Electrochimica Acta 222 (2016) 888–897

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Using corrosion-like processes to remove poisons from electrocatalysts: a viable strategy to chemically regenerate irreversibly poisoned polymer electrolyte fuel cells

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ARTICLE INFO

Article history:
Received 31 July 2016
Received in revised form 7 November 2016
Accepted 9 November 2016
Available online 15 November 2016

Keywords:
Fuel cell
SO_2 Poisoning
Regeneration
Oxygen reduction

ABSTRACT

Poisoning of Pt/C catalysts due to SO_2 on a rotating disk electrode (RDE), and as part of the cathode layer in a single cell fuel cell and fuel cell stack are studied in terms of the system performance, and the effect of electrochemical and chemical post treatment to remove the adsorbed sulphur-containing species. It is found that external polarisation can only recover the ORR performance of catalyst on an RDE after SO_2 poisoning when an applied potential of 1.6 V(RHE) is used for 1 ks. An alternative approach is to use ozone, as in the presence of this species, the electrode potential is raised to ~1.6V(RHE) due to the high potential of the ozone reduction reaction. The high open circuit potential leads to a mixed potential and was found also to be highly efficient at removing the poison via coupled ozone reduction and poison oxidation. The ozone process is found to work efficiently at the catalyst level as shown through rotating disk electrode studies and also in single cell fuel cells. Furthermore we demonstrate for the first time the recovery of a SO_2 poisoned fuel cell stack using the mixed-potential approach and ozone as a reactant. The cleaning process is fast (~10 minutes), occurs at room temperature, and does not require any special modification to the fuel cell. The process may be applicable to a wide range of poisons which can be oxidatively removed from platinum at high potentials.
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1. Introduction

The use of Polymer Electrolyte Fuel Cell (PEFC) as an alternative to conventional automotive engines and portable power sources receives ever growing attention due to its modularity, system robustness, high power density, low operating temperature, near zero emissions, quiet operations, etc. Large scale commercialisation of the PEFC is currently underway with an installed base (2015) of over 100,000 combined heat and power (CHP) units in Japan alone [1]. At the same time, a number of manufacturers have released fuel cell powered vehicles with clear goals of ramping up the manufacturing rate. However, cost and durability still remain a potent issue [2]. The cost of the PEFC has been reduced significantly in recent years. For large scale commercialisation of PEFCs, efforts must turn to issues relating to the environments in which the fuel cells are expected to operate. As most of the PEFCs use air from the atmosphere, impurities and pollutants present in the surrounding environment may adversely affect their performance as well as durability [3]. Much literature is available on the effect of air pollutants on the electrochemical activity of fuel cell catalysts [4–8]. Similarly, academic studies are available on the susceptibility of PEFCs to degradation or performance and durability shortfalls upon exposure to airborne contaminants [3,4,9–14]. However, very little work has been performed on the reactivation of the contaminated PEFC, and those works have hitherto not been so promising. Hence commercial systems typically rely on removal of aerial contaminants before they reach the cell by using absorption media, such as high surface area carbon filters. Use of such filters create three problems: (a) they increase the cost of the entire system; (b) they increase the energy cost of the air circulation system as they impose a hindrance to air flow; and (c) it is not possible to know the state of the filter and when "breakthrough" of contaminants will occur unless expensive sensors are installed. Hence there is always the possibility that some contaminants will enter the fuel cell, especially towards the end of life of the filter.

The composition and degree of pollution vary from place to place. The pollutants present in the immediate environment can be

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http://dx.doi.org/10.1016/j.electacta.2016.11.054
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subdivided into two categories. Firstly, the common pollutants, such as sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon dioxide (CO_2), carbon monoxide (CO), etc. Secondly, pollutants that will be present as a consequence of burning fuels and other waste. St-Pierre (2012) proposed a list of 97 airborne contaminants which was later extended to 260 during research activities supported by the US Department of Energy [15]. Among them, SO_2 is one of the major contaminants present in the atmosphere as a result of the combustion of fossil fuels. The maximum urban level of SO_2 may be as high as 0.35–0.70 ppm during peak hours. [16] Indeed, in some places, for instance around marine ports, or factory areas, significantly higher levels of pollutants may be present. It is likely that high levels of SO_2 along with NO_x and CO_x would be observed in vehicle-dense urban areas. In such an environment the performance of a PEFC may degrade substantially as such contaminants, especially SO_2, are irreversibly detrimental even at the sub-ppm level [3,4]. Consider an air breathing PEFC powered vehicle driving in a city behind a fossil fuel powered internal combustion engine (ICE) vehicle. The pollutants emitted by the ICE vehicle may be entrained into the cathode of the PEFC of the following vehicle. In such cases, the local concentration of SO_2 in the air might reach several ppm, especially as there are no European emission standards covering the production of SO_2 in vehicular exhausts. Eventually the PEFC powered vehicle will suffer severe performance degradation without some mitigation strategy to remove the SO_2. A similar situation may arise in stationary PEFC powered sources (e.g. combined heat and power systems) which are installed near an industrial area. At present, once a PEFC system is contaminated with sulfur from SO_2, it has to be replaced with a new one which is not a commercially feasible option.

Little information about recovery of PEFCs contaminated with airborne contaminants is available from the literature. All of the previous work has involved single cells rather than stacks, and the method of recovery has involved electrochemical methods relying on external polarisation of the fuel cell – something which is operationally difficult to perform on commercial systems. Mohtadi et al. (2004) studied the effects of common air pollutants e.g. NO_2, H_2S, and SO_2 on the durability of single-cell PEFCs [9]. They reported a loss of 78% performance in the presence of air containing 5 ppm SO_2. They were unable to totally recover the performance of the fuel cell even after externally polarising the cell to 1.4 V. Similarly, SO_2 contamination of PEFCs was studied by Gould et al. who reported only partial recovery after poisoning by SO_2 and subsequent external polarisation of the PEFC to 1.1 V. [17,18] The recovery of SO_2 contaminated single cell PEFCs was also studied by Jayaraj et al. (2014) [19]. They reported that only 80% of the initial performance could be recovered even after external polarisation of the cell for 9 h. Moreover, external polarisation of a multiple cell PEFC stack is not a feasible option. Exposure to high voltage during external polarisation may lead to corrosion and complete failure of the stack, as it is not possible to regulate the voltage applied to each individual cell, only the total stack, and the distribution of voltage across the cells will be highly non-uniform.

