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Solid state potentiometric oxygen gas sensors

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Oxygen gas sensors, operating in the potentiometric (zero current) mode, based upon oxygen ion conducting solid electrolytes are reviewed. Detailed consideration is given to practical aspects of their composition, construction and operation.

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1. Introduction

Solid state potentiometric oxygen gas sensors are being used in increasing numbers in industry for a variety of applications. As cheaper devices become available they will routinely be used in domestic appliances and internal combustion engines. It is the purpose of this article to review recent literature particularly with respect to the practical aspects of these sensors including construction, accuracy and range of oxygen pressures measurable, and to suggest possible directions of further development.

2. Background

2.1. *Theory*

The cell

$$O_2(P'_{O_2}),\ \mathrm{Me}\ \left|\ \begin{array}{c} O^{2-}\ \text{conducting} \\ \text{solid electrolyte} \end{array}\ \right|\ \mathrm{Me},\ O_2(P''_{O_2}) \qquad (1)$$

develops an e.m.f., E, between the metal electrodes, Me, given by [1]

$$E = (RT/4F) \int_{P'_{O_2}}^{P''_{O_2}} t_{\mathrm{ion}}\, d \ln P_{O_2} \qquad (2)$$

In practice the metal electrodes may be platinum, silver or other precious metals. R is the gas constant, T the absolute temperature, F the Faraday number and t_{ion} the transport number of the ions in the solid phase. If t_{ion} is close to unity then Equation 2 simplifies to

$$E = (RT/4F) \ln (P''_{O_2}/P'_{O_2}) \qquad (3)$$

In practice one of the gases is used as a reference of known oxygen partial pressure (P'_{O_2}) and the other is the sample gas (P''_{O_2}). In this case Equation 3 may be written

$$E = E_1 + (RT/4F) \ln P''_{O_2} \qquad (4)$$

where E_1 is a constant of value $-(RT/4F) \ln P'_{O_2}$. Commonly used reference gases are pure oxygen ($P'_{O_2} = 1$) or air ($P'_{O_2} = 0.21$). Equation 4 shows that a decade change in P''_{O_2} results in a change in E of approximately 50 mV at 1000 K.

2.2. *Applications*

The principal applications of oxygen gas sensors include the following.

(i) Control of combustion in boilers burning fossil fuels to maximize efficiency and minimize the generation of CO[2, 3]. The efficiency of domestic and other systems may be raised by partial condensation of the water vapour in the flue and consequent extraction of latent heat: minimization of excess air is advantageous to raise the dew point of exhaust gases. Control may be effected continuously with a permanently installed monitor or intermittently using a portable instrument to make periodic checks and adjustments of the system.

(ii) Monitoring and control of atmospheres in metallurgical heat treatment furnaces [4].

(iii) Control of car exhaust gases for protection of three-way catalyst systems [5].

(iv) The control of P_{O_2} in laboratory applications using pump-gauge devices [6, 7]. The range of oxygen pressures which may be realized using such equipment covers the very wide range from approximately 10^{-27} to 1 atmosphere [2].

(v) The proposed 'lean-burn' car engine requires the development of a suitable oxygen sensor, combining ruggedness in the aggressive environment of the exhaust, adequate speed of response (~ 100 ms), long-term stability ($> 20\,000$ miles) and low price when produced in high volumes. The attraction of lean-burn is improved fuel economy combined with low emissions of CO, NO_x and hydrocarbons. However, a precise air–fuel (A/F) ratio must be maintained for smooth running of the internal combustion engine. In the lean region the e.m.f. of the potentiometric sensor is only weakly dependent upon A/F ratio and the development of suitably sensitive devices has not yet been achieved [3].

3. Practical aspects

3.1. *Electrolytes*

Potentiometric oxygen sensors incorporate oxygen-ion conductors, e.g. ZrO_2, CeO_2, ThO_2, Bi_2O_3, as electrolytes. Ionic conductivity of the quadrivalent oxides is improved by doping with aliovalent oxides which generate high concentrations of anionic vacancies and also tend to stabilize the structure in the high-temperature form (fluorite).

In a measurement of P_{O_2} the total impedance of the sensor should be negligible compared with the input of the voltmeter, both to minimize errors due to iR effects and to reduce noise in the circuit. A value of 1 MΩ has been suggested [2] as an acceptable upper limit for the impedance of a sensor. The conductivity of the electrolyte increases as the temperature is raised, the ionic mobility being a thermally activated process with a typical activation energy of 100 kJ mol^{-1}.

A requirement for accurate measurements is that, at the working temperature, the electronic partial conductivity should be very small [8] so that t_{ion} in Equation 2 is close to unity. Further, the physical permeability of the electrolyte should be negligible to prevent mixing of the reference and sample gases, and thermal shock resistance should be sufficient to prevent cracking during operation.

Electrolytes based upon ZrO_2 (e.g. ZrO_2–Y_2O_3 or ZrO_2–CaO) are most commonly used at the present time. Conductivity varies with the type of dopant in the order $Yb_2O_3 > Y_2O_3 > CaO > MgO$ [9] and is maximized at the minimum dopant level necessary to achieve full stabilization of the cubic phase. Lower dopant levels achieve partial stabilization resulting in a cubic phase with tetragonal precipitates. Commonly, sensors incorporate polycrystalline fully stabilized ZrO_2 (FSZ) to take advantage of the high conductivity. However, this material has lower thermal shock resistance than partially stabilized material (PSZ) or the metastable polycrystalline tetragonal material (TZP). Recent work has shown that suitably prepared PSZ or TZP can have conductivities adequate for sensors, with the high fracture toughness providing a distinct advantage [10]. In fact, at temperatures below 400° C TZP is expected to have superior conductivity to FSZ if grain boundary effects can be ameliorated by improved fabrication procedures [11]. A further advantage of Y_2O_3-doped PSZ and TZP over FSZ is that the fraction of costly Y_2O_3 is reduced.

