AAN 104 How Electrochemical Gas Sensors Work

Alphasense toxic gas sensors are electrochemical cells that operate in the amperometric mode. That is, they generate a current that is linearly proportional to the fractional volume of the toxic gas, such as CO or H_2S. Figure 1 shows schematically the structure of a toxic gas sensor.

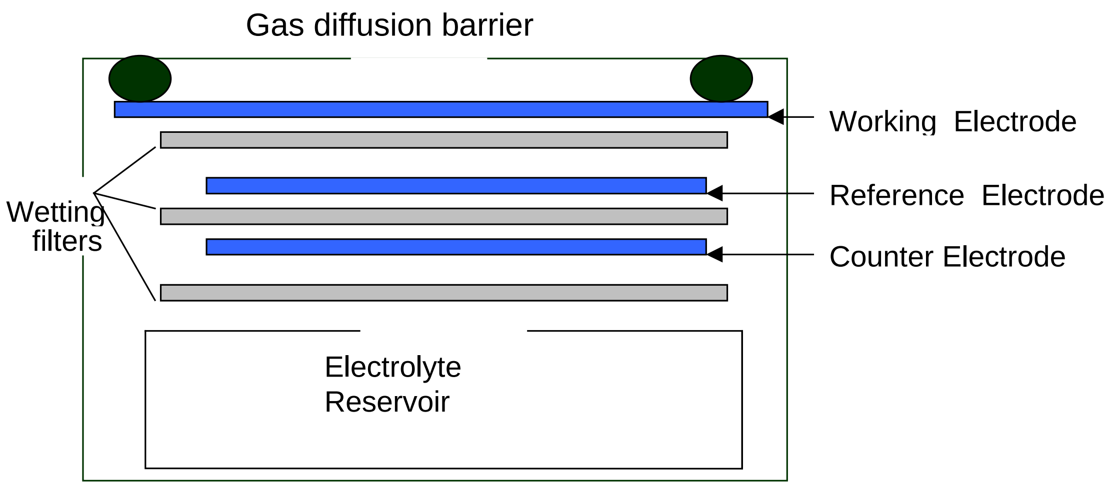

Figure 1. Schematic diagram of electrochemical toxic gas sensor. Three metal strips connect each electrode to the three pins outside of the sensor body.

Three electrodes in a toxic gas sensor
The **working electrode** (also called the sensing electrode) is designed to optimise the oxidation or reduction of the toxic gas to be measured. This electrode allows the gas to come in contact with both electro catalyst and electrolyte to create a three-phase interface of gas, liquid and solid.
The other two electrodes in the cell, the counter electrode and the reference electrode usually have a similar chemical composition to the working electrode. In Alphasense sensors all three electrodes are stacked parallel to each other, as illustrated in Fig. 1.

The cell electrolyte provides ionic electrical contact between the electrodes, usually with the aid of hydrophilic separators (labelled “wetting filters” in figure 1) to allow capillary transport of the electrolyte which is usually sulfuric acid between 3 and 7 Molarity.
See Application Note AAN 106 for further information. A potentiostatic circuit maintains the potential of the working electrode at a fixed value with respect to the reference electrode potential. See Application Note AAN 105 for more information on electronic circuit design.

The working electrode is the surface where the electrochemical oxidation (CO, H_2S, NO, SO_2) or reduction (NO_2, Cl_2) occurs. A high surface area catalyst is used to optimise the sensor performance, resulting in a high sensor capacitance: typically 50 to 200mF, leading to susceptibility to electromagnetic interference; see Application Note AAN 103.

Sensor Technology House, 300 Avenue West, Skyline 120, Great Notley. Essex.CM77 7AA. UK
Tel: +44 (0) 1376 556700 - Fax: +44 (0) 1376 335899
Email: sensors@alphasense.com - Web: www.alphasense.com

This electrode is exposed to the outside air and hence is directly exposed to all gases in the air including the gas to be measured. Therefore this electrode may be poisoned if exposed to certain gases that either adsorb onto the catalyst (e.g. acetylene onto CO sensors), or react, creating by-products which inhibit the catalyst (e.g. NO_2 or aromatics onto H_2S sensors). This is the same problem as poisoning in fuel cells and car catalytic converters.

The **counter electrode** balances the reaction of the working electrode – if the working electrode oxidises the gas, then the counter electrode must reduce some other molecule to generate an equivalent current, in the opposite sense. For example, where carbon monoxide will be oxidised on the working electrode, oxygen will be reduced on the counter electrode. The two reactions are:

Working electrode	$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$
Counter electrode	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$
The overall cell reaction is:	$CO + 1/2O_2 \rightarrow CO_2$

The higher the CO concentration the harder the counter electrode must work to keep up and hence the more oxygen it will consume at the counter electrode. Unlike the working electrode, the counter electrode potential is allowed to vary. The counter electrode potential in clean air is close to the working electrode, but as current is demanded from the counter electrode, the potential increases, so the main responsibility of the potentiostat circuit is to ensure that adequate current is fed to the counter electrode and that the counter electrode can operate at its preferred potential.

Although for most sensors reduction of oxygen at the counter electrode is the most common reaction the counter electrode will do whatever it must do to keep up with the working electrode. At low gas concentrations the working electrode produces a small current and hence the counter electrode quite easily reduces small amounts of oxygen to maintain the electrochemical balance, but If the sensor is starved of oxygen (for example when measuring H_2S in biogas where the oxygen concentration is a few hundred ppm) then the counter electrode will begin to reduce protons, generating hydrogen gas when it runs out of oxygen

Alphasense toxic gas sensors are three electrode systems: they include a third electrode, the **reference electrode**. This reference electrode anchors the working electrode potential to ensure that it is always working in the correct region of the current-voltage curve – see figure 2 below. It is important that the reference electrode has a stable potential, keeping the working electrode at the right electrochemical potential to maintain a constant sensitivity, good linearity and minimum sensitivity to interfering gases. The potentiostat circuit described in Application Note AAN 105 ensures that the counter electrode is provided with as much current as it needs, also maintaining the working electrode at a fixed potential, irrespective of how hard it is working.

