

Chapter I.1 Factors Influencing the Stability of Polarographic Oxygen Sensors

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1 Introduction

An ideal polarographic oxygen sensor (POS) exhibits a time-independent relationship between the current it delivers, throughout its specified operating temperature range, and the activity of oxygen contacting its membrane. All applications of POS require stability in some measure, and long-term monitoring applications demand stability over periods up to 1 year.

Available sensors approach more or less closely to this ideal, depending upon their makeup, their design, and the evolution of certain thermodynamic variables of the system. This article presents a systematic examination of those factors which influence the steady-state current output of POS, includes an attempt to weigh the relative importance of these various factors, lists the symptoms which enable the user to recognize individual effects, and gives cures, when these are possible, for the troubles.

At the outset a distinction must be drawn between a drift of steady-state sensitivity, and the short-term transient approach to stabilization following any major change in operating conditions, such as a change of membrane, of temperature, of applied voltage, or of oxygen activity. Such a transient change of sensitivity is easily recognizable, and operating procedure is easily adapted to it. It is usually sufficient to wait for a certain predetermined time, the stabilization time, before resuming measurements after such a perturbation. Typically, the stabilization time lasts for several minutes.

After this stabilization time has elapsed, the output from the POS settles down to a level which can appear to be constant over a period of several hours, but which nevertheless can drift noticeably, at constant oxygen activity, over a period of months. It is this drift which is discussed in detail in this section.

2 Theory of the Sensitivity of POS

The causes of instability of POS are best discussed with reference to a theory of the dependence of POS-sensitivity upon relevant dimensions and other parameters. Such

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theories have been elaborated by a number of workers specializing in different fields [1–5, 9, 11, 13, 18, 23]. In drawing these works together, therefore, the opportunity has been taken here to generalize the results and to extend their significance.

2.1 Oxygen Fugacity, Partial Pressure, Activity and Concentration

Theories of POS sensitivity are based upon Faraday's laws and the diffusion equation, but also upon an assumption that thermodynamic equilibrium exists at the two-phase boundaries: membrane/sample and membrane/electrolyte solution. This assumption leads to the boundary conditions, employed in the solution of the diffusion equation, that the chemical potential, or equivalently the fugacity of oxygen, is the same on each side of the two-phase boundaries. When this assumption is valid, it is the fugacity of oxygen which is really measured by a POS.

The fugacity of a component in a nonideal solution is a true measure of its escaping tendency [10, 20]. It is equal to the partial vapor pressure of the component if the vapor behaves as an ideal gas, as is the case for oxygen at the low pressures normally monitored with POS; hence it is correct to say that the signal from a POS is a measure of the partial pressure of oxygen contacting the membrane. Deviations of the fugacity from partial pressure are discussed in standard works on thermodynamics.

It is also correct to say that the signal from a POS is a measure of the relative activity a_s of oxygen in a solution, since the activity of a gas is proportional to its fugacity by definition:

$$a_s = f_{O_2} / f_{O_2}^\circ \quad (1)$$

$f_{O_2}^\circ$ is the fugacity of a freely chosen standard state of the gas, and is therefore a constant. The activity is a dimensionless quantity (cf. Chap. I.3).

The user of a POS should always bear in mind, however, that the concentration, c_s , of oxygen in a solution can vary independently of the fugacity. These quantities are related through the activity coefficient γ_s of oxygen in the particular sample medium

$$a_s = \gamma_s \cdot c_s / c_s^\circ = f_{O_2} / f_{O_2}^\circ \quad (2)$$

and γ_s can vary, at constant fugacity, due to variations in the concentrations of other components of the sample solution [24, 25]. This phenomenon has long been understood, and accounted for, in the field of oceanography, where oxygen measurements are made in saline water and substantial variations of γ_s occur, but is less appreciated in other fields. These points are relevant when testing the stability of POS, by comparison with the results of a chemical titration method such as that due to Winkler ([26], App. D), because titrations determine concentrations rather than fugacities. In this case the composition of the sample solution must be maintained constant during the test, to keep γ_s constant.

