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Short Communication

Poly(3-methylthiophene) oxidation under chemical control. Rate coefficients change with prepolarization potentials of reduction

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Abstract

A kinetic study based on the potentiostatic oxidation of poly(3-methylthiophene) is presented. The influence of different initial states obtained by the reduction of the film at rising cathodic potentials for the same prepolarization time was studied. At the chronoamperometric maxima, the oxidation occurs under chemical control as shown by the semilogarithmic relationships between current and chemical concentrations. The oxidation rate coefficient changes as a function of both the oxidation overpotential, as for any other electrochemical oxidation, and the reduction potential of prepolarization. This dependence on the cathodic prepolarization shows two ranges: constant rate coefficients were obtained after reduction by prepolarization at low cathodic potentials and an exponential decrease of the rate coefficient after reduction at increasing cathodic prepolarizations. The conformational relaxation model allows a good description and quantification of these results.

Keywords: Poly(3-methylthiophene); Oxidation; Rate coefficients; Closing potential; Conformational packing

1. Introduction

Oxidation–reduction reactions taking part in films of conducting polymers are electrochemical reactions involving reverse swelling/shrinking and packing processes [1,2]. Movements in artificial muscles [3,4] and transversal ionic conductivities through smart membranes under control of the membrane oxidation state [5–7] constitute applications of these changes of volume. Most of the kinetics and mechanistic aspects of these chemical reactions involving polymer gels, ions and solvent remain untreated. A basic question is, if during some time along the complex chronoamperometric response promoted by potentiostatic oxidation of films of conducting polymers after prepolarization at high cathodic potentials, the involved chemical reaction can control the process, as stated for polypyrrole [8] some years ago.

When an anodic potential is applied to a neutral poly(3-methylthiophene) (p3-MTh) film having strong polymer/polymer interactions and a packed folding polymeric structure, electrons are extracted from the polymer and positive charges (polarons) are stored along the chains (p3-MTh^{+}). Repulsion forces emerge between charges on neighboring chains and the simultaneous transformation of the distribution of double bonds along the chains producing conformational unfolding movements. Free volume is generated between chains and forcing the entrance of counterions (A^-) and solvents (S) from the solution, in order to balance positive charges on the chains [9–14]. The reaction is summarized as

$$\underset{\text{neutral chains}}{(\text{p3-MTh})_s} + n(A^-)_{aq} + mS \rightarrow \underset{\text{oxidized chains}}{[(\text{p3-MTh}^{n+})(A^-)_n(S)_m]_{gel}} + (ne^-)_{metal} \quad (1)$$

where s means solid and aq, aqueous solution. The reaction includes physical aspects, like relaxation from packed

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conformations to gel, as a controlling rate step for the beginning of the electrochemical oxidation. Both physical and chemical aspects were included by the electrochemical stimulation of conformational relaxations (ESCR) model [9–11,13–16] in order to get a good physicochemical description, without adjustable parameters, of chronoamperometric, voltammetric or chronocoulommetric responses. When the open structure of a swollen oxidized polymer is reduced by a cathodic potential sweep (Fig. 1a), the polymer first shrinks (1.2–0.5 V), closes (0.5–0.0 V) still under partial oxidation (the average interchain distances become lower than the counterion diameter: counterions, and the same number of positive charges, remain trapped inside the material), and finally attains increasing conformational packing of the folded polymeric chains at rising cathodic potentials (0.0 to −3.5 V): the trapped counterions require high overpotentials to open their way towards the solution by pushing the packed chains. Any subsequent oxidation from rising packed initial states is initiated on nuclei, which expand and coalesce [15] giving chronoamperometric maxima (Fig. 1b) at rising oxidation times. Consumed charges are similar (they increase slowly for rising cathodic potentials) pointing to similar initial redox states. But a great difference exists between the chronoamperometric shapes (kinetics) due to the different initial physical states.

