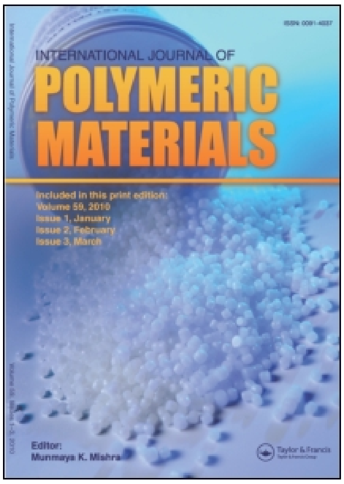

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Electrocatalytic Response of Poly(2-Chloroaniline)/Cobalt Phthalocyanine Modified Electrodes

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The electrochemical response of poly(2-chloroaniline) (PANiCl) synthesized by chemical oxidation at low temperature is described. The polymer obtained is soluble in methylpyrrolidone and it is possible to cast films which are good substrates for supporting metal complex catalysts such as cobalt phthalocyanine (CoPc) and are very stable to potentials upto 0.8 V *vs.* SCE. Films of PANiCl containing 1% of CoPc exhibit catalytic activity for the electrochemical oxidation of 2-mercaptoethanol, glutathione and hydrazine in acid medium. Evaluation of the electrocatalytical response of PANiCl/CoPc films suggests that the diffusion rate of electroactive species into the film is improved when the polymer reaches the oxidized state.

Keywords: Polyaniline; polymer modified electrodes; electrocatalysis; electro-oxidation; cobalt phthalocyanine; 2-mercaptoethanol; glutathione; hydrazine

INTRODUCTION

In recent years, conductive polymers have been widely investigated. An important goal of this research has been the development of materials with high electroactivity, as alternatives to conventional electrode materials for a great variety of applications [1–3] such as electrochromic devices, active materials for rechargable batteries and

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as conductive supports for electrocatalytic systems. This kind of polymeric electrodes should have good processability, high stability and well-known physical properties.

Many efforts have been focused on polyaniline (PANi) [4–6] and PANi composite films [7, 8]. PANi is a particularly interesting material as a catalyst support due to its large surface area, high conductivity and storage stability. The entrapping of heteropolyanions in PANi has found applications in the oxidation of methacroleine to metha-acrylic acid [9]. The inclusion of platinum dispersed in PANi films [10, 11] has provided electrode materials for methanol and CO oxidation [10, 11].

Metal phthalocyanines are well known as catalysts for the reduction of O_2 [12–14]. It has been shown that it is possible to incorporate Fe and Co tetrasulphonated phthalocyanines (MTSPc) in PANi films during the electropolymerization of aniline. These systems exhibit high activity for the electroreduction of O_2 [15–18]. These complexes also catalyze several electrochemical reactions, apart from the reduction of O_2 [14], many of them involving oxidation processes. However, due to the low stability of PANi-modified electrodes at potentials higher than 0.7 V *vs.* SCE [19–21], it is not possible to study electrocatalytic oxidation reactions as thiol and hydrazine oxidation which are promoted by metallophthalocyanines [14]. Therefore, PANi/MTSPc modified electrodes are limited to reactions occurring at potentials lower than 0.7 V *vs.* SCE. These modified electrodes are obtained by oxidative electropolymerization of metallo-4,4′,4″,4‴-tetra-aminophthalocyanine (MTAPc) on a graphite substrate [22]. Poly-MTAPc modified electrodes have been used successfully for the oxidation of hydrazine, thiols, oxalic acid, and NADH and also for O_2 reduction [23–27]. This kind of electrodes have been synthesized by electropolymerization in organic medium [22]. On the other hand, there are few reports on polyanilines substituted with electron-withdrawing groups. This kind of materials should present more stability at high positive potentials compared to polyaniline. Because of this, films obtained with polyaniline substituted with chlorine should be good support materials for metal-complex catalysts for studying electro-oxidation reactions.

In this work, we report a simple way for obtaining modified electrodes based on poly (2-chloroaniline) (PANiCl) and cobalt phthalocyanine (CoPc) for studying the electro-oxidation of 2-

mercaptoethanol, glutathione and hydrazine. In order to understand the electronic properties of the poly(2-chloroaniline) some theoretical calculations were performed using the semiempirical HF-AM1 method [28].

