# How Oxygen, Electrochemical Toxic, and Metal Oxide Semiconductor Sensors Work *

1. Oxygen sensor detection principle

Most portable or survey instruments used for workplace evaluation of oxygen concentrations make use of "fuel cell" type oxygen sensors. "Fuel cell" oxygen sensors consist of a diffusion barrier, a sensing electrode (cathode) made of a noble metal such as gold or platinum, and a working electrode made of a base metal such as lead or zinc immersed in a basic electrolyte (such as a solution of potassium hydroxide). Oxygen diffusing into the sensor is reduced to hydroxyl ions at the cathode:

$O_2 + 2H_2O + 4e\text{-} \rightarrow OH\text{-}$
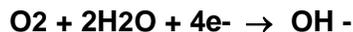
Hydroxyl ions in turn oxidize the lead (or zinc) anode:

$2Pb + 4OH \rightarrow 2PbO + 2H_2O + 4e\text{-}$

This yields an overall cell reaction of:

$2Pb + O_2 \rightarrow 2PbO$

Fuel cell oxygen sensors are current generators. The amount of current generated is proportional to the amount of oxygen consumed (Faraday's Law). Oxygen reading instruments simply monitor the current output of the sensor.

An important consideration is that fuel cell oxygen sensors are used up over time. In the cell reaction above, when all available surface area of the lead (Pb) anode has been converted to lead oxide (PbO), electrochemical activity ceases, current output falls to zero, and the sensor must be rebuilt or replaced. Fuel cell sensors are designed to last no more than one to two years. Even when installed in an instrument which is never turned on, oxygen sensors which are exposed to atmosphere which contains oxygen are generating current, and being used up.

Oxygen sensors are also influenced by the temperature of the atmosphere they are being used to measure. A warmer atmosphere leads to faster electrochemical reactions. For this reason oxygen sensors usually include a temperature compensating load resistor to hold current output steady in the face of fluctuating temperature. (Microprocessor based instrument designs usually provide additional signal correction in software to further improve accuracy.) Another limiting factor is cold. The freezing temperature of electrolyte mixtures commonly used in oxygen sensors tends to be about 5F (- 20C). Once the electrolyte has frozen solid, electrical output falls to zero, and readings may no longer be obtained. There are two basic variations on the fuel cell oxygen sensor design. These variations have to do with the mechanism by which oxygen is allowed to diffuse into the sensor. Dalton's Law states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the various gases. The partial pressure for oxygen is that fraction of the total pressure due to oxygen. Partial atmospheric pressure oxygen sensors rely on the partial pressure (or pO 2) of oxygen to drive molecules through the diffusion barrier into the sensor. As long as the pO 2 remains constant, current output may be used to indicate oxygen concentration. On the other hand, shifts in barometric pressure, altitude, or other conditions which have an effect on atmospheric pressure will have a strong effect on pO 2 sensor readings. To illustrate the effects of pressure on pO 2 sensors, consider a sensor located at sea level where atmospheric pressure equals 14.7 PSI (pounds per square inch). Now consider that same sensor at an elevation of 10,000 feet. Although at both elevations the air contains 20.9 percent oxygen, at 10,000 feet the atmospheric pressure is only 10.2 PSI! Since there is less force driving oxygen molecules through the diffusion barrier into the sensor, the current output is significantly lower.

"Capillary pore" oxygen sensor designs include a narrow diameter tube through which oxygen diffuses into the sensor. Oxygen is drawn into the sensor by capillary action in much the same way that water or fluid is drawn up into the fibers of a paper towel. While capillary pore sensors are not influenced by changes in pressure, care must be taken that the sensor design includes a moisture barrier in order to prevent the pore from being plugged with water or other fluids.
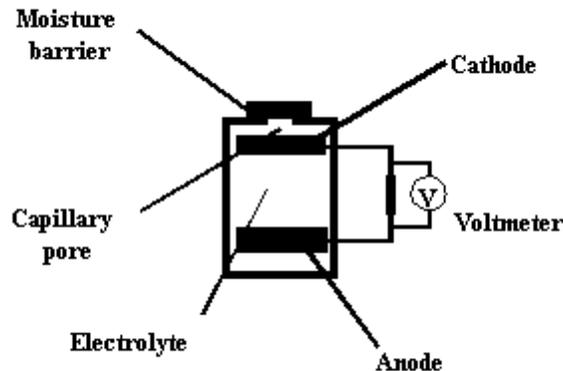
Figure 1.0: Capillary pore type oxygen sensor

1.1. Effects of contaminants on oxygen sensors

Oxygen sensors may be affected by prolonged exposure to "acid" gases such as carbon dioxide. Most oxygen sensors are not recommended for continuous use in atmospheres which contain more than 25% CO_2.

