Chapter 2

Electrochemical Sensors

The oldest electrochemical sensors date back to the 1950s and were used for oxygen monitoring. More recently, as the Occupational Safety and Health Administration (OSHA) began requiring the monitoring of toxic and combustible gases in confined space applications, new and better electrochemical sensors have been developed.

Fig. 1. Electrochemical Sensors

By the mid-1980s, miniaturized electrochemical sensors became available for detection of many different toxic gases in PEL ranges, with the sensors exhibiting good sensitivity and selectivity. Currently, a variety of electrochemical sensors are being used extensively in many stationary and portable applications for personal safety. Figure 1 shows a small collection of such electrochemical sensors.

The physical size, geometry, selection of various components, and the construction of an electrochemical sensor usually depends on its intended use. Quite often, the final design results in a compromise between various performance parameters of the electrochemical sensor. The most common misconception about electrochemical sensors is that they are all the same. In fact, the appearance of the electrochemical sensors used to detect various gases may be similar, but their functions are markedly different. Consequently,

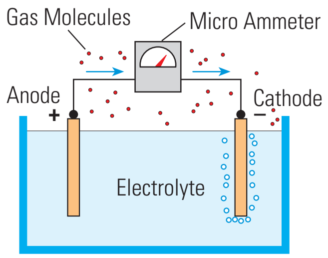

Fig. 2 Basic Sensor

one can expect varying performance from each of these sensors, in terms of sensitivity, selectivity, response time, and operating life.

For example, a low concentration gas sensor with very high sensitivity uses a coarse-porosity hydrophobic membrane and less restricted capillary to allow more gas molecules to pass through to produce enough signal for better sensitivity. However, this design also allows more of the electrolyte's water molecules to escape out to the environment. In other words, an electrochemical sensor with high sensitivity would have a relatively short operating life due to evaporation of moisture through the porous membrane.

Similarly, the electrolyte composition and the sensing electrode material is selected based on the chemical reactivity of the target gas. By careful selection of the electrolyte and/or the sensing electrode, one can achieve the selectivity towards the target gas, but the sensitivity may be reduced.

In summary, different electrochemical sensors may appear very similar, but are constructed with different materials including such critical elements as sensing electrodes, electrolyte composition, and porosity of hydrophobic barriers. Additionally, some electrochemical sensors use external electrical energy to make them reactive to the target gas. All components of the sensors play a crucial role in determining the overall characteristics of the sensors.

Principle of Operation

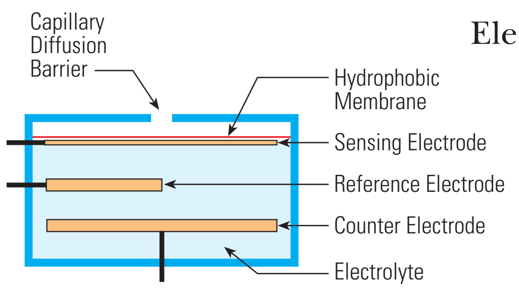

Fig. 3 Typical Electrochemical Sensor Setup

Electrochemical sensors operate by reacting with the gas of interest and producing an electrical signal proportional to the gas concentration. A typical electrochemical sensor consists of a *sensing electrode* (or working electrode), and a *counter electrode* separated by a thin layer of electrolyte, Figure 3.

Gas that comes in contact with the sensor first passes through a small capillary-type opening and then diffuses through a *hydrophobic barrier*, and eventually reaches the electrode surface. This approach is adopted to allow the proper amount of gas to react at the sensing electrode to produce a sufficient electrical signal while preventing the electrolyte from leaking out of the sensor, Figure 4.

