Response of electrochemical oxygen sensors to inert gas–air and carbon dioxide–air mixtures: Measurements and mathematical modelling

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ABSTRACT

Electrochemical oxygen gas sensors are widely used for monitoring the state of inertisation of flammable atmospheres and to warn of asphyxiation risks. It is well established but not widely known by users of such oxygen sensors that the response of the sensor is affected by the nature of the diluent gas responsible for the decrease in ambient oxygen concentration. The present work investigates the response of electrochemical sensors, with either acid or alkaline electrolytes, to gas mixtures comprising air with enhanced levels of nitrogen, carbon dioxide, argon or helium. The measurements indicate that both types of sensors over-read the oxygen concentrations when atmospheres contain high levels of helium. Sensors with alkaline electrolytes are also shown to underestimate the severity of the hazard in atmospheres containing high levels of carbon dioxide. This deviation is greater for alkaline electrolyte sensors compared to acid electrolyte sensors. A Computational Fluid Dynamics (CFD) model is developed to predict the response of an alkaline electrolyte, electrochemical gas sensor. Differences between predicted and measured sensor responses are less than 10% in relative terms for nearly all of the gas mixtures tested, and in many cases less than 5%. Extending the model to simulate responses of sensors with acid electrolytes would be straightforward.

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1. Introduction

Oxygen sensors are widely used for workplace air monitoring to warn of asphyxiation risks, particularly in confined spaces [1]. Examples include tunnels, sewers and cellars, inert gas welding sites, locations near landfill sites, water treatment plants and breweries. In these locations there is the potential for the release of large quantities of inert or low toxicity gas that could reduce the concentration of oxygen in the immediate environment and cause asphyxiation. Oxygen sensors are also employed in process safety applications where inerting of flammable atmospheres is required. In the EU, standards for both general performance in all the above applications [2] and use specifically with flammable atmospheres [3] exist for oxygen sensors.

There are currently two main types of sensor that are used for the detection of oxygen deficiency in workplaces: electrochemical and paramagnetic [3]. The former are the most common type and are often used in portable and fixed monitors. Typically, the alarm level of the oxygen sensor is set at 19 or 19.5% (v/v). The response of electrochemical gas sensors, however, depends upon the nature of the diluent gases in the sampled atmosphere. There is a potential for such gas sensors to over-read the oxygen concentration in

certain environments, i.e. under-estimate the hazard. The varying effect of different diluent gases on the response of electrochemical sensors is due to differences in the diffusivity (dependent on molecular mass) and, in some cases, chemical reaction of the diluent gas with the electrolyte in the sensors. These effects are well known in the gas detection industry but are less well known to users.

The standard approach to determine the response of oxygen sensors is to measure directly the sensor's response with diluent gas mixtures of known concentrations. Analytical models for the response of electrolytic sensors to binary gas mixtures have been produced by, amongst others, Hobbs et al. [4], based on mass transport considerations. A more detailed, general treatment of mass transport, applicable to electrochemical sensor behaviour, can be found in Foust et al. [5] and Taylor and Krishna [6], for example.

The purpose of the present work is to present measurements of the response of electrochemical oxygen sensors of both acid and alkaline electrolyte types to atmospheres containing varying concentrations of nitrogen, carbon dioxide, argon or helium, which are common diluents in industry. A numerical modelling approach based on Computational Fluid Dynamics (CFD) is presented that predicts the gas sensor response based on the known properties of the gas and assumed conditions inside the sensor. Fundamentals of the finite-volume CFD approach used here can be found in Versteeg and Malasekera [7]. The CFD results are also compared to two simpler models for one-dimensional steady-state diffusion.

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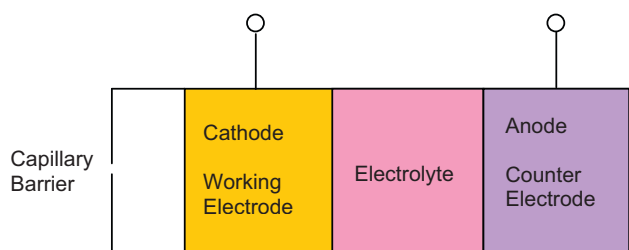*E-mail address:* peter.walsh@hsl.gov.uk (P.T. Walsh).

