



# Electrochemical Sensors for CO/NO<sub>x</sub> Detection in Automotive Applications

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**Abstract.** Recent progress in the development of a  $\beta$ -alumina gas sensor for automotive applications is reported. The sensing device consists of two solid electrolytes (namely a thin film of sodium sulfate deposited on  $\beta$ -alumina by appropriate treatment in a gaseous atmosphere), with two electrodes having different catalytic properties, one made of platinum, the other of gold. The  $\beta$ -alumina component was prepared as sintered pellets by pressing and as thick films by screen-printing. The electrical response of these materials at different temperatures in the range 300° to 800°C and under various gases (CO, NO, NO<sub>x</sub>) with dilution in pure air in the range 5 ppm to 5 vol% was investigated and studied as a function of the preparation technique. The dense ceramic and the thick film designs behave similarly. A sensor prototype based on the thick film design was then developed and tested. All the experimental results prove that the sensor can be successfully used for selective detection of CO and NO<sub>x</sub>. The selectivity results from an appropriate choice of the working temperature of the sensing element. At low temperatures (300 to 400°C) NO<sub>2</sub> can be selectively detected in the presence of CO; the opposite happens in the higher temperature range (550 to 650°C).

**Keywords:** electrochemical sensor,  $\beta$ -alumina, CO/NO<sub>x</sub> detection, screen printing, selectivity

## 1. Introduction

World wide recommendations and laws for limiting environmental pollution are becoming more and more strict for both industrial and domestic sources of pollution [1]: public organizations for environmental control require new tools for a more effective monitoring of emissions. Many investigations are therefore devoted to develop new gas sensors able to selectively detect various gases such as CO, SO<sub>2</sub>, NO<sub>x</sub>, HC, especially in exhausts from combustion processes [2].

The largest application of these sensors is expected to be in automobiles; the automotive use ranges from monitoring air quality in the passenger compartment to measuring exhaust gas emissions for engines and

emissions control, and for on board diagnostic (OBD) of the efficiency of catalytic converters.

Today the most common industrial gas sensors available on the market are based on semiconductor oxides like tin dioxide and their detection principle is based on the variations of their electrical resistance with the surrounding atmosphere. When tested for motor vehicle applications, these devices revealed the disadvantage of responding to CO and NO<sub>2</sub> in an opposite sense that is prejudicial to the efficient operation. In fact, these two gases induce opposite variations of the electrical conductance. CO acts as a reducing gas and therefore conductance increases, whereas NO<sub>2</sub> being an oxidizing gas leads to a conductance decrease. Thus the response of SnO<sub>2</sub>-based sensors could be sometimes very low even if in

the presence of an atmosphere at high CO and NO<sub>2</sub> concentration.

Some other semiconductor sensors for NO<sub>x</sub> detection have been proposed in literature, e.g. based on WO<sub>3</sub> [3] or on doped TiO<sub>2</sub> [4]. Also in these cases the influence of NO<sub>2</sub> presence on the sensing performances, for example in NO detection, was not clearly explained. In addition to these sensors, a great deal of research has been also carried out on potentiometric sensors, like zirconium oxide for O<sub>2</sub> monitoring for automotive application. This kind of sensors has been recently used for NO<sub>x</sub> detection by combining two ZrO<sub>2</sub> cells [5] or by a single ZrO<sub>2</sub> cell with one platinum electrode covered by a metal oxide film which modifies the platinum activity [6]. This last sensor, however, shows at 500°C a positive e.m.f. for NO<sub>2</sub> and a negative e.m.f. for NO.

A new NO sensor obtained by a thick film technology has been also reported, in which a separate section for the reference electrode was not required [7]: however, in this study, the variation of sensor selectivity as a function of the temperature of the sensitive element was not investigated.

Some authors [8] have studied pure sodium nitrate for the detection of NO<sub>x</sub> and sodium carbonate for the detection of CO<sub>x</sub>; but the major problem connected with such devices seems to be their unstability, specially in the harsh conditions of the exhaust (high temperatures, presence of water vapor).

On the basis of such electrochemical principles, a new sensing device using SO<sub>2</sub> pre-treated β-alumina as sensing material has been recently proposed and patented [9] for detection of SO<sub>2</sub> and CO. It uses the electrochemical properties of some solid electrolytes like β-alumina and sodium sulfate associated with two electrodes with different catalytic properties, for instance one made of platinum, the other of gold. Unlike conventional electrochemical devices like zirconia sensors for oxygen [10,11] which are based on two separate gas atmospheres, this sensor includes two electrodes which are in contact with the same gas mixture.

This sensor also being sensitive to other gases, namely NO<sub>2</sub> and NO, a model for explaining its sensing ability (Fig. 1) can be proposed and extended to reductive or oxidant gases [12]. The created potential is controlled by the electrochemical reaction of oxygen at each electrode (reaction 1) and the difference of potential is generated by a difference of consumption of adsorbed oxygen at one electrode

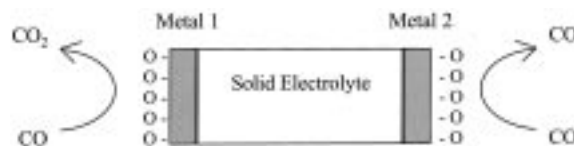


Fig. 1. Scheme of the electro-catalytic principle of the patented device.

compared to the other one (for instance, reaction 2 or 2', in the case of CO or NO, respectively)



The e.m.f. measured under an oxygen/nitrogen gas flow depends on the difference of O<sup>2-</sup> concentrations on the two electrodes by a thermodynamics model and the variations of the e.m.f. with the pollutants gases like CO, NO, NO<sub>2</sub> depends on the O<sup>2-</sup> concentrations by a kinetic model.

