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Current mode operation: a technique for improving the reliability of zirconia oxygen probes in reducing atmospheres

W. E. BORBIDGE, P. T. WHELAN

CSIRO Division of Chemical Physics, P.O. Box 160, Clayton, Victoria, Australia 3168

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A technique is described whereby zirconia oxygen sensors with platinum electrodes can be protected from deterioration in reducing atmospheres, typical of metallurgical heat treatment conditions. By the application of current to the sensor, the technique provides a form of anodic protection, while at the same time the oxygen concentration in an atmosphere varying in temperature and composition can be continuously detected and measured.

1. Introduction

The use of zirconia solid electrolyte oxygen sensors for atmospheric control in industry has become widely accepted as a technology with many benefits over alternative techniques. There are two main areas of application where zirconia oxygen probes have had the most impact. One area of importance is in combustion control, for example in furnaces, boilers and power stations; the other is in the heat treatment of metals for surface treatments such as case hardening, carbonitriding and annealing. Of the two the latter has proven to impose the most severe conditions on zirconia oxygen probes, causing deterioration of the outer electrode of the sensor in the heavily reducing atmospheres encountered in heat treatment applications.

An electronic technique has been developed, referred to as 'current mode' operation, which can provide the outer electrode of a sensor with a form of anodic protection so as to extend the life of an oxygen sensor operating in a reducing atmosphere. The technique is applicable to most types of zirconia sensor operating with platinum electrodes but will be described in detail using the 'reaction bonded zirconia oxygen sensor'.

1.1. *The reaction bonded oxygen sensor*

Reaction bonded oxygen sensors are a development of the CSIRO Division of Chemical Physics, based on the Division's patented reaction bonding process for joining metals and ceramics [1–3].

The probe is basically a high temperature solid electrolyte cell, constructed from a closed end tube of ZrO_2 to which are attached internal and external platinum electrodes. The zirconia solid electrolyte, which at high temperatures has a high conductivity for oxygen ions, is used as a membrane to separate the environment being measured from a reference environment of known oxygen content.

When the outer electrode is exposed to the sample gas (for which the oxygen partial pressure P_1 is to be measured) and the inner electrode is exposed to the reference gas (of known oxygen partial pressure P_2, usually air, $P_2 = 0.2$ atm) a potential difference E will be set up between the two electrodes, according to the Nernst equation:

$$E_{\text{Nernst}} = \frac{RT}{4F} \ln \frac{p_2}{p_1} + C \qquad (1)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, and C is a constant for the particular cell. For the reaction bonded sensor C is usually low (< 0.2 mV).

The sensor is constructed from a zirconia thimble (calcia or yttria stabilized) reaction bonded via a platinum foil washer to an alumina shank of a length to suit the installation (see Fig. 1). The zirconia thimble is platinized using platinum paste on both the inner and outer surfaces to form the electrodes of the oxygen

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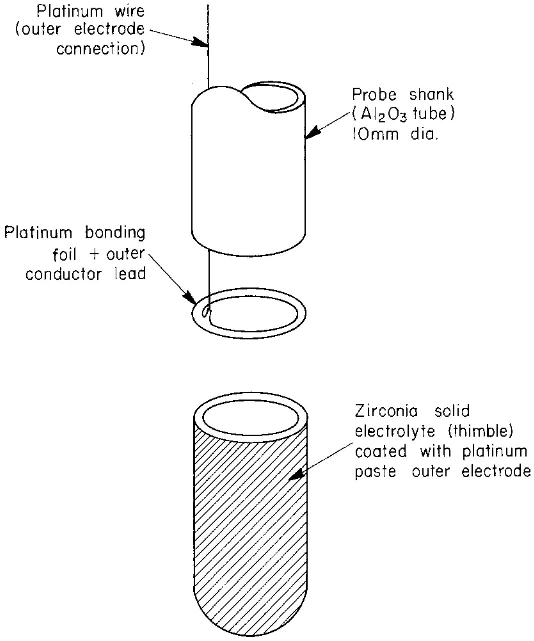

Fig. 1. Exploded view of reaction-bonded oxygen sensor. Thermocouple pair not shown.

sensor. The outer electrode is connected by the platinum foil bond to a platinum wire inside the sensor, which connects to the terminal head as the outer electrode wire. A thermocouple element (Pt–Pt/13%Rh) is fitted within the body of the sensor so as to contact the inner platinized surface of the zirconia; the negative lead of the thermocouple also acts as the inner electrode wire.

The sensors are generally robust and can withstand continuous operation at high temperatures. They are suitable for use in most industrial atmospheres, particularly those typically encountered in combustion control. Their performance can be impaired however by operation under severely reducing conditions where the oxygen potential is extremely low.

In this paper, the problems of operating under these conditions are discussed, and a novel technique is presented which can help to overcome these problems.