Steele *et al.* [12] have discussed the requirements for electrolytes and made the following observations. When a sensor is subjected to a P''_{O_2} change, the composition of the surface, and more slowly that of the bulk, come to equilibrium with the final oxygen pressure. The rate of which the bulk achieves this is many orders of magnitude slower than the process at the surface. The correct e.m.f. is observed, however, after only a few milliseconds even though the diffusion process is continuing, because t_{ion} is effectively a constant and can be placed in front of the integral in Equation 2. Conseqently the e.m.f. is determined only by the boundary conditions at the two gas–solid interfaces. However, where an electrolyte contains impurity second phase then theoretical analysis [13] indicates that the e.m.f. developed is dependent upon the concentration profile in the bulk and hence an equilibrium e.m.f. is developed only slowly. The magnitude of deviation from correct values depends upon the transport properties of the second phase. If t_{ion} in the second phase is close to unity then erroneous e.m.f. effects should be absent.

Under reducing conditions (10^{-20} atm), volatilization of a grain boundary phases may occur.

$$SiO_2 \rightarrow SiO\uparrow + \tfrac{1}{2}O_2\uparrow \tag{5}$$

$$MgO \rightarrow Mg\uparrow + \tfrac{1}{2}O_2\uparrow \tag{6}$$

This can generate permeability in the ceramic which is undesirable. Thus zirconia-based ceramics should be as pure as possible for potentiometric applications.

3.2. *Electrodes*

The oxygen electrode reaction is (in Kroger–Vink notation)

$$\tfrac{1}{2}O_2 + 2e' + V_O^{\cdot\cdot} \rightleftharpoons O_O^x \tag{7}$$

Clearly this process involves the gas phase (O_2), the electrode (e′) and the electrolyte ($V_O^{\cdot\cdot}$, O_O^x) and this has prompted the suggestion that the reaction occurs at the three-phase boundary. Certainly, the steps making up the overall process shown in Reaction 7 take place at or close to the boundary and this indicates that requirements of the electrode should include good adhesion between the porous electrode and electrolyte and a long three-phase boundary [14–16].

Suitable electrodes may be obtained by the application of a platinum paint [17] which is first dried and then fired in air to burn off organic binders and to promote adhesion. Some commercial paints contain mineral binders: these are undesirable, particularly if their components change valency in the operational pressure range or if they form a glassy phase [18]; the former introduces sluggish response, particularly in unbuffered systems at low P_{O_2} values, while the latter renders the electrode inactive resulting in voltage drift and slow response. If the firing temperature is high, then recrystallization and sintering of the platinum takes place which decreases both the porosity and length of the three-phase boundary. This happens, albeit more slowly, during operational use [19]. Hence firing and operating temperatures should be minimized to maintain the activty of the electrodes [20].

Platinum electrodes, which may be applied by techniques other than painting (for example sputtering, printing, evaporation), behave catalytically, and at elevated temperatures bring the components of the gas phase at the gas–solid interface to thermodynamic equilibrium. The measured e.m.f. then relates to the equilibrium P''_{O_2} rather than actual, non-equilibrium value. In many, but not all, cases it is the equilibrium P''_{O_2} which is required. Haaland [21] investigated the catalytic properties of electrodes and found that platinum could be poisoned with lead so that the measured P''_{O_2} then corresponded with the bulk non-equilibrium value at temperatures above 500–550° C; at lower temperatures even lead-poisoned platinum electrodes are catalytic. Silver electrodes are also non-catalytic.

At P_{O_2} values greater than 10^{-3} atm the electrode system at 700° C has a characteristic frequency, from a.c. impedance analysis, in the range 10^2–10^3 Hz [12]. This indicates that the electrode responds to changes in P_{O_2} within a few milliseconds.

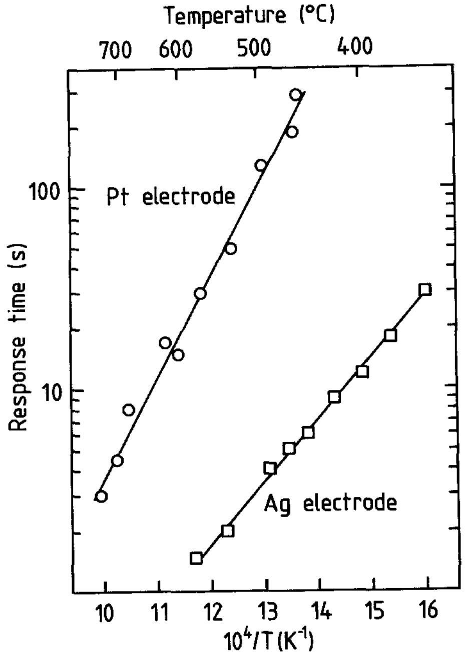

Fig. 1. Time for 99% change in e.m.f. in response to a change in air pressure from 760 to 300 torr for platinum and silver electrodes as a function of temperature [22].

Fouletier *et al.* [22] measured response times of platinum and silver electrodes as functions of temperature (Fig. 1). These data represent a 99% change in the e.m.f. between the initial and final states. They show firstly that silver electrodes respond faster than platinum electrodes and secondly that the response deteriorates rapidly with decreasing temperature. Gold may also show an order of magnitude improvement in response time compared with platinum [23]. At 500° C the response time at these relatively high oxygen pressures is $\sim 2\,\text{min}$ on platinum. As is shown later, this deteriorates significantly at lower P''_{O_2} values.

