

Interpretation of the output signal from a zirconia oxygen sensor operating under applied current

P. T. WHELAN, W. E. BORRIDGE

CSIRO Division of Materials Science and Technology, Locked Bag 33, Clayton, Victoria, Australia 3168

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Under conditions of applied current flow, oxygen can be transported through a ZrO_2 sensor so as to create a localized, relatively oxygen-rich atmosphere at the measuring electrode and thereby provide protection for the sensor in hostile reducing atmospheres. The rate of dissipation of this protective atmosphere can be controlled by the use of a porous ceramic muffle around the sensor's measuring electrode. Analysis of the output signal from the sensor not only allows the oxygen content in the bulk atmosphere to be determined, but can also yield much useful information relevant to the operation of the sensor, such as the onset of electrode limiting and electronic conduction.

1. Introduction

The use of solid-state zirconia based oxygen sensors has become widespread in many areas of industry. These sensors function according to the Nernst equation (1), whereby a potential difference E_{Nernst} is set up between two electrodes (generally platinum), one of which is exposed to the sample gas (for which the oxygen partial pressure P_1 is to be measured) and the other is exposed to a reference gas of known oxygen partial pressure P_2 , usually air:

$$E_{\text{Nernst}} = \frac{RT}{4F} \ln \frac{P_2}{P_1} \quad (1)$$

where R is the gas constant, T is the absolute temperature and F is the Faraday constant.

There are certain applications which are hostile to these sensors when operating with platinum electrodes, in particular, those involving reducing atmospheres and contaminants such as sulphur. For example, in metallurgical heat-treatment furnaces the combination of low partial pressures of oxygen and elevated temperatures provides conditions whereby zirconia can be dissociated in the presence of platinum, with the formation of intermetallic phases or compounds [1]. Also, in oxygen sensing for combustion control, low excess air or fuel rich conditions can cause sulphur in the fuel to react with the platinum electrodes to form platinum sulphide. In both cases electrode deterioration is the result, causing downgrading in performance and lifetime of sensors operating under these circumstances.

The current mode technique uses to advantage the phenomenon of oxygen ion transport through a zirconia cell to provide a relatively oxygen rich protective atmosphere at the sensing electrode, whilst at the same time permitting measurement of oxygen content in the bulk surrounding atmosphere. Maintaining the electrode at an oxidizing condition in this way has been shown to greatly inhibit the deleterious reactions which would otherwise normally occur in a reducing

atmosphere. Results to this effect, and also the basic principles of the current mode technique, have been published previously [2].

This paper describes some further developments of the technique, especially in interpreting the output signal from the sensor and suggests ways to further improve protection of the sensor, in particular the use of ceramic muffles to restrict dissipation of the protective atmosphere.

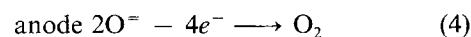
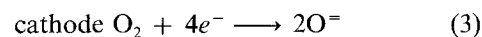
1.1. Oxygen transport

Zirconia cells can be used as a selective source or getter for oxygen; over a defined operating range the amount of oxygen transported is related to the current flow through the cell:

$$O = \frac{I}{4F} \quad (2)$$

where O is the amount of oxygen transported in mol s^{-1} , I is the current in amperes and F is the Faraday in C mol^{-1} .

The current can be generated within the cell by resistive loading its output or by the application of an external voltage source, resulting in electrode reactions departing from equilibrium such that



For a sensor with the outer sensing electrode as the anode, oxygen will be taken up from the internal reference atmosphere, transported as oxygen ions in the zirconia and liberated as pure oxygen at the anode. Provided the sensor temperature is such as to allow high ionic mobility within the zirconia and the platinum electrodes are porous, oxygen can be pumped linearly over many orders of magnitude of applied current.

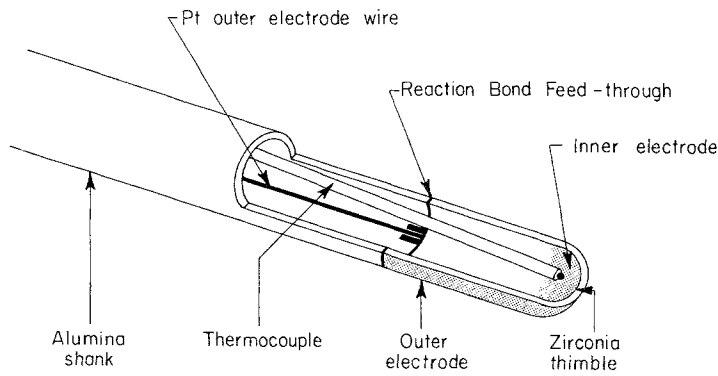


Fig. 1. Sectioned view of the reaction-bonded sensor, showing the internal construction.