1.2. *Problems of operating probes in reducing conditions*

Under normal atomospheric conditions platinum is an inert noble metal, being very stable and possessing good corrosion resistance and freedom from oxidation. The main limitation to its use in oxidizing atmospheres is vaporization at high temperatures, the rate of volatilization is reported as $9.19 \times 10^{-3}\,\mathrm{mg\,cm^{-2}\,h^{-1}}$ at 1400° C [4]. In these atmospheres, typical of combustion control applications normally running at about 5% excess oxygen, zirconia oxygen sensors with platinum electrodes can give long trouble-free life. However, in reducing atmospheres, such as are found in metallurgical heat treatment furnaces, platinum and hence the outer electrode of the sensor ceases to be inert.

At low oxygen pressures platinum becomes reactive with a wide range of otherwise highly stable substances. For example, refractory oxides such as alumina and zirconia can be dissociated in the presence of platinum. resulting in the evolution of oxygen and the formation of low melting point intermetallic phases of Al and Zr with Pt [5]. This type of reaction is well known between platinum and silica, where under reducing conditions, silica can be readily converted to silicon, forming low melting point eutectic phases with platinum, as low as 830° C, leading to premature failure in the metal. Silica is a common impurity in commercial grade alumina and zirconia used for making oxygen sensors; in zirconia, the siliceous impurities tend to be concentrated in the grain boundaries of the polycrystalline ceramic [6].

The severity of the reactions occurring between platinum and the refractory oxides is largely controlled by the geometry of the reacting system, in particular by the amount of surface area in contact between the reacting materials, and also by the ability of oxygen to escape from the reaction zone [7].

Such reactions impose restrictions on the use of zirconia oxygen sensors with porous platinum electrodes in reducing atmospheres, where problems of poor electrode contact with the zirconia can arise. These reactions are particularly detrimental to the reaction bonded sensor which relies for its integrity on a solid state bond of Al_2O_3–Pt–ZrO_2 which by its nature involves intimate contact between platinum and the oxide ceramics.

The deleterious reactions described above can only proceed when the atmosphere is reducing and virtually no reactions with platinum will occur if atmospheric conditions are maintained strongly oxidizing.

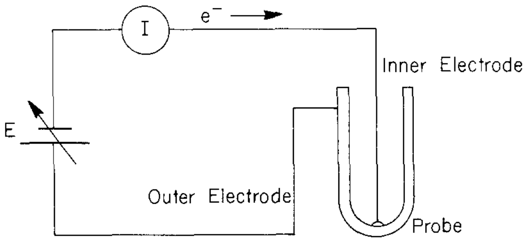

Fig. 2. Basic oxygen probe current pump.

The technique described in this paper of operating the reaction bonded oxygen probe as an oxygen pump, or in 'current mode', was therefore developed as a method of providing the outer platinum electrode and bond area of a probe operating in conditions of low oxygen pressure with a localized, relatively oxygen rich atmosphere, so that the platinum of the electrode and bond will remain inert.

1.3. *Oxygen probe current pump*

A probe will act as an oxygen pump when connected in a circuit as shown in Fig. 2.

By the application of an external voltage source current will pass through the zirconia solid electrolyte in the form of ionic charge movement, and through the platinum connecting electrode wires in the form of electron flow. At the platinum electrodes the exchange reaction 2 occurs

$$O_2 + 4e^- \rightleftharpoons 2O^{2-}. \tag{2}$$

As a result of this reaction oxygen is taken up at the cathode side of the probe, and liberated at the anode in an amount exactly equivalent to the charge passed through the cell [6].

The amount of oxygen evolved is related to the current by the Faraday law:

$$Q = \frac{I}{4F} \tag{3}$$

where Q is the quantity of oxygen, mol h^{-1}; I, the current in amperes and F, one Faraday. There are certain limitations to this behaviour of the probe as an oxygen pump. Firstly, the temperature of the probe must be sufficiently high to allow ionic mobility within the zirconia, and secondly, the platinum electrodes need to be porous, to allow free passage of the gaseous oxygen. In practical terms, the pump responds linearly over many orders of magnitude of applied current and can therefore be used to inject a stream of pure oxygen uniformly from the outer electrode of the probe into the surrounding gas.

The technique can be used to load a stream of carrier gas with a precisely known percentage of pure, dry oxygen, which can be used for calibration of instruments such as spectrometers. It can be shown that the oxygen pressure pO_2 in a gas stream is related to the current passing through the pump by the expression:

$$\frac{pO_2}{P} = \frac{4FCD + 22.4I}{4FD + 22.4I} \tag{4}$$

where C is the oxygen mole fraction upstream in the gas carrier, D, the flow rate of the gas and P the total pressure of the gas [8, 9].

