Description of ceramic oxygen sensor
Oxygen Analyzer

Introduction

Oxygen sensors based on ceramic oxygen ion conductors are increasingly used in equipment for monitoring and controlling industrial processes. Essential advantages of these sensors include their extremely short response time, extensive measuring range, good temperature resistance, and long-term stability.

Another significant advantage is the low cross-sensitivity of these sensors to other gases, making them particularly suitable for measuring oxygen in mixed gases, humid atmospheres, and combustion processes.

Measurement principle

A ceramic oxygen sensor can physicochemically be characterized as an oxygen ion concentration cell of the type:

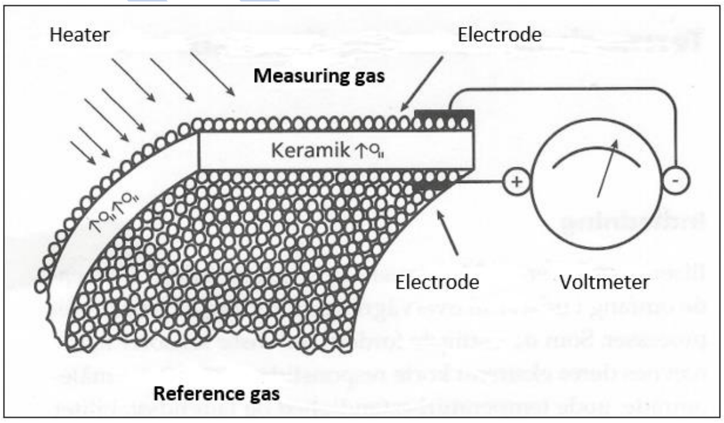
O_2 (pO_2'), Pt – ceramic oxygen ion conductor **– Pt, O_2 (pO_2'')**

The prerequisite for a sensor of this type to work is that the ceramic oxygen ion conductor used as a solid electrolyte has a good conductivity for oxygen ions, the electronic conductivity is minimal, and is entirely gas-tight.

If these conditions are met, the sensor generates a voltage E (EMF) expressed by Nernst's equation:

$$E = \frac{RT}{4F} \ln \frac{(pO_2'')}{(pO_2')}$$

R is the gas constant. T is the absolute temperature. F is Faraday's number. pO_2' and pO_2'' are the oxygen partial pressure on the two sides of the ceramic oxygen ion conductor. Assuming that pO_2'' is known (reference gas), typically atmospheric air (O_2 = 20.9%), and E and T are measured, pO_2'' can therefore easily be calculated from this equation.
The figure shows the principle in a ceramic oxygen sensor:



Materials
By alloying zirconia with either potassium oxide (CaO), magnesium oxide (MgO), or yttrium oxide ($Y2O_3$), a sensor ceramic is obtained, which at temperatures above 500°C is conductive for oxygen ions, and at the same time insulating for electrons.

Depending on the amount of alloyed material, a crystal structure is obtained, which is either pure cubic, or a mixture of cubic tetragonal and/or monoclinic. If the crystal structure is exclusively cubic, the material is called fully stabilized zirconia (FSZ), whereas a material that contains several crystal structures (cubic, tetragonal, monoclinic) is called partially stabilized zirconia (PSZ) from the English abbreviation Partially Stabilized Zirconia.

Generally, fully stabilized zirconia has better ionic conductivity than partially stabilized zirconia, but because the partially stabilized zirconia has significantly higher strength and better thermal shock resistance, it is today the dominant one as a solid-state electrolyte in ceramic oxygen sensors.

The choice of alloy oxide for zirconia in connection with sensor ceramics depends entirely on the use of the oxygen sensor - there are both advantages and disadvantages. Good thermal shock resistance is achieved with magnesium oxide, but this is at the expense of rapid aging at temperatures > 1000°C. Yttrium oxide is relatively expensive, but not least due to several acceptable properties, the most widely used alloying element in sensor ceramics.

