Sensors and Actuators B 134 (2008) 647–653

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

$FeSrTiO_3$-based resistive oxygen sensors for application in diesel engines

G. Neri[a,*], G. Micali[a], A. Bonavita[a], R. Licheri[b], R. Orrù[b], G. Cao[b], D. Marzorati[c], E. Merlone Borla[c], E. Roncari[d], A. Sanson[d]

[a] Department of Industrial Chemistry and Materials Engineering, University of Messina, Contrada di Dio, Vill. S. Agata, I-98166 Messina, Italy
[b] Department of Chemical Engineering and Materials, INSTM and University of Cagliari, Italy
[c] Centro Ricerche FIAT, Strada Torino 50, 10043 Orbassano, To, Italy
[d] CNR ISTEC, Faenza, Italy

ARTICLE INFO

Article history:
Received 31 March 2008
Received in revised form 5 June 2008
Accepted 6 June 2008
Available online 17 June 2008

Keywords:
$FeSrTiO_3$
Resistive oxygen sensor
Diesel engines

ABSTRACT

$SrTi_{0.4}Fe_{0.6}O_{2.8}$ (STFO60) powders were prepared by self-propagating high-temperature synthesis (SHS) and subsequent ball-milling (BM) treatment, and then deposited on an interdigited alumina substrate by screen-printing to fabricate a planar resistive oxygen sensor for direct injection (DI) diesel engines.

The electrical characteristics and response to oxygen of the STFO60 sensor have been carefully examined first in a bench system with synthetic gases thus simulating diesel exhaust composition. The results obtained highlighted the promising performances of the sensor in terms of the temperature resistance independence as well as sensor response at the high oxygen concentrations typical of diesel engines. Cross-sensitivity tests also indicated that the sensor response is not influenced by main components in the exhausts, such as HC, CO_2, NO_x, CO.

The STFO60 sensor was then tested as an oxygen probe on a diesel engine car under real driving conditions. Road tests confirmed that the performances of the resistive sensor are comparable with those of a commercial lambda probe.

1. Introduction

Oxygen sensors are a part of the closed loop fuel feedback control device, associated with modern emission control systems [1]. The closed loop fuel feedback control system is responsible for controlling the air/fuel, A/F, ratio (λ factor) of the catalytic converter feed gas. Nearly every passenger car is nowadays equipped with at least one lambda probe measuring the air-to-fuel ratio to control engine operation. Additionally, a second lambda sensor downstream catalyst is used for monitoring catalyst functionality continuously for on-board diagnosis (Scheme 1).

In conventional engines, the λ factor oscillates between 0.95 and 1.05 [2–5]. In order to increase fuel efficiency, modern internal combustion engines are operated under lean conditions. In lean-burn engines the air–fuel mixture contains excess oxygen, i.e., the lambda parameter λ is greater than 1. A direct injection (DI) diesel engine, for example, operates in a large area of its performance map with a λ factor between 1.8 and 5, i.e., to an oxygen concentration >10 vol.%.

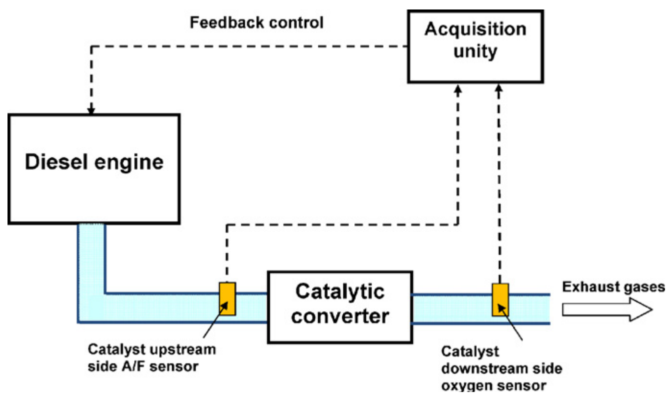
The wide use of air/fuel ratio and emission control systems has led to the development of different types of oxygen sensors [2–7]. Zirconia-based lambda sensors are most widely used in gasoline engines. For diesel engines special care must be given to the choice of the sensor and to its installation in order to obtain reproducible results and rise times characterized by higher oxygen concentration. Indeed, typical exhaust gas compositions of gasoline and diesel engines (see Table 1) show remarkable differences among them, in particular as far as the concentration of oxygen is concerned [8]. For this scope a wide band lambda oxygen sensor is required for diesel engines [9].

Planar resistive oxygen sensors based on TiO_2 or Fe-doped $SrTiO_3$ have attracted specific interest as promising alternatives to conventional zirconia sensors, because of their simpler design and manufacturing process, with potential cost reduction [9–13]. Furthermore, these planar sensors have a better thermal conductivity with respect to conventional lambda probe and, therefore, they reach the operating temperature in few seconds, guaranteeing quick start operation.

Two basic requirements should be fulfilled by an oxygen sensor for this application: its output should depend as far as possible only on the oxygen content of the exhaust gas, and its response time should be as short as possible. In resistive semiconductor-based sensors, the corresponding conductivity (σ) value is dependent on

* Corresponding author.
E-mail address: neri@ingegneria.unime.it (G. Neri).

