

The Rank Brothers Oxygen Electrode

Operating Manual

Manufactured by:

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1. Additional Items

Each electrode is supplied with the following additional items:

- A screened lead connected to a DIN plug.
- 50mm x 450mm of PTFE membrane.
- 1 stirring bar (flea).
- 1 spare PTFE 'O' ring.

2. Introduction

The name 'Oxygen Electrode' is just one of the many titles often used to describe this electrochemical sensor for oxygen. Other names include: 'Clark Cell', after its generally recognised inventor (1956) Leyland C Clark and 'Oxygen Membrane Polarographic Detector' (O₂-MPD for short), because of the mode of action of the electrochemical device.

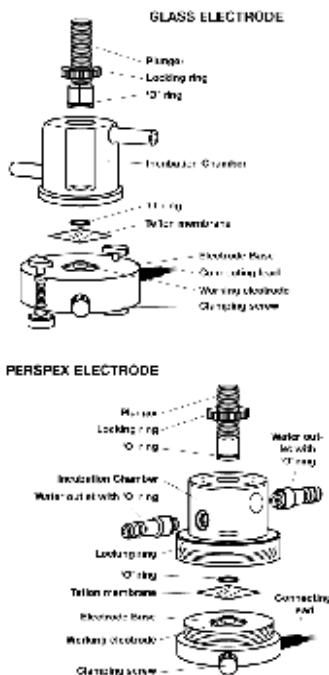
The Oxygen electrode remains one of the most commonly used devices for measuring the partial pressure of oxygen (sometimes referred to as 'oxygen tension') in the gas phase or, more commonly, dissolved solution. The Oxygen Electrode finds application in a wide variety of diverse subject areas including areas such as:

- Environmental studies (e.g. O₂-levels in natural waters).
- Sewage treatment (vital in monitoring the progress of bacterial attack).
- Alcohol production (O₂-levels in fermentation tasks need to be continuously monitored and controlled).
- Medicine (invasive and non-invasive monitoring of a key physiological analyte).

The typical range of detection of O₂ of this device is from 10⁻⁴atm (i.e. 0.01%) to 1atm (i.e. 100%). The key to continuing supremacy of the Oxygen Electrode over other electrochemical devices for O₂ detection is the utilisation of a gas-permeable, ion-impermeable, membrane that separates the test system from the sensing electrode (the platinum cathode). This membrane prevents many problems of electrode passivation or poisoning that arise when the sensing electrode is placed in direct contact with the system (usually an aqueous solution) under test.

3. The Cell

The Rank Brothers Oxygen Electrode comprises two electrodes. The first is a small (typically 2mm in



diameter) central platinum disc working electrode (this is the cathode and it is at this electrode that the O₂ diffusing through the membrane is reduced). Set in a well surrounding this is a silver ring counter and reference electrode (about ten times larger in surface area than the Pt cathode). Conduction between the two electrodes is achieved using a 3M potassium chloride solution to saturate the paper tissue covering the two electrodes. On top of this is placed the key gas-permeable membrane, usually 12.7µm thick PTFE, sealed from the test sample in the incubation chamber by a silicone rubber 'O' ring.

The controller supplied by Rank Brothers is used to apply a voltage to the central platinum electrode that is sufficiently negative, with respect to the silver electrode, that all the oxygen diffusing through the membrane and reaching this electrode is reduced. The resultant current which flows between the two electrodes is proportional to the oxygen partial pressure in the test system, P(O₂). The controller converts this current directly into a voltage and depending on the model will display this in units of percentage saturation. It can also be measured continuously using a x/t chart recorder or a data logger.

4. Principles of Operation

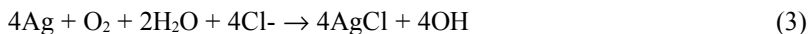
When the platinum electrode is polarised at -0.6V with respect to the silver electrode, every oxygen molecule that reaches its surface from the test medium, via the gas-permeable membrane, is reduced to water through the following reaction:



For every reduction reaction there must be an oxidation and this occurs at the silver electrode as follows:



Thus the overall electrochemical process that occurs in an Oxygen Electrode is as follows:



As the oxygen electrode is repeatedly used the bright silver ring electrode rapidly becomes 'tarnished'. Eventually an even coat of brown silver chloride forms on the silver electrode. The presence of this silver chloride layer is desirable (it stabilises the overall behaviour of the electrode) and should not be removed except if it grows very thick (after many months of use).

The polarising voltage at the platinum electrode is so negative that the current, i_d is related to the P(O₂), via the following expression:

$$i_d = 4 \cdot F \cdot P_m \cdot A \cdot P(O_2) / b \quad (4)$$

Where F = Faraday's constant ($9.64 \times 10^4 \text{C} \cdot \text{mol}^{-1}$), $P_m = O_2$ permeability of the PTFE membrane (typically $1.05 \times 10^{-12} \text{mol} \cdot \text{atm}^{-1} \cdot \text{s}^{-1}$), A = surface area of the Pt working electrode (typically 0.031cm^2) and b = thickness of the PTFE membrane (typically $12.5 \times 10^{-4} \text{cm}$). Thus in a test medium which is air-saturated water, $P(O_2) = 0.2 \text{atm}$, the oxygen electrode would have a value for i_d of $2 \mu\text{A}$ approximately.