In this paper we examine an approach to use "corrosion-like" or mixed potential processes to remove poisons from fuel cell catalysts. The process works by producing a local electrochemical cell associated with reduction of an oxidant to water coupled to oxidation of a contaminant adsorbed on the platinum nanoparticle surface – a process which is quite similar to mixed potential corrosion of metals in oxygenated environments, Fig. 1(a). In this case the oxidant being reduced is ozone (although we also show that this process works to a limited extent using oxygen), and that the process is coupled to the oxidation of the fuel cell contaminant through the underlying carbon substrate and adjacent ionically

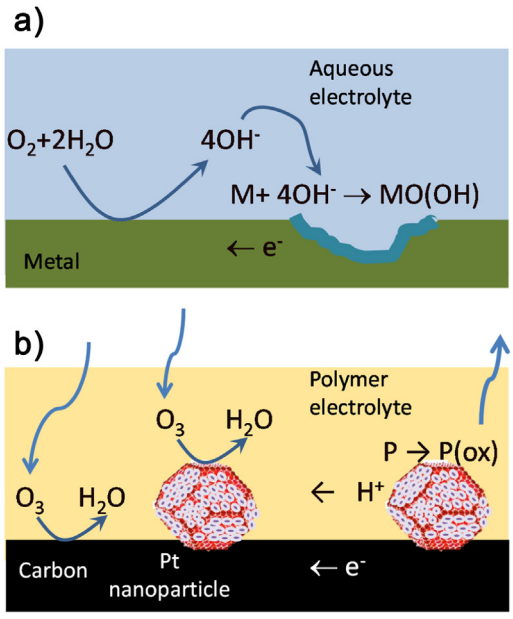


Fig. 1. Cartoons comparing the mixed potential corrosion process in which oxygen reduction is coupled to metallic corrosion (a); to the mixed potential catalyst cleaning process in which poisons deposited on the catalyst are oxidised coupled to the reduction of ozone, (b) P represents a poison which is oxidised.

conducting phase (Fig. 1(b)):

$$O_3 + 6H^+ + 6e^- \rightleftharpoons 3H_2O \quad (1.)$$

$$S_{ad} + 2H_2O \rightleftharpoons SO_2 + 4H^+ + 4e^- \quad (2.)$$

$$\text{Net reaction}: 3S_{ad} + 2O_3 \rightleftharpoons 3SO_2 \quad (3.)$$

$$S_{ad} + 4H_2O \rightleftharpoons SO_4^{2-} + 8H^+ + 6e^- \quad (4.)$$

$$\text{Net reaction}: S_{ad} + O_3 + H_2O \rightleftharpoons H_2SO_4 \quad (5.)$$

We show that this process is efficient for the room temperature chemical cleaning of SO_2 contaminated PEFC single cells and stacks utilising ozone (O_3). The approach is easily applicable to commercial systems as it simply requires flushing the cathode with ozone diluted in air at room temperature whilst the fuel cell is not operating. This process does not require any external polarisation and thus avoids the risks and difficulties of connecting a stack to an external power supply. We show the effect of SO_2 contamination and its subsequent recovery by O_3 at the catalyst level, single cell level and in a fuel cell stack.

2. Experimental

2.1. Materials

ACS reagent grade H_2SO_4 acid (95%), $HClO_4$ acid (95%), hydrogen peroxide (35 wt.%), potassium permanganate (99%), and anhydrous propan-2-ol (99.5%) were procured from Sigma-Aldrich, UK. Ultra-pure DI water (Millipore Milli-Q, 18.2 MΩ cm) was used to prepare various solutions. Fuel cell electrodes with a nominal Pt loading of 0.4 mg cm^{-2} were procured from Alfa Aesar, UK. Nafion PFSA NR212 membranes were procured from DuPont, USA. Hydrogen, Oxygen, Nitrogen, and 100 ppm SO_2 in Argon cylinders were

procured from Air Products. Compressed air was used for fuel cell tests. The N6 grade gases (Air products, BIPA) were controlled with N6 rated regulators (GCE Druva) and connected with specially cleaned (SC-11) tubing and fittings from Swagelok. Room temperature during all the experimental measurements was $25 \pm 2\,^{\circ}C$.

2.2. Catalyst ink preparation for electrochemical studies

The catalyst ink was prepared by mixing 8.33 mg 60 wt.% Pt/C (HiSpec™ 9100; Johnson Matthey, metal area of 89 $m^2\,g^{-1}$ [20]) catalyst in 10 ml ultrapure DI water and 3 ml propan-2-ol in a 20 ml sample bottle. Approximately 52 μl of 5 wt.% nafion solution (Aldrich) was added to the above mixture. The sample bottle was then placed in a temperature controlled ultrasonicator (BANDELIN, SC255) for 60 min. The well dispersed ink was then kept aside in a fridge for electrochemical studies.

A glassy carbon rotating disk electrode (AFE5T050GC, Pine Research Instrumentation) was micro-polished on a polishing pad with 0.05 μm alumina abrasive (PK-3 Electrode Polishing kit, ALS Co. Ltd., Japan) and subsequently cleaned by mild sonication in ultrapure DI water followed by rinsing with copious DI water. The required amount of catalyst ink was taken and drop coated over the polished RDE. The catalyst ink coated RDE was left to dry for 30 min while rotating at 700 rpm.

2.3. Cyclic voltammetry and RDE studies

A three compartment electrochemical cell was used for CV and RDE studies. The glassware was rigorously cleaned before using for any electrochemical analysis. The glassware was initially soaked in acidified $KMnO_4$ for 12 h, followed by rinsing with acidified H_2O_2 and ultra-pure DI water, respectively. The glassware was again soaked in piranha solution for 6 h and thoroughly washed with ultra-pure DI water. The glassware was boiled for 1 h before using it in any electrochemical studies. A high surface area Pt-wire was used as a counter electrode and a reversible hydrogen electrode was used as a reference electrode (HydroFlex®; Gaskatel GmbH, Germany). All the ex-situ electrochemical measurements were carried out in 0.5 M $HClO_4$ solution at 25 °C using a potentiostat/galvanostat (PGSTAT302N; Metrohm Autolab B.V., The Netherland). The CV studies were carried out under an inert environment, with a scan rate of 20 mV s^{-1} utilising an analogue integrator. The oxygen reduction reaction (ORR) measurements were carried out at 1600 rpm. The step size was 1 mV.

The effect of SO_2 on CV and ORR of the catalyst were carried out by purging 100 ppm SO_2 through the solution. The solution was changed with a fresh solution and purged with N_2 and O_2 to study electrochemical performance of the catalyst after SO_2 contamination. The SO_2 contaminated electrodes were later cleaned with 0.4% O_3 and electrochemical performance of the O_3 cleaned/recovered electrodes were studied again in a fresh electrolyte as

