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Application of advanced morphology Au-X (X = YSZ, ZrO₂) composites as sensing electrode for solid state mixed-potential exhaust NO_x sensor.

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Abstract

Among various NO_x sensors developments, mixed potential sensor based on Yttria Stabilized Zirconia (YSZ) with a simple planar architecture Au/YSZ/Pt is of practical interest. Au composites electrodes were investigated to improve sensing performances. Such potentiometric solid-state gas sensors - were fabricated by screen-printing and tested for NO₂ detection. Electrochemical impedance spectroscopy has shown that the addition of YSZ in the Au electrode decreased the polarization resistance in air. In addition, the (Au+10 wt% YSZ)/YSZ/Pt sensor has a shorter response time and higher sensitivity to NO₂ (range 20-100 ppm) at 450-550 °C in comparison with a reference Au/YSZ/Pt sensor. On the other hand, the addition of non-conductive ZrO₂ doesn't significantly modify the electrochemical property but strongly damages the sensor responses toward NO₂.

1. Introduction

Continuous stringent legislations in automotive exhausts oblige the vehicles manufacturers to optimize combustion operations and to monitor pollutants such as nitrogen oxides [1, 2]. From

2014, Euro 6 standards require the utilization of a NO_x (NO and NO₂) catalytic after-treatment device for Diesel engines. Selective catalytic reduction (SCR) of nitrogen oxides by ammonia or urea [2, 3] is the most advanced technology used in heavy diesel engine trucks but also in Diesel passenger cars. Conversion of NO_x depends on oxygen partial pressure as well as on NH₃/NO and NO/NO₂ ratios, and could reach above 99% at 573 K [3]. In this context, fast and accurate on-board diagnostics of NO_x concentration in the exhaust are strongly required.

Due to this strong demand, there are numerous studies dealing with the development of NO_x sensors for on-board detection in light and heavy duty vehicles. In this paper, we will focus only on potentiometric gas sensor designed with two electrodes and working in the same atmosphere, according to the mixed potential principle. A recent development of such a sensor is reported in [4]. Most of these sensors are composed of a solid electrolyte based on yttria-stabilized zirconia (YSZ) [4-10], but other electrolyte may be used: β -alumina (2Na₂O–11Al₂O₃) [11] or samaria-doped-ceria (SDC) [12]. Two electrodes, a reference one and a sensing one are associated with the electrolyte. These two electrodes must present different electrocatalytic activity to detect NO_x, such as the couples Pt-Au [5, 11], Pt-MnCr₂O₃ [8], Pt – (Au-oxide) [9, 13], or Pt with other oxide [4]. The signal of a two electrode potentiometric sensor, in a complex gas environment, shows a non-Nernstian behavior due to the establishment of a mixed potential [4, 5, 6, 8] on the sensing electrode. This latter is linked to the superposition of parallel electrode reactions occurring at the triple phase boundaries (TPB) [8, 9, 10, 14], such as the oxygen electrode reaction and the electrochemical reduction (oxidation) of NO₂ (NO). The sensitivity of NO₂ is always higher than that of NO. In addition, by using the Au/Pt couple of electrodes interfaced on YSZ, NO₂ and NO exhibit opposite responses, positive for NO and negative for NO₂ [5].

The morphology of the two electrodes plays a significant role in the number of TPB [8, 14], then on the kinetic of the electrode reactions and finally on sensing performances. For instance, a sensor with two Pt based electrodes showing asymmetric morphologies can be effective for NO₂ detection [15, 16]. Composite electrodes made of Pt or Au mixed with an oxide [7, 13, 17-19] are also strongly investigated to improve the sensing performances. Recent studies have reported the sensing performances of Au+YSZ [19] and Au-NiO [13, 20] composite electrodes.

Cross sensitivity to exhaust gases as CO and hydrocarbons can be eliminated by using a catalytic filter [5, 21] deposited on the top of the electrodes. This catalytic layer can fully oxidize these molecules into CO₂ which is not detected by the sensor. It can also catalyze the NO oxidation into NO₂ to reach the thermodynamic equilibrium. Therefore, the NO/NO₂ ratio is only dependent on the temperature for a fixed partial pressure of oxygen. Our aim is to develop a potentiometric sensor highly sensitive to NO₂ equipped with a catalytic filter. Then, at a constant tem-

perature and oxygen partial temperature, this system could provide concentrations of NO₂, NO and overall NO_x.

