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YSZ-based electrochemical sensors: From materials preparation to testing in the exhausts of an engine bench test

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Abstract

Planar sensors based on tape-cast YSZ layers with parallel Pt finger electrodes, one coated with WO_3 thick film as sensing electrode, were fabricated. The sensors were tested in the laboratory at various concentrations of NO_2 and CO at different temperatures and oxygen partial pressures. Field tests were also performed; planar sensors were located close to a commercial oxygen sensor, downstream the three-way catalytic converter of a FIAT fire 1242 c.c. spark ignition engine coupled to a dynamometer. The performance of the gas sensors was measured at the air/fuel ratio stoichiometric point (A/F ∼ 14.3) at different engine regimes (RPM and torque) and thus at different operating temperatures. The response of gas sensors was compared with the response of the commercial lambda probe and related to the exhaust gas concentrations measured by spectroscopic analytical equipment at the engine exhaust end. Preliminary measurements showed promising results in terms of sensitivity, stability and reproducibility.

Keywords: Sensors; ZrO_2; Electrical properties; Automotive applications

1. Introduction

Strict norms on pollution control are being enforced worldwide, especially for what concerns emissions of vehicles. To satisfy the automobile emission regulations, the on-board diagnostic (OBD) system has been introduced inside the vehicles to monitor all the components related to the anti-pollution processes. At present, the OBD system consists of two solid state oxygen sensors (lambda sensors), one placed upstream the three-way catalytic converter (to control the fuel/air ratio), the second one located downstream in the exhaust to control, through an electronic unit, the efficiency of the catalytic converter. New, reliable and fast NO_x, HCs and CO solid-state sensors will allow a direct and precise analysis of the pollutants, easily integrable in the OBD system. Solid state gas sensors developed to directly measure the concentrations of gases in the exhaust pipes of an internal combustion engine (ICE) could be, in fact, easily used as a feed-back element in engine control systems.

Solid-state electrochemical sensors with metal oxide auxiliary phases seem to be the most suitable for applications at high temperatures and in harsh environments. Several reports are available in the relevant literature concerning the study of sensors based on ceramic electrolytes combined with metal oxides electrodes for NO_x[1–12] and CO/HCs[9,11–16] detection. The authors of this paper have investigated the sensing properties of electrochemical sensors based on coupling YSZ with *p*-($LaFeO_3$),[4–6] n-type semiconducting oxides (WO_3, In_2O_3),[7–9] and mixed conductors ($La_xSr_{1-x}FeO_3$).[11,12] The sensing mechanism of the sensors was also studied and it was found that the adsorption mechanism characteristic of the semiconductor can play a role in the sensing performance of the devices.[11]

This work summarizes the whole way from materials preparation to field tests in the exhaust of an engine bench test for electrochemical sensors. Planar sensors based on tape-cast YSZ with WO_3 as sensing and Pt as reference electrodes were fabricated. WO_3 sub-micrometric powders were prepared in the laboratory. Previous work[7–9] on YSZ-based sensor with WO_3 sensing electrode, both in bulk and planar form, refer to WO_3 commercial powders. The sensors were measured at various concentrations of NO_2 and CO at

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different temperatures. The influence of the oxygen partial pressure on the sensors performance was also studied. Some measurements were performed in an engine bench test. Planar sensors were located close to a commercial oxygen sensor, downstream the three-way catalytic converter of a FIAT fire 1242 c.c. spark ignition engine.

2. Experimental

YSZ tape-cast layers of 150 μm in thickness were used as solid electrolyte materials for planar sensors. Commercial Pt ink was used for the preparation of the metallic electrodes and deposited on one side of the layers as parallel fingers. The firing temperature of Pt paste was 750 °C for 10 min. For the fabrication of the sensing electrode, WO_3 oxide was mixed with a commercial screen-printing oil and the slurry thus obtained was painted on the area of one metallic electrode and fired at 750 °C for 3 h. Fig. 1 shows a scheme of a planar sensor.

