

# Revisiting the Electrochemical and Polymeric Behavior of a Polypyrrole Free-Standing Electrode in Aqueous Solution

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A procedure to obtain homogeneous free-standing polypyrrole (ppy) films 10–20  $\mu\text{m}$  thick is described. The resulting films have mechanical characteristics good enough to be used as a working electrode for electrochemical measurements and applications. Structures and uniformity of both film surfaces and the cross section were studied by SEM. Three different procedures were used to determine the film thickness. The free-standing film can be reduced in aqueous solution up to  $-3.0$  V without any presence of hydrogen release or polymer degradation. Voltammetric experiments show the usual voltammograms, but they only involve a partial oxidation and reduction of the film capabilities: voltammetric charges increase for decreasing sweep rates. A deep reduction of the film is achieved by polarization times longer than 300 s at  $-0.6$  V or more cathodic potentials. The second cathodic maximum, appearing on the voltammograms between  $-0.7$  and  $-0.9$  V, is related to slow kinetic and structural processes since the film reduction is completed by long polarization time at  $-0.6$  V; the concomitant equilibrium potential is then more anodic than  $-0.6$  V. All of these results are consistent with the electrochemically stimulated conformational relaxation (ESCR) model. The swelled and oxidized film shrinks progressively along the voltammetric reduction. Around  $-1.0$  V the polymeric structure is closed when still 35% to 60% (depending on the scan rate) of the material remains oxidized. The reduction is then completed by slow migration of the counterions through the increasingly compacted polymeric entanglement by stimulating conformational relaxation processes of the ppy chains. A constant and low cathodic current is observed on the voltammograms up to  $-3.0$  V. Oxidation potentials higher than  $+0.6$  V promote the electrochemical degradation of the ppy. Three potential windows are distinguished for these films in aqueous solutions: from potentials as low as  $-3.0$  to  $-0.6$  V they are a compacted semiconductor electrode without hydrogen release; from  $-0.6$  to  $+0.5$  V they are a progressively more oxidized and swelled conducting polymer electrode; and potentials higher than  $+0.6$  V bring on ppy over-oxidation processes and degradation of the electrochemical activity.

## 1. Introduction

Among the conducting polymers (CP), polypyrrole (ppy) is characterized by its high conductivity, good environmental stability, and easy synthesis.<sup>1</sup> Some of the most interesting properties of CPs are based on the change of the film macroscopic properties (conductivity, stored charge, volume, porosity, color, etc.) during the oxidation/reduction processes under electrochemical control.<sup>1,2</sup> Thus, electrochemical methods are important tools for investigating the behavior and properties of intrinsically conducting polymers. Since Kanawaza et al. reported the electropolymerization and the high conductivity of ppy,<sup>3,4</sup> many experimental electrochemical studies of ppy and its derivatives have been reported.<sup>5–20</sup> These and many others works show voltammograms, chronoamperograms, chronopotentiograms, chronocoulograms, and other types of electrochemical experiments of polypyrrole and its derivatives. An overview of all these experimental results and their discussion reveals that the electrochemical behavior of ppy films depends on numerous variables related to the electropolymerization conditions, the morphologic structure of the film, and also on the electrochemical experiment (applied potentials or currents, supporting electrode, electrolyte nature, temperature, pH, etc.).

However, most of the above refereed studies have been restricted to very thin layers onto metallic electrodes;<sup>9–20</sup> only a few reports have been devoted to the electrochemical behavior of free-standing ppy films.<sup>5–7</sup> Free-standing films are also of great interest for some applications such as ion-exchange membranes, polymeric batteries, or artificial muscles.<sup>1–2,7,17–18</sup> Extrapolation from supported thin films (less than several microns) to thicker free-standing films (typically more than 10  $\mu\text{m}$ ) is not so evident. Indeed, in the former the ppy film exchanges counterions at the polymer/electrolyte interface and only electrons at the polymer/metal interface, while the latter has mainly polymer/electrolyte interfaces and the electrons are conducted by the polypyrrole film. On the other hand, the film thickness may be also a determinant parameter.<sup>21–23</sup> Differences in the appearance of cyclic voltammograms have been attributed in the literature to the use of a thick free-standing film or a thin deposited layer for performing the electrochemical experiment.<sup>8,14,22</sup> Nevertheless, in other works results obtained with both types of films are discussed all together without paying attention to this point.<sup>9–10,15</sup>

The relevance of electrochemical stability for some applications has been also pointed out in the literature.<sup>7,24–25</sup> Degradation of the electrochemical response has been related to the “over-oxidation” of ppy,<sup>25–26</sup> an irreversible chemical degradation provoked by the attack of nucleophilic agents that has been

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well characterized by spectroscopic and analytical techniques.<sup>27–30</sup> Some efforts have also been made to study this degradation by electrochemical methods and determine the potential range to avoid electrochemical overoxidation of the ppy film.<sup>7,31–38</sup> A dependence on the type of ppy system, the electrolyte nature and conditions (pH, solvent, temperature), and also on the hardness of the electrochemical treatment have been shown. From the point of view of developing commercial applications, stability of the ppy material system must be tested at experimental conditions as close as possible to working conditions in its final application.

In this paper, we develop a homogeneous free-standing polypyrrole electrode and revisit the electrochemical behavior and stability in aqueous solutions of thick free-standing polypyrrole films, which are suitable to be applied for different electrochemical devices.

## 2. Experimental Section

**2.1. Film Preparation.** Polypyrrole films were prepared at room temperature ( $23 \pm 2$  °C) in a one-compartment electrochemical cell from 0.1 M LiClO<sub>4</sub> and 0.2 M pyrrole acetonitrile solutions. The reference (Crison Ag/AgCl in 3 M KCl(aq)), working, and counter (6 cm<sup>2</sup> stainless steel plate) electrodes were connected to a EG&G M-283 PAR potentiostat/galvanostat and introduced directly into the cell. The electrolyte was purged with dry nitrogen, and inert atmosphere was maintained over the solution throughout polymerization. Square potential waves (+0.88 V anodic potential for 8 s, −0.33 V cathodic potential for 2 s) were applied between the counter and the working electrode during the film growth.<sup>11,39</sup> The polymerization took place on both faces of the flat working electrode, and it was stopped at different polymerization charges, which is defined as the anodic charge minus the cathodic charge. The coated electrodes were rinsed with acetonitrile and dried in the atmosphere for 2 h before each film was peeled and fixed to the holder. The electrical contact was established by attaching a copper ring wire with conductive carbon tape. Four different polypyrrole free-standing films were used for performing the electrochemical experiments described below.

