ELECTROCHEMICAL OXYGEN SENSORS: for the measurement of percent and trace oxygen in process streams

by

Richard F. Bobeck

Manager, Sensor Development
Chief Chemical Engineer
Teledyne Analytical Instruments
San Gabriel, California 91776

The monitoring of process streams for efficiency and safety has always been a major plant concern. Recent developments in electrochemical sensing techniques now make analysis fast, accurate, repeatable and applicable to almost all plant processes.

Different types of analytical methods have been used for many years to determine the amount of oxygen in an industrial sample. As early as 1942, for example, Hartmann and Brown developed an oxygen analyzer that took advantage of the fact that oxygen is unique in being a strongly paramagnetic gas. Oxygen has a magnetic susceptibility of about 3449 x 10^{-6} cgs at 20°C while most other gases commonly found in industrial processes have relatively low magnetic susceptibility. The large difference in susceptibility makes this method reasonably specific to oxygen.

The paramagnetic method of analysis 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 the earlier paramagnetic analyzers. Other variations using the paramagnetic property of oxygen have also been used 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 for a number of years, 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 as well. A few paramagnetic analyzers, not affected by many of the disadvantages cited, are extremely expensive and best suited for laboratory analysis.

Wet chemical analysis has also lent itself to the monitoring of 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 solution is then systematically exposed to three different liquid chemical reagents that absorb oxygen (O_2), carbon monoxide (CO) and carbon dioxide (CO_2), respectively, from the solution. After each reagent has absorbed a specific gas, the solution is returned to a graduated cylinder for measurement before being exposed to the next reagent. The concentration of O_2, CO and CO_2 in the gas sample is determined from the change in the amount of total sample as a result of their absorption in the reagent. Use of the Orsat apparatus was the first really satisfactory attempt at employing a wet chemical technique for process monitoring. Certain problems, however, are inherent to this kind of analysis. The analysis is often inconsistent and requires the averaging of two to three readings. About 15 minutes is required for each reading. Direct readout is not available; readings are estimations based upon the fluid level in a graduated cylinder. Skill of the operator in making and interpreting the measurement is a major factor that can influence the actual analysis.

Although all of these analyzers have been, and are still being, used in continuous monitoring applications, the use of electrochemical oxygen detectors is becoming more prominent.

There are three general classes of electrochemical sensors now being used for the measurement of percent and trace oxygen concentration in a process stream. Recently, considerable effort has been made into improving the design of these electrochemical sensors. They can now be utilized in many of the difficult application areas often overlooked by a large number of process instrumentation manufacturers. Electrochemical sensing devices such as the solid-state ceramic oxygen sensor, the Micro-Fuel Cell, and the polarographic sensor were designed as high-accuracy transducers capable of selectively monitoring a particular component in a process sample, in particular, oxygen. Elimination of many of the disadvantages of other techniques has resulted in electrochemical sensors capable of fast, repeatable, accurate analysis.

The most frequently utilized electrochemical oxygen detector is the solid-state ceramic oxide sensor. Its primary application is in flue gas or other combustion-related processes. The sensor, which is responsive to changes in the partial pressure of oxygen in a sample, is made of a high-temperature zyttria stabilized zirconium-oxide ceramic electrolyte coated on both its inside and outside surface with porous platinum (see Figure 1). The two electrodes, both the anode and the cathode, are porous to the extent that gas may readily diffuse through them. To the outer side of the cathode there is supplied oxygen or an oxygen-containing gas such as air; to the outside side of the anode there is supplied a sample gas. 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:

Cathode: $O_2 + 4e^- \longrightarrow 2(O^{2-})$

Anode: $2(O^{2-}) \longrightarrow O_2 + 4e^-$

Therefore, an emf output is produced which is a function of the difference in oxygen partial pressure on either side of the cell. The emf can be expressed in volts given by the Nernst equation:

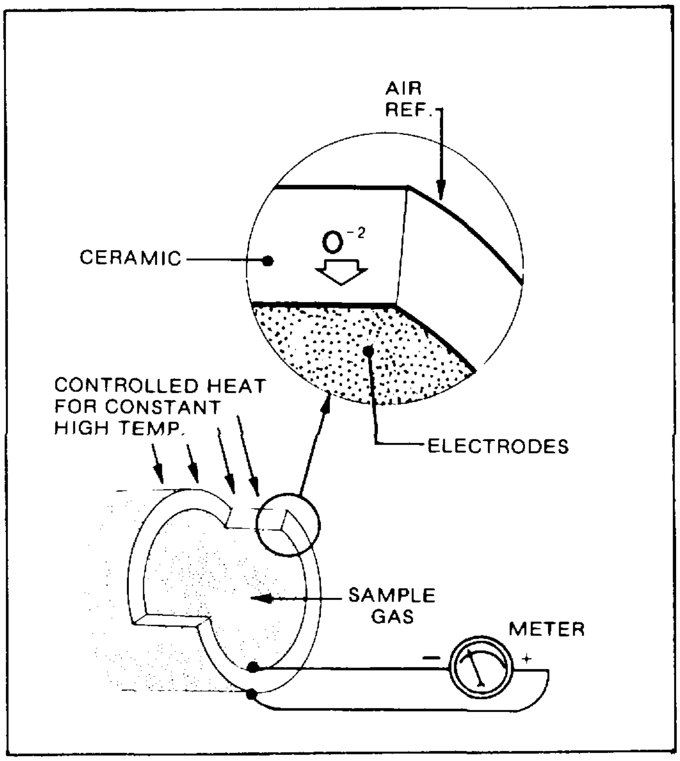

Figure 1. ZrO_2 Ceramic Sensor

$$\text{emf} = \frac{RT}{4F} \ln \left[\frac{P_R(O_2)}{P_S(O_2)}\right] + C$$

Where:

R = gas constant

T = absolute pressure 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

C = cell constant

In actual operation, air provides 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. It can be readily seen, using the Nernst equation, that when the sample gas is air, the output is zero. Consequently, as the oxygen concentration decreases, the voltage output increases, enhancing sensitivity at usual oxygen control levels. From the graph in Figure 2, it can be seen that this technique is useful for very low *level (less than 1% O_2) measurements as well,* although it is most widely used for percent level measurement.

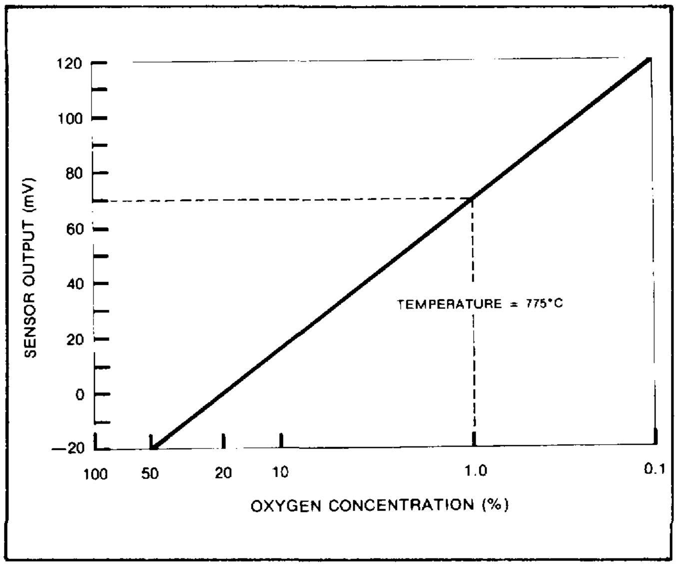

Figure 2. ZrO_2 Sensor Output vs. Concentration

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. Ionic conductivity 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 losses within the cell. Experimental data verifies the necessity for a high operating temperature (see Figure 3). From the curve, it can be seen that the cell temperature should be maintained and operated in the range of 600°C to 800°C.

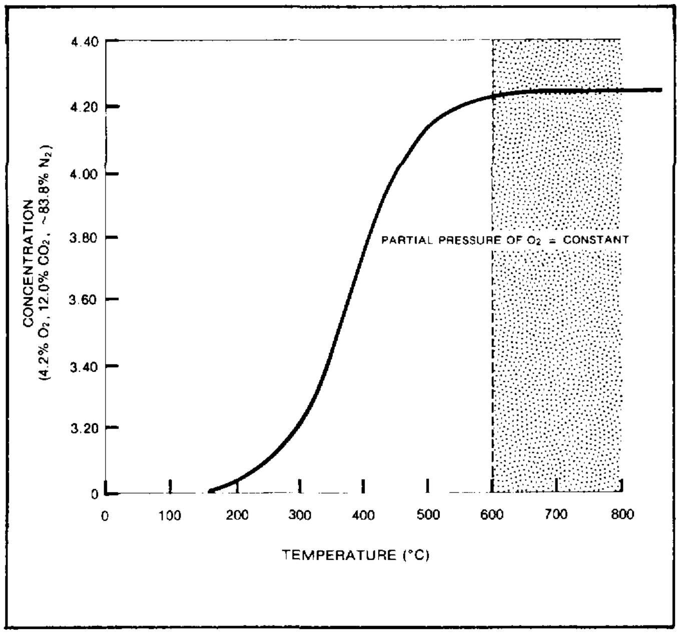

Figure 3. ZrO_2 Sensor Temperature Response

At extremely high temperatures (about 1300°C), certain factors become significant which offset the increase in conductivity. A major factor is the chemical stability of the electrodes. This is a considerable problem in practical design.