WO_3 powders were prepared by precipitation method: 1 g of $((NH_4)_{10}W_{12}O_{41})$ was dissolved in 20 ml of water. The solution was heated in an ultrasonic bath. By continuous stirring, a 20 ml water solution 0.1 M HNO_3 was added. The obtained precipitated was dried at 110 °C for one night and then heated to 600 °C.

The X-ray diffraction (XRD) analysis was performed using a Philips X-Pert Pro 500 Diffractometer for phase identification of the synthesized oxide. XRD patterns showed only the peaks of monoclinic WO_3. Microstructures of the electrodes were observed by a field emission scanning electron microscope (FE-SEM).

Sensing experiments were carried out in a conventional gas-flow apparatus equipped with a controlled heating facility. The sensor was alternatively exposed to air and NO_2 or CO (200–1000 ppm in air) at the total flow rate of 100 ml/min in the temperature range between 500 and 650 °C. Electromotive force (EMF) measurements were performed between the two electrodes of the sensors using a digital electrometer. During the EMF measurements, the electrode with the oxide coating was always kept at the positive terminal of the electrometer and both the electrodes were exposed to the same gas environment.

For tests at the engine bench, the gas sensor packaging used was similar to that of a commercial lambda probe provided with a heating facility. The planar sensor was

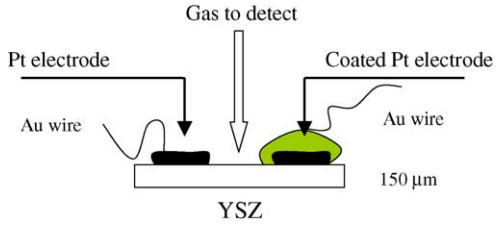

Fig. 1. Scheme of the planar sensor.

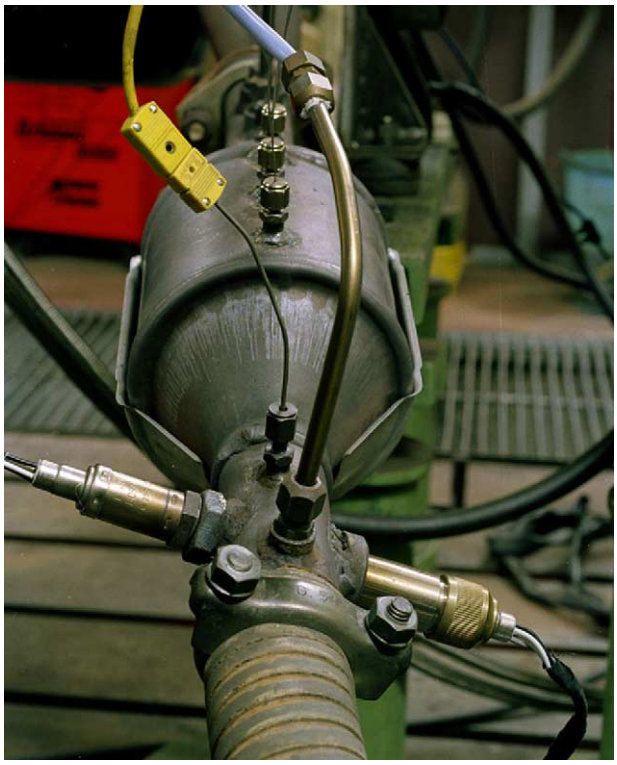

Fig. 2. Three-way catalytic converter equipped with a lambda probe (on the left) and a gas sensor (on the right).

positioned on the top of the inside alumina tube using a ceramic paste. The electric contacts were performed using Ni alloy wires. A cylindrical steel cover was fabricated with holes on top to ensure the gas flowing. The gas sensor was positioned close to a commercial oxygen sensor, downstream the three-way catalytic converter of a FIAT fire 1242 c.c. spark ignition engine coupled to a dynamometer (Fig. 2). The EMF response of the gas and oxygen sensors were simultaneously recorded and compared. Another commercial oxygen sensor was located upstream the catalytic converter to control the air/fuel ratio (A/F) of the engine. The performance of the gas sensors was measured at the stoichiometric point (A/F ∼ 14.3) at different engine regimes (RPM and torque), and thus at different operating temperatures. All the parameters for the engine adjustment were set up using the Test Point software. The exhaust gas concentrations were measured by spectroscopic analytical equipment at the engine exhaust end. Non-dispersive infrared spectrometer (NDIR) was used for CO and CO_2 measurements, chemiluminescence spectrometer for NO_x, and flame ionised detector (FID) for unburned hydrocarbons.

