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Polypyrrole: Diffusion Coefficients and Degradation by Overoxidation

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The electroactivity of electrogenerated polypyrrole films was degraded by applying consecutive anodic potential pulses (overoxidation). After each degradation step, the electroactivity of the material was recorded by voltammetric and chronoamperometric measurements. The charge consumed during each degradation step was calculated by the difference between the degradation and the control chronoamperograms. The diffusion coefficients of the counterions within the material were obtained from the control chronoamperograms by applying the electrochemically stimulated conformational-relaxation model. As the materials became increasingly degraded, slower oxidation processes were observed, and decreasing diffusion coefficients were obtained. These observations point to growing cross linking between neighboring polymeric chains during the degradation process, thus reducing conjugation lengths and increasing the rigidity of the conformational electro-chemo-stimulated movements on the chains. An electroactivity degradation of 50% induces a 15% increase in the weight of the material, pointing to the presence of rigid and oxidized islands entrapped by cross-linking points that prevent any ionic interchanges.

Introduction

Oxidized conducting polymers are nonstoichiometric materials[1] constituted of polymeric chains, counterions, and solvents; that is, they act as a polymeric salt. The nonstoichiometry indicates that the balancing counterion content can evolve through consecutive steady states in a continuous, uniform, infinitesimal, and reverse way from zero to 30−60% (w/w), depending on the chemical nature of the counterion, under electrochemical control. This means that any property related to the composition, electro-chemo-mechanical volume,[2] electrochromicity,[3] charge storage,[4] electroporosity,[5] electron−ion transduction,[6] and so forth can also change in a continuously infinitesimal and reverse way[7] by as many orders of magnitude as the driving composition under electrochemical control. As a consequence, any function related to the electrochemical properties, for example, electro-chemo-mechanical actuation or artificial muscles,[8] smart windows or electrochromic devices,[9] supercapacitors[10] and all polymeric batteries,[4] nervous interfaces,[11] and intelligent medical dosages,[12] and so forth, must have a similar flexibility in its actuating devices.

Electrochemical reactions, properties, and applications of conducting polymers are linked to swelling/shrinking processes. These reactions occur under kinetic control of the counterion diffusion when the molecular structure of the polymer is open. The conformational relaxation−migration process (electrochemical stimulation of the conformational movements of the polymeric chains and the correlated migration of counterions

along the generated channels) is the limiting step of reduced and compacted films.[13] The kinetic limiting step, diffusion, and conformational-relaxation processes take place inside the material.

Besides these kinetic limitations, the polymer of any device will also undergo, during its lifetime, a progressive degradation process. This degradation acts on both the range of any property linked to a potential increase and the kinetics of its change. To improve our understanding of the relationships between degradation and diffusion processes, we present a study about the evolution of the diffusion coefficients inside increasingly degraded materials. The degradation was induced by anodic polarization, described in the literature as overoxidation. Voltammograms and chronoamperograms allow for perfect control of the material's electroactivity and the charge involved in the degradation processes and permit the diffusion coefficient inside the material to be obtained.

Experimental Details

Lithium perchlorate, $LiClO_4$, from Fluka and potassium nitrate, KNO_3, from Merck, both analytical reagents, were used as received. Pyrrole (Fluka) was distilled under vacuum before use. Water from a Milli-Q purifier with a resistivity of 18 MΩ·cm was used for the preparation of the solutions. Nitrogen gas of high purity was used for the deaeration of the solutions.

The electrochemical measurements were carried out using an EG&G PAR 273A potentiostat/galvanostat connected to a PC and controlled through M270 electrochemical software.

A single-compartment electrochemical glass cell was used; the working electrode and counter electrode were platinum sheets with surface areas of 1 and 4 cm^2, respectively, and the reference electrode was Ag/AgCl (KCl 3 M) from Radiometer. All of the experiments were performed at room temperature.