**Fig. 1.** Simplified schematic of oxygen sensor.

2. Principles of sensor performance

Most electrochemical oxygen sensors comprise a cell containing two electrodes, a cathode of flat PTFE tape with an active catalyst, and either a lead-based anode in combination with a semi-solid alkaline electrolyte paste or a non-lead-based anode in combination with a semi-solid acidic electrolyte paste. A recent development is the use of solid polymer electrolyte (SPE) electrochemical sensors [1] but these are not considered here. The cell is sealed apart from a small capillary tube which controls the rate at which oxygen can enter (Fig. 1).

In sensors with an alkaline electrolyte, when oxygen reaches the working electrode (cathode), it is reduced to hydroxyl ions by taking water from the electrolyte and electrons from the electrode, as follows:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (1)$$

The hydroxyl ions migrate through the electrolyte to the lead anode where they oxidise by converting the lead of the counter electrode into lead oxide, i.e. slowly consuming the lead, releasing water into the electrolyte and electrons to the counter electrode:

$$2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^- \qquad (2)$$
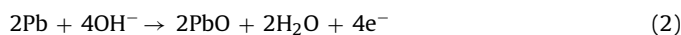
The flow of electrons from the anode to the cathode via an external circuit produces a measurable electrical current that is proportional to the rate at which the reactions occur. This therefore allows determination of the oxygen concentration.

As part of the measuring process, oxygen is consumed by the sensor, producing a flow of oxygen along the capillary tube. The transport of oxygen is therefore not governed solely by diffusion; there are non-negligible convective transport effects due to the bulk flow of oxygen. Even in simple binary nitrogen–oxygen mixtures, this makes the response of the oxygen sensor non-linear [4].

If the atmosphere being measured using an alkaline electrolyte sensor is diluted by an acid gas such as carbon dioxide, sulphur dioxide or nitrogen dioxide, some or all of the acid gas will react with the electrolyte. This increases the bulk flow along the capillary tube, enhancing the non-linearity in the sensor response, and causing an increase in signal of about 0.3% of signal for every 1% of

diluent gas in the case of carbon dioxide [4]. This does not apply to sensors with acid electrolytes (or SPEs) as the acid gases do not react.

3. Oxygen sensor measurements

Four types of monitors using alkaline electrolytes and one example of a monitor using an acid electrolyte electrochemical sensor were tested. Details of the characteristics of all the sensors are given by Dowker [8]. Each of the sensors investigated was calibrated in clean air to 20.9% (v/v) oxygen prior to each set of tests and the calibration checked upon completion of the test.

The sensors were exposed to air from the monitored, clean laboratory supply, diluted in turn by nitrogen, carbon dioxide, argon, and helium to concentrations from 20.9% oxygen to approximately 10% (v/v) oxygen. The air and diluent mixing was performed using a gas mixing pump (Digamix Gas Dilution System, Wösthoff GmbH, Bochum, Germany), which mixes the gases by volume, and has an output flowrate of approximately 500 ml/min. The air mixtures were fed into the monitor/sensor in the same way as the monitor would be calibrated: for a monitor sampling by diffusion (i.e. no internal pump) a dedicated mask or fitting was used to expose the sensor to the gas; for a monitor having an internal pump, the gas mixtures were introduced from the output of the Digamix Gas Dilution System via a 'Y tube' allowing the monitor to control the flow rate of the air mixture to the sensor.

The exposures were of approximately 5 min duration, well in excess of the response times of the sensors (typically around 15 s to 90% of the final response).

4. CFD model

The CFD model geometry consisted of a straight-sided capillary tube with a cylindrical region at one end representing a small volume of air, and the electrode/electrolyte reaction surface at the opposite closed end (Fig. 2). It was assumed that the sensor was of alkaline electrolyte type and therefore at the electrode/electrolyte surface both oxygen and any acid gases were removed from the air, inducing a continuous flow of gas along the capillary tube. The rate at which these gases were removed was calculated to be just sufficient to bring their concentrations to zero at the reaction surface. This set up a concentration gradient along the capillary tube, from ambient levels (20.9%, v/v oxygen in fresh air) at the open end of the capillary to zero at the other, as shown in Fig. 2.

