ELECTROCHEMICAL INVESTIGATION OF THE LEUCOEMERALDINE/EMERALDINE REDOX COUPLE OF POLYANILINE

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Abstract

Polyaniline (PANI) was prepared electrochemically by the pulse and potential cycling methods at gold and platinum electrodes, respectively. Thin and thick films were prepared by the latter method. Square-wave and ac-voltammetric methods were employed to investigate the leucoemeraldine/emeraldine redox couple. Two well-separated current peaks were observed in the thick films suggesting a two-step reaction in the oxidation process. The effect of supporting electrolytes on the ac-voltammetric behavior of PANI was also investigated. The positions of the current peaks seem to be influenced by the size of the anion. The observed two-current peaks might be due to a two-step reaction in the transformation of leucoemeraldine to emeraldine.

1. Introduction

Polyaniline has been known for more than 100 years [1]. It is a very attractive conducting polymer because of its ease of preparation, substantial stability, and potential technological applications in batteries and electrochromic devices [2-4,11]. The polyaniline film as a typical electroconductive organic polymer has been prepared by Diaz and Logan [6] by means of anodic oxidation of aniline in aqueous sulphuric acid. Several works on the electrochemical study of polyaniline have been done [1,7,8,10]. Quite recently, there has been considerable interest in the development of probes for the detection of biologically significant molecules using PANI [9].

Inspite of the many investigations carried out on polyaniline, several aspects of the system are still unclear [2,4,5,12,35,42].

It is the aim of this project to elucidate the mechanism of the redox reaction in the transformation of leucoemeraldine to emeraldine by applying square-wave voltammetry and ac-voltammetry, since these techniques have so far not been employed for such investigations.

2. Literature Review

2.1. Mechanism of charge conduction in polyaniline

In the neutral leucoemeraldine form, the PANI band gap (Eg) between the highest occupied π electron band (valence band) and the lowest unoccupied one (conduction band) (Fig. 1a) is approximately 3.9 eV [46]. Removing an electron from the chain leads to the formation of a polaron (Fig. 1b). In chemical terminology the polaron is just a radical cation [47]. When a second electron is taken out of the chain, a bipolaron (Fig. 1c) is formed [47]. A bipolaron is defined as a pair of like charges (a dication). In the partially oxidized undoped emeraldine base, an absorption band appears around 2 eV. At high protonation levels in emeraldine, the 2 eV band completely disappears in to a 1.5 eV band, consistent with the disappearance of quinoid units to form the semiquinoid structures along the polymer chain [46].

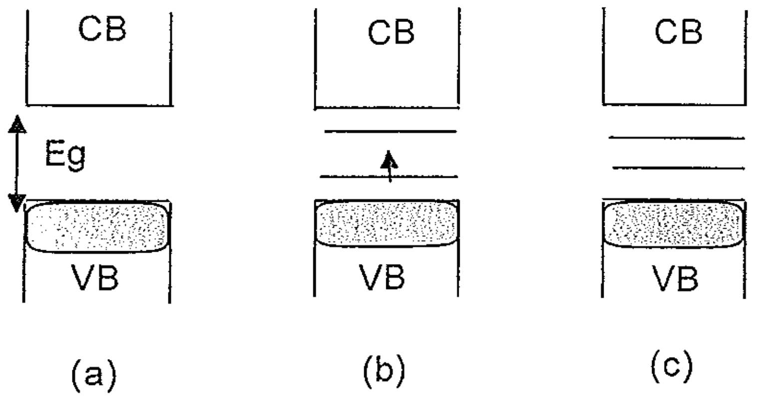


Fig. 1 Band structures of a polymer (a) undoped state (b) a polaron (c) a bipolaron
VB = valence band ; CB = conduction band.

There is quite a large difference in opinion concerning the charge carriers in polyaniline. Nechtschein and co-workers [13] have observed spinless bipolarons as responsible carriers in most of their samples [5]. Epstein and co-workers[15] strongly favour spin-carrying polarons for the charge transport process. Furthermore, some other groups suggest the possibility of polaron-bipolaron transformation [2,14].

The schematic representation for the polaron-biplaron states of PANI proposed by Genies and Lapkowski [14] is shown in Fig. 2.

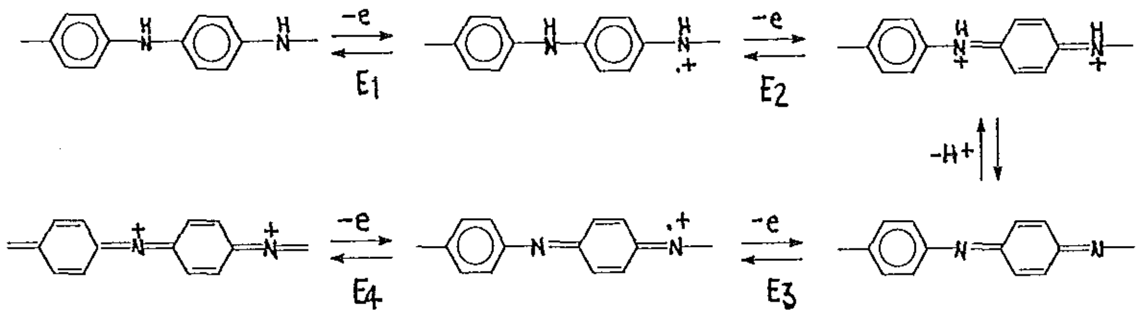


Fig. 2. The electroactive sites in polyaniline and their redox mechanisms

2.2. Synthesis of PANI by Electropolymerization

Several variations of basic reaction mechanisms have been proposed [4-6,17-22] which differ in some details but all involve the formation of radical cation intermediates from the aniline. A general reaction scheme is shown in Fig. 3 [4]. At relatively low potential it is the radical cation (1) which is supposed to be the major intermediate. But experimental evidence [23] also show the formation of nitrenium cation (4) at more positive potentials than is needed for the formation of the radical cation.

Polyaniline (PANI) is usually produced by the anodic oxidation of aniline in acidic aqueous solution [6,20-22], but can also be produced by chemical oxidation [24]. The polymerization appears to involve a nucleation process similar to that of the deposition of metals, and electrochemically-prepared polyaniline will form dense, non-fibrillar thin films; thicker films (> 150 nm) become less densely packed and more fibrous. This may be due to a change in the deposition mechanism when the film become ssufficiently thick to inhibit direct access to the electrode by unreacted monomer [4,34,38].

