

The effects of battlefield contaminants on PEMFC performance

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Abstract

The effects of contaminants on the performance of an air breathing proton exchange membrane fuel cell (PEMFC) were investigated, by introduction into oxidant air fed to the fuel cell. The impact of the common pollutants sulphur dioxide, nitrogen dioxide, carbon monoxide, propane and benzene and the chemical warfare agents, sarin, sulphur mustard, cyanogen chloride (CNCl) and hydrogen cyanide (HCN) were assessed. At the concentrations studied, the common contaminants had either no effect on performance or caused a reversible depression. The chemical warfare agents all seriously compromised the performance of the fuel cells in an irreversible manner. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) continue to be the subject of intensive research and development efforts, owing to the high power densities they offer. Additionally, their characteristic low operating temperatures, low emissions, quiet operation and potential for system robustness has resulted in them being targeted at a wide range of applications.

The use of the PEMFC as an electrochemical replacement for the internal combustion engine receives ever growing attention, and increasingly in the fields of portable power and primary power generation, the potential benefits of using such fuel cell technology are being recognised.

As large scale commercialisation of PEMFCs draws closer, efforts must turn to issues relating to the environments in which the fuel cells will be expected to operate. Unless the oxidant is supplied to the cells from a contained source (e.g., bottled oxygen or air), impurities present in the immediate atmosphere may adversely affect their performance. This is of particular concern for military applications where any working fuel cell systems must also be hardened against contamination by chemical and biological weapons.

A great deal of research has been carried out into the poisoning of fuel cell catalysts. This has, however, been primarily concerned with the effect of carbon monoxide [1–4], which is present in hydrogen reformed from an organic fuel, such as methanol. Little information has been published on the susceptibility of PEMFCs to damage or performance shortfall when exposed to air contaminants. The authors are not aware of any published study into the effects of contaminants that might be encountered under battlefield conditions.

It is difficult to define the environmental conditions of the battlefield, unless specific combat scenarios are introduced. Pollution levels will vary greatly from near zero in remote regions to those encountered in city centres or close to industrial and chemical plant. Exposure times to battlefield contaminants might generally be expected to be less than for normal fuel cell operation but the concentrations experienced could be high.

With respect to the impurities present in the immediate environment of the battlefield, two general types of contaminants were considered. Firstly, those that will be present independently of the combat; common pollutants such as sulphur dioxide, nitrogen oxides, carbon monoxide and benzene. Secondly, those that will be present as a consequence of combat, such as burning fuel and organic vapour, and those introduced deliberately by the combatants such as chemical warfare agents.

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Table 1
Contaminants investigated and concentration

Contaminant	Concentration
Carbon monoxide	20 ppm
Sulphur dioxide	500 ppb
Benzene	50 ppm
Propane	90 ppm
Nitrogen dioxide	400 ppb
Cyanogen chloride (CNCl)	780 ppm and 1560 ppm
Hydrogen cyanide (HCN)	1780 ppm and 3560 ppm
Sulphur mustard	15 ppm
Sarin	170 ppm and 340 ppm

Carbon monoxide is generated in the atmosphere both as a result of combustion processes and from the oxidation of organic compounds, the maximum recorded city centre concentrations in the UK are of the order 20 ppm [5]. Nitrogen oxides are released into the atmosphere as a result of fossil fuel combustion, mostly in the form of nitric oxide which is then oxidised to nitrogen dioxide. Elevated NO_x levels (400 ppb) are usually observed in built-up areas under stable weather conditions. Sulphur dioxide occurs mainly in the atmosphere as a result of fossil fuel combustion, and maximum urban levels of < 500 ppb have been recorded in the UK [5].

It is likely that elevated NO_x , carbon monoxide, and sulphur dioxide levels would also be observed in a vehicle dense battlefield environment.

Organic pollutants can broadly be split into two categories; volatile organic compounds (VOCs) which include benzene, butadiene, toluene and ethylene and are typically found in the 1–30 ppb levels in urban environments, and persistent organic pollutants (POPs) which include DDT, dieldrins (pesticide residues), dioxins, furans and PCBs, and are usually found in low to sub parts per billion levels

in the atmosphere. This latter group of organic pollutants have not been included in this study.

Table 1 shows a list of the air pollutants assessed in this initial stage of the battlefield contaminants study and their concentration.

The concentrations of carbon monoxide, sulphur dioxide, and nitrogen dioxide, represent maximum hourly atmospheric readings recorded in the UK [5]. The benzene and propane levels are those which might be associated with a localised chemical release or incident, and for the benzene, the siting of the fuel cell in close proximity to an internal combustion engine exhaust.