**2.2. Characterization Techniques.** The total mass of electropolymerized films was determined with a precision balance (0.1 μg sensibility) by weight difference between coated and uncoated electrodes. Film thickness was measured using a TRIMOS Sylvac digital micrometer with 0.1 μm sensibility. Scanning electron microscopy (SEM, Hitachi S-3500N microscope) was used to inspect both faces of the ppy film and for determining the film thickness, the electron energy being 3 kV. Cyclic voltammograms and chronoamperograms were recorded by an EG&G M-270 potentiostat-galvanostat using the free-standing polypyrrole film as working electrode and a Ag/AgCl reference electrode. The electrochemical measurements were carried out using 0.5 M LiClO<sub>4</sub> aqueous solutions. The cell was purged with dry nitrogen before performing electrochemical experiments at room temperature.

## 3. Results and Discussion

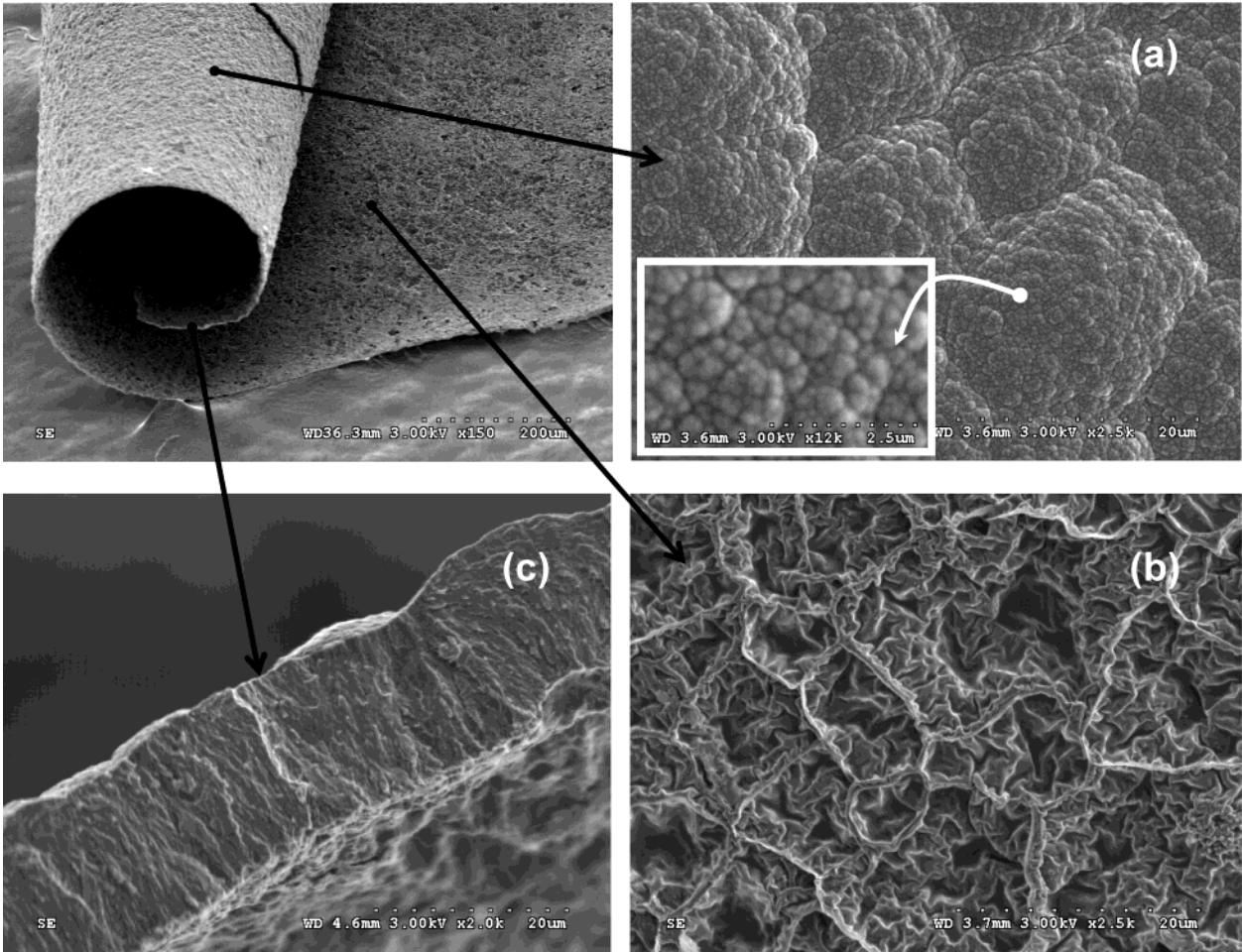
**3.1. The Free-Standing Ppy Electrode.** After being peeled from the stainless steel electrode the ppy film rolls easily, as can be observed in the panoramic SEM image shown in Figure 1. At a microscopic scale, the face being in contact with the solution during the polymerization process shows a cauliflower texture (Figure 1a). The fractal nature of these surface structures can be more clearly observed in the inset of the image at high magnification ( $\times 12$  k). The other face of the film, which was

in contact with the electrode during polymerization, looks like a creased tissue (Figure 1b). As can be observed in the cross section of the film (Figure 1c), the thickness is very uniform despite that both faces look quite rough, as guarantees the used electropolymerization procedure.<sup>39</sup> No pores or cracks were systematically observed either on both faces, or on the cross section up to  $\times 30$  k magnifications. Therefore, the ppy film looks like a dense material within SEM resolution, and it can be used as a working electrode in an electrochemical cell.