2. Substance-specific electrochemical sensors

One of the most useful detection techniques for toxic contaminants is the use of substance-specific electrochemical sensors installed in compact, field portable survey instruments. Substance-specific electrochemical sensors consist of a diffusion barrier which is porous to gas but nonporous to liquid, reservoir of acid electrolyte (usually sulfuric or phosphoric acid), sensing electrode, counter electrode, and (in three electrode designs) a third reference electrode. Gas diffusing into the sensor reacts at the surface of the sensing electrode. The sensing electrode is made to catalyze a specific reaction. Dependent on the sensor and the gas being measured, gas diffusing into the sensor is either oxidized or reduced at the surface of the sensing electrode. This reaction causes the potential of the sensing electrode to rise or fall with respect to the counter electrode. The current generated is proportional to the amount of reactant gas present.

This two electrode detection principle presupposes that the potential of the counter electrode remains constant. In reality, the surface reactions at each electrode causes them to polarize, and significantly limits the concentrations of reactant gas they can be used to measure. In three electrode designs it is the difference between the sensing and reference electrode which is what is actually measured. Since the reference electrode is shielded from any reaction, it maintains a constant potential which provides a true point of comparison. With this arrangement the change in potential of the sensing electrode is due solely to the concentration of the reactant gas.
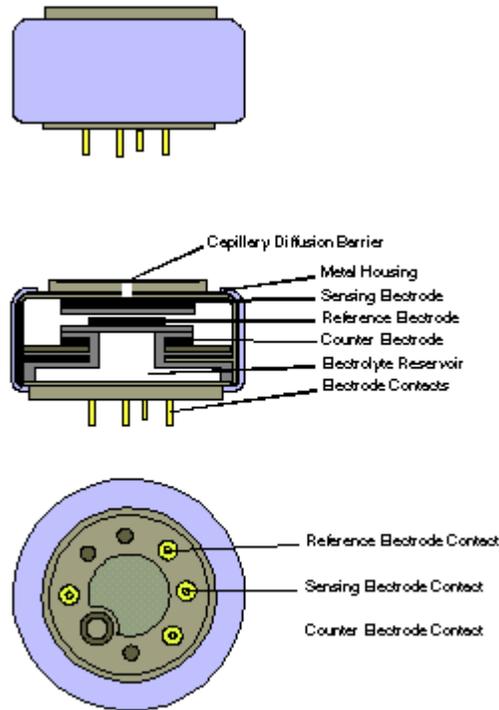
Figure 2.0: Three electrode electrochemical sensor

The oxidation of carbon monoxide in an electrochemical sensor provides a good example of the detection mechanism:

Carbon monoxide is oxidized at the sensing electrode:

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

The counter electrode acts to balance out the reaction at the sensing electrode by reducing oxygen present in the air to water:

$1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$
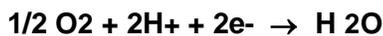
Similar reactions allow for the electrochemical detection of a variety of reactant gases including hydrogen sulfide, sulfur dioxide, chlorine, hydrogen cyanide, nitrogen dioxide, hydrogen, ethylene oxide, phosphine and ozone. A bias voltage is sometimes applied to the counter electrode to help drive the detection reaction for a specific contaminant. Biased sensor designs allow for the detection of a number of less electrochemically active gases such as hydrogen chloride and nitric oxide. Several other contaminants (such as ammonia) are detectable by means of other less straight forward detection reactions.

Electrochemical sensors are stable, long lasting, require very little power and are capable of resolution (depending on the sensor and contaminant being measured) in many cases to 0.1 ppm. The chief limitation of electrochemical sensors are the effects of interfering contaminants on toxic gas readings. Most substance-specific electrochemical sensors have been carefully designed to minimize the effects of common interfering gases. Substance-specific sensors are designed to respond only to the gases they are supposed to measure. The higher the specificity of the sensor the less likely the sensor will be affected by exposure to other gases which may be incidentally present. For instance, a substance-specific carbon monoxide sensor is deliberately designed not to respond to other gases which may be present at the same time, such as hydrogen sulfide or methane.

Even though care has been taken to reduce cross-sensitivity, some interfering gases may still have an effect on toxic sensor readings. In some cases the interfering effect may be "positive" and result in readings which are higher than actual. In some cases the interference may be negative and produce readings which are lower than actual. Electrochemical sensor designs may include a selective external filter designed to remove interfering

gases which would otherwise have an effect on the sensing electrode. The size and composition of the filter are determined by the type and expected concentration of the interfering contaminants being removed.

The following table lists the cross sensitivity of a commonly used brand of electrochemical toxic sensors to gases other than their target gas. (Responses may differ with other brands of sensors and detectors.) Depending on the nature of the reaction each gas has with the sensor, the effect can either decrease the signal (negative cross sensitivity) or increase the signal (positive cross sensitivity). Each figure represents the reaction of the sensor to 100 ppm of gas, thus providing a percentage sensitivity to that gas relative to its target gas.

