

NO₂-selective electrochemical sensors for Diesel exhausts

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Summary

Electrochemical NO_x sensors based on yttria-stabilized zirconia (YSZ) are commercialized to detect overall NO_x concentrations in Diesel exhausts without distinction between NO and NO₂. To overcome this inconvenient, a high-sensitive sensor for NO_x detection based on selective electrochemical reduction of NO₂ is proposed. An electrochemical cell consisting of three metallic electrodes on solid-state electrolyte (YSZ) operating under electric polarization between a gold working electrode and a platinum counter electrode allows selective NO₂ detection at 400-550°C with high sensitivity, and without any significant interferences to other gases like hydrocarbons, carbon monoxide and also ammonia and nitrogen monoxide. A mechanism based on cathodic overpotential is proposed.

Motivation and results

The interest of reliable electrochemical gas sensors for automotive exhausts application to on-board control nitrogen oxides emissions is growing with the strengthening of international legislations. Although commercial sensors still exist and despite numerous studies on mixed potential YSZ based devices, there are few solutions to distinguish NO and NO₂ [1-2]. However, NO₂ is much more harmful than NO because at the origin of acidic rains and acting as a precursor of ozone formation. In addition, studies on air quality in European urban zones have evidenced that the ratio NO₂/NO_x slightly increases year after year mainly due to Diesel Oxidation Catalysts which equipped Diesel cars. Hence, the objective is to develop a NO₂-selective electrochemical sensor for Diesel exhausts.

An electrochemical planar sensor composed of an YSZ porous layer and three metallic electrodes on it was prepared by screen-printing. Low currents (10/100 nA) were applied between the working gold electrode (WE) negatively polarized, and the platinum counter electrode (CE) to induce electrochemical reductions at the Au/YSZ interface. The sensor response (ΔV) was measured as the potential difference between WE and the reference platinum electrode (RE) (Fig. 1). NO_x sensitivity and selectivity of this sensor were investigated in a test bench in the temperature range 400-550°C for atmospheres containing O₂ (12 vol.%), H₂O (2 vol.%) and various NO and NO₂ concentrations (25-300 ppm). At temperatures lower than 500°C, the sensor was found to be highly sensitive and selective to NO₂. For instance, at 450°C, for an applied current of 100 nA, ΔV value drastically decreases from 2.1 V in O₂/H₂O atmosphere down to 1.7 V when 100 ppm of NO₂ is introduced (Fig. 2). For low NO₂ concentrations (< 100 ppm), the sensitivity of the sensor is around 5 mV/ ppm of NO₂. Furthermore, when reducing gas are introduced, such as NO (200 ppm), CO (300 ppm), H₂ (300 ppm), hydrocarbons (300 ppm of a mixture 25 vol.% methane, 25 vol.% butane, 50 vol.% propene) or NH₃ (50 ppm), the sensor signal is practically not modified (Fig. 3). Hence the sensor is selective to NO₂. Regarding mechanism detection, the sensor response is found to be mainly linked to the cathodic overpotential at the Au (WE)/ YSZ interface which is drastically reduced by the presence of NO₂.

Word count: 480

References

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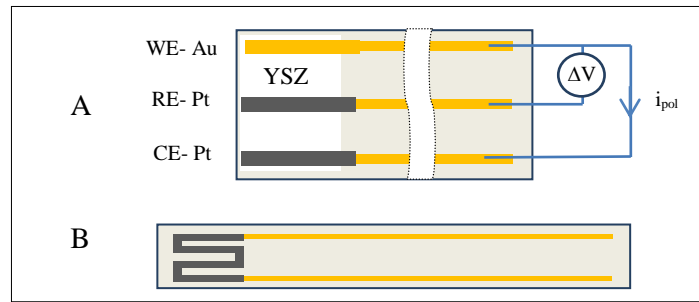


Figure 1: Schematic representation of sensing (A) and heating (B) sides of YSZ planar sensor

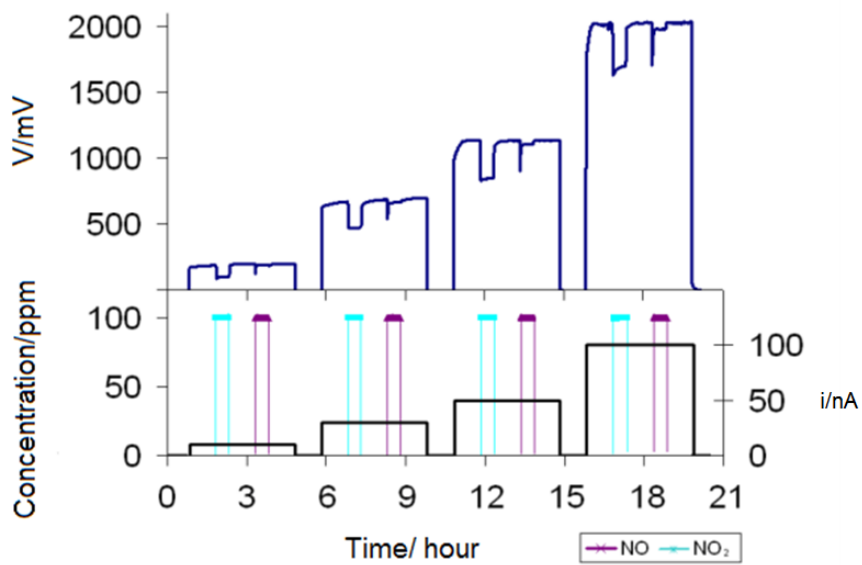


Figure 2: Sensor signal (ΔV /mV) at 450°C to 100ppm NO₂/NO at different polarizations (i/nA).

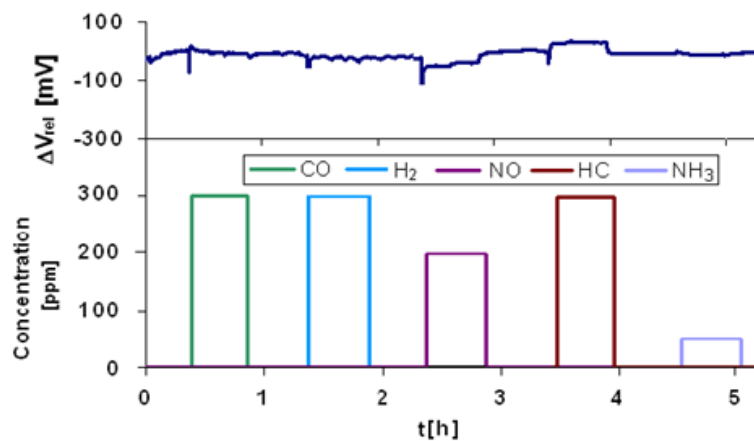


Figure 3: Relative sensor response at 450°C to 300 ppm CO, 300 ppm H₂, 200 ppm NO, 300 ppm HC (25 % methane, 25 % butane, 50 % propene), 50 ppm NH₃ (Gas flow: 30 l/h, polarization +100 nA)