3. Results and discussion

3.1. Laboratory tests

SEM observations were performed on WO_3 oxide thick films deposited on Pt electrodes. WO_3 films showed a porous

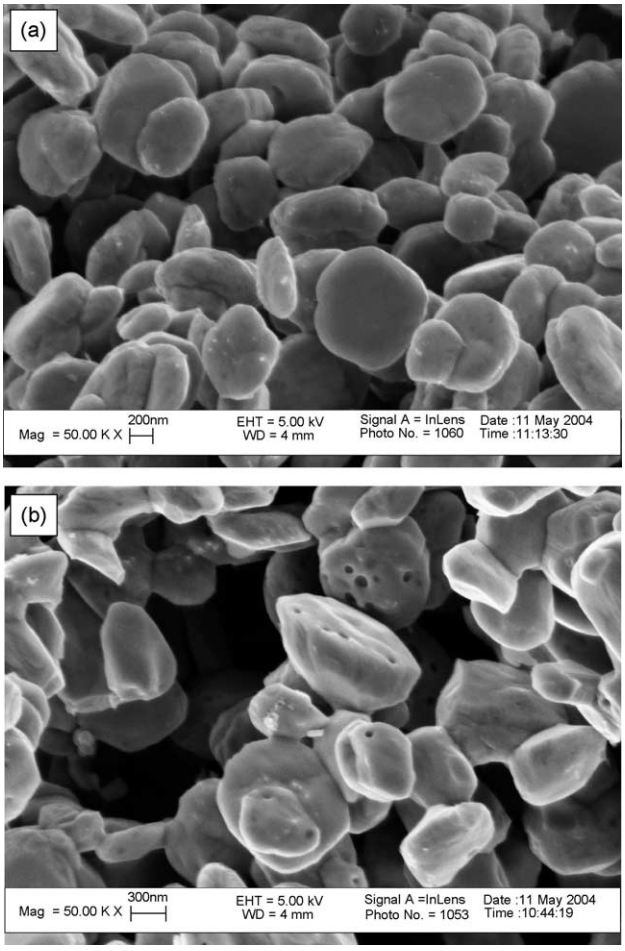

Fig. 3. SEM micrography of the "as prepared" WO_3 coating (a) and after the engine bench test (b).

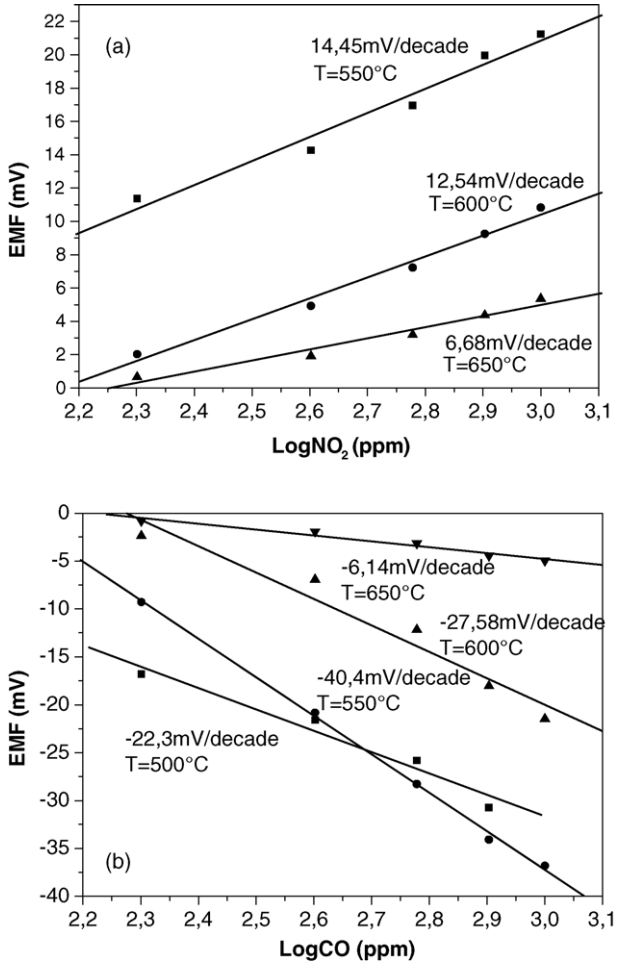

Fig. 4. EMF of WO_3 sensors vs. log of NO_2 (a) and CO (b) concentrations in air at different temperatures.

