High-Temperature Operation of Oxygen Electrode Giving Fast Response for Respiratory Gas Sampling

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The 98% response time of the membrane-covered Clark-type polarographic oxygen electrode may be reduced to 0.4 sec. by heating the electrode and the gas sample flowing past it to 80° when the electrode is covered with 0.25-mil (6 μ) Teflon membrane. The design of the microcathode electrode has been modified slightly to prevent drying out of the electrolyte and pressure changes within the electrolyte cavity. The relationship of output current to temperature approaches a plateau at this temperature which suggests that for reasonably accurate operation, temperature regulation may not be as crucial as it is at body temperature.

THE RATE of response of the membrane-covered Clark-type* polarographic oxygen electrode is limited by the rate of diffusion of oxygen through the membrane. Kreuzer (*1*) and Staub (*2*) have used Teflon membranes 5 μ thick to reduce response times to about 1 sec. Kreuzer, using his catheter electrode in the airway, was able to record approximate oxygen plateaus in expired alveolar gas during slow respiration and reported 95% response in 1 sec. However, the electrode output current was sensitive to airway temperature which varied from inspiration to expiration. This variation is in part due to the high-temperature permeability coefficient of Teflon (*3*). At higher temperatures the current derived at a given oxygen tension increases and the response time decreases. It has therefore been found possible to shorten the response time and stabilize the temperature by placing the electrode in a thermostated metal cuvet (kept at elevated temperature) through which a gas sample is pulled.

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Methods

The commercially available Clark-type pO_2 electrodes with the micro platinum cathodes (25-μ diameter) have almost no electrolyte cavity and no opening for relief of pressure from this electrolyte space. When temperature is elevated, they tend to dry quickly, and dissolved air in the electrolyte escapes to form gas bubbles which increase the pressure within the electrolyte space. An electrode was constructed with dimensions comparable to the standard electrodes but with an electrolyte chamber having openings for filling and for pressure relief (Fig. 1). The platinum cathode diameter was 25 μ. For high-temperature operation it was found that if the glass surrounding the platinum were too smooth, evaporation of water through the Teflon membrane resulted in loss of continuous film between the anode and cathode. If the

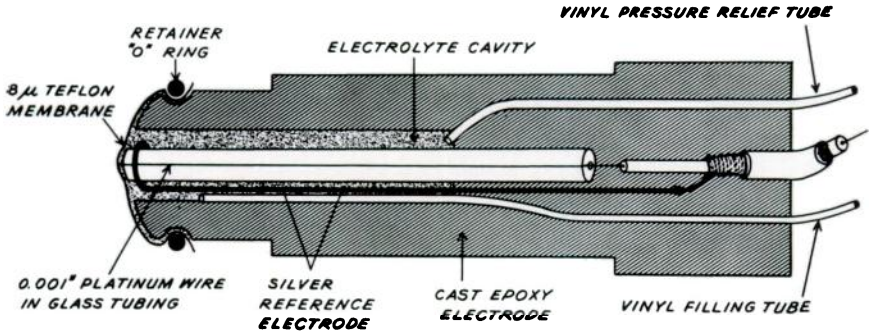

Fig. 1. Modification of oxygen electrode for use at high temperature. Catheters built into electrode permit it to be filled or flushed with electrolyte and prevent pressure build-up due to heating and bubble formation.

surface was too rough, edgewise diffusion of oxygen resulted in a slow component or tail in the response. The surface was prepared by very gentle grinding under water on a fine-grain carborundum stone. Teflon membranes of 6–8 μ were used. A buffered electrolyte, prepared by adding 1 ml. of saturated KCl to 30 ml. of undiluted, pH 7 phosphate buffer stock concentrate, was used to eliminate the effect of CO_2 and the nonlinearity seen at high pO_2. A commercially available,* stainless-steel, water-jacketed, 25-μl. cuvet intended for capillary blood pO_2 analysis was slightly modified (Fig. 2). Temperature was regulated to 0.1° by a circulating thermostat. Gas samples were pulled through the cuvet at 100–150 ml./min. using PE 90 polyethylene catheter. The hub of the No. 19 needle inlet was cut off to permit the sampling cathe-

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ter to be mounted directly on the needle tubing. The output of the electrode was amplified and recorded using a Grass, low-level DC preamplifier* and ink writer. A suitable input coupling circuit is indicated in Fig. 3.

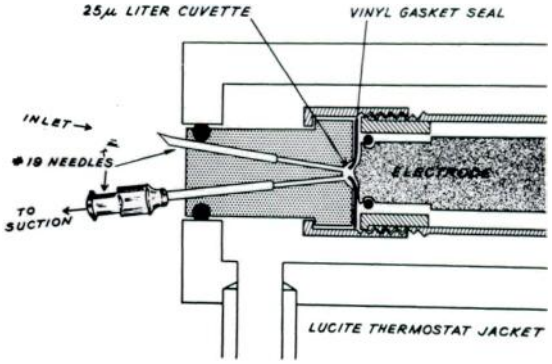


Fig. 2. A 25-μl. cuvet with water jacket. Electrode is sealed in by vinyl gasket between cuvet and front of electrode. Inlet and outlet were drilled out to accept needle tubing.