The aim of this paper is to present recent progress in this sensor development, particularly on the preparation of the sensing material, on the structure of the device and on the response of these sensors to CO, NO and NO<sub>2</sub>.

## 2. Material Preparation

### 2.1. Structure of the Sensing Devices

This original device, which has been patented [9], uses a solid electrolyte associated with two electrodes with different catalytic properties, one made of platinum, the other of gold (Fig. 2). The conductor

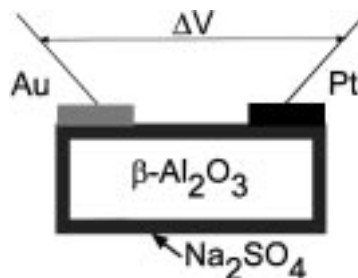


Fig. 2. Structure of the sensing devices.

material between the two electrodes is obtained by a  $\text{SO}_2$  pretreatment of  $\beta$ -alumina. This treatment yields a sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) film which becomes a part of the ionic conductor. This structure was found to limit crack formation due to allotropic modifications which occur in the temperature range 200 to 300°C with pure sintered sodium sulfate. In fact, it can be reasonably supposed that  $\text{SO}_2$  adsorption on the surface  $\text{Na}^+$  ions of  $\beta$ -alumina lattice gives rise to a thin and not completely dense layer of sodium sulfate; the porosity of this thin film is able to dampen the mechanical constraints involved in the allotropic transformation of  $\text{Na}_2\text{SO}_4$ . Consequently, the first goal in using a thin sodium sulfate film supported on  $\beta$ -alumina is the increasing of stability for the electrical properties. The other advantages connected to the presence of this film are the protection of  $\beta$ -alumina from undesired reactions with water vapor and  $\text{CO}_2$  (for instance, carbonate formation) and also the improving of the sensor sensibility to pollutants.

It was verified that the catalytic activity of metal electrodes is higher when they are supported on  $\text{Na}_2\text{SO}_4$  film than when they are directly deposited on  $\beta$ -alumina.

In all cases presented in this paper, the sensing devices consist of  $\beta$ -alumina covered with a film of sodium sulfate and two electrodes, one made of platinum, the other of gold. For the studies on sensing materials before sensor production, two types of samples have been tested: sintered pellets obtained by cold pressing of  $\beta$ -alumina powders and  $\beta$ -alumina thick films obtained by screen printing. The thick films have been deposited on two types of substrates: on standard pure  $\alpha$ -alumina substrates for the material tests and on appropriate complex substrates for the development of sensor prototypes (Fig. 3).

Even if the final goal is the preparation of thick film sensor devices appropriate for automotive applications, the investigation on sintered materials is necessary as a reference and for the validation of the  $\beta$ -alumina synthesis.

## 2.2. Synthesis of $\beta$ -Alumina Powder

Aluminum isopropoxide was hydrolyzed at 80°C in an aqueous solution of sodium oxalate, yielding an amorphous precipitate which was oven dried at 105°C. Its crystallization was observed at 1115°C (heating rate of 10°C/min) by DTA and the final product was identified by XRD as a mixture of  $\beta$ - and

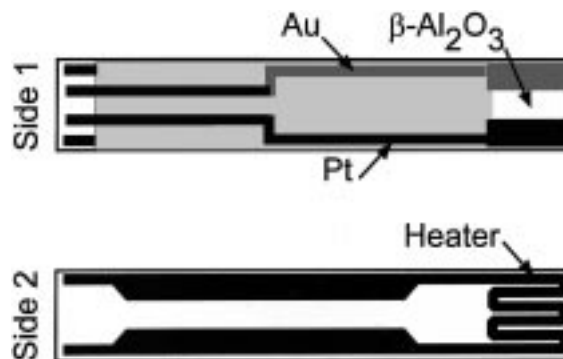


Fig. 3. Thick film sensor prototype with the sensing material on one side (with gold and platinum electrodes) and the platinum heater on the other side.

$\beta''$ -alumina (JCPDS files 31-1263 and 31-1262, respectively).

The amorphous powder was therefore calcined at 1200°C for 30 min in order to obtain a well-crystallized product, showing a negligible residual weight loss. After calcination, the powder presented agglomerates having a mean size of about 45  $\mu\text{m}$ . A grinding step of an alcoholic suspension of this powder was thus performed in a planetary mill, to obtain a fine powder with mean particle diameter of about 5  $\mu\text{m}$ . This powder was used for preparing the sensitive elements as sintered pellets or as thick screen-printed films.

## 2.3. Sintered Material

Pellets were obtained by cold uniaxial pressing followed by isostatic pressing at 200 MPa. These pellets were then sintered at 1650°C (soaking time of 5 min) using a thermal cycle optimized for this material, with a limited stay at temperatures higher than 1200°C to minimize the sodium oxide loss due to volatilization.

The sintered pellets had a high final density of 99.5% of the theoretical value and a mean pore diameter of about 0.005  $\mu\text{m}$ , as determined by Hg porosimetry.

