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Criticality of human breath detection with a portable device I: nanotechniques for improving sensing materials

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ABBREVIATIONS AND ACRONYMS

ABS	Acrylonitrile butadiene styrene
ACDs	Atherosclerotic Cardiovascular Diseases
CAWS	computer-aided wet-spinning
CSA	camphorsulfonic acid
EDS	Energy Dispersive X-ray Spectroscopy
EtOH	Ethanol
GC	Gas Chromatography
HME	Heat and Exchange Moisturizers
min	minute
ml	milliliter
PANi	polyaniline
PC	Personal Computer
PHBHHx	poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate]
Ppm	parts per million
PTFE	Polytetrafluoroethylene
RH	Relative Humidity
s	seconds
SEM	Scanning Electron Microscope
VOC	Volatile Organic Compounds
Vol	Volume
WS	Wize Sniffer

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1. INTRODUCTION

Human breath is largely composed of oxygen, carbon dioxide, water vapor, nitric oxide, and numerous volatile organic compounds (VOCs) [1, 2]. Changes in the concentration of the molecules in VOCs could suggest various diseases or at least changes in the metabolism. Indeed, breath gases are recognized to be excellent indicators of the presence of diseases and clinical conditions. Such gases have been identified as biomarkers using accurate but expensive benchtop instrumentations such as gas chromatography (GC) or electronic nose (e-nose) [1]. As a consequence, in recent years, it has been stimulated the necessity to develop a portable device for breath analysis, easy to use, and feasible for patients living far from medical structures or physicians.

In the framework of SEMEOTICONS (SEMEiotic Oriented Technology for Idividual's CardiOmetabolic risk self-assessmeNt and Self-monitoring) European Project, we developed a low cost, portable, easy-to- use device for the analysis of breath composition: the Wize Sniffer (WS). The first prototype of such device is based on commercial, semiconductor-based gas sensors.

This type of sensors is very robust and easy to be integrated. Nevertheless, they are not selective, thus impeding the discrimination of each type of molecule they are able to detect.

In this report we describe a method to improve the sensitivity of semiconductor-based gas sensors. In particular, we focus our attention on the development of a hybrid, ad-hoc sensor, based on Polyaniline sol-gel nano-film, to detect Nitric Oxide.

Why Nitric Oxide?

NOx (Nitrogen (di)Oxide) is a VOC that plays an important role as an indicator of metabolic since it is related to endothelial function [8]. In addition, it is a vasodilator and it modulates inflammatory response (operating in combination with CO and Hydrogen Sulfide). It is also a good indicator for asthma diseases.

Detection of NO presents some challenging problems, because low cost sensors are not available. As a consequence, the development of a sensor for NO to be used in a portable device for breath analysis and taking advantage by nano-scale sensing materials imposed us to work harmonizing existing commercial sensors with innovative sensing materials.

2. THE COMMERCIAL GAS SENSORS

The choice of gas sensors has been made taking into account the breath compounds to detect and the working principle of the sensors. The aim of WS is to detect those compounds, present in human exhaled gas, correlated to cardio-metabolic risk. As a consequence, our interest, during a first phase of the work, was focused on: oxygen, carbon dioxide, carbon monoxide, ammonia, hydrogen, hydrocarbons, ethanol, hydrogen sulfide, also according to the suggestions by SEMEOTICONS' physicians.
In a subsequent step, our efforts were addressed to the development of PANi nano fiber-based gas sensors in order to detect substances such as nitrogen oxide.
Criteria for choosing sensors' working principle, was based on their ease of use. So, we selected metal oxide semiconductor gas sensors. Their functioning is based on a variation of resistance from R_0 to Rs when the sensor senses the gas particles. An analogue voltage is measured as indirect measure of change in resistance (see Figure 1):

(1)
$$R_S = \frac{V_C - V_{RL}}{V_{RL}} \times R_L$$

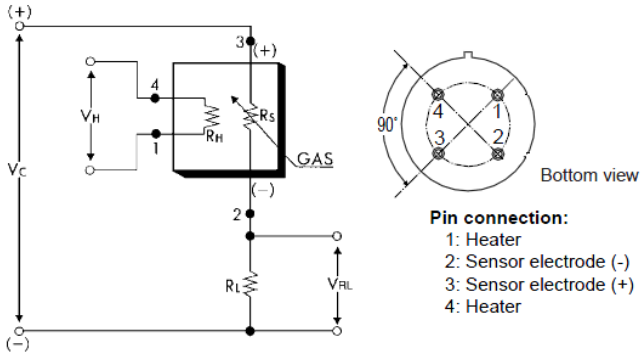

Figure 1- The inner electrical circuit

Furthermore, basing on the study of Guo et al. [1], we chose chemical gas sensors manufactured by Figaro Engineering, because such kind of sensors are very robust, sensitive, resistant to humidity and ageing. We selected the following 6 gas sensors:

- **TGS 2602**: sensitive to hydrogen, ammonia, ethanol, hydrogen sulfide, toluene, cigarette smoke;
- **TGS 2620**: sensitive to hydrogen, carbon monoxide, ethanol, methane, isobutane;
- **TGS 4161 and its module AM-4-4161**: sensitive to carbon dioxide;
- **TGS 2442**: sensitive to carbon monoxide;
- **TGS 2444**: sensitive to ammonia;
- **TGS 821**: sensitive to hydrogen.

3.2 TEMPERATURE AND HUMIDITY SENSOR

The sensitivity characteristic of each sensor varies according to humidity percentage present in the chamber or, generally, in the environment where the sensors are placed (see Figure 2A). For this purpose, a temperature and humidity sensor, Sensirion SHT11 was integrated into the store chamber (Figure 2B).

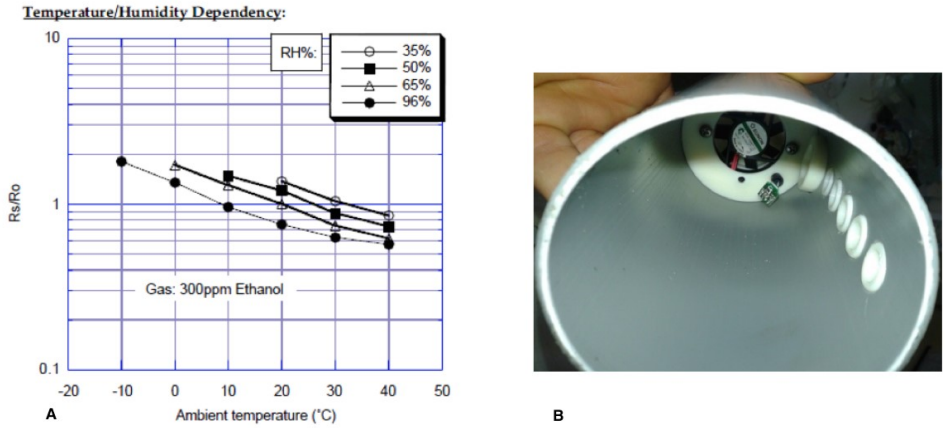

Figure 2 (A) An example of the effects of temperature and humidity on gas sensors' sensitivity (TGS2602 in this case). (B) Sensirion SHT11 temperature sensor inside the store chamber.

Sensirion SHT11 has a humidity accuracy of about +/-3.5% and a temperature accuracy of about +/-0.5°C@25°C. It has a digital output, in contrast to other sensors (the gas ones) which have an analogue output.