The film thickness was estimated by three different methods: from the polypyrrole density,<sup>13</sup> the film area, and mass ( $x_d$ ); from SEM images of the film cross section ( $x_{SEM}$ ); and directly using a micrometer ( $x_{micro}$ ). Table 1 lists the obtained thicknesses for three electrogenerated films by consumption of different polymerization charges. The thickness calculated from polymerization parameters ( $x_d$ ) appears to be closer to  $x_{SEM}$  than to  $x_{micro}$ . Differences between  $x_{SEM}$  and  $x_{micro}$  are higher than the experimental dispersion obtained for each experimental method. It should be noted that both the pressure applied by the micrometer and the vacuum of the electron microscope could modify the film thickness. Moreover, the ppy film is a soft matter that can vary its volume depending on the polymer oxidation state and even on the relative humidity. This can be the origin of the high thickness obtained by the micrometer for the thinnest film (ppyF1). Polymerization charge of the ppy films used for the electrochemical experiments was approximately 4.7 C/cm<sup>2</sup>, and the average thickness of these films was approximately 15 μm, according to the results obtained by all of the above methods.

This free-standing ppy film is brittle, especially when it is in a reduced and dry state. Nevertheless, its mechanical resistance is high enough to allow it to be peeled from the stainless steel electrode and mounted in a holder that keeps it in a flat position. Figures 2a–d show pictures of the different fabrication stages of the free-standing ppy electrode. Taking into account that the volume of the film changes with both the oxidation state and the water content, we selected an elastic material for manufacturing the holder (Figure 2b). In this way, small movements of the polymeric chains are guaranteed to preserve the physical integrity of the film during oxidation/reduction processes. From these starting ideas, different configurations were tested to establish the electric contact and to hold the film. Finally, the best results, i.e., easiest handling and minimum deformation and physical damages during the electrochemical experiments, were obtained with the transversal configuration schematized in Figure 2e. One face of the ppy free-standing film (black circle) is fixed to a thick ring of water-resistant nonconducting tape (left side of the holder). The electrical contact was guaranteed by a copper ring wire attached to the ppy film by conducting carbon tape (Figure 2c), and this ensemble was isolated by a second ring of nonconducting sticky tape that completes the holder at the right side (Figure 2d). In this way, both faces of 1.54 cm<sup>2</sup> of free-standing polypyrrole film are in contact with the electrolyte solution during the electrochemical experiments.

**3.2. Electrochemical Response by Cyclic Voltammetry.** The electrochemical properties of the free-standing polypyrrole film were investigated by cyclic voltammetry at different scan rates and potential intervals. Figure 3a and b shows voltammograms recorded from +0.4 V (Ag/AgCl 3 M reference electrode) to different cathodic potentials (−0.4, −0.6, −0.8, −0.9, and −1.0 V) at 6 mV/s and from +0.4 to −1.0 V at different scan rates between 20 and 1 mV/s, respectively. At 6 mV/s or slower scan rates, the voltammograms show at least an anodic and two cathodic maxima between +0.4 and −0.1



**Figure 1.** SEM images of the ppy film. (a) Face in contact with polymerization solution during the electropolymerization. (b) Face in contact with the stainless steel electrode. (c) Film cross section.

**TABLE 1: Film Thickness Calculated from Polymerization Parameters (mass and area) and the Ppy Density ( $\rho_a$ ), Determined from SEM Images of the Film Cross Section ( $x_{SEM}$ ) and Directly Measured by a Micrometer ( $x_{micro}$ ) for Three Films of Different Polymerization Charge ( $Q_{pol}$ )**

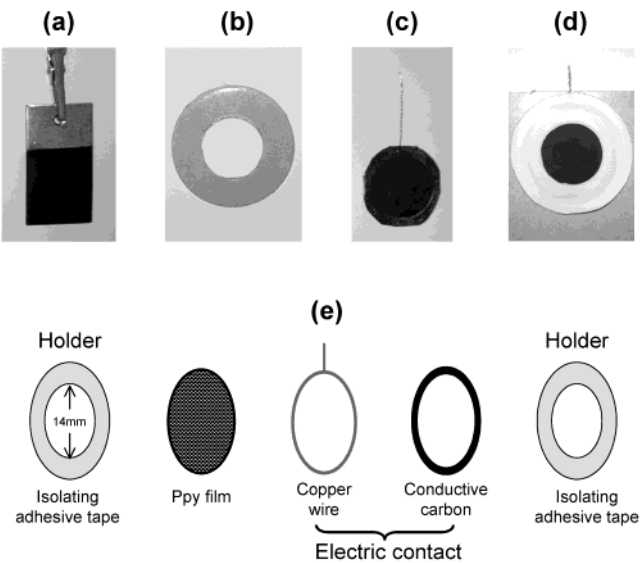
	$Q_{pol}$ (C/cm <sup>2</sup> )	$\rho_a^a$ (μm)	$x_{SEM}^b$ (μm)	$x_{micro}^b$ (μm)
ppyF1	2.85	8.9	10 ± 4	16 ± 2
ppyF2	4.69	14.6	13 ± 2	14 ± 2
ppyF3	5.09	17.5	16 ± 4	21 ± 2

<sup>a</sup> Polypyrrole density = 1.54 g/cm<sup>3</sup>.<sup>13</sup> Estimated error <1%. <sup>b</sup> Statistic errors of 10 experiments.

V. The shape of the voltammograms is very similar to that previously reported for Pt electrodes coated by a thin film (~2 μm) of ppy in aqueous solutions,<sup>12</sup> although there the scan rate was varied between 10 and 200 mV/s in the same potential range.

At increasing scan rates, the intensity of the voltammetric peaks rises, the anodic one almost two times faster than the cathodic ones, and the potential of the anodic peak shifts anodically and both cathodic peaks shift cathodically (Figure 4). Both current increase and potential shifting indicate kinetic limitations of the concomitant electrochemical reactions.

