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Electrochemical sensors for oxygen analysis

Developments in electrochemical sensing techniques now make the analysis for trace or percentage amounts of oxygen in many process streams fast, accurate and repeatable.

□ There are three general classes of electrochemical sensors for measuring oxygen concentrations (percentage or trace amounts) in a process stream. Recently, considerable improvements have been made in their design.

These devices include the solid-state ceramic oxygen sensor, the Micro-Fuel cell and the polarographic sensor. They are designed as high-accuracy transducers capable of selectively monitoring a particular component in a process sample, especially oxygen. By eliminating many of the disadvantages of other techniques (see box on next page), electrochemical sensors are now capable of making fast, repeatable and accurate analyses for the oxygen content of certain process streams.

Ceramic-oxide sensor

The most frequently used electrochemical oxygen detector is the solid-state ceramic-oxide device. Its primary application is for flue gas or other combustion-related processes. The sensor is responsive to changes in the partial pressure of oxygen in a sample. It is made of a high-temperature yttria-stabilized zirconium-oxide ceramic electrolyte, and coated on inside and outside surfaces with porous platinum (Fig. 1a).

The anode and cathode are porous to the extent that gas can readily diffuse through them. Oxygen, or an oxygen-containing gas such as air, is supplied to the outer side of the cathode. The sample gas is supplied to the outer side of the anode.

At the cathode, oxygen is electrochemically reduced at the interface between the electrode and the electrolyte. Electrons are supplied by the conductive electrode, and the oxygen ions become a part of the electrolyte crystal structure. Ions migrate through the solid electrolyte and are electrochemically oxidized at the anode. Hence, oxygen is produced and electrons are released at the anode. The simultaneous reactions are:

$$\left.\begin{array}{ll} \text{Cathode:} & O_2 + 4e^- \rightarrow 2O^{-2} \\ \text{Anode:} & 2O^{-2} \rightarrow O_2 + 4e^- \end{array}\right\} \qquad (1)$$

Therefore, a voltage (E) is produced that is a function of the difference in the oxygen's partial pressure on either side of the cell. This voltage can be evaluated from the Nernst equation:

$$E = \left(\frac{RT}{4F}\right) \ln \left(\frac{P_R(O_2)}{P_S(O_2)}\right) + C \qquad (2)$$

where R = gas constant, T = absolute temperature of the cell, F = Faraday's constant, P_R = partial pressure of oxygen in the reference gas, P_S = partial pressure of oxygen in the sample gas, and C = cell constant.

In actual operation, air serves as a convenient reference gas with a constant partial pressure of O_2 on one side of the cell, while the other side is exposed to the sample gas. By using Eq. (2), we can readily find that the voltage output is zero when the sample gas is air. Consequently, as the oxygen concentration decreases, the voltage output increases, enhancing sensitivity at the usual oxygen-control (percentage amounts) levels as shown in Fig. 1b. This technique is also useful for very low levels (less than 1% O_2).

The ceramic-oxide electrolyte becomes an oxygen-ion conductor only when operated in the proper temperature range. The electrolyte material is chosen for its high oxygen-ion conductivity, which is found to be temperature-dependent and is greater at higher temperatures. This high operating temperature is necessary as a result of the theoretical heat losses associated with the electrochemical reaction as well as I^2R (I is current, R is resistance) losses within the cell. Experimental data verify the necessity for a high operating temperature (Fig. 1c), showing that cell temperature should be maintained in the range of 600 to 800°C.

At extremely high temperatures (about 1,300°C), certain factors become significant that offset the increase in conductivity. One such factor is the chemical stability of the electrodes. This is a considerable problem in practical design.

Although a wide range of applications are feasible with ceramic-oxide sensors, most units are used for combustion, exhaust-gas and furnace-atmosphere control. The major advantages of this technique are speed of response and specificity for oxygen in the absence of combustibles.

