How Oxygen Sensors Work

Galvanic oxygen sensors are the most popular technology for measuring oxygen concentration in air. These oxygen sensors can be divided into two types:

- Mass flow control using capillary
- Partial pressure control using solid polymer membrane

Oxygen Sensor Chemistry

Alphasense oxygen sensors operate like a metal/air battery. Oxygen in contact with the cathode is reduced to hydroxyl ions, with a balancing reaction of lead oxidation at the anode. The reaction equations are:

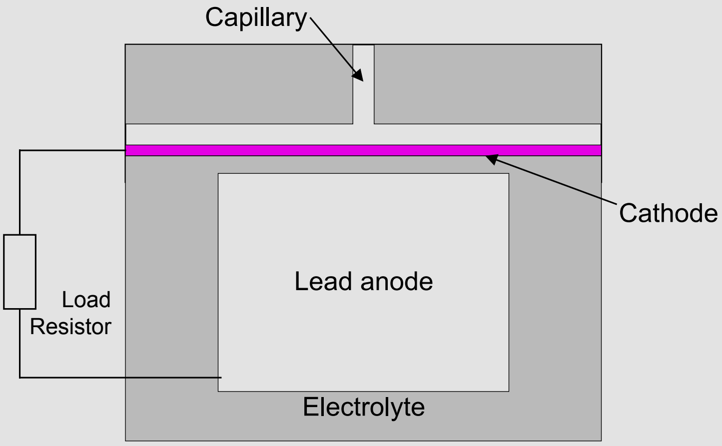
Cathode $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Anode $2Pb + 4OH^- \rightarrow 2PbO + 2H2O + 4e^-$

Overall $O_2 + 2Pb \rightarrow 2PbO$

Alphasense oxygen sensors generate a current, which is proportional to the rate of oxygen consumption, following Faraday's Law. This current is easily measured by placing a load resistor between the cathode and the anode (the 2 pins on an oxygen sensor) and measuring the resultant voltage drop. This load resistor value is typically between 10 and 100 Ω – a low resistance results in a small voltage drop which is difficult to measure and a high resistance imposes a voltage across the anode and cathode which can cause unfavourable side reactions.

Figure 1. Mass flow controlled oxygen sensor.



Most galvanic oxygen sensors use a platinum electrode to reduce the oxygen and an oxidisable lead anode to complete the electrochemical reaction. Sensor lifetime depends on the availability of lead: the oxygen sensor dies when all the lead has oxidised. The output remains nearly constant until most of the lead is oxidised so oxygen sensor end of life due to consumption of the anode cannot be predicted until about three weeks before the anode is exhausted.

The most common electrolyte in oxygen sensors is potassium hydroxide (KOH): lead oxidation is best controlled in an electrolyte with a pH between 10 and 12. Sensors for use in high carbon dioxide atmospheres (e.g. combustion gases) sometimes use an acidic electrolyte to avoid carbonate deposition within the sensor.

As lead oxidises, lead oxide occupies more volume than pure lead, so the combined anode and electrolyte volume inside the oxygen sensor expands. If the sensor is not properly designed then the internal pressure builds up in the sensor splitting the sensor case, causing leakage.

Mass Flow Control Oxygen Sensors

Figure 1 shows a mass flow control oxygen sensor using a capillary; these are less than 100µm diameter, controlling the flow of air to the cathode. Since all oxygen that diffuses through the capillary to the platinum cathode is reduced, control of the output current is driven by the physics of gas diffusion through the capillary. The consequences of mass flow control are:

1. The amount of oxygen available for reduction at the cathode depends on the oxygen concentration in the air, not the oxygen partial pressure. Sensor output is nearly independent of ambient pressure.
2. As oxygen is consumed at the cathode, the pressure at the cathodic side of the capillary decreases; this pressure drop increases the rate of oxygen diffusion through the capillary. This is the reason that the output current from mass flow controlled oxygen sensors is non-linear with respect to oxygen concentration. Over a narrow range (typically 19% to 23% oxygen for safety applications) the non-linearity is insignificant; however, at high oxygen concentrations the non-linearity is severe, but very repeatable. See Application Note AAN 003.
3. The rate of gas diffusion through the capillary is only weakly temperature dependent. The dependence is due to the change of gas viscosity with temperature, which varies as the square root of the Kelvin temperature: a weak dependence of 0.2%/K at 20°C.
4. Since gas diffusion through a capillary is faster than gas diffusion through a solid membrane, the response time of mass flow oxygen sensors is faster than partial pressure sensors.
5. When subjected to a positive pressure step mass flow oxygen sensors show a positive pressure transient which lasts typically 10-20 seconds before recovering to the initial output (remember that these sensors are only weakly pressure dependent). Negative pressure steps show a much smaller output transient. See Application Note AAN 004.

