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NO₂ Gas Sensing Using a CF/Pani Composite as Electrode

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Gas sensors based on CF/PAni composite electrodes were synthesized using the polymerization chemistry. These sensors were used for detection of toxic gases like NO₂. Three different deposition times were used in the synthesis of the CF/PAni composite: 30, 60 and 90 min. The morphology and the structural characteristics of the composites were analyzed by scanning electron microscopy and Raman spectroscopy, respectively. Experiment results confirmed that the NO₂ gas sensor using CF/PAni composite has good response characteristics to different NO₂ gas concentrations. Furthermore, the NO₂ gas sensor using CF/PAni-90 composite showed the best sensitivity. This behavior was attributed to its largest content of PAni on the carbon fiber, which induced to its largest surface area. This morphology favors the adsorption of gas molecules leading to the highest current variation with the oxidation process.

Introduction

Nowadays, the need to search more efficient materials and devices to apply to environmental pollution control has widely increased. The environmental analyses have been made by random sampling followed by extraction and laboratory instruments. The sensors have performed an important role in the several research groups being a promising new approach to control future environmental problems. The main advantages of a sensor versus conventional analytical techniques of environmental monitoring consist in analyzing multiple pollutants in complex samples, miniaturization and its possible use in real time (1, 2). Thus, the development of new material applied to environmental sensors becomes essential (3). Common chemical sensors differ in terms of the sensing material associated to their properties, such as: electrical conductivity, optical, temperature, etc.

Besides of the advantageous characteristics listed above, some obstacles still limit their use, such as: the gradual formation of a passive layer on the electrode/analyte interface and the slow kinetics of the electron transfer between some compounds and the electrode materials (4,5). In this context, conducting polymers, carbon fiber (CF) and carbon nanotube (CNTs) are very promissory to use as sensor electrodes (6,7).

Conducting polymer systems are a field of scientific and technical interest, offering the opportunity to obtain a broad variety of promising new materials, with a wide range of properties and applications (8,9). Polyaniline (PAni) is one of the most investigated and commercialized conducting polymers. The great interest in this material stems from its ability to be rapidly and reversibly cycled between the conductive and the insulating states, associated with its good stability, facility of preparation, and the monomer low cost (10-13).

The interaction of conducting polymers with the environment, mainly related to exposure to humidity or gases, drastically alters the conductivity of the polymer, being this property valued when composes the sensor. In this sense, carbonaceous materials have been intensively studied as materials for sensors due to its strong electrocatalytic activity and minimum encrusting formation in their surface. These characteristics have been attributed to its electronic structure and high electrical conductivity (14, 15). Sensors based on carbonaceous materials are very interesting for several environmental substance interests, such as: heavy metals and gas sensors (SO_2 , CH_4 , NO , NO_2) (16,17). Particularly, nitrogen dioxide (NO_2) is important to be detected because it is colorless, flammable, and dangerous, even at a very low concentration.

In this work, we report the use of polymer composite material formed by Polyaniline (PAni), chemically deposited on the carbon fiber (CF), as an electrode for a NO_2 gas sensor. The composite materials were morphologically and physically characterized by scanning electron microscopy (SEM) and Raman spectroscopy, respectively. The electrical resistivity of the CF/PAni composites was investigated by potentiostatic experiments and by electrochemical impedance spectroscopy, during NO_2 gas exposure at room temperature.

