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Improvement of the NO_x selectivity for a planar YSZ

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Abstract

The present work aims to develop a sensor that can leave the laboratory and be industrialised. For this reason potentiometric sensors based on a solid electrolyte YSZ and 2 metallic electrodes (platinum and gold) were fabricated by screenprinting technology and were tested in a laboratory test bench for different concentrations of CO, NO and NO₂ in oxygen rich atmosphere. By depositing a catalytic filter consisting of 1.7%Pt dispersed in alumina directly on the electrodes, it was shown that the selectivity towards NO_x could be highly reinforced. This filter was characterized by the use of SEM, TPD, and XRD technology.

Keywords:

NO_x sensor; catalytic filter; selectivity

1. Introduction

Since many years researchers have been working on the development of a reliable potentiometric gas sensor for automotive exhausts application. However, one of the major problems accounted with these sensors, as for other types, has been the limited selectivity [1, 2]. As the European Commission has focused in their latest emission requirements proposals (Euro V and Euro VI) specifically on the reduction of the NO_x emission, one of the major challenges today is the enhancement of the NO_x selectivity [3].

In the present work, a planar potentiometric YSZ sensor with a catalytic filter directly deposited on the sensitive part of the sensor is suggested to reduce the influence of CO.

2. Experimental

For the fabrication of planar potentiometric sensors, screen-printing technology was used to deposit a solid YSZ electrolyte and two metallic electrodes (commercial pastes), one in gold and one in platinum on an alumina sheet (Fig. 1). Gold paste was equally used to establish the connection between the sensor and the acquisition system. On the back side of the sensor a platinum heating element is printed to ensure the control of the temperature.

In order to produce sensors with enhanced selectivity towards NO_x a catalytic filter layer (40-80 μm) consisting of 1.7% Pt dispersed in alumina was deposited over the sensing elements.

The fabricated sensors were tested in a conventional flow apparatus (Fig. 2). The gas flow in the sensing chamber consisted basically of a synthetic gas containing 12 vol.% O₂, 2 vol.% H₂O and nitrogen balance.

Pollutant gases such as CO, NO and NO₂ were added to the base gas in a concentration range of 50-300ppm. The total flow rate amounted to 30l/h. While the

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entering gas mixture had ambient temperature, the sensors were heated to 400-550°C in order to establish an optimal working temperature. The measured electromotive force was the potential difference between the gold and the platinum electrode ($V_{Pt-V_{Au}}$).

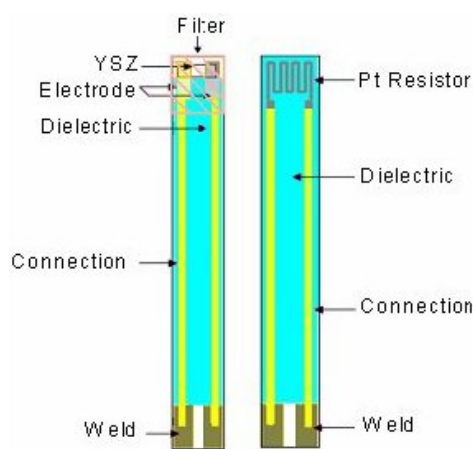


Figure 1. Schematic of the YSZ sensor with Pt and Au electrode

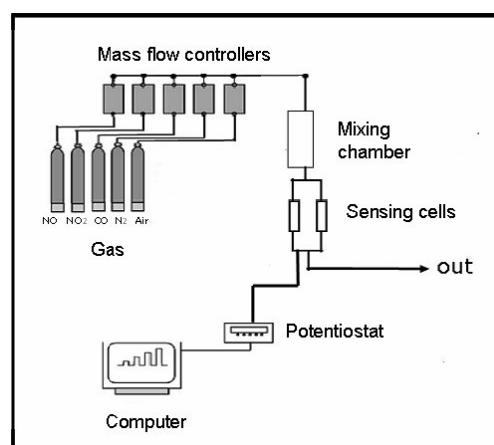


Figure 2. Schematic of the test bench

By applying XRD and SEM technologies the crystal structure and the surface morphology of the deposited catalytic filter layer was analysed.

Furthermore the adsorption-desorption behaviour of NO_2 was investigated by means of TPD. In a Ushaped quartz tube 0.1g of the 1.7% Pt dispersed in alumina powder, used to fabricate the catalytic layer, was placed and heated to 450°C. The sample was then exposed to a gas mixture consisting of 300ppm NO_2 , 3.5% oxygen and helium balance for 12 hours successively. The sample was then cooled down to room temperature and treated 10 minutes with pure helium. For the desorption, the sample is heated under helium up to 700°C with a heating rate of 15°C/min and a helium flow rate of 3l/h. The NO , NO_2 desorption could be followed by a mass spectrometer.