EXPERIMENTAL

Poly(2-chloroaniline) (PANiCl) was prepared using a variation of a method developed to obtain polyaniline using low temperatures [3, 27]. PANiCl was synthesized from 2-chloroaniline. 2-chloroaniline (Aldrich Chemical Co.) was distilled twice under reduced pressure and stored in the dark. Equimolar ratio (0.25 M) of 2-chloroaniline and ammonium peroxydisulfate (Merck p.a.) in 1 M HCl were used. These solutions were mixed and kept at 0°C during 20 hours. The resulting polymeric material was filtered and rinsed with 1 M NH_4OH and double-distilled water. The product was then rinsed with methanol to remove soluble reaction products. Finally, this polymer was dried under nitrogen dynamic vacuum at 65°C. The PANiCl films were obtained by casting-off solutions containing 1g of PANiCl powder dissolved in 100 mL of 1-methyl-2-pyrrolidone (NMP). Modified films were prepared in a similar fashion, except that the appropriate weight of CoPc was added to the solution. The concentration of the phthalocyanine in these films is defined as a percentage basis of the weight of the CoPc added to 1g of PANiCl powder.

The supporting electrolytes were prepared from analytical grade chemicals from Merck and double-distilled water. CoPc was purchased from Aldrich Chemical Co. and used as received. Analytical grade 2-mercaptoethanol (ME) obtained from Fluka, was distilled before use and stored in the dark. Reduced glutathione (G-SH) was obtained from Sigma Chemical Co. and used without further purification. Hydrazinium sulfate was used as obtained from Merck. An ordinary pyrolytite graphite (OPG) disk (geometric area, 0.44 cm^2) from Pine Instrument Co. was used as working electrode and as support for the samples. Prior to polymer casting, its surface was renewed with 1200 grit silicon carbide paper and polished with filter paper followed by sonication for a few minutes in double distilled water. All measurements were conducted at 25°C under nitrogen in a conventional three-compartment glass cell with individual compartments separated with fritted glass, for the working, reference and counter electrodes. The reference was a saturated calomel electrode. The electronic equipment consisted of a POS73 Wenking Potentioscan and Pine ASR electrode rotator with servo control for the rotation frequency. The electrode surface was coated with a PANiCl or PANiCl/CoPc by taking 5 μL of stock polymer or polymer + CoPc solutions in NMP. The electrodes were dried under nitrogen atmosphere for 45 minutes and then kept in a dessicator at 20°C for 8 hours. UV–vis spectra (Shimadzu UV-160) of the emeraldine and leucoemeraldine form were obtained in dimethylsulfoxide (DMSO). The reduced form (leucoemeraldine) was obtained reducing the emeraldine with hydrazinium sulfate [30, 31] in the same solvent that was used to record the UV–vis spectra. FT-ir spectra were recorded using a Bruker IFS 66 v spectrometer in the range 4000–400 cm^{-1} at a spectral resolution of 4 cm^{-1} (256 scans) using KBr pellets.

Theoretical calculations were performed using the semiempirical method Hartree-Fock AMl. The structures studied were 2-chloroaniline tetramers in several oxidation stages (reduced, 50% oxidized (emeraldine-like), 100% oxidized (pernigraniline-like) structures). The final optimized structures were obtained without symmetry restrictions. We have shown that tetramer analysis is a good approximation for studying the polymer study [32, 39].

RESULTS AND DISCUSSION

1. General Characteristics of PANiCl Chemically Synthesized

PANiCl prepared as emeraldine was soluble in DMSO, 1,4-dioxane, dimethyl formamide (DMF) and NMP. Also, the yield obtained is remarkably high (82%) compared to that reported by Wang *et al.* [33] using a similar procedure who reported a yield of 30%. They obtained a material slightly soluble in chloroform and tetrahydrofuran, and soluble in DMF. Our results confirm that the PANiCl synthesized at low temperatures is highly soluble in common solvents [3].

