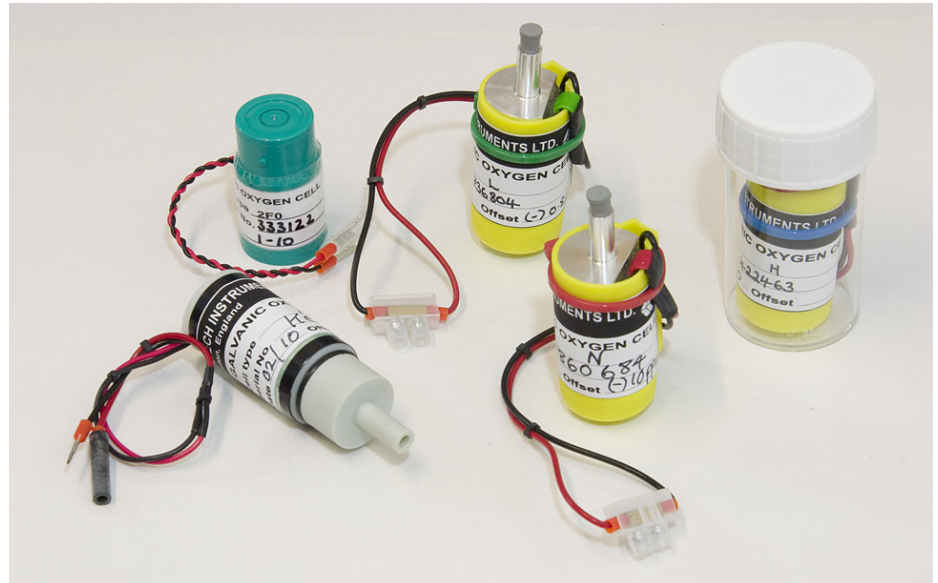


Oxygen sensors

theory & application

Hitech Instruments use one of two types of oxygen sensor in their oxygen analysers. Several models, between them, cover the very wide variety of applications for which the techniques can be used. This Technical Note describes the theory behind the operation of the two types of cells used, viz. the 'zirconia cell' and the 'galvanic cell' (or 'metal/oxygen' battery) and explains some of the advantages and limitations of each.



ZIRCONIA CELLS - HOW THEY WORK.

A Hitech zirconia oxygen sensor (see Figure 1) is an impervious tube-shaped zirconia (zirconium oxide) element with a closed end and is coated externally and internally with porous metal electrodes, typically platinum. At temperatures, above about 400°C, the zirconia becomes an oxygen ion conductor, which results in a voltage being generated between the electrodes. The value of the voltage is dependent upon the differences between the partial pressures of the oxygen in the sample and the oxygen in a reference gas (generally air) and is determined by the Nernst equation:-

$$\text{Cell output} = \frac{2.303RT}{4F} \log \frac{P1}{P2}$$

where:-

- R = molar gas constant
- T = absolute temperature of cell in Kelvin
- F = Faraday constant
- P1 = partial pressure of oxygen in the reference gas (air in most cases)
- P2 = partial pressure of oxygen in the sample

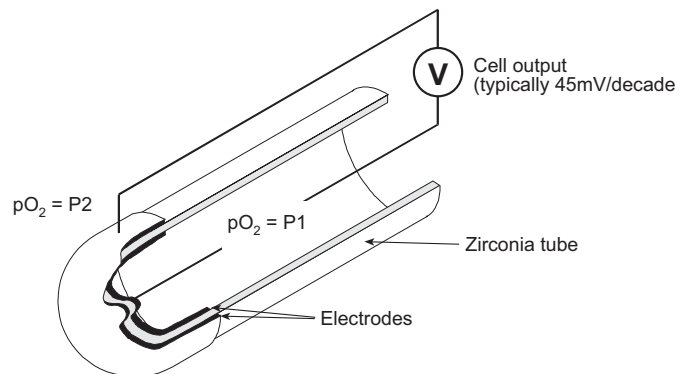


Figure 1 - Zirconia cell structure

Thus, with air on both sides of the cell, the output is zero (log1 = 0). The reference electrode is negative with respect to the sample electrode for sample concentrations of oxygen higher than that of air and positive for concentrations less than that of air. Depending on the application either the internal or external electrode can be used as the reference.

The output voltage is processed electronically to provide signals suitable for display or for process control purposes.

GALVANIC CELLS - HOW THEY WORK

The cell is a diffusion-limited metal/air battery, shown diagrammatically in Figure 2. The oxygen in the sample diffuses through the barrier and reaches the cathode. Here it is reduced to hydroxyl ions which, in turn, pass through the electrolyte to oxidise the metal anode.