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

In actual applications, there are some shortcomings when utilizing the ceramic oxide sensor in other than inert gas samples. Because of the necessity for high operating temperatures, any combustible gas present at the sensor will burn after combining with oxygen in the sample. The sensor, therefore, gives an indication of oxygen concentration present after combustion takes place, i.e., the sensor gives a net oxygen reading, which may not be sufficient for optimizing a combustion process.

Because of the necessity for the high operating temperature of the sensor, it is most convenient in applications involving the continuous monitoring of oxygen.

More recent developments have led to the use of another type of electrochemical sensor for industrial applications: the Micro-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 being oxygen.

The Micro-Fuel Cell, like the solid-state ceramic oxide sensor, is a galvanic cell. The principle of operation is identical to the already described solid-state ceramic sensor. The fuel cell operates on the principle that oxygen is reduced at the sensing electrode, resulting in the generation of a current directly proportional to the partial pressure of oxygen present. Figure 4 shows the essential parts of the Micro-Fuel Cell.

A sample gas is passed over the cell such that the oxygen molecules present can diffuse through the protective sensing membrane. The membrane itself is made of a polyethylene or Teflon film varying in thickness depending upon 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

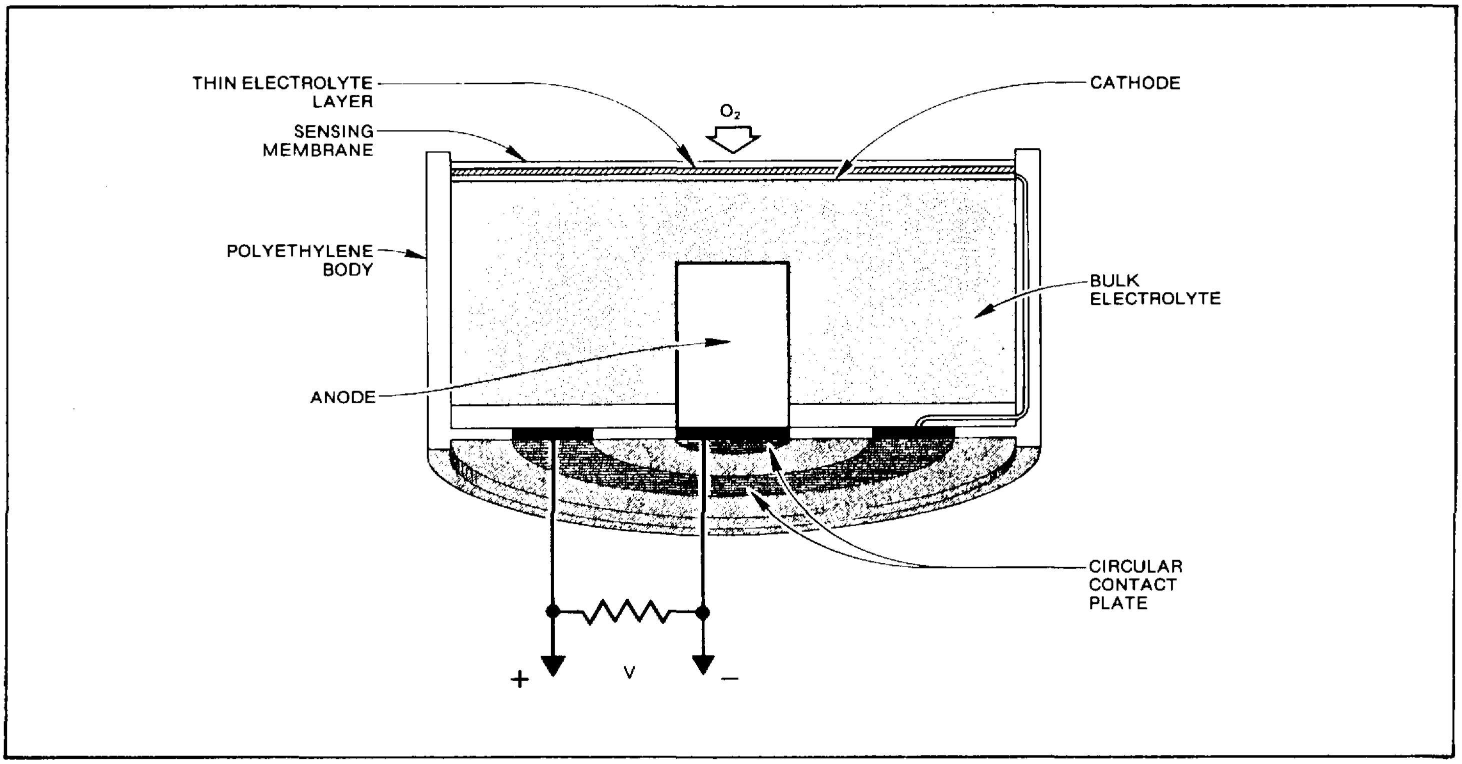

Figure 4. Micro-Fuel Cell

absorbed to form an activated species capable of undergoing reduction. The general cell reactions are:

Sensing electrode (cathode):

$$4e^- + 2H_2O + O_2 \longrightarrow 4OH^-$$

Counter electrode (anode):

$$4OH^- + 2Pb \longrightarrow 2PbO + 2H_2O + 4e^-$$

Overall cell reaction:

$$2Pb + O_2 \longrightarrow 2PbO$$

