

# Oxygen Sensors: Lead-Free vs Standard Lead Type

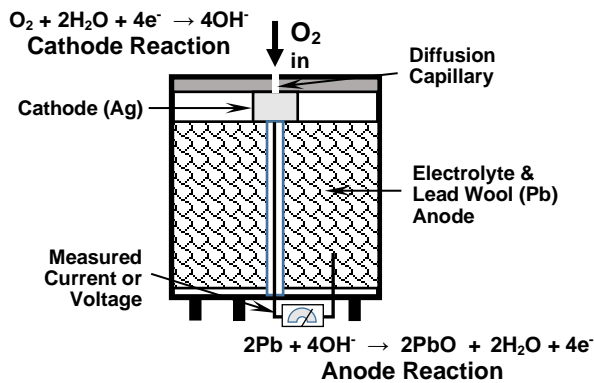
## Why Use a Lead-Free Oxygen Sensor?

Compared to standard oxygen sensors, lead-free sensors:

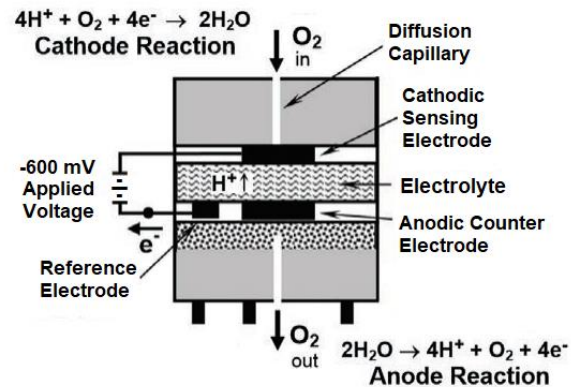
- Are higher cost but longer-lived, not prone to leakage, lighter weight, contain no toxic materials, but use more power.

## Sensor Design

The **Conventional “standard” Oxygen Sensor** is a galvanic cell, which uses a sacrificial anode of lead wool and an inert cathode. The cell is low-cost and the reaction proceeds without external power by the net oxidation of lead to lead oxides:  $2\text{Pb} + \text{O}_2 \rightarrow 2\text{PbO}$ . Once the lead is consumed, or the solid  $\text{PbO}/\text{Pb}(\text{OH})_2$  completely coats the Pb surface, the sensor stops working. The resulting lead oxyhydroxides have higher volume than the original lead wool, and therefore the contents expand and build pressure, causing a tendency to leak. The life of the sensor depends on the rate at which oxygen diffuses in, which is controlled by the diameter of the inlet capillary. A narrow capillary allows sensor lives of up to 3 years, but can result in transient pressure effects and false alarms.



Galvanic Oxygen Sensor with Lead



Catalytic Lead-Free Oxygen Sensor

The **Lead-Free Oxygen Sensor** uses catalysts and an applied voltage to reduce oxygen at the cathode and regenerate it at the anode. Because there is no consumable material, the sensor can last a long time, typically 5 or more years, until somehow the catalyst becomes deactivated, the inlet capillary becomes plugged, or the electrolyte dries out. There is also no significant volume change and thus these sensors are not prone to leakage. The need for an applied voltage causes lead-free sensors to use more power and therefore they are most commonly employed in instruments with rechargeable batteries such as the POLI or MUNI. However, by using a narrow inlet capillary the power draw has been reduced enough that lead-free oxygen sensors can be used in the UNI, albeit with more frequent battery replacements. Note also that the outlet pore must not be blocked, so that the regenerated oxygen can escape out the bottom of the sensor.

## Further Comparison and Summary

The table below summarizes the advantages and disadvantages of both types of sensors. Although the lead-free sensor has a higher initial purchase cost, its longer life means that the cost is usually lower for long-term use. Both sensors have a fast response time of about 10 seconds or less, although direct comparisons show the lead-free sensor to be a bit faster, and the galvanic sensor slows a bit with age as the lead wool gets coated. A significant advantage for the lead-free sensor is the absence of toxic lead, which may need to be treated as hazardous waste upon disposal of the standard galvanic sensor.

## Comparison of Oxygen Sensors

Factor	Standard Lead-Containing Galvanic Cell	Lead-Free Electrochemical Cell
Cost	Lower purchase price; higher long-term	Higher purchase price; lower long-term
Life	1-3 years, ends when Pb is used up	5 years or more; indefinite end
Start-up	Useable immediately after installation	Few hours stabilization time after installation
Power	Low power: OK for non-rechargeable monitors	Moderate power: Better for rechargeable monitors, but non-rechargeable work OK with more frequent battery changes
Range	0 - 30% Vol	0 - 30% Vol
Resolution	0.1% Vol	0.1% Vol
Response time	$t_{90} \sim 10$ s (slows with age)	$t_{90} \leq 10$ s (slightly faster)
Leakage	Prone to leakage	No leakage
Weight	High	Low
Electrolyte	Alkaline: Acid gases at % levels cause high readings; cannot use above 25% CO <sub>2</sub>	Acidic: Unaffected by acid gases (alkaline gases like NH <sub>3</sub> may cause high readings)
Waste	Lead (Pb) may be hazardous waste	Non-hazardous
Pressure Effects	Low on short-lived cells; high on long-lived cells	Moderate

Small inlet capillaries used in either sensor (to extend sensor or battery life) can result in transient low or high readings with rapid pressure changes, such as when going quickly up or down an elevator or mine shaft. Such transients can cause the sensors to go into alarm, but they tend to settle back down to normal readings within several seconds to a few minutes.

