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Influence of counter ions in electrochemical properties and kinetic parameters of poly tyramine electroactive film

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ABSTRACT

This work present that the electrodeposited poly tyramine (PTy) film by using potentiostatic method on the surface of the graphite electrode is fractal object with semiconductor properties. Electro synthesized polymers in the presence of the different anions have been characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The effect of different anions and electro synthesis parameters on the morphology, kinetic parameters and fractal dimension of the polymer was evaluated. Diffusion coefficient of counter ions calculated from the slope of the Warburg line in the Nyquist plot. A value of γ that is the characteristic of anomalous diffusion is obtained by EIS method and then the relation between fractal dimension and anomalous diffusion has been investigated.

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1. Introduction

Conducting polymers such as polypyrrole, polythiophenes or poly aniline represent a group of conjugated π -electron materials which process a combination of various electrical, optical and other semiconductor properties as a organic semiconductors that with respect to electronic energy levels hardly different from organic semiconductors [1]. Aminophenols are interesting members of the class of substituted anilines [2–6]. It is known that the electrooxidation of phenols produces phenoxy radicals, which, reacting with a phenol molecule yield to a para-linked dimer; further oxidation leads to oligomers and eventually to the formation of a passivating insulating film. For phenol derivatives with amino groups, the reported voltammetric studies have been interpreted by analogy with the well-established aniline oxidation, i.e. a $E(CE)_n$ mechanism; the oxidation of o-aminophenol was described as producing a ladder-structured film and reactive intermediates of 2-amino-phenoxazin-3-1 formation in solution. In the case of tyramine (4-(2-aminoethyl)phenol) (Ty), because the amino function is separated from the phenolic ring by two methylene groups, it is expected that only the phenol moiety is oxidized to perform the polymerization [7–9].

It is well-known that without redox species in solution the charge-transport process of an electrode modified by an

electroactive polymer film is affected by ionic transfer at the polymer|electrolyte interface, ionic and electronic charge carrier transport inside the polymer and an electronic transfer at the metal|polymer interface [10–12]. These processes would only be dependent on the degree of oxidation of the polymer. However, it has also been suggested that the external supporting electrolyte contacting the polymer film could be incorporated into the polymer phase [13]. This internal electrolyte phase can play an important role in the charge-transport and charge transfer processes of the polymeric material. In this way, a certain fraction of the ionic charge could be transported across the polymer film by this excess of electrolyte and another one by the charge-balancing ions.

Electrochemical impedance spectroscopy (EIS) is one of the most universal and powerful electroanalytical techniques for fine characterization of chemical kinetics and transport process occurring in thin coated and ion insertion electrodes [14,15]. Boundary conditions have a strong influence on the control of diffusion processes in electrochemical systems. For these systems, with mobile ions, diffusion fluxes implies a Warburg like impedance; this impedance is an $\omega^{1/2}$ function

$$Z(i\omega) \propto (i\omega)^{-1/2} \quad (1)$$

However, in many cases impedance measurements of diffusive processes give rise to power laws in frequency which deviate more or less from the exact 1/2 exponent law [16].

$$Z(i\omega) \propto (i\omega)^{-\gamma/2} \quad (0 < \gamma < 2) \quad (2)$$

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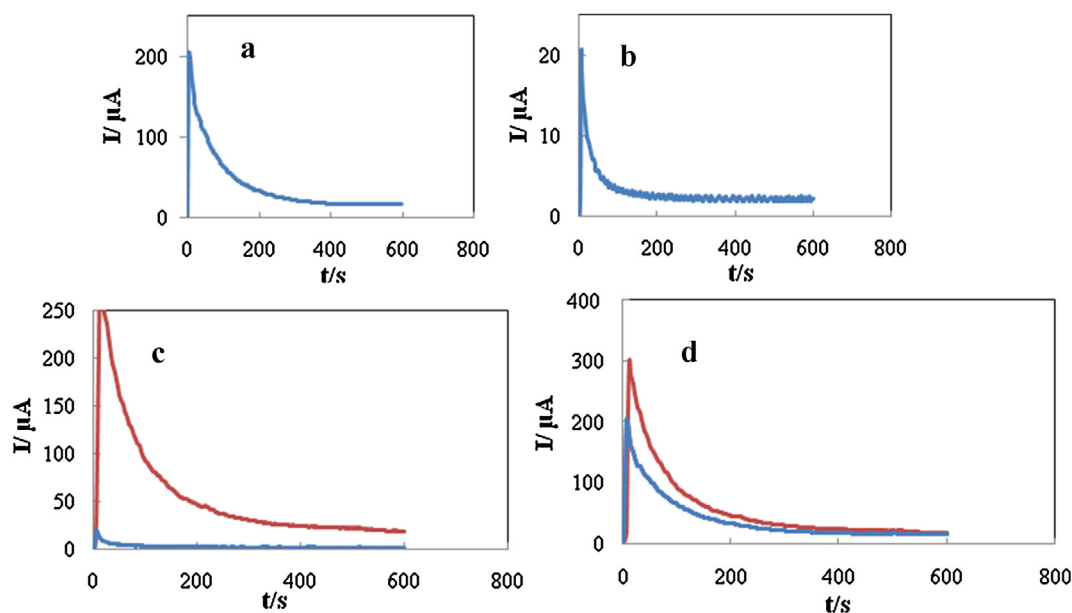


