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Development of a NOx gas sensor for exhaust

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Summary

A high-sensitive sensor for ***NOx detection*** based on ***selective electrochemical*** reduction of NO_2 is proposed. Electrochemical cell consisting of three metallic electrodes and ***YSZ*** electrolyte operates under electric polarization and allows selective NO_2 detection in exhaust gases at 400-550°C. ***Electrical polarization*** applied between working and counter electrodes accelerates partial electrochemical reaction: oxygen reduction on cathode and oxygen-ion oxidation on anode. Variation of working electrode potential, where NO_2 reduction is possible, is proportional to NO_2 concentration. Cross-sensitivity of sensor to hydrocarbons, NO and CO was not observed. Combination with a **catalytic filter** allows NO measurement and distinction between NO and NO_2, given that oxygen concentration is known and ammonia concentration remains negligible.

Motivation

The interest for reliable electrochemical gas sensors for automotive exhausts application to on-board control the emissions of nitrogen oxides is still challenging with the strengthening of international legislations. Electrochemical NOx sensors based on yttria-stabilized zirconia (YSZ) solid electrolyte have been and are still extensively studied, focusing either on materials approach [1,2] or on running mode (polarization) [3,4]. In a past project, a planar potentiometric YSZ based sensor with platinum and gold electrodes associated with a catalytic filter covering the sensing element was shown to be fully selective to NOx but unable to distinguish between NO and NO_2 [5]. Without a catalytic filter, the Au/YSZ/Pt sensor is sensitive to reducing gas (CO, hydrocarbons, NO…) with a positive response ($\Delta V = V_{Pt}-V_{Au}$) while opposite behavior is observed for oxidant gas NO_2. A catalytic filter removes interferences from CO and hydrocarbons and leads to NO/NO_2 thermodynamic equilibrium so that a similar response is obtained either for NO or NO_2 (Figure 1). Hence, the objective is to improve such sensor to overcome this inconvenient; a strategy based on electrode polarization was developed.

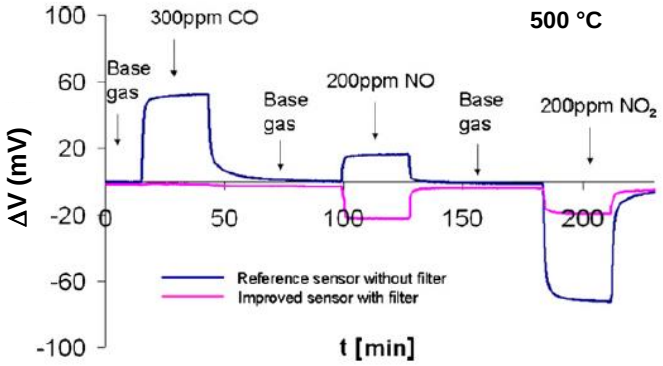

Fig. 1: Responses ($\Delta V = V_{Pt}-V_{Au}$) of Au/YSZ/Pt planar sensors with and without catalytic filter (from [5]).

Experimental

The sensor is developed by screen-printing technology. In order to polarize the gold working electrode (WE) in the range 0-100nA, a third platinum counter-electrode (CE) is added to the starting Au/YSZ/Pt sensor. The initial platinum electrode is considered as the reference one (RE) and the sensor response is measured as $\Delta V = V_{RE\text{-}Pt}-V_{WE\text{-}Au}$ (Figure 2). A platinum heating resistance is deposited on the opposite side of the alumina substrate in order to heat and monitor the sensor temperature. Test conditions are

summarized hereafter: sensor temperature 400-550 °C, gases: CO 0–1000 ppm, NO_2 0–2000 ppm, NO 0–2000 ppm in H_2O (2 vol.%), O_2 (12 vol.%) balanced with N_2.

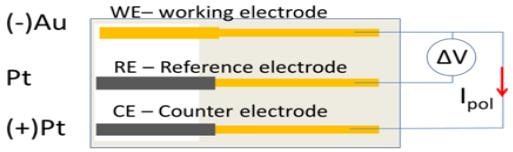

Fig. 2: Schematic representation of 3-electrodes YSZ polarized planar sensor.

