OP19
4OxLL / 5OxLL CiTiceL® Operating Priciples

Contents

Document Purpose	1
Introduction	2
Operating Principles	2
Recommended Circuitry	3
Reaction Mechanisms	4
Sensor and Instrument Venting	4
Calibration Guidelines	5
Effects of Temperature, Pressure and Humidity	6
Temperature Dependence	
Pressure Effects	
Humidity Effects	
Carrier Gas Effects	7
Linearity	8
Sensor Mounting	8
Handling and Storage	9

Document Purpose

The purpose of this document is to describe the functionality of the 4OXLL and 5OXLL longlife oxygen sensors, and to provide information and advice regarding the appropriate use of these sensors.

This document and the information contained within does not constitute a specification. This document should be used in conjunction with the Product Datasheet, the Product Characterisation Note and the Product Safety Datasheet (PSDS 5).

Operating Principles

Introduction

The 4/5OxLL is a lead free oxygen sensor designed to measure oxygen in the range 0-30%. It has been specifically developed for use in industrial safety applications where its compact size makes them an ideal choice for portable instrumentation where size is important.

The 4/5OxLL oxygen sensor builds on the company's extensive experience in the design and manufacture of toxic gas sensors. Based on field-proven toxic sensor design principles, the new 4OxLL is available in the industry-standard 4 Series housing and the 5OxLL in the standard 5 Series housing..

Operating Principles

This oxygen pump is designed to be maintenance-free and stable for long periods. It uses technology from both the original oxygen and toxic gas CiTiceLs, which results in a direct response to volume concentration rather than partial pressure. A feature of the design is the capillary diffusion barrier, which limits the access of gas to the *sensing* electrode. The electrode is therefore able to react all target gas as it reaches its surface and still have electrochemical activity in reserve. This high activity reserve ensures each CiTiceL has a long life and excellent temperature stability.

However, where the original Oxygen CiTiceLs used lead, the 4/5OxLL uses a lead free electrode system similar to the subsequently developed toxic gas CiTiceLs (CO, H_2S etc.).

The 4/5OxLL is designed to work in a potentiostatic circuit with the *reference* electrode at a more positive potential than the *sensing* electrode. This is known as 'biased' operation, with the *sensing* electrode held at 600 mV below the reference electrode.

The recommended biased operation circuit is essentially the same as for a standard 3 electrode sensor. It is modified however, such that the non-inverting input of IC1 is at the required potential below the circuit common, and this provides the bias voltage. As oxygen is reduced at the *sensing* electrode, the output from IC2 will always be **negative** with respect to common.

The bias voltage must be applied via IC1 so as not to draw any current from the *reference* electrode. It must not be applied by connecting a battery directly to the *reference* and *sensing* electrodes. It is strongly recommended that a bias potential is maintained at all times, even when an instrument is switched off. Applying bias to a new CiTiceL, or to a CiTiceL which has been off bias, will produce a transient and rapidly decreasing offset - **a period of stabilisation time will be required before meaningful measurements can be taken.** Refer to the Characterisation Note for further details of stabilisation times.

