Reducing Risks and the Cost of Gas Detection

Every day, throughout the world, workers in potentially hazardous locations trust their lives to gas detection instruments. Whether entering a confined space where oxygen depletion presents a real danger to life or working in an industrial plant where toxic levels of gas may have leaked from a nearby process, portable or stationary gas detectors are often the only means of protection from these invisible dangers. They are designed to react quickly to a rise in toxic, flammable or asphyxiant gas and produce an audible and visible alarm to alert workers and plant operators so that the hazard can be addressed and personal safety can be maintained.

Given an appropriate warning by the instrument, the user then has sufficient time to replace the sensor in a planned fashion or indeed move the unit to a less demanding environment. Every gas detector contains one or more internal gas sensors, optimised for each target gas. In fixed systems, typically one sensor is fitted; in portable instruments up to six gas sensors may be present. Gas sensors are designed to convert the ambient concentration of target gas into a measureable electrical signal which the detector can interpret and generate an alarm if pre-set levels are exceeded. For the detection of combustible gases, the predominant technologies used are catalytic bead (pellistors) sensors or non-dispersive infra-red (NDIR), the latter is also commonly utilised for the sensing of carbon dioxide. Where a toxic or oxygen depletion hazard is likely to occur, the prevailing gas sensors are electrochemical.

Electrochemical Sensors

For more than thirty years, electrochemical sensors have been deployed to detect low levels of toxic gases or percentage levels of oxygen. They offer small size, excellent sensitivity, fast response times, high selectivity, a linear output, low power and are available at a reasonable cost. A generic overview of an electrochemical sensor construction is depicted in Figure 1.



are surrounded by a conductive electrolyte, typically a strong mineral acid to provide mobility for the generated ionic species. The chemical reactions that take place at the sensing and counter electrodes (see Figure 2) result in a small electrical current; this current is proportional to the atmospheric concentration of the target gas.

Reaction at the Sensing electrode CO + H₂O \longrightarrow CO₂ + H⁺ + 2e⁻

Reaction at the Counter electrode $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Figure 2: Electrochemical sensor reactions for a carbon monoxide sensor

With a suitable potentiometric circuit, the current can be amplified into a useable voltage which the host instrument can analyse and monitor to determine whether a hazardous level of gas has been reached.

Since they work on a catalytic basis with no consumable components, in theory electrochemical sensors will work indefinitely - in many cases working lifetimes of greater than five years are achieved in benign environments and light usage profiles. In a limited number of cases however the working life of an electrochemical sensor can be adversely affected, leading to loss of sensor performance or indeed premature failure. See Figure 3 for a list of the most common sensor failure modes.

Determining sensor failure

Many sensing technologies are inherently fail-safe, that is if a sensor

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Figure 1: Typical construction of an electrochemical sensor

At the heart of every sensor are the electrodes, highly active catalysts optimised for each target gas. Most electrochemical sensors contain three electrodes; a sensing or working electrode which reacts with the gas species as it enters the sensor, a counter electrode which provides a compensating electrochemical reaction and an inert reference electrode which is included to provide a stable potential against which the potential of the other electrodes can be measured. The electrodes stops working correctly, it generates a fault condition which can be detected by the instrument into which it is fitted and the user can then act accordingly. For some electrochemical sensors this is also true – for example a lead-based oxygen sensor produces a drop in output as it nears end of life which can be identified electronically and an impending sensor failure message created by the instrument. However, the majority of electrochemical sensors have a number of failure modes which are fail dangerous, which means that in some, admittedly rare, instances the sensor might not detect a hazardous condition if it arose, the instrument would be unaware and the user could be placed in a potentially dangerous situation.

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Since sensors are relied upon to protect workers and plants, users of gas detection instruments are highly motivated to ensure that their equipment does what it is designed to do; detect dangerous gases. As a minimum, all gas detection apparatus is calibrated with target gas before first use and periodically during its lifetime - calibration intervals of one or three months are most common. In addition, some industries, particularly those where a large number of portable units are in operation, have adopted a 'bump check' whereby instruments are exposed to target gas daily and before every use to ensure correct performance. If an instrument fails a bump check, it is quarantined before new sensors are fitted and recalibrated. This may result in a shortage of instruments available for a particular shift and reduce the number of personnel able to work, or may require a surplus of 'back-up' instruments to be available. Both scenarios increase the cost of ownership of gas detectors.