2.2 The Oxygen Diffusion Impedances of the Sample, the Membrane, and the Electrolyte Solution

The electrical signal I_1 [A] delivered by a POS is proportional, by Faraday's laws, to the flux of oxygen J_{O_2} [mol m⁻² s⁻¹], arriving at the cathode and originating in the sample:

$$I_1 = nFA J_{O_2} \quad (3)$$

Here $n = 4$ is the number of electrons added to each oxygen molecule arriving at the cathode, F [C mol⁻¹] is the Faraday, and A [m²] is the area of the cathode. Further discussion will be restricted to the "one-dimensional" case, when the cathode is sufficiently large relative to the membrane thickness for edge effects to be ignored. Conditions at the cathode are so arranged that the fugacity of oxygen is reduced to zero at its surface; then the flux of oxygen is maximized, and is determined in the steady state by the resistance to oxygen diffusion offered by the sample, the membrane and the electrolyte layer (cf. Chap. I.3).

$$J_{O_2} = f_{O_2} / [(z_s / D_s S_s) + (z_m / D_m S_m) + (z_e / D_e S_e)] \quad (4)$$

Here f_{O_2} [kPa] is the fugacity of oxygen in the bulk of the sample, and the three terms in the denominator represent the diffusion impedances of the boundary layer in the sample, the membrane, and the electrolyte layer respectively. Z [m] is the thickness of the layer, D [m² s⁻¹] is the diffusion coefficient of oxygen and S [mol m⁻³ kPa⁻¹] the solubility of oxygen in the layer. The boundary layer is that region of the sample, adjacent to the sensing membrane, within which the concentration of oxygen is lower than in the bulk of the sample due to consumption by the sensor itself.

Clearly, the output from the POS can be stable only if the total diffusion impedance is constant, and the causes of instability must be sought among those factors which can influence the magnitudes of the individual contributions to this impedance. These factors are considered below.

The largest contribution to the total diffusion impedance is normally that due to the membrane. Table 1 lists magnitudes of the relevant parameters, and the derived values of the corresponding diffusion impedances, $z_m / D_m \cdot S_m$, for six commonly used membrane materials.

In aqueous electrolytes at 25°C, the oxygen solubility S_e and diffusion coefficient D_e are of the order of $8.5 \cdot 10^{-3}$ mol m⁻³ kPa⁻¹ [17] and $2 \cdot 10^{-9}$ m² s⁻¹ [27] respectively. Ideally, the electrolyte layer should have a thickness z_e of 1 μm, so that its diffusion impedance would be approximately 6.0 m² s kPa mol⁻¹.

In the sample, assumed for example to be pure water at 25°C, $S_s = 0.0125$ mol m⁻³ kPa⁻¹ [17] and $D_s = 2.6 \cdot 10^{-9}$ m² s⁻¹ ([14], Chap. I.4). The thickness z_s of the boundary layer, however, depends upon the type and vigor of agitation of the sample. One convenient example which can be treated in detail with exact mathematical methods is that in which the sensing face of the POS is disk-shaped and is rotated relative to the sample fluid about an axis through the center of the disk. In this case the boundary layer thickness is uniform and is given by [16]:

$$z_s = 17 D_s^{1/3} \nu_s^{1/6} \omega^{-1/2} \quad (5)$$

Table 1. Solubility and diffusion parameters for 1 mil (0.001 inch or 25.4 μm) membranes of various materials, at 25°C

Material	D_m [$\text{m}^2 \text{s}^{-1}$]	S_m [$\text{mol m}^{-3} \text{kPa}^{-1}$]	$z_m/D_m S_m$ [$\text{m}^2 \text{kPa s mol}^{-1}$]	$0.53 z_m^2/D_m$ [s]
Polytetrafluoroethylene (PTFE)	2.54×10^{-11}	0.106	0.943×10^7	25.4
Perfluoroalkoxy (PFA)	2.69×10^{-11}	0.093	1.02×10^7	24.0
Fluorinated ethylene-propylene (FEP)	1.73×10^{-11}	0.088	1.67×10^7	37.3
Ethylene-tetrafluoroethylene (Tefzel) ^a	1.34×10^{-11}	0.017	1.12×10^8	48.1
Polytrifluoro-monochloro ethylene	3.43×10^{-13}	0.040	18.5×10^8	1881

