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Electrochemical Preparation and Properties of Novel Conducting Polymers Derived from 5-Amino-2-naphthalensulfonic Acid, Luminol and from Mixtures of Them

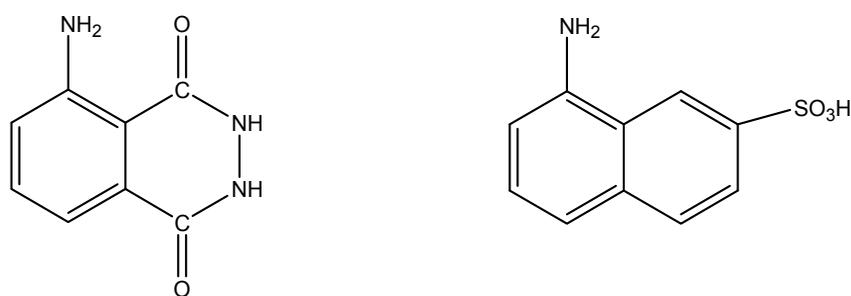
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1. Introduction

Polyanilines contain anionogenic functional groups are denominated self-doped polyanilines. These polymers possess properties different from those of polyaniline (PANI) as suppressed or no need on anion doping during oxidation or reduction processes, solubility in aqueous base, extended redox activity for neutral and basic solution, making them promising applications such as biosensors as a result of physiological pH values, and rechargeable batteries due to the fact that self doping polyanilines are capable of storing more specific energy than PANI as a function of self-doping (Malinauskas, 2004). Therefore it is important the development of these types of polymers, the electrochemical oxidation of 5-amino-2-naphthalensulfonic (ANS) and the luminol can be done a self-doped homopolymer, however the electropolymerization of these compounds has not been studied. The chemical structures of these monomers are similar in three aspects (Figure 1): (a) both ANS and luminol contain into their chemical structure the aniline; (b) It is difficult obtain a film of homopolymers to these monomers, because the electrooxidation in milium acid of luminol produce a dimmer (De Robertis et al., 2008; Ferreira et al., 2008) in fact the solubility of luminol is bass in this milieu, in these conditions is favored the formation of dimmers; on the other hand no deposition of a polymer onto the electrode has been observed when others amino naphthalensulfonic acid has been electrochemically oxidate, probably for the reason that oligomers are very soluble (Mažeikienė & Malinauskas, 2004). (c) A self-doped polymer can be obtained by copolymerization with aniline and whoever of these monomers (De Robertis et al., 2008; Ferreira et al., 2008, Mažeikienė & Malinauskas, 2004).

So large of our knowledge there are no reports of the homopolymerization of ANS and luminol, the importance of the synthesis of each films consist in the case of ANS in obtain information of the effect of the separation of group sulfonic to aniline in the ion exchange of film, because the charge compensation has been evaluated principally for ring substituted

anilines (Barbero et al., 1994; Cano-Márquez et al., 2007; Mello et al., 2000; Varela et al., 2001). In the case of homopolymer of luminol should be studied as influence the chemical nature of film in the properties obtain and in the activity electrocatalytic; in fact these properties are only reported for the dimer of luminol (Chen & Lin, 2002). On other hand as the polymer obtained to luminol not is water soluble, in consequence the copolymerization of these two monomers can be result of a deposition a self doping polymer film. The goal of this study is the electrosynthes of three novel conducting polymers: polyANS, polyluminol (only has been reported dimmers of luminol) and copolymer, obtained to ANS, luminol and both respectively, the evaluation of properties of films obtained as well as: activity electrocatalytic to ascorbic acid, electrochemical activity in pH neutral and study the charge compensation using the electrochemical quartz crystal microbalance (EQCM) during the redox process only for polyANS.



Luminol (3-aminophthalhydrazide)

5-Amino-2-naphthalenesulfonic acid

Fig. 1. Chemical structure of monomers used in the present study.

2. Experimental

2.1 Materials

The commercial chemicals: luminol (Fluka), ANS (Aldrich), graphite powder (sigma), nujol (Alfa- Aesar), HCl (Fermont), HClO₄ (Fermont), HNO₃ (Caledón), H₂SO₄ (Fermont) and camphorsulfonic acid (Aldrich) were of analytical reagents grade and were used without further purification except the aniline (Sigma) which was distilled before use at stored to low temperature in the dark. The aqueous solutions were prepared using deionized water, and the solutions were deoxygenated by purging with nitrogen gas. After this, a nitrogen atmosphere was kept over the solution during each run.

2.2 EQCM measurements

EQCM measurements were conducted using a PAR 273A (Princeton Applied Research) potentiostat-galvanostat coupled to an electrochemical quartz crystal microbalance Seiko model QCA922, both controlled by WinEchem V. 1.5 installed in a personal computer. The quartz crystal resonator was mounted in a home-made acrylic cell (Figure 2). This cell is characterized by the commercial holder of quartz and it is united to made in home solution container, so the sample container also hold the quartz crystal. As the sample container is acrylic only aqueous solutions can be used with this cell.