1.4. *The current mode technique*

When operating as an oxygen pump a current is applied to the probe via a high impedance current source, the direction of current application chosen so as to evolve gaseous oxygen on the outside of the outer electrode. The atmosphere in close proximity to the probe will be modified by the additional oxygen pumped through the solid electrolyte, and is referred to as the 'micro-atmosphere' as distinct from the 'bulk atmosphere' which will continue to exist in the furnace gases further removed from the electrode. An equilibrium between the micro-atmosphere and the bulk atmosphere will be set up resulting in a steady total oxygen level in the system. Normal diffusion of the pumped oxygen can be expected to occur, as well as reactions between the oxygen and components of the reducing gas atmosphere, such as carbon monoxide, hydrogen and carbon. Such reactions result in the uptake of oxygen at a faster rate than would be expected for normal diffusion processes alone.

The corresponding voltage across the probe will now be a combination of the Nernst voltage (as produced by the resulting 'mixed' atmosphere) and the voltage drop across the electrolyte as a result of its resistance. The probe can therefore no longer be directly used to measure the oxygen level in the bulk atmosphere, as the outer electrode is partially shielded by the micro-atmosphere produced as a result of the oxygen pumping.

To overcome this problem a combination pump-gauge could be used [8], where the probe consists of two separate cells, one operating as a pump, the other detecting Nernst voltage, in the usual way, upstream.

By the use of a current scan technique on a probe operating in 'current mode' it will be shown that a single element sensor can be used both to continuously measure the oxygen pressure and to pump into an unknown dynamic system.

The technique is based on the assumption that for a fixed oxygen pumping rate (i.e., fixed current), a state of equilibrium will be produced and the oxygen gradient across the micro-atmosphere will be stable provided there are no large variations in temperature and gas flow rate in the system. Any variation in oxygen content of the bulk atmosphere will alter the position of the equilibrium and be reflected back through the micro-atmosphere to the outer electrode, producing detectable signal changes to the probe voltage.

The aim of the experimental work therefore has been to find the optimum pumping rate of oxygen to provide maximum protection of the reaction bond and platinum electrodes, and to develop a technique to continuously measure the Nernst voltage (i.e., to measure the oxygen concentration in the bulk atmosphere) while simultaneously passing this optimum protection current through the probe.

2. Experimental technique

When current is flowing through an oxygen probe, in the direction so as to evolve oxygen at the electrode of lowest oxygen partial pressure, a voltage drop is developed across the probe resistance with polarity that opposes the Nernst voltage. The voltage measured across the probe (V_0) is then an arithmetic sum of the Nernst voltage (representative of the oxygen level in the atmosphere seen by the probe i.e., the micro-atmosphere) and the IR drop across the probe resistance R,

$$V_0 = E_{\text{Nernst (m)}} + IR \tag{5}$$

where $E_{\text{Nernst (m)}}$ is the Nernst voltage representative of the micro-atmosphere.

At low current levels, the composition of the micro-atmosphere around the probe can be considered to be similar to that of the bulk atmosphere, the oxygen concentration of which the probe is required to measure, i.e.,

$$E_{\text{Nernst (m)}} \approx E_{\text{Nernst (bulk)}} \tag{6}$$

and

$$V_0 \approx E_{\text{Nernst (bulk)}} + IR \tag{7}$$

However, as the current level is increased, and the composition of the micro-atmosphere becomes richer in oxygen, $E_{\text{Nernst (m)}}$ will no longer be equivalent to $E_{\text{Nernst (bulk)}}$ and an error will be introduced to Equation 7, the magnitude of the deviation (in mV) depending on the magnitude of the current.

$$V_0 = E_{\text{Nernst (bulk)}} + IR + \text{mV deviation} \tag{8}$$

It follows therefore that if the resistance R, and the magnitude of the deviation are known, for a known applied current I, and measured probe voltage, V_0, the Nernst voltage appropriate to the bulk atmosphere can be calculated from Equation 8.

2.1. *Probe resistance*

Although the d.c. resistance of a probe can be measured in the laboratory under zero Nernst voltage conditions (i.e., an air atmosphere) it is necessary in a practical situation for the probe resistance to be continually measured *in situ*, in the reducing atmosphere, while the current is flowing, since the resistance is known to vary greatly with time (ageing of the electrodes), temperature and even concentration of oxygen in the atmosphere.

2.1.1. Electrical characteristics. The simplified equivalent circuit of a zirconia cell with platinum electrodes can be drawn as in Fig. 3, where R_B and R_{E1}, R_{E2} are the d.c. resistance of the electrolyte and electrodes, and C_B and C_{E1}, C_{E2} are the electrolyte and electrode capacitances.

