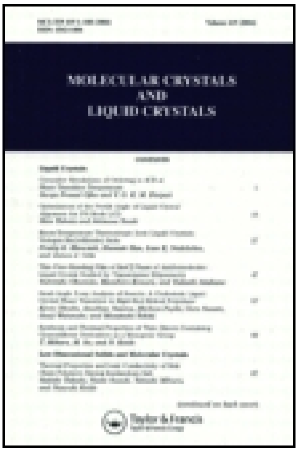

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Electrochemical Kinetics in Dense, Reactive and Wet Gels. Biomimicking Reactions and Devices

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Electrochemical Kinetics in Dense, Reactive and Wet Gels. Biomimicking Reactions and Devices

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Both p-doping and n-doping processes kinetics were studied by potential steps using different polymers from initial states having different conformational compaction degree. At the chronoamperometric maxima exist, in both cases, a chemical kinetic control. The kinetic coefficient, k, and the reaction order related to the active sites in the polymer chains, β, decrease for increasing packed conformations of the initial state. Rising packed conformations are obtained at rising cathodic potentials for p-doping polymers, or inside the band-gap for both p- and n-doping polymers. These materials can be used as sensors: their electrochemical responses change with the electrolyte concentration or temperature.

Keywords Biomimetic materials; concentration sensor; conducting polymers; electrochemical kinetics; temperature sensor

Introduction

Electrochemical reactions in presence of liquid electrolytes involve exchanges between conducting polymer, as films or powders, and the electrolytic media: ionic exchange for charge balance and solvent exchange required by osmotic pressure balance [1]. The reactive material is a dense ionic gel. Reactions involve reactive polymeric chains, electrons, ions and solvent. Both, the nature of the reactive system and the involved components mind protoplasmic environment in biological cells [2]. In cells thousands of simultaneous reactions, involving a similar number of different reactive macromolecules and ions of different chemical nature, occur. In conducting polymers only one reactive polymer, one cation and one anion are involved: the simplest system if compared with cells. Different electrochemical methodologies are available to follow those electrochemical kinetics. Conducting polymers swell and shrink during electrochemical reactions controlling the conformational state of the chains, a key aspect in biological reactions. Thus, moreover the concentration of the reactants and the temperature influence, different conformational states can be selected as initial states for the reaction. The emerging question is: are reaction kinetics and kinetic quantities influenced when the conformational movements become the rate

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*Address correspondence to Toribio F. Otero, Departamento de Arquitectura y Tecnología de la Edificación, Aulario general II, Universidad Politécnica de Cartagena, Spain E-30203. E-mail: toribio.fotero@upct.es determining step?. If this happens, could kinetic quantities include and provide information about conformational structures?

In this paper we got different initial packed conformations by reduction of p-doping conducting polymers at different cathodic potentials for the same time. Using the same initial state every time the oxidation reaction is studied, by potential step to an anodic potential, for different concentrations of the reactants. The reaction coefficients and the reaction orders were obtained. The procedure was repeated under the same chemical and physical conditions for different initial states of packed conformations. In this way it is possible to control if the conformational structure of the initial states influence the reaction kinetics.

The same procedure was used for the study of n-doping kinetics. The reaction kinetic was studied by potential step from the initial state got by polarization inside the band-gap to a cathodic potential inside the n-doped potential range. The procedure was repeated starting from a different initial state of packed conformations for every kinetics.

Experimental

Pyrrole (Fluka 97% content) and 3-methylthiophene were distilled under vacuum before use. 2-ethylheptyl-DTCPD was synthesized as previously indicated [3,4]. Acetonitrile (Lab Scan, HPLC grade) and dichloromethane (Fluka) were used after drying using a UOP Type 3A molecular sieve (Fluka). Two lithium salts ($LiClO_4$, $LiBF_4$, from Sigma-Aldrich) and tetrabutylammonium hexafluorophosphate (Fluka) ($TBAPF_6$) were used as received. All prepared solutions were used after being de-aerated by bubbling N_2 gas for 20 min.

All the electrochemical experiments were performed in a Metrohm one compartment electrochemical cell connected to an Autolab PGSTAT-100 potentiostat/galvanostat controlled by a personal computer using the GPES electrochemical software. A platinum electrode having 1 cm^2 area (0.5 cm^2 by each side) was used as working electrode. Two steel plates having 4 cm^2 of surface area were used as counter electrodes. The reference electrode was a Crison Ag/AgCl (3M KCl) electrode. All potentials in this work are referenced to this electrode. When the effect of the temperature was studied, a Julabo T25 Cryostat/Thermostat ($\pm 0.1^\circ$C) was used. All the other experiments were performed at 20°C (room temperature).