2. Experimental details

2.1. The reaction-bonded oxygen sensor

The current mode of operation could be applied to most types of zirconia sensor, however all test work for this study was undertaken using reaction-bonded sensors. These are constructed by bonding a zirconia crucible (calcia or yttria stabilized) onto an alumina extension shaft via a platinum foil washer (see Fig. 1), using a direct solid-state process known as reaction bonding [3]. Porous platinum electrodes are fired on the inner and outer surfaces of the zirconia solid electrolyte. The inner reference electrode is typically 1 cm² in area and is fired to 1450° C for 4 h during construction of the sensor. The platinum outer sensing electrode is considerably larger in area, ~8 cm² and is fired to only 1000° C.

2.2. The current mode technique

2.2.1. Hardware. The current mode technique involves applying current to the sensor by a form of chronopotentiometry using a computer controlled current source (see Fig. 2). The main advantage with this circuit arrangement is the minimal external loading of electrode potentials under conditions of applied current flow, i.e. a Nernstian voltage component can still be measured from the sensor.

2.2.2. Software. The sensor current is incremented from zero by the programmable current source in an increasing series of plateaus of fixed increments, to form a linear current ramp, as shown in Fig. 3a. The length of each plateau is designed such as to allow charging of the sensor's internal capacitances C_s (typically 50 ms). After stabilization of the output voltage V₀, the IR drop across the sensor can be calculated

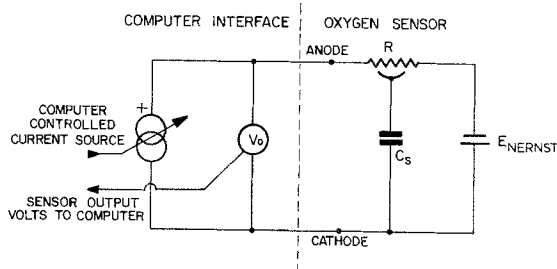


Fig. 2. Mini-computer interface used to control current flow and record output voltage response from the sensor.

using the change in current and voltage from sequential plateaus.

$$IR = \frac{\Delta V_0}{\Delta I} I \tag{5}$$

2.3. Furnace atmosphere

The sensor was heated in an electric tube furnace, with hydrogen being used to provide the reducing atmosphere (in the form of a mixture of 10% H₂ in N₂, at a flow rate of ≈ 1.5 l min⁻¹). Although an industrial heat-treatment atmosphere would normally consist of a number of different reactive gases, hydrogen is a typical component, and was considered appropriate as a standard test gas in these experiments. Small quantities of air were introduced into the gas stream to control the oxygen partial pressure at the required levels.

3. Sensor output response

3.1. General form of the scan

For a sensor operating according to the current mode

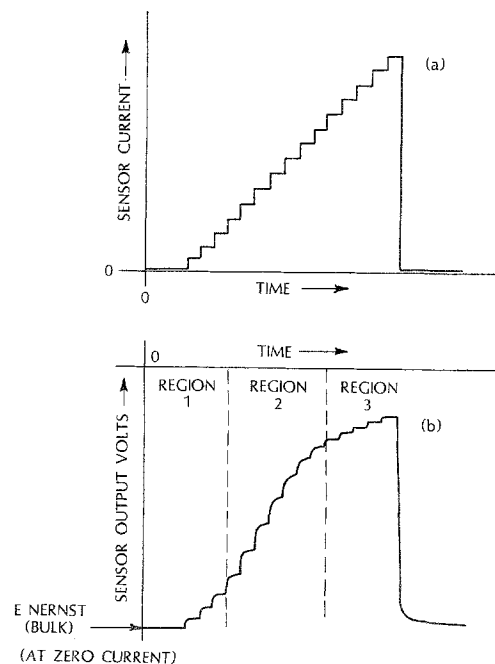


Fig. 3. Sensor current waveform and resulting output voltage transfer characteristic.

technique, the output scan or transfer characteristic can take many forms, depending on operating conditions. Generally however, three distinct regions can be identified, which can be related to phenomena occurring within and around the sensor. Fig. 3b shows these regions in the simplest form of the output scan.