This paper describes the sensing performances for NO₂ detection of YSZ-based solid state planar sensors using Pt as a reference electrode and Au-composites as sensing electrodes. The objective was to increase the porosity and then the number of TPBs of the sensing electrodes. These latter were composed of Au mixed either with YSZ or ZrO₂. The addition of YSZ into the Au electrode could provide a mixed electronic and ionic conductivity into the sensing electrode in order to delocalize the TPBs in the overall volume, while the incorporation of ZrO₂ should only act on the porosity. Electrochemical performances for the oxygen electrode reaction were investigated by impedance spectroscopy and compared with those of pure Au sensing electrode. Finally, the sensing performances for NO₂ were evaluated between 450 and 550°C.

2. Experimental

Solid state planar sensors (Figure 1) were fabricated by screen-printing (Aurel C890) on alumina substrates (CoorsTek). A functional and porous layer 5x5 mm of solid electrolyte (YSZ: (ZrO₂)_{0.92}(Y₂O₃)_{0.08} provided by Superconductive) was deposited by screen-printing (200 mesh) from a home-made ink containing 4 g of YSZ powder, 1.7 g of organic binder (ESL V400A) and 1 g of solvent (ESL 404) mixed 10 minutes in a three-roll mill (Exakt 80E). Then, the samples were dried for 15 min in air at 120°C and sintered at 1380 °C in air for 2 hours with a ramp of 5°C/min. Platinum and gold electrodes, of 1 mm width and 4 mm length, were screen-printed on the surface of the YSZ layer using a commercial paste of Pt (ESL 5545) and Au (ESL 8880-H). The distance between the electrodes was 2 mm. The deposited electrodes were further dried for 15 minutes at 120°C and then sintered at 850°C for 2 hours in air with a ramp of 5°C/min. The gold and platinum electrodes were denoted as the sensing (SE) and the reference (RE) electrode, respectively.

Gold based composite electrodes were prepared by mixing the Au commercial paste (ESL 8880-H) with 10 wt% YSZ (denoted as AuY) or with ZrO₂ (denoted as AuZ) homemade inks. YSZ ink is the same as for electrolyte. ZrO₂ ink was composed of 4 g of ZrO₂ powder (Merck), 1.7 g of organic binder (ESL V400A) and 1 g of solvent ESL (59 wt % of ZrO₂). This ZrO₂ ink (10 wt%) was mixed in a three roll mill with the Au commercial paste. The depositions were further dried for 15 minutes at 120°C and then sintered at 850°C for 2 hours in air with a ramp of 5°C/min. Final amount of ceramic fraction in composite electrodes is 9.5 %wt.

The powders (YSZ and ZrO_2) were characterized by using laser granulometry (MASTER-SIZER 2000 MALVERN) and BET measurements with nitrogen (ASAP 2020). Specific area of YSZ powder after calcination at 850 °C in air was found to be 15 m²/g while that of ZrO_2 was 3.8 m²/g. Mean particle size of agglomerates was 1.6 µm and 0.288 µm, for YSZ and ZrO_2 , respectively.

Number and nature of impurities in the commercial ink of Pt (ESL 5545) and Au (ESL 8880-H) were controlled by ICP (Jobin-Yvon JY138 Ultrace). The presence of 1500 ppm of Cu and around 30 ppm of Al, Na, and Zn have been detected in the Au paste whereas significant loadings of Ti (29000 ppm), Zn (9000 ppm), Fe (2500-3500 ppm), Cr (1500 ppm) and Al (1500 ppm) have been analyzed in the Pt ink sample.

Scanning electron microscopy (JEOL JSM 6500F) was used to investigate the morphology of the electrodes and of the YSZ layer. Samples were placed in epoxy resin and polished to obtain cross section. Surface of samples was covered with a conductive carbon layer (Quorum Q150R ES).

