Development of a YSZ based Oxygen and Hydrocarbon sensors for combustion control unit

JP. Viricelle *, P. Breuil, G. Tournier, M. Minot, C. Pijolat

Ecole Nationale Supérieure des Mines, Centre SPIN, 158 cours Fauriel, 42023 Saint-Etienne Cedex 02, France.

Abstract

This paper describes the development of a chemical sensor based on a YSZ (8 mol.% Yttrium doped Zirconia) thimble tube associated with three metallic electrodes: one internal in platinum in contact with ambient acts as a reference and two externals ones, one in platinum and the other in gold respectively measure oxygen and hydrocarbon concentrations. This device is dedicated to combustion control in industrial processes. Optimization of this sensor concerning electrodes geometry’s and temperatures in regards of responses to oxygen and carbon monoxide in laboratory conditions is presented.

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1. Introduction

There is still a need of robust gas sensors for automotive or industrial processes, able to measure various gases such as oxygen, hydrogen, hydrocarbons, carbon monoxide, nitrogen oxides, ammonia ... For oxygen, lambda sensors are successfully used in automotive since four decades. For other gases, most of recent developments are also focused on YSZ based sensors. In our laboratory, we have a long experience of planar single chamber sensor where two metallic electrodes, gold and platinum, are set on the same side of an electrolyte layer, beta alumina or YSZ, and in contact with the target atmosphere [1, 2]. Another original device consisting of one internal platinum electrode in air and two external electrodes in gold and platinum in contact with target gas, on both side of a quartz layer was patented: the external platinum electrode at 570°C was mainly sensitive to oxygen while the gold one was sensitive to both

* Corresponding author. Tel.: + 33 4 77 42 02 52; fax: + 33 4 77 42 94 94.
E-mail address: viricelle@emse.fr.
This device was a complex laboratory device. So the objective of this study was to develop a robust sensor based on the same concept, but built on a YSZ thimble tube and able to work in harsh environment, in order to control both oxygen and reducing gases concentrations.

2. Experimental

For the sensor development a YSZ (8 mol.% Yttrium doped Zirconia) thimble tube (outer diameter 6mm, length 100mm) was used, associated with three metallic electrodes (fig. 1). The internal one is deposited by painting a platinum ink in the internal part of the YSZ tube. The external ones were also depositing by painting: the platinum one (5 mm width) is deposited near the closed part of the tube, and the gold one (5 or 23 mm width) was deposited at various distance from the previous one. All connections were reported to the open side of the tube with metallic pastes of the same nature as the electrodes. Two signals (emf (V)) were measured respectively between external gold and platinum electrodes and the platinum internal one: \( \text{emf(Au)} = V_{\text{Au,ext}} - V_{\text{Pt, int}} \) and \( \text{emf(Pt)} = V_{\text{Pt,ext}} - V_{\text{Pt, int}} \).

For the temperature control of the probe, two solutions were used. For the comprehensive study, our device was introduced in a furnace with a thermocouple as shown in Fig. 1 and positioned in order to set the temperature of one external electrode, either gold or electrode, and we focused only on the signal of the considered electrode. This has allowed studying the optimum temperature regarding sensing properties, independently for each electrode. Then, for real application, an external heater has been designed by RB Technology, which allows to set a temperature gradient along the YSZ thimble and thus to set the temperature for each external electrode at the optimum temperature determined previously with tests in a furnace (Fig. 2).

![Fig. 1. Schematic of YSZ thimble tube (100mm length, 6mm external diam.) with external Pt and Au electrodes (internal Pt electrode, not represented inside the tube), in a tubular furnace for laboratory testing.](image1)

![Fig. 2. Temperature profile inside the heater.](image2)
In each case, furnace and autonomous heater, gases in contact with external side were generated with mass flow controllers. The total gas flow was set at 6 l/h. Oxygen content was varied between 1 and 20vol.%, balanced with nitrogen. Carbon monoxide was added in the concentration range 0-300ppm. The internal part of the probe was maintained under static ambient air.

