PREPARATION AND CHARACTERIZATION OF ELECTRODES MODIFIED WITH METALLOPORPHYRINS. APPLICATION TO REDUCTION OF NITRITE

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Dedicated to Professor Sergio Roffia on the occasion of his retirement.

Six type-modified electrodes by electropolymerization of tetrakis(x-aminophenyl)porphyrins, where x = 2, 3 or 4, and their Cu(II) and Ni(II) complexes in HCl solution were prepared and characterized by cyclic voltammetry, atomic force microscopy and UV-VIS spectroscopy. The morphology of the polymers depends on the position of the amino groups. The modified electrodes show interesting electrocatalytic activity toward reduction of nitrites. The catalytic behavior strongly depends on the nature of the metal and the position of the amino groups.
Keywords: Modified electrodes; Electropolymerization; Tetraaminophenylporphyrins; Nitrite reduction; Porphyrins; Copper complexes; Nickel; Cyclic voltammetry; Electrochemistry.

In the last years modification of electrode surfaces with polymeric materials has been subject of a great interest. Incorporation of metalloporphyrins and metallophthalocyanines anchored on electrode surfaces as electropolymerized films has received special attention due to their electrocatalytic properties in many chemical reactions[1–4]. The electrochemical polymerization process of metalloporphyrins and the catalytic activities of the films depend on peripheral substituents. In particular, amino substituted porphyrins and derivatives can be electropolymerized by radical coupling reactions after reduction or oxidation of the monomer precursor[4–7].

In this study, we present the modification of conducting glass surfaces by polymer films of tetrakis(x-aminophenyl)porphyrin (x = 2, 3 or 4). The electropolymerization mechanism implies oxidation of amino groups, forming radical cationic species that react with the monomer[8]. The film formation depends on the position of the amino substituents. The electrocatalytic activity of these electrodes has been recently proven for reduction of nitrate in two aqueous media[8]. In the present work, this type of modified electrodes is employed for reduction of nitrite in aqueous sodium perchlorate (pH 6). The single porphyrins are not soluble in this medium and their immobilization in an electropolymerized film is therefor a prerequisite to obtain catalytic activity. Preliminary results are analyzed hereinafter.

Electrocatalytic reduction of nitrite using modified electrodes with polymer materials based on metalloporphyrins was investigated[9,10], the major products formed being ammonia, nitrous oxide, molecular nitrogen and hydroxylamine. The proposed mechanism involves interactions between NO and iron porphyrin film in acid media or NO, nitrite and iron porphyrin film in neutral media. From our results we cannot establish a possible mechanism. However, a better electrocatalyst of the nitrite reduction in sodium perchlorate has been found.

EXPERIMENTAL

Tetrakis(x-aminophenyl)porphyrins (tapp) (x = 2, 3 or 4) and their complexes with copper(II) and nickel(II) were obtained from MidCentury Co. and used without further purification. Electropolymerization and electrochemical measurements were performed using a VoltaLAB PGZ 100 electrochemical instrument (Radiometer Analytical, France). The three-electrode electrochemical cell was equipped with a platinum counter electrode and a Ag/AgCl reference electrode. Working electrode was a conducting transparent electrode (2 cm^2 apparent surface area), prepared by SnO$_2$:F deposition on a polished glass sheet. Electropolymerization was accomplished using 1 M HCl aqueous solution containing 1×10^{-3} M porphyrin or 1×10^{-3} M metalloporphyrin monomer, by cycling 25 times the potential between +0.2 and +1.2 V *vs* Ag/AgCl, at the scan rate of 50 mV s^{-1}. The electrolyte solutions were purged with pure N$_2$ and kept at room temperature for all the experiments. After the polymerization, the modified electrodes were rinsed with double-distilled water. Their stable voltammetric response was obtained by successive potentiodynamic cycles at the scan rate of 100 mV s^{-1} in the 1×10^{-1} M NaClO$_4$ electrolyte.

