FIRB “SQUARE” PROJECT: NANO-STRUCTURED SENSORS FOR THE DETECTION OF THE POLLUTING IC ENGINE EXHAUST GASES AND FOR INDOOR AIR QUALITY MONITORING

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abstract.

- The present work is a final dissemination of activities carried out and main results obtained in the national founded project Firb “Square”. The project is leaded by Centro Ricerche Fiat and it involves the most qualified national public Research Institutes and Universities active in the fields of nanomaterials synthesis, nanotechnology and gas sensors development.

1. Introduction

The project aims are to develop the technologies necessary to realise micro-sensors with nanometric structure to detect the emissions of internal combustion engines and to monitor the indoor air quality. These sensors, by means of benefits given by the nanometric structure and thanks to the innovative nanotechnologies developed, offer several important advantages:

- High sensitivity and selectivity to the chemical pollutants
- Fast response time
- Low dimensions
- Low raw material costs

Main technical objectives of the project are:

- Synthesis of nano-materials for sensing element: SHS, Gel Combustion, Sol Gel and Spry Coating technologies;
- Film deposition technologies: PMCS, Spin coating and Spry/drop coating (thin film); Screen Printing (thick film);
- Micro-injection moulding technology of ceramic nano-powders for sensor holder production;
- Development of specific gas sensors prototypes for automotive application (exhaust gas monitoring, indoor air quality, olfactory perception).

2. Experimental

The technical activities are organized in four main line:

1. Synthesis of nano-materials:

the most promising materials obtained were $SrFe_xTi_{1-x}O_3$ (SHS) and SnO_2 + CuO (GC) for exhaust application; In_2O_3 (Sol Gel), ZnPc-TiO_2 (PMCS) for indoor air quality application; cluster of Me TPP (Cu, Co, Zn, Mn, Fe, Sn Ru, Cr) for indoor olfactory perception. Figures 2-4 show three different sensitized materials.

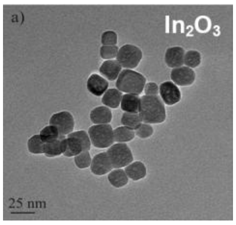

Figure 2 – Sol gel In2O3

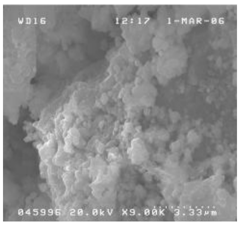

Figure 3 – SHS SrFexTi1-xO3

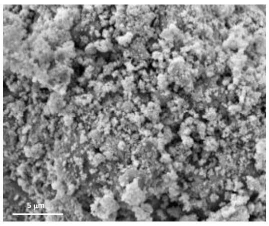

Figure 4 – Gel combustion SnO2

2. Thick and thin film deposition:

the processes used in the final prototypes production were: screen printing for both exhaust and IAQ application; plasma & supersonic beam for IAQ; spry coating for olfactory application. Figures 5-7 show the three different deposition process prototypes.

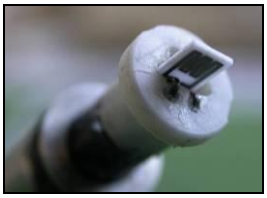

Figure 5 – Screen printing

Figure 6 – PMCS deposition

Figure 7 – Spry coating

1. Sensor prototypes manufacturing:

several kind of materials and deposition technologies have been characterized in order to select the most promising solution for the different applications.

2. Sensors validation:

the selected sensors have been tested in two specific bench capable to reproduce the working automotive condition (exhaust & indoor applications). The most promising prototypes for both applications have been implement in two Fiat Auto cars for an extensive road test campaign.

3. Results & Discussion

$SrFe_xTi_{1-x}O_3$ oxygen sensor vehicle tests:

to verify its performance in real operating conditions, the $SrFe_xTi_{1-x}O_3$ sensor was installed in an exhaust pipe of a diesel car together with a commercial Bosch probe (Figure 8).

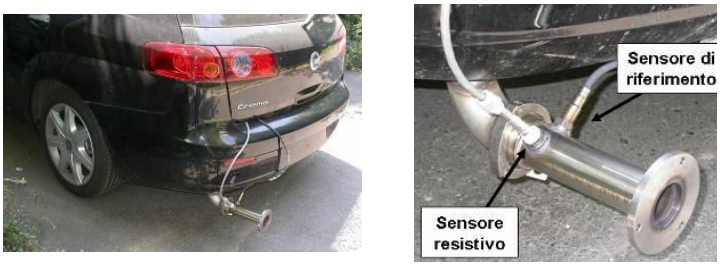

Figure 8: SrFe0.6Ti0.4O3 sensor prototype equipped on a Fiat Croma exhaust line.