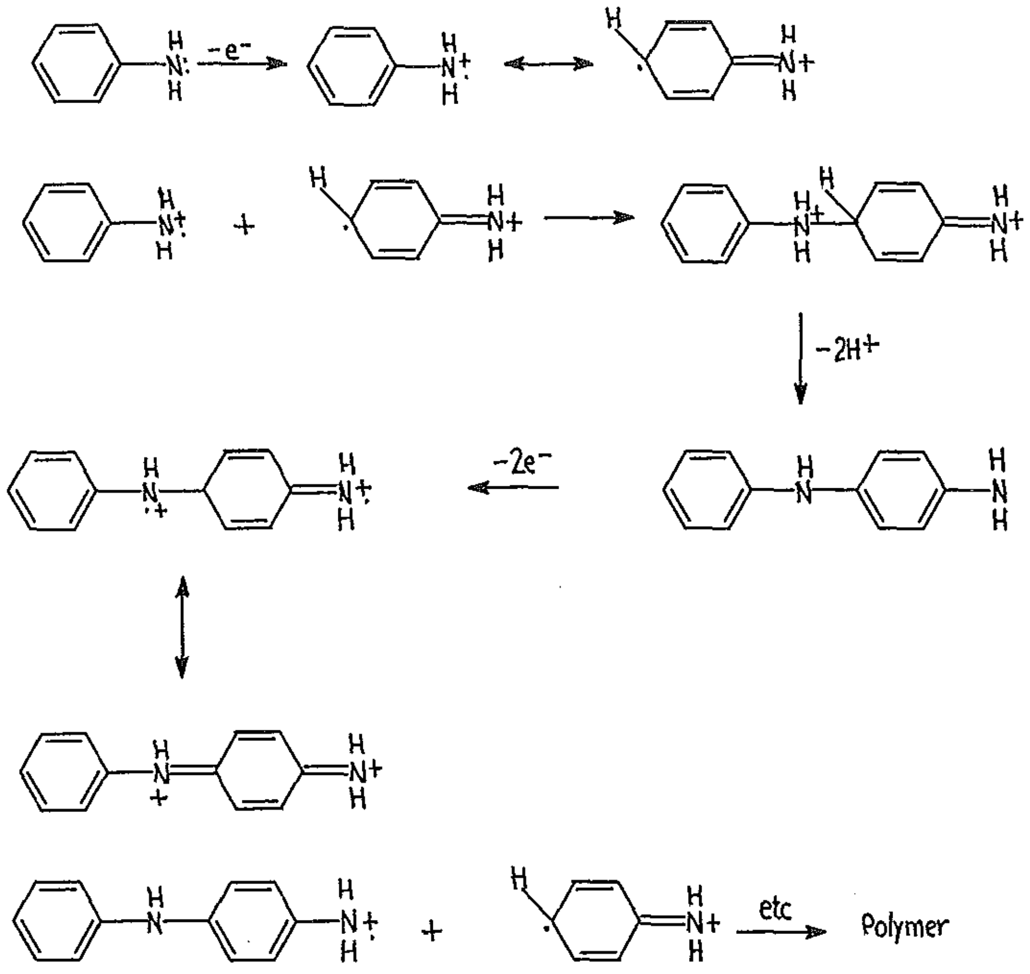


Fig. 3. General reaction scheme for the polymerization of aniline

It has been suggested that in the first step of the electrochemical aniline oxidation, the following intermediates might be formed (see Fig. 4) [23].

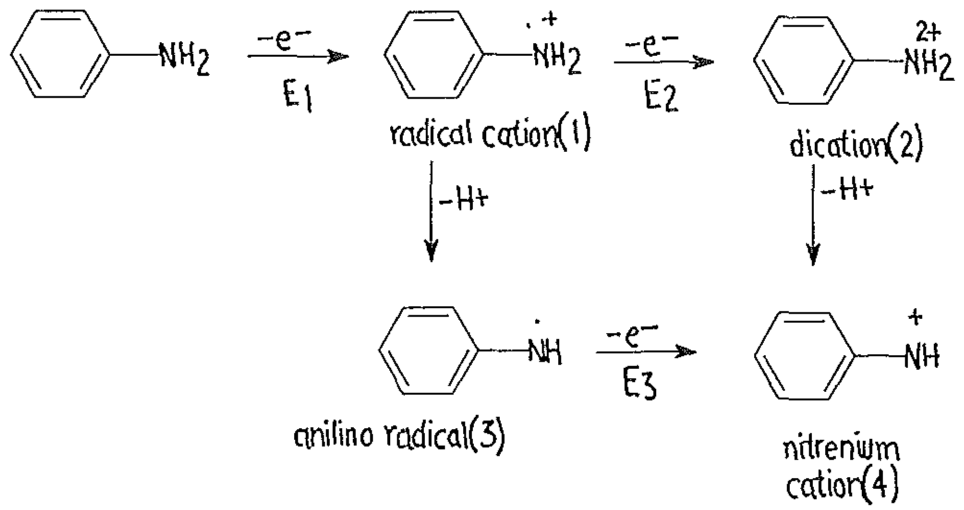


Fig. 4. Schematic representation of possible intermediates formed in the course of the anodic aniline oxidation

The fiberlike structures found in the thicker films are clearly electronically conductive since microscopic examination of the film during oxidation and reduction shows rapid changes in the color of the fibers during potential cycling [34]. An autocatalytic mechanism has been suggested which proceeds by a mediated electron transfer process (Fig. 5) [12].

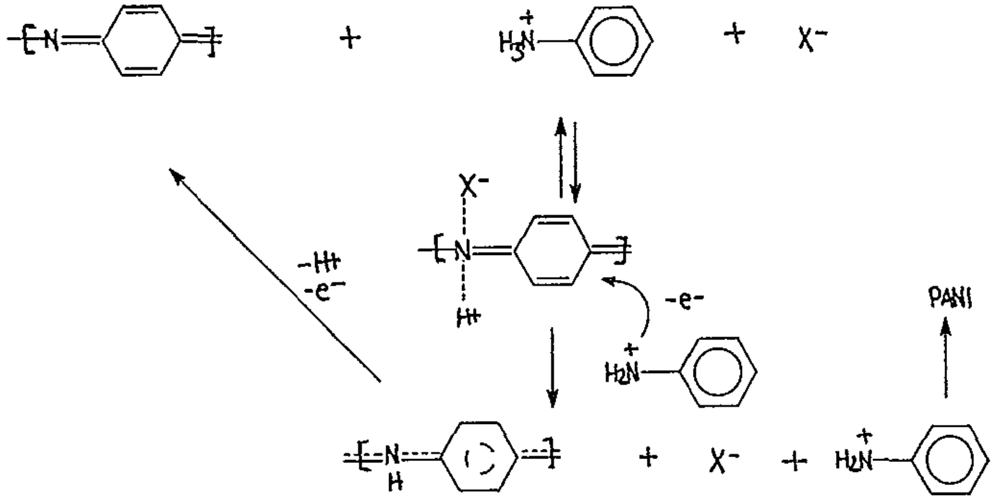


Fig. 5. Mechanism for aniline oxidation onto PANI

The potential for the catalytic deposition of polyaniline corresponds with the potential of the most positive oxidation peak obtained in the cyclic voltammogram of polyaniline [12]. Kitani and co-workers [25] studied the effect of supporting electrolytes in the preparation of PANI. The increase of doping charge per unit cycle was used as a measure of the rate of film growth. The growth rate of PANI film is 2.7-2.8 times faster in sulphuric acid than in perchloric, nitric or hydrochloric acid. This may be partly attributed to the bivalency of the sulphate ion [25]. Hyodo and co-workers [26] studied the effect of polymer electrolytes on the polymerization of PANI. The result of their investigation show that the very small amount of polymer electrolytes such as poly (vinylsulfonic acid sodium salt) (PVS), poly (styrenesulfonic acid sodium salt) (PSS) accelerate the film growth rate. The surface morphology of the films was also changed dramatically from fibrillar morphology to a granular one. The electropolymerization of aniline in solutions containing such polyelectrolytes forms electroconductive polymer-polymer composites in which the ion-exchange groups of the polyelectrolytes (e.g., sulfonate; $-SO_3^-$) act as immobilized dopants. The alteration of oxidation state (or charge) in the polymer during the electrochemical redox reaction is compensated by doping (or undoping) of cation from (or to) the electrolyte solution [33].