Other methods for oxygen analysis

Different types of analytical methods have been used to determine the amount of oxygen in an industrial sample. For example, Hartmann and Brown in 1942 developed an oxygen analyzer that took advantage of oxygen's unique property of being strongly paramagnetic. Oxygen has a magnetic susceptibility of about $3{,}449 \times 10^{-6}$ as a magnetic moment (cgs units) at 20°C, while most other gases commonly found in industrial processes have relatively low magnetic susceptibility. This large difference in susceptibility provides for a method of analysis that is reasonably specific for oxygen.

The paramagnetic method was followed by the development of the magnetic-wind (or thermal/magnetic) analyzer. Except for a few modifications, the principle of operation of the magnetic-wind analyzer is essentially the same as that of the paramagnetic analyzer. Other variations using the paramagnetic property of oxygen also have been made, such as the paramagnetic pressure analyzer (based on the Quinche effect) and the paramagnetic susceptibility analyzer.

While these instruments have been used with moderate success, numerous disadvantages make their application to industrial processes somewhat problematical. Since most units are position-sensitive, installation can often be a problem. The delicate suspension of the magneto-dynamic analyzer makes it sensitive to vibration and physical shock. Magnetic-wind analyzers are less sensitive to vibration but more susceptible to interferences. The necessity for zero and calibration gases has led to additional inconveniences. A few paramagnetic analyzers, not affected by many of the disadvantages cited, are extremely expensive and best suited for laboratory analysis.

Wet chemical analysis also has been used to monitor some industrial processes. The Orsat apparatus is probably the most widely used. A gas sample is manually drawn into the apparatus with an aspirator and mixed with water. The sample is then systematically exposed to three different liquid chemical reagents that absorb carbon dioxide, oxygen, and carbon monoxide. After each reagent has absorbed a specific gas, the sample is returned to a graduated cylinder for measurement, before being exposed to the next reagent. The concentrations of CO_2, O_2 and CO in the gas sample are determined from the change in the amount of total sample as a result of their absorption in the reagent.

The Orsat apparatus was the first satisfactory attempt for process monitoring. Certain problems, however, are inherent in this type of analysis. It is often inconsistent and requires the averaging of two to three readings, each of which requires about 15 minutes. Direct readout is not available; readings are based upon the liquid level in a graduated cylinder. Skill of the operator in making and interpreting the measurement is a major factor that can influence the actual results.

Although all of these analyzers are still being used in continuous monitoring applications, electrochemical oxygen detectors are becoming more prominent.

In actual applications, the ceramic-oxide sensor has some shortcomings when used in other than inert-gas samples. Because of the need for high operating temperatures, any combustible gas present at the sensor will burn by combining with the oxygen in the sample. Therefore, the sensor gives an indication of the oxygen concentration that is present after combustion takes place. That is, the sensor gives a net oxygen reading, which may not be sufficient for optimizing a combustion process.

The requirement for high operating temperatures makes this sensor most convenient in applications involving the continuous monitoring of oxygen.

Micro-Fuel cell

More recent developments have led to another type of electrochemical sensor for industrial applications, known as a fuel cell.

The fuel cell is an energy converter (a transducer) and not a source of stored energy. The fuel cell will not operate until a fuel is supplied; in this case, the fuel is oxygen.

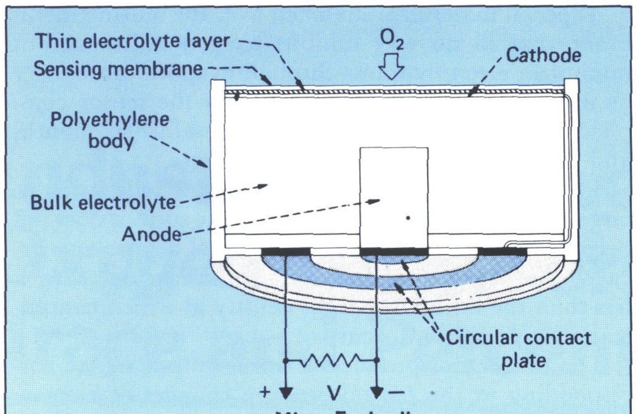
Like the solid-state ceramic-oxide sensor, the Micro-Fuel cell is a galvanic device. Its principle of operation is identical to that of the solid-state ceramic sensor; i.e., oxygen is reduced at the sensing electrode, resulting in the generation of a current that is directly proportional to the partial pressure of the oxygen present. The essential parts of such a cell are shown in Fig. 2a.

