Raman Spectroelectrochemical Study of Adsorption of N_2O at Salt Polyaniline

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ABSTRACT

Recent research shows the ability of the polyaniline (PANI) to detect the presence of different gases through changes in their electrical properties. This methodology is based on exposing the polymer at a concentration of gas and measure the adsorption process polianiina film (PANI) has been studied by Raman spectrometry insitu with green laser excitation (532 nm). The Raman characteristics have been identified and their changes during the presence of nitrous oxide have been analyzed. It has been shown that an increase of gas concentration causes an increase in the ratio content of the reduced form of polyaniline within the film. From this it is concluded that the physisorption of gas molecules only influence on the film surface and not on the chemical structure thereof.

INTRODUCTION

The essence of all optical spectroscopy interact consists in a beam of electromagnetic radiation with a system whose characteristics are to be determined. Generally speaking, different from the incoming beam by projecting effect of this interaction. From the changes suffered by the incoming beam can, in principle, information on the structure of the system under study. If there is already a general model of the system, the study of changes in the incoming beam allows quantitative information associated with the internal processes of the system and details not covered in the general model. Consequently, we first describe the mechanism of interaction of radiation with matter.

Although it is possible that all solids adsorb gases to some degree, adsorption generally not very pronounced, unless the adsorbent possesses a considerable area per unit mass. The amount of gas adsorbed by a solid depends on the nature and area of the adsorbent and the adsorbed gas as well as temperature and gas pressure, for this reason, an increase in the surface area of adsorbent increases the total gas quantity adsorbed. Because the surface area of the agents are not generally easily determined, it is customary to use the mass as a measure of the available surface and express the amount of adsorption per unit absorbent agent used (Maron, 1994). This paper aims to demonstrate the reversibility in material properties after being exposed to the presence of nitrous oxide (N_2O) and then can be used as a sensor in more than one occasion. PANI was used to sense other gases such as NH_3, CO_2 and NO_2 satisfactory results by the application of electrochemical techniques, on this basis were tested for impedance detection N_2O and then adjusted the temperature of the system to achieve the desorption of gas from the polymeric material, the results obtained under controlled conditions, ie at laboratory level, however it is intended that the end use of the detection device is in an open N2O.

Experimental Methods

The Raman spectrometry experiments were made at an open system environment temperature and injecting N_2O gas directly on the PANI deposited on copper combs. The incident beam Micro RAMAN team Labram model VIS-63 was placed at a distance of about 5 mm. The device is fastened to a support which can receive the direct flow of gas with a concentration of 99% nitrous oxide. To reduce the heating effects of the beam and a possible degradation of the polymer film, the cell holder periodically moved relative to the laser beam to 1 mm from the starting point every 10 min (Figure 1).

Figure 1. Infrastructure for Raman spectrometric measurements

Before each experiment, the device has been cleaned for 2 h in a solution of pure acetone, then PANI was deposited with the previously used technique, and is dried by exposure to fluorescent light.

The first measurements were performed with continuous flow at different concentrations, then the flow is stopped again and the result measured spectrum. To demonstrate the effect of the N_2O on polyaniline, increases the temperature of the system supplying hot air at a distance of 30 cm at a temperature of approximately 90 ° C.

Results and Discussion

To check the composition of the PANI salt, and to analyze the effect that it occurs when exposed to an atmosphere different, Figure 2 shows the Raman spectrum of pure PANI, the characteristic peaks at 1598 and 1562 cm-1 DC link are assigned to content in the quinoid ring in the emeraldine base and emeraldine salt, respectively. The peak at 1489 cm-1 corresponds to the DC link of the benzenoid ring leucoemeraldine component (XB Yan, 2007). The peaks at 1302 and 1162 cm-1 corresponding to CN of the secondary amine. The peaks at 1110 and 824 cm-1 are attributed to aromatic CH bending in the plane and off the plane of the 1,4-disubstituted aromatic ring (R. Cross-Silva, 2004). Peaks between 800 and 600 cm -1 can be assigned to vibration of the CH bands in the benzene rings. The technique of resonance Raman spectroscopy is sensitive to the electronic structure and vibration properties of conducting polymers (Y. Furukawa, 1988).

