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## Electrochemical study of polyaniline deposited on a titanium surface

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**Abstract** The electrochemical synthesis of polyaniline on a titanium surface in aqueous sulfuric acid solutions with various concentrations of added aniline has been investigated by cyclic voltammetry. By utilizing a more cathodic potential range (up to  $-0.6$  V) for the cyclization than is usual (up to  $-0.2$  V) on Pt and Au electrodes, the new voltammetric waves have been deconvoluted from the already well-known ones for polyaniline.

By simultaneous electrochemical and in situ Raman spectroscopic measurements, the Raman bands of polyaniline electrodeposited on a Ti electrode, were assigned for potentials of  $-0.15$  V and  $-0.6$  V. It was found that the new monitored waves were closely related to the so-called “middle” peaks and appear only when the polyaniline reaches an overoxidized state.

**Key words** Ti electrode · Polyaniline film · Cyclic voltammetry · Raman spectroscopy · Degradation products

### Introduction

Polyaniline (Pani), which is readily synthesized by the chemical or electrochemical oxidative polymerization of aniline in aqueous acid solutions, has attracted attention, especially in the last ten years, because of its good stability in air, electroactive and conductive properties, attractive application prospects in electrochemistry and also as a very promising material in the development of advanced technologies.

The fundamental questions about this polymer concern the polymerization mechanism, the structure of polymer components in their oxidation states, the redox mechanisms, the electronic and ionic conducting mechanisms, and the mechanism of doping and undoping reactions etc. [1–5]. Much detailed structural information has been obtained in recent investigations employing coupled physicochemical, electrochemical and spectroscopical methods [6–7]. It has been shown that the morphology of electrochemically prepared Pani depends strongly on the experimental conditions: the nature, geometry and surface preparation of electrodes, the supporting electrolyte, the potential, current density, agitation, sweep rate, temperature etc. [8–11]. In spite of many investigations, the exact mechanism of the electrochemical polymerization of aniline and of redox mechanisms in Pani film, especially for the overoxidized state and the formation of degradation products, have still not been completely elucidated. This is very often because of the use of electrodes prepared from noble metals (Au and Pt) and inert substrates (graphite, glassy carbon, ITO etc.), where the cathodic potential during the cyclization has to be limited as a result of hydrogen gas evolution.

The introduction of the titanium electrode into polymer electrochemistry gives the possibility to widen the cathodic potential range for investigations and to obtain new electrochemical data for redox reactions and degradation products in polymer film. To our knowledge, very few papers have so far been devoted to the electrosynthesis of Pani on a Ti surface [11–13]. The first electrosynthesis of Pani on a Ti electrode, presented by Geskin [11] and later Abalyaeva and Kogan [12], included voltammograms with the usual limit of cathodic potentials [ $-0.2$  V (sce)], like those used with noble metal electrodes Au and Pt.

The purpose of this work is to enlarge the initially studied domain of electrochemical synthesis of Pani on a Ti electrode, and we report here some preliminary results of a correlation between the electrochemical response of Pani deposited on Pt and Ti surfaces.

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## Experimental

### Electrode

Two types of working electrode (Pt and Ti) plates with an area of 24 mm<sup>2</sup> and two types of working microelectrode (Pt and Ti) wires with an area of 0.5 mm<sup>2</sup> embedded in epoxy resin (Struers) were utilized. Prior to performing each measurement, the working surfaces of the Ti and Pt electrodes were machined flat and polished to a final smoothness of around 0.1 μm on successively finer grades of alumina powder lubricated with distilled water. Then, the electrodes were cleaned ultrasonically and rinsed with ethanol. A Pt plate was used as counter electrode in the case of the Pt working electrode, and a Ti plate in the case of the Ti working electrode.

After each experiment, the formed Pani film was chemically dissolved by immersing the Pt electrodes in concentrated HNO<sub>3</sub> and the Ti electrodes in diluted (1:1) HNO<sub>3</sub>. The reference saturated calomel electrode (sce), was used with a Luggin probe. The potential of the working electrode was measured against the reference sce.