Type of Sensor	Interfering Gas										
	CO	H_2S	SO_2	NO	NO_2	Cl_2	H_2	HCN	HCl	NH_3	Ethylene
Carbon Monoxide (CO)	100	< 10	< 10	< 30	< 15	< 10	< 40	< 15	< 3	0	approx. 50
Hydrogen Sulfide (H_2S)	0	100	approx. 15	< 5	approx. -20	< -25	0	0	0	0	0
Sulfur Dioxide (SO_2)	0	0	100	0	< -120	< 5	0	< 50	0	0	0
Nitric Oxide (NO)	0	approx. 35	approx. 5	100	< 40	0	0	0	< 15	0	0
Nitrogen Dioxide (NO_2)	0	approx. -20	< -0.5	0	100	90	0	< 1	0	0	0
Chlorine (Cl_2)	0	approx. -20	0	0	120	100	0	0	0	0	0
Hydrogen Cyanide (HCN)	< 5	approx. 350	approx. 160	0	approx. -120	approx. -55	0	100	approx. 35	0	approx. 50
Hydrogen Chloride (HCl)	< 5	approx. 60	approx. 100	approx. 240	approx. 15	approx. -30	approx. 0	0	100	0	2
Ammonia (NH_3)	0	approx. 130	approx. 70	approx. 20	approx. 0	approx. -50	0	approx. 30	approx. -5	100	0

Table 2.0: Cross sensitivity of Biosystems, Inc. "7 Series" toxic sensors

In some cases, cross sensitivity is used to deliberate advantage. Carbon monoxide and hydrogen sulfide are the two most common toxic gases associated with confined space entry. In addition to "substance specific" sensors designed to measure these toxic hazards, several manufacturers offer a dual purpose sensor designed to detect both carbon monoxide and hydrogen sulfide. Dual purpose sensors of this kind are useful in situations requiring use of a single sensor to monitor simultaneously for both toxic hazards. It should be pointed out that since dual purpose sensors have been designed to respond to both hazards at the same time, they cannot determine which of the two hazards is producing the reading. A dual purpose sensor cannot determine which hazard is present in what specific concentrations, but may still be capable of providing an immediate indication when conditions become unsafe.

When a specific contaminant such as hydrogen sulfide is known to be potentially present, the best approach is usually to use a direct reading substance specific sensor. The OSHA standard for permit required confined space entry (29 CFR 1910.146) explicitly requires the use of direct reading, substance specific sensors whenever a

particular toxic hazard is known to be present. If hydrogen sulfide is known to be potentially present, one of the toxic sensors selected should be specifically for the detection of H 2S, and calibrated directly to this hazard.

3. Metal oxide semiconductor sensors

Metal oxide semiconductor (or MOS) sensors may be used for toxic as well as combustible gas monitoring. As discussed previously in the combustible gas monitoring section, MOS sensing elements consist of a metal oxide semiconductor such as tin dioxide (SnO 2) on a sintered alumina ceramic bead contained within a flame arrestor. In clean air the electrical conductivity is low, while contact with reducing gases such as carbon monoxide or combustible gases increases conductivity. Sensitivity of the sensing element to a particular gas may be altered by changing the temperature of the sensing element.
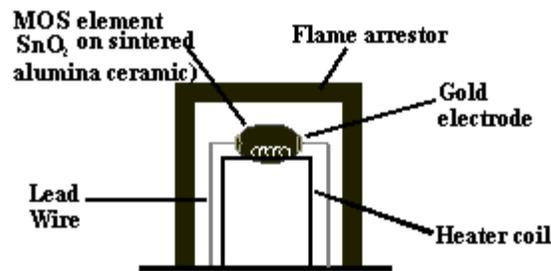

Figure: Metal oxide semiconductor (MOS) sensor

MOS sensors are "broad range" devices designed to respond to the widest possible range of toxic and combustible gases, including chlorinated solvent vapors and other contaminants difficult to detect by other means. This non-specificity can be advantageous in situations where unknown toxic gases may be present, and a simple go / no go determination of the presence of toxic contaminants is sufficient.

Since sensitivity of the sensing element to a particular gas is mathematically predictable, a commonly used strategy is to preprogram the instrument with a number of theoretical specific response curves. If the exact nature of the contaminant is known, an identification code can be entered, and readings of the sensor will be adjusted to reflect the expected sensitivity of the sensor to the contaminant being measured. MOS sensors offer the ability to detect low (0 - 100 ppm) concentrations of toxic gases over a wide temperature range. The chief limitations concerning use of this kind of sensor are the difficulty in the interpretation of positive readings, the potential for false positive alarms, and the effects of humidity on sensor output. As humidity increases sensor output increases as well. As humidity drops to very low levels, sensor output may fall to zero even in the presence of gas. In addition, caution must be exercised when making assumptions about the contaminants which are presumed to be present. If a user keys in the preprogrammed response curve for a contaminant which is highly detectable by the sensor, but actually encounters one which is less detectable, the result may be erroneously low readings.

* Excerpted (with permission) from Corporate Health and Safety: Managing Environmental Issues in the Workplace; Eric George, Editor. Published by Ergonomics, Inc., Southampton, Pennsylvania, Copyright 1996; Robert E. Henderson, *"Assessment and Management of Air Quality in the Workplace."*