Polypyrrole films were electrogenerated under galvanostatic

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SCHEME 1: Potential Program Used for the Progressive Electrochemical Degradation and Electrochemical Control of Polypyrrole Films[a]
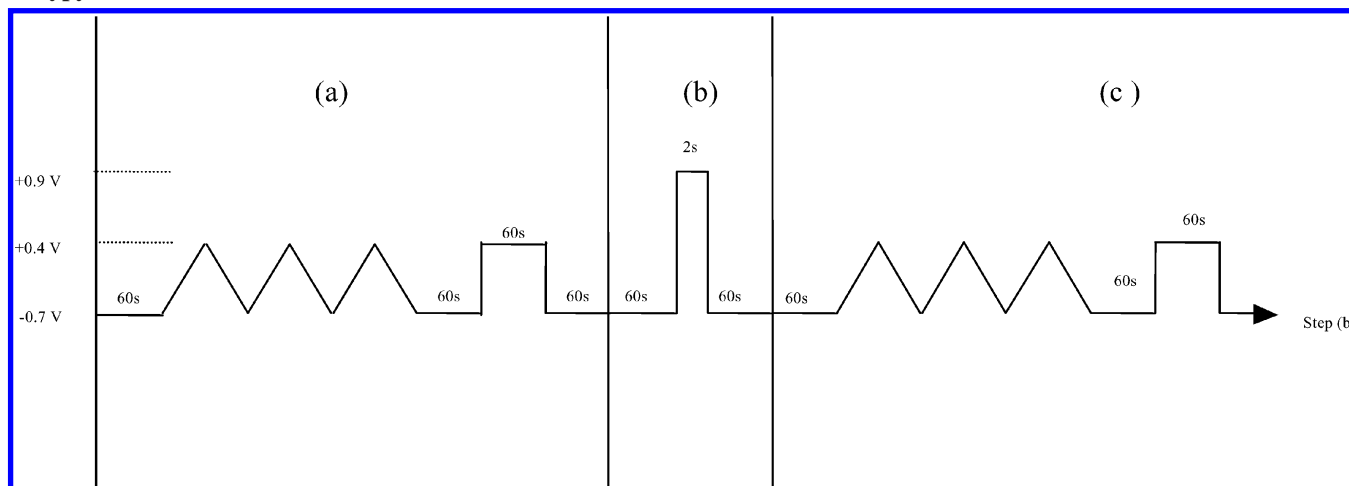
[a] (a) Consecutive cyclic voltammogram of control, from −0.7 to +0.4 V (vs Ag/AgCl, 3 M) at a scan rate of 20 mV·s⁻¹, and the control potential step between −0.7 to 0.4 and back to −0.7 V. (b) Degradation pulse from −0.7 V, kept for 60 s, to +0.9 V, kept for 2 s and transient to −0.7 V. (c) Consecutive cyclic voltammograms and potential steps of control, after each degradation pulse, under those conditions stated in a.

conditions by a current density of 1 mA·cm⁻² flowing through a Pt electrode in 50 mM pyrrole and 0.1 M KNO₃ aqueous solution for 400 s. A 1-μm-thick polypyrrole film, calculated by considering a formation rate of ca. 400 mC·cm⁻²·μm⁻¹, as reported by Díaz et al.,[14] was obtained. The coated electrode was then transferred to a 0.1 M LiClO₄ aqueous solution where the electroactivity of the material could be recorded after consecutive steps of electrochemical degradation. Consecutive voltammograms were taken until a stationary state was attained in the new electrolyte at 20 mV·s⁻¹ between −0.7 and +0.9 V. One stationary voltammogram was recorded to check the electroactivity of the film.

The polypyrrole film was submitted to consecutive treatments (Scheme 1) of degradation polarization, voltammetric control, and potential step. Every potentiostatic degradation step consisted of a square potential wave from −0.7 V, kept for 60 s (reduction of the film), to the selected degradation potential of +0.9 V, which was applied for 2 s (oxidation + degradation−overoxidation of the film) and returned to the initial potential of −0.7 V (60 s) (reduction of the remaining electroactive film). All of the concomitant chronoamperograms between both states were recorded. The difference between the anodic and cathodic charges gives the charge consumed for the degradation (or overoxidation) process.