5. Setting up the Oxygen Electrode

Apart from the electrode itself you need to have the following items:

- Small pair of sharp scissors
 - 3M potassium chloride solution
 - Teat pipette
 - PTFE membrane (supplied by Rank Brothers)
 - Tissue paper (lens tissue is ideal, but one ply of ordinary tissue is fine)
1. Using the teat pipette, wet both electrodes and fill the small well containing the silver electrode with the potassium chloride solution.
 2. Cut a 1.5cm square piece of tissue paper with a 2mm hole in its centre and float this on the potassium chloride in the well ensuring that the hole is central above the platinum electrode.
 3. Touch the empty teat pipette against the tissue paper and use it to suck off the excess electrolyte so that the paper is wet (but not very wet) and clings to the surface of the electrode.
 4. Cut a 1.5cm square piece of PTFE membrane and place it so that it covers both electrodes, ensuring that the platinum electrode is underneath the centre membrane and that there are no air bubbles trapped under the membrane.
 5. Gently push the silicone rubber 'O' ring over the platinum electrode so as to hold the PTFE membrane in place when the plastic base and the incubation chamber are clamped together (you can use the incubation chamber to gently push the 'O' ring into place).
 6. Carefully clamp the electrode base and the incubation chamber together. It is important to ensure that the incubation chamber is not rotated on the base during clamping, as this will damage the membrane. The locking ring should be tightened by hand only. Over tightening may cause problems.
 7. Connect the electrode to the controller, adjust the polarising voltage to 0.6V and adjust the stirring speed to a suitable level. Connect the water jacket of the incubation chamber to a constant temperature water bath and allow the sample temperature to stabilise. The electrode is now ready for calibration.

6. Calibrating the Oxygen Electrode

It is necessary to refer to the individual controller manuals for precise instructions for calibration, however the following general information is still useful. The controllers all convert the current from the electrode to a voltage thus if S is the voltage from the controller, it is proportional to the partial pressure of O_2 in the medium under test, i.e.:

$$S = K \cdot P(O_2) \quad (5)$$

Where K is the proportionality constant. All our controllers (excluding the Electrochemical Processor) allow the adjustment of K via a sensitivity control so that S can be adjusted to a suitable value when the test sample contains a known level of oxygen. Typically the sensitivity is adjusted with an air saturated aqueous test sample to give a display reading of 100.0 (100% saturation) or until a chart recorder gives a full-scale reading. The readings will then be the percentage air saturation for the test solution being monitored.

Some useful conversion factors are as follows: for 100% air saturated water, $P(O_2) = 0.2095$, atm = 159mm, Hg $[O_2] = 2.4 \times 10^{-4} \text{mol.dm}^{-3} = 8\text{ppm} = 8\text{mg.dm}^{-3}$. It should be noted that the electrode has a small residual current i.e. there is a small current flow even with no oxygen present. Thus when low levels of O_2 are under study (i.e. $P(O_2) < 0.002\text{atm}$) Equation 5 is not accurate enough and should be modified to:

$$S - S_0 = K \cdot P(O_2) \quad (6)$$

Where S_0 is the background signal when $P(O_2) = 0\text{atm}$. This can normally be trimmed out on either the controller or the chart recorder during calibration.

7. Oxygen Consumption of the Electrode

The oxygen electrode consumes oxygen from the test medium reaction (see Equation 3). However, if the electrode is to function properly it is important that the partial pressure of O_2 at the interface between the membrane and the test medium should be the same as that in the bulk of the medium. As a result, when the test medium is an aqueous solution it must be continuously stirred, failure to do so will lead to a signal that drifts downward and general erratic behaviour. For the Rank Brothers oxygen electrode it can be shown that the percentage of the total amount of oxygen lost per minute (%D) from an aqueous solution of low ionic strength is given by the following expression:

$$\%D = 12.5 \cdot i_d / P(O_2) \cdot V_{\text{test}} \quad (7)$$

Where V_{test} = volume of the test solution in dm^3 and i_d is the current flow through the electrode. For example, if we take $i_d = 2\mu\text{A}$ for a sample where $P(O_2) = 0.2\text{atm}$ (i.e. an air saturated solution) we can estimate that only if $V_{\text{test}} < 0.125\text{cm}^3$ will the electrode consume $> 1\%$ of the total number of oxygen molecules present per minute. It follows

from Equation 7 that measurements of $P(O_2)$ carried out on small isolated volumes of aqueous solution using the oxygen electrode should be avoided since it is likely to lead to a downwardly drifting signal as monitoring proceeds (due to oxygen consumption by the electrode). In such circumstances it is better that the electrode is operated for short times (e.g. monitor for 1-2 minutes, every 10-20 minutes) rather than continuously. It is possible to reduce the oxygen consumption by reducing the diameter of the platinum electrode, however the current flow is also reduced putting more demands on the controller.