Polypyrrole films were electrochemically obtained from 0.1 M pyrrole, 0.1 M $LiClO_4$ and acetonitrile solution with 1% water by potentiostatic polarization at 0.90 V, until the consumption of the necessary electropolymerization charge. The small amount of water added allows to obtain films with better electrochemical properties, limiting the chemical polymerization pathway [3]. The obtained polymer films are very reproducible. We checked the reproducibility of the generated film by three consecutive potential sweeps. After that, the film is rinsed with acetonitrile and acetone to obtain the weight using a Sartorious SC2 balance with a precision of 10^{-6} g.

The copolymerization of DTCPD derivative and 3-methylthiophene was performed by cyclic voltammetry (CV) in 0.001M 2-ethylheptyl-DTCPD + 0.005M 3-methylthiophene solutions in dichloromethane and 0.1 M $TBAPF_6$ as electrolyte. The electrochemical control of the generated films and the ionic exchanges were carried out in 0.1M $TBAPF_6$ acetonitrile solution.

After polymerization, the working electrode was transferred into the background solution consisting in one of the electrolytes indicated before in dry acetonitrile in absence of monomer. Then, the polymer film was submitted to chronoamperometric analysis to study oxidation (p-doping) or reduction (n-doping) reactions.

Results and discussion

Reaction Kinetics

p-doping. The simplified general expression for p-doping/dedoping process in conducting polymers is represented by equation 1:

$$[Pol^{*}]_{s} + n \cdot (A^{-})_{sol} + m \cdot (Solvent) \leftrightarrow [Pol^{n+}(A^{-})_{n}(Solvent)_{m}]_{gel} + n \cdot (e^{-})_{met} \tag{1}$$

Where Pol* represents the active sites in the polymer able to store a positive charge after oxidation becoming into Pol^{+}; A^{-} is the anion of the electrolyte required for charge balance, Solvent, are solvent molecules required for osmotic pressure balance inside the polymer, and the subscripts s, sol, gel and met are solid, solution, gel and metal states, respectively.

The empirical reaction kinetics of the reaction (1) is:

$$r = k \cdot [A^{-}]^{\alpha} \cdot [Pol^{*}]^{\beta} = A \exp\left(\frac{-E_a}{RT}\right)[A^{-}]^{\alpha} \cdot [Pol^{*}]^{\beta} \tag{2}$$

where k ($L\ mol^{-1}\ s^{-1}$) is the rate coefficient of the oxidation reaction, with A the pre-exponential factor, E_a the activation energy, R the universal gas constant ($R = 8.314\ J\ K^{-1}\ mol^{-1}$) and T the temperature; r ($mol\ s^{-1}\ L^{-1}$) is the oxidation reaction rate, being proportional to the electrical current passing through the electrode; α is the reaction order related to the counterion concentration in solution, β is the reaction order related to the concentration of active sites, on chains, in the polymer film.

The reaction rate, r, of the electrochemical reactions is controlled by the current flowing through the electrode, i (A):

$$r = \frac{i \cdot \rho}{m \cdot F} \tag{3}$$

where F is the Faraday's constant (96485, $C \cdot mol^{-1}$), m is the mass of the polymer film and ρ is the polymer density, ($1540\ g\ L^{-1}$) [4] for polypyrrole.

[Pol*], the active sites concentration, understood as those points on the chains where a positive charge will be present after oxidation, can be calculated as follows:

$$[Pol^{*}] = \frac{Q_{ox} \cdot \rho}{m \cdot F} \tag{4}$$

Where Q_{ox} is the charge required to oxidize the film (C), obtained by integration of the chronoamperometric response obtained during oxidation.

