

# Electrochemical and chromogenic relaxation processes in polyaniline films

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## Abstract

One critical feature for practical applications of polyaniline (PAni) in electrochromic devices is the rate of color change when an electric perturbation is applied. The electrochemical and chromogenic reactions of PAni were quantified running chronoamperometric experiments coupled to spectrophotometry in the visible region. It was verified that the process of color change does not follow the charge injection, depending on the sweep rate and also if the process is oxidation or reduction. It was shown that the reduction and oxidation processes have different kinetics, mainly related to the different polymer conformations in both redox states and it was also shown that the chromogenic process must be related to conformational changes produced by the transformation of benzenoid to quinoid character and these changes are slower than the injection charge. © 2002 Published by Elsevier Science Ltd.

*Keywords:* Polyaniline; Electrochromism; Relaxation

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## 1. Introduction

The incessant research and development of new materials is a great challenge for chemists, physicists and material scientists. Among recent advances, intrinsically conducting polymers (ICP) show exceptional characteristics combining properties of conventional polymers with inorganic semiconductors and metallic elements [1]. The origin of unusual physico-chemical properties of ICP like low energy electronic transitions, low ionization potential, and high electronic affinity is due to the  $\pi$ -conjugated bonds [2]. As a result, ICPs can be easily oxidized, building new electronic states in the energy gap, changing drastically the coloration state and the conductivity.

Nowadays, polyaniline (PAni) is the most attractive ICP due its superior characteristics and versatility. This polymer can exist in several oxidation states, each one characterized by the amine to imine nitrogen units ratio. PAni can be synthesized chemically or electrochemically by oxidative polymerization. However, the electro-oxidative polymerization method has been preferentially used for the prep-

aration of PAni films, because the deposition can be easily controlled by electrochemical techniques. One of the most interesting characteristics of PAni is the marked electrochromism, a property that some materials show by changing their color in a reversible way, as response to an applied potential [3]. It was reported that PAni exhibits multiple color changes in aqueous media (transparent yellow, green, blue, and violet) depending on both, the applied potential and the pH [4,5]. In the reduced state, the absorption occurs in the ultraviolet region due to transition  $\pi \rightarrow \pi^*$ . The yellow color in this state is due to probably radical species deeply inserted in the polymeric sites. In the semi-oxidized state, the green color can be associated with two characteristics absorption bands at 425 and 800 nm. These bands can be relate with the population of quinone rings depending on the degree of oxidation, also the band at 425 nm can be related with polaronic species (or the magnitude of protonated sites). Finally, the blue-violet color can be associated with transitions of the bipolaronic form [6–8]. However, a critical factor for practical applications of PAni is the rate of color change when a potential is applied, or in other words, the rate of change of the absorption bands. Despite the excellent optical contrast showed by PAni, the chromogenic response is relatively slow with respect to the electrochemical perturbation [9]. When a charge is injected in a polymeric network during an

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electrochemical oxidation process, the behavior as a whole can be understood considering two sequential reactions: an electrochemical reaction that corresponds to a charge injection and a structural change of the polymer as a result of this redox reaction. The redox reaction, with simultaneous insertion/expulsion of ionic species to preserve the electroneutrality [10,11], is a very fast process (the transport of electrons may occur via electron hopping between neighboring redox sites and by the motion of delocalized electrons through conjugated systems [12]). To stabilize the injected charge and better accommodate counterions in specific polymeric sites, a distortion of the structure must occur. In polyheterocyclic polymers like polypyrrole, polythiophene or polyaniline, the electronic structure changes from aromatic to quinoid forms (it is accepted that when the polymer is more oxidized, its quinoid character is larger), which induces structural changes as chain torsion [13].

Otero et al. [14,15] demonstrated that some effects could be explained and quantified if electrochemical switching is controlled by a 'conformational relaxation of the polymeric chain'. In agreement with these authors, oxidative or reductive electrochemical processes are controlled by transitions from compact, or neutral, films to open, or oxidized ones (in other words, the redox kinetics can be driven by the rate at which structural changes in the solid matrix occur). Other factors as interchain charge transport, flow of counterion interactions and cross-linking should be considered but, practically, all these phenomena may be considered as the structural changes of the polymer and, with some simplifications, they may be characterized by a conformational relaxation time [16]. Naturally, in the electrochemical/electrochromic response of PANi, the time of conformational relaxation of the polymeric chain proposed by Otero et al. [14,15] can be considered as the relaxation time of the electrochemical reaction and the chromogenic response may be related exclusively to the time necessary for the complete modification of molecular orbitals and the ionic accommodation.