3.3 CITYTECHNOLOGY AND SERVOMEX GAS SENSORS

Two additional sensors, MOX20 sensitive to **oxygen and** manufactured by CityTechnology, IR1507 sensitive to **carbon dioxide and** manufactured by Servomex, were inserted in our device. These sensors work in *flowing-regime*: they sense gases' stream that is injected at a constant rate (120ml/s) by the sampling pump. This electro-mechanic pump takes gas samples from the store chamber, injects them where the O2 and CO2 sensors are placed. Then, gases are brought back to store chamber.
About oxygen and carbon dioxide sensors' outputs, COSMED s.r.l. reported us the following informations:

- Warm-up time: 30min (for both sensors)
- Oxygen sensor's output: from 0 to 4V+/-0.01V @20.93% O2
- Carbon dioxide sensor's output:

- 0.02V +/-0.01V @ 0.03%
- 0.67V +/-0.01V @ 0.70%
- 1.75V +/-0.01V @ 2.00%
- 3.5V +/-0.01V @ 5.00%

Here, a table that summarizes the commercial sensors used for WS 1.0 and WS 1.1 and the molecules to be detected (Table 1).

Table 1. Sensors, detected molecules and optimal detection range.

SENSOR	DETECTED MOLECULE(S) / PHYSICAL QUANTITY	OPTIMAL DETECTION RANGE
FIGARO TGS2602	hydrogen, ammonia, ethanol, hydrogen sulfide	1-10 ppm
FIGARO TGS821	hydrogen	1-1000 ppm
FIGARO TGS2620	hydrogen, carbon monoxide, ethanol	50-5000 ppm
FIGARO TGS2442	ammonia	10-1000ppm
FIGARO TGS2444	carbon monoxide	10-100ppm
FIGARO TGS4161	carbon dioxide	350-10000ppm
Servomex IR1507	carbon dioxide	0%-5%
MOX20 CityTechnology	oxygen	20.93%+/-10%
SENSIRION SHT11	temperature and humidity	-40°C-123°C 0%-100%

3. A GENERAL APPROACH TO IMPROVE COMMERCIAL SENSORS WITH NANO-MICROSCALE SENSING MATERIALS

NOx (Nitrogen (di)Oxide) is a VOC that plays an important role as an indicator of metabolic risks and various diseases [8]. In addition, it is a vasodilator and it modulates inflammatory response (operating in combination with CO and Hydrogen Sulfide). It is also a good indicator for asthma diseases. Detection of NO presents some challenging problems, because low cost sensors are not available. One widely used commercial sensor for NO is the Quark NObreath (http://www.cosmedusa.com/en/products/pulmonary-function/quark-nobreath-nitric-oxide-monitor), which cost is more expansive of the entire WS. As a consequence, the development of a sensor for NO to be used in a WS system and taking advantage by nanoscale sensing materials imposed us to work harmonizing existing commercial sensors with innovative sensing materials.

The philosophy inspiring our improvement of commercial sensors with new nanoscale techniques, such as electrospinning or wet-spinning or sol-gel approach is based on the idea of hybrid sensor [9]. The hybrid sensors combine the basic functionality of commercial sensors with a new sensing material manufactured at small scales improving the surface-volume ratio so that the surface of the sensing material interacting with gas to be detected is increased. Chemical gas sensors, such as FIGARO ENG sensors used in WS, present an interface setup truly straightforward if compared to other transduction methods. At present, more commercial chemical gas sensors exploit metal oxide semiconductors because they offer the most favored sensor architecture due to their low-cost, high sensitivity, and simplicity in function. As a consequence, it is possible to combine several functional elements in the same device, such as the sensitive layer, signal converter, and control electronics. However, despite the simple working principles of metal oxide gas sensors, the gas sensing mechanism at the microscopic level is very complex and is still not adequately understood. Gas sensors made of the same metal oxide materials can have different properties and sensing response depending on the fabrication techniques and preparation conditions. It is generally recognized that catalytic reduction/oxidation at the microscopic surface, underlies the chemo-resistive property of the metal oxides. Such reactions are dependent by the electronic structure, chemical composition, crystal structure and relative orientation of the oxide surface to the analyte molecules, thereby allowing their gas sensing properties to be tuned by modifying these parameters. The most successful approach for optimizing the gas sensing properties of metal oxides is to modify the structure of sensing material. Metal oxides can be doped by a small amount of metals, such as Sn, Pd, Cu, Nb, etc, in order to modify structural and electronics properties. The principle of our hybrid surface sensor approach is based on the following assumption: since the sensing mechanism of metal oxides semiconductors is based on the surface reactivity of the materials to incoming analyte gases where electron transfer will play a major role, doping the pristine metal oxide with an additional conductive layer, given in our case by the polymer polyaniline (PANi). Apart from metal dopants as mentioned before, PANi has several advantages over other composite materials. Conducting polymers are currently used in various applications ranging from metallic interconnects in circuits, to active material in electronics devices, electromagnetic radiation shielding, and obviously chemical sensors. PANi is one of such polymers that has been investigated the most. It can be doped during the chemical synthesis to directly yield the conducting emeraldine salt or it can be doped after synthesis by protonation of the insulating emeraldine base. Figure 3 show the monomer structure of emeraldine PANi.

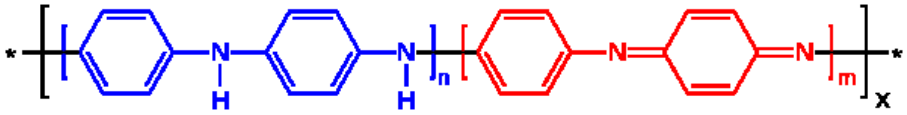

Figure 3 -Emeraldine PANI monomer structure, N is the nitrogen atoms, and H is hydrogen atom, any corner is filled by carbon atoms.

One main problem for creating an hybrid surface Metal-oxide/PANi is represented by the confinement of the additional polymer surface on the pristine metal oxide surface. Figure 8 shows the real dimension of the TGS2602 on which to depose the polymer layer. The real dimensions are approximately less than 300μm×300μm.

3.2 POLYANILINE NANO-MICROFIBER-BASED GAS SENSORS

The hybrid sensing layer combining pristine metal oxide layer with PANI has been prepared with three different techniques: (i) electrospun nanofibers; (ii) wet-spun microfibers; and (iii) dip-coating sol-gel nanofilms. The necessity to use different deposition techniques was due to hard problems on the confinement of PANi layer on the sensing region of the pristine commercial sensor, Figure 4.

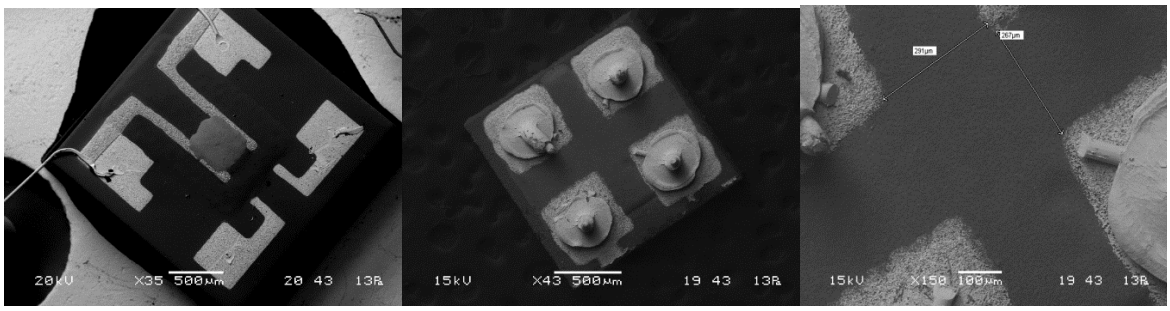

Figure 4- Example of sensing surfaces for two different FIGARO sensors. The images were recorded with a Scanning Electron Microscope

The hybrid surfaces after PANI deposition are shown in Figure 5.

