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Carson, Jr. et al.

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[54] **VOLTAMMETRIC OXYGEN SENSOR**

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[52] **U.S. Cl.** ..... **204/195 P;** 204/1 T; 204/195 R

[51] **Int. Cl.²** **G01N 27/46**

[58] **Field of Search** ..... 204/1 T, 195 R, 195 P, 204/195 T

[56] **References Cited**

UNITED STATES PATENTS

2,928,774	3/1960	Leisey	204/195 T
2,928,775	3/1960	Leisey	204/195 T
3,673,069	6/1972	Neidrach et al.	204/195 P
3,719,575	3/1973	Neidrach et al.	204/195 P
3,763,025	10/1973	Chand	204/195 R
3,794,575	2/1974	Neidrach et al.	204/195 P

FOREIGN PATENTS OR APPLICATIONS

1,124,534	8/1968	United Kingdom	204/195 T

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[57] **ABSTRACT**

A voltammetric oxygen sensor is described which includes a pair of spaced apart and electrically insulated noble metal wire electrodes, and a reference electrode associated with the pair of electrodes to provide a cathode-reference voltage readout.

2 Claims, 2 Drawing Figures

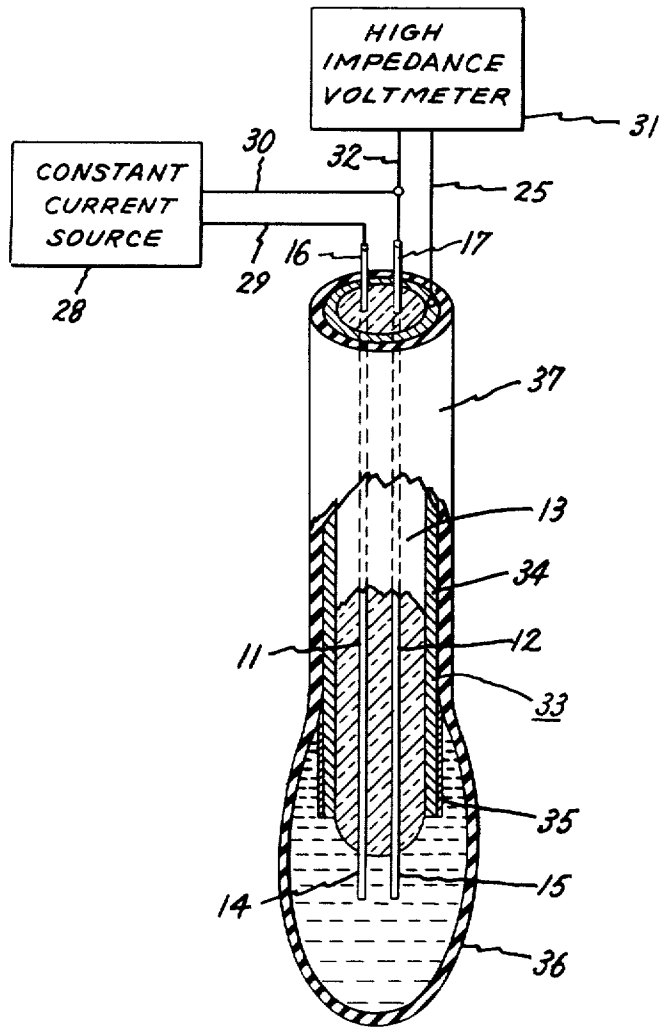


Fig. 1.

