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NO₂-selective electrochemical sensors for Diesel exhausts

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Abstract

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 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.

Keywords: NO_x sensor, exhaust, YSZ, mixed potential, polarization, overpotential.

1. Introduction

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.

2. Experimental

2.1. Elaboration of 3 electrodes YSZ based sensor and gas response measurement

An electrochemical planar sensor composed of an YSZ porous layer and three metallic electrodes was prepared by screen-printing on an alumina substrate equipped with a platinum heater on reverse side (Fig. 1). 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 the reference platinum electrode (RE) and WE. 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 (1–20 vol.%), H₂O (2 vol.%) and various NO and NO₂ concentrations (25–300 ppm).

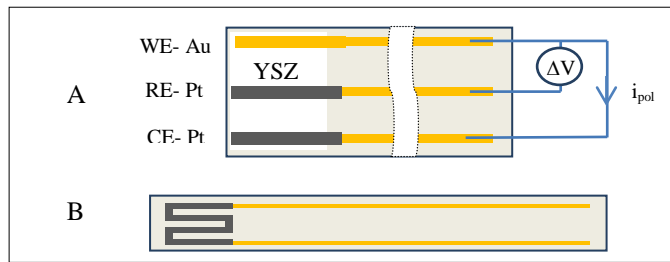


Fig. 1. Schematic representation of sensing (A) and heating (B) sides of YSZ planar sensor

2.2. Electrochemical measurement and overpotential calculation

In galvanostatic mode, the measured signal, ΔV , which is the sensor response, is defined by equation (1).

$$\Delta V = V_{RE} - V_{WE} \quad (1)$$

where V_{RE} and V_{WE} are respectively the potentials of the Pt reference and Au working electrode, under the applied current (i_{pol}). Value of ΔV can also be expressed by equation (2).

$$\Delta V = \Delta V^o + R' i_{pol} + \eta_{WE} \quad (2)$$

where R' is the electrical resistance of solid electrolyte between RE and WE;

i_{pol} is the polarization current between WE and CE,

ΔV^o is the open-circuit voltage (when $i_{pol}=0$),

η_{WE} is the electrochemical overpotential of the working electrode.

The overpotential of the reference electrode η_{RE} is negligible as no current is issued from the reference electrode.

ΔV and ΔV^o can be measured respectively at fixed i_{pol} and $i_{pol}=0$. Electrolyte resistance R' can also be determined experimentally from impedance spectroscopy measurement. Therefore, the overpotential of the working electrode can be calculated, for a fixed temperature and gas conditions, directly from equation (3).

$$\eta_{WE} = \Delta V - \Delta V^o - R' i_{pol} \quad (3)$$

In a same way, it is possible to consider platinum counter electrode CE versus reference electrode RE. The polarisation voltage ΔV_{pol} applied to fix the desired current can be expressed by equation (4).

$$\Delta V_{pol} = V_{CE} - V_{WE} = \Delta V^o + Ri_{pol} + \eta_{WE} + |\eta_{CE}| \quad (4)$$

where R is the electrical resistance of solid electrolyte between CE and WE;

i_{pol} is the polarization current between WE and CE,

ΔV^o is the open-circuit voltage (when $i_{pol}=0$),

η_{WE} and η_{CE} are respectively the electrochemical overpotential of the working and counter electrodes.

The experimental measurement of ΔV , ΔV^o and R allows to calculate the sum $\eta_{WE} + \text{abs}(\eta_{CE})$ from equation (4), and finally combining with equation 3 to determine both η_{WE} and η_{CE} . Their variations were recorded upon various applied currents in a wide range of oxygen partial pressure, in addition with injections of NO_2 (10 to 100 ppm).

3. Results and discussions

3.1. Gas sensor responses

At temperatures lower than 500°C , the sensor was found to be highly sensitive and selective to NO_2 . For instance, at 450°C , for an applied current of 100 nA, ΔV value drastically decreases from 2.1 V in $\text{O}_2/\text{H}_2\text{O}$ atmosphere down to 1.7 V when 100 ppm of NO_2 is introduced (Fig. 2). For low NO_2 concentrations (< 100 ppm), the sensitivity of the sensor is around 5 mV/ ppm of NO_2 . Furthermore, when reducing gases are introduced, such as NO (200 ppm), CO (300 ppm), H_2 (300 ppm), hydrocarbons (300 ppm of a mixture 25 vol.% methane, 25 vol.% butane, 50 vol.% propene) or NH_3 (50 ppm), the sensor signal is practically not modified (Fig. 3). Hence the sensor is selective to NO_2 .

