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ScienceDirect
Procedia Engineering 5 (2010) 164–167
Procedia Engineering
www.elsevier.com/locate/procedia

Proc. Eurosensors XXIV, September 5-8, 2010, Linz, Austria

Effect of nanostructured WO_3 layers in the sensitivity to nitrogen oxide in YSZ-based electrochemical sensors for automotive applications

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Abstract

The sensitivity to nitrogen monoxide (NO) is studied and compared when using several YSZ-based electrochemical gas sensors with identical characteristics but covered by different porous layers over one of their catalytic Pt electrodes. Sensors are exposed to several exhaust gas mixtures containing nitrogen monoxide. The gases are composed by a low concentration of NO dissolved in N_2 atmosphere or by a low concentration of NO dissolved in a multi-component mixture similar to exhaust gases from internal combustion engines. The optimum layer thickness and preparation temperture to enhance NO sensitivity are studied. Regarding the composition of the layers, layers made of nanostructured WO_3 mixed with porous YSZ seem to maximize the NO sensitivity and decrease crossed sensitivities.

Keywords: YSZ; WO3; NOx sensor; monolithic ceramic technology.

1. Introduction

Detecting and minimizing nitrogen oxides (NOx) emissions in exhaust gases coming from combustion engines has been an important subject in the last decades. American and European vehicle emission regulations focus on the control of NOx emissions in automotive exhaust gases, particularly in lean combustion exhaust gases (non stoichiometric combustion mixtures with an excess of air, or lack of fuel). Low response times and no crossed sensitivities in multi-component gases environments are necessary to meet regulations and help minimizing of NOx emissions. Commercial sensors are already available to detect and minimize NOx. However, their structure is too complex as demands two connected electrochemical cells with electronic signal control. A more simple structure with good sensing properties is still necessary.

The objective of this work is comparing the response and behavior of potentiometric gas sensors with different diffusive layers covering their measuring electrode. Most of the layer configurations contain nanostructured tungsten

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doi:10.1016/j.proeng.2010.09.073

trioxide (WO_3). Responses in front of several nitrogen monoxide concentrations and in front of gas mixtures similar to exhaust gases from combustion engines are studied and compared for each layer configuration.

2. Experimental

2.1 Sensors preparation

Sensors consisted in the schematic structure

(exhaust gas)+porous layer+Pt electrode+YSZ electrolyte+Pt electrode+(air reference) (1)

A schematic cross-section of the sensors can be seen in Figure 1. Apart from the implementation of the porous layer, the fabrication of the sensors consisted in monolithic ceramic planar techniques such as tape casting, ceramic stacking and sintering. Starting from Y_2O_3 4.5%wt-doped ZrO_2 (yttria stabilized zirconia, YSZ) powders, several YSZ films of 20 μm thickness were prepared. These films were superposed with appropriate holes, cavities, electrodes and electrical contacts to get the desired 3D structure seen in Figure 1. Electrodes and contacts were printed by means of screen printing. The obtained structures were sintered at 1450ºC for 30 minutes, thus leading to YSZ-based sensors with dimensions of 55 mm x 4 mm x 1.5 mm, still without the porous layer over one of the Pt electrodes. More details about the structure of these sensors and its preparation technique can be found at [1-3].