### Calibration

**NOTE: Oxygen sensors in MUNI, POLI and VOXI EC monitors require N<sub>2</sub> calibration upon first installation (but not thereafter, nor in UNI series monitors).**

For POLI firmware v1.0.3 and MUNI v2.0.3 and later, and all VOXI O<sub>2</sub> firmware, the scheme below is implemented. The purpose is to provide a good calibration by using nitrogen initially at the factory but then not requiring this second gas cylinder during routine calibration by the end user.

- 1) The calibration curve is set using Fresh Air Zero for 20.9% span and pure N<sub>2</sub> for 0% O<sub>2</sub>.
- 2) The pure N<sub>2</sub> zeroing is done at the factory or upon first installation of a replacement sensor in the field.
- 3) The user generally does not need to recalibrate at 0% O<sub>2</sub> because this raw value does not change much over the life of a sensor.
- 4) During Fresh Air Calibration, the oxygen span is set at 20.9%, and the previously-calibrated N<sub>2</sub> response is used for 0% O<sub>2</sub>.
- 5) During Span Calibration with gas mixtures, typically including 18% O<sub>2</sub>, no O<sub>2</sub> calibration is actually done, only the other sensors are span calibrated. The O<sub>2</sub> response is just a Calibration Check to test whether the sensor reads back within an acceptable range. Calibration Certificates list this read-back value.
- 6) If the user is working at low O<sub>2</sub> concentrations and wants to recalibrate the 0% O<sub>2</sub> response, they can do so with N<sub>2</sub> using the Single-Zero menu on POLI, Single Span menu on MUNI, or setting the span value to 0% on O<sub>2</sub> VOXI.
- 7) Pure N<sub>2</sub> (0% O<sub>2</sub>) recalibration is more commonly needed for lead-free oxygen sensors than for galvanic, and when operating in inert gas environments.
- 8) Note that Lead-free oxygen sensors have a bias voltage and therefore require at least an hour stabilization time after installation and before calibration (preferably overnight stabilization).

UNI series monitors do not use the above scheme. They use fresh air to set 20.9% O<sub>2</sub> and can use any lower concentration of 18% or less for span calibration. For UNI O<sub>2</sub> Inert models, regular calibration at 0% O<sub>2</sub> is highly recommended.

## Matrix Gas Effects

When other gases are present in % levels, beside the components of air, there are three potential effects on oxygen sensor readings:

- Displacement of O<sub>2</sub>
- Diffusion Rate
- Absorption into Electrolyte

The first two effect both galvanic and lead-free sensors because they both sample the same way by diffusion through a capillary.

**Displacement Effect:** This is the usual effect one is trying to measure: if some other gas enters the work space, it takes the place of some of the oxygen.

**Diffusion Rate Effect:** Oxygen sensors are most commonly calibrated in ambient air containing 20.9% O<sub>2</sub> and 78.1% N<sub>2</sub>, and small amounts of other gases\* including argon and carbon dioxide. When other balances gases beside nitrogen are present in high (% level) concentrations, oxygen response can be affected because diffusion rates through the capillary inlet depend on the molecular weight of the gas mixture. With gases heavier than N<sub>2</sub>, such as argon, diffusion is slowed and the O<sub>2</sub> response is reduced, while with lighter gases such as hydrogen or helium, diffusion is faster and O<sub>2</sub> response is increased:

$$\text{Response new gas matrix} = \text{Response with N}_2 \text{ balance} \times \sqrt{28/mw}$$

Where “mw” is the average molecular weight of the new gas.

**Example 1**, new matrix gas contains 10% CO<sub>2</sub> (mw = 44) in place of N<sub>2</sub>:

Average molecular weight is:  $(10/79) \times 44 + (69/79) \times 28 = 30$ ; therefore  $\sqrt{28/30} = 0.966$

New response at 20.9% = 20.9%  $\times$  0.966 = 20.2%

If the 10% CO<sub>2</sub> has displaced both N<sub>2</sub> and O<sub>2</sub>, we combine both effects: 20.9  $\times$  0.9  $\times$  0.966 = 18.2%.

\* For simplicity in the calculations presented, these gases are ignored and combined as part of the nitrogen.

**Example 2**, new matrix gas contains 10% helium (He, mw = 4):

Average molecular weight is:  $(10/79) \times 4 + (69/79) \times 28 = 25$ ; therefore  $\sqrt{28/25} = 1.06$

New response at 20.9% = 20.9%  $\times$  1.06 = 22.1%

**Absorption Effect:** Conventional leaded sensors use an alkaline electrolyte, which absorbs acid gases like CO<sub>2</sub> and SO<sub>2</sub>. Under typical atmospheric conditions this is not an issue, but when the measured gas contains percent levels of acid components, they are sucked into the sensor along with additional oxygen, initially causing slightly high readings, but eventually causing the sensor to fail. Therefore, corrections are needed for elevated acid gas levels, and the lead-galvanic cells cannot be used with CO<sub>2</sub> levels above 25%. Conversely, the lead-free sensor uses an acidic electrolyte which is unaffected by acid gases but can be affected by high levels of alkaline gases such as ammonia.

**Calibration with new matrix gas:** The simplest way to avoid the need for mathematical corrections is to calibrate the O<sub>2</sub> sensor with a standard prepared in the new matrix gas. This is especially useful for acid gases, because the absorption effect is difficult to quantify because it depends on the age and conditions of use of the sensor.