

"INNOVATORS IN GAS DETECTION"



Technical Discussion Papers

Sensors

- ▲ *Electrochemical Oxygen Sensors*
- ▲ *Hydrogen Sulfide Detection:
Electrochemical vs. Solid State
Semiconductor Sensors*
- ▲ *Electro-catalytic Combustible Sensors*
- ▲ *Electrochemical "TwinTox" Sensors*

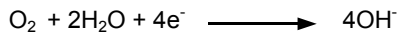
ELECTROCHEMICAL OXYGEN SENSORS

Technical Discussion

The oxygen sensors used in BW instruments are of the self-powered, diffusion-limited, metal-air battery type. They are comprised of an anode, an electrolyte and an air cathode, as shown in Figure 1.

Oxygen sensors are current generators, and the current is proportional to the rate of oxygen consumption (Faraday's Law). This current can be measured by connecting a resistor across the output terminals to produce a voltage signal. If the passage of oxygen into the sensor is purely diffusion-limited, the signal is a measure of oxygen concentration.

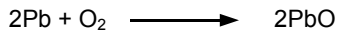
At the cathode, oxygen is reduced to hydroxyl ions according to the equation:



The hydroxyl ions in turn oxidize the metal anode as follows:



Overall, the cell reaction may be represented as:



Capillary-pore oxygen sensors, such as the ones used in BW instruments, utilize 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.

Capillary-pore sensors are minimally influenced by changes in atmospheric pressure. Although rapidly changing pressure leads to a change in sensor output, once the diffusion barrier capillary has stabilized at the new pressure, the output will return to the previous level. Because the volume of atmosphere contained in the diffusion barrier capillary is very small, stabilization at the new pressure is usually achieved within 10 to 30 seconds. This effect can be seen clearly when a properly calibrated capillary-pore oxygen sensor is taken on board a commercial jet. Initially the sensor reads 20.9%. As the jet takes off and begins to gain altitude, the pO₂ drops, causing a drop in oxygen sensor readings. When the jet reaches cruising altitude (actually, when cabin pressure is stabilized at normal operational levels), the readings return to 20.9%. As the jet begins its descent prior to landing, pO₂ increases causing a rise in readings. As soon as the sensor is back at ground level (and the cabin is once again depressurized), readings will return to 20.9%.

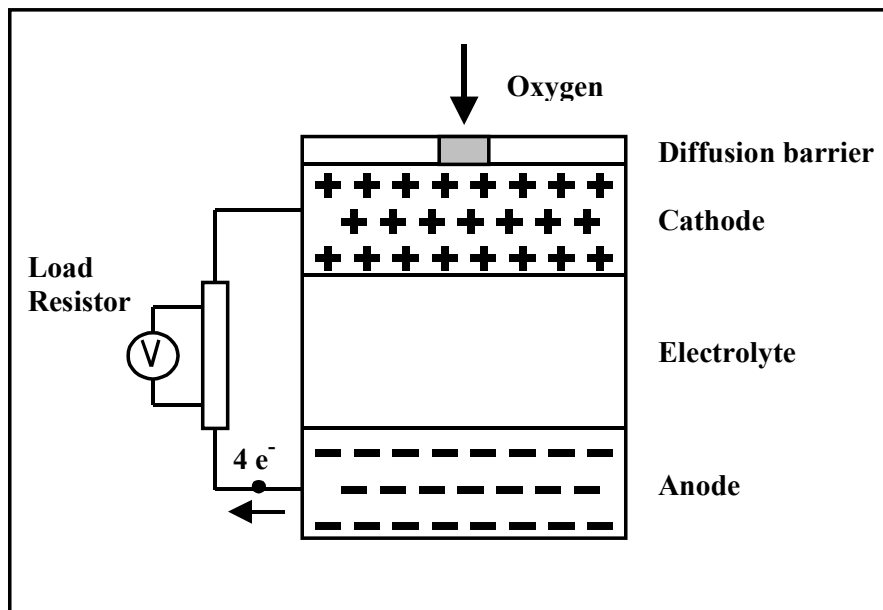


Figure 1. Capillary-pore oxygen sensor

HYDROGEN SULFIDE DETECTION: Electrochemical vs. Solid State Semiconductor Sensors