In the CFD model, the length of the capillary tube was subdivided into a large number of small cells. Within each cell the gas velocity, pressure and gas species concentration were calculated by solving numerically the laminar flow equations governing the conservation of mass, momentum and chemical species. The model took into account convective effects, which are largely responsible for the non-linear response of oxygen gas sensors. The resulting predictions were dependent upon boundary conditions in the model
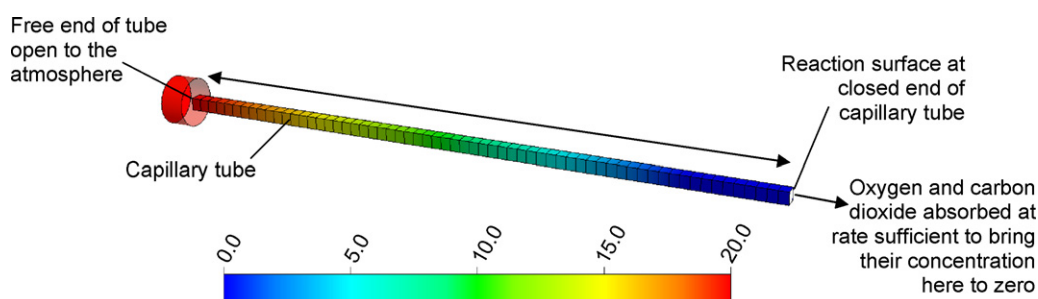

Fig. 2. CFD model of the capillary tube in the sensor showing the concentration of oxygen, varying from 21% (v/v) at the open end to zero at the reaction surface.

Table 1
CFD model boundary conditions.

Location	Boundary condition
Electrode/electrolyte surface	Zero concentration of oxygen and any acid gases[a]; zero-gradient conditions for all other chemical species; zero velocity
Capillary tube walls	Zero slip or no-slip walls, i.e. zero-gradient of chemical species and either zero or zero-gradient velocity
Circular end face of cylindrical volume	Inlet with prescribed oxygen, nitrogen and third species concentrations (see Table 2a–d) at a velocity normal to the face of 0.1 m/s
Side walls of cylindrical volume	Zero pressure opening; zero-gradient conditions for chemical species

[a] This condition was enforced by a sink term in the species conservation equation in the computational cell nearest to the electrode/electrolyte surface, for details see Gant et al. [14].

that specified the concentration of each species at the open end of the capillary and the rate at which species were reacted at the electrode/electrolyte surface of the sensor.

Outside the open end of the capillary tube, the environment usually provides a large reservoir of air to maintain constant ambient conditions. To simulate this in the model, air was pumped through the small cylindrical volume on the end of the capillary tube by imposing a small velocity on the circular end face of 0.1 m/s. The flow of air needed only to be sufficient to make up for the depletion of oxygen, and in some cases carbon dioxide, due to their removal at the reaction surface. Without this flow of air, the oxygen and carbon dioxide would have eventually fallen to zero along the full length of the capillary tube. Tests were undertaken using a larger velocity of 1 m/s to show that the magnitude of this velocity had no significant effect on the resulting model predictions. A summary of the CFD model boundary conditions is provided in Table 1.

The model was developed using the commercial CFD software ANSYS-CFX11 [9]. The molecular diffusivities were determined using the default approach in CFX11 which assumes the Schmidt number is unity, i.e. the rate of diffusion of chemical species was assumed to be equal to rate of diffusion of momentum. Hence, the molecular diffusivity was assumed to be equal to the molecular viscosity of the gas mixture. This molecular viscosity (or diffusivity) was determined in each computational cell from the mass-weighted sum of the molecular viscosities of the different species, based on standard temperature and pressure conditions of 0 °C and 1 atm. An iterative method was used to solve the CFD model equations and the simulations typically took a few minutes to run on a desktop computer.

The CFD model predictions are compared to the results of two simpler models for one-dimensional multi-component diffusion: the effective-diffusivity model of Wilke [10] and the linearised theory model of Toor [11] and Stewart and Prober [12]. In the former model, the effective diffusivity for the transport of species i in a mixture comprising n component gases is determined from:

$$D_{i,eff} = \frac{1 - x_i}{\sum\limits_{\substack{j=1 \\ j \neq i}}^{n} (x_j/D_{ij})} \quad (3)$$

where x_i is the molar fraction of species i, and D_{ij} is the diffusivity of the binary i–j mixture. The flux of species i is determined from:

$$J_i = -c_t D_{i,eff} \nabla x_i \quad i = 1, 2, \ldots, n \quad (4)$$

where c_t is the mixture molar density and ∇x_i is the gradient of the molar fraction of species i. Following the approach adopted by Wilke [10], the molar fractions in Eq. (3) are evaluated from the arithmetic average of their values at the ends of the capillary tube, and the gradients are evaluated assuming linear variation between these two values.

