

A METHOD FOR REDUCING THE FLOW-SENSITIVITY OF A POLAROGRAPHIC DISSOLVED-OXYGEN SENSOR

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Summary—A method for reducing the flow-sensitivity of polarographic dissolved-oxygen sensors has been modelled mathematically and tested experimentally. The improved probe uses a two-layer membrane: the first layer is made of Teflon and the second of silicone rubber, which is more permeable than Teflon to oxygen. This arrangement reduces the flow-sensitivity to about 4% of that for a single-membrane 1-mil Teflon; second membrane 2.5-mil silicone rubber. (b) First membrane 0.5-mil Teflon; second membrane 5-mil silicone rubber.

Membrane-covered dissolved-oxygen (DO) probes have found acceptance in a wide range of research and industrial applications.¹ Most, if not all, practical sensors may be termed polarographic devices (although the method is clearly voltammetry) following the concepts of Clark's design.² The sensor is composed of a pair of electrodes immersed in an electrolyte solution and separated from the test-solution by a gas-permeable membrane. Oxygen diffuses through the membrane and is reduced cathodically at the surface of a noble metal. The electrolytic current thus generated is proportional to the partial pressure of oxygen at the surface of the membrane and to the diffusivity of oxygen through the membrane. The consumption of oxygen by the probe necessitates a certain rate of flow at the surface of the membrane to replenish the oxygen removed; otherwise the sensor will register a pO_2 lower than the true value for the test-solution. The effect of the flow-rate on the response is referred to as the flow-sensitivity of the probe, and it should be kept as low as possible.

The requirement of solution flow past DO sensors is a major disadvantage of conventional probes: it calls for a pump or other flow-producing mechanism (such as a stirrer) if an accurate reading is to be obtained. Here we describe a method for reducing the flow-sensitivity of polarographic DO sensors. Its use should eliminate the need for pumping or stirring in most applications.

THEORETICAL CONSIDERATIONS

Various methods for reducing flow-sensitivity of DO sensors have previously been reported.³⁻⁵ Unfortunately, these attempts have generally resulted in sluggish probes with long response-times, ranging

from minutes to hours. In most applications, such long response-times are unacceptable, and in addition, calibration and standardization of very slow sensors is impractical.

Butler *et al.*⁵ demonstrated that the flow-sensitivity of DO electrodes can be considerably reduced if the cathode is made hair-like. This approach is an application of the well-known fact that sensors with an extremely small cathode are relatively insensitive to changes in flow. Unfortunately, the output current of the DO sensor is proportional to the cathode size, and this sets a practical lower limit to the size of the cathode. Butler *et al.* improved the situation somewhat by using a spiral of 40- μm thick platinum as the cathode, which resulted in a sensor with the flow-sensitivity of a 40- μm thick cathode but with a much higher output current, owing to the relatively larger area. We have found that sensors of this type still require stirring in most applications.

The flow-sensitivity of DO sensors may be improved by reducing the oxygen consumption and distributing it over a larger volume of the test-solution. Once the consumption per unit area is reduced to a low enough level, eddy diffusion within the solution may suffice to replenish the oxygen consumed by the sensor. With large-area cathodes, oxygen diffusion paths are approximately perpendicular to the surface of the cathode and hence the oxygen is consumed from the solution directly overlying the cathode area (Fig. 1). It is therefore evident that in this case oxygen consumption per unit area can be reduced only by reducing the permeability of the membrane separating the cathode from the test-solution. Unfortunately, this will slow down the response of the electrode and reduce its sensitivity.³ However, at the edge of the cathode, oxygen is consumed from a larger area