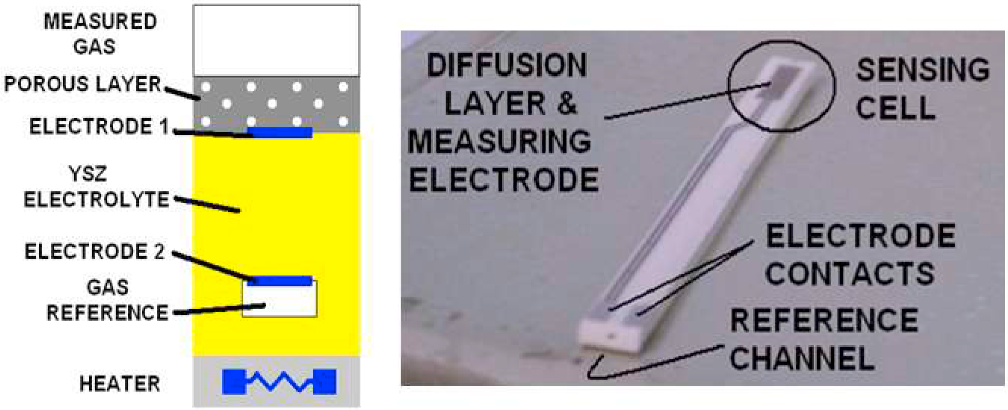

Fig. 1. (Left) schematic structure of a planar ceramic electrochemical oxygen sensor; (Right) Real image of a planar sensor.

2.2 Porous layers preparation

After sintering, the porous layer was added by printing the desired material ink over the measuring electrode and heating again the structure up to 700C or 900C. The reason why this layer was added after sintering is that tungsten trioxide evaporates above 900C and layers containing this material would not work. Layers were made of nanostructured WO_3, nanostructured WO_3 mixed with porous YSZ and porous YSZ. Also, some sensors were left with no layer over the electrode to use as reference sensors.

Pores were generated by mixing the layer materials with sacrificial materials such as graphite. Those sacrificial materials should disappear when heating up to 900C and, subsequently, they shoud generate pores in the layer structure. Regarding nanostructured WO_3, it had been obtained after a sol-gel chemical route starting from tungstic acid dissolved in methanol and water. Details on its preparation and XRD, TEM and Raman characterization can be found at [4].

The effect of the layers diffusivity was studied as well. Layers were prepared with two different thicknesses: 20 and 40 micrometers. As a result, up to eleven different sensor configurations were studied, with the only differences in their porous layer configurations: sensors with no layer, layers made of YSZ, YSZ+WO_3, WO_3, thick (40 micron) and thin (20 micron) layers and two different temperatures for the layer preparation: 700C and 900C. Several samples were prepared for each layer configuration, to ensure repeatability of the results (no less than 6 samples for each layer configuration, including the no-layer reference sensors).

2.3 Experimental tests

The sensors were exposed to several gas mixtures in a controlled gas testing system at high temperature (600C) to ensure a high ionic conductivity in YSZ. Two sets of measurements were carried out: first, the sensors were exposed to several nitrogen monoxide concentrations (ppm of NO) dissolved in a nitrogen atmosphere. Second, sensors were exposed to different synthetic exhaust gas mixtures with some content of O_2, CO_2, C_3H_8, CO, N_2 and a small amount of NO. These gas mixtures corresponded to three different combustion parameters λ [5]: one of the mixtures was a rich exhaust gas mixture (λ<1, excess of fuel, air-fuel ratio lower than the stoichiometric ratio) and the remaining two were lean mixtures (λ>1, excess of air, air-fuel ratio higher than the stoichiometric ratio). For each one of those λ compositions, the NO concentration ranged from 10 ppm to 9000 ppm.

1. Results

3.1 Sensors exposed to NO dissolved in N_2

Figure 2 shows the output open circuit voltages measured between the sensor electrodes when exposing to several N_2 atmospheres containing low loadings of nitrogen monoxide. A thin layer (20 micrometer thickness) made of only WO_3, with no porous YSZ content, and prepared at 900C gave the highest sensitivity in front of nitrogen monoxide dissolved in a N_2 atmosphere.

