

Electropolymerization of aniline monomer and effects of synthesis conditions on the characteristics of synthesized polyaniline thin films

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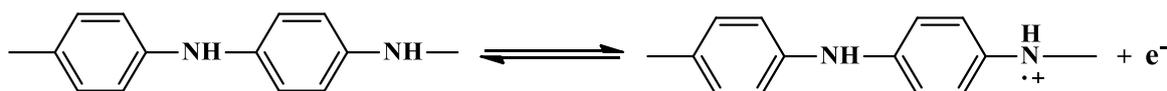
Abstract: Electrochemical polymerization of aniline was carried on platinum (Pt) wire electrode in sulfuric acid (H₂SO₄) solution by cyclic voltammetry using a conventional three-electrode cell at room temperature (20°C). The effects on the electrodeposition of the monomer concentration, anodic potential and potential scan rate are discussed. The conductive layer of emeraldine base polyaniline (Pani) was prepared in this work by repeating potential cycling between -0.24 and 0.9 V/SCE at 50 mV/s in 1 M H₂SO₄ solution containing 0.1 M aniline monomer.

Keywords: Electropolymerization, Polyaniline, Conducting polymer, Cyclic voltammetry.

1. Introduction

The use of conductive polymers has made significant progress in the last few decades due to its various applications in energy storage devices ^{1,2}, biosensors ^{3,4}, electrocatalysts ^{5,6}, etc. Polyaniline (Pani) has been at the leading of the global search for commercially viable conductive polymers due to its unique protonic dopability, excellent redox recyclability, chemical stability, variable electrical conductivity, low cost and facile synthesis ⁷. Therefore, Pani can be used as an electrode material ^{8,9}, corrosion protection of metals ^{10,11}, in the manufacture of secondary batteries ¹², in microelectronics ¹³ and as an electrochromic material ¹⁴⁻¹⁶. Future high-tech applications in the domain of chemical sensors have also been proposed ¹⁷⁻¹⁹. Pani can be prepared by various techniques, namely electrodeposition ^{20,21}, template synthesis ^{22,23}, seeding ²⁴, and interfacial polymerization ²⁵. Electrochemical polymerization also called electropolymerization using for this study is a typical method generally used for the synthesis of Pani coating ^{26,27}. Electropolymerization has many

advantages related to the direct production of polymers in the doped and undoped state ²⁸. This synthesis is performed by anodic oxidation of the monomer on inert electrodes such as platinum, carbon, gold and others ^{29,30}. These polymers can be electrochemically deposited on metal or semiconductor electrodes in film format. The most acceptable start of an electropolymerization mechanism of an aromatic monomer is the formation of a radical cation in two units of the monomer, followed by a dimer formation with the exit of two protons and reconstitution of the aromatic system. The reaction continues with the dimer, and another monomer charged to form a trimer and so on until the polymer is formed. The cyclic voltammograms of Pani deposited on the Pt electrode are characterized by three main pairs of redox peaks. The redox peaks were assigned using the formalism of Pekmez ³¹: The first redox peak appearing between 0.36 V/SCE and 0.45 V/SCE is the oxidation leucoemeraldine oxidation to leucoemeraldine radical cation interpreted by the following reaction:

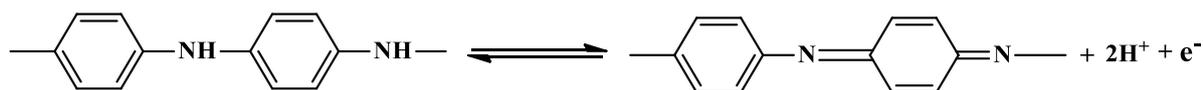


The second redox peak is the emeraldine radical cation to emeraldine and the third redox peak in the range of 0.8 and 1 V/SCE is the transformation of

the cation of the pernigraniline radical to pernigraniline as illustrated by the following reaction:

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The determinant factor for obtaining a polymer with a high degree of conjugation is the equilibrium of the stability of the monomeric radical cation. The electrical and physicochemical properties of the electrosynthesized material depend strongly on the synthesis conditions. In early studies, Rajapakse and co-workers³² reported that polyaniline is non conducting if grown from a medium of pH above 3. Pekmez et al.³³ reported that the optimum monomer concentration is about 100 mM on a Pt surface in acetonitrile + 0.1 M tetrabutylammonium perchlorate solution. Mello Mulato³⁴ reported that the monomer concentrations of 0.2 M represent the optimized case in HCl (1 M) solution on the FTO electrode. Pournaghi-Azar and Habibi³⁵ show that the Pani begin to deposit on the Al electrode in 0.1 M H₂SO₄ in aniline solutions higher than 0.35 M. Babaiee et al.³⁶ reported that aniline fibers with excellent stability and conductivity could be produced on graphite electrode yet, there exists an optimum electropolymerization condition where the scan rate is 25 mV/s, and the switching potential is 1000 mV causing the formation of aniline nanofibers with diameters ranging from 65 to 70 nm and having good electroactive properties. This study aims to investigate the electropolymerization of aniline (Fig.1) by cyclic voltammetry method using Pt wire as a working electrode in H₂SO₄ (1 M) medium. The effects of monomer concentration, anodic potential and potential scan rate are studied.

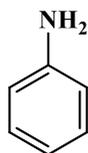


Figure 1. Chemical structure of aniline

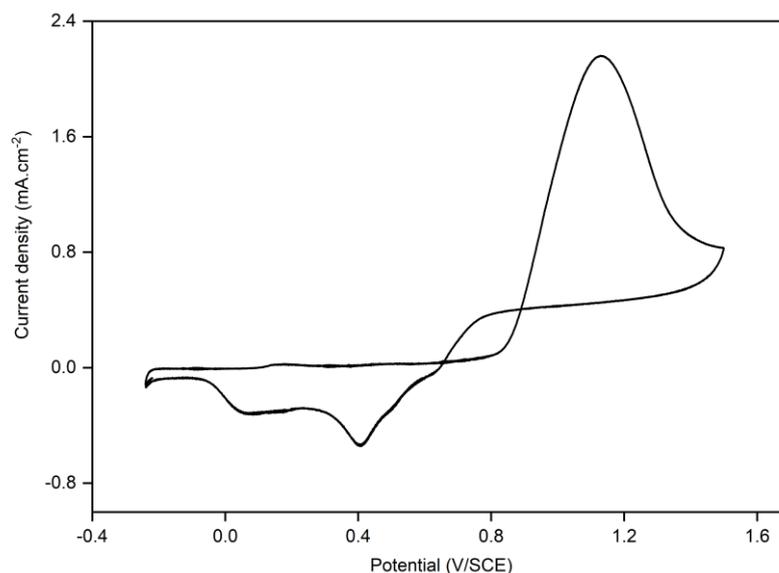


Figure 2. Cyclic voltammogram during electropolymerization of 1 M H₂SO₄ solution containing 0.02 M aniline on the Pt wire electrode at a scan rate of 100 mV/s

2. Experimental

2.1. Materials

Aniline and H₂SO₄ were purchased from Sigma-Aldrich. All chemicals used were analytical grade. The monomer aniline was distilled under reduced pressure and stored in the refrigerator (about 4°C) before use. All aqueous solutions were prepared using double distilled water.

2.2. Electropolymerization of aniline

At first, before each scan the Pt electrode was prepared to ensure a reproducible surface by polishing, rinsing with distilled water and then electrochemically cleaned by cyclic voltammetry in 1 M of H₂SO₄ solution until a reproducible voltammogram was obtained. The electropolymerization of the aniline was performed on a PGZ 301 Potentiostat/ Galvanostat monitored by VoltMaster 4 software with a three-electrode system, containing a Pt wire (0.2 cm²) as the working electrode, a saturated calomel electrode (SCE) as a reference electrode and glassy carbon as a counter electrode. All potentials recorded are referred to this reference electrode. Pani films were prepared on the platinum working electrode by the cyclic voltammetry in 1 M H₂SO₄ solution containing aniline at room temperature (20°C). After the electropolymerization of the aniline, the Pani electrode was repeatedly washed with doubly distilled water.

3. Results and Discussion

3.1. Electropolymerization of aniline on the Pt electrode by cyclic voltammetry

Fig.2 illustrates the first cycle of the voltammogram for a solution of H_2SO_4 1 M, containing 0.02 M aniline monomer on Pt wire electrode, recorded over a potential range of -0.24 to 1.5 V/SCE, at a potential scan rate of 100 mV/s.