^a Tefzel is a registered trademark of DuPont de Nemours

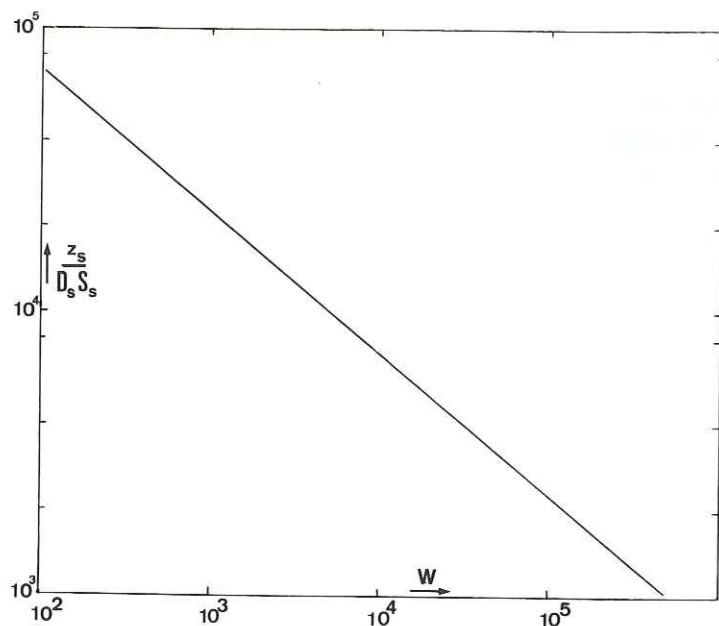


Fig. 1. Dependence of the diffusion impedance of the boundary layer in the sample upon rotation rate of the stirrer (see text)

where ν_s [$\text{m}^2 \text{s}^{-1}$] is the kinematic viscosity of the sample fluid and w is the rotation speed in rotations per minute. It is clear that the thickness and diffusion impedance of the boundary layer decrease with increase of rotation rate. Figure 1 illustrates this conclusion for $\nu_s = 10^{-6} \text{ m}^2 \text{ s}^{-1}$, other parameters having previously quoted magnitudes typical of an aqueous sample at 25°C. Further studies on the subject of diffusion limitations due to the sample are reported in [23].

2.3 Mechanical Requirements for Stability

In order to achieve highly stable output from a POS, conditions should be chosen such that the membrane-diffusion impedance is precisely determined and outweighs the contributions of the electrolyte layer and of the sample by as great a margin as possible. This means that the electrolyte and boundary layer thicknesses must be less than certain critical values, so that membrane tension and sample agitation must be carefully controlled. These critical values become smaller as the membrane permeability increases or as the membrane thickness decreases.

In order to express these requirements more quantitatively, Eqs. (1) and (2) are rewritten in the form:

$$I_1/I_m = (1+r)^{-1}, \quad (6)$$

where

$$I_m = nFAD_m S_m f_{\text{O}_2} / z_m \quad (7)$$

and

$$r = [(z_s/D_s S_s) + (z_e/D_e S_e)] / (z_m/D_m S_m). \quad (8)$$

I_m would be the magnitude of the sensor current if the membrane alone were responsible for limiting the supply of oxygen to the cathode, and r is the ratio of the sum of the diffusion impedances of the electrolyte layer and the sample, to the diffusion impedance of the membrane.

Clearly, $I_1 = I_m$ when $r = 0$, and for any value of r greater than zero, the current I_1 is smaller than I_m . Figure 2 plots the dependence of the ratio of the sensor current to the "membrane" current, upon the ratio of diffusion impedances r . For small values of r , $I_1/I_m \cong 1 - r$.

It often happens that POS are operated under conditions for which the diffusion impedances of the electrolyte and/or boundary layers are poorly controlled and, therefore, variable. Variations of 100% are not unlikely. Figure 2 shows that such variations will result in poor stability of the output from the sensor if r is large, but will have little influence if r is small.

2.4 Electrochemical Requirements for Stability

In connection with Eq. (1), it was mentioned that the fugacity of oxygen at the cathode surface must be zero during operation of a POS. For this to be so, the rate