The UV-VIS experiments were performed in a one-compartment quartz cuvette, using a Varian Cary 1E spectrophotometer run by CaryWinUV 2.5 software. A NANOSCOPE IIIA (Digital Instruments Inc. Santa Barbara, CA) atomic force microscope (AFM), operating in a contact mode, was employed to investigate the surface-polymer morphology. Solvent and electrolytes were of analytical grade. The electrolytes (NaClO$_4$, NaNO$_2$) were of analytical grade from Fluka and Merck, respectively, and were used without further purification.

RESULTS AND DISCUSSION

Preparation and Characterization of Polymer-Modified Electrodes

The schematic structure of the metalloporphyrins used to form the polymeric materials is shown in Fig. 1. The aminophenyl groups are nearly perpendicular to the plane of the molecule. The amino substituents can be located at positions 2, 3 or 4. The complexes could be electropolymerized on the conducting glass substrate only when the amino substituents were in positions 2 or 4[8], but the reason is yet unknown. Figure 2 shows the voltammetric response to the film formation from Cu-2-tapp, Ni-2-tapp and Ni-4-tapp complexes, respectively. A similar behavior was observed for Cu-4-tapp complex and the uncoordinated ligands. In all the cases, the anodic current diminishes during the first 5 voltammetric scans, reaching a constant profile afterwards. In general, thin films are obtained. In the initial cycles, the formation of radical complexes is achieved directly on the bare electrode surface. Later, the electrode is modified with oligomers and the subsequent oxidation takes place on a different surface. This is probably the reason for the change in the current. The values of the final charge density obtained after the electropolymerization are shown in Table I. From the results it is clear that the thinnest polymer is poly-H₂-2-tapp. For the metalloporphyrin complexes of Ni(II), the substituent in the ortho position favored formation of a thicker film. In the case of the Cu(II) complexes, the charge densities are very similar for the ortho and para substitutions.

In Fig. 2, there is a strong anodic wave at *ca* 1 V *vs* Ag/AgCl corresponding to the oxidation of the amino groups. Also, it is possible to observe a small voltammetric wave appearing at *ca* 0.6 V for all the compounds stud-
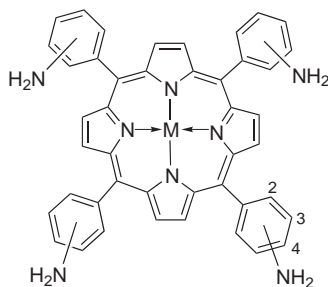

FIG. 1
Structure of tetrakis(x-aminophenyl)porphyrin (where x = 2, 3 or 4) and its complexes with M = Ni(II), Cu(II)
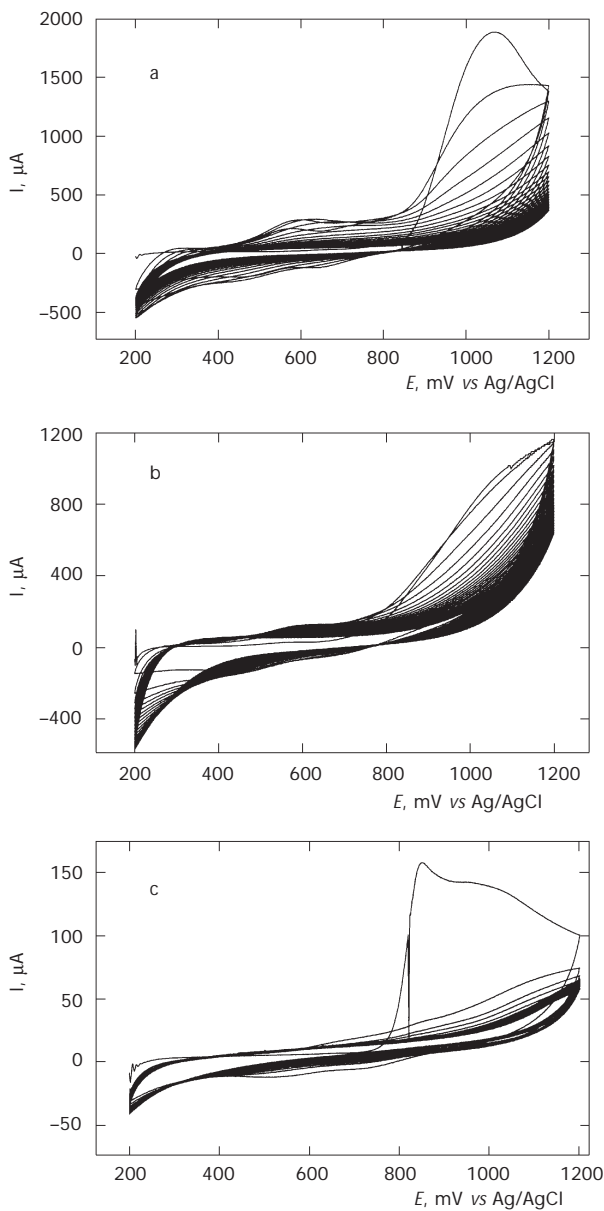
FIG. 2

