A Two Electrode Electrochemical Amperometric Sensor for NO_2 Detection.

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***Abstract*-**In this work a new and simple two electrode amperometric sensor for NO_2 detection is described. The sensor consists of a Nafion® proton exchange membrane (PEM), a Graphite working electrode, and a *NiO* counter electrode. The developed sensor presents a good sensitivity to NO_2 and very small cross sensitivity to CO and O_2. A dedicated measurement system was developed, and a measurement protocol was found, ensuring satisfactory performance also in terms of repeatability.

I. Introduction

Reliable and simple chemical sensing systems for the assessment of NOx concentration are required in many applications fields. In the last years a huge amount of research has been devoted to the development of such systems, based on different solid state sensor types. In particular both conductive metal oxide sensors as well as electrochemical sensors have been widely studied [1-7]. Nevertheless, several problems remains open, and the development of measuring devices ensuring the required performance is still a research issue. In particular, semiconductor sensors present in general a high sensitivity but a low selectivity, and the cross-sensitivity remains therefore an unsolved problem. As far as electrochemical sensors are concerned [6][7], most of these sensors ensure a good sensitivity and a significantly higher selectivity than conductive sensors but often, again, a non negligible cross-sensitivity to other products [6] such as CO, and to other gases including oxygen and water vapor.
As a further issue, an exhaustive knowledge of the chemical reactions responsible for the sensor behavior is still lacking, and therefore the sensors have to be experimentally characterized. Also the measurement protocol has to be experimentally tailored to the application, and its design is an important step of the development of the measurement system.
In this work a new and simple two electrode amperometric sensor consisting of a Nafion® proton exchange membrane (PEM), a Graphite working electrode, and a *NiO* counter electrode is presented. The developed sensor presents a good sensitivity to NO_2 and very small cross sensitivity to CO and O_2. As a drawback, the sensor response is highly sensitive to both humidity and temperature (that have therefore to be controlled). A compact and flexible measurement system is also presented, together with a measuring protocol ensuring a good performance in terms of repeatability.

II. Sensor and measurement system development

The amperometric sensor described in this work is a two electrode cell consisting of three layers: *NiO*/PEM/Graphite.
The *NiO* layer acts as reference/counter electrode, whereas the graphite layer is the sensing electrode. The interface *NiO*/PEM was already investigated, and it was proved to posses a moderate reversibility; the exchange current density was found of the order of 2 $\mu A/cm^2$, using Zirconium Phosphate as electrolyte [4]. This value allows its use as reference/counter electrode in electrochemical devices, provided that the current densities are maintained lower than some tens of nA/cm^2

A. Sensor structure

The *NiO* electrode is obtained by a pressed (40 kN/cm^2) pellet (10 mm diameter, 0.15 mg) of a mixture of the oxide (Aldrich 99.99%) with 10% Nafion®. The powder to be pressed is obtained by drying in mild condition a mixture of the oxide with the proper amount of Nafion® solution (Aldrich w 20%) diluted in n.propanol. One side of the pellet is connected to the external circuit using silver glue, and it is fixed on an insulating support, while the other side is covered by a layer of Nafion®, that is obtained

by drying at room temperature the above solution. This layer can be reinforced by a glass tissue imbued with it. The sensing electrode is prepared by mixing 20 mg of Graphite with 0.5 ml of a Nafion® solution diluted to 2.5 % w/w in n.propanol. The slurry is placed as a spot over the Nafion® layer and dried at room temperature.
For this sensor the reaction of interest at the Graphite electrode are expected to be:

$$NO_2 + H^+ + e \leftrightarrow HNO_2 \qquad (1)$$

where equation (2) is valid only in presence of NO_2.
At the *NiO* electrode, on the other hand, the following reaction is considered:

$$2NiO + H_2O \leftrightarrow Ni_2O_3 + 2H^+ + 2e \qquad (2)$$

the reaction kinetics of (1) is described by the following equations:

$$r_1 = \frac{d[H^+]_C}{dt} = -k_{-1}[NO_2]_{gas}[H^+]_t n_e \qquad (3)$$

where k_X are the reaction rate constants, $[X]_{C,t}$ indicates the concentration of the reactant X produced at the graphite, or the total amount available respectively, n_e denotes the density of free electrons.
and the faradaic current density linearly related to the NO_2 concentration, is given by:

$$j = -Fr_1 + Fr_2 \qquad (5)$$

where r_2 is the rate of reaction (2) and F id the Faraday.