Technical Discussion

Hydrogen sulfide (H₂S) is one of the most common chemicals used or encountered by industry. Well over 150,000 workers in North America are exposed or potentially exposed to this flammable and highly poisonous gas every year. Hydrogen sulfide is also known for its corrosive effects, particularly on sensitive electronic equipment.

Hydrogen sulfide is a common hazard in a wide range of industries, including oil and gas drilling and production, oil refining, petrochemical processing, gas transmission and storage, chemical processing, wastewater treatment, pulp and paper production and mining.

To avoid the hazards associated with possible personnel exposure, H₂S sensors are provided by industry in portable and fixed detection systems to give an early and reliable warning that H₂S is present in ambient air. This paper discusses two H₂S detection techniques: electrochemical sensors and solid state sensors.

Principles of Operation

To fully appreciate the relative merits of each of these detection techniques, it is important to have a basic understanding of each technique's principle of operation.

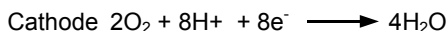
The solid state semiconductor consists of four main parts: the substrate, a ceramic wafer on which the other parts are built; the heater, to maintain proper operating temperature; the interdigitated track, which contains the electrodes for sensing purposes; and the semiconductor layer—usually a metal oxide film, such as tungsten oxide or tin oxide.

Normally, the semiconductor layer has a low electrical conductivity, but in the presence of H₂S, a surface reaction occurs, which releases electrons within the semiconductor layer dropping its resistance. This fall in resistance is registered via a sensor signal output change in H₂S gas concentration.

Electrochemical sensors are classified as fuel cells. They may have either two or three electrodes. In the three-electrode cells, the third electrode acts as a reference. The principle of operation is the same for each type.

In electrochemical sensors, H₂S enters the cell through a diffusion barrier and gas-permeable membrane. A reaction takes place at the working electrode (anode), releasing electrons that flow to the counter electrode (cathode), where a counter reaction occurs. These reactions may or may not

consume the electrolyte. It reacts as follows (see also Figure 1):



This flow of electrons is registered as a concentration value, which is commonly displayed on a local LCD or LED transmitter readout—a companion control module or PLC/DCS control system.

Response Characteristics

Figures 2 and 3 show samples response curves for solid state and electrochemical sensors, respectively. Solid state sensors are typically logarithmic in response, while electrochemical sensors exhibit a linear response curve.

The normal resistance (no H₂S present) of a solid state sensor can be as high as 20 meg ohms. The resistance needs to decrease to about 100K ohms before the instrument will move off the meter zero point. Full scale deflection (100 ppm H₂S) is approximately 10 to 15K ohms.

The logarithmic response of a solid state sensor can lead to significant problems. One problem is that either a linearized circuit or a non-linear scale must be implemented in the control circuitry. Another inconvenience is the need to expose the sensor to two different concentrations of gas during calibration for "low span" and "high span" adjustment, as there is no true zero point on the logarithmic curve.

An additional problem is the inherent instability of the semiconductor layer, which results in a changing baseline resistance. The results are barely noticeable at the zero end of the scale, where large resistance changes represent small concentration changes; however, the results are significant at the high end of the scale, where small resistance changes represent large concentration changes. In electrochemical sensors, the number of electrons released in the chemical reaction is linearly dependent on gas concentration. A significant feature is the gas diffusion controlled operation of the working electrode. The design of this barrier allows only a small quantity of sample atmosphere to reach the electrode. As a result, only a small fraction of the active electrolyte is reacted, leaving a large quantity "in reserve" for higher concentrations of H₂S. Cell output remains linear at concentrations of 1,000 ppm and above.