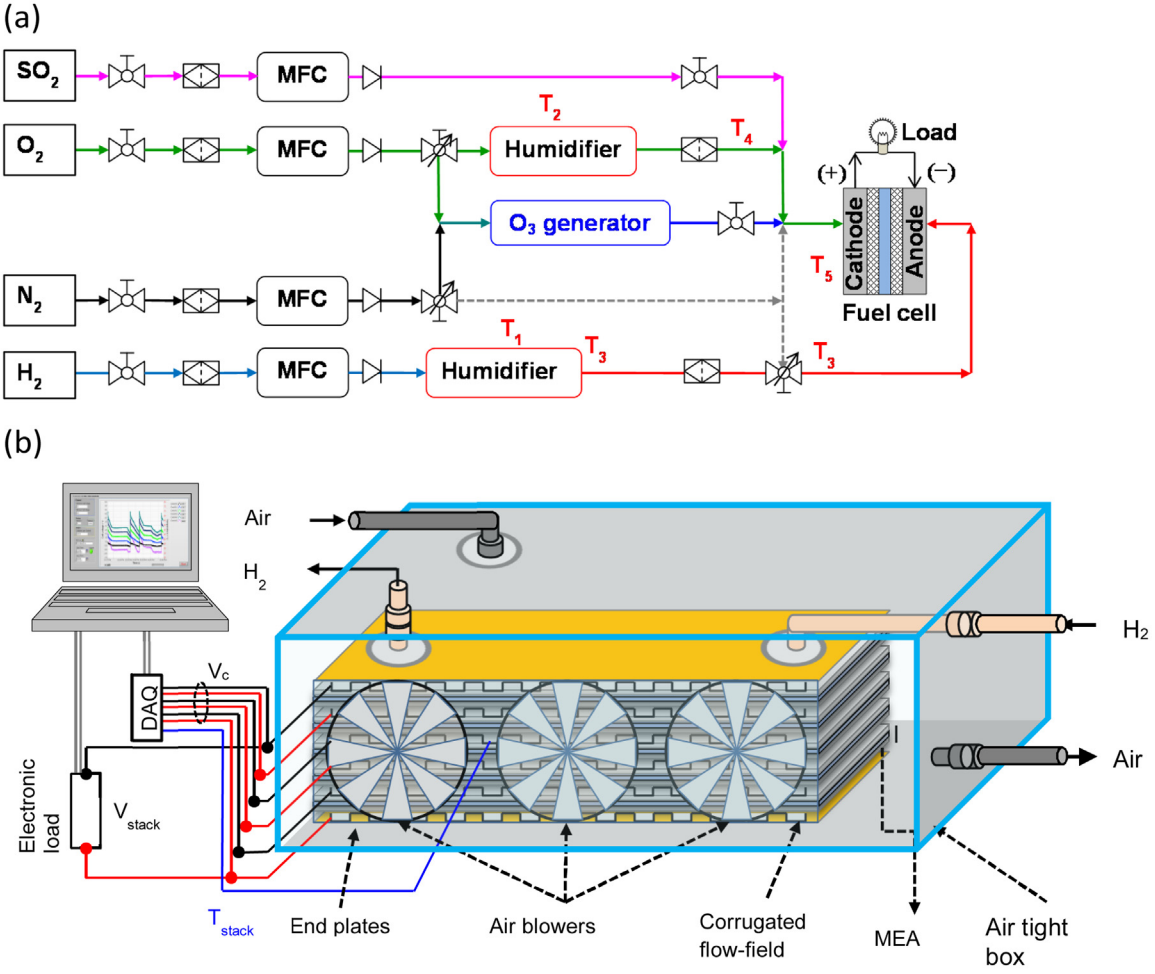


Fig. 2. (a) Block diagram of configuration used to poison and regenerate the single cell fuel cell utilising ozone. (b) Schematic of experimental set-up used to study SO_2 contamination of open-cathode PEFC stack followed by its O_3 recovery. The stack was run without any external humidification and external heating. The stack is enclosed in a specially designed airtight container to study SO_2 contamination and O_3 recovery.

mentioned earlier. The electrochemical cleaning of the SO_2 contaminated catalyst was carried out by stepping up the potential of the electrode to 1.6 V. The performance of the electrochemically cleaned electrodes in CV and ORR were also tested as per the methodology described earlier.

Correction of the ORR results to specific kinetic current density was performed using

$$j_{k,sp} = \frac{j_{MT} j_{Expt}}{\left(j_{Expt} - j_{MT}\right)} \frac{1}{L \times SA} \quad (6.)$$

Where j_{MT} [A m^{-2}] is the mass transport limited current density at the specific rotation rate used, j_{Expt}[A m^{-2}] is the experimentally measured current density, L [g m^{-2}] is the catalyst loading and SA [m^2 g^{-1}] is the catalyst specific area.

2.4. Fuel cell studies

The Nafion membranes were pretreated to remove any organic and inorganic impurities. The pretreatment carried out by boiling the membrane in 1 M H_2O_2 solution at 80 °C for 1 h. The membrane was then carefully rinsed with ultrapure water and again boiled in 1 M H_2SO_4 solution at 80 °C for another 1 h. The treated membrane was then washed thoroughly and boiled in ultrapure DI water for another 30 min before it was used for MEA fabrication. The pretreated membrane was then sandwiched between two 25 cm^2 electrodes (#45372, 0.4 mg_{Pt} cm^{-2}; Alfa Aesar) and hotpressed at 160 °C under 5 MPa pressure for 210 s. The prepared MEA was then used in fuel cell hardware (FC-01-02; Electrochem Inc., USA) to study its performance at various conditions.

A schematic of the single-cell fuel cell setup for the SO_2 contamination and recovery studies is shown in Fig. 2(a). The fuel cell was operated at 80 °C and 65% RH to study its performance. A fuel cell load/impedance analyser (KFM2030; Kikusui, Japan) was used to study the PEFC performance. The H_2 and O_2/Air stoichiometries were maintained at 1.5 and 2.0 relative to the maximum current density, respectively. The MEAs were galvanostatically broken in for 12 h at 1.0 A cm^{-2} with pure H_2 and O_2 as anode and cathode gases. The polarisation studies were later studied using Air and 10% O_2 in N_2 as cathode gas, respectively. The contamination studies of the PEFCs were carried out by mixing the required amount of SO_2 in the cathode gas. The contamination studies were carried out at different concentrations of SO_2. After contamination, the PEFCs were purged with nitrogen before any performance testing. O_3 recovery of the SO_2 contaminated fuel cell was carried out by passing an O_2 stream through an O_3 generator (BMT801; BMT Messtechnik GmbH, Germany). The required O_3 concentration was tuned by varying the concentration of O_2 in inlet gas, supply voltage and current to the generator. The concentration of O_3 produced was measured with an UV/Vis dual beam spectrometer (UV4-200, ATI-Unicam) at the known ozone UV absorption peak (λ_{max} = 253.7; $\varepsilon = 3000 \pm 30$ dm^3 mol^{-1} cm^{-1}) [21]. Fig. 2(b) shows the physical experimental configuration to study the in-situ cathode contamination of the PEFC stack. The stack was enclosed in an air-tight box to study the effect of airborne contaminant SO_2 on its durability and performance. The basic configuration for SO_2 contamination and subsequent O_3 recovery can be found in earlier reported literatures [22,23]. To study the cathode contamination of the stack, compressed air was premixed with the required concentration of SO_2 and connected to the inlet of the airtight box. The premixed air was later blown through the open-cathodes with the help of two fans. The anodes and cathodes were flushed with neat N_2 after contaminating the stack with the respective contaminants and before admission of the O_3. The contaminated stack was then treated with 0.4 vol% O_3 to recover its performance. The O_3 recovered stack was again purged with N_2 before going for further fuel cell studies.

3. Results and discussion

3.1. Electrochemical studies of SO_2 contamination and recovery in aqueous acid electrolytes

Voltammetric studies were carried out on the electrochemistry behind SO_2 contamination of commercial Pt/C catalyst (60 wt.% HiSpec™ 9100; Johnson Matthey). Fig. 3(a) shows the voltammograms of the catalyst under different conditions. The CV of the electrode in SO_2 free N_2-satd. electrolyte is shown in Fig. 3(a)(i).