In the present paper a systematic spectroelectrochemical study of PANi films, obtained by electrochemical synthesis in aqueous media, was carried out. It was analyzed the effect of the scan rate in the potentiodynamic cycles on the electrochromic response of PANi and, with the adjustment of chronoamperometric/absorptiometric curves, it was possible to quantify the response time of the electrochemical/electrochromic reactions showing that the chromogenic relaxation time is slower in many cases than the electrochemical relaxation time.

## 2. Experimental

The reagents used were aniline (Aldrich) and hydrochloric acid 37% (Merck). Before utilization, aniline was distilled in the presence of zinc powder (Merck) in order to

obtain a monomer free of impurities. The transparent liquid obtained was immediately used to prepare the aniline polymerization solution. The other reagents were used as received. PANi films were grown using an aniline acid solution  $1.0 \text{ mol l}^{-1}$  HCl and  $0.5 \text{ mol l}^{-1}$  aniline. All spectroelectrochemical studies were performed in  $1.0 \text{ mol l}^{-1}$  HCl electrolytic solutions free of the monomer.

The voltammetric synthesis of PANi was carried out at  $50 \text{ mV/s}$  in the  $-0.25$  and  $0.75 V_{\text{SCE}}$  potential range to avoid the formation of undesirable products [17]. As working electrode an optically transparent glass coated with indium–tin oxide ( $\text{In}_2[\text{Sn}_x]\text{O}_{3-y}$  from Delta Technologies, sheet resistance  $20 \Omega$ ) was employed. Before use, the working electrode was rinsed with detergent and deionized water and after that it was immersed in acetone. As counter electrode a platinum wire was used and all potentials are referred to the saturated calomel electrode (SCE). Cyclic voltammetry experiments and potential steps were carried out using a potentiostat/galvanostat AUTOLAB model PGSTAT 30 from Ecochemie. The electrochromic process was followed simultaneously in a MICRONAL B 295 spectrophotometer coupled to the potentiostat. Absorption spectra of PANi at different potentials were obtained with a VARIAN 5G UV–VIS–NIR spectrophotometer and a potentiostat/galvanostat FAC 2001.

For the calculation of both relaxation times the fitting of the chronocoulometric and absorptiometric curves was done using the MICROCAL ORIGIN<sup>®</sup> 5.0 software. The method of adjustment was that of Levenberg–Marquardt, that minimizes the sum of the squares of the differences between the experimental and theoretical curves.

## 3. Results and discussion

The electrochemical polymerization of PANi is shown in Fig. 1(a) that presents the typical voltammogram of film growing in  $1.0 \text{ M HCl}$ . The first redox couple corresponds to the leucoemeraldine/emeraldine transition and the second redox couple, at more positive potentials, is associated to the emeraldine/permanganiline transition and also to the oxidation of aniline monomers. The fact that an intermediary redox couple is not detected when the potential is cycled up to  $0.75 V_{\text{SCE}}$  shows that there is no production of species from a hydrolysis reaction involving the overoxidation of the monomer or of sites in the polymeric chains.

Fig. 1(b) and (c) show an increase of charge and absorbance as a function of time during the electrodeposition of PANi. It must be pointed out that the maximum and minimum of absorption at  $700 \text{ nm}$  occur when the polymer is oxidized (permanganiline form, violet) and reduced (leucoemeraldine form, transparent yellow), respectively. An appreciable increase in the deposition charge is only visualized after  $1000 \text{ s}$ ; this behavior being dependent on other factors as the potential window used, the nature of the substrate, and the scan rate.

