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Electrodeposition and Characterization of Polyaniline on Stainless Steel Surface via Cyclic, Convolutive Voltammetry and SEM in Aqueous Acidic Solutions

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The electrodeposition of polyaniline on stainless steel electrode was carried out in aqueous media at two different concentrations of sulphuric acid under potentiodynamic conditions. It was found that the nature of the voltammograms in 0.5M and 1M of H_2SO_4 are simillar. The first voltammetric wave (A_1 & C_1) of the cyclic voltammograms corresponding to transition from leucoemaraldine (LE) state to emeraldine (EM) state. The deposited films were characterized electrochemically and microscopically. The deposition of polyaniline appears to occur over the passive metal oxide film and the electron transfer between the polymer and the metal occur. Polyaniline films on stainless steel appear to be promising for metal anodic protection in corrosive aqueous media. The electrochemical parameters of the electrodeposited polyaniline were determined using cyclic voltammetry, convolution- deconvolution transforms and derived chronoamperograms.

Keywords: Electrodeposition; polyaniline; stainless electrode; convolution – deconvolution transform; SEM.

1. INTRODUCTION

Polyaniline *(PANI*) is one of the most intensively investigated conducting polymers due to its excellent environmental stability, ease of synthesis, and relatively high level of electrical conductivity[1– 4]. *PANI* has been widely studied for potential applications in many domains such as electrochromic devices, rechargeable batteries, electromagnetic interference shielding, and sensors [5,6]. Nanostructure *PANI* carries many specific physical and chemical properties, such as specific light absorption, catalytic and magnetic properties due to the surface, quantum and macroscopic quantum tunneling influences [7-9].

Although polyaniline is the most widely studied conductive polymer and is readily formed in aqueous solutions on various substrates (mainly inert metals and semiconductors), it is used less for the formation of protective coatings on oxidizable metals [10 - 13]. Certainly, aniline electropolymerization is more feasible in acidic aqueous solutions where, however, these metals are highly corroded.

Polyaniline (*PANI*) has different oxidation states, the most stable one is called emeraldine. Usually aniline is polymerised using strong inorganic [14,15] and organic acids [16]. *PANI* has been shown to protect SSs both when prepared with a dopant [17] and when undoped [18].

In this work, we explain the electrodeposion of *PANI* on 304 stainless steel from two different concentrations of sulphuric acid solutions; the deposited films are investigated by using varying techniques. The electrochemical parameters and the electrode behavior of the electrodeposited films were extracted experimentally via cyclic voltammetry and convolution – deconvolution transforms methods**.**

2. EXPERIMENTAL

Aniline (BDH) was distilled before use. We used grade reagents of sulphuric acid (Fluka) for electropolymerisation and other measurements. Electrochemical experiments were conducted in a single compartment three electrode cells with 304 stainless steel rods as the working electrode. We used a platinum sheet as a counter-electrode and the reference electrode was Ag/AgCl (3 mol dm^{-3} KCl). Before each experiment, the working electrode was polished with wet emery papers of different grit sizes (180, 400, 800, 1000 and 1500). After polishing, the working electrode was washed with doubly distilled water and acetone before immersion in test solution. *PANI* was electrochemically synthesized from aqueous acidic solution containing aniline monomer by cycling the working electrode potential between −0.18 and 1 V. The thickness of the polymer layer was estimated from the amount of charge, Q, necessary to switch from the leucoemeraldine (LE), the reduced form of *PANI*, to the emeraldine (EM), the oxidised form of *PANI*. The charge of the final voltammogram during the deposition was taken as a measure of the thickness of *PANI*. The thickness of polymer layer was calculated from the equation:

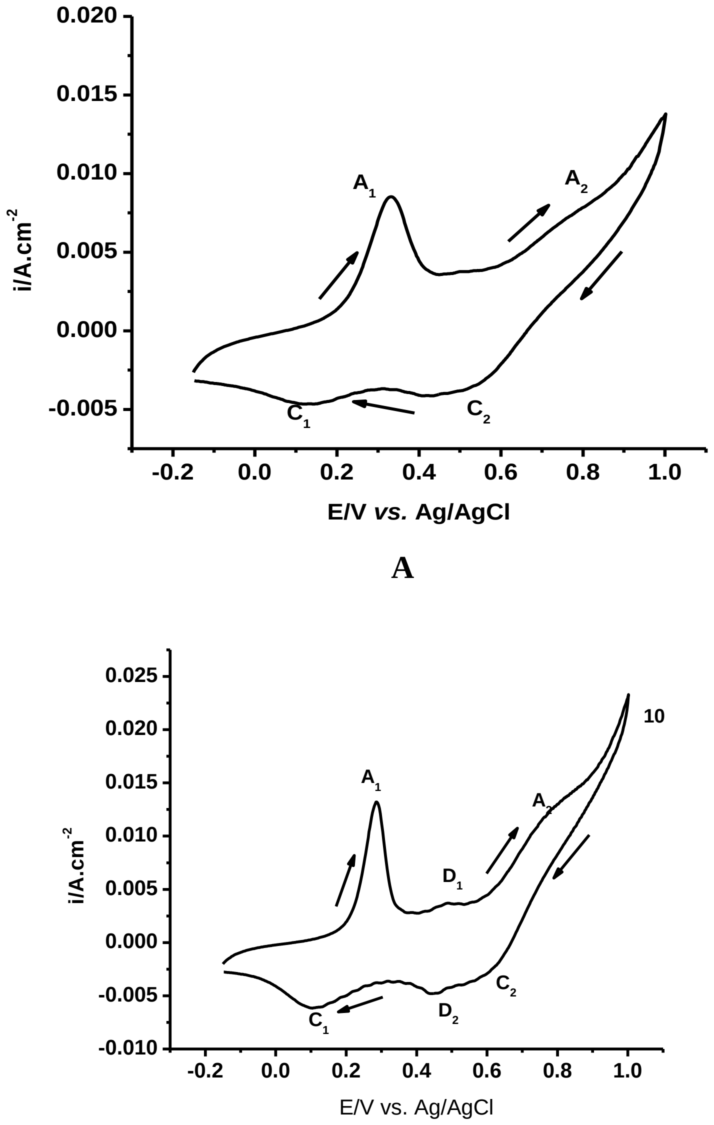
$$d = QMw / zFA\rho \qquad (1)$$

where Q is the charge; Mw is the molecular weight of monomer; z is the number of electrons/monomer unit; A is the area of the electrode; ρ is the specific density of monomer; F is Faraday’s constant. The underlying steel surfaces were investigated after peeling off the polymer layer with a tape paste, washed with redistilled water, and finally rinsed with acetone in ultrasonic bath. Electropolymerisation and electrochemical characterizations were carried out using the computerised Autolab PGSTAT 30 electrochemical instrument with GPES software. Scanning electron microscope (SEM) images were obtained by using Joel JSM-6360LVSEM. Convolution – deconvolution transforms of the data for cyclic voltammetric experiments was performed using EG & G condesim software package. Algorithms for the program were coded and implemented into the condesim software package supplied by EG & G.

All working solutions were thoroughly degassed with oxygen free nitrogen and a nitrogen atmosphere was maintained above the solution throughout the experiments.

3. RESULTS AND DISCUSSION

3.1. Electrodeposition of polyaniline



A

B

Figure 1. 10th cyclic voltammetry for electrodeposition of *PANI* from 0.5M H_2SO_4 (A) and from 1M H_2SO_4 (B) .