### Electrolytic cell

The electrochemical measurements were carried out in a classical three-electrode cell at room temperature. A fine porosity fritted glass disk was used to separate the working electrode from the counter electrode. Prior to use, the electrolytic cell was cleaned in concentrated HNO<sub>3</sub> and rinsed thoroughly in distilled water. Before each measurement the solution in the cell was initially deaerated by passing argon gas through it for at least 1 h. During the run the flow was discontinued. The gas was passed through a gas purifier and then through a gas bubbler filled with doubly distilled water to minimize evaporation in the cell. The electrolyte was changed after each measurement in order to avoid the possible build-up of any soluble species and oligomers.

### Solutions

The chemicals were all reagent grade or better. The sulfuric acid (Merck) was used as received. Aniline (Merck) was distilled to eliminate the oxidized impurities. The distilled aniline was stored in the dark under an argon atmosphere. All of the aqueous solutions were prepared with triply distilled and deionized water.

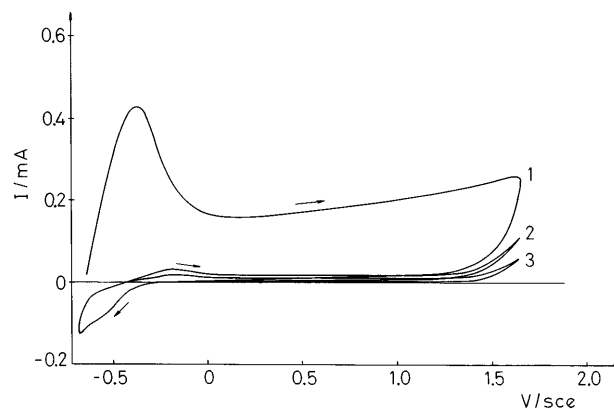
### Apparatus

The electrochemical measurements were carried out with a Heka Model 488 potentiostat/galvanostat interfaced with a personal computer and connected to a Philips X-2Y recorder model PM 8272.

The Raman spectra were recorded on a Spex 1877 spectrograph with a silicon photodiode array detector (IRY 512). The measured spectral range was from 500 to 1800 cm<sup>-1</sup> with a spectral resolution of 3 cm<sup>-1</sup>. The spectra were excited by the 514.5-nm line of an Ar<sup>+</sup> laser with power of 100 mW measured on the spectroelectrolytic cell.

## Results

Figure 1 shows typical voltammograms recorded on a virgin Ti electrode immersed in aqueous sulfuric acid solutions. The first cycle always shows an active region

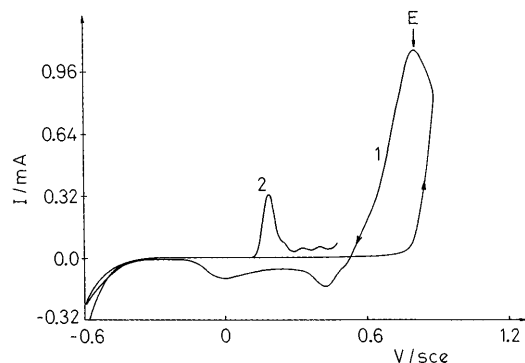


**Fig. 1** Voltammograms of Ti electrode immersed in 1 M H<sub>2</sub>SO<sub>4</sub> ( $v = 50$  mV/s). 1, 2 and 3 represent number of cycles

followed by the large current plateau of a passive region. The primary passivation potential of titanium shifts in the noble direction on increasing the acid concentration and sweep rate [14]. The critical current density for passivity and the dissolution current density in the passive range increase also on increasing the acid concentration and sweep rate [14]. The reverse sweep shows no reduction of the formed passive film, i.e. the passive film becomes chemically and electrochemically stable. The titanium electrode becomes passive by growing an anodic oxide film. Note that the electrochemical depassivation of titanium surface is a very slow process [15]. Depassivation could be accelerated by cathodic polarization, but the extensive cathodic reduction is not able to reactivate completely the titanium electrode. The electrochemical reduction is incapable of producing an oxide-free bare titanium surface because of the formation of a surface hydride layer during cathodic polarization. This indicated that during the cyclization, the cathodic current has only a minor effect on depassivation of the titanium surface. It is evident that after the first cycle the titanium electrode remained passive in all investigated potential regions.