3.3. *Temperature effects*

In this section, only effects relating to sensors with gaseous references will be considered: effects with metal–metal oxide references are discussed later. There are three principal temperature effects resulting in errors in the measured value of P''_{O_2}. The first effect arises simply from the presence of the T term in Equations 2–4 and may be quantified for small $\Delta P''_{O_2}/P''_{O_2}$ values by the equation [24]

$$\Delta P''_{O_2}/P''_{O_2} = 4FE\Delta T/RT^2 \tag{8}$$

This relationship shows that error in the measured P''_{O_2} is proportional to both E and ΔT. Thus the error may be minimized by using a gaseous reference oxygen pressure similar to that of the sample gas. Values of $\Delta P''_{O_2}/P''_{O_2}$ calculated using Equation 8 for sample gases over a wide P''_{O_2} range using an air reference are shown in Fig. 2a. An important region of measurement in the flues of small boilers is that around 2% O_2 (this corresponds to approximately 10% excess air in a gas-burning system). Fig. 2 shows that an error in the temperature of $\pm 20°$ C would only result in an error in P''_{O_2} of 5%, i.e. $P''_{O_2} = 0.02 \pm 0.001$ which for the purposes of control is negligible. The temperature of the sensor is normally measured with a thermocouple and the above calculation shows that for this particular application, cold-junction compensation is not necessary. At much lower P''_{O_2} values, for example in the reducing region at $P''_{O_2} = 10^{-18}$, an error of 1° C would introduce an error in the calculated pressure of 4% and clearly for accurate work cold-junction compensation for the thermocouple becomes important.

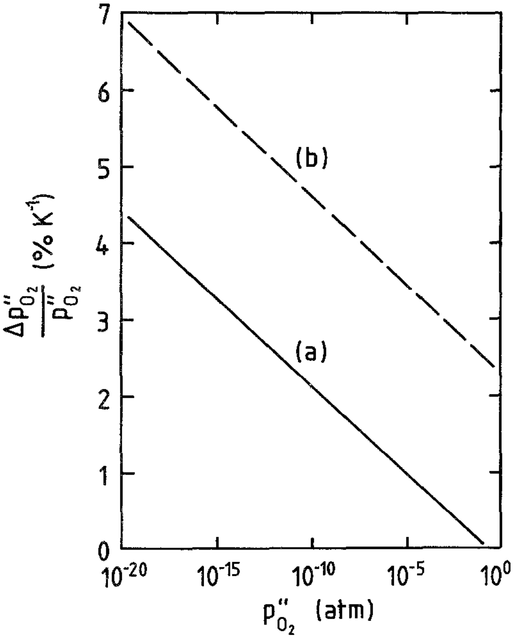

Fig. 2. Error in measured pressure resulting from each degree error in temperature for gauge operated at approximately 1000 K, (a) with an air reference or (b) a metal–metal oxide reference. Temperature coefficient of oxide reference (dE_A/dT) versus O_2 (1 atm) taken as $0.5\,\text{mV}\,\text{K}^{-1}$.

The second effect results from differences in temperature between the two electrodes giving rise to a thermoelectric e.m.f. Fouletier *et al.* [22] have derived an equation relating to this e.m.f. with the temperature difference. It has been shown [24] that if the cell temperature is measured at the reference electrode, the thermoelectric e.m.f. (mV) for temperatures close to 1000 K is given by

$$\Delta E_R = (0.52 + 0.05 \log P''_{O_2})\,\Delta T \qquad (9)$$

and if measured at the sample electrode

$$\Delta E_S = (0.52 + 0.05 \log P'_{O_2})\,\Delta T \qquad (10)$$

The advantage in determining the temperature at the sample electrode is that the error varies only with the temperature difference as the reference oxygen pressure, P'_{O_2}, is constant. It follows from Equation 10 that if an air reference is used,

$$\Delta E_S = 0.49\Delta T\,(P'_{O_2} = 0.21) \qquad (11)$$

An e.m.f. offset of 0.5 mV is therefore anticipated for each degree difference in temperature between the electrodes. This can be detected with the same gas (e.g. air) in contact with both electrodes. At 1000 K an error of 0.5 mV in the cell voltage corresponds to an error of 2.3% in the measured P''_{O_2} value [24]. For accurate work the temperature differential must be minimized by paying attention to furnace design in order to achieve a flat temperature profile over the working region.

The third effect arises where there are temperature variations across a single electrode; a particular case in point is where the electrode is extended by painting a 'stripe' on the electrolyte from the electrode to a cooler region to act as an electrode connection. As a result the porous metallic coating has an electrochemical potential which varies along its length and this causes circulating currents to flow. The voltage measured is a mixed potential which may differ substantially from the true equilibrium potential at the sensor tip [22]. This problem can be solved by using electrodes which do not extend beyond the constant temperature region of the furnace and making connection via a platinum wire.

3.4. *Range of operation*

The range of oxygen pressures over which potentiometric sensors can operate is more than 20 orders of magnitude under appropriate conditions. The situation where O_2 is measured diluted with an inert gas, e.g. argon, will be considered first. In this case a most important limitation is semipermeability of the electrolyte. As the P''_{O_2} value is decreased, the partial electronic conductivity increases as a result of electron generation.

$$O_O^x \rightleftharpoons \tfrac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e' \qquad (7)$$

A similar effect can also occur at high P''_{O_2} values with the consequent generation of holes (h).

$$V_O^{\cdot\cdot} + \tfrac{1}{2}O_2 \rightleftharpoons O_O^x + 2h^{\cdot} \qquad (12)$$