The electrooxidation of aniline leading to polymerization follows a two electron transfer process

$$x\text{-ph} - \mathrm{NH_2} \rightarrow (\mathrm{Ph} - \mathrm{NH})x + 2x\,\mathrm{H}^+ + 2x\,\mathrm{e}^- \qquad (2)$$

Although many electrochemical methods are suitable for nucleation and growth of *PANI* on inert electrodes, cyclic voltammetry produces uniform and compact *PANI* layers [19]. Here, *PANI* is electrodeposited onto a SS surface from H_2SO_4 solution using two concentrations of 0.5 M H_2SO_4 and 1M H_2SO_4 aqueous acidic solutions containing 1M aniline. It was found that in case of 0.5 M H_2SO_4 solution the cyclic voltammogram of polyaniline exhibits two oxidative peaks (A_1 & A_2) coupled with two reductive peaks (C_1 and C_2) associated with two ill defined peaks D_1 and D_2 (Fig.1 A) while in case of 1M H_2SO_4 acid solution the cyclic voltammograms exhibits the growth of two ill defined intermediate peaks (D_1 & D_2) (Fig. 1B).

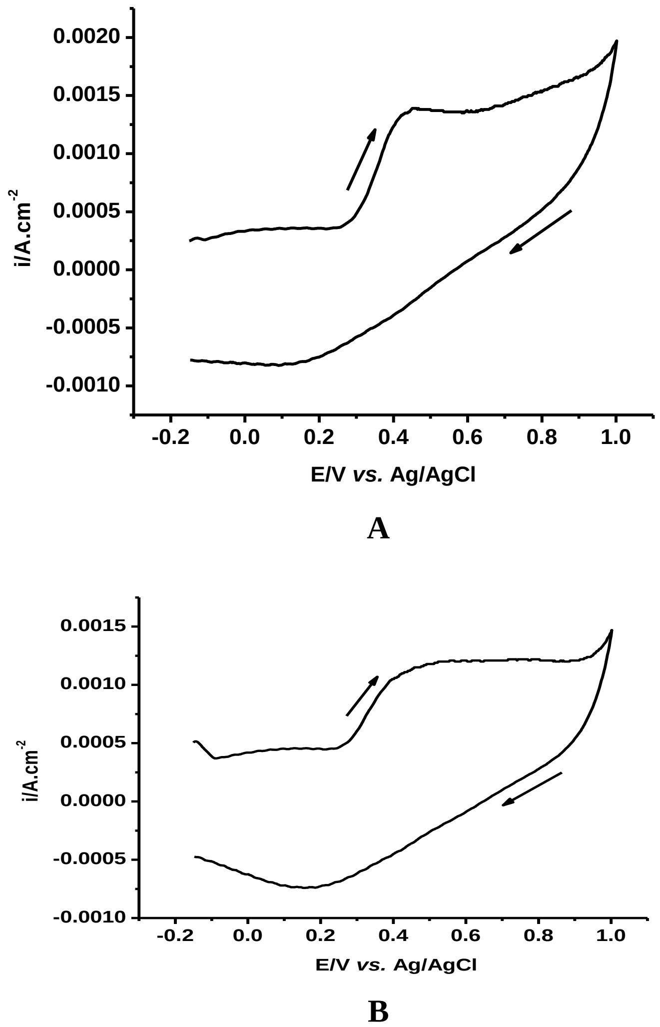
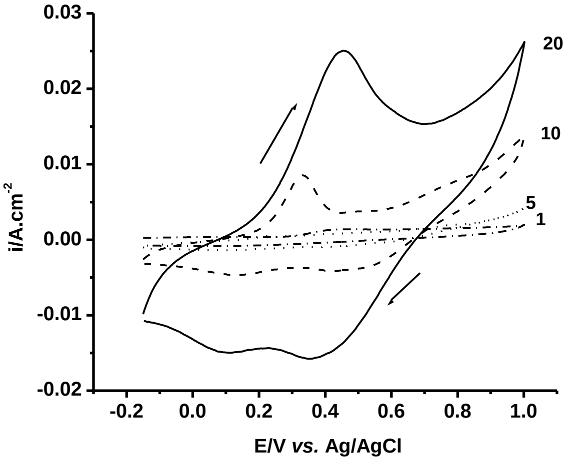
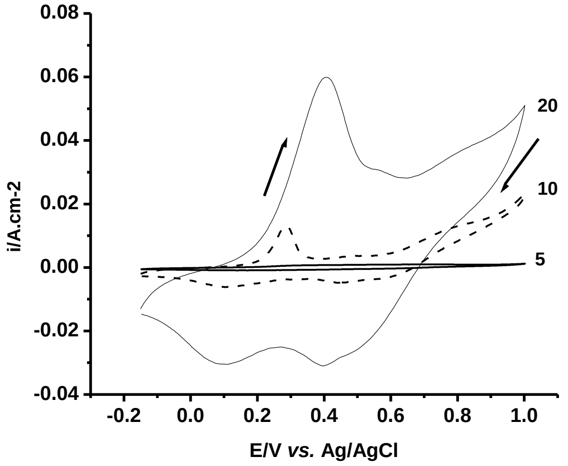


