



The Theory of Zirconia Oxygen Sensors

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1 Abstract

This white paper describes the chemistry and mineralogy of zirconia and why its properties make it a perfect candidate as a solid electrolyte material in oxygen gas sensors. The theory of Nernstian zirconia oxygen sensors and how their electrochemical signals can be used to calculate oxygen partial pressures is explained with formulae and charts. Some important considerations about using zirconia sensors in real-World applications are reviewed.

2 Background

The birth of solid electrolyte gas sensing came in 1957 when Kiukkola and Wagner discovered that partially stabilised zirconium dioxide (ZrO_2 - zirconia) was an oxygen ion conductor at elevated temperatures $>300^\circ C$. They demonstrated that this material could be used to measure oxygen partial pressures in gases using an electrochemical cell or 'oxygen sensor'.

3 Morphology of Zirconia

Zirconia is a stable ceramic material that once fired (or sintered) in a kiln is an extremely stable, chemically resistant refractory material capable of withstanding very high temperatures. Certain types of zirconia are known to be ionic conductors of oxygen and are therefore referred to as solid electrolyte materials. There are three common crystal structures of zirconia known: pure zirconia crystals are monoclinic at room temperatures, then change to tetragonal and finally cubic form as the temperature rises further.

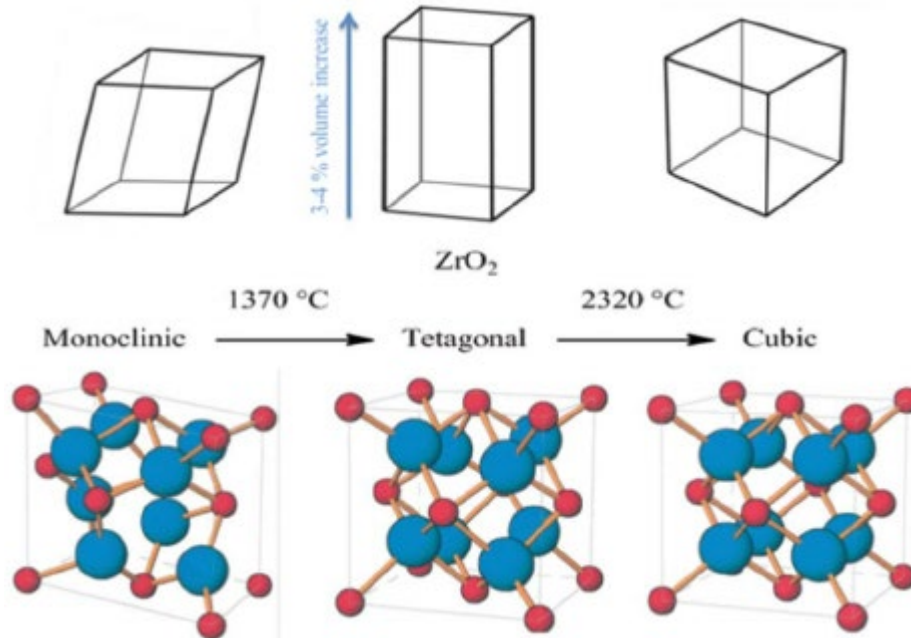


Figure 1: The three common crystal structures of zirconia.

Monoclinic zirconia does not conduct oxygen ions to any significant degree and cubic zirconia is not particularly strong or stable. Instead, partially stabilised (tetragonal) zirconia is preferred as the solid electrolyte material to use for making oxygen sensors. It is structurally very strong and chemically stable and is an excellent conductor of oxygen ions when heated above 300°C.

4 Chemical Doping of Zirconia

Partially stabilised zirconia is manufactured by adding dopants such as calcium, magnesium or yttria to the ceramic powder before sintering. Typically, a dopant level of between 3 and 8% by weight is added, and yttria is the most potent type. Therefore, yttria doped partially stabilised zirconia is the preferred material to use as an oxygen sensor solid electrolyte material.

At high sintering temperatures (>1500°C) the presence of these dopants creates defects in the ceramic crystal lattices and locks the tetragonal form permanently in place as the



ceramic cools down. The sintering process produces a dense off-white material without any porosity. Inside the crystals, the network of induced lattice defects is what allows charge carrying oxygen atoms (anions) to pass through the material unimpeded when the temperature is hot enough ($>300^{\circ}\text{C}$). The hotter the temperature, the faster the anions move, and the ionic conductivity of the material increases. The term ionic conductivity is used as opposed to electronic conductivity because the charge is carried by atoms rather than electrons.