Results and discussions

Sensors without catalytic filter were firstly investigated. Under negative polarization of gold working electrode, electrochemical reaction of oxygen reduction, eq.(1), is favored at this electrode. In presence of NO_2, WE overpotential decreases due to NO_2 electrochemical reduction, eq.(2). On the contrary, reducing gases cannot be reduced at WE, so that the sensor is only selective to NO_2.

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}_{YSZ} \qquad (1) \qquad\qquad NO_2 + 2e^- \rightarrow O^{2-}_{YSZ} + NO \qquad (2)$$

Figure 3a illustrates NO and NO_2 responses at 450°C of a sensor polarized at 25 and 50nA and clearly points out the significant response (ΔV decrease) to NO_2, while no response is observed to any tested reducing gases (Figure 3b).

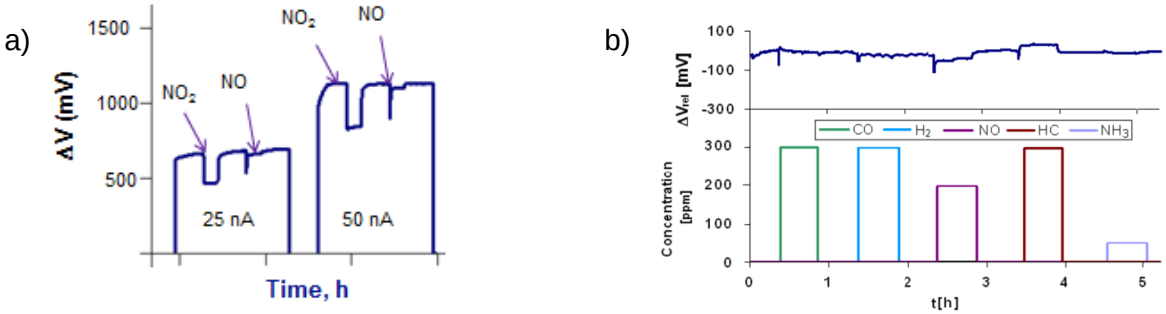

Fig. 3: Sensor response (ΔV) at 450°C, in H_2O (2 vol.%), O_2 (12 vol.%), balanced with N_2 a) to 100ppm NO_2/NO at different polarizations, b) to reducing gases(CO, H_2, NO, HC= hydrocarbons, NH_3) under 50nA.

From the measurement of both the sensor response (ΔV) and of the polarization voltage ($\Delta V_{pol} = V_{CE\text{-}Pt} - V_{WE\text{-}Au}$), it is possible to calculate gold WE electrode overpotential (η_{Au}). Figure 4 confirms that η_{Au} is dependent on NO_2 concentrations with no significant influence on oxygen content (tested range 2-18 vol.%).

As a conclusion, the polarized NO_x sensor without filter allows to measure selectively NO_2. If the catalytic filter is added while maintaining polarization, the sensor measures NO_2 concentration resulting from NO/NO_2 thermodynamic. Hence, if the equilibrium constant is known (oxygen content required), it's possible to calculate both NO_2 and then NO by combination of systems with and without catalytic filter.

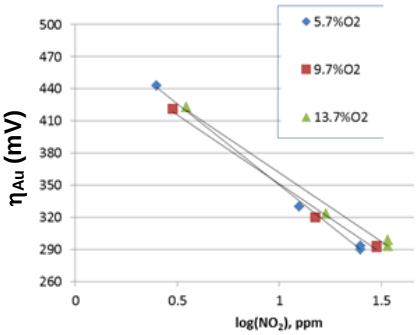

Fig. 4: Overpotential of gold WE electrode as a function of NO_2 concentration, at 450°C, 25nA, in H_2O (2 vol.%), O_2 (≈6, 10, 14 vol.%), balanced with N_2

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