Amperometric Sensors Based on Nafion as Proton Conductor: a Comparison between Two Different Structures

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Abstract- -In this work the authors propose the development and the characterization of two NO_2 amperometric detection systems, based on two different solid state electrochemical sensors. Both sensors have a Nickel Oxide counter electrode, a Graphite working electrode, and Nafion as protonic conductor. The first detection system exploits a two-electrode sensor that presents a satisfactory sensitivity to NO_2, a very low cross-response to interfering gases (CO, O_2), a short response time, and that requires simple front-end electronics. Nevertheless, the usage of this sensor is limited to the detection of low NO_2 concentrations (below 10 ppm). A similar performance can be obtained by a system based on a three-electrode version of the sensor which can be used in a wider NO_2 concentration range, but requires a more complex front end electronics.

I. Introduction

Nitrogen Oxides derivates (NO_x) are commonly generated by combustion processes. Dioxide nitrogen (NO_2) is a highly toxic gas, and one of the main causes of air pollution. Low concentrations of NO_2 (a few ppm) are harmful for human beings and plants. For this reason there is a large request for sensitive NO_2 detection systems suitable for continuous air-quality monitoring. The scientific community is studying new solutions to detect NOx, based both on conductive metal oxide sensors, and on electrochemical sensors. These latters, usually based on ceramic ionic conductors, work at high temperatures (300°C - 800°C) [1-4]. Detection systems exploiting electrochemical sensors based on solid polymer ionic-conductors, and able to work at lower temperatures are also interesting and are at present studied by several research groups [5-11]. In this work the authors propose a comparison between two different systems based on similar amperometric electrochemical sensors, working at ambient temperature, which proved to be highly selective toward NO_2. Both sensors uses Nafion as polymeric protonic conductor. The first sensor is based on a Nickel Oxide-Graphite (NiO-C) two-electrode structure, requires a very simple front-end electronics [11], and is very selective toward NO_2, but it requires a careful selection of the measurement protocol, and can be used only for detection of NO_2 in low concentrations. The second one is a three-electrode version of the previous structure, which requires a less critical set-up of the measurement, and can be used in a wider measurement range in terms of NO_2 concentration.

II. Proposed approach

A. Sensor construction

Two different electrochemical sensors are proposed in this work: the first is based on a two electrode structure, it consists of a Graphite (C) working electrode, where the reaction with the sensed gas, NO_2, is promoted, and of a NiO counter-electrode. The electrodes are separated by Nafion that acts as a protonic conductor. The second sensor proposed in this work is the three electrode version of the first sensor that is provided with an additional electrode (reference), with the same structure as the counter electrode. The NiO counter 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 n.propanol solution. In detail, the powder to be pressed is obtained by drying in mild conditions a mixture of the oxide with the proper amount of Nafion solution (Aldrich w 20%) diluted in n.propanol. In the three electrode version the pellet is divided into two portions in order to obtain also the reference electrode. The NiO pellet (or pellet parts) is placed on an insulating support, and covered by a layer of Nafion, obtained by drying at room temperature the above solution. This layer can be reinforced by a solution imbued glass tissue. The working 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 over the Nafion layer, and dried at room temperature.

For the proposed sensors, the reaction of interest at the Graphite electrode in presence of NO_2 is expected to be:

$$NO_2 + H^+ + e \longrightarrow HNO_2 \tag{1}$$

At the NiO electrode, the following reaction is considered:

$$2NiO + H_2O \longleftrightarrow Ni_2O_3 + 2H^+ + 2e \tag{2}$$

The output current, due to the exponential dependence from the sensing electrode potential, can be expressed by the equation:

$$i_C \propto K[NO_2]e^{-\alpha_C\left(\frac{FV}{RT}\right)} \tag{3}$$

where K is a kinetic constant, $[NO_2]$ indicates the gas concentration, α_C denotes the cathodic transfer coefficient, F the Faraday constant, V the sensing electrode interface potential, and R and T are the universal gas constant and the absolute temperature respectively. From (3), if V can be considered as a constant during sensor operations, a linear dependence of the sensor output (current) on NO_2 concentration is expected.