Figure 2. First cyclic voltammogram for electrodeposition of *PANI* from 0.5 M H_2SO_4 (A) and from 1M H_2SO_4 (B).

The first cycle of cyclic voltammograms of *PANI* synthesis in two different concentrations of acidic H_2SO_4 solutions are shown in Fig. 2. The SS in both acid concentrations (0.5 M H_2SO_4 & 1 M H_2SO_4) shows active dissolution current (Fig. 2) in the anodic scan and followed by broad anodic peak which coupled with broad cathodic peak in the reverse scan. The positive scan on curves indicates that no sensible current attributed to faradaic reactions is found at potentials below 0.19 V while a large increase in anodic currents commences at potentials above 0.30 V. The latter result implies that the formation of aniline radicals on the passivated steel commences at ~ 0.33 V, initiating the polymerization of aniline. On the negative sweep of this curve, an obvious but relatively broad reduction peak is found in the potential region from 0.55 to 0.00 V.



A



B

Figure 3. Cyclic voltammograms (1st , 5th, 10th and 20th cycles) from 0.5 M H_2SO_4 (A) and (5th, 10th and 20th cycles) from 1 M H_2SO_4 (B). during deposition of *PANI.*

Fig. 3 shows the successive cycles for the growth of PANI from 0.5M H2SO4 and 1 M H_2SO_4 solutions, respectively. The first oxidative peak is related to the LE/EM redox couple. The second one, related to formation of diradical cation (bipolaronic pernigraniline) [20]. As mentioned before a medial small redox peaks (D_1 & $D_2^{\backslash}$) , which is related to the degradation product of BQ/HQ couple, is observed in 1M H_2SO_4 acidic solution more than in 0.5 M H_2SO_4. The interpretation of the middle peaks D_1/D_2 has not been unanimous [21 - 23]. It has been attributed to the presence of ortho coupled polymers formed under certain experimental conditions [24]. Another assignment associates peaks D_1/D_2 with the products of *PANI* degradation, soluble species such as benzoquinone (BQ) and hydroquinone (HQ), and/or insoluble fragments containing quinonic functional groups at their ends [25].

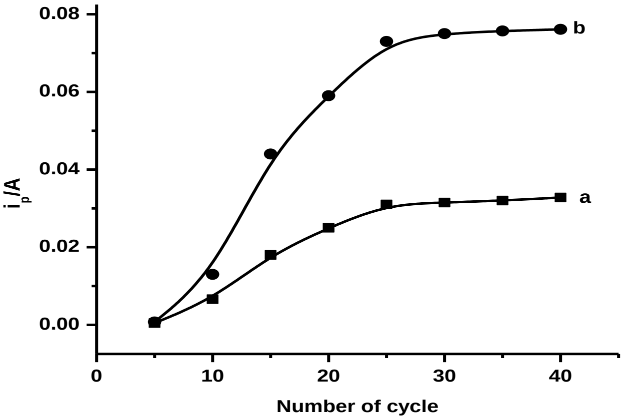


Figure 4. peak current versus sweep cycles of electrodeposited *PANI* in 0.5 M H_2SO_4 (a) and 1 M H_2SO_4.