In the second cycle (Fig. 1), the formed passive film blocked all possible redox reactions in the interface Ti/passive film/electrolyte. Continued polarization in the anodic direction resulted in the formation of thicker films [16]. From electron diffraction patterns and Raman spectroscopic measurements it has been shown that the passive film is amorphous and primarily composed of TiO<sub>2</sub> [17, 18].

In the next cycles, the voltammograms have similar shapes to the second one, manifested by large plateaus with anodic and cathodic currents of approximately zero. It is evident that after the first cycle the Ti electrode becomes electrochemically "inert". In such an electrode it is possible to study potentiodynamically the electro-synthesis and electrodeposition of the Pani film. All variations of current density during the sweep will depend only on aniline polymerization and deposition, and on redox reactions in the formed polymer film.

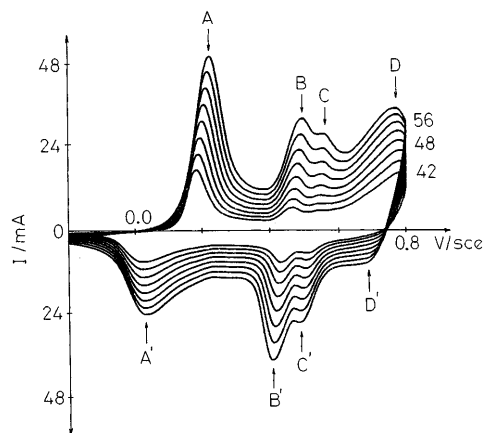


**Fig. 2** Voltammograms of Ti electrode immersed in 1 M  $\text{H}_2\text{SO}_4$  + 0.05 M aniline ( $\nu = 1$  mV/s): 1 first cycle, 2 part of the second cycle. For clarity the second cycle is not completely represented

Figure 2 shows the first and part of the second cyclic voltammogram (CV) curve recorded on a Ti electrode from the starting potential of  $-0.6$  V(sce) up to  $0.9$  V(sce). The voltammogram's shape is very similar to that recorded for a Pt electrode and reported in [6]. But, for the same experimental conditions, the voltammogram in the case of the titanium electrode shows lower values of current density than in the case of Pt electrode. This suggests that the initial oxidation of aniline on a Pt electrode is much more favorable than on a Ti electrode.

At the first positive sweep, monomeric aniline is oxidized, exhibiting a distinct irreversible broad anodic current peak E at about  $0.8$  V (sce). Part of the monomeric aniline oxidation products are deposited on the electrode, i.e. the polymer growth process begins to take place. In the first reverse cycle, the new cathodic peaks, which are almost reversible, appear, confirming the initial deposition of electrooxidized products. As cycling continues, the height of peak E decreases and finally essentially disappears. On the contrary, the already formed cathodic peaks rise in intensity and new anodic well-defined peaks, which are ascribable to the electrochemical response of Pani deposits, gradually form. The point to be emphasized is that monomeric aniline is incorporated into the growing polymer and the resultant chain is again oxidized electrochemically to incorporate another monomeric aniline from the solution phase. However, the polymer growth cannot occur at potentials lower than  $0.5$  V (sce). This indicates that in order to incorporate the neutral aniline molecule, the polymer itself must be in a certain oxidized state.

In Fig. 3, the voltammograms recorded during the continuously applied cyclic voltammetric scans on the Ti electrode are shown. The increasing current in each successive cycle reflects the regular growth of the polymer film. The voltammograms in Fig. 3 have very similarly shaped CV curves and almost the same redox potentials as the corresponding waves registered on Pt electrode [19]. This indicates that, during the run, the same redox processes occur on Pt as on Ti electrode surfaces. However, the redox potential ranges for all detected waves are smaller for the Ti than for the Pt



**Fig. 3** Voltammograms of Ti electrode recorded after multicyle scan in 1 M  $\text{H}_2\text{SO}_4$  + 0.05 M aniline ( $\nu = 20$  mV/s). 42–56 represent number of cycles. For clarity each second cycle is omitted

electrode. It can be concluded that on the Ti electrode the Pani film formed is thinner and involves more reversible redox processes than on the Pt electrode.