In the first region, at relatively small current levels, the sensor is effectively acting as a linear resistance, at each step giving an output voltage drop (ΔV_0) proportional to the applied current. Oxygen is being transferred freely through the sensor from the inner reference atmosphere into the bulk atmosphere surrounding the anode. The voltage drop developed across the sensor resistance will be of a polarity opposing the Nernst voltage.

The sensor voltage, V_0 , is now the arithmetical sum of the Nernst voltage and IR drop across the probe resistance:

$$V_0 = E_{\text{Nernst}} + IR + \eta \quad (6)$$

where η is the overpotential.

As the current is increased into the second region of the scan, the change in sensor output voltage appears to become non-ohmic. Either the sensor resistance would appear to be increasing with applied current, or, more likely, there is an actual localized change in the Nernstian component of the voltage being measured across the sensor. Assuming under these conditions that the oxygen concentration in the bulk surrounding atmosphere has not altered, then this localized change or deviation, in the form of a voltage term, E_{dev} , must be included in equation 6 such that:

$$V_0 = E_{\text{Nernst}} + IR + E_{\text{dev}} \quad (7)$$

At higher current still, in region 3 of the scan, the sensor response becomes distinctly non-linear, as the size of the output voltage step, ΔV_0 , decreases with applied current. This behaviour would suggest electrode limiting at high applied current levels, resulting from changes occurring in electrode reaction mechanisms under these conditions.

Overall the scanning technique is very sensitive to any variations in sensor characteristics which cause the transfer characteristics to deviate from a linear output with current. These variations can be observed and recorded graphically in the scan output, and show up clearly in the magnitude and sign of the E_{dev} term calculated from equation 7.

3.2. The E_{dev} term

The E_{dev} term can be related to changes in localized oxygen concentration at the sensor's electrodes, provided that there is no major variation in sensor resistance as current is passed. If however a resistance change does take place during a scan, which can for example occur with electrode limiting, the sensor IR drop will be affected and as a result E_{dev} will now include the change in this term as well as that resulting from oxygen concentration variations at the sensor's electrodes.

Another factor relevant to E_{dev} is overpotential. When current is passed through the sensor, electrode reactions depart from equilibrium by an amount which is a function of the overpotential, η , developed at each electrode [4]. Electrically, η represents a non-ohmic opposition to current flow within the sensor, excluding the E_{Nernst} potential. At low applied current levels overpotential is small and it is considered that only at high current, especially after limiting, does η become significant. Current mode calculations include any overpotential as a component of the E_{dev} term.

Despite its complex nature, E_{dev} can be used as a calibrating factor for a scan run under a particular set of conditions, the calibration remaining valid for minor changes in those conditions, for example, in changes of oxygen partial pressure in the bulk surrounding atmosphere.

3.3. Cathode characteristics

At the cathode, molecular oxygen from the sensor's internal reference atmosphere is electrochemically dissociated to form atomic oxygen in the zirconia solid electrolyte, at a rate proportional to the applied electrical current.

The mechanism by which this process occurs involves a number of steps, although it is generally unresolved as to which is the rate-determining step of the reaction [5]. The possibilities include:

- (1) Molecular diffusion of oxygen through the pores of the platinum electrode.
- (2) Adsorption and dissociation of molecular oxygen to atomic oxygen on the electrode surface.
- (3) Diffusion of atomic oxygen to or from the three-phase electrode–electrolyte–gas boundary.

Fig. 4 is a schematic representation of the various steps involved in the cathode reaction [6].

During a scan, onset of limiting at the cathode typically takes the form shown in Fig. 5b. Initially the size of the output voltage step ΔV_0 increases, resulting in a negative E_{dev} term, as calculated from equation 7. As the current is increased further during the scan, there is a definite decrease in ΔV_0 causing the E_{dev} term to peak and start increasing positively. These two

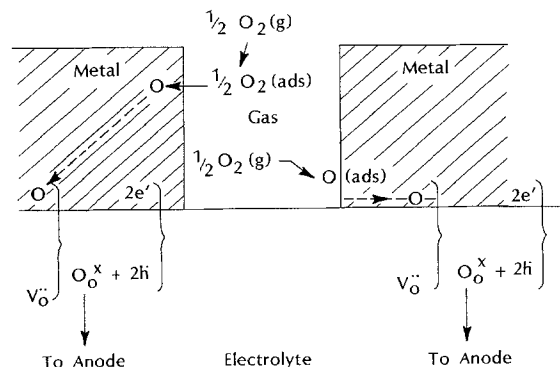


Fig. 4. Schematic representation of oxygen transport mechanisms near the cathode–electrolyte interface. V_0 represents a vacant oxygen ion site, O_0^x an oxygen on its lattice site, h a positive hole and \bar{e} an excess electron.