A. Measurement system

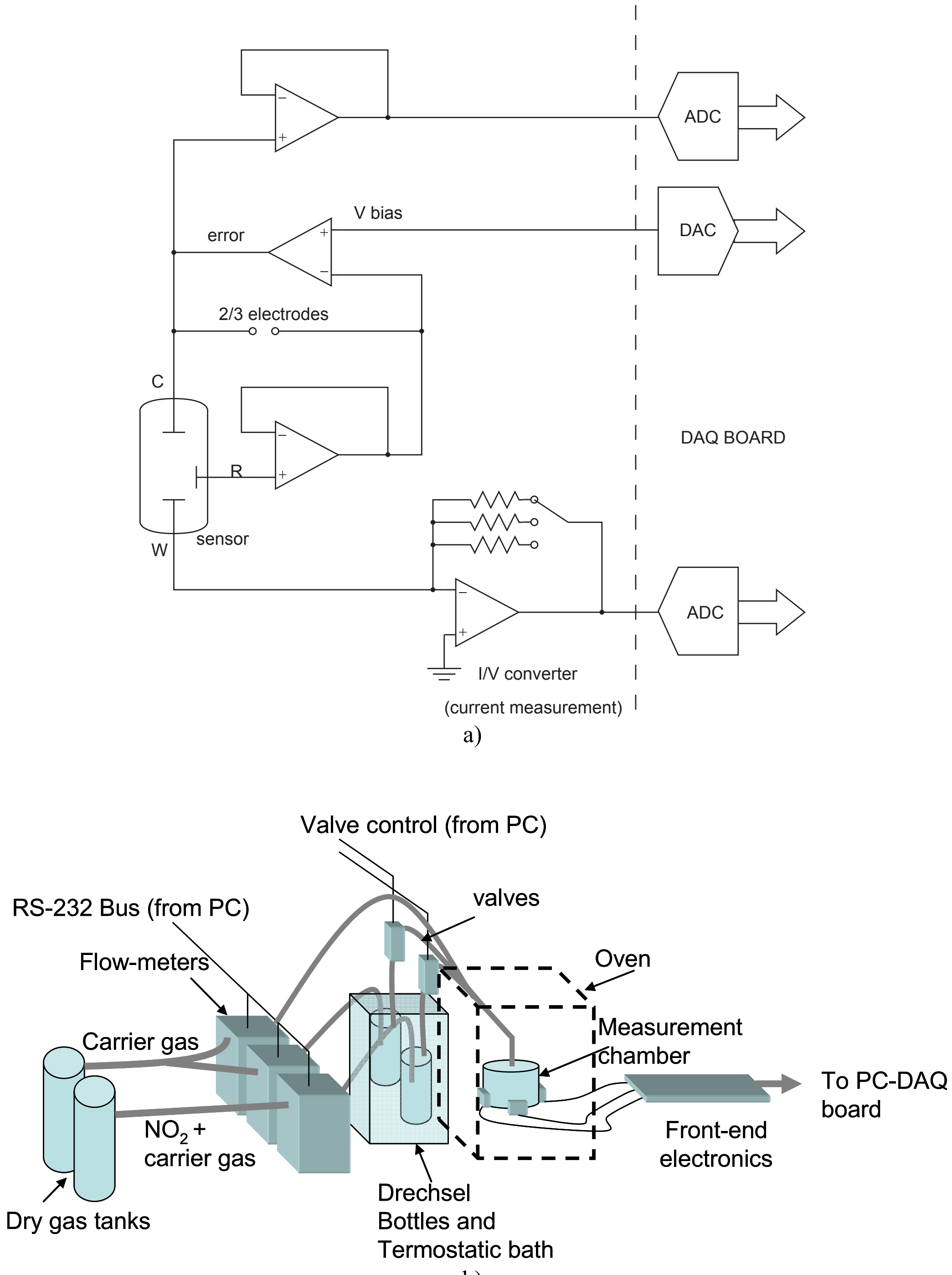
Two different dedicated front-end electronic circuits were developed for the proposed amperometric sensors, able to set the voltage across the devices to a selectable value, and to measure the generated current (see figure 1 a). They allow to set a bias voltage in the range (-1V,1V), with 1 mV accuracy, between the sensor electrodes: working-counter for the two-electrode version, and working-reference for the three-electrode version. To this purpose, the front-end electronics of the three electrode sensor comprises a feedback control loop, in which the error signal is obtained by reading the reference-to-working electrode voltage drop with a high impedance circuit, and by comparing it to a constant voltage. The error signal is used to change the voltage across the series of the working electrode-Nafion, and counter electrode-Nafion interfaces, that is to change the counter electrode voltage. With this solution the voltage drop across the series of the two interfaces Nafion-working, Nafion-reference electrodes, this latter always operating close to the zero current condition, can be set to a desired value. Therefore, if the Nafion-reference electrode interface is stable, the working electrode-Nafion interface potential is also kept at to a constant value, irrespective of the current flowing through the device.