After surface polishing, the mechanical behavior of the sintered bodies was evaluated by microhardness and flexural tests. The microhardness was measured by a Vickers microindenter under different applied loads (1.961; 2.942; 4.903 N); the flexural strength was obtained by a biaxial flexural tests, using a

loading cell of 1 kN and a crosshead rate of 0.1 mm/min.

The microhardness was  $980 \pm 90$  HV and the flexural strength was  $300 \pm 30$  MPa: these values are close to those typical of  $\alpha$  alumina substrates for electronic packaging.

#### 2.4. Thick Film Preparation

A hand operated screen-printing equipment with a fabric meshed screen was used to prepare thick  $\beta$ -alumina films having an area of about  $0.4 \text{ cm}^2$  and a thickness of  $150 \mu\text{m}$  on  $\alpha$ -alumina substrates, using an appropriate ink. For this purpose, calcined  $\beta$ -alumina and a sodium aluminosilicate glass powder, having a softening temperature of about  $780^\circ\text{C}$ , were first mixed in an alcoholic suspension in a planetary mill. The glass powder was added to aid the film adhesion to the substrate during the heat treatment. Mixtures having different  $\beta$ -alumina/glass weight ratios were prepared, namely 50:50, 60:40 and 75:25, in order to investigate the influence of the glass content in the film on the electrical responses.

After drying, ceramic mixtures were mixed with an organic vehicle formed by a volatile organic liquid containing a polyvinylacetate for adjusting the ink viscosity, and mixed in a ball mill for several hours. The total inorganic/organic weight ratio was about 2:1. Finally, the inks were deposited on the  $\alpha$ -alumina substrates through the fabric screen.

After drying in air at room temperature, the films were heat treated up to  $1000^\circ\text{C}$  (soaking time of 1 h), controlling the heating and cooling steps in such a way as to achieve a good adhesion to the substrate and avoid crack formation. A slow cooling rate was adopted between  $1000^\circ$  and  $700^\circ\text{C}$ , in the softening range of the glass. Even if this secondary component of the ink increased the adhesion properties of the film, the presence of a glassy phase can lead to local differential thermal contractions during cooling and consequently to the inhomogeneous shrinkage of the films. In addition, while the organic portion is eliminated by combustion during heat treatment, the glassy phase still remains at the end of the process as a component of the sensitive film, preferentially located at the  $\beta$ -alumina grain boundaries and in the intergranular porosity. Its presence is important for the electrical response of the material, as described below.

### 3. Electrical Tests on Laboratory Samples

#### 3.1. Preliminary Measurements

A special testing bench was developed for the electrical measurements. It allows the recording of the electrical response of the materials at different temperatures in the range  $300^\circ$  to  $800^\circ\text{C}$  and under various gases ( $\text{CO}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ) with dilution in pure air in the range 5 ppm to 5 vol%. During this investigation the tests were performed in the range of 0.5 ppm to 0.2 vol%. The exact control of the different concentrations is set with massflowmeters and measured with analytical apparatus: I.R. analyzer for  $\text{CO}$  and  $\text{NO}$  and U.V. chemiluminescence analyzer for  $\text{NO}_x$ .

This bench includes two test cells: one has a furnace, in order to test the materials with mechanical points made of gold as electrical contacts; the other is a small glass cell for testing sensing devices with their own heater. This testing bench is controlled by a computer.

The two metallic electrodes were prepared by sputtering for most of the experiments. Because of the importance of the two electrodes for the sensor behavior, special attention was given to the deposition conditions of the gold and platinum thin films. The parameters considered were thickness, area, mechanical adhesion and impurities.

The electrical e.m.f. which results between the two electrodes was measured versus temperature or time at a fixed temperature. Typical responses versus time to injection of 300 ppm  $\text{CO}$  at  $500^\circ\text{C}$  are reported on Fig. 4 for the sintered material and on Fig. 5 for a thick film deposited onto a standard ceramic substrate ( $\alpha$ -alumina).

The response time for reaching 90% of the final signal value is about 30 s. Considering the test conditions (flow = 5 l/min; cell volume = 0.5 l), it can be reasonably supposed that the response time of the sensors will be sufficient when they will be directly placed in atmosphere for monitoring, without the dead space of the apparatus. In addition, the recovery times and sensitivities (100 to 200 mV) are appropriate for the proposed application.

The sensor response to second injections of  $\text{CO}$  showed that the samples do not exhibit any memory or hysteresis effect (irreversible adsorption). Similar experiments with long injections of  $\text{CO}$  (few days) show the absence of signal drift.

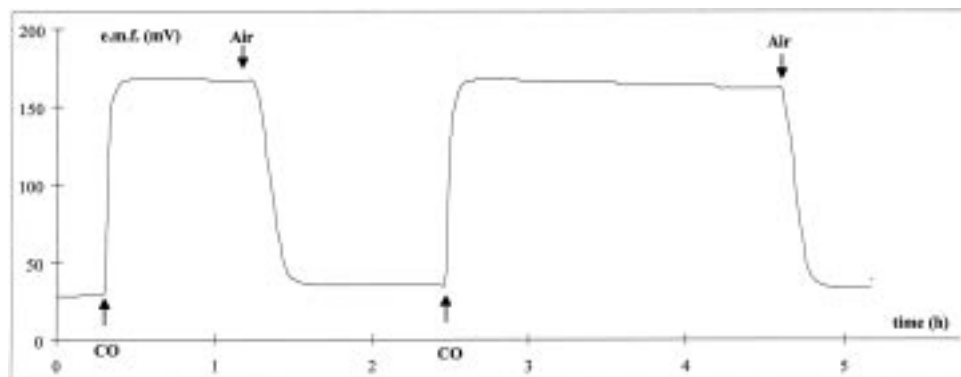


Fig. 4. Typical electrical response of a sintered material ( $\beta$ -alumina cold pressed at 200 MPa; annealing at 1400°C). Two injections of 300 ppm CO (repeatability and reversibility).