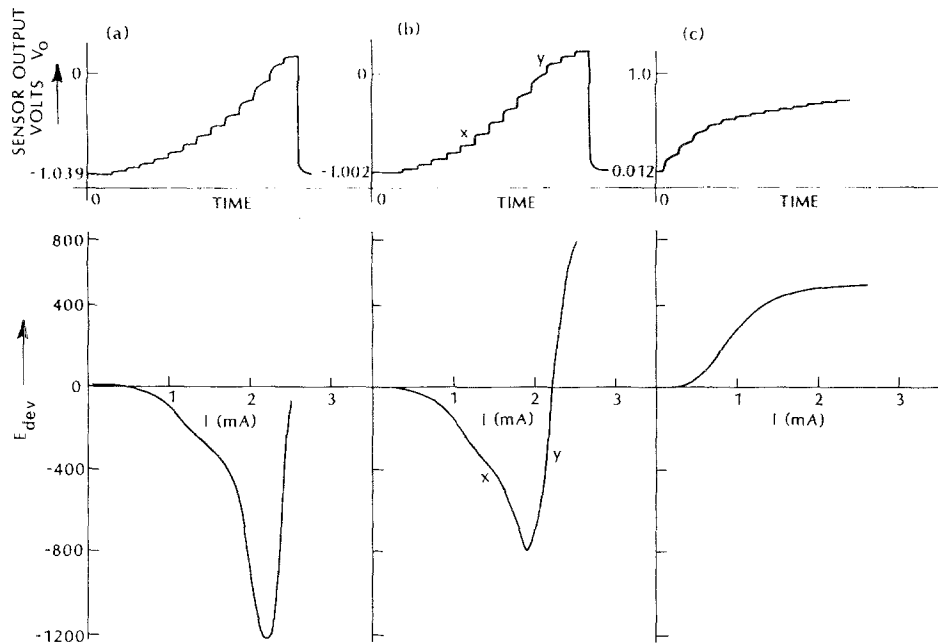


Fig. 5. Cathodic polarization for different reference atmospheres. (a) 100% O₂, (b) air, 21% O₂, (c) 10% H₂ in N₂.

effects are marked as regions *x* and *y* respectively in Fig. 5b.

We have found that the ability of the cathode to take up oxygen is dependent on the partial pressure of the oxygen with which it is in contact, i.e. limiting currents are reached at an earlier point in the scan, the lower the oxygen concentration in the reference atmosphere at the cathode. Fig. 5 shows data illustrating this effect from three scans run with 100% O₂, air (21% O₂) and then a reducing mixture of 10% H₂ in N₂ as the reference atmosphere. Here it can be seen that in all cases, the end result of limiting is a strong swing towards the positive for the E_{dev} term.

3.4. Anode characteristics

At the anode, oxygen ions combine to form molecular oxygen that in the absence of limiting effects is evolved proportional to the sensor current flow (as per equation 2).

Factors affecting the production and dissipation of oxygen at the anode are:

- (a) diffusion of gas through the porous electrode;
- (b) the kinetics of reactions at the three-phase interface;
- (c) the reactivity of gases in the bulk surrounding atmosphere, especially hydrogen;
- (d) the flow rate of gas past the electrode.

It is generally accepted that the anodic reaction proceeds at a faster rate than that of the cathode [5].

3.5. Anode protection-muffles

Oxygen sensors can be required to operate in reducing atmospheres for extended periods at temperatures up to about 1300°C. At high operating temperatures, a higher current density is required through the sensor to form a protective atmosphere at the anode, due to

the increased reactivity and greater mobility of the gases in the furnace.

In order to maintain the anode at a relatively oxidizing atmosphere under all conditions it was considered that some form of muffle would be required to restrict the dissipation of pumped oxygen away from the anode. We have found that a suitable muffle can allow the protective oxygen atmosphere to be developed at a lower current level. This is an advantage as high currents can alter electrode morphology and cause unpredictable changes in characteristics.

Most of the test work on muffles for this study was performed with a muffle of the type shown in Fig. 6. This is an impervious ceramic crucible (zirconia), sealed to the shank of the sensor with alumina cement, so that the leak rate is determined by the seal.

