Amperometric Nitrous Oxide Gas Sensor: Preparation of Cu/PANI/Cu Electrodes and Sensing Behavior

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Received: November 10, 2012 / Accepted: November 27, 2012 / Published: December 20, 2012.

Abstract: The authors studied the changes in the electrical properties of PANI (polyaniline) when exposed to the presence of N₂O (nitrous oxide). The techniques used to determine the adsorption of gas in the polymer were the electrochemical impedance, steps voltammetry and transmission electron microscopy. The objective of this work was to determine the ability of adsorption and desorption of PANI to be used as sensor in an open environment. Measurements were performed in a controlled atmosphere, temperature and flux. The gas was passed through a glass capsule in which an electrochemical cell was designed with copper electrodes and PANI as electrolyte. The change in electrical properties of the material is analyzed using a potentiostat/galvanostat in situ. Subsequently, the material was analyzed by TEM (Transmission Electron Microscopy) elemental analysis. The measurements were performed with different concentrations of N₂O with a purity of 99%. As a result of measurements, it was found that the change in electrical resistance of PANI is caused by the physical interaction that occurs when in contact with N₂O and even a change in the morphology of polymer, however, the binding is weak and sufficient to increase the temperature at which 25% PANI film regains its original properties.

Key words: Polymer, electrochemical, gas sensor, nitrous oxide, impedance.

1. Introduction

The NOx gases are global interest due to effect on the climate change, which have a significant contributing in the atmospheric reactions that produce ground-level ozone [1]. Specifically, N₂O (nitrous oxide gas) that has decrement in emission from transportation and industry, but increase in emissions from agricultural activities results from an incomplete process of soil denitrification or the use of synthetic fertilizers [2].

The N₂O gas monitoring is crucial in the emission control to mitigate the environment impacts. This requires improved accuracy and has created a need to improve the conventional gas sensor systems, e.g., infrared [3] and to explore new solutions.

Actually, the organic molecules like conductive polymers have proven highly sensitive to ambient temperature to a wide range of inorganic-organic toxic gases in a low concentration [4]; some of these compounds are being studied to develop new chemical sensors, e.g., PANI (polyaniline) is a polymer semiconductor 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 [5-10].

In the literature, PANI has been demonstrated to be a good candidate for a sensor of NH₃, NO₂ and CO₂ gas [11], but lack information for N₂O gas. This paper aims to demonstrate that PANI can be used as a sensor.
in more than one occasion, additionally for N₂O, also, to explain the reversibility in material properties after being exposed to the presence of this gas [12-14].

In this study, a characterization was reported of the system N₂O-PANI. In the following sections, a description of the used techniques is explained. These include: the PANI synthesis and electrochemical (impedance detection). Finally, the results and discussions on the desorption process of N₂O from PANI samples.

2. Material and Methods

PANI synthesis: The film was obtained by oxidative polymerization of aniline using the oxidation state of emeraldine base. The conditions of synthesis were a chemical oxidation of aniline via sodium styrene sulfonate C₈H₇NaO₃S, where the proton acid was hydrochloric acid HCl and the initiator was ammonium persulfate (NH₄)₂S₂O₈ in liquid aniline (99% w.t.) at a temperature of -3 °C [14].

Sensor design: The device consisted of a nonconductive material base, which was clamped on two conducting comb-like structures of copper placed into a planar configuration, where the protruding teeth were arranged in mutually symmetrically order. The separation was 1.0 mm between teeth and the total area was of 1.0 cm². After, the copper comb surfaces was covered with PANI 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.

Variable measuring: To determine material properties like the impedance, was used the Advanced Electrochemical Interface (model 1287, Solartron Electrochemical) as part of a computer controlled system, which is composed of a potentiostat with the four three-terminal cell connection that 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 (Fig. 1).

The operating conditions were a alternating current (AC) applied with an excitation voltage of 10 mV amplitude and a frequency range between 1 Hz and 100 Hz M.

Material properties were measured before, during and after in contact with the N₂O subsequently to compare the results and then determine the degree to which exhibits the phenomenon of adsorption and desorption. The experiment was carried out with a

![Fig. 1](image) Fig. 1  Design diagram the gas sensor.
concentration of 0% N₂O system is stabilized at a temperature of 40 °C and a test is performed with an impedance voltage of 50 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 N₂O 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.

3. Results and Discussions

When PANI thin film samples were in contact with N₂O gas of different concentration, their electrical properties signals at started to increase, as shown in Fig. 2. The resistance of the PANI sensing material changed, due to the N₂O molecule adsorption, and it is quite logical to observe in the same figure that the magnitude of the electrical properties change (ΔR) is proportional to the gas concentration. The response time of the sensing system for 100 mL N₂O gas is about min to reach 70% of the equilibrium value.

