Process Absorption-Desorption N₂O in a Resistive Sensor Based Chemically Polyaniline

Extended Abstract 2012-A-391-AWMA

Luisa Y. Quiñones, Carmen J. Navarro, Balter Trujillo, Isela Rodríguez, Eduardo Herrera Centro de Investigación en Materiales Avanzados, S.C. (CIMAV), Departamento Medio Ambiente y energía, Miguel de Cervantes 120, C.P. 31109 Chihuahua, Chih. México.
Laura Ortega Instituto Tecnológico de Chihuahua II (ITCHII), Av. De las Industrias 11101, C.P. 31130 Chihuahua, Chih. México.
Yadira Gochi Instituto Tecnológico de Oaxaca (ITO). Av. Ing. Victor Bravo Ahuia #125 esq. Calz

Instituto Tecnológico de Oaxaca (ITO) Av. Ing. Victor Bravo Ahuja #125 esq. Calz. Tecnológico. C.P.68030. Oaxaca.Oax. México.

INTRODUCTION

Organic molecules, as well as conductive polymers have proven highly sensitive to ambient temperature to a wide range of inorganic and organic toxic gases in a low concentration; some of these compounds are being studied to develop new chemical sensors.¹ The N₂O gas is a result of an incomplete process of soil denitrification and is considered a greenhouse gas. Global interest is the monitoring of emission sources. The requirements for emission control more accurate on this and other pollutants have created a need to improve new sensor systems. Polyaniline (PANI) is a conducting polymer able to modify their electronic structure due to the presence of an agent in the environment, which interacts with the polymer surface and then this is altered in its chemical and electrical properties, the polymer chain is restructured making it difficult to return to its original natural form. This paper aims to demonstrate the reversibility in material properties after being exposed to the presence of nitrous oxide (N₂O) and then can be used as a sensor in more than one occasion. PANI has been used to sense other gases such as NH3, NO₂ and CO₂ 2 satisfactory results through the application of electrochemical techniques, on this basis were tested for impedance detection of N₂O and then adjusted the temperature of the system to achieve desorption of gas from the polymeric material, and the results were obtained under controlled conditions, however it is intended that the final use of the device is the detection of N₂O in an open environment.

BACKGROUND

The discovery of conducting polymers has opened up many new possibilities for devices combined with optical, electrochemical, and electrical properties. Among them, PANI has received widespread attention on the mechanics of its flexibility, high environmental stability, ease of processing, simple and reversible (doping / dedopaje) and its modified chemical electrical conductivity ³. Gas sensors based on materials such as PANI have drawn attention dramatically in recent years due to its unique properties: the conductivity of these types of polymers depends on the ability to conduct electrical charge along the chain polymer as the jumping ability of electrical charges between polymer chains.

Experimental Methods

PANI was obtained by oxidative polymerization of aniline using the oxidation state of emeraldine base. The synthesis is based on the chemical oxidation of aniline by using an oxidizing agent, which process is carried out with 99% liquid aniline, sodium styrene sulfonate (C₈ H₇ NaO₃ S) as oxidizing agent, hydrochloric acid (HCl) as the acid proton and ammonium persulfate ((NH₄)₂ S₂ O₈) as initiator, the synthesis was on at a temperature of $-3 \degree C^4$. The design of the sensor consists of a base of a nonconductive material which was placed on a copper base as two combs found as shown in Figure 1, the metal combs are not touching each other, have a separation between each tooth 1 mm and the total area is 1cm2, copper is covered with PANI deposited with the airbrush technique being able to obtain a thin film that closes the circuit and make way for the electric current between the electrodes. The material is sensitive to temperature changes by what is required by means of a control thermostat thus kept constant during the measurements at 40 ° C. We used the computer model interface Solatron Electrochemical 1287 was applied alternating current (AC) with an excitation voltage of 10 mV amplitude and a frequency range between 1 Hz and 100 Hz M. The team is composed of a potentiostat with 4 terminals, which were connected as follows: in the absence of reference electrodes, cable for reference 1 joined the working electrode, the reference cable 2 is joined to the counter electrode, and thus only two terminals are obtained. Was considered to, each of the combs of copper as an electrode and counter electrode respectively, and PANI content between them as the electrolyte.

Voltenctor Genitalist Sensor

Figure 1. Design diagram with the Temperature Control Sensor.