Glarum and co-workers made simultaneous measurements of ESR absorption and current (I) for a 100 nm PANI film on Pt in 0.5 M H_2SO_4. Concurrent measurements of ESR absorption and injected charge during a potential scan between 0.2 and 0.8 V reveal a major increase in paramagnetism within the conducting regime, with sharp maxima near 0.2 and 0.8 V [31,39].

Many workers agree that the cyclic votammograms recorded during the electropolymerization of PANI show two peaks which are ascribed to the electrochemical response of PANI deposits [19,27,29,31]. Degradation of the PANI film was observed if the anodic limit of the potential exceeded 0.7 V [22,28]. It was found that when degradation commenced, a pair of redox waves appeared at ca. 0.5 V vs SCE [22]. Kobayashi and co-workers [28] proposed p-benzoquinone as the degradation product . The degradation mechanism of the PANI film is shown in Fig.6.

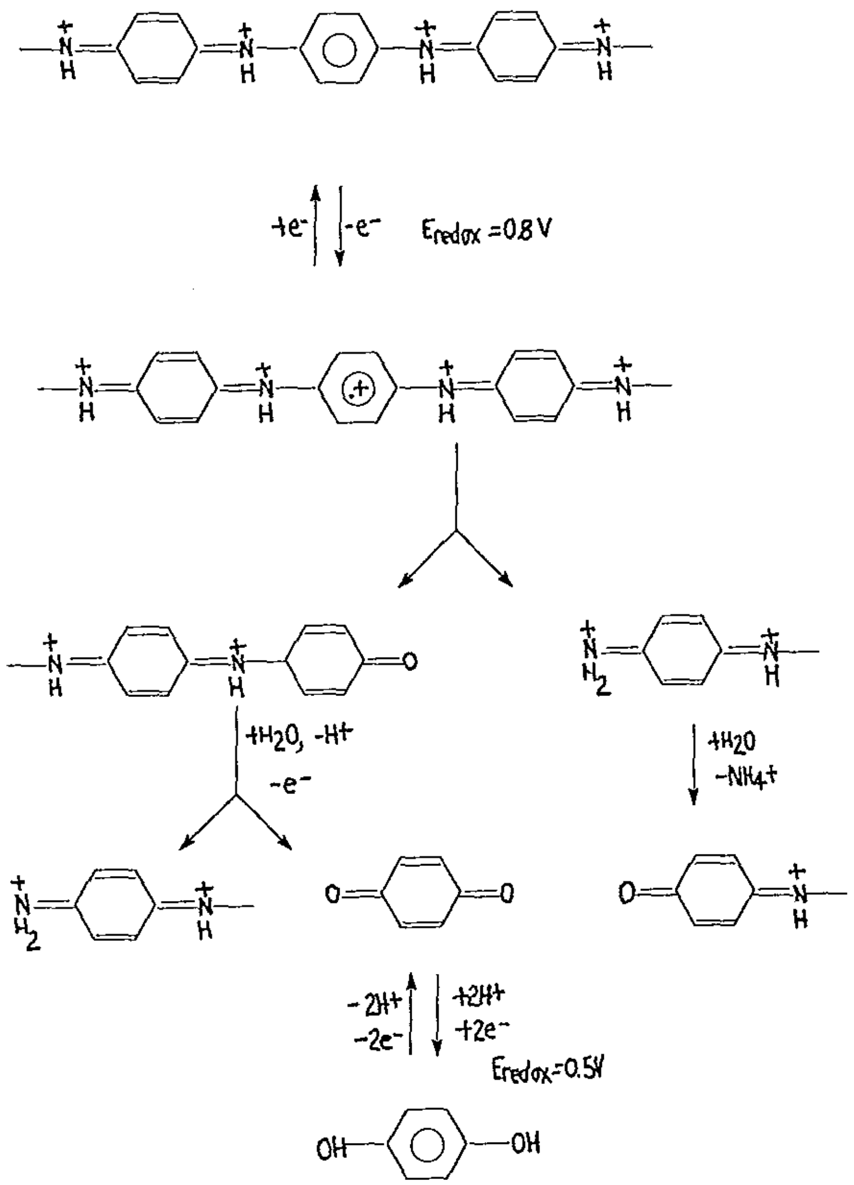


Fig.6. Oxidative degradation pathway of a polyaniline film

2.3. Structures of Leucoemeraldine, Protoemeraldine and Emeraldine

It was concluded at an early stage that the basic structural unit in polyaniline was that of an aniline octamer [4,18,29]. The smallest number of -NH-ϕ- and = ϕ = N- repeat units which can be used in the interconversion from leucoemeraldine to pernigraniline is eight [24]. The idealized formulae of leucoemeraldine, protoemeraldine and emeraldine are given in Fig. 7 [24,29].

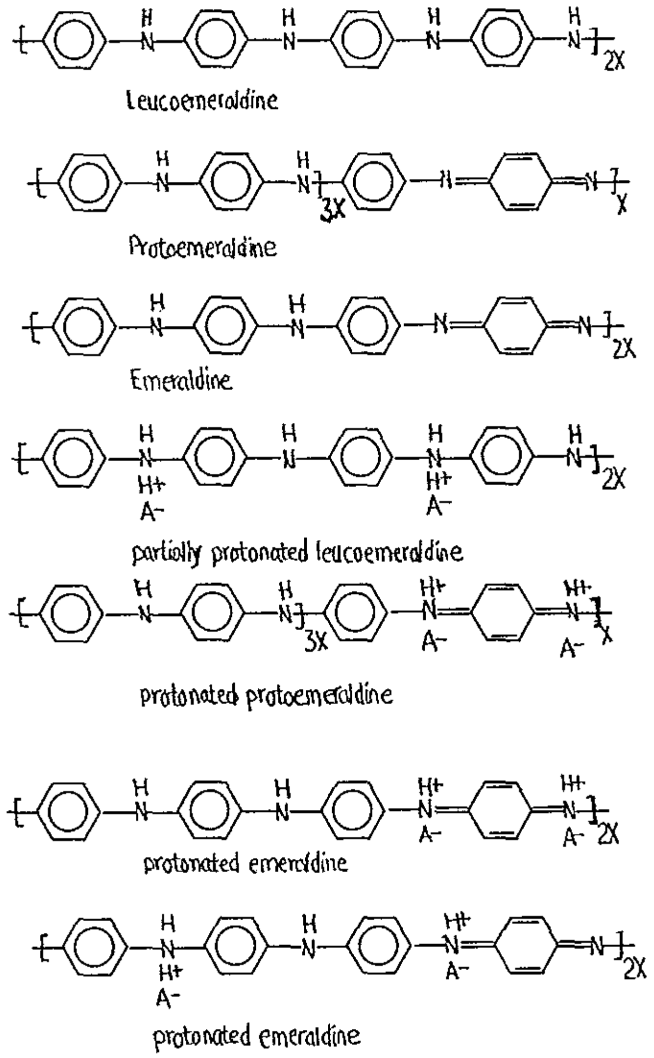


Fig.7. The idealized formulae of leucoemeraldine, protoemeraldine and emeraldine at different oxidation states

2.4. Electrochemistry of polyaniline

The electrochemistry of polyaniline is more complex than that of other conducting polymers. This is because its property is influenced by many factors such as pH, degree of oxidation, water content and the nature of anions [4,24,30,43,45]. Some of the factors that affect the electrochemistry of PANI are:

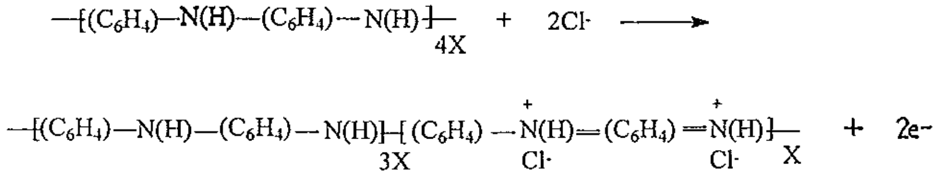
(1) pH

PANI is structurally unique in that it has nitrogen atoms occupying the bridging position in its backbone structure. These nitrogen atoms are the protonation sites which result in the modification of its electronic properties. This protonation- induced insulator- to - conductor transition has been called protonic acid doping.