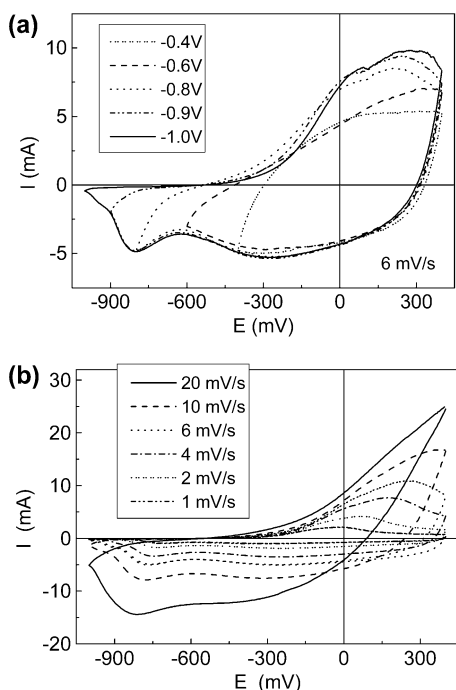
The charges involved in oxidation and reduction of voltammetric branches are plotted in Figure 5 versus the scan rate. Both oxidation and reduction charges decrease at increasing scan rates: oxidation and reduction processes are never completed under those experimental conditions. Two main questions



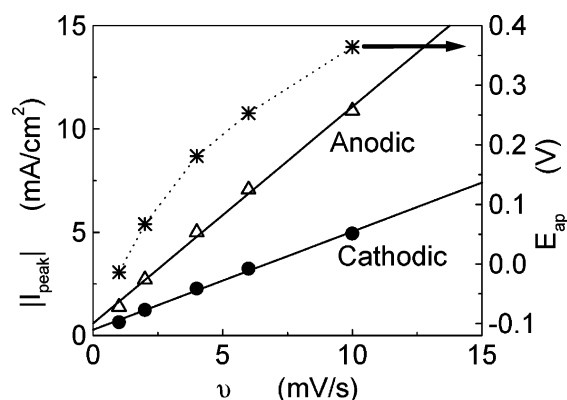
**Figure 2.** (a) Ppy film polymerized onto the stainless steel electrode. (b) Holder made of flexible isolating adhesive tape. (c) Free-standing ppy film with electrical contact. (d) Final free-standing ppy electrode (14 mm diameter). (e) Schematic representation of the transversal sequence of components in the final free-standing ppy electrode.

emerge from these results: how slow should the sweep be to attain a complete oxidation and reduction of the ppy film, and which potential limits are suitable to complete both processes in absence of polymeric degradation.

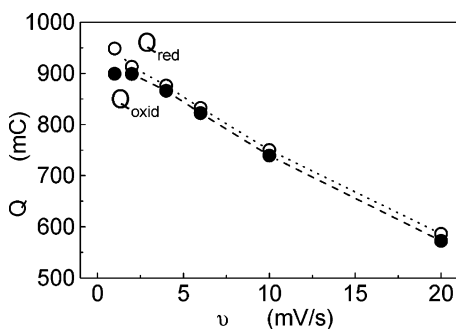




**Figure 3.** (a) Cyclic voltammograms recorded at 6 mV/s in different potential ranges from +0.4 to -0.4, -0.6, -0.8, -0.9, and -1.0 V. (b) Cyclic voltammograms between +0.4 and -1.0 V recorded at different scan rates from 20 to 1 mV/s. Ag/AgCl reference electrode; 0.5 M LiClO<sub>4</sub> aqueous solutions and room temperature. Electrode area: 1.54 cm<sup>2</sup>.

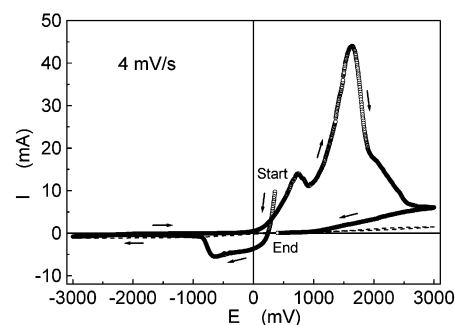


**Figure 4.** Evolution of the current density of the anodic (Δ) and the main cathodic (●) peak (left axis) and the potential of the anodic maximum (E<sub>ap</sub>, right axis) of the voltammogram shown in Figure 3b versus the scan rate.



**Figure 5.** Oxidation (●) and reduction (○) charges obtained from voltammograms in Figure 3b as a function of the scan rate.

**3.3. Potential Limits.** To check the stability of the free-standing ppy electrode at large negative and positive potentials in aqueous solution, a voltammetric experiment in a broader

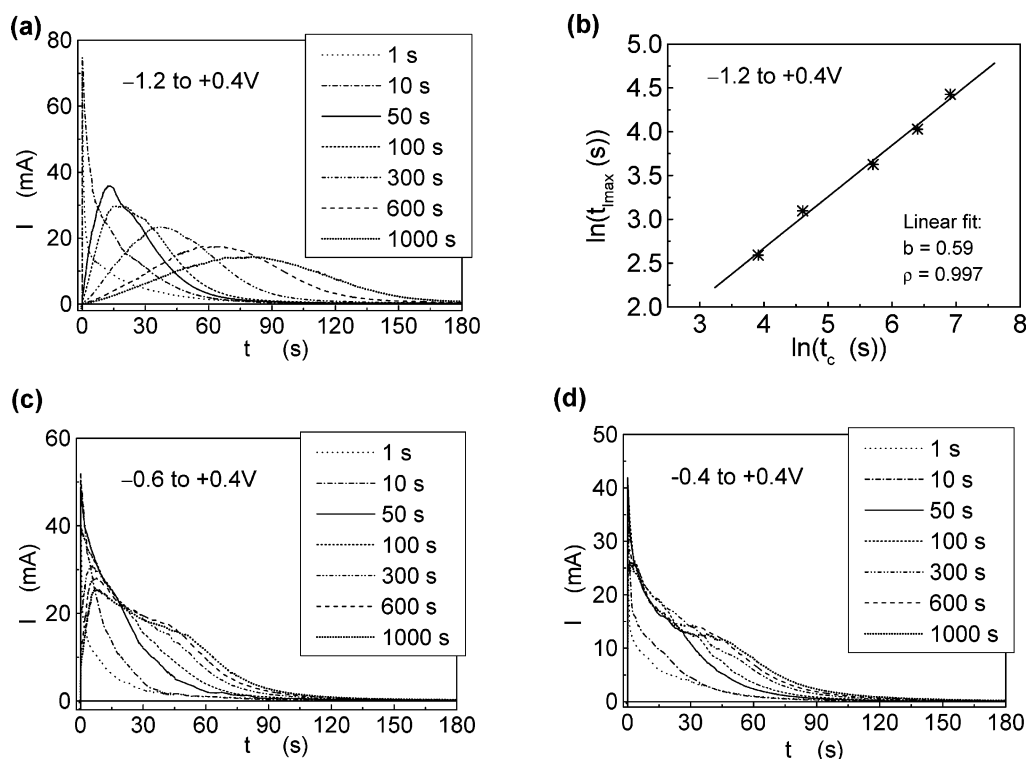


**Figure 6.** Cyclic voltammogram recorded at 4 mV/s in the potential range -3.0 to +3.0 V. The potential scan starts at +0.4 V, goes down to -3.0 V, goes up to +3.0 V, and finally comes back to +0.4 V. The second cycle of the voltammogram is plotted as a dashed line. Ag/AgCl reference electrode; 0.5 M LiClO<sub>4</sub> aqueous solutions and room temperature. Electrode area: 1.54 cm<sup>2</sup>.