After each of the degradation processes, the electroactivity of the material was recorded by consecutive voltammograms between −0.7 and +0.4 V at 20 mV·s⁻¹ until reaching a stationary state. The material was then submitted to a square potential wave of −0.7 to +0.4 V to determine the diffusion coefficient.

Results

A clean and dried platinum electrode was weighed using an ultramicro (model SC2) Sartorius balance with a precision of 10⁻⁷ g. After electrogeneration of a polypyrrole film, the coated electrode was rinsed with water and methanol and then dried and weighed. The weight of the electrogenerated polymer film was 0.1323 mg. Figure 1 shows the experimental degradation and control chronoamperograms obtained in 0.1 M LiClO₄ aqueous solution by square waves of a potential between −0.7 to +0.9 and returning to −0.7 V during successive degradation cycles, such as those indicated by Scheme 1. The integration
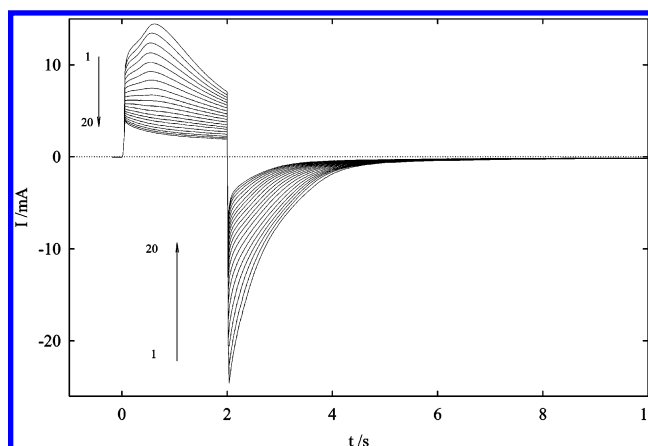

Figure 1. Experimental degradation (anodic) and control (cathodic) chronoamperograms obtained in 0.1 M LiClO₄ aqueous solution by square waves of potential between −0.7 to +0.9 and back to −0.7 V for consecutive degradation cycles, such as those indicated by Scheme 1, applied to a polypyrrole (weighing 0.1323 g)-coated platinum (0.5 cm²) electrode.

of the anodic chronoamperogram shows the charge consumed to oxidize and partially degrade the film, and that of the cathodic chronoamperogram shows the charge consumed to reduce the remaining electroactive material. The difference between both charges can be considered to be the charge consumed to degrade the material: the degradation charge. As expected during a degradation process, decreasing current densities and decreasing electroactive charges were observed in the chronoamperograms that were obtained after consecutive degradation processes. Moreover, the anodic chronoamperograms showed a maximum that is characteristic of a nucleation processes, as explained by the electrochemically stimulated conformational-relaxation model, ESCR.[13]

Figure 2 shows the evolution of the control voltammograms that were obtained after each of the 20 consecutive degradation processes (Scheme 1). As expected from the chronoamperometric results, a continuous decrease in the currents (and charge) involved is observed in the consecutive voltammograms; that is, the electroactivity of the material is degraded by the treatment. Both the anodic and cathodic voltammetric peaks showed a continuous shift toward more positive potentials on

