Intrinsic Asymmetry, Hysteresis, and Conformational Relaxation during Redox Switching in Polypyrrole: A Coulovoltametric Study

Intrinsic Asymmetry, Hysteresis, and Conformational Relaxation during Redox Switching in Polypyrrole: A Coulovoltametric Study

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Theoretical coulovoltammograms associated with the evolution of anodic charges when a polypyrrole film, which was previously compacted at a strong negative potential in a 0.1 M LiClO$_4$ propylene carbonate solution, was submitted to anodic potential sweeps were compared with experimental responses. The electrochemically stimulated conformational relaxation (ESCR) model provides a good description of either the influence of the negative potential limit, the sweep rate, the temperature, or the electrolyte concentration on the rate of electrochemical oxidation, this being initiated through conformational relaxation processes and completed under counterions diffusion control. An analysis of both anodic and cathodic experimental branches, together with theoretical conformational relaxation curves, allows to detect four different structural rearrangement processes affecting electrochemical responses: the well-known conformational relaxation effect observed only in anodic branches, a hysteresis effect on cathodic curves at potentials lower than −600 mV vs SCE, an intrinsic asymmetry between anodic and cathodic branches, and a like-capacitive effect at the beginning of the anodic sweep. The combination of both hysteresis effects in cathodic branches and relaxation effects in anodic ones gives rise to a hysteresis cycle, whose integration yields the electrochemical energy required to expand the compacted polymer structure. On the other hand, the intrinsic asymmetry between anodic and cathodic branches has been related to the different values of coefficients z_r and z_c which, according to the ESCR interpretation, are associated with the electric charge required to open or close a mole of polymeric segments, respectively. This fact opens the possibility for a complete theoretical description of electrochemical responses of conducting polymers as a function of their structure.

1. Introduction

A conspicuous separation between the anodic and cathodic peak potentials, i.e., the so-called "redox asymmetry" or "hysteresis", is an usual phenomenon observed in voltammetric experiments performed on conducting polymer-coated electrodes. Electrochemical models predict fully symmetrical doping (or oxidation) and dedoping (or reduction) waves, with identical peak potentials and currents.[1,2] Redox asymmetry can be therefore considered as an anomalous effect related to a complex nonequilibrium behavior, thus suggesting that either doping or dedoping reactions have some kinetic limitations.[3] This means that its interpretation cannot be based on a purely thermodynamic analysis, but it should also include some irreversible processes taking place inside the polymer or at the interfaces. Until now, a variety of explanations to this old problem have been proposed. Among interfacial processes, a slow heterogeneous electron transfer across the metal/polymer boundary has been proposed in order to interpret the peak potential difference,[4−6] but so strong predicted variations in the positions of the peaks were not experimentally observed. Concepts of two-step polaron−bipolaron reactions[7,8] and of conservation of mass and charge in the different regions of the electrode system[9] were also developed. One of the most promising attempts was performed by Heinze et al.,[10−14] who interpreted the observed asymmetries in cyclic voltammograms of conducting polymers in terms of local modifications of the chain geometry, i.e., transitions between benzoid and quinoid structures taking place in a different manner during doping and dedoping.[12−14]

The experimental results we present in this work are in general accordance with this hypothesis of conformational relaxation as responsible for the observed asymmetry in voltammetric responses. It will be demonstrated that differences between anodic and cathodic branches can be varied by modifying parameters that either affect the energetic availability of polymeric chains in order to undergo conformational changes (potential scan rate and temperature) determine the amount of free volume left inside the polymeric structure after reduction (negative potential of departure), or influence the rate of formation of positive charges on polymeric chains (counterion concentration in the solution). For a better understanding of processes causing redox asymmetry in electrochemical responses, we will make use of coulovoltammograms or charge−potential curves instead of voltammograms or current−potential curves. The experimental data have been completed with theoretical simulations performed on the basis of the electrochemically stimulated conformational relaxation (ESCR) model, which was presented by the authors in previous works[15−19] in an attempt to explain other anomalous effects observed in electrochemical responses of conducting polymers, as memory[20] and first oxidation cycle effects.[21,22] This work represents a further contribution in this direction: we test the validity of the ESCR treatment to describe the anodic branches of coulo-