Another muffle, of porous alumina ceramic (Sillimant 60 NG Haldenwager) was used in some experiments, results for which are confined to Section 3.8, Fig. 9. This was of the same general form as the zirconia muffle and both types of muffle fitted over the sensor tip with a clearance of ~0.5 mm.

3.6. The stoichiometric point

With the use of a muffle around the sensor it is possible, by current pumping, to greatly alter the atmos-

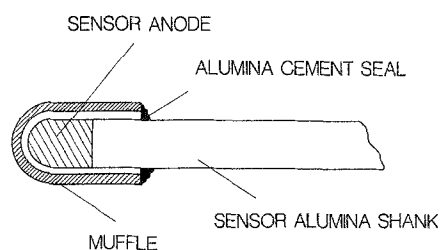


Fig. 6. Muffle around the sensor outer electrode to restrict the dissipation of evolved oxygen away from the anode region.

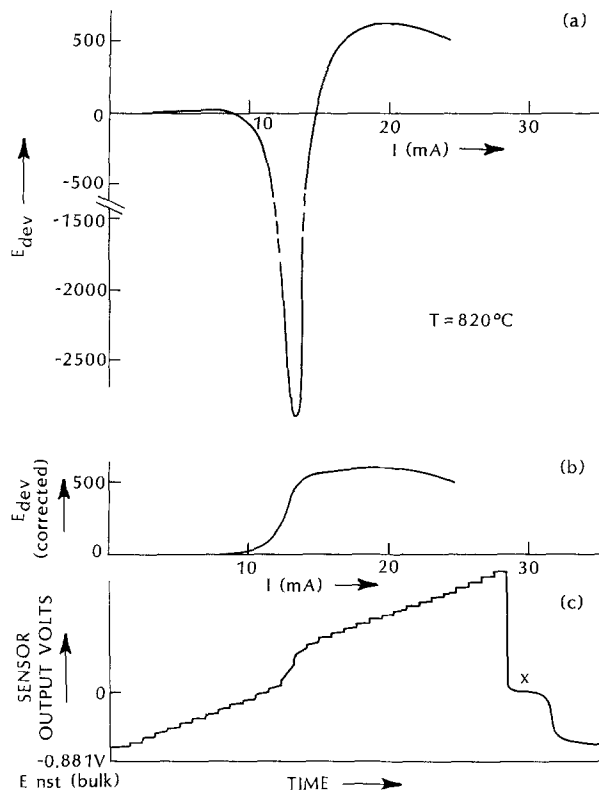
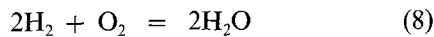


Fig. 7. Abrupt change of sensor output when gas components within the muffle are in stoichiometric proportions.

phere at the anode, from reducing conditions, i.e. $10^{-20}\%$ O_2 to almost 100% O_2 .

As the current is increased during a scan, and the oxygen concentration increases within the muffle, the oxidation of hydrogen proceeds (as per equation 8) until the reacting gas components are in stoichiometric proportions for a particular operating temperature.



From this point on, the atmosphere inside the muffle contains an increasing excess of oxygen.

At stoichiometry, the oxygen partial pressure around the sensor changes rapidly through many orders of magnitude; the result is a sudden dramatic variation in sensor Nernst voltage, of the order of 600 mV [7]. This can be observed as a pronounced shift on the output scan, and also as a large change in the calculated E_{dev} term, see Fig. 7.

The rapidly changing nature of the sensor output voltage in this region of the scan makes accurate resistance measurements difficult. The data plotted in Fig. 7a have been calculated by the computer, using the extremely distorted value of R which the computer has measured around the stoichiometric point. The result is a large negative swing in the calculated E_{dev} term.

In the absence of electrode limiting however, it can be observed, as in Fig. 7c, that there is very little real change in sensor resistance as the atmosphere in the muffle passes through stoichiometry. By interpolating between the resistance values in linear parts of the scan, i.e. before and after the stoichiometric point, and substituting this new value of R into equation 7, more

realistic values of E_{dev} can be calculated for the period of the stoichiometric transition. Fig. 7b is a plot for E_{dev} data 'corrected' in this way, and compared to Fig. 7a, now shows a positive swing where the stoichiometric transition occurs, in this case at a sensor current of about 12 mA .

The region x in Fig. 7c, at the end of the scan is, in effect, the Nernstian output from the sensor after the current source has been switched off. It can be seen that the output voltage passes back through a stoichiometric transition as the atmosphere inside the muffle returns to reducing conditions.