The circuit is completed by a low noise current-voltage converter whose output voltage is A/D converted and acquired by a DAQ board (see figure 1a).

To test the proposed detection systems a chemical sampling system was implemented (see figure 1 b) by means 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 set 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 measurement chamber is placed in an oven kept at a reference temperature (1°C accuracy). If not differently stated, the experiments are performed by keeping both the sensors and the Drechsel bottles at 30°C, that is imposing a 100% RH.

Both the chemical sampling system and the developed electronics are configurable in order to implement different kinds of measurement: it is possible to track the sensor response under abrupt flow composition changes, to perform voltammograms, to dynamically change the biasing voltage, and to evaluate sensor sensitivity as a function of different flows or different flow compositions.



a)

b)

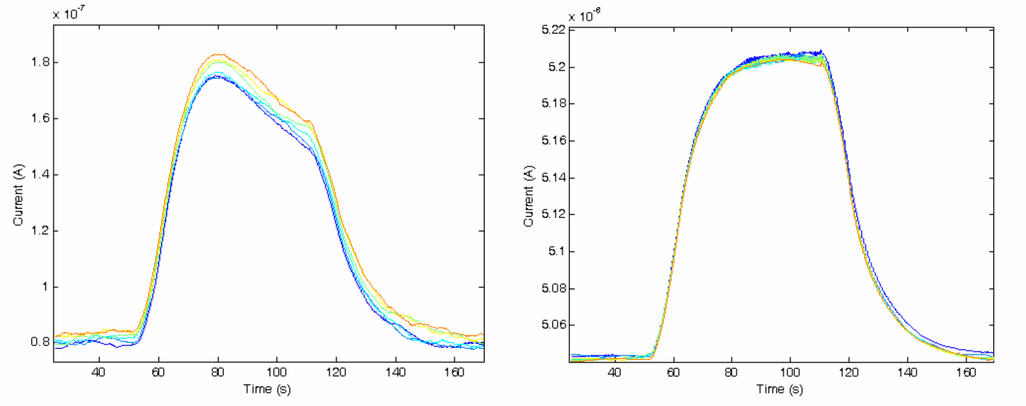
Figure 1. a) 2 and 3 electrodes front-end circuit structures. b) Chemical test sampling system.

C. Difference in two and three electrode sensor operations.

In the two electrode design the potential V across the working electrode-Nafion interface can not be efficiently controlled, since the electronics sets the voltage difference between the working electrode and counter electrode, i.e. it sets the voltage across the series of the two interfaces (counter-Nafion, working-Nafion), independently from the current flowing through the device. Therefore the linear behaviour, suggested by (3), can be granted only when low currents are generated for short time intervals. The authors already pointed out that the counter electrode interface is not very stable, and that its potential changes as the products of the reaction (2) accumulates at this surface [11]. This results in a current decay when the sensor is exposed to large quantities of NO_2. The authors showed that in any case satisfactory results can be obtained by using the sensor for the detection of low concentrations of NO_2 with short NO_2 exposure times (few minutes), and sufficiently long recovery times (about ten minutes). This limit can be partially overcome by the three electrode structure where the reference electrode is devoted to the control of the potential V at the working electrode-nafion interface. This grants a better control of the voltage V at the working -Nafion interface that remains stable during measurements.