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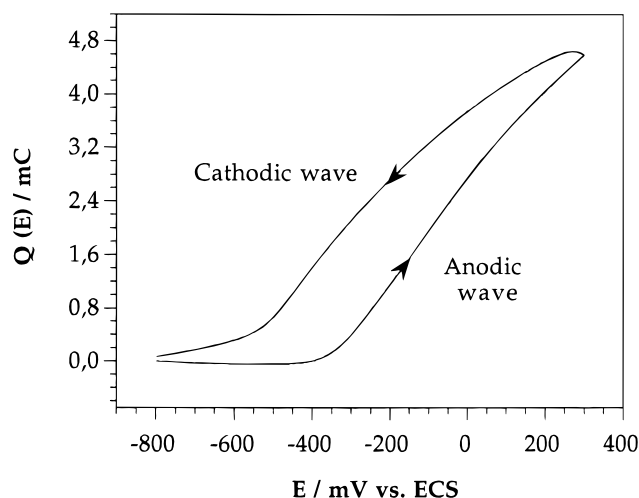* Corresponding author. Fax 34-943-21 22 36. E-mail qppfeott@sq.ehu.es.

Figure 1. Complete charge–potential plot of a thin polypyrrole film in response to a potential sweep carried out between −800 and 300 mV vs SCE, the scan rate being 30 mV s^{-1} and the temperature of the cell 22 °C (room temperature). The hysteresis effect is observed as a separation between anodic and cathodic waves.

voltametric responses, and we show the way of extracting new structural information from experimental responses.

2. Experimental Details

Pyrrole (Jansen) was distiled under vacuum before use and stored under N$_2$ at −10 °C. Acetonitrile (Lab Scan, HPLC grade), propylene carbonate (Merck, >99% content), and anhydrous lithium perchlorate (Aldrich, 95% content) were used without further purification. A one-compartment electrochemical Metrohm cell, connected to a PAR M273 potentiostat–galvanostat and controlled by an IBM PS/2 computer, was used for both electrogeneration and checking of polypyrrole films. Working electrode and counter electrode were platinum sheets having 1 and 2 cm^2 of surface area, respectively. A saturated calomel electrode (SCE) from Crison Instruments was used as reference electrode. The temperature of the cell was maintained constant with a Huber ministat. All the solutions were degassed prior to use by bubbling N$_2$ for 10 min.

Electrogeneration was carried out using acetonitrile, with a 2% of water content, as solvent, 0.1 M LiClO$_4$ as electrolyte, and 0.1 M pyrrole as monomer, by passing 50 mC at 800 mV vs SCE at room temperature (22 °C). Polypyrrole films of about 0.1 mm of thickness were obtained, showing electrochromic properties (yellow in reduced state and blue when it was oxidized). After generation, the polymer-coated electrode was rinsed with acetone, dried in air, and transferred into the background solution (0.1 M LiClO$_4$ in dry propylene carbonate) in the absence of the monomer, where it was submitted to electrochemical analysis. The solvent/electrolyte system was chosen because of its wide potential window and stability.

3. Results and Discussion

Let us consider a polypyrrole film obtained as described above. Figure 1shows the coulovoltammogram or charge–potential transient (those two variables will be represented by $Q(E)$ and E, respectively) corresponding to a potential sweep between −800 mV (which was maintained for 120 s, this time being long enough to attain the neutral state) and 300 mV at 30 mV s^{-1}. When the potential is swept toward more positive potentials, the charge consumed for doping remains close to zero until about −500 mV. Then, the oxidation charge increases

rapidly, and finally, at high applied potentials, it approaches a straight line. Along the cathodic sweep, the discharging curve shows an asymmetry related to the charging one: the charge remaining in the polymer is, at each potential, larger than the charge consumed during the anodic wave. Disagreements of as much as 1.63 mC in charge values (which represents almost a 34% of the overall doping charge) are inquestionably associated with significant differences between doping and dedoping mechanisms. Although the shape of both anodic and cathodic waves has been related, in a simplified view, to a counterion diffusion-controlled process,[22] it must not be disregarded as the different time scale at which counterion diffusion and conformational relaxation processes occur. Successive increments in the doping depth require the polymeric matrix to expand in order to allow the penetration of counterions and solvent molecules from the surrounding solution. In contrast, dedoping involves the outflow of solvated counterions from an already opened structure, thus requiring no previous conformational changes to proceed. In other words, doping has a stronger energetic consumption than dedoping, this being reflected in the position of the anodic wave which is displaced toward more positive potentials. This effect can be considered as a structural feature of each conducting polymer, which we will express in this work in terms of an intrinsic asymmetry.