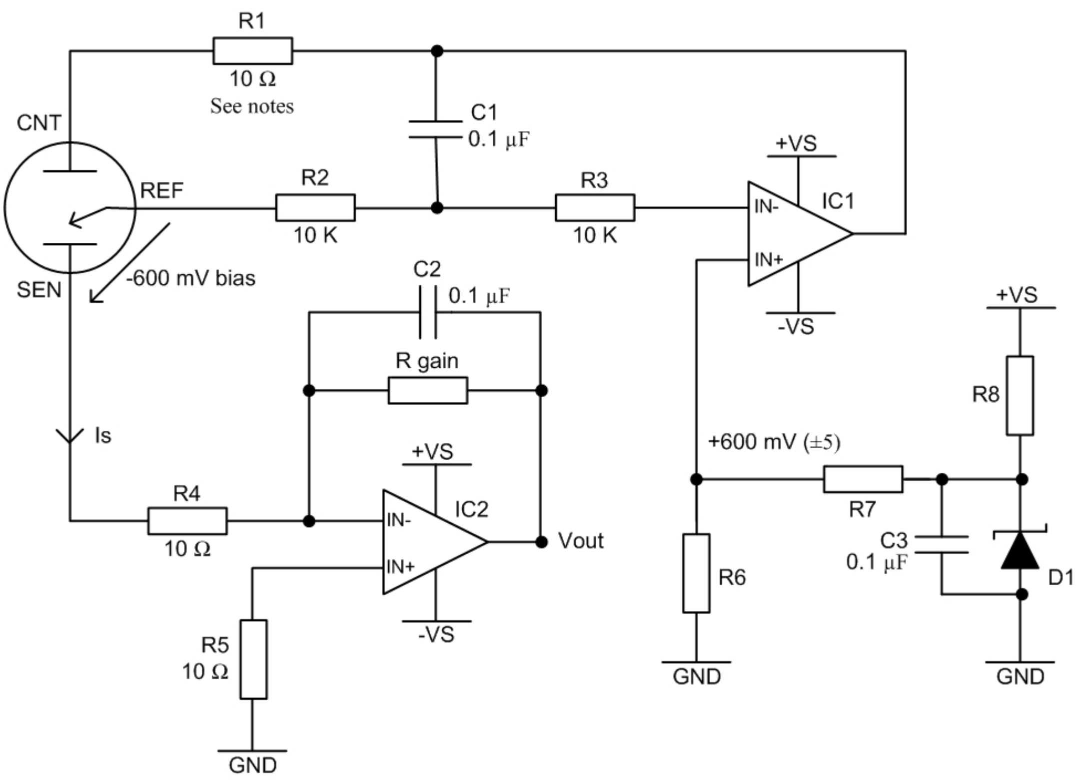
The recommended bias voltage of -600 mV has been shown to offer the greatest balance of features for operational use. The negative bias voltage indicates the *reference* electrode will be more positive than the *sensing* electrode.

Caution: Due to the fact that the *reference* and *sensing* electrodes of the 4/5OxLL and other CiTiceLs requiring biased operation are meant to have different potentials, they are despatched from City Technology without a shorting link. As shorting can result in prolonged recovery times, the 4/5OxLL must be stored with the electrodes un-shorted. For this reason, the shorting FET used in the unbiased circuit is omitted from the recommended biased circuit.

Caution: For correct operation, CiTiceLs require a small supply of oxygen to the *reference* electrode. Continuous exposure to an anaerobic sample gas may cause the sensor to malfunction in spite of the oxygen access paths. The sensor must not therefore be completely potted with resin or totally immersed in an anaerobic gas mixture - potting may also seal the vent.

Operating Principles

Recommended Circuitry



Notes

1. IC1/IC2: LT1078, OPA2251. (Rail to rail, low input offset voltage, etc Op Amps).

2. D1: MAX6006, LT1004-1.2, ZXRE125. (Precision Voltage Reference).

3. R1 is optional and can be replaced with a link.

4. Recommended minimum supply voltage : 3 VDC (+VS: 2.5 VDC minimum and -VS: -0.5 VDC).

5. Determination of R_{gain}, use $V_{out} = -I_s \times R_{gain}$. Recommended R_{gain} = 1 KΩ (for V_{out} = -100 mV in air).

6. If a different supply voltage or gain is used, the sensor circuit may take more time to recover after exposure to overload conditions. Higher supply voltages will allow a larger gain to be set without circuit saturation.

7. R6 and R7 should be selected such that the bias voltage is as specified in the schematic. Based on +VS of +2.5V, the following values result in a bias voltage of 598 - 604 mV

D1	ZXRE125CFTA – reference voltage from DiodesZetex (1.22V, 0.5%)
R6	102K 1%
R7	105K, 1%
R8	51K

8. Oxygen pump sensors need a larger positive supply rail than most toxic sensors as the counter electrode needs to be continuously driven to a sufficiently high positive voltage to maintain sensor operation over all conditions (especially at temperature extremes). Using a minimum positive rail of +2.5V ensures enoughheadroom for correct operation.

Operating Principles

Reaction Mechanism

Oxygen is reduced at the *sensing* electrode

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

Water is oxidised at the *counter* electrode

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

For further more detailed background on the fundamental design and operating principals of electrochemical sensors and the associated operating circuitry, please contact City Technology.

Sensor and Instrument Venting

As can be seen from the reaction mechanism, oxygen is generated on the counter electrode during operation of the sensor. This must have an escape route from the sensor. To ensure that it does not migrate through the internal electrode stack and onto the *sensing* electrode (resulting in a high false reading), a vent is incorporated into the sensor design, directly below the *counter* electrode where the oxygen is generated. This allows the generated oxygen to exhaust to atmosphere / instrument.

When the sensor is mounted on the PCB, the sensor edge gives adequate clearance for the vent hole. However, if the sensor vent hole is blocked (for example, by glue or epoxy), sensor performance will be compromised. When installing the sensor into instrumentation, care must be taken to ensure that the sensor vent hole is not blocked.