The effect of pH on the redox transformation of leucoemeraldine to emeraldine has been investigated by Huang and co-workers [24]. The result of their investigation is presented below.

(a) Oxidation reactions between pH 1 - pH 4

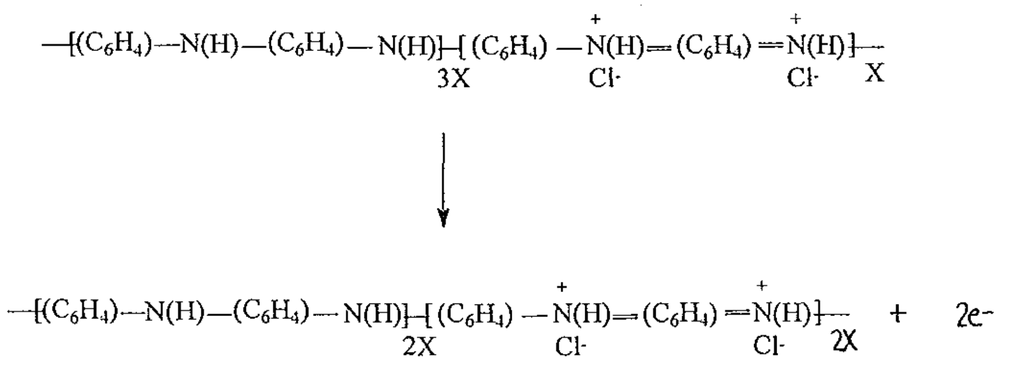
In this pH range, the oxidation is experimentally found to be independent of pH; hence no protons are involved in the oxidation reaction. The first half of peak 1 is believed to involve the conversion of pale yellow leucoemeraldine to the protonated form of light green protoemeraldine [24].



$$-[(C_6H_4)-N(H)-(C_6H_4)-N(H)]_{4X}- + 2Cl^- \longrightarrow$$

$$-[(C_6H_4)-N(H)-(C_6H_4)-N(H)]_{3X}-[(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)=(C_6H_4)=\underset{Cl^-}{\overset{+}{N}}(H)]_X- + 2e^- \quad (1)$$

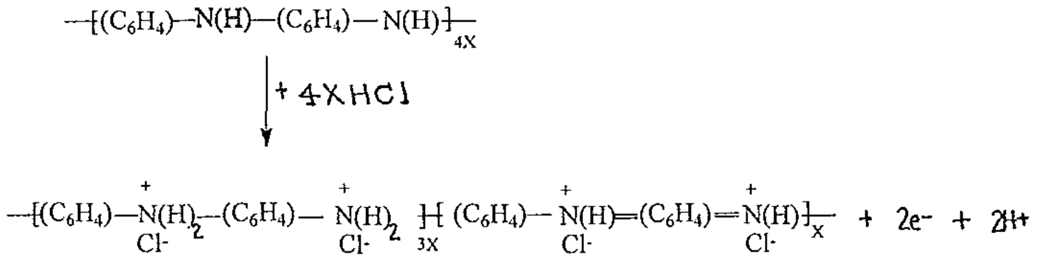
The second oxidation reaction occurs during the second half of peak 1 (Fig. 10) in the cyclic voltammogram to give the dark green protonated form of emeraldine :



$$-\!\left[(C_6H_4)-N(H)-(C_6H_4)-N(H)\right]_{3X}\left[(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)=(C_6H_4)=\underset{Cl^-}{\overset{+}{N}}(H)\right]_{X} \longrightarrow -\!\left[(C_6H_4)-N(H)-(C_6H_4)-N(H)\right]_{2X}\left[(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)=(C_6H_4)=\underset{Cl^-}{\overset{+}{N}}(H)\right]_{2X} + 2e^- \tag{2}$$

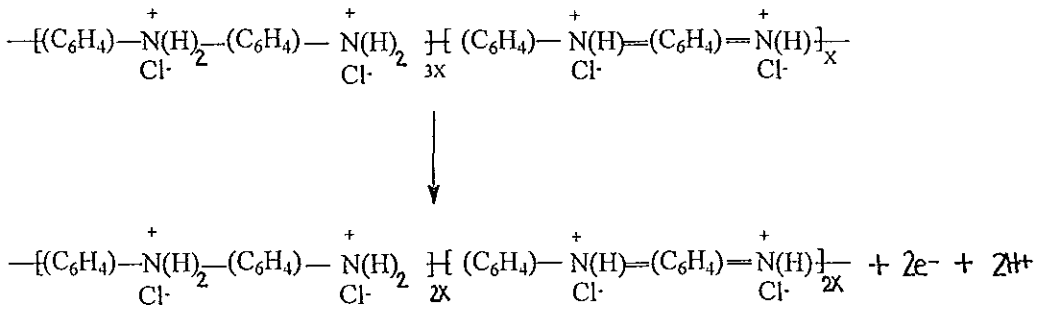
(b) Oxidation reactions between ca. pH -0.2 and -2.12

The potential of peak1 in the cyclic voltammogram of PANI decreases ca. 58 mV per pH unit with increasing pH in the pH range ca. -0.2 (1.0 M HCl) to ca. -2.12 (6.0 M HCl). In these more acidic solutions it is believed that the amine nitrogen atoms in leucoemeraldine will be completely or partly protonated.



$$-\!\left[(C_6H_4)-N(H)-(C_6H_4)-N(H)\right]_{4X} \xrightarrow{+\,4XHCl} -\!\left[(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)_2-(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)_2\right]_{3X}\left[(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)=(C_6H_4)=\underset{Cl^-}{\overset{+}{N}}(H)\right]_{X} + 2e^- + 2H^+ \tag{3}$$

This is then followed by further oxidation and deprotonation during the second part of peak 1, to give a protonated form of emeraldine.



$$-\!\left[(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)_2-(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)_2\right]_{3X}\left[(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)=(C_6H_4)=\underset{Cl^-}{\overset{+}{N}}(H)\right]_{X} \longrightarrow -\!\left[(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)_2-(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)_2\right]_{2X}\left[(C_6H_4)-\underset{Cl^-}{\overset{+}{N}}(H)=(C_6H_4)=\underset{Cl^-}{\overset{+}{N}}(H)\right]_{2X} + 2e^- + 2H^+ \tag{4}$$

(c) Oxidation reactions between ca. pH -0.2 and 1

In this pH range, -0.2 to +1, reactions (1), (2), (3) and (4) occur simultaneously to varying extents.

(2) Degree of oxidation

By changing the oxidation state the conductivity of polyaniline is switched "on" at the initial stage of doping and is switched "off" at high levels of doping. This switching behavior is unusual among other conducting polymers [24,25,32].