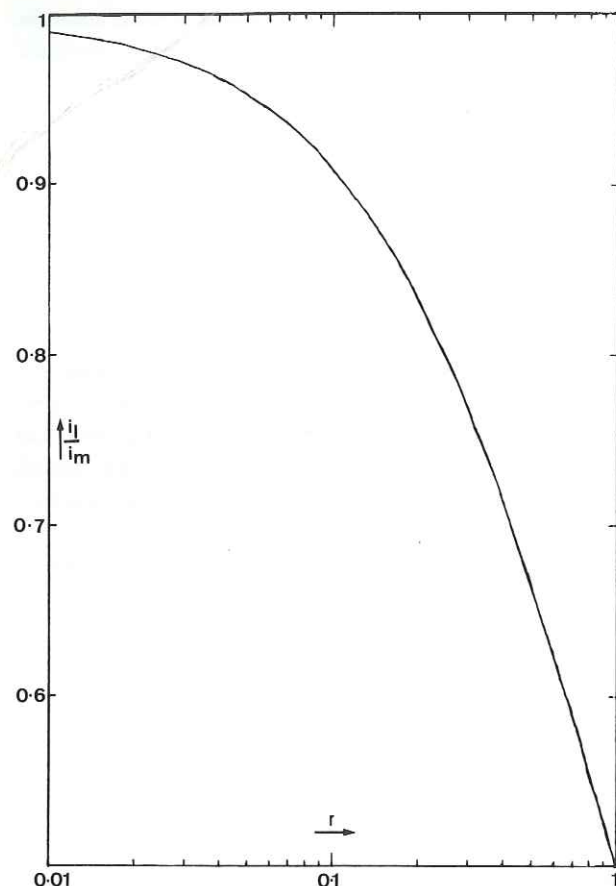


Fig. 2. The influence of the diffusion impedance of the electrolyte and boundary layers upon the current output from a POS

constant k for the electrochemical conversion of oxygen to hydroxide ions at the cathode surface must be large. If k is insufficiently large, the output current is smaller than the idealized current considered previously, being given by

$$I_1 = nFA f_{O_2} / [(1/kS_e) + (z_s/D_s S_s) + (z_m/D_m S_m) + (z_e/D_e S_e)]. \quad (9)$$

Electrochemical rate constants depend upon the interfacial voltage difference U_i between the cathode and the electrolyte, in an exponential manner [22]:

$$k \sim k_0 \exp(\alpha e U_i / RT), \quad (10)$$

where α is a dimensionless constant ($0 < \alpha < 4$), e is the charge on a proton, R is the gas constant and T the absolute temperature. By design, the applied voltage is made sufficiently large initially for the current to become independent of this voltage. Yet there are certain phenomena which may occur during operation of the sensor, which can influence the magnitude of the rate constant k , and hence of the sensor output.

POS are most commonly operated with a constant total applied voltage, which is shared between the anode/electrolyte interface, the cathode/electrolyte interface, and the electrolyte conductor. Ideally, the electrolyte solution (Chap. I.5) should be chosen such that it represents an almost perfect conductor, and its share of the applied voltage is virtually zero. Also ideally, the anode should be operated under practically equilibrium conditions so that its interfacial voltage is fixed by the thermodynamic parameters of the system. Ideally, therefore, the cathode interfacial voltage U_i should remain constant.

The electrolytic conductor may take an increasing share of the applied voltage with the passage of time, either because it becomes progressively depleted of salt due to the anode reaction, or because it becomes gradually diluted with sample water due to faulty sealing of the membrane to the sensor body (Chap. I.6).

The anode interface may take a variable fraction of the applied voltage, either because it becomes increasingly blocked by the deposition of nonporous insulating products, or because the penetration of electroactive vapors into the cell from the sample interfere with the intended anode reaction.

In the presence of such phenomena, the cathode voltage U_i is also variable, usually in the sense that it decreases with time, causing a downward drift in sensor output.

The oxygen electrode reaction is also subject to interference by deposits on the cathode surface, either of electroplated metals (the anode metal is frequently plated onto the cathode during operation), or of organic substances adsorbed from the electrolyte, or of products of side reactions at the cathode of interfering vapors from the sample. Again, a downward drift of sensor output at constant oxygen activity is the usual consequence.

3 The Factors Responsible for Instability of POS

Two types of instability are observed during the operation of POS [6, 19, 21]. Often, there is a gradual monotonic drift of sensitivity — usually in the sense that a decreasing current per unit oxygen activity is output, with the passage of time. Secondly, there are positive and negative fluctuations of sensitivity superimposed on the general drift, some of very short duration, of the order of seconds or minutes, and others of longer time constant of the order of days. Table 2 lists various causes for each of these observable symptoms.

The effects of most of these causes of instability can be eliminated, or at least minimized, by careful design.

3.1 Overstressed or Understressed Membranes

The most important single factor determining the sensitivity of a POS is the membrane tension. Because the membranes used for POS are normally thin, and partially elastic, their thicknesses, and hence the impedances they offer to oxygen diffusion, can be substantially altered if they become stretched when being mounted over the sensing

Table 2. Causes of instability of POS

General drift	Osmotic effects (downward) Release of membrane stress (downward) Leakage or evaporation of a gross excess of electrolyte (upward) Deposition of anode metal at edge of cathode causing increase of cathode area (upward) Membrane erosion (upward) Membrane clogging (downward) Anode blocking (downward) Dilution of electrolyte with sample water (downward) Cathode deactivation by anode metal or poisons
Short-term fluctuations	Poorly stabilized anode supply voltage Poorly compensated temperature variations Flow rate variations of sample Gravitational (orientational) effects Applied pressure effects Vibrational effects
Intermediate-term fluctuations	Barometric pressure effects Residual current variations

face. One of two deleterious effects may then occur. Either the membrane may gradually slip under the restraining means, to return to its original thickness, or it may suffer "cold flow" as a result of the constant stress, with a consequent change of thickness. These thickness changes often continue during a period of months following mounting and are observed as a gradual drift of output signal. Experience suggests that true stability can only be achieved if membrane stretching is avoided during mounting.