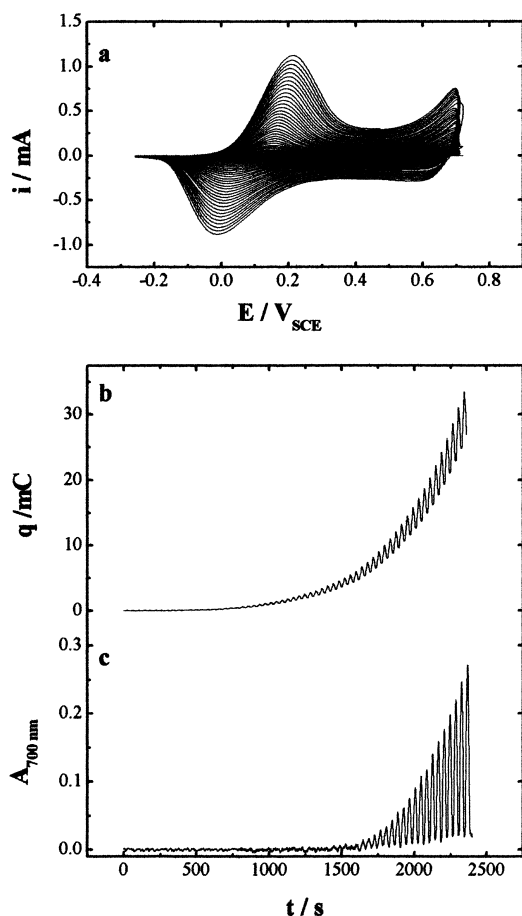


Fig. 1. (a) Growing of PANi film with potentiodynamic conditions; (b) charge and (c) absorbance as a function of time. Electrolytic solution:  $1\text{ mol l}^{-1}$  HCl +  $0.5\text{ mol l}^{-1}$  aniline.  $\nu = 50\text{ mV/s}$ .

In order to verify the band structure of PANi as a function of potential, for a later study of chromogenic kinetics, absorption spectra in the visible region were obtained for different applied potentials (Fig. 2). The main absorption bands at 425 and 800 nm are due to partial oxidation of the

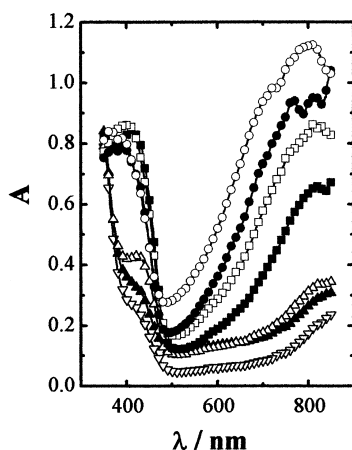


Fig. 2. Spectral absorption of polyaniline at different applied potentials. ( $\nabla$ )  $-0.2\text{ V}$ , ( $\blacktriangle$ )  $0.0\text{ V}$ , ( $\triangleleft$ )  $0.1\text{ V}$ , ( $\blacksquare$ )  $0.2\text{ V}$ , ( $\square$ )  $0.3\text{ V}$ , ( $\bullet$ )  $0.4\text{ V}$  and ( $\circ$ )  $0.5\text{ V}$ . Electrolytic solution:  $1\text{ mol l}^{-1}$  HCl.

polymer. When the potential was varied from  $-0.2$  to  $0.5\text{ V}$ , the polymer showed reversible color changes from pale yellow to green. The band seen at  $425\text{ nm}$  is attributed to the presence of polaron states in the doped form of polyaniline [18]. This band shows a high sensitivity to the potential; the maximum of absorption occurs at  $0.3\text{ V}_{SCE}$ , and for more positive values, the band decreases in intensity and shifts to smaller wavelength. These phenomena occur because the polaronic band always becomes more destabilized on moving to higher energy values [8]. The broad band at  $800\text{ nm}$  shows a steady increase from  $0.2\text{ V}$  and can be related to the superimposed bands of polaronic and bipolaronic species [19–21].

Chromogenic changes as a function of potential were studied by following the absorbance change at a single wavelength. In order to investigate the main electronic transition of PANi, wavelengths of  $425$  and  $700\text{ nm}$  were chosen and the absorbance was recorded simultaneously with cyclic voltammetry experiments. When both processes, the color change and the insertion charge occur simultaneously, the differential of the absorbance curve ( $dA/dt$  vs  $E$ ) coincides with voltammetric profile [22–25]. When both processes, charge transfer and color change do not occur simultaneously, current can be used for kinetics studies of the charge transfer reaction and absorbance for kinetics study of the chromogenic process because absorbance only measures concentration changes of colored species.