Additional support to the above interpretation comes from the application of different negative potentials to the polymer film before the realization of the potential sweep. According to the ESCR model,[15,17] a strong cathodic polarization implies interchain free volume destruction, together with the compacting of the polymeric structure. Moreover, below a given potential (about −900 mV in polypyrrole) the polymeric structure closes, making difficult any further movement of counterions within the polymer network.[19] This results in increasing energetic requirements for the beginning of subsequent oxidation as higher than the initial compactness was, so the anodic branch of the curve should be expected to move toward more positive potentials, giving a stronger asymmetry, i.e., a higher separation between doping and dedoping curves. Normalized charge–potential curves performed from different initial potentials (E_c), ranging between −3000 and −800 mV, which were maintained for 120 s, to the same upper limit of 300 mV at 30 mV s^{-1} are depicted by Figure 2(solid lines). It can be observed that the oxidation process requires higher overpotentials to proceed as more negative the initial potential was. This fact has been linked to the opening of the compacted structure by means of conformational rearrangements of the polymeric chains, which is followed by a diffusion-controlled completion of the oxidation process.[15] The more negative the initial potential was, the longer are times required to open the compacted structure and to initiate the oxidation process. The final diffusional region remains substantially unchanged whatever the initial potential was. So the observed differences between oxidation branches can only be assigned to variations in the rate of conformational relaxation, this being a consequence of the initially different degrees of closure of the polymeric structure attained by polarization at potentials more negative than about −900 mV. In the context of the ESCR treatment, this phenomenon will hereafter be named the conformational relaxation effect.

A slight growth in the initial charging slopes was also observed as the departure potential is moved toward more negative values. Another outstanding point in the obtained coulovtametric curves is that cathodic branches are almost not affected by changes in the initial conditions, at least in the region of high potentials, thus proving that asymmetry between
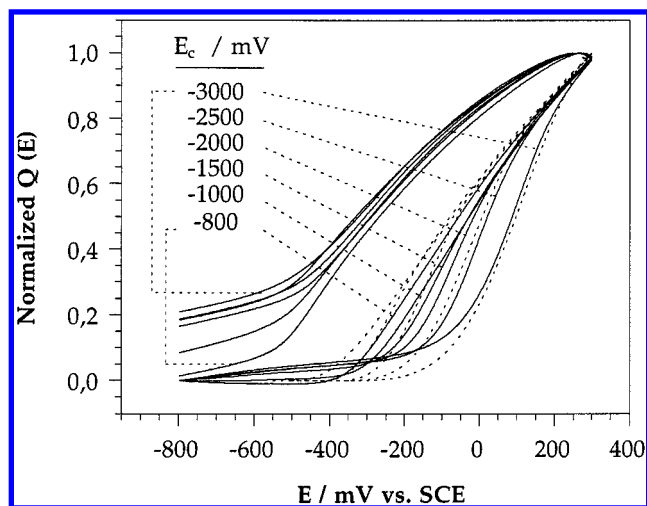
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Figure 2. Experimental (solid lines) and theoretical (dashed lines) normalized charge−potential responses to potential sweeps carried out on a polypyrrole electrode in a 0.1 M LiClO$_4$ propylene carbonate solution from different departure potentials, indicated in the figure, to 300 mV vs SCE at 30 mV s^{-1} and room temperature. Theoretical data were extracted from eqs 1 and 4.

Figure 3. Experimental (solid lines) and theoretical (dashed lines) normalized charge−potential responses to potential sweeps carried out on a polypyrrole electrode from −2000 to 300 mV in a 0.1 M LiClO$_4$ propylene carbonate solution, at different sweep rates, which are indicated in the figure. Theoretical data were extracted from eqs 1 and 4.

branches is due to kinetic limitations during oxidation but not during reduction. Nevertheless, a careful examination of the final part of the cathodic branches shows that a given amount of the charge consumed for oxidation is not recovered during reduction, arriving up to 20% of the overall charge when the film was previously polarized to −3000 mV vs SCE. This effect is responsible for the appearance of hysteresis effects, as it will be seen later in this work. Returning to the beginning of the cathodic wave, we now observe that despite the similitude of the curves, the reduction process is a few slower when the film is previously polarized at more negative potentials. Hence, the application of high positive potentials during the oxidation sweep does not reach the point of erasing completely the structural effect of the initial potential of reduction. In any case, all the reduction curves undergo a change in slope below −600 mV, giving a straight variation ahead with higher remaining charges for experiments starting at more negative potentials. We will come back to this point later in this work.

