
Operating principle and construction of XYA zirconium dioxide oxygen sensors

Application note



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1. Physical background

1.1 Partial pressure

Definition:

The partial pressure is defined as the pressure of a single gas component in a mixture of gases. It corresponds to the total pressure which the single gas component would exert if it alone occupied the whole volume.

In biology and medicine above all the partial pressures of oxygen and carbon dioxide are of importance. Here, the term partial pressure is also used for the concentration of gases dissolved in liquids, e.g. in blood or water. Thereby the partial pressure of a gas dissolved in a liquid is the partial pressure of that gas which would be generated in a gas phase in equilibrium with the liquid at the same temperature.

Dalton's law:

The total pressure (p_{total}) of a mixture of ideal gases is equal to the sum of the partial pressures (p_i) of the individual gases in that mixture.

$$p_{total} = \sum_{i=1}^k p_i \quad (1)$$

From equation (1) it can be derived that the ratio of the number of particles (n_i) of an individual gas component to the total number of particles of the gas mixture equals the ratio of the partial pressure (p_i) of the individual gas component to the total pressure (p_{total}) of the gas mixture.

$$\frac{n_i}{n_{total}} = \frac{p_i}{p_{total}} \quad (2)$$

n_i : Number of particles in gas i
 n_{total} : Total number of particles
 p_i : Partial pressure of gas i
 p_{total} : Total pressure

Example 1:

The atmospheric pressure at sea level under standard conditions is 1013.25 hPa. Here the main components of dry air are nitrogen (78.09 %Vol.), oxygen (20.95 %Vol.), argon (0.927 %Vol.) and carbon dioxide (0.033 %Vol.). The volumetric content (%) can be equated to the number of particles (n) since the above gases can be approximated as ideal gases.

Equation (2) can be solved for the partial pressure of an individual gas to get:

$$p_i = \frac{n_i}{n_{total}} \cdot p_{total} \quad (3)$$

The oxygen partial pressure then equates to:

$$p_i = \frac{20.95\%}{100\%} \cdot 1013.25 \text{ hPa} = \underline{\underline{212.28 \text{ hPa}}}$$

However, this value is only relevant when the atmosphere is dry (0 % humidity). If moisture is present a proportion of the total pressure is taken up by water vapour pressure. Therefore the partial oxygen pressure (ppO_2) can be calculated more accurately when relative humidity and ambient temperature are measured along the total barometric pressure.

Firstly water vapour pressure is calculated:

$$WVP = H_{Rel} \cdot WVP_{Max} \quad (4)$$

WVP : Water vapour pressure [mbar]
 H_{Rel} : Relative humidity [%]
 WVP_{Max} : Max. water vapour pressure [mbar]

For a known ambient temperature, maximum water vapour pressure (WVP_{Max}) can be determined from Table 1. The maximum water vapour pressure is also referred to as the dew point.

Partial oxygen pressure then equates to:

$$ppO_2 = (BP - WVP) \cdot \left(\frac{20.95}{100} \right) \quad (5)$$

ppO_2 : Partial pressure O_2 [mbar]
 BP : Barometric pressure [mbar]
 WVP : Water vapour pressure [mbar]

Operating principle and construction of XYA zirconium dioxide oxygen sensors

Example 2:

The effect of humidity reducing the partial oxygen pressure and therefore the volumetric content of oxygen is shown using the following meteorological data:

Temperature : 22 °C
 Humidity : 32 %
 Barometric pressure : 986 mbar

Using Table 1, WVP_{Max} for 22 °C can be found to be 26.43 mbar. Equation (4) then gives:

$$WVP = \left(\frac{32}{100} \right) \cdot 26.43 = 8.458 \text{ mbar}$$

Partial oxygen pressure then equates to:

$$ppO_2 = (986 - 8.458) \cdot \left(\frac{20.95}{100} \right) = 204.795 \text{ mbar}$$

As we now know the oxygen partial pressure and the total barometric pressure we can work out the volumetric content of oxygen as:

$$O_2 \text{ \%Vol.} = \frac{204.8}{986} \cdot 100 = \underline{\underline{20.77 \%}}$$