It should be noted that although $P(O_2)$ and therefore i_d is independent of salinity, the actual concentration of O_2 in solution decreases with increasing salinity (see Reference 1). As a result of this the factor '12.5' in Equation 7 increases with increasing salinity (it is $\cong 29$ in 3M sodium chloride). Thus care should be taken when monitoring low oxygen levels in isolated low volume solutions of high ionic strength.

8. Temperature Sensitivity of the Oxygen Electrode

The oxygen electrode is temperature sensitive and should be thermostatted whenever this is possible. If no thermostating is employed the signal is likely to increase with increasing temperature. If the thermostating is inadequate the signal will fluctuate as the oxygen electrode and sample change temperature. Any light shining on the electrode may cause a change in signal due to heating effects.

9. Cleaning and Storing the Oxygen Electrode

When the electrode is not in use for a few hours (e.g. overnight) it is best dismantled and the electrodes left to soak in distilled water, we can supply a storage cell for this purpose. If the electrode assembly must be left intact, but non-operational for a few hours, it is best if the electrode is left on, but with the stirrer switched off. The platinum electrode needs to have a 'mirror' finish, any surface damage will affect the response of the electrode, and it will thus need to be cleaned approximately once every 5-7 days of use or when it has lost its shine. A suitable polish can be made by mixing a thick slurry of $0.3\mu\text{m}$ polishing alumina (obtainable from BDH Chemical UK for instance) in distilled water. A piece of cotton wool can then be used to polish the platinum electrode until it is smooth, bright and clean (this should only take a few minutes). The silver electrode will need to have the layer of silver chloride removed and the surface polished every 2-3 months of use. A 10% ammonia solution on cotton wool can be used to remove the silver chloride layer. (Ensure that the appropriate handling precautions are observed.) The silver electrode can then be made smooth, bright and clean by polishing with the alumina slurry as described above for the platinum electrode.

10. Troubleshooting

Simply dismantling the electrode, washing it in distilled water and then re-assembling with a new membrane and fresh potassium chloride can solve most problems encountered with the oxygen electrode. A useful check to see if the electrode is

responding properly is to alter the $P(O_2)$ in the test solution. This can be done by saturating with air, or by removing all oxygen from the test medium by purging with nitrogen (or any inert gas, such as He or Ar) or by adding sodium dithionite. The signal should change very rapidly (typically giving a 90% response within 15 seconds) with a sudden change in $P(O_2)$. The observation of some signal noise that is synchronised with the stirrer flea rotations is a useful indication that the electrode is working well.

Symptoms	Possible Causes	Suggested Remedies
Noisy signal.	<ul style="list-style-type: none"> Electrical interference. Stirrer flea in contact with the membrane. 	<ul style="list-style-type: none"> Remove the electrode from the source of noise. Ensure the flea is the correct size (it is usual to have some signal noise synchronised with the stirrer flea rotations).
Sluggish or no change in signal with changes in oxygen level.	<ul style="list-style-type: none"> Incubation Chamber clamped too tight. Insufficient electrolyte soaking the tissue. An air-bubble above Pt electrode. Membrane damaged. Stirrer flea stopped. Platinum electrode damaged. 	<ul style="list-style-type: none"> Reassemble the electrode. The locking ring should be hand tight only. Reassemble the electrode. Remove the air bubble with teat pipette. Reassemble the electrode. Check stirrer is switched on and operating OK. Polish the electrode or return to us for repair.
Step change in signal.	<ul style="list-style-type: none"> Stirrer flea had stopped turning and now has started again. 	<ul style="list-style-type: none"> Check stirrer is functioning correctly and the flea is OK.
Smooth but rapid increase in signal.	<ul style="list-style-type: none"> Hole in membrane (the test solution has begun to leak into the electrolyte well). 	<ul style="list-style-type: none"> Reassemble the electrode with a new membrane.
Smooth but slow increase in signal with constant oxygen level.	<ul style="list-style-type: none"> Inadequate thermostating. The electrode is being warmed up (e.g. by direct sunlight). 	<ul style="list-style-type: none"> Improve the thermostating. Shade from direct sunlight.
Downwardly drifting signal.	<ul style="list-style-type: none"> Air bubble above platinum electrode. Hole in membrane. Stirrer flea stopped turning. Inadequate thermostating. 	<ul style="list-style-type: none"> Remove the bubble. Reassemble the electrode. Check the stirrer and flea are OK. Improve thermostating.

	<ul style="list-style-type: none"> • Electrode consuming too much oxygen. 	<ul style="list-style-type: none"> • This is a problem in samples high in ionic strength, low in volume (< 1cm³) and low in oxygen (< 5% saturated).
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11. Technical Data

Oxygen Electrode	
Size	50mm x 100mm x 50mm approx.
Weight	100g approx.
Response-time	100% - 0% air saturation in less than 15 seconds

12. Suggested Further Reading

1. M L Hitchman, *Measurement of Dissolved Oxygen*, 1978, Wiley-Interscience, London, ISBN 0-471-03885-7.
2. Y H Lee and G T Tsao, *Advances in Biochemical Engineering*, 1979, Volume 13, Page 35.

13. Acknowledgements

We gratefully acknowledge the help and assistance given by Professor Andrew Mills, University of Strathclyde in compiling this manual.