From the reactions above, it can be clearly seen that as a result of the oxidation of Pb (anode material), four electrons are generated. These four electrons are then utilized for the reduction of oxygen at the cathode. It is this flow of electrons from one electrode to the other that constitutes an electric current which is directly proportional to the partial pressure of oxygen in the sample (see Figure 5). Of course, in the absence of oxygen, no oxidation or reduction will take place and no current is produced. The cell has an absolute zero with no offset.

The current output of the cell which is directly proportional to oxygen partial pressure is dependent upon the diffusion path. The rate of diffusion of oxygen to the electrode surface is controlled by movement through the sensing membrane and the thin film of electrolyte between the sensing membrane and the sensing electrode.

The diffusion current i is expressed as follows:

$$i = \frac{nFDC}{a}$$

Where:

i = current in amperes

n = number of electrons per mole of gas

F = Faraday's constant

D = diffusion coefficient of the gas

C = concentration of the dissolved gas in the thin layer

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 at the sensing electrode. This concentration gradient is created because of the removal of oxygen at the sensing

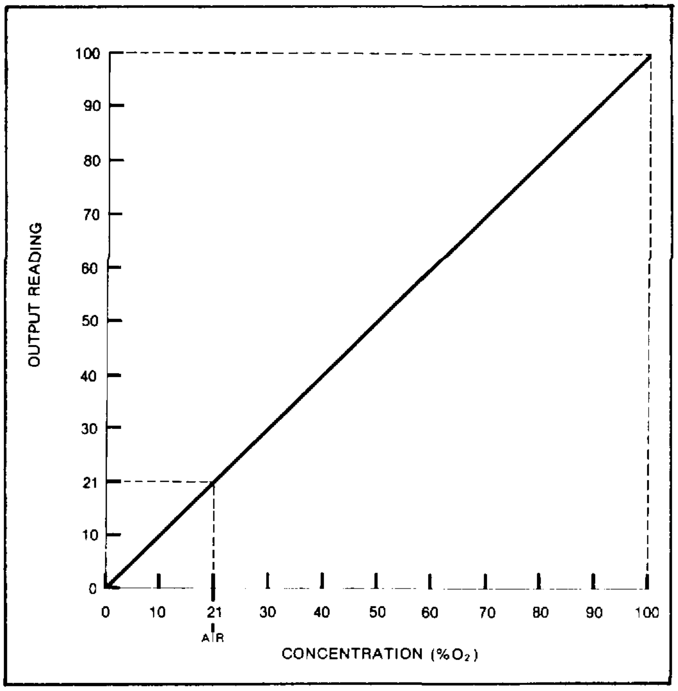

Figure 5. Micro-Fuel Cell Output vs. Concentration

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 as follows:

$$D = D_o \exp\left(-\frac{E}{RT}\right)$$

Where:

D = diffusion coefficient

D_o = relates to a reference temperature

E = activation energy for diffusion

R = gas constant

T = temperature

It is important to note concerning the temperature dependence of D that the rate of diffusion increases as the temperature increases for the Micro-Fuel Cell: typically, +2.5% per degree Centigrade. There are a number of techniques available to compensate for changes in output due to temperature. The simplest and one of the best is through the use of negative temperature coefficient thermistors. A typical curve is shown in Figure 6.