Peak A is assigned to the oxidation of the reduced form of Pani to the semiquinone radical cation of paraphenylene amine polymer units, (polaron state) [20], or protonation reactions of Pani [21]. In the case of the Ti electrode, there is a very narrow peak, with the width at half maximum down to  $65$  mV at the 56th cycle compared with about  $100$  mV for a Pt electrode. Peak A' is broad, with a potential of about  $180$  mV on a Pt and  $150$  mV on the Ti electrode and is more negative than peak A. This peak corresponds to the reduction of the polaron state [20], or deprotonation reactions of Pani [21] in the polymer chain.

The second peak D is assigned to the further oxidation of polymer to the form of quinoid diradical dications of paraphenylene amine polymer units (bipolaron state). Note that in the later stage of polymer growth, after about 10 cycles, the so-called "middle" peaks B–B' and C–C' grow and become more and more pronounced. These peaks can be attributed to the oxidation and reduction of degradation products [22] and to the presence of a polymer containing phenazine rings [23].

The "middle" peaks B–B' and C–C' begin to appear only when the limit anodic potential on Fig. 3 reaches the value of peak D. Pani prepared on the Ti electrode at lower anodic potentials, for instance at  $0.6$  V (sce), exhibits only a single pair of redox waves A–A' and has a different structure from that of Pani prepared at higher anodic potentials.

In Table 1 are summarized the registered (CV) waves from Fig. 3 and assigned species from Raman spectroscopy measurements.

For lower concentrations of aniline, below  $0.1$  M, the "middle" peaks B–B' and C–C' are more pronounced. For higher concentrations of aniline these two middle peaks are superimposed and form a single, broader peak.

**Table 1** Assigned species on Pt and Ti electrode during the CV run

Wave	Assigned species	Redox potential range $E_a - E_k$ (V)	
		Pt	Ti
A/A'	Semiquinone radical cations polaron states of Pani (0/+1)	0.18	0.15
B/B'	Benzoquinone/hydroquinone	0.10	0.03
C/C'	<i>p</i> -Aminophenol/quinoneimine	0.07	0.03
D/D'	Quinoid diradical dications bipolaron states of Pani (+1/+2)	0.08	0.03

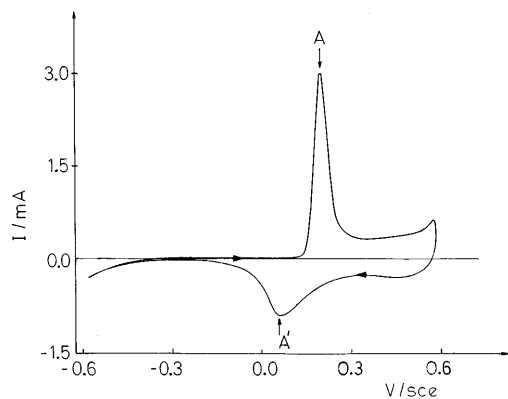
In the case of microelectrode voltammograms, it is possible to sweep many times through the second oxidation peak D without any indication of degradation products (the appearance of B–B' and C–C' is minimized). By comparison, degradation is clearly severe at the low sweep rate in the case of the microelectrode.

It is well known that on a Pt electrode, for potentials more negative than  $-0.2$  V (sce) in acidic aqueous solutions, hydrogen gas evolution begins, manifested by abrupt increase of cathodic current. On the contrary, on the Ti electrode the increase of cathodic current begins for cathodic potentials more negative than  $-0.7$  V (sce) [14]. This phenomenon gives us the possibility to extend the cathodic potential limit from  $-0.2$  V (sce) to  $-0.7$  V (sce).

Figure 4 shows the voltammogram recorded after a multicycle scan for a cathodic potential limit of  $-0.6$  V (sce) and anodic potential limit of  $0.6$  V (sce), before the appearance of second peaks D–D' and the formation of degradation products. Peak A is sharp and symmetrical, indicating the oxidation of only one type of species.

In this potential range, the film is fairly stable, giving the reversible color change from transparent yellow, at  $-0.6$  V (sce), to green, at  $0.6$  V (sce).