As soon as the testing gas was cut off and a purging gas (dried Ar) was introduced into the test chamber, the increase in (ΔR) stopped and its last value was maintained during the purging process for all the PANI samples kept at room temperature. This means that the introduction of the dried Ar gas only interrupted the N₂O adsorption process on PANI samples and did not purge out any already adsorbed N₂O molecules from them.

Further introduction of N₂O gas renewed the adsorption process, and the same unrecoverable resistance phenomenon was observed again during the subsequent purging process. Fig. 4 shows the change of the electrical resistance at of PANI sample at different sample temperature during the purging process to visualize the effect of thermal energy on the N₂O desorption process. Initially the test chamber was filled with a 100 mL/min N₂O gas which causes the increase of the electrical resistance in PANI samples. After about 10 min of N₂O gas circulation, this was cut off and the dried Ar flux was introduced into the chamber to purge the test gas by keeping the PANI sample at 40 °C temperature. As expected, the change in the electrical properties of the PANI samples was small enough to be considered negligible by taking into account the high sensitivity of the electrochemical system. Toxic gas with the same concentration was re-introduced into the test chamber for another 10 min, causing again an increase in the electrical resistant.

Fig. 3 shows the change in electrical resistance of the material, measured from the cyclic voltammetry test, where it can be seen that the presence of N₂O gas surface PANI film leads differently. Initially the test chamber was filled with 100 mL of N₂O gas that causes increased electric resistance PANI samples. After about 10 min of the N₂O gas flow of this stream was cut and Ar is introduced into the chamber to purge gas to keep test samples at ambient temperature PANI. As expected, the change in the resistance electrical signals of the PANI samples was small enough to be considered negligible by taking into account the high sensitivity of the electrochemical system. Toxic gas whit the same concentration was
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Fig. 3  The relationship of sensing current and time for using PANI as solid electrolyte applied potential 50 mV; gas flow rate 50 mL min; system two terminals: Cu; temperature: 40 °C.

![Graph showing the relationship of sensing current and time.]  

Fig. 4  TEM-micrographs of the polyaniline film. The images show that the PANI :(a) TEM image PANI magnification, 100,000×; (b) TEM image of PANI after expose 100 mL N2O/min magnification, 100,000×.

re-introduced into the test chamber for another 10 min, causing again an increase in the resistance electrical of the polymer samples. At the end of desorption process, the switch of heating element on the PANI sample holder was turned on and the polymeric samples were heated to 50 °C (curve a in Fig. 3) and 60 °C (curve b in Fig. 3). Now the resistance electrical signals began to decrease and the speed of this decrease increased with the sample temperature. The recovery time was about 60 min at 60 °C under Ar ambient in comparison with an almost infinite time for recovery at 20 °C. More adsorption-desorption cycles could be observed with an additional system around the heating element to accelerate desorption process, which is under construction (Fig. 3).

The surface morphologies of PANI before and after being exposed to the flow of N2O is illustrated in Fig. 4. The morphology of the film surface undergoes a change due to Van Der Waals forces which allow adsorption of molecules on the N2O molecules PANI. EDS analysis indicated that the electrolyte was changed after being exposed to the gas (Table 1).
Table 1  TEM-EDS analysis of PANI film before and after being exposed to N$_2$O flux.

<table>
<thead>
<tr>
<th>Element</th>
<th>PANI film</th>
<th>PANI-N$_2$O adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight %</td>
<td>Atomic %</td>
</tr>
<tr>
<td>C</td>
<td>74.36</td>
<td>80.25</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>23.10</td>
<td>18.71</td>
</tr>
<tr>
<td>S</td>
<td>2.53</td>
<td>1.02</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td>-</td>
</tr>
</tbody>
</table>

Each of the polyaniline redox state is associated with a specific electronic structure that the absorption process of various molecules can be detected by changes in its resistance and/or electrical conductivity and because of the alteration of the chemical structure it is difficult for the PANI back to its original state [14]. The interaction of the gas with the polymer produces not only an adsorption and absorption, the bond can be cleaved with the temperature rise of the system [15].

5. Conclusions

In this study, polyaniline was used as detector material of N$_2$O. Analyses provide detailed information on the surface of the polyaniline film after being exposed to the gas, which could be useful in the quantification of the analyte molecules in an environmental gases mixture.

The polyaniline can be used as a sensor of N$_2$O based on change of its chemical-resistive in the presence of an external agent. The desorption or the rupture in the molecular junction between the polyaniline and N$_2$O on the surface was by the temperature increased.

The signal emitted can be used to determine the exact concentration of N$_2$O.

Acknowledgments

This work was supported by the Research Center for Advanced Materials, S.C. National Council of Science and Technology of Mexico. The authors acknowledge technical support of Carlos Ornelas, Jorge Carrillo, Ramón Gómez and Ivan Templeton.

References