The control of the sensor heating was performed with a Pt-resistance element (ESL 5545) placed on opposite side of the alumina support (Figure 1A). Before testing, all sensors were aged at 800°C for 120 hours in air. Symmetric sensors were also made to investigate the electrochemical performances of the Au based electrodes (Figure 1B). Three series of symmetric sensors were prepared by screen-printing with the same procedure than used for the electrolyte layer and the electrodes: Au/Au as a reference sample, AuY/AuY and AuZ/AuZ.

Resistivity of the YSZ porous layers and electrochemical properties of the Au composite electrodes were measured by using electrochemical impedance spectroscopy (EIS, VersaSTAT 3 - Princeton Applied Research). Each symmetric sensor was placed in a tubular furnace (CARBOLITE) in ambient air. AC signal amplitudes of 150 mV were applied between the two electrodes in the frequency range 10⁵ Hz – 10⁻³ Hz. EIS measurements were performed between 550°C and 700°C with a step of 25°C both during heating and cooling down. Impedance diagrams were recorded during a temperature plateau of 3 h. EIS measurements were not possible below 550°C, due to the extremely high resistivity (higher than 10 MΩ) of the YSZ porous layer. Fitting of the Nyquist plots was realized in ZView interface.

The sensing performances for NO₂ of the solid state planar sensors (Figure 1A) were measured in a synthetic gas bench (Figure 2) with a “base gas” containing 12 vol% O₂, 1.5 vol% H₂O, balanced with N₂. Amounts of 20, 50 and 100 ppm of NO₂ for 15 min were added in the

base gas. The total flow rate was 15 L h⁻¹ per cell, simultaneously four sensors were tested. For heating control and signal processing, an electronic card coupled with a LabView interface was used. Response and recovery times of the sensor responses were compared taking into account that the dead volume in the sensor cell is around 30 cm³. Therefore, considering the flow rate in the sensor cell (15 L h⁻¹), around 35 seconds are necessary to deeply change the NO₂ concentration. Response (and recovery) times were measured and correspond to the time to reach (or to recover) 90% of the maximum sensor response.

Sensors have been tested between 450 and 550 °C. The open-circuit voltage (OCV) was measured as follow:

$$OCV = E_{RE} - E_{SE} \quad (1)$$

where E_{RE} was the potential of the reference electrode (Pt) and E_{SE} was the potential of the sensing electrode (Au, AuY or AuZ). The responses of the sensors toward NO₂, ΔV , were calculated according to the following relationship:

$$\Delta V = OCV_{NO_2} - OCV \quad (2)$$

when OCV_{NO_2} was the stabilized sensor signal measured during NO₂ injection.

3. Results and discussion.

3.1. SEM characterizations

Figures 3 and 4 display that the YSZ layer is extremely porous, probably due to the presence of evaporated binder (30 wt%) and solvent in the initial paste. However, the surface of this layer evidences percolation between micrometric YSZ grains ensuring bulk ionic conductivity.

Figure 4A shows that the Au sensing electrode is dense and totally covers the surface of the electrolyte. The interactions between the gold film and the porous YSZ layer are poor. In this case, TPB electrode/electrolyte/gas is limited by the perimeter of the Au dense film. Addition to the gold paste of 10 wt% of ZrO₂ or YSZ ink, produces strong modifications of the electrodes morphology (Figures 4B, 4C). The Au-Z composite electrode presents open pores in which the gas can diffuse from the electrode surface to the electrolyte layer. The diameter of these pores varies from 0.5 to 5 µm. Metallic phase contain a wide size distribution of Au grains from 1 to 20 µm. Agglomerates of ZrO₂ larger than 2 µm can be observed inside the composite electrode Au-Z. Au particles in the Au-Y composite layer present a similar size from 1 to 20 µm. YSZ particles,

between 1 and 5 μm , are dispersed in the vicinity of the electrode layer. High porosity with continuous electric contact between Au and YSZ electrolyte grains forms an electrode with a higher number of TPBs. Contrary to the Au electrode, the platinum reference electrode (Figure 4D) is highly porous. This Pt electrode contains micrometric Pt particles (1 - 5 μm) smaller than the Au grains observed in the Au-composite electrodes.