Visible and near-UV absorption spectra of PANI were measured at three different potentials [36]. The film oxidized at 0.6 V Vs SCE showed absorption peak at 740 nm, while that reduced at -0.2 V showed its absorption maxima at 305 nm. These features of the absorption spectra are consistent with the observed electrochromism of the PANI film, i.e., green for the oxidized state and transparent yellow for the reduced state of the film. When the PANI film was kept at 0.15 V vs SCE where the redox reaction of the film occurred appreciably, an absorption shoulder at 420 nm became more distinct, suggesting strongly that an intermediate "yellowish green" state exists between the oxidized "green" state and the reduced "yellow" state [36].

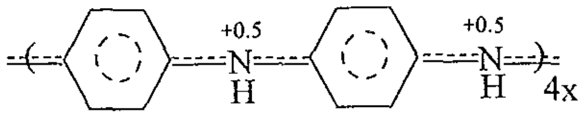
2.5 Properties of PANI

Conductivity

The conductivity of polyaniline , unlike all other conducting polymers, depends on two variables instead of one, namely the degree of oxidation and the degree of protonation of the polyaniline [29].

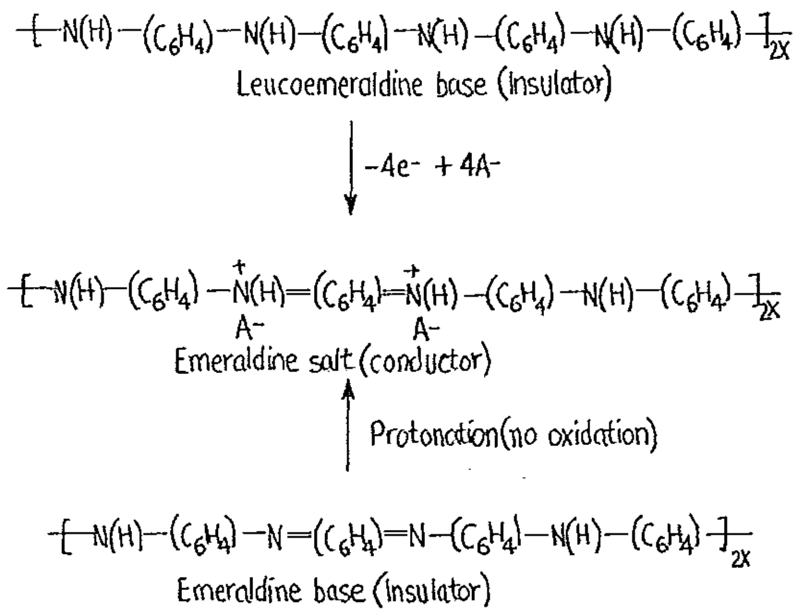
It is proposed that the emeraldine salt form of polyaniline shows high conductivity because of extensive π - conjugation in the polymer chain.

From the resonance structures each nitrogen atom would bear a +0.5 charge, all -C_6H_4 rings would be intermediate between benzenoid and quinoid, viz.



The resulting highly conjugated π -system, in addition to contributing to high conductivity, would also be expected to impart extra stability to this form of PANI [24].

The emeraldine salt can be formed in two different ways [24,30,32] as depicted below.



$[-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-]_{2X}$

Leucoemeraldine base (Insulator)

$\downarrow -4e^- + 4A^-$

$[-N(H)-(C_6H_4)-\underset{A^-}{\overset{+}{N}}(H)=(C_6H_4)=\underset{A^-}{\overset{+}{N}}(H)-(C_6H_4)-N(H)-(C_6H_4)-]_{2X}$

Emeraldine salt (conductor)

$\uparrow$ Protonation(no oxidation)

$[-N(H)-(C_6H_4)-N=(C_6H_4)=N-(C_6H_4)-N(H)-(C_6H_4)-]_{2X}$

Emeraldine base (Insulator)

Recently, Macdiarmid and co-workers [37,40] introduced the concept of secondary doping. Secondary doping is the treatment of a polymer, already doped by a primary dopant, with an apparently "inert" substance (secondary dopant). Such treatment may increase the conductivity of the polymer by several orders of magnitude with concomitant changes in electronic spectra and, frequently, degree of crystallinity. It differs from primary doping in that the changes, depending on the primary/secondary dopant combination employed, may frequently persist, possibly to a reduced extent, upon removal of the secondary dopant. The observed phenomena originate from the fact that doped (protonated) PANI, being a polyelectrolyte, acts like a macromolecule bearing a large number of ionizable groups. When the PANI film is treated with an appropriate "inert" solvent or vapor of an inert substance, its molecular conformation changes from that of a compact coil structure to that of a more open, expanded, coil-like structure. Attainment of the expanded molecular conformation acts to reduce π -conjugation defects in the polymer backbone due to ring twisting; this results in an increase in the component of the bulk conductivity due to intra-molecular effects. The opening-up of the coil tends to promote the linear conformation necessary for crystallization, thus increasing the crystallinity of the polymer with enhancement of the inter-molecular component of the bulk conductivity.

2.6. Electrochromic Behavior

Polyaniline shows multicolour changes depending on the redox process involved at different potential as well as protonation level [1]. Kobayashi and co-workers in 1984 [22,36] indicated that to improve significantly PANI's switching-life in acid aqueous solution, the potential pulse has to be narrowed to the first redox process, the colour changes from transparent yellow to green. There are slight variations in the reports about colour changes [5,16,22,23,28]. Huang and co-workers report the following colour changes [24].

Table 1. Electrochromic behavior of PANI

Form of PANI	Unprotonated	Protonated
Leucoemeraldine	pale yellow	pale yellow
Protoemeraldine	blue	light green
Emeraldine	dark blue	green
Nigraniline	blue	dark blue
Pernigraniline	violet	violet

3. Experimental

Aniline was purified under reduced pressure. All solutions were prepared with doubly distilled water. The electrochemical cell used was a three electrode cell. The working electrodes were Pt and Au disc electrodes in polytetrafluoroethylene (PTFE) with a geometrical area of about 0.07 cm^2. The electrodes were polished with alumina, rinsed with double distilled water and dried before each set of experiments. A silver-silver chloride electrode in saturated KCl served as a reference electrode. A platinum wire was used as a counter electrode. The electrolyte solutions were purged with nitrogen for 10 minutes prior to the experiments. All electrochemical investigations were carried out with the BAS 100W electrochemical analyzer at laboratory temperature (20 ± 2)° C.

PANI films were grown on the electrodes by: (i) Sweeping the potential (between -100 and 800 mV at a scan rate of 50 mVs^{-1}) in 1M perchloric, 0.5M sulphuric and 1M p-toluene sulphonic acids in aqueous solutions containing 0.1M aniline each. Thin film of PANI was grown by taking 25 cycles and the thick film by taking 50 cycles; (ii) the pulse method, by switching the electrode potential between -100 mV and +800 mV in a solution of 0.5 M H_2SO_4 containing 0.1 M aniline. The pulse duration was 250 ms at each potential.

4. Result and Discussion

4.1. Preparation of PANI film

Two methods were used for the preparation of polyaniline.

4.1.1. Pulse Method

The Au electrode was switched in the potential range of -0.1 and +0.8V in a solution containing 0.5 M H_2SO_4 and 0.1 M aniline. The pulse duration was 250 ms at each potential. The current response for the differential pulse time base (DPTB) recorded during the film growth is shown in Fig. 8b. Fig. 8a shows the potential excitation waveform for DPTB.

