

A COULOMETRIC OXYGEN ANALYZER BASED ON A POROUS CATALYTIC ELECTRODE WITH VACUUM CONTROLLED ACTIVE SURFACE AREA

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A coulometric analyzer for oxygen is described, based on the use of a porous catalytic silver electrode where the active surface area is controlled by applying a pressure difference across the cell. Oxygen concentrations over the range 100–0.007% can be measured.

A new type of porous silver electrode¹⁻⁴ initially developed for use in fuel cells has recently found several valuable applications in analysis⁵⁻¹⁰. A continuous analyser, based on a coulometric principle, has been developed and applied to the direct determination of oxygen in gases⁵, and of dissolved oxygen in water and waste water⁶. In addition several indirect procedures have been devised based on reaction with a reagent which liberates oxygen. The determination of permanganate and dichromate⁷, chemical oxygen demand (C O D) of trade waste and industrial effluent⁸, hypochlorite or peroxide strength of textile bleaching baths⁹, and oxygen capacity of whole blood¹⁰ are examples of the use of the devices as an end-point sensor in automatic analysis.

The detailed operation of porous electrodes has been described by the original authors^{1-4,11}, but the principle can be explained briefly. The porous structure of the catalytic operating layer contains pores of two distinct sizes, the smaller pores (c. 3 μm) consist essentially of the intergranular spaces while the larger pores (c. 50 μm) are formed by the addition of a thermally labile pore forming agent during the sintering process. The function of the larger pores is to act as a diffusion path for the gas while the smaller pores enable the electrolyte to wet the working surface by capillary action. The outer protective layer contains pores of uniformly small diameter and serves to prevent the escape of gas into the cell compartment until a certain pressure is reached within the electrode body. In the case of the Type LD 848 electrodes this is about 1.5 atmospheres. When the oxygen containing gas sample is introduced into the electrode under a slight overpressure it diffuses into the catalytic operating layer and is reduced electrochemically.

The control of pressure can be achieved in two ways; firstly by using a differential pumping system where the effluent gas from the electrode is partly recycled into the inlet line. Alternatively a spring loaded diaphragm valve may be connected to the cell exit.

An alternative to using a high pressure to introduce the gas to the working surface is to pass the gas to the electrode at atmospheric pressure and at the same time lower the ambient pressure in the outer cell compartment¹². By applying a slight vacuum to the air space above the electrolyte a pressure difference is established across the

electrode in an analogous manner to the high pressure system. The latter system has the important advantage that the pumping system for manipulation of samples and reagents can now be located subsequent or downstream of the electrode assembly. This enables glass or metal sampling manifolds to be employed and eliminates entirely the errors associated with the diffusion of atmospheric oxygen into the flexible plastic pump tubing. The present paper describes the operation of the system using a sub-atmospheric pressure cell.

EXPERIMENTAL

Electrode system. The porous catalytic silver electrodes were type¹⁻⁴ 857 (J. Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, Prague). The design of this electrode is somewhat different than the earlier type 817 in that the central annular space in the latter is completely filled with catalytic operating layer. This arrangement, as well as improving the response time also enables higher currents to be drawn through the electrode as it increases the effective area of contact between gas and working electrode surface. At a flow rate of 10 ml min⁻¹ the pressure drop across the electrode from inlet to outlet manifold is 2--5 mm Hg. The gas inlet and outlet connections are made *via* a nickel tube which also provides electrical contact. In the present electrode assembly two electrodes are connected in series, the geometric surface area of each being 10 cm².

Cell and control circuitry. A conventional three-electrode system with an operational amplifier potentiostat was used (Fig. 1). The reference voltage was obtained from a 1.5 V dry cell *via* a 1 k Ω potentiometer. A mercury/mercuric oxide reference electrode is used and connection to the working electrode compartment is by a Luggin probe. The platinum spiral counter electrode (0.05 . 50 cm) was contained in a separate compartment with a sintered glass contact to the main cell assembly. A potential of -0.60 V vs Hg/HgO was applied to the working electrode, corresponding to the limiting current region for oxygen reduction. The maximum current load in the present system of 200 mA is governed by the output capability of the booster amplifier although the electrodes could support a much higher current.

The cell assembly (Fig. 2) was constructed from Plexiglass with the electrode compartment sealed with a neoprene gasket and tight fitting lid. The space (6) above the electrolyte was con-

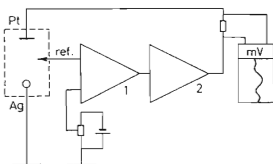


FIG. 1

Potentiostat and Electrical Connection

1 Philbrick PF85AU operational amplifier; 2 booster Philbrick P66A.

nected to the inlet of the peristaltic pump. By pumping in this way it was possible to decrease the pressure to 200–500 mm Hg below atmospheric. A sub-pressure of 330 mm Hg controlled by the adjustable mercury valve (12) was found to be satisfactory for most measurements.