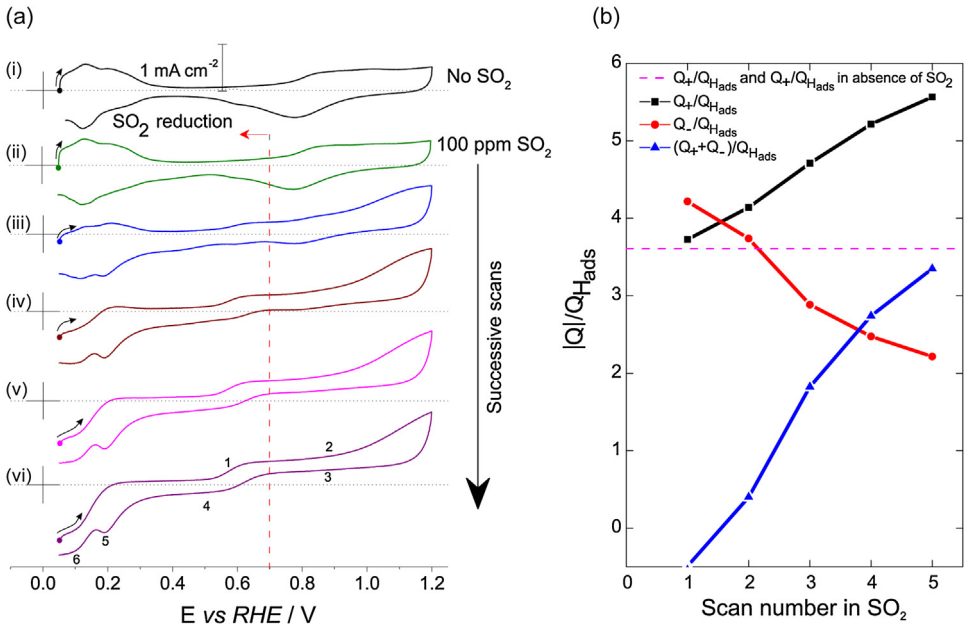


Fig. 3. (a) Successive cyclic voltammograms of a 20 μg_{Pt} cm^{-2} catalyst layer on a glassy carbon electrode in 0.5 mol dm^{-3} $HClO_4$ solution purged with pure N_2, (i); and then N_2 + 100 ppm SO_2 (ii)-(f). The CVs were performed at 20 mV s^{-1} and 298 K.

The anodic peaks for H_2 desorption and oxide formation and reduction peaks are clearly visible. The integrated anodic charge and cathodic charges of this voltammogram balance to within 1.5%. The anodic H desorption peaks at 130 and 200 mV are attributed to the weakly bonded H atom at Pt(110) and Pt(100) crystal facets. Similarly, Pt is oxidised from 0.8 V onwards. The cathodic oxide reduction peak at 0.775 V is due to the reduction of platinum oxide back to the metal.

The effects of 100 ppm SO_2 added to the nitrogen bubbling through the electrolyte on consecutive voltammograms of the catalyst are shown in Fig. 3(a)(ii)-(vi) for successive scans. As the pKa of the water complex formed on bubbling SO_2 through water (sometimes referred to as H_2SO_3) is 1.85, only a small amount of the dissolved sulfur is liable to exist as HSO_3^- (~3% at the pH of this experiment). It is observed that upon exposure to SO_2, there is not much change in the hydrogen peaks in the anodic potential range 0.05-0.4 V. However, there is a slight decrease in the onset of oxidation and an increase in the oxidation current. There is also a progressive and general change to the voltammograms on successive scans. At higher potentials, the currents become more anodic, with suppression of the platinum oxide reduction peak. Indeed after the second scan, the reverse going scan remains anodic, implying that an oxidation process continues during the reverse scan. In these acidic solutions the SO_2 will exist as a hydrated molecule, $SO_{2,aq}$. It seems reasonable to assume that the anodic process occurring is composed of either the oxidation of the SO_2 to sulphate, or the oxidation of an adsorbed sulfur species deposited on the electrode surface. The net reactions for which may be written as

$$SO_{2,aq} + 2H_2O \rightleftharpoons HSO_4^- + 3H^+ + 2e \quad (7.)$$

$$SO_{x,ads} + (4-x)H_2O \rightleftharpoons HSO_4^- + (7-2x)H^+ + (8-2x)e \quad (8)$$

Reduction of the SO_2 is complex and may go through a range of adsorbed intermediates [24,25]. In the voltammograms there is a general shift in the currents in a cathodic direction, especially at lower potentials. Indeed, careful comparison of the voltammetric scan in the absense of SO_2 with the first scan in the presence of SO_2 shows that there is a slight excess of current seen starting at about 0.4 V (RHE). The peak associated with platinum oxide also undergoes some significant changes. At first it shifts to lower potential and then it becomes weaker and is eventually replaced by a broad plateau. This indicates that a general reductive process is occurring leading to a species which can be oxidised at higher potential to either SO_2 (equation 2) or to sulfate (equation 4). Consecutive cycling in the presence of SO_2 leads to an almost complete disappearance of the hydrogen adsorption/desorption peaks indicating the presence of a blocking species on the surface. A clear reduction process starting at about 0.7 V indicates the point at which significant amounts of SO_2 reductive adsorption commences, although even at 0.9 V, some sulfur adsorption is present [26]. XANES data indicates that below this potential $SO_{2\,(ads)}$ and then progressively S_{ads} are formed on the platinum nanoparticle surface [26]. Similarly, an onset potential for the oxidation of the adsorbed sulfur species occurs at 0.5 V. At higher potentials there is a very broad oxidation process which becomes significantly evident at 0.9 V. However, close comparison of the initial scan (a)(i) and the first scan in SO_2 containing solution, (a)(ii), shows that the excess current is initially evident at potentials down to 0.4 V(results not shown). The voltammetry towards SO_2 oxidation/reduction seems to improve with increasing coverage of sulfur species on the surface, an aspect which has been previously commented upon, see also below [27].