Figura 2. Raman spectra of pure PANI

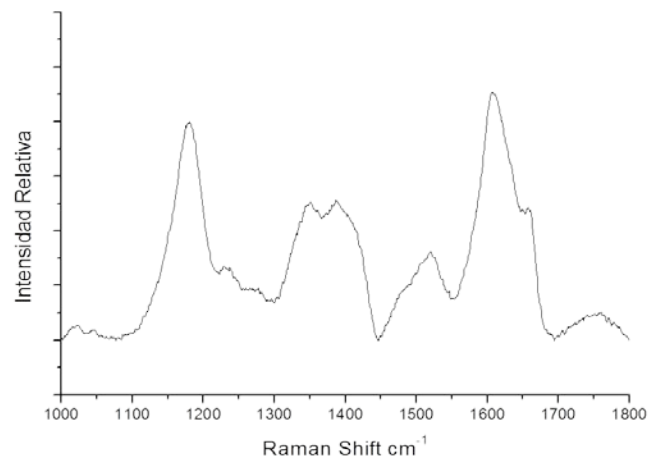
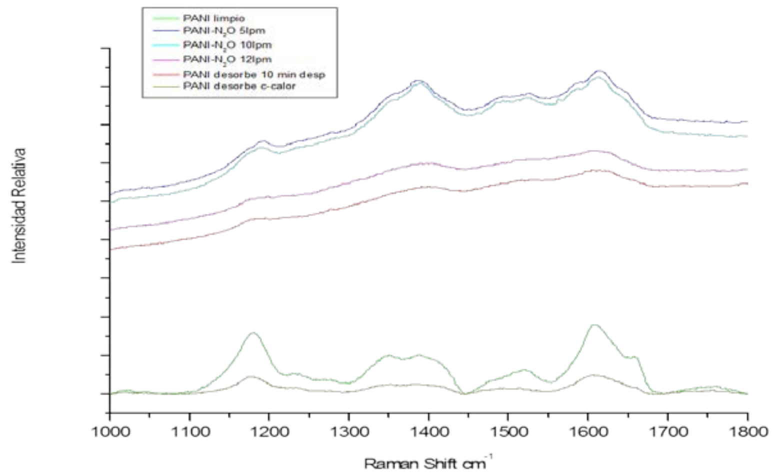


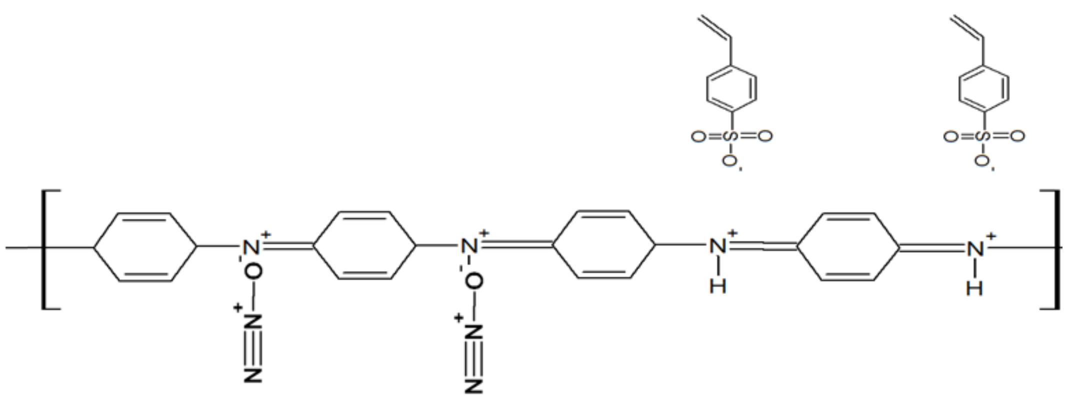
Figure 3 shows a Raman spectrum modified according to the presence of an external agent chain PANI salt, such measurements correspond to the response over time to reach a stable point that we call "saturation" sample from there because there is not any significant change.
In Raman spectrum, we can see based on the increase of temperature, it returns to its original form as a product of physisorption occurred between PANI and N_2O.

Figure 3. Raman spectrum physisorption-desorption of N_2O



Now, if we consider the possibility that the N_2O molecule may interact with certain sites with partial positive charges on the polyaniline chain found that this interaction would be conducted through a hydrogen bond which is a special type of molecular interactions ion-induced dipole type between the nitrogen atom of a polar N - H (as in the structure of the polyaniline) and an atom of high electronegativity such as oxygen into dinitrogen oxide. The structure of PANI could now represent like that in Figure 4.

Figure 4. Proposed reaction mechanism between polyaniline and nitrous oxide



SUMMARY

In this study we found that the adsorption of N_2O by the PANI film is related to the temperature surrounding the system. Maintaining a temperature of 40 ° C the desorption takes place is not however a way that the temperature was increased up to 80 ° C the film returns to its initial electrical properties. On reaching this temperature the difference in impedance between the clean material and after having passed throughout the experiment is less than 100 kΩ.cm^{-2}.

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KEYWORDS

polymer, raman, gas sensor, nitrous oxide, adsorption