The voltammogram is characterized by a very significant increase in the anode current from 0.8 V/SCE corresponding to the oxidation of the

aniline monomer to form the polymer. On the return scan, a reduction wave is observed at about 0.4 V/SCE attributed to the reduction of the aniline formed during its oxidation³⁰.

3.2. Influence of aniline concentration

Fig.3 shows the cyclic voltammograms recorded during the continuous scan over 20 cycles at 50 mV/s potential scan rate between -0.24 and 1.6 V/SCE on Pt wire electrode in H_2SO_4 (1 M) solution containing different concentrations of aniline (0.01, 0.02, 0.05 and 0.1 M).

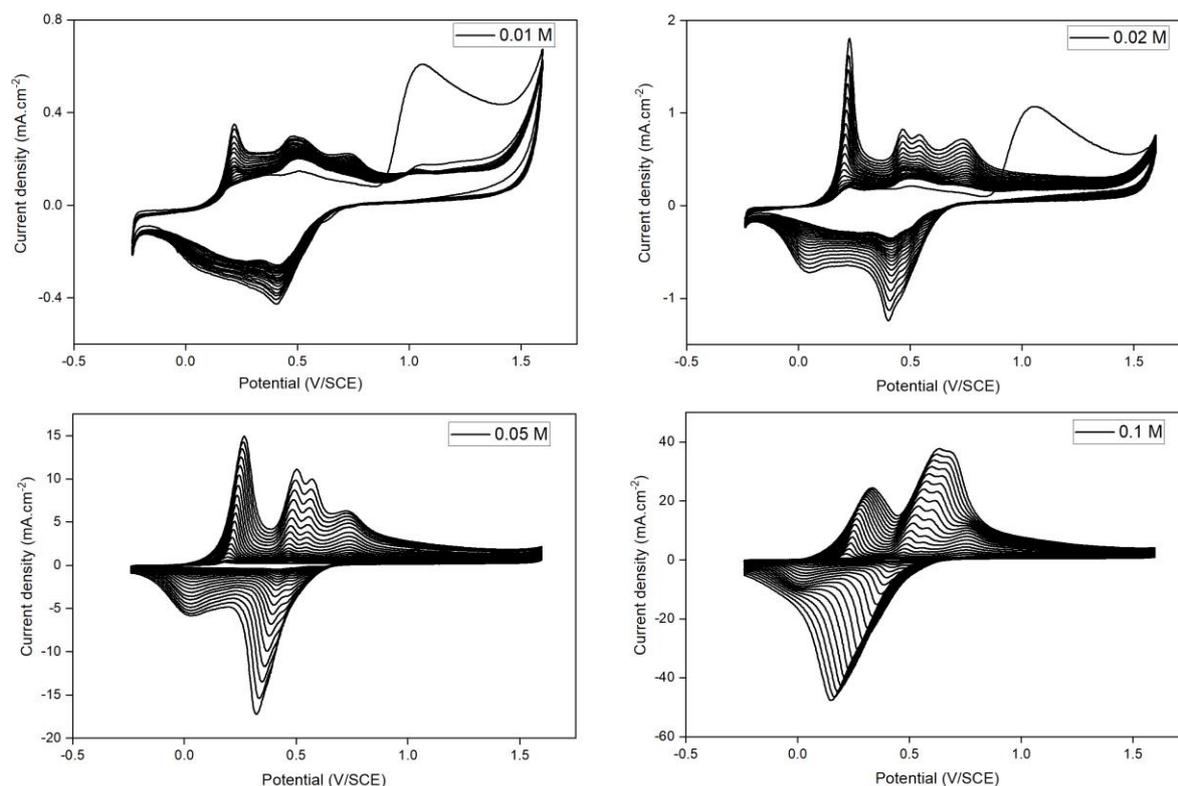


Figure 3. Cyclic voltammograms (20 cycles) of Pani obtained at different concentrations of aniline (0.01, 0.02, 0.05 and 0.1 M) in H_2SO_4 (1 M), recorded in a potential range between -0.24 and 1.6 V/SCE and at a scan rate of 50 mV/s