The increase in voltammetric current peak or charge with sweep number is an indication for the growth of *PANI*. The peak current is measured and shown as a function of scan number in Fig. 4). Since the voltammetric charge increases on repeated potential scan, and deposition of the *PANI* layer is visually observed, it is inferred that the oxidation potential of aniline overlaps with the potential of oxidation of SS surface. It is likely that the initial layer of the deposit is a composite, which consists of the surface oxide on SS and *PANI*. On further continuation of the potential sweeps, the magnitude of current of the voltammograms increases suggesting an increase in thickness of the *PANI* on the SS (Fig. 4).

Fig. 4 indicates that the growth rate of *PANISO4* after 40 cycles are high. This indicates that the H_2SO_4 as supporting electrolytes help the mobility of radical cations to the electrode surface for the formation of *PANI*. Thus one usually selects solutions with good mass transport and limited ion pairing. Therefore, the higher concentration of H_2SO_4 is capable of enhancing the mass transport [26]. Other important factors can also be considered. For example, the rate of formation of the conductive species is closely related to the mobility of anions inside the film which compensates for the polymeric positive charge [27].

Table 1. Values of peak characteristics and thickness (d) of electrodeposited *PANI* films in 0.5 M and 1 M H_2SO_4 at different sweep cycles.

Sweep cycle	d (um)	E_p^{A1} (V)	E_p^{A2} (V)	E_p^{C1} (V)	E_p^{C2} (V)	E_p^{A1-C1} (V)	E_p^{A2-C2} (V)
0.5 M H_2SO_4							
10	0.534	0.330	0.760	0.130	0.430	0.200	0.330
20		0.450	0.940	0.096	0.360	0.354	0.580
30		0.510	1.009	0.086	0.305	0.425	0.704
1 M H_2SO_4							
10	0.716	0.279	0.775	0.110	0.570	0.168	0.205
20		0.406	0.840	0.099	0.490	0.307	0.350
30		0.495	0.984	0.098	0.541	0.397	0.443

As shown in Table 1, the peak separatipns $E_p^A – E_p^C$ of *PANI* in case of 0.5 M H_2SO_4 are wider than that in case of 1 M H_2SO_4. This is indicative of a more difficult charge transfer of *PANI* in 0.5 M H_2SO_4 acid solution. Also, The data in Table 1 indicate quasireversibility of the redox process.

As indicated, the SS metal undergoes surface oxidation during the initial potentiodynamic scan of the *PANI* deposition. The surface oxidation of the metal does not prevent nucleation and growth of the *PANI*. As adsorption of aniline is the primary step for deposition of the *PANI*, it is inferred that adsorption of the monomer takes place on the electrode surface followed by the oxidation step. Once the electrode is passivated with the *PANI* deposited in the initial cycle, surface oxidation of the metal is prevented, and therefore, it is expected that the kinetics of *PANI* deposition during the subsequent potentiodynamic cycles may not depend on the substrate. It is therefore, likely that the surface nature of a SS metal electrode plays an important role in the electron transfer process to outer layers of the *PANI*. The thickness of the films estimated via Eq. 1 is cited in Table 1.

3.2 Convolutive voltammetry of PANI

For the following reaction, in which a given species undergoing only electron transfer

$$R \rightleftharpoons Ox + ne \qquad (3)$$

and no subsequent processes other than 'linear' diffusion out in the solution from a planar electrode, i.e. the Fick's Second Law is expressed as [28]

$$[\partial C_{Ox}/\partial t_{\,x} = D_{Ox}[\partial^{2} C_{Ox}/\partial x^{2}]_{\,x} \qquad (4)$$

then the solution of the above via Laplace methods yields [29]

$$(C^{bulk} - C^{s}) = I_{1} / n\, FSD^{1/2}{}_{Ox} \text{ and} \qquad (5)$$

$$C^{bulk} = I_{lim} / n\, FSD^{1/2}{}_{Ox} \qquad (6)$$

where C^{bulk} & C^{s} is the bulk and surface concentrations respectively and the convolution I_1 is given by