voltage range was planned. Figure 6 shows cyclic voltammograms recorded at 4 mV/s in a potential range between -3.0 and +3.0 V. The voltage scan starts at +0.4 V, goes cathodically to -3.0 V and later anodically to +3.0 V, before coming back to +0.4 V. From +0.4 to -1.0 V, the voltammogram reproduces the features described above for the cathodic scan of this potential region. Then the current drops to a low and constant cathodic value approximately at -1.0 V, showing a large plateau up to -3.0 V in aqueous solution. This points to the presence of kinetic limitations as those described by the electrochemically stimulated conformational relaxation (ESCR) model.<sup>40-42</sup> The drop of the current at -1.0 V in the cathodic scan (Figures 3 and 6) does not indicate the complete reduction and shrinking of the polymer, but the end of the reduction under diffusion control of the counterions toward the solution. Now the structure is closed and the reduction and compaction of the film goes on under conformational relaxation and migration kinetic control, giving lower cathodic currents. The conductivity of the polymer ( $5 \times 10^{-2}$  S/cm by the four points method) is high enough to support electrochemical metal deposition at high cathodic potentials, as will be shown in a future work. Moreover, the small and constant current up to -3.0 V indicates that the H<sub>2</sub> evolution does not take place (at least significantly) on the compacted ppy film, in contrast with the high hydrogen evolution observed on ppy-coated platinum electrodes at such cathodic potentials.<sup>17</sup>

In this dynamic experiment, the film still shows a good electrochemical response after being polarized at -3.0 V since it was reoxidized during the anodic scan. However, the deep compaction of the ppy chains requires some energy to open the structure and allow the penetration of counterions. Thus, the oxidation maximum is shifted more than 400 mV (from +0.30 V to +0.74 V) when, for the same scan rate, the voltammogram is reversed at -1.0 V (Figure 3b). This anodic shifting of the voltammetric maximum has been observed also for polypyrrole films onto platinum electrodes and has been described by the ESCR model.<sup>42</sup> Therefore, to get a deep electrochemical reduction and compaction of the free-standing ppy film, cathodic potentials as large as -3.0 V can be applied, at least for short times.

The second maximum in the anodic scan (approximately at +1.64 V) corresponds to the irreversible electrochemical degradation of polypyrrole, since the electrochemical response disappears and the current density is close to zero when the potential is scanned back from +3.0 to +0.4 V. The second cycle of the voltammogram confirms the electrochemical degradation after applying so large anodic potentials (dashed line in Figure 6).



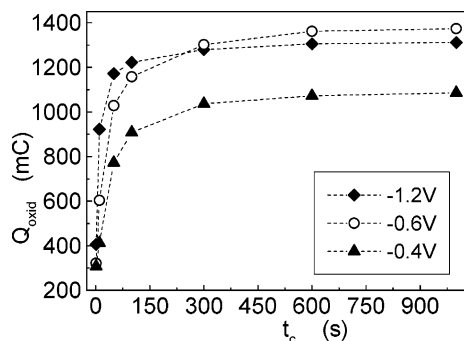
**Figure 7.** Chronoamperograms recorded to show the influence of the polarization time ( $t_c$ ) at a cathodic potential ( $E_c$ ) in the subsequent oxidation by anodic potential step ( $E_a$ ): (a)  $E_c = -1.2$  V,  $E_a = +0.4$  V,  $t_c$  varying from 1 to 1000 s; (c)  $E_c = -0.6$  V,  $E_a = +0.4$  V,  $t_c$  varying from 1 to 1000 s; (d)  $E_c = -0.4$  V,  $E_a = +0.4$  V,  $t_c$  varying from 1 to 1000 s. (b) Double logarithmic plot of the time at the current maxima ( $t_{\text{Imax}}$ ) versus the polarization time at  $-1.2$  V; the attained linear dependence is predicted by the ESCR model.

**3.4. Deep Reduction and Oxidation by Anodic Potential Steps.** As stated above, the degree of oxidation and reduction attained by voltammetric methods depends on the sweep rate, which indicates the presence of kinetic limitations provoked by the compaction and closing of the polymeric structure during the electrochemical reduction. Electrochemical step methods such as chronoamperometry are therefore more suitable to study stationary reduction and oxidation states and the extension of these slow processes. The free-standing ppy electrode was reduced at a cathodic potential ( $E_c$ ) for a polarization time ( $t_c$ ), and then it was oxidized by potential step to an anodic potential ( $E_a$ ) applied for a time long enough to complete the oxidation (typically 300 s). After each chronoamperometric experiment, the relative electroactivity of the film was checked by cyclic voltammetry between  $+0.4$  and  $-0.4$  V at 6 mV/s. We have considered that the ppy film still has a good electrochemical performance and can be used for subsequent experiments if the voltammetric oxidation and reduction charges (obtained from the second cycle of the voltammogram) remain similar to their initial values ( $\pm 5\%$ ).