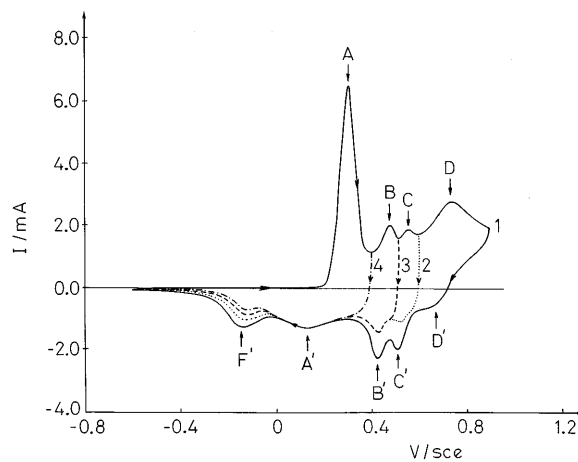
Figure 5 curve 1 shows the voltammogram recorded under multicycle condition during 50 continuously ap-



**Fig. 4** Voltammogram of Ti electrode immersed in 1 M  $\text{H}_2\text{SO}_4$  + 0.1 M aniline, recorded after 50 CV cycles between  $-0.6$  and  $0.6$  V ( $v = 20$  mV/s)

plied CV scans in the potential range from  $-0.6$  V (sce) to  $0.9$  V (sce). For the first time, the cathodic peak F' on the Ti electrode for potentials more negative than  $-0.2$  V (sce) is monitored. The “middle” peaks B–B' and C–C' are well pronounced and separated, which is characteristic for a lower concentration of aniline. The first anodic peak A shows asymmetry. This asymmetry is not due to an additional ohmic drop across the film thickness because it changes from the right to the left side of the peak A, depending on the experimental condition (concentration of aniline, sweep rate, number of cycles, range of potential sweeping etc.). The cathodic peak F' only appears if CV measurements are performed with higher anodic potential limits through the peak D, i.e. with formation of degradation products (peaks B–B' and C–C'). It seems that the first anodic peak in reality consists of two peaks A and F. This assumption can be proved by voltammograms recorded for various anodic potential limits on the same electrode (Fig. 5). If the anodic potential is limited after the peak C, between the peaks C and B, and before the peak B, at potentials of:  $0.6$ ,  $0.5$  and  $0.4$  V (sce) respectively, the rest of the voltammograms (CV curves 2, 3 and 4), show a similar shape to curve 1. Only slight diminishing of the ratio  $I_{F'}/I_A$  of peak intensity is noticed. On the curves from Fig. 5 it is evident that the cathodic peak F' is not redox related with anodic peaks B and C. In the potential range from  $-0.6$  V (sce) to  $0.9$  V (sce) the electrodeposited thin Pani film shows multiple color changes, from transparent yellow at  $-0.6$  V (sce) to green at  $0.6$  V (sce) and dark blue at  $0.9$  V (sce). The electrochromic behavior of the film was unstable in the repetition of these color changes. For thicker films, the polymer has various shades of black in its oxidized form.

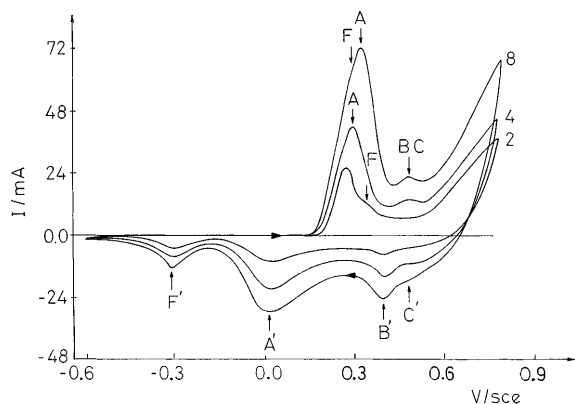
Taking into account the fact that the cathodic peak F' is more pronounced at higher concentrations of aniline, our next measurements were performed in solutions containing  $0.3$  M aniline.