Another critical parameter in connection with sensor ceramics is the purity of the material. The presence of, e.g., iron, nickel, cobber and cobalt will contribute to electronic conductivity. The content of other components must be extremely minimal < 0,01. For example, alumina and silica will contribute to the formation of glass phase in the grain boundaries. The result is a reduction in ionic conductivity.

Sensor construction
Most often, the ceramic sensor itself is designed as a tube closed at one end. The tube is both internally and externally coated with a porous platinum electrode and mounted electrode outlet.

Oxygen sensors based on alternative measurement principles can usually only measure dry gases. In contrast to these, measuring equipment can be built with ceramic oxygen sensors for two completely different measuring methods.

In-situ measurement, where the sensor is located directly at the measuring point. The measuring gas is added to the sensor, untreated and in the same condition as in the process. Therefore the method does not require a separate sampling system, and the measuring system requires minimal maintenance.

Extractive measurement, where the sensor is located outside the process itself. The measuring gas is added to the sensor with a pump or an injector system.

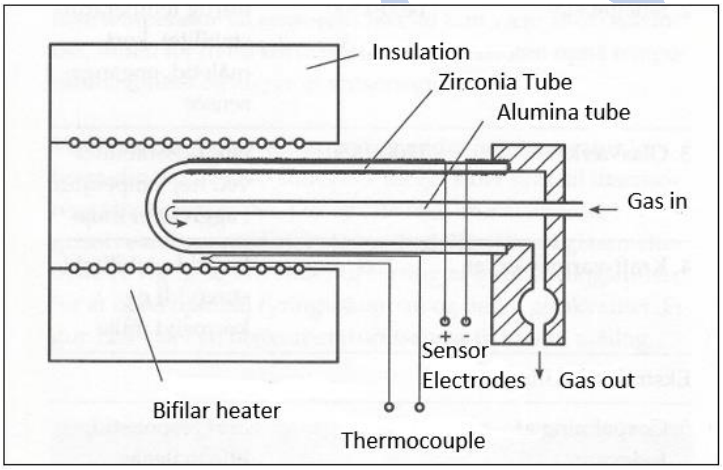
Extractive measurement can be divided into "dry measurement" and "wet measurement", respectively. For dry measure, the measuring gas must be clean and free of moisture. Therefore, a process gas typically needs to be conditioned, meaning it is dried for moisture and cleaned of particles (dust and soot) and other harmful elements before it is added to the sensor. In wet measurement, where the sensor is located immediately outside the process, the measuring gas is added to the sensor untreated and at a temperature above the dew point of the concerned measuring gas.

Sensor Ceramics

Tubes of stabilized zirconia are manufactured commercially by extrusion or by isostatic pressing and are delivered in lengths up to 1000 mm. When using diffusion bonding, a small piece of tube or a thimble of stabilized zirconia can be attached to a carrier tube of the much cheaper alumina ($Al2O_3$). However, a sensor made by assembling different ceramic materials places great demands on the coefficient of expansion of the individual materials, just as dimensional differences affect the thermal sensors thermal shock resistance and stability at high temperatures.

In an in-situ measurement probe, the ceramic oxygen sensor is often surrounded by a protective tube made of $Al2O_3$. The protective tube partly shields the oxygen sensors platinum electrode from being sandblasted, partly to increase the sensor systems' overall heat capacity, thereby reducing the oxygen sensors load for thermo chock.

For extractive measurement, the sensor is built into a separate electric heater which keeps the oxygen sensor at a constant temperature of approx. 700°C The figure shows the construction of an oxygen sensor for extractive measurement:



Practical use of oxygen sensors

As previously described, the ceramic oxygen sensor has a wide range of purposes and is superior to alternative measurement principles in almost all areas. However, when the use so far has been relatively limited, it is mainly because it has only been possible in recent years to produce sufficiently good ceramic materials.