The FT-ir spectrum of PANiCl is depicted in Figure 1a. Key bands assignments are as follows: The 1590 and 1500 cm^{-1} bands are

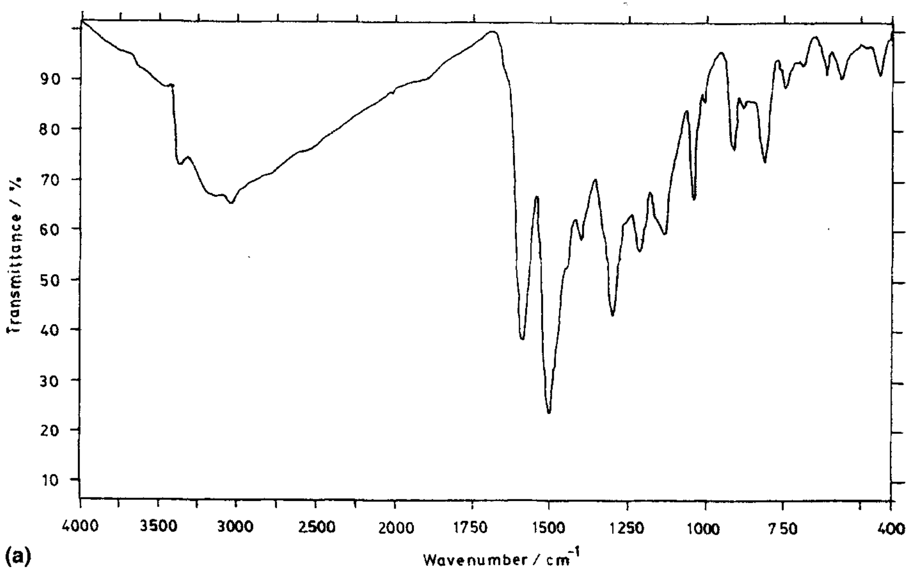

FIGURE 1 (a) FT-ir spectrum of poly(2-chloroaniline), (b) UV–vis absorption spectra of poly(2-chloroaniline). Solid line: emeraldine form. Dashed line: reduced form.

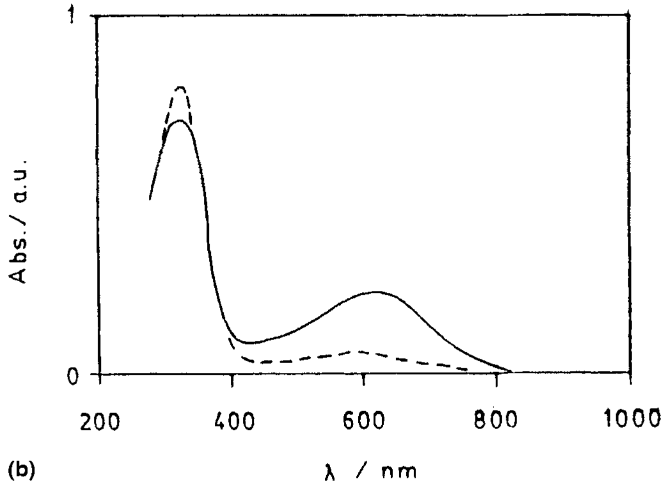

FIGURE 1 (Continued).

assigned to non-symmetric C_6 ring stretching modes. The higher frequency vibration has a major contribution from the quinoid ring units. Therefore the 1500 cm^{-1} band is attributed to an aromatic ring stretching mode. The degree of oxidation of PANIs is generally estimated from the intensity ratio of these two bands which suggest the oxidation state of the material [34]. In our case, from the ratio between these two bands, it is possible to estimate that 40% of the rings are quinoid-type and 60% are aromatic-like. This ratio has been reported previously for PANi and it was described as corresponding to the emeraldine base form [35]. Therefore, in our case it is possible to establish that the PANiCl obtained is mainly in its emeraldine base form. The 1298 cm^{-1} band is a C—N stretch, indicative of secondary (2°) aromatic amine groups [36, 37]. The single band at 1043 cm^{-1} is a C—Cl stretch in aromatics and the band at 1006 cm^{-1} may be assigned to C—Cl stretching in a quinoid moiety [38].

Figure 1b shows the UV–vis spectra of poly(2-chloroaniline) in two oxidation states. The reduced form only exhibits a peak at 318 nm. This peak corresponds to a $\pi \rightarrow \pi^*$ transition. The π orbital corresponds to the π of benzene interacting with pz of the nitrogen, whereas the π^* is a benzene orbital. The oxidized form shows a new peak at around 686 nm. This peak corresponds to a $\pi \rightarrow \pi$ quinone transition. UV–vis absorption values obtained for polyaniline are compared with those of PANiCl in Table I. Energy transitions of PANiCl occur at lower values than those of PANi.

