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CALORIMETRIC STUDY OF INTERACTION BETWEEN OXYGEN AND β-Al_2O_3, β-Al_2O_3+Au AND β-Al_2O_3+Pt

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Abstract

In an attempt to improve the understanding of the electrochemical effects observed on an original potentiometric gas sensor, interactions of oxygen with the device were investigated. These calorimetric measurements have evidenced the existence of a weakly bounded endothermal oxygen species. Moreover these species may be regarded to be responsible for the electrical response developed by the sensor. Such results, which are in agreement with a previously proposed model, validate the underlying hypothesis and shed light on the role of oxygen in the sensor's responses.

Keywords: β-alumina, endothermal oxygen species, gas sensor, oxygen

Introduction

As part of our research activities on new gas sensors, we have developed an original device which consists of a solid electrolyte (Na-β-alumina) associated with two different electrodes, one in platinum, the other in gold, located in the same gas mixture [1–4].

Generally speaking, the electromotive force delivered by the sensor between the two electrodes depends on the surrounding gases (nature, partial pressure) and on the working temperature.

The potentiometric response read *vs.* oxygen pressure is particularly significant of the role that can be attributed to this gas on the behaviour of this device [5, 6] (Fig. 1).

Electrochemical phenomena producing such electrical signals have already been modelled with some capacitance effect occurring at the electrode-solid electrolyte interface [5, 7].

In fact the validity of this model based on the competitive adsorption of several chemisorbed oxygen species is correlated to the existence of weakly bound species characterised by a positive enthalpy of formation.

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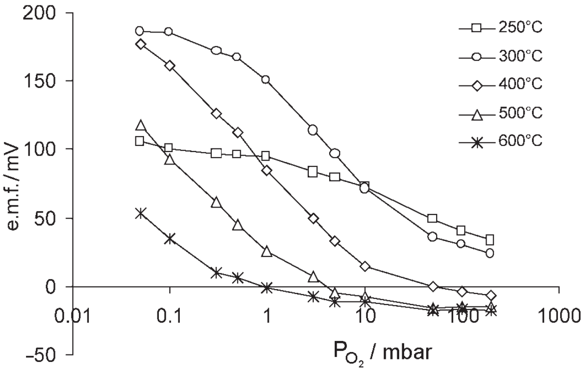

Fig. 1 Electrochemical response of the sensor *vs.* oxygen partial pressure and temperature

In order to verify such a hypothesis, we have chosen to study the interaction between oxygen and the various materials of the sensors by a calorimetric method. This paper intends to describe and analyse the results obtained with this technique.

Experimental

Experiments have been conducted on a Tian & Calvet calorimeter (Setaram High Temperature). The reactor is made up of two identical quartz tubes (external diameter: 17 mm) respectively placed in the two microcalorimetric elements. The first tube will be the measurement cell and will receive the samples while the second, empty one, will be considered as a reference cell.

These two tubes are connected to the same gas circuit that includes a vacuum pump, microleak valves and gauges used for gas introduction and pressure control since experiments are carried out under static conditions (Fig. 2).

Calibration has been done between 0 and 2 mW with various Joule effects produced by an electrical resistance of 500 Ω; we have verified that the output voltage of the calorimeter is proportional to the power dissipated by the Joule effect and the coefficient of proportionality (11.1 mV mW^{-1}) does not depend on working temperature.

In consideration of the electrical responses read on the sensor, we have restricted our study to the pressure and temperature range involving the most significant sensor response variations; i.e. with oxygen pressure enclosed between 0.1 and 100 mbar and limited to the 200–400°C temperature range.

Studied samples

As described previously, the sensing device is a juxtaposition of several materials, namely, a solid electrolyte (Na-β-alumina) in contact with two metallic electrodes, one in platinum, the other in gold. In order to study such a configuration and to appreciate the exact role of each material, we have chosen to test separately the β-alumina, gold, and platinum and besides β-alumina associated with each metal.

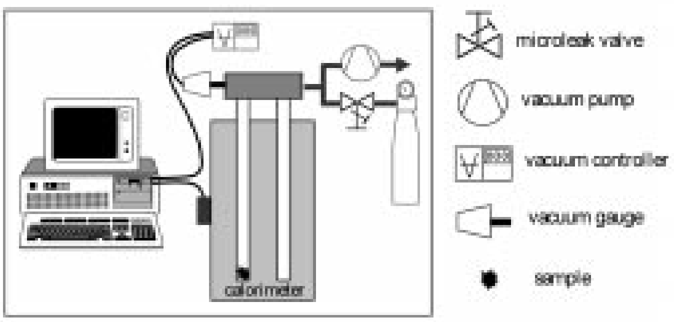

Fig. 2 Schematic view of the experimental set-up

β-alumina

Samples of β-alumina used were pellets of powder [8] (200 mg) of relatively small specific surface (<1 m^2 g^{-1}) sintered at 1050°C for one h. Experiments have always been conducted using three pellets (600 mg).