Nerve agents such as sarin are potent inhibitors of cholinesterase, an enzyme that hydrolyses a neurotransmitter called acetylcholine. The blister agent sulphur mustard, attacks the human body through many mechanisms, including binding to different proteins within cells, via the active sites of enzymes.

The levels of the chemical warfare agents chosen are realistic battlefield concentrations, and in the cases of HCN and CNCl represent standards used by the UK's Ministry of Defence [6] and NATO for the examination of protective carbon based filters.

2. Experimental

For all experiments membrane electrode assemblies (MEAs) obtained from W.L. Gore & Associates of active area 11 cm^2 and a platinum catalyst loading of 0.3 mg/cm^2 on both anode and cathode were utilised.

An ambient air PEMFC test cell, manufactured by Advanced Power Sources Ltd. was utilised for the testing of the common contaminants. Ambient air cells, similar in

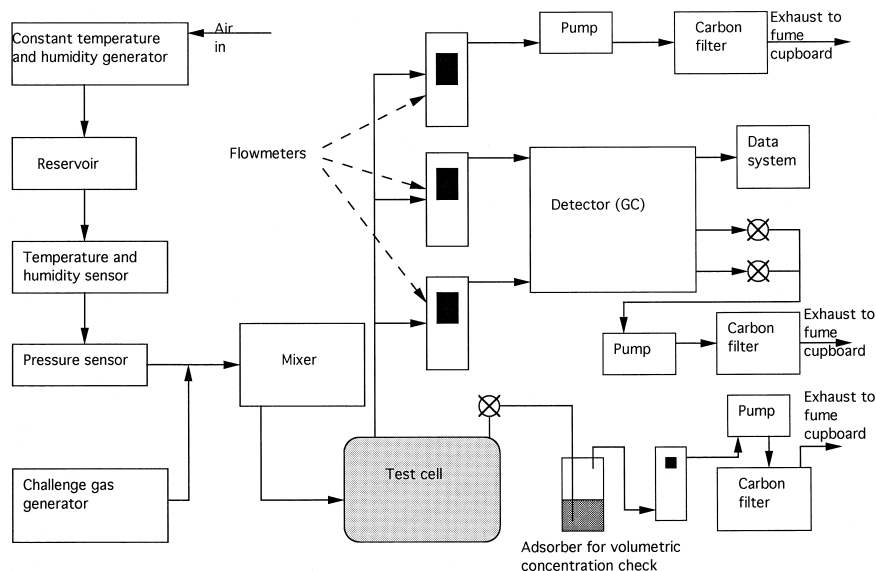


Fig. 1. Schematic of CNCl and HCN toxic gas test rig.

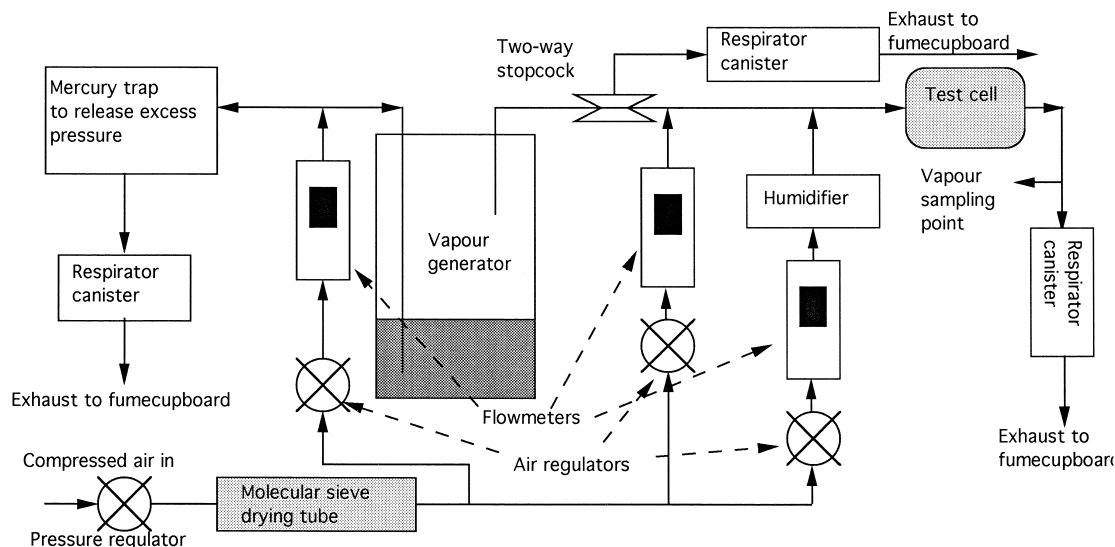


Fig. 2. Schematic of sarin and sulphur mustard toxic vapour test rig.

operation, and fabricated at DERA Haslar, were used to assess the effects of the chemical warfare agents. Both types of cells featured stainless steel 316L cathode plates and utilised reactant hydrogen at a pressure of 1 bar (g).

