

# Characterisation of an oxygen sensor based on In/In<sub>2</sub>O<sub>3</sub> reference electrode

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## Abstract

A potentiometric sensor for measuring oxygen activity in LBE has been developed since 2000 until today at 'Institut Químic de Sarrià' electrochemistry laboratories. This sensor is based on In/In<sub>2</sub>O<sub>3</sub> reference electrode. The last experiments performed with this sensor have been directed to characterise the sensor. For this purpose, the following experiments in stagnant conditions have been performed: effect of the operating temperature from 300 to 500 °C, different covering gases (N<sub>2</sub> + 5% H<sub>2</sub>, Ar 99.999%, and N<sub>2</sub> + 10 mg/L O<sub>2</sub>) and comparison of different solid electrolytes (ZrO<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>/MgO). Long-term experiments have also been performed to see the stability of the signal with time.

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## 1. Introduction

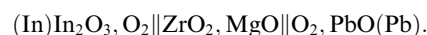
The measure of oxygen activity and its control is a key parameter of the accelerator driven systems (ADS) reactors that use 44.5% Pb–55.5% Bi (LBE) as coolant [1]. Oxygen activity is related with the thermodynamic stability of the oxide layers that protect the structural materials [2,3]. A low oxygen activity will mean the destruction of the oxide layers. A structural material immersed in LBE without a passive oxide layer will be dissolved by the action of LBE, and this dissolution means corrosion [4,5], and all the serious problems related with this phenomenon. In the other side, a high oxygen activity in LBE will produce the formation of solid PbO, which is not soluble in LBE and can generate problems to the LBE flowing.

The measure of oxygen activity is performed using oxygen sensors [6]. In order to have accurate measures of the oxygen activity, it is necessary to have the sensor employed totally characterised. For this reason, it is necessary to know the sensor performance in different environments and the effect on the sensor's signal of metallic impurities dissolved in LBE [7].

In this paper, we show the results obtained with a potentiometric oxygen sensor based on In/In<sub>2</sub>O<sub>3</sub> reference electrode [8]. The experiments performed are directed to characterise the sensor.

## 2. Experimental

The potentiometric oxygen sensor employed is based on In/In<sub>2</sub>O<sub>3</sub> reference electrode, and it is described in a previous work [8]. In electrochemical terms, the sensor is represented by the following equation:



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The oxygen partial pressure in the LBE is related to the sensor electrochemical potential according to the Nernst equation:

$$E = \frac{RT}{4F} \ln \frac{P_{O_2,RE}}{P_{O_2,WE} a_{Pb}^2},$$

where  $P_{O_2,RE}$  is the oxygen partial pressure in the reference electrode ( $\text{In}/\text{In}_2\text{O}_3$ ),  $P_{O_2,WE}$  is the oxygen partial pressure in the working electrode, that is in the LBE, and  $a_{Pb}$  is the activity of lead in the LBE.

The dependence of the electrochemical potential with temperature in the case of oxygen saturation in the lead–bismuth is:

$$E(V) = -0.468 + 4.31 \times 10^{-5} T.$$

Using this sensor, the following experiments have been performed:

- Effect of the operating temperature.
- Effect of different covering gases over LBE.
- Comparison of different solid electrolytes of the sensor.
- Long-term experiments.

All the experiments have been performed in stagnant conditions in an autoclave. The LBE is contained in a ceramic crucible.

### 3. Results and discussions

#### 3.1. Effect of the operating temperature

The effect of the operating temperature of LBE on the sensor has been evaluated from 300 to 500 °C. These experiments have been performed shifting the covering gas from nitrogen + 5% hydrogen to air. We assume that, the potentials recorded when the covering gas is air correspond to oxygen saturation in LBE, because the oxygen content of air is so high (20%) and the volume of LBE is only 15 mL. In this experimental conditions saturation will be achieved in a short period of time. Fig. 1 shows a summary of the experiments performed.

It can be seen how the sensor gives signal at 300 °C. The range of the potential goes from 220 mV in reductive environment ( $\text{N}_2/5\% \text{H}_2$ ) to –190 mV in air. From 350 to 500 °C the maximum value of the potential recorded keeps, approximately, constant. It moves around 300 mV. The minimum value of the potential, that is, the corresponding to oxygen saturation, evolves to more negative values. At 350 and 400 °C, the value of this electrochemical potential is –200 mV. At 450 °C, the potential is –250 mV, and at 500 °C is –438 mV, and, in these conditions, it achieves the theoretical values. In the whole range of temperature tested, the response

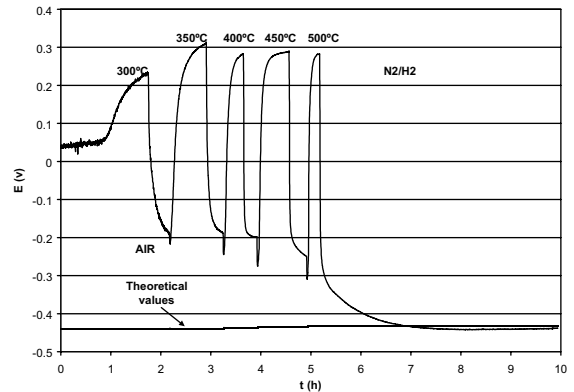


Fig. 1. Electrochemical potential of the sensor in LBE using  $\text{N}_2 + 5\% \text{H}_2$  and air as covering gases at different working temperatures.

of the sensor is fast when the covering gas changes, only few minutes.