It is good practice to ensure that the instrument is also adequately vented, to prevent elevated oxygen levels and pressure buildup across the cell.

The minimum cross sectional area of the instrument vent hole can be calculated using the formula below.

Minimum Vent Cross Sectional Area (square mm) = 4.4×10^{-3} x V x G

Where V is the internal ‘free’ instrument volume (ml)
G is the instrument ‘vent membrane’ Gurley number (Gurley seconds)

The coefficient 4.4×10^{-3} has the units $\frac{\text{square mm}}{\text{ml x Gurley seconds}}$

IMPORTANT NOTE
If the instrument is not adequately vented, sensor performance may be compromised.

Web: www.citytech.com Email sales@citytech.com Call +44(0) 23 9228 8100

Calibration Guidelines

CiTiceLs® provide very stable signals over time and for many applications, instruments containing CiTiceLs® only require periodic recalibration. The time interval required between initial calibration and subsequent recalibrations is dependant on various factors. In strenuous applications involving extremes of operation, or for sensors used in safety applications, frequent instrument calibration may be required.

Safety Note : Many CiTiceLs are designed to be used in safety critical applications. To ensure that the sensor and/or instrument in which it is used, is operating properly, it is a requirement that the function of the device is confirmed by exposure to target gas (bump check) before each use of the sensor and/or instrument. Failure to carry out such tests may jeopardize the safety of people and property.

Calibration Gas Concentration

For maximum accuracy, the sensor should be calibrated using a gas mixture in the range where most measurements are to be made. Where this is not possible, a mixture towards the top of the CiTiceL range should be chosen. Calibration gases exceeding the range of the CiTiceL must not be used as this may not provide an accurate calibration.

Calibration Period

The calibration and, if necessary, adjustment procedures demonstrate that the gas detection apparatus is able to measure the target gas with sufficient accuracy. However, between calibrations, the performance of the apparatus is unknown and the deviations are likely to increase with time.

When choosing a suitable calibration period, factors such as sensor characteristics, type of apparatus, static and dynamic conditions of temperature and humidity, dust, poisoning, corrosive atmospheres and experience of the user in similar situations should be considered.

Appropriate calibration periods can range from days to months. It is good practice to determine the calibration period as follows:

a) if there is sufficient reliability and stability data available for the apparatus and sensors used in a specific application, the calibration period can be derived from this data for applications with similar operating conditions.

b) if sufficient data is not available, two calibrations should be conducted at short intervals following commissioning. If it is not necessary to adjust the apparatus at these calibrations, the interval can be increased. This procedure should be repeated until the calibration period specified in the instruction manual is reached. An appropriate short interval could be four weeks, as an example.

c) if adjustment is necessary at two successive calibrations, the calibration period should be shortened until no such adjustment is necessary. If the final calibration period is unreasonably short, a more suitable measuring principle should be considered.

An adjustment is necessary if the deviation of the measured value is outside the limits required by the application or if the minimum requirements for stability of the apparatus as defined in EN 45544-2 are not met. EN 45544-2 states that the deviation within one calibration period should not exceed the lower limit of measurement in clean air and 20 % of the measured value in test gas.

Calibrating to Cross Sensitive Gases

Electrochemical CiTiceLs are cross sensitive to certain non-target gases. Information regarding cross sensitivities for particular sensors can be found on the product datasheets. It is important to remember however, that cross sensitivity data is only very approximate and cross sensitivities will vary between sensors and sensor batches. Therefore, it is not advisable to calibrate sensors to non-target gas as this may result in some degree of measurement error.

Operating Principles

Effects of Temperature, Pressure and Humidity

Temperature Dependence

The output of the 4/5OxLL varies slightly with gradual changes in temperature. The sensor output will increase slightly with increasing temperature, and will decrease slightly with decreasing temperature.

When exposed to a step change in temperature, these sensors exhibit a transient response - a decrease in signal for a sharp rise in temperature and an increase in signal for a sharp drop in temperature. The transient temperature response will rapidly fall away, returning to the steady state value after several seconds.

Pressure Effects

The 4/5OxLL will give a transient response to step changes in pressure: - an increase in signal for increased pressure and a decrease in signal for decreased pressure changes. This transient usually fades away after a short time.

This can be a particular problem when using sampling pumps, as pumps can introduce pressure fluctuations into the gas stream. Pressure pulsations can be avoided by ensuring the sensor is positioned at the atmospheric end of the sample train. Alternatively a flow restriction placed upstream from the CiTiceL® will also help to damp out pressure oscillations.