3. Sensor working principle

The concept of the sensor is derived from a combination of two existing types of sensors. For oxygen measurement, the concept is the conventional one, based on YSZ probe with two metallic electrodes (platinum) and a reference chamber (internal part), as for the well-known lambda sensor. If the temperature is set at a sufficiently high value, typically above 600°C, to reach thermodynamic equilibrium of oxygen adsorption and diffusion inside YSZ, oxygen content can be calculated from the measured potential and the Nernst law (1).

\[ \Delta E = \frac{RT}{nF} \ln \left( \frac{PO_2}{PO_2_{\text{ref}}} \right) \]  

where \( \Delta E \) is the measured potential (V), \( T \) the temperature (K), \( R \) the gas constant, \( n=4 \) (electrons involved in oxygen electrochemical reaction), \( F \) the Faraday constant, \( PO_2 \) is the external oxygen pressure, \( PO_2_{\text{ref}} \) is the oxygen pressure in the reference chamber.

For carbon monoxide measurement, a gold additional electrode was added on previous sensor. The sensing principle is the one of a single chamber sensor where the two electrodes of different nature (different catalytic activity) are set on the same side of an electrolyte. In this case, at lower temperature (range 300-600°C), the device behaves as a non-Nernstian sensor, and the difference of potential is the result of different kinetics of the reaction of target gas on the two electrodes [1, 2]. In the present configuration, the potential of gold electrode was measured in regards of reference internal electrode for practical reason, but it could also be measured in regards of the platinum external one.

4. Results

We firstly studied the influence of external electrodes temperatures on their sensitivity to oxygen and carbon monoxide, in order to define adequate temperature which has rise to the temperature profile shown in Fig.2. At 700°C, platinum is only sensitive to oxygen and doesn't present any significant response to carbon monoxide: for example in Fig. 3, a constant signal around -35mV for 3% oxygen is observed. The injection of 100ppm of CO doesn't change. On the contrary, for gold electrode maintained at 370°C, a CO response is observed: the signal is around +65mV under 3% oxygen and falls down to +25mV when CO is introduced (Fig. 3).

The optimum gold electrode size and temperature regarding CO response has been defined through tests in furnace. The maximum CO relative response (emf \( \text{CO}_2 \) – emf \( \text{O}_2 \)) was measured in the range 330-370C depending on gold electrode geometry (Fig. 4). The reported gold temperature is the value taken on the warmer side. The chosen configuration was a wide gold electrode (23mm) at 370°C. Then, the sensor was calibrated versus oxygen content with platinum electrode using Nernst law. For CO response on gold, Fig. 5 shows that the oxygen level influences the emf value, but the relative CO response is almost unaffected by oxygen (in the range 1-5%). CO relative responses have been calibrated (Fig. 6). Hence, as the oxygen level is known using platinum external electrode, gold electrode signal allows determining relative response and finally CO concentrations.
Fig 3: Response of gold (370°C, 23mm) and platinum (700°C) electrodes to 100ppm of CO in a base of oxygen 3% (balanced in nitrogen). Test with external heater.

Fig 4: Relative response of gold electrode to 100ppm CO, versus its temperature (warmer point) and depending on its size: S1: 5mm width – S2: 23mm width (2 probes of each size). Test in furnace.

Fig 5: Response of gold electrode (370°C, 23 mm width) to 100ppm of CO in various bases of oxygen in the range 1.5 to 5% (balanced in nitrogen).

Fig 6: Calibration of CO relative response on gold electrode (370°C, 23 mm width), for various oxygen contents in the range 1.5 to 5% (balanced in nitrogen), (4 calibration tests at O2 3%).

5. Conclusions

In this study, a new YSZ probe with three electrodes was designed and laboratory investigations demonstrated the possibility to measure both the oxygen and CO concentration. Complementary tests have to be performed to check the behavior of other interfering reducing or oxidizing gases in order to fulfill the application of combustion control.

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