T (°C)	WVP _{Max} (mbar)	T (°C)	WVP _{Max} (mbar)
0	6,10	31	44,92
1	6,57	32	47,54
2	7,06	33	50,30
3	7,58	34	53,19
4	8,13	35	56,23
5	8,72	36	59,42
6	9,35	37	62,76
7	10,01	38	66,27
8	10,72	39	69,93
9	11,47	40	73,77
10	12,27	42,5	84,19
11	13,12	45	95,85
12	14,02	47,5	108,86
13	14,97	50	123,38
14	15,98	52,5	139,50
15	17,04	55	157,42
16	18,17	57,5	177,25
17	19,37	60	199,17
18	20,63	62,5	223,36
19	21,96	65	250,01
20	23,37	67,5	279,31
21	24,86	70	311,48
22	26,43	75	385,21
23	28,11	80	473,30
24	29,82	85	577,69
25	31,66	90	700,73
26	33,60	95	844,98
27	35,64	100	1013,17
28	37,78	110	1433,61
29	40,04	120	1988,84
30	42,42	130	2709,58

Table 1: Maximum water vapour pressure (WVP_{Max})

Operating principle and construction of XYA zirconium dioxide oxygen sensors

1.2 Nernst voltage

Two different ion concentrations on either side of an electrolyte generate an electrical potential known as the Nernst voltage. This voltage is proportional to the natural logarithm of the ratio of the two different ion concentrations.

$$\Delta U = -\frac{k_B T}{e_0} \cdot \ln\left(\frac{c_1}{c_2}\right) \quad (6)$$

k_B : Boltzmann constant ($k_B=1,38 \cdot 10^{-23}$ J/K)

T : Temperature [K]

e_0 : Elementary charge ($e_0=1,602 \cdot 10^{-19}$ C)

c_i : Ion concentration [mol/kg]

2. Sensor function

2.1 Sensor construction

First Sensors XYA oxygen sensors consist of two zirconium dioxide (ZrO_2) discs coated with thin porous layers of platinum which serve as electrodes (see Fig.1). The two discs are attached to a platinum ring, forming a hermetically sealed chamber. At the outer surfaces of the ZrO_2 discs there are two further platinum rings to provide for the sensors electrical contacts. The first disc is connected to a reversible current source, at the second disc a voltage (Nernst voltage) can be measured.

Two outer alumina (Al_2O_3) elements prevent any ambient particulate matter from entering the sensor and also remove any unburnt gases. This prevents contamination of the cell which may lead to unstable measurement readings. The complete assembly is surrounded by a heating coil which provides for the necessary operating temperature of the sensor (not shown in Fig. 1).

1.3 Zirconium dioxide (ZrO_2)

At high temperatures >650 °C zirconium dioxide (ZrO_2) exhibits two mechanisms:

1. ZrO_2 partly dissociates to produce oxygen ions which can be transported through the material when a voltage is applied.
2. ZrO_2 behaves like a solid electrolyte for oxygen. If two different oxygen pressures exist on either side of an ZrO_2 element a voltage (Nernst voltage) can be measured across that element (see 1.2 Nernst voltage).