B. Measurement system

The measurement system is sketched in figure 1. The sampling system is composed of a gas tank system feeding two PC controlled flow-meters (BronkHorst F-201C). Each controlled flow (carrier gas and mixture under test) passes through a Drechsel bottle (filled with water and placed in a thermostatic bath whose temperature is fixed, with 1°C accuracy), and through a 3-way valve. Also the 3-way valves are PC controlled: they allow switching each flow to the measurement chamber or to the ambient. The presence of the valves allow to reduce as possible the fluidodynamic transients due to variations of the flowmeter set-points.

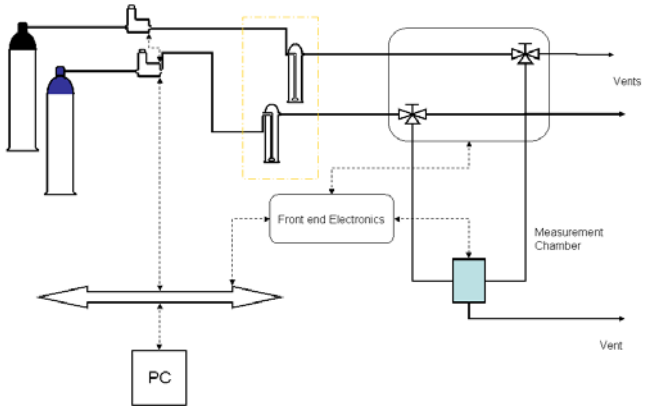

Figure 1. Measurement set-up. The system is composed by gas reservoirs, a flowmeter bench, a mixing control station and a front end electronics interfaced to a data acquisition and control system.

The measurement chamber is placed in an oven kept at a reference temperature (1°C accuracy). If not stated differently, in what follows the experiments are performed by keeping the sensor at 40°C. The thermostatic bath temperature is set at 25°C. The RH is also measured by a humidity sensor (Humirel HTS2330) inside the measurement chamber. An accurate humidity control is necessary when using

Nafion® based sensors, because their behavior depends on the ionic conduction related to water content in the PME and to the H^+ ion generation/combination phenomena taking place at both the sensor electrodes in presence of water [2],[6]. Moreover water weakens the $SO3^-$-H^+ bonds within the Nafion® structure, allowing the proton conduction phenomenon between the sensor electrodes (actually, a humidity excess can also induce flooding, which causes an anomalous sensor behavior [8]).
The developed measurement system is composed of the sensor, of a dedicated front-end electronics (a I-V converter), and of a PC controlled acquisition and processing system. The system allows to apply a voltage difference between the electrodes in the range (-1V,1V), with a 1 mV accuracy. Moreover, it allows controlling, as mentioned before, both the flowmeter bench and the electro-valve system described in figure 1, and it allows measuring both the relative humidity (2% accuracy) and the temperature (by a J type thermocouple, 10^{-1} °C accuracy) in the measurement chamber. Summarizing, with this system it is possible to implement different measurement protocols: to track the sensor response to abrupt changes of the flow composition, to performi voltammograms, to evaluate sensor sensitivity as a function of different flows or different flow compositions.

I.Experimental Results

The developed sensor was tested with different mixtures of nitrogen and NO_2 with concentrations from 2 ppm to 10 ppm.
The different mixtures were obtained by mixing the two variable flows controlled using the two flowmeters in figure 1, always keeping the total flow constant during a measurement. The measurement chamber temperature was kept at 40°C, and the Drechsel temperature was fixed at 25°C (RH =43%).

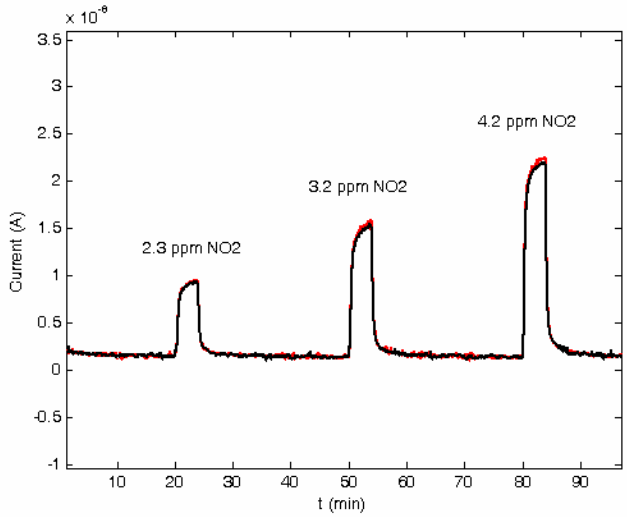

Figure 2. Two sensor response curves obtained in different days (black solid line and dashed red line) with a total flow of 150ml/min and with 2.3, 3.2, 4.2 ppm of NO_2.

