



Gas phase recovery of hydrogen sulfide contaminated polymer electrolyte membrane fuel cells[☆]



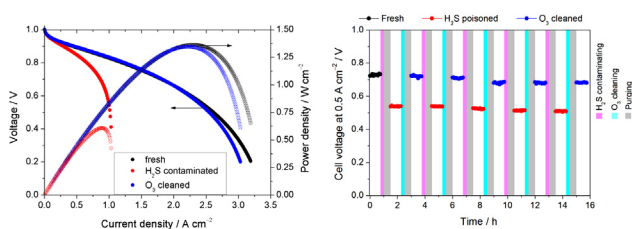
Biraj Kumar Kakati, Anthony R.J. Kucernak*

Department of Chemistry, Imperial College London, London SW7 2AZ, UK

HIGHLIGHTS

- Recovery of H₂S contaminated PEMFC is studied via external polarization and O₃ cleaning.
- The room temperature O₃ cleaning process completely rejuvenates the H₂S contaminated fuel cell in 600–900 s.
- O₃ cleaning at room temperature avoids excessive carbon corrosion as seen by low CO₂ generation.
- The in-situ O₃ cleaning process proceeds through both a chemical and electrochemical route.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of hydrogen sulfide (H₂S) on the anode of a polymer electrolyte membrane fuel cell (PEMFC) and the gas phase recovery of the contaminated PEMFC using ozone (O₃) were studied. Experiments were performed on fuel cell electrodes both in an aqueous electrolyte and within an operating fuel cell. The ex-situ analyses of a fresh electrode; a H₂S contaminated electrode (23 μmolH₂S cm⁻²); and the contaminated electrode cleaned with O₃ shows that all sulfide can be removed within 900 s at room temperature. Online gas analysis of the recovery process confirms the recovery time required as around 720 s. Similarly, performance studies of an H₂S contaminated PEMFC shows that complete rejuvenation occurs following 600–900 s O₃ treatment at room temperature. The cleaning process involves both electrochemical oxidation (facilitated by the high equilibrium potential of the O₃ reduction process) and direct chemical oxidation of the contaminant. The O₃ cleaning process is more efficient than the external polarization of the single cell at 1.6 V. Application of O₃ at room temperature limits the amount of carbon corrosion.

Room temperature O₃ treatment of poisoned fuel cell stacks may offer an efficient and quick remediation method to recover otherwise inoperable systems.

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1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is considered to be the one of the most promising portable power sources due to its fast start-up, high power density, quick load following, and ease of electrolyte handling, low corrosion and system robustness [1–4]. The purity of the hydrogen (H₂) should be relatively high to achieve high efficiency, power density and long

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* Corresponding author. Tel.: +44 20 75945831; fax: +44 20 75945804.

E-mail address: anthony@imperial.ac.uk (A.R.J. Kucernak).

life time. Nowadays, H₂ is produced most likely from fossil fuels, through steam reforming of methane and partial oxidation of hydrocarbon fuels. The reformed hydrogen might have various impurities like nitrogen, CO_x, NO_x, SO_x, ammonia, hydrogen sulfide (H₂S) and trace amount of hydrocarbons [5]. The PEMFC research involving fuel side contaminants are mainly focused on the effects of CO and tolerance to it [6–20]. In the case of sulfides, more precisely H₂S, research is mainly focused on the effects of the contaminant on the electrochemical performance of the catalyst or on the performance of the fuel cell [21–26]. Unlike CO, the detrimental effect of H₂S on the performance of the fuel cell is cumulative and highly irreversible [23,27]. Furthermore, the normal CO mitigation approaches, better known as Pt–Ru alloy catalyst and/or air bleeding, do not provide a satisfactory remedy for H₂S contamination [21]. The first experimental work on the contamination of platinum catalyst by sulfur compound was carried out by Loučka et al., in 1971 [28,29]. Heinzel et al. (2002) reported a decrease in cell performance due to the presence of H₂S at as low a concentration as 0.5 ppm [30].

The in-situ research on the effect of sulfides on the performance of PEMFC has been performed [21,31–37]. However, only a handful of literature studies are available on the effort to recover H₂S contaminated fuel cells [32,38–40]. Uribe et al. (2001) reported that a partial recovery could be achieved by potential scanning of the electrode between 0 and 1.4 V vs dynamic hydrogen electrode [27]. Mohtadi et al. [21] reported that the degree of recovery of a PEMFC anode contaminated with H₂S depended on the degree of oxidation of the two surface species Pt–S and Pt–S₂. They later studied the effect of operating temperature on the severity of the contamination of fuel cell with H₂S [41]. The presence of two forms of chemisorbed sulfur on platinum was reported by Contractor and Lal [42]. Shi et al. [40] carried forward the study on the severity of H₂S poisoning on the performance of fuel cell with different H₂S concentration, current density and the cell temperature. They used a high voltage pulse to recover the performance of the 5 ppm H₂S contaminated fuel cell [39]. Gould et al. used potential cycling and potential hold techniques to study the recovery of SO₂ [32] and H₂S [25] contaminated PEMFCs in nitrogen and air environments. They reported that partial recovery of PEMFC polarization curve performance (92% of original power at 0.6 V) was possible but strongly dependent on the external polarization program. It seems clear that electrokinetic remediation or external polarization (cycling and/or potential hold) of the contaminated cell is not a viable solution for a large stack.