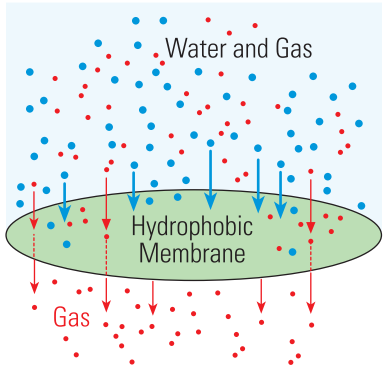

Fig. 4 Hydrophobic Membrane: prevents liquid electrolyte from leaking out.

The gas that diffuses through the barrier reacts at the surface of the sensing electrode involving either an oxidation or reduction mechanism. These reactions are catalyzed by the electrode materials specifically developed for the gas of interest.

With a resistor connected across the electrodes, a current proportional to the gas concentration flows between the anode and the cathode. The current can be measured to determine the gas concentration. Because a current is generated in the process, the electrochemical sensor is often described as an *amperometric gas sensor* or a *micro fuel cell.*

Importance of a Reference Electrode. For a sensor requiring an external driving voltage, it is important to have a stable and constant potential at the sensing electrode. In reality, the sensing electrode potential does not remain constant due to the continuous electrochemical reaction taking place on the surface of the electrode. It causes deterioration of the performance of the sensor over extended periods of time. To improve the performance of the sensor, a reference electrode is introduced.

This reference electrode is placed within the electrolyte in close proximity to the sensing electrode. A fixed stable constant potential is applied to the sensing electrode. The reference electrode maintains the value of this fixed voltage at the sensing electrode. No current flows to or from the reference electrode. The gas molecules react at the sensing electrode and the current flow between the sensing and the counter electrode is measured and is typically related directly to the gas concentration. The value of the voltage applied to the sensing electrode makes the sensor specific to the target gas.

The micro fuel cell-type electrochemical sensors do not require an external driving voltage. For example, an electrochemical sensor specific to oxygen has an anode, either Pb or Cd, that supplies electrons for the reduction of oxygen at the cathode. During the oxidation of the anode, the electrons are released which then travel via an external circuit to the cathode where oxygen molecules consume the electrons as follows:

In acidic electrolyte

Oxidation at the anode: $2Pb + 2H_2O \rightarrow 2PbO + 4H^+ + 4e^-$

Reduction at the cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

In basic electrolyte

Oxidation at the anode: $2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^-$

Reduction at the cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

The overall reaction in both cases is: $2Pb + O_2 \rightarrow 2PbO$. These types of sensors do not require a reference electrode.

Major Components

An electrochemical sensor consists of the following major components:

A. ***Gas Permeable Membrane*** (also called hydrophobic membrane): This is used to cover the sensor's sensing (catalyst) electrode and, in some instances, to control the amount of gas molecules reaching the electrode surface. Such barriers are typically made of thin, low-porosity Teflon membranes. Such sensors are called *membrane clad* sensors. Alternatively, the sensing electrode is covered with a high-porosity Teflon and the amount of gas molecules reaching the electrode surface is controlled by a capillary. Such sensors are referred to as *capillary-type sensors.* Besides offering a mechanical protection to the sensor, the membrane performs the additional function of filtering out unwanted particulates. Selecting the correct pore size of the membrane and capillary is necessary to transfer the proper amount of gas molecules. The pore size should be such as to allow enough gas molecules to reach the sensing electrode. The pore size should also prevent liquid electrolyte from leaking out or drying out the sensor too quickly.

B. ***Electrode:*** The selection of the electrode material is very important. It is a catalyzed material which performs the half cell reaction over a long period of time. Typically, the electrode is made from a noble metal, such as platinum or gold, and catalyzed for an effective reaction with gas molecules. Depending on the design of the sensor, all three electrodes can be made of different materials to complete the cell reaction.

C. ***Electrolyte:*** The electrolyte must facilitate the cell reaction and carry the ionic charge across the electrodes efficiently. It must also form a stable reference potential with the reference electrode and be compatible with materials used within the sensor. If the electrolyte evaporates too quickly, the sensor's signal will deteriorate.

