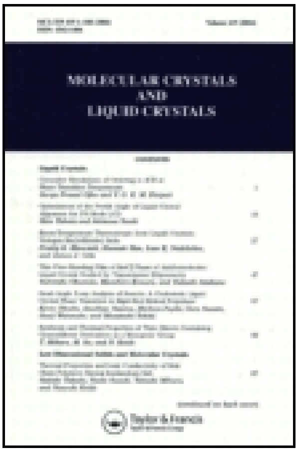

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Preparation and Electrochemical Characterization of Poly(pyrrole) Films Modified by Cobalt Particles

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Preparation and Electrochemical Characterization of Poly(pyrrole) Films Modified by Cobalt Particles

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ABSTRACT

The electrochemical preparation and characterization of poly(pyrrole) / cobalt stable composites were investigated in this work. Using cyclic voltammetry, a new redox couple was identified in the composite compared to poly(pyrrole) films. In addition, cobalt modifies the polymer redox process displacing the peak potential. The morphological results indicate structural changes in the polymer and the composite.

Keywords: poly(pyrrole); cobalt; composite; complexation

INTRODUCTION

Generally, the development of polymer electrodes modified with metallic particles aim at the increasing electrocatalytic activity[1-2]. Other applications involves sensor development[3]. The inclusion of metal into polymer matrices is also studied by others authors

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intending to improve the conductivity and stability of polymeric films. In recent paper, Hwang *et al.* [4] showed the effect of valence Cu in the stability of the poly(pyrrole), Ppy, films when exposed in the oxygen atmosphere for 50 days. A common technique for the incorporation of metals is the reduction of metallic ions in the electropolymerization solution. A different way was proposed by Marawi *et al.* [5], using an active metal substrate to promote the metallic inclusion into poly(3-methylthiophene) electrodes. Many studies[6-8] have been devoted to understand the interaction between metal and the polymer. However, the mechanistic of this interaction is still not clear. Commonly, it is attributed to metallic deposition [3] or complexation between metal and Ppy, as reported by Chen *et al.* [7,9] for the Au(I), Au(III) and Ag(I). In the present work a stable composite of Ppy / cobalt was synthesized and the influence of metallic particles on the electrochemical and structural properties of the conducting polymer was investigated.

EXPERIMENTAL

Pyrrole (Alfa Aesar) was purified by vacuum distillation before use and was stored at 5 °C in low light conditions to suppress degradation. $LiClO_4$ was used as the supporting electrolyte. The working solution was deaereted by bubbling nitrogen for 20 minutes before each experiment. Pt sheets were used as working ($A = 0.4$ cm^2) and counter electrodes ($A = 1.0$ cm^2). As reference electrode, a saturated calomel electrode was employed. Potentiostatic depositions were carried out at 750mV during the time to grow films of 800mC/cm^2 charge. The solutions for electropolymerization were prepared from pyrrole and $LiClO_4$, each at 0.1M concentration, in the absence or presence of 0.01M $CoSO_4$. After the synthesis, the films were rinsed with water and immersed in monomer-free and cobalt free 0.1M $LiClO_4$ aqueous solutions. Then, the polymer films were characterized by cyclic voltammograms at different scan rates. An EG&G PARC model 283 potentiostat was used to carry out electrochemical measurements. SEM measurements were accomplished using ZEISS model DSM 940A equipment.

RESULTS AND DISCUSSION

Cyclic voltammograms for the Ppy films (dash line) and for the composite of Ppy / cobalt (solid line) are shown in figure 1. It was observed a large difference in the electrochemical behavior of the materials. Both films were synthesized at 750 mV under conditions described at experimental section.

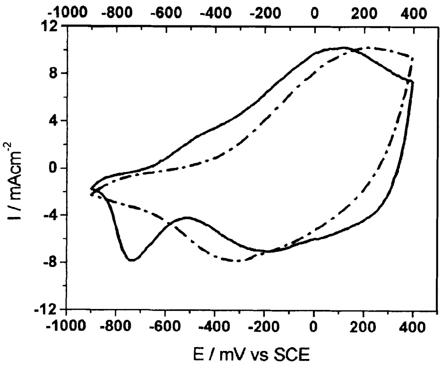

FIGURE 1: Cyclic voltammograms for the fifth cycle in the process of Ppy films (dash line) and the composite of Ppy / cobalt (solid line) at 100mV/s in 0.1M $LiClO_4$(aq).