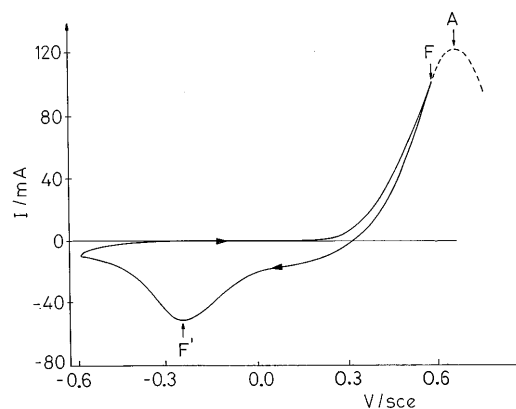
**Fig. 5** Voltammograms of Ti electrode immersed in 1 M  $\text{H}_2\text{SO}_4$  + 0.03 M aniline ( $v = 20$  mV/s). 1 50th scan, 2 51st scan, 3 52nd scan, 4 53rd scan

Figure 6 shows voltammograms recorded in 1 M  $\text{H}_2\text{SO}_4 + 0.3 \text{ M}$  aniline, where the peaks B and C are merged into one broader peak BC. The deconvolution of peaks A and F is obviously a result of the mutual shift of the potential positions of peaks A and F. In the second cycle, peak F appears as right hand side asymmetry of peak A. Then, in the eighth cycle, the asymmetry appears on the left hand side, near the top of the peak A. On the fourth cycle the first anodic peak A is symmetrical and the anodic peak F does not appear. In this case, during the shift of anodic peaks A and F with cycle number, the more intense peak A completely convolutes peak F. With augmentation of sweep rate, the first anodic peak shifts in the anodic direction while the corresponding cathodic one shifts in the cathodic direction and becomes more pronounced. Also, under multicycle conditions, the cathodic peak F' also shifts in the cathodic direction while the asymmetry of peak A moves from right to left.

In order to determine whether the redox pair F-F' originated from some oligomers, after the prolonged Pani film growth in the potential range between  $-0.6 \text{ V}$  (sce) and  $0.9 \text{ V}$  (sce) on the same electrode (Fig. 6), the aniline solution was suctioned away. The film was rinsed many times and the solution was replaced with 1 M  $\text{H}_2\text{SO}_4$ . The potential was then scanned for various values of anodic and cathodic limit potentials. Such an approach can exclude possible complications related to splitting of two or more peaks due to monomer present in the electrolytic solution. For an anodic potential limit of  $0.6 \text{ V}$  (sce), there is no change in voltammogram shapes with number of cycles. The first anodic peak A shows asymmetry of its left side. For a faster sweep rate, if the anodic potential limit is just stopped at the left side asymmetry of peak A, the only well-defined peak F' appears, and this corresponds to anodic peak F (Fig. 7). With the number of cycles, there is no change in voltammogram shapes. For a lower anodic potential limit of  $0.2 \text{ V}$  (sce), the polymer electroactivity is completely eliminated, because the oxidation processes are omitted.



**Fig. 6** Voltammograms of Ti electrode immersed in 1 M  $\text{H}_2\text{SO}_4 + 0.3 \text{ M}$  aniline ( $v = 20 \text{ mV/s}$ ). 2, 4 and 8 represent number of cycles



**Fig. 7** Voltammogram of Ti electrode, with previously formed Pani film, immersed in 1 M  $\text{H}_2\text{SO}_4$  ( $v = 200 \text{ mV/s}$ )

For a new, more positive anodic potential on the same electrode, the electrochemical activity in the polymer film restarts.

From all these measurements we can conclude that the redox pair F-F' originates from some species of degradation products, which are incorporated into the polymer chain and participate in redox reactions in the polymer film.

## Discussion

The appearance of third redox waves F-F' during the continuously applied voltammetric scans on the Ti electrode in aqueous acid solutions with aniline added and in acid solutions of already formed Pani films is closely related to the so-called "middle" peaks B-B' and C-C'. In literature data there exists some controversy over the interpretation of the "middle" peaks in the cyclic voltammograms, and a number of key questions remain still unanswered. It is generally accepted that the "middle" peaks originate mostly from the redox reactions of dimers, oligomers and the degradation products including *p*-benzoquinone, quinoneimines, *p*-aminodiphenylamine, hydroquinone and *p*-aminophenol.

