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Polymerization of Pyrrole and Thiophene on Polyethylene Adipate Electrodes

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Polymerizations of pyrrole and thiophene on a platinum foil coated by polyethylene adipate (PEA) were carried out in acetonitrile by electrochemical methods. Different compositions of semi-conducting composite films of PEA/Polypyrrole(PPy), PEA/Polythiophene(PT) were prepared by the electrochemical polymerization of pyrrole and thiophene on PEA electrode. The polymerization was possible only for a certain thickness of the polyethylene adipate(PEA) on the platinum. Conductivities of PEA/PPy, PEA/PT, films at different compositions were obtained. The films were examined by FTIR spectroscopy. The topography of surface films were analyzed by a scanning electron microscope(SEM). The conductivity behaviour of (PEA/PPy), (PEA/PT) films at different compositions when exposed to Ar, N_2, C_3H_8 and H_2 gases indicated that these films cannot be used as gas sensors.

Keywords: Polyethylene adipate, Polyethylene adipate / Polypyrrole composite, Polyethylene adipate / Polypyrrole composite.

Introduction

Modification of an electrode surface by means of layers of conducting polymers has been constituted an area of major interest in recent years.[1–5] One of the reasons for this interest is that the catalytic activity of films change with the polymer coatings. The preparation of such composites by electrochemical polymerization of pyrrole and thiophene on the insulating polymer coated working electrodes is one of the best method used to improve some properties of PPy, PPy/Polyesteramid[6], PPy/Polystyrene[7], PPy/Polyethylene[8], PPy/Polyurethane[9], PPy/Polybishenol A Carbonate[10] and PPy/Polyamide[11].

Great effort has been devoted by various research groups to the electrochemical synthesis of conducting polymer films such as polypyrrole and polythiophene[12–14]. It has been found that the film formation and the electrical and physical properties of the resulting films are strongly affected by the preparation conditions.[15–18]

The aim of this paper is to show that pyrrole and thiophene can be polymerized in a polymer matrix of conventional insulating polymer by an electrochemical method. The main objective of this study is to obtain a semi-conducting polymer which can be used as a gas sensor.

In this study, PEA/PPy, PEA/PT composite films were obtained for this purpose by the electrochemical polymerization of pyrrole an thiophene on PEA coated electrodes.

Experimental

The chemicals: polyethylene adipate (PEA), acetonitrile, tetrabutylammonium tetrafluoroborate (Bu_4BF_4) were all Aldrich reagent grade, at highest purity and therefore no further purification was done. The pyrrole and thiophene (merck) were distilled between under vacuum 64 and 68 °C. All solutions were deaerated by bubbling N_2 through at room temperature for 5 min. before polarization has started.

Preparation of the Working Electrode

Two Pt foils were used as the working and the counter electrodes. The surface area of the working electrode was 1.5 cm^2 and the counter electrode was 1.0 cm^2. The working and counter electrodes were burned in a reducing flame. Both surfaces of the Pt were coated by the polyethylene adipate which was dissolved in chloroform and dried until constant weight was obtained.

Electrochemical Measurements

A Wenking POS 73 model potentiostat and Rikadenki RW-11T X/Y recorder were used for electrochemical measurements. The conventional three-electrode system consisting of a Pt as the working electrode and a platinum as the counter electrode was used. The reference electrode was $Ag/AgBF_4(s)/BF_4(0.01M)$. Sweep rates were 50 mVs^{-1} and 5mVs^{-1} for cyclic voltammetry(CV).

Results and Discussions

One of the first questions related to the growth of a polymer was based on the influence of the chemical nature of the electrode surface on the polymerization process. In this way, the voltammograms depicted in Fig. 1 were obtained using the same working electrode which was coated with the polyethylene adipate. The oxidation peak potentials of 0.01M pyrrole and 0.01M thiophene were determined by cyclic voltammograms (see curves A, B, C).