HYDROGEN SULFIDE DETECTION:

Electrochemical vs. Solid State Semiconductor Sensors

Technical Discussion (cont'd)

The currents generated by the oxidation reaction are quite low—typically 0.4 $\mu\text{A/ppm H}_2\text{S}$. However, the intrinsically low background current and low noise output of the cell results in excellent repeatable sensitivity to H_2S .

External Influences on Response

Sensor response may also be influenced by a variety of environmental conditions. Solid state semiconductor and electrochemical detectors vary quite differently in how they are affected by these often uncontrollable environmental factors.

Lack of H_2S Exposure – A common trait of solid state semiconductor sensors is their tendency to “go to sleep” when exposed to H_2S free air for prolonged periods of time. This effect is generally caused by the localizing of electrons within the metal oxide film, which drives the zero resistance into the high meg ohm range. This normally high zero resistance prevents a quick or repeatable response. Most electrochemical cells have an absolute zero, which eliminates the “going to sleep” syndrome.

Rain and Humidity – The metal oxide film on a solid state semiconductor sensor is vulnerable to changes caused by exposure to water. A gradual conversion of the film to a metal hydroxyl state occurs, which eventually deadens the sensor's sensitivity to H_2S .

Even brief exposures to water through rain or washdown will cause surface changes that prevent absorption of hydrogen sulfide; recalibration of the sensor is advisable after exposure to moisture. To minimize susceptibility to moisture damage, surface temperature should be greater than 100 °C. This is often accomplished with a built-in heater.

Changes in humidity or direct exposure to moisture have little effect on the electrochemical cells. All reactions take place at the working electrode, where moisture is continually present. The electrolyte reservoir has sufficient overcapacity to allow the cell to accommodate all but the most prolonged periods of very high or very low humidity. The cell has been tested for three months at a relative humidity of 0% without ill effects. In addition, once the RH was increased, the cell reabsorbed all lost moisture.

Temperature – Maintaining a constant chip surface temperature is important to keeping the response time and stability of solid state sensors within acceptable limits. For this reason, heaters are often built into the sensor surface.

Equally important is the need to set each individual sensor's operational temperature to compensate for

variations in chip manufacturing and the process of metal oxide deposition. A sensor operating too cold will respond very slowly; a sensor operating too hot will respond very quickly but will also demonstrate a tendency toward non-repeatability. However, only a few manufacturers address the critical importance of this issue by thermostatically controlling the heater to prevent surface temperature fluctuations.

The temperature effects on the sensitivity of the electrochemical sensor are predictable and repeatable from cell to cell. From 0 °C to 40 °C, the span changes by less than $\pm 10\%$ of the reading given at 20 °C. From 0 °C to -40 °C, there can be a further fall of 5% of the reading.

The zero shifts by less than 3 ppm for a temperature change from 20 °C to 40 °C. Below 20 °C, baseline shifts are negligible. The electrolyte does not freeze at -40 °C.

Operating Considerations

There are certain operational costs affected with any gas monitoring system. Calibration and power consumption are two of the major factors that should be considered in the selection process.

Calibration – In general, the manufacturers of solid state sensors recommend monthly or three-month calibration intervals. However, many companies have adopted a daily calibration schedule for these systems. This is due primarily to the lack of repeatability caused by the sensor's vulnerability to surface changes. In addition, and as previously mentioned, calibration at two or more concentration levels is required to assure proper response all along the logarithmic response curve; this multi-concentration calibration process often requires 15 minutes or more per sensor.

The linear nature of the electrochemical sensor, along with its absolute zero and excellent repeatability, allows single point calibration at up to six-month intervals.

Reproduceability between electrochemical cells is outstanding. Direct replacement without calibration will produce a response within 10% of the original; with calibration, the response will be within 2% of the original.

Power Consumption – The sensor heater and associated circuitry is a major power draw in solid state semiconductor systems. This can be a major drawback in applications for portable monitors or for fixed systems needing solar power or battery backup. Power consumption for systems using the electrochemical sensor is significantly reduced.