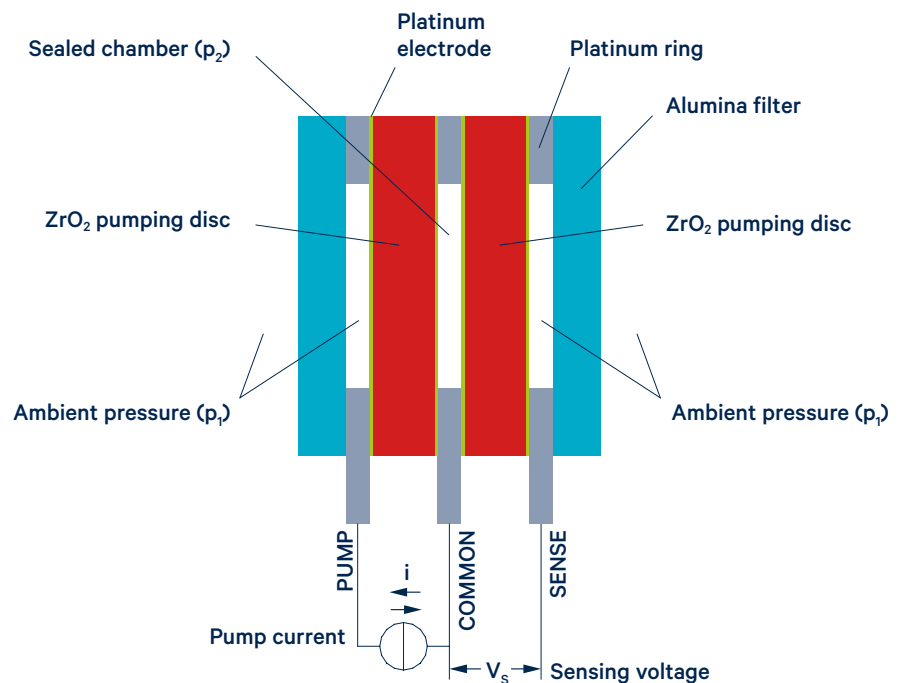


Fig. 2.1: Sensor construction

Operating principle and construction of XYA zirconium dioxide oxygen sensors

Additionally, First Sensors XYA series is housed in stainless steel caps to protect the sensors against dirty environments and mechanical destruction.

For more information about other gases and chemicals which have an influence on the measuring results and life of the sensor please see chapter 4 Cross Sensitivity.

2.2 Pumping disc

The first ZrO_2 disc (pumping disc) works as an electrochemical oxygen pump, evacuating or pressurising the sealed chamber. Depending on the direction of the connected reversible constant current source the oxygen ions move through the disc from one electrode to the other thus changing the oxygen concentration and therefore the pressure (p_2) inside the chamber (see Fig. 1).

2.3 Sensing disc

A difference in oxygen pressure across the second ZrO_2 disc (sensing disc) generates a Nernst voltage which is logarithmically proportional to the ratio of the oxygen ion concentrations (see 1.2 Nernst voltage).

This voltage is sensed and compared with two reference voltages V_1 and V_5 (see Fig. 2). Each time either of these two references is reached the constant current source is reversed and the Nernst voltage approaches its other reference value. Thereby V_1 is the sensing voltage for the highest and V_5 the sensing voltage for the lowest oxygen pressure achieved in the chamber.