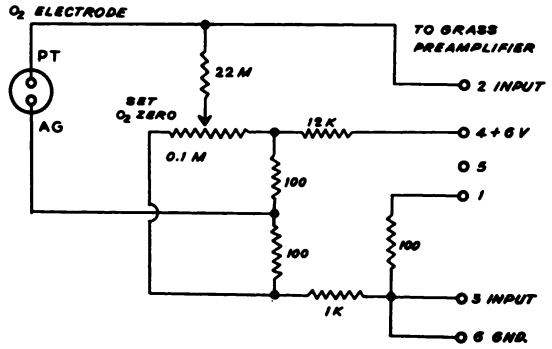


Fig. 3. Circuit used to provide 0.50 v for driving electrode and a zero O_2 adjustment and to couple electrode into low-level DC preamplifier and recorder.

Results

The output current of the electrode with 8-μ Teflon membrane at 70° in air was approximately 3×10^{-9} amp. The polarographic plateau at higher temperatures, as shown in Fig. 4, was shifted to lower voltage. At 80° the zero O_2 (background) current was found to rise rapidly with polarizing voltages above 0.5 v, whereas at 37° this occurred well above 0.8 v. With time, this background current tended to fall towards zero (circled points on Fig. 4), resulting in unstable readings. At 0.5 v, background current fell to a constant value within a few minutes of operation. Accordingly, 0.5 v was selected for the following studies.

The effect of temperature on the response time expressed both as the

*Model 5P1G.

time constant (time to 63% of maximum) and as the 98% response (four time constants if response is exponential) is shown in Fig. 5. The electrode responds about twice as fast at 70° to 80° as at 37°. The current through the electrode increased about 50% over the same range and was less sensitive to temperature change at the high than at

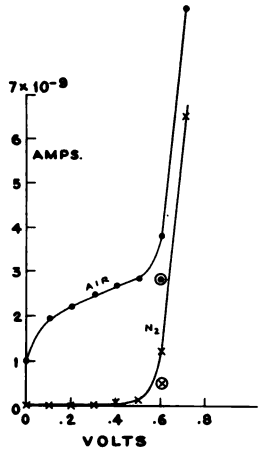


Fig. 4. Polarogram of electrode at 80° with air and O_2 free gas. Circled points at 0.6 v were obtained after waiting 30 min., indicating gradual fall in background current. This was avoided by operation at 0.5 v.

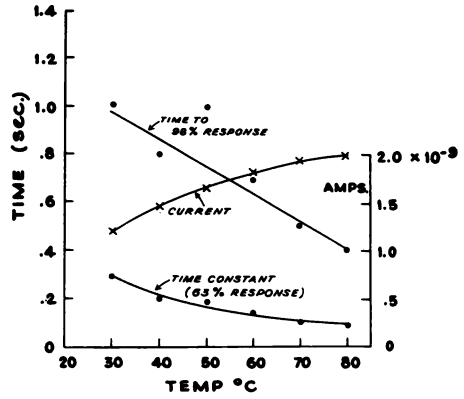
the low temperature range. This is of interest in that small temperature changes will produce less drift at high temperature. The response of the oxygen electrode at 80° to an instantaneous change from air to nitrogen and back to air is compared in Fig. 6 with the response of an infrared CO_2 analyzer* to a sudden introduction and withdrawal of CO_2. The response was found to be approximately a single exponential provided the surface of the glass surrounding the platinum was uniformly ground, eliminating pock marks and cracks at the edge of the platinum; such irregularities tended to introduce a slow component in the response curve. The electrode was linear to within 1% at 80° over the range 0-100% oxygen (Fig. 7).

The pO_2 is, of course, dependent on the water vapor concentration in the gas sample. In air saturated at body temperature, water vapor decreased the current about 5% (Fig. 8). When using polyethylene sampling catheters, there was a considerable delay in response to water vapor changes particularly in substituting dry for wet gas. Water vapor clung to the inside of the tubing and cuvet and continued to saturate the inflowing air for many seconds after the shift to dry gas. For practical purposes, when sampling an air stream through a catheter, it

*Model LB-1, Beckman Instruments, Inc., Spinco Division.

may be assumed that the water vapor pressure does not change between inspiratory and expiratory readings because of this lag effect.

At high operating temperatures it was more difficult to obtain stable electrode operation. Electrodes have been assembled which have remained stable over many hours and in which no membrane change has



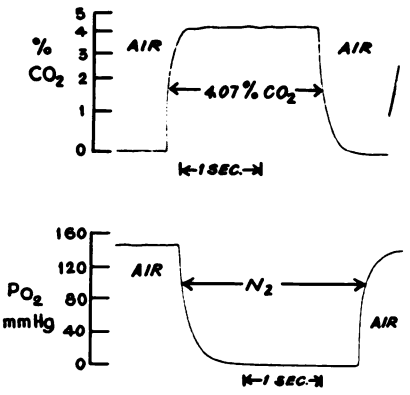


Fig. 5 (*left*). Effect of temperature upon response time and current of modified pO_2 electrode. Teflon membrane, 8μ; sampling catheter length, 5 cm.; gas flow, 150 ml./min. **Fig. 6** (*right*). Comparison of response to step change in concentration of oxygen electrode at 80° with infrared CO_2 analyzer, using low-pressure, high-velocity sampling with a 5-cm. catheter.