structure made of disk like grains of sub-micrometric dimension of about 200–400 nm, as shown in Fig. 3(a). The "as prepared" WO_3 coating and the oxide coating after the gas tests in the laboratory showed the same morphology. No difference in grain size and morphology was detected. The same WO_3 sensing electrode tested at the engine bench showed the same grain size and the presence of holes, as a chemical etching on the grain surface, as shown in Fig. 3(b). It is known that the WO_3 is highly sensitive to strong acids, halogenated species and hydrocarbons that may be all present in the harsh conditions of the engine exhaust. Thus, the formation of volatile tungsten species can justify the presence of the observed holes.

Fig. 4 shows the dependence of EMF of WO_3 planar sensors versus the logarithm of NO_2 (Fig. 4(a)) and CO (Fig. 4(b)) concentrations in air at different temperatures. A linear correlation was observed between the EMF values and the NO_2 and CO concentrations in log. scale. The EMF response, performed at fixed temperatures (550–650 °C), was in opposite direction upon exposure to NO_2 and CO. Positive EMF values were measured at different NO_2 concentrations and negative EMF values at different CO concentrations. At 500 °C the response to NO_2 was very slow, unstable and in the negative direction. In the temperature range 550–650 °C the response was stable and reproducible. At 550 °C the EMF magnitude was 21 mV and −37 mV upon exposure to 1000 ppm of NO_2 and CO, respectively. The response times to NO_2 and CO at 550 °C were, respectively, 2 min and 40 s. The response time became faster with increasing the operative temperature of the sensors. The best sensitivity to both NO_2 and CO gases was observed at 550 °C.

In order to investigate the effect of oxygen concentration on the response of WO_3 planar sensors, the EMF values at different NO_2 and CO concentrations in a lower oxygen atmosphere were measured at fixed temperature in the range 500–650 °C. Fig. 5(a) and (b) shows the EMF response to different NO_2 and CO concentrations at different oxygen concentrations at 550 °C. In the presence of both NO_2 and CO gases the EMF increases with decreasing the oxygen concentration in the atmosphere. The plot of the EMF response to 200 ppm of NO_2 (Fig. 6(a)) and to 400 ppm of CO (Fig. 6(b)) versus different oxygen concentrations in logarithmic scale at different temperatures showed a linear correlation. The highest oxygen dependence was obtained at 550 °C that is also