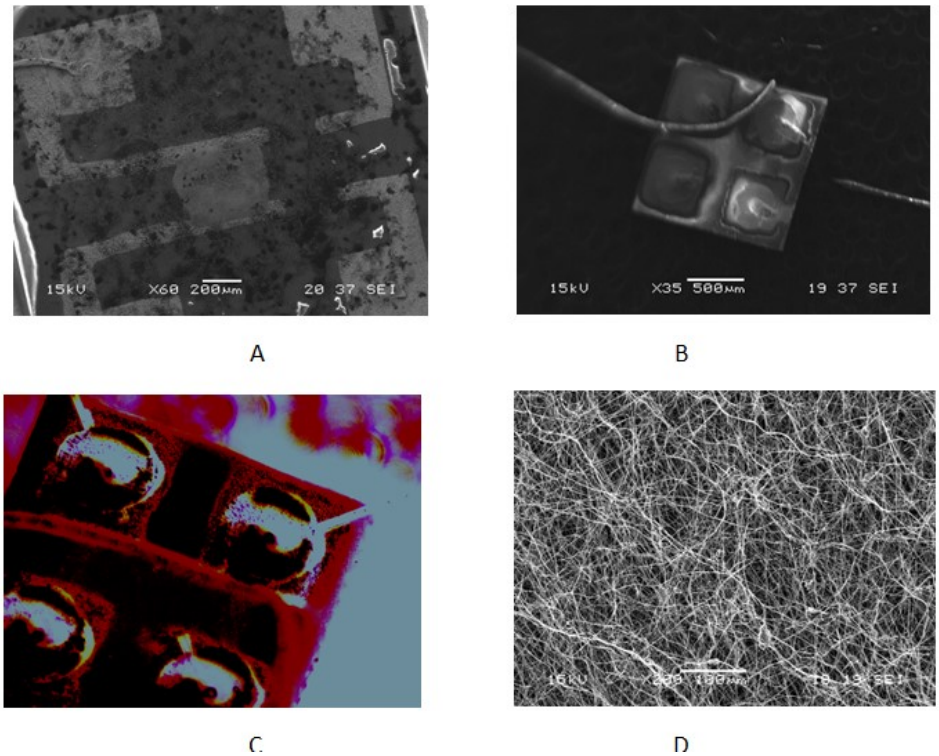

Figure 5- Surfaces of hybrid sensors (metal-oxide/PANi) as observed using a SEM. A, PANi nanoislands produced with the dip-coating technique; B and C single wet-spun microfiber PANi; D, electrospun nanofibers.

The formation of the mat, as shown in Figure 5D, as manufactured with the electrospinning technique has given many problems due to the confinement of the PANi nanofibers on the pristine metal oxide surface

and covering the sensors pins producing a short circuit of the same. Consequently, this technique was unable to produce a satisfactory hybrid sensor.

The preparation of electrospun nanofibers has been detailed on previous reports; here, we focus the attention on the wet-spinning technique.
This research activity was aimed at investigation of the experimental parameters for the manufacturing on a lab scale of microstructured membranes to be employed as part of gas sensor materials. For this purpose, a blend of polyaniline emeraldine base (PAni) doped with 10-camphorsulfonic acid (CSA), and poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (PHBHHx) was investigated as electrically conducting material to be processed by means of a computer-aided wet-spinning (CAWS) technique based on Additive Manufacturing principles [10-12]. PAni is one of the most investigated electrically conductive polymers for sensing materials development due its low cost, ease of synthesis, environmental stability, adequate level of electrical conductivity, and wide range of technological applications [13].
However, one the main drawbacks of PAni is the limited processability due to its poor solubility and rigid backbone related to molecule high aromaticity and low molecular weight. The blending of PAni with Poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (PHBHHx), a polyester produced by biotechnological microbial fermentation with piezoelectric properties and a relatively high dielectric constant [14], was investigated as strategy to improve solution viscoelastic properties for the development of microstructured membranes by CAWS.

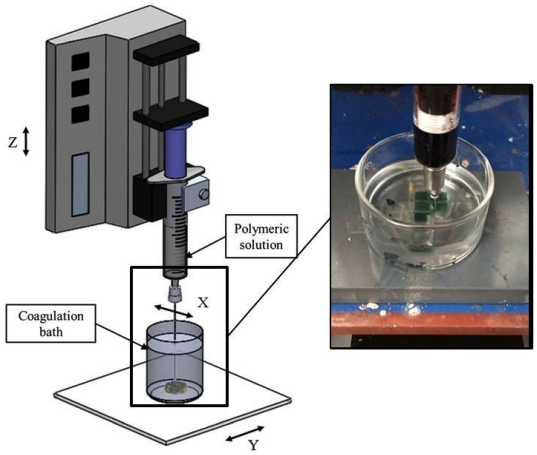

Figure 6 -Schematics of the computer-aided wet-spinning (CAWS) system employed for the preparation of PHBHHx/PAni blend microstructured membranes.

Materials and Methods

Materials

Polyaniline emeraldine base (PAni, Mw = 65,000), 10-camphorsulfonic acid (CSA), ethanol (EtOH) and chloroform (CHCl3) were purchased from Sigma-Aldrich (Italy) and used without further purification. Poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (PHBHHx; 12 mol% HHx, MW=300 000 g/M) was kindly supplied by Tsinghua University, Beijing, China. PHBHHx was purified before use according to the following procedure: (a) the polymer was dissolved in 1,4-dioxane (5% w/v) under stirring at room temperature for 1 h; (b) the solution was filtered under vacuum, using filter paper; (c) the filtrate was slowly dropped into 10-fold volume water to precipitate PHBHHx; (d) after precipitation, the polymer was collected by filtering; (e) the polymer was washed with distilled water and then ethanol, and vacuum-dried and stored in a desiccator.

Membranes manufacturing

PAni solutions were prepared by dissolving at room temperature 100 mg of PAni in 5 mL of $CHCl_3$ (2% w/v) under stirring for 4 h. 128 mg of CSA (0.5 molar ratio of CSA per repeat unit of PAni) were then added to the solution that was left under magnetic stirring at room temperature for 16h. The solution was filtered

using a 0.2 µm PTFE filter (Millipore, Italy) to obtain a homogeneous mixture. 1,25 g of PHBHHx (25% w/v) were then dissolved in the PAni solution under stirring for 2 h at 30 °C. Membranes manufacturing was performed by means of a computer-controlled rapid prototyping machine (MDX-40A, Roland DG Mid Europe Srl, Italy), modified in-house to allow the production of 3D scaffolds composed of wet-spun polymeric fibres (Figure 10) [11]. The prepared solution was placed into a glass syringe fitted with a stainless steel blunt needle, i.d. 0.34mm (gauge 23). A syringe pump (NE-1000, New Era Pump Systems, Wantagh, NY, USA) was used to control the extrusion flow rate of the polymer solution into the coagulation bath. A beaker containing ethanol was fixed to the fabrication platform and used as a coagulation bath. An initial distance between the needle tip and the bottom of the beaker (Z_0) of 1mm was set in all the performed experiments. The geometrical membrane parameters, including the distance between parallel fibre axis (d_F), the number of deposition layers (N_L), the membrane size and geometry, were designed using an algorithm developed in Matlab software (The Mathworks, Inc.). The combination of the X-Z axis needle motion and the Y axis platform motion allowed the fabrication of membranes layer-by-layer with a 0-90° lay-down pattern. The prepared samples were left in the coagulation bath for 12 h and then dried under a fume hood.