The relaxation effect being supported by the slow rearrangement of the polymeric structure, it would be expected that any increase in the potential sweep rate (v) should promote a larger separation between anodic and cathodic branches. This fact can be well observed from normalized coulovoltammograms recorded during potential sweeps between −2000 and 300 mV at sweep rates varying between 10 and 50 mV s^{-1} (see Figure 3). This was the expected result, since conformational relaxation processes require time to occur. If the potential sweep is performed at a low sweep rate, conformational changes have time enough to evolve, so the separation between anodic and cathodic waves decreases. As the sweep rate is increased, shorter times are available to cross over to the same potential interval. In those conditions, oxidation becomes controlled by the ability of polymeric segments to undergo conformational rearrangements rather than by the diffusion of dopant counterions, so the anodic wave is displaced toward higher potentials, and a stronger relaxation effect is observed. On the other hand, the cathodic branches obtained at different sweep rates overlap, thus showing that counterion diffusion processes across opened structures need lower times to occur. In the same way, the initial slope of the charging curves is not affected by changes in the sweep rates.
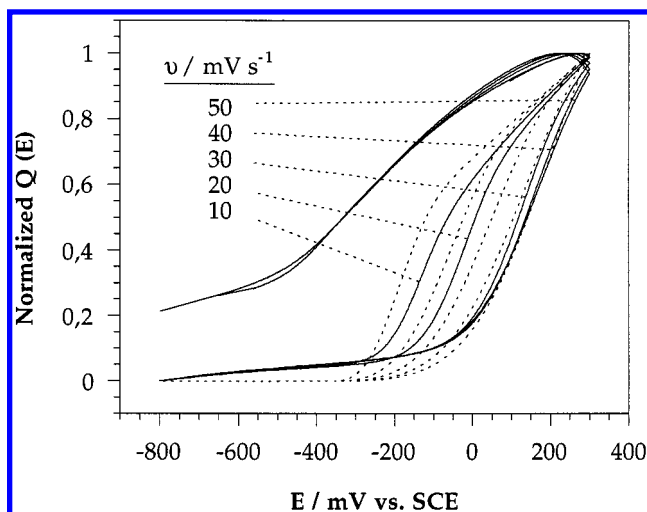
As is evident from the above results, conformational movements are faster as more electrochemical energy is given to polymeric chains through anodic overpotentials. Another way to supply the energy required for conformational relaxation is by means of changes in the temperature (T) of the system. So it would be expected that the separation between anodic and cathodic curves is markedly affected by the temperature. To confirm this prediction, we changed the experimental procedure as follows. A polypyrrole-coated platinum electrode was reduced and compacted by cathodic polarization at −2000 mV in a 0.1 M LiClO$_4$ propylene carbonate solution at room temperature for 2 min. The electrode was then extracted from the background solution, and it was maintained in N$_2$ gas; meanwhile, the temperature of the solution was regulated to a new value. The compacted and reduced electrode was again immersed in the solution and immediately submitted to a potential sweep between −2000 and 300 mV at 30 mV s^{-1}. Different temperatures, in the range between −10 and 30 °C, were studied following this procedure. Normalized charge−potential curves are represented by Figure 4. As the polymer was always reduced under the same experimental conditions, the compactness attained during reduction was also the same. Thus, when the polymer was later submitted to potential sweeps at different temperatures, the changes observed on the wave separation have to be attributed to differences in the thermal energy available by polymeric segments to undergo conformational changes. As expected, conformational relaxation occurs faster at increasing temperatures, promoting a shift of the oxidation curve to lower potentials. Note that at −10 °C the conformational relaxation rate was so slow that oxidation was not completed once the upper limit of potential was reached. So the charge keeps on increasing during the first moments of the cathodic wave, which is shifted cathodically in comparison to that obtained at higher temperatures.