$I_1 = i^*(\pi t)^{-1/2}$ or more 'fully' as

$$I_1(t) = 1/\pi^{-1/2} \int_{0}^{t} i(u) / (t-u)^{1/2} du \qquad (7)$$

The limiting value of I_1 at 'extreme' potentials gives limiting convoluted current (I_{lim}) i.e. when the concentration at the electrode C^s is effectively reduced to zero by rapid redox conversion and the current is thus controlled solely by the maximum rates of diffusion to (and from) the electrode.

Table 2. Values of electrochemical parameters of electrodeposited PANI in 0.5 M and 1 M H_2SO_4

Conc. of H2SO4	E_1^0/V	E_2^0/V	D($cm^2.s^{-1}$)	k_{s1} (cm.s^{-}1)	k_{s2}(cm.s^{-1})
0.5 M	0.23	0.59	$6.17x10^{-6(a)}$ $5.23x10^{-6(b)}$ $4.85x10^{-6(c)}$ $5.23x10^{-6(d)}$	$2.21x10^{-3}$	$3.62x10^{-3}$
1 M	0.19	0.67	$7.19x10^{-6(a)}$ $6.53x10^{-6(b)}$ $6.85x10^{-6(c)}$ $7.11x10^{-6(d)}$	$3.24x10^{-3}$	$4.26x10^{-3}$

Values of D from (a) cyclic voltammetry, (b) convolution transform, (c) from deconvolution transform and (d) from derived chronoamperometry.

In cases of straight forward electron transfer or subsequent chemical reaction, the I_1 convolution [30 – 34] allows to determine the diffusion coefficient of the bulk species from Eq. (8) [28]:

$$I_{lim} = nFAC^{bulk}\sqrt{D} \qquad (8)$$

where I_{lim} is the limiting value achieved for I_1 when the potential is driven to a sufficiently extreme value past the wave; the other terms have their usual significance. The values of diffusion coefficients (D) of the investigated *PANI* was calculated via Eq. (8) and listed in Tables 2.

The obtained I_1 convolution of the first redox peak ($A_1 + C_1$) of *PANI* in 0.5M H_2SO_4 at a scan rate of 0.5 $V.s^{-1}$ is indicated in Figure 5. The I_1 convolution shows a large separation between the forward and backward sweep and return to zero current value, confirming the sluggish of the electrons transferred of the redox couple LE/ EM.

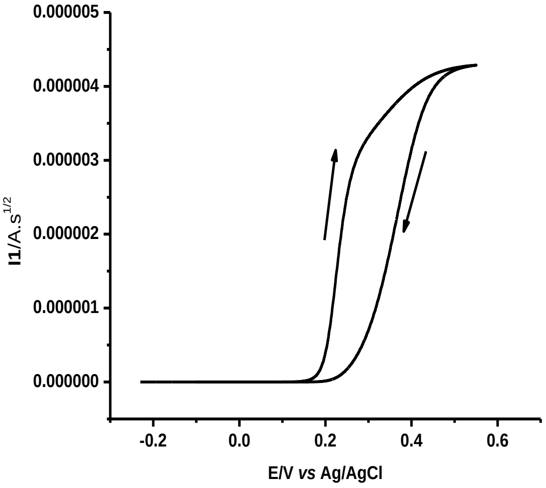


Figure 5. Convoluted current of the first redox peak of 10th cycle of electrodeposited *PANI* in 0.5 M H_2SO_4 .

The *i* - *t* plot derived from cyclic voltammogram of the *PANI* at sweep rate of 0.5 $V.s^{-1}$ is presented in Fig 6A. By selecting the data points of the decay part of the oxidative i-t plot a Cottrell plot are obtained and presented in Fig. 6B. The slope of Cottrel plot yields a diffusion coefficients cited in Tables 1. As shown the i - t plot produces discontinuity Δi_c at t = 2.9 s due to the reversibility of the scan. Inspection of Fig. 6A revealed that, the equality of the height of the forward and backward peaks confirming that the equality of the amount of charge for forward and backward peaks of oxidative and reductive couple process.