Some theoretical calculations were performed in order to understand the electronic properties of the polymer. In a previous work [32], we discussed the variation of some physicochemical properties of oligoaniline with the chain length. We concluded that tetramers could serve as model systems for performing theoretical calculations of longer chain polyanilines. Figure 2 shows the structures obtained from calculations using the semiempirical AMI method. Results of tetra(2-chloroaniline) show torsional angles between adjacent benzenic rings larger than those of tetraniline. This is probably due to a steric hindrance caused by the large volume of the chlorine atom. The energy level values obtained for the emeraldine structure show lower energy $\pi \rightarrow \pi q$ transitions than in tetraniline (for tetraniline: 7.36 eV and for tetra(2-chloroaniline): 7.28 eV). Also, for tetra(2-chloroaniline) a strong stabilization of the HOMO is observed. This suggests an increase in the ionization potential (IP). (Reduced tetraniline: 7.80 eV emeraldine tetraniline: 8.08 eV; Reduced tetra(2-chloroaniline): 8.22 eV, emeraldine tetra(2-chloroaniline): 8.33 eV). These results are in qualitative agreement with electrochemical data and UV–vis spectra. It is important to point out that the AMI method does not provide accurate energy level values. From these calculations it is possible to predict a large increase of the IP (related to electrochemical oxidation potential) produced by adding chlorine substituents to the backbone of the polyaniline chain. Also a band-gap lowering is predicted. This fact has been confirmed above by the UV/vis spectra (Tab. I). This shows then that tetra(2-chloroaniline) model systems provide a good approximation for understanding the electronic properties of poly(2-chloroaniline).

TABLE I Absorption values from UV vis spectra of polyaniline and poly(2-chloroaniline) in DMSO

Reduced structures	*Oxidized structures*
Polymer λ max. (nm)	Polymer λ max. (nm)
PANiCl $\frac{566}{306}$	PANiCl $\frac{612}{344}$
PANiCl $\frac{577}{318}$	PANiCl $\frac{686}{318}$

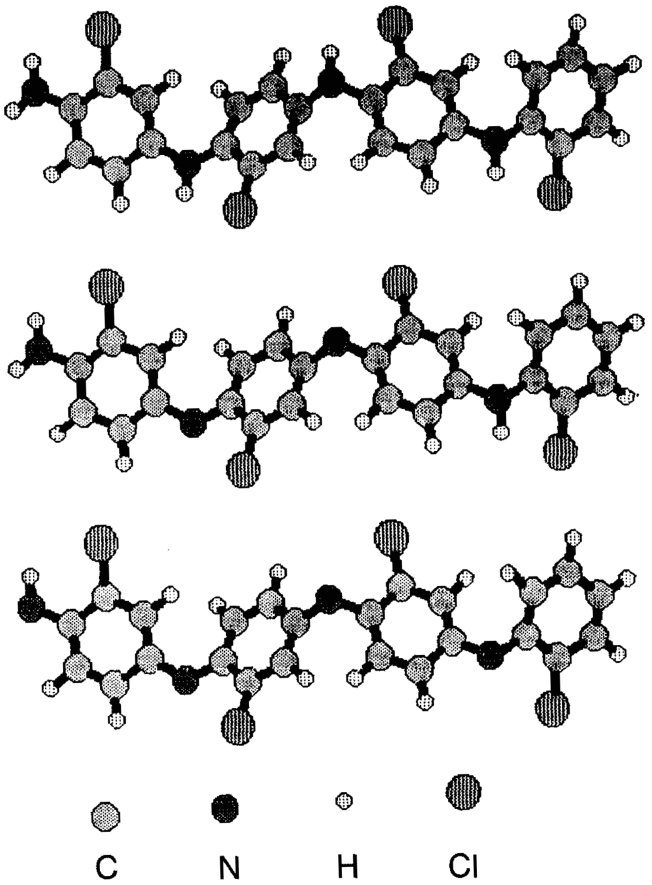

FIGURE 2 Schematic representation of tetra(2-chloroaniline). (a) reduced, (b) 50% oxidized, and 100% oxidized.