In this paper we report the use of a gaseous reactant, ozone (O₃), as a means to treat a fuel cell poisoned with H₂S. This process does not require external polarization of the cell and thus can easily be performed on a fuel cell stack. Although we use H₂S as an example of a poison, this process might equally be applicable to other poisons. For instance, it is interesting to note that SO₂ seems to follow a similar pathway in deposition of S_{ads} on platinum, so the remediation process we describe here would also be suitable for fuel cell electrodes exposed to SO₂ [42].

2. Experimental

2.1. Materials

ACS reagent grade sulfuric acid (95%), hydrogen peroxide (35 wt.%), potassium permanganate (99%), and anhydrous propan-2-ol (99.5%) were procured from Sigma–Aldrich, UK. Ultra-pure 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 from Alfa Aesar, UK. Nafion PFSA NR212 membranes were procured from DuPont, USA. Hydrogen, Oxygen,

Nitrogen, and 1000 ppm H₂S in Argon cylinders were procured from Air Products. Compressed air was used for fuel cell testing. The N6 grade gas cylinders were controlled with N6 rated regulators (GCE Druva and Air products) and connected with specially cleaned (SC-11) tubing and fittings from Swagelok. Room temperature during experimental measurements was 25 ± 2 °C.

2.2. Electrochemical measurements

Experiments in this paper have been performed in both a three-electrode electrochemical cell utilizing an aqueous acid electrolyte (ex-situ measurements), and within a fuel cell (in situ measurements). The electrodes used in the three-electrode electrochemical cell were the same as those used in the fuel cell and were poisoned and cleaned with O₃ in an external flow-field (Fig. 1(b)) in order to (a) replicate the process that occurs within a fuel cell; and (b) avoid contamination of the electrochemical cell by hydrogen sulfide or O₃ during the experiments. The only time that O₃ was utilized in the three-electrode electrochemical cell was during the measurements of the open circuit potential (OCV) of the electrode during exposure to O₃ (Fig. 3(a)).

2.2.1. Ex-situ electrochemical analysis of fuel cell electrodes

The glassware was rigorously cleaned before using for any electrochemical analysis. The glassware was initially soaked in acidified KMnO₄ for 12 h, followed by rinsing with acidified H₂O₂ and ultra-pure water, respectively. The glassware was again soaked in piranha solution for 6 h and thoroughly washed with ultra-pure water before use. All the ex-situ electrochemical analyses were carried out in 1.0 M H₂SO₄ solution in a 5 neck jacketed cell. All electrochemical measurements were carried out using a Potentiostat/Galvanostat/ZRA (Reference 3000, Gamry, USA). For aqueous electrochemical studies, the working electrode was a 1 cm² of fuel cell electrode (Johnson Matthey, Alfa Aesar catalog # 45372, 0.4 mg_{Pt} cm⁻²) in a platinum wire holder. 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). Fig. 1(a) shows the schematic of the ex-situ electrochemical cell of the fuel cell electrodes. All the ex-situ cyclic voltammetry (CV) analyses were carried out at room temperature (25 ± 2 °C), unless otherwise specified. The electrochemical surface areas (ECA) of the electrode were calculated from the hydrogen desorption area in the cyclic voltammetry [43]. Further discussion is provided in supplementary material.

2.2.2. H₂S contamination and O₃ recovery in an ex-situ flowfield

For all the ex-situ electrochemical experiments, the H₂S contamination and O₃ cleaning processes were carried out at room temperature utilizing an external flowfield, Fig. 1(b). The electrode was placed in a flowfield (parallel channels, 1 mm land, 1 mm channel) and the relevant gases were passed over its surface. Flow rates of 75 sccm were used, which in this geometry corresponds to a space velocity of 12.5 s⁻¹. Utilizing an external flowfield for the contamination and cleaning processes avoided contamination of the electrolyte, RHE, and counter electrodes with H₂S. The external flowfield was purged with N₂ after contaminating the electrode with H₂S (100 ppm, balance hydrogen, effective dose 23 μmol cm⁻²) and again after O₃ treatment. After contamination and/or cleaning with O₃, the electrode was transferred from the flowfield to the electrochemical cell for characterization. The effective dose is calculated assuming all the H₂S is absorbed by the electrode and none leaves the flowfield.

The O₃ cleaning process of the H₂S contaminated electrode was monitored with the help of an online gas analyzer (HPR-20 QIC Hiden analytical, UK). The mass spectrometer was typically allowed

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