Thus at high and low P''_{O_2}, t_{ion} may depart significantly from unity, which results in an error in the calculated value of P''_{O_2} when the assumption $t_{\text{ion}} = 1$ in Equation 3 is made. The e.m.f. is modified by an overpotential due to the passage of current [2] which also results in transport of oxygen from the high to the low pressure side. The evolution of O_2 into the low pressure region causes substantial deviations in the P''_{O_2} value measured at the electrode when P''_{O_2} is small (e.g. p.p.m. levels). The latter effect may be aleviated in two ways. The first is to use a ZrO_2-tip electrode in the sample gas compartment [25]. This allows the measurement to be made in the bulk of the sample gas rather than at the surface of the electrolyte separating the two gases. The second method is to use a differential gauge [26] in which the cell

$$P'_{O_2},\ \text{Pt}\,|\,\text{solid electrolyte (SE)}\,|\,\text{Pt},\ P''_{O_2} \qquad (13)$$

is replaced by the coupled cells

$$P'_{O_2},\ \text{Pt}\,|\,\text{SE}\,|\,\text{Pt},\ P'''_{O_2},\ \text{Pt}\,|\,\text{SE}\,|\,\text{Pt},\ P''_{O_2} \qquad (14)$$

The two platinum electrodes in the centre compartment are electronically connected so that the theoretical e.m.f.s of cells (13) and (14) are identical. P'''_{O_2} is chosen to lie between P'_{O_2} and P''_{O_2} but closer to the latter. This reduces the semipermeability flux into the sample compartment which contains the electrode most sensitive to permeability perturbations.

The problems due to semipermeability are most serious at high and low oxygen pressures and at high temperatures as summarized in Fig. 3 for a ZrO_2-based and a ThO_2-based electrolyte [8]. Similar diagrams may be drawn for other solid electrolytes. CeO_2–Y_2O_3, for example, has a higher

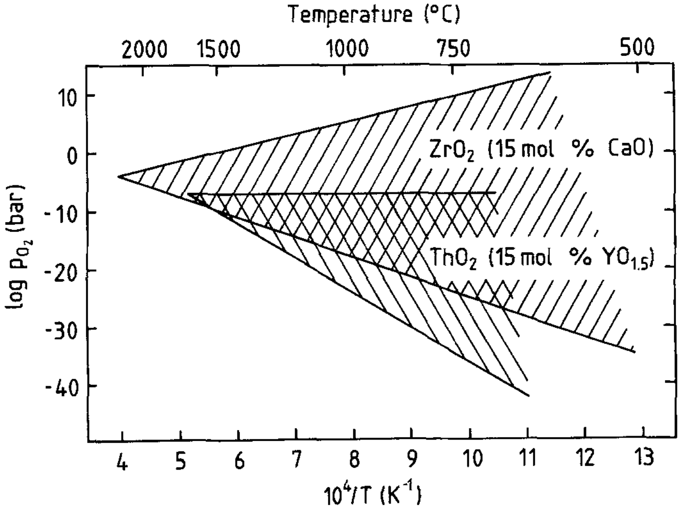

Fig. 3. Range of temperatures and partial pressures (shown shaded) in which the electronic partial conductivity amounts to < 1% of the total conductivity [8].

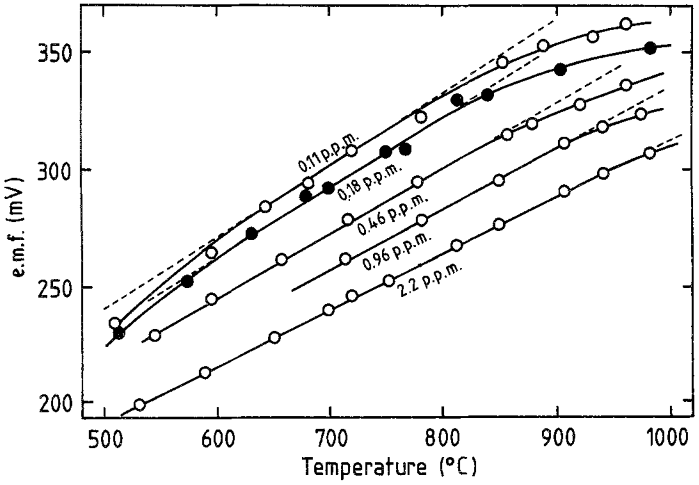

Fig. 4. Oxygen pressure measurements in unbuffered gas mixtures between 550 and 1000° C [18]. Theoretically predicted results shown as broken lines for the indicated oxygen levels.

conductivity than ZrO_2–Y_2O_3 (by a factor of 3–4) but has too high a semipermeability for accurate use [27].

Data for a ZrO_2–5.5 wt % CaO tube at low oxygen partial pressures (in argon) [18] are shown in Fig. 4. The results indicate that it is possible to make measurements of P''_{O_2} in unbuffered gas mixtures down to 0.1 p.p.m. O_2, provided the operating temperature is chosen as a compromise between the overpotentials generated by the semipermeability current; the current increases at higher temperatures and the electrode impedance increases at lower temperatures [18].

The above discussion relates to an equilibrium situation where the P''_{O_2} may be held constant for an extended period (several hours if necessary). However, for most applications a reasonably rapid response is required to detect changes in P''_{O_2}. Response times were measured by Fouletier *et al.* [22] and are shown in Fig. 5. If extrapolation is legitimate the response time for $P''_{O_2} = 10^{-6}$ atm at 700° C is ~2 h with a platinum electrode. This is an indication of the small exchange current densities at the p.p.m. level and suggests that in this region the sensor output could be drastically perturbed by the presence of other redox systems such as H_2–H_2O, CO–CO_2 or dust particles containing variable valency elements. Anthony *et al.* [24] reported a sharp change in sensor voltage at oxygen contents below 0.1 p.p.m. which they attributed to traces of CO_2 and H_2O. Etsell and