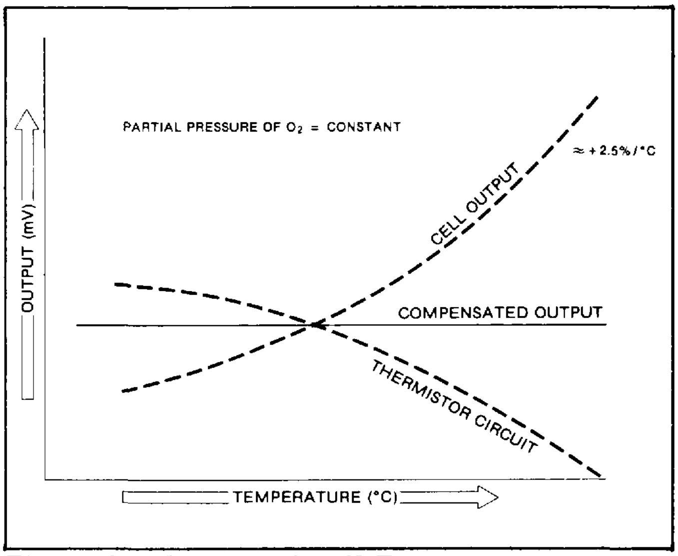

Figure 6. Micro-Fuel Cell Temperature Compensation

The Micro-Fuel Cell is not vibration or position sensitive. It is also insensitive to changes in flow rate.

Application of the Micro-Fuel Cell has been extremely successful in the area of trace oxygen analysis for some time. Unlike the earliest cells developed by Paul Hersch which had limited range capability and short life, the Micro-Fuel Cell can detect parts-per-million concentrations of oxygen as low as 1 ppm, and have a continuous process life of 12 months and more. Application areas where the Micro-Fuel Cell is now gaining attention is percent oxygen analysis for combustion control.

Another galvanic cell that operates very similar to the Micro-Fuel Cell is the Open-Cathode Cell (see Figure 7). This cell is also an electrochemical transducer specific to oxygen, although its construction is somewhat unique so as to facilitate the measurement of oxygen at trace levels (less than 1 ppm). The general cell reactions are identical to that of the Micro-Fuel Cell.

The cathode of this type of cell is constructed of silver screen elements that have a very large surface area. This assembly is mounted in an acrylic cell block so that only the lower edge of the

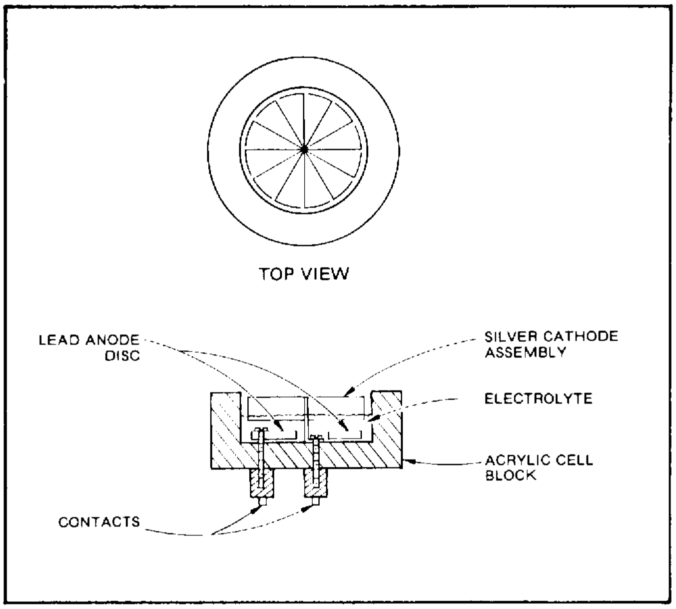

Figure 7. Open-Cathode Oxygen Cell

silver screen elements 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 disc positioned under the screens provides the necessary counter electrode. Since there is no sensing membrane, as in the Micro-Fuel Cell, a gas stream is passed directly over the cathode screens. A current is produced that is proportional to the concentration of oxygen in the sample.

The open-cathode cell is specifically designed for applications requiring high sensitivity at very low ppm levels of oxygen.