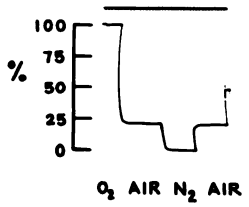
been necessary from day to day. However, with the extremely thin membranes and high temperatures the membranes may develop holes and fail within a few minutes after assembly. Some of the sources of failure have been identified as follows.

1. Gas bubbles arising in the electrolyte from dissolved gases break the continuity of the electrical cell. To avoid this, it has been found helpful to drive off the dissolved gases by boiling the electrolyte before injecting it into the electrode.

2. Negative pressure in the cuvet ruptures the very thin membrane. Hence, negative pressure in the cuvet must be held at a minimum. If a constant flow suction is used the membrane will rupture if the sampling tip orifice is temporarily obstructed for even a fraction of a second, as it may be when the sampling needle tip is pushed through a rubber mouthpiece. Therefore, the suction to the electrode should be stopped when any manipulation of the sampling tip is being done.

3. Particulate dirt punctures the membrane. To avoid this, the cuvet and the vinyl gasket as well as the plastic and glass portions of the electrode which come in contact with the membrane must be kept scrupulously clean and smooth.

4. The membrane is stretched in applying it over the tip of the electrode. This must not be done not only because of the danger of creation of holes but because, when the membrane presses too tightly on the electrode tip, the thin film of water may dry out, resulting in a reduction of the output current to zero.



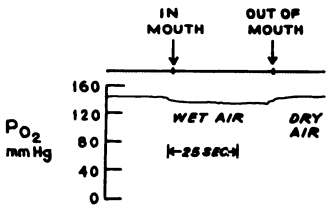


Fig. 7 (*left*). Linearity of O_2 electrode (80°). **Fig. 8** (*right*). Effect of water vapor on hot O_2 electrode. Water vapor saturated at body temperature by sampling from closed mouth filled with air reduced reading about 5%. Time markers appear displaced because of curvilinear recording. With longer (20-cm.) sampling catheter, water vapor variation during respiratory cycle was avoided due to water vapor's clinging to catheter walls.

An upward drift of the current in the electrode generally occurs after long periods of operation. It is believed that this results from the electrolytic deposition of trace metals, probably mostly silver, on the edges of the cathode, increasing the effective area of the cathode. These trace metals may be removed by mild polishing of the tip with a kitchen abrasive or may require the use of the fine carborundum stone.

Drift of the electrode tends to be somewhat more than that observed at 37° operation principally because of the tendency of the electrolyte film to dry. It was found important to avoid change in flow rate through the cuvet since such changes altered both electrode tip temperature and total gas pressure.

The electrode may be calibrated in use if the inspired oxygen concentration is known. Since zero does not ordinarily drift, the gain of the amplifier may be reset to make the recorder deflect correctly during inspiration. In an experiment in which the inspired concentration was

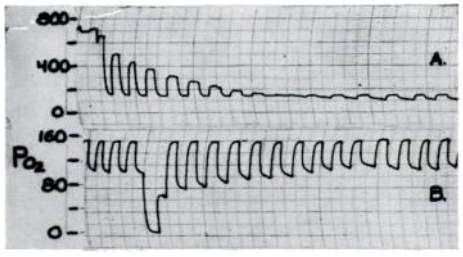


Fig. 9. Recording of pO_2. **A** indicates trace after washout with air after breathing 100% O_2; **B**, effect of single breath of 100% N_2.

varied we have used a paramagnetic recording oxygen analyzer* to record inspired concentration continuously, and have adjusted the calibration of the rapid responding polarographic electrode to agree with this reading during inspiration.

Discussion

An oxygen pressure sensor responding sufficiently rapidly to follow oxygen tension changes in the airway makes possible recordings comparable to those now commonly available with the infrared CO_2 analyzer (Fig. 9). The other instrument available commercially which can offer fast response to changing oxygen tensions is the mass spectrometer, which is not available in most laboratories because of its high cost and complexity of operation. The oxygen electrode, with a suitable cuvet and circulating thermostat, is available for less than $500. The plateau of oxygen electrode current with temperature at the high-temperature range suggests the construction of a self-thermostated cuvet, which is now under construction in this laboratory.

References

1. Kreuzer, F., Rogeness, G. A., and Bornstein, P., *J. Appl. Physiol.* **15,** 1157 (1906).
2. Staub, N. C., *J. Appl. Physiol.* **16,** 192 (1961).
3. Rayment, R. B., *Anal. Chem.* **34,** 1089 (1962).

*Model F, Beckman Instruments, Inc.