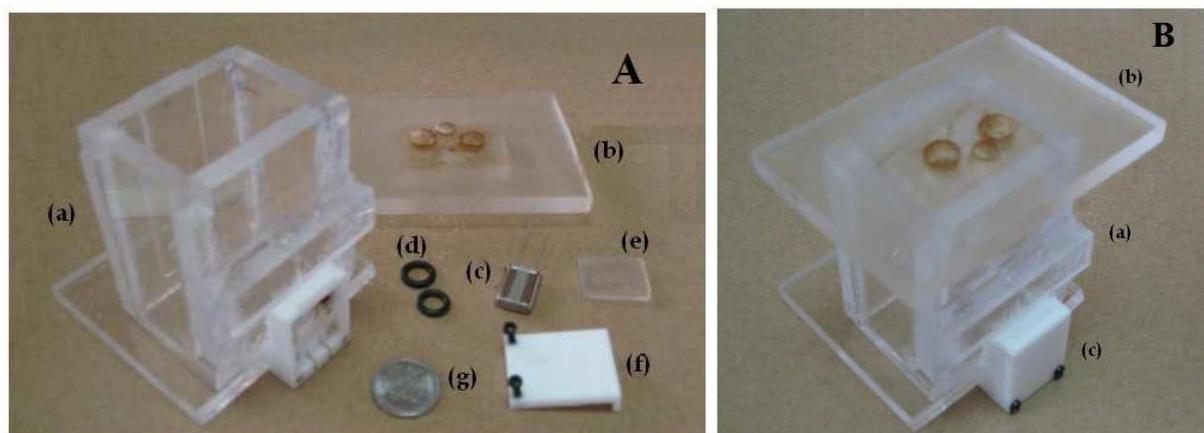


Fig. 2. Photograph of A) disassembled and B) assembled cell: (a) acrylic sample container, (b) acrylic cell cover, (c) teflon quartz crystal and his container, (d) O-rings, (e) acrylic cover of quartz crystal container, (f) teflon cover of quartz crystal container and (g) coin ($\phi = 0.8$ cm).

2.3 Electrochemical measurements

Electrochemical experiments were carried out in a three-compartment cell in a high purity nitrogen atmosphere at room temperature. The electrode reference consisting of $\text{Ag}|\text{AgCl}|3 \text{ mol dm}^{-3} \text{ NaCl}$ (BAS) and the counter electrode was a platinum wire. The working electrodes were: carbon paste electrode (0.1452 cm^2), glassy carbon, Au and Pt (0.0707 cm^2) and a 9 MHz AT-cut quartz crystal coated with gold (0.1963 cm^2). Two types of carbon paste electrode were prepared the first by intimately mixing 1.0 g of finely ground graphite powder with 1.0 g of Nujol. The second type of electrode is characterized by included the monomer into the carbon paste bulk, the electrode is prepared mixing graphite powder, nujol and the monomer. In both cases the resulting paste was then packed into a plastic 1 mL syringe in which a piece of copper wire was wound to produce the electrical contact. The surface was smoothed by a weight paper before each experience. The glassy carbon, Au and Pt electrodes were systematically polished successively with 3 and $1 \mu\text{m}$ polish diamond (BAS) on a Microcloth felt disk (BAS). Following this, the electrodes were thoroughly rinsed with deionised water and sonicated in an ultrasonic bath for 10 minutes. The precoated PANI film for electrodeposition of polyANS was carried out by realizing 10 cycles of potential between -200 and 1200 mV , except for the three first cycles for which the upper limit was 1100 mV . The scan rate was 50 mVs^{-1} , and the electrolyte solution was $0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M aniline}$.

3. Results and discussion

3.1 Electrosynthesis and characterization of polyANS

The electrosynthesis of a film of polyANS was tested by chronopotentiometry and cyclic voltametry in five different electrodes: Au, Pt, glassy carbon, carbon paste and Au modified with PANI. No deposition of a polymer onto the Au, Pt and glassy carbon electrodes was observed, in agreement to reported for aminonaphthalen disulfonics acids (Mažeikienė & Malinauskas, 2004) probably because the products formed during the oxidation are very solubles. On the contrary film growth was presented onto carbon paste and Au/PANI electrodes, the syntheses and properties obtained in each electrode are presented to continuation.

3.1.1 Electrosynthesis and electrogravimetric study of polyANS synthesized onto Au/PANI electrodes

The syntheses electrochemical of film of PolyANS onto the Au/PANI electrode was carried out by cyclic voltametry, this modified electrode was used as working electrode for the reason that in earlier work it was demonstrated that contrary to the metallic electrodes a film of sulfonated PANI is obtained onto Au/PANI electrodes since, during electrooxidation of PANI positive charges are generated at the polymer chain, which are compensated by incorporation of anions from the solution. Consequently, the $-\text{SO}_3$ group of sulfonated PANI is incorporated to the PANI film as a dopant anion, anchoring sulfonated monomers on the PANI surface. Then, when the oxidation potential of monomers is attained the monomer is polymerized on PANI. During the reduction the anion cannot be ejected of PANI because the polymer synthesized is trapped within the PANI chains. (Cano-Márquez et al., 2007). Figure 3 shows curves obtained in diverse stages of growth of polyANS. At the very beginning of the electrodeposition the curve obtained is very similar to those of PANI (Shin-Jung & Su-Moon, 2002), in fact, in this stage the polyANS produced is small in comparison to those of PANI as a result the response obtained is those of PANI, which is characterized by three well redox centered pair centered at around 250, 780 and 500 mV corresponding to leucoemeraldine to emeraldine, emeraldine to pernigraniline redox transitions and sobreoxidation products respectively. When the cycle increase the response change gradually until become in those of polyANS, in fact the peaks attributed to oxido-reduction of film shift until overlapping (Figure 3). The reduced separation of the two peaks for sulfonated polyaniline has been associated with steric effects caused by the bulky sulfonic acid substituent (Wei et al., 1996; Yue et al., 1991). Additionally to the two oxido-reduction process of polyANS situated between 200 and 500 mV, the cyclic voltammogram of polyANS present a redox pair centered at around 540 mV, at present time no clear assignation can be proposed for this peak, however it can be speculated that have as origin the oxido-reduction of degradation products because is located of same potential of degradation products of PANI.