Hand and Nelson [24] suggested that the "middle" peaks arise from the product of the oxidative reaction of aniline in acidic solution, which should be *p*-benzoquinone when the potential is sufficiently high. Kobayashi et al. [25] and Stilwell and Park [19] also proved the existence of *p*-benzoquinone as the product of oxidative degradation of Pani using voltammetry and UV-Visible spectroscopy, and proposed that the CV current peak B is likely to arise from the *p*-benzoquinone/hydroquinone pair. However, *p*-benzoquinone may be produced from the very beginning of the aniline oxidation and/or another intermediate leading to the benzoquinone may give a similar CV peak. This intermediate molecule is likely to be *p*-aminophenol, which produces *p*-benzoquinone upon oxidation [26].

Yang and Bard [26] designed other pairs of “middle” peaks to distinguish them from B–B’ and C–C’, formed at a later stage of cyclization. They suggest that the “middle” peaks may result from a small oligomer with the diphenylamine structure. According to these authors, the “middle” peaks on a Pt electrode and slow scan rates result from the redox pairs *p*-hydroxydiphenylamine and *p*-aminodiphenylamine in the early stages, and benzoquinone and *p*-aminophenol in the later stage. At fast scan rates, oxidative hydrolysis can be suppressed, and the “middle” peak is only a result of a redox reaction of *p*-aminodiphenylamine or small oligomers formed from *p*-aminodiphenylamine units.

Note that all the above-mentioned reports describe the Pani deposits as a unique *para*-coupling phenomenon and have neglected a probable *ortho*-coupling in the polymer structure. A very few papers, so far, have been devoted to the possibility of the cross-linking reactions and *ortho*-coupling mechanism in the polymer chain.

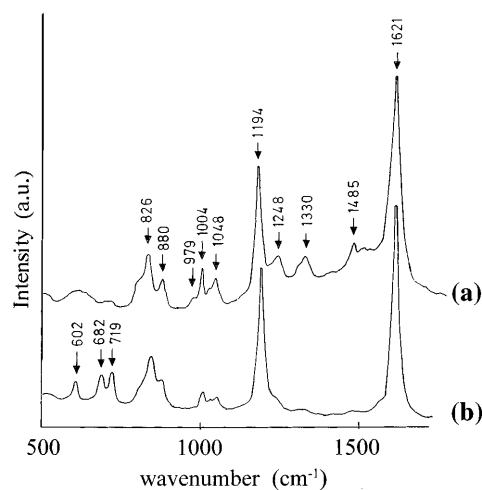
Genies and Tsintavis [28] pointed out the possibility of *ortho*-coupled aniline rings in addition to the *para*-coupled ones during the process of polymerization of aniline at higher anodic potentials. They have attributed the “middle” peaks to the presence of a polymer containing phenazine rings.

Note that before us Park et al. [26] have recorded on a Pt electrode a very low intensity of anodic peak F on the right hand side of the first anodic peak A during the CV measurements made using solutions containing 50 mM aniline in 1 M H<sub>2</sub>SO<sub>4</sub> with scan rates of 50 mV/s. They claimed that this peak should be assigned to larger oligomers than dimers, but smaller than the polymer, and it might originate from the redox reaction of the phenazine-type intermediate, which is regarded as a cross-linked oligomer, as proposed by Genies et al. [23]. The cross-linking reaction should give rise to an interruption in the delocalization of both the charge and the electron along the polymer chain. The experiments performed with phenazine in H<sub>2</sub>SO<sub>4</sub> solution with aniline added showed that the phenazine cannot be oxidized in just the potential range F–F’. The formation of waves F–F’ should be correlated to the presence of an intermediate which could react to phenazine rings, as in aromatic electrophilic substitution reactions.

It is very possible that on a Pt electrode the voltammetric peak F’ convolutes with the cathodic peak A’, which is many time larger than the corresponding anodic peak A. Of course, this cannot be a strong proof, because on a Pt electrode it is not possible to deconvolute the cathodic peak in aqueous solutions for cathodic potentials more negative than –0.2 V (sce).

In order to characterize the origin of peaks F–F’, we have performed additional spectroelectrochemical measurements on the Ti electrode for various values of cathodic potential during the scan. Figure 8 shows the Raman spectra recorded at potentials of –0.15 V and –0.6 V, i.e. before and after the cathodic peak F’. Spectrum a is very similar to that monitored on a Pt electrode for the fully reduced form of Pani [29]. Assignments of Raman bands are given in Table 2.