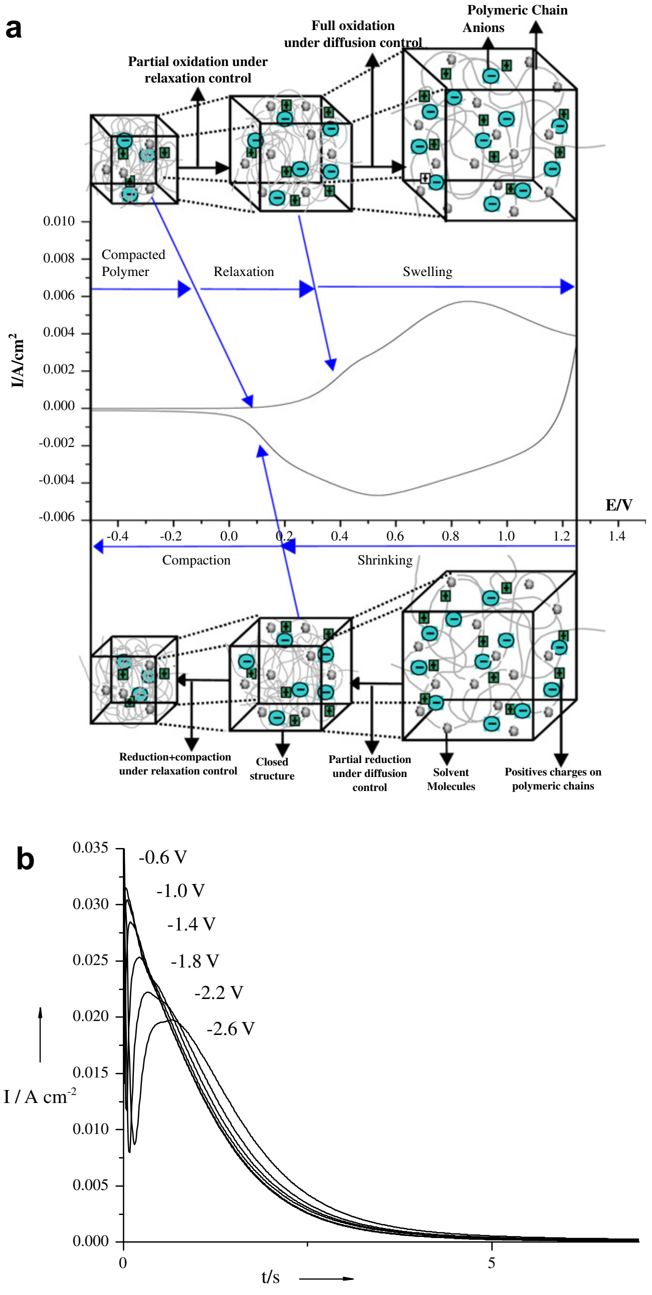

Fig. 1. (a) Voltammogram obtained from a p3-MTh film in 0.1 M $LiClO_4$ acetonitrile solutions, between −0.6 and 1.25 V vs. Ag/AgCl, at 0.1 V s^{-1} and 25 °C showing relaxation/swelling and shrinking/packing processes. (b) Chronoamperograms obtained by potential steps from different initial cathodic potentials (applied for 60 s) indicated in the figure, to the same final potential of 1.10 V. The area under the chronoamperograms is the consumed charge.

The model states that the oxidation of a packed structure starts with the formation of nuclei of oxidized material, under conformational relaxation kinetic control, promoting the progressive rise of the oxidation current. Once the structure is open, the oxidation of the film is completed under diffusion of counterions giving an exponential decay of the current. Hence oxidation starts under the control of the electrochemical stimulation of the conformational relaxations (rising currents) and finishes under diffusion control (final exponential decay of the current). The question investigated here is, if the chemical reaction kinetics is the limiting rate control step at the intermediate stages: on the chronoamperometric maximum.

Our aim here is, according to the relaxation model, revisiting the influence of the initial packed state of the polymeric conformations on the empirical chemical kinetics (the chemical part of the electrochemical reaction) of the oxidation process. At the same time, we can check the availability of the usual methodologies from the chemical kinetics, when applied to those reactive materials having an intermediate structure between solid and gel.

2. Experimental

Acetonitrile (Lab Scan) and anhydrous lithium perchlorate (Fluka) were used as received, and 3-M-thiophene (Merck) was distilled under vacuum before use. The working electrode was a platinum sheet having 1 cm^2 surface area. The counterelectrodes were two stainless steel sheets having a 3 cm^2 of surface area. A saturated Ag/AgCl supplied by Crison Instruments was the reference electrode. A one-compartment electrochemical cell was used. The experiments were performed under a nitrogen atmosphere. The electrochemical techniques were applied by means of an EG&G 273 PAR potentiogalvanostat. The temperature of the cell was maintained by means of a Selecta cryostat.

Polythiophene films were electrochemically obtained from 0.1 M $LiClO_4$ and 0.25 M 3-M-thiophene acetonitrile solution by passing 300 mC cm^{-2} through the working electrode, under polarization at a constant potential of 1600 mV vs. Ag/AgCl. After polymerization, the coated