2. Electrochemical Behaviour

Figure 3 shows cyclic voltammograms of PANiCl and PANiCl + CoPc modified electrodes with different CoPc contents. These films were cycled for 30 minutes in 1 M HCl or 0.5 M H_2SO_4 at 100 mVs^{-1} before recording the voltammograms of Figure 3 in the same electrolyte used for the pre-treatment. These electrodes were subjected to potential cycling at 100 mVs^{-1} between –0.2 to + 0.8 V *vs.* SCE for more than

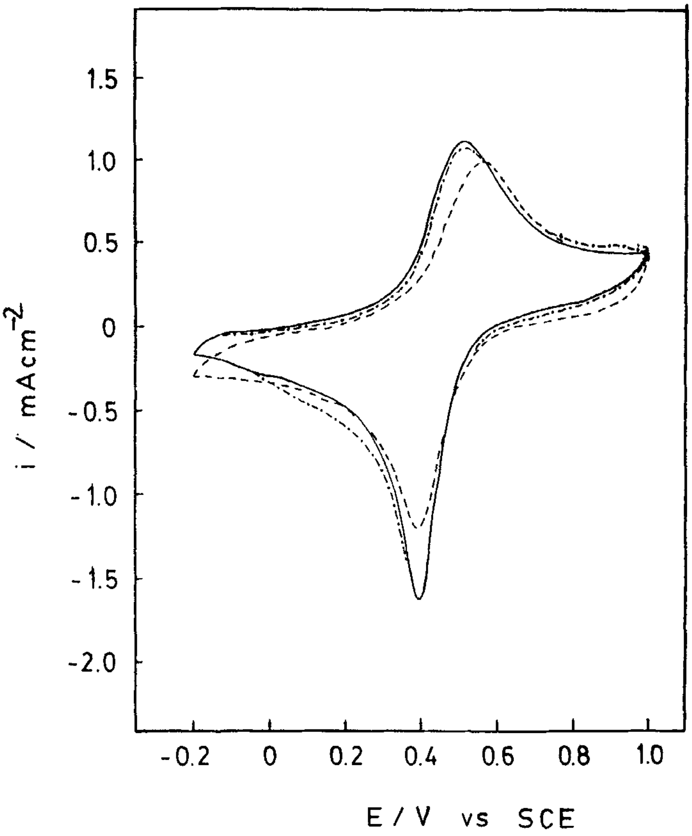

FIGURE 3 Cyclic voltammograms of PANiCl films containing 1% CoPc in 1 M HCl (dashed line), 1% CoPc in 0.5 M H_2SO_4 (dashed-dotted line) and without CoPc in 0.5 M H_2SO_4 (solid line). N_2 saturated Scan rate: 10 mVs^{-1}.

8 hours. After that, both anodic and cathodic charges remain constant which illustrated the high electrochemical stability of these polymers. The potentiodynamic profiles of all studied films display the typical redox process of poly(2-chloroaniline). In 1 M HCl, the anodic peak is observed at around 0.56 V. The current peak for polymer electroreduction appears at ca. 0.40 V. In 0.5 M H_2SO_4 the anodic peak is shifted to more negative potentials (0.52 V). The c.v. profiles remain unchanged when 1% of CoPc is present in those films. At 1% CoPc concentration the redox process attributed to the Co(II)/Co(III) reversible couple that

should appear at ca. 0.7–0.8 V *vs.* SCE [40] is masked because of the large capacity of the polymer film.

Figures 4a and b depicts the electrocatalytical response of an OPG disk electrode modified with PANiCl/CoPc films in electrolytes containing 10^{-2} M mercaptoethanol (RSH) or 10^{-2} M reduced glutathione (GSH) in 1 M HCl or 10^{-2} M hydrazine in 0.5 M H_2SO_4. In Figure 4a the irreversible wave for RSH oxidation starts at ca. 0.3 V and the *Ep* value is reached at ca. 0.75 V. The main process