Electropolymerization of 10^{-3} M tapp metalloporphyrins in 1 M HCl aqueous solution on a SnO$_2$:F electrode by cyclic voltammetry. Scan rate 50 mV s^{-1}, 25 voltammetric cycles. a Cu-2-tapp, b Ni-2-tapp, c Ni-4-tapp (monomers)

ied, including the free ligands. The latter wave can be attributed to a porphyrin anodic response. Although, in the case of the Ni complexes, there are also reports about "hybrid" redox couples involving metal and ligand[11].

The morphologies of the ortho and para Cu polymers can be seen in Fig. 3 as the AFM images (in contact mode). The ortho polymers (Fig. 3a) form

TABLE I
The final charge density after the electropolymerization

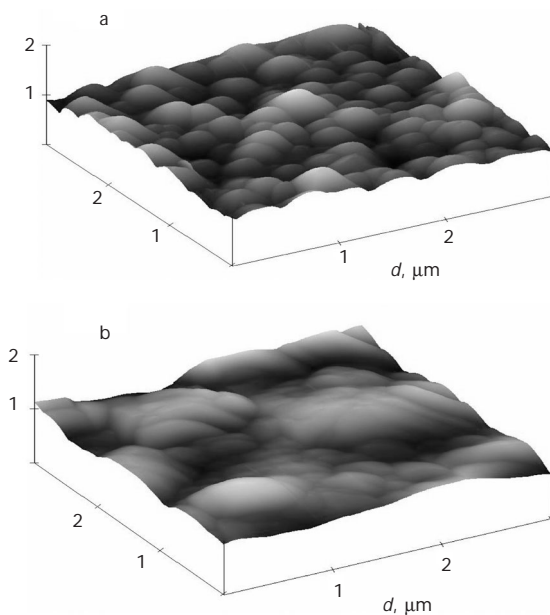| Polymer	σ, μC cm^{-2}
Poly-Cu-2-tapp	6818
Poly-Cu-4-tapp	5743
Poly-Ni-2-tapp	11683
Poly-Ni-4-tapp	1064
Poly-H$_2$-2-tapp	455
Poly-H$_2$-4-tapp	2795

FIG. 3
AFM 3D-image of a SnO$_2$:F/poly-Cu-2-tapp and b SnO$_2$:F/poly-Cu-4-tapp

globular structures that grow in the interstices of the surface. Similar images have been obtained for the Ni and free-base ligand with the substituents in the same position. However, the complexes and the free ligand with the substituent in the para position form smoother films, without defined globular structures that practically cover the surface of the electrode (Fig. 3b). These results are in accordance with the evolution of the electropolymerization charge. In the former case a more regular surface coverage is obtained. The similarities in morphology among the polymers that have the amino substituent in the same position could indicate a similar pattern in the way of polymerization depending on the position of the amino groups. However, the kinetics of the process may be very different because of the change in the charge obtained for the same number of potentiodynamic cycles.

All the modified electrodes are very stable when exposed to air and visible light, and are conductive, as previously verified[8]. The modified electrodes present big charge in comparison with the conducting glass (except for poly-Ni-4-tapp), indicating that the polymers are capacitor-like systems that contain electrolyte between the inner layers.