5 Zirconia Oxygen Sensor Theory

With zirconia identified as a suitable solid electrolyte material, an oxygen sensor cell can be constructed (normally) into a thimble shaped ceramic tube so the outer surface is exposed to the unknown measurement gas and the inner surface is exposed to fresh air, which acts as a fixed and known reference point. High temperature platinum metal electrodes are then painted onto the two surfaces and connected to a high impedance voltmeter by electrode wires as shown in the schematic below:

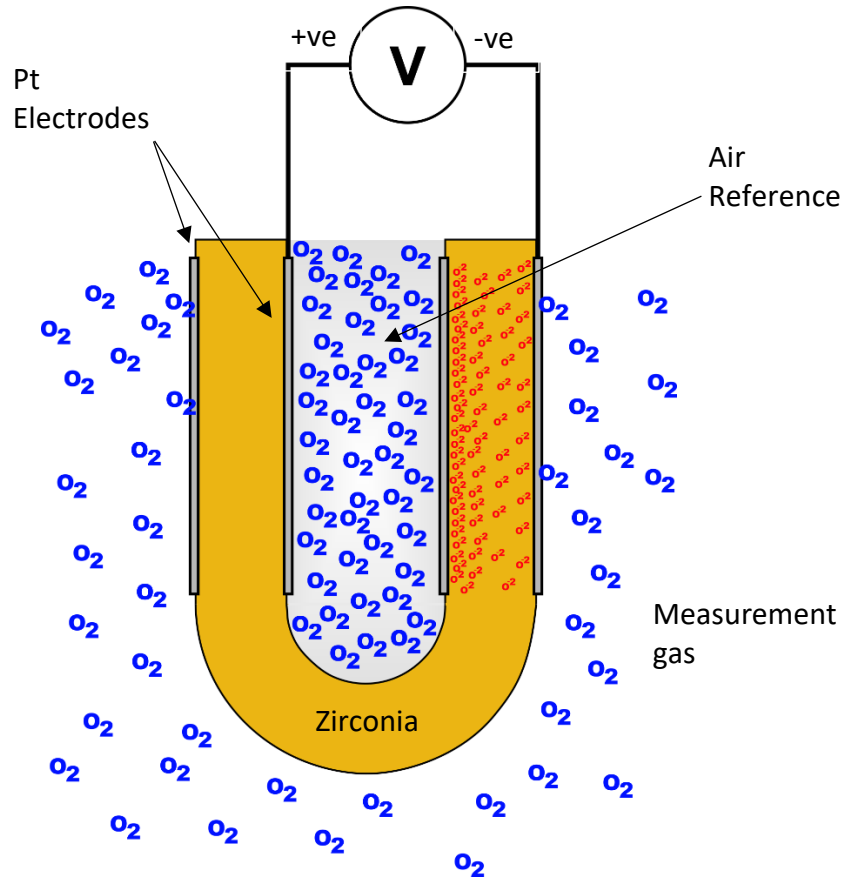


Figure 2: Schematic of a zirconia solid electrolyte oxygen sensor cell.

When the whole cell is heated to an optimum temperature of 650°C the charged oxygen anions within the zirconia become highly mobile and quickly migrate across the cell wall so as to maintain an equilibrium with the oxygen partial pressures on both surfaces of the cell. As shown above, if the oxygen pressure is different, this creates a charge imbalance (or charge gradient) across the cell wall. The resulting voltage generated between the electrodes is then related to the oxygen content (or partial pressure) of the unknown measurement gas by the well-known Nernst equation:

$$EMF = \frac{RT}{zF} \ln \left[\frac{pO_2(\text{reference gas})}{pO_2(\text{measurement gas})} \right] \quad 1$$

where:	<i>EMF</i>	= Electro-motive force (V)
	<i>R</i>	= Molar gas constant (8.3144 J. mol ⁻¹ .K ⁻¹)
	<i>T</i>	= Absolute temperature (°K)
	<i>z</i>	= Number of charge units transferred (z = 4 for oxygen)
	<i>F</i>	= Faraday's constant (9.6485 x 10 ⁴ C. mol ⁻¹)
	<i>pO₂ (reference)</i>	= Partial pressure of oxygen in the air reference
	<i>pO₂ (measurement)</i>	= Partial pressure of oxygen in the measurement gas

