# ELECTROCHEMICAL CELLS

The electrochemical sensors, also known as a fuel cells, are available to measure percent or trace (ppm) levels of oxygen in a gas or gas mixture. Variations to both of these cell types for measuring in hydrogen or hydrogen containing atmospheres are also available. There are a number of cell housing types so the cell can be optimised for the chosen application.

Principle of Operation

All electrochemical oxygen sensors are of the self-powered, diffusion limited, metal-air battery type comprising an anode, a semi-solid electrolyte paste and an air cathode. The cell comprises an enclosure containing two electrodes, a flat PTFE tape with an active catalyst the cathode and a block of lead (anode). The enclosure is sealed apart from a small capillary that controls the rate at which oxygen can enter the cell.

Capillary Barrier
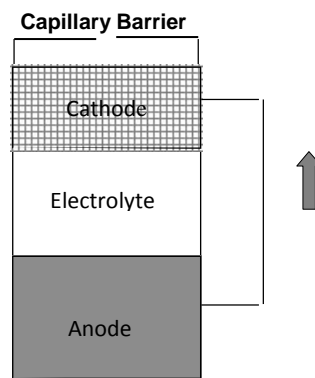
Oxygen enters the sensor through the capillary where it comes in contact with the cathode, and is immediately reduced to hydroxl ions:

$$O_2 \; + \; 2\,H_2O \; + \; 4\,e^{--} \qquad\qquad 4\,OH^{--} \qquad\qquad (1)$$
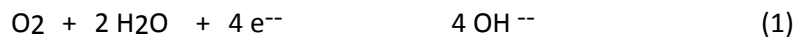
These hydroxyl ions then migrate through the electrolyte to the lead anode. The hydroxyl ions react with the lead anode which is then oxidised to lead oxide.

$$2\,Pb \; + \; 4\,OH^{--} \qquad\qquad 2\,PbO + 4\,e^{--} \quad + \quad 2\,H_2O \qquad (2)$$
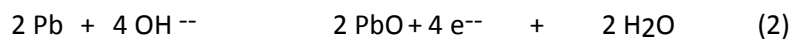
As these two processes take place a current is generated which can be measured by the instrument. This current is proportional to the oxygen concentration and leads to an accurate determination of oxygen.

Sensor lifetime

As the electrochemical reaction results in the oxidation of the lead anode, the electrical / chemical properties of the cell change requiring periodic calibration. The oxidation of the lead anode also means the sensors have a limited life, once all the available lead has been oxidised the cell will no longer produce an output, and must be replaced. Consequently, the lower the oxygen level the sensor is exposed to the longer it will operate. The cell life also depends on the humidity level of the sample gas. A more humid sample gas will prolong the life of the cell because it reduces drying out of the electrolyte.

Systech Illinois ppm cells measuring low levels of oxygen should have lifetimes in excess of 3 years. Percent cells, measuring air, should have lifetimes around 5 years. Some components of the gas stream increase the rate of oxidation, or form other lead compounds, thus shortening the life of the sensor. These include CO_2 and Cl_2. Gas streams containing these gases should be avoided where possible.

Concentration or Partial Pressure

All Systech Illinois electrochemical cells use capillary diffusion and measure oxygen concentration. Membrane type diffusion barriers measure partial pressure.

Pressure Effects

The current generated by the cell is proportional to the volume fraction of oxygen and this is independent of the pressure of the gas. If, however the cell is subjected to a small change in the pressure or small pressure pulses, for example by a pump, then a transient current can be generated which will be seen as change in oxygen reading on the analyser.

When the pressure changes, gas is forced through the capillary barrier (known as bulkflow). This results in an enhanced (or reduced) flux of gas to the cell and hence a transient on the output signal. The transient quickly settles once the pressure pulse is complete and diffusion conditions are re-established. Systech Illinois cells are fitted with an anti-bulkflow mechanism, which damps pressure changes resulting in a considerable reduction of the transient signal.

Some pumps can subject the cell to a barrage of pressure pulses, which overcome the anti bulkflow device and result in an enhanced oxygen reading. In these cases, it is necessary to design the sample system to minimise the pulses.

If the pressure pulse is sufficiently large the cell barrier will rupture, often accompanied by the electrolyte leaking from the cell. Pressures as low as 1 Bar can cause over-pressure if incorrectly applied. Care must be taken to prevent over-pressure of the cells as damage of this nature is not covered by Systech Illinois' warranty.

Temperature Effects

The electrochemical cells are sensitive to temperature, although the effect is relatively small. Changing the temperature from +20 to –20 deg C will result in approximately a 10% loss of output signal. To minimise the effects of temperature change the, cells for some instruments eg 900 series have temperature compensation built in, other instruments can have temperature compensation fitted.

Linearity

The signal from a Systech Illinois cell is:

$$O/P = constant * \ln[1/(1-C)]$$

Where C is the fractional concentration of oxygen

In practice, the output from the cells is effectively linear up to 30% oxygen. Oxygen concentrations above 30% would present difficulties both due to the non-linearity and also due to reduced lifetime.