At the same time it is necessary to create conditions, during the membrane mounting operation, which do not permit a thick electrolyte layer to remain between the membrane and the sensing cathode. This requirement follows from the rule that the diffusion impedance of the electrolyte layer should be as small as possible relative to that of the membrane.

Membrane mounting is therefore a rather delicate operation, which can be accomplished reproducibly only with a mechanical aid. Such a tool can be simple, but its design is not as trivial as it would seem at first sight.

3.2 Membrane Erosion and Membrane Clogging

Two problems encountered when operating POS in harsh environments are the erosion of the membrane by suspended solid particles, and the deposition on the membrane of films of algae, microorganisms, or grease [6]. Erosion of the membrane leads to erroneously high measurements, because of the connection between sensitivity and the reciprocal of membrane thickness. Clogging of the membrane produces erroneously low measurements.

Membrane erosion can be countered by using thicker, tougher membranes, whenever the consequent increase of response time of the sensor is of minor importance, and by filtering or settling out suspended particles in other circumstances.

The rate of membrane clogging has been found to vary greatly in different culture media [6]. It has been suggested that attachment of strongly acidic groups (e.g., sulfonate — HSO_3^-) to the surface of the membrane contacting the sample medium might be an effective means of prevention of clogging [8], because these groups, when ionized, would repel the predominately negatively charged colloidal species responsible for the clogging. Until such specially treated membranes become available, the only recourse to counter membrane clogging seems to be to locate the sensor in a turbulent region of the sample, where "sticking" of deposits becomes less likely.

3.3 Osmotic, Gravitational, Pressure or Vibrational Effects

The role of the electrolyte layer intervening between the membrane and the cathode, in determining the sensitivity of a POS, was detailed above. Hence physical phenomena which influence directly the thickness of the electrolyte layer can give rise to instability of the response from a sensor.

The membrane which encloses a POS is semipermeable in the sense employed in discussions of osmotic effects, that is, it allows the passage of water vapor but blocks the passage of ions. When a POS is immersed in pure water, therefore, water vapor enters the sensor, diluting the electrolyte. If the walls of the electrolyte chamber were completely rigid, the internal pressure would rise concomitantly, until the water vapor pressure in the electrolytic solution equals the water vapor pressure in the water outside the sensor. Equilibrium would then be attained. In practice, however, the hydrostatic pressure inside the sensor at equilibrium, known as the osmotic pressure, can be as high as 10^4 kPa at equilibrium [20], and could not be restrained by the tension in the membrane. Distillation of water into the sensor continues, therefore, with movement of the membrane to adapt to the increased volume of electrolyte.

This entry of water into the sensor causes an increase in the electrolyte layer thickness, z_e , and a consequent decrease in the output from the sensor.

As an example, we calculate the rate of decrease of the signal delivered by a POS containing 2 mol dm^{-3} KCl as electrolyte, and provided with a $25 \mu\text{m}$ thick Tefzel membrane, assuming the sensor to be immersed in pure water at 25°C . The vapor pressures of water inside and outside the sensor are 2.96 kPa and 3.03 kPa respectively [12]. From the water permeability of Tefzel, it then follows that the rate of increase of thickness of the electrolyte layer dz_e/dt , is about $1 \mu\text{m/month}$. From Eq. (6) we derive:

$$\frac{d}{dz_e} (I_V/I_m) = -\frac{D_m S_m}{z_m D_e S_e} \sim -10^{-3} \mu\text{m}^{-1}. \quad (11)$$

Hence, the downward drift of the signal due to this cause amounts to about 0.1% per month.

This effect increases in significance as the oxygen and or water permeability of the membrane increases.

A hydrostatic pressure in the sample influences the signal from a POS because the activity of dissolved oxygen at constant concentration is changed by this applied pressure. Assuming that the partial molar volume of oxygen V_m ($0.032 \text{ dm}^3 \text{ mol}^{-1}$) is indepen-

dent of applied pressure in the range of interest, the activity of oxygen and the signal from the sensor are *increased* by an *overpressure* w_p by the factor ([20], p. 318)

$$\exp(V_m \cdot w_p / RT).$$

The effect is not large: at 2000 kPa overpressure or 200 m water head, for example, the signal is 2.5% higher than at atmospheric pressure (App. A).