In summary, mass flow control oxygen sensors show a weak temperature dependence, almost no pressure dependence and respond rapidly, but have a strong output spike when subjected to a positive pressure step, although they recover quickly to their original output.

Partial Pressure Oxygen Sensors

The other electrochemical method of measuring oxygen in gas uses a solid Teflon-like membrane: the same technology as dissolved oxygen electrodes for measuring oxygen in water.

The rate of gas diffusion through the membrane is linearly proportional to the partial pressure of the oxygen on the two sides of the membrane, following Fick's Law. Since oxygen is reduced at the cathode, the partial pressure on the cathodic side of the membrane is virtually zero, giving a driving force which is linearly dependent on oxygen partial pressure, so the rate of gas diffusion (and hence sensor output) is linearly dependent on the oxygen partial pressure. These types of oxygen sensors show the following characteristics:

1. Sensor output varies linearly with oxygen concentration from 0 to 100%.
2. Any change in atmospheric pressure affects linearly the oxygen partial pressure, so partial pressure sensors are linearly dependent on ambient pressure.
3. Since the gas must diffuse through a solid polymer membrane, the rate of diffusion is dependent not only on the gas partial pressure but also on the diffusivity of the membrane. Unfortunately the diffusivity of polymer membranes have a high temperature dependence, typically 2 to 3%/K; this is usually corrected by using a thermistor sensor inside the body of the oxygen sensor to compensate for temperature changes. However, during thermal transients the membrane diffusivity and compensating temperature sensor will not be in phase and significant thermal transient errors can result.
4. Since diffusion through a polymer membrane is slower than through a capillary the response time (as t90) of partial pressure sensors is typically 20 to 40 seconds while it is between 5 and 10 seconds for mass flow sensors.
5. Since partial pressure sensors are linearly dependent on pressure, a pressure step will result in an output step. However, since the response time of partial pressure sensors is slower, the transient pulse is smaller than for mass flow sensors.

In summary, partial pressure sensors show a linear pressure dependence, require temperature compensation, show a slower response time but have a smaller transient behaviour when exposed to pressure changes.

Carrier Gas Dependence

Alphasense oxygen sensors are normally calibrated in ambient air. Certain applications may involve oxygen measurements in an atmosphere where the balance ("carrier") gas is not nitrogen. Examples are argon or helium in nuclear reactors or deep-sea applications. This different carrier gas affects the rate of diffusion of oxygen through the capillary: Carrier gases that are smaller and lighter molecules increase the oxygen flux through the capillary and give a higher reading. Conversely, larger molecules slow down oxygen diffusion through the capillary, resulting in a lower sensor output. Graham's Law is a simplification of the kinetic theory used to predict the effect of carrier gases on oxygen diffusion. In its simple form, Graham's Law states that the rate of gas diffusion increases by the square root of the ratio of the average gas molecular weight.

output (in new carrier gas) = output (in air) x √ (28.0/ M)

Where M = mean molecule weight of carrier gas

28.0 = molecular weight of nitrogen

Certain molecules such as helium do not exactly follow Graham's Law because the ratio of the mean free path to molecular weight is not the same as for diatomic molecules. However, an approximation of the effect of a different carrier gas can be easily calculated.

Example

If the carrier gas were 30% helium and 70% nitrogen then the mean molecular weight of the carrier gas would be:

(28.0 x0.7) + (4.0x0.3) = 20.8

Therefore the output signal would be:

signal (30%/70%) = output (in air) x √ (28/20.8) = output (in air) x 1.16

For further advice, contact Alphasense.