To select a polarization time high enough to deeply reduce the free-standing ppy electrode, this parameter was varied for fixed cathodic and anodic polarization potentials. Figure 7a shows the chronoamperograms obtained after reducing the film at  $-1.2$  V for different polarization times ranging between 1 and  $10^3$  s, followed by a potential step to  $+0.4$  V. When the electrode is polarized for 1 or 10 seconds, the chronoamperogram shows a sharp initial maximum followed by an exponential decay, which is typical of the charge of a double layer followed by the oxidation of the polymer film under diffusion kinetic control of the counterions inside the polymer.<sup>41</sup> However, for longer polarization times a well-defined maximum appears, which shifts toward longer oxidation times as the cathodic polarization time rises. These maxima are characteristic of

oxidation processes that occur under conformational relaxation and nucleation and have been described by the ESCR model.<sup>41</sup> A double-logarithmic scale dependence between the oxidation time of the maximum ( $t_{\text{Imax}}$ ) and the polarization time was observed (Figure 7b), the slope being 0.6. The same relationship has been previously described for platinum electrodes coated with thin films (ca.  $0.1 \mu\text{m}$ ) of polypyrrole and polyaniline, and it has been interpreted in terms of the ESCR model.<sup>16,43</sup> This experiment was also performed for cathodic polarizations at  $-0.6$  and  $-0.4$  V and the subsequent oxidation at  $+0.4$  V for a time long enough to attain a steady state. The chronoamperograms show the evolution of shoulders and well separated maxima for the ppy film pre-polarized at  $-0.6$  V (Figure 7c) for increasing polarization times, while at  $-0.4$  V they show only the evolution of shoulders (Figure 7d).

The attained reduced state (or reduction depth) after every polarization time at  $-1.2$ ,  $-0.6$ , and  $-0.4$  V was quantified by the charge consumed to oxidize the film by the anodic step to  $+0.4$  V. Figure 8 shows that the oxidation charge increases with the polarization time and evolves to a plateau, whatever the studied reduction potential. After polarizations at  $-0.6$  V, the oxidation charge on the plateau was slightly higher than that attained after polarizations at  $-1.2$  V. Even by polarization at  $-0.4$  V the charge on the plateau (around 1080 mC) is higher than that obtained by cyclic voltammetry between  $+0.4$  and  $-1.0$  V at the slower of the studied scan rates (around 900 mC, Figure 5). Those results indicate that the steady state of the reduction process, whatever the studied potential of reduction, can be completed only after a long reduction times ( $> 50$  s at  $-1.2$  V,  $> 300$  s at  $-0.6$  V or  $-0.4$  V). This fact is also consistent with the ESCR model: the reduction of our oxidized and swelled free-standing film starts under diffusion kinetic control of the counterions and water toward the solution; the reduction by cathodic polarization induces the progressive film



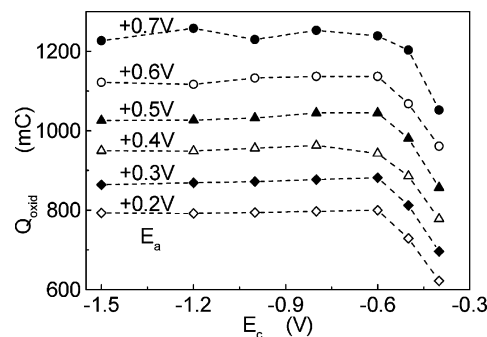
**Figure 8.** Oxidation charges ( $Q_{\text{ox}}$ ) determined from chronoamperograms recorded after anodic potential steps (from  $-1.2$ ,  $-0.6$ , and  $-0.4$  to  $+0.4$ ) versus the polarization time ( $t_c$ ) at the cathodic potential.

shrinking and closing of the polymeric structure when the ppy is still partially reduced, entrapping counterions. Then both reduction and polymer compaction progress by migration and relaxation processes under kinetic control. Relaxation and migration processes are much slower than diffusion processes, since counterions have to open their way throughout the closed polymeric matrix by stimulation of the conformational movements of the polymeric chains, the driving force being the electric field imposed by the cathodic polarization.

A comparative view of Figures 8 and 5 also allows us to conclude that along a cathodic voltammetric sweep up to  $-1.0$  V only a fraction of the oxidized polymer (40 to 65%, depending on the scan rate) is reduced, which confirms that the drop of the current density at  $-1.0$  V is related to the compaction and closing of the polymeric structure entrapping a significant fraction of oxidized polymer units. The presence of these oxidized polymer units after applying cathodic potentials agrees with high electrical conductivity shown by the deeply reduced ppy film (after 30 min at  $-2.0$  V; the film conductivity determined by the four point method was  $5 \times 10^{-2}$  S/cm).

To attain a deep reduction of the ppy film, a sufficiently high cathodic potential and polarization time are required. Although reduction and compaction require longer times at  $-0.6$  V than at  $-1.2$  V, a deeper reduced state is finally attained for polarization times longer than 300 s at  $-0.6$  V, as can be deduced from the higher anodic charge consumed to oxidize the film polarized at  $-0.6$  V than that polarized at  $-1.2$  V (Figure 8). This indicates that a softer compaction is attained at  $-0.6$  V that allows a deeper reduction despite the lower driving force. As predicted by the ESCR model,<sup>41</sup> the softer compaction at  $-0.6$  V is confirmed by the shorter times of the chronoamperometric maxima compared with those attained at  $-1.2$  V for all polarization time.

Whatever the reduction potential, Figure 8 shows that a polarization time of 600 s is long enough to attain a stationary reduction state of the free-standing film. To know the lower cathodic potential allowing a complete reduction of the film, new chronoamperometric experiments were performed, varying  $E_c$  from  $-0.4$  to  $-1.5$  V and keeping fixed the polarization time ( $t_c = 600$  s) and the anodic potential. The experiment was performed for different oxidation states stepping to different anodic potentials ( $+0.2 \text{ V} \leq E_a \leq +0.7 \text{ V}$ ). For all the studied anodic potentials, the oxidation charge increases with the pre-polarization cathodic potentials until a constant value is reached for  $E_c$  equal or more negative than  $-0.6$  V (see Figure 9). This is consistent with the above-described results and corroborates that  $-0.6$  V is a potential negative enough for attaining a full reduction of the ppy film. This is a surprising fact, as long as we know never before mentioned in the literature, since



**Figure 9.** Dependence of the oxidation charges ( $Q_{\text{ox}}$ ) on the cathodic potential ( $E_c$ ) for 600 s of polarization time and different anodic steps ( $+0.2 \text{ V} \leq E_a \leq +0.7 \text{ V}$ ). The charges have been obtained from the corresponding chronoamperometric experiments.