A sample gas is passed over the cell so that the oxygen molecules present can diffuse through the protective sensing membrane. This membrane is made of a polyethylene or Teflon film of a thickness that depends on the application. Oxygen that has diffused through the membrane will dissolve in the electrolyte solution and migrate to the surface of the sensing electrode, where it becomes absorbed to form an activated species capable of undergoing reduction. The general cell reactions are:

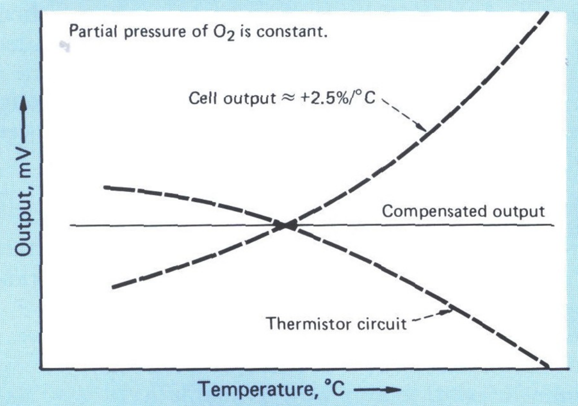
$$\left.\begin{array}{l}\text{Cathode (sensing electrode):}\\ \qquad 4e^- + 2H_2O + O_2 \rightarrow 4OH^- \\ \text{Anode (counter electrode):}\\ \qquad 4OH^- + 2Pb \rightarrow 2PbO + 2H_2O + 4e^- \\ \text{Overall cell reaction:}\\ \qquad 2Pb + O_2 \rightarrow 2PbO\end{array}\right\} \quad (3)$$

From these reactions, we find that four electrons are generated as a result of the oxidation of the lead (Pb) anode. The four electrons are then used to reduce oxygen at the cathode. This flow of electrons from one electrode to the other constitutes an electric current that is directly proportional to the partial pressure of oxygen in the sample. In the absence of oxygen, no oxidation or reduction takes place and no current is produced. The cell has an absolute zero with no offset.

The electrical current produced by the cell (directly proportional to oxygen partial pressure) is dependent upon the diffusion path. The rate of diffusion of oxygen



a. Micro-Fuel cell



b. Compensating for temperature dependence

Operating principles of Micro-Fuel cell **Fig. 2**

to the sensing electrode surface is controlled by movement through the sensing membrane and the thin film of electrolyte between the membrane and the electrode. The diffusion current, i, is expressed as:

$$i = nFDC/a \tag{4}$$

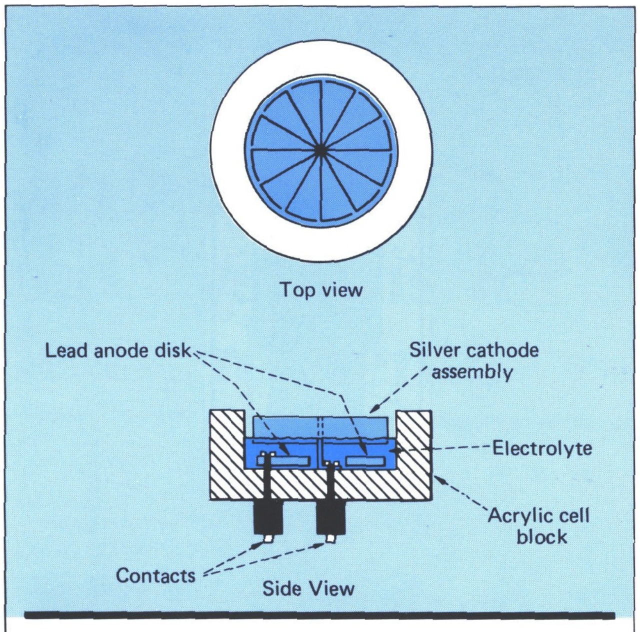
where n = number of electrons per mole of gas, F = Faraday's constant, D = diffusion coefficient of the gas, C = concentration gradient of the dissolved gas in the thin layer, and a = thickness of the diffusion layer.