With the simple two electrode sensor arrangement it is of the utmost importance the selection of a suitable measurement protocol. In fact for this sensor the response to a constant concentration of NO_2 eventually tends to a very small value due to the change of the electrode potentials with time. To obtain satisfactory measurements the average value of the current has to be kept low to maintain as constant as possible the average reaction potentials. To this purpose a pulsed measurement technique is used, i.e. the gas under test is delivered to the measurement chamber for short periods, during which the current rises, and after that the reference gas (humid nitrogen) is fed to the sensor in order to restore the reference conditions. To better illustrate this point, see the results shown in figure 2 and compare them with those of figure 3. In both cases the sensor was tested by keeping a constant total flow of 150 ml/min and delivering some pulses of nitrogen and NO_2 mixtures with different concentrations and durations. The responses in figure 2 are obtained by flowing nitrogen for 20 minutes, the gas under test (nitrogen + NO_2, maximum NO_2 concentration of 5 ppm.) for the following 4 minutes, and again nitrogen for the following 6 minutes.
In figure 3 the sensor response to pulses with higher concentrations of NO_2 followed by shorter recovery times in nitrogen is shown.

It is possible to see in figure 3, that when the concentration rises over 9 ppm the baseline changes. This can be explained considering the reaction potentials (interface electrode/electrolyte) and the reaction expression:

$$A + e \leftrightarrow D \tag{4}$$

where A is the reacting specie (acceptor), e is the electron and D is the donor. Actually the electrode potential (E) can be expressed using the following Nernst equation:

$$E = \frac{\mu^0}{e} + \frac{kT}{e} \ln\left(\frac{[A]}{[D]}\right) \tag{5}$$

where μ^0 is the standard chemical reaction potential, k is the Boltzmann constant, T is the temperature, e is the electron charge, and $[X]$ is the concentration of the involved species x. Note that the use of such formulation implies a thermodynamic steady state. Nevertheless eq (5) can be used to approximately analyze the different experimental dynamic conditions.

Initially, in the absence of NO_2 at the equilibrium and with an external voltage difference applied across the electrodes of 0 V the sensor current is close to zero, that is the potentials of the two electrodes is equal (E_{NiO}=E_C, where E_C is the working electrode potential, and E_{NiO} is the counter electrode potential).

The counter electrode potential can be written as:

$$E_{NiO} = k_1 + k_2 \ln(CF) \tag{6}$$

Where CF is expressed by (7),

$$CF = \left(\frac{\left[Ni^{3+}\right]^0}{\left[Ni^{2+}\right]^0}\right) \tag{7}$$

and where k_1 and k_2 are two reaction constants as in (5), and $[X]^0$ indicates the equilibrium concentration of x. When the NO_2 pulse is supplied, the working electrode potential grows higher than that of the NiO electrode, electrons entering the working electrode reduce NO_2 to HNO_2. At the same time Ni^{3+} ions are produced at the Nafion®-NiO interface and also the potential of this electrode starts to grow . The ratio CF grows with the concentration of NO_2 and at the equilibrium, if the NO_2 concentration is maintained, the two potentials tend to become equal and consequently the measured current tends to zero.

When the NO_2 pulse is removed, the NiO electrode has a higher potential with respect to the C electrode and this justifies a negative current. The excess of Ni^{3+} ions at the interface tends to diffuse slowly in the electrode bulk, and hence also the baseline is slowly recovered. This sets a specific limit to the use of such sensor, related to the NO_2 maximum concentration.

As a conclusion, if the NO_2 pulse duration and the recovery time in humid nitrogen are not properly set as a function of the maximum NO_2 concentration to be detected, both the baseline and the NO_2 response amplitude drift.

Nevertheless it was observed that for the concentration range of interest (lower than 10 ppm), the measurement protocol shown in figure 2 is a satisfactory trade-off in terms of repeatability and measurement time, even at higher sensor biasing voltages (up to –200 mV).

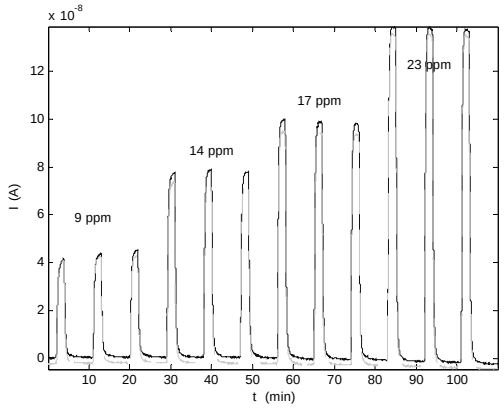

Figure 3. Sensor response obtained with a total flow of 150ml/min and with 9,14, 17 and 23 ppm of NO_2 .