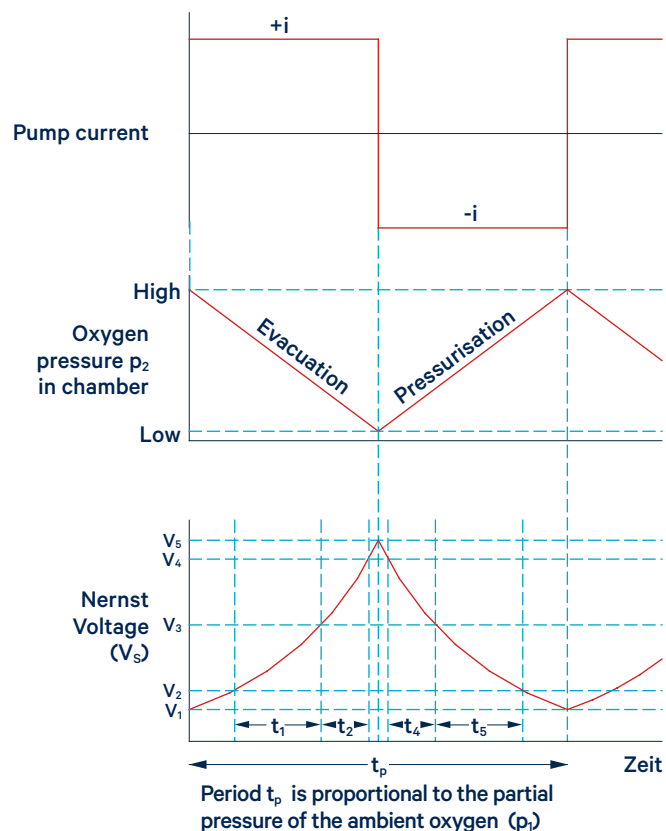


Fig. 2.2: Nernst voltage as a function of the oxygen pressure p_2 in the chamber

Operating principle and construction of XYA zirconium dioxide oxygen sensors

3. Measurement

The duration of a complete pump cycle, i.e. the time taken to once evacuate and refill the chamber, depends on the partial pressure of the ambient oxygen (see Fig. 3). This time is equivalent to the cycle duration of the Nernst voltage (t_p). The higher the ambient oxygen pressure is, the longer it takes for the oxygen pump at constant pump current to reach the same reference voltages. This is because a greater number of oxygen ions are required to be pumped in order to create the same ratio-metric pressure difference across the sensing disc. Thus, the pumping cycle and therefore the cycle time of the Nernst voltage is a measure of the ambient oxygen partial pressure.

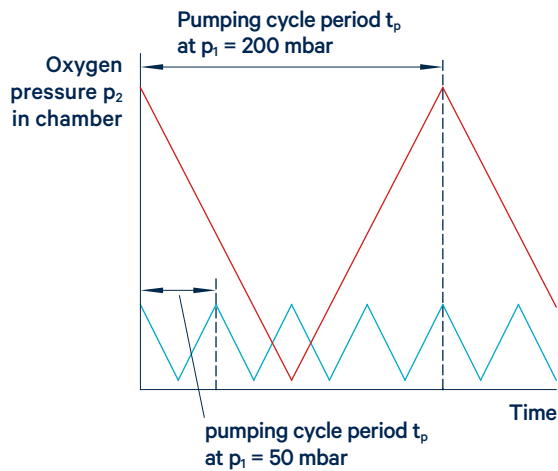


Fig. 3: Pumping cycle period depending on the ambient oxygen partial pressure p_i

3.1 Practical considerations

In theory any two values can be chosen for V_1 and V_5 , in practice they are chosen to:

1. Eliminate the effect of an electric double layer in the ZrO_2 square formed by space charges.
2. Create the best response time for the application.
3. Eliminate temperature dependence.

Compensating for the electric double layer

Not all of the charge supplied by the constant current source contributes to a pressure change in the chamber, some is absorbed by an electric double layer formed at the platinum/ ZrO_2 interface as the current source is reversed. This effect is particularly noticeable at the extremes of pressure and near the pump reversal voltages. As pressure increases the amount of charge required to change the

chamber pressure also increases. To reduce this effect the working chamber pressure should only vary 1-10 % from the ambient pressure. To overcome the influence of the double layer near the pump reversal points, Nernst voltages are chosen well away from V_1 and V_5 . (see V_2, V_3 and V_4 in Fig. 2)

Response time

Because the pump cycle time increases as the oxygen pressure increases, at higher oxygen pressures V_1 and V_5 should be made close to each other in order to ensure a fast response.

Compensating for temperature dependence

It can be seen that the Nernst voltage (equation (6)) is temperature dependant. However the temperature dependence is such that under

certain operating conditions, the combined temperature dependence of Nernst law and the gas laws that govern oxygen can be vastly reduced. Again much of this temperature dependence occurs around the pump reversal points so by choosing to measure Nernst voltages at V_2, V_3 and V_4 we can make the temperature co-efficient (TC) virtually equal zero.

When operating in this $TC = 0$ mode the time taken to reach V_2, V_3 and V_4 are measured. These are highlighted as t_1, t_2, t_4 and t_5 in Fig 2. The revised cycle time (t_d) is then calculated as follows:

$$t_d = (t_1 - t_2) + (t_5 - t_4) \quad (7)$$

Operating principle and construction of XYA zirconium dioxide oxygen sensors

Not only does t_d give a linear output proportional to the ambient oxygen pressure but unlike t_p , it also goes through the origin. One of the major benefits of having a linear response that goes through the origin is that sensor calibration (gain) can occur at one point anywhere on the slope. By measuring t_p , two point calibration is required not only to set the gain but also to remove the zero offset.

Sensitivity

Sensitivity is defined as the cycle time (t_d or t_p) in milliseconds divided by the ppO_2 in mbar of the known calibration atmosphere.