In Fig. 3(a), cyclic voltammograms at different scan rates for PANi films in  $1.0\text{ M HCl}$  electrolyte solution are shown. Assuming that the processes are diffusion controlled, the current should be proportional to the scan rate for a finite diffusion and proportional to the square root of the scan rate for semi-infinite diffusion. So, in order to compare the profiles the currents were normalized by the scan rate. The position of the current peak depends on many factors such as pH, solvent, substrate, thickness and homogeneity of the films [26]. The potential range was chosen between  $-0.2$  and  $0.5\text{ V}$ , in order to avoid possible degradation reactions. The complete superposition of  $dA/dt$  curves with the cyclic voltammograms means that the electrochemical reaction is exclusively related to the transformation of chromogenic species. The curves of  $dA_{700\text{ nm}}/dt$  are close to the cyclic voltammograms at slow scan rate, which shows the relation between the charge injection and the transformation from leucoemeraldine to emeraldine. The analysis of these profiles shows that in the potential range where the peaks of  $dA_{700\text{ nm}}/dt$  for  $5$  and  $10\text{ mV/s}$  appear, is the same region where it is observed the oxidation peak in the cyclic voltammogram, indicating that both the electrochemical and the electrochromic reactions during the oxidation process take place at practically the same rate. When the scan rate is increased to  $50$  and  $100\text{ mV/s}$ , the anodic peak of the voltammogram shifts to more positive potentials, which is a typical effect observed in electrochemical processes limited by diffusion. However, the  $dA_{700\text{ nm}}/dt$  peaks observed at  $50$  and  $100\text{ mV/s}$  are more affected than the current peaks in the

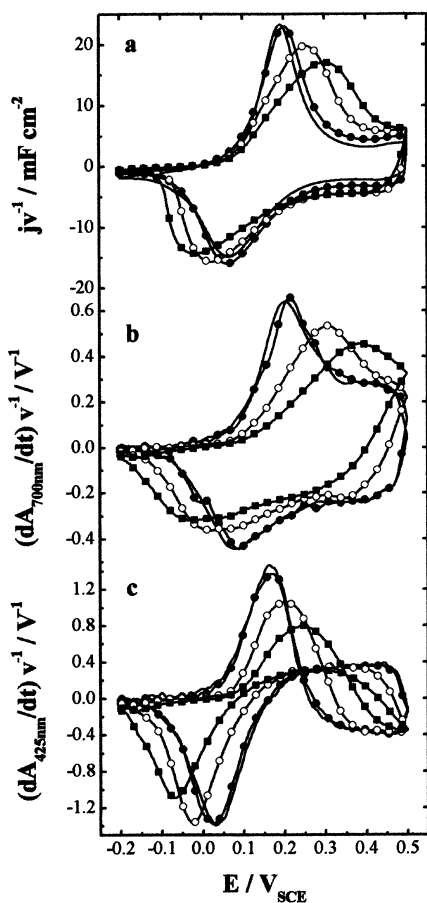


Fig. 3. (a) Cyclic voltammogram, (b)  $dA_{700\text{nm}}/dt$  vs  $E$  and (c)  $dA_{425\text{nm}}/dt$  vs  $E$  profiles at (—) 5 mV/s, (—●—) 10 mV/s, (—○—) 50 mV/s and (—■—) 100 mV/s. Electrolytic solution:  $1 \text{ mol l}^{-1}$  HCl.

voltammograms. This fact clearly shows that the rate of charge injection occurs faster than the chromogenic change. The same behavior is observed during the reduction process: at higher scan rates, the  $dA_{700\text{nm}}/dt$  peak does not follow the changes in the current peaks of the voltammograms.