Under these operating conditions, the leak rate of the muffle now becomes an important factor in determining the rate of build up of oxygen as the current is increased during a scan. Oxygen can be considered to be evolved into the muffle at a rate equal to or faster than it is diffusing out or being reacted with the furnace gases, when E_{dev} (corrected) tends positive. For a given current level, the oxygen concentration within the muffle will be related to the oxygen content in the bulk surrounding atmosphere. Thus the stoichiometric point also will occur at different current levels, depending on the original oxygen concentration. Fig. 8 shows data from four scans, all run at the same temperature, where it can be seen that the more reducing the atmosphere in the furnace, then the higher the current required to reach stoichiometry inside the muffle. The atmosphere inside the muffle would appear to be quite sensitive to oxygen partial pressure changes in the bulk surrounding atmosphere; the four scans in Fig. 8 show clearly differentiated stoichiometric points (particularly on the E_{dev} plots), despite there being only small variations in the E_{Nernst} (bulk) for each scan.

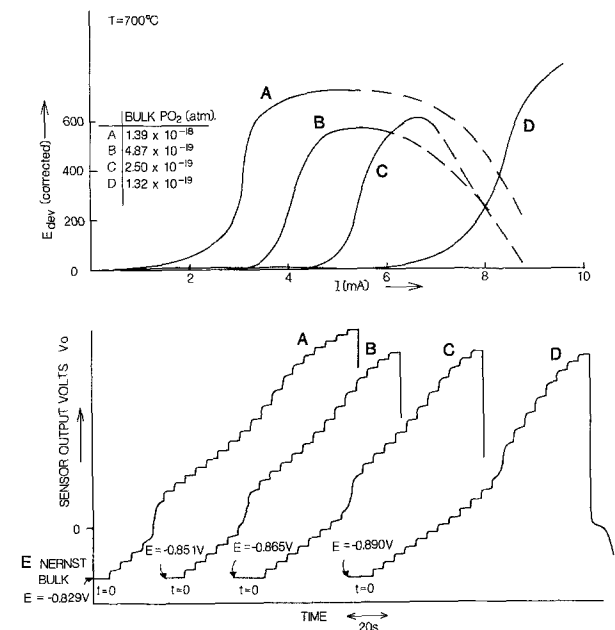


Fig. 8. Stoichiometric transition at different current levels, due to change in furnace oxygen concentration.

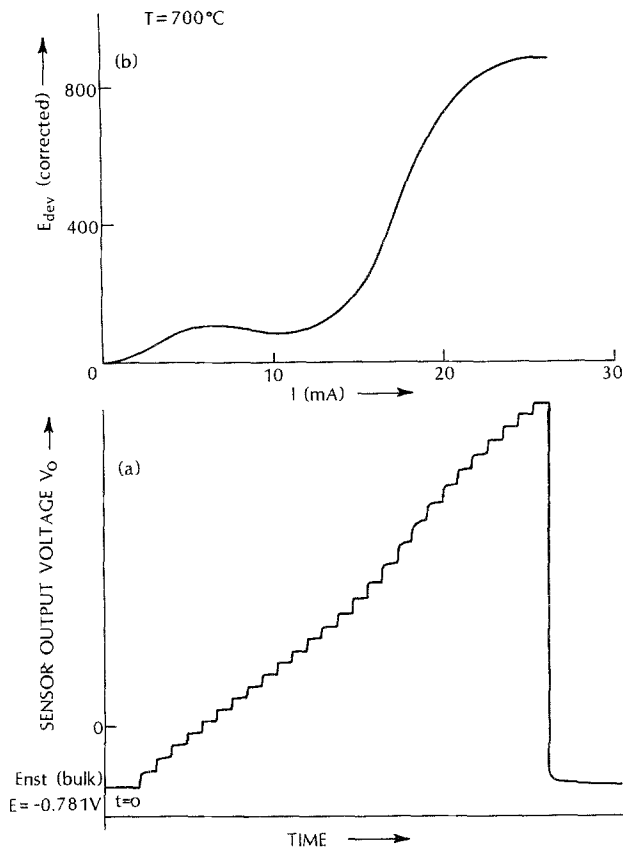


Fig. 9. Use of porous muffle allowing a gradual build up of oxygen near the stoichiometric region.

3.7. Effect of temperature

When the furnace temperature alters, there will be a change in the sensor resistance due to the thermal dependence of both the electrode reactions and ionic conduction of the electrolyte. Similarly, the oxygen gradient developed across the muffle will change, as gas diffusion processes and reaction rates between hydrogen and oxygen vary with temperature.