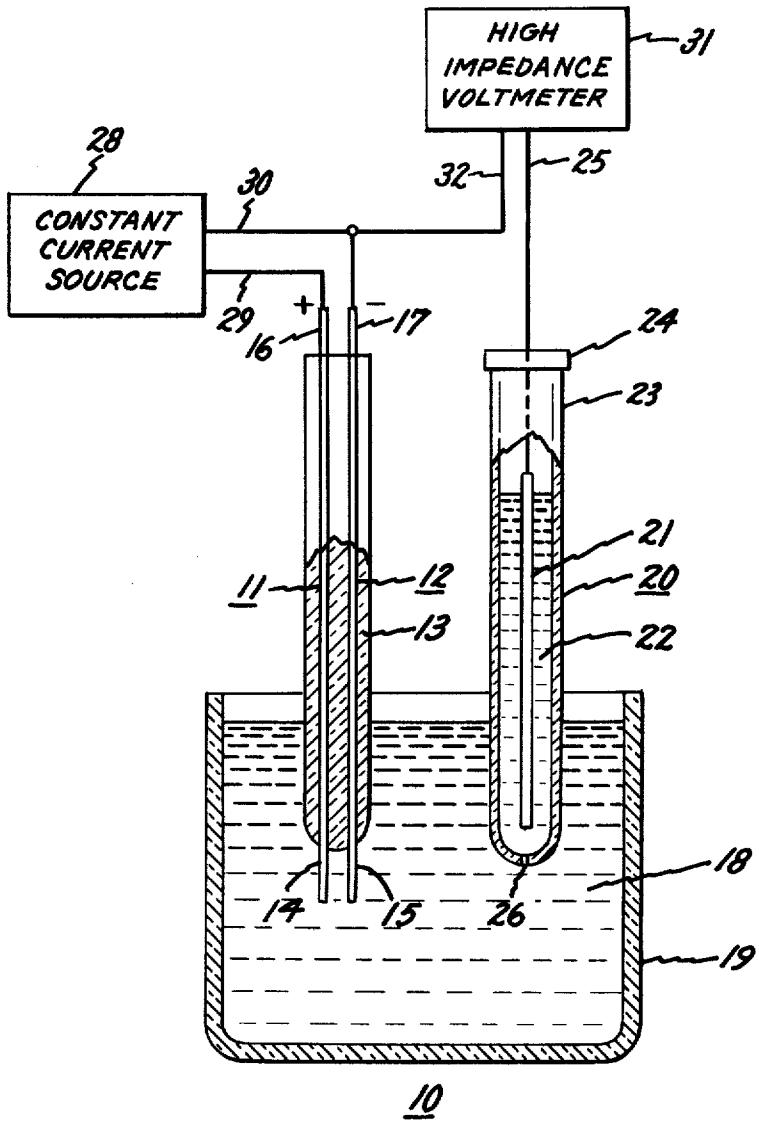
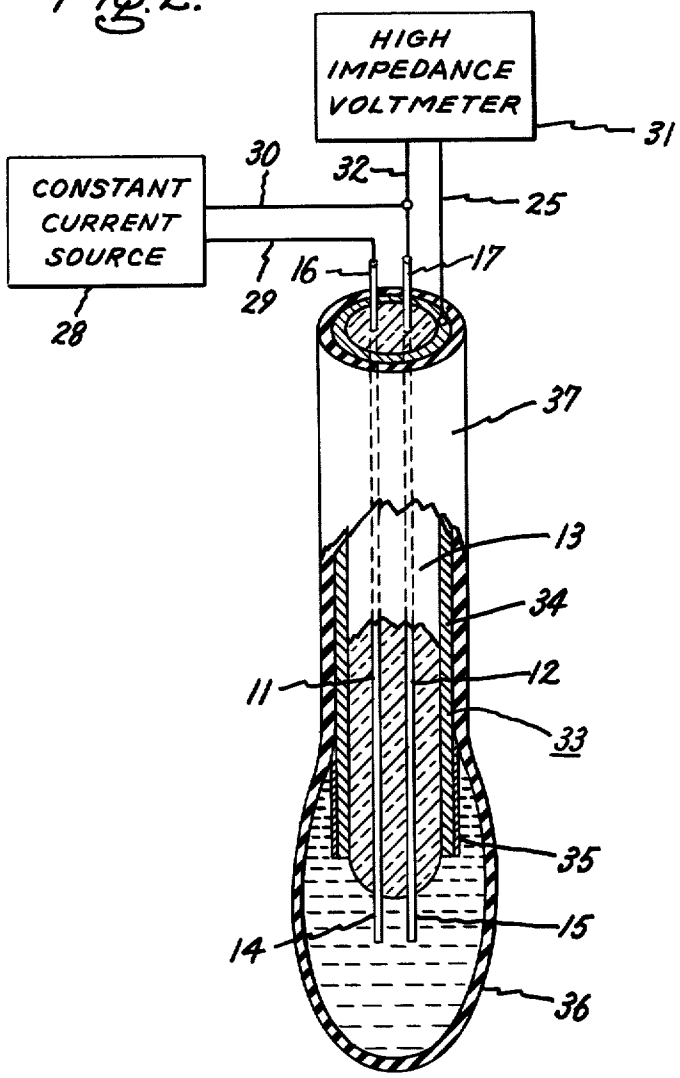