The behavior shown by the  $dA_{425\text{nm}}/dt$  profile (Fig. 3(c)) is completely different to that observed at 700 nm. The physical meaning of the  $dA_{425\text{nm}}/dt$  curves is the rate of production of absorbing species at 425 nm and, depending on the potential range, a peak in  $dA_{425\text{nm}}/dt$  is related to the maximum rate of formation of polaronic species. The curve decay observed at more positive potentials indicates that the formation rate of those species decreases and the negative values suggest the consumption of these species. At this wavelength, the increase in the scan rate produces a decrease in the chromogenic response, mainly at 100 mV/s, where the peak of  $dA_{425\text{nm}}/dt$  is shifted to more positive potentials in relation to the same peak at 5 mV/s. An interesting fact is that there is not an exact superposition of both, the  $dA_{425\text{nm}}/dt$  and the voltammetric current peaks; the  $dA_{425\text{nm}}/dt$  peak is reached at lower potentials than the current peak. This indicates that, before the current maximum is reached, the production of polaronic species decreases. This diminution is related to the transformation of polaronic species

into bipolaronic spineless ones. This agrees with earlier ESR studies [19] showing that the band at 425 nm can be related exclusively to polaronic species. In the cathodic scan it is observed the same behavior that in the anodic scan: at higher scan rates, the peak of  $dA_{425\text{nm}}/dt$  appears at lower potentials than the voltammetric one.

Chronoamperometric and absorptiometric experiments were carried out in situ at 700 and 425 nm (Fig. 4(a)–(c)). As it can be seen, the chronoamperometric and absorption curves at 700 nm are similar, indicating that the injected charge can be directly related to the formation of species that absorb in this region. However, measurements made at 425 nm showed that after performing an anodic potential step from  $-0.2$  to  $0.2$  V, the absorbance grows and stabilizes at a maximum value. At more positive values ( $0.4$  and  $0.6$  V), the absorbance value increases and then drops, reaching a constant value. In these cases, a clear peak in the absorption curve appears in both the oxidation and the reduction step. This is an indication that intermediary species are quickly produced and consumed when the potential is higher than  $0.2$  V. As mentioned earlier, the electrochemical oxidation processes modifies the electronic band structure generating new electronic states in the energy

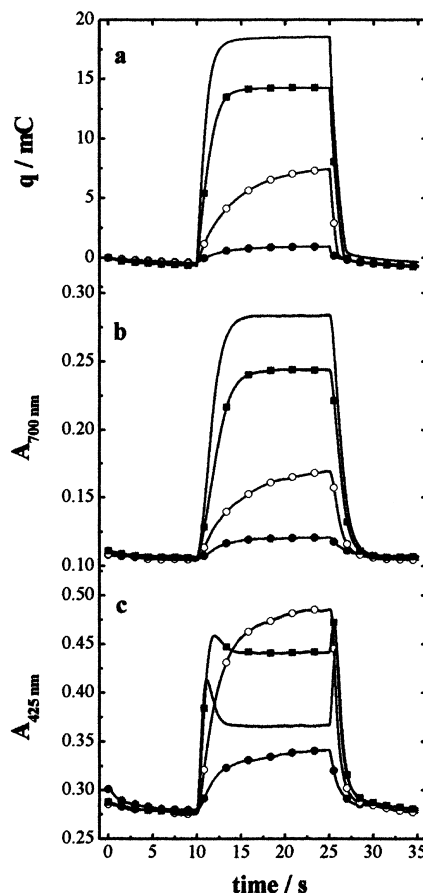


Fig. 4. Charge (a), 700 nm absorbance (b) and 425 nm absorbance (c) as a function of time for PANi. Potential steps: (—●—)  $-0.2 \rightarrow 0.1 \rightarrow -0.2$  V, (—○—)  $-0.2 \rightarrow 0.2 \rightarrow -0.2$  V, (—□—)  $-0.2 \rightarrow 0.4 \rightarrow -0.2$  V and (—)  $-0.2 \rightarrow 0.6 \rightarrow -0.2$  V. Electrolytic solution:  $1 \text{ mol l}^{-1}$  HCl.

gap, the so-called polaronic band. For potentials more positive than 0.2 V, the production of bipolaronic species leads to the diminution of the polaronic population, which is verified by a decrease of absorbance at 425 nm. This agrees with an absorption increase at 700 nm, favoring stronger charge localization on the nitrogen atoms of the charge carriers and, consequently, a change of structure to quinoid diimine (or bipolaronic) species.