D. ***Filter:*** Sometimes a *scrubber* filter is installed in front of the sensor to filter out unwanted gases. There is a limited selection of filters, each with different degrees of effectiveness. The most commonly used filter medium is activated charcoal, as shown in Figure 5. The activated charcoal filters out most chemicals with the exception of carbon monoxide and hydrogen gases. By properly selecting the filter medium, an elec-

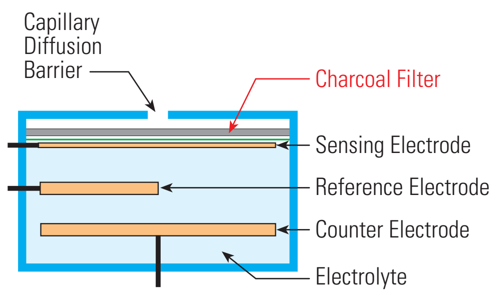

Fig. 5 Filtering with Activated Charcoal

Typical Gases and the Range of Measurement of Electrochemical Sensors

GAS NAME	PPM RANGE
Ammonia, NH_3	10
Arsenic Hydride, AsH_3	1
Bromine, Br_2	30
Carbon Monoxide, CO	300
Chlorine, Cl_2	5
Chlorine Dioxide, ClO_2	5
Diborane, B_2H_6	1
Fluorine, F_2	10
Germane, GeH_4	2
Hydrogen, H_2	2000
Hydrogen Chloride, HCl	30
Hydrogen Cyanide, HCN	30
Hydrogen Fluoride, HF	10
Hydrogen Sulfide, H_2S	30
Nitric Oxide, NO	100
Nitrogen Dioxide, NO_2	50
Oxygen	ppm levels to 100% by vol.
Ozone, O_3	3
Phosphine, PH_3	1
Silane, SiH_4	50
Sulfur Dioxide, SO_2	100

trochemical sensor can be made more selective to its target gases.

Choosing the suitable materials for the above components, and *arranging* the geometry of all these components to determine the optimum operating performance presents a challenge to scientists. Minor variations in the details of the sensor design can have a profound influence on the sensor's accuracy, response time, sensitivity, selectivity, and life expectancy.

Importance of Oxygen. The reactions at the sensing electrode (*anode*) for some gases are as follows:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

$$H_2S + 4H_2O \rightarrow H_2SO_4 + 8H^+ + 8e^-$$

$$NO + 2H_2O \rightarrow HNO_3 + 3H^+ + 3e^-$$

$$H_2 \rightarrow 2H^+ + 2e^-$$

$$2HCN + Au \rightarrow HAu(CN)_2 + H^+ + e^-$$

Simultaneously, the reactions at the counter electrode (*cathode*) need oxygen molecules to complete the process:

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

An inadequate supply of oxygen to complete the reaction will shorten the life of the sensors, hence the sensors will not operate properly.

Sensors involving a reduction reaction of the target gas—such as the reduction of nitrogen dioxide, chlorine, and ozone—at the cathode produce water as a byproduct. At the anode, water is simultaneously oxidized. Such sensors do not require the presence of oxygen to function properly, as shown by the following:

$$NO_2 + 2H^+ + 2e^- \rightarrow NO + H_2O$$

$$Cl_2 + 2H^+ + 2e^- \rightarrow 2HCl$$

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$$

Characteristics

There are many different ways that electrochemical sensors are constructed, depending both on the gas to be detected as well as the manufacturer. However, the main characteristics of the sensors are essentially very similar. Following are some of the common characteristics of electrochemical sensors:

1. With a three-electrode sensor, there is normally a jumper which connects the working and reference electrodes. If it is removed during storage, it will take a long time for the sensor to stabilize and be ready to be used. Some sensors require a bias voltage between the electrodes, and in such cases, the sensors are shipped from the factory with a nine-volt battery powered electronic circuit. It takes anywhere from thirty minutes to twenty-four hours for the sensor to stabilize, and it will continue to stabilize over a three-week period.