For the purposes of this experimental work, it is proposed to represent the probe by the simplified equivalent circuit of Fig. 4 where the resistance R_s represents the total d.c. resistance in the circuit, and has associated with it a complex impedance that is capacitive (typical value $100\,\mu\text{F cm}^{-2}$); The double layer capacitance generated at each electrode is the dominant source of this impedance, and is represented as a shunt

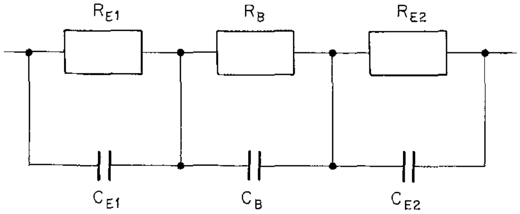

Fig. 3. Simplified equivalent circuit.

component distributed throughout the resistance of the probe, shown in Fig. 4 as C_s.

R_s is basically a combination of two components, the electrolyte resistance and the electrode resistance. The electrolyte resistance varies only with temperature and composition of the material, and is independent of oxygen pressure.

The electrode resistance component is the most complicated parameter; it is intimately involved with the exchange reaction:

$$O_2 + 4e^- \rightleftharpoons 2O^{2-}$$

and is therefore affected by temperature, oxygen pressure, applied voltage and current and electrode condition. Any variation in these parameters will be reflected in changes in the total d.c. resistance.

2.1.2. Measurement of probe resistance. The d.c. resistance, R_S, can be measured by a circuit as shown in Fig. 5.

The resistance is measured by a differential technique, that is, varying the applied current by a small amount, and measuring the corresponding change in V_0, ΔV and probe resistance $R_S = \Delta V/\Delta I$. This technique allows R_S to be determined even when a large standing current is flowing through the probe.

The main limitation to the rate of these transient measurements of resistance is the effect of C_S, which limits the rate of change in V_0 for a ΔI transient. For reaction bonded probes the response time for the voltage to stabilize is normally less than 50 ms at 800° C. Fig. 6 shows the typical response.

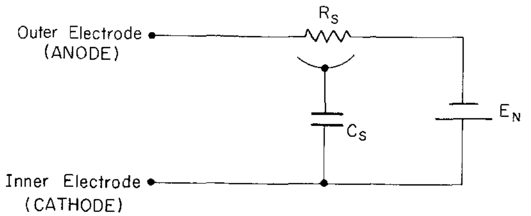

Fig. 4. Equivalent circuit used for current mode operation.

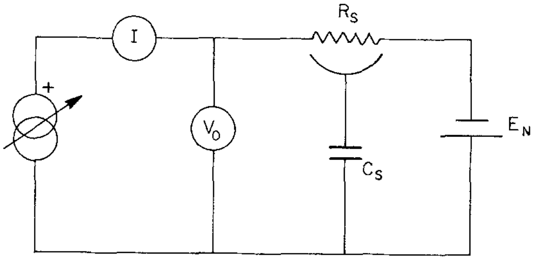

Fig. 5. Circuit arrangement for d.c. resistance measurements.

The probe voltage shows typical exponential rise and decay response, with negligible over voltage polarization effects.

2.2. *Measurement of mV deviation*

The mV deviation for a particlular applied current level can be determined by a current scanning technique, in which the current is increased from zero in fixed increments, the probe voltage being measured and recorded at each current plateau.

As the current is increased, oxygen builds up at the outer electrode of the probe forming the micro-atmosphere as described above. At each plateau, the measurements of I and V_0 can be taken and used to calculate R_S by the differential method and hence the IR drop across the probe. If there is no accumulation of oxygen at the outer electrode due to the application of the current, then Equation 9 applies:

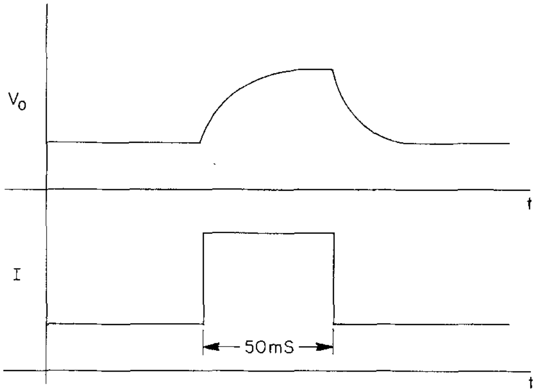

Fig. 6. Response of the probe voltage to a current transient.

$$V_0 = E_{\mathrm{Nernst\,(bulk)}} + IR \tag{9}$$

$E_{\mathrm{Nernst\,(bulk)}}$ is measured at the start of the scan, with zero applied current.