Predicting Sensor Failure

As identified in Figure 3, dehydration is a relatively frequent mechanism that can lead to sensor failure. Since all electrochemical sensors rely on ionic conductivity between the electrodes internally, they contain an acidic or alkali electrolyte. This is in equilibrium with the ambient environment and as a result, if the sensor is placed in hot, dry atmospheres, water is lost from the electrolyte and conversely in hot, wet environments, the electrolyte can absorb water. The absorption of water is rarely a problem as sensors are designed with sufficient internal free space to accommodate it. In extreme dry conditions however, the efficacy of the electrolyte can be impaired such that it is no longer able to support ionic transfer within the sensor, which leads to a loss in sensitivity. Normally this condition can only be detected by application of target gas.

Solidsense has developed an interrogation method, the Capa Test, which allows the condition of the electrolyte to be assessed without the need for application of gas. By performing an electronic charge-discharge cycle to their solid electrolyte sensors and analysing the capacitive response of the sensor, a numeric value can be generated which gives a quantitative ("Capa") value to the quality, ionic mobility and hydration level of the electrolyte. The Capa value of each electrochemical sensor can be generated as frequently as required and the host instrument can assess whether the sensor is likely to fail in the near future; if an impending failure is identified the sensor can be replaced before it actually fails. The Capa test requires simple electronic componentry and can be performed using existing instrument architecture.

Figure 4 shows the gas sensitivity and Capa value of a carbon monoxide sensor which has been subjected to a high temperature, low relative humidity environment and monitored for a prolonged period. The sensitivity to target gas remains stable throughout the first six weeks but as the sensor nears total dehydration, the output begins to drop dramatically and reaches a point at which the sensor would not have sufficient output to generate an alarm signal in the presence of dangerous levels of carbon monoxide. However, during this time, the Capa value also drops steadily and at the end of week six, plummets to a very low value. At this point, the sensor is still active to gas but by analysing the Capa value, the

Frequency Misuse/Damage **False Alarms Poisoning/Inhibition** Environmental Interaction Physical mistreatment Exposure to dry, hot Cross sensitivity to Contaminant gas of sensor/instrument, environments can lead non-target gases or species can react with dirt, grease or paint to sensor losing water alarms due to shock, or bind to the blocking gas access. from the internal vibration or rapid electrode catalysts and electrolyte and a reduce gas sensitivity. pressure and resultant loss in temperature changes. sensitivity.

Figure 3: Common failure mechanisms for electrochemical sensors

instrument has a mechanism to anticipate imminent failure. Given an appropriate warning by the instrument, the user then has sufficient time to replace the sensor in a planned fashion or indeed move the unit to a less demanding environment. Since the loss of water is reversible, if the sensor is placed in a benign relative humidity atmosphere, it will reabsorb water and recover sensitivity. This can be seen in the traces from week eight on the graph; at this point the carbon monoxide sensor was rehydrated in a 50% RH atmosphere and sensitivity was restored.

Given the ability to predict sensor failure, users of gas detection instrumentation can better plan maintenance of their equipment. Sensors can be replaced in a systematic and not ad-hoc fashion which reduces inventory levels of replacement components and can reduce instrument down time. Furthermore, sensor replacement on fixed systems can be planned into existing maintenance/calibration schedules. This can significantly reduce cycle times and lower the cost of ownership of gas detection apparatus.

Since there remain some failure modes which are undetectable using the Capa test methodology, it does not replace any bump testing or calibration with target gas which should be carried out as per the manufacturers recommendations or in accordance with local legislation. The Capa test has been developed to work uniquely with the Solidsense range of solid electrolyte sensors, and while some functionality can be achieved with traditional liquid based sensors, the prediction of failure cannot.



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