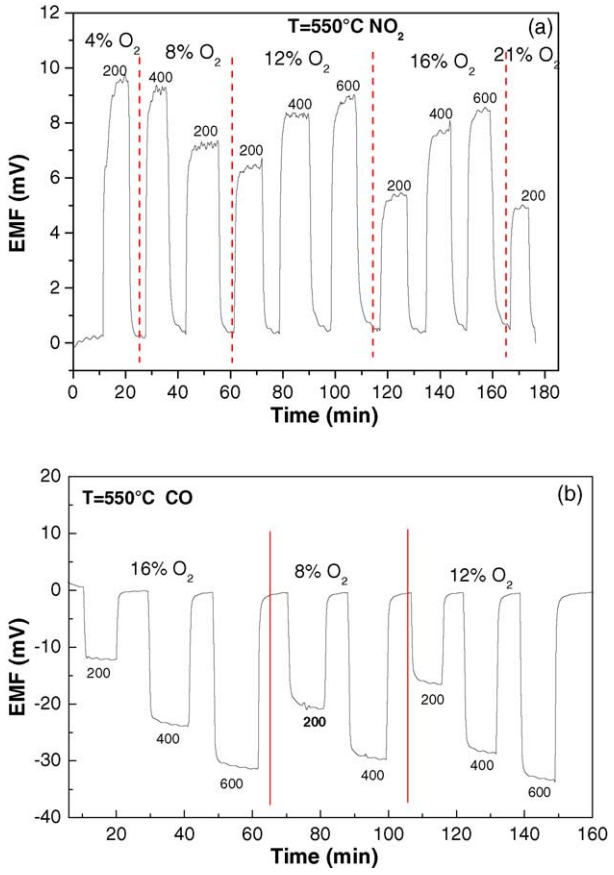

Fig. 5. EMF response to different NO_2 (a) and CO (b) concentrations at different oxygen (4 vol.%, 8 vol.%, 12 vol.%, 16 vol.%, 21 vol.%) concentrations at 550 °C.

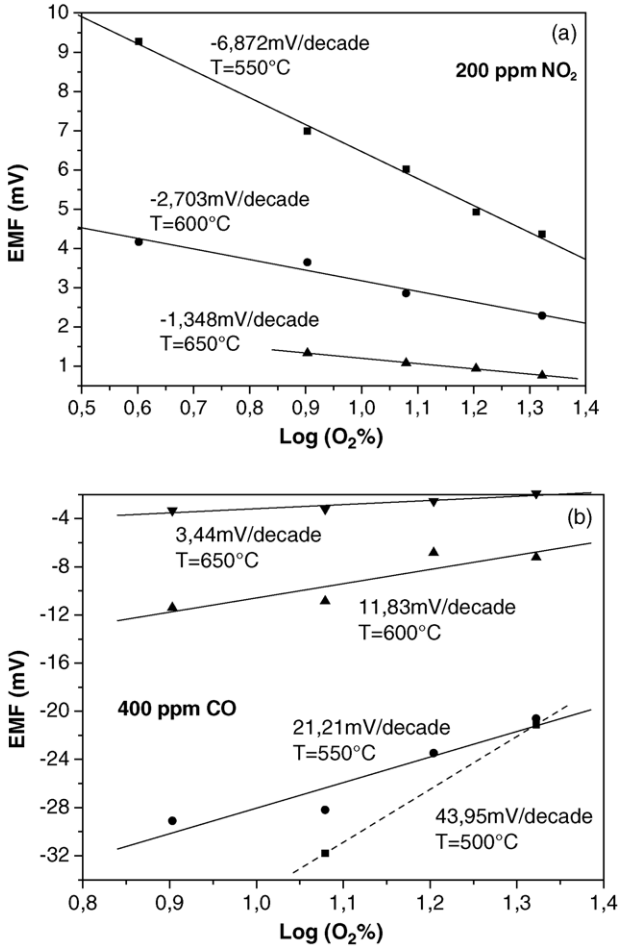

Fig. 6. EMF response to 200 ppm of NO_2 (a) and to 400 ppm of CO (b) vs. log of oxygen concentration at different temperatures.

the best operating temperature of the sensor. According to several authors, the sensing mechanism of solid state electrochemical sensors with semiconducting electrodes can be explained by mixed potential theory.[10,16] It is has been reported that the mixed potential is strongly dependent on the electrode material, because of catalytic and kinetics factors. The oxide electrode can play an important role in promoting the electrochemical reaction of NO_2 and CO.[11] The electrochemical reactions occurring at the three-phase boundary between solid electrolyte, electrode and gas, are:

for NO_2

$$NO_2 + 2e \Leftrightarrow O^{2-} + NO \quad (1)$$

$$O^{2-} \Leftrightarrow 1/2O_2 + 2e \quad (2)$$

for CO

$$CO + O^{2-} \Leftrightarrow CO_2 + 2e \quad (3)$$

$$1/2O_2 + 2e \Leftrightarrow 2O^{2-} \quad (4)$$

In the cases reported in the literature, these are the reactions occurring at the sensing electrode with metal oxide that give rise to the mixed potential. In the case of our sensors where both electrodes are exposed to the same gas environment, both reactions take place at both the electrodes, though reactions (1) and (3) prevail at the sensing electrode and reactions (2) and (4) at the metal electrode side. The dependence of the EMF response to NO_2 and CO on the oxygen partial pressure is consistent with the mixed potential theory. The behaviour of the WO_3 planar sensors observed at temperatures below 500 °C under NO_2 exposure cannot be explained only by the mixed potential theory. This is in agreement with results previously reported.[11,12] Thus, other sensing mechanisms such as different electrocatalytic activity and chemical sorption–desorption behavior of the semiconducting electrodes can be claimed.[17]

