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Electrochemical Modification of Graphite Electrodes with Poly(4-aminophenol)

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Summary: It was observed the formation of polymeric films derived from 4-aminophenol on the graphite electrode in aqueous medium (pH 0.5, 8.0 and 12.0). The electrochemical behavior of formed films was studied by voltammetry cyclic and impedance. These analyses indicate that the preparation in acid medium favors the charge transfer rate of the polymer. Polymers formed at pH 8.0 present higher coverage of the electrode surface and impedance increase. Scanning electron microscopy showed that the formed polymer present globular morphology.

Keywords: 4-aminophenol; coatings; cyclic voltammetry; electropolymerization; films

Introduction

Electrochemical methods are a powerful tool for surface modification, substrate cleaning, films formation and bulk material.[1] These methods are widely preferred because they are not aggressive to the environment. They show high reproducibility, simple methodology and can be used at ambient temperature. They present great efficiency on the coating of conducting and non-conducting polymers with precise electrochemical control of their formation rate and thickness.[1–3]

Polymers are being discarded for their traditional roles as electric insulators to literally take charge as conductors with a range of novel applications.[4]

The conductivity of conducting polymers is influenced by various factors, including polaron length, conjugation length, overall length and the charge transfer to adjacent molecules.[4,5] They can be classified as redox polymers, electronically conducting polymer (organic metals) and ion exchange polymers.[6] The main interest in this area is related with the wide range of possible applications of modified electrodes in electrocatalysis,[7–9] electrochromic devices[10,11] photoelectrochemistry,[12] sensors,[13,14] ion gate membrane for controlled release of anionic drugs[15] and others.

Non-conducting polymers present high resistivity, growth self-limited, being therefore permselectives. They are useful in preventing interfering species from approaching of the electrode surface. In addition, its use for sensors presents high sensitivity, fast response time and good reproducibility because of the ultra-thin non-conducting film used.[2]

The use of non-conducting polymers of phenol and its derivatives for the development of biosensors has been reported.[2,16,17] The electropolymerized films of phenol are produced by ortho- or para-coupling of phenolate radicals generated by oxidation of the phenolate anion. Subsequent reactions produce oligomers and finally, poly(phenylene oxide) films are polymerized on the surface of the electrode.[2]

Studies[18–20] about the formation of polymeric films indicate that monomers

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containing aromatic groups bounded directly to oxygen atom presents ease in the polymerization, high mechanic resistance of the formed film providing greater stability to the modified electrode.

Aminophenols are interesting electrochemical materials since, unlike aniline[21] and other substituted anilines[22,23], they have two groups (–NH_2 and –OH), which could be oxidized. Therefore, they could show electrochemical behavior resembling anilines[21] or phenols.[24,25]

Recent study[26] suggest that the electrooxidation of 4-aminophenol involve the uptake of two electrons and two protons, producing a quinoneimine; in the next step, quinoneimine suffers hydrolysis, producing *p*-benzoquinone. Also, these authors suggests that the secondary chemical reactions between *p*-benzoquinone and 4-aminophenol becomes increasingly important as the pH value is increased, making possible the occurrence of 1,4-coupling reactions and film generation on the electrode surface upon the electrooxidation of 4-aminophenol.

Various studies do not mention the detection of polymeric material derived from 4-aminophenol on electrodes of mercury drop,[27] gold[28] and platinum,[29] however, reaction conditions can affect film formation.[23,30]

Alteration of the medium pH affects the electropolymerization due to the differences in the protonation of the OH and NH_2 groups giving different polymeric films on the electrodes surfaces indicated by optical and electrochemical analyses.[31]

In the present work was investigated the electropolymerization of 4-aminophenol on graphite carbon electrodes, the electrochemical behavior of the films produced, the surface morphology of modified electrodes and electrochemical impedance in different pH values.

Materials and Method

The monomer employed for the polymerization reaction was 4-aminophenol 97.5% purchased from Acros Organics. $HClO_4$ solution ($0.5\ mol \cdot L^{-1}$) was used for all experiments and pH adjustment was carried out using NaOH solution. Ultrapure water (18.2 MΩ cm) from the system Milipore-Mili-Q plus, was employed in all experiments.

A three compartment electrochemical cell of 25 mL capacity was used for all electrochemical experiments. The working electrode employed for the electrochemical studies was a graphite disk with 29.7 mm^2 of geometrical area. The auxiliary electrode was a platinum plate. All potentials were measured *versus* a saturated calomel electrode (SCE). The experiments of cyclic voltammetry and impedance measurements were performed on Potentiostat CH Instrument model 420A and an Autolab PGSTAT20 with module FRA (Frequency Response Analyser), respectively. Frequency sweeps extended from 10^{-3} a 10^5 Hz using amplitude wave of 5 mV. Spectroscopy measurements were performed on Shimadzu UV-visible spectrophotometer (model UV-1650PC).