Applied pressure can have a substantial influence upon sensor response if gas bubbles are enclosed in the electrolyte by the membrane, for compression or expansion of these bubbles lead to large changes in the thickness of the electrolyte layer. Such problems are minimized by choosing sensors having uncluttered electrolyte reservoirs which present a minimal risk of trapping of air bubbles.

Gravitational effects upon the electrolyte layer are conceptually simpler to understand, for the membrane may sag to some extent if it supports the whole weight of the electrolyte. The effect is most significant if the electrolyte volume and the membrane area are large, and if the membrane is poorly tensioned and supported. It can be minimized by clamping the sensor in a fixed orientation.

Vibrations of the sensor or turbulence in the sample sometimes causes the sensor to deliver a noisy signal. This problem is particularly acute if either the membrane is poorly tensioned, or if air bubbles are enclosed in the sensor. The explanation is thought to be that convection currents are caused in the electrolyte, thus transporting oxygen from the electrolyte reservoir to the cathode.

3.4 Flow Rate Variations of the Sample

Variations of the flow rate of the sample cause variations of the thickness of the boundary layer z_s . A specific example of a "rotating disk" was presented above, but similar conclusions may be drawn for other modes of convection of the sample fluid. It was pointed out that the sample agitation must exceed a certain critical magnitude, characteristic of the particular membrane used, in order that the sensor output be independent of flow rate. Estimates of the critical velocity for a flowing sample stream are usually given in the published specifications of commercially available POS.

3.5 Plating of Anode Metal on Cathode

Ideally, the electrochemical reaction at the anode of a POS should result in the creation of an insoluble porous solid phase which adheres firmly to the anode metal. In practice, the products generated at most of the commonly chosen anode metals, such as silver, lead, cadmium, thallium, or zinc, are soluble in the electrolyte to some extent because of the formation of complexes between the metal ions and the anions of the electrolyte. Diffusion of these ions and subsequent plating of the anode metal on the cathode is therefore a common phenomenon.

The plating is less rapid when the membrane is well tensioned, and when the zone surrounding the cathode, through which diffusion of the metal ions occurs, is long and narrow. Also the useful life of the sensor is longest, for any particular sample, for

membranes of low permeability, since the initial rate of formation of the metal ions is proportional to the membrane permeability.

Sometimes the plating occurs over the whole of the area of the cathode, an effect which is most easily noticeable at gold cathodes because of the change of coloration. This is not too troublesome if the anode is silver, but can lead to a decrease in cathode activity when the anode metal is more basic. The cathode should be polished in these circumstances to restore its activity.

Otherwise the plating occurs at the periphery of the cathode, as tree-like dendritic formations, thus extending the sensing area and leading to an increase in displayed concentration at constant sample concentration. Again, the cathode must be polished at regular intervals.

3.6 Anode Blocking

The continuous operating lifetime of a POS is often limited by the blocking of its anode by nonporous reaction products.

It usually occurs when a particular quantity of anode product has been deposited on each unit area of the anode, and therefore the lifetime is longer the larger the area of the anode, the lower the permeability of the membrane, and the lower the concentration of oxygen to which the sensor is exposed. Activity is easily restored by stripping the product off the anode with a suitable cleaning solution. A silver anode, for example, may be cleaned with a commercial detarnishing fluid, or with an ammoniacal solution.

3.7 Drying Out of the Sensor or Dilution of the Electrolyte with Sample Water

In order to function properly, a POS must be filled with an electrolyte having at least a minimum conductivity for current flow. This conductivity is decreased if either the sensor dries out, or if the electrolyte becomes diluted by sample water entering through a "leak" in the membrane sealing system. The symptom manifested by the sensor in this case is a gradual decrease of signal at constant oxygen concentration. To cure the problem, it is only necessary to renew the electrolyte, and to ensure adequate sealing of the membrane to the sensor body.

3.8 Poorly Stabilized Applied Voltage

Theoretically, the output current from a POS should be independent of small (≤ 0.2 V) variations of the applied voltage, since the slope of the current voltage curve should be zero at the chosen operating voltage. In practice a sudden change in applied voltage usually has two effects: (1) it triggers a transient "kick" of the current — and hence in the displayed oxygen concentration — which can be of substantial proportions, e.g., equivalent in order of magnitude to the signal in air saturated water, followed by an exponential decay to the steady state, lasting some minutes; (2) the steady-state sen-

sitivity of the sensor changes in some degree, depending upon the design of the sensor and the choices of cathode metal and electrolyte.