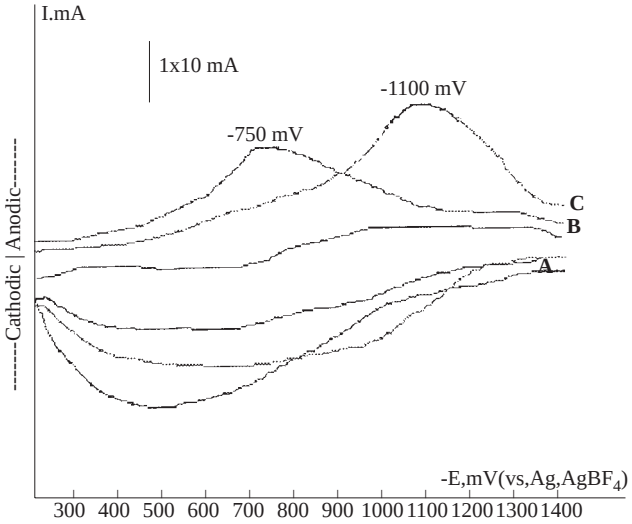


Figure 1. Voltammetric study of the working electrode coated with polyethylene adipate in nonaqueous solution(acetonitrile) of 0.01M Bu_4BF_4 (curve A), in the presence of 0.01M pyrrole (curve B) and 0.01M thiophen

(curve C).

The conductivity of PEA/PPy and PEA/PT films obtained in different compositions and the change in their conductivity with gases are given in Tables 1 and 2.

Table 1. The conductivity behavior of PEA/PPy films at different compositions exposed to H_2, C_3H_8 and N_2 gases.

composites	%21 PPy+%79PEA	%48PPy+%52PEA	%84PPy+%16PEA
conductivity	1.0×10^{-3} SCm^{-1}	1.25×10^{-3} SCm^{-1}	7.14×10^{-3} SCm^{-1}
exposed to H_2	34.8×10^{-3} SCm^{-1}	36.1×10^{-3} SCm^{-1}	26.8×10^{-3} SCm^{-1}
exposed to C_2H_8	43.1×10^{-3} SCm^{-1}	42.5×10^{-3} SCm^{-1}	41.5×10^{-3} SCm^{-1}
exposed to N_2	2.3×10^{-3} SCm^{-1}	19.5×10^{-3} SCm^{-1}	62.8×10^{-3} SCm^{-1}

Table 2. The conductivity behavior of PEA/PT films at different concentration exposed to H_2, C_3H_8 and N_2 gases.

composites	%29 PT+%71PEA	%50 PT+%50PEA	%71 PT+%29PEA
conductivity	1.0×10^{-5} SCm^{-1}	1.0×10^{-4} SCm^{-1}	2.5×10^{-4} SCm^{-1}
exposed to H_2	2.5×10^{-7} SCm^{-1}	1.12×10^{-7} SCm^{-1}	2.5×10^{-7} SCm^{-1}
exposed to C_3H_8	7.12×10^{-7} SCm^{-1}	1.02×10^{-6} SCm^{-1}	0.98×10^{-5} SCm^{-1}
exposed to N_2	6.86×10^{-6} SCm^{-1}	1.35×10^{-5} SCm^{-1}	2.23×10^{-5} SCm^{-1}

Polymer oxidtion reactions:

$(PPy) + nBF_4^- \longrightarrow (PPy)^{n+} (BF_4)_n + ne^-$

$(PTy) + nBF_4^- \longrightarrow (PTy)^{n+} (BF_4)_n + ne^-$

When the electrode is coated with a non-conducting polymer film electrochemical processes take place in the polymer/electrolyte interface. We have two different electrodes;

(a) the initial polyethylene adipate/Pt electrode:

(b) polyethylene adipate/polypyrrole electrode.

From the voltammograms obtained with a platinum/polyethylene adipate electrode we conclude that:

(a) electrochemical processes responsible for the polymerization process take place on the platinum electrode;

(b) the polyethylene adipate, as the host matrix, does not interact with the polymer, the polypyrrole and the polythiophene. This means, the conducting polymer components do not attach to the polyethylene adipate backbone;

(c) The conductivity of the film was found to be within the same order of magnitude with pure PPy synthesized in the same manner (10 S/cm);

(d) the initial monomer oxidation/polymerization process depends on the film thickness of the polyethylene adipate. The reaction takes place at the interface between Pt and the porous polymer material. While initially the working electrode was Pt/PEA after the oxidation reactions it turns to Pt/PEA+PPy or Pt/PEA+PT. To clarify the structure of films FTIR spectrums are given in Fig. 2 and the topographic structure SEM results are given in Figures (3a-b).