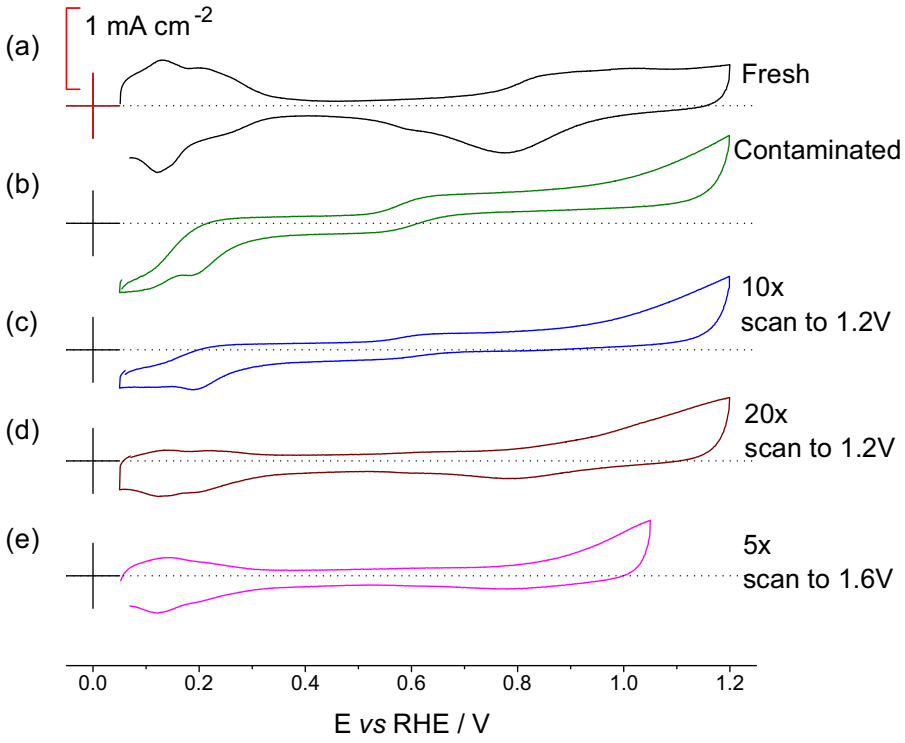


Fig. 4. Cyclic voltammograms of electrochemical recovery of a platinum electrode after being exposed to 100 ppm SO_2; (a) Electrode before exposure to SO_2; (b) Voltammogram of electrode after five electrochemical cycles (0.05-1.2 V RHE) in a solution saturated with 100 ppm SO_2/N_2. (c) Voltammogram after ten cycles in fresh electrolyte cycling up to 1.2 V. (d) Voltammograms after 20 further cycles to 1.2 V; (e) Voltammogram after the electrode has been scanned to 1.6 V for five cycles. The electrode is formed by spin coating a 20 $\mu g_{Pt}\,cm^{-2}$ catalyst layer on a glassy carbon electrode. The experiments were carried out in SO_2-free 0.5 mol dm^{-3} $HClO_4$ solution at 25 ±2 °C, with a scan rate of 20 mV s^{-1}.

It is observed that the reduction peak associated with platinum oxide reduction completely disappears from the third cycle onwards. In fact it is superseded by the SO_2 adsorption peaks. The reduction of SO_2 occurs mainly in three stages as seen in the voltammograms in Fig. 3(a) which show similar voltammetry to that seen for electrodeposited platinum on glassy carbon [28]. The electrochemistry of adsorbed sulfur involves intermediates for which three reduction zones/peaks are evident under potentiodynamic cycling. The reductive plateau commencing at "4" in the cathodic sweep is due to the initial reduction of SO_2 commencing at about 0.71 V. At peaks "5" and "6", commencing at about 0.35 V, there is a subsequent reduction process. These latter reductive processes seem correlated with the position of the hydrogen adsorption peaks, suggesting some interplay of adsorbed hydrogen in the reactions. During the subsequent anodic scan, the surface is inactive towards reduction of SO_2 and also shows a very low double layer current, suggesting that it is effectively blocked towards any electrochemical reaction. It is only when the potential exceeds about 0.5 V that this species is oxidised (1), presumably to SO_2 on the basis of the position. At still higher potentials beginning at (2) there is growth of a very broad oxidation peak associated with removal of sulfur from the surface. Further details of this process are provided in Fig. 3(b). This shows the total anodic and cathodic charges (and their sum) for each successive scan. These charges are

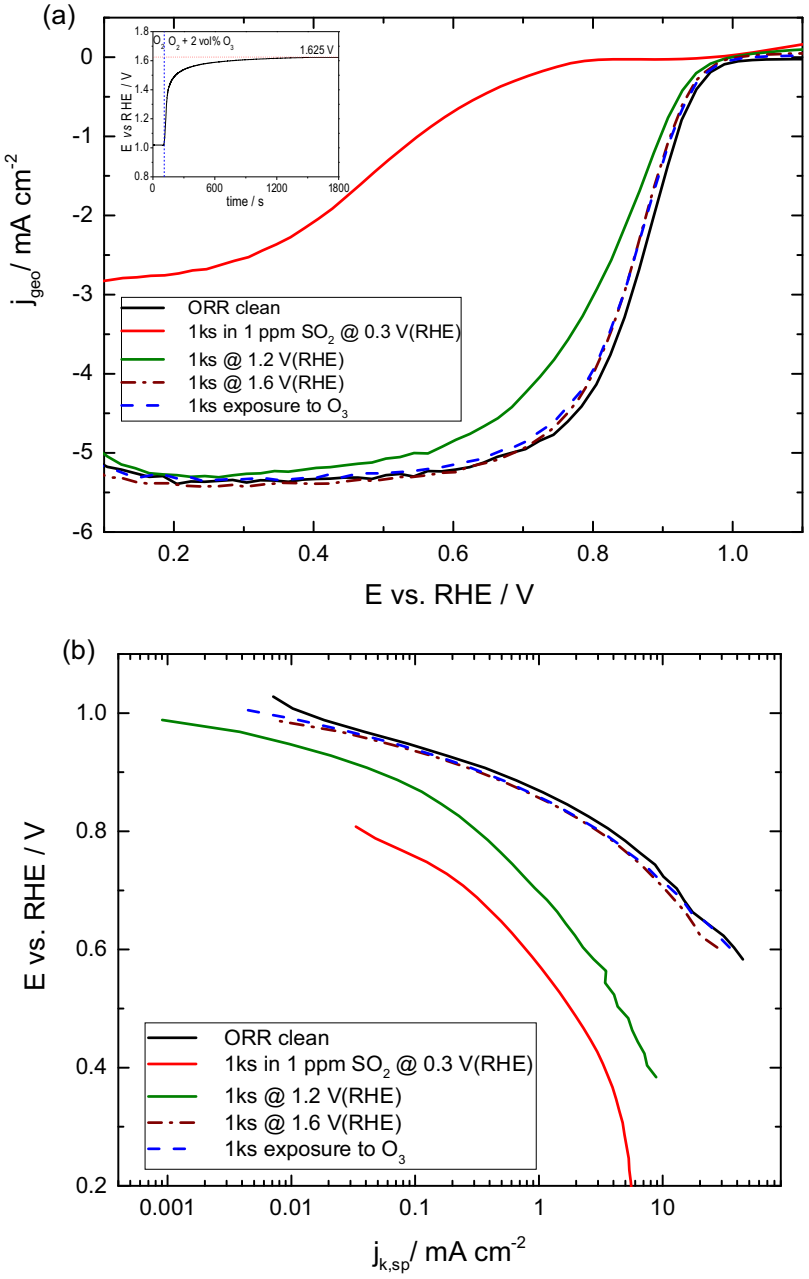


Fig. 5. (a) Potentiostatic curves for the oxygen reduction reaction on a glassy carbon rotating disk electrode coated with Pt/C catalyst (20 μg_{Pt} cm^{-2}) in O_2-satd. 0.5 M $HClO_4$ solution (—); ORR performance after exposure to a solution containing 1 ppm SO_2 at a potential of 0.3 V(RHE) for 1ks and then returned to fresh electrolyte to obtain the ORR result (——); ORR performance after SO_2 exposure (as previously performed) and then polarisation in SO_2-free electrolyte for 1ks at 1.2 V before performing the ORR as above (——); ORR performance after SO_2 exposure (as previously performed) and then polarisation in SO_2-free electrolyte for 1ks at 1.6 V before performing the ORR as above (·····); ORR performance after SO_2 exposure (as previously performed) and then immersion in an O_3 solution for 1 ks before performing the ORR as above (- - - -). Inset: open circuit potential with time for an un-poisoned electrode showing the transition from O_2 saturated electrolyte to exposed to O_3 (b) electrokinetic plots of the data in (a) corrected for the mass transport limited current and for the specific surface area of the catalyst (see text). 20 mV s^{-1} scan rate at 1600 rpm and 298 K.

ratioed to the hydrogen UPD charge in order to give a sense of the coverage of the sulphur species. We also plot the average anodic and cathodic charge for the platinum in the absence of SO_2 (we find that in the absence of SO_2 the anodic and cathodic charges agree to better than 1.5%). It is clear that on the first scan there is a net cathodic charge, but on subsequent scans there is a net anodic charge suggesting that net SO_4^{2-} (or other high oxidation state oxo-sulfur species) is produced, with the surface becoming more active towards sulfur dioxide oxidation on successive scans.