The rate at which the gas species will reach the sensing electrode is directly proportional to the concentration gradient of the gas there. This concentration gradient is created because of the removal of oxygen at the electrode during reduction. Consequently, the oxygen concentration at the surface of the sensing electrode is much lower than that in the bulk of the thin-layer electrolyte. The magnitude of the concentration gradient is directly proportional to the oxygen concentration in the electrolyte layer and, hence, to the partial pressure of oxygen in the sample. This electrolyte layer also includes the membrane thickness. Therefore, the effect of membrane thickness on sensor response is an important design parameter. For example, cells are now available that can respond as fast as 90% of full scale in less than 7 seconds.

The effect of temperature on the process of diffusion of gases in membranes is also an important design parameter. The relationship between diffusion and temperature is:

$$D = D_o \exp(-E/RT) \tag{5}$$

where D = diffusion coefficient, D_o = diffusion coefficient at a reference temperature, E = activation energy for diffusion, R = gas constant, and T = temperature.



Open-cathode cell for trace amounts of oxygen Fig. 3

Because of the temperature dependence of D, the rate of diffusion increases as the temperature increases for the Micro-Fuel cell. Typically, this rate is +2.5%/°C. There are a number of techniques that compensate for changes in output due to temperature. The simplest is through the use of negative-temperature-coefficient thermistors. A typical curve is shown in Fig. 2b.

The Micro-Fuel cell is not vibration- or position-sensitive, and is insensitive to changes in flowrate. This cell has been extremely successful in trace-oxygen analysis, detecting oxygen concentrations as low as 1 ppm.