Therefore, it is also natural that examples of practical use are found in the areas where the benefits of ceramic oxygen sensors are exploited. The table shows some typical data for different practical utilizations:

Application	Temperature [°C]	Important features
In-situ measurements		
Automobiles	500-900	Good thermal shock resistance and mechanical strength, short response time, and low price
Molten steel	1400-1500	Fast temperature stability, short measurement time, disposable sensor
Glassworks	1200-1450	Long-term stability at high temperature in aggressive environments
Electricity and district heating	750	Long-term stability in dusty and corrosive environments
Extractive measurements		
Gas packaging of food	750	Short response time on small measuring volume
Welding processes	750	Robustness, measuring range in ppm O_2
Atmospheric control	750	Large measuring range (100% - 0,1 ppm O_2), high measuring accuracy, and long-term stability

In the following, the individual examples are reviewed more detailed:

Automobiles - The oxygen sensor, also called a Lambda probe, is located in the exhaust system of cars, and the sensor signal is used to measure and control the fuel/air ratio supplied to the engine. On the market exists both Lambda probes heated by the exhaust gas alone and probes with a small built-in electric heater to keep the sensor temperature constant.

Great demands are placed on the thermal shock resistance of the Lambda probe (temperature changes of 50-100 °C/second) and mechanical strength, as the probe is exposed to strong vibrations.

Molten steel - When measuring oxygen in molten steel, the sensor itself is inserted into the molten steel. This requires extreme demands on the thermal shock resistance, so this type of oxygen sensor is made of magnesium stabilized zirconia. Due to the very high temperature, the life of the sensor will be 15-20 seconds. Within this short period, the sensor must achieve temperature stability and emit a sensor signal.

Description of ceramic oxygen sensor
Oxygen Analyzer

When measuring oxygen in glass melting heaters and other high-temperature combustion processes, very high demands are placed for the long-term stability of the oxygen sensor. Oxygen measurement in glass melting heaters is essential and is used to control the combustion air to achieve optimal firing economy and the best glass quality. Often it is used in aggressive environments with high dust density.

Electricity and district heating - Oxygen measurement in connection with electricity and heat production is carried out exclusively with ceramic oxygen sensors. Also, here, the purpose is to control the combustion air to achieve optimal combustion economy and minimize the emission of sulfur dioxide (SO_2) and nitrogen gases (NO and NO_2).

Gas packaging of food - Measurement of residual oxygen in connection with gas packaging of food is done during the packaging process itself. Fast measurements are required (10-30 times/minute), and the amount of gas available is a few milliliters (1/1000 liters).

A mixed gas consisting of carbon dioxide (CO_2) and nitrogen (N_2) is typically used in gas packing. The mixing ratio depends on what is being packed. For example, slaughter products are usually packed in 20-30% CO_2, while cheese and coffee are packed in pure CO_2. However, the quality criterion is in all cases that the content of residual oxygen forms a vital part of the ongoing quality control and helps to provide greater certainty for the indication of correct shelf life.

Welding processes - Control of residual oxygen in the shielding gas on the back of a stainless steel weld during the welding process is essential for the ability of the weldings to resist corrosion. When welding ordinary stainless steel, the residual oxygen content must be less than 30 ppm (30 millionths). This can be achieved by using a suitable rear gas tool connected to an oxygen meter. Due to the low oxygen content in the welding gas, the ceramic oxygen sensor for this use is superior to other measurement principles.

Atmospheric control - Oxygen measurement in connection with atmospheric control covers a wide range of utilization, from process monitoring in the production of gases to laboratory measurements in the range of 100% - 0.1 ppm oxygen. There are strict requirements for the sensors measurement accuracy and long-term stability, but here too, the ceramic oxygen sensor is superior to competing measurement principles, not least due to its very large measuring range and less cross-sensitivity to the presence of other gases.

The memo is authored by Henning Jensen, co-author of the book "Material Knowledge - Technical Ceramics". ISBN 87-7756-237-2. Published by the Danish Academy of Engineering, Danish Institute of Technology, the FORCE institutes, Research Center Risø.