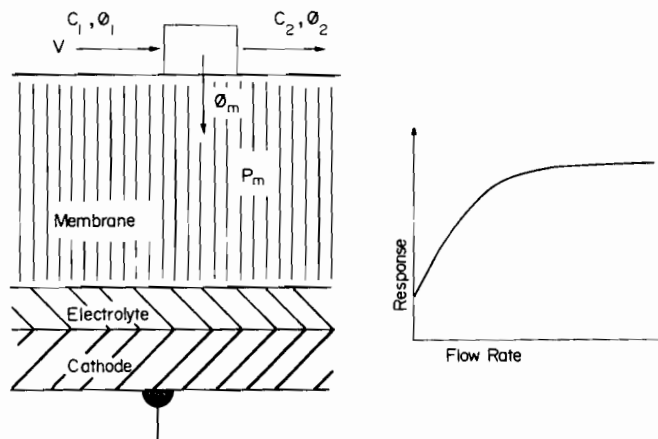


Fig. 1. Schematic representation of the origin of flow-sensitivity in a membrane-covered polarographic sensor with large surface area. (a) Cross-section of cathode and membrane. V is the solution flow-rate, ϕ the flux of the electroactive species and P_m is the permeability of the membrane. (b) Resulting flow-sensitivity of a large-area cathode sensor.

owing to the spreading out of the diffusion paths. This "edge effect" becomes much more important if the total surface area of the cathode is reduced (Fig. 2).

A further reduction of oxygen consumption per unit area (or volume) of solution can be obtained by further spreading out the diffusion stream-lines. This could be accomplished by introducing a second gas-permeable membrane between the primary membrane and the solution. The second membrane should have a much higher permeability to oxygen than the primary membrane has. An analogue of this configuration would be a point heat-source separated from a solution by a layer of a thermal insulator, above which there is a layer of a thermal conductor. It is obvious, intuitively, that the layer with high thermal conductivity will help in distributing the heat over a larger area than would be the case in its absence. This approach, of using two gas-permeable membranes, is considered here.

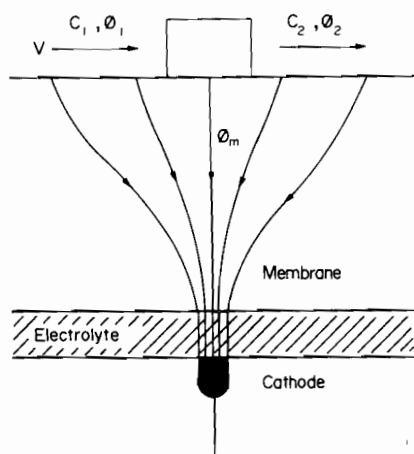


Fig. 2. Schematic representation of diffusion paths in a polarographic sensor with a small-area cathode. Since consumption of electroactive species per surface area is smaller than for a large-area electrode, the sensor is less sensitive to flow.

Among the various gas permeable-membranes applicable for DO sensors, Teflon (Trade-Mark of Du-Pont) is usually preferred on account of its relatively high diffusivity to oxygen, and its mechanical strength, mechanical stability and inertness.⁶ The extra layer required for reducing flow-sensitivity should thus have a much higher permeability to oxygen than that of Teflon. Only one material, silicone rubber, was found to meet this criterion. Its permeability to oxygen is about 60 times that of Teflon.⁷

MODEL CALCULATIONS

Migration of gases through membranes is usually treated in terms of the permeability coefficient (P) rather than the diffusion coefficient (D). This simplifies calculations because the gas transport can be treated as a function of the partial pressure, which is a continuous function for boundary layers. Permeability is related to diffusivity by⁷

$$P = SD \quad (1)$$

where S is the solubility coefficient of the gas in the membrane.

The diffusion flux of oxygen, J , at any point in a cross-section through a membrane can thus be expressed as:

$$J = -P \left(\frac{dv}{dx} + \frac{dv}{dy} \right) \quad (2)$$

where v is the partial pressure of oxygen and the permeability P is assumed to have no directional dependence but may vary along the plane.