In order to compare quantitatively the electrochemical and chromogenic processes, relaxation times can be estimated using experiments similar to those shown in Fig. 4. For this purpose, only 700 nm curves will be used because, as it was discussed above, the response at 425 nm shows a complicated behavior at positive potentials due to the conversion of polaronic species into bipolaronic ones.

The current density decay, as a consequence of a potential step, can be written in a simple form considering finite diffusion as [27]

$$j = j_{\max} e^{-(1/\tau_e)t} \quad (1)$$

where  $j_{\max}$  is the maximum current density and  $\tau_e$  is the relaxation time of the electrochemical reaction. As the optical variable considered is absorbance, an integral quantity, the current density must be integrated to obtain the charge density

$$q = j_{\max} \tau_e - j_{\max} \tau_e e^{-(1/\tau_e)t} \quad (2)$$

As  $j_{\max} \tau_e$  is equal to  $q_{\max}$ , the equation is re-written in the form

$$q = q_{\max}(1 - e^{-(1/\tau_e)t}) \quad (3)$$

As it was shown in the potentiodynamic experiments, there are different relaxation times for both, charge transfer and chromogenic processes. So that, it is possible to consider that after the redox process, the formed species suffer a transformation, which can be associated to the color change. Assuming that this process has only one relaxation time, the absorbance-time dependence can be described as

$$A = A_{\max}(1 - e^{-(1/\tau_a)t}) \quad (4)$$

where  $A$  is the absorbance,  $A_{\max}$  the maximum absorbance and  $\tau_a$  is the chromogenic relaxation time. Thus, by fitting experimental curves by using either Eqs. (3) or (4),  $\tau_e$  and  $\tau_a$  can be calculated for different applied potentials, for both oxidation and reduction processes. In the special case of both relaxation time are the same, Eqs. (3) and (4) can be associated and a direct relation is obtained between current and  $dA/dt$  as it was done in Ref. [22].

The use of  $\Delta A$ s rather than absolute values of the absorbance is necessary to satisfy an indispensable requirement for the fitting of experimental curves, that is that the curves must pass through the origin. The form to present the curves for oxidation and reduction processes, that is a steady grow until reaching a maximum, does not affect the interpretation of the data, since it must be taken into

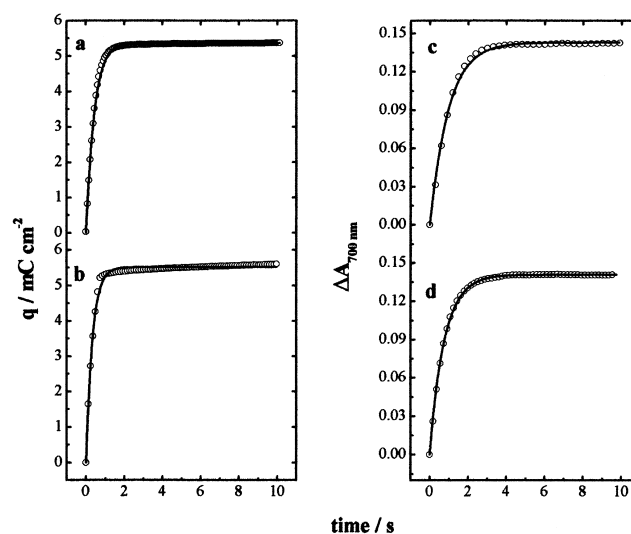


Fig. 5. Charge as a function of time for the oxidation process (a) and the reduction process (b) of a PANi film. Absorbance at 700 nm as a function of time for the oxidation process (c) and the reduction process (d). Adjusted curves using equations (3) or (4) (—) and experimental ones (—○—). Charge and absorbance were registered for a potential pulse  $-0.2 \rightarrow 0.4$  V for the oxidation reaction and  $0.4 \rightarrow -0.2$  V for the reduction reaction. Electrolytic solution:  $1 \text{ mol L}^{-1}$  HCl.