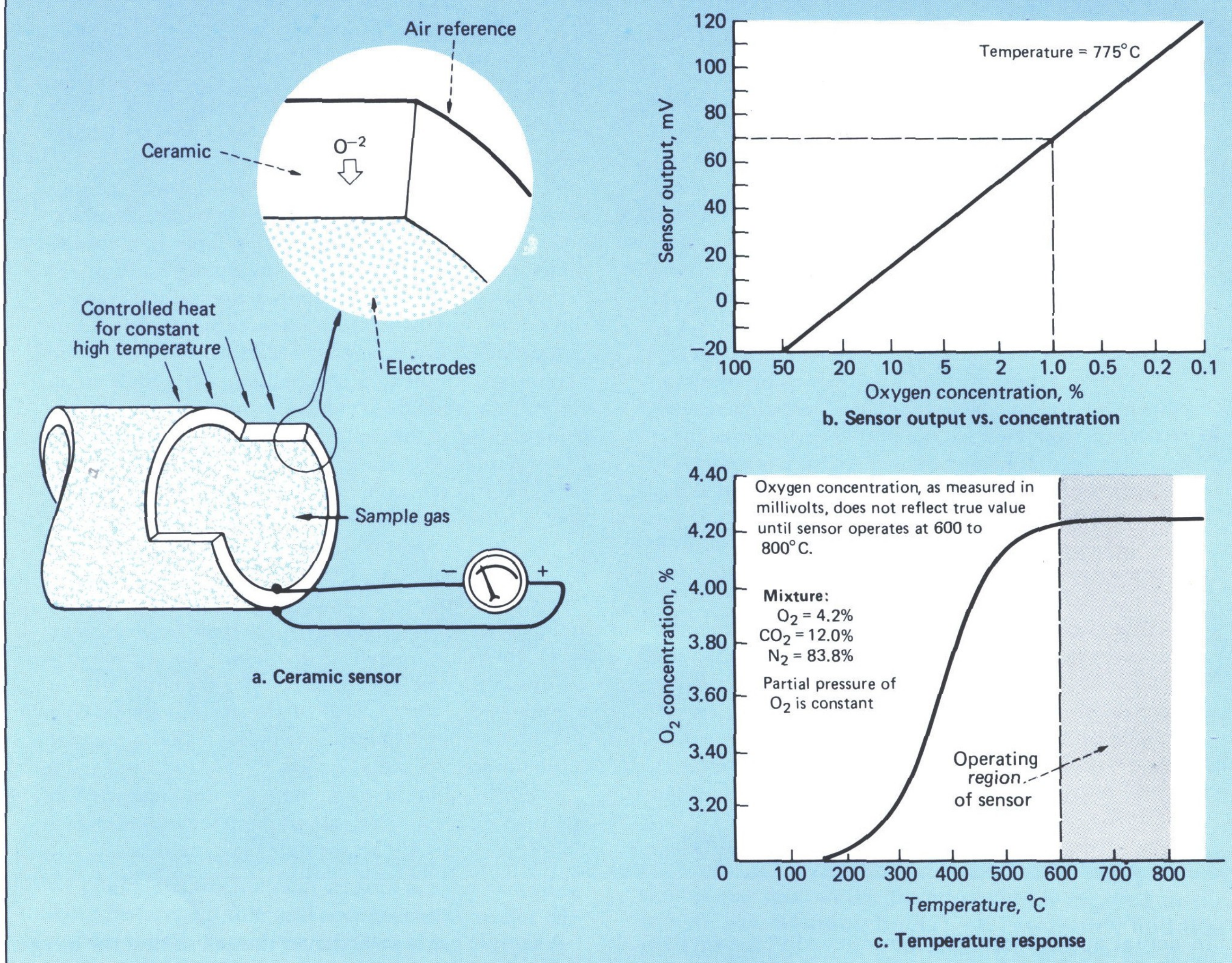
Open-cathode cell

Another galvanic cell is the open-cathode cell (Fig. 3). This is also an electrochemical transducer that is specific for oxygen. Its construction is somewhat unique so as to facilitate the measurement of oxygen at levels less than 1 ppm. The general cell reactions are identical to those of the Micro-Fuel cell.

The cathode of this cell is made of silver screen elements that have a very large surface area. The assembly is mounted in an acrylic block so that only the lower edge of the screens is under the surface of the electrolyte. By capillary action, a thin layer of electrolyte is maintained over the surface of the screens.

A lead disk, positioned under the screens, provides the necessary counterelectrode. Since there is no sensing membrane, a gas stream is passed directly over the cathode screens. A current is generated that is proportional to the concentration of oxygen in the sample.