The results obtained in this experiment show that, this sensor could be used from 350 °C, because the signal range is so wide. Moreover, the values of the potential achieve the theoretical predictions only at 500 °C. From 300 to 400 °C, the potential in air as covering gas evolves only –10 mV. From 400 to 450 °C, the change in the potential of the sensor in the same experimental conditions is –50 mV. From 450 to 500 °C, the potential changes –180 mV.

These results can be explained by the increase of the ionic conductivity of the solid electrolyte with temperature.

#### 3.2. Effect of different covering gases over LBE

Three different covering gases have been tested independently at 500 °C:

- $\text{N}_2 + 5\% \text{H}_2$ ,
- Ar 99.999%,
- $\text{N}_2 + 10 \text{ mg/L O}_2$ .

These covering gases correspond to a reductive environment ( $\text{N}_2 + 5\% \text{H}_2$ ), to a high purity gas with an oxygen concentration lower than 1 mg/L (Ar 99.999%), and to a gas with a moderate oxygen concentration ( $\text{N}_2 + 10 \text{ mg/L O}_2$ ). The tests have been performed with the same flow of covering gas (40 mL/min), with experimental setups built using the same design, and with different oxygen sensors, previously calibrated. The results obtained are shown in Fig. 2.

We can see how, with  $\text{N}_2 + 5\% \text{H}_2$ , the potential of the sensor keeps constant around 430 mV for a long period of time, more than 160 h. It means that the oxygen partial pressure in the LBE is about  $10^{-42}$  bar. This low

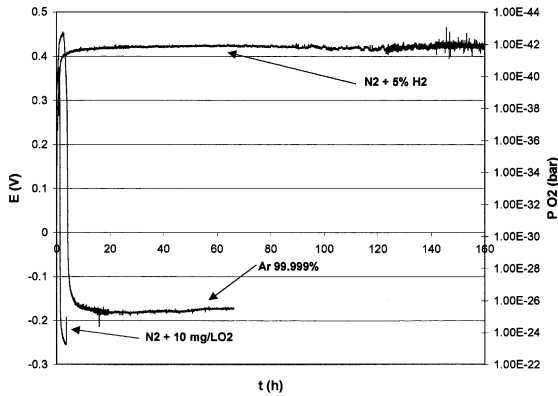


Fig. 2. Electrochemical potential of the sensor in LBE at 500 °C as a function of time using  $N_2 + 5\% H_2$ , Ar 99.999% and  $N_2 + 10 \text{ mg/L } O_2$  as covering gases.

oxygen partial pressure can be expected in a reductive environment as  $N_2 + 5\% H_2$  is.

In Ar 99.999%, the sensor potential keeps constant around 430 mV ( $P_{O_2} \approx 10^{-42}$  bar) for only 3 h. After this time, the potential evolves to negative values, and it indicates that oxygen content of LBE is increasing. The low oxygen concentration in the high purity Ar (<1 mg/L) diffuses into the LBE. Oxygen saturation in LBE isn't achieved due to formation of a lead oxide layer on the LBE surface and to the low gradient of oxygen between the covering gas and the LBE.

In  $N_2 + 10 \text{ mg/L } O_2$ , the sensor potential keeps constant around 370 mV for only 1.3 h. It is necessary to note that the oxygen partial pressure in LBE is about  $10^{-40}$  bar, slightly higher than in  $N_2/H_2$  and in high purity Ar. After this short time, the potential evolves to negative values, indicating diffusion of oxygen into LBE. If we compare this test with the test performed in high purity Ar, we can see several differences:

- The time necessary to detect oxygen diffusion in LBE is lower in  $N_2 + 10 \text{ mg/L } O_2$  than in Ar 99.999%. It indicates that the oxygen gradient between the covering gas and the LBE regulates the oxygen diffusion rate.
- The maximum oxygen partial pressure detected in the LBE is higher when the covering gas is  $N_2 + 10 \text{ mg/L } O_2$  than in Ar 99.999%, but in any case, the oxygen partial pressure corresponding to saturation in LBE has been measured. In both cases ( $N_2 + 10 \text{ mg/L } O_2$  and Ar 99.999%), an oxide layer has been observed on the LBE surface. If the lead oxide is not porous, this layer would avoid the diffusion of oxygen from the covering gas to the LBE, and the potential recorded would be independent of the oxygen concentration of the covering gas tested. In the same way, the lead oxide would feed with oxygen the LBE

and electrochemical potentials corresponding to oxygen saturation would be achieved. These last two facts have not been observed in these experiments. Combining previous results [8] and the results obtained in these experiments, we deduce that the lead oxide layer of the LBE surface is a porous layer. So dynamic equilibrium between oxygen concentration in the covering gas and oxygen partial pressure in LBE can be achieved at a fixed time, and the oxygen partial pressure of saturation in LBE cannot be reached.