HIGH IMPEDANCE VOLTMETER
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CONSTANT CURRENT SOURCE
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Fig. 2.


HIGH IMPEDANCE VOLTMETER
31
CONSTANT CURRENT SOURCE
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VOLTAMMETRIC OXYGEN SENSOR

The present invention relates to a voltammetric oxygen sensor and, more particularly, to such a voltammetric oxygen sensor in which a reference electrode is associated with a pair of electrodes to provide a cathode-reference voltage readout.

Oxygen sensors are known in the prior art for determining oxygen content of a sample. Such sensors include a pair of electrodes that are connected by means of an electrolyte medium. The electric circuit parameters of this device change when exposed to materials having different oxygen content as, for example, oxygen from a sample when passing into the sensor electrolyte changes the voltage or current between the two electrodes and the changes are a well-defined function of the oxygen content of the sample.

A specific type of voltammetric sensing of end points in redox titrations has been described in an article entitled "Derivative Polarographic Titrations" by C. N. Reilley et al. at pages 1223–1226 in "Analytical Chemistry," Volume 23, No. 9, September, 1951. We found that we could measure oxygen content with the system described in the above publication. Such an oxygen measurement has not been reported previously to the best of our knowledge. While the above system had high sensitivity and adequate stability, it had the serious problem of undesirable sensitivity to IR drop and the associated polarization of the non-oxygen sensitive electrode.

The primary objects of our invention are to provide a rugged and dependable voltammetric oxygen sensor which is suitable for biomedical, environmental control, and other applications.

In accordance with one aspect of our invention, a voltammetric oxygen sensor includes a pair of spaced apart and electrically insulated noble metal wire electrodes, and a reference electrode associated with the pair of electrodes to provide a cathode-reference voltage readout.

These and various other objects, features and advantages of the invention will be better understood from the following description taken in connection with the accompanying drawing in which:

FIG. 1 is a partial sectional view of a voltammetric oxygen sensor made in accordance with our invention; and

FIG. 2 is a partial sectional view of a modified voltammetric oxygen sensor made in accordance with our invention.

In FIG. 1 of the drawing, there is shown generally at **10** a voltammetric oxygen sensor embodying our invention. Sensor **10** is shown with generally parallel and spaced apart elongated noble metal wire anode and cathode electrodes **11** and **12**, respectively. Such wires are made, for example, of platinum. Electrodes **11** and **12** are electrically insulated by electrical insulation **13** which is shown as an electrically insulating glass rod in which the electrodes are embedded. Ends **14** and **15** of electrodes **11** and **12** are exposed. Ends **16** and **17** of electrodes **11** and **12** are also exposed. Exposed ends **14** and **15** are shown immersed in a pHydrion buffer 6.8 solution **18** within a container **19**.

A reference electrode **20** is associated with electrodes **11** and **12** by being immersed partially in solution **18** within container **19** and spaced from exposed ends **14** and **15** of electrodes **11** and **12**. Reference electrode **20** is shown with a silver-silver chloride electrode **21**, a salt solution **22**, a glass envelope **23**, a cover **24**, an electrical lead **25** from electrode **21**, and a capillary opening **26**.

Constant current source means **28** in the form of a battery and large value resistor is connected by electrical leads **29** and **30** across anode **11** and cathode **12**. A high impedance voltmeter **31** is connected across cathode **12** by an electrical lead **32** and across reference electrode **20** by electrical lead **25**. The resulting structure is a voltammetric oxygen sensor made in accordance with our invention which sensor is shown immersed partially in a solution sample within a container.