III. Results and conlcusions

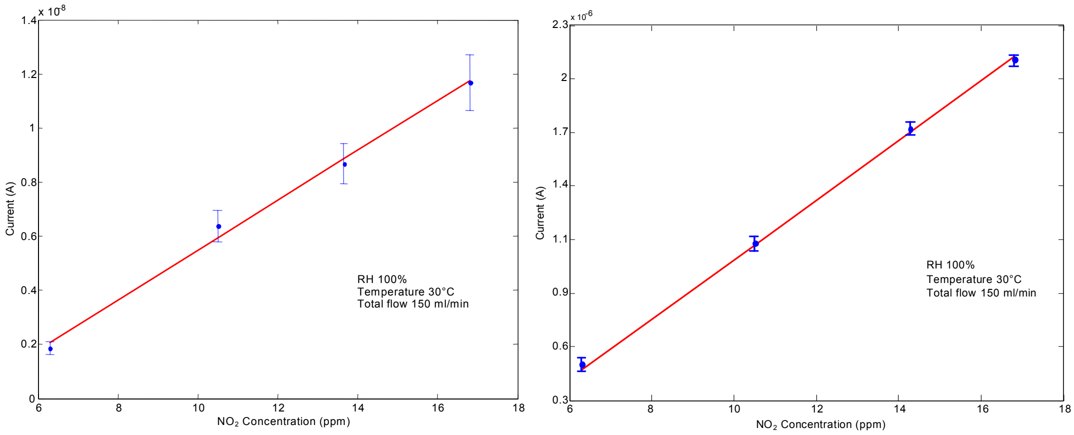
Preliminary results showed good characteristics of sensitivity and response repeatability as shown in figure 2. To make a comparison among the different sensor responses, the following measurement protocol was used: 1 minute exposure to N_2, 1 minute exposure to NO_2 plus N_2 mixtures in different concentrations, and 1 minute of exposure to in N_2 (recovery phase). The flow is always constant during these three measurement phases, and set in the range 100-200 ml/min [10]. As can be seen comparing figure 2a) (NiO-C two-electrode structure) with figure 2b) (NiO-C three-electrode structure), there is an evident difference between the three-electrode version and the two-electrode version of the sensor in terms of both response sensitivity, and capability to show a plateau under steady chemical conditions (phase 2 of the measurement protocol).



a) b)

Figure 2. In this picture some responses of the sensors obtained with a 3 minutes measurements at 200 ml/min total flow, with a 1 minute exposure to NO_2 (15 ppm) at -0.2V biasing, are shown: a) NiO-C two-electrode structure responses b) NiO-C three-electrode structure responses,

Figures 3a) and 3b) show the sensor responses to different NO_2 concentrations (measurement conditions : 100% RH, 30°C, 0V biasing, 150 ml/min flow, 4 min N_2 flow, 4 min NO_2 + N_2 mixture flow, 5 min N_2 flow). Both sensors responses are fairly linear, but the sensitivities are different. For the NiO-C two-electrode sensor shown in figure 3a) the sensitivity is about 1 nA/ppm, whereas the three electrode version has a sensitivity of 170 nA/ppm, i.e. more than two orders of magnitude larger than the first one. In these experimental conditions (up to 17 ppm of NO_2 in N_2) the three electrode sensor shows a stable and satisfactory behaviour, whereas the lower stability of the two electrode sensor causes a higher standard deviation of repeated measurements at the higher concentrations. Note that a significantly higher sensitivity (close to 100 nA/ppm) can be achieved also with the two electrode sensor by biasing it with a voltage of –0.5 V as stated in [11]. Nevertheless, as above explained, when delivering large currents this sensor becomes unstable, so in this conditions, if exposed to NO_2 concentrations in the order of 10 ppm, the sensor largely drifts, and long recovery times are required.



a) b)

Figure 3. Responses to NO_2 concentrations a) NiO-C two-electrode sensors b) NiO-C three electrode sensor. Experimental conditions: 100% RH, with 0V biasing, 30°C, 150ml/min total flow. The dots represent the mean value over 14 measurements for each concentration whereas the bars quantify the std deviation.

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