During the scan from –0.15 V to –0.6 V, the difference between the two spectra confirmed the transition of the semiquinoid and quinoid parts and also the polaronic part of benzene to *para*-disubstituted benzene rings. The bands located in spectrum (a) at 1248, 1485 cm<sup>–1</sup> (characteristic of stretching vibrations of a



**Fig. 8** In situ Raman spectra of Ti electrode with formed Pani film after 5 cycles (potential range between –0.6 and –0.9 V) in aqueous 1 M H<sub>2</sub>SO<sub>4</sub> + 0.1 M aniline, recorded for potentials of: a –0.15 V, b –0.6 V

**Table 2** Raman frequencies in the 500–1800 cm<sup>–1</sup> range for various redox forms of Pani. B, benzene ring; Q, quinoid or semiquinoid ring; s, strong; m, middle, w, weak, sh shoulder. The peaks located at 979, 1004 and 1048 cm<sup>–1</sup>, which appear in all Raman spectra, belong to the background solution of 1 M H<sub>2</sub>SO<sub>4</sub> + 0.1 M C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>

Potential, –0.15	V vs (sce) –0.6	Raman assignment	Wilson notation
/	602 (m)	$\delta_{C-C}$ in mono-disubstituted B ring	6 b
/	682 (m)	$\delta_{C-C}$ in <i>para</i> -disubstituted B ring	6 b
/	719 (m)	$\gamma_{C-C}$ in <i>para</i> -disubstituted B ring	4
/	826 (m)	$\delta_{C-C}$ in B ring	1
880 (m)	880 (sh)	$\gamma_{C-H}$ in B and Q ring	10 a
1194 (s)	1194 (s)	$\delta_{C-H}$ in B ring	9 a
1248 (m)	/	$\nu_{C-N}$ in Q ring (semiquinoid and quinoid part)	
1330 (m)	/	$\nu_{C-N} + \nu_{C-C}$ in B (polaronic part)	
1485 (m)	/	$\delta_{C=N}$ head-to-tail polymerization in Q (semiquinoid and quinoid part)	
1621 (s)	1621 (s)	$\nu_{C=C}$ in B ring	8 a

semiquinoid and quinoid part) and  $1330\text{ cm}^{-1}$  (characteristic of a polaronic part in the benzene ring) disappear in spectrum (b). Several new bands located at 602, 682 and  $826\text{ cm}^{-1}$  characteristic of benzene and *para*-disubstituted benzene rings appear.

The strongest Raman bands, 1194 and  $162\text{ cm}^{-1}$ , which are the key bands of *para*-disubstituted benzene rings, are located on the same wavenumber on the two spectra, indicating that the chemical structure of the Pani film does not change significantly at the potential before and after the peak  $F'$ . No Raman evidence of *ortho*-coupling and phenazine structure was monitored. The polymer chain consists of *para*-disubstituted semiquinoid, quinoid and benzene rings in a ratio which depends on the applied potential.

## Conclusion

The study of the evolution of the voltammetric curves of aniline and electrodeposited polyaniline on a Ti electrode as a function of the anodic potential limit indicates that the mechanically polished Ti surface is suitable for the electrochemical synthesis of polyaniline and the investigation of redox reactions in a polymer film.

The mechanism of electrosynthesis on a Ti electrode is similar to that on a Pt electrode. The formed Pani film on the Ti electrode, for the same electrochemical condition, is thinner, with more reversible redox processes than on a Pt electrode.

For cathodic potentials more negative than  $-0.2\text{ V}$  the new redox peaks  $F-F'$ , which are closely related to the "middle" peaks, were detected.

The formation of waves  $F-F'$  should be correlated to the presence of an intermediate which could react to form phenazine rings, as in aromatic electrophilic substitution reactions.

Tentative assignments of Raman bands of the Pani film provide support for the assumption that at a potential of  $-0.6\text{ V}$  the polymer chain mostly consists of *para*-disubstituted benzene rings. At this potential, the yield of the transition from the fully oxidized to the fully reduced Pani form is nearly 100%.

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