Finally, the dependence of the relaxation effect on the electrolyte concentration in the surrounding solution (C_s) comes from the need for counterions to compensate the positive charges generated along the chains as the conformational relaxation process goes on. The influence of this variable was followed by potential sweeps from −2000 to 300 mV, at 30 mV s^{-1} and room temperature, changing each time the concentration the salt
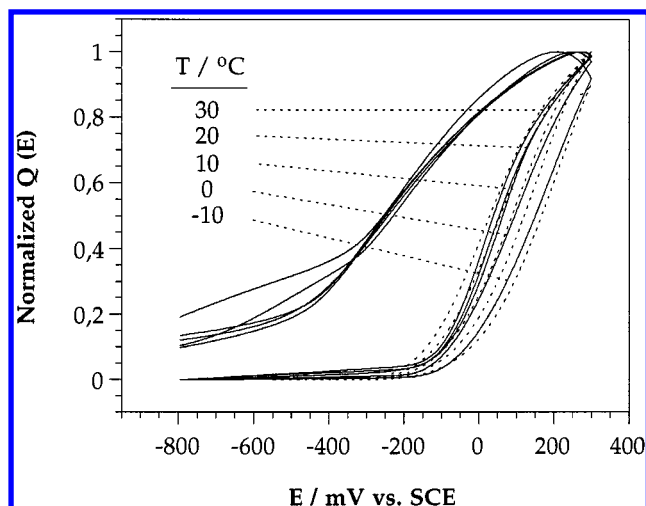
Figure 4. Experimental (solid lines) and theoretical (dashed lines) normalized charge−potential responses to the application of potential sweeps from −2000 to 300 mV in a 0.1 M LiClO₄ propylene carbonate solution, at temperatures varying in the range between −10 and 30 °C. Reduction temperature was always 22 °C (room temperature). Theoretical data were extracted from eqs 1 and 4.
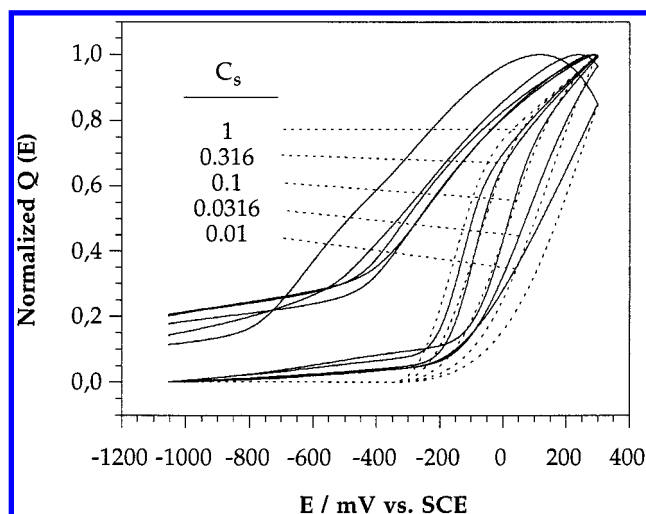

Figure 5. Experimental (solid lines) and theoretical (dashed lines) normalized charge−potential responses obtained for thin polypyrrole films. Potential sweeps were carried out from −2000 to 300 mV vs SCE at 30 mV s⁻¹ and room temperature. The concentration of the electrolyte in the solution changed each time in the range between 0.01 and 1 M. Theoretical data were extracted from eqs 1 and 4.

in the solution in a range between 0.01 and 1 M. Normalized coulovoltametric responses are shown by Figure 5(solid lines). As was expected, increasing values of the salt concentration promote higher oxidation rates and a lower separation between doping and dedoping branches, thus showing that conformational relaxation can be treated as an electrochemical reaction in the solid state, in which dopant counterions participate as reactants. The curve corresponding to an electrolyte concentration of 0.01 M does not reach its maximum charging level during the anodic wave. That means that the expansion of the polymeric structure has not enough time to be completed during the anodic scan, so both oxidation and conformational relaxation processes go on during the cathodic branch. As a consequence, the reduction process becomes shifted cathodically.

The experimental curves obtained for the different studied experimental variables (departure potential, potential sweep rate, temperature, and counterion concentration) can be theoretically simulated on the basis of the ESCR model, whose mathematical

statements have been extensively described in previous papers.[17,18] According to the ESCR treatment, the overall charge spent for oxidation and recovered during reduction can be separated into two parts. The first component reflects the opening of the polymeric structure in the first stages of the oxidation process, so it is known as conformational relaxation charge. To calculate it, the model takes into account that oxidation does not occur simultaneously in all the polymer bulk, but it is initiated from a few nuclei on the external film surface once the nucleation overpotential is reached. This fact was included in Avrami's treatment,[24] leading finally to the following expression for the charge consumed for conformational relaxation at each applied potential:[18]