By taking logarithms from Eq. (2):

$$\ln(r) = \ln(k) + \alpha \cdot \ln[A^{-}] + \beta \cdot \ln[Pol^{*}] \tag{5}$$

Equation (5) indicates that α can be obtained from the oxidation kinetics, by submitting the polypyrrole film to potential steps. The polymeric film is reduced at a cathodic potential for a constant time and then submitted to an anodic potential step. The anodic potential is kept for a time enough for the oxidation completion. The procedure is repeated for different

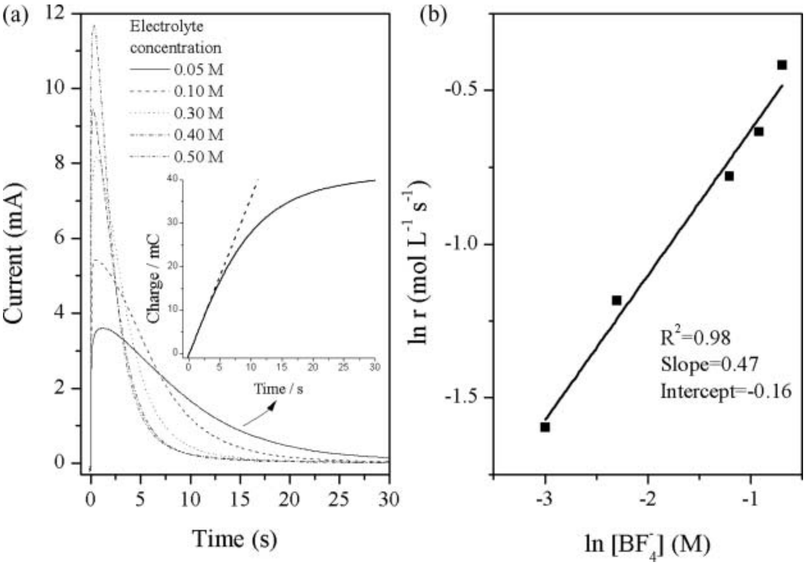

Figure 1. a) Chronoamperometric responses obtained from a polypyrrole thin film-coated Pt electrode in different concentrations of $LiBF_4$ acetonitrile solutions. Cathodic potential applied before oxidation was −1.10 V during 30 s. Oxidation was performed at 0.20 V. In the inset the chronocoulogram obtained by integration of chronoamperometric experiment in 0.05 M. b) Double logarithmic plot of the oxidation rate of polymer versus concentration of electrolyte.

concentrations of the electrolyte at constant temperature and it can be repeated for different initial states, applying different cathodic potentials.

Figure 1 shows the oxidation chronoamperograms after reduction of the polymer films at −1.10 V for 30 seconds; then the material is oxidized by potential step to 0.2 V for 30 seconds. The oxidation is repeated in different concentrations of the electrolyte. By integration of those chronoamperograms the chronocoulograms were obtained (inset Fig. 1.a) and by applying Eq. 4 those are changed to kinetic representations of the concentration variation with time. The initial reaction rates are defined by the current at the chronoamperometric maximum and calculated using Eq. 3. Figure 1a shows that for increasing concentrations of the electrolyte the current at the maximum increases: the reaction is a sensor of the concentration. Figure 1.b presents a double logarithmic plot of the reaction rate versus the concentration of electrolyte. A high correlation coefficient is obtained, corroborating the chemical kinetic control stated by Eq. 5 for the polymer oxidation (p-doping) in solution around the chronoamperometric maxima. The reaction order related to electrolyte concentration, α, is the slope (Eq. 5). After repeating the procedure from initial states having different packed conformations, Table 1 shows the values of slopes (α), intercepts and correlation coefficients of linear regression using different cathodic potentials (different initial states for the oxidation kinetics). The value of reaction order is constant 0.49 ± 0.03 for the different initial states.

The kinetic methodology was repeated now by potential steps to different final anodic potentials, that means different Q_{ox} and different concentrations of active centres [Pol*], under constant concentration of counterions in solution, $[A^-]$, and constant temperature. From Eq. 5 the reaction order β can be obtained if the reaction occurs under chemical kinetic control. Fig. 2.a shows the experimental oxidation chronoamperometric responses.

Table 1. Values of α, intercept and correlation coefficient for polypyrrole oxidation kinetics in $LiBF_4$ obtained from initial states of packed conformations obtained at different cathodic potentials for 30 s every time

Cathodic potential (V)	−0.30	−0.50	−0.70	−0.90	−1.10	−1.30	−1.50	−1.70
α	0.52	0.52	0.51	0.52	0.47	0.47	0.45	0.44
Intercept	0.13	0.02	0.00	−0.03	−0.16	−0.23	−0.30	−0.39
R^2	0.99	0.99	0.99	0.99	0.98	0.98	0.98	0.97

The double logarithmic representation of the current at the maxima, as a function of the active sites concentration in the film shows (Fig. 2.b) a high correlation coefficient value, corroborating the chemical kinetic control of the oxidation at the maxima as required for fitting Eq. 5. The reaction order related to polymer active sites concentration, β, is the slope.