Results

The developed manufacturing process allowed for preparation on a lab scale of customized PHBHHx/PAni blend microporous membranes with good accuracy, reproducibility and degree of automation. As summarized in table 2, the most influent parameters for the obtainment of microstructured membranes constituted by overlapped layers of aligned fibers were deposition velocity (V_{dep}) and solution feed rate (F).

Table 2. PHBHHx/PAni membrane prototypes by computer-aided wet-spinning; dF= distance between parallel deposition lines; NL=number of overlapped fibrous layers; Vdep= deposition velocity; F=solution feed rate.

Sample	Structural parameters		Processing parameters	
	d_F (mm)	N_L	V_{dep} (mm/min)	F (mL/h)
PHBHHx/PAni-d_F0.2N_L4	0.2	4	100	0.10
PHBHHx/PAni-d_F0.2N_L8	0.2	8	100	0.10
PHBHHx/PAni-d_F0.5N_L4	0.5	4	150	0.15
PHBHHx/PAni-d_F0.5N_L8	0.5	8	120	0.15

By optimizing the processing parameters, PHBHHx/PAni microstructured membranes with different structural features were developed. In particular, four membrane prototypes with different distance between parallel fiber deposition lines (dF = 0.5 or 0.2 mm) and different number of overlapped layers (N_L = 4 or 8) were successfully manufactured (Figure 7 a and b).

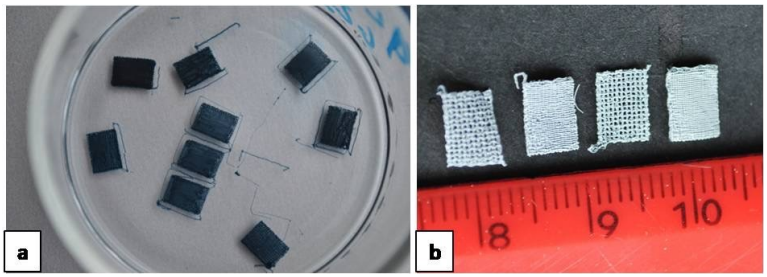

Figure 7 -(a) Wet-spun microstructured membranes. (b) Dried microstructured membrane prototypes; from left to right: PHBHHx/PAni-dF0.2NL4, PHBHHx/PAni-dF0.5NL4, PHBHHx/PAni-dF0.5NL8 and PHBHHx/PAni-dF0.2NL8.

3.3 DEVELOPMENT OF A GAS SENSOR BASED ON PANI FIBERS AS SENSING ELEMENT

Our aims were:

- to improve the sensitivity of a commercial gas sensors settling a film of Polyaniline on its sensing element, and for this purpose we used TGS2602 because easy to open;
- to evaluate the sensitivity of the new gas sensor to nitrogen oxide.

First, we demonstrated that this sensor is not sensitive to nitrogen (di)oxide. The tests were conducted in collaboration with the Institute of Geoscience and Earth Resources (IGG) of CNR of Pisa. In figure 8 A, B, C is shown the tests set up. A system of thin tubes and valves allowed flowing the gases from the tanks at a fixed vol/min. The flux was controlled by means of a flowmeter.

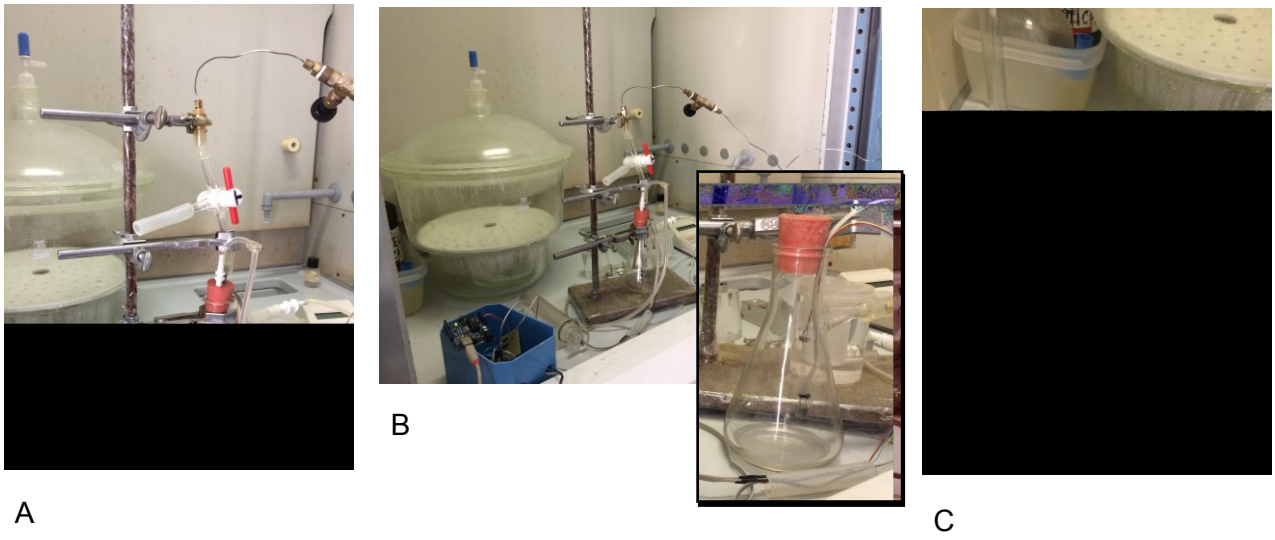

Figure 8 A,B,C- Tests set up. The gas sensor TGS2602 and the temperature and humidity sensor Sensation SHT11 were placed in a vial of 600ml. An Arduino Mega2560 was used to read the output values from the sensors.

The sensors' output voltages in ambient air were the following (Figure 8):

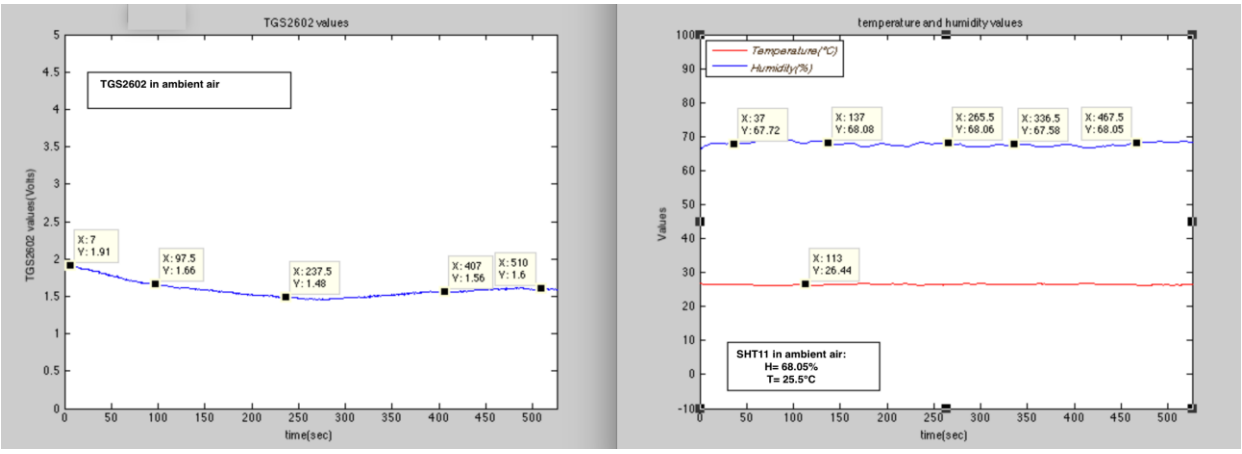

Figure 8- Sensors' output voltages in abient air

that is, 1.60V for TGS2602, a temperature equals to 26.44°C and a humidity at about 68.05%.