After substituting numerical constants, the Nernst equation can be rewritten more conveniently like so:

$$EMF = 2.1543 \times 10^{-5} \times T \left[\ln (P_{O_2}^{\text{reference}}) - \ln (P_{O_2}^{\text{unknown}}) \right] \quad 2$$

The equation reveals that as long as the temperature of the sensor (T) is fixed and known and the reference gas is also fixed and known then the resulting EMF generated is always proportional to the natural LOG (ln) of the oxygen partial pressure of the unknown measurement gas. The zirconia sensor is therefore described as a potentiometric logarithmic sensor. It can also be noted that if both the reference gas and the measurement gas are fixed and known (but are not the same, since then the log expression to the right of T would be zero) then the sensor will act like a thermocouple and the measurement voltage will be proportional to the temperature (T). Therefore, accurate measurement of the cell temperature is just as important as the measurement of the gas itself.

The Rapidox gas analyser uses a simplified version of the above formula when calculating oxygen. For the Bosch type oxygen sensors, the following formula applies when operating them in potentiometric measurement (Nernst) mode:

$$EMF = A \times LOG \left(\frac{O_2}{100} \right) + B \quad (Assume LOG_{10}) \quad 3$$

Where:

<i>EMF</i>	= Nernst voltage obtained
<i>A</i>	= Temperature variable
<i>B</i>	= Nernst EMF in pure oxygen, mV
<i>O₂</i>	= Volume % oxygen

In terms of oxygen, formula 3 is expressed as:

$$LOG \left(\frac{O_2}{100} \right) = \frac{EMF-B}{A} \quad 4$$

Which in turn can be rewritten as

$$\left(\frac{O_2}{100} \right) = 10^{\left(\frac{EMF-B}{A} \right)} \quad 5$$

Which can in turn be rewritten as:

$$O_2 = 100 \times 10^{\left(\frac{EMF-B}{A} \right)} \quad 6$$

This equation is used to calculate the oxygen partial pressure of the measurement gas by reading the signal voltage coming from the cell. The equation shows that the voltage is proportional to the LOG of the oxygen partial pressure. This is important because it is what gives Rapidox zirconia sensors such a wide dynamic range of measurement from as low as 10E⁻²⁶ppm to 100% O₂. When both measurement and reference chamber are the same gas, the output of the sensor is theoretically 0mV and if the measurement gas is of a higher partial pressure (e.g., 100% oxygen) then the output is a negative voltage of approximately -50mV. If the measurement gas has a very low oxygen partial pressure (e.g., 1ppm) then the output is a positive voltage of approximately 200mV as shown in the plots below.

The two plots demonstrate the unusual logarithmic nature of the sensor output which allows it to measure over a huge range of oxygen values. The sensor output is perfectly linear on a logarithmic scale chart, allowing easy calibration and quality checking using R-squared statistics. The linear plot shows that the sensor signal increases to infinity at ultra-low oxygen levels, thus giving a very large signal resolution per point of oxygen at ppm levels. This feature makes zirconia sensors the best choice for sensitive ppm levels of gas measurements. Conversely, above 21% oxygen the signal resolution is dramatically reduced making zirconia sensors not so attractive for measurements in enriched oxygen atmospheres.