According to Fig.3, in all cases, as increasing of cyclic voltammograms number, the oxidation peaks shift to the higher potential values, and the reduction peaks shift to the lower potential values with an increase in current density for all peaks. The intensity of the first peak current density at 0.85 V/SCE (oxidation peak of the aniline monomer) decreases and eventually disappears as the number of cycles increases³⁰. The cyclic voltammograms show that the current density increases in each successive cycle, which confirms the electrodeposition of Pani films. By simple comparison between the values of the current densities of the first anodic peak of the 20th cycle, we can see that the polymerization rate increases with the concentration of monomers (for a monomer concentration of 0.01 M, we have $I = 0.35 \text{ mA.cm}^{-2}$, for a concentration of 0.02 M, we have $I = 1.80 \text{ mA.cm}^{-2}$, for a concentration of 0.05 M, we have $I = 14.90 \text{ mA.cm}^{-2}$, while for a

monomer concentration of 0.1 M, we have $I = 24.45 \text{ mA.cm}^{-2}$). Polymerization under cyclic voltammetry conditions provided information about the growth of the film. Oxidation of the monomer began at 0.85 V and eventually disappeared as the number of cycles increases. For the three low aniline concentrations (0.01, 0.02 and 0.05 M), we can see the presence of four redox peaks. The first redox peak at around 0.2 V/SCE corresponded to the first step of oxidation of the species HN-R-NH (R: C_6H_4) in the main chain to a cation radical or polaron system HN-R-NH^+ . The cation radical was then oxidized, practically at the same potential, to the dication or bipolaron $\text{HN}^+=\text{R}=\text{NH}^+$. The middle redox peaks (second and third peaks) at around 0.5 V/SCE are attributed to the oxidation of intermediate compounds or secondary oxidation products. The fourth redox peak observed at around 0.75 V/SCE related to the bipolaron redox^{30,37}. For

the aniline concentration of 0.1 M, we can see the presence of the three first redox peaks mentioned above. The resulting voltammograms indicate that only Pani formed in the medium with the highest aniline concentration (0.1 M) has three identified redox waves with currents associated with redox transitions between these different species significantly higher compared to films made in more diluted monomer solutions^{34,38}.

3.3. Influence of the anodic potential

The electropolymerization of aniline (0.1 M) in H_2SO_4 (1 M) by cyclic voltammetry at a potential scan rate of 50 mV/s on Pt wire electrode for different anode potential values ranging from the same starting potential (-0.24 V/SCE) to gradually increased anode return potentials, is shown in Fig.4.