We measured material properties before, during and after being in contact with the N_2O to subsequently compare the results and then determine the degree to which exhibits the phenomenon of absorption and desorption. The experiment was carried out with a concentration of 0 % N_2O system is stabilized at a temperature of 40 °C and a test is performed with an impedance voltage of 22 mV and a frequency range 100 Hz to 1 MHz from this step the only variable to change is the temperature held fixed voltage and frequency, is injected N_2O at 100 % and makes a new impedance measurement with the initial conditions. Concentration and keeping unchanged the closed system, the temperature is raised to 50 °C and measured impedance. Keeping the above conditions, the temperature is raised to 60 °C and again measured impedance finally opens the system, again establishing the initial conditions of temperature, a new measurement is performed and compared with previous measurements.

Results and Discussion

PANI film when in contact with N_2O at a concentration of 100 % the curve with the impedance measurement is altered as shown in Figure 2. PANI resistance increases as the gas is absorbed by the film, the time taken to stabilize and saturate the film is proportional to the gas concentration.

Figure 2. Adsorption of N2O by Impedance Analysis with Different Concentrations.

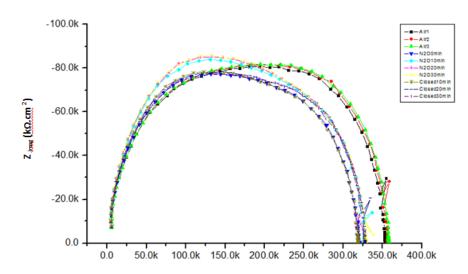
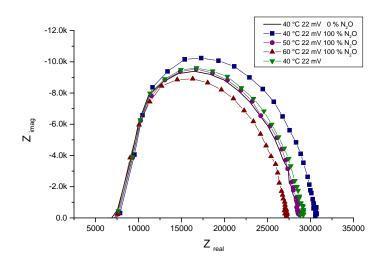


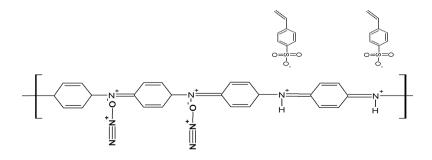
Figure 3 shows the results of the experiment to demonstrate the absorption-desorption process described above.

Figure 3. Absorption-Desorption of N₂O in the Temperature Dependence.



The black line represents the system in its initial form, where PANI is found only in the presence of argon is passed then a concentration of 100 % nitrous oxide represented by the red line, the blue line represents the measurement starts to a temperature of 50 °C, the temperature rises again and further decreases the semicircle which coincides with the aforementioned relation between the resistance and temperature of a material, then the system is opened again set of initial conditions temperature and 5 graphs comparing the results of the 5 measurements can be observed as the final measurement is very close to the initial one. Whereas the molecule of dinitrogen oxide has a structure where one of the nitrogen atoms shown as the central atom attached at one end to another nitrogen atom by a triple bond, and the other end to the oxygen through a single bond, we can determine the ionic character of each link by an analysis of electro negativities and finding that the two nitrogen atoms link presented is pure covalent, while the central link between nitrogen and oxygen is polar covalent with a difference of electro negativities (according to Pauling's scale) of 0.5. From this value and knowledge of the geometry of the molecule is linear we can infer that the molecule is polar. Now if we analyze the possibility that the N₂O molecule could interact with specific sites with partial positive charges in the chain of PANI found that this interaction would take place through a hydrogen bond which is a special type of molecular interaction ion-induced dipole type between the nitrogen atom of a polar N - H (as in the structure of PANI) and a high electro negativity atom such as oxygen in the dinitrogen oxide. PANI structure could now be represented as show in Figure 4.

Figure 4. Proposed reaction mechanism between polyaniline and nitrous oxide.



SUMMARY

In this work, it was observed that desorption of N₂O by PANI film is related to the temperature surrounding the system. Maintaining a temperature of 40 °C, desorption takes place, however a temperature of 60 °C must be reached for the film to returns to its initial electrical properties. Upon reaching this temperature the impedance mismatch between the clean material and after having passed through the whole experiment is less than 100k Ω cm⁻².

REFERENCES

- 1. A. M. Bond, S. Fletcher, F. Marken, S.J. Shaw, P.G. Symons, J. Chem. Soc. Faraday Trans. 92 **1996**.
- Fatmanur Kasapoglu F., Ayse Onen A., Niyazi Bacak N., Yagci Y., Photoinitiated Cationic polymerization using a novel phenacyl anilinium salt, Polymer 2002 pp 2575-2579
- 3. G. Natta, G. Mazzanti, P. Corradini, Atti. Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend., 25 1958.
- 4. J. Elizalde-Torres, Hailin Hu, A. Guaderrama-Santana, A. García-Valenzuela and J.M. Saniger. Revista Mexinaca de Física 54 (5) **2008** pp 358-363

KEYWORDS

polymer, chemiresistive, , gas sensor, nitrous oxide, impedance