HYDROGEN SULFIDE DETECTION: Electrochemical vs. Solid State Semiconductor Sensors

Technical Discussion (cont'd)

Summary

There are inherent weaknesses in the design and response of semiconductor sensors. Temperature, humidity and other ambient conditions can significantly affect detection and measurement performance. Their logarithmic nature and tendency to "go to sleep" necessitate frequent calibration. Finally, power consumption may be substantial.

Electrochemical devices are better suited to the realities of modern H₂S monitoring applications.

They can withstand environmental extremes with little or no loss of detection accuracy, require less frequent calibration and have significantly lower operating costs.

While each application should be judged on its merits, electrochemical cells generally prove more reliable, offer greater operator confidence and provide maximum performance in early warning detection of hazardous concentrations of hydrogen sulfide.

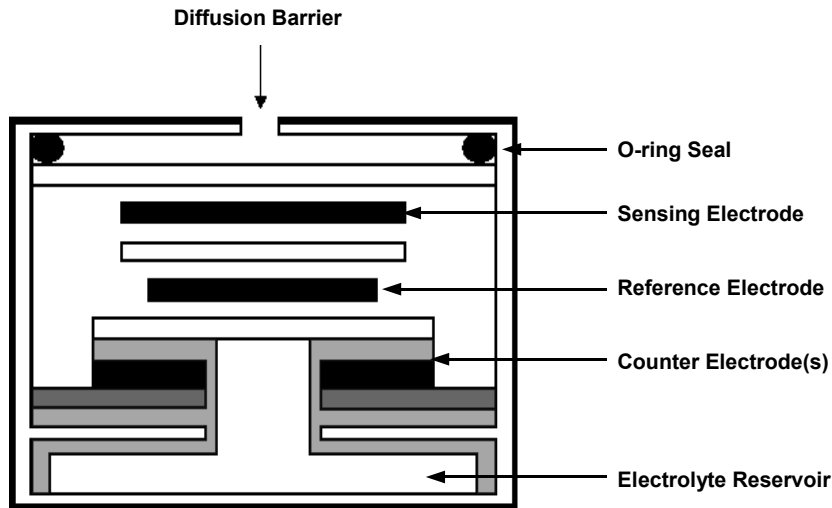
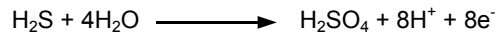
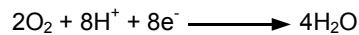


Figure 1. Electrochemical sensor

Working Electrode Reaction:



Countering Electrode Reaction:



0.70 microAmps per ppm H₂S

HYDROGEN SULFIDE DETECTION: Electrochemical vs. Solid State Semiconductor Sensors

Technical Discussion (cont'd)

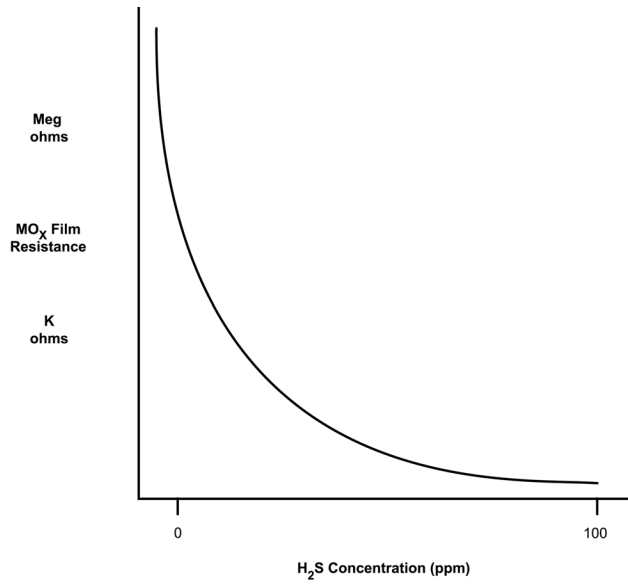


Figure 2. Sample solid state sensor response curve (simplified)