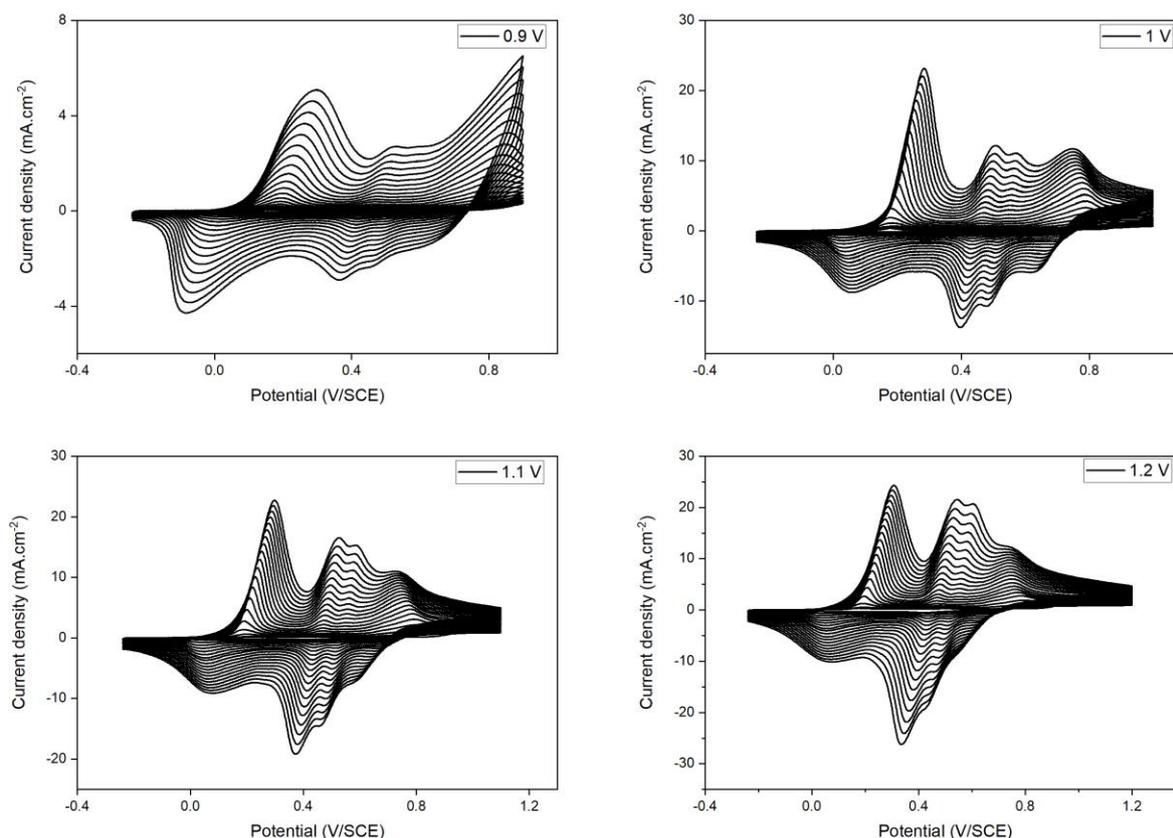


Figure 4. Cyclic voltammograms (20 cycles) during electropolymerization of aniline on the Pt wire electrode in 1 M H_2SO_4 solution containing 0.1 M aniline at a scan rate of 50 mV/s

As illustrated in Fig.4, for the four cases, the oxidation peaks shift to the anodic direction, and the reduction peaks shift to the cathodic direction with an increase in current density for all anodic peaks with the increase of the number of cycles. The electrochemical behaviour indicates that the conductive polymer is formed and that a polymer deposit is visible. The anodic return potential has a significant influence on the electrochemical stability of Pani films. In the case of a minimum return potential of 0.9 V/SCE, only one pair of redox peaks are present in the cyclic voltammograms corresponding to the transition value of leucoemeraldine. For the three return potential

voltammograms of 1, 1.1 and 1.2 V/SCE have four pairs of redox peaks that appear to be more marked in cyclic voltammograms (i.e. other forms of aniline that are less conductive). During the oxidation process, the aniline monomer exhibits an electrochromic behaviour, being yellow at low potential value and passing through green and blue to black at higher potentials³⁹⁻⁴¹.

3.4. Influence of the potential scan rate

We plotted the cyclic voltammograms of a 1 M H_2SO_4 solution containing 0.1 M aniline, recorded in a potential range of -0.24 to 0.9 V/SCE for different potential scan rate from 10 to 100 mV/s (Fig.5).