   When installed in a portable or stationary instrument, the sensor cannot be removed from power for an appreciable amount of time. It is wise to double-check the instrument before use if batteries or power were removed at some point. The portable instrument's circuitry provides a small current needed to maintain the sensor in the ready-to-use condition, even if the instrument is turned off.

   Two-electrode sensors do not require any bias voltage. For example, oxygen sensors do not require a bias voltage.

2. Most of the toxic gas sensors require a small amount of oxygen to function properly. There is a vent hole on the side or back of the sensor for this purpose. It is wise to double-check with the manufacturer in applications that use non-oxygen background gas.

3. Electrolyte within the sensor cell is an aqueous solution separated by a hydrophobic barrier which will not allow the aqueous solution to leak out. However, water vapor can pass through, just as other gas molecules can. In high humidity conditions, prolonged exposure can cause excessive water to build up and create leakage. In low humidity conditions, the sensor can dry out. Sensors that are designed to monitor high gas concentrations have less porous barriers to limit the amount of gas molecules that pass through, and therefore are not affected by the humidity as much as sensors that are used to monitor low gas concentrations, which have more porous barriers and allow a more free exchange of water molecules.

Pressure and Temperature

Electrochemical sensors are minimally affected by pressure changes. However, it is important to keep the entire sensor within the same pressure since differential pressure within the sensor can cause sensor damage. Electrochemical sensors are also quite sensitive to temperature and, therefore, the sensors are typically internally temperature-compensated. However, it is better to keep the sample temperature as stable as possible.

In general, when the temperature is above 25°C, the sensor will read higher; when it is below 25°C, it will read lower. The temperature effect is typically 0.5% to 1.0% per degree centigrade, depending on the manufacturer and type of sensor.

List of Typical Gas Interference Ratios for CO Sensors

Gas	Without Filter	With Filter
H_2S	0.3:1	10:1
SO_2	2:1	20:1
NO	3.3:1	10:1
NO_2	1.6:1	10:1
H_2	2:1	2:1

The higher the interference ratio, the less effect an interference gas has on the sensor.

Selectivity

Electrochemical sensors are generally fairly selective to the target gas they are designed for. The degree of selectivity depends on the type of sensor, the target gas, and the concentration of gas the sensor is designed to detect. The best electrochemical sensor is for the detection of O_2, which has good selectivity, is very reliable, and has a long life expectancy. Other electrochemical sensors are subject to interference from other gases. A typical list of interference ratios for CO sensors is shown on page 34 as an example.

The higher the ratio, the less the effect of interference gas on the sensor. The interference data are taken using relatively low gas concentrations. In actual applications, interference concentrations can be quite high, causing false readings and/or alarms.

Life Expectancy

The life expectancy of an electrochemical sensor depends on several factors, including the gas to be detected and the environmental conditions in which the sensor is used.

Generally, a one- to three-year life expectancy is specified. In reality, the life expectancy will be highly dependent on the total amount of gas exposed to the sensor during its life, as well as other environmental conditions, such as temperature, pressure and humidity.

Summary

Electrochemical sensors require very little power to operate. In fact, their power consumption is the lowest among all sensor types available for gas monitoring. For this reason, the sensors are widely used in portable instruments that contain multiple sensors. They are the most popular sensors in confined space applications.

A sensor's life expectancy is predicted by its manufacturer under conditions that are considered normal. However, the life expectancy of the sensor is highly dependent on the environmental contaminants, temperature, and humidity to which it is exposed.

Typical Toxic Gas Electrochemical Sensor Specification

Sensor Type: 2 or 3 electrodes; mostly 3 electrodes

Range: 2-10 times permissible exposure limit

Life Expectancy: 12 to 24 months normal; depends on manufacturer and sensor

Temperature Range: –40ºC to +45ºC

Relative Humidity: 15-95% noncondensing

Response Time T_{80}: < 50 sec.

Long Term Drift: drift down 2% per month