3. Results and discussion

3.1. Sensing characteristics of the sensor without a catalytic layer

In absence of a catalytic filter layer and at the optimum temperature determined of 450°C (maximum sensitivity to NO_x), a positive response in regard to the base line was obtained for reducing gases such as CO and NO (Fig. 3), whereas the oxidizing gas NO_2 responds negatively. This was due to the difference in the Redox potential of the gases and the different

catalytic/electrical properties of the electrodes. Similar sensing behaviour has been reported already in literature [4]. Remarkable is the fact that NO₂ has a higher sensitivity than NO.

3.2. Sensing characteristics of the sensor with aPt/alumina catalytic layer

As it is seen, the strong sensor response to CO would influence significantly the NO_x signal if not eliminated. By depositing a catalytic layer consisting of 1.7% platinum in alumina the sensor response to CO could be suppressed as CO was oxidized to the non-reactive gas CO₂ (Fig. 4).

If furthermore NO and NO₂ were considered, it was necessary to transform the response to NO and NO₂ into the same direction in order to get a total NO_x output and to avoid cancelling out of the signals in case of co-existence. Platinum is said to be a good catalyst to put NO and NO₂ to the thermodynamic equilibrium. At the working temperature of 520°C the ratio of NO to NO₂ according to the equilibrium thermodynamic should be close to 1.

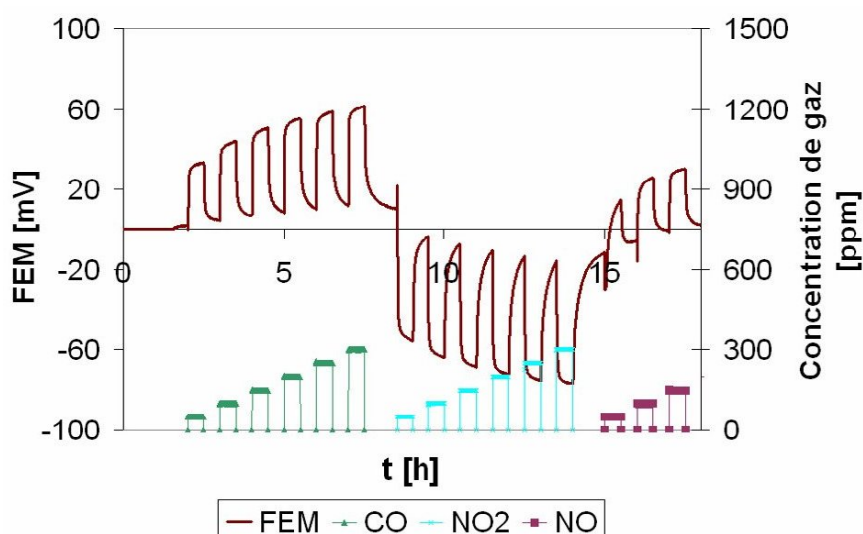


Figure 3. Sensing characteristics of a Au/YSZ/Pt sensor without a catalytic filter layer at 450°C in presence of 12% O₂

This is to say, that independent whether it is NO or NO₂ which arrives at the sensor, the same response should be obtained. This theory corresponded very well with the experimental results as a response with a similar magnitude (approximately 20mV) was obtained for NO and NO₂. As the sensor is more sensitive to NO₂ than to NO, the sensor signal was negative.

It is to be noted that the working temperature here was shifted from the optimum temperature 450°C, mentioned in section 3.1, to 520°C with a loss of sensibility of approximately 5mV. However, this shift of the platinum in the catalytic layer which was observed to take place upon a long term exposition to NO₂ in presence of oxygen and at temperatures lower than 500°C. The reason for the deactivation will be discussed in the next section.

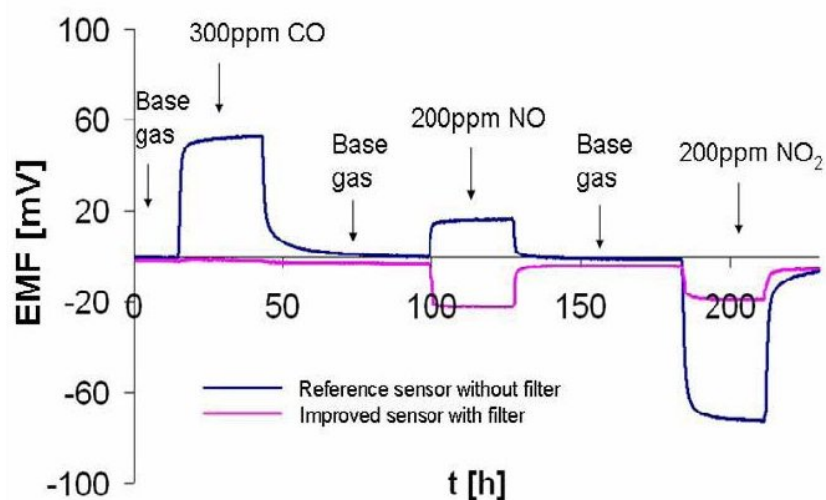


Figure 4. Sensor response to CO, NO and NO₂ at 520°C (Base gas: 12vol.% O₂, 2vol.% H₂O, N₂ balance)