To electropolymerization of poly(4-aminophenol) the experiments were performed at room temperature. The work electrodes were polished with alumine oxide (0.3 μm), before each electrochemical assay. After polishing, the electrode was rinsed with water from a Millipore Milli-Q system. The electrodes were then sonicated in ultrasound bath and rinsed again with water.

The monomer solutions were deoxygenated with N_2 prior to electropolymerization. Poly(4-aminophenol) films were grown by potentiodynamic deposition on graphite electrodes from solution containing 4-aminophenol ($2.5 \times 10^{-3}\ mol \cdot L^{-1}$). $HClO_4$ solution ($0.5\ mol \cdot L^{-1}$) was used for all experiments and pH adjustment was carried out using NaOH solution. The graphite electrode behavior was analyzed in $K_3[Fe(CN)_6]$ ($5.0\ mmol \cdot L^{-1}$)/$K_4[Fe(CN)_6]$ ($5.0\ mmol \cdot L^{-1}$)/KNO_3 ($0.1\ mol \cdot L^{-1}$) solution, and $HClO_4$ solution ($0.1\ mol \cdot L^{-1}$), before and after 4-aminophenol electropolymerization.

The morphology of the poly-4-aminophenol films, in different pH values, was observed by scanning electron microscopy using a LEO 940A Zeiss microscopy.

Results and Discussion

Structural Variations of 4-aminophenol with the Variation of pH Values

The prediction of the structural variations of 4-aminophenol in function of the pH was made using the simulation program of titration curves CurTiPot 3.1 (Figure 1). The pKa values to 4-aminophenol was obtained by according with Linn.[32]

In highly acid media, 4-aminophenol is found on the cathionic form (structure I). With the increase of the pH values occurs the deprotonation of the ammonium group (structure II). When the pH becomes equal to the pK_1 value the concentrations of the protonated and deprotonated forms are equivalents (structures I and II). At pH equal to the isoelectric point ($pH = 7.66$) occurs only the structure II in solution. With the increase of the pH occurs the deprotonation of the phenolic group. At pH equal to the pK_2 value, the equimolar equilibrium phenol/phenoxide is established (structures II and III). In highly basic pH the concentration of the phenoxide ion will increase until its total conversion (structure III).

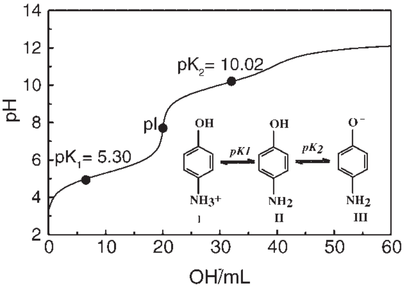

Figure 1.
Simulation of titration curve of 20 mL of 4-aminophenol (50×10^{-3} mol · L^{-1}) with NaOH (50×10^{-3} mol · L^{-1}).

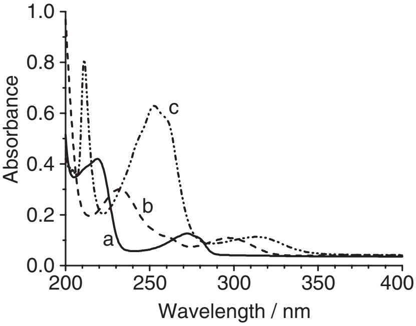

Figure 2.
UV spectra of 4-aminophenol in aqueous solution at pH: (a) 0.4; (b) 8.0; (c) 12.0.

Figure 2 shows the spectra of 4-aminophenol at different pH values.

Due the presence of $-NH_2/NH_3^+$ and $-OH/-O^-$ groups (auxochromes) attached to benzene, occurs alterations in the wavelength and intensity of the absorption spectra. These wavelength values are represented in Table 1.

When 4-aminophenol is converted to the anilinium (structure I, see Figure 1), the pair of nonbonding electrons of the nitrogen is no available for interaction with the π electrons of the ring, and the spectrum is almost identical of phenol, that absorbs in 210.5 and 270 nm.

Conversion of 4-aminophenol (structure II) to the corresponding phenolate anion (structure III) results in a bathochromic shift of the bands and an increase in ε_{max} because the nonbonding electrons in the anion are available for interaction with the π-electron system of the ring.[33]

Poly(4-aminophenol) Film Synthesis and Characterization

The polymerization was done in acid and basic aqueous medium. Strongly adhering

Table 1.
Wavelength values of UV spectra of 4-aminophenol in different pH values.

pH	Wavelength (nm)		Structure
0.4	219	272	I
8.0	232	297	II
12.0	252	312	III

poly(4-aminophenol) films were deposited to the surface of a graphite disk working electrode by cycling between −0.30 V and +1.20V vs. SCE, with 100 potential scans.