The linearised theory model for steady-state multi-component diffusion with no net flux is described in detail by Taylor and Krishna [6]. It is based on solution of the generalised Fick's law,

which in matrix form for a three-component mixture is written:

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = -c_t \begin{bmatrix} D'_{11} & D'_{12} \\ D'_{21} & D'_{22} \end{bmatrix} \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix} \quad (5)$$

where $[D']$ is the matrix of Fick diffusion coefficients, which has components:

$$D'_{11} = \frac{D_{13}[x_1 D_{23} + (1 - x_1)D_{12}]}{S} \quad (6)$$

$$D'_{12} = \frac{x_1 D_{23}(D_{13} - D_{12})}{S} \quad (7)$$

$$D'_{13} = \frac{x_2 D_{13}(D_{23} - D_{12})}{S} \quad (8)$$

$$D'_{22} = \frac{D_{23}[x_2 D_{13} + (1 - x_2)D_{12}]}{S} \quad (9)$$

where

$$S = x_1 D_{23} + x_2 D_{13} + x_3 D_{12} \quad (10)$$

The fluxes of components 1 and 2 are then given by:

$$J_1 = -c_t(D'_{11}\nabla x_1 + D'_{12}\nabla x_2) \quad (11)$$

$$J_2 = -c_t(D'_{21}\nabla x_1 + D'_{22}\nabla x_2) \quad (12)$$

and, assuming zero bulk flow, the flux of the third component is found from continuity:

$$\sum_{i=1}^{n} J_i = 0 \quad (13)$$

For multi-component diffusion, the linearised theory model accounts for the driving force for all of the components, unlike the effective diffusivity model. This can be important to resolve the correct qualitative behaviour in certain ternary systems, such as the diffusion of nitrogen through a mixture of hydrogen and carbon dioxide [6], and other interaction phenomena such as osmotic and reverse diffusion [13].

Both the effective diffusivity and the linearised theory models tested here assume the net flux along the capillary tube to be zero, i.e. for the gas to be stagnant. More sophisticated models based on linearised theory have been developed that account for finite fluxes, see for example Taylor and Krishna [6]. However, these more complex models require iterative solution methods and are outside the scope of the present work.

5. Results

The different ambient conditions measured and simulated in the present work are summarised in Table 2a–d. For each diluent gas, two additional data points for which experimental data were not available were also modelled to explore the likely response of the gas sensor to very low oxygen concentrations.

It was found that the four monitors with the alkaline electrolyte oxygen sensor behaved very similarly under all conditions, therefore the results are shown only for one monitor. Table 2a–d

Table 2
Model predictions of oxygen concentrations and acid and alkaline electrolyte sensor measurements (denoted AC1 and AL1 respectively) for mixtures of air with (a) nitrogen, (b) carbon dioxide, (c) argon or (d) helium. Concentrations shown are in % (v/v) and the % errors (relative) are between the model predictions and AL1 values.

Fixed O_2 conc.	Fixed N_2 conc.	Detected O_2 concentration					% Error	
		AL1	AC1	Wilke	CFD		Wilke	CFD
(a) Nitrogen								
20.9	79.1	20.9	20.9	20.9	20.9		0.0	0.0
18.8	81.2	18.6	18.9	18.8	18.6		1.1	−0.2
16.7	83.3	16.3	16.8	16.7	16.3		2.5	0.0
14.6	85.4	14.1	14.8	14.6	14.1		3.5	−0.2
12.5	87.5	11.9	12.7	12.5	11.9		5.0	0.1
10.5	89.6	9.8	10.7	10.5	9.9		7.1	1.0
6.0	94.0	–	–	6.0	5.5		–	–
3.0	97.0	–	–	3.0	2.7		–	–

Fixed O_2 conc.	Fixed CO_2 conc.	Detected O_2 concentration					% Error		
		AL1	AC1	Wilke	Linear Theory	CFD	Wilke	Linear theory	CFD
(b) Carbon dioxide									
20.9	0.0	20.9	20.9	20.9	20.9	20.9	0.0	0.0	0.0
18.8	10.0	19.5	18.9	18.5	18.7	19.2	−5.0	−3.9	−1.6
16.7	20.0	17.9	16.8	16.2	16.6	17.5	−9.4	−7.2	−2.4
14.6	30.0	16.4	14.8	14.0	14.5	15.8	−14.7	−11.7	−3.9
12.5	40.0	14.7	12.7	11.8	12.4	14.0	−19.6	−15.9	−4.4
10.5	50.0	13.0	10.7	9.8	10.4	12.4	−24.6	−20.3	−4.6
6.0	71.3	–	–	5.5	5.9	8.4	–		–
3.0	85.6	–	–	2.7	2.9	5.3	–		–