In practice Equation 9 only holds true for very small currents. As the current is increased during the scan, and the micro-atmosphere becomes steadily more oxygen rich, Equation 9 begins to be in error by increasingly larger amounts, i.e.,

$$E_{\mathrm{Nernst\,(bulk)}} = V_0 - IR_S - \mathrm{mV\ deviation}. \tag{10}$$

The value of the mV deviation is equivalent to the amount that the Nernst voltage of the bulk atmosphere has been modified by changes in the micro-atmosphere due to the build-up of oxygen for a particular value of applied current I. The relationship between I and mV deviation can be expected to vary with temperature, electrode condition and gross changes in gas flow rate and composition of the bulk atmosphere in the furnace. For this reason, it is necessary to re-initiate current scans at periodic intervals, as these conditions vary with time.

2.3. *Computer techniques for control and measurement*

To facilitate long term testing under various conditions of temperature and furnace atmosphere, a mini-computer controlled system was arranged to enable current scans to be easily and routinely performed. The system layout is shown in Fig. 7.

In this system the current is incremented by a programmable current source controlled by a mini-computer; the computer also reads and stores the values of probe voltage measured by the digital voltmeter.

Calculations as described above to determine the values for mV deviation and probe resistance at each current plateau are also performed by the computer, which can then be used to provide a continuous measurement of oxygen concentration in an atmosphere changing in composition and temperature.

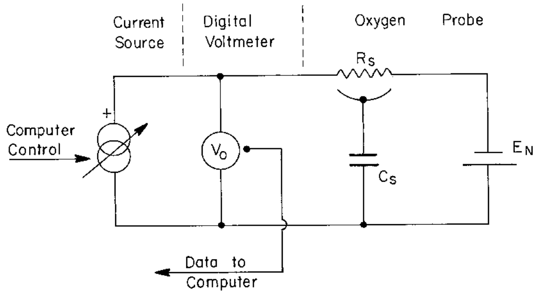

Fig. 7. System layout for computer interface to probe.

The mini-computer can be programmed to periodically run a scan, and then set the current to a level which corresponds to a known mV deviation. This in effect re-establishes the micro-atmosphere to the same equilibrium state which applied at that current level during the scan. With the current set at this point Equation 11 can therefore be directly solved for $E_{\mathrm{Nernst\,(bulk)}}$:

$$E_{\mathrm{Nernst\,(bulk)}} = V_0 - IR_S - \mathrm{mV\ deviation} \tag{11}$$

If the composition of the bulk atmosphere in the furnace changes, the probe volts V_0 will respond immediately, and the change in probe volts will be the effective change in Nernst voltage of the probe.

If the temperature changes, Equation 11 will still hold true provided an accurate figure for R_S can be obtained at the new temperature. The value of R_S is very sensitive to temperature, and it needs to be updated several times per minute to allow for any temperature changes in the furnace.

The value of mV deviation could be expected to remain constant for a particular current level, provided the temperature does not vary to a large degree.

Operation under changing conditions of gas composition and temperature can therefore be considered in terms of first and second order effects. First order effects are the R_S variations with temperature and V_0 variations with gas composition. The second order effects are the drift in mV deviation with temperature and R_S variations with gas composition.

2.3.1. Bi-stable mode. For moderate variations in temperature and gas composition the second order effects listed above can be disregarded, and the first order effects can be handled with a bi-stable mode of operation. This involves repeated measurements of R_S and V_0 so as to continually solve Equation 11 to determine a changing $E_{\mathrm{Nernst\,(bulk)}}$. R_S can be repeatedly measured, while the standing current is applied to the probe, by applying a fast current step ΔI, measuring the

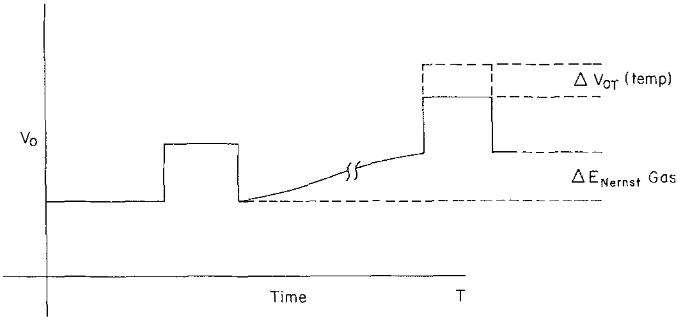

Fig. 8. Diagrammatic representation of the effect on probe volts of variation in gas composition and temperature. When operating in the bi-stable mode, the computer generates a series of current transients which result in corresponding transients in V_0.

voltage V_0 before and after the transient, and calculating R_S by the $\Delta I/\Delta V$ method.

The use of this technique means that the dynamic resistance of the probe can be continuously updated at a rate of up to about ten readings per second, which is more than fast enough to compensate for the normally slow temperature variations in a large furnace.

This also implies that by processing Equation 11, $E_{\text{Nernst (bulk)}}$ can also be calculated at this rate, permitting on-line continuous control of furnace atmosphere conditions.