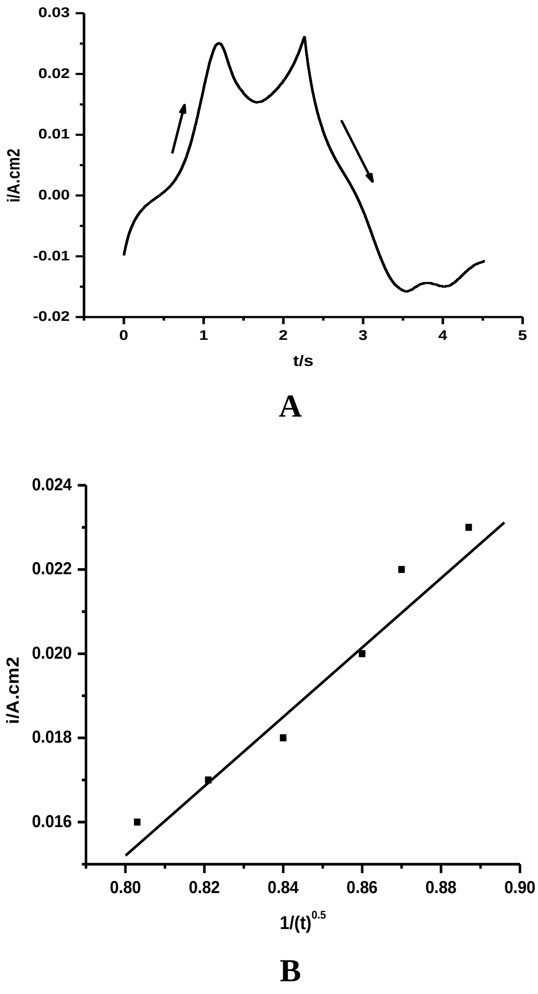


Figure 6. Presentation of derived chronoamperogram (i – t) plot (A) and i *vs* 1/√t (B) of *PANI* of 10th cycle from 0.5 M H_2SO_4.

The diffusion coefficient (*D*) of the *PANI* species was determined from the following equation [29]:

$$I_{\mathrm{limd}} = i_p / 3.099(\alpha n_a v)^{1/2} \qquad (9)$$

Where I_{limd} is the deduced limiting convoluted current and the other symbols have their usual meaning. The calculated value of the diffusion coefficient was listed in Tables 2.

3.3. Deconvolution transforms

The deconvolution transforms of the current ($d I_1 /dt$) as a function of *E* is defined as [35]

$$(dI_1/dt) = nFAC\sqrt{D}\, a\zeta / (1+\zeta)^2 \qquad (10)$$

where $$a = nvF/RT \quad (11)$$

and $$\zeta = exp\ [nF/RT\ (E - E^0) \quad (12)$$

and the representation of this equation at v = 1 V.s^{-1} of the investigated *PANI* are indicated in Fig 7. The width of deconvoluted peak (*w*p) in the case of fast charge transfer is equal to 3.53 *RT/nF* = 90.5 /n mV for fast charge transfer.

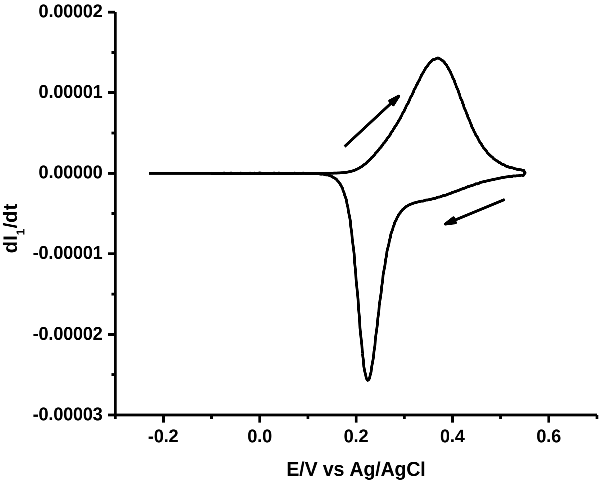


Figure 7. deconvoluted current of the first redox peak of 10th cycle of electrodeposited *PANI* in 0.5 M H_2SO_4.