Under the steady-state conditions, the net flux at any given point must be zero. This can be simulated numerically by calculating the gradients of pO_2 from each point, along the co-ordinates of the cross-section, deriving the net flux and setting it to zero. From this

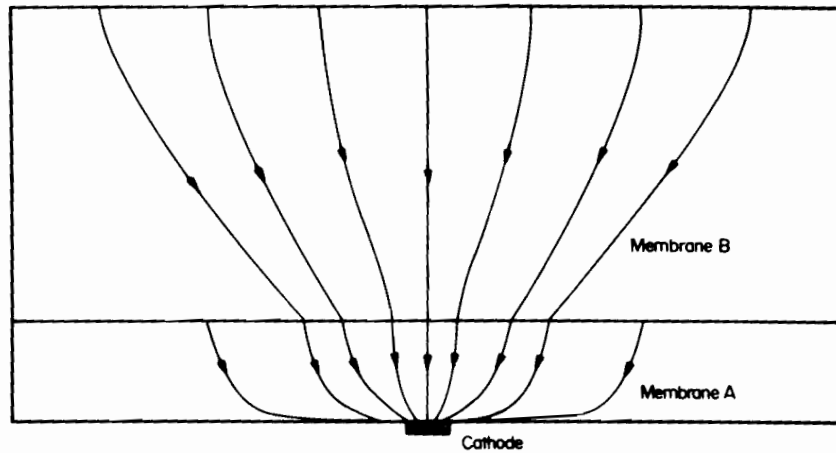


Fig. 3. Diffusion path of a double-membrane polarographic sensor, computed for the model given. The permeability of the silicone rubber membrane (B) was assumed to be 60 times that of the Teflon membrane (A).

equality $v_{i,j}$ at the centre point can be derived:

$$v_{i,j} = \frac{P_{i-1}v_{i-1,j} + P_i(v_{i,j-1} + v_{i,j+1} + v_{i+1,j})}{P_{i-1} + 3P_i} \quad (3)$$

where i is the line number of the grid, j the column number, and the grid is assumed to be perpendicular

to the cathode surface, *i.e.*, it represents a cross-section through the membrane. The cathode is assumed to be a long and narrow bar so that diffusion parallel to its length (the z axis) is negligible. The boundary conditions are $v = 0$ at the cathode surface and $v = 1$ in the test-solution. It is also assumed that