In FIG. 2 of the drawing, there is shown a modified voltammetric oxygen sensor embodying our invention. As in FIG. 1, there are shown generally parallel and spaced apart elongated noble metal wire anode and cathode electrodes **11** and **12** which are embedded in electrical insulation **13**. Ends **14** and **15** of electrodes **11** and **12** are exposed. Ends **16** and **17** of electrodes **11** and **12** are also exposed. A reference electrode **33** surrounds at least partially electrodes **11** and **12** and is electrically insulated therefrom by insulation **13**. Electrode **33** is shown as a silver tube **34** with a silver chloride region **35**. A suitable aqueous electrolyte, such as a buffered saline solution, is in contact with the anode, cathode and reference electrodes. It will, of course, be appreciated that a gelling agent may be employed with the electrolyte to fabricate more easily the sensor. A diffusion barrier **36**, which is electrically insulating and has an appropriate permeability coefficient for the particular substance to be sensed, such as oxygen, encapsulates the electrodes and electrolyte. Further, since barrier **36** is electrically insulating, it is employed to cover the exterior of the sensor at **37**. As in FIG. 1, current source **28**, leads **29** and **30**, high impedance voltmeter **31**, and leads **25** and **32** are also employed in the same manner.

We found that we could form a voltammetric oxygen sensor which eliminated the undesirable sensitivity to IR drop and the associated polarization of the non-oxygen sensitive electrode.

Our present voltammetric oxygen sensor is formed by providing a pair of generally parallel and spaced apart elongated noble metal wire cathode and anode electrodes. While we prefer platinum, other noble metals are suitable. The electrodes are preferably embedded in electrical insulation. A variety of conventional electrically insulating materials can be employed.

In our first embodiment the opposite ends of the electrodes are exposed. One exposed end of the glass rod with associated electrodes is immersed in a sample solution, such as pHydrion buffer 6.8 solution, within a container. A conventional silver-silver chloride salt bridge reference electrode is associated with the cathode and anode by being immersed in the same solution. Other solutions can be also employed, such as 0.1 M K_2SO_4.

A constant current source in the form of a battery and large value resistor is connected by electrical leads across the opposite exposed ends of the cathode and anode. A high impedance voltmeter is connected by electrical leads across the exposed end of the cathode and the exposed end of the reference electrode. The resulting structure is a voltammetric oxygen sensor made in accordance with our invention.

The above described sensor was operated by employing a quiescent pHydrion buffer 6.8 solution saturated with gas at room temperature. The voltage in the above solution saturated by air and then by oxygen was measured by an electrometer. The voltage measurement is the voltage of the cathode versus the reference electrode which provides high sensitivity with good stability.

In the second embodiment of our invention the opposite ends of the electrodes are exposed initially. A reference electrode surrounds at least partially the anode and cathode electrodes and is electrically insulated therefrom by the insulation in which the anode and cathode are embedded. The reference electrode is silver with a silver chloride region agent at one end thereof. The silver-silver chloride electrode can be provided, for example, to silver paint, a silver tube, a silver spiral or a configuration. The exposed region of the silver is provided with a silver chloride layer, which region is adjacent to one end of the silver. A suitable aqueous electrolyte such as a buffered saline solution is in contact with the anode, cathode and reference electrodes. Such an electrolyte can be applied for contact with the above electrolytes by adding a small amount of a conventional gelling agent to the electrolyte solution. A diffusion barrier which is electrically insulating and has an appropriate permeability coefficient for the particular substance to be sensed, such as oxygen, encapsulates the electrodes and the electrolyte. Since the barrier is electrically insulating, it is also employed to cover the exterior of the sensor. A silicone-polycarbonate block copolymer is a suitable diffusion barrier material. Additional materials for providing diffusion barriers which are also electrically insulating materials are described in U.S. Pat. No. 3,714,015. The application of such diffusion barriers and related information on forming sensors is also provided in this patent. This patent is incorporated by reference in the present application, which patent is assigned to the same assignee as the present application.