The variables R_S and V_0 are very sensitive to the conditions in the atmosphere around the probe, and therefore the amount of variation of these variables can be used as a monitor to determine if conditions have changed sufficiently for a new current scan to be required. This will then provide a new current set point, suitable for the new atmosphere conditions, and an updated value of mV deviation, corresponding to that current set point.

Figure 8 shows the effect on probe volts V_0 of variation in the two main variables, gas composition and temperature, while operating in the bi-stable mode. A change in gas composition will produce a drift in V_0, shown in Fig. 8 as ΔE_{Nernst} Gas. A variation in temperature will cause the probe resistance R_s to vary, which in turn will alter the value of ΔV arising from the same current step ΔI, by the amount ΔV_{OT}.

When suitably programmed then, the minicomputer can be used to provide the optimum protection current for the probe at all times, taking account of changes in temperature and gas composition, and probe resistance drift. At the same time as this protection current is applied, with the probe volts vastly modified from the original Nernst voltage, the program in the bi-stable mode can detect and quantify a continuously changing Nernst voltage; that is, a continuous and accurate read-out of oxygen concentration can be obtained.

3. Results and discussion

All experimental work was performed using reaction bonded oxygen sensors set up in a small laboratory furnace of 50 mm working diameter with a flow rate of reducing gas of 0.2 $\text{dm}^3\,\text{min}^{-1}$. Commercial grade 10% Hydrogen in Nitrogen was used to provide the reducing atmosphere, the oxygen partial pressure of which was $\leqslant 10^{-18}$ atm.

Several oxygen probes were used for the experimental work. The actual numerical data obtained varied slightly from one probe to another, however, the data presented here can be regarded as typical in form.

Table 1 shows current scan data for a probe operating at 900° C. At each sequential current level the probe volts (V_0) have been measured, R_S calculated ($\Delta V/\Delta I$), E_{Nernst} calculated – ($V_0 - IR_S$) and the mV deviation determined ($E_{\text{Nernst (bulk) (zero}\,I)} - E_{\text{Nernst (calc)}}$).

It can be observed from the scan data, that as the current level increases the mV deviation also increases in magnitude (with negative polarity) until at a certain current level, referred to as $I_{\text{break-point}}$, a turning point is reached when the mV deviation changes polarity and begins to increase in a positive direction. A plot of mV deviation against current level is shown in Fig. 9.

Figure 10 shows an oscilloscope trace of the step response of the probe volts as the current is incremented during a scan on a probe.

It is apparent from Figs. 9 and 10 that as the current is scanned from zero, the response of the probe can be considered in three distinct stages.

For very small applied current levels (zero and the first two or three steps of the scan) the probe is effectively acting as a linear resistance, producing an IR drop proportional to the current. The oxygen evolved at the outer electrode is being dispersed into the bulk atmosphere at such a rate as to have no appreciable effect on the calculated Nernst voltage (that is $E_{\text{Nernst (calc)}} \approx E_{\text{Nernst (bulk)}}$). Because this region shows no non-ohmic characteristics both electrodes can be assumed not to be rate-limiting and the exchange reaction (2) fully applies that is, ionic current is the only mechanism of charge movement. At these low current levels the micro-atmosphere has not been created to the extent which can be detected by the probe.

At slightly higher current levels of the scan the probe resistance appears to become non-ohmic in character. The effect observed is that of an increasing IR drop with increasing applied current, that is the probe resistance is increasing with current.

The rise in resistance, as measured by the differential ΔI, ΔV method, could be explained in two ways. One explanation is that electrodes of a fixed porosity tend to impose an increasing restriction upon the transfer of oxygen as the current is increased. This may be occurring to some extent; however the increasing magnitude of the mV deviation in this region of the scan suggests that the dominant cause of the apparent resistance rise is a decreasing value of Nernst voltage, with increasing current the oxygen evolved at the outer electrode is forming an oxygen rich micro-atmosphere around the probe, that is $E_{\text{Nernst (micro)}} < E_{\text{Nernst (bulk)}}$. By the nature of the $\Delta I/\Delta V$ method of resistance measurement, an apparent increase in resistance will occur if the Nernst voltage is decreasing in magnitude as the current is incremented during a scan.