Then, only the temperature and humidity sensor SHT11 was placed into the vial. On the bottom of the vial a saturated solution of Sodium Chloride was placed to keep the humidity at a constant value, equals to 75% at each temperature, because, as explained in previous sections, the humidity affects the semiconductor

gas sensors' behavior. The sensor's output signal in the vial with the saturated solution of Sodium Chloride was the following (Figure 9):

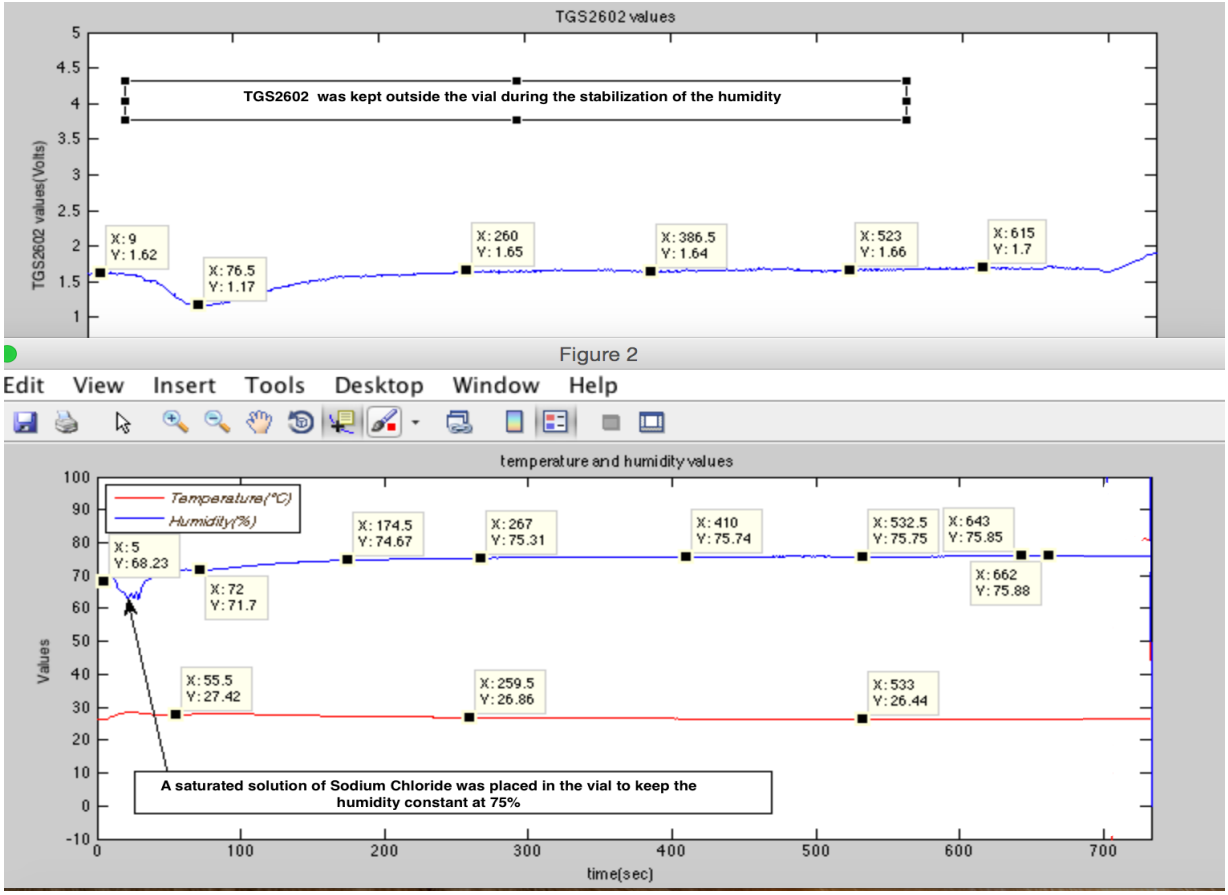

Figure 9- The humidity in the vial was kept constant at 75% by means of a saturated solution of Sodium Chloride

Then, TGS2602 was inserted into the vial and after 90sec a valve was opened to flush the vial with Nitrogen at 206ml/min for 15 min. The flux was monitored by a flowmeter. During the flushing, the humidity decreased at 9.76% (the air into the vial became dry) and the gas sensor's output increased at 3.78V. This shows how the sensor's behavior is affected by the humidity. Figure 10 shows this second step of our tests.

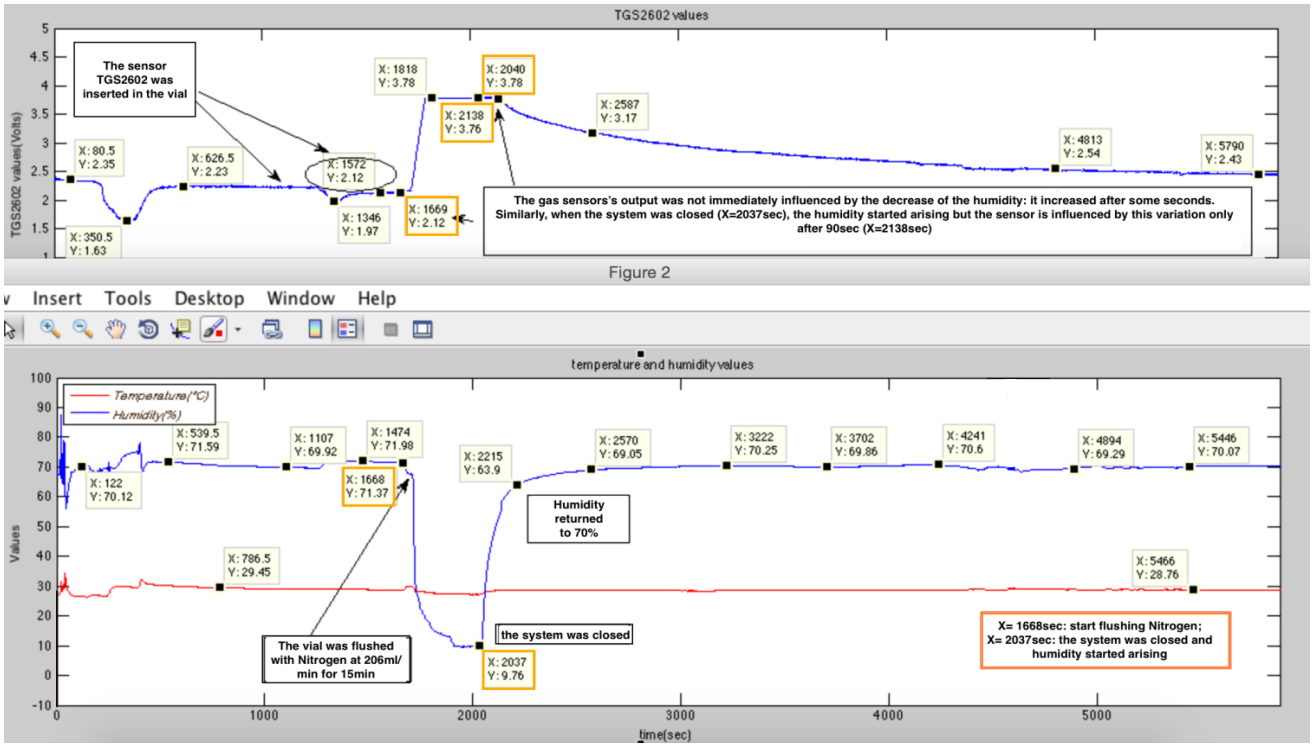

Figure 10 - TGS2602 was inserted into the vial; then the vial was flushed with Nitrogen at 206ml/min for 15min.