3.2. Electrochemical characterizations

Electrochemical Impedance Spectroscopy was used to investigate the electrochemical properties of the symmetric sensors Au/Au, AuY/AuY and AuZ/AuZ. Experiments below 550°C were not possible to carry out due to the extremely high resistivity of the sensors, of the order of 10 M Ω . This is due to the high porosity of the electrolyte layer. Indeed, literature data reports high increase of the YSZ electrolyte resistance with the porosity [22, 23].

Figure 5 shows a typical Nyquist plot of the Au-Au sample at 551°C in air. Impedance spectra exhibit two well-defined semicircles that could be separated and resolved. The first semicircle, in the high frequency (HF) domain, represents the resistivity of the YSZ solid electrolyte layer (R_{SE}) which is mainly due to the blocking of the conduction by the pores [22]. The second contribution, in the low frequency (LF) range (from 10^2 to 10^{-3} Hz), corresponds to the overall polarization resistance (R_{pol}) at the two symmetrical electrodes linked with the kinetic of the electrode reactions [7, 17, 23, 24].

The SE semi-circle can be reasonably fitted with a parallel $R_{\text{SE}}C_{\text{SE}}$ element [7, 24] with R_{SE} and C_{SE} , the resistance and the capacitance of the YSZ layer (Figure 5). The resistance of the YSZ layer is extremely high, around $2 \times 10^6 \Omega$ at 550°C and is almost similar for the three sensors (Figure 6). This underlines the good repeatability of the preparation method. This value is higher than the ones reported in previous studies [22, 23]. This could be related to the high porosity of the screen printed YSZ layer. The activation energy is similar for the three symmetrical sensors, at around 1.13 eV. This value is in good agreement with that reported for porous YSZ membranes impregnated with 1 wt% Pt [23]. On the other hand, Kleitz et al [22] have found similar activation energies, at around 1.04 eV for both bulk and pores conductivity.

Modeling of LF part of impedance spectra can be performed with a RC element [7, 18], but better fits were obtained by using a parallel combination of a resistance (R_{pol}) with a constant

phase element (CPEpol) [24-27]. [Figure 7](#) depicts the Arrhenius diagram of the polarization resistance in air between 550 and 700 °C. From a general point of view, polarization resistances of the two symmetrical electrodes are one order of magnitude lower than resistances of the YSZ layer. The two samples Au/Au and AuZ/AuZ show similar values of polarization resistances as well as of the apparent activation energy (1.54 ± 0.03 eV). Therefore, the enhancement of the electrode porosity with the addition of an insulating material such as zirconia seems to not significantly modify the oxygen electrode kinetic. Opposite results were reported in the literature data for Pt composites electrodes containing Ga_2O_3 [7] deposited on a dense YSZ sheet. The presence of the oxide phase was found to inhibit the cathodic electrode reaction.

The electrode composite of Au with YSZ shows the highest electrochemical performances ([Figure 7](#)) and the lowest apparent activation energy (1.43 ± 0.3 eV). For instance, at 550°C, the value of R_{POL} decreases from $5 \cdot 10^5 \Omega$ for Au and AuZ down to $3 \cdot 10^5 \Omega$ for AuY. The apparent activation energy values at the Au/YSZ interface in oxygen, reported in the literature data, are in the order of 0.9 - 1 eV [25, 28]. For instance, Woo et al. [25] have recently performed experiments on a symmetrical Au/YSZ/Au sensor using thin Au plates contacted on a porous spray-coated YSZ layer. In the temperature range 600-700°C, they found an activation energy value of 1.02 eV under oxygen.

Our experimental data evidence high E_a values. Blocking process of the charge transfer may occur at the Au/YSZ interface which could be linked with the extremely high YSZ layer porosity as well as with the presence of impurities (Cu ~1500 ppm, Al, Na, Zn ~30ppm) in the Au paste.