Metals

Concerning gold and platinum, we have studied metallic sheets (0.1 mm thick) with a nominal area close to 10 cm^2. The surface of these sheets may be considered as greatly higher than those of the sensors electrodes (~15 mm^2).

β-alumina associated with metals

In this case, we have used pellets of β-alumina partially covered with a thin sputtered metal layer (~500 nm), as it is for the sensors [5].

Experimental procedure

Before the experiments, the calorimeter was stabilized at the working temperature with a very small temperature oscillation (<0.3°C). The samples were placed in the measurement cell, and the system is stabilized again for 12 h under a controlled residual pressure of oxygen (0.1 mbar). The experiments were then conducted, introducing pure oxygen in the gaseous circuit. Several pressure variations were chosen: 0.1 to 1, 0.1 to 10, 0.1 to 50, and 0.1 to 100 mbar. After each gas injection and stabilisation of the calorimetric signal, oxygen was pumped back to the pressure of 0.1 mbar.

Results

In order to evaluate the symmetry of the calorimetric device, we have introduced various pressures of pure oxygen without any sample in the measurement cell at several temperatures. The results obtained are given in Fig. 3. We can note that the gas injections produce an exothermic signal in the measurement cell with regard to the refer-

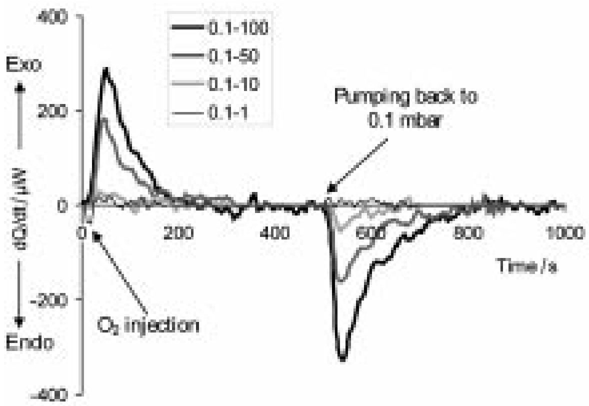

Fig. 3 Reference signal (empty cell) recorded at 300°C for various oxygen pressure variations

ence cell. This signal is perfectly reversible and we observe an endothermic effect when pumping back to 0.1 mbar. Moreover, it increases with the oxygen pressure admitted, to attain a maximum heat flow of 300 µW for a 0.1 to 100 mbar injection.

We have verified that the working temperature only slightly affects these results. In all cases, these curves will be used as reference signals, in particular for the evaluation of the reaction enthalpy.

β-*alumina*

Figure 4 shows the calorimetric signal recorded at 300°C on β-alumina pellets represented on curve (a) for an oxygen pressure variation from 0.1 to 10 mbar (b). It may be compared to the curve (c), which is the reference signal noted for the same experimental conditions without any sample.

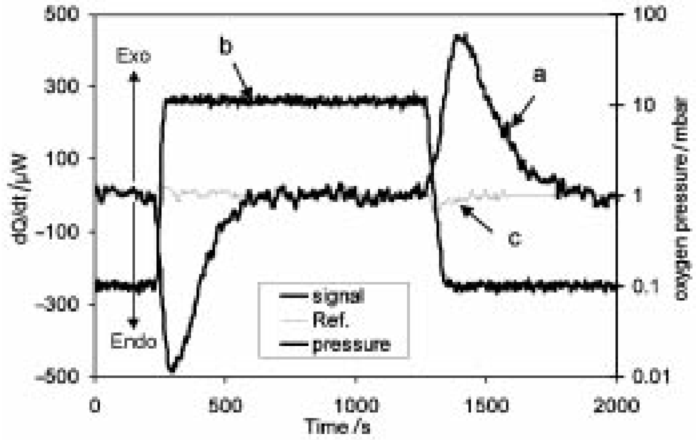

Fig. 4 a – calorimetric signal; b – recorded at 300°C for a 0.1 to 10 mbar oxygen pressure variation; c – comparison with reference signal

This calorimetric curve is representative of all the results obtained with β-alumina pellets, namely, an endothermic signal after oxygen admission and a same intensity exothermic signal when pumping back to 0.1 mbar.