Stability and Drift

The design of the cell requires that the cells speed of reaction should be sufficient for diffusion through the capillary and all other stages in the process should be significantly faster. Systech Illinois cells have highly active electrodes so the cells have a large activity reserve. This is a factor in ensuring excellent long-term stability and low drift.

Hydrogen Cells

Hydrogen cells are specially designed to have low hydrogen cross interference. They must be used in hydrogen and hydrogen containing gas streams, including gases such as ethylene. Hydrogen cells can be used on any other gas streams, e.g. nitrogen, but their lower signal output requires modification to the instrument to display the correct readings.

Correction for Carrier Gas Molecular Weight

The molecular weight of the carrier, or background, gas will affect the rate that oxygen can enter the cell through the capillary, this will result in a different current output for the same oxygen concentration dependent on the carrier gas. Correction for this difference will be required if the measurement carrier gas is different from the calibration carrier gas.

The error is dependent on the molecular weight of the carrier gas. Some examples molecular weights are:

Nitrogen - 28.02
Hydrogen - 2.02
Argon - 39.91
Helium - 4.00

When calibrating using one carrier gas and measuring using another the magnitude of the error can be easily calculated and the correct oxygen concentration known.

The formula is:

$$O_2 = \text{Reading} / \sqrt{(C_{mwt}/ M_{mwt})}$$

(O_2 – is the true oxygen reading)
(reading – is the reading of the instrument)
(C_{mwt} – is the molecular weight of the carrier gas used for calibration)
(M_{mwt} – is the molecular weight of the carrier gas used for the measurement)

For example; an instrument calibrated in N2 (or Air) and then used to measure oxygen in hydrogen is reading 12ppm. The true oxygen content of the gas would be:

$$12\text{ppm} / \sqrt{(28.02/2.02)} = 3.2\text{ppm}.$$

To correct the readings for these errors there are a number of options

[1] Calibrate the instrument as normal and calculate the true reading using the formula above.

[2] Correct the calibration gas value using the formula, set the instrument to that value during calibration and then read the correct values from the instrument.

e.g. To calibrate using N2 (Air) and then measure oxygen in hydrogen.
Air contains 20.9% O2 so applying the formula gives a hydrogen reading of:

$$20.9\% / \sqrt{(28.02/2.02)} = 5.61\%$$

So the instrument is set to read 5.61% when calibrated in nitrogen and will then read correctly when measuring oxygen in hydrogen.

[3] Use a calibration cylinder with the correct carrier gas.

When using carrier gases that contain a mixture of gases the molecular weight can be calculated by summing the proportions of the gases. For a mix containing 50% N2, 30% Ar and 20% He the molecular weight would be:

Nitrogen	Argon	Helium		Total
(0.5 x (28.02)) +	(0.3 x (39.91)) +	(0.2 x (4))	=	26.8

This figure can then be used in the formula as before.

Note: When changing the carrier gas it will take some time to flush the cell. Ensure the analyser is allowed sufficient time to reach a stable reading before taking measurements.

Acceptable gases for the measurement stream

Electrochemical cells are very tolerant of many components in the gas stream requiring measurement. This makes these analysers especially suitable for measurements in hydrocarbons, furnaces and soldering ovens, where many contaminants can be present. However, some compounds interfere with the operation of the cell, and others shorten the cell lifetime by reacting with the components of the cell.

Solvents are a particular problem, often they attack the cell materials, causing the capillary to swell and prevent the oxygen reaching the cell. Gas streams containing solvents should be avoided.

Acidic gases can interfere with the operation of the electrolyte, again preventing the oxygen from being measured correctly. Gas streams containing acidic or corrosive compounds should also be avoided.

The lists below outlines some of the gases that are successfully measured using Systech Illinois fuel cell analysers and some of the known problem gases.

Acceptable Gases	Special Care Required	Gases to Avoid
Nitrogen	Carbon dioxide	Chlorine (Cl_2)
Argon	(low concentrations only)	Ammonia
Helium		Acetaldehyde*
Hydrogen*	Carbon Monoxide*	Ethylene Glycol*
Xenon	(Reduces cell lifetime)	Formaldehyde*
SF6		Vinyl Chloride*
Butadiene*		Methyl-dioxolane*
Ethylene*		Hydrogen sulphide (H_2S)
Acetylene*		
* Use H2 cell		* Acceptable if concentration below 5ppm

For applications involving gases other than those listed above, please contact Systech Illinois for advice.

Applications

The applications for the Systech Illinois electrochemical analysers are with industrial gas producers, industrial gas users and for safety monitoring.

Gas Producers	- for ensuring product quality by measuring for an oxygen impurity.
Gas Users	- to ensure reliability of inert gas blankets - to ensure quality of gases used as production materials. - for monitoring and controlling the oxygen content in Soldering ovens, furnaces and manufacturing processes
Safety Monitoring	- to ensure sufficient oxygen is present in a working atmosphere where the atmosphere can become oxygen deficient.