Modelling Amperometric Electrochemical Gas Sensors

When designing circuits, electronic engineers frequently ask for an equivalent model of a sensor. This equivalent model allows simulation of the potentiostatic circuit, which is required to both measure and control an amperometric electrochemical gas sensor.

Application Note AAN 105 explains how to design a potentiostatic circuit, and Application Note AAN 104 explains how an amperometric electrochemical gas sensor operates.

This Application Note demonstrates how a gas sensor may be modelled with an equivalent circuit. Of course, electrochemical sensors are more complex, so the limitations of this model are also explained.

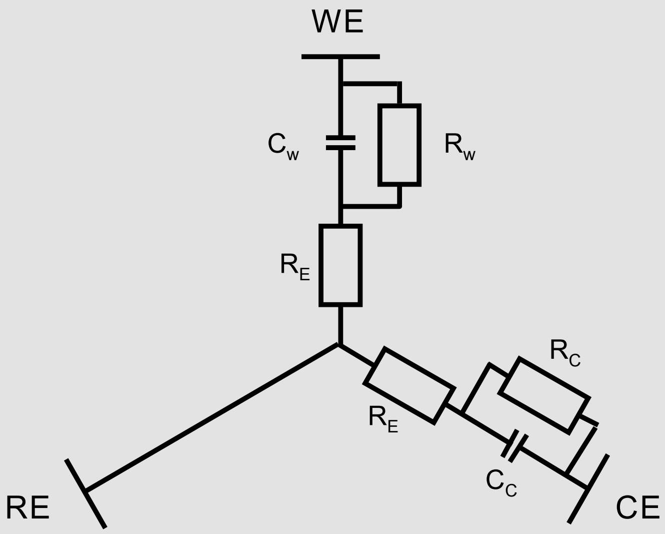
The Model

Alphasense amperometric electrochemical gas sensors use three electrodes:

- **Working electrode** reacts with the target gas to generate a current
- **Counter electrode** supplies a current that balances that generated by the working electrode current
- **Reference electrode** sets the operating potential of the working electrode

All three electrodes are connected internally through the electrolyte, so a common central node is an essential part of the model. The electrolyte can be modelled simply as a resistor, R_E. The reference electrode has no equivalent circuit since the potentiostatic circuit is designed with a high input impedance to this electrode and therefore, ideally, carries no current.

The working and counter electrodes can be modelled simply as a combination of resistors and capacitors as illustrated below. R_w and R_c is the charge transfer resistance of the working and counter electrodes. C_w and C_c is the capacitance of the working and counter electrodes. The electrolyte resistance is indicated by R_E.



The following table shows approximate values of the elements described earlier for A and D series CO and H_2S sensors.

Physical Element	Equivalent. circuit element	CO-AF	CO-DF	H2S-A1	H2S-D1
Electrolyte	RE / Ω	2	2	2	2
Working electrode	RW / Ω	300	2000	130	1000
	CW / mF	130	80	260	90
Counter electrode	RC / Ω	300	2000	130	1000
	CC / mF	260	160	520	180

Electrochemical Considerations

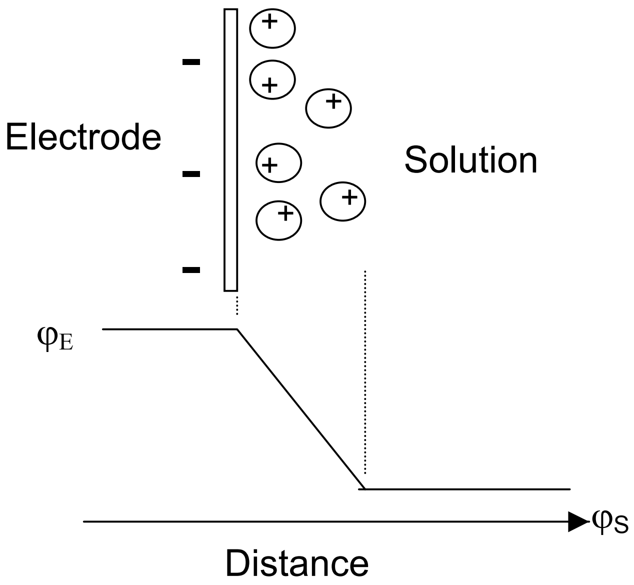
The elements described in the first section of this application note can be derived from a basic knowledge of electrochemical interfaces.

R

The resistor elements describe the ohmic resistance associated with the electrodes. For best sensor operation, these values are minimised.This may be achieved with the use of a high ionic strength electrolyte and optimisation of the electrode geometry.

C

Consider an electrode immersed in an electrolyte in which the electrode is biased negative to the potential of zero charge (pzc), such that the electrode has an excess of electrons at the surface. An excess of positively charged ions resides on the solution side of the interface in order to maintain electroneutrality. This situation is described schematically below :-



where φ_E and φ_S are the potentials of the electrode and solution respectively. Most of the potential drop occurs in the region close to the electrode where a net accumulation of positively charged species has occurred. This situation can be described electrically as a capacitor.

Limitations of the model

The model presented here is a simplified version of a more complicated, lumped element equivalent circuit. It is beyond the scope of this note to include all of the details of the system such as a constant phase element to account for the non-ideal capacitance behaviour of real electrodes. Therefore, for the purposes of simulating toxic sensors a few points should be considered:

- Capacitance is frequency dependent and, in particular, low frequency measurements are dominated by the capacitance associated with the porous nature of the electrode. At high frequencies, capacitance becomes dominated by solution resistance, but potentiostatic circuits are low frequency circuits. See Application Note AAN 103.
- Capacitance is a complex function of the bias potential. Meaningful results will only be obtained at a constant stable bias. Any instantaneous shift in bias potential will result in charging/discharging of the electrode, resulting in an unstable reading for several minutes.
- If sensors are used in low humidities, loss of electrolyte will increase the internal resistance from about 1 ohm to 10 ohms. This will change the RC time constant of the sensor, which may affect noise immunity and possibly circuit stability.