The amplitude of the signal depends on the oxygen pressure variation, it increases from 350 μW for a weak oxygen injection (0.1 to 1 mbar) and reaches a ceiling to 500 μW for injections higher than 10 mbar. However, the length of the signal is weakly affected by the admitted oxygen quantity and is always about 400 s.

For a 0.1 to 10 mbar oxygen injection (Fig. 4), we can note that the reference curve (c) is negligible with regard to the heat flow produced by the interaction between oxygen and β-alumina (a). Consequently, the noticed endothermic signal can only be attributed to an endothermal reaction between oxygen and β-alumina.

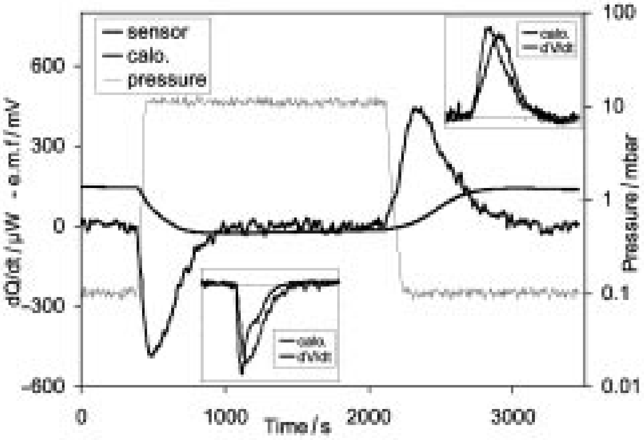

Fig 5 Comparison between heat flow and response of a sensor set in the same gas phase at 300°C

On the other hand, the length of the heat flows may be compared to the potentiometric response time of a sensor put in the same gas phase. These results are given in Fig. 5 and show a rather good agreement between the calorimetric signal and the derivation *vs.* time of the sensor response.

Metals

In opposition to the previous results, the measurements carried out on gold and platinum sheets have not shown any heat flow variation with the various oxygen pressure changes. At least, for the experimental conditions and with the operating sensitivity range used for the β-alumina samples.

β-*alumina partially covered with metals*

Generally speaking, and for the same experimental conditions, the curves read on β-alumina pellets partially covered by metal show a lower maximum than pellets without metal. In order to explain this difference, we have represented in Fig. 6 the energy exchanged *vs.* the oxygen pressure variation and the metal nature. This exchanged energy has been calculated by geometric integration of the heat flow after correction with the reference signal.

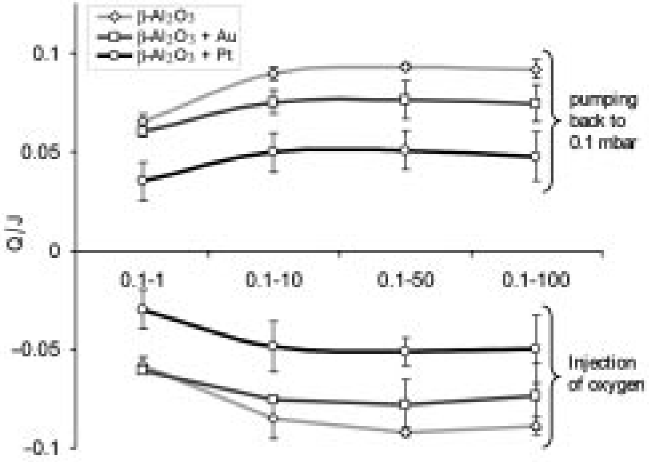

Fig. 6 Energy exchanged by samples *vs.* oxygen pressure variation at 300°C

We ascertain that metals perceptibly reduce the exchanged energy quantity, moreover, platinum effects are more important than the gold one. However, we can verify that these phenomena are perfectly reversible and seem to stabilize beyond an oxygen pressure of 10 mbar.

The fact that platinum seems more active than gold agrees with an asymmetrical effect on the electrodes. This effect could explain the electrochemical potential, which appears between the sensor electrodes.

Working temperature influence

The same experiments conducted for various temperatures included between 200 and 400°C indicate an increasing of the exchanged energy with temperature. This is illustrated in Fig. 7 for an oxygen pressure variation from 0.1 to 100 mbar. On β-alumina, such a result agrees with an endothermic effect, for which temperature promotes the reaction and increases the number of species produced.

Interpretation of results

The calorimetric measurements have evidenced some endothermal effects when oxygen is injected onto the materials. Moreover, these fully reversible processes are certainly responsible for the electrostatic potential developed by the sensor.