Fixed O_2 conc.	Fixed Ar conc.	Detected O_2 concentration					% Error		
		AL1	AC1	Wilke	Linear theory	CFD	Wilke	Linear theory	CFD
(c) Argon									
20.9	0.0	20.9	20.9	20.9	20.9	20.9	0.0	0.0	0.0
18.8	10.0	18.5	18.7	18.6	18.6	18.1	0.8	0.8	−2.2
16.7	20.0	16.2	16.6	16.4	16.4	15.5	1.4	1.4	−4.3
14.6	30.0	14.0	14.5	14.3	14.3	13.1	1.8	1.8	−6.3
12.5	40.0	11.8	12.4	12.1	12.1	10.9	2.7	2.7	−7.6
10.5	50.0	9.7	10.4	10.1	10.1	8.9	4.3	4.3	−8.0
6.0	71.3	–	–	5.7	5.7	4.8	–	–	–
3.0	85.6	–	–	2.8	2.8	2.4	–	–	–

Fixed O_2 conc.	Fixed He conc.	Detected O_2 concentration					% Error		
		AL1	AC1	Wilke	Linear theory	CFD	Wilke	Linear theory	CFD
(d) Helium									
20.9	0.0	20.9	20.9	20.9	20.9	20.9	0.0	0.0	0.0
18.8	10.0	20.0	20.2	20.6	21.0	20.2	3.1	5.0	1.0
16.7	20.0	19.0	19.2	20.2	20.8	19.4	6.1	9.4	2.1
14.6	30.0	17.7	18.3	19.5	20.2	18.5	10.1	14.2	4.7
12.5	40.0	16.3	17.0	18.6	19.3	17.5	13.8	18.2	7.6
10.5	50.0	14.7	15.5	17.4	18.0	16.4	18.0	22.3	11.9
6.0	71.3	–	–	13.0	13.3	13.1	–	–	–
3.0	85.6	–	–	8.0	8.1	9.2	–	–	–

summarises the gas concentrations measured using the two different types of sensor: with an alkaline electrolyte (referred to as 'AL1') and an acid electrolyte (referred to as 'AC1'). For comparison purposes, the model results should be compared to the AL1 sensor measurements. The final column in Table 2a–d provides the relative percentage error between the models and the AL1 sensor readings.

The tabulated results are presented graphically in Fig. 3. In each of the graphs the dotted line shows the idealised linear response, i.e. a straight line from 20.9% (v/v) oxygen to the origin. The model behaviour between the eight discrete points simulated is interpolated using a line of best fit, shown in the graphs with solid lines.

The measurement results show that of the gas mixtures tested, those containing helium produced by far the largest non-linear response. This was a consequence of the rapid diffusion of oxygen in helium–nitrogen mixtures. For a helium-enriched atmosphere containing an oxygen concentration of 18.8%, electrochemical oxygen sensors using either acid or alkaline electrolytes registered an oxygen concentration of 20.0% or more. This clearly has serious implications in terms of the sensors under-responding to the severity of the hazard. Moreover, both types of sensor responded slowly and showed anomalously large transient behaviour compared to the other diluents.

