Capillary Oxygen Sensors

A capillary oxygen cell consists of an enclosure which holds two electrodes: an active catalyst cathode coating on porous PTFE tape and a lead anode. This enclosure is airtight apart from a small capillary at the top of the cell which allows oxygen access to the working electrode. The entire cell is filled with conductive electrolyte which allows ionic transfer between the electrodes (see figure 1).

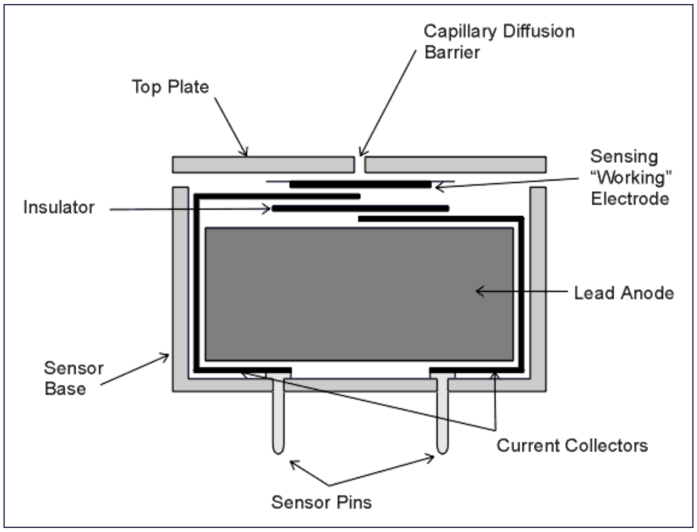

Figure 1 – Schematic of oxygen sensor.

The rate at which oxygen can enter the cell is controlled by the diameter and length of the capillary on the top of the sensor. When oxygen reaches the working electrode, it is immediately reduced to hydroxyl ions:

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

These hydroxyl ions migrate through the electrolyte to the lead anode where they are involved in the oxidation of the metal to its corresponding oxide.

$$2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^-$$

As the two processes above take place, a current is generated which can be measured externally by passing it through a known resistance and measuring the potential drop across it. Since the current produced is proportional to the rate at which these reactions occur, its measurement allows accurate determination of the oxygen concentration.

As the electrochemical reaction results in the oxidation of the lead anode these sensors have a limited life of 1 – 2 years, however this can be lengthened by increasing the size of the anode or restricting the amount of oxygen that gets to the anode.

The current generated by a capillary controlled oxygen sensor is proportional to the volume fraction (i.e. volume %) of oxygen present and this is independent of the total pressure of gas.

Capillary and Partial Pressure Oxygen Sensors

Capillary control of gas diffusion is not the only method of limiting the rate of oxygen entry into the sensor. It is also possible to use a very thin, plastic membrane over the top of the working electrode – the membrane operates as a solid barrier in which the oxygen molecules must dissolve in order to reach the sensing electrode.

The flux of oxygen to the working electrode is dependent on the partial pressure gradient of oxygen across the barrier. This means that the output signal from the cell is proportional to the partial pressure of oxygen in the gas mixture. Any changes in atmospheric pressure will therefore result in an equivalent change in the output current of the cell. It is important that this characteristic is considered when designing instruments to ensure that back pressure is not applied to the cell when using a pump.

The signal from a capillary controlled oxygen sensor is non-linear and follows the following relationship with the fractional oxygen concentration (C);

$$\text{Signal} = \text{constant} * \ln [1/(1-C)]$$

In practice, the outputs from the cells are effectively linear up to 30% oxygen and only oxygen concentrations higher than these cause measurement difficulties. In contrast, partial pressure sensors offer a linear output up to 100% oxygen (or 1.0 fractional oxygen concentration).

Both capillary and solid membrane oxygen sensors are sensitive to changes to temperature; but to differing extent.

The effect of temperature on the performance of a capillary barrier oxygen sensor is relatively small, and typically changing the temperature from +20°C to –20°C will result in 10% loss of the output signal. In contrast, temperature has a much greater effect on solid membrane oxygen sensors. The diffusion of gas across the membrane is an activated process and as a result has a large temperature coefficient. Typically a 10°C change in temperature doubles the output signal from the sensor. Solid membrane oxygen sensors require temperature compensation as a result, and many have thermistors designed in.