Interest of these calorimetric results is enhanced to account for a model proposed to fit the whole electrical responses read on the sensor in various gaseous surrounding. This

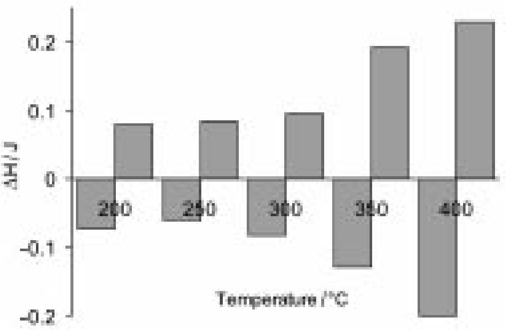

Fig. 7 Energy exchanged for a 0.1 to 100 mbar oxygen injection on β-alumina *vs.* temperature

is particularly important that the validity of the model is linked to the existence of a weakly bound species characterised by an endothermal formation process.

It should be noticed that the presence of mobile or weakly bonded oxygen species has already been mentioned many times in literature; that is the case for systems calling upon metal oxides or systems in which a metal is associated with a solid electrolyte [9–11]. Some authors have also, within the frame of studies conducted on oxygen adsorption on metal oxide surfaces, proposed the existence of endothermal-type species [12–14].

Results obtained with gold and platinum tends to show that the endothermic phenomenon preferentially occurs on β-alumina. The signal of the metal-coated alumina pellets is indeed always weaker, mainly with platinum. Great differences observed between the samples cannot be attributed to a simple specific surface difference and are linked to the metal nature. On the other hand, we have not detected any calorimetric signals with the metallic sheets.

Consequently, with regard to the calorimetric results noted on the various samples, we propose that a chemical interaction between oxygen and β-alumina takes place, producing weakly bounded endothermal oxygen species. Then, such mobile and highly reactive species, would chemisorbs on active sites at the metal/solid electrolyte interface with an exothermic reaction.

It is usually accepted that a fast and reversible dissociative adsorption of oxygen on vacant sites of platinum surface takes place at elevated temperatures. However, in the case of gold, even if opinions are divided, oxygen adsorption is questionable [16, 17].

Anyway, platinum effects are much more important than gold ones and would induce a significant asymmetric effect between the two metallic electrodes.

If s_β is an adsorption site at the surface of the β-alumina, and $(\text{O–s})_\beta$ the endothermal species, the reaction process may be expressed as follows:

$$\frac{1}{2}\text{O}_2 + \text{s}_\beta \leftrightarrow (\text{O–s})_\beta \qquad \text{with } \Delta H_1 > 0 \tag{1}$$

[1] - oxygen – β-alumina endothermal interaction

then, the chemisorption of such species on an active site σ associate to the metal may produce the charged species O^--σ:

$$(\mathrm{O{-}s})_{\beta} + (\sigma + e^{-})_{\mathrm{Me}} \leftrightarrow (\mathrm{O}^{-}\text{-}\sigma)_{\mathrm{Me}} + \mathrm{s}_{\beta} \qquad \text{with } \Delta H_2 < 0 \tag{2}$$

[2] - chemisorption at the β-alumina – metal interface

If n_1 and n_2 are respectively the quantity of species produced by reaction (1) and (2), the calorimetric results presented in Fig. 6 imply:

$$n_1|\Delta H_1| + n_2|\Delta H_2| > 0 \;\text{ then }\; n_1|\Delta H_1| > n_2|\Delta H_2| \;\text{ and }\; (n_2|\Delta H_2|)_{\mathrm{Pt}} > (n_2|\Delta H_2|)_{\mathrm{Au}} \tag{3}$$

The last condition agrees with the fact that oxygen adsorption on platinum electrode is more significant than on gold one. And this activity difference is able to explain the electrochemical potential, which appears between the sensor electrodes.

Conclusions

This work has contributed to a better understanding the nature of interactions between oxygen and the various materials used for our potentiometric gas sensor.

Calorimetric investigations have evidenced endothermal interactions of oxygen with β-alumina. Even if the exact nature of the endothermal oxygen species remains an open issue, its formation seems to be the first step of the electrochemical mechanism involving the sensors electrical response.

The proposed mechanism is keeping with the three-phase-boundary concept often put forward about zirconia-based oxygen sensors. It involves an associatively oxygen adsorption on the solid electrolyte followed by a diffusion to the metal/solid electrolyte interface and a dissociative reaction with metal.

With such a hypothesis, metal only plays a part as an electron source and a measuring electrode.

All these results are in good agreement with the model previously proposed and have allowed us to validate underlying hypothesis as endothermal oxygen species existence. Other aspects as surface potential, influence of the electrode size and nature are actually studied. These experiments would allow us to improve the understanding of the various electrochemical phenomenon occurring on such devices.

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