For atmospheres with high levels of carbon dioxide, the measurements show clear differences between the response of sensors with acid and alkaline electrolytes. In an atmosphere with an oxygen concentration of 18.8%, the alkaline-based sensor registered a concentration of 19.5% while the acid-based sensor registered a concentration of 18.9%. At typical alarm setpoints of 19 or 19.5%, the deviation for the alkaline-based electrolyte sensor was approximately 0.5% (v/v) (absolute) while that for the acid-based electrolyte sensor was less than 0.1% (v/v) (absolute). The observed positive deviations at carbon dioxide concentrations below 10–20% (v/v) (i.e. at oxygen concentrations of approximately 19–17% (v/v) respectively) are in agreement with the value of +0.3% of signal per % carbon dioxide quoted by Hobbs et al. [4]. This deviation is due to the reaction of the acidic carbon dioxide gas with
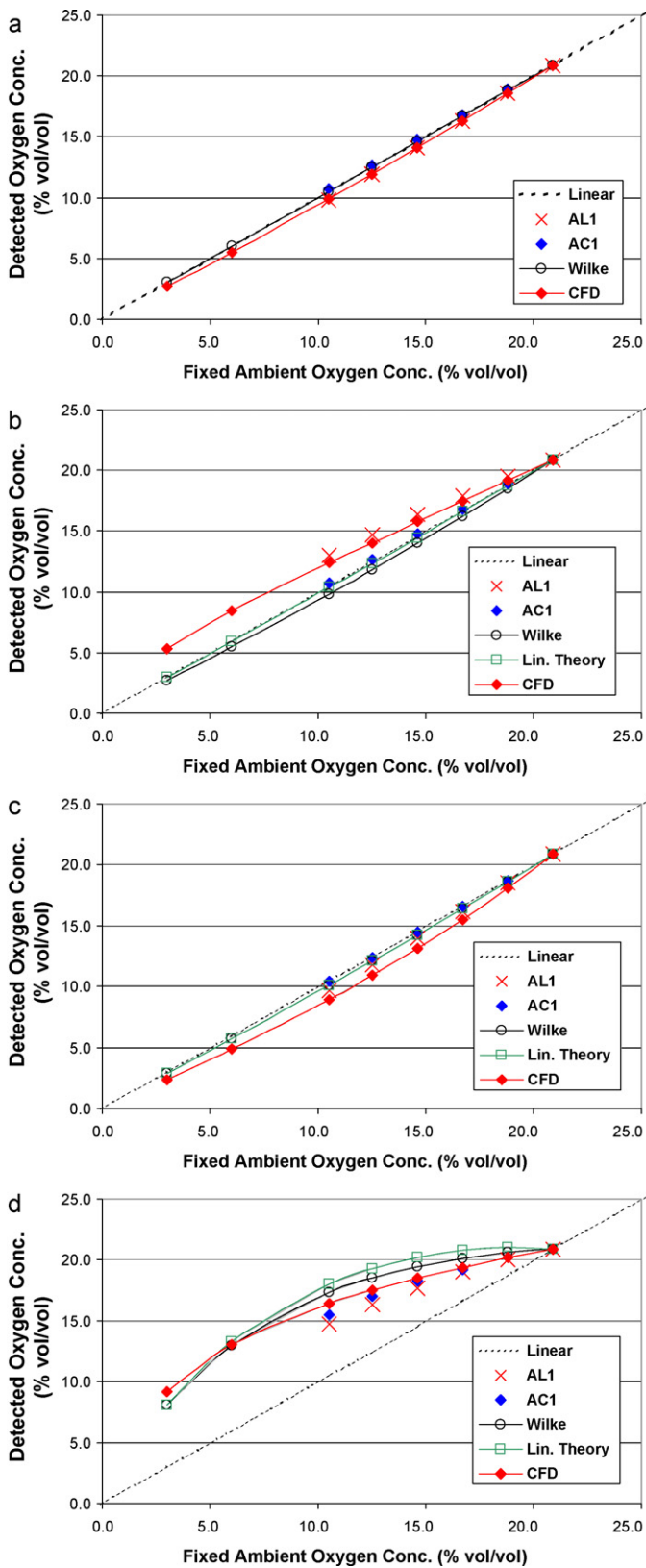
Fig. 3. Comparison of model predictions of oxygen concentrations to acid and alkaline electrolyte detector measurements (denoted AC1 and AL1, respectively) for mixtures of air with (a) nitrogen, (b) carbon dioxide, (c) argon or (d) helium.

the alkaline electrolyte enhancing bulk flow of oxygen to the electrode.

The response of sensors with either acid or alkaline electrolytes to atmospheres containing high concentrations of either nitrogen or argon was less non-linear than for helium or carbon dioxide gas mixtures. Both types of sensors recorded oxygen concentrations in reasonably good agreement with the set levels. The maximum absolute deviation of 0.8% (v/v) was recorded by the sensor with an alkaline electrolyte at very low oxygen concentrations of 10.5% (v/v).

The CFD model predicted the correct trend for the sensor to under- or over-read the actual ambient gas concentration in all of the cases examined experimentally. When air was diluted with nitrogen, the CFD model predictions agreed very well with the AL1 sensor readings, with a relative deviation of less than 1% (v/v). For the higher molecular mass gases (carbon dioxide and argon) the CFD model slightly under-predicted the experimental values while for the lighter gas (helium) the oxygen concentration was slightly over-predicted. In all but one of the cases, the predicted oxygen concentration was within 1.2% (v/v) (absolute) of the value measured by the AL1 sensor or in relative terms, a relative difference of less than 10%. In comparison, the repeatability of the experimental measurements (two standard deviations) was 0.2% (v/v), in absolute terms.