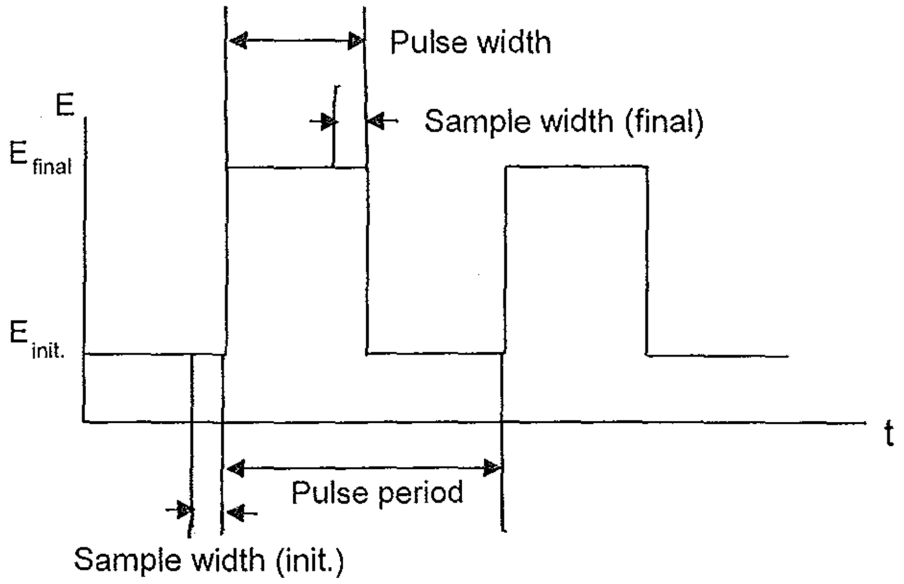


Fig. 8a. Potential excitation waveform for DPTB.

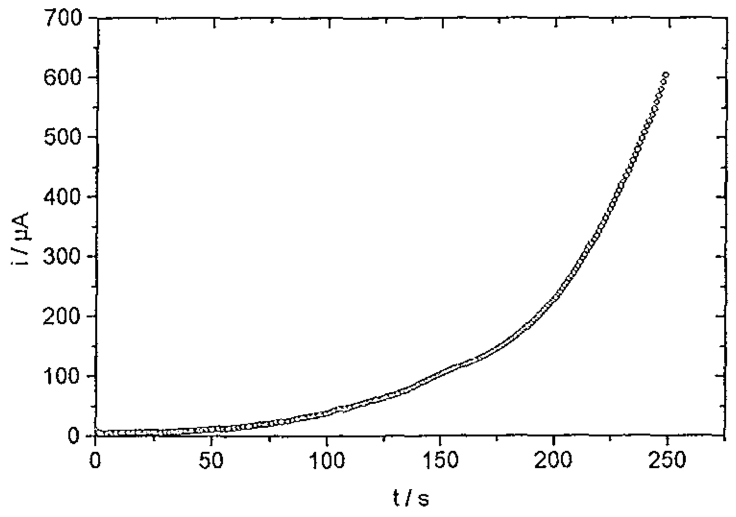
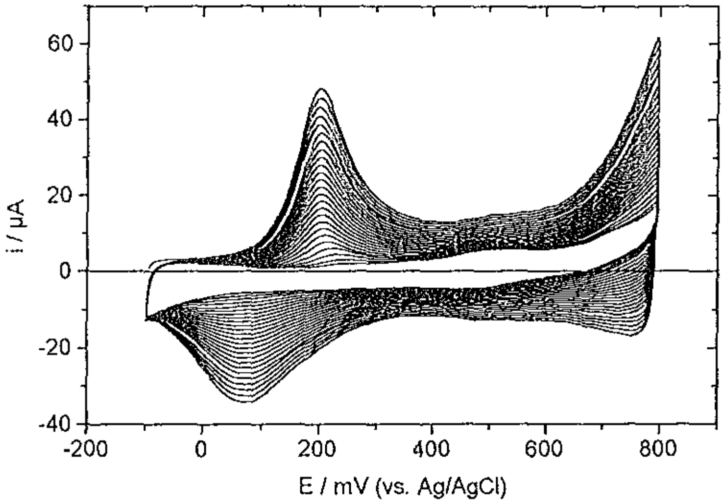


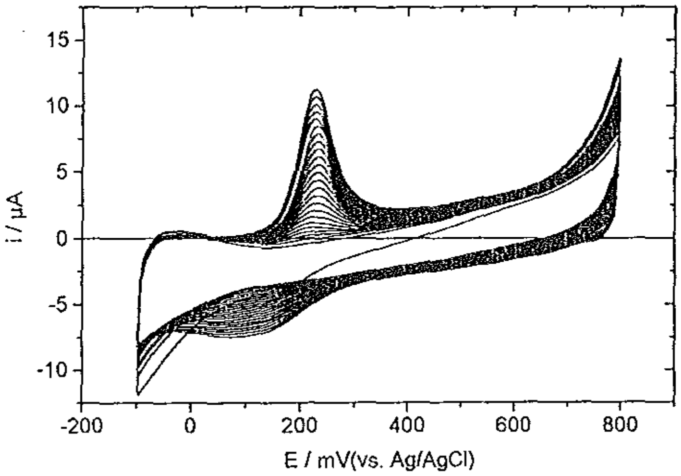
Fig. 8b. Current response for DPTB recorded during the growth of PANI

4.1.2. Potential cycling

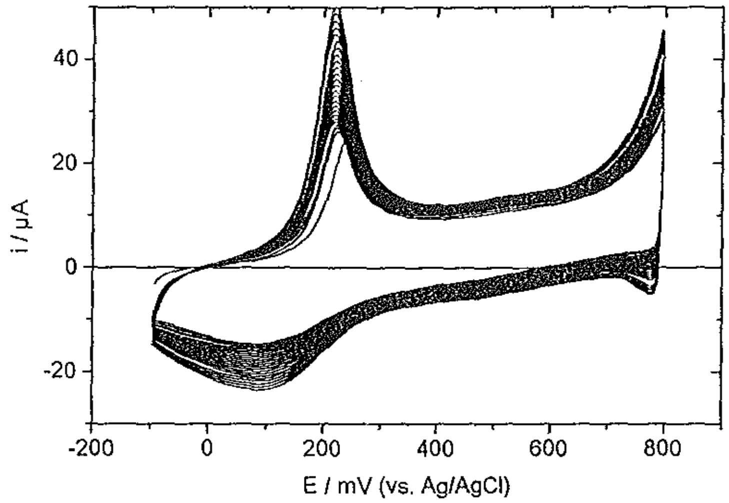
Thin and thick films were prepared on Pt by potential cycling between -0.1 to +0.8 V in different supporting electrolytes. The voltammograms for the thin and thick films grown in different supporting electrolytes are shown below (Fig. 9a-c).



9 a)



9 b)



9 c)

Fig. 9 Cyclic voltammograms recorded during growth of PANI on Pt electrode from a solution containing (a) 0.5 M H_2SO_4 and 0.1 M aniline (b) thin and (c) thick films in 1M p-toluene sulphonic acid and 0.1M aniline. Sweep rate 50 mV/s

PANI films were prepared by potential cycling . Thin films were prepared by taking 25 cycles while the thick films were prepared by taking 50 cycles. The peak responsible for the degradation product was absent in the voltammograms (Fig. 9a-c).