$$Q_r(\eta) = Q_r[1 - \exp[-c^2 a(\eta)[1 - [a(\eta_N)/a(\eta)]]^{1/2}]^2] \quad (1)$$

where Q_r represents the overall conformational relaxation charge, c is a characteristic oxidation time, which depends on the inverse of the sweep rate ($c \sim v^{-1}$), η is the anodic overpotential applied during oxidation, η_N represents the nucleation overpotential, and $a(\eta)$ varies along the potential sweep as follows:

$$a(\eta) = [\pi N_o \lambda^2/\tau_0^2 A] \exp[-2\Delta H/RT] \quad (2)$$

Here N_o denotes the number of oxidation nuclei generated per cm⁻² of film surface, λ is the length of a single polymeric segment, τ_0 is the conformational relaxation time in the absence of any external perturbations, which depends on the counterion concentration according to a potential law ($\tau_0 \sim C_s^{-0.25}$),[15] A is the area of the film, T is the temperature, and ΔH represents the activation energy for the conformational relaxation process. We likewise accept that this energy depends linearly on both anodic and cathodic overpotentials (η and η_c, respectively), so we have

$$\Delta H = \Delta H^* + z_c \eta_c - z_r \eta \quad (3)$$

ΔH^* being the conformational activation energy in the absence of any external electric field. According to eq 3, the closure of the polymeric matrix is proportional to the reduction overpotential, which is related to both the potential of reduction (E_c) and the potential at which the polymer structure closes along a negative potential sweep (E_s), so $\eta_c = E_s - E_c$. The parameter z_c, defined as the coefficient of cathodic polarization, expresses the charge consumed to compact 1 mol of polymeric segments. On the other hand, the thermal energy needed to relax 1 mol of polymeric segments decreases when an anodic overpotential is applied to the polymer. As the oxidation level (the number of charges consumed to oxidize a polymeric segment) depends on the applied potential, this electrochemical energy will be proportional to an anodic overpotential, referred to the oxidation potential of the conducting polymer (E_o); thus $\eta = E - E_o$. Finally, the parameter z_r is defined as the coefficient of electrochemical relaxation, and it is related to the charge needed to relax 1 mol of polymeric segments.

The second component of the doping charge is supposed to be consumed under counterion diffusion control into the partially oxidized polymer, so it will hereafter be named diffusion charge:

$$Q_d(\eta) = Q_{ds}(\eta)\frac{\exp[-b(\eta)\eta/2v]}{v^2\eta} \int_{\eta_N}^{\eta} \frac{I_r(\eta')}{Q_r}[\int_{\eta'}^{\eta} \eta b(\eta) \times$$
$$\exp[b(\eta)\eta/2v]\, d\eta]\, d\eta' \quad (4)$$

In eq 4, $Q_{ds}(\eta)$ is the diffusion charge consumed in the steady state at a given potential, $I_r(\eta)$ is the conformational relaxation
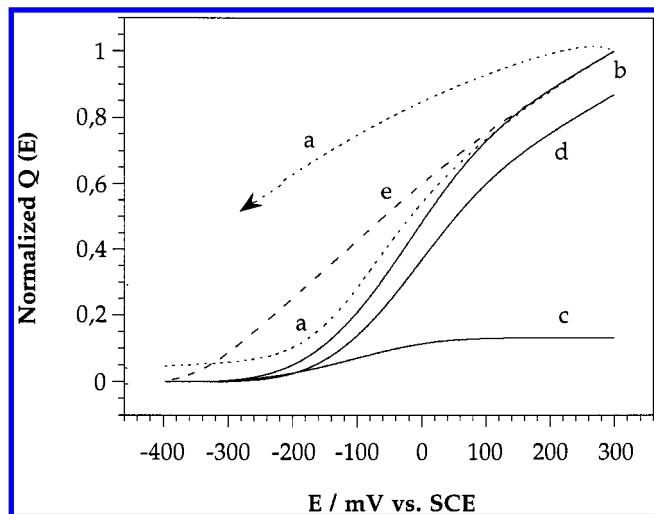
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Figure 6. Normalized charge−potential experimental response to a potential sweep from −2000 to 300 mV vs SCE (a), all the other electrochemical magnitudes having the same value as in Figure 1. The experimental curve is compared to the theoretical one (b), which can be separated into its conformational relaxation (c) and counterion diffusion (d) components. A comparison is also made with the experimental response corresponding to a reduction potential of −800 mV (e).