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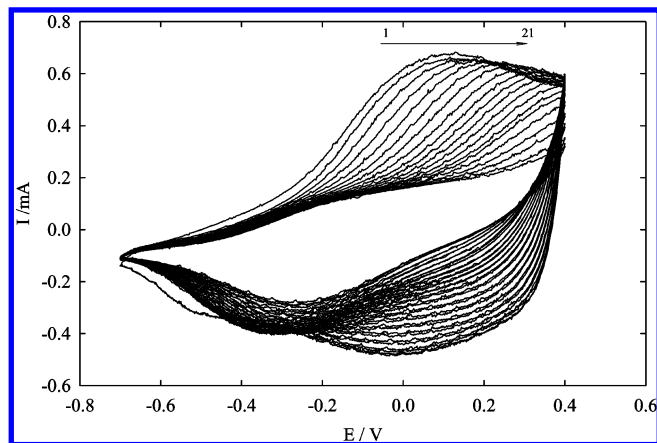
Figure 2. Control voltammograms from the pristine polypyrrole electrode (Scheme 1a and from the third *c* cycle after each treatment, obtained in 0.1 M LiClO$_4$ aqueous solution, from −0.7 to +0.4 V at 20 mV·s^{-1}, after consecutive degradation cycles. The potentials refer to Ag/AgCl (3 M KCl).
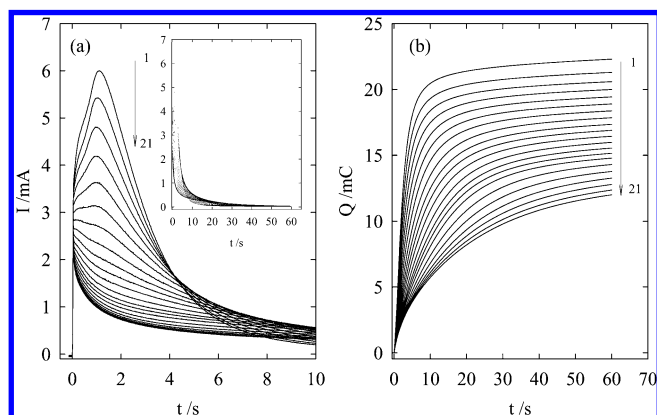

Figure 3. (a) Control chronoamperograms (a and c from Scheme 1) performed in 0.1 M LiClO$_4$ aqueous solution by potential step between −0.7 V, kept for 60 s, and +0.4 V, kept for 60 s (inset). The initial 10 s were presented in the larger plot. (b) Chronocoulograms obtained by numerical integration of the experimental chronoamperograms after each degradation cycle.

the anodic branches or toward a more negative potential on the cathodic branches for increasing degradation treatments, in others words, increasingly resistive behavior. Such an observation indicates the presence of increasing resistance for the electrochemical reactions and for the concomitant interchange of counterions during polymeric oxidation and reduction processes.

After 20 degradation cycles, 20 mC had been consumed to degrade the polymer. This charge was calculated by adding up the degradation charges that were obtained from each of the consecutive treatments. At the end of the treatment, the coated electrode was dried and weighed, with a weight increase of 20.3 μg over the weight of the dry film before treatment. This represents a weight increase of 15% during the degradation process.

Figure 3a shows the control anodic chronoamperograms that were obtained for the pristine electrode (number 1) and after each of the 20 consecutive degradation cycles (numbered from 2 to 21). The maximum current is observed in the chronoamperogram that was obtained for the pristine polypyrrole, for which it rapidly falls to zero, the oxidation process being complete after 8−10 s. The maximum current decreases very quickly for consecutive degradation treatments, and oxidation times gradually increase (Figure 3a, inset). After 14 degradation
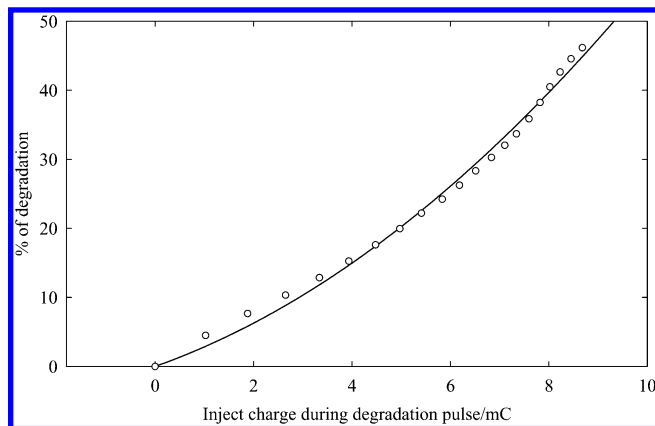
Figure 4. Parabolic dependence of the accumulated degradation charge on the consecutive cycles of treatment and the attained degradation percentage. A quadratic equation (— fits the experimental results: % of degradation = 2524 (Q_{inject}) + 304 646 (Q_{inject})^2.

treatments, the maximum becomes a shoulder, and the oxidation process is not completed after 10 s. By the integration of each of those chronoamperograms, the chronocoulograms shown in Figure 3b were obtained. As will be seen later, chronocoulograms are more suitable than chronoamperograms for obtaining the diffusion coefficients.