The voltammograms of a graphite electrode for 100 cycles in solution of 4-aminophenol is shown in Figure 3.

During continuous potential cycling a gradual increase in current between +0.3 to +0.5 V (pH 0.4) and −0.2 to +0.0 V (pH 8.0) after the first cycle, reflects the covering of the electrode surface by electroactive polymer film.

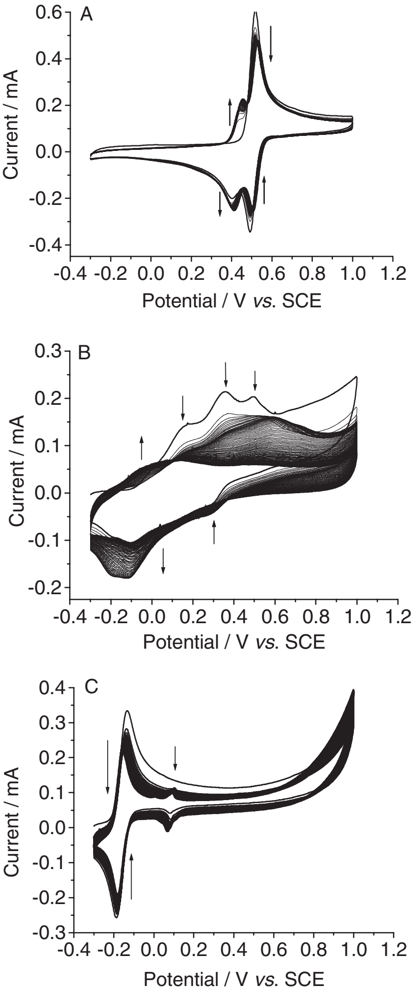

Figure 3.
Potentiodynamic growth of poly(4-aminophenol) (2.5×10^{-3} mol · L^{-1}) in aqueous solution containing 3-aminophenol (2.5×10^{-3} mol · L^{-1}), 50 mV · s^{-1}, 100 scans. (A) pH 0.4 (B) pH 8.0 (C) pH 12.0. The arrows indicate scans increase.

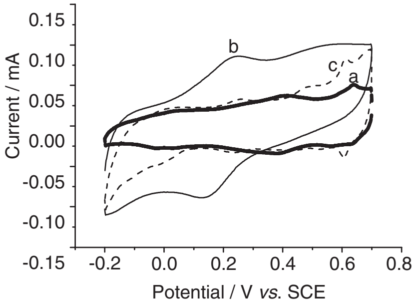

Figure 4.
Cyclic voltammogram of graphite electrode or electrodes modified with poly (4-aminophenol) in 0.5 mol · L^{-1} $HClO_4$ solution, 50 mV^{-1}. Modified electrode at (a) pH 0.4 (b) pH 8.0, (c) pH 12.0.

Figure 4 shows the cyclic voltammograms of graphite electrode coated with poly(4-aminophenol) prepared at pH 0.4, 8.0 and 12.0.

Polymers prepared at pH 0.4 gives four waves: +0.40V and +0.64V (oxidation) and +0.38V and +0.62V (reduction). Films prepared at pH 8.0 presents wave of oxidation in +0.24V and of reduction in +0.14V. In electrode modified prepared at pH 12.0 are observed waves of oxidation in +0.26V, +0.48V and +0.61V, and waves of reduction in 0.0V, +0.23V and +0.60V. The decrease of the redox peaks in basic media is related with the way which the species are present on the solution where the oxidation of the deprotonated phenolic groups tend to form insulating films, as observed on others films.[26,33–36]

The Figure 5 shows the modified electrodes prepared in different pH values in solution containing $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$.

Analysis in redox solution is a parameter used to indirect investigation of the conducting properties of the modified electrode. Figure 5 show that, in low pH values, the deposited film keeps the electron transference similar route of the electrode without modification. However, small potential shifts are observed. With the increase of the pH, occurs decrease on

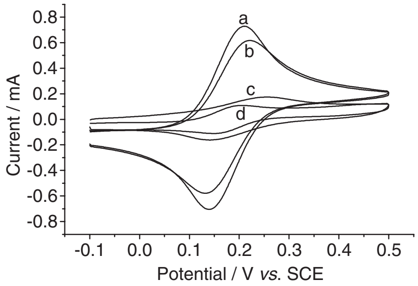

Figure 5.
Cyclic voltammogram of a graphite electrode and a graphite electrode modified with poly(4-aminophenol) in aqueous solution containing $K_3Fe(CN)_6$ (5 mmol · L^{-1}), $K_4Fe(CN)_6$ (5 mmol · L^{-1}) and KNO_3 (0.1 mol · L^{-1}), 100 mV · s^{-1}. (a) bare graphite electrode and modified with poly(4-aminophenol) at (b) pH 0.4; (c) pH 8.0; (d) pH 12.0.

the electronic transference, insulating the electrode surface in basic pH values.