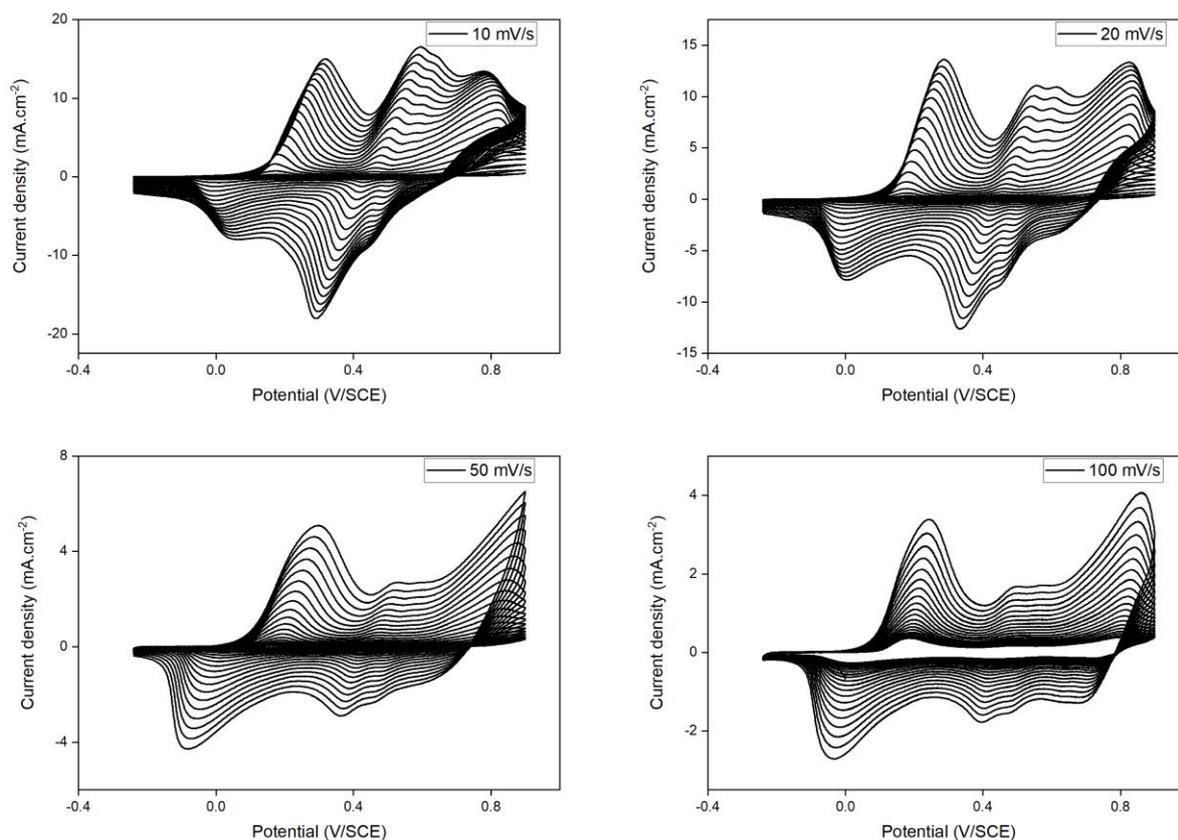


Figure 5. Cyclic voltammograms (20 cycles) during electropolymerization of aniline on the Pt wire electrode in 1 M H₂SO₄ solution containing 0.1 M aniline at different potential scan rate (from 10 to 100 mV/s)

As the scan rate increases, the oxidation peaks shift slightly to a more positive potential, while the reduction peaks shift to a more negative potential. For the potential scan rate of 50 mV/s only one pair of redox peaks is present in the cyclic voltammograms corresponding to the oxidation of

leucoemeraldine to emeraldine. On the other hand, the other scans rates (10, 20 and 100 mV/s) have three pairs of redox peaks, i.e. other forms of less conductive aniline. It can be seen that the current density of the oxidation peaks decreases with increasing potential scan rate⁴².

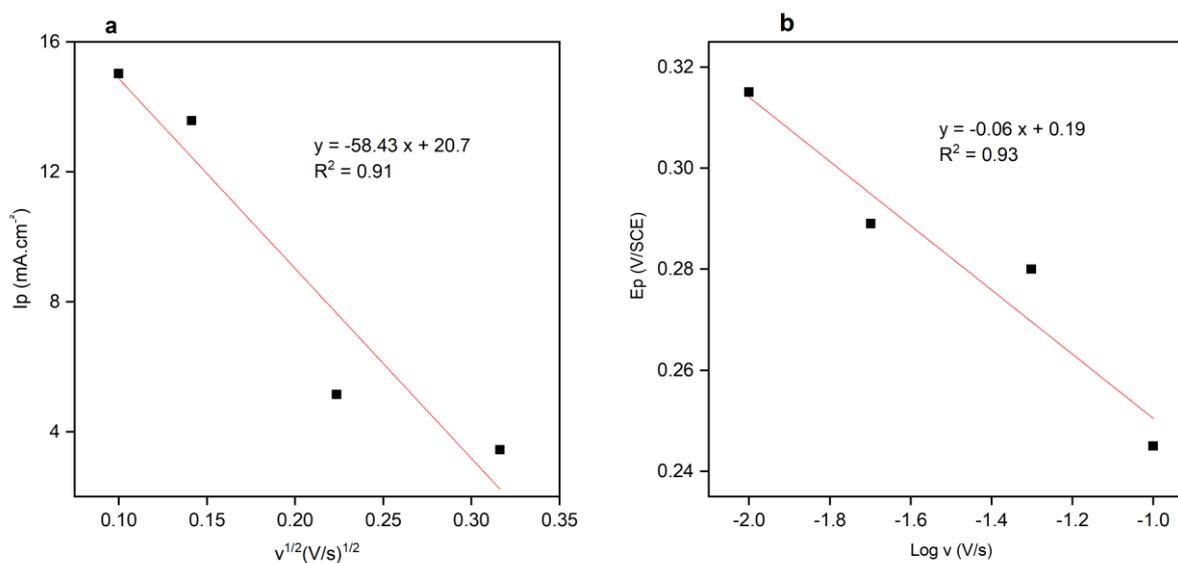


Figure 6. a-Dependence of the oxidation peak current on the square root of the potential scan rate. b- Dependence of the oxidation peak potential on log potential scan rate

The linear variation of the anode current peak (last cycles) with the square root of the potential scan rate (Fig.6a) shows that the electrochemical reaction at the electrode-electrolyte interface is controlled by the diffusion process. On the other hand, there is a significant increase in the difference between the oxidation peak potential and the reduction peak potential associated with a given redox couple when the potential scan rate increases. This reflects a slight decrease in the reversibility of redox couples for highest potential scans rates (Fig.6b).