Accepting that decreasing control charge indicates electroactivity degradation for the conjugated material, this degradation can be quantified as the fraction (or percentage) of electroactivity loss by the material after each treatment; therefore, the charge involved in the pristine voltammogram, or chronoamperogram, of the control (Q_0) minus the control charge obtained by the same experimental method after *n* degradation treatments (Q_n), divided by the pristine charge (Q_0) and multiplied by 100, gives the experimental degradation percentage after *n* treatments: [(Q_0 − Q_n) /Q_0]100 = % of degradation.

To determine the efficiency of the charge involved in the degradation process in diminishing the electroactivity of the polypyrrole film, we plotted this charge versus the attained degradation percentage (Figure 4). A pseudoparabolic dependence, $Q_{deg} \propto$ (% of degradation)^2, was obtained, which means that the efficiency of the charge to degrade the polymer increases when the degradation percentage of the treated material increases; that is, a lower charge is consumed to attain the same increase in the degradation percentage.

The control chronocoulograms of Figure 3 can be used to calculate the diffusion coefficients of the counterions using the ESCR model.[13a]

According to the ESCR model

$$\ln\left[1 - \frac{Q}{Q_t}\right] = -bt \qquad (1)$$

where the diffusion coefficient, *D*, from the already oxidized material toward the oxidation front is included in *b*

$$D = \frac{bh^2}{2} \qquad (2)$$

Here, *h* is the thickness of the polypyrrole film. The constant *b* can be obtained by plotting $\ln(1 - Q/Q_t)$ versus *t*, using the final part of the chronoamperogram where the oxidation occurs under pure diffusion control, *Q* is the charge consumed at every time *t* (Figure 3b) after the potential step (the numerical method of the trapezoid was used for the integration at every *t*), and Q_t is the total charge obtained by integration of the chronoamperograms.
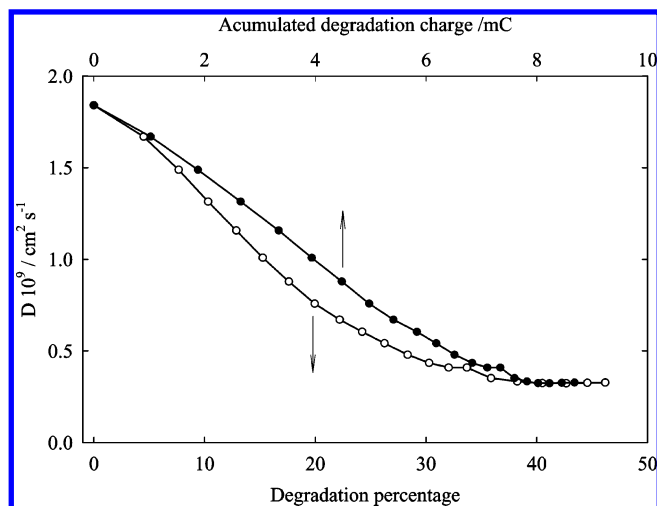
Figure 5. Variation of the perchlorate diffusion coefficient inside the polypyrrole film as a function of both the degradation percentage of the polymeric electroactivity and the accumulated degradation charge during consecutive degradation cycles.

The evolution of the diffusion coefficients as a function of both the degradation percentage and the charge involved in the degradation process can be seen in Figure 5. A decreasing sigmoidal shape is obtained: the diffusion coefficient of the counterions inside the polymer during oxidation decreases when the degradation percentage increases. A similar result was obtained when the attained diffusion coefficients were repre-

sented versus the accumulated charge for the consecutive degradation cycles.

Figure 6a shows a parallel evolution of both the diffusion coefficient and the charge consumed per cycle to degrade the polymer as a function of the number of treatment cycles. Moreover, the degradation charge consumed during a degradation cycle decreases in consecutive degradation cycles; the same degradation cycle is less efficient at degrading the polymer when it is applied to a pristine polymer than when applied to a partially degraded polymer film. Another way to observe this effect is by plotting the accumulated degradation charge on consecutive cycles versus the number of cycles, as Figure 6b shows.