The presence of cobalt modifies the polymer film behavior shifting the peak potential for the redox process in Ppy. In addition, a pronounced cathodic peak arises near at -730 mV. This process could be attributed to the reduction of cobalt ions to metallic cobalt. Another possible reaction, Co^{3+} to Co^{2+} reduction, should not interfere considering that Co^{3+} species is in very low concentration in aqueous solution, once it is reduced to Co^{2+} by water[10]. It was also observed an anodic shoulder for potentials more negatives than the redox process for the Ppy, which was associated with cobalt oxidation.

Some experiments related to the bare Pt sheet background in the cobalt salt / $LiClO_4$ were made (figures not shown). It was observed that the deposition of cobalt on Pt electrode presents a cathodic peak at -940 mV. From these results, an interaction between polymer and cobalt must be responsible for the changes in the voltammetric behavior of the polymer. Due to the large shift of the cathodic peak for cobalt in the modified electrode related to the peak potential in the bare electrode, a complexation could be proposed. In the literature, a complex formation has been proposed by Chen *et al.* [7,9] to explain the interaction between Ppy and cations of noble metals, such as Au(III) and Ag(I). However, these authors had suggested weak interactions for metals belonging to the fourth period in the periodic table, such as Cu, Pb and Co[9], and polymeric films, but without complexation. On the other hand, Hwang *et al.*[4,11] had studied Cu-modified Ppy and Cu(I)-Ppy complexes. They verified an electron transfer from Cu to N^+ of Ppy, suggesting a strong interaction. They proposed also a complex formation for the monovalent Cu, responsible for the increase of the conductivity and the improvement in the adhesion of the deposited Cu with the Ppy matrix. Further experiments are being carried out to clarify the complex formation and the oxidation state of the.cobalt in the Ppy matrix.

In our work, we observed a morphological change for the composite related to the pure Ppy, as reported by Hwang *et al* when the metal incorporated was the Cu. The surface morphologies for Ppy in (a) absence and in (b) presence of cobalt ions during the synthesis are shown in figure 2. The nodular structure for the Ppy is feature for films prepared in aqueous media[12-14]. The formation of Ppy nodules is related to the production of gas at the working electrode during the electrochemical deposition. A more compact surface was obtained for the Co-modified Ppy. Similar results were found for the Cu-modified Ppy[4]. This morphology contributes to the relative stability of metal-modified Ppy due to the decrease in permeability of the Ppy films by the gas production (oxygen).

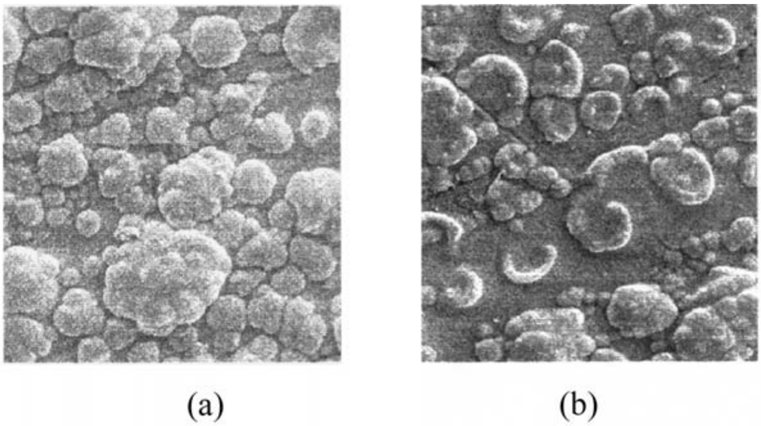

FIGURE 2: SEM micrographs for Ppy in (a) absence and in (b) presence of cobalt ions during the synthesis. In both cases, potential synthesis was 750mV. Magnification 1000x.

CONCLUSIONS

In this work, we studied the electrochemical preparation and characterization of Ppy / cobalt composite. We have observed that the electrochemical behavior of the polymer was modified by the cobalt inclusion, which leads to a displacement in the peak potential of Ppy and a new redox reaction with a peak at –730 mV during the cathodic sweep. From the voltammetric features, we have proposed a complexation between polymer and incorporated particles.

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