current, which can be obtained by deriving eq 1, and $b(\eta)$ is a diffusional magnitude:

$$b(\eta) = 2D_{app}/h^2 \qquad (5)$$

Here h is the film thickness and D_{app} is the apparent diffusion coefficient of counterions throughout the polymer, being a function of both the concentration of counterions in the solution ($D_{app} \sim C_s^{-1/2}$)[25] and the applied potential ($D_{app} \sim \eta$).[18] Addition of eqs 1 and 4 gives the theoretical charge−potential transient for the oxidation of a conducting polymer during a potential sweep. In Figures 2−5 theoretical curves (dashed lines) are plotted together with experimental results (solid lines) for each variable. As is apparent from the figures, the model provides a reasonably good description of experimental charge−potential transients.

Now we focus our attention on the experimental curve corresponding to a potential sweep from −2000 to 300 mV, at 30 mV s⁻¹ and room temperature (see Figure 6, curve a), which clearly resembles other structural relaxation-controlled transients, particularly magnetization curves in ferromagnetic materials.[26] Two differences can be pointed out. On one hand, the charge consumed for the electrochemical doping is higher the more positive the applied potential is; i.e., doping charge never attains a saturation level, provided that overoxidation or degradation processes are neglected.[27] On the other hand, any increase in the doping level of the polymer originates not in a single process but in at least in two different events, as has been indicated above. In fact, the corresponding theoretical curve (Figure 6, curve b) can be separated into its conformational relaxation (Figure 6, curve c) and counterion diffusion (Figure 6, curve d) parts, according to eqs 1 and 4, respectively. Among those two events, only conformational relaxation is responsible for the separation between anodic and cathodic branches. To clarify this point, let us compare curves a and e in Figure 6, which represent the coulovoltametric responses to potential sweeps initiated from −2000 and −800 mV, respectively. At high potentials, once the opening of the structure has finished, both curves overlap. In other words, the diffusion component does
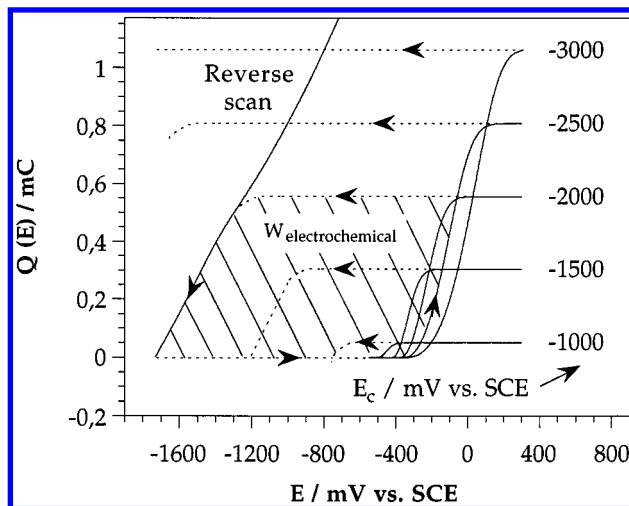

Figure 7. Evolution of the conformational relaxation component by changing the initial potential as indicated in the figure. The electrochemical work consumed for the conformational relaxation of the polymer structure has been extracted from the area covered by the hysteresis loop. The theoretical data were obtained by fitting eq 1.

not vary by itself as the separation between branches changes, thus proving that it has no relevant meaning in the understanding of the hysteresis mechanism.

What is remarkable about the above result is that we can make use of the theoretical relaxation curve (given by eq 1) to study the influence of structural rearrangements on the hysteresis phenomenon. In this sense, we could suppose that if diffusion processes were hindered, the hysteresis cycle would be much smaller. This fact is shown by Figure 7 for a potential sweep initiated from −2000 mV. Experiments in this direction are in progress. In any case, the stripped area defined by the experimental reduction and theoretical relaxation branches can be considered as an electrochemical work required to expand the structure during oxidation by means of conformational rearrangements. Therefore, we can write

$$W_{electrochemical} = \oint Q(E)\, dE \qquad (6)$$

By integration of the stripped area in Figure 7, we deduce that the work required to oxidize and relax a polypyrrole structure compacted at −2000 mV is of around 2.95 kJ mol⁻¹, this value being very close to the obtained in a previous work[17] from the last term in eq 3 (around 2.68 kJ mol⁻¹). Figure 7 shows also the conformational relaxation curves at different potentials of departure. The area inside the hysteresis cycle increases as the potential of departure is displaced to more negative values, as was expected: more negative potentials applied during reduction lead to closer macromolecular structures at the beginning of the oxidation and, hence, to stronger energetic requirements in order to open and relax it. This result is in agreement with experimental results reported by the authors in an earlier work.[15]