0925-4005/$ – see front matter
doi:10.1016/j.snb.2008.06.007



Scheme 1.

oxygen partial pressure, P_{O_2}, according to the following equation:

$$\sigma(P_{O_2}, T) \propto P_{O_2}^{1/m} \exp\left(-\frac{E_A}{kT}\right) \quad (1)$$

where the m factor displays a negative or positive value depending upon the n- or p-type behaviour of the semiconductor, while E_A represents the activation energy of the electric conduction. In order to avoid cross-sensitivity linked to temperature fluctuations and to obtain a sensor able to operate in a thermally fluctuating environment, it is necessary to reduce the E_A term near to zero [10–13]. Regarding the response time, it should be as low as possible, i.e., values of the order of 200 ms are required.

In a previous paper we reported the preparation by self-propagating high-temperature synthesis (SHS) and successive ball-milling (BM) treatment of Fe-doped strontium titanate (STFO) [13]. It was found that STFO films, having a Fe loading corresponding to the composition $SrTi_{0.4}Fe_{0.6}O_{2.8}$ (STFO60), show a resistive behaviour which does not depend on temperature in the range between 500 and 700 °C. Oxygen sensing tests there reported have also shown the good properties of the STFO60 thick film-based sensor.

As a natural continuation of the above activity, in this work the potential practical application of this sensor in diesel engines is tested. Then, the electrical characteristics and response to oxygen concentrations typical of diesel engines are examined in detail in bench tests simulating exhausts conditions. Finally, the STFO60 sensor was put in an exhaust pipe of a diesel car together with a commercial Bosch probe to test the sensor performance under real operating conditions.

2. Experimental

2.1. Powders synthesis

Powders of $SrTi_{0.4}Fe_{0.6}O_{2.8}$ were prepared by SHS according to the stoichiometry of the following reaction:

$$SrO_2 + 0.4TiO_2 + 0.6Fe \rightarrow SrTi_{0.4}Fe_{0.6}O_{2.8}$$

The experimental SHS set-up used and the preparation procedure are described in detail elsewhere [13]. First, reactants (SrO_2, TiO_2 and Fe) were mixed in the presence of acetone, as dispersing agents, for about 2 h using a centrifugal mill (Tecnotest, Italy). The resulting mixture was uniaxially pressed to form cylindrical pellets with a diameter of 16 mm, 20 mm height and a green density in the range of 50–60% of the theoretical value. The combustion front was generated at one sample end by using a heated tungsten coil, which was immediately turned off as soon as the reaction was initiated. Then, the reaction self-propagates until it reaches the opposite end of the pellet. The temperature during reaction evolution was measured using thermocouples (W–Re, 127 μm diameter, Omega Engineering Inc.) embedded in the pellet.

The synthesized combustion product was further processed by BM in a SPEX 8000 shaker mill (SPEX CertiPrep, USA) by using stainless steel vials. A ball to powder ratio of about 3.2 was used by loading vials with 5 g of SHS products that were milled with two stainless steel balls (weight, 8 g; diameter, 16 mm). The milling time was 5 h. After each run, powders were removed and vials and balls were cleaned by using a slurry of silica and acetone with the aim to eliminate all residual powders of previous milling experiments.

2.2. Bench sensing tests

Sensors were fabricated by depositing thick films (thickness about 30 μm) of the synthesized STFO powders by screen-printing on alumina substrates (6 mm × 3 mm sized), supplied with comb-like electrodes and a Pt heater on the back side. Subsequently, the devices were treated at temperatures between 650 and 850 °C in air for 2 h to stabilise film texture and microstructure.

Sensing tests were accomplished in the measurement apparatus shown in Fig. 1. All equipments are controlled by a PC by using a specifically developed software running on Lab View platform. Sensing tests were carried operating the sensor at a temperature of 650 °C and with a total flow of 200 cm^3/min.

2.3. Road tests

In order to verify the oxygen sensor performances under real-like operating conditions, the prototypal STFO60 sensor has been installed and tested directly on a Fiat Croma 1.9JTD 16V Euro4 compliant. The sensor installation on the exhaust line is shown in Fig. 2 . In parallel a reference oxygen sensor (Bosch LSU4.9 planar wide band lambda sensor with pumped O_2 reference) was also installed. The two sensors have been fixed on the exhaust pipe by means of a standard UHEGO sensor cap. The sensing element temperature of the STFO60 sensor has been fixed at approximately 600 °C, while the signals coming from the prototypal sensor and the reference one have been acquired continuously using a data logger.

3. Result and discussion

3.1. Electrical characteristics of $SrTi_{0.4}Fe_{0.6}O_{2.8}$ powders

In a previous paper we reported the preparation of STFO powders synthesized by SHS and their electrical properties as temperature and oxygen concentration were varied [13]. The iron loading in the STFO powders formulation and a further ball-milling treatment were found to be crucial to synthesize the above mate-

Table 1
Typical exhaust gas composition of gasoline and diesel engines

	NO_x (ppm)	HC (ppm)	CO (ppm)	H_2 (ppm)	O_2 (%)	CO_2 (%)	H_2O (%)	SO_2 (ppm)	N_2 (%)
Gasoline	900	350	5000	1700	0.5	10	10	15–60	Bal.
Diesel	1135	30	490	n.i.	10.5	7.1	4–5	30	Bal.

n.i.: not indicated.