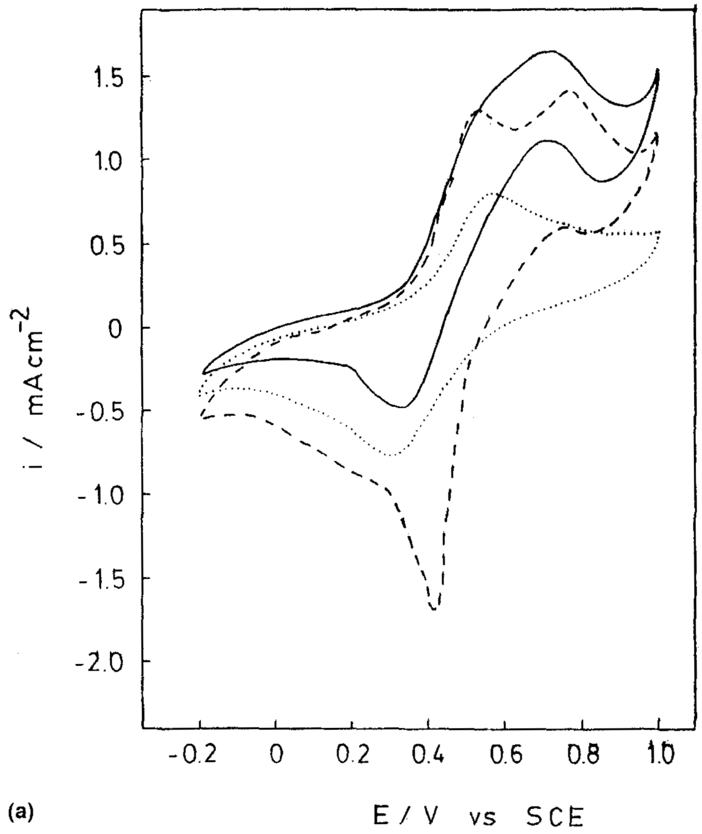

FIGURE 4 Rotating/disk electrode polarization curves for: (a) 10^{-2} M 2-mercaptoethanol (solid line) 10^{-2} M glutathione (dashed line) and on 1% CoPc/PANiCl films. Electrolyte: 1 M HCl, N_2 saturated. Scan rate: and 10 mVs^{-1}. Rotation speed: 1600 rpm. (b) 10^{-2} M hydrazine, scan rate: 10 mVs^{-1}. Rotation speed: 1600 rpm. The dotted lines illustrate the response of PANiCl films without CoPc.

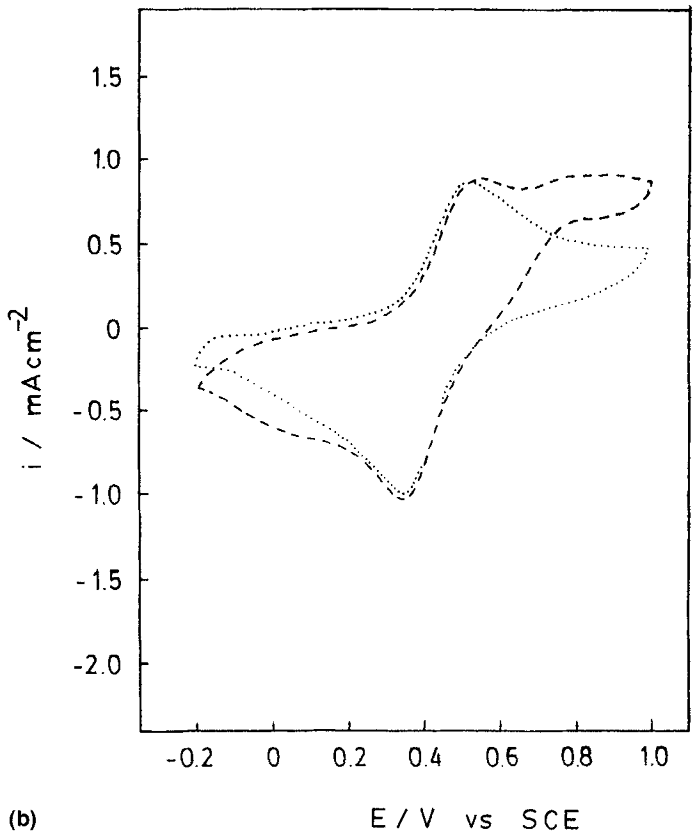

FIGURE 4 (Continued).

appears as a shoulder at ca. 0.55 V. This potential value is close to that corresponding to the first redox process of PANiCl.

For GSH, two waves are present in the positive scan (see Fig. 4a). The first peak is located at around 0.54 V and corresponds to the PANiCl redox process. The second wave resolved at ca. 0.78 V is attributed to GSH oxidation.