Finally, Nitrogen Oxide (NOx) at 1ppmv was injected into the vial at 250ml/min for 3min. The gas sensor output variations were only due to a decrease in humidity during the flushing with NOx. Indeed, when the valve was closed and the humidity returned at about 75%, also the TGS2602's output returned to its baseline value. So we can affirm that TGS2602 is not sensitive to Nitrogen (di)Oxide. This is shown in Figure 11.

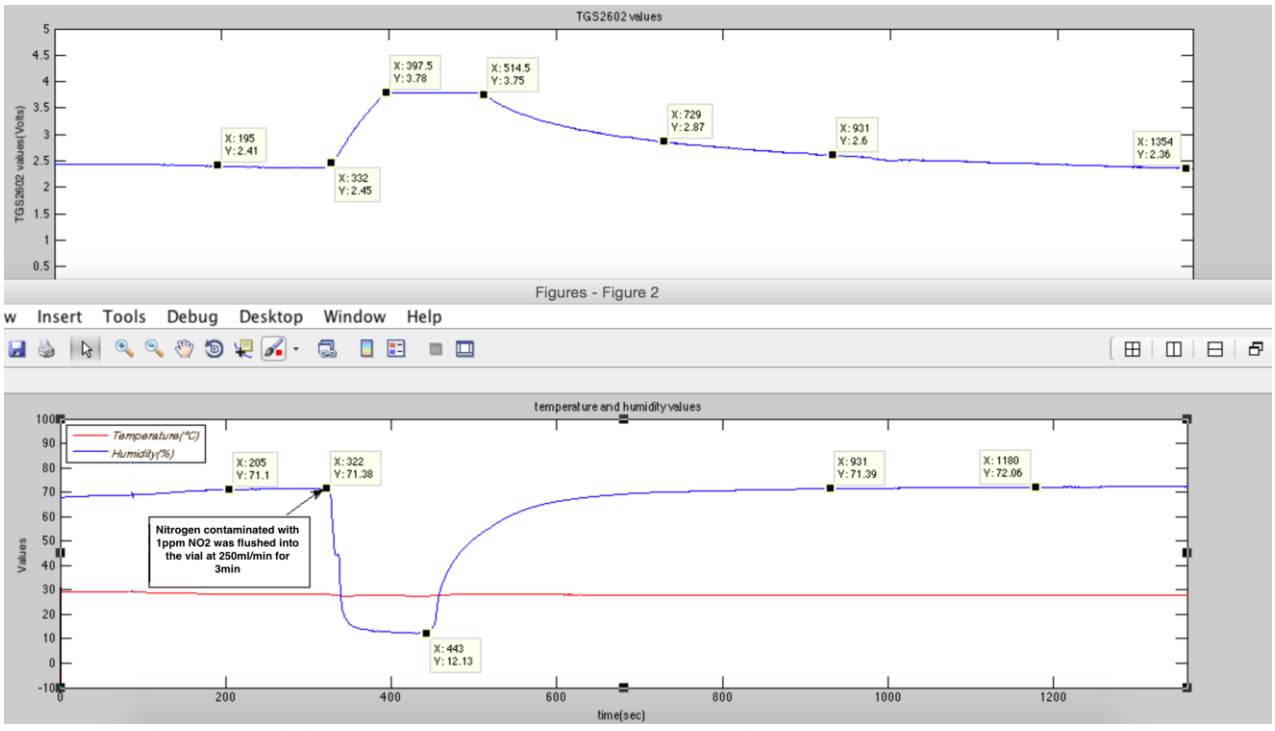

Figure 11- We demonstrated that TGS2602 is not sensitive to Nitrogen Oxide

Then, a PANi sol-gel nanofilm as described in Section 3.2 was settled on the sensing surface of TGS2602, developing the NOx hybrid sensor. The characterization of the NOx hybrid sensor has been essentially

making use of a SEM. In figure 12, we report the image of the sensing surface with the 4-pins connections. The white areas denote the underlying metal oxide surface, while the dark regions represent the PANi coating.

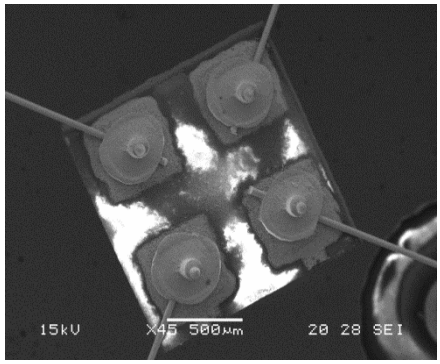

Figure 12- SEM overview of the hybrid sensor metal oxide/PANi

A detail of the PANi film surface is reported in Figure 13.

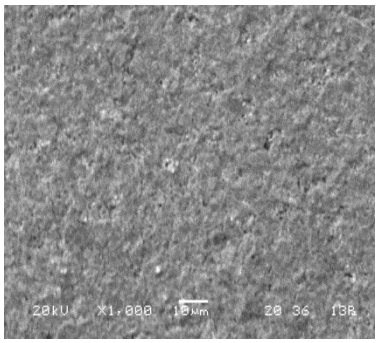

Figure 13- SEM image of the PANi film surface.

The complex chemical structure of the metal oxide composition combined with the PANi has been investigated with the Energy Dispersive X-ray Spectroscopy (EDS) analysis. EDS is an analytical technique used for the elemental analysis and chemical characterization of the hybrid structure. Its characterization capabilities are due to the fundamental principle that each chemical element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. Figures 14 and 15 report the EDS analysis on the metal oxide surface. It is interesting to note that the chemical composition of the metal oxide structure shows as prevalent compound the ZnO2, with several doping atoms, such as Zr, Si, and Bi.

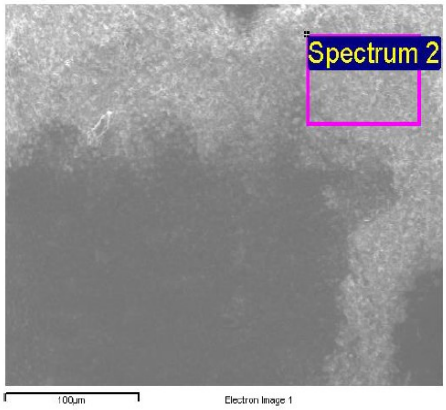

Figure 14- Portion of the metal oxide surface under EDS investigation.