2.1. Common contaminants

Dry air was fed into a chamber above the cathode face of an ambient air PEMFC test cell at a flow rate of 0.5 SLPM and atmospheric pressure. Pressurised air cylinders containing the contaminant at the required concentration were purchased from BOC Speciality Gases.

Air was passed into the cell for 30 min, followed by a challenge with the contaminated air for a further 30 min, before returning to a flow of pure air. A flow meter was utilised in order to ensure that the oxidant flow remained unchanged after switching from pure to 'contaminated' air.

The effects of the contaminants were assessed galvanostatically using a constant current load unit at 50, 100 and

200 mA/cm², with the potential of the cell recorded at intervals as a function of time. A temperature controller was used to keep the cell at a constant 30°C.

2.2. Chemical warfare agents

For CNCl and HCN contaminants the ambient air fuel cells were placed in a Bruhl jar and connected into a standard toxic gas test rig used for filter absorbent testing (Fig. 1). The conditioned, influent test air was provided using a Miller Nelson control unit with the temperature and relative humidity (RH) monitored using a Mitchell dew point hygrometer. The air flow rate was 15 SLPM and the temperature and RH were controlled at 24°C and 80%, respectively.

The CNCl challenge was generated from a gas cylinder maintained at 22°C in a water bath. The gas was passed through a liquid trap and flow controller before being introduced into the influent air prior to the mixing cham-

Table 2
Summary of the effect of the contaminants on fuel cell output

Contaminant	Concentration	Percentage of original output during challenge	Percentage of original output during recovery
Carbon monoxide	20 ppm	96%	100%
Nitrogen dioxide	400 ppb	100%	100%
Sulphur dioxide	500 ppb	100%	100%
Benzene	50 ppm	95% (50 mA/cm ²)	95%
		93% (100 mA/cm ²)	
		72% (200 mA/cm ²)	
Propane	90 ppm	100%	100%
HCN	1780 ppm	13%	45%
HCN	3560 ppm	9%	35%
CNCl	780 ppm	11%	32%
CNCl	1560 ppm	12%	50%
Sulphur mustard	15 ppm	13%	13%
Sarin	170 ppm	30%	30%
Sarin	340 ppm	23%	23%

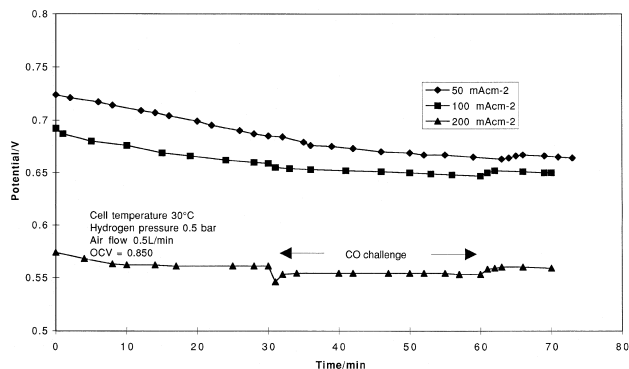


Fig. 3. Effect of 20 ppm carbon monoxide in air on PEMFC performance.

ber. The flow controller was used to establish the desired challenge concentration.

The HCN challenge was generated by passing air through liquid HCN contained in a Dreschel bottle, maintained at 10°C in a water bath. The vapour laden air was passed through a liquid trap before being introduced into the influent air prior to the mixing chamber. The challenge concentration was adjusted by controlling the air flow to the vapour generator. The challenge concentration was determined by electrometric titration of a 5 litre sample of test air taken from the Bruhl jar.