By repeating the described kinetic methodology starting every time from a different initial state of packing conformations, obtained by reduction of the polymer film at increasing cathodic potentials every time, semilogarithmic plots similar to that presented by Fig. 2.b were obtained.

Table 2 shows the values of β, intercepts and correlation coefficients of regressions. Both, the reaction order β and the intercepts present a strong dependence, β increases and the intercept decreases for rising conformational packed conformations of the initial state for the oxidation.

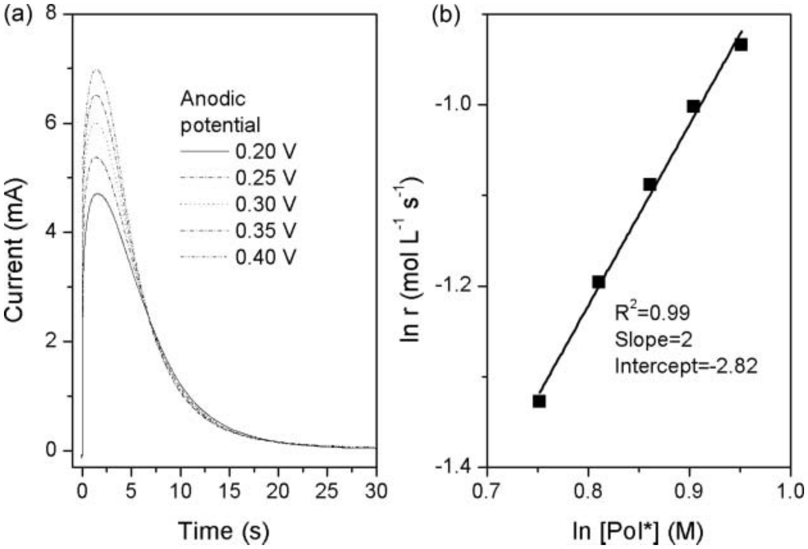

Figure 2. a) Chronoamperometric responses of polypyrrole thin film-coated Pt electrode in 0.10 M $LiBF_4$ acetonitrile solution applying different anodic potentials during oxidation. Cathodic potential applied before oxidation was −0.90 V. b) Double logarithmic plot of the oxidation rate of polymer versus concentration of active sites in polymer.

Table 2. Values of β, intercept and correlation coefficient for polypyrrole oxidation in $LiBF_4$ obtained applying different cathodic potentials before oxidation during 30 s

Potential (V)	−0.30	−0.50	−0.70	−0.90	−1.10	−1.50	−1.70
β	0.91	1.39	1.92	2.00	1.86	1.93	3.87
Intercept	−1.31	−1.82	−2.52	−2.82	−2.68	−3.14	−4.71
R^2	0.99	1.00	0.95	0.99	1.00	0.98	1.00

The rate coefficient k can be calculated using α and intercepts from Table 1 through Eq. 6.

$$\ln(k') = \ln(k) + \alpha \cdot \ln[A^-]$$
$$k = \cdot\frac{k'}{[A^-]^\alpha} \tag{6}$$

A second value of rate coefficient k can be obtained using β and intercepts from Table 2, as indicated in Eq. 7:

$$\ln(k'') = \ln(k) + \beta \cdot \ln\left[Pol^*\right]$$
$$k = \cdot\frac{k''}{[Pol^*]^\beta} \tag{7}$$

Figure 3 shows reaction coefficients, k, obtained from the kinetics in different concentrations of electrolyte (squares) or for different concentrations of active sites (circles). Decreasing kinetic coefficients were obtained for the polymer oxidation from rising packed conformations of the initial state.