When calculating t_d (one calibration point), sensitivity is defined as:

$$\text{Sensitivity} = \frac{t_d}{ppO_2} \quad (8)$$

When calculating t_p (two calibration points), sensitivity is defined as:

$$\text{Sensitivity} = \frac{t_p - \text{offset}}{ppO_2} \quad (9)$$

Sensitivity for a nominal sensor, when calculating t_d , is typ. 1.05 ms/mbar. Though due to many factors that may influence the sensitivity (chamber volume, ZrO_2 thickness etc), there is a production tolerance of $\pm 15\%$. This makes calibration a necessity to ensure good sensor to sensor repeatability.

3.2 Recommended values

When using the sensor to measure ppO_2 of approx 1..1000 mbar (0.1..100 % of typical barometric pressure), the following values are recommended:

t_d (TC=0 mode)

Constant current source: $i=40 \mu A$
 Pump reversal voltages: $V_1=40 \text{ mV}, V_5=90 \text{ mV}$
 Sense voltages: $V_2=45 \text{ mV}, V_3=64 \text{ mV}, V_4=85 \text{ mV}$

t_p (basic period calculation)

Constant current source: $i=40 \mu A$
 Pump reversal voltages: $V_1=25 \text{ mV}, V_5=115 \text{ mV}$

When using the sensor in higher O_2 pressures alternate values can be recommended on request.

Due to the many benefits of operating the sensor in TC = 0 mode (calculating t_d), this is the recommended mode of operation. Calculating t_p , as it is relatively simple, is only recommended for basic applications where high accuracy is not necessarily required.

3.3 Calibration

First Sensors XYA zirconium dioxide oxygen sensors do not directly measure the concentration (volumetric content) of the ambient oxygen but instead measure the partial oxygen pressure. However, the volumetric content can easily be calculated from Dalton's law (see equation 2) if the total pressure of the gas mixture is known.

If a relative content (percent by volume) is to be determined, the oxygen sensor has to be calibrated in the actual measurement environment with a known oxygen concentration. Typically this would involve calibration in normal air to 20.7 % (not 20.95 %) to take into account average humidity levels. In order to maintain

accuracy, calibration should occur regularly to remove variance caused by fluctuations in barometric/application pressure. As barometric pressure changes relatively slowly daily calibrations are recommended. Regular calibration also removes any sensor drift which is typical in the first few hundred hours of operation.

First Sensors control circuit boards (ZBXYA, ZBXYAF) offer oxygen measuring ranges of 0..25 % Vol., 0..100 % Vol. and custom ranges. For further details please refer to the ZBXYA and ZBXYAF data sheets.

Typical calibration procedure

1. Sensor placed in calibration gas, typically normal air (20.7 % O_2), though can be any gas of known concentration.
2. Oxygen sensor heats up until the correct operating temperature is reached, ~100 s from cold.
3. Pumping cycles commence.
4. Sensor is left at the operating temperature for 5-10 min. to fully stabilise.
5. Output (t_d or t_p) is calculated. Usually over at least ten cycles to average out any noise. The greater the averaging the better.
6. Output value is normalised to equal the known % of the calibration gas. When calculating t_d the calibration process is now complete.
7. When calculating t_p if better accuracy is required it is recommended that a second calibration at a lower % is completed. This two point calibration will remove any zero offset. If accuracy is not critical single point calibration is sufficient.

Operating principle and construction of XYA zirconium dioxide oxygen sensors

3.4 Initial sensor drift and active burn-in

In the first 200 h the sensor output can drift by up to ±3 %. This is due to a number of factors including:

1. Impurities in the zirconium dioxide migrating to the surface of the platinum electrode bond which alters the catalytic properties.
2. Heater coil ageing.
3. The internal stainless steel surface of the cap becoming less reflective due to thermal oxidation.

Regular calibration removes the effect of initial sensor drift as the sensor output is constantly re-referenced against the known calibration gas. However if regular calibration is not possible and the output is required to have stabilised prior to use in the application then it may be necessary to actively burn-in the sensor .