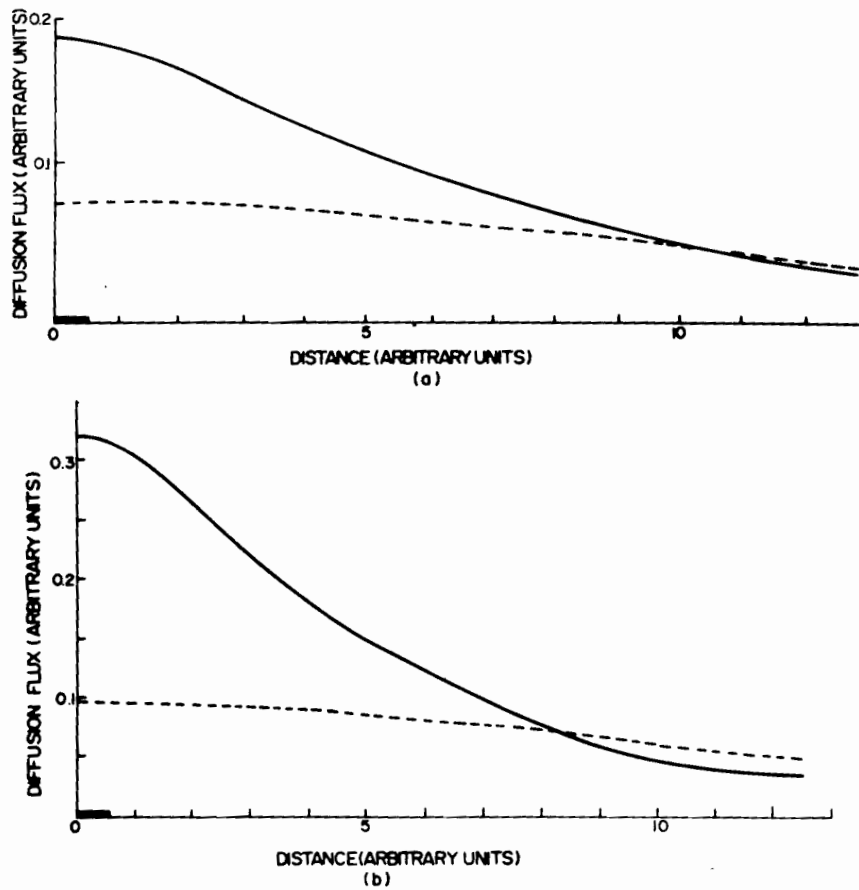


Fig. 4. Vertical diffusion of oxygen at the surface of a DO sensor with a single (solid line) and two (broken line) gas-permeable membrane(s), computed for a cross-section perpendicular to the cathode. Only one half of the plane is shown. The heavy bar represents one half of the cathode width. (a) First membrane 1-mil Teflon; Second membrane 2.5-mil silicone rubber. (b) First membrane 0.5-mil Teflon; second membrane 5-mil silicone rubber.

a thin electrolyte layer separates the cathode and the first membrane.⁸ The calculations are done for the two membranes in contact.

Model calculations of this type confirm the assumption that a layer with high diffusivity will reduce the oxygen consumption per unit surface area of test-solution. This is illustrated in Figs. 3 and 4 which summarize three computer runs. It is clear that the introduction of a second membrane, of high permeability, has the effect of spreading out the oxygen consumption (Fig. 3). Furthermore, the localized high-consumption peak of the single membrane sensors is significantly damped out (Fig. 4) in the two-membrane sensors.

EXPERIMENTAL

The performance of the double-membrane electrode was tested with the sensor shown in Fig. 5. It comprised a Plexiglas body in which a cavity was formed. The anode was a 1-mm thick silver wire, about 5 cm long, wound around the central stem in which the gold cathode was cast. The gold cathode surface was shaped in the form of a thin bar 3 mm long and about 15 μm wide.

Sensitivity to flow was tested in demineralized water in a 500-ml beaker at room temperature ($25 \pm 2^\circ$). The solution was stirred with a magnetic bar and was kept saturated with respect to the atmosphere by bubbling air through it. All measurements were made with a 0.8 V polarization potential and 2M potassium chloride as internal electrolyte solution.

The signal processor was a home-made electronic circuit built around a MOSFET operational amplifier (RCA CA 3130).

The sensitivity of the sensor to stirring, for a given membrane pair, was found by comparing the response at full stirring speed and the response with no stirring or air-bubbling. A rest period of about 15 min was allowed before the response for the unstirred system was read. It should be noted, though, that even if forced stirring is not used, some solution movement is still expected, because of convective diffusion. However, since a similar effect is expected in practical applications we consider the present results to represent a realistic measure of the flow-sensitivity of the sensor.

RESULTS AND DISCUSSION

The flow-sensitivity of the DO sensor was tested for various membrane pairs (Table 1). The response was

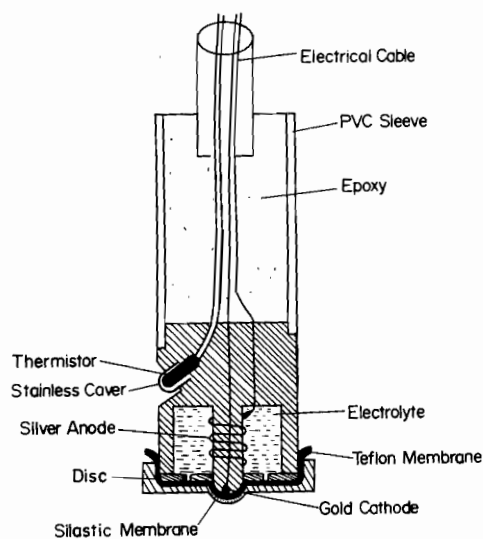


Fig. 5. Cross-section of the DO sensor used in the present study.