It was found that *w*p in the range of 235 - 280 ± 2 mV, indicating and confirming the quasi-reversibility nature of charge transfer of redox processes. The separation between the forward and backward peaks of the deconvolutogram confirms the deviation of charge transfer from nernstain behaviour. The asymmetry of the forward and reverse peak, further confirming the sluggish of electron transfer nature of the redox process. From the above discussion it was found that, the I_1 *vs E* and (dI_1/dt) *vs E* curves were easier to interpret than *i vs E* curve. Also, the values of the diffusion coefficient of the investigated compound was calculated via Eq. 13 [29].

$$e_p = \frac{\alpha n^2F^2vCD^{1/2}}{3.367\ RT} \quad (13)$$

where *ep* is the peak height (in Ampere) of the forward deconvolution sweep and the remaining terms have their usual meanings. Value of the diffusion coefficient estimated from this method is given in Table 2.

It was found that the value of diffusion coefficient calculated from Eq. (13) agree well with the values calculated from cyclic voltammetry and convolutive voltammetry (Table 2).

From the above discussion the electrode behaviour of electrodeposited polyaniline (*PANI*) can be suggested to proceed as:

x-ANI $\rightarrow$ PANI + $2xH^+ + 2\,xe^-$ (polymerization step)

PANI $\leftrightarrow$ LE $\leftrightarrow$ EM $+2e^- + 2H^+$ (first wave A_1 / C_1)

EM $\leftrightarrow$ PE $+ 2e^- + 2H^+$ (second wave A_2 / C_2)

3.4. SEM images

The morphology of deposited *PANI* from H_2SO_4 in the potential range of the electrodeposition was examined by scanning electron microscopy (SEM) (Fig. 8). The *PANI* film deposited for 40 cycles is a spongy, connected, and grainy layer with high porosity which may be attributed to the higher growth rate in using H_2SO_4 . The indicated figure displays a better defined fibrous structure due to the regulation of the growth rate by lowering of the anodic potential limit in CPS to 820 mV.

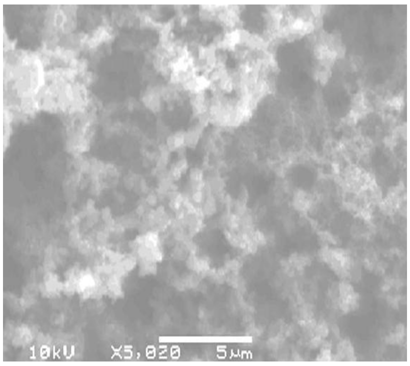


Figure 8. SEM image of *PANI* film in 0.5 M H_2SO_4.

4. CONCLUSION

In the present paper the electrochemical characterization of *PANI* as well as obtaining a thin polyaniline films on SS electrode were performed in aqueous acidic solutions. The study was carried out by cyclic voltammetry, convolution deconvolution transforms and derived chronoamperometry techniques in aqueuos medium within the potential range of –0.2 to 1.0 V at various scan cycles using stainless steel (SS) electrode and supporting electrolyte 0.5M & 1M H_2SO_4. Voltammetric characteristics of *PANI* (E_p^a, E_p^c) were estimated, the reversibility of the electrode processes (E_p(a-c)) was investigated and the electrode reaction was correlated with the shapes of the obtained voltammograms. The morphology of the deposited *PANI* films from the selected media H_2SO_4 in the potential range of the electrodeposition was examined by scanning electron microscopy (SEM).

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