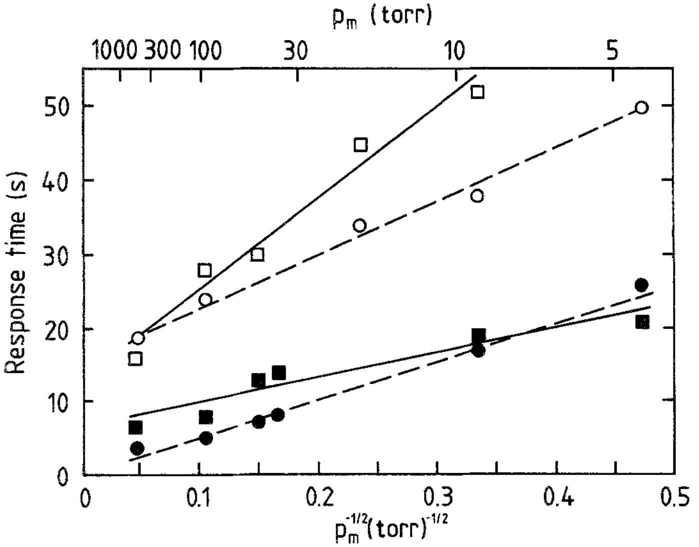

Fig. 5. Time for 99% change in e.m.f. in response to a 25% pressure increase for platinum (○, ●) and silver (□, ■) electrodes [22]. Temperatures: ○, 620° C; ●, 730° C; □, 440° C; ■, 500° C. P_m is the mean of the initial and final oxygen pressures.

Flengas [28] point out that for purified argon, P''_{O_2} is controlled by small amounts of CO, CO_2, H_2 and H_2O present.

Attention will now briefly be turned to buffered systems such as $CO-CO_2$ and H_2-H_2O. Appropriate ratios of these gases allow generation of P_{O_2} values in the ranges $10^{-5}-10^{-21}$ and $10^{-20}-10^{-23}$ atm, respectively [8], according to

$$CO_2 \rightleftharpoons CO + \tfrac{1}{2}O_2 \tag{15}$$

and

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2}O_2 \tag{16}$$

These mixtures are much less sensitive to errors resulting from semipermeability flux. The reasons for this are, firstly, that O_2 coming through from the high P_{O_2} to the low P_{O_2} side reacts rapidly with the reduced species in Equations 15 and 16 and as a result only marginally perturbs the P_{O_2} at the measuring electrode. Secondly, the exchange current density is high in the buffered mixtures and principally involves the oxidized and reduced species

$$CO_2 + V_{O}^{\cdot\cdot} + 2e' \rightleftharpoons CO + O_{O}^{\times} \tag{17}$$

and

$$H_2O + V_{O}^{\cdot\cdot} + 2e' \rightleftharpoons H_2 + O_{O}^{\times} \tag{18}$$

As a result, overpotentials due to the semipermeability electronic current are small and the measured e.m.f. is close to the theoretical value. The high exchange current density in well-buffered systems has a further consequence: although the P_{O_2} is very small the electrode response is not excessively long [29]. With $CO-CO_2$ mixtures in the ratio range $10^{-2}-10^{2}$ the response time was a few minutes. Weakly buffered mixtures with ratios $< 10^{-3}$ or $> 10^{3}$ showed response times ~ 1 h at 900° C.

3.5. *Reference oxygen systems*

The most commonly used reference gas is air because of its ready availability and the fact that the dry gas is of very constant composition. However, if the air is not dried before presentation to the reference electrode an error is introduced. Verdin [30] has pointed out that the oxygen content of dry air is 21% while that of air at 20° C and 80% relative humidity is only 20.6%. The resulting error in the measured P''_{O_2} in this case is 2%. Alternatively, where air at the measuring point may be polluted, dry oxygen may be used as the reference gas.

Errors due to semipermeability of the electrolyte may be reduced by using a reference gas of similar oxygen partial pressure to that of the sample gas. This can sometimes be achieved by use of a metal–metal oxide reference which generates a P'_{O_2} fixed by the temperature of operation. Selection of an appropriate redox system may be made from thermodynamic data. This, of course, does not solve the problem of temperature effects as the oxygen pressure in thermodynamic equilibrium with a given metal oxide is itself temperature sensitive. Consider the following metal–metal oxide couple

$$xM + yO_2 \rightleftharpoons M_xO_{2y} \tag{19}$$

with standard free energy of reaction ΔG^0. The equilibrium oxygen partial pressure is given by

$$\Delta G^0 = RTy \ln P'_{O_2} \tag{20}$$

For the passage of n faradays of charge, one mole of M_xO_{2y} is transformed in the cell

$$M,\ M_xO_{2y},\ O_2(P'_{O_2}),\ Pt\,|\,SE\,|\,Pt,\ O_2\,(1\,\text{atm}) \tag{21}$$

which has an e.m.f. E_A. Then

$$E_A = -\Delta G^0/nF\;(n = 4y) \tag{22}$$

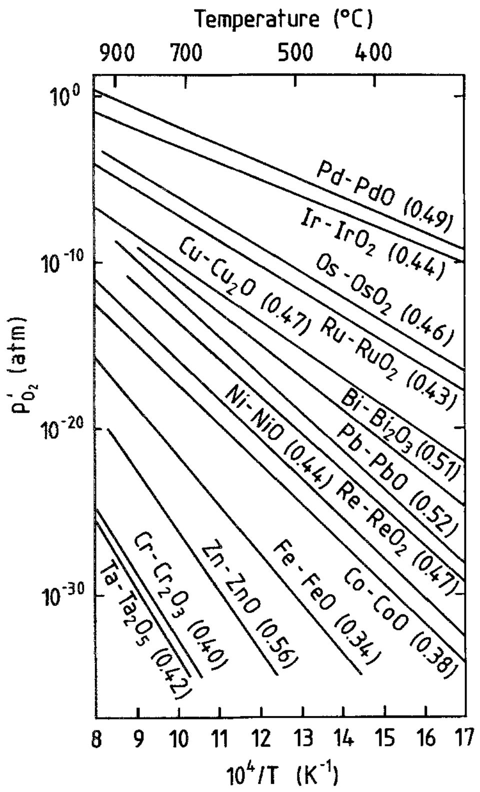

Fig. 6. Oxygen pressure in equilibrium with a range of metal–metal oxide couples versus reciprocal temperature. Temperature coefficients of e.m.f. versus O_2 (1 atm) shown in parentheses (mV K^{-1}); estimated accuracy ± 0.03.