Active burn-in involves operating the sensor normally in a controlled atmosphere where the exact partial oxygen pressure (ppO₂) is known. If this is normal air then all weather data must be recorded and the ppO₂ calculated as previously described in chapter 1.1, Example 2. With the ppO₂ known the sensor output (t_d or t_p) can be normalised as described in Equation 8. By calculating slope any variance in the sensor output can be considered to be drift and not due to environmental fluctuations. The level

of stability required will be dependant on the application specifications. However, in general the output can be considered stable when the slope value has varied by less than ±0.2 % of reading in the last 48 h.

When performing active burn-in at First Sensor, measurements are taken at 12 h intervals and the environmental temperature is also kept constant to negate any temperature dependence the sensor output may exhibit.

3.5 Using a barometric pressure sensor to scale the XYA output

If regular calibrations in normal air are not possible it may be necessary to use a barometric pressure sensor in conjunction with the XYA sensor to automatically compensate the output. This is a relatively simple process as variations in the barometric pressure change the output of the oxygen sensor by the same proportion. So if the barometric pressure changes by 1 % the sensor output will also change by 1 %.

Ideally the initial system calibration should be performed after the sensor has burned in for 200 h. This will ensure any sensor drift, which may effect future accuracy, has occurred beforehand.

Typical calibration procedure when using a barometric pressure sensor:

1. Sensor is placed in the calibration gas, typically normal air (20.7 % O₂), though can be any gas of known concentration.
2. Oxygen sensor heats up until the correct operating temperature is reached, ~100 s from cold.
3. Pumping cycles commence.
4. Sensor is left at the operating temperature for 5-10 min. to fully stabilise.
5. Output (t_d or t_p) is calculated. Usually over at least ten cycles to average out any noise. The greater the averaging the better.
6. Output value is normalised to equal the known % of the calibration gas.
7. The barometric pressure at the time of the calibration is stored.

Subsequent O₂ and barometric pressure readings are then entered into following equation:

$$O_{2\text{ comp}} = O_{2\text{ cur}} \cdot \left(\frac{p_{\text{cal}}}{p_{\text{cur}}} \right) \quad (10)$$

Example:

The sensor output is calibrated to 20.7 % and the barometric pressure is measured at 1000 mbar. The following day the pressure has changed by 1 % to 990 mbar. Without compensation the O₂ output would also reduce by 1 % to 20.493 %.

Using equation (10) the compensated O₂ value is:

$$O_{2\text{ comp}} = 20.493\% \cdot \left(\frac{1000\text{mbar}}{990\text{mbar}} \right) = 20.7\%$$

Operating principle and construction of XYA zirconium dioxide oxygen sensors

4. Cross sensitivity

The XYA oxygen sensors measure partial oxygen pressure as explained above and show some cross sensitivity with other gases. Described below are gases or chemicals that will have an influence on the life of the sensor or on the measuring results.

The sensors have been primarily developed for boiler combustion control applications. Therefore, life tests have been performed in a laboratory atmosphere, in exhaust gases of natural gas fired boilers as well as in exhaust gases of light oil.

4.1 Combustible gases

Small amounts of combustible gases will be burned at the hot platinum electrode surfaces or alumina filters of the sensor. In general combustion will be stoichiometric as long as enough

oxygen is available. The sensor will measure the residual oxygen pressure which leads to a measurement error. The sensor is not recommended for use in applications where there are large amounts of combustible gases present and an accurate O₂ measurement is required.

Investigated gases (stoichiometric combustion) are:

- H₂ (hydrogen) up to 2 %;
- CO (carbon monoxide) up to 2 %;
- CH₄ (methane) up to 2.5 %;
- NH₃ (ammonia) up to 1500 ppm;

4.2 Heavy metals

Vapours of metals like Zn (zinc), Cd (cadmium), Pb (lead), Bi (bismuth) will have an effect on the catalytic properties of the platinum electrodes. Exposures to these metal vapours has to be avoided.

4.3 Halogen and sulphur compounds

Small amounts (< 100 ppm) of halogens and/or sulphur compounds have no effect on the performance of the oxygen sensor. Higher amounts of these gases will in time cause readout problems or, especially in condensing environments, corrosion of sensor parts.