It has been reported that the species resulting from the reduction at around 0.21 V blocks the active sites of the Pt and is desorbed or re-oxidised only at very high potential [25]. The adsorbed sulfur may undergo further reduction in the region "6" and below to form poly-sulfide.

Prolonged adsorption of sulfur on Pt may lead to gradual penetration of sulfur into the bulk of the metal. At potentials higher than 0.9 V, the sulfur adsorbed on Pt is electro-oxidized to sulphite (or SO_2) or sulfate through reactions shown in (2), (7) and (8). However, this process is not particularly effective, and it is almost impossible to remove all adsorbed sulfur. For instance, Fig. 4(b)-(d) shows voltammetry in SO_2-free electrolyte of the electrode contaminated in the same manner as described in Fig. 3, and subsequent gradual recovery of the electrode when scanned up to a potential of 1.2 V and then 1.6 V, Fig. 4(e). For comparison voltammetry of the electrode in the same electrolyte before poisoning is shown in Fig. 4(a). Potentiodynamic cycling of a SO_2 contaminated electrode cannot recover the original active area of the catalyst even after 30 cycles to 1.2 V Fig. 4(c)-(d) (~20 min.). Even cycling the electrode to 1.6 V does not recover all the platinum surface area with more than 50% of the H_{UPD} region still being lost, Fig. 4(e). Such significant blocking of the platinum surface is crucial in understanding the loss in performance of fuel cell cathodes in the presence of SO_2, even after attempted cleaning using external polarisation. Furthermore, although external polarisation is an option for the simple electrodes used in electrochemistry, and even the simple single test cells used in laboratories, it is very difficult and costly to implement on a fuel cell stack in the laboratory, and virtually impossible for a fuel cell in an operational device.

Fig. 5 shows the oxygen reduction reaction (ORR) performance of the catalyst in O_2 saturated 0.5 M $HClO_4$ solution before and after exposure to 1 ppm SO_2 in solution for 1 ks. In both cases the ORR reaction was performed in fresh electrolyte in the absence of SO_2. The onset potential of the fresh electrode in SO_2 free electrolyte is observed to be close to 1.0 V, and a limiting current is quickly reached by about 0.7 V. The limiting current for the ORR studies was observed to be 5.5 mA cm^{-2}, in good agreement to the value expected on the basis of rotation rate and oxygen solubility.

However, after exposure at a potential of 0.3 V(RHE) in a solution containing 1 ppm SO_2 for 1 ks the electrode is found to be significantly blocked towards the oxygen reduction reaction and the electrode fails to achieve a limiting current. The onset for oxygen reduction is shifted to below 0.8 V(RHE). This poisoning effect is quite similar to that observed in the cathodic scan of the CV in the presence of SO_2. It is well known that platinum catalysts poisoned using sulphite [8,29] or dissolved SO_2 [28,30,31] during potentiostatic polarisation show decreased performance towards the ORR and increased yields of hydrogen peroxide [29]. Furthermore, attempts to electrochemically remove the adsorbed sulfur containing compounds only show limited success [30] unless excessive polarisation is used [32]. After exposing the electrode to SO_2 as above, we have tried to remove the adsorbed sulfur species by polarisation for 1ks at either 1.2 V(RHE) or 1.6 V (RHE). In each case a freshly poisoned electrode was prepared. In the case of polarisation at 1.2 V(RHE), moderate recovery of the performance of the electrode is achieved, whereas at 1.6 V, almost complete recovery. Recently we discovered that ozone can be used to totally recover the anode of a fuel cell exposed to hydrogen sulphide – a potent poison to many chemical processes [33]. Hence we decided to study whether the O_3 recovery technique was suitable for the recovery of SO_2 contaminated electrodes. After exposure to SO_2 as previously described, the catalyst coated electrode was cleaned in a solution saturated with 0.4% O_3 and rinsed with water before returning to fresh electrolyte to perform the ORR. It is observed that O_3 cleaning almost totally reinstates the ORR activity of the catalysts, Fig. 5(a). This effect is more easily seen in the electrokinetic plots for the *ORR*, Fig. 5(b), in which the currents have been corrected for the mass transport limitation of the system due to the performance of the rotating disk electrode, and also the specific surface area of the catalyst. Hence treatment of catalysts contaminated with SO_2 can be quickly and quantitatively recovered by a short treatment with a low concentration of O_3. The mechanism of operation seems to be due to the high open circuit potential that the electrode achieves in the presence of ozone, as shown in the inset to Fig. 5(a). It is seen that during exposure to ozone, the potential rises up to 1.625 V, at which potential the sulfur species on the electrode surface are oxidised. This is confirmed by the similarity in performance improvement seen when the electrode is polarised at almost the same potential for the same period, Fig. 5(a).

We believe that two processes are responsible for the removal of the poison. In the first, as described in the introduction, reduction of O_3 to water is coupled to the simultaneous oxidation of the sulfur species on the surface (Fig. 1) through an *electrochemical* reaction. Crucially, the region at which O_3 reduction occurs and that at which poison oxidation occurs may be some distance apart as governed by the distance that the protons (and electrons) required to complete the reaction can travel without incurring too much of an energetic penalty. It has already been shown that a fuel cell can be operated on an ozone rich oxygen stream by Bussayajarn et al. and that such a fuel cell has an open circuit cell voltage >1.6 V(RHE), and is capable of sustaining current densities of a few 10's mA cm^{-2} at a cell voltage greater than 1.2 V[34]. Hence it reasonable to expect that O_3 can act as an appreciable oxidant which can drive the poison oxidation at a sufficiently high potential, and with a sufficiently low impedance to allow complete oxidation of the poison. As was shown in Fig. 5, the effect of O_3 exposure on the removal of poison can be replicated by polarising the electrode at the same potential. The second possibility is associated with the direct reaction of the ozone, or one of the products of ozone decomposition in aqueous solutions [35,36] with the poison through a direct *chemical* reaction:

$$O_3(aq) \rightarrow O_2(aq) + \dot{O}(aq) \quad (9.)$$

$$\dot{O}(aq) + H_2O \rightarrow 2OH^{\cdot}(aq) \quad (10.)$$

$$Pt - S_{ads} + 3[O] \rightarrow SO_2(g) + Pt - O \quad (11.)$$

$$Pt - (SO_2)_{ads} + [O] \rightarrow SO_2(g) + Pt - O \quad (12.)$$

Where [O] represents the active oxygen species produced e.g. O_3, $\dot{O}$ and $OH^{\cdot}$ radicals.