3.5. Study of the Pani films in H₂SO₄

Pani films were prepared on the Pt wire working electrode by the cyclic voltammetry within the

potential of -0.24 V/SCE to 0.9 V/SCE for 10 cycles in a solution containing 0.1 M aniline and 1 M sulfuric acid. Moreover, the potential scan rate of electropolymerization was set at 50 mV/s. After the electropolymerization of the aniline, the electrodeposited Pani electrode is cleaned several times with deionized water to remove the rest of the aniline solution and then activated in an H₂SO₄ solution, then we plotted the cyclic voltammograms of Pani modified electrode in a 1 M H₂SO₄ solution without aniline, recorded in a potential range of -0.24 to 1.0 V/SCE at a potential scan rate of 10 mV/s (Fig.7).

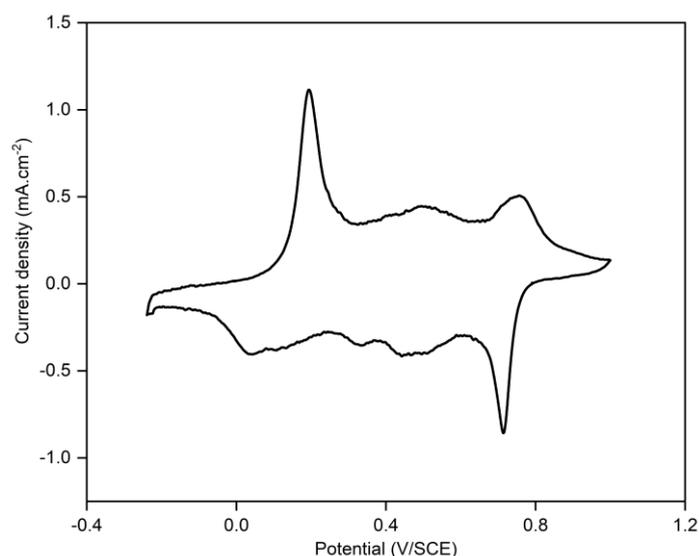


Figure 7. Cyclic voltammogram at Pt wire electrode modified with a Pani film in 1 M H₂SO₄ solution, obtained at a potential scan rate of 10 mV/s and between -0.24 and 1 V/SCE

The electrode modified by a Pani film placed in H₂SO₄ solution without monomer has the same electrochemical behavior as that observed in H₂SO₄ solution in the presence of monomer at the end of electroplating. The major features of this curve are the appearance of two pairs of peaks corresponding to the oxidation-reduction transitions of polyaniline, namely the transition from leucoemeraldine to emeraldine and from emeraldine to pernigraniline⁴³. The peaks in the middle are caused by degradation products. These peaks are attributed to the presence of phenazine cycles. The formation of phenazine structures in the polymer is attributed to the electropolymerization of high potential aniline, which is related to the reaction of aniline nitrenium cations in ortho position on another ring or to crosslinking between two Pani chains⁴⁴.

4. Conclusion

Pani films were electrochemically deposited by cyclic voltammetry of Pt wire electrode in H₂SO₄ solution contains aniline with varying aniline concentration, anodic potential and potential scan rate. Aniline electropolymerization results show that

the rate of polymerization increases with increasing monomer concentration. The aniline concentration of 0.1 M, has three identified first redox waves with significantly higher currents densities for redox reactions between these different species for films produced in more dilute monomer solutions. The voltammograms of the anodic return potential of 0.9 V/SCE and the potential scan rate of 50 mV/s, have a single redox peak, corresponding to the oxidation of leucoemeraldine to emeraldine conductive layer of Pani. A linear relationship between the density of current and the square root of the potential scan rate was observed, which indicates that the electrochemical reaction at the electrode-electrolyte interface is controlled by the diffusion process.

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