4. Hysteresis, Intrinsic Asymmetry, and Conformational Relaxation

Experimental results shown here reveal the existence of four different structure rearrangement processes during redox switching in conducting polymers (see Figure 8):

1. A conformational relaxation process, responsible for the positive shift of the oxidation wave when initiated from more negative potentials.
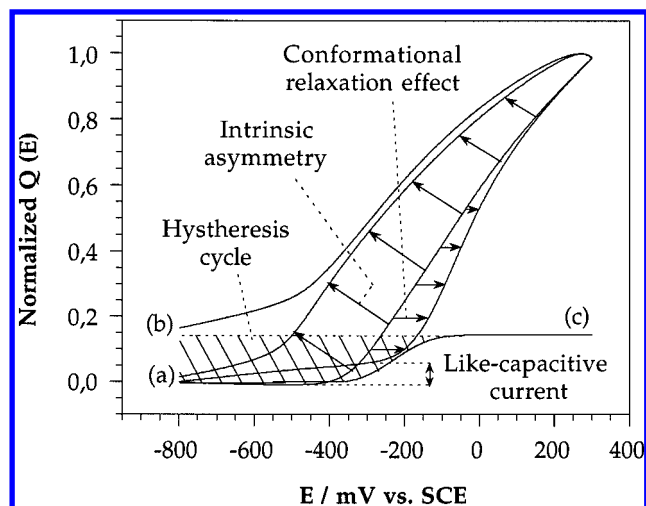
Figure 8. Charge−potential transients for potential sweeps performed from (a) −800 mV and (b) −2000 mV vs SCE, together with the theoretical conformational relaxation component of this last curve (c). The conformational relaxation effect, the hysteresis cycle, the intrinsic asymmetry, and like-capacitive currents are indicated in the figure (see Figure 7 for a complete description of the hysteresis cycle).

2. A hysteresis, that is, an effect that is symmetric to the theoretical anodic relaxation curve, showing that the structural memory is not extinguished by passing through the oxidized state.

3. An intrinsic asymmetry between anodic and cathodic branches remains even in the absence of any relaxation process. This property of the polymer is also related to structural changes, as has been detected, studied, and applied in membranes.[28]

4. Finally, increasing linear charges are observed from the beginning of the experimental curves to the starting relaxation process. On the basis of their linear variation with the applied potential, we named them like-capacitive charges. Experimental results show that they are probably related to a redistribution of dipoles and remaining charges within the reduced polymer.

Conformational relaxation and hysteresis were proved in this paper to be related processes, since they are a consequence of the conformational relaxation control of both oxidation (opening) and reduction (closure) processes. The asymmetric effect is an intrinsic structural property of conducting polymers, affecting in a different way oxidation or reduction kinetics. It has been detected, in the context of the ESCR model, through differences between coefficients z_r (charge required to relax 1 mol of polymeric segments) and z_c (charge required to compact 1 mol of polymeric segments).[15−19] If that is confirmed, further conformational relaxation experiments will allow us to quantify asymmetric processes and their connection with structural features of the polymer. This is the subject of our actual work.

5. Conclusions

The validity of the ESCR treatment to describe theoretically anodic coulovoltametric responses of conducting polymers has been stated. A good fitting between experimental and theoretical curves whatever the experimental variable studied (departure potential, sweep rate, temperature, or electrolyte concentration) was obtained.

Studies showed that the oxidation of a compacted polymer film under initial conformational relaxation control and subse-quent diffusional full completion does not attain to erase a deep structural memory, thus promoting the appearance of a hysteresis cycle related to both the reduction curve and the conformational relaxation component of the oxidation branch. Additionally, this hysteresis effect is revealed as a slowing down in the reduction rate at potentials more negative than about −600 mV vs SCE. On the other hand, the asymmetry between anodic and cathodic charge−potential curves has been related to an intrinsic structural feature of the polymer as is the difference in the values of coefficients z_r and z_c. It has been shown that the separation between oxidation and reduction branches can be increased by applying more negative potentials during reduction. This has been considered as a conformational relaxation effect. Finally, a like-capacitive charge was detected from the beginning of the potential sweep, which structural meaning is out of the scope of this paper.

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