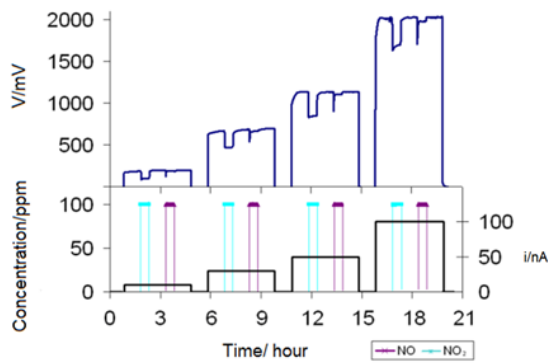


Fig. 2. Sensor response (ΔV / mV) at 450°C to 100ppm NO_2/NO (O_2 12vol.%, H_2O 2vol.%) at different polarizations (i / nA).

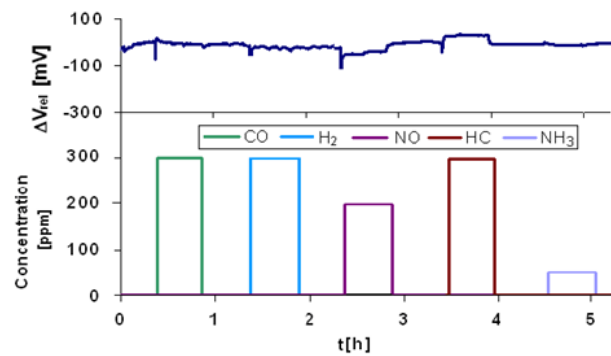


Fig. 3. Relative sensor response at 450°C to 300 ppm CO, 300 ppm H_2 , 200 ppm NO, 300 ppm HC (25 % methane, 25 % butane, 50 % propene), 50 ppm NH_3 at $i_{pol}=100$ nA (O_2 12vol.%, H_2O 2vol.%).

3.2. Detection mechanism

It is known that the modification of sensitivity and selectivity can be enhanced by the polarization of the sensing electrode [3, 4]. If the electrode is polarized negatively as a cathode like WE gold electrode here, only reducible gas can modify its potential and then can be detected. The obtained experimental result proves that in the used temperature and polarization conditions, only O_2 and NO_2 can be electrochemically reduced on the cathodic polarized gold working electrode (equations 5, 6).



where $V_{O^{\circ}}$ is an oxygen vacancy and O_{O^x} is a lattice position of O^{2-} ion in YSZ. Calculations of Au-WE and Pt-CE overpotential during NO_2 (Fig. 4) and NO, CO (not shown here) injections confirms that the sensor response is mainly linked to the cathodic overpotential at the Au (WE)/ YSZ interface which is drastically reduced by the presence of NO_2 . Pt-CE overpotential (absolute value) is quite lower than Au-WE one and do not vary significantly under any gases, neither NO_2 nor reducing gases.

The influence of oxygen concentration on Au-WE overpotential was also investigated (Fig. 5). The overpotential linearly depends on the logarithm of the NO_2 partial pressure. The slopes are respectively 151, 129 and 129 mV/decade for 5.7%, 9.7% and 13.7% O_2 . These values are more than two times higher than those measured for the similar sensor in potentiometric sensor (no polarization): 52 mV/decade at 450°C [5], or 35 mV/decade at 500 °C [6]. They are also higher than the ones reported (112 mV/decade) for a polarized device based on lambda probe [1]. Such high sensitivity to NO_2 is related to the effect of polarization. In potentiometric mode, the mixed potential of the electrodes [3-6] is mainly linked to the difference in electrocatalytic properties of the two electrodes. In galvanostatic mode, the sensitivity is only driven by the overpotential of the sensing electrode. In case of polarized sensing electrodes, the applied current fixes the rate of the electrode reactions, both the electrochemical reduction of oxygen and NO_2 . As demonstrated by study of the exchange current (not presented here), the rate of NO_2 electrochemical reduction is higher than the one of oxygen; NO_2 can be more easily electrochemically reduced than O_2 . The strong decrease of the overpotential is a consequence of the fast electrochemical reduction of NO_2 and is proportional to the logarithm of its concentration. Moreover, the impact of O_2 on NO_2 sensitivity is quite weak in the studied range. As a conclusion, a high sensitive and selective NO_2 sensor running in a polarized mode was developed, based on the overpotential drop of the Au-WE electrode.