found to be mainly dependent on the thickness of the Teflon membrane. This would be expected, considering that the permeability of silicone rubber to oxygen is about 60 times the permeability of Teflon. Hence, the diffusion is primarily controlled by the Teflon membrane. The flow-sensitivity is expressed as the relative difference in response for the stirred and unstirred systems.

The flow-sensitivity of the sensor is greatly reduced when a two-membrane configuration is used (Table 1), as predicted by the model calculation. The highest flow-sensitivity (*ca.* 58% change in response) was registered with the thinnest Teflon membrane (0.5 mil), in complete agreement with our assumption that the flow-sensitivity is a function of the rate of oxygen consumption per unit area. The 0.5-mil Teflon membrane had the lowest resistance to diffusion and hence the rate of oxygen consumption should be the largest. This is substantiated by the magnitude of the response in an air-saturated solution (440 nA), the largest value for this set of experiments.

Table 1. Performance of the proposed sensor with different membranes

Membrane thicknesses, mil		Response in air nA	Response in stirred air-saturated solution nA	Decrease in response,* %	Response time,† sec	
Teflon	Silicone rubber				t_{63}	t_{90}
0.5	—	490	440	58	0.9	1.2
1	—	331	320	25	3.0	6.5
2	—	281	268	23	4.5	14
1	10	238	240	9	18.0	32
2	10	270	269	4	14.5	24
1	40	285	301	4	115	220

* Difference in response to well-stirred and unstirred solutions, expressed as fraction of response in stirred solution.

† Time to reach 63% (t_{63}) or 90% (t_{90}) of final value.

The flow-sensitivity of a sensor with a single Teflon membrane decreases progressively as thicker membranes are used (Table 1). With a 1-mil membrane the reduction in response is about 25%, much too high for most practical applications. However, this flow-sensitivity is already considerably smaller than that expected for a cathode of large area, because of the enhanced "edge effect" of the hair-like electrode (Fig. 2). The addition of the extra membrane, highly permeable to oxygen, was found to be effective in further reducing the sensitivity to flow (Table 1), the difference in response between stirred and unstirred solutions decreasing with increasing thickness of the silicone rubber membrane. Minimum flow-sensitivity was obtained with a combination of a 1-mil Teflon film and a 40-mil silicone rubber membrane. However, the response time to reach 90% of maximum signal ($t_{90\%}$) for this membrane pair was about 220 sec, which is probably too high for most applications. Fortunately, a similar flow-sensitivity (ca. 4%) was found for the 2-mil Teflon film and 10-mil silicone rubber membrane combination. The response time for this pair ($t_{90\%} = 24$ sec) is considerably shorter and probably acceptable even for manual individual measurements.

A second bonus of the double-membrane system is the similarity in response to air (the gas phase) and air-saturated solution. Ideally, these responses should be identical because the electrode is sensitive to pO_2 , which is identical in the two phases. However, experience has shown that the response of conventional DO sensors to solutions is much lower than that to the

gas phase. This could be explained by the existence of a hydrodynamic boundary layer⁹ adjacent to the membrane when it is in contact with a stirred solution. This stationary film provides an extra resistance to diffusion and hence the diffusion flux should be smaller than the diffusion flux obtained in the gas phase, where there is no additional resistance to oxygen migration towards the cathode. An equality of response to air and air-saturated solution has an important practical advantage. Sensors exhibiting this behaviour can be calibrated with air instead of an air-saturated solution (or any other standard solution), because the pO_2 in air is constant. This calibration procedure is very convenient and time-saving in field measurements with portable instruments.

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