With respect to laboratory measurements, in road tests the sensor is exposed to an harsh ambient. Therefore an adequate protection is necessary to preserve the sensor life and stability. The probe for car testing was then fabricated by mounting the housing of a commercial lambda probe on the $SrFe_xTi_{1-x}O_3$ sensor, in order to protect and eliminate turbulence near the sensing film due to high spatial velocity of the gases. Another problem to solve is the wide temperature fluctuation of the exhaust gases. A temperature control has been achieved by means of a Proportional Integrated Derivative (PID) controller that finely adjusts the power delivered to the sensor by the heater. Fig. 9 shows the output responses of the resistive $SrFe_xTi_{1-x}O_3$ sensor and Bosch commercial probe acquired at the exhaust pipe during a time period of the road test, in response to wide variations of oxygen concentration (in the range 4-20 vol. %). It should be note that the sensors output are opposites. The resistive sensor increases its resistance with the increase of O_2 concentration, whereas the voltage of the Bosch oxygen sensor decreases correspondingly.

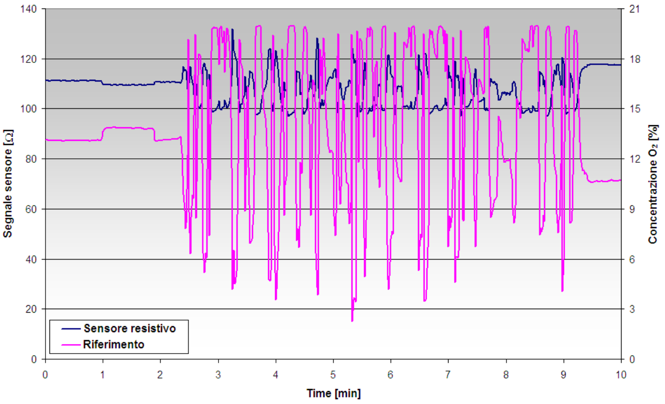

Figure 9: SrFe0.6Ti0.4O3 sensor experimental results.

During road test the concentration of exhaust gases changes very quickly. Then, an essential requirement of the oxygen probe is, a prompt response. The strict signal overlapping between sensor response and lambda sensor signal indicate that the $SrFe_xTi_{1-x}O_3$ sensor responds quickly to oxygen concentration variations as the Bosch probe.

These promising results demonstrate the feasibility of resistive oxygen sensor based on cost effective raw materials and with good performances; anyhow furter investigation on the sensor behaviour during long-term operation are required in order to verify the stability, reproducibility and life-time of the $SrFe_xTi_{1-x}O_3$ sensor in real operating conditions.

AQS sensors:

The laboratory screening on AQS sensors of two types (thin and thick film) allowed to select the ones with best performances. The next step has been a test on board in order to check their sensibility to air pollutant (CO and NO_2) in actual conditions (see Fig. 10).

Figure 10: In_2O_3 sensor prototype equipped on a Fiat Idea cabin inlet air duct

The location and casing in the inlet air duct were adapted from those of commercial sensors.

Figure 11 show the good results obtained: sensibility and selectivity to the air pollutants and besides a low response time. All that confirms the maturity of these technologies for the automotive field.

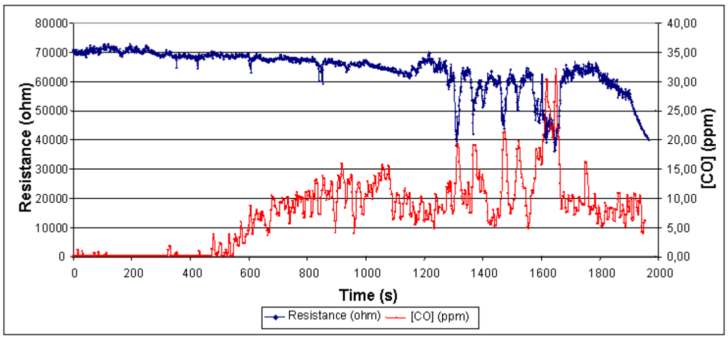

Figure 11: **In_2O_3 sensor Experimental results**

<u>Olfactive sensors:</u>

This type of sensors were tested in laboratory with a prototype Electronic Nose supplied by the “Tor Vergata” Rome University (see Fig. 12).

The metalloporfirine cavity, hosting the suitable metal ion, are able to produce a frequency variation in the quartz assembly.

The aim of this research is to collect these signal and create a sensorial map, in order to discriminate among the various gases influencing the air quality.

Advanced mathematical techniques, such as Principal Component Analysis (PCA), were used to show this behaviour.

Figure 12: Kit of MeTPP sensor prototype on bench test

The overall results showed in Fig. 13 are promising, but the great spread caused by the varying operating condition (umidity, temperature) suggests further development and research study.

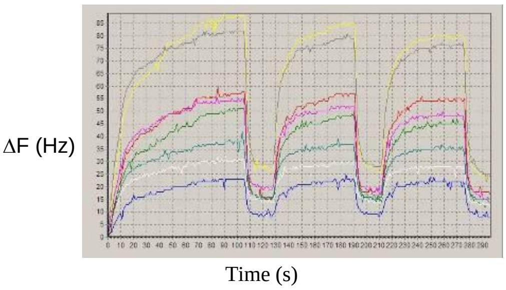

Figure 13: Experimental results

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