The open-cathode cell is specifically designed for



a. Ceramic sensor

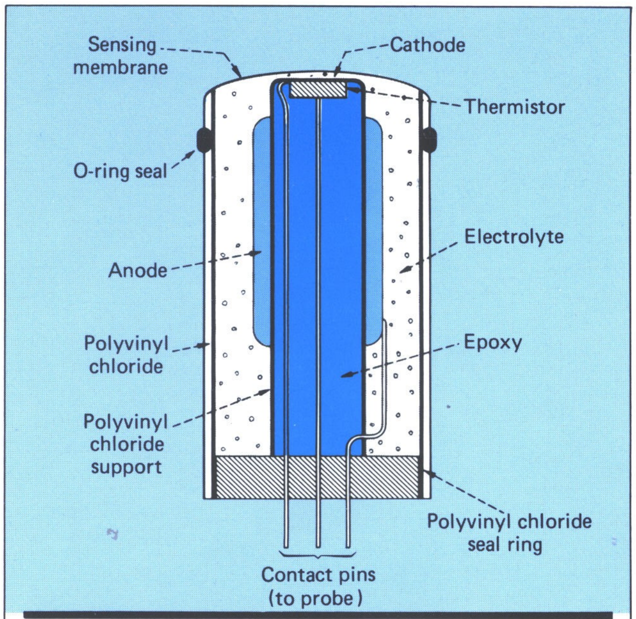
b. Sensor output vs. concentration

c. Temperature response

Properties of zirconium-oxide ceramic sensors **Fig. 1**

Comparison of operating characteristics of electrochemical sensors

Feature	Ceramic-oxide sensor	Micro-Fuel cell	Open-cathode cell	Polarographic sensor
Analytical range	0.1 ppm-100%	1 ppm-10 atm.	0.1 ppm-10,000 ppm	1-100%
Type of analyzer	Online	Portable, online	Online	Portable, online
Major application	Flue gas	Trace O_2, % O_2	Trace O_2	Flue gas, CO_2 streams
Certified calibration-gas requirement	Yes	No	No	No
Zero-gas requirement	Yes	No	No	No
Gas-phase measurement	Yes	Yes	Yes	Yes
Liquid-phase measurement	No	Yes	No	Yes
90% response time	1-2 s	7-30 s	30 s	7-10 s
Expected life	12 mo.	6-18 mo.	6 mo.	6 mo.
Operating temperature	600-800°C (1,100-1,480°F)	Thermistor-compensated	50-52°C (122-125°F)	Thermistor-compensated
Sensor maintenance	Replaceable	Disposable	Replaceable	Disposable
Approximate cost (sensor replacement)	$325	$50-100	$225	$95



Polarographic sensor responds to partial pressure of oxygen **Fig. 4**

applications requiring high sensitivity at very low (ppm) levels of oxygen.

Polarographic sensor

Due to significant improvements over the past few years, the polarographic sensor has now become a major contender for continuous process monitoring—especially of oxygen in process streams.

The polarographic (POL) sensor (Fig. 4) is another electrochemical transducer that responds to changes in the partial pressure of the oxygen in a sample. In order for this sensor to respond, a predetermined external voltage must be applied across the measuring and the reference electrodes. In the absence of oxygen, this voltage polarizes the system to reduce the current between the electrodes substantially to zero. Only when the measuring electrode is exposed to oxygen will current begin to flow. The general reactions that take place when oxygen is present are:

$$\left.\begin{array}{l}\text{Cathode (sensing electrode):}\\ \qquad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\\ \text{Anode (reference electrode):}\\ \qquad 4Ag + 4Cl^- \rightarrow 4AgCl + 4e^-\\ \text{Overall cell reaction:}\\ \qquad O_2 + 4Ag + 4H^+ + 4Cl^- \rightarrow 4AgCl + 2H_2O\end{array}\right\} \quad (6)$$

Consumption of the electrolyte solution and, more importantly, the anode material is a major design consideration. Sensor consumption is expressed by:

$$t_c = nFN/i \qquad (7)$$

where t_c = consumption time of the reference electrode, n = number of electrons per electrode reaction, F = Faraday's constant, N = number of moles of the reference electrode, and i = average current output over the time t_c.

A special material is stretched over the sensing membrane that in no way inhibits oxygen diffusion, but minimizes electrolyte loss through evaporation by dry or warm samples. This design makes the sensor completely disposable at the end of its useful life (six months and more in most continuous processes).

The surface area of the reference electrode must be large enough so that polarization at the surface does not become controlling. This usually is not a problem, because the current density at the reference electrode is less than the limiting current density at which concentration polarization occurs.

The POL sensor produces a linear output signal, corresponding to the partial-pressure changes of oxygen. The output can be expressed in volts, as calculated from Eq. (2). The diffusion path through the sensing membrane and the thin layer of electrolyte to the cathode surface is most critical. Linearity is directly dependent upon this diffusion path as well as the response time of the sensor. Since mass transport by diffusion through the membrane is the slowest step in the overall process, the response time can be approximated from:

$$t = KM^2/D \qquad (8)$$

where t = time (s), K = proportionality constant, D = diffusion coefficient for oxygen in the membrane, and M = membrane thickness.

Early polarographic sensors had response times of 90% of full scale in 20 s, or more, and were in most cases nonlinear. POL sensors now available have a 90%-of-full-scale response in less than 10 s, and have a completely linear output with changes in oxygen partial pressure.

The most significant advantages of the new POL sensors are the relatively fast response time, long shelf life, linear output, zero offset, and complete disposability.

Comparison of electrochemical sensors

The sensing techniques described in this article offer a means of monitoring oxygen for most processes. The accompanying table summarizes the guidelines generally considered by the user, and points out the versatility of electrochemical oxygen sensors. Electrochemical sensors can be used for oxygen monitoring in almost every industrial process. Combining oxygen analysis with the procedures for other critical parameters such as CO, CO_2, and total combustibles, we obtain techniques that can be used as part of process control systems.