Another effective measure is to ensure that the back pressure downstream from the CiTiceL® is effectively zero, so allowing an unrestricted flow of gas to ambient air. However, it is important to prevent back diffusion from the ambient air diluting the gas stream and affecting the gas concentration being measured. Back diffusion can be reduced, for example, by the provision of an exhaust gas tube of 4mm internal diameter and 8mm length.

The sensor may also give a temporary increase in signal if it receives a mechanical shock. These shock responses can largely be eliminated by using polythene foam or other suitable cushioning material as padding around the sensor.

Humidity Effects

Changes in relative humidity of a gas sample will affect the volume % concentration of oxygen, and therefore the output of an oxygen sensor. As humidity increases, a dilution effect is caused by increasing water vapour pressure. The current given by the sensor is only affected in as much as the concentration of oxygen varies. The graph below shows the change in oxygen concentration of ambient air over the range 0-100% RH at different temperatures.

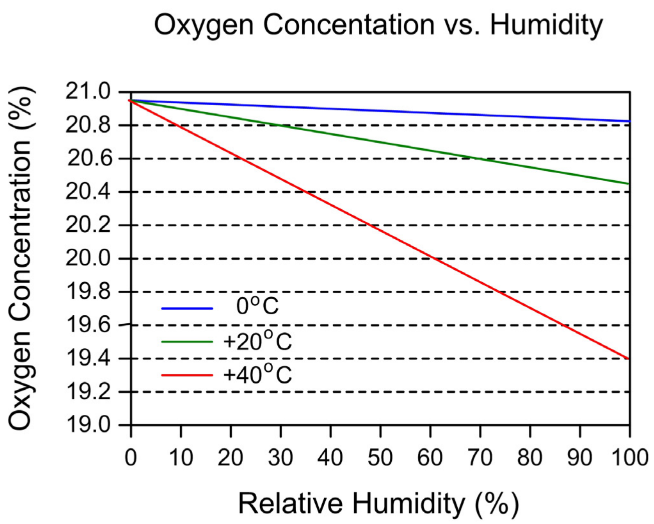


Figure 2. Effect of Humidity on Oxygen Concentration

Operating Principles

The 4/5OxLL has been designed to work between 20% and 90% RH. In continuous operation in low relative humidity, water will diffuse out of the sensor and once the volume of electrolyte has decreased by 25%, operational problems will occur. Provided the sensor is not left under these conditions long enough for a reduction in electrolyte volume to take place to this extent, the sensor can be restored by exposing the sensor to higher relative humidity. Water ingress will occur and over time the water balance will be restored.

Under continuous operation in high relative humidity, water will slowly diffuse in. Water uptake is, however, only harmful when the liquid volume increase extends beyond the free space available. When this happens the sensor becomes prone to leakage, increasingly so as more water is taken up by the sensor. Placing the sensor back into a lower relative humidity before leakage occurs will gradually restore the sensor to its original condition and no permanent harm will result from this exposure.

Conditions where liquid condensation may occur should be avoided. Under such conditions liquids may form in the region of the gas access hole, which will restrict the flow of gas to the sensor. With gas access restricted, sensor signal will be low. Under no circumstances should the sensors be heated to dry them out.

Continuous sensor operation at temperatures at the upper temperature specification limit in combination with extremes of humidity will affect performance and sensor lifetime. Further details of the 4/5OxLL temperature, humidity and pressure performance can be found in the Characterisation Note.

Carrier Gas Effects

For most purposes, the 4/5OxLL may simply be calibrated in ambient air. In the presence of high concentrations of gases other than air however, the effect of the carrier gas (i.e. mixture less oxygen) on the output signal becomes important.

The rate of diffusion of oxygen (and hence the signal from the sensor) is proportional to the molecular weight of the carrier gas (Graham's Law). Dry air may be considered to consist of 20.95% oxygen in nitrogen (which has a molecular weight of 28). When using the sensor with a different carrier gas, with a significantly different molecular weight from nitrogen, the signal from the sensor will be affected. The difference in signal to the nitrogen standard may be calculated using the following:

$$\text{New signal} = \text{Signal with nitrogen carrier gas} \times (28 / M)^{1/2}$$

Where 28 = molecular weight of nitrogen
M = mean molecular weight of carrier gas

Example

If the 4OxLL is working in a carrier gas consisting of 60% nitrogen (molecular weight: 28) and 40% helium (molecular weight: 4) the mean molecular weight of the carrier gas is:

$$((28 \times 60) + (4 \times 40)) / 100 = 18.4$$

Hence:

$$\text{New signal} = \text{Signal with nitrogen carrier gas} \times (28 / 18.4)^{1/2}$$
$$= \text{Old signal} \times 1.23$$

Carrier gas mixtures having a mean molecular weight significantly different from nitrogen will require a special calibration test gas, due to the effect this has on the output signal.