For sarin and sulphur mustard the fuel cells were placed in an enclosure formed from two large glass flange joints which were modified to provide inlet and outlet ports for the hydrogen gas supply and the electrical connections. This was then connected to a standard toxic vapour test rig (Fig. 2). The laboratory supply compressed influent air was passed at ambient temperature (20–25°C) through a molecular sieve drying tube and then divided into three streams. Each stream was passed through a flow regulator and a rotameter with one stream going to the vapour generator and one stream going to the humidifier. These streams were then recombined with the third before being fed into the fuel cell enclosure at challenge flow rates of 1–2 SLPM. The RH of the challenge was kept in the range 1 to 5% to minimise agent decomposition.

For the sarin challenges the concentration was determined by collecting vapour samples on Poropak tubes at

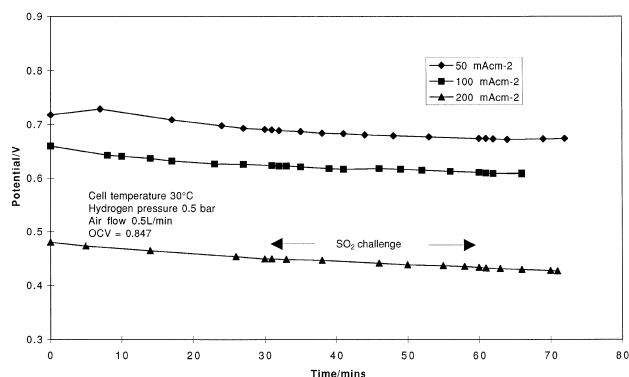


Fig. 4. Effect of 500 ppb sulphur dioxide in air on PEMFC performance.

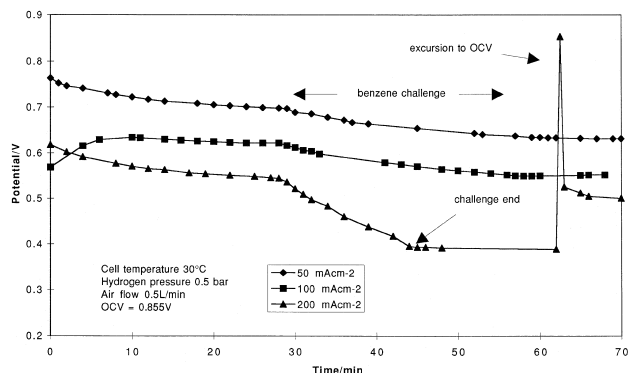


Fig. 5. Effect of 50 ppm benzene in air on PEMFC performance.

the start and end of each experiment. The agent was eluted using propan-2-ol and the resulting solution was subjected to chromatography using a DB17 column, at 70°C for 1 min, increasing at 30°C min⁻¹ to 250°C and holding at this temperature for 1 min.

For sulphur mustard the challenge concentration was determined using the same method as for sarin except that the final temperature during chromatography was 220°C.

The fuel cells were set up in series with a battery, providing a bias voltage, and a constant current load unit to provide a constant current density of 50 mA/cm².

The effects of the introduction of the challenge chemicals for 15 min on the performance of the fuel cells were assessed by monitoring the cell potential galvanostatically at 50 mA/cm² and a cell temperature of 25°C.

3. Results

Table 2 gives a summary of the effect of the various contaminants on the fuel cells after 15 min had elapsed, as a percentage of the cells' original power prior to the contaminant challenge. In a similar manner, recovery of the cells is indicated by their performance 15 min after the contaminant challenge ceased.

The effect of 20 ppm of carbon monoxide on the cathode side, was to produce a depression in performance

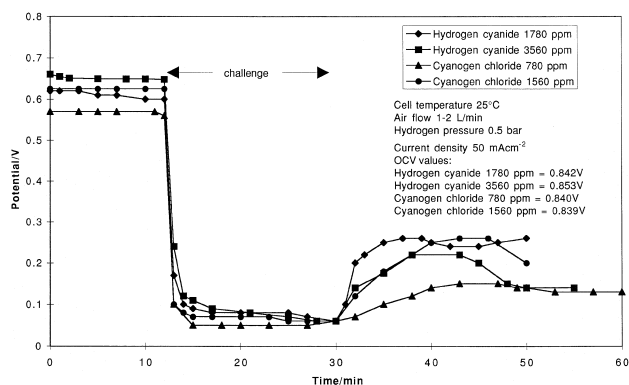


Fig. 6. Effect of HCN and CNCl in air on PEMFC performance.