Table 1. Typical computer output of data generated during a current scan. V_0 at zero I represents $E_{Nernst(bulk)}$

I (mA)	V_0 (V)	R_S (Ω)	$E_{Nernst\ calc}$	*Deviation* (mV)
0	−0.9978	–	–	–
1.4740	−0.9593	26.1371	−0.9978	−0.0
2.9500	−0.9205	26.2872	−0.9980	−0.2
4.4240	0.8808	26.9335	−0.9999	−2.1
5.8990	−0.8412	26.8474	−0.9995	−1.7
7.3710	−0.8014	27.0380	−1.0006	−2.8
8.8450	−0.7616	27.0013	−1.0004	−2.6
10.3200	−0.7210	27.5254	−1.0050	−7.2
11.7910	−0.6802	27.7362	−1.0072	−9.4
13.2740	−0.6386	27.0512	−1.0109	−13.1
14.7490	−0.5970	28.2033	−1.0129	−15.1
16.2250	−0.5545	28.7940	−1.0216	−23.8
17.7020	−0.5113	29.2484	−1.0290	−31.2
19.1750	−0.4675	29.7352	−1.0376	−39.8
20.6500	−0.4239	29.5593	−1.0342	−36.4
22.1250	−0.3805	29.4237	−1.0314	−33.6
23.6010	−0.3382	28.6585	−1.0145	−16.7
25.0500	−0.2976	28.0193	−0.9994	−1.6
26.5530	−0.2559	27.7445	−0.9925	5.2
28.0310	−0.2160	26.9959	−0.9727	25.0
29.5080	−0.1767	26.6079	−0.9618	35.9
30.9890	−0.1382	25.9959	−0.9437	54.0
32.4630	−0.0999	25.9837	−0.9434	54.3
33.9420	−0.0619	25.6930	−0.9339	63.8
35.4190	−0.0240	25.6601	−0.9328	64.9

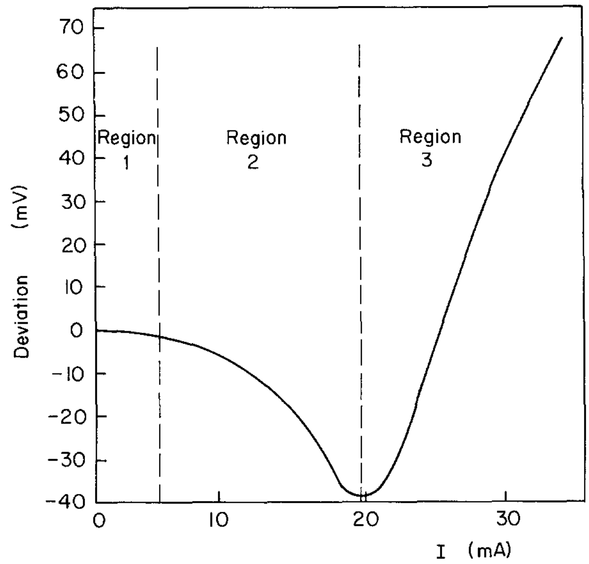

Fig. 9. Plot of mV deviation against current level for a typical scan.

It is most probable therefore that at these current levels in the middle range of the scan, the probe is still obeying the exchange reaction and that the non-linearity shown in Figs. 9 and 10 is due to modification of the micro-atmosphere by oxygen evolved at the outer electrode.

At the high current end of the scan a marked change in character can be observed, which corresponds to a decrease in the IR drop across the probe with increasing current. The decreasing resistance in this most distinctly non-linear section of the scan implies that there is some change occurring in the mechanism of current flow.

It has been shown by other workers in this field [6, 8, 10–14] that direct electron injection can take place at high applied potentials, and that this is reflected in abnormally high current flow, or reduced resistance. It is most likely that this is the effect observed here; that is with increasing applied current no further oxygen is evolved at the outer electrode, and the micro-atmosphere ceases to become more oxidizing. The exchange reaction is no longer obeyed fully for higher currents and further current through the electrolyte is via electron, rather than oxygen ion, flow. This behaviour would be the result of a rate limiting effect of the platinum electrodes, where the electrodes are unable to transfer oxygen at the rate demanded by the high applied current.

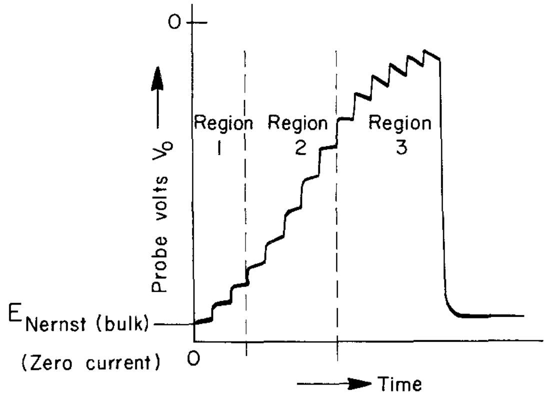

Fig. 10. Typical voltage transfer characteristic for a current scan.

The point on the current scan at which this third stage commences, $I_{\text{break-point}}$, or the onset of electronic injection is temperature dependent. Figure 11 is drawn from data obtained for a probe operating at temperatures between 800° C and 1100° C, and shows a plot of $I_{\text{break-point}}$ against temperature. Also shown in the same figure is the relationship between probe resistance and temperature.