Although polarographic techniques have been described in a number of publications in the last decade, few have devoted attention to applications for continuous process monitoring. It is only during the past few years, due to significant improvements in design, that the polarographic sensor has become a major contender for oxygen monitoring of industrial processes.

The polarographic (or POL) sensor is also an electrochemical transducer that responds to partial pressure changes in the amount of oxygen in a sample (see Figure 8). However, in order for the sensor to respond, a predetermined external voltage must be applied across the measuring electrode and the reference electrode. 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 once again begin to flow. The general reactions that take place when oxygen is present are:

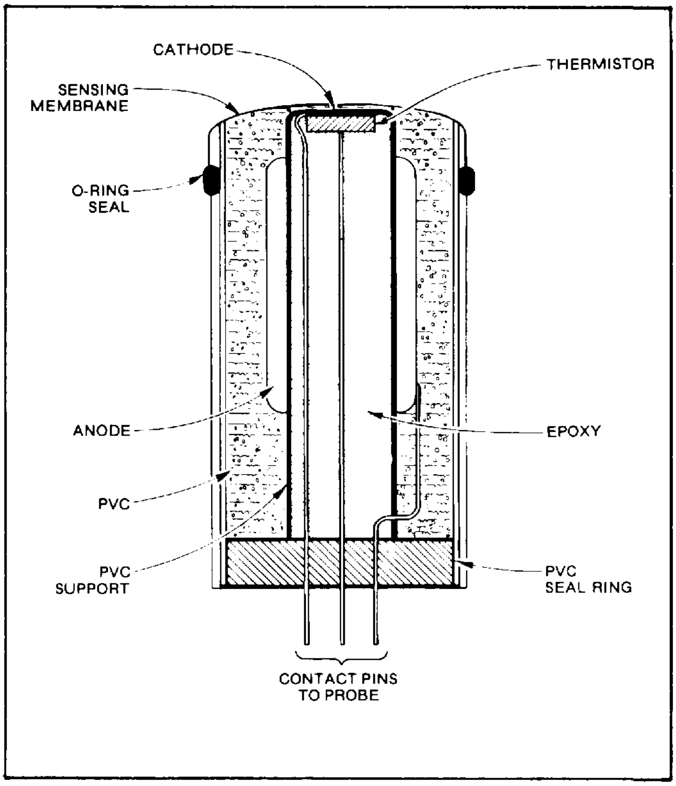

Figure 8. POL Sensor

Sensing electrode (cathode):

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

Reference electrode (anode):

$$4Ag + 4Cl^- \longrightarrow 4AgCl + 4e^-$$

Overall cell reaction:

$$O_2 + 4Ag + 4H^+ + 4Cl^- \longrightarrow 4AgCl + 2H_2O$$

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

$$tc = \frac{nFN}{1}$$

Where:

tc = 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

i = average current output over the time tc

A special material is stretched over the sensing membrane which in no way inhibits oxygen diffusion, but minimizes electrolyte loss through evaporation in dry or warm samples. This type of design makes the sensor completely disposable at the end of its useful life. POL sensors are now designed to last six months and more in most continuous processes.

It is also important that the reference electrode surface area be large enough so that polarization at the surface does not become a potential controlling factor. This is not usually a problem since the current density at the reference electrode is much less than the limiting current density where concentration polarization takes place.

The POL sensor produces a linear output signal corresponding to partial pressure changes of oxygen. The output can be expressed in volts given by the Nernst equation. As with the Micro-Fuel Cell, it is the diffusion path through the sensing membrane and the thin layer of electrolyte to the cathode surface that 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 by:

$$t = \frac{KM^2}{D}$$

Where:

t = time in seconds

K = proportionality constant

D = diffusion coefficient for oxygen in the membrane

M = membrane thickness

Early polarographic sensors had response times of 90% of full scale in 20 seconds or more, and were, in most cases, non-linear. POL sensors now available have a 90% of full scale response in less than 10 seconds, 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 response, no offset, and complete disposability.

Electrochemical sensors can be used for oxygen monitoring in almost every industrial process. By combining oxygen analysis with additional critical parameters such as CO, CO_2 and total combustibles, these techniques can be used as part of process control systems.

It is primarily because of the proper application of electrochemical techniques to process systems that use of the sensors described is becoming so widespread. Electrochemical techniques once used only for laboratory work are now one of the primary analytical tools for continuous process monitoring when speed, accuracy and reliability are essential.