In figure 4 the sensor responses (current peak values) obtained in the described experiments are shown as a function of the NO_2 concentration, for different flows. Using the measurement protocol of Figure 2, the sensor response is found to be linearly related to the NO_2 concentration (rms fitting error lower than 10%). The sensitivity varies from 4nA/ppm (50 ml/min) to 9 nA/ppm (200 ml/min) (see figure 5).

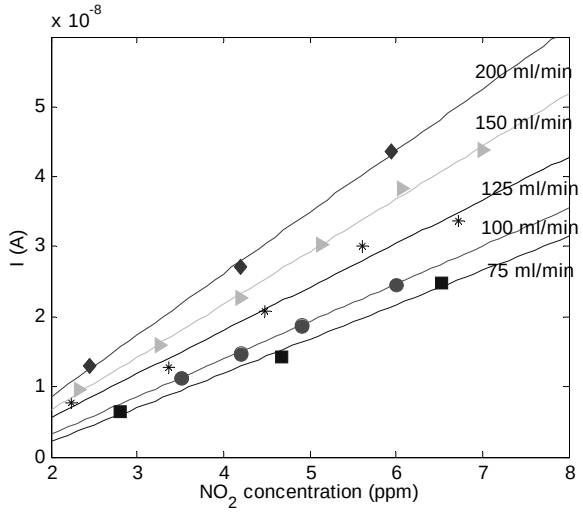

Figure 4. Sensor response (peak values) obtained in the described experiments as a function of the NO_2 concentration, for different flows.

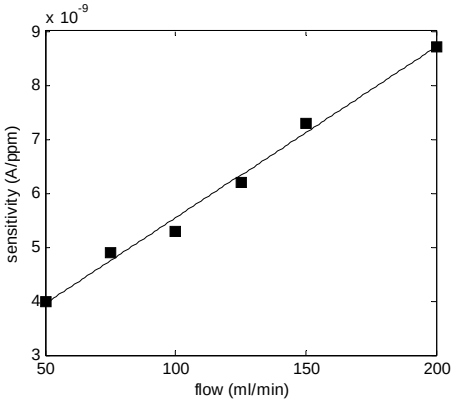

Figure 5. sensitivity to NO_2 concentration as a function of the total flow.

In figure 6 the voltammograms are reported for two different concentrations of NO_2. The sensor sensitivity becomes 90 nA/ppm at a bias voltage of -0.5V (total flow 150 ml/min). The higher

sensitivity in this biasing condition has to be traded with a longer measurement time, as discussed before, and with a more complex measurement system.

To conclude this investigation some experiments have been carried out with *CO* and oxygen as a first analysis of the sensor sensitivity to interfering gases. The experiments have been performed in the same manner as described before, with 0V biasing and 150 ml/min of total flow. The response peak is 4 nA for mixtures of nitrogen and 300 ppm of *CO*, and 5 nA for mixture of nitrogen and 3000 ppm of oxygen, showing sensitivities that are 2 and 3 order of magnitude smaller than that to NO_2, respectively.

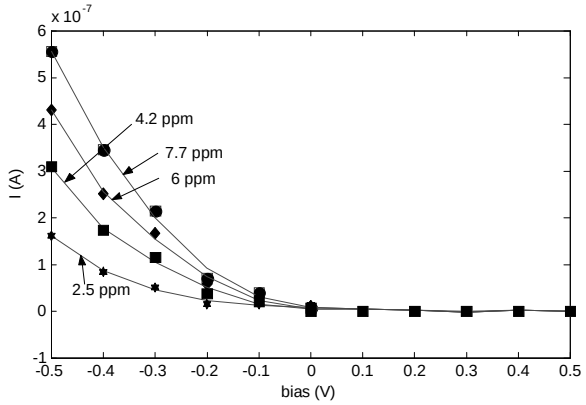

Figure 6: Voltammograms performed with different concentrations of NO_2. Total flow 150 ml/min

II. Conclusions

A novel simple electrochemical two electrodes C/Nafion®/NiO amperometric sensor has been proposed and characterized. A chemical sampling system and a front end electronics has been designed to acquire small current signals. The sensor showed good characteristics in terms of response repeatability, sensitivity, response time and cross-sensitivity to interfering gases, even with 0V biasing.

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