Figure 4 shows differences in electronic spectra of the complexes in solution and electropolymerized ones. The complexes were dissolved in 1 M HCl where they are very soluble; the electropolymerized systems are in 5×10^{-1} M perchloric acid in order to obtain similar pH and prevent dissolution of the films. In the case of the complexes in solution, the UV-VIS spectra correspond to typical "etio-type porphyrins" according to the Stern definition[12]. They exhibit an intense Soret band near 400 nm corresponding to the allowed transition $^1A_{1g} \rightarrow {}^1E'_u$, and two quasi-forbidden Q bands. The spectra correspond to metalloporphyrins, M-tapp, having D_4h symmetry. Accordingly, etio-type metalloporphyrins present two Q bands: band I and its vibrational satellite-band, II. When polymerized, the relationship between the intensity of the Soret and Q bands, S/Q, decreases, because Soret band becomes diminished and Q bands ("ill-defined") rise. Q bands appear as wide, non-defined transitions but present two zones of higher intensity positioned in the same region as the original Q bands. The Soret band decreases its intensity but widens. Also, its maximum shifts to the red. These changes can be attributed to the polymerization because similar patterns are obtained when phthalocyanines are polymerized[13]. In those cases, the Soret band also shifts to lower energies and the Q band (only a single Q band in the case of phthalocyanines) widens and decreases in intensity.

Application to Nitrite Reduction

The voltammetric responses of the bare conducting glass and the modified poly-Cu-2-tapp with and without nitrite in the solution are shown in Fig. 5. In the case of the bare conducting glass, there is no reduction process. However, the profile of the modified electrode changes drastically when the nitrite is in the solution. The pronounced quasi-reversible peak, which
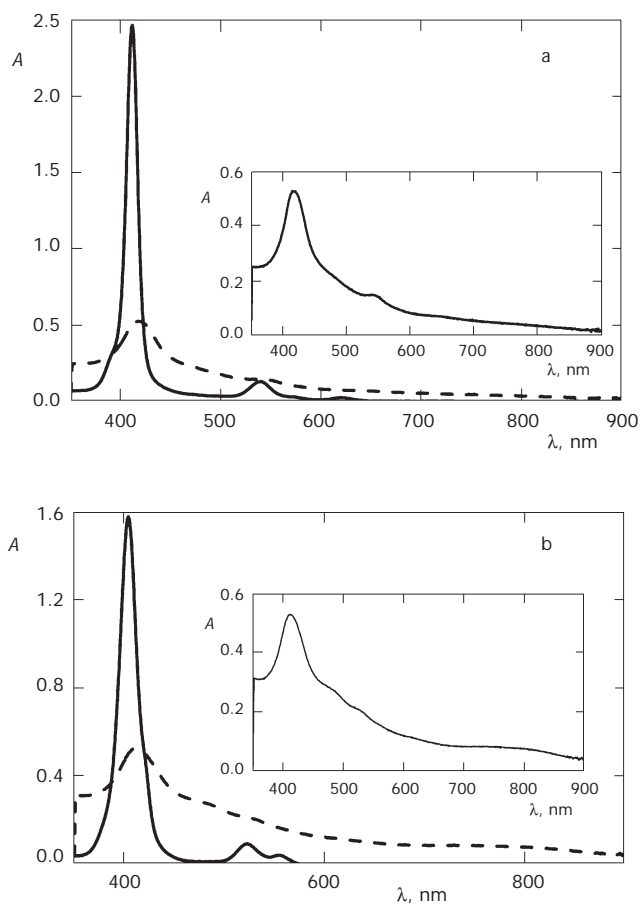