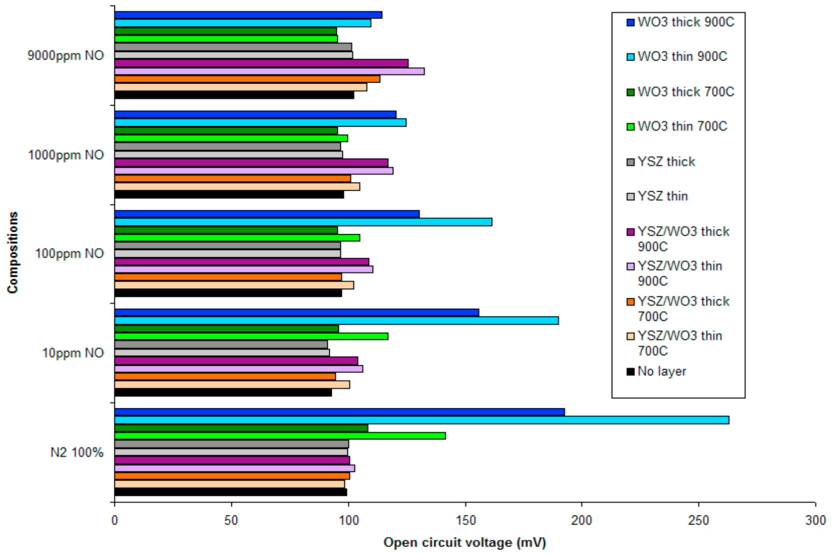

Fig. 2. Detected voltages in front of the nitrogen monoxide concentrations dissolved in the N_2 atmosphere. Note that sensors with no WO_3 content in their layer or with no layer lead to the most unsensitive response in front of NO.

3.2 Sensors exposed to NO in exhaust gas compositions

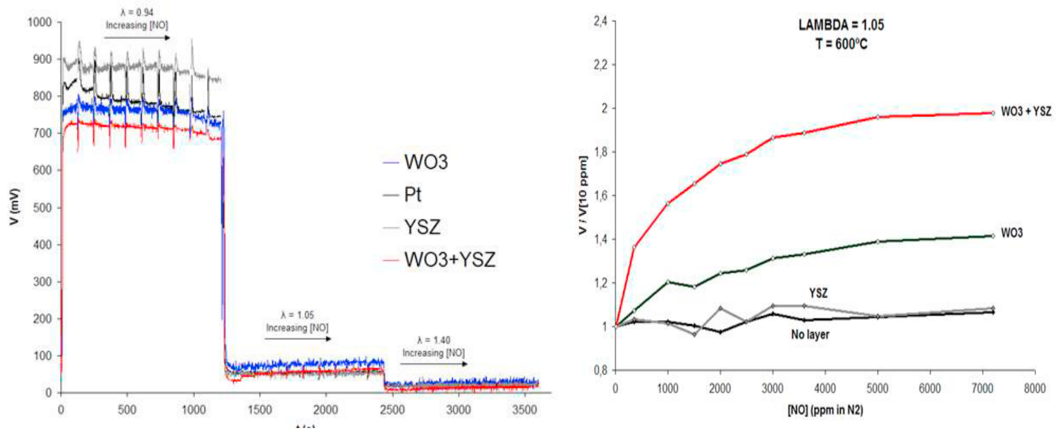

Fig. 3. (Left). Response of sensors with 4 different layer configurations in front of 3 combustion conditions: one rich exhaust gas mixture (first 1200 seconds) and two lean mixtures (rest of the experiment). The sensor marked as 'Pt' was the sensor with no layer over its Pt electrode. Fig.3. (Right) Detail of the stationary responses in the case of the parameter λ=1.05 (lean mixture) with respect to the lowest NO concentration (10ppm). Layers with no WO3 content are unsensitive to NO but layers with WO_3 and YSZ are more sensitive than layers with only WO_3.

Fig.3 shows the responses of the sensors in front of the λ compositions. The response in front of the different NO concentrations under one of the lean mixtures (λ=1.05) is depicted with respect to the response measured at [NO]=10ppm. It was seen that the most sensitive layer was made of a mixture of YSZ+WO_3. Layers with no tungsten trioxide were unsensitive to nitrogen monoxide, but layers with the mixture of YSZ and WO_3 led to sensors with higher sensitivities than layers with just WO_3. The observed behaviours were attributed to a competition between promotion of nitrogen monoxide catalysis (due to WO3) and the molecular filtering before reaching the electrode due to porous YSZ.

Acknowledgements

C.L.G. acknowledges his grant FIE from the AGAUR de la Generalitat de Catalunya.

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