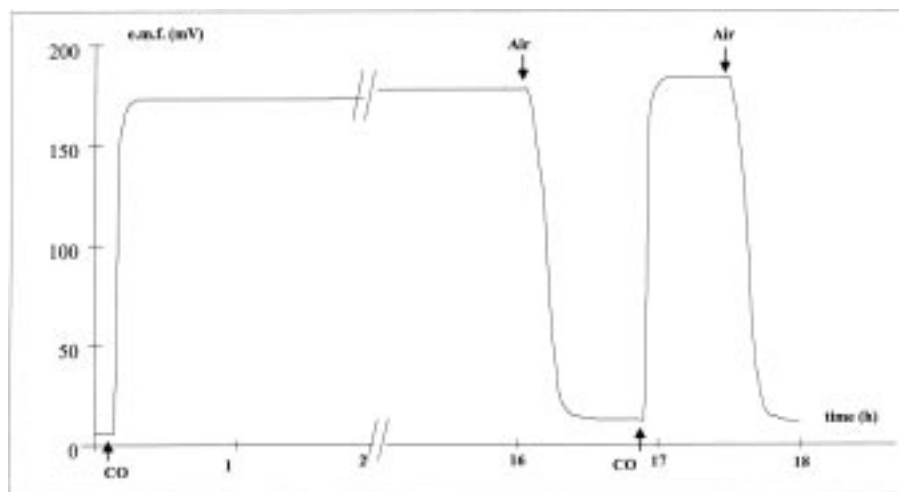


Fig. 5. Typical electrical response of a thick film. Elaboration conditions: 60%  $\beta$ -alumina/40% glass; 900°C annealing. Two injections of 300 ppm CO: repeatability, reversibility and long term stability.

A comparison between the electrical responses of the two types of samples as a function of temperature is reported on Fig. 6. In both cases, the response to CO is basically the same.

Therefore, taking in account that thick film technology is more appropriate for technical and industrial applications, the research was focused on the thick film development.

### 3.2. Electrical Tests on Thick Films

Many parameters have been investigated and optimized for yielding high-performance thick films, namely the composition and softening temperature of the binder (a sodium aluminosilicate glass was

used), the  $\beta$ -alumina/binder weight ratio, the particle size distribution of their mixture, the composition (organic/inorganic component ratio, type and amount of the liquid vehicle and the rheological agent) and viscosity characteristics of the ink, the thermal cycle and the annealing temperature. After this optimization step, an extended investigation was performed on samples prepared under fixed conditions (mixture of 60 wt%  $\beta$ -alumina and 40 wt% glass; annealing at 900°C, SO<sub>2</sub> pretreatment).

The first important result is the fact that the temperature dependence of the sensitivities is largely dependent on the different gases present in the atmosphere. Figures 7 to 9 show the variations of the electrical signal (e.m.f.) under various concentra-

tions of CO, NO and NO<sub>2</sub> at three temperatures: 320°, 520° and 720°C. At low temperatures (Fig. 7), the three gases produce negative signals, relative to that measured under pure air (Pt electrode as positive connection and Au electrode as negative connection). When the temperature increases, the signal becomes positive under CO, very weak under NO and remains negative under NO<sub>2</sub>.

At intermediate temperatures (Fig. 8), the devices show a large positive response to CO, a negative response to NO<sub>2</sub> (only for high concentrations) and a very slight response to NO.

At high temperatures (Fig. 9), there is essentially only a positive response to CO (no signal for NO and very low negative response to NO<sub>2</sub>).

These results suggest that it is possible to detect selectively CO and NO<sub>2</sub>. At low temperatures (300° to 400°C), NO<sub>2</sub> can be detected with a good selectivity,

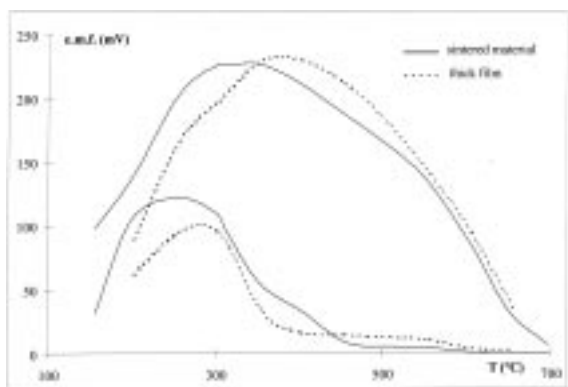


Fig. 6. Electrical response versus temperature for a sintered material and a thick film. Comparison between pure air and CO 300 ppm.