For the atmosphere diluted with nitrogen, the effective diffusivity model of Wilke [10] gave a linear response, as anticipated, and hence over-predicted the oxygen concentration detected by the AL1 sensor by up to 7.1%. Predictions using the linearised theory model were not made for this case. For the atmosphere diluted with carbon dioxide, both the Wilke and linearised theory models predicted qualitatively incorrect behaviour. The AL1 sensor detected overly high oxygen concentrations for this case, whereas the Wilke model predicted it to under-read and the linearised theory predicted an approximately linear response. For argon, the two models gave identical predictions of the detected oxygen concentration in good agreement with the AL1 sensor measurements, with a maximum relative error of 4.3%. For the final helium case, however, the Wilke and linearised theory models tended to over-predict the degree of non-linearity of the sensor response, with maximum relative errors of 18.0% and 22.3%, respectively. Overall, the performance of these two simple models was inferior to the CFD model in all cases except where the atmosphere was diluted with argon. Both models assumed that there was zero net flux along the capillary tube, whereas the CFD model accounted for convective fluxes. This is considered to explain the relatively poor performance of the Wilke and linearised theory models in the carbon dioxide and helium enriched atmospheres, i.e. the bulk flow of gas along the capillary tube was non-negligible in these cases.

A number of tests were undertaken with the CFD model to try to identify the possible causes of the differences between its predictions and the oxygen concentrations detected by the AL1 sensor. These explored the sensitivity of the model predictions to the orientation of the sensor with respect to gravity, the flow of air over the open end of the capillary tube, use of free-slip or no-slip boundary conditions on the capillary walls, the length of capillary tube and the numerical methods used by the model (i.e. use of a one-dimensional or three-dimensional representation for the tube, and grid resolutions of $1 \times 1 \times 64$ cells, $10 \times 10 \times 64$ cells, and $20 \times 20 \times 128$ cells). None of these factors was found to influence the model predictions to any significant degree. Details of the tests are described in Gant et al. [14].

A possible explanation for the differences between the CFD model and the helium dilution measurements is that in reality the oxygen concentration may not have fallen completely to zero at the reaction surface, although it was assumed to do so in the model. Under ideal conditions for the electrochemical sensor, where the

kinetics of reduction of oxygen are diffusion controlled rather than reaction rate controlled at the electrode–electrolyte interface, the effective oxygen concentration at this boundary is zero. All the oxygen reaching the electrode is effectively and immediately removed. However, in helium, the rate of diffusion of oxygen is considerably faster than in the other diluent gases (proportional to the inverse square root of the molecular weight). Consequently, the electrode reduction rate may not be so much greater than the diffusion rate, resulting in a low but non-zero level oxygen concentration at the electrode surface, i.e. the reduction reaction is now not quite fast enough to remove all the oxygen as it arrives. To investigate this matter, tests were performed using a modified CFD model that reduced the oxygen concentration to 2, 3, 4 or 5% (v/v) at the reaction surface, rather than zero. The case where the ambient oxygen concentration was only 10.5% (v/v) in helium and nitrogen was studied since this exhibited the greatest difference between model and measured oxygen concentrations. The results showed that as the oxygen concentration at the reaction surface was increased in the model, so the predicted non-linearity of the sensor response decreased. This trend was due to the non-linearity of the sensor response being largely due to the bulk flow of gas along the capillary tube in response to the oxygen consumption at the electrode/electrolyte surface. Model predictions were found to be in good agreement with the AL1 sensor measurements with an oxygen concentration of 3% (v/v) at the reaction surface. It is unclear, however, whether this concentration needs to be adjusted on a case-by-case basis to obtain agreement with the measurements.

For the other diluent gases, variations between the CFD model and the experiments cannot be explained by a non-zero oxygen concentration at the electrode as this would lead to poorer agreement. However, the differences for gases other than carbon dioxide, which has an effect dependent on the type of electrolyte (acid or alkaline), are not as great as with helium and may be due to normal variability in sensor response and other effects such as temperature. The CFD model presented here uses a single effective diffusivity for all of the components. In a ternary mixture, this approach is likely to provide best predictions when the binary diffusivities of the three component gases are similar. The CFD predictions may be improved by using a more accurate diffusivity model, for instance, the linearised theory approach. This could be explored in future studies.