3.2. Testing in the exhausts of an engine bench test

Fig. 7 shows the signal output (EMF) of the WO_3 planar sensor compared to that of the commercial lambda probe both positioned in the engine bench. The engine was switched off and started up many times in different operating conditions to study the response time, the reproducibility, and the stability of the gas sensor. The air/fuel ratio was always kept constant at the stoichiometric value A/F ∼ 14.3. The engine regime

Table 1
Exhaust concentrations and sensor performances measured during the engine bench test

	Temperature (°C)	CO (%)	NO_x (ppm)	HC (ppm)	CO_2 (%)	EMF sensor (mV)	EMF λ probe (mV)	Response time (s)	Recovery time (s)
A	694	4.63	2.21	297.9	11.17	−328.6	−898.8	40	60
B	697	4.93	0.44	78.5	11.17	−410.5	−910.2	40	40
C	693	5.37	2.24	298.8	10.78	−406.1	−903.2	20	60

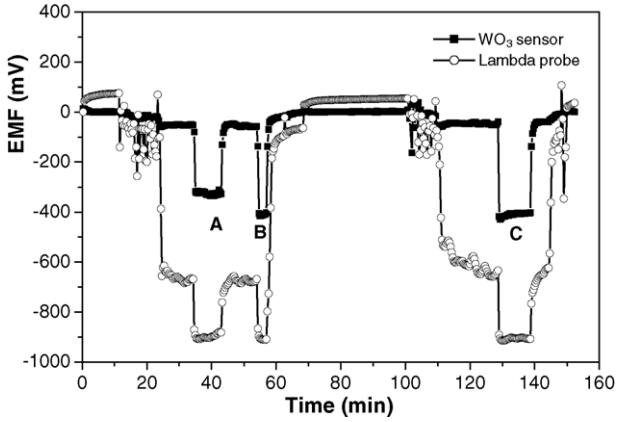

Fig. 7. EMF of the WO_3 planar sensor compared to that of the commercial lambda probe at the engine bench.

was about 3000 round/min and the torque was changed to have high or low CO concentrations in the exhausts. Three peaks (A, B, C) have been measured by setting the engine parameter to have approximately the same high CO partial pressure in the exhausts. Table 1 reports the temperature measured close to the sensors, the exhaust gas concentrations measured by the analytical equipments, the EMF response of the lambda probe and of the WO_3 gas sensor, and finally the response and recovery times of the WO_3 sensor. The response of the WO_3 sensor to CO was large and stable. The reproducibility of peaks B and C was very good taking into account that the EMF response is influenced by small variations in the oxygen partial pressure and temperature. The response and recovery times of the sensor, calculated at 90% of the stable value, were less than 40 s and 60 s respectively. The peak A showed a lower EMF value compared to the peaks B and C, probably due to the fact that it is the first signal recorded under gas exposure. Other measurements were performed at the engine bench changing the RPM and thus the operating temperature. The EMF response was stable, reproducible and consistent with the previous measurements. At lower temperatures, the response and recovery times became higher.

4. Conclusions

Among the metal oxides previously studied[6,9,11,12] as sensing electrode for high temperature applications, WO_3 showed the best performance. A chemical method was set up to obtain pure WO_3 sub-micrometric powders. The prepared sensors were preliminary tested in the laboratory showing good sensing response to different CO and NO_2 concentrations in different oxygen partial pressures. Measurements in an engine bench test at air/fuel stoichiometric value (A/F ∼ 14.3), at temperatures up to 700 °C, showed good performances in terms of sensitivity, stability and response time. Further studies are needed to investigate the long term stability of the sensors in the exhausts.

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