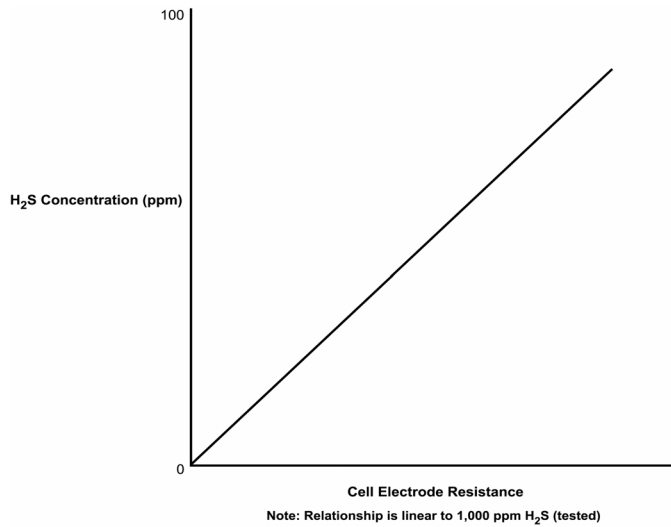


Figure 3. Sample electrochemical sensor response curve (simplified)

ELECTRO-CATALYTIC COMBUSTIBLE SENSORS

Technical Discussion

Combustible gases and vapors may be ignited and propagate flame only between the limits of flammability known as the Lower Explosive Limit (LEL) and the Upper Explosive Limit (UEL). Mixtures of combustible gases in air below the LEL are too lean to permit propagation of flame, while mixtures above the UEL are too rich to permit combustion due to the lack of oxygen. The LEL and the UEL are usually expressed as percentages, by volume, of combustible gas in air. These values differ from gas to gas. In practice, values of LEL and UEL are established empirically, and different authorities have established different values for the same gases.

While some industrial gas alarm systems are required to indicate alarms at preset levels above the limits of flammability (e.g. as for use with methane drainage systems in coal mines), most are required to indicate alarms at preset levels below the LEL. The gas detection technology adopted in each case is different—thermal conductivity or infrared detectors are commonly used for the detection of high concentrations (above the LEL), and electro-catalytic detectors being very widely used for the detection of concentrations below the LEL. This paper is concerned only with the latter. The principles of operation and some practical examples are described.

Principle of Operation

Despite a great deal of research and development in the field of gas detection during the past decade or so, industry has yet to devise a more cost-effective form of a selective combustible gas detector for use at sub-LEL levels than that of the long established electro-catalytic detector. Such detectors have been in widespread use for more than 50 years—in portable, transportable and fixed, multi-point gas alarms. Although many design improvements have been made to detectors of this type over the years, in essence, the basic concept has not changed.

The principle of operation depends upon the oxidation of combustible gases on an electrically heated catalytic “filament” (otherwise known as the “sensitive,” “active” or “detector” element), which causes the temperature of this filament to rise so as to electrically unbalance a Wheatstone bridge circuit of which it forms a part (see Figure 1). This sensitive filament may take the form of a simple length of platinum wire or it may be in the form of a coil of platinum wire coated with a suitable noble metal oxide, e.g. palladium/ thoria on an alumina base. The latter configuration is designed to enhance the catalytic activity at lower filament temperatures and so to extend the life of the filament. A second

filament, made inactive to gas by sealing or “poisoning” but electrically matched with the sensitive filament, is connected electrically with the latter as part of the Wheatstone bridge and is located adjacent to it in the detector housing so as to provide compensation for the effects of ambient temperature variations upon the sensitive filament. This second filament is known as the “non-sensitive” or “compensator” element.