and

$$\frac{dE_A}{dT} = -\frac{1}{4yF}\frac{d\Delta G^0}{dT} \tag{23}$$

Oxygen partial pressures for a number of systems are shown in Fig. 6 from data extracted from [31–34]. As can be seen, a very wide range of P'_{O_2} values can be generated using an appropriate redox system. Also shown on Fig. 6, in parentheses, are temperature coefficients for the various systems. They generally lie in the range 0.4–0.5 mV K^{-1} and are similar because the free energy of the reaction is dominated by the entropy change of the condensation process (gaseous oxygen $\rightleftharpoons$ solid oxide). The couples Fe–FeO, Cr–Cr_2O_3 and Co–CoO have the most favourable temperature coefficients, while the commonly used Pd–PdO is at the upper end of the range.

In order to estimate the error due to uncertainty in the temperature when using a redox system as reference it is convenient to consider Cells 21 and 24.

$$O_2(1\,\text{atm}),\ \text{Pt}\,|\,\text{SE}\,|\,\text{Pt},\ O_2(P''_{O_2}) \tag{24}$$

Cell 24 has an e.m.f. E_B. The e.m.f. of the cell

$$\text{M},\ \text{M}_x\text{O}_{2y},\ O_2(P'_{O_2}),\ \text{Pt}\,|\,\text{SE}\,|\,\text{Pt},\ O_2(P''_{O_2}) \tag{25}$$

is E_C where

$$E_C = E_A + E_B \tag{26}$$

Then

$$dE_c/dT = dE_A/dT + dE_B/dT \tag{27}$$

The term dE_A/dT has been determined using Equation 23 and is always negative because the oxygen pressure above the redox system increases with temperature. The e.m.f. E_B is given by

$$E_B = (RT/4F) \ln P''_{O_2} \tag{28}$$

$$dE_B/dT = (R/4F) \ln P''_{O_2} \tag{29}$$

The sign of dE_B/dT is therefore the same as that of ln P''_{O_2}, i.e. negative for P''_{O_2} values less than that of pure O_2 at 1 atm, which is the usual case. Hence both E_A and E_B are both normally negative and therefore additive (for $P''_{O_2} < 1$). The error resulting per degree for Cell 25 in the case where $dE_A/dT = 0.5\,\mathrm{mV\,K^{-1}}$ is shown in Fig. 2b. Over the whole P''_{O_2} range shown, the error when using a metal–metal oxide reference is clearly greater than when using an air reference.

At first sight it seems surprising that reference systems such as $Cr–Cr_2O_3$, Fe–FeO or $Cu–Cu_2O$ operate as well as they do in view of earlier comments regarding the exchange current density at P_{O_2} values below 10^{-6} atm. This suggests that either the redox systems participate via a direct solid state reaction or that the atmosphere above the metal–metal oxide contains a buffer such as CO_2 or H_2O. The solid state process is possible for material directly in contact with the electrode but not for more remote material. It is suggested, therefore, that the redox systems would probably lose their effectiveness if care were taken to eliminate CO_2, and more particularly H_2O, during their preparation. These gases can act as intermediaries, effectively carrying O_2 between the redox system and the electrode.

A final point which should be made is that the thermodynamically calculated P'_{O_2} is only achieved while both components of the redox system are present. If either becomes totally exhausted then the oxygen pressure will deviate from the calculated value. Consideration should therefore be given, when preparing the reference electrode, to whether leakage of O_2 is likely to occur into or out of the reference and this will be determined by the likely pressure differential between the reference and sample gases. In cases where there is an equal likelihood of transport in both directions then equivalent amounts of metal and oxide according to Reaction 19 should be incorporated.

3.6. *Sampling*

In order to measure the P''_{O_2} value of a sample the gas must be introduced to the measuring electrode. This may be accomplished by diffusion or by pumping, and the selection of the process depends upon the response time required of the sensor and on practical factors specific to the particular application. Where sampling occurs by diffusion [35] the sensor must be located close to the source of the sample gas or alternatively in the sample gas stream so that response times do not become excessively long. This approach has the advantage that gas pumps can be omitted, condensation of water vapour in gas lines is obviated and dust is not pumped into the sensor. For applications such as the continuous trimming of large boiler installations, a response time of 1–2 min is of no consequence and may even damp out oscillations of the system. In general, however, rapid response is preferred and this entails flowing the sample gas into the sensor. Condensation problems may be aleviated by heating sample lines. This mode of operation has advantages other than rapid response. The furnace maintaining the sensor at constant temperature may more easily be isolated from the sample gas and being remote from the system may be controlled very precisely; the orifice which must be made to allow sampling need only be small and hence physical alteration and damage to the system is minimized; the sensor is external to the system so that servicing is simplified. A disadvantage of pumping is leakage of air into the sample which is most likely to occur in a suction system [30]. If a sample contains 2% O_2 but on reaching the sensor has been mixed with 2% air due to leakage then the sensor reading would be 19% high. Hence samples should be pressurized as early in the sample train as possible. This, of course, still does not solve the problem, since where the P_{O_2} in the line is lower than that in the atmosphere, back diffusion through the leak will still occur.