4.2. Characterization of PANI film

4.2.1 Film formed by pulse method

The film formed was characterized by cyclic voltammetry in 0.5 M H_2SO_4 .A voltammogram obtained with a gold electrode is shown in Fig. 10.

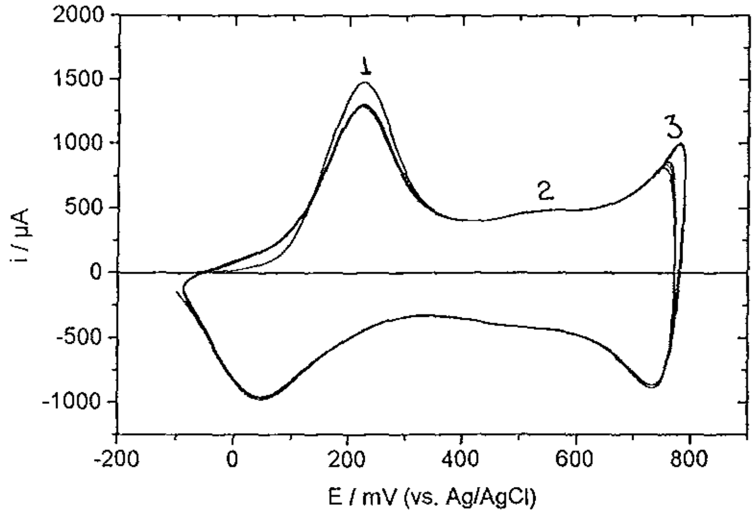


Fig. 10 Cyclic voltammogram of a PANI film on a gold electrode in 0.5 M H_2SO_4. Sweep rate : 50 mV/s

The charge obtained by integration of the anodic and cathodic part of the voltammogram (Fig. 10) was found to be the same and was therefore used as a relative measure of the film thickness. Peak 1 stands for the conversion of leucoemeraldine to emeraldine. Peak 2 is due to the degradation product. While peak 3 is due to the transformation of emeraldine to nigraniline. The charge for the anodic part was 12.1 mC/cm^2 . While the charge for the cathodic was 12 mC/cm^2 .

Further investigations on the PANI film were carried out in the potential range -0.1 to +0.4 V in order to study the transition between the completely reduced form (leucoemerldine analog) to the partially oxidized form of polyaniline (emeraldine analog). Fig. 11 shows the voltammogram of the film obtained in the potential range of interest. The charge of the first anodic section was found to be 7.1 mC cm^{-2} and by less than 4% larger than the charge consumed in the anodic section of the second cycle (6.85 mC cm^{-2}). The charges due to the reduction of the PANI film were 6.91 mC cm^{-2} and 6.88 mC cm^{-2} for the first and the second cycle, respectively.The charges consumed in the anodic and cathodic sections were approximately equal.

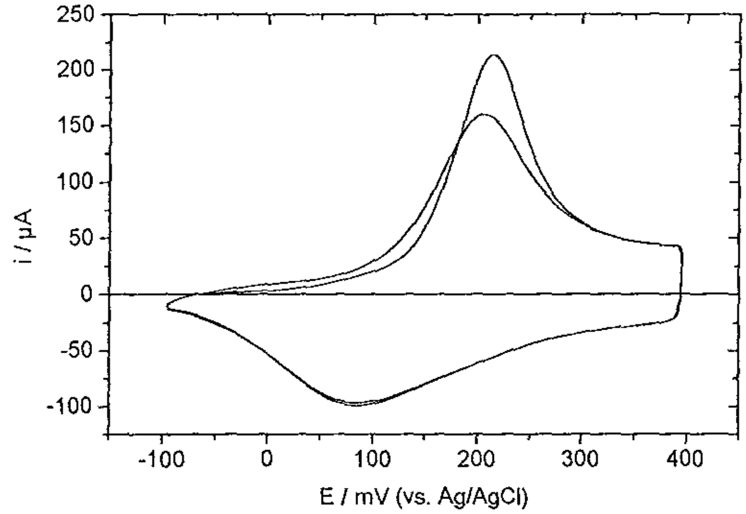


Fig. 11 Cyclic voltammogram of a PANI film on a gold electrode in 0.5 M H_2SO_4. Sweep rate 50 mV/s

4.2.2. Film formed by potential cycling

The thin and thick films were characterized by cyclic voltammetry and chronoamperommetry. The anodic and cathodic charges for both films were evaluated. Table 2 shows the anodic and cathodic charges obtained by integration of the area under the curve for both cyclic voltammograms and chronoamperograms of the PANI films.

Table 2. Anodic and cathodic charges for the thin and thick PANI films

S.No.	Film type	Anodic charge mC/cm^2		Cathodic charge mC/cm^2	
		cyclic voltammetry	chronoamperometry	cyclic voltammetry	chronoamperometry
1	thin film	1.43	1.23	1.46	1.1
2	thick film	4.99	5.3	5.24	5.12

The anodic and cathodic charges obtained from the voltammograms were found to be approximately equal. The results obtained from chronoamperometry were in good agreement with those extracted from cyclic voltammetry. Therefore, the film shows good coulombic efficiency.

4.3. Linear Sweep voltammetry

A series of LSV experiments was conducted to investigate the degree of hydrogen and aniline coverage of a platinum electrode in pure 0.5 M H_2SO_4 and 0.5 M H_2SO_4 containing 0.1 M aniline, respectively. The potential range was -0.2 to +0.4 V. The following result was obtained.

Table 3. Charge due to hydrogen and aniline, degree of coverage (θ) of aniline and effective surface area of Pt in 0.5 M H_2SO_4 containing 0.1 M aniline calculated from LSV experiments.

S.N.	Time/ s	.2V +0.4V - -0				-0.2V - +0.4 V			
		Q(H)/ μC	Q(An)/ μC	degree of cov.	A/cm^2	Q(H)/ μC	Q(An)/ μC	degree of cov.	A / cm^2
1	1	79.5	55	0.31	0.03	74.8	50.1	0.33	0.03
2	2	79.7	52.9	0.34	0.03	70.9	47.9	0.36	0.03
3	3	78.9	51.5	0.35	0.03	68.9	46.7	0.38	0.03
4	4	78.1	50.7	0.36	0.03	67.5	45.9	0.39	0.03
5	5	76.1	50.7	0.36	0.03	65.9	44.9	0.4	0.03

Bowden and co-workers [41] found that 9×10^{-4} C/real cm^2 are involved in stripping a monolayer of H. The number of monolayer hydrogen atoms was

1.6×10^{15} H/real cm^2 . An attempt was made to estimate the effective surface area of the electrode based on the above assumption. The above table shows the data obtained from LSV experiments. The effective surface area was evaluated by using the following equation .

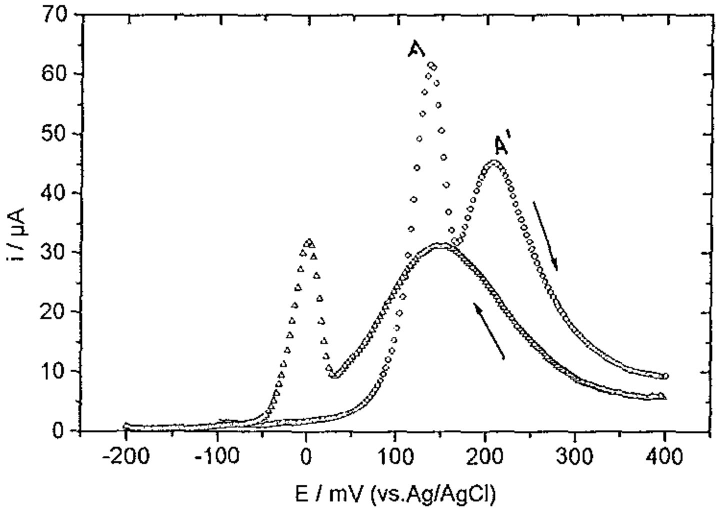
$$\text{effective surface area} = \frac{Q(H)-Q(An)}{900\ \mu C\ cm^{-2}} \qquad (5)$$

As can be seen from the table the effective surface area was calculated to be 0.03 cm^2. This result could be used to calculate the number of aniline molecules that participate in the first step of aniline oxidation.