Fig. 1. The typical chronoamperogram during electropolymerization of Ty in the presence of different counter anions. (a) PTy- ClO_4 , (b) PTy-Cl, (c) comparison of (a) and (b) diagrams (d) PTy- ClO_4 in different monomer concentration (0.03 and 0.05 M Ty).

where ω is the angular frequency of the external electric field. When anomalous diffusion is considered some properties will be different from the case of normal diffusion. When normal diffusion occurs, dimension of diffusion coefficient D is cm^2/s . But in the case of anomalous diffusion the dimension of D will be $\text{cm}^2/\text{s}^\gamma$, where γ is the characteristic of anomalous diffusion.

Anomaly behavior is related to the unusual dimension of surface geometry, i.e. fractal dimension. Fractal structures are arisen during specific condition of polymerization dynamic and have non-integer dimensions which could be easily calculated [17,18]. Fractals have been characterized by several methods that can be classified as physical, chemical and electrochemical [18–21].

The aim of this paper is to present more insight into the processes appearing during oxidation and reduction of a PTy film electrode in different aqueous electrolytes, role of the electrosynthesis parameters (monomer concentration and electrolyte nature) on the kinetics and on the morphology of the PTy and relationship between the fractal dimension of PTy film and diffusion coefficients using electrochemical methods.

2. Experimental

The chemicals used in this work were of Merck origin and used without further purification. All electrochemical measurements were carried out in a conventional three electrodes cell, powered by a potentiostat/galvanostat (EG&G 273A) and a frequency response analyzer (EG&G, 1025). The system was run by a PC through M270 and M398 software via a GPIB interface. The frequency range of 100 kHz to 10 MHz and modulation amplitude of 5 mV were employed for impedance studies. PTy films electrodeposited on a graphite rod of 0.22 cm^2 area were employed as working electrode. Saturated calomel electrode (SCE) and a platinum wire were used as reference and counter electrodes respectively. The electropolymerization of PTy was performed potentiostatically using 0.1 M aqueous KClO_4 and KCl solution and different monomer concentrations (5×10^{-3} , 1×10^{-2} , 3×10^{-2} , 5×10^{-2} and 7×10^{-2} M respectively). The electrochemical measurements were carried out in acidic solution (pH 2) of HClO_4 , HCl and potassium salt (0.1 M) as supporting electrolyte. The electrical impedance is calculated without subtracting the uncompensated resistance and the

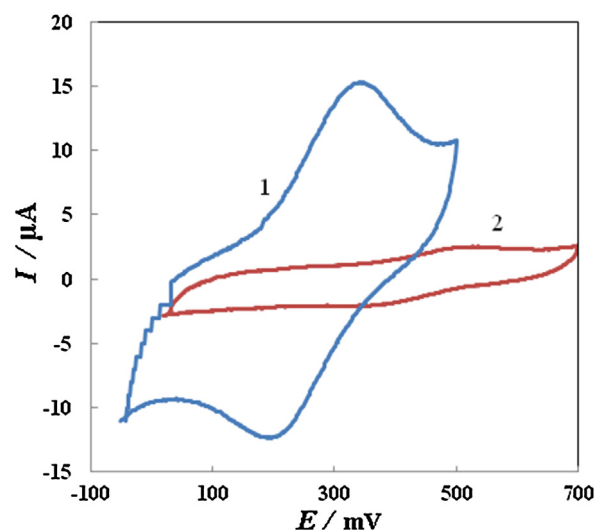


Fig. 2. Cyclic voltammograms of PTy films on graphite electrode in presence of (1) ClO_4^- and (2) Cl^- anions.

double layer capacitance. Fitting of experimental data to the proposed theoretical models was done by means of homemade and Z-view software.

3. Results and discussion

Chronoamperometry (CA) was used to deposit PTy coatings from an electrolyte containing monomer and supporting electrolytes at a constant potential on working electrode. Fig. 1 shows the typical chronoamperogram during electropolymerization in the presence of different counter anions. The current of polymerization increased considerably in the presence of perchlorate anions.

Fig. 2 shows the cyclic voltammogram of PTy film that prepared as described in Section 2 (0.03 M tyramine) and presenting the influence of the incorporated anions, while voltammograms in Fig. 3 obtained at various potential sweep rates. A pair of peaks signifying polymer's redox processes is present in all studies. In the presence of ClO_4^- anions, the polymer oxidation potential was

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