Sometimes water-scrubbing is used to clean a gas sample, e.g. from an oil-fired furnace because of the content of tar, soot and sulphur compounds, and then consideration must be given to the effect that this has on the measured P_{O_2}. Water washing removes CO_2 which, in the flue of a boiler, represents a substantial fraction of the gas; the water vapour pressure is also changed. A further possible error arises from the liberation of air from the water used for scrubbing. Gas flow can also generate a differential pressure which can introduce an error [24], and can cool the sample electrode [28].

Anderson and Graves [36] measured the response time of a potentiometric sensor to a change of P''_{O_2} in O_2–N_2 mixtures. They showed an asymmetry in the e.m.f. response, the device apparently being more rapid in changing from low to high P''_{O_2} than in the reverse direction. This effect has been confirmed in other work [22] and arises from the logarithmic dependence of e.m.f. upon P''_{O_2} (Equation 3). Examination of the computed pressure (rather than e.m.f.) against time curves reveals elimination of the asymmetry, the response time for a given percentage change in computed pressure being independent of the direction of the pressure change.

3.7. *Practical designs*

Generally, devices must separate the sample and reference gases and this has been achieved in a number of ways. Two similar devices, one using an open-ended and the other a closed-end tube are shown in Fig. 7. In Fig. 7a the sample gas flows through the tube and the e.m.f. is measured between the inner and outer electrodes. If the tube is sufficiently long, the ends are relatively cool and connections to the tube present no difficulty. The same applies to the closed-end tube in Fig. 7b. These

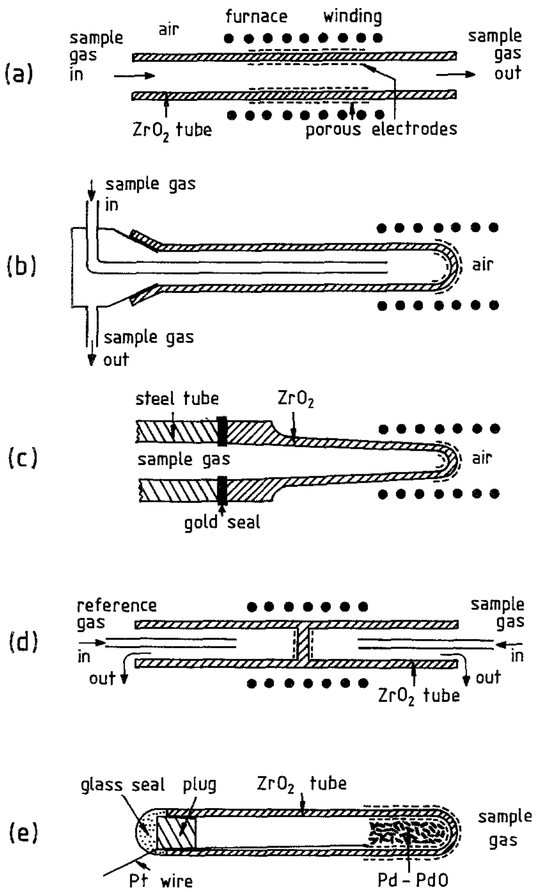

Fig. 7. Various configurations of potentiometric sensors.

designs are often used in laboratory applications, but long ZrO_2 tubes are expensive and industrial sensors are usually more compact as they incorportate less ZrO_2. The thimble type is shown in Fig. 7c [35] and in this case the electrolyte which is only a few centimetres long is hermetically sealed onto a support such as stainless steel. This can be done using a gold seal [e.g. 37, 38], care being taken to select the steel for close matching of the thermal expansion coefficients of the metal and ceramic. A similar design has been used by Whelan and Borbidge [39], but this time using a platinum seal between a ZrO_2 thimble and an alumina tube. Where a metal seal is used to make an electrode connection, it should not be too close to the hot electrode region or mixed potentials may arise [12].

The so-called lambda sensor developed for use in motor car exhausts incorporates an electrically conducting graphite seal [40]. Stringer and Johnston [41] used an asbestos fibre seal in a compression fitting. Seals can also be fabricated using glass, glass-ceramic and fused ceramic, but close matching of thermal expansion coefficients is then essential if a durable seal is to be made.

In order to reduce the cost, a number of designs [42, 43] have consisted of a disc of electrolyte sealed into the end of a tube of non-electrolyte. It is difficult to make a leak-tight seal in this configuration. Bannister *et al.* [44] have addressed the problem of expansion mismatch by mixing electrolyte and non-electrolyte intimately to tailor the material to match the non-electrolyte tube. The resulting disc has a lower ionic conductivity than the pure electrolyte, but still adequate for a potentiometric device.

Kocache *et al.* [45] have virtually eliminated the problem of the temperature differential between the electrodes by using a symmetrical system (Fig. 7d). Sealing to the electrolyte is achieved using a flexible metal diaphragm and a glass seal.

A gauge incorporating a Pd–PdO reference electrode [46, 47] is shown in Fig. 7e. It has small dimensions which tend to reduce cracking due to thermal shock. The encapsulating material for the reference electrode is a glass which would need to be carefully chosen if a lasting seal is to be produced: leakage would quickly terminate the life of this device.

3.8. *Behaviour in some applications*

In some instances substantial deviations of the sensor reading from theoretical values may occur. Two areas of particular importance are unbuffered or poorly buffered systems at low P_{O_2}, and measurements in vehicle exhausts which are non-equilibrium systems containing agents which can poison electrodes.