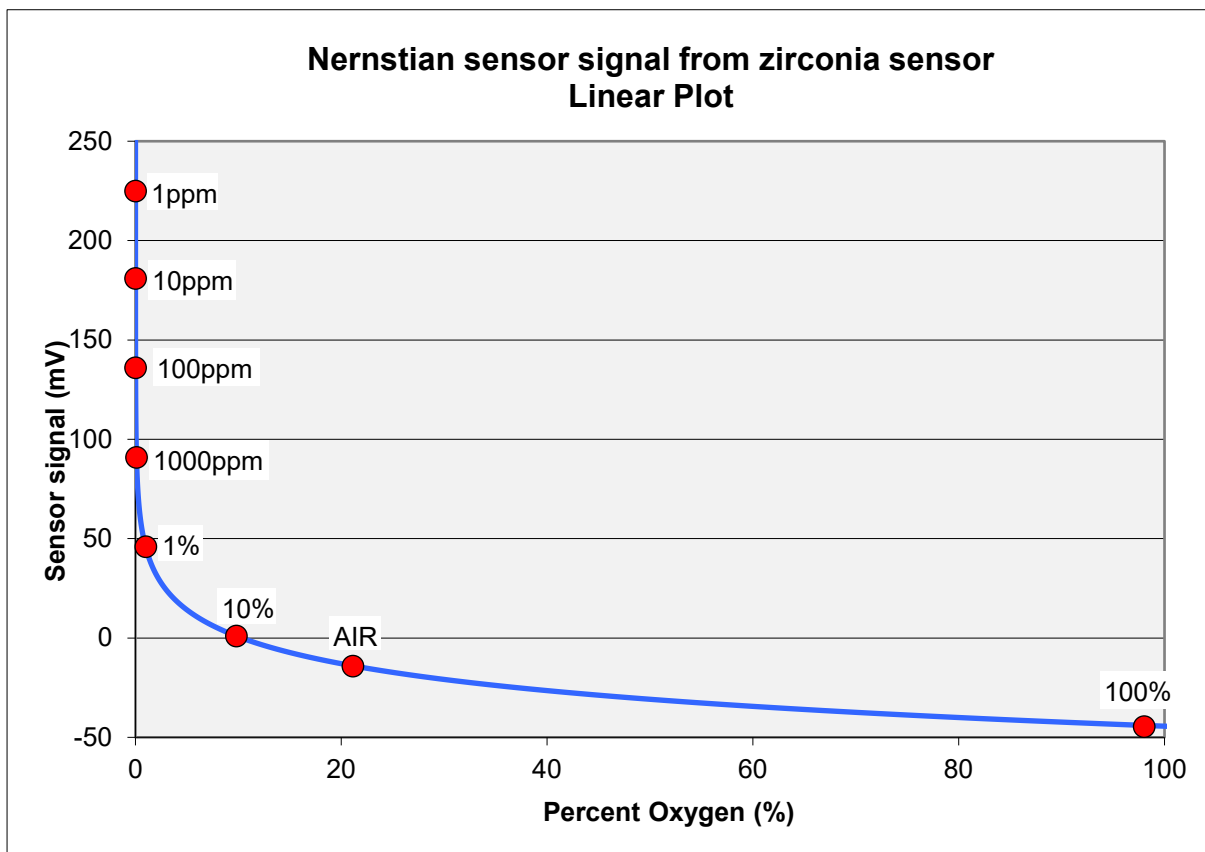


Figure 3: Signal output of a zirconia oxygen sensor plotted on a linear x-axis.