FIG. 4

UV-VIS spectra at open circuit potential of: a 1×10^{-4} M Cu-2-tapp (monomer) dissolved in 1 M HCl (full line) and SnO_2:F/poly-Cu-2-tapp in 5×10^{-1} M $HClO_4$ (dashed line). Inset: UV-VIS spectrum of SnO_2:F/poly-Cu-2-tapp in 5×10^{-1} M $HClO_4$. b 1×10^{-4} M Ni-2-tapp (monomer) dissolved in 1 M HCl (full line) and SnO_2:F/poly-Ni-2-tapp in 5×10^{-1} M $HClO_4$ (dashed line). Inset: UV-VIS spectrum of SnO_2:F/poly-Ni-2-tapp in 5×10^{-1} M $HClO_4$

appears at *ca* 0 V in the absence of nitrite, disappears when nitrite is added. Also, the charge decreases in the presence of the ion. However, a current discharge that begins at *ca* 0 V, corresponding to the reduction of nitrite, indicates that the polymer is not completely inhibited. Normally, the electroreduction of nitrite and nitrate requires low scan rates to be enhanced. Probably, the scan rate used herein is excessive to allow the recovery of all the active sites. For that reason, the charge becomes diminished and the redox couple at 0 V disappears. Figure 6 depicts the polarization curves for all the studied systems. It is noticeable that the cathodic current begins at very similar potentials for all the cases. However, the current and redox behavior are very different, depending on the metal centre and the position of the amino substituent. The highest reduction currents originate when the amino groups occupy the ortho position in the Cu complex. In the Ni case, the situation changes. At more positive potentials, the poly-Ni-4-tapp is better but this situation changes when the potential is shifted more negatively. Poly-Ni-2-tapp then becomes a better catalyst. For the free ligands, the ortho and para polymers show a similar behavior but at negative potentials, the para system becomes better. Comparing the current of the six modified electrodes at –100 mV (Table II), it is clear that the poly-Cu-2-tapp is the most active electrode.

It is noteworthy that except the case of the polymerized free ligands, the position of the amino groups drastically modified the catalytic behavior of
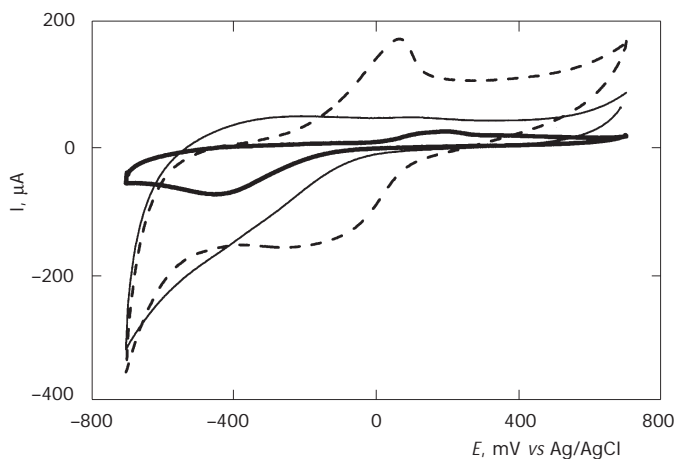