3.2. Regeneration of irreversibly poisoned fuel cells: Single cell system

To assess whether this approach is applicable to fuel cell systems, we tested the effect of SO_2 on the performance of a single cell fuel cell operating at a current density of 1.0 A cm^{-2}. It is well known in the literature that operation of a fuel cell in which the

cathode air is contaminated with SO_2 leads to a degradation in performance dependent on the fuel cell operating conditions [3,4,37–41]. The degree of poisoning of the cathode is a complex function of SO_2 concentration [40], temperature [41] and cathode potential [42]. In our experiments we found that even at elevated levels of SO_2 in the cathode air supply, we saw little cell potential degradation unless the cathode potential was less than 0.65 V, as seen by others [13]. Hence we chose a current density of 1 A cm^{-2} which allowed us to operate in a regime in which poisoning occurred. Fig. 6(a) shows the performance of a fuel cell operated on an impure air supply containing 10 ppm SO_2 over 7.2 ks, corresponding to a cumulative dose of 1.8 μmol_{SO_2} cm^{-2} of electrode assuming all the SO_2 is adsorbed. Over this period the cell voltage drops by 60 mV. Increasing the SO_2 concentration in the cathode feed air to 50 ppm for 300 s (0.4 μmol_{SO2} cm^{-2}) causes an even more severe drop in cell voltage of 150 mV. Thus the degree of cell voltage loss is not directly related to the total dose of SO_2 applied to the system, but rather related to the dose history and to the specific cell operating conditions (specifically cathode potential) during the poisoning process. As seen in the RDE results in Fig. 3, there is significant evolution of the sulfur coverage of the catalyst during exposure which changes the response of the surface. During the periods when no SO_2 is in the fuel cell cathode air supply there is some recovery of the cell voltage, as might be expected from Fig. 4, as the operating voltage of the fuel cell is in the region at which adsorbed sulfur will be oxidised. Zhai et al. performed similar research on SO_2 contamination and subsequent recovery in a single cell fuel cell [13,41]. They also reported a partial recovery of initial performance after operating the fuel cell on air alone. However, their results showed that even after 70 hours the fuel cell still shows a 200 mV loss in cell potential [41].

Allowing the cell voltage of the cathode to rise to the OCV has an even bigger effect. If the cell is shut down and left under air at OCP for 43 ks, then there is an 80 mV improvement in cell potential when the cell is restarted – this is undoubtedly due to a more aggressive cathode potential being able to oxidise more of the adsorbed sulfur species off of the surface. However, the initial performance of the fuel cell is not recovered. Furthermore, subsequent exposure to even a small concentration of 10 ppm SO_2 in the cathode air for 360 s (a dose of 0.1 μmol_{SO_2} cm^{-2}), causes a significant drop in performance. SO_2 reduction to adsorbed sulfur has been shown in Fig. 3(a) to start at about 0.7 V (RHE) and become progressively more facile as the potential is lowered. Hence it is unsurprising that the rate of fuel cell poisoning is a function of the cathode performance (i.e. degree to which it is poisoned). As the cathode potential drops due to poisoning the rate of poisoning increases. This occurs because the overpotential for SO_2 reduction increases. Such non-linear effects in poisoning have been seen in fuel cell poisoning before, for instance in propene poisoning of a fuel cell stack [43].

Work by others has shown that potentiostatic polarisation of the fuel cell can lead to significant improvements in performance following SO_2 poisoning. For instance potential cycling in air between 0.09 and 1.1 V for 30 minutes can recover ≥98% of the performance [18]. Although potentiostatic treatment may be suitable for single cells it is difficult to see how this approach could realistically be applied to stacks, as it is difficult to ensure that the voltage is evenly applied to individual cells when a multi cell stack is externally polarised. Furthermore, in any operational system such a polarisation would be physically difficult to perform. Hence we have examined a simple chemical treatment that can be performed at room temperature. It is seen in Fig. 6(a) that a 900 s exposure of 0.4% O_3 almost completely recovers the fuel cell (>95% of initial performance at currents up to 1 A cm^{-2}). This amount of O_3 is equivalent to a dose of 22 μmol_{O3} cm^{-2} of electrode, and represents about a 40-fold excess compared to the dose of SO_2 applied. In much the same way as the O_3 treatment of the catalyst totally regenerated its ORR performance in Fig. 5, the O_3 treatment removes the adsorbed sulfur species from the catalyst surface. Furthermore, the performance is stable after the treatment and the performance shows no decay for the remaining 7.6 ks of the experiment.

We have previously shown that in the case of anode poisoning by H_2S, in which the blocking species are similar to those present here, O_3 treatment leads to the adsorbed sulfur species being oxidised to SO_2 which then exits through the cathode exhaust [33]. Under these conditions SO_2 is prevented from re adsorbing on the platinum catalyst because of the high potential, hence allowing it to be removed in the cathode exhaust. Comparison of the fuel cell I-V curves at the points labelled A, B and C in Fig. 6(a) is shown in

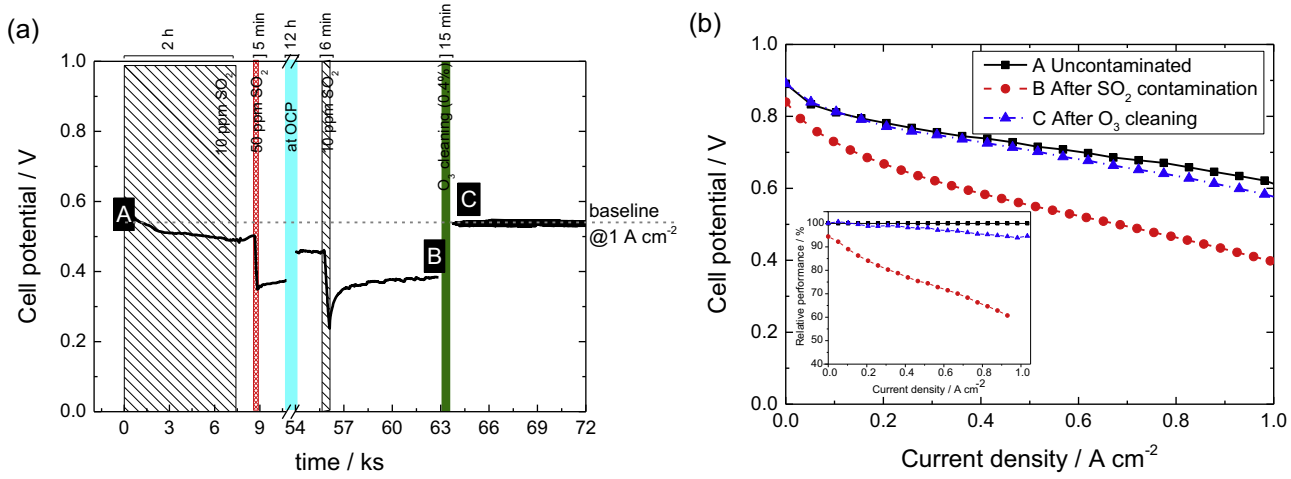


Fig. 6. (a) Long term performance curve of a single cell fuel cell operated in the presence of SO_2, and regeneration utilising O_3 at room temperature. Fuel cell operated at a current density of 1 A cm^{-2}. During unlabelled periods the fuel cell was operated using clean air. (b) Polarisation curves of the PEFC at each of the labelled positions in (a) A: at beginning of run, B: after poisoning with SO_2 (total dose 2.2 μmol_{SO2} cm^{-2}); C: after 900 s 0.5% ozone cleaning. Inset shows the relative performance of the fuel cell scaled to the initial performance. The polarisation measurements were carried out at 80 °C, with 65% relative humidity, H_2/air. The anode and cathode gas stoichiometries were maintained at 1.5 and 2.0, respectively. A back pressure of 10 psi was applied during these experiments.