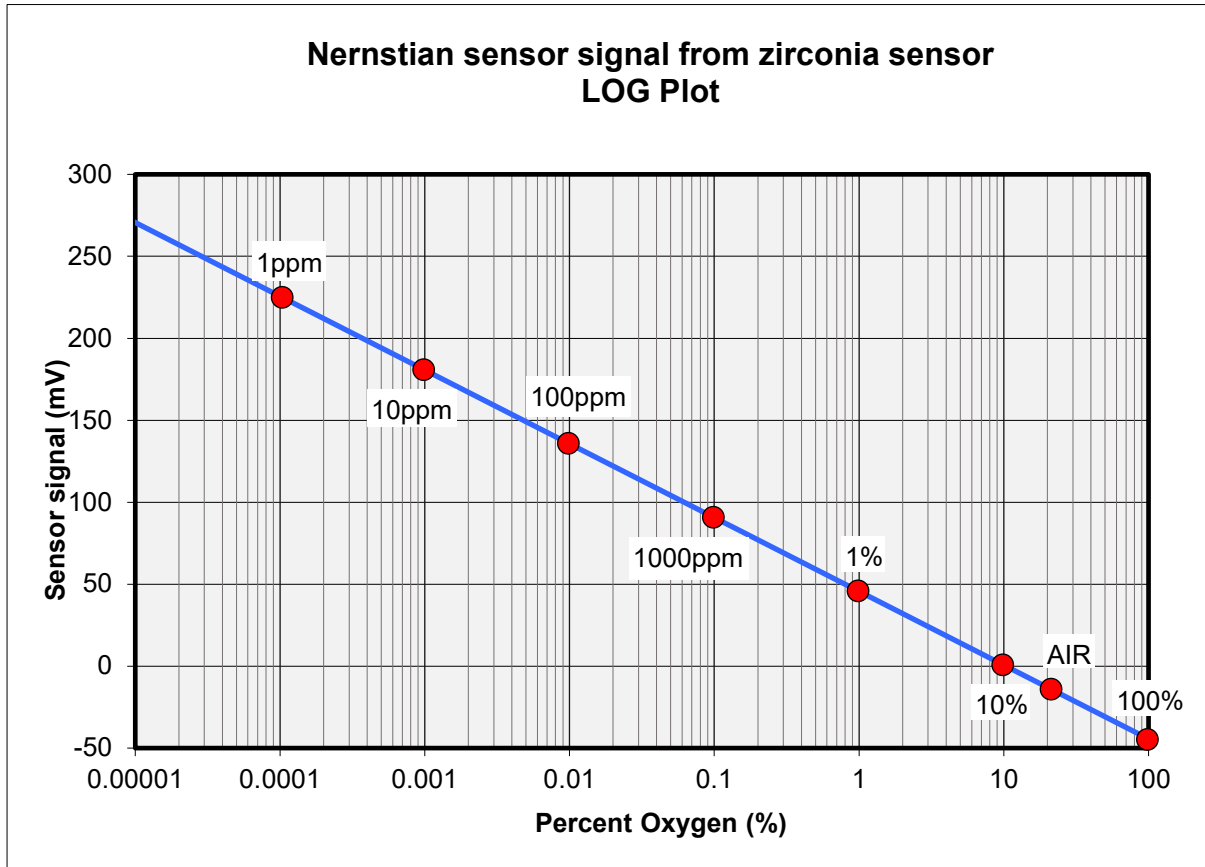


Figure 4: The same curve plotted on a logarithmic x-axis scale.

6 Special Considerations for Sensor Operation

As mentioned previously, zirconia sensors measure oxygen as a partial pressure. This corresponds to oxygen concentration only when the gas being measured is at 1 bar atmospheric pressure (assuming that is the local ambient pressure). The Rapidox gas analysers display oxygen concentration (in terms of a percentage or in ppm) but this is only correct if the measurement gas reading has been pressure corrected using an independent pressure sensor measurement. Apart from the Rapidox 2100 analyser which has a sensor designed to operate under high pressures or even under vacuum, all Rapidox instruments are equipped with on-board pressure sensors to automatically correct for changes in gas



pressure. In the case of the Rapidox 2100 readings of up to 1000% oxygen are permissible which would be equivalent of taking measurements in pure oxygen at 10bar gauge pressure.

Likewise, it was mentioned that the temperature of the oxygen sensor must be maintained carefully at approximately 650°C to give good accuracy. The Rapidox analysers all have complex heater control circuitry to monitor and maintain the sensor temperature at exactly the right setting no matter what the external thermal effects are.

The design of the sensor as described means that a fresh air path must be maintained to the reference chamber otherwise the Nernst equation becomes invalid. Air is a highly suitable reference point because it exists everywhere on the planet and is a stable 20.954%.

However, the chemistry of air is affected by humidity and should this be high then the reference chamber may be temporarily depleted of a small amount of oxygen since humid air is no longer 20.954%. Whilst this is hard to predict, the latest versions of Rapidox analysers include on-board humidity measurement to allow correction factors to be applied to the reference chamber calculations. Likewise, the sensor must be positioned in a location where the atmosphere is guaranteed to be fresh air. If the air has unexpected oxygen enrichment (e.g., in a hospital) or depletion (e.g., if nitrogen blanketing is being used and gas is escaping) then the shift in reference gas oxygen content will impact the readings of the gas analyser.

Most importantly the sensor design must be such that the measurement gas and the reference gas are sealed from each other, so it is impossible to cross-contaminate the gases. The basic design of a thimble shaped zirconia sensor has been optimised over many years and is now more often of a planar design. The concept of a walled tube of zirconia ceramic remains, however. Normally the sensor has a metal thread and gas seal allowing the sensor to be screwed tightly into a gas manifold, pipe or flue. In this way the reference chamber can be replenished with fresh air using the spaces around the multi-strand electrode and

heater wires used. An example of a typical sensor installation is shown in the schematic below.