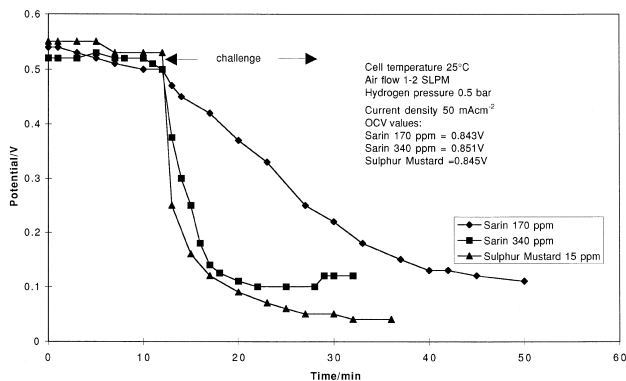


Fig. 7. Effect of sarin and sulphur mustard in air on PEMFC performance.

of a few millivolts (Fig. 3). This appeared to be completely reversible, and when the flow of CO ceased the performance of the cell returned to its original level.

Sulphur dioxide, at 500 ppb (Fig. 4), and nitrogen dioxide at 400 ppb, did not have a detrimental effect on cell performance over the time interval tested. Similarly, 90 ppm of propane in the air stream did not have any observable effect on the cell potential.

Benzene (Fig. 5) had a marked effect on cell performance, the cell potential decreased for as long as the benzene was present in the air stream, in contrast to the carbon monoxide where a lower, but stable performance was observed. Although withdrawal of the contaminant did arrest the performance decline, the cell did not return to its original performance. It was noted that once electrical load was removed the cell began to recover. In a separate experiment, subsequent to the benzene challenge, an excursion to open circuit potential was effected for 1 min. This resulted in the cell performance almost recovering to that obtained prior to the introduction of the benzene.

The chemical warfare agents seriously compromised performance of the fuel cells. Steady state for CNCl and HCN (Fig. 6) was reached within 1–2 min of exposure, and both showed a partial recovery when the contaminant challenge was ended, however, no return to original performance was observed even after leaving the cells to recover for several days. The fuel cells challenged by sarin and sulphur mustard (Fig. 7) exhibited a more gradual degradation, reaching steady state values in 5 to 25 min. These cells did not show any tendency to recover and the effects appeared to be permanent.

To further investigate the relationship between concentration of the chemical warfare agent and fuel cell degradation. A series of experiments were performed with varying concentrations of sarin.

Fuel cells were operated galvanostatically at 50 mA/cm² and the sarin introduced. The cell voltage before and after 10-min exposure was measured (Fig. 8).

Over the time interval studied, concentrations up to 5 ppm showed only small effects if any. At the higher concentrations, which are thought to be representative of the concentrations one might expect if sarin was released into the atmosphere, catastrophic failure of the cells was observed.

4. Discussion

Platinum is the catalyst of choice for the majority of PEMFC developers. It is the most effective catalytic surface for both hydrogen oxidation and oxygen reduction. It is, however, rapidly deactivated by carbon monoxide at operational PEMFC temperatures. This poisoning of the platinum surface by CO has been thoroughly researched and is well-understood [1–4].

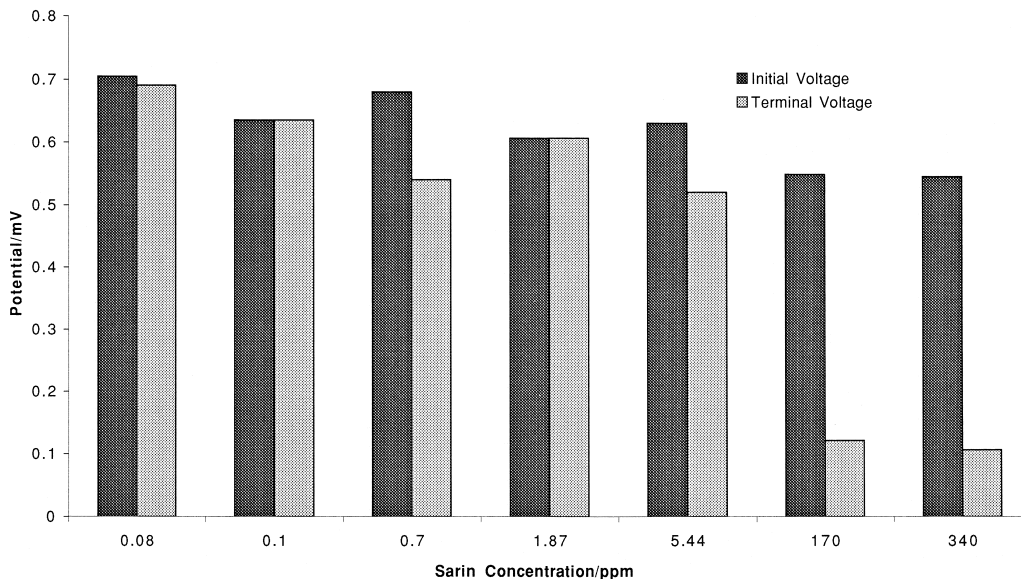


Fig. 8. Effect of varying sarin concentration.