Morphologic Properties

The morphology of the poly(4-aminophenol) film, in different pH values, observed by scanning electron microscopy (Figure 6) shows an irregular polymeric film. The coating presents a globular structure randomly distributed on the electrode surface.

For all pH studied the coating is not capable of filling the graphite cavities, possibly due to the formation of a passiving layer of poly(4-aminophenol).

For pH 8.0 was observed increase of the covering of the area of the modified electrode in relation to others pH, compatible with current increase showed $HClO_4$ solution (Figure 4).

Impedance Analyses

Impedance spectroscopy is an effective method to probe the electron transfer rates from the electrode to the redox active specie in solution.[37] This analysis is shown in Figure 7.

All impedance plots had been constructed of a semicircle with different charge transfer resistance (Rct) and a straight line. This indicates that the electrode reaction of the polymer is under kinetic control at high frequencies and is under mass transfer control at low frequences.[38] Their charge transfer resistance at pH 0.4, 8.0 and 12.0 are 58, 84 and 71 Ω, respectively. The reduction of the electron transfer resistance in acid medium is in agreement with the voltammetric cyclic

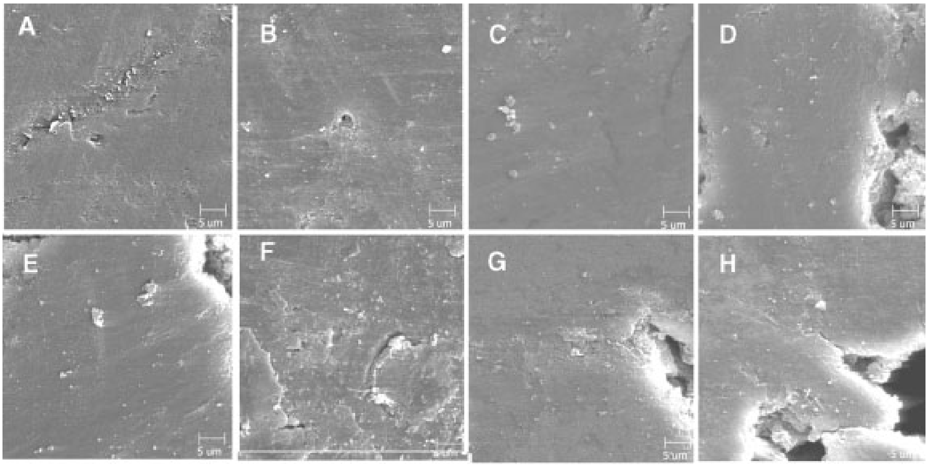

Figure 6.
Scanning electron micrograph of bare graphite electrode (A) and poly(4-aminophenol) modified electrode (B) pH 0.4; (C) pH 2.0; (D) pH 6.0; (E) pH 7.0 (F) pH 8.0 (G) pH 10.0; (H) pH 12.0 Magnification: 2000×.

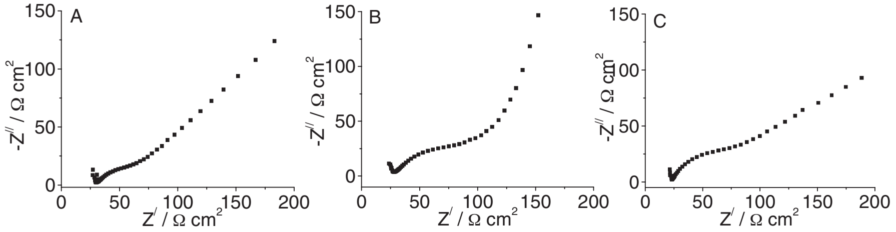

Figure 7.
Nyquist-diagram (Z″ vs. Z′) for the AC impedance measurement in $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple and 0.05 mol · L^{-1} KCl of modified graphite electrode with poly-4-aminophenol in different pH values. (A) 0.4, (B) 8.0, (C) 12.0.

analysis observed in $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple (see Figure 5).

Conclusion

It was observed the formation of the electroinative and electroactive polymeric films derived from 4-aminophenol on the graphite surface in different pH values.

The films formed show reduction in electron transport across the polymeric matrix in $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple.

Surface analyses of polymers prepared at pH 0.4 and 12.0 showed a lesser amount of deposited film, possibly due to the formation of passiving layer that was not enough to fill the graphite cavities. The poly(4-aminophenol) films showed globular morphology in all pH values studied.

The impedance studies indicate that the polymer prepared in acid medium favors lower charge transfer impedances on the surface of modified electrode with poly-4-aminophenol.

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