Reaction kinetics for p-doping process have been widely studied from chronoamperometric responses for different conducting polymers such as polypyrrole in different solvent

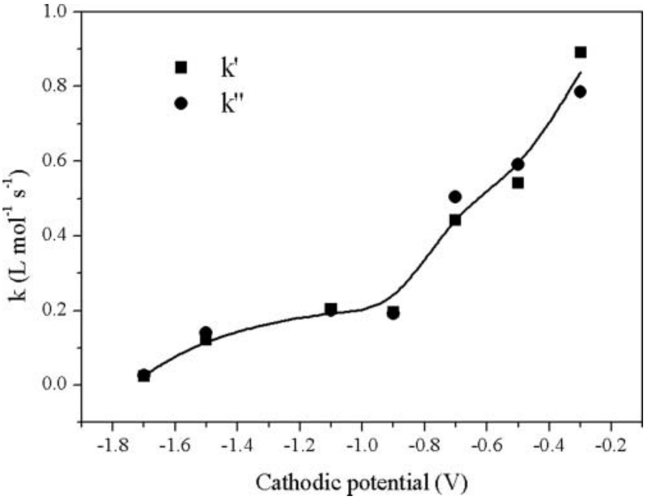

Figure 3. Values of kinetic coefficient for the p-doping (oxidation) reaction of polypyrrole in $LiBF_4$ acetonitrile solution, applying different cathodic potentials before oxidation.

[5] and electrolytes [6], polyaniline [7,8], polythiophenes [9,10] or PEDOT [11]. Similar results to those presented by Table 1, Table 2 and Fig. 3 were obtained there. Variations of the reaction order β and the kinetic coefficient as a function of the initial state of the packed conformations for the oxidation of conducting polymers are in good agreement with predictions from the electrochemically stimulated conformational relaxation (ESCR) model [12,13].

n-doping. The n-doping processes have received rather limited attention from a kinetic point of view, compared with p-doping. The high negative potentials usually required for n-doping promote parallel reactions with residual water and oxygen causing partial degradation. Kinetic studies become quite difficult under those conditions.

Figure 4 shows the result of the voltammetric characterization of poly(2-ethylheptyl-DTCPD-co-3-methylthiophene) by potential cycling between -1.60 and 1.00 V, showing that 4 redox processes can be observed. The oxidation-reduction maxima at 0.84 V and 0.74 V, respectively (standard potential $E^0 = 0.79$ V) overlaps the oxidation/neutralization potentials of the parent poly(3-methylthiophene) polymer [14]. That should mean the extraction of electrons from the polymeric chains during the oxidation sweep, with generation of positive charges (p-doping) and entrance of charge balancing anions from the solution. The processes should be reversed during the reduction sweep.

Two redox processes, with standard potentials -0.80 and -1.38 V are related with injection of electrons during the reduction sweep with generation of negative charges on the chains (n-doping) and entrance of balancing cations from the solution. Equation 8 corresponds to simplified n-doping reaction of conducting polymers:

$$[Pol^*]_s + a \cdot (C^+)_{sol} + b \cdot (Solvent) + a \cdot (e^-) \leftrightarrows [Pol^{a-}(C^+)_a(Solvent)_b]_{gel} \qquad (8)$$

Where Pol* represent the active sites in the polymeric chains able to store negative charge to become Pol^-, C^+ is the cation of the electrolyte required for charge balance during reaction, and Solvent, gel, s, and sol where defined in the previous section.

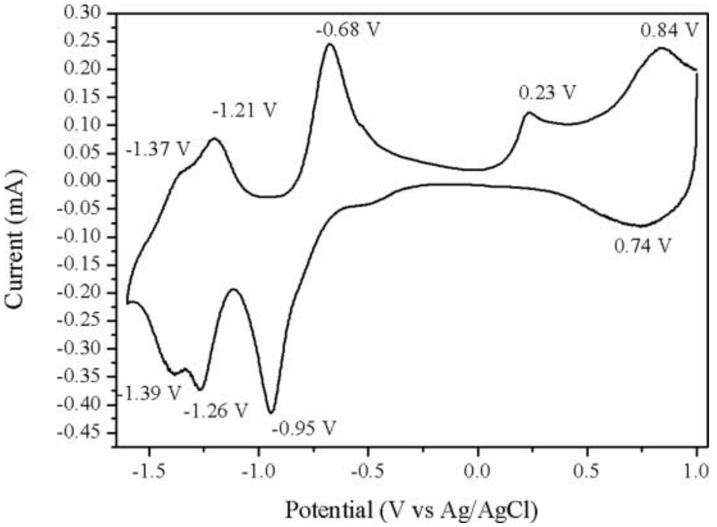

Figure 4. Voltammogram obtained from poly(2-ethylheptyl-DTCPD-co-3-methylthiophene) film from -1.60 to 1.00 V at 50 mV s^{-1}.