### 3.3. Comparison of different solid electrolytes of the sensor

Two solid electrolytes have been compared:  $ZrO_2/Y_2O_3$  and  $ZrO_2/MgO$ . Two sensors build using these solid electrolytes have been tested at 500 °C with  $N_2 + 5\% H_2$ , and air. Fig. 3 shows the results obtained in two different experiments, one with  $ZrO_2/Y_2O_3$  sensor and the other with  $ZrO_2/MgO$  sensor.

We can see how, in both sensors (zirconia/yttria and zirconia/magnesia), the electrochemical potential in  $N_2 + 5\% H_2$  is around 400 mV, that is an oxygen partial pressure of  $10^{-42}$ , and in air the potential is around -430 mV, that is oxygen partial pressure of saturation in LBE. The potentials recorded with  $ZrO_2/Y_2O_3$  show a higher drift that the  $ZrO_2/MgO$  sensor. The  $ZrO_2/MgO$  sensor gives more accurate potentials according to theoretical calculations than  $ZrO_2/Y_2O_3$  sensor. The potentials of both sensors evolve equally when the covering gas changes from  $N_2 + 5\% H_2$  to air.

From this test, it can be concluded that from a practical point of view, either zirconia/yttria or zirconia/magnesia can be used as solid electrolyte for oxygen potentiometric sensors applied to LBE.

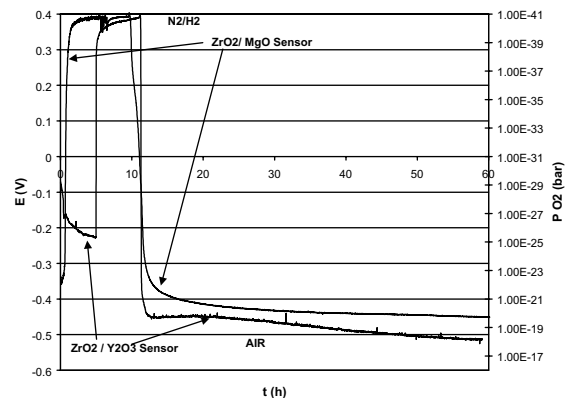


Fig. 3. Comparison of the potentials of the sensors build using  $ZrO_2/Y_2O_3$  and  $ZrO_2/MgO$  as solid electrolytes in  $N_2 + 5\% H_2$  and air as covering gases of LBE.

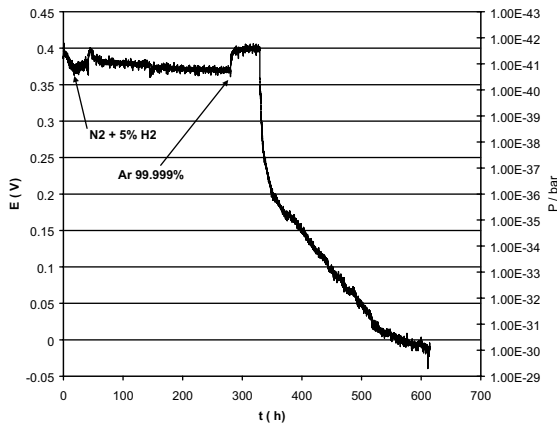


Fig. 4. Electrochemical potential of the sensor in LBE at 500 °C during the first 600 h of a long term experiment. During 200 h, the covering gas has been  $N_2 + 5\% H_2$ , and in the rest of experiment is Ar 99.999%.

### 3.4. Long-term experiments

The sensor has been tested up to 700 h of continuous operation. During 200 h it has been tested in  $N_2 + 5\% H_2$  as covering gas, and in the rest of the experiment the covering gas has been Ar 99.999%. In  $N_2 + 5\% H_2$  the potential keeps constant 380 mV, that is an oxygen partial pressure in LBE of  $10^{-41}$  bar. In Ar 99.999%, the potential slowly evolves to oxygen saturation values in LBE. Fig. 4 shows the results obtained in the first 600 h of operation.

## 4. Conclusions

1. The oxygen sensor shows an electrochemical signal from 300 °C. If the sensor has to be used for performing measurements according theoretical predictions, the recommended operating temperature for this sensor is from 500 °C.
2. The oxygen gradient between the covering gas and the LBE regulates the oxygen diffusion rate. Equilibrium between oxygen concentration in the covering gas and oxygen partial pressure in LBE has been

achieved. The oxide layer formed on LBE surface when oxygen is present in the covering gas, even when high purity gases as Ar 99.999% have been employed. The dependence of the electrochemical potential with the covering gas tested and previous experimental results [8] let us to conclude that the lead oxide layer is porous.

3. It does not exist practically any difference between using zirconia/yttria or zirconia/magnesia as solid electrolyte for oxygen potentiometric sensors applied to LBE.
4. The sensor has been tested in continuous operation up to 700 h. In reductive environment, the signal keeps constant, whereas in Ar 99.999% the potential evolves to oxygen saturation values.
5. In order to get a complete characterisation of the sensor, it is necessary to perform tests in experimental loops.

## Acknowledgments

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