The scan data is valid only for a particular set of operating conditions, and so any major change in those conditions, especially temperature, will necessitate the electronics initiating a new scan. Data relevant to the prevailing gradient conditions will then be collected and processed. With sensor electrical response time of < 50 ms per current plateau under most conditions, this can be achieved rapidly.

3.8. Interpreting the complete output scan

During a scan, we have seen that there are two main effects which cause the sensor output to deviate markedly from a linear response; these are the transition through stoichiometry and the onset of electrode limiting.

The stoichiometric transition is characterized by a large shift in sensor output voltage, while the sensor resistance remains approximately constant throughout, with the result that the E_{dev} (corrected) term exhibits a strong positive change around this point as

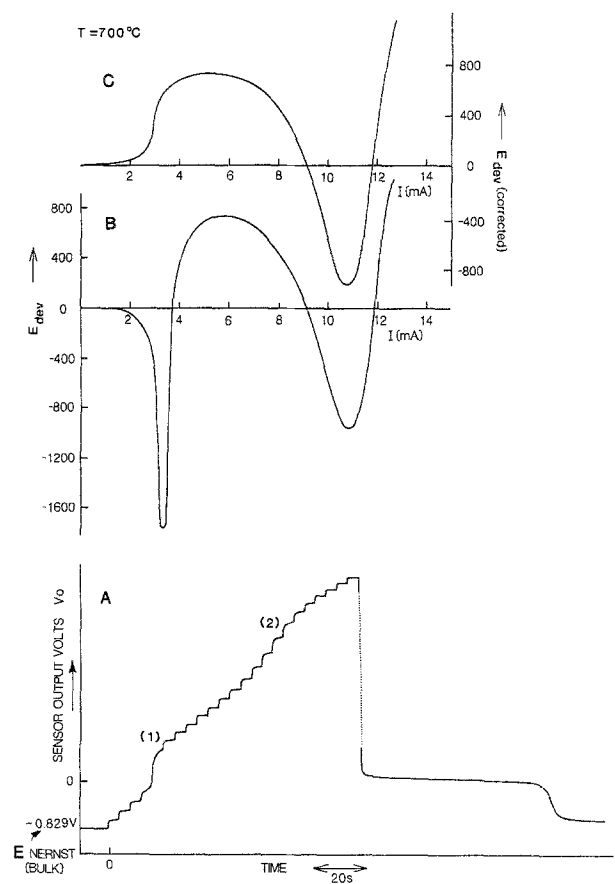


Fig. 10. Data showing stoichiometry (A1) and cathodic polarization (A2) occurring during the same scan.

the current is increased during the scan (refer to Section 3.6, also Fig. 10).

With electrode limiting on the other hand (marked as region 2 on Fig. 10), the transfer characteristic shows at first a gradual increase in size of the output voltage step ΔV_0 . This suggests a rise in resistance, but may at least in part be attributed to a change in the Nernstian component of the sensor voltage, which could arise if the three-phase region associated with the cathode electrode had become depleted of oxygen, due to the high rate of uptake of molecular oxygen as demanded by the applied current flow. This would effectively lower the oxygen partial pressure at the cathode, bringing it closer to that of the anode, and hence decreasing the Nernst voltage of the sensor.

After the initial increase in ΔV_0 with the onset of electrode limiting, there follows a region where ΔV_0 starts to decrease as the current increases. This indicates a further change taking place in cathode characteristics, resulting in opposition to current flow within the sensor decreasing. Under these conditions of high applied current flow, the onset of mixed conduction through the electrolyte is likely. There are a number of possible ways in which this could occur:

(1) After limiting, increasing current flow through the sensor electrolyte is provided by electronic conduction only. This could be likened to insulation breakdown between cathode and anode; or

(2) The dissociation of molecular oxygen at the cathode still proceeds at an increasing rate with

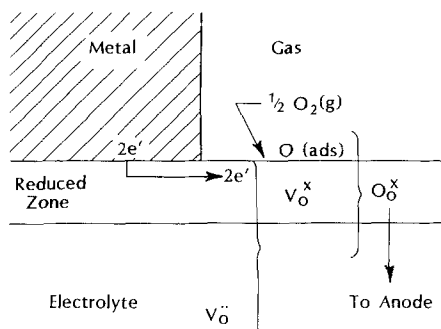


Fig. 11. Schematic representation of oxygen transport mechanisms near the cathode-electrolyte interface, for high applied voltage or large overpotential.

current, but at a rate less than in direct proportion to the applied current flow; the difference being taken up by electronic conduction; or

(3) New reaction mechanisms may come into play, such as those proposed by Yanagida *et al.* [6]. At high current levels, it is considered that electronic conduction, whereby electrons are directly injected into the electrolyte, would give rise to reduction or blackening of the electrolyte at the cathode, and that this would in itself lead to an increase in ionic conductivity of the electrolyte, i.e. under these conditions, the electrolyte would be able to directly adsorb molecular oxygen from the gaseous atmosphere, reaction occurring via the zone of electronically-conductive reduced zirconia adjacent to the cathode. This mechanism is illustrated schematically in Fig. 11.