The kinetics of n-doping reaction can be studied following a similar procedure to that presented for the p-doping reaction. From reaction (8) the empirical kinetic equation should be:

$$r(mol \cdot L^{-1} \cdot s^{-1}) = \frac{dQ}{F \cdot V \cdot dt} = k \cdot [C^{+}]^{\alpha} \cdot [Pol^{*}]^{\beta} \tag{9}$$

The different initial states of packed conformations were now attained by polarization in the potential range from −0.25 to 0.25 mV (Fig. 4), inside the potential band-gap. Then the potential was stepped to more cathodic potentials than −0.50 V correspond to n-doping (reduction) reactions, like reaction (8). For calculations in this case we use a value of density of copolymer of 1550 g L^{-1} [15].

Figure 5a shows the chronoamperometric responses from the coated platinum electrode in 0.1 M $TBAPF_6$ acetonitrile solution when the material was submitted to potential steps from 0.25 V, maintained for 10s, to different cathodic potentials ranging from −1.00 to −1.30 V. The responses related to the reaction from the neutral state to the reduced state show a reduction maximum, in a similar way to the above presented oxidation maxima obtained for the transition from the neutral state to the oxidized state (p-doping). At the maxima the current increases by potential steps to rising cathodic potentials. Figure 5.b shows the double logarithmic plot of the reduction rates versus different concentrations of active sites for n-doping; β reaction orders close to 2 were obtained. This result could be interpreted in the sense that every cation approaching from the solution during reaction interacts with two active sites on neighbour polymeric chains. A good fit of the experimental data is obtained, corroborating the chemical kinetic control of the n-doping process.

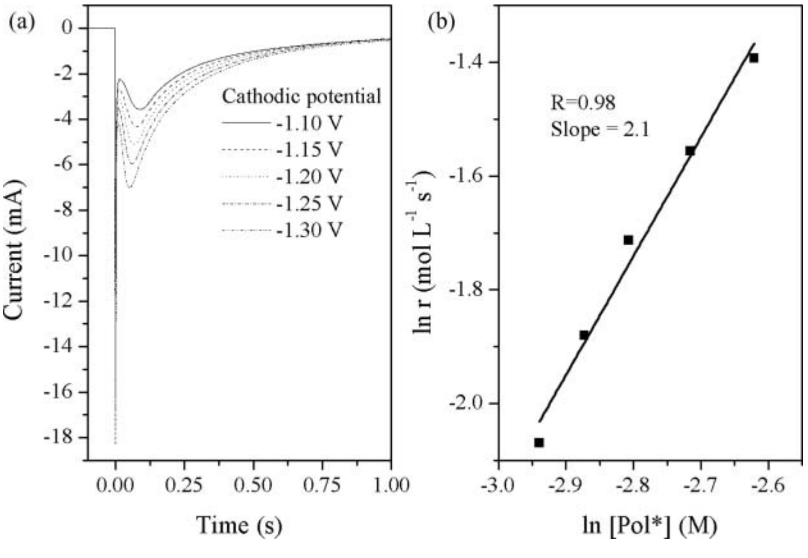

Figure 5. a) Chronoamperometric responses of a poly(2-ethylheptyl-DTCPD-co-3-methylthiophene)-coated platinum electrode in 0.1 M $TBAPF_6$ acetonitrile solution, submitted to potential steps from 0.25 V anodic potential maintained for 10 s to different cathodic potentials indicated. b) Double logarithmic plot of the oxidation rate of copolymer versus concentration of active sites.

Conducting Polymer Films as Reactive Temperature Sensors

The chemical kinetic control of the reaction states, through the empirical reaction rate (Eq. 2), the quantitative influence of the temperature on the oxidation reaction rate. If the concentration of ions in solution and the concentration of active sites on the film are kept constant, then:

$$\ln(r) = k''' - E_a/RT \tag{10}$$

Where $k''' = \ln A + a\cdot\ln [A^-] + b\cdot\ln [Pol^*]$.