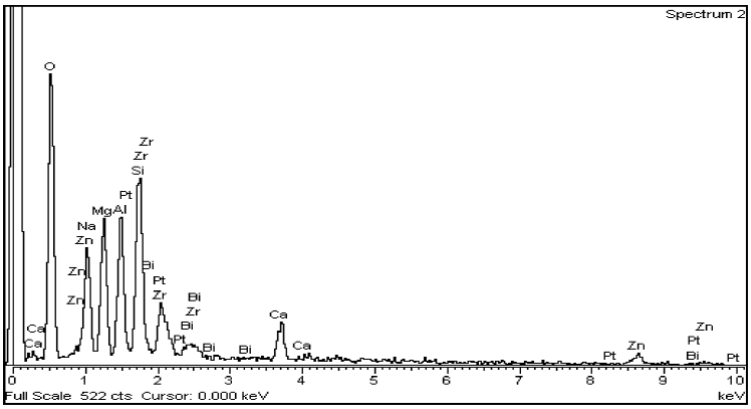

Figure 15- Chemical composition of the metal oxide structure. The results show that the prevalent compound is the ZnO2, with several doping atoms, such as Zr, Si, and Bi.

Similar EDS investigation has been performed on the PANi surface, Figure 16 and 17. The chemical composition of the PANi structure is evidenced by the presence of N atoms, since the carbon atoms form the great initial peak. The presence of more atoms as in the pattern represented in Figure 17 can be easily explained because the EDS rays have a deep penetration depth so that the EDS analysis collect the atoms from all the hybrid bi-layer surface containing both the metal oxide film and the overlaying PANi surface.

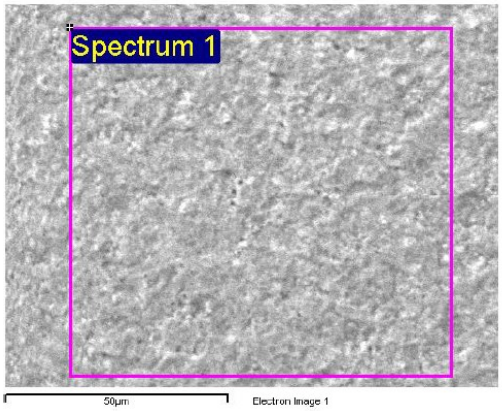

Figure 16- Image of the PANi surface under EDS investigation.

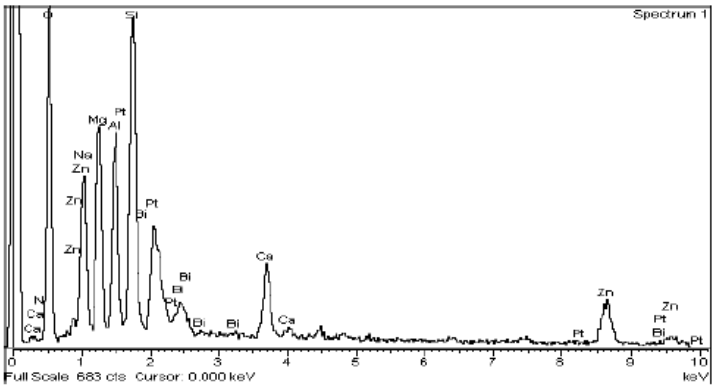

Figure 17- Since carbon atoms form the initial high peak, the PANi structure's chemical composition is evidenced by the presence of N atoms, between Ca and O atoms.

Finally, the NOx Hybrid Sensor's sensitivity to NOx was evaluated. The hybrid sensor was tested as done for TGS2602. The tests were conducted in collaboration with the IGG Institute, CNR of Pisa. The test set-up was the same, as shown in Figure 18. The so developed NOx Hybrid Sensor was placed into a vial with

Temperature and Humidity Sensor SHt11 and a saturated solution of NaCl to keep the humidity constant @75% (as done for the previous tests).

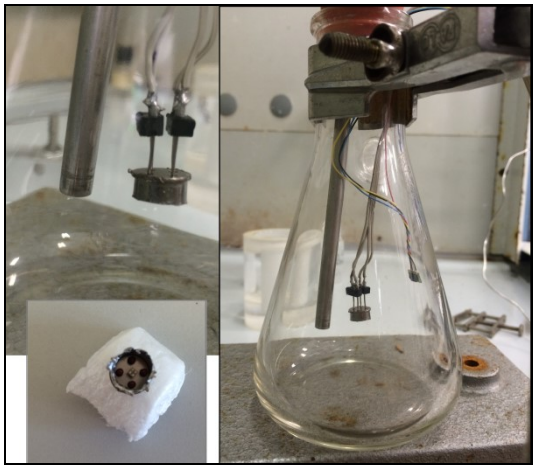

Figure 18- Test set-up for NOx Hybrid-Sensor. Here the TGS2602 "cut" in order to settle PANi sol-gel nanofilm on its sensing element.

First, the vial was "washed" with Nitrogen for 10 min at 250ml/min. A flowmeter allowed monitoring the flux. In figure 19 we can see the NOx Hybrid Sensor's response. The temperature was constant at 26.56°C, while the humidity was influenced by the flux of Nitrogen, essentially dry air. Indeed, its value decreased at 9.78%. Since the semiconductor gas sensors, as explained in the previous sections, are strongly influenced by the humidity, a variation in NOx Hybrid Sensor's response occurred: its output rose at 3.75V. When the Nitrogen valve was closed, both the sensors returned to their baseline value, that is 1.89V @69.31% humidity for NOx Hybrid Sensor.