In order to further investigate the mechanisms affecting limiting, a scan was arranged so that the electrode limiting would occur at a low current level (by lowering the oxygen concentration at the sensor's cathode reference electrode from 21% (air) to 1% O_2 in N_2). The transfer characteristic of this scan is shown in Fig. 12. At the high current end of the scan, after cathodic limiting has taken place, a typical stoichiometric transition can be seen to have occurred at the anode. This indicates that the uptake of oxygen from the reference atmosphere at the cathode has continued to proceed at an increasing rate, after cathodic limiting. This result discounts the first of the proposed forms of mixed conduction as outlined above. If, after limiting, increasing current levels were accounted for by electronic conduction only, then there should be no

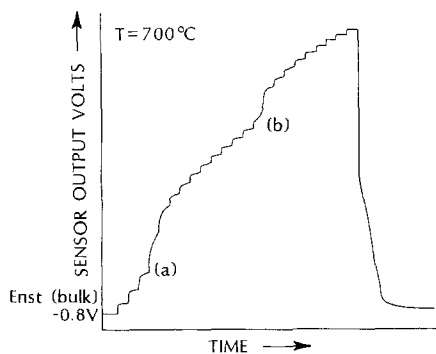


Fig. 12. Transfer characteristic showing cathodic limiting (a) occurring at a lower current level than that for stoichiometry (b).

increase in the rate of molecular oxygen transfer from the reference atmosphere to the anode as current is increased during the scan. Once this form of limiting was reached, there would be no increase in oxygen concentration at the anode for higher current levels. As shown in Fig. 12, the opposite effect is observed — oxygen continues to be pumped through the sensor in increasing amounts after the onset of cathode limiting.

This confirms then, that at least a proportion of the increasing current after limiting arises from increasing ionic conduction. The exact mechanism by which this occurs has yet to be established. However, if the mechanism proposed by Yanagida *et al.* [6], i.e. ionic conduction via reduced zirconia, is largely responsible, then the practical operation of a sensor under these conditions would probably need to be restricted, in that reduced zirconia is known to be associated with loss of mechanical strength within the ceramic electrolyte. For the best long-term operation then, it is important that the cathode reaction should not be limiting at current levels below those necessary to build up a protective atmosphere at the outer electrode of the sensor.

3.9. Operation of the sensor

Under normal operating conditions, the sensor would be 'biased' to a particular current level, at which a steady-state oxygen gradient would be present across the muffle. Variations in gas composition in the bulk atmosphere would alter this gradient and so produce a modification to the atmosphere inside the muffle which would be detected by the sensor. Operation on either the oxygen lean or rich side of stoichiometry should be possible.

Taking the E_{dev} data obtained during a scan and solving for E_{Nernst} in equation 7:

$$V_0 = E_{Nernst} + IR + E_{dev} \quad (7)$$

the continuous measurement of oxygen partial pressure in the bulk atmosphere can be obtained. The E_{dev} term itself can be used as a guide for setting the level of the protective oxidizing atmosphere to be held at the anode.

The differential allowed between the oxygen concentration inside the muffle and that in the bulk atmosphere may have to be determined for a particular operating situation, so as to maintain a high sensitivity to oxygen partial pressure changes in the bulk atmosphere.

4. Conclusion

The current mode technique can enable a sensor operating under reducing conditions to be protected from deterioration, by providing a localized, relatively oxygen rich atmosphere around the sensor. With the addition of a ceramic muffle to the sensor, the oxygen partial pressure at the anode can be altered radically, over many orders of magnitude, during the current pumping process. Yet at the same time, changes in

oxygen concentration can be detected and measured through this protective atmosphere.

The output transfer characteristic from the current scanning process can yield much useful information concerning operation of the sensor; in particular, possible detrimental effects, such as electrode limiting or the onset of electronic conduction, can be readily detected under conditions of applied current flow.

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