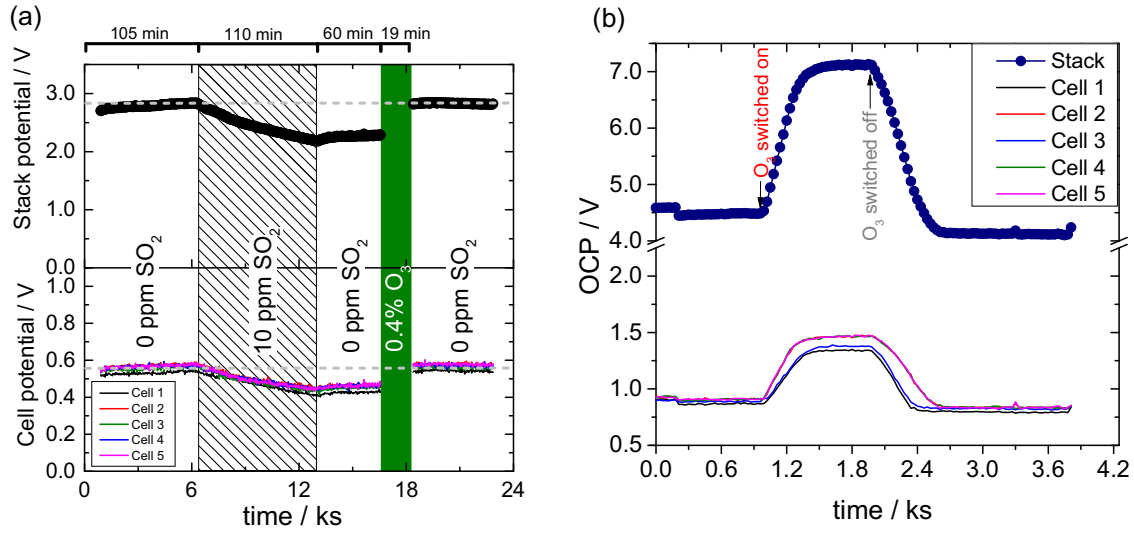


Fig. 7. (a) Long term durability studies of a PEFC fuel cell stack (5-cells in series) operating on H_2/Air showing both the full stack voltage and the individual cell voltages. The effect of short term ozone treatment on the regeneration of the fuel cell. (b) Expansion of the period during which an ozone purge is used to remove adsorbed poisons from the cathode surface.

Fig. 6(b). It can be seen that following the O_3 treatment there is almost complete recovery of the fuel cell performance curve. In fact at higher potential, the performance is slightly better (~1% performance improvement), suggesting activation of the performance in the low overpotential region. We saw such an effect in our previous paper too, suggesting that O_3 might be useful in cleaning catalysts before their use [23]. The improvement in performance matches or exceeds that seen during potentiostatic polarisation regeneration by Gould et al. [18], especially taking into account the high 7-fold higher dose of SO_2 applied to the electrodes in this study compared to that study.

However, long term exposure of fuel cell electrodes to ozone is not without its risks. For instance, it is well known that exposure of fuel cells to ozone during operation (i.e. when the electrodes are at elevated temperature), can lead to degradation of performance [44,45]. As we have shown in our previous paper, prolonged exposure to ozone at room temperature (used to regenerate poisoned fuel cell electrodes) also leads to some degradation of the performance of the fuel cell at high current densities [23]. This degradation is related to increased hydrophilicity of the catalyst layer leading to an increase in mass transport losses at high currents [23]. However the low temperature of our treatment means that the degradation rate is much slower than seen in operating fuel cells. This result is also confirmed by Maruyama et al. who show that at room temperature it takes 10 hours to show significant degradation, and for short time treatments there is even an improvement in performance [46].

3.3. Regeneration of irreversibly poisoned fuel cells: Fuel cell stack

Although some work has been performed on regenerating individual fuel cells exposed to poisons, to our knowledge, there are no examples of such approaches being applied to fuel cell stacks. This is partially because the typical approach used, which involves external polarisation, is unsuitable to apply to stacks because of the issues of maintaining uniform potential distribution across all cells. In order to test whether our approach works on fuel cell stacks, we examined the poisoning and regeneration of an air breathing open cathode five-cell fuel cell stack provided by Intelligent Energy. Fig. 7(a) shows the performance of the fuel cell stack in terms of the individual cells and the stack voltage when the system was operated at a target current density of 1 A cm^{-2}. On exposure to 10 ppm SO_2 the stack voltage progressively falls losing on average 110 mV per cell over a period of 6.6 ks. On removal of the SO_2 from the air feed, the fuel cell stack recovers a little in voltage.

Treatment of the system with ozone was performed by flushing the entire system with 0.4% ozone in air. Transients for all five cells and the entire stack voltage for this process is shown in Fig. 7(b). It can be seen that the stack voltage increases from an OCV value of about 4.4 V to over 7 V (about 1.4 V per cell). There are small differences in the potential excursion that each cell sees, but they all exceed 1.3 V. Returning the fuel cell to operation mode, shows that following the O_3 cleaning process, the stack and cell voltages return to their previous values. Hence it is shown that the O_3 treatment approach can also recover fuel cell stacks.

4. Conclusions

We have shown how ozone treatment can be used to successfully remove adsorbed sulfur species on Pt/C cathode catalysts produced through the interaction of those catalysts with SO_2. The process occurs predominantly through a mixed potential process in which reduction of ozone to water is coupled to oxidation of the sulfur containing species on the catalyst surface. During exposure to ozone, the electrode potential is raised to 1.4–1.6 V. The process is fast and occurs at room temperature. It is shown that the catalyst regeneration process occurs equally well for catalyst on a rotating disk electrode, single cell fuel cell and five cell fuel cell stack. Especially in the low current region, exposure to O_3 can lead to beneficial effects. At higher current densities, it may not be possible to recover all of the initial activity due to increases in mass transport losses.

It is interesting to consider whether the O_3 treatment process is applicable to other chemical contaminants. Certainly, it would appear that this process should be applicable to any species which can be oxidatively removed from platinum surfaces when applying 1.6 V(RHE). This suggests that the process may be applicable to a

broad range of poisons encountered in cathode contamination, especially those with hydrocarbon fragments.

Acknowledgements and Data Availability

The authors would like to acknowledge the Engineering and Physical Sciences Research Council for financial support under project EP/I037024/1 and the Technology Strategy board under the IDP11 framework for project 102283. The authors would like to thank Intelligent Energy for the use of one of their fuel cell stacks and especially Dr Paul Adcock and Dr Niall Lafferty for their help. The data used in the production of the figures in this paper is available at doi:10.5281/zenodo.167109.

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