Examples of voltammetric oxygen sensors made in accordance with our invention are as follows:

EXAMPLE I

A voltammetric oxygen sensor was formed as above-described and as shown in FIG. 1 of the drawing. The sensor was formed by a pair of generally parallel and spaced apart elongated platinum wire cathode and anode electrodes. Each of these electrodes had a 0.005 inch diameter and was 0.2 centimeter in length. The electrodes were spaced 0.1 centimeter apart. The electrodes were then embedded in a rod of electrically insulating glass. This embedding was accomplished by setting the wires within a fixture into which molten glass was poured. The glass rod covered the electrode substantially except that the opposite ends of the electrodes were exposed. A separate conventional silver-silver chloride salt bridge reference electrode was associated with but spaced from the cathode and anode. A constant current source in the form of a battery and large value resistor was connected by electrical leads across one opposite exposed end of the cathode and anode. A high impedance voltmeter was connected by electrical leads across the same exposed end of the cathode and the exposed end of the reference electrode. The resulting structure was a voltammetric oxygen sensor made in accordance with our invention.

EXAMPLE II

The voltammetric oxygen sensor of Example I was tested by having the cathode and anode at one exposed end immersed separately in two different solution samples at different times. Each solution was contained within a container. The reference electrode was also immersed separately in the same solutions. Two separate tests were made in quiescent solutions which were saturated with gas at room temperature. In each of these tests the battery voltage was 1.35 volts, the resistance was provided by a 15 megohm resistor, and the polarization current was 0.1 microampere. The voltage was measured by an electrometer, which voltage was the voltage of the cathode versus the reference electrode. Each solution was first saturated by air and the voltage measurement obtained. The solution was then saturated with oxygen and the voltage measurement obtained.

EXAMPLE III

The results of the tests of the voltammetric oxygen sensor described above in Example II are set forth below in Table 1. In this Table there is set forth the solution, the voltage in solution saturated first by air and then by oxygen, and the difference in voltage between air and oxygen.

Table I

Solution	Voltage in Solution Saturated By Air	Oxygen	Voltage Change
Hydrion buffer pH 6.8	-1.1542V.	-0.830V.	0.0712V.
0.1 M K_2SO_4	-0.1708V.	-0.0922V.	0.0786V.

Our voltammetric oxygen sensor eliminates the undesirable sensitivity to IR drop and the associated polarization of the non-oxygen sensitive electrode. Thus, the placement of the anode with respect to the cathode is not critical. The cathode reaction is the more sensitive one with respect to oxygen concentration, and is also subject to fewer variances than the anode reaction, resulting in a more stable output.

While other modifications of the invention and variations thereof which may be employed within the scope of the invention have not been described, the invention is intended to include such as may be embraced within the following claims.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A voltammetric oxygen sensor comprising

a. a pair of parallel spaced apart elongated platinum wire electrodes, said platinum electrodes being electrically insulated from each other by electrical insulation but having their opposite end portions exposed,

b. constant current source means connected across said platinum electrodes coupled electrically to each proximal end portion thereof, said constant current source polarizing the platinum electrodes producing a platinum cathode and a platinum anode,

c. an associated silver-silver halide reference electrode surrounding at least partially said platinum electrodes and being electrically insulated therefrom,

d. a high impedance voltmeter connected across and coupled electrically to the said proximal end portion of said platinum cathode and the silver of said reference electrode providing a cathode-reference electrode voltage readout,

e. an electrolyte solution in mutual contact with at least the distal end portions of said platinum anode, said platinum cathode and said silver halide of said reference electrode, and

f. an oxygen permeable electrically insulating diffusion barrier material encapsulating said electrolyte solution and at least the distal portions of said electrodes.

2. A voltammetric oxygen sensor as in claim **1**, in which the electrode insulation is an electrically insulating epoxy resin, the electrolyte solution is a buffered saline solution, and the diffusion barrier material is a silicone-polycarbonate block copolymer.

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