When such a gas detector is exposed to increasing concentrations of a combustible gas in air, its response (as measure electrically across the Wheatstone bridge) typically increases approximately linearly through the LEL, peaking at around the stoichiometric mixture, and then falls to zero when the combustible gas concentration reaches 100% by volume (see Figure 2). From this, it will be evident that the gas detector is coherent only with the LEL range, and that anomalous response can occur at gas concentrations greater than the stoichiometric mixture. This defines its limitation of measurement, although it is possible to devise a means of preventing anomalous readings of the gas detection system at concentrations in excess of the LEL.

Detection Elements

The detection elements may take various forms according to the origin of their design. The simplest form is the platinum wire filament, still used in some gas detection instruments. However, this has the disadvantage of requiring a high operating temperature for efficient combustion (methane –900 °C), resulting in short life to failure due to evaporation of the platinum wire.

The two particular forms of detection considered in this paper are the “filament” and the “bead.” Each has unique characteristics.

The filament configuration is generally as shown in Figure 3. It is comprised of a silica fiber tubular former upon which is spirally wound a length of fine gauge platinum wire. The spaces between the turns of the wire are critical to the performance of the detector. The sensitive (active) filament is coated with one of several alternative palladium/platinum/ thoria catalysts, each designed to give the best possible relative response to a particular range of gases. The non-sensitive filament is made chemically inert to gas or is sealed with, for example, glass. The sensitive filament is electrically self-heated to a temperature between 300 °C and 600 °C, according to the gas(es) to be detected. Both filaments are mounted in ceramic or similar frames to suit the various designs of gas detection instruments.

ELECTRO-CATALYTIC COMBUSTIBLE SENSORS

Technical Discussion (cont'd)

The "bead" (see Figure 4) takes the form of a ceramic pellet supported on a platinum wire coil and/or in the case of the sensitive element, coated with a palladium thoria, or other catalyst, or in the case of the non-sensitive element, deactivated with potassium hydroxide, glass or similar material. This glass or ceramic pellet works to minimize coil wire evaporation as well as to provide mechanical support. The sensitive element is normally electrically self-heated to between 400 °C and 600 °C for methane and other gases.

Much has been said of the effects of "poisons" or "inhibitors" on electro-catalytic beads. The most common poisons are silicons, sulfides, phosphates and leads. These materials exhibit an affinity for the catalyst and tend to coat the sensor bead, which prevents the gas being monitored from reaching the sensing element. In some cases, the effect is so dramatic that some sensors have been rendered useless in a matter of a few days.

This problem has been resolved by using a method to apply a sponge-like coating around the glass bead and applying the catalyst throughout the porous coating. This greatly increases catalytic surface area, thereby increasing the amount of poison that can be tolerated and extending sensor life.

Usually the bead is much smaller than the filament, and it operates at lower input power with correspondingly lower output sensitivity (usually stated in terms of millivolts bridge out-put per percent LEL or percent volume of gas in the air).

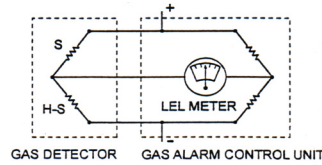


Figure 1. Basic gas detection circuit (The Wheatstone Bridge)

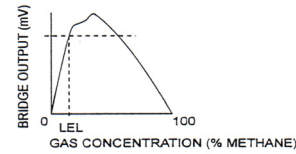


Figure 2. Typical response characteristic (bead)

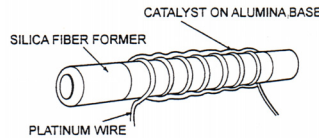


Figure 3. The filament (sensitive)



Figure 4. The bead (sensitive)

ELECTROCHEMICAL “TWIN TOX” SENSORS

Technical Discussion

The “Twin Tox” gas sensor used in BW Technologies BW Defender multi-gas detection instruments is a unique approach for sensing hazardous levels of hydrogen sulfide (H₂S) and carbon monoxide (CO) gas.