Operating Principles

Linearity

The signal from the 4/5OxLL is slightly non-linear and follows the law:

$$S = K \ln (1/(1-C))$$

N.B. If the sensor is calibrated in dry air to read 20.9% (S=20.9, C=0.209), then K = 89.14

In the example below the two lines are arranged to be the same at 20.9% oxygen which represents the condition when calibrating in air. The maximum error within the operating range then occurs at about 10% oxygen when the sensor output is approximately 0.5% lower than a linear response would indicate. In most circumstances this error is insignificant, although digital techniques may provide compensation if required.

Operation in oxygen levels above 30% will result in greater measurement error and slower sensor recovery.

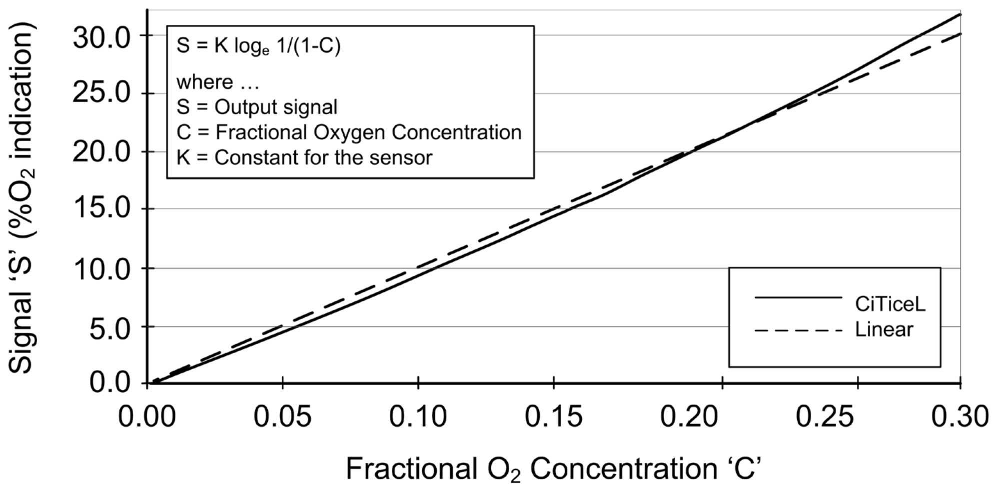


Figure 3. Output Signal vs Concentration

Sensor Mounting

If the 4/5OxLL is incorporated into a fixed application, then the cell should be mounted in the inverted orientation ie pins up. This will ensure that the internal wick remains wet with electrolyte in the reservoir. In portable applications, any orientation is acceptable since the cell will regularly be subjected to changes in orientation.

IMPORTANT NOTES

- Sensor pins must not be soldered to as excessive heat will damage the sensor.
- The vent hole must not be blocked, as leakage due to the buildup of oxygen pressure within the sensor is likely to result in damage to the instrument.

Operating Principles

Handling and Storage

CiTiceLs are relatively insensitive to mishandling and following the simple guidelines given below should ensure correct operation.

- CiTiceLs may be stored for up to six months, during which time they should be kept sealed in the container in which they were supplied or in clean air and within the temperature range given on the product data sheet.
- CiTiceLs should not be stored in areas containing solvent vapours.
- It is important to be aware that reactive species can diffuse into and reside un-reacted on a CiTiceL until the instrument they are in is switched on and the sensor is operational. Once powered, the resulting reaction can cause a temporary high baseline.
- It is important to avoid using CiTiceLs in close proximity to alcohol containing antiseptic products, such as wipes and sanitizing gels, or handling CiTiceLs if these products have recently been used. CiTiceLs can respond to the alcohol based solvents contained within these and generate an output, which could manifest itself as an exaggerated baseline signal or prolonged recovery time.
- CiTiceLs must not be subjected to any pressure when handling or clamping.
- At the end of its life, please dispose of CiTiceLs in accordance with local regulations. The hazardous waste disposal regulations depend on geographic location, and local regulations should be checked before discarding sensors. Product Safety Datasheets (PSDS's) are available for all City Technology products, detailing their hazardous content.

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