3.3. Sensor performances

3.3.1. OCV measurements in the base gas.

The evolution of OCV in the base gas (12% O_2 , 1.5% H_2O) was monitored as a function of time ([Figure 8](#)) at 450°C. These responses correspond to potential differences between the Pt electrode and the Au-based one ([Figure 1a](#)). Initial signal abrupt variations are due to the temperature regulation. Regarding the Au sensor, OCV values significantly increase with time during the first two hours and then gradually raise but never reach a steady-state. After 18 hours on stream, the OCV value of the Pt/Au sensor is + 57 mV. The OCV, in oxygen atmosphere, between Au and Pt electrodes is generally attributed to a difference in the O_2 electrode kinetic rate linked with different oxygen activity [29]. A positive value indicates that the oxygen activity is higher on Pt than on Au, in good agreement with the morphology of the two electrodes ([Figure](#)

4). The two Au composites present similar behaviors with an initial increase followed with a gradual decay of the OCV with time. Responses of AuZ and AuY sensors reach a steady-state value of +10 mV and +2 mV after 6.5 and 13 hours on stream, respectively. These results underline that the electrode porosity increases the surface specific area and the number of TPB, active for the oxygen adsorption. Therefore, the electrochemical properties of AuY for the oxygen electrode reaction become closest to those of the Pt electrode, in good agreement with EIS data (Figure 7).

3.3.2. NO_2 sensing performances

NO_2 sensing performances such as the response time and the signal stability were monitored as a function of the morphology and the composition of the sensing electrodes. In oxygen-rich atmosphere, in presence of NO_2 , a mixed potential is established between the oxygen electrode reaction and the electrochemical reduction of NO_2 [3, 30].

As already reported in the literature [5, 19], whatever the temperature and the nature of the electrodes, the responses to NO_2 and NO are opposite. As expected, the sensors responses to NO_2 are negative (Figure 9). At 450°C, the AuZ sensor presents a strange and non usable behavior, suggesting extremely slow and complex interactions of NO_2 with the porous electrode. On the opposite, the AuY sensor shows stable and reversible responses. In addition, this electrode exhibits the highest sensing performances with sensitivity to NO_2 of around -52 mV/decade. The recovery time of pure Au electrode is extremely high, most probably because a slow diffusion of NO_2 into the dense Au layer.

By increasing temperature to 500°C and 550 °C, the sensitivity decreases for all sensors. For instance on AuY, the response drops from 42 mV/decade at 500°C down to 28 at 550°C. In parallel, response and recovery times are strongly decreased (Figure 10). Responses of both Au and AuZ electrodes become reversible. However, the response time of AuZ remains much longer. Whatever the temperature, AuY exhibits the highest sensitivity and the lowest response time. Sensitivity of AuY sensor is two times higher than that of Au at 500°C and 550°C. Nevertheless, the AuY response tends to decrease with time during the NO_2 injections.

For example, Figure 11 allows to compare responses and recovery times of the three sensors during addition of 100 ppm NO_2 at 500°C. Response time for AuY is the shortest one, at approximately 50 s. The Au sensor shows a longer response time around 120 s. The AuZ

sensor is extremely slow: even after 15 min, the signal is not stable. Whatever the electrode, several minutes are necessary to recover the initial response after the end of the NO₂ exposure at 500°C. The utilization of Au-Y composite can strongly reduce this recovery time which is 8 min instead of 45 min for both Au and AuZ. These long recovery times are probably linked with a strong adsorption of NO₂ onto the electrodes. At higher temperature (550°C) and for a lower concentration of NO₂ (20 ppm), the recovery times become reasonable (considering the dead volume of the cell) on AuY (130 s) and Au (70 s).