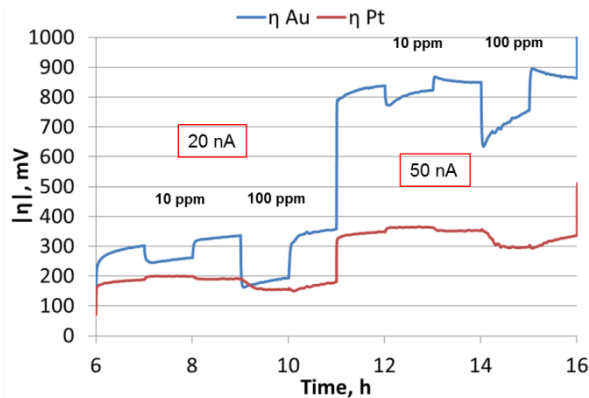


Fig. 4. Overpotential of Au-WE and Pt-CE electrodes (η /mV) at 450°C with various polarization (20, 50nA) and NO_2 concentrations (10, 100ppm) (O_2 12vol.%, H_2O 2vol.%).

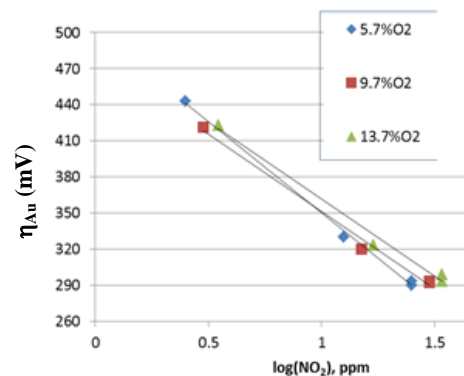


Fig. 5. Overpotential of Au-WE electrode (η /mV) as a function of NO_2 concentration, at 450°C, 25nA, in H_2O (2 vol.%), O_2 (\approx 6, 10, 14 vol.%), balanced with N_2 .

References

- [1] S. Fischer, R. Pohle, B. Farber, R. Proch, J. Kaniuk, M. Fleischer, R. Moos, Method for detection of NO_x in exhaust gases by pulsed discharge measurements using standard zirconia-based lambda sensors, *Sensors and Actuators B* 147 (2010) 780-785.
- [2] D. Wang, D. Racine, H. Husted, and S. Yao, Sensing Exhaust NO_2 Emissions Using the Mixed Potential Principle, SAE Technical Paper (2014) doi:10.4271/2014-01-1487.
- [3] Miura N., Lu G., Ono M., Yamazoe N., Selective detection of NO by using an amperometric sensor based on stabilized zirconia and oxide electrode, *Solid State Ionics*, 117 (3-4) (1999) 283-290.
- [4] Sekhar P.K., Brosha E.L., Mukundan R., Li W., Nelson M. A., Palanisamy P., Garzon F.H., Application of commercial automotive sensor manufacturing methods for NO_x/NH_3 mixed potential sensors for on-board emissions control, *Sensors and Actuators B*: 144(1) (2010) 112-119.
- [5] Romanytsia I., Viricelle J.-P., Vernoux P., Pijolat C., Application of advanced morphology Au-X (X = YSZ, ZrO_2) composites as sensing electrode for solid state mixed-potential exhaust NO_x sensor, *Sensors and Actuators B* 207, (2015), 391-397.
- [6] Gao J., Viricelle J.-P., Pijolat C., Breuil P., Vernoux P., Boreave A., Giroir-Fendler A., Improvement of the NO_x selectivity for a planar YSZ sensor, *Sensors and Actuators B* 154 (2011) 106-110.