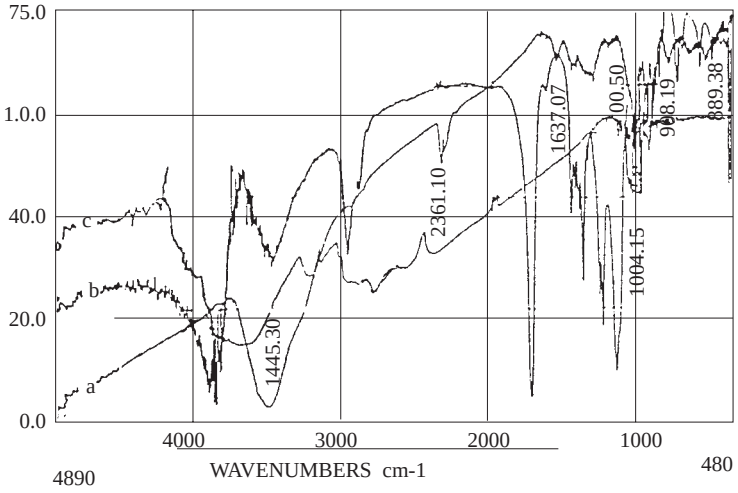


Figure 2. The FT-IR spectra A) PEA film B) PEA/PPy film and C) PEA/PT film

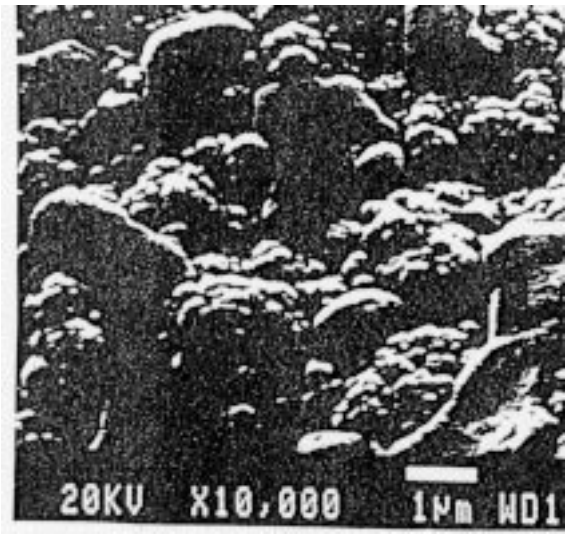


Figure 3a. The top and bottom cross section morphology of PEA/PPy film.

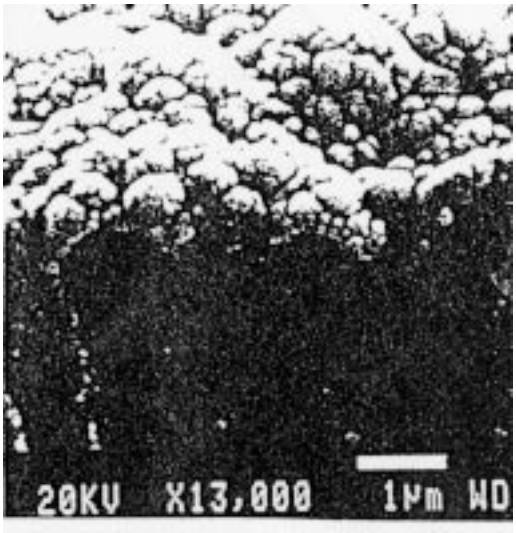


Figure 3b. Surface topography of PEA/PT film.

The first penetrating pyrrole and thiophene form a very fine particle of PPy and PT on the electrode surface due to fast oxidation. These polymers gradually clug the pores and reduces the conductivity, hence reduces the oxidation rate. Therefore, due to slow reaction the crystal sizes get lager and lager. This fact can be seen

in Figs. 3a-b taken by SEM. As can be seen in surface topography the crystals are scartered randomly and their particles sizes are not uniform. According to these observations, structure of PEA/PPy and PEA/PT can be composite. The conductivity of composite materials are less than those of pure PPy and PTx. The composite film obtained on the surface of electrode is less fragile as compared to pure PPy and PT. At the same time the removal of thin composite material from the Pt surface is much easier than the removal of material from PEA/PPy and PEA/PT.

Lastly, it was observed that the conductivity of composite material used are increasing up to a certain point and then remain at a constant value when gases are in contrast to the citation given in the literature[19−20].

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