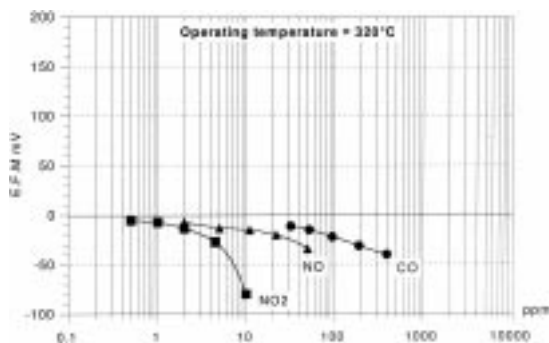


Fig. 7. Electrical response (EMF: electrical potential between the two electrodes) versus gas concentrations of CO, NO and NO<sub>2</sub> at 320°C.

for instance few ppm in the presence of 100 ppm of CO. On the contrary, at high temperatures (600 to 700°C), it is possible to detect CO in the range 10 to 100 ppm and with a good selectivity with respect to NO<sub>x</sub>. This can be seen in Fig. 10 for the response of a thick film at 650°C for two injections of 500 ppm CO (Fig. 10(a)) and for the same injections of CO added with 70 ppm of NO<sub>2</sub> (Fig. 10(b)). The signal is decreased from about 145 to 125 mV but the detection is still possible. The peak observed at the first injection on Fig. 10(b) can be explained by the laboratory experimental conditions which affect and limit the response time due to the dead space in the testing apparatus. This result must be compared to those obtained with semiconducting oxide sensors which present very large decreases in the electrical conductivity under few ppm NO<sub>2</sub> [13] and consequently these devices are not suitable for automotive applications.

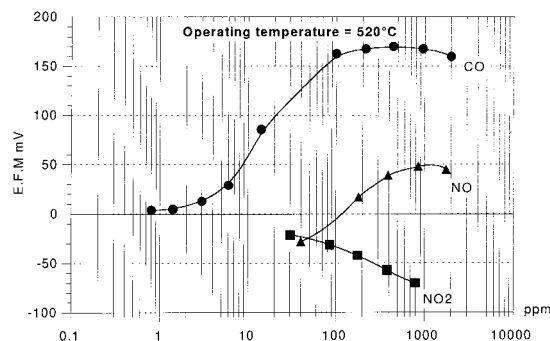


Fig. 8. Electrical response (EMF: electrical potential between the two electrodes) versus gas concentrations of CO, NO and NO<sub>2</sub> at 520°C.

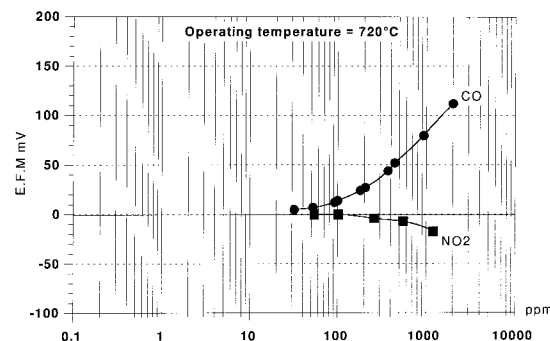


Fig. 9. Electrical response (EMF: electrical potential between the two electrodes) versus gas concentrations of CO, NO and NO<sub>2</sub> at 720°C.

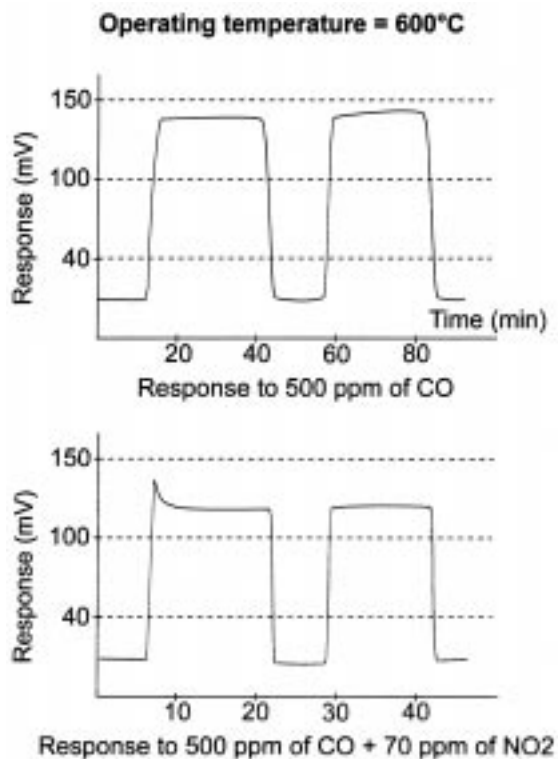


Fig. 10. Electrical response of a sintered material at 600°C: influence of the presence of NO<sub>2</sub> on the response under CO: (a) two injections of 300 ppm CO; (b) two injections of 300 ppm CO added with 70 ppm NO<sub>2</sub>.

#### 4. Electrical Tests on Sensor Prototypes

##### 4.1. Fabrication

On the basis of the above results obtained on thick films tested in a furnace, sensor prototypes have been developed for the detection of exhaust gases, at temperatures as high as 600° to 700°C. For these prototypes it was decided to develop strongly built sensors without a great miniaturization like the micro-sensors developed with micro-machining used in silicon technologies. As a consequence, the thick film technology appears suitable.

The sensor substrates (0.85 × 5.1 cm) include a platinum heater and the two metallic electrodes (platinum and gold). The β-alumina solid electrolyte is deposited onto these substrates by screen printing technology using the above described ink. Different sets of samples were prepared by varying the electrode geometry or their deposition method

(thin or thick films) and by the position of the heater: on the same side of the sensing material or on the back side.