Experimental Procedure

CF/PAni composites were synthesized by oxidative polymerization. The synthesis solutions were following:

- Monomer solution: distilled aniline (12.6 mmol L^{-1}) and 1.0 mol L^{-1} HCl, 3.0 mol L^{-1} NaCl.
- Oxidizing agent solution: 1.0 mol L^{-1} HCl, 3.0 mol L^{-1} NaCl and 0.03 mol L^{-1} ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

In a ring-shaped support, six carbon fibers (size $2 \times 1 \text{ cm}$) were attached equally spaced and fully immersed in a monomer solution at -10°C . The oxidizing agent solution was added in the center of the support at different deposition times of the 30, 60 and 90 minimum at -10°C with vigorous stirring. The samples were named as CF/PAni-30, CF/PAni-60, and CF/PAni-90. The composite was washed in 1.0 mol L^{-1} HCl. All samples were dry in air atmosphere until a constant mass. After completely dried, the samples were weighed using an analytical balance to six decimal places. Morphological characterization was carried out by using a scanning electron microscopy JEOL model JSM-5900LV. Raman spectra were recorded using a micro - Raman scattering spectroscopy (Renishaw microscope system 2000) with an excitation of Ar, 514.5 nm laser with a 500x objective.

The gas sensing measurements were carried out in a closed glass chamber. The porous polymer composite was facing against the NO_2 gas inlet. Different concentration of NO_2 gas was placed in the sensing chamber at room temperature. Before of the gas insertion, the chamber was purged for 30 min with ultra pure N_2 gas. The transient resistance responses of the CF/PAni electrode were obtained by applying a 0.1V DC across both terminals of the electrodes. The resistance variation of the CF/PAni composite electrodes was evaluated by electrochemical spectroscopy impedance (EIS) before and after NO_2 gas insertion. All impedance spectra were recorded at 0.0V with ac amplitude of 10 mV applied in the frequency range of $10^5 - 1 \text{ Hz}$.

Results and discussion

SEM images, in Figure 1 (A1,B1,C1), exhibit the CF/PAni composites before NO₂ exposition while the images concerning A2, B2 and C2 show these composites after NO₂ gas insertion, in all deposition times studied. For the whole samples, the polyaniline effectively covered the CF substrates. However, the coating was more uniform for composites formed at 30 min. The others ones showed the clusters formation of polyaniline among the CFs. This suggests that the interaction between polymer molecules and CFs overcomes the Van der Waals interaction between CFs, with the effective interaction between the π - bonds in the aromatic ring of the polyaniline. Hence, the CF strongly facilitates the charge-transfer reaction between the two components. In these composites, CFs can offer a good mechanical support to PAni and also ensure the electronic conduction in the composite electrode. Afterwards, the NO₂ gas measurements, the CF/PAni morphologies are quite similar, with the partial disappearance of PAni clusters. Apparently, the oxidation-reduction process, caused by the NO₂ gas insertion, promoted a chemical corrosion on the composite surface.

(A1)

(A2)

(B1)

(B2)

Figure 1. SEM images of the CF/PAni at different deposition times: (A1) 30, (B1) 60 and (C1) 90 min before NO₂ gas exposure and (A2) 30, (B2) 60 and (C2) 90 min after NO₂ gas insertion, 7500x.

Figure 2 (a-c) shows the Raman spectra of the composite before (i) and after (ii) the insertion of NO₂ gas. For composites formed with 60 and 90 min all the peaks are more pronounced with the gas insert. This fact can be related to the oxidation of polyaniline by the NO₂ gas. This oxidation process promotes an increase in the intensity of the peaks, due to the polymer change from esmeraldine to pernigraniline state. This effect is presented in the shift at the band associated with ν C= N that varied from 1489 to 1498 cm⁻¹ after NO₂ gas insertion. The pernigraniline represents a maximum oxidation state of PAni and this state is irreversible. However, for the CF/PAni-30 composite, this increase was not significant. This fact can be related to the close contact between the polyaniline film and carbon fiber due to the thin layer of PAni in this composite. So, the electron transport is more efficient and dominated by the CF substrate. This effect decreases the impact of the oxidation process with the insertion of NO₂ gas upon the PAni.

Figure 2. Raman spectrum of CF/PAni composite before (i) and after (ii) NO₂ gas insertion to (a-c) CF/PAni – 30, 60 and 90 min, respectively.