The best cure for this problem, of course, is to eliminate the instabilities in the applied voltage, using filtering techniques well known in the electronic art.

Particular attention should be paid to this phenomenon when current measurements are made by following the voltage drop across a resistor in series with the sensor. With this method, the voltage across the sensor changes linearly with the steady-state current, and the system is potentially "noisy". "Galvanic" sensors having an applied voltage of 0 V are usually operated in this fashion. Details of better methods of current measurement are to be found in Chapter I.10.

3.9 Temperature Variations

The current delivered by a POS changes by about 3% to 4% per °C, at constant oxygen activity. This temperature coefficient is greatest for the least permeable membranes [15].

When temperature changes occur during the course of measurements, as they inevitably do during field work, for example, this temperature coefficient is recalled from a previous determination in order to interpret the measured current in terms of oxygen activity. Hence one is concerned not only with the stability of sensor output at constant temperature, but also with the stability of the temperature coefficient of oxygen solubility and diffusivity in the membrane, and perhaps also, of properties of the electrolyte layer and diffusion boundary layer.

Extra care is necessary when a POS is to be operated well above room temperature, to avoid enclosing an air bubble in the sensor. The reason is that this bubble expands more than the displaced electrolyte would have done, and the additional volume might be created by "inflation" of the membrane. This, of course, leads to a diminished output from the sensor, and sometimes to an irreversible stretching of the membrane.

3.10 Residual Currents

The residual current of a POS is the current produced by the sensor when exposed to a medium containing no oxygen. It is never zero, although the sensor should be selected such that it is negligible in comparison with the signals of interest in any particular study. Commercial sensors are available having residuals in the range from 0.01% to 1% of the signal generated in air-saturated water. Hence the stability of residual currents is of little interest when measurements are to be made in well-aerated clean water, but becomes of crucial importance when measurements are made in anaerobic media.

Even a cursory study of residual currents reveals that they are rarely constant in time (Chap. I.2). For example, a current spike followed by an exponentially decaying current tail is observed whenever a sensor is switched on after being exposed to air whilst off circuit. The time constant for this decay can be minutes or even hours, depending upon the particular sensor, and upon the state of cleanliness of the cathode.

Because of the transient nature of the residual current, the practice of electronically adjusting the zero point of a sensor by subtraction of a constant current is of limited usefulness.

The residual current is completely internal in origin, and so becomes of less relative importance as the oxygen permeability of the membrane increases, because the signal level increases in comparison with the constant error level.

4 The Compromise Between Stability, Speed of Response, Residual Current, and Stirring Requirement

The membrane permeability (Chap. I.3) has been mentioned in several places in the foregoing discussion, in the context of POS stability. This is because the oxygen must pass through the diffusion boundary layer and the electrolyte layer, as well as the membrane, and these two additional impedances are likely to vary during operation; therefore stability can be expected only when the membrane impedance exceeds those of the other two by a safe margin. This reasoning alone would dictate a choice of a low permeability membrane for a POS, whenever stable, long-term monitoring of oxygen is of primary importance.

Another advantage also accrues from the use of a low permeability membrane, namely that the rate of stirring required to reduce the impedance of the diffusion boundary layer to a negligible value in comparison with that of the membrane, is least for these membranes. Indeed, as has been seen, very high stirring rates are needed to supply oxygen at the rate required by thin PTFE, PFA, or FEP membranes.

Why, then, are highly permeable membranes most commonly chosen for POS?

The reason is that, in some applications, speed of response and the ability to measure traces of dissolved oxygen are of predominating importance.

The response time of a POS for 99% of a signal change is [4]

$$\tau_{99} \cong 0.53 z_m^2 / D_m, \quad (12)$$

assuming that the transient is controlled by the membrane alone. This time is shortest for thin permeable membranes. Relevant values are recorded in Table 1, and it is clear that the lower permeability membranes would be totally unsuitable for any application where speed of reaction is necessary.

Secondly, the lower limit of oxygen concentration c_{lim} which can be measured with any particular sensor is:

$$c_{\text{lim}} = I_r / \phi, \quad (13)$$

where I_r is the residual current of the sensor and ϕ is the sensitivity of the sensor expressed as current per unit concentration. Since the residual current is independent of the membrane chosen, while the sensitivity is proportional to the permeability of the membrane toward oxygen, the concentration limit is inversely proportional to the permeability. Hence, any sensor is more capable of measuring to lower concentration limits, when it is fitted with a permeable membrane, than when fitted with an impermeable one.