Investigated gases are:

- Halogens, F₂ (fluorine), Cl₂ (chlorine)
- HCL (hydrogen chloride), HF (hydrogen fluoride)
- SO₂ (sulphur dioxide)
- H₂S (hydrogen sulphide)
- CFC's, HCFC's (Freons)
- CS₂ (carbon disulfide)

5. Application hints

5.1 Fail safe operation

One of the main benefits of the dynamic and active cell employed within the XYA oxygen sensor is that it is inherently fail safe. The continual cycling and measurement of the generated Nernst voltage is effectively the heart beat of the sensor, if this stops something fatal has occurred with the cell. This can very quickly be detected by a microprocessor which can generate the relevant error code.

5.2 Sensor asymmetry

The generated Nernst voltage shown in Fig. 2 is symmetrical, which is a strong indication of sensor health. If an asymmetric output waveform is detected it could be one of the following causes:

1. The heater voltage is too low
2. The sensor has been contaminated meaning the cell is not pumping correctly.
3. The hermetic seal which surrounds the sensing chamber has a leak. This means it is far more difficult to evacuate the chamber than it is to re-pressurise it.
4. The cell has been excessively loaded with capacitive impedance.

To measure asymmetry we can simply calculate the following at the same time as measuring t_d or t_p.

$$\text{Asymmetry} = \frac{(t_1 + t_2)}{(t_5 + t_4)} \quad (11)$$

The result of this calculation should ideally be 1 to indicate perfect sensor health. In production the sensor asymmetry has a tolerance of ±2.5 % (0.975 to 1.025).

Operating principle and construction of XYA zirconium dioxide oxygen sensors

5.3 Operation in humid environments

When operating the sensor in warm, humid environments it is important the sensor remains at a higher temperature than its surroundings, especially if there are corrosive components in the measurement gas. During operation this is not a problem due to the 700 °C generated by the heater, but this means when the sensor or application is being powered down the sensor heater must be the last thing to be turned off after the temperature of the surroundings have suitably cooled. Ideally the sensor should be left powered or at a lower standby voltage (2 V typically) at all times in very humid environments.

Failure to adhere to these rules will result in condensation forming on the heater and sensing cell as these will be the first components to cool due to their connections to the outside world. When the sensor is re-powered the condensation will evaporate, leaving behind corrosive salts which very quickly destroy the heater and cell .

5.4 Protecting from water droplets

In environments where falling water droplets are likely the sensor should be protected since water falling directly onto the very hot sensor cap can cause massive temperature shocks to the cell and heater. Popular methods include a hood over the sensor cap or for the sensor to be mounted in a larger diameter cylinder.

At a very minimum the sensor cap should be angled downwards as this will deflect any falling moisture and prevent the sensor cap from filling with water.

5.5 Using the sensor with silicones (rubbers, plastics)

The XYA oxygen sensors, like all other zirconium dioxide sensors, are damaged by the presence of silicone in the measurement gas. Vapours (organic silicone compounds) of RTV rubbers and sealants are the main culprits and are widely used in many applications. These materials are often made of cheaper silicones,

that when heated still outgas silicone vapours into the surrounding atmosphere. When this reaches the sensor the organic part of the compound will be burned at hot sensor parts, leaving behind a very fine divided SiO₂ (silicon dioxide, also known as silica). This SiO₂ completely blocks the pores and active parts of the electrodes. If RTV rubbers are used we advise to use high quality, well cured materials.

5.6 Reducing atmospheres

The sensor by definition requires at least some ambient oxygen to operate. Otherwise the sensor, due to applied constant current source, will try to pump the O₂ within the ZrO₂. This will in time damage the ZrO₂ and degrade sensor performance. It is therefore imperative that the sensor is not used for prolonged periods in very low oxygen environments (less than 1 mbar ppO₂), especially in reducing atmospheres (an atmosphere in which there is little free oxygen and oxygen is consumed).

Note:

Detailed information on the design of your own evaluation electronics can be found in our application note "[Designing Interface Electronics for Zirconium Dioxide Oxygen Sensors of the XYA Series](#)". Please contact First Sensor for further information.