the poisoned Pt cathode, cyclic voltammetry is used to oxidize the sulfur adsorbed on the Pt at approximately 0.89 and 1.05 V.

Preliminary ADTs show that the cell performance could be recovered from NO₂ in neat air after exposing the cell to 5 ppm NO₂ for 12 h for three cycles, it also shows that sustained partial recovery from SO₂ takes place in all the five poisoning cycles applied.

Acknowledgments

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References

- [1] US Environmental Protection Agency, Air trends, 2004. <http://www.epa.gov/airtrends/sixpoll.html>.
- [2] J.M. Moore, P.L. Adcock, J.B. Lakeman, G.O. Mepsted, J. Power Sour. 85 (2000) 254–260.
- [3] A. Contractor, L. Hira, Electroanal. Chem. 96 (1979) 175.
- [4] R. Mohtadi, W.-k. Lee, S. Cowan, M. Murthy, J.W. Van Zee, Electrochem. Solid States Lett. 6 (12) (2003) A272–A274.
- [5] M. Mathieu, M. Primet, Appl. Catal. 9 (1984) 361.
- [6] T. Loučka, J. Electroanal. Chem. 31 (1971) 319.
- [7] A.J. Bard, Encyclopedia of Electrochemistry of the Elements, Marcel Dekker Inc., NY, 1986.
- [8] H. Sotro, W.-k. Lee, M. Murthy, J.W. Van Zee, Electrochem. Solid States Lett. 6 (7) (2003) A133.
- [9] A. Contractor, L. Hira, Electroanal. Chem. 93 (1978) 99–107.