Measurements in inert gases at p.p.m. levels of O_2 can be difficult to make accurately. The exchange current density due to O_2 is low, and parasitic side reactions can become potential-determining, e.g. [48]

$$H_2O + 2e \rightleftharpoons H_2 + O^{2-} \tag{30}$$

$$CO_2 + 2e \rightleftharpoons CO + O^{2-} \tag{31}$$

Small amounts of H_2O and CO_2 can produce large e.m.f. deviations and the presence of metal–metal oxide couples on the electrodes perhaps deposited from dust can perturb the measured e.m.f.: readings can be in error by up to 700 mV [2].

The performance of the lambda sensor has been discussed in detail by Logothetis [40]. At 700° C the device is shown to respond closely to the theoretically predicted behaviour (Fig. 8), but there are substantial deviations below 500° C which may be due principally to CO adsoption. This is manifested as a shift in the potential step away from the stoichiometric point: oscillations of the e.m.f. may also occur [49]. Blocking can substantially increase the response time [50]. The presence of the porous spinel layer, applied to protect the electrodes and improve their catalytic activity in non-equilibrium environments [3, 40], can produce displacement of the voltage step due to differences in the diffusion coefficients of the gases present in the exhaust: this causes the lean–rich response time to become shorter than the rich–lean, which is the reverse of that noted in unbuffered O_2–inert gas

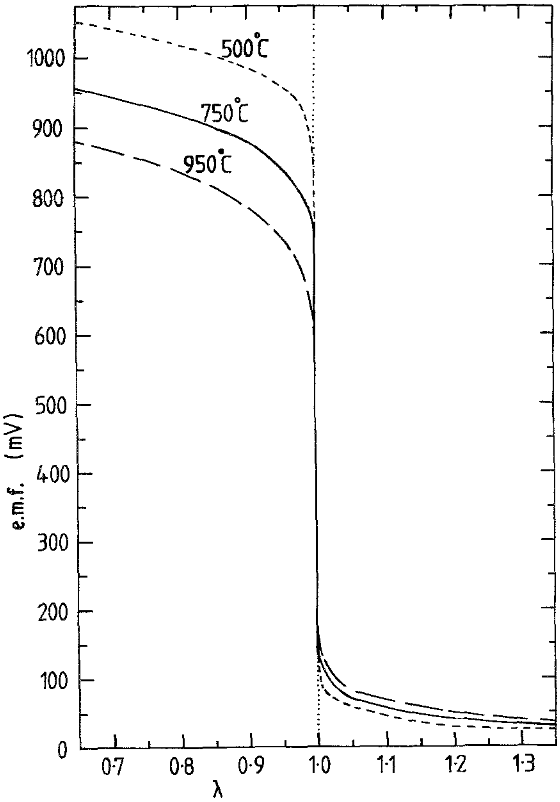

Fig. 8. Theoretical e.m.f. of a potentiometric sensor versus λ, the actual air–fuel ratio divided by the stoichiometric air–fuel ratio. The data were computed for air–methane mixtures with air as reference gas.

mixtures [36]. Also the use of leaded fuel tends to poison the platinum electrodes decreasing their catalytic activity [51].

As a general rule, potentiometric sensors are unreliable for low temperature operation with non-equilibrium systems [49].

4. Directions for future developments

Future work will probably concentrate on three principal aspects:

(i) lower cost devices
(ii) miniaturization
(iii) lower temperature of operation.

These areas are, of course, not mutually exclusive. Achievement of these aims will require improvements in electrolytes, electrodes and cell design.

The pump–gauge devices [52–54] may prove particularly attractive commercially. These miniaturized sensors consist of a pump for transmitting oxygen into a small sealed or semi-sealed volume, and a potentiometric gauge for determining the ratio of the partial oxygen pressure in the sample gas and in the enclosed volume. The internal gas acts as a reference and the need for connection to a reference gas (e.g. air) or use of a redox reference is obviated.

At present, sensors are operated above 500° C, but there would be attractions to reducing this temperature. Advantages would include lower power requirement to maintain the device at its operating temperature, greater portability of the device because a low power requirement could be satisfied with an electrochemical power source, less tendency to ignite inflammable or explosive mixutures of gases and in some applications involving hot gases the device might require no additional source of heat.

Velasco and Schnell [55] are pursuing the miniaturization of devices using microelectronic techniques. Thin films of electrolyte may be deposited with low resistance as a result of their small thickness. The heater can also be printed onto the substrate. A particularly interesting development is the incorporation of a pump onto the gauge which effectively displaces the large voltage step normally at the stoichiometric point to an appropriate point in the lean region.

Fluoride electrolytes (e.g. $PbSnF_4$ [56] and LaF_3 [57]) have been operated in oxygen sensors below 200° C and developments here may prove fruitful. The mechanism of the oxygen reaction on these solids is not immediately obvious. The probable reaction is

$$\tfrac{1}{2}O_2 + V_F^{\cdot} + 2e \rightleftharpoons O_F'$$

i.e. oxygen ions can be inserted into fluoride vacancies. Interestingly, initial results indicate that at these lower temperatures the oxygen may be reduced only to peroxide (O^-) rather than to oxide (O^{2-}), i.e.

$$\tfrac{1}{2}O_2 + e \rightleftharpoons O^-$$

However, the work of Badwal *et al.* [58] indicates that electrodes limit the low temperature operation of solid state oxygen sensors. These studies have shown that electrodes composed of urania–scandia are superior to platinum electrodes in terms of response at low temperatures and ageing properties. A range of mixed electronic–ionic conductors (e.g. [59]) will be investigated in the future as possible replacements for electronic electrodes and such work will benefit from previous studies on fuel cells and electrolysers [60].

Application of a large voltage across the electrodes has been found to modify the sensor properties beneficially [39] so that a usable response may be obtained at 250° C. The processes involved here are still uncertain but investigation and clarification of the influence of high electric fields may lead to advances in low temperature operation.

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