account that in the oxidation process the polymer changes from transparent to colored, while in the reduction process, the reverse change occurs. Fig. 5 shows the fitting at one potential for both, oxidation and reduction processes for HCl electrolytic solution. It can be seen that the fits (solid line) are very precise for both charge and absorbance variables. The values of  $\tau_a$  and  $\tau_e$  as a function of the applied potential obtained from the fittings, for a film grown up to  $25 \text{ mC cm}^{-2}$ , are shown in Fig. 6. It can be seen the process of chromogenic relaxation occurs more slowly than the process of electrochemical relaxation ( $\tau_e < \tau_a$ ), as it was already deduced from the voltammetric results (Fig. 3) and qualitatively verified by Malinauskas and Holze [9]. Analyzing the oxidation process, it can be noted that  $\tau_e$  for the oxidation reaction diminishes when the potential increases. This is in agreement with a diminution of the charge transfer resistance with the applied potential. The reduction reaction occurs faster than the oxidation one. This fact is observed for both optical and electrochemical processes. This behavior is in agreement with the structural modification of the polymeric entanglement: in the open and oxidized polymer, the reduction occurs faster because the channels formed during oxidation favor the flux of counterions. On the other hand, when the polymer is compact in the reduced state, the entrance of counterions is more difficult and the relaxation time for the oxidation is higher.

In order to study the influence of the chemical nature of the counterion, experiments with HCSA 1 M as electrolytic solution were performed. The results obtained are shown in Fig. 7.

It was observed that for all potentials, during the

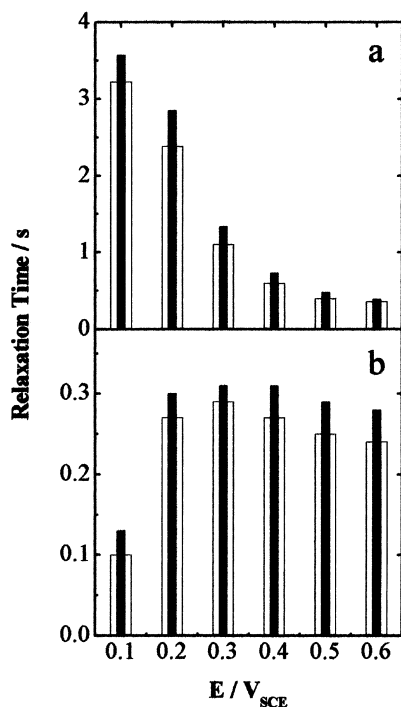


Fig. 6. Relaxation time at different applied potentials for both electrochemical ( $\square$ ) and electrochromic ( $\blacksquare$ ) reactions during (a) oxidation and (b) reduction processes. HCl electrolytic solution.

oxidation process, the chromogenic relaxation time is higher than the electrochemical one. This fact clearly shows that the change of coloration is related not only to charge injection but also to a structural accommodation produced as a consequence of the redox processes. Thus, in the oxidation process the quinone character of the polymer increases leading to the opening of the torsion angle and the

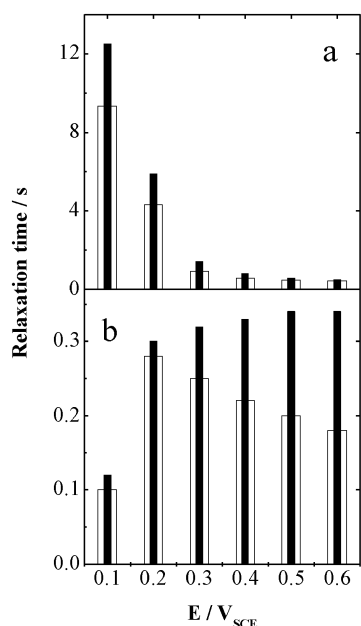


Fig. 7. Relaxation time at different applied potentials for both electrochemical ( $\square$ ) and electrochromic ( $\blacksquare$ ) reactions during oxidation (a) and reduction (b) processes. HCSA electrolytic solution.

change in color must follow this transformation. It is also evident that the relaxation time of the oxidation process is greater than  $\tau_c$  for HCl solution. This fact is related to the fact that the volume of the camphorsulfonate anion is bigger than the volume of chloride anion provoking a diminution in the rate of the ionic insertion in the polymer matrix. As charge transfer and ionic insertion are concomitant process to maintain film electroneutrality, the global charge transfer kinetics is modified by changing the chemical nature of the electrolyte. The effect of the chemical nature of the anion is more evident in the oxidation process than in the reduction one. This fact shows that as the oxidized polymer matrix is more open than the reduced one, even the big camphorsulfonate anion can move easily to compensate charge during the reduction reaction.