##### 4.2. Electrical Tests

The evaluation of the response of the sensors to different gases has been performed on the same testing bench used for the evaluations of the materials. The performances of the sensors are very similar to those obtained directly on the material: the dependency with temperature is still preserved, and consequently selective detections are possible. Large sensitivities to CO (150 mV under 300 ppm CO) are obtained at 650°C without the influence of NO (500 ppm) and NO<sub>2</sub> (50 ppm). On the contrary, it is possible to monitor the NO<sub>2</sub> concentrations at low temperature (400°C).

Figures 11 and 12 show the responses of a sensor consisting of a thick film of β-alumina (60 wt% β-alumina to 40 wt% glass; annealing at 900°C; SO<sub>2</sub> pretreatment) and the responses of the analytical instrumentation used to measure the concentration of gases. The tests include injections of three gas concentrations (increasing and decreasing) with pure air injections between each gas injection (Figs. 11–12(a)) and steps in gas concentrations (increasing and decreasing) without pure air injections (Figs. 11–12(b)). Figure 11 shows the response at 570°C for CO (180, 350 and 500 ppm) and Fig. 12 shows the response at 330°C for NO<sub>2</sub> (60, 150 and 240 ppm).

In the investigated CO concentration range, the sensor response allows to well distinguish the transition between two CO concentrations. On the contrary, signal saturation is quickly achieved under low NO<sub>2</sub> concentration (see Fig. 7), hindering the observation of the transition steps (see Fig. 12(b)).

The selectivity has been also studied. The same experiments as above have been performed under NO<sub>2</sub> at high temperature and CO at low temperature. A part of these results are summarized on Fig. 13. It is interesting to underline the good agreement between the results obtained with the sensors and those obtained on materials tested in furnace. Concerning the selectivity, it appears necessary to better define the working temperatures, for instance 650 to 700°C for the CO detection and 300 to 350°C for the NO<sub>2</sub> detection.

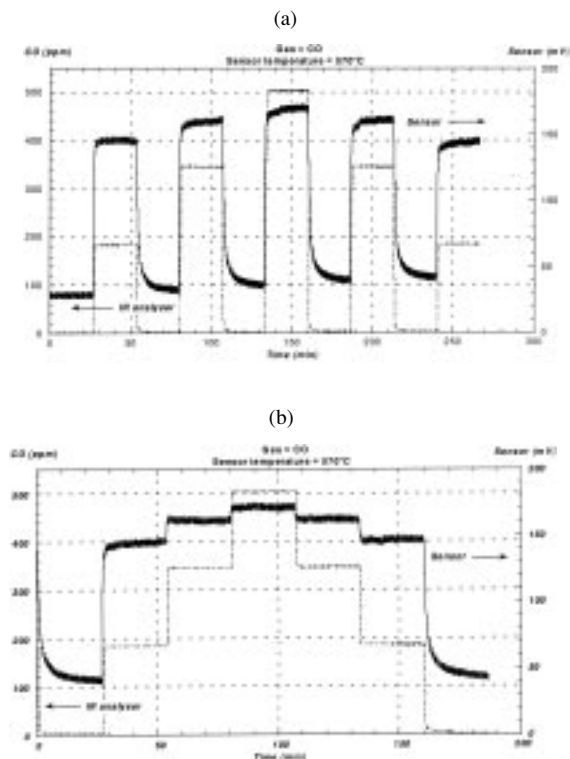


Fig. 11. Response of a sensor at 570°C versus time for different concentrations of CO: (a) comparison with the I.R. analyzer (dotted line) for gas injections (increasing and decreasing concentrations) with desorption under pure air between each injection; (b) comparison with the I.R. analyzer (dotted line) for gas injections without desorption under pure air: increasing and decreasing steps.

### 5. Industrial Applications

An industrial application program for these sensors is in progress. The main application is to use these sensors for car exhausts analysis. An electronic device including the encapsulated sensor and an electronic circuit for the control of the sensor (dc alimentation, temperature regulation and e.m.f. measure with amplification and calibration) is currently tested on an experimental car. This car is also equipped with an on board analytical apparatus to control CO and NO<sub>x</sub> concentrations. These analyzers are placed in the car trunk and the gases are sampled with gas pipes connected to different places in order to perform a control according to the future targets in industrial applications (for instance, air quality control in the passenger compartment or exhaust control). A computer placed inside the car allows the direct

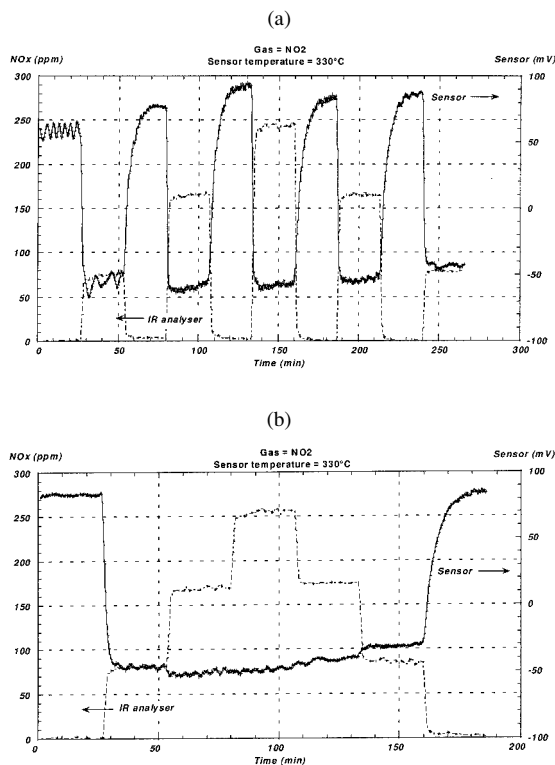


Fig. 12. Response of a sensor at 330°C versus time for different concentrations of NO<sub>2</sub>: (a) comparison with the I.R. analyzer (dotted line) for gas injections (increasing and decreasing concentrations) with desorption under pure air between each injection; (b) comparison with the I.R. analyzer (dotted line) for gas injections without desorption under pure air: increasing and decreasing steps.