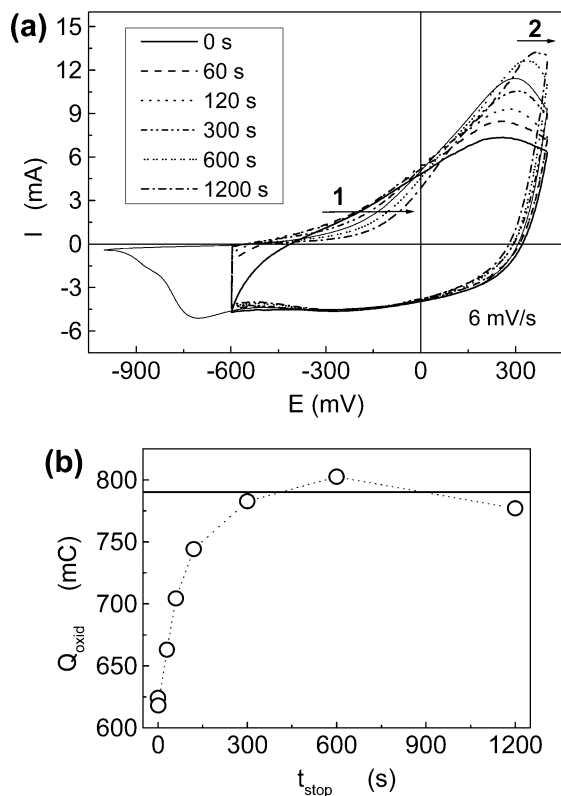
voltammograms are taken as the redox spectra of the electroactive species; thus, considering voltammetric results (Figures 3.a and b) and the literature related to the electrochemical behavior of electrode-supported ppy films, it should be expected that the ppy only could be completely reduced by polarization at potentials more cathodic than  $-0.9$  or  $-1.0$  V. A nonsolved conflict between thermodynamic and kinetic processes seems to emerge from the above results. We will come back to this point in the next subsection devoted to the second cathodic peak of the voltammograms.

Looking at a fixed  $E_c$  in Figure 9, the oxidation charge rises with the anodic potential, in the same proportion for all the studied cathodic potentials (see almost parallel  $Q_{\text{ox}}$  versus  $E_c$  curves). Thus, the final oxidation degree depends on the oxidation potential as well as on the pre-polarization conditions. For large anodic potentials, the polypyrrole could be degraded by overoxidation. Since both the reversible oxidation and the overoxidation increase the total oxidation charge, the limit of potential to avoid degradation is not well defined from these data. We must use the control voltammograms that were recorded after each chronoamperogram to detect the beginning of the electrochemical degradation: voltammetric oxidation and reduction charges fell significantly after polarization at  $+0.6$  V, which indicates the first stages of degradation. Therefore,  $+0.5$  V is a safe anodic potential: high enough to achieve the relaxation, oxidation, and swelling of the compacted and reduced polymeric structure but low enough to prevent the polymer degradation.

All of these results have shown that the free-standing films of polypyrrole can be deeply reduced at potentials equal to or more cathodic than  $-0.6$  V by long reduction time ( $>300$  s). This is an unexpected result according to previous literature. On the other hand, the oxidation depth or oxidation degree of the free-standing ppy electrode can be reversibly controlled by polarization potentials between  $-0.6$  and  $+0.5$  V. These potentials are key points for developing any kind of smart device based on the electrochemistry of this free-standing ppy film.

### 3.5. Second Cathodic Peak of the Cyclic Voltammograms.

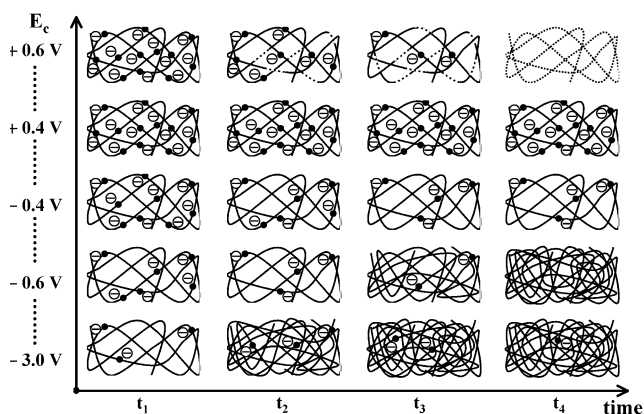
As was pointed out above, the deep reduction attained at  $-0.6$  V seems to contradict the presence of a broad reduction peak with two relative maxima (Figure 3) going up to  $-1$  V in the voltammograms. Two different cathodic processes have also been described in the literature for thin ppy films onto metallic electrodes and in different electrolytic media.<sup>12,22,44</sup> The second cathodic process (between  $-0.7$  and  $-0.9$  V) has been attributed to the formation of polaronic couples<sup>44</sup> or, alternatively, to the incorporation of small cations<sup>12</sup> as an easier process for charge balance than the expulsion of big anions when the polymeric matrix is already shrunk and closed. In this way, it should be



**Figure 10.** (a) Comparison of a cyclic voltammogram between +0.4 and -1.0 V and successive voltammograms between +0.4 and -0.6 V with increasing stopping times at -0.6 V. (b) Oxidation charge ( $Q_{\text{oxid}}$ ) determined from these voltammograms versus the stopping time ( $t_{\text{stop}}$ ).

expected that the ppy reduction could be achieved only by polarization at potentials more cathodic than this second cathodic maximum. However, we have just shown that a deeper reduction of the free-standing ppy electrode can be attained before this maximum (at -0.6 V) rather than after it (at -1.2 V).