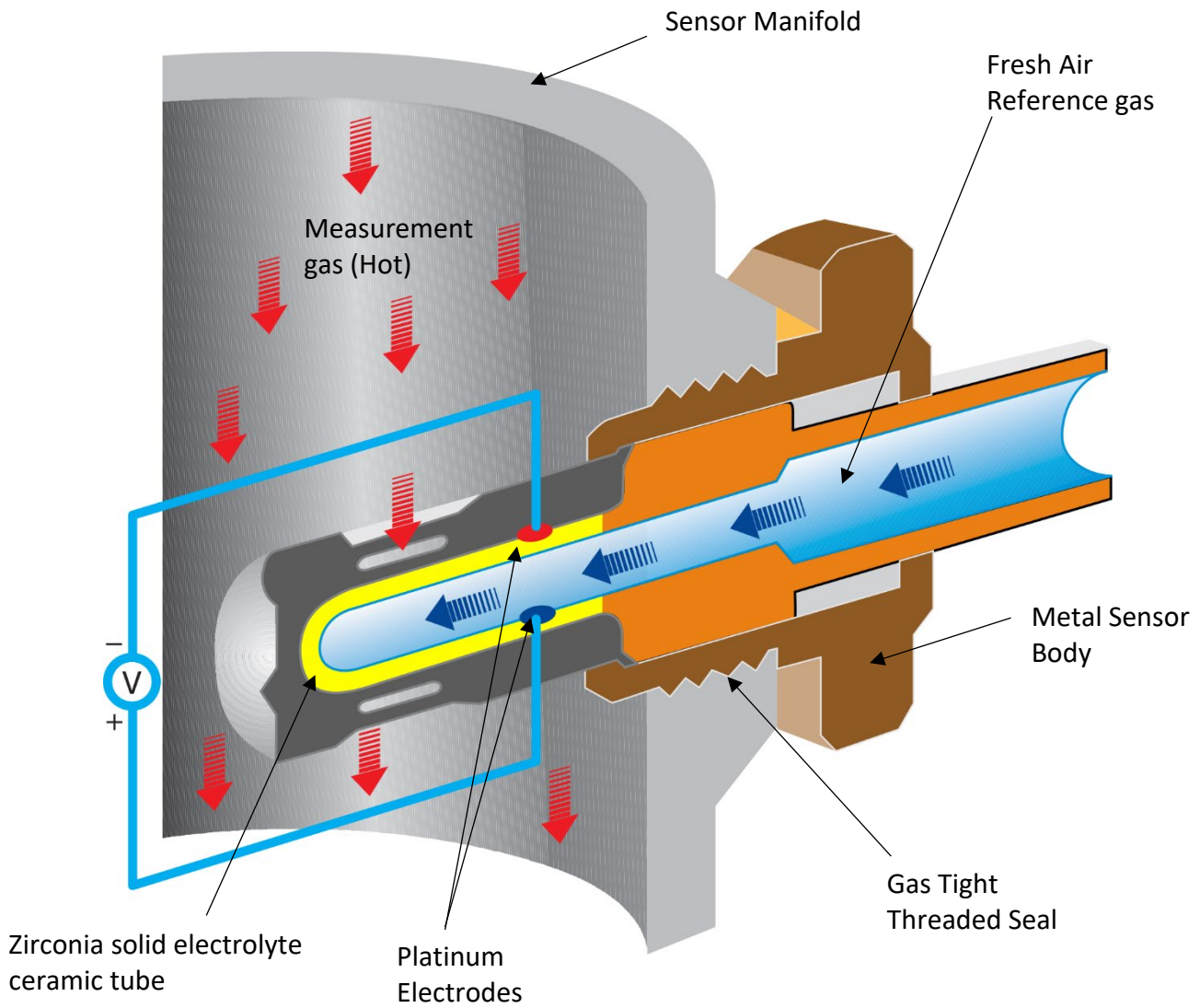


Figure 5: Schematic of an oxygen gas sensor installed into a flue.