Manifold. A peristaltic pump (Technicon Corp., New York, U.S.A.) was used for metering samples and also for the control of pressure in the cell compartment. A schematic diagram of the manifold is shown in Fig. 3. In order to minimise errors due to diffusion of atmospheric oxygen into the system the inlet side of the manifold was constructed from glass with the minimum number of connections made by butt-jointing inside a thick walled PVC sleeve. Oxygen-free nitrogen or argon is used as the carrier gas. In the present system three individual cell assemblies were employed. The first of these acts as an electrolytic purification unit to remove traces of oxygen from the carrier gas. The second is the analyzer unit itself while the third is used to check on the current efficiency of the oxygen reduction in the analyzer cell. The absence of a significant current in the latter unit provides a simple and instantaneous check on the 100% current efficiency of the working unit.

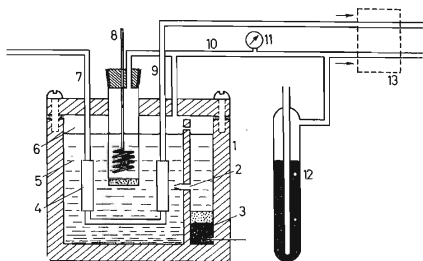


FIG. 2

Coulometric Analyzer

1 Electrolytic cell; 2 Luggin capillary; 3 mercuric oxide reference electrode; 4 working pores Ag electrode; 5 5M-KOH; 6 gas compartment over the electrolyte; 7 analyzed gas inlet; 8 platinum common electrode; 9 gas outlet; 10 suction tube; 11 subpressure gauge; 12 mercury valve; 13 proportioning pump.

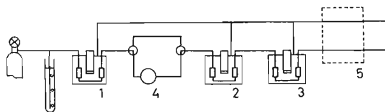


FIG. 3

Experimental Assembly

1, 2, 3 Oxygen analyzers; 4 calibrating electrolyzer; 5 proportioning pump.

Calibration — current readout. The analyzer was calibrated with electrogenerated oxygen produced at a platinum anode in 5M-KOH. The anode in the calibration cell was situated in a separate compartment in order to avoid contamination of the calibration gas stream with hydrogen. It should be pointed out that interference from hydrogen (and carbon monoxide) in the present system gives rise to a non-electrochemical catalytic reaction to form H_2O (or CO_2) with consequent lowering in the measured oxygen level.

The calibration electrolyzer was fed by a constant current from a 100 V d.c. source with a series current controlling resistor. The currents from the analyzer and the calibration electrolyzer were monitored on a potentiometric recorder with 6 mV full-scale deflection. It is possible to measure the current flowing through the analyzer in the integrated and non-integrated modes. The choice depends on the type of sample being measured. For discrete samples integration of the current gives a significant enhancement in precision while for continuous monitoring a non-integrated signal is more convenient.

RESULTS AND DISCUSSION

The feasibility of using the electrode assembly under sub-atmospheric conditions was proved experimentally. The results obtained for the analysis of oxygen in gases over the concentration range 100–0.007% were essentially the same as those obtained for the analyzer working at above atmospheric pressure. A rectilinear dependence of current on oxygen concentration was obtained. For a given oxygen level the current is independent of temperature and is unaffected by small variations in the sub-pressure. The current efficiency is, however, influenced by the flow rate of the gas (Fig. 4). At high flow rates ($>16.9 \text{ ml min}^{-1}$) the reduction efficiency is flow dependent while at flow rates lower than 10 ml min^{-1} 99.5% efficiency is achieved even at a current load of 200 mA. This latter value corresponds to a mass flow of $0.7 \text{ ml O}_2 \text{ min}^{-1}$.

The response time of the system under these conditions is of the order of several minutes hence it is preferable to dilute high oxygen containing samples with nitrogen thus enabling higher flow rates and response times of 30 s or less to be attained. The limit of detection with the present system is defined by the magnitude of the residual current ($15–50 \mu\text{A}$) although unless extreme care is taken diffusion of oxygen from the counter electrode compartment can increase this to c. $8–10 \cdot 10^{-5} \text{ A}$.

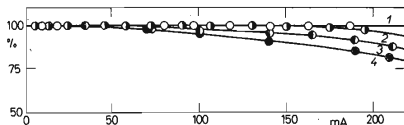


FIG. 4

Dependence of the Current Efficiency on Gas Flow Rates

$E = -0.6 \text{ V vs Hg/HgO}$, subpressure 330 mm Hg. Flow rate, ml min^{-1} : 1 10.0; 2 16.9; 3 22.6; 4 30.0.

With the present system using a peristaltic pump maintenance of the slight vacuum on the cell presents little problem as it is necessary only to compensate for any slight leaks in the system and to remove the oxygen formed in the counter electrode compartment.

The use of an analyzer as a purification unit is more convenient than conventional chemical systems. The absolute level of oxygen in the purified gas has so far not been measured but a solid MgO electrolyte potentiometric sensor is being developed for this purpose.

The principle advantage of the present system is that it eliminates the possibility of errors due to diffusion of oxygen into the sample inlet line. The measurement of oxygen in gases at low pressures is also feasible. Work is at present in progress to develop an analyzer for low (*i.e.* sub-v.p.m.) levels of oxygen.

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