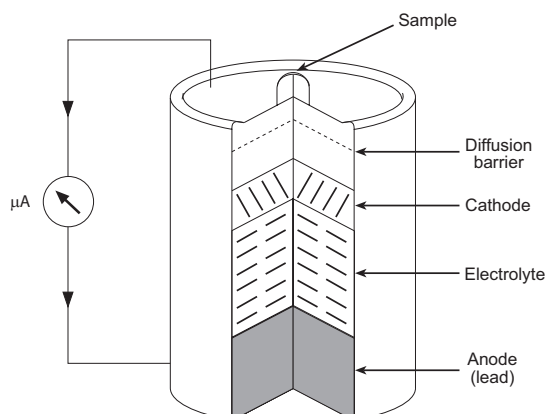


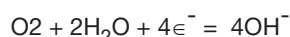
Figure 2 - Galvanic cell structure

A current, proportional to the rate of consumption of oxygen, is generated when the cathode/anode circuit is completed, the cell operating in what is virtually a short-circuit condition. Since the rate at which oxygen reaches the cathode is limited by the diffusion barrier, the cell current is a direct function of this rate, this in turn being a direct function of the concentration of oxygen in the sample. The general equations for the cell are as follows:-

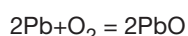
Anode reaction:



Cathode reaction:



Overall cell reaction:



$$\text{Output } (\mu\text{A}) = K \log (1/1-C)$$

where K is a constant and C is the partial pressure of oxygen in the sample. For 'ppm' and percentage measurements up to 25%, a linear approximation is usually adequate, although all of our microprocessor based analysers linearise exactly.

Our 'E' type cell operates in a slightly different way. This enables it to measure oxygen in samples containing high amounts of carbon dioxide. It is linear up to 100% and provides a millivolt, rather than a current, output.

Being batteries with consumable anodes, these cells have a finite life which varies according to type:- 'L' type (for ppm) 25,000 oxygen percent hours; 'N' (general purpose 200ppm to 25%) 100,000 oxygen percent hours; 'E' (up to 100% in neutral and mildly acid gas backgrounds) 1,000,000 oxygen percent hours.

When it comes to choosing a particular type of cell for any given application, the most significant factors to take account of are: a) High operational temperature of zirconia resulting in changes of sample composition. b) Speed of response – galvanic sensors are much slower than zirconia ones.

COMPARISONS - ZIRCONIA AND GALVANIC CELLS

When using zirconia cells, a sampled gas must be heated to the cell's operating temperature typically in the presence of platinum. These conditions usually mean that any components in the sample that can react with each other will react. Thus any hydrogen, carbon monoxide, and/or organic material will react with any oxygen present, thereby reducing the oxygen level measured by the cell. The cell will thus modify mixtures containing these components and the measurement of 'free' oxygen present in a cold sample is not possible. This effect can, however, be used with advantage to monitor the quality of atmospheres used in metal treatment furnaces since the extracted sample is analysed in very similar conditions to those prevailing in the process. By checking the sample before it enters the furnace, some pre-emptive corrective action is possible if the quality deteriorates. Zirconia cells can also analyse hot samples straight from the process, a big advantage if cooling the sample causes condensation as, for example, is the case for combustion gases from high sulphur content fuels. Hitech can supply instruments fitted with cell that have non-catalytic electrodes. These types of cell are particularly useful for monitoring parts per million levels of oxygen in the presence of trace levels of combustibles. These conditions are frequently found in nitrogen and argon gases produced by air liquefaction plants. The dynamic range of zirconia cells is very wide, being about 23 decades for most practical purposes, and the speed of response is very fast as they can respond to a step change from percentage levels down to sub ppm levels in a few seconds. The need to heat the sensor using precise temperature control circuits makes zirconia cell based analysers more expensive than the galvanic type, as well as requiring a warm-up time of around 10 minutes. (Note: this time is for Hitech zirconia sensor heaters; others will typically take significantly longer.)

Galvanic cells, since they operate at ambient temperatures, can measure 'free' oxygen in samples that also contain oxidisable materials. Most benign gases can be handled but corrosive and other strongly oxidising gases must be avoided. Three different range versions are needed to cover concentrations from 100% down to low ppm levels. Galvanic cells need no high power supporting circuitry (such as the zirconia cell heater). This enables battery powered portable instruments to be designed using this type of sensor. Although they are consumable, galvanic cells have very acceptable working lives (see earlier section) and are easy and inexpensive to replace. Speed of response is significantly slower than for zirconia cells, especially when moving down to ppm levels of oxygen from percentage levels. Nevertheless, the response speed compares favourably with the response speed for other 'cold' sensors. Analysers are available from Hitech which use a dual cell technique that improves the response rate significantly.

Note: The sensor used in Hitech instruments is reflected in their model number:

Galvanic sensors in G series e.g. G1010, G610, G210.

Zirconia sensors in Z series e.g. Z1030, Z230, Z130, Z1110.

OTHER RELATED HITECH TECHNICAL NOTES

TN02: "THE USE OF HITECH ZIRCONIA OXYGEN ANALYSERS FOR DEWPOINT MEASUREMENT"

TN03: "THE USE OF HITECH ZIRCONIA OXYGEN ANALYSERS IN HEAT TREATMENT"