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Voltammetric response of the bare conducting glass in the presence of 1×10^{-1} M nitrite in 1×10^{-1} M NaClO$_4$ (thick line), and of the modified SnO$_2$:F/poly-Cu-2-tapp with (full line) and without (dashed line) 1×10^{-1} M nitrite in 1×10^{-1} M NaClO$_4$. Scan rate 100 mV s^{-1}
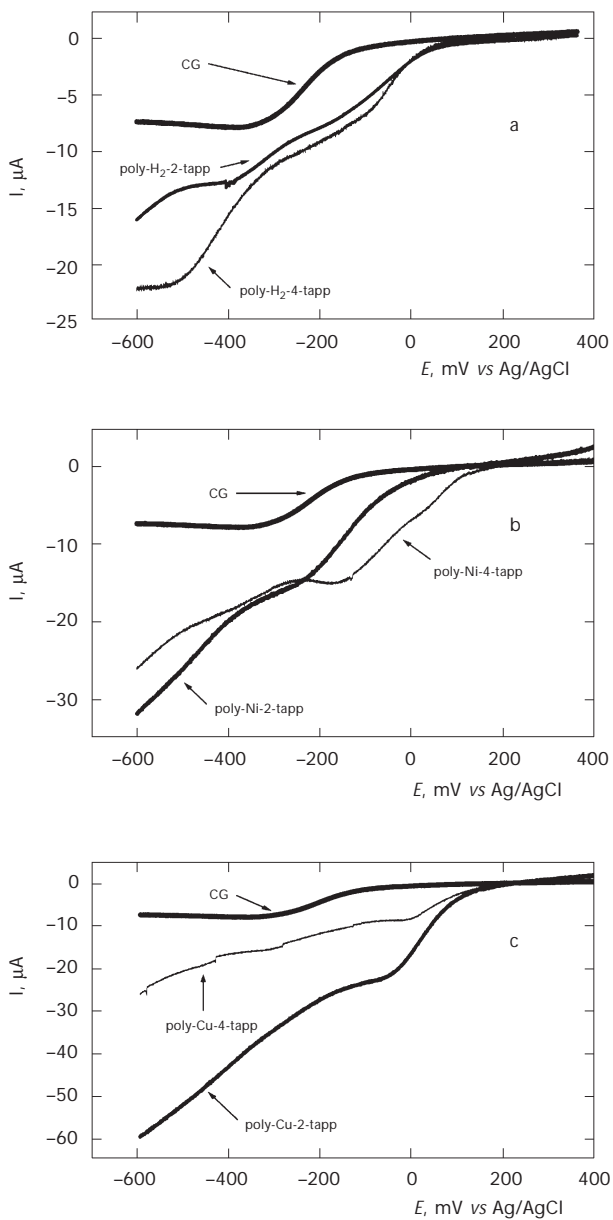
FIG. 6
Polarization curves of SnO_2:F/polymeric-tapp electrodes in the presence of 1×10^{-1} M nitrite in 1×10^{-1} M $NaClO_4$. Scan rate 5 mV s^{-1}

the films. However, there is no common pattern, as the poly-Cu-2-tapp is 2.5 times more active than the poly-Cu-4-tapp, while in the case of the Ni sytems, the para film is better than the ortho film in terms of current. However, this change can be attributed to the different quantity of active sites in these cases. In order to obtain a kind of comparison, in Table III, we present the cathodic current at a constant potential divided by the charge density of the film.

From the results in Table III it is ratified that there is no common pattern for the ortho and para systems. The catalytic effect changes from this new point of view because now the best catalysts are poly-Ni-4-tapp and poly-H_2-2-tapp. However, it is possible than only the active sites in the outer layers of the polymeric films react with the nitrite and the compari-

TABLE II
Comparison of the modified electrodes

Polymer	I, μA^a
Poly-Cu-2-tapp	21.8
Poly-Cu-4-tapp	8.2
Poly-Ni-2-tapp	5.8
Poly-Ni-4-tapp	12.6
Poly-H_2-2-tapp	6.1
Poly-H_2-4-tapp	7.1

[a] E = –100 mV *vs* Ag/AgCl.

TABLE III
Comparision of the modified electrodes at constant potential

Polymer	I, μA /σ, μC cm^{-2}
Poly-Cu-2-tapp	3.2×10^{-3}
Poly-Cu-4-tapp	1.4×10^{-3}
Poly-Ni-2-tapp	4.9×10^{-4}
Poly-Ni-4-tapp	1.2×10^{-2}
Poly-H_2-2-tapp	1.3×10^{-2}
Poly-H_2-4-tapp	2.5×10^{-3}

son between current and thickness (measured as charge) has no sense. In order to elucidate this matter, electrochemical impedance spectroscopic measurements are in progress.