Conclusions

The objective of this study was to study the influence of gold composite electrodes on the performances of a mixed potential Au/YSZ/Pt sensor. The effect of YSZ and ZrO₂ additions to the gold electrode on the response toward NO₂ was investigated between 450°C and 550°C. The initial gold electrode was quite dense. SEM characterizations evidenced that the porosity and then the number of triple phase boundaries were increased when ZrO₂ and YSZ were incorporated into the Au electrode. However, with ZrO₂ addition, polarization resistance was not modified compared to reference Au/YSZ/Pt sensor. In this case, the presence of porosity in the electrode damages the sensor performances both in terms of NO₂ sensitivity and of signal stability. On the contrary, as shown by electrochemical impedance measurements, the polarization resistance was significantly reduced in the case of Au-YSZ electrode. Such a result indicates that the electrochemical properties for the oxygen electrode reaction were only improved for the Au-YSZ composite electrode because the ionic conductivity of YSZ can delocalize the electrode reaction in the overall electrode volume. Furthermore, the addition of YSZ improved the sensitivity toward NO₂ as well as the response time of Au-based electrodes. As a conclusion, porous Au-YSZ composite electrodes in a YSZ-based sensor have a beneficial effect compared to pure gold electrode.

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Figure captions

Figure 1: A) Schematic drawing of solid state gas sensors and B) symmetric samples for EIS measurements

Figure 2: Test bench 1 – Humidifier, 2 – Mixing chamber, 3 – Control card/potentiostat

Figure 3: Surface SEM images of the screen-printing YSZ layer

Figure 4: SEM images of electrode/YSZ interface (Au :white, YSZ or ZrO_2 grey): A – Au; B – AuZ; C – AuY; D – Pt.

Figure 5: Experimental and fitted Nyquist plot of Au-Au sample at 550°C in air (numbers with arrow indicate the $\log_{10}$ of the measuring frequency)

Figure 6: Arrhenius diagrams of the solid electrolyte resistance (R_{SE})

Figure 7: Arrhenius diagrams of the polarization resistance (R_{POL}) of the three symmetric sensors Au/Au, AuZ/AuZ and AuY/AuY.

Figure 8. Sensor Pt/YSZ/SE baseline at 450°C in 12% O_2 , 1.5% H_2O

Figure 9: Sensor responses (ΔV) Au, AuZ and AuY sensors to different concentrations of NO_2 in presence of 12% O_2 and 1.5% H_2O at 450°C

Figure 10: Sensor responses (ΔV) of Au, AuZ and AuY sensors to different concentrations of NO_2 in presence of 12% O_2 and 1.5% H_2O at A) 500°C and B) 550°C

Figure 11: Sensor responses (ΔV) of Au, AuZ and AuY sensors to 100 ppm of NO_2 in presence of 12% O_2 and 1.5% H_2O at 500°C

Figure 1: A) Schematic drawing of solid state gas sensors and B) symmetric samples for EIS measurements

Figure 2: Test bench1 – Humidifier, 2 – Mixing chamber, 3 –Control card/potentiostat

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Figure 3: Surface SEM images of the screen-printing YSZ layer

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Figure 4: SEM images of electrode/YSZ interface (Au :white, YSZ or ZrO_2 grey): A – Au; B – AuZ; C – AuY; D – Pt.

Figure 5: Experimental and fitted Nyquist plot of Au-Au sample at 550°C in air (numbers with arrow indicate the $\log_{10}$ of the measuring frequency)

Figure 6: Arrhenius diagrams of the solid electrolyte resistance (R_{SE})

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Mis en forme : Retrait corps de texte, Interligne : 1,5 ligne

Figure 7: Arrhenius diagrams of the polarization resistance (R_{POL}) of the three symmetric sensors Au/Au, AuZ/AuZ and AuY/AuY.

Figure 8. Sensor Pt/YSZ/SE baseline at 450°C in 12% O_2 , 1.5% H_2O .

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Figure 9: Sensor responses (ΔV) Au, AuZ and AuY sensors to different concentrations of NO_2 in presence of 12% O_2 and 1.5% H_2O at 450°C

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Figure 10: Sensor responses (ΔV) of Au, AuZ and AuY sensors to different concentrations of NO_2 in presence of 12% O_2 and 1.5% H_2O at A) 500°C and B) 550°C

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Figure 11: Sensor responses (ΔV) of Au, AuZ and AuY sensors to 100 ppm of NO_2 in presence of 12% O_2 and 1.5% H_2O at 500°C .

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