Sensor Technology House, 300 Avenue West, Skyline 120, Great Notley. Essex.CM77 7AA. UK
Tel: +44 (0) 1376 556700 - Fax: +44 (0) 1376 335899
Email: sensors@alphasense.com - Web: www.alphasense.com

Current- voltage curves

The working electrode current changes when the applied potential is varied, producing a current-voltage curve; a schematic diagram of a typical current voltage curve is shown in Figure 2.

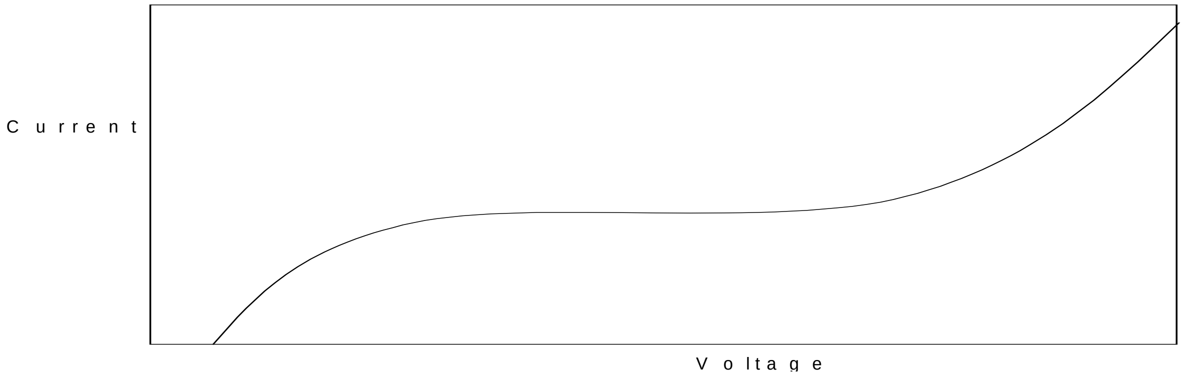

Figure 2. Schematic diagram of a typical current-voltage curve.

Importantly, note that there is a plateau region up to several hundred millivolts where the generated current is almost independent of the applied potential. This region of the current-voltage curve is known as the diffusion or transport limited current plateau. This plateau occurs because the current is controlled completely by the diffusional flux or mass transport of the electroactive gas (for example CO or H_2S) to the working electrode; this flux is independent of the potential applied to the electrode. On either side of this plateau region the current is controlled by the electrochemical kinetics at the electrode/electrolyte interface and the current in these regions is exponentially dependent on the electrode potential. The toxic gas sensor should be operated with the working electrode potential in the diffusion limited plateau region so that the output current is not critically sensitive to the applied potential, or to small fluctuations in the reference electrode potential (for example, reference electrode potentials vary with temperature).

For many toxic gas sensors it has been found that a zero voltage applied to the working electrode with respect to reference electrode corresponds conveniently to the plateau region. However, certain sensors (e.g. nitric oxide: NO) require a bias voltage to ensure NO reduction rather than NO_2 oxidation. Application Note 105 explains methods of biasing the working electrode, relative to the reference electrode.

When operating in the transport limited current plateau the measured current (I_L) should be linearly dependent on the concentration or fractional volume of the toxic gas (C_T) in the external environment:

$$I_L = k\ C_T$$

where k is a proportionality constant.

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This equation holds true over the entire range of the sensor; for example, Alphasense CO-AF sensors are linear from 1 ppm to over 10 000 ppm CO.

Although electrochemical toxic gas sensors are designed to operate in the plateau region to reduce sensitivity to small reference electrode-potential changes, one cannot conclude that small changes in the reference electrode potential can be ignored. Remembering that the working electrode has a high capacitance of typically 50-200 mF, then any change in the reference electrode or electronics potential will be forced upon the working electrode by the potentiostat circuit. The “double charge layer” of the working electrode will either dump or adsorb current as it adjusts to its new operating potential. This will be observed as an output current transient whenever the set potential changes.

Controlling range and sensitivity

The working electrode is usually designed to maximise the current generated in response to the presence of an electrochemically active gas. In order to tailor the gas concentration range and the sensitivity (expressed as nA/ ppm), a gas diffusion barrier above the working electrode controls the flux of the toxic gas to the working electrode. Quite simply, the larger the diffusion hole the greater the sensitivity and the smaller the concentration range. Therefore, for example, Alphasense H_2S sensors using the same electrode have different ranges and sensitivities by varying the gas diffusion barrier hole size. These holes vary in size from 0.3 to 10 mm diameter and also affect the rate that electrolyte absorbs water or dries out: see Application Note AAN 106. A simple rule to follow: sensors with lower sensitivity and larger concentration range dry out slower in low humidities and absorb water slower in high humidities.

Summary

Alphasense toxic gas sensors are three electrode amperometric electrochemical cells.

The working electrode either oxidises or reduces the target gas with the counter electrode balancing the generated current.

The reference electrode anchors the working electrode at the correct potential to ensure that it stays in the transport limited current plateau of the current-voltage curve.

Good design of a potentiostatic circuit will minimise current transients by keeping the working electrode at a stable potential.

The current path to the counter electrode and generated by the working electrode is provided by metal strips; the ionic current between the counter and working electrodes is transported by the electrolyte.

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