6. Conclusions

The response of electrochemical oxygen sensors with acid or alkaline electrolytes to air atmospheres containing enhanced levels of nitrogen, carbon dioxide, helium and argon have been measured. The results have shown that sensors with either acid or alkaline electrolytes over-read the oxygen concentration, i.e. underestimate the asphyxiation hazard, when atmospheres contain high levels of helium. Sensors calibrated simply by exposure to atmospheres diluted by nitrogen should therefore not be utilised in atmospheres contaminated by helium. Indeed, great care should be taken when measuring oxygen in helium–air mixtures with electrochemical sensors because of their long response times and anomalous behaviour.

Sensors with alkaline electrolytes have also been shown to underestimate the severity of the hazard in atmospheres containing high levels of carbon dioxide. Alkaline electrolyte sensors exhibit significant deviations from the true value whereas acid electrolyte sensors do not. At concentrations around 19 and 19.5% (v/v), which are typically set as oxygen deficiency alarm levels, the deviation is approximately 0.5% (v/v) oxygen (absolute) for alkaline electrolyte sensors. Although the deviation is not large, it can be compensated for by calibration in carbon dioxide–air

mixtures, if carbon dioxide is known to be the only asphyxiating hazard.

Also, it is worth noting that if carbon dioxide is suspected in the atmosphere, then a carbon dioxide monitor should also be used in conjunction with an oxygen monitor since toxic levels of carbon dioxide are reached well before the oxygen concentration is depleted to typical alarm levels of 19.5–19% (v/v) oxygen. Workplace Exposure Limits for carbon dioxide are 5000 and 15,000 ppm for 8-h time-weighted average and 15-min exposures respectively [15]. When carbon dioxide displaces air containing 20.9% (v/v) oxygen, 5000 ppm (0.5%, v/v) carbon dioxide results in an oxygen concentration of approximately 20.8% (v/v), while 15,000 ppm (1.5%, v/v) carbon dioxide results in an oxygen concentration of approximately 20.6% (v/v). At oxygen concentrations around the alarm level (19%, v/v) carbon dioxide levels could be much greater (approximately 10%, v/v) if caused by dilution of air by pure gas. The IDLH (immediately dangerous to life or health) level for carbon dioxide is 4% (v/v) [16] while at 10% (v/v) carbon dioxide the threshold of unconsciousness is approached in 30 min; and at 20% (v/v) carbon dioxide, unconsciousness occurs in less than 1 min [17].

Reasonably accurate measurements of oxygen concentrations have been obtained using either acid or alkaline-based sensors in atmospheres with high levels of either nitrogen or argon. It is always good practice to calibrate around the region of interest, which for occupational personal exposure measurements is the alarm level of 19–19.5% (v/v) oxygen. However, the error arising from calibration at the normal atmospheric level of 20.9% (v/v), which is convenient to use, is small. When lower oxygen concentrations are required to be measured, e.g. in process safety, as would occur in inerting operations, then deviations from the linear oxygen in nitrogen response are larger and calibration with the appropriate diluent concentrations becomes necessary.

A CFD model has been developed to predict the response of sensors with alkaline electrolytes and predictions have been compared to the measurement data. For all of the gas mixtures tested, the trend for the sensor to under- or over-read the actual gas concentration was correctly predicted by the model. In all but one of the cases, which featured a very low oxygen concentration in a helium-enriched atmosphere, the difference between predicted and measured sensor responses was less than 10% in relative terms (an absolute difference of 1.2% oxygen by volume), and in many cases the relative difference was less than 5%. Tests showed that the small errors between the model and measured values may have been due to the oxygen concentrations falling to a low but still finite value at the reaction surface with the sensor in a helium-enriched atmosphere, whereas in the model it was assumed to fall to zero. The CFD model was also shown to produce more accurate predictions of the detector response than the effective diffusivity model of Wilke [10] or the linearised theory model of Toor [11] and Stewart and Prober [12] (assuming zero net flux), for all of the cases examined, with the exception of the argon-enriched atmospheres, where the detector response was nearly linear in any case.

Further possible applications of this CFD-based model include interpolation or extrapolation of sensor response beyond the conditions tested in the laboratory, and prediction of the likely sensor response to the presence of gases not previously measured. Extending the model to simulate sensors with acid electrolytes would be straightforward.

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