A new voltammetric experiment was planned to study if the second cathodic peak corresponds to an additional thermodynamic process, as has been suggested in the literature, or to a slow kinetic process of which equilibrium potential is less cathodic than this voltammetric maximum. A reference voltammogram at 6 mV/s between +0.4 and -1.0 V was recorded. Then new limits between +0.4 and -0.6 V were set, and different stopping times at the cathodic limit of -0.6 V ( $0 \leq t_{\text{stop}} \leq 1200$  s) were studied. Results are shown in Figure 10a. As expected from our previous chronoamperometric results, increasing currents are involved on the anodic maxima when the stopping time rises, exceeding even that of the reference voltammogram for stopping times longer than 300 s. The corresponding oxidation charge (Figure 10b) also rises for increasing stopping times at -0.6 V and surpasses the oxidation charge of the reference voltammogram (horizontal solid line in Figure 10b) for  $t_{\text{stop}} > 300$  s. The charge decrease observed for  $t_{\text{stop}} = 1200$  s is an effect of the anodic shifting of the maximum when it starts to be significant, which again is consequence of the compaction of the reduced polymeric chains. Here, the presence of conformational relaxation is clearly shown by the anodic shifting of both the beginning of the oxidation (arrow 1 in Figure 10a) and the oxidation maximum (arrow 2), as predicted by the ESCR model for voltammetric experiments.<sup>42</sup> In complete agreement with the chronoamperometric results, these effects appear for polarization times at -0.6 V equal or higher than 300 s.



**Figure 11.** Schematic representation of the temporal evolution of the reduction/oxidation degree and compactness of the ppy free-standing electrode depending on the polarization potential. Positive charges in the oxidized polymer chains are represented by black dots in the solid line. Dashed white circles represent adsorbed anions to balance the polymer charge. Dotted lines represent degraded ppy units. For all the polarization potentials, the initial state ( $t = 0$ ) is a stationary oxidized state like that schematized for +0.4 V. For all the polarization potentials a stationary state is finally attained at long times, the degree of reduction or oxidation depending on both the initial state and the polarization potential.

These results corroborate that the ppy free-standing film can be deeply reduced and compacted by polarization at -0.6 V. As conclusion, the reduction maximum approximately between -0.7 and -0.9 V, which has been observed for free-standing and electrode-supported polypyrrole films and at scan rates between 1 and several hundreds of mV per second, is a kinetic consequence of slow reduction processes of which thermodynamic potential is more anodic than -0.6 V.

**3.6. Three Potential Regions with Different Electrochemical Behavior.** Taking into account all the above results, the electrochemical response of the free-standing polypyrrole electrode, which can be used for multiple electrochemical applications in electromechanic and electrochromic devices, charge storage, electron/ion transduction, ionic delivery, or medical dosage, etc., show three well differentiated regions of potential: (i) for increasing polarization times, a progressively more reduced and compacted ppy film entrapping part of the counterions is obtained for increasing cathodic potentials equal to or higher than -0.6 V; (ii) a progressively more swelled and oxidized steady state of the film is obtained from -0.6 to +0.5 V; (iii) potentials more anodic than +0.6 V provoke a progressive degradation of the electrochemical properties.

Figure 11 shows schematically the time evolution of the charge and compactness of the ppy film under polarization at different potentials within each of these regions. (i) Any polarization at potentials more cathodic than -0.6 V (for example -3.0 V in the figure) requires times long enough to get a stationary state of deep reduction and compaction of the polymeric network. At increasing cathodic potentials, the reduction/compaction is faster but a lower reduction degree is finally attained. Despite the high degree of reduction and compaction, the free-standing film is conductive enough to be used as a semiconducting electrode in aqueous media up to -3.0 V without any significant hydrogen release and without any degradation or loss of its electrochemical properties. (ii) In an intermediate potential region, approximately from -0.6 to +0.5 V, stationary states of increasing degrees of oxidation and swelling are achieved in a reversible way. Here, the oxidation and reduction processes take place mainly by diffusion of counterions from and toward the electrolytic solution, respec-



tively. Thus, potentials within this region ( $-0.4$  and  $+0.4$  V in Figure 11) are suitable for the electrochemical control of the macroscopic properties of the ppy electrode in order to develop smart electrochemical devices. (iii) Any polarization at  $+0.6$  V or more anodic potentials promotes the polypyrrole overoxidation and degradation (schematized by dotted line in Figure 11) and the subsequent loss of electrochemical activity.

#### 4. Summary and Conclusions

Free-standing films of polypyrrole had been electrochemically synthesized by consecutive potential step onto stainless steel electrodes and then removed from its metallic support. The film thickness ranges between 10 and 20  $\mu\text{m}$ , according to results obtained by three different methods (SEM, micrometer, and calculation from polymerization parameters and the film density). The film looks like a dense and uniform material by scanning electron microscopy of both its cross section and faces.

A disk electrode of 14 mm in diameter of free-standing polypyrrole has been made. The electric contact is guaranteed through a metallic ring wire fixed to the working electrode by a ring of conducting tape. Both sides of the structure are covered with thick rings of nonconducting tape, having a inner diameter of 14 mm, to isolate the electric contact and give mechanical consistency to the free-standing ppy electrode.

Voltammetric experiments between  $+0.4$  and  $-1.0$  V involve only a partial reduction of the oxidized electrode capabilities, even at scan rates as slow as 1 mV/s. The film shrinks along the reduction branch and closes when still a high amount of polymer units are oxidized, entrapping up to 60% of the counterions at 20 mV/s. After that, the reduction can be completed only under slow migration processes driven by cathodic polarization that requires both sufficiently long times and high potentials.

The free-standing ppy electrode can be deeply reduced and compacted by polarization in aqueous solution at potentials ranging between  $-0.6$  and  $-3.0$  V for a sufficiently long time (several minutes). Thus, it can be used as a semiconducting electrode up to  $-3.0$  V without hydrogen release or electrochemical degradation. The reduction and compaction by polarization at  $-0.6$  V is also a new and surprising observation, since from the voltammetric results and from the literature we expected that these processes might require potentials equal to or more cathodic than  $-1.0$  V. The second cathodic maximum that appears between  $-0.7$  and  $-0.9$  V in voltammograms is not related to a thermodynamic process but rather to a kinetic one, of which the equilibrium potential is less cathodic than  $-0.6$  V.

The stationary reoxidation of a deeply reduced and compacted free-standing ppy film is achieved very slowly compared to supported ppy films ( $t_{\text{oxid}} > 180$  s is required at the anodic potential). Stationary states of increasingly oxidation and swelling degree are obtained by polarization at potentials between  $-0.6$  and  $+0.4$  V. Oxidation potentials higher than  $+0.6$  V applied for several minutes promote an irreversible degradation of the electrochemical response of the electrode.

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