#### 4. Conclusions

By using the two main absorption bands of Pani located at 425 and 700 nm was possible to compare the rate of color change (chromogenic process) and the rate of charge injection. It was shown that the reduction and oxidation processes have different kinetics, mainly related to the different polymer conformations in both redox states: a more open structure in the oxidized form of PANi than the reduced one. Also, it was shown that the chromogenic process must be related to conformational changes produced by the transformation of benzenoid to quinoid character and the rate of these changes is slower than the injection charge. Also, it was shown that the chemical nature of the anion plays an important role mainly during the oxidation process, modifying the rate of the injection charge and as consequence, the rate of color change.

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#### References

- [1] Mattoso LHC. *Quím Nova* 1996;19(4):388–99.
- [2] Varela H, Torresi RM. *J Electrochem Soc* 2000;147(2):665–70.
- [3] de Oliveira SC, Torresi RM, de Torresi SIC. *Quím Nova* 2000;23(1): 79–87.
- [4] Watanabe A, Mori K, Iwasaki Y, Nakamura Y, Niizuma S. *Macromolecules* 1987;20(8):1793–6.
- [5] Stejskal J, Kratochvíl P, Jenkis AD. *Polymer* 1996;37(2):367–9.
- [6] Yano J, Terayama K, Yamasaki S, Aoki K. *Electrochim Acta* 1998; 44:337–43.
- [7] Bernard MC, Hugot-Le Goff A, Bich TV, Zeng W. *Synth Metals* 1996;81:215–9.
- [8] Córdoba de Torresi SI, Bassetto AN, Trasferetti BC. *J Solid State Electrochem* 1998;2:24–9.

- [9] Malinauskas A, Holze R. *Synth Metals* 1998;97:31–6.
- [10] Varela H, Malta M, Torresi RM. *J Power Sour* 2001;92(1–2):50–5.
- [11] Varela H, Torresi RM, Buttry DA. *J Braz Chem Soc* 2000;11(1):32–8.
- [12] Inzelt G, Pineri M, Schultze JW, Vorotyntsev MA. *Electrochim Acta* 2000;45:2403–21.
- [13] Bredas JL, Street GB. *Acc Chem Res* 1985;18:309–15.
- [14] Otero TF, Grande H, Rodríguez J. *Electrochim Acta* 1996;41(11–12):1863–9.
- [15] Otero TF, Grande HJ. *Electroanal Chem* 1996;414:171–6.
- [16] Csahók E, Vieil E, Inzelt G. *J Electroanal Chem* 2000;482:168–77.
- [17] Torresi RM, Maranhao SLD. *J Electrochem Soc* 1999;146(11):4179–82.
- [18] Chinn D, Dubow J, Li J, Janata J, Josowicz M. *Chem Mater* 1995;7:1510–8.
- [19] Neudeck A, Petr A, Dunsh A. *J Phys Chem B* 1999;103:912–9.
- [20] Abd El-Rahman HA. *Polym Int* 1997;44:481–9.
- [21] Geniès EM, Lapkowski M. *J Electroanal Chem* 1987;220:67–82.
- [22] Mello RQM, Torresi RM, Córdoba de Torresi SI, Ticianelli EA. *Langmuir* 2000;16:7835–41.
- [23] Stilwell DE, Park SM. *J Electrochem Soc* 1989;136(2):427–33.
- [24] Koziel K, Lapkowski M, Lefrant S. *Synth Metals* 1995;69:217–8.
- [25] Gazotti Jr. WA, Jannini MJDM, Córdoba de Torresi SI, De Paoli M-A. *J Electroanal Chem* 1997;440:193–9.
- [26] Gazotti Jr. WA, Faez R, De Paoli M-A. *J Electroanal Chem* 1996;415(1–2):107–13.
- [27] de Albuquerque Maranhão SL, Torresi RM. *Electrochim Acta* 1998;43(3–4):257–64.