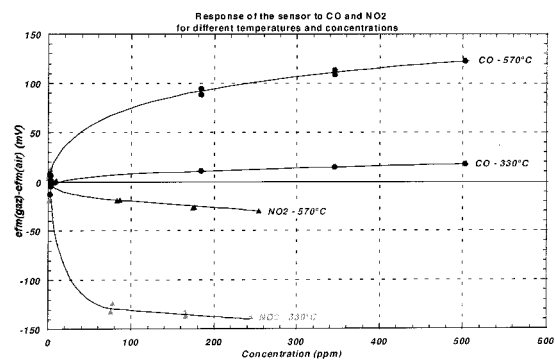


Fig. 13. Response (EMF) of a sensor versus gas concentrations, at two temperatures (330° and 570°C) and for CO and NO<sub>2</sub>. Level under pure air: 40 mV.

comparison between the gas concentrations and the sensor response.



In some preliminary experiments, a  $\beta$ -alumina sensor (named ECONOX sensor) and an oxygen zirconia-based sensor are directly placed at the exit of the exhaust duct. The oxygen sensor is not a lambda type, but an UEGO sensor, manufactured by NGK (Japan): its signal is proportional to air to fuel ratio. For technical reasons, the on board analyzers were not connected to the exhaust pipe.

The responses versus time are reported in Figs. 14 and 15 for various accelerations of the motor. It can be observed that the dual behavior of the sensor with the temperature is in agreement with the bench tests: the response is positive when the temperature of the sensor is set at 700°C (Fig. 14) and, on the contrary, the response is negative at low working temperature of 300°C (Fig. 15). An important point is the fact that the response times are very fast in both cases and comparable to that of the O<sub>2</sub> sensor.

The sensor response is about 0.5 s delayed compared to r.p.m. signal (see the loop effect on Figs. 14(b) and 15(b)): it clearly appears considering the peak after a sudden engine acceleration; consequently the response time can be considered lower than 0.5 s.

For the industrial application, the main point will be devoted to the comparison between the sensor response and the exact values of the concentrations of CO, NO, NO<sub>2</sub> measured in the exhausts in order to

check the selectivity with the sensor temperature. The problem is more complicated with NO than for the differentiation of CO and NO<sub>2</sub>. Secondly, it is necessary to realize long term experiments in order to test the stability of these sensors. The difficulty is connected to the fact that the stability depends on many parameters (sensing material; configuration, nature and surface quality of the metallic electrodes; thermal stability of the heater; . . .). Different interfering gases must be also checked, especially hydrocarbon compounds and water vapor which appear of prime importance for the automotive applications, both for long term stability and for selectivity. At last, the tests of the sensors need an electronic device. For the development of the electronic circuit, it is necessary to take into account the values of sensor impedance. Some prototypes are currently developed.

## 6. Conclusions

These preliminary experiments seem to prove that these  $\beta$ -alumina thick sensors could be successfully used for various industrial applications, especially when selective information on CO and NO<sub>x</sub> is claimed. The applications which should be more immediately envisaged are related to the control of the

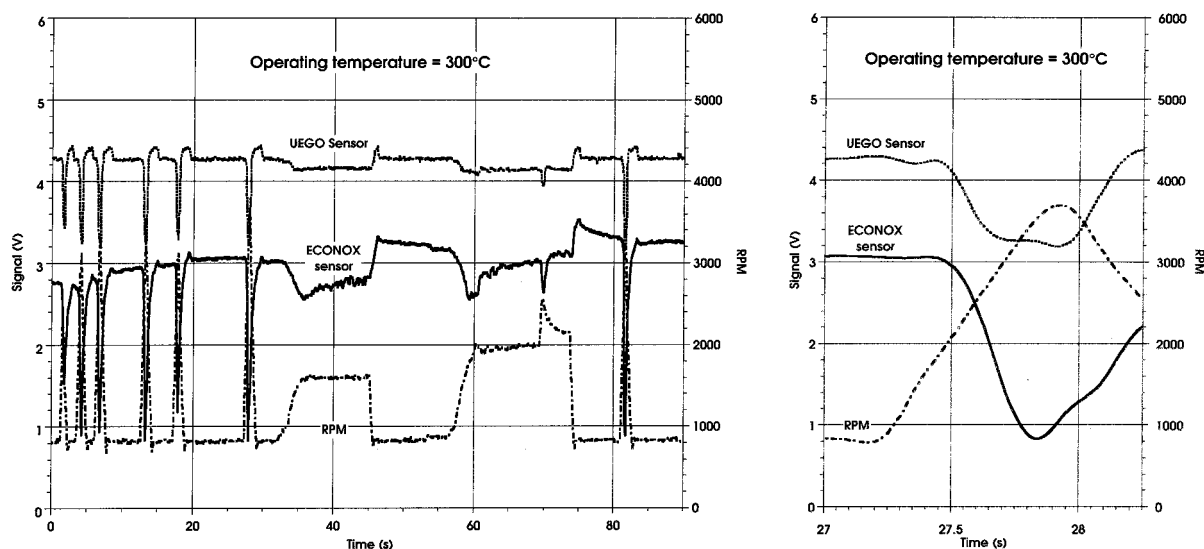


Fig. 14. Responses of a  $\beta$ -alumina sensor (named ECONOX) in an exhaust for a sensor operating temperature of 320°C. Comparison with an oxygen sensor (UEGO) as a function of the acceleration rate (RPM). (a) Large time scale; (b) loop for the acceleration step on the 28th second