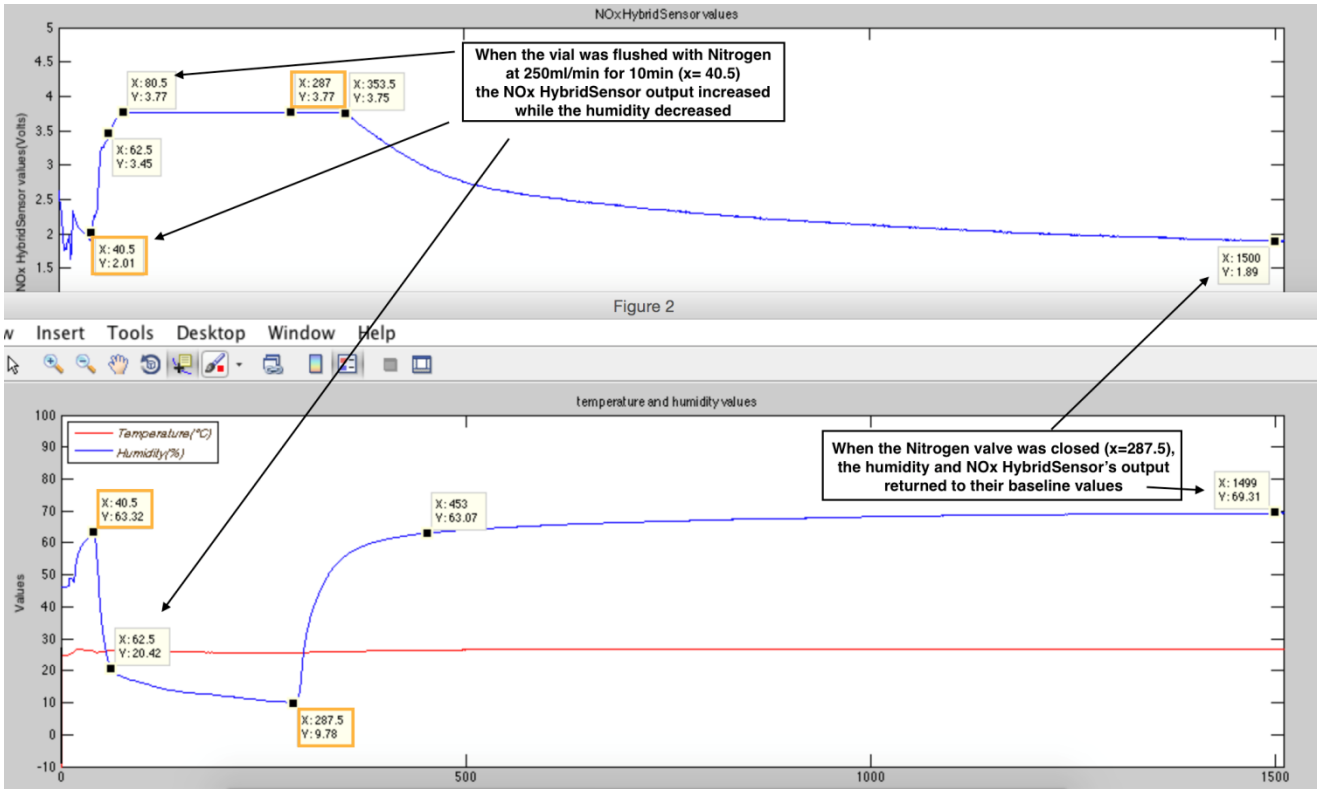

Figure 19- Flush with Nitrogen at 250ml/min for 10min. When the Nitrogen valve was closed, both the sensors returned to their baseline value, that is 1.89V @69.31% humidity for NOx Hybrid Sensor.

Finally, the sensitivity to NOx was tested. The outcome is reported in Figure 20.

The vial was flushed with NOx (1ppmv) at 250ml/min for 3 min. As usual, the humidity decreased in value, as well as NOx Hybrid Sensor's output. A semiconductor gas sensor variation in output (toward higher/lower value with respect to the baseline) is always expected consequently to a variation in humidity values.
When the NOx valve was closed, the NOX Hybrid sensor's response raised at 1.99V, thus exceeding its baseline value (1.09V @75%humidity). The hybrid sensor didn't return to its baseline value even for long times (more than 1 hour). The unavoidable decrease in voltage was essentially due to the fact that the vial was not hermetically closed.
This demonstrated that the PANi sol-gel nanofilm was sensitive to NOx and interacted whit it, causing a rise in voltage output.

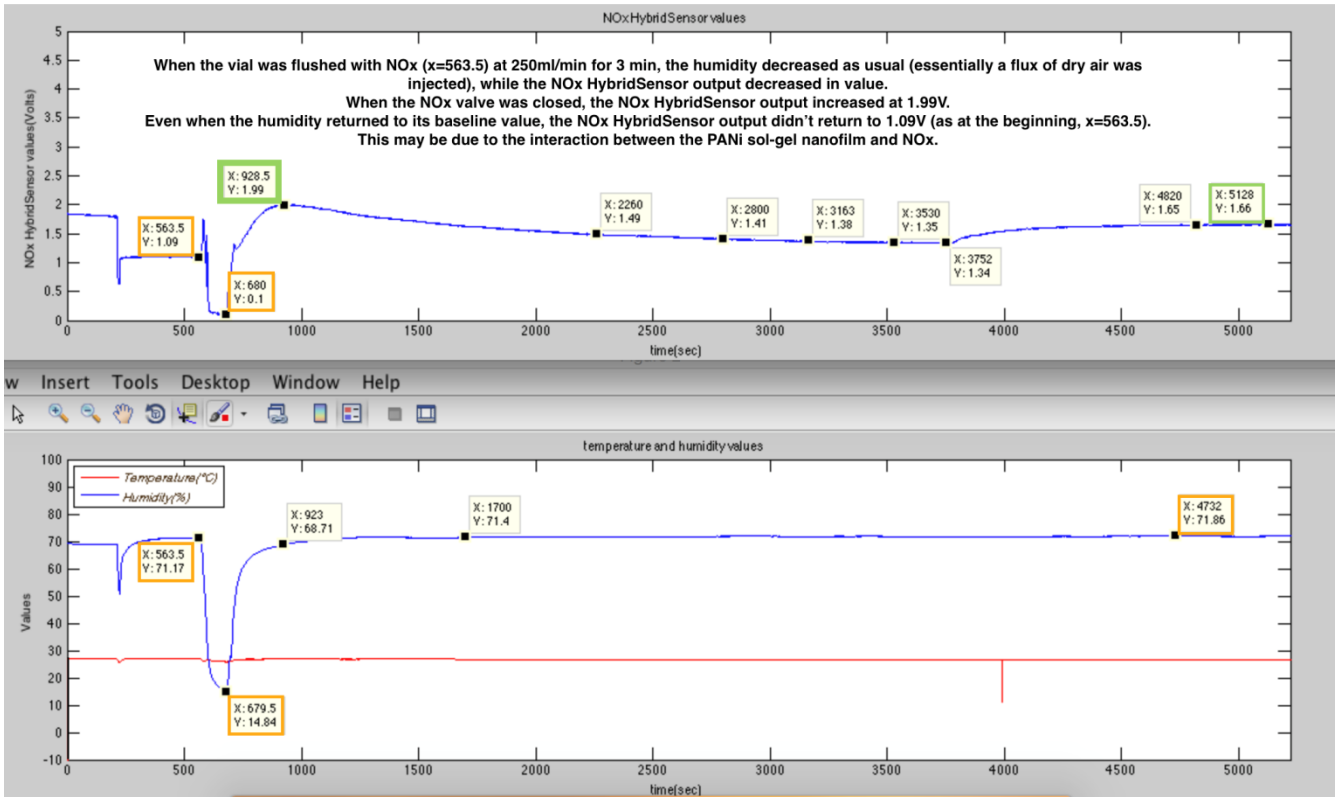

Figure 20- NOx Hybrid Sensor's sensitivity to Nitrogen Oxide.

This may be considered, to all purposes, a feasibility study which demonstrated that **the sensitivity of a semiconductor gas sensor, based on a Zinc Oxide (ZnO) sensing element, can be improved making it "hybrid" by means of a PANi nanofilm settled on its sensing surface. In this case we demonstrated the improved sensitivity to NOx**, a molecule considered not only as biomarker for asthmatic disorders, but also very important as biochemical mediator in numerous functions (cerebral, gastrointestinal, renal, respiratory functions). In addition, a good bio-availability of this mediator enhances the endothelial function, lipid metabolism, and contrasts hypertension [8].

4. CONCLUSIONS

The focus of the activity presented in this report has been on the improvement of the Wize Sniffer sensors' performance.

The Wize Sniffer is an innovative device able to operate with a limited number of breath VOCs, principally related to those noxious habits for cardio-metabolic risk (alcohol intake, smoking), thus giving information to physicians on the possible state of wellness of an individual. The functionality of the commercial gas sensors, as well as the manufacturing and the characteristics of the nanofiber-based gas sensors have been described.

The results obtained during this activity give us the opportunity to have a final hardware/software configuration of the Wize Sniffer as considered as a standalone device. In addition, a new customized sensor for the detection of NOx involving a conductive polymer, PANi, has been manufactured exploiting nanoscale techniques. The new sensor presents still some open questions about its accuracy and reproducibility; however, we consider its creation as a new possible tool to improve our portable device.

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