The “Twin Tox” is basically two gas sensors in one. It utilizes toxic gas sensing technology that has been field proven over the last decade and is the present standard for the detection of hazardous gases in the industrial hygiene industry, particularly those found in the oil and gas, municipal, pulp and paper, fire/hazmat sectors and other confined space entry applications.

The BW Technologies “Twin Tox” has two separate chambers within the single sensor package, which provide independent gas sensing and resulting signal outputs for H₂S and CO. This allows the “Twin Tox” to be gas specific to either H₂S or CO or both simultaneously. Figure A graphically illustrates the inner workings of the sensor. Note that there are two layered and independent sensing chambers, each containing a sensing electrode (S1 & S2). The first sensing electrode chamber (S1) will react only to H₂S gas molecules and the second sensing electrode chamber (S2) reacts with CO. Both S1 and S2 sensing electrodes share a reference electrode and the common electrolyte solution reservoir.

The gas sensing reactions are shown at the bottom section of Figure 1. The key advantages are that:

- 1) sensor signal output is linear to the exposed gas concentration;
- 2) power consumption is minimal because the actual sensing chemical reaction creates the base sensing signal—each molecule of H₂S produces 8 electrons of signal (the sensing circuitry is normally quiescent); and
- 3) the working electrode reaction regenerates the exact amount of water (H₂O) that was used on the sensing electrode to react with the target gas (H₂S or CO) (it refills itself).

The “Twin Tox” sensor should not be confused with the Dual Tox type sensor, which is simply a non-filtered CO electrochemical cell that will indiscriminately detect H₂S and/or CO based on its cross-interfering response. Unlike the BW Technologies “Twin Tox,” the Dual Tox type sensor contains only one sensing electrode chamber, gives only one gas sensing signal output and cannot distinguish between H₂S and CO.

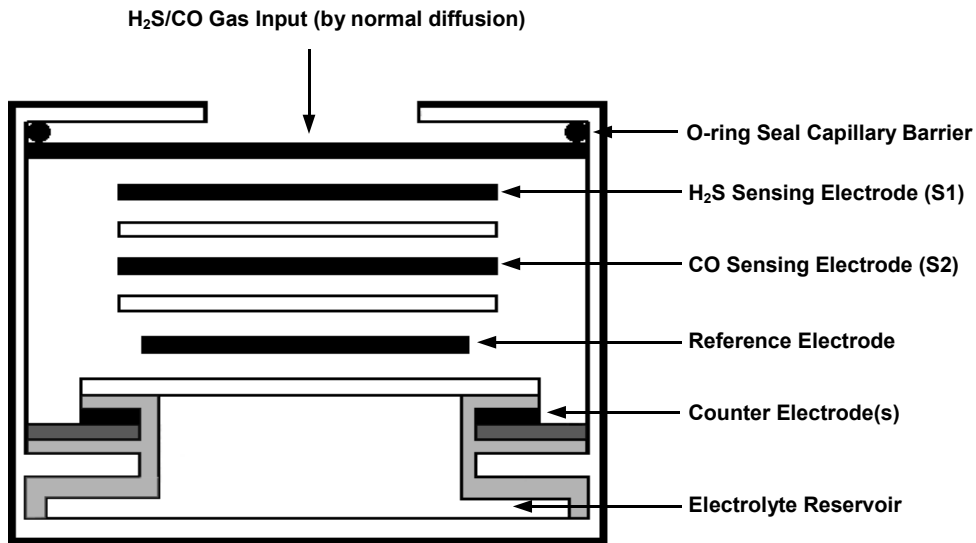
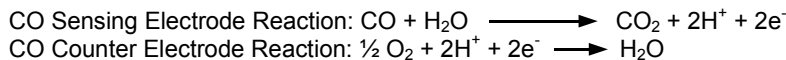
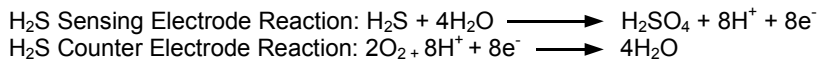


Figure 1. Electrochemical “Twin Tox” Sensor



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