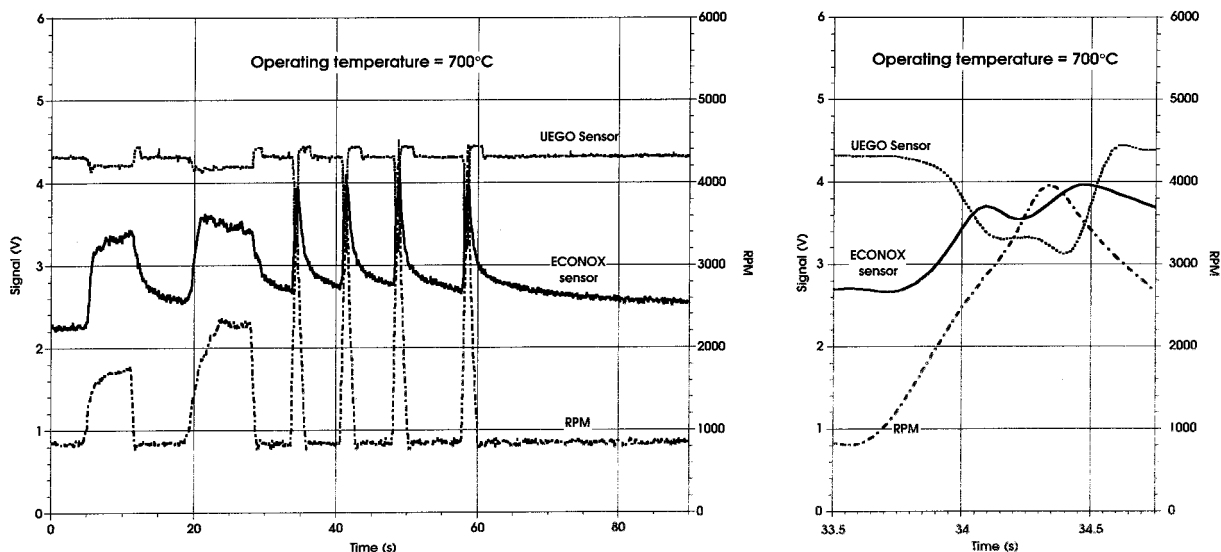


Fig. 15. Responses of a  $\beta$ -alumina sensor (named ECONOX) in an exhaust for a sensor operating temperature of 700°C. Comparison with an oxygen sensor (UEGO) as a function of the acceleration rate (RPM). (a) Large time scale; (b) loop for the acceleration step on the 34th second.

atmospheric pollution and obviously to car emission control.

The selectivity results from an appropriate choice of the working temperature of the sensing element. At low temperatures (300° to 400°C)  $\text{NO}_2$  can be selectively detected in the presence of CO; in the higher temperature range (550° to 650°C) CO can be selectively detected in the presence of  $\text{NO}_2$ . In CO detection, quantitative data can be obtained in the compositional range 0 to 500 ppm of CO, whereas a signal saturation was observed starting from concentration of about 100 ppm  $\text{NO}_2$ . On the other hand, this provides higher sensitivities for low  $\text{NO}_2$  concentrations.

The sensor prototypes developed by a thick film technology have demonstrated their ability to operate in the exhaust gas. At a laboratory scale, they are not deteriorated and they behave similarly than on the bench tests (temperature dependence of the response, fast response times). The response time of about 0.5 s seems consistent with a large number of applications, including the automotive ones.

Concerning the automotive field, it is certain that the exhaust applications need hard specifications especially for the long term stability of the sensors and their durability. The experiments presented in this

paper only pointed out a future potentiality of these sensors in relation to their performance for  $\text{CO}/\text{NO}_x$  selective detection. For this goal, a special effort and attention will be focused in the future on the long term studies in real conditions of exhaust applications, for instance with various types of motors (diesel or gasoline) or of catalytic converters.

Since a key operating principle of these sensors is based on the differences in catalytic reactions which occur at each electrode, from a fundamental point of view, it is necessary to measure the real catalytic activities of the two metals (and also other metals than Pt and Au) under the three gases (CO, NO and  $\text{NO}_2$ ) and at different temperatures range from 300 to 700°C.

On the other hand, these experiments must be performed under various oxygen pressures in order to take into account the influence of the oxygen concentration on the sensing process, especially for the oxygen dissociation reaction at each electrode.

Concerning the sensing material, it is important to determine its exact action and especially in order to distinguish the contribution due to the chemical nature of the material and the part due to the value of the electrical impedance. To this effect experiments are currently in progress with different materials (pure

$\beta$ -alumina, pure sodium sulfate, thick films with various concentrations of glass, . . .).

In addition, considering that a fundamental role is played by the catalytic activity of the two electrodes, efforts must be also devoted to the optimization of the choice of the electrode materials and of the technologies for electrode deposition.

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