The general form of these relationships between $I_{\text{break-point}}$, R_S and temperature is the same for all probes tested, however, the actual numerical data can vary from one probe to another depending on electrode area and condition.

The main objective when using the current mode technique is to protect the electrodes and bond from the deleterious effects of the reducing atmosphere, by providing a relatively oxygen rich micro-atmosphere around the probe. For this purpose it would be expected that the maximum

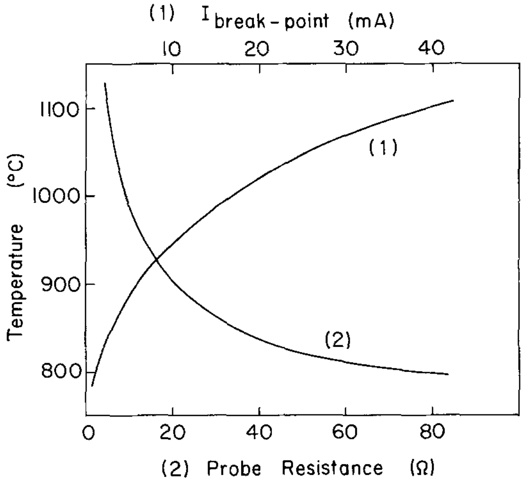

Fig. 11. Plot of $I_{\text{break-point}}$ and resistance against temperature.

current would provide the maximum protection. However, from the results discussed above it is clear that there are limits to the current which can be applied to a probe; that is, long term operation in the high current area, causing electronic injection, would probably be harmful both to the electrolyte and electrodes. The optimum operating point therefore, lies within the medium current range.

To test the effect on a probe of operation within different current regimes, two similar probes were arranged with different current levels. Probe A was set with applied current at $0.5 \times I_{\text{break-point}}$. Probe B was set with applied current equal to $1.2 \times I_{\text{break-point}}$, that is, just within the electronic conduction range.

Probe A was tested over 300 h continuous operation at 1000° C in reducing atmosphere, with $E_{\text{Nernst (bulk)}} = 1.086$, equivalent to $pO_2 = 1.2 \times 10^{-18}$ atm. Repeated current scans over this period showed that $I_{\text{break-point}}$ was holding steady at 8 mA. Current applied to the probe was set at 4 mA, so that the probe was operating in the medium current range, with some oxygen enrichment of the microatmosphere. Over the 300 h test period the probe resistance drifted slightly from 20Ω–25Ω. At the conclusion of the test period the probe was examined, and it was observed that the outer platinum electrode was still in good condition with no apparent deterioration over the test period. The Al_2O_3–Pt–ZrO_2 reaction bond was still intact.

Probe B was tested over 130 h continuously under similar conditions to probe A, the only difference being that the current was set to $I = 1.2 \times I_{\text{break-point}}$, this is the current level where mV deviation becomes positive. The value of $I_{\text{break-point}}$ was initially 17 mA, over the 130 h test period, the value fell to 3 mA. This suggests that some deterioration of the probe was occurring, that the ability of the electrodes to transfer oxygen was decreasing. This is also supported by the resistance measurements over the period, during which R_S increased from 15Ω to 57Ω. When the probe was examined at the conclusion of the test, the outer platinum electrode was seen to have become distinctly thinner, and was slightly flaky in patches. The platinum reaction bond was still intact however.

These results indicate the importance of selecting the correct operating point for the probe, and when compared to the behaviour of probes without current protection, show the improvement in lifetime which can be achieved by the current mode technique. Experimental work has shown that probe life can be extended by a factor of up to 100 times that of probes operating under the same reducing atmosphere and temperature, without any current protection, that is, operating normally in the voltage mode.

Both the reaction bond and the platinum electrodes appear to be well protected by the technique. However, as the experimental work described above shows, the electrodes are sensitive to the level of current applied, excessively high current causes problems with flaking and separation of the electrodes from the zirconia electrolyte.

These results apply only to probes operating in the laboratory under hydrogen atmosphere. Future research will be directed towards proving that the technique is also of benefit to probes operating in industrial heat treatment furnaces, where the atmosphere usually consists of propane or methane derived mixtures, with CO and CO_2 being the main components.

4. Conclusion

Current mode operation involves applying current to a probe at an optimum level so as to generate a relatively oxygen rich protective atmosphere around the probe. This will impede deterioration of the outer platinum electrode, and for the reaction bonded probe, prevent failure at the bond interface. The technique appears promising in that the results show extended lifetimes for probes operating under laboratory conditions in hydrogen reducing atmosphere. The principles of the technique would also apply to carbon monoxide based atmospheres, normally used in industry, and would provide protection for an oxygen probe while simultaneously allowing on-line continuous measurement and control of oxygen potential.

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