It is known that carbon monoxide levels of up to several hundred parts per million present in reformed hydrocarbon fuel anode gas stream have an adverse, yet reversible effect on performance [1]. It is not surprising therefore, that upon cessation of the CO flow, and under cathode conditions of high oxidising potential, a platinum oxide surface and the presence of oxygen, oxidation rapidly occurs through to carbon dioxide.

Sulphur dioxide showed no apparent effect on cell performance after 30 min of exposure. Work reported by Veldius et al. [7] has shown a $\leq 10\%$ decrease in PEMFC current density with 500 ppb sulphur dioxide in the air stream. This work, was however, carried out at an elevated temperature of 80°C, 2 bar (g) hydrogen and air reactant gas pressure, current densities of approximately 800 mA/cm² and over time periods of many hours. In a separate study by Pino et al. [8], challenges with sulphur dioxide contaminated air over several hours of operation, did not produce major degradation in performance at a concentration of 50 ppm, performed at 75°C, 3 bar (g), and 400 mA/cm².

This study is primarily concerned with short-term exposures thought to be realistic under battlefield conditions. Long-term testing with sulphur dioxide, nitrogen dioxide and propane, may provide additional information as to the nature of the reaction of the MEAs of PEMFCs with these contaminants.

It is known that benzene is adsorbed onto metal surfaces to form 2D structures [9]. On introduction to the fuel cell cathode benzene appears to have been adsorbed onto the catalyst sites and gradually ‘smothers’ the cell. The phenomenon appears to be related to potential as the effect was more marked at higher current densities, where a lower oxidising potential was experienced, and recovery of the cell was initiated by an excursion to higher cell potentials (Fig. 5).

The response of the cell to challenges by HCN and ClCN in the cathode feed were similar, and is consistent with platinum catalyst sites being preferentially occupied by the gases, leading to a very rapid decrease in oxygen reduction and an almost complete cell failure. The partial recovery observed after the challenge was ended could be explained by considering the heterogeneous nature of the platinum. Catalytic sites that lead to the greatest heats of adsorption would be occupied first by the poison, these will also be the ones from which desorption is the most difficult to achieve. The contaminants adsorbed onto sites other than the preferential locations, are most easily desorbed, but these are also least effective for oxygen reduction. From the observed results it may be inferred that the platinum to cyanide bond may be broken at these sites.

The effects of the introduction of sarin (CH₃POFOCH(CH₃)₂) and the sulphur mustard (ClCH₂CH₂SCH₂CH₂Cl) to the fuel cell cathode appeared distinct from the two simple chemical warfare agents mentioned above. Although still catastrophic, the decrease in cell performance

to a steady value was more gradual and subsequent to the vapour challenge there was no indication of cell recovery.

Sarin and sulphur mustard affect the fuel cell much more slowly than the previous chemical agents. The systematic introduction of sarin (Fig. 8) showed that at the lower concentrations little noticeable effect was observed over the 10-min test period. At higher concentrations where performance losses were observed, these were found to be irreversible. The phosphate (sarin) and sulphur (sulphur mustard) atoms are likely to bind irreversibly with the catalytic platinum site, but the size of the agent molecules will reduce the rate of this reaction and may prevent neighbouring platinum sites from being rapidly poisoned. Smaller oxygen molecules could then react with remaining catalyst sites allowing some fuel cell reaction to occur.

It should be noted that at high concentrations of the chemical warfare agents, cell failure could be due to other poisoning mechanisms than adsorption–desorption, parasitic side electrochemical reactions and chemical decomposition of the agents could play a part in cell degradation.

5. Conclusion

It is evident from this study that if fuel cells, utilising atmospheric air as oxidant, are to be considered as a viable power source for applications in contaminated battlefield environments, then research to establish methods of mitigation against the degrading effects of exposure to contaminant gases and vapours needs to be undertaken. Owing to the wide range of possible contaminants, this mitigation is unlikely to take the form of increasing the tolerance of the fuel cell catalyst, and a strategy of encasement combined with various filter systems is the most likely route.

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