The main oxidation process of RSH and GSH display similar *Ep* values at the cathodic and anodic sweep. It is well known the electro-oxidation of thiols is catalyzed by the Co(II) state [14]. In Figure 4a, the voltammograms show a decrease of the activity when the potential is close to the standard potential of the Co(III)/Co(II) couple

(0.70 – 0.80 V). The reaction is inhibited probably because the Co(III) state in the phthalocyanine is inactive for the reaction. During the cathodic sweep the current increases as more Co(II) centers are generated electrochemically inside the film and the *Ep* values are reached at ca. 0.72 V for RSH, and 0.75 V for glutathione.

Figure 4b shows the rotating disk polarization curve for hydrazine oxidation. Two waves are observed, that correspond to the polymer redox process at ca. 0.54 V, and hydrazine oxidation that starts at ca. 0.77 V. In the negative sweep when the potential is equal to 0.77 V the current density decreases, tracking the PANiCl potentiodynamic profile. It is interesting to note that at sweep rates as low as 2 mVs^{-1}, a limiting current is obtained, (see Fig. 5). These curves were recorded

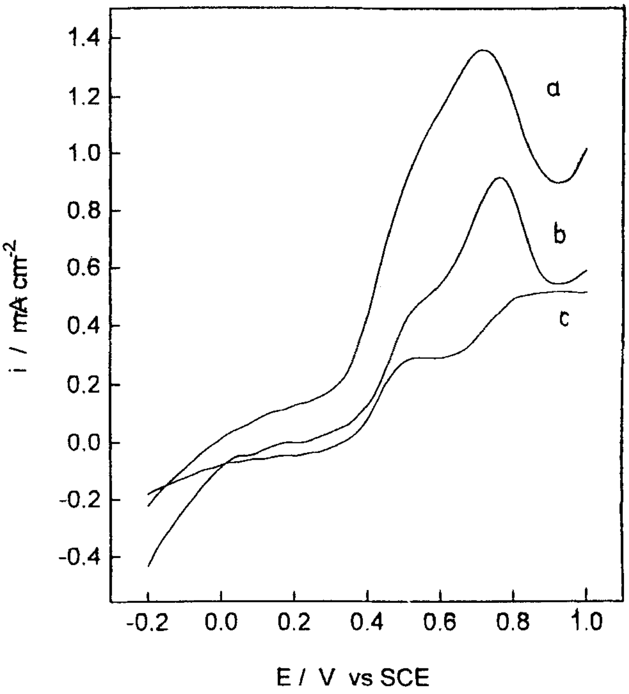

FIGURE 5 Rotating disk polarization curves on 1% CoPc/PANiCl films. (a) 10^{-2} M 2-mercaptoethanol + 1 M HCl, (b) 10^{-2} M glutathione + 1 M HCl, and (c) 10^{-2} M hydrazine + 0.5 M H_2SO_4. N_2 saturated. Scan rate: 2 mVs^{-1}. Rotation speed: 1600 rpm.

at lower potential scan rates in order to decrease the background currents of PANiCl. This limiting current is achieved after the potential corresponding to the Co(III)/Co(II) redox couple is attained. In contrast to what is observed for the oxidation of the thiols, the Co(III) state seems to be active for the electro-oxidation of hydrazine. These results differ from those previously reported for the electro-oxidation of hydrazine on CoTSPc [41, 42] and on polymeric CoTAPc [23]. In those systems the Co(II) state has been considered to be active species for hydrazine oxidation.

From the rotating disk polarization curves depicted in Figures 4a and b and Figure 5 it is possible to conclude that the electro-oxidation of RSH, GSH and hydrazine depends on the oxidation state of PANiCl. These films display a significant electrocatalytical activity only after reaching the first redox process of PANiCl (0.54 V) during the positive scan. The diffusion of the species into the film seems to improve when the polymer reaches the oxidized state. This phenomenon has been reported previously for polyaniline thin films by Schmidt *et al.* [43].

As a final conclusion, the chemical synthesis of soluble poly(2-chloroaniline) described in this work facilitates the preparation of modified PANiCl/CoPc films. These films are stable and resistant to oxidation compared to those of unsubstituted polyaniline. They are promising substrates for preparing films with activity for electro-oxidation reactions. They exhibit catalytic activity for the electro-oxidation of 2-mercaptoethanol, glutathione and hydrazine. The oxidation process of electroactive species seems to be controlled by the oxidation state of the polymer.

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