The influence of the potential scan rate on the reduction process is shown in Fig. 7. Three different scan rates are compared, *viz.* 0.005, 0.05 and 0.1 V s^{-1}. The voltammetric responses for the nitrite reduction depend in all cases on the scan rate. The process is favored in some cases at 0.05 V s^{-1}, because although the currents are very similar at 0.05 and 0.1 V s^{-1}, the reduction wave begins at lower potentials at 0.05 V s^{-1}. For poly-Cu-2-tapp
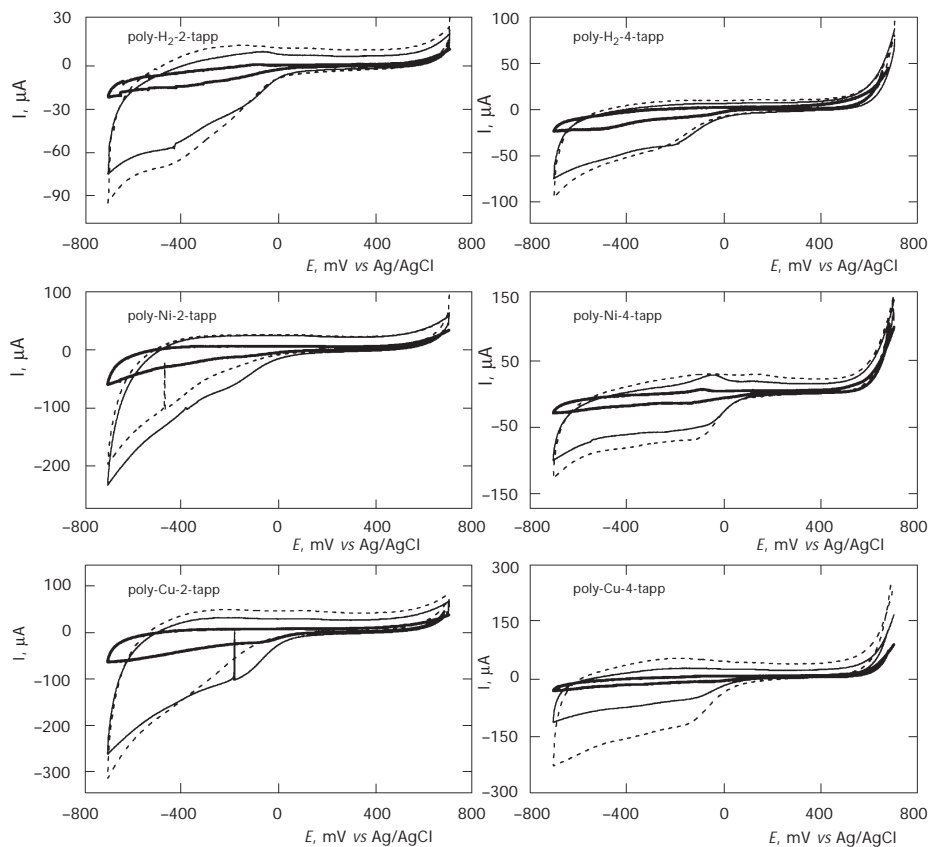

FIG. 7
Voltammetric response (first cycle) at three different scan rates: 100 (dashed line), 50 (full line) and 5 (thick line) mV s^{-1} of SnO$_2$:F/polymeric-tapp electrodes in the presence of 1×10^{-1} M nitrite in 1×10^{-1} M NaClO$_4$

there is a potential shift of almost 100 mV and for poly-Ni-2-tapp, 50 mV. The current is higher at 0.05 V s^{-1}. For the other systems the current and potential at the two scan rates (0.05 and 0.1 V s^{-1}) are very similar, except for poly-Cu-4-tapp where the current is higher at 0.1 V s^{-1}. In general, the current of a voltammetric wave increases with the scan rate. In our case this is not observed, except for the last system. An explanation for this behavior is the slowness of the reduction process. If an intermediate is generated, which blocks the active site for a long time, the film will not react as expected when the scan rate is increased.

CONCLUSIONS

This study presents new examples of modified electrodes prepared by immobilization of porphyrins and metalloporphyrins, *viz.* tetrakis(x-amino-phenyl)porphyrin (where x = 2 or 4), and their Cu(II) and Ni(II) complexes, in electropolymerized films. Different types of films are originated, depending on the position of the amino substituent. The morphological characteristics are independent of the metal centre. The amino groups in the same position give the same behavior. Para polymers form smooth films that cover the electrodic surface, while ortho polymers form globular films that grow in the interstices of the surface defects. The electrocatalytic activity for the nitrite reduction depends both on the amino substituent position and the nature of metal centre. However, from these results we can hardly suggest a possible nitrite reduction route and further experiments are necessary. In this way, controlled potential electrolyses and electrochemical impedance spectroscopic measurements are in progress.

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