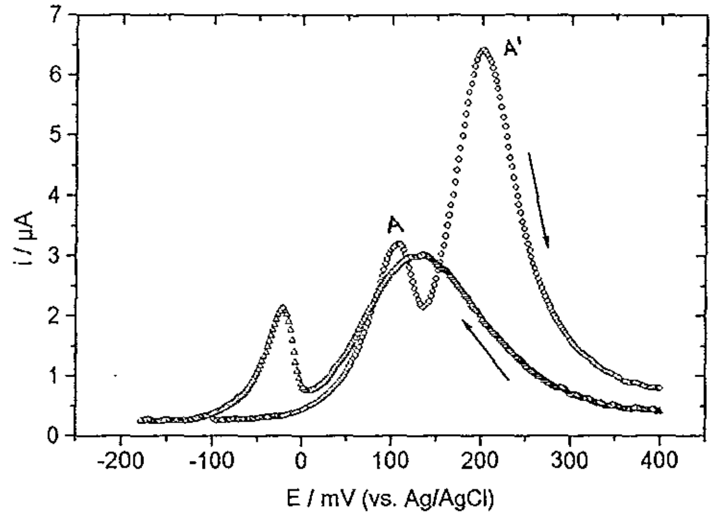
4.4. Square wave voltammetry

The response of a PANI coated gold electrode to square wave voltammetry at low frequencies and a small amplitude was investigated. Both Barker square wave voltammetry (BSWV) and Osteryoung square wave voltammetry (OSWV) experiments show two distinct peaks in the range of potential between -0.2 to +0.4V. The colour of the PANI film changes from yellow to yellowish green and then to green as the potential was switched on from the negative to the positive potential. Kobayashi and co-workers [36] observed similar colour changes in the range -0.2 to +0.6 V. The observed two current peaks would be due to two reaction steps in the transformation of leucoemeraldine to emeraldine. The following two reaction steps were suggested for the observed two current peaks (peaks A and A').

Peak A could be due to the transformation of leucoemeraldine to protoemeraldine salt while A' could be due to the transformation of protoemeraldine salt to emeraldine salt. Reactions (1) and (3) are suggested for peak A while reactions (2) and (4) for peak A' (see pp. 9 and 10).



12 a)



12 b)

Fig. 12 Square wave voltammograms of PANI on a gold electrode in 0.5 M H_2SO_4. (a) BSWV and (b) OSWV frequencies. This might suggest that the first reaction step is slow as compared to the second. As the frequency was increased, the faster second reaction step become more important. A possible explanation for this observation would be the difference in the stability between the two structures- protoemeraldine salt and emeraldine salt. Emeraldine salt is more stable than protoemeraldine salt [24].

4. 5. 2. Ac- voltammetric behavior of PANI grown by potential cycling

4. 5. 2. 1. Effect of supporting electrolytes

The in- phase ac- response of PANI film at low frequency and small ac-amplitude was investigated. Fig. 14 (a) and (b) show the effect of supporting electrolytes on th ac- voltammetric behavior of PANI films. In the thick films two well separated current peaks were observed. But the first peak (peak A) appeared as a shoulder in the case of bigger anions such as p-toluene sulfonate anion. This might be due to the relatively smaller mobility of the bigger anions.

4. 5. 2. 2. Effect of film thickness

The effect of film thickness on the ac-voltammetric behavior of PANI was investigated (Fig. 16). One peak is observed in the case of the thin films. As the thickness of the film increases the appearance of two peaks is observed. This might be due to the change of the film from non- fibrillar to a fibrillar morphology.

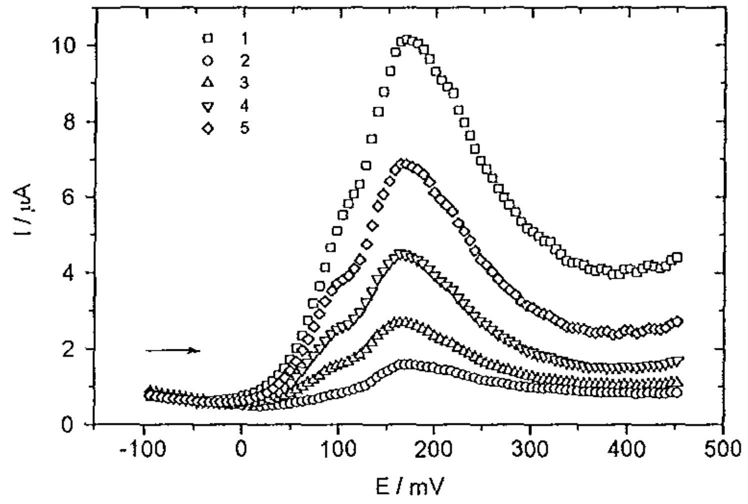


Fig. 15. Effect of film thickness on the ac-voltammetric behavior of PANI prepared in perchloric acid (1 = 150 cycles, 2 = 25 cycles, 3 = 50 cycles, 4 = 75 cycles and 5 = 100 cycles)

5. Conclusion

In this project the leucoemeraldine / emeraldine redox couple has been investigated electrochemically. For this investigation PANI films were prepared by the pulse and potential cycling methods at gold and platinum electrodes, respectively. Thin and thick films were also prepared by controlling the number of cycles using the latter method.

Square-wave and ac-voltammetric techniques were employed since these methods can discriminate the capacitive current and result in a response which is mainly due to Faradaic processes.

While there was no indication for two redox reactions in the dc-voltammograms, the square-wave and the in-phase ac-voltammetric methods resulted in two well-separated current peaks in the potential range where the transition from leucoemeraldine to emeraldine occurs. This indicates the presence of a two-step reaction in the oxidation process.

Reaction schemes (1) and (3) were suggested for peak (A) while (2) and (4) were suggested for peak (A'). These reaction schemes were proposed for the first peak of the dc-voltammogram at intermediate pH range by MacDiarmid [24].

In the first peak leucoemeraldine is converted to the protoemeraldine salt form. While in the second peak the protoemeraldine salt is transformed to the emeraldine salt form of PANI.

Further studies on the effect of supporting electrolytes on the ac-voltammetric behavior of PANI were made. The result of our investigation showed that the position of the current peaks seem to be influenced by the size of the anion. But the charges calculated by integrating the area under the voltammograms were approximately equal.

The thickness dependence of the ac-voltammetric behavior of PANI was also investigated. While thin films resulted in a single peak, thick films resulted in two distinct peaks.

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DECLARATION

I, the undersigned, declare that this thesis is my original work and has not been presented for a degree in any other university and all sources of materials used for the thesis have been dully acknowledged.

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Date of submission	June 1997

This thesis has been submitted for examination with our approval as University Advisors

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