A compromise between speed of response and high sensitivity, on the one hand, and stability and low stirring requirement on the other is therefore necessary when selecting a sensor for any particular application. When rapid response is indispensable, frequent recalibration is inevitable, and when stability is of prime importance, a sluggish response must be tolerated.

References

1. Aiba S, Huang SY (1969) Oxygen permeability and diffusivity in polymer membranes immersed in liquids. *Chem Eng Sci* 24:1149–1159
2. Aiba S, Ohashi M, Huang SY (1968) Rapid determination of oxygen permeability of polymer membranes. I + *EC Fundam* 7:479–502
3. Benedek AA, Heideger WJ (1970) Polarographic oxygen analyzer response: The effect of instrument lag in the non-steady state reaction test. *Water Res* 4:627–640
4. Berkenbosch A (1967) Time course of response of the membrane-covered oxygen electrode. *Acta Physiol Pharmacol Neerl* 14:300–316
5. Berkenbosch A, Riedstra JW (1963) Temperature effects in amperometric oxygen determinations with the Clark electrode. *Acta Physiol Pharmacol Neerl* 12:131–143, 144–156
6. Borkowski JD, Johnson MJ (1967) Long-lived steam sterilizable membrane probes for dissolved oxygen measurement. *Biotech Bioeng* IX:635–639
7. Corrieu G, Touzel JP (1978) Comparaison de sonde de mesure de la concentration en oxygène dissous: Essais au laboratoire. *Tech Sci Munic* 73:349–356
8. Gregor HP, Gregor CD (1978) Synthetic-membrane technology. *Sci Am* 239:88–101
9. Hale JM, Hitchman ML (1980) Some considerations of the steady state and transient behavior of membrane covered dissolved oxygen detectors. *J Electroanal Chem* 107:281–294
10. Hitchman ML (1978) Measurement of dissolved oxygen. Orbisphere Laboratories, Geneva, p 7
11. Jensen OJ, Jacobsen T, Thomsen J (1978) Membrane covered oxygen electrodes. I. Electrode dimensions and electrode sensitivity. *J Electroanal Chem* 87:203–211
12. Kaye GWC, Laby TH (1972) Tables of physical and chemical constants, 14th edn. Longman, London, p 222
13. Kok R, Zajik JE (1973) Transient measurement of low dissolved oxygen concentrations. *Can J Chem Eng* 51:782–787
14. Kolthoff IM, Miller CS (1941) The reduction of oxygen at the dropping mercury electrode. *J Am Chem Soc* 63:1013–1017
15. Krevelen van DW (1972) Properties of polymers. Elsevier, Amsterdam, p 286
16. Levich VG (1962) Physicochemical hydrodynamics. Prentice Hall, Englewood Cliffs NJ, p 69
17. Linke WF (1965) Solubilities of inorganic and metal-organic compounds, vol II. Am Chem Soc, Washington DC
18. Mancy KH, Okun DA, Reilley CN (1962) A galvanic cell oxygen analyzer. *J Electroanal Chem* 4:65–92
19. McKeown JJ, Brown LC, Gove GW (1967) Comparative studies of dissolved oxygen analysis methods. *J Water Pollut Control Fed* 39:1323–1336
20. Moore WJ (1972) Physical chemistry, 5th edn. Longman, London, p 250, 300
21. Pijanowski BJ (1971) A quantitative evaluation of dissolved oxygen instrumentation. Joint conference on sensing of environmental pollutants, Palo Alto, Calif
22. Randles JEB (1952) Kinetics of rapid electrode reactions, part 2. Rate constants and activation energies of electrode reactions. *Trans Faraday Soc* 48:828–832
23. Schuler R, Kreuzer F (1967) Rapid polarographic in vivo oxygen catheter electrodes. *Respir Physiol* 3:90–110
24. Schumpe A, Deckwer WD (1978) Oxygen solubilities in synthetic fermentation media. Preprints, 1st Eur Cong Biotechnol, Interlaken, pp 154–155

25. Setschenow J (1889) Concerning the constitution of salt solutions on the basis of their behavior to carbonic acid. *Z Phys Chem* 4:117–125
26. Winkler LW (1889) The determination of dissolved oxygen in water. *Ber Dtsch Chem Ges* 22:1764–1774
27. Yatskovski AM, Fedotov AN (1969) Solubility and diffusion of oxygen in solutions of potassium hydroxide and phosphoric acid. *Elektrokhimiya* 5:1052–1053