3.3. TPD experiments

TPD experiments have been carried out to investigate the deactivation behaviour mentioned in section 3.2. Fig. 5 shows the NO_x and oxygen desorption profile of the 1.7% Pt/alumina powder. Two major desorption peaks of 30 amu could be observed. However 30 amu can be linked to different nitrogen oxide species beside NO, as it is the major decomposition product of NO₂, nitrate or nitrite. The first peak centred at 100°C is believed to represent NO bound to platinum [5] and amounts to 11 μmol/g.

As the desorption of this species is already completed at around 150°C, it seems to be justified to presume that it will not affect the sensor function at 450°C.

The second desorption peak starts at approximately 200°C and continues up to 460°C. The amount of NO desorbed is calculated to be 88 μmol/g. As oxygen desorption (at amu 32) takes place at the same time, this peak is believed to belong to nitrate or nitrite adsorbed on the alumina support [6]. It is therefore advisable to work at a temperature higher than 500°C to ensure that nitrate or nitrite desorption will not lead to a deactivation of the catalyst.

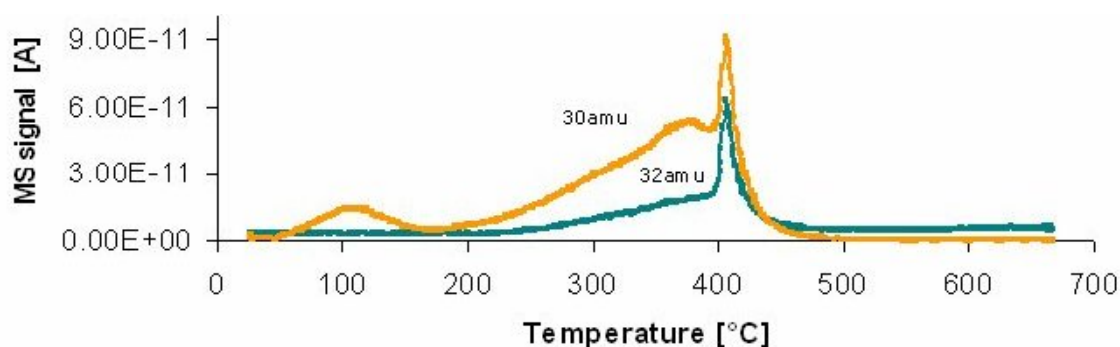


Figure 5. TPD profile of 1.7%Pt dispersed in alumina for NO_x ions (at 30 amu) and O₂⁺ (at 32 amu)

3.4. XRD and SEM characterisation of the filter layer

Using XRD analysis, only alumina and platinum phase were detected which meant that there was no major pollution in the catalytic layer. Furthermore, the filter characterisation with SEM showed that the surface of the catalytic layer was non-fissured. The electron retro diffused image (Fig. 6) showed that alumina areas of about 5 μm² were present which were not covered with Pt. However this was sufficient to oxidize all CO to CO₂.

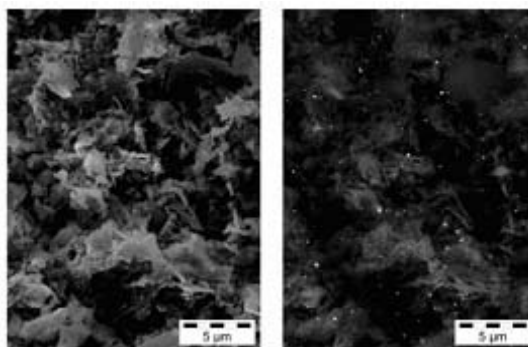


Figure 6. SEM images of the catalytic filter surface (1.7%Pt dispersed in alumina)

4. Conclusions

A simple robust Pt/YSZ/Au NO_x sensor is presented in this work. It is shown that by depositing a catalytic filter layer over the sensing elements CO interference can be totally cancelled and a higher NO_x selectivity is achieved. By using TPD analysis an optimal working temperature can be found to avoid the deactivation of the catalyst. However once selectivity is achieved, an improvement in the sensitivity is necessary to grant industrial application.

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