The response time of a CF/PAni-90 electrode with different concentrations of NO₂ gas, from 10 to 300 ppm, is shown in Figure 3. In this concentration range, the ohmic resistance increased two times over its initial value. In the case, the oxidation state of PAni in the composite is esmeraldine salt, which has the highest conductivity. When it is exposed to the gas, an over-oxidation process occurs decreasing the composite conductivity.

Figure 3. Sensor response to NO₂ gas vs. time at room temperature for CF/PAni – 90 min composite to 10, 25, 50, 75, 100, 150, 200 and 300 ppm of NO₂ gas. The NO₂ gas was balanced with N₂, and the sensors were purged by N₂ during 30 min.

The sensor response (S) was given by $S = (R_{\text{gas}} - R_{\text{N}_2}) / R_{\text{air}} (\Delta R / R_{\text{N}_2})$, where R_{gas} and R_{N_2} are the electrical resistance of the sensor in the tested NO₂ gas and N₂, respectively. The sensor response vs concentration plot shows a linear slope at low concentration levels, Figure 4. The extrapolation of this linear region gives the sensor sensitivity. The sensitivity values were 2.16×10^{-3} , 8.0×10^{-3} and $8.9 \times 10^{-3} \text{ ppm}^{-1}$, for CF/PAni - 30, 60 and 90 min respectively. Similar behaviors were observed for CF/PAni-30 and CF/PAni-60. However,

the CF/PAni-90 composite presented the best response. These sensors provided a reproducible performance.

Figure 4. Sensor response to NO₂ gas vs. concentration at room temperature.

The ac impedance spectra of CF/PAni-90 composite electrode are illustrated in Figure 5 for high frequency range in the whole NO₂ concentrations studied. The results were represented graphically using a complex plane also known as Nyquist plot. The system CF/PAni shows the electrical behavior of a resistor in series with a capacitor. In this frequency range the resistive component is dominant and each plot is shown as set of very close points. So, each mark in Figure 5 represents the resistive component for each concentration of gas insertion. Figure 5 inset show the zoom for one gas concentration. The resistance of the CF/PAni - 90 composite varied from 8.0 (0 ppm) to 32.5 Ω (300 ppm).

Figure 5. Nyquist plot for CF/PAni – 90 min composite electrodes at 0.0V for 0, 50, 75, 100, 150, 200 and 300ppm NO₂ gas.

From EIS measurements, the sensor response vs concentration plot shows a linear slope at the same region analyzed by the potentiostatic technique, Figure 6. However, the

sensitivity values obtained by the EIS technique were greater than those for the potentiostatic technique. This difference in sensitivity values may be related to the fact of the EIS is much more sensitive to resistance variation than the potentiostatic technique. As EIS measurements are carried out in high frequencies, predominantly the electron transport is analyzed that is intrinsically related to the sensor/gas interface. In this case, the sensitivity values were $14,8 \times 10^{-3}$, $18,2 \times 10^{-3}$ and $25,5 \times 10^{-3} \text{ ppm}^{-1}$, for CF/PAni - 30, 60 and 90, respectively.

Figure 6. Sensor response to NO₂ gas vs. concentration in room temperature.

Conclusion

In summary, we present the sensor development using composites formed by the chemical polymerization of polyaniline on carbon fiber with. This approach was based on the possibility of the resistivity change of polyaniline according to their oxidation degree. Furthermore, the large surface area and good electronic properties of the carbon fibers were explored. In general, the high surface area and porous nature of the CF/PAni composites showed a significant performance, in both sensitivity and time responses. Nevertheless, for both potentiostatic and EIS techniques, the composite with the highest sensitivity was the CF/Pani-90. This behavior was attributed to CF/Pani-90 min composite has a highest content of PAni on the carbon fiber. The largest PAni content in CF/Pani-90 promoted its highest resistivity variation associated to its state change from esmeraldine to pernigraniline.

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