This expression provides a different way to explore the chemical control of the reaction kinetics: by changing the temperature under constant concentration of anions $[A^-]$ and active sites [Pol*]. A polypyrrole film was oxidized at 0.20 V during 30 s in order to erase structural memory on the material. Then the polymer was reduced and compacted at −1.20 V for 60 s at room temperature. The coated electrode was then extracted from the solution into the nitrogen atmosphere of the closed cell. The temperature of the solution was adjusted to the working temperature. Then the coated electrode was returned into the solution and submitted to oxidation potential step, readapted now by prepolarization at −1.20V (the previous applied potential), kept for only 1 second to 0.2 V. The experimental procedure was repeated in different temperatures −10, −3, 4, 11, 18, 25 and 32°C. The chronoamperometric responses are presented in Fig. 6a.

By plotting the logarithm of the reaction rate obtained from the maxima, Eq. (3), versus T^{-1}, a semilogarithmic relationship is obtained, as expected for a chemical reaction (Eq. 10). This plot can be used as a calibration curve of a reactive temperature sensor.

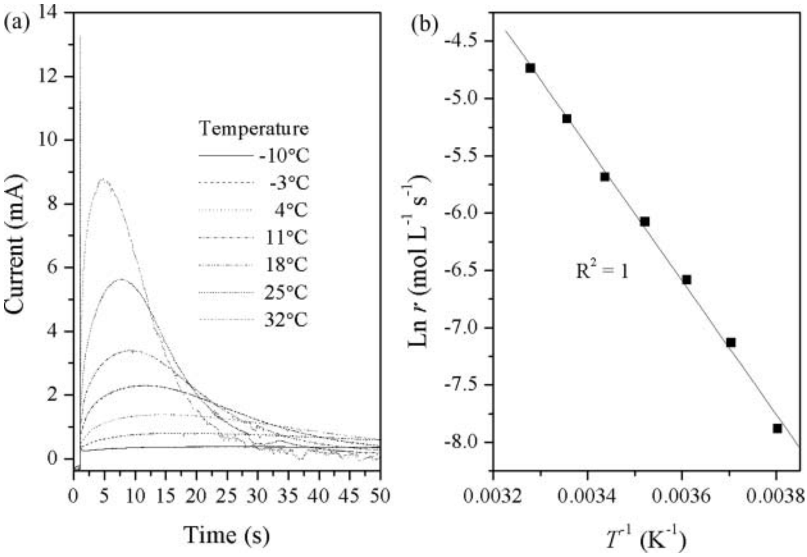

Figure 6. a) Chronoamperograms obtained from a polypyrrole film having 4.01 μm thickness in 0.1 M $LiClO_4$ acetonitrile solution. The coated electrode was reduced every time at −1.20 V at room temperature for 60 s, after that, the temperature was varied to different values (indicated on the figure) and an oxidation step was applied to the polymer film from −1.20 V, kept now for 1 s to 0.20 V. b) Arrhenius plot for the polypyrrole oxidation obtained from the chronoamperograms showed in a).

Conclusions

The p-doping and n-doping kinetics of conducting polymer films were studied. A chemical kinetic methodology similar to those used for any other chemical reaction was followed studying the effect of reactants concentrations. One of the reactants (the active sites) is located in the polymeric chains. The second reactant (anions or cations) is present in solution. The reaction coefficient and the reaction orders related to either reactant were obtained from different initial states of the film, attained by electrochemical prepolarization at different potentials.

The expected double logarithmic dependencies (Eq. 5) between reaction rates and reactant concentrations, or the semi-logarithmic variation of the reaction rate with 1/T assure the chemical kinetic control of the electrochemical process at the chronoamperometric maxima.

The reaction kinetics changes (Tables 1 and 2), if the conformational movements become the rate determining step. In that case the chronoamperometric responses present a maximum, when the reaction starts from initial states having different conformational packed structures. In those dense and reactive gels the kinetic coefficient (k) and the reaction order related with concentration of active sites in chains (β) are a function of the initial packed state of the polymer: lower values of k and bigger of β are obtained when rising cathodic potentials are applied before oxidation. The reaction coefficient and the reaction order include structural information about the packed conformations of the initial state for the oxidation.

These materials can be used as sensors, due to the variation in their response with the electrolyte concentration or temperature. Electrochemical devices as: artificial muscles, polymeric batteries, smart electrochromic windows, smart membranes, drug delivery devices, artificial nervous interfaces, etc, which actuation is driven by the same electrochemical reaction, should be expected to work, simultaneously, as a sensor of the working conditions, mimicking biological organs.

Acknowledgments

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