Discussion

The rapid decrease in the charge stored by the material, as seen from the anodic control voltammograms or chronoampero-grams after several treatments at 0.9 V for 2 s each, confirms the rapid deterioration of the polypyrrole electroactivity (charge stored per mass unit). The electroactivity degradation reaches 50% at the end of the process, with a weight increase of 15%.

All of the electrochemical responses (Figures 1, 2, and 3a) indicate a slower rate of oxidation and reduction (Figure 2) with increased degradation of the electroactivity. The increasing irreversibility of the anodic and cathodic voltammetric processes indicates the increasingly resistive behavior of the material related to the interchange of ions.

The evolution of the voltammetric controls indicates that the structural rigidities induce either slow conformational changes
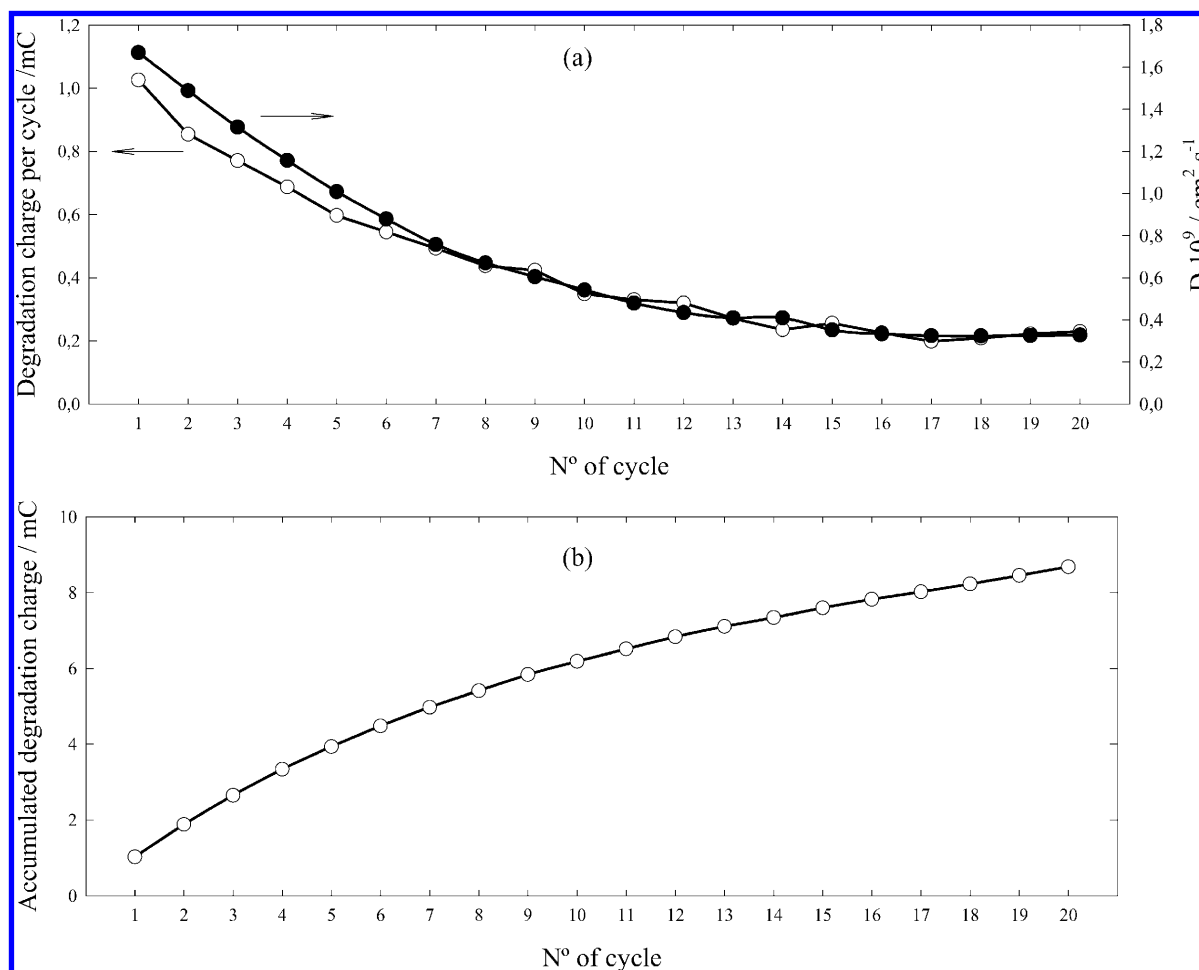
Figure 6. (a) Evolution of the charge consumed to degrade the polymer per degradation cycle and the diffusion coefficient of the counterions inside the swelling polymer as a function of the number of degradation cycles. (b) Evolution of the accumulated degradation charge during the consecutive degradation cycles.

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along the chains, slow generation of free volume, or slow penetration of counterions during the oxidation process. On the basis of the ESCR model, the maxima present on the control chronoamperograms from Figure 3 indicate that the oxidation processes occur under conformational relaxation kinetic control of the generation of nuclei of oxidized material on a compacted and reduced film.[13] At the maximum, the nuclei start to coalesce, and at the inflection point after the maximum, the coalescence was finished and the oxidation goes on under pure diffusion kinetic control. The evolution of the current and charges from that point was used to determine the diffusion coefficient of the counterions inside the polymer. The overall oxidation rate is under counterion-diffusion control of the counterions from those regions where the polymeric oxidation (at the studied potential) already was completed toward the partially oxidized regions. As expected, decreasing diffusion coefficients were obtained for increasing degradation percentages. Figure 5 supports the relationships between the degradation processes and their influence on the diffusion coefficient, being quite close the evolution of the diffusion coefficient as a function of the degradation percentage or the charge accumulated during the consecutive degradation processes. Even more explicit is this parallelism when we followed both the evolution of the diffusion coefficient and the charge consumed per treatment cycle, Figure 6, as a function of the number of cycles of treatment.

A surprising fact is that for increasing cycles of treatment the charge consumed per cycle to degrade the material decreases, and as they do, the relative variation of the diffusion coefficient does also (Figure 6) but the degradation percentage increases pseudoparabolically (Figure 4). Those results suggest the formation of rigid islands in the material with a minimum number of chemical attacks inside the islands and surrounded by a cross-linking net that hinders the ionic interchange. The large weight increment observed during the degradation should be attributed to the entrapment of counterions in those rigid and electrochemically inactive islands. The presence of those islands of conducting material could explain the use of the overoxidized conducting polymers for electroanalytical applications as conducting electrodes keeping a high electronic conductivity.[15] The confirmation of those islands will require new experimental work.

From a chemical point of view, the structural resistance for the counterions' diffusion can be induced by nucleophilic attacks on some radical cations of the oxidized chains giving sp^3 carbons on the chain, interrupting the conjugation and diminishing the conjugation length.[16] Shorter conjugation lengths will induce much slower conformational relaxation processes of the polymeric chains, promoting increasing material rigidity.

The second origin of the presence of structural resistance can be attributed to the recombination of two radical cations from neighboring oxidized chains giving a cross-linking process. A low fraction of cross-linking processes between neighboring chains can promote the total rigidity of an island in the material. The island should become electrochemically inactive because the dimensions between cross-linking points are lower than the counterion diameter.

Conclusions

When the electroactivity of a polypyrrole film is degraded by consecutive overoxidation treatments, the oxidation and reduction processes gradually take longer, as observed by voltammetry or chronoamperometry

The diffusion coefficients of the counterions inside the polymer, obtained by the ESCR model, decrease when the degradation of the polymer increases.

A parallel evolution is observed between the charge needed per cycle to degrade the polymer and the decrease in the diffusion coefficient, suggesting the increasing resistance of the material for ionic interchange during electrochemical processes. Cross-linking processes probably occur between neighboring polypyrrole chains as a result of the degradation process.

The sharp increase in the degradation percentage when the degradation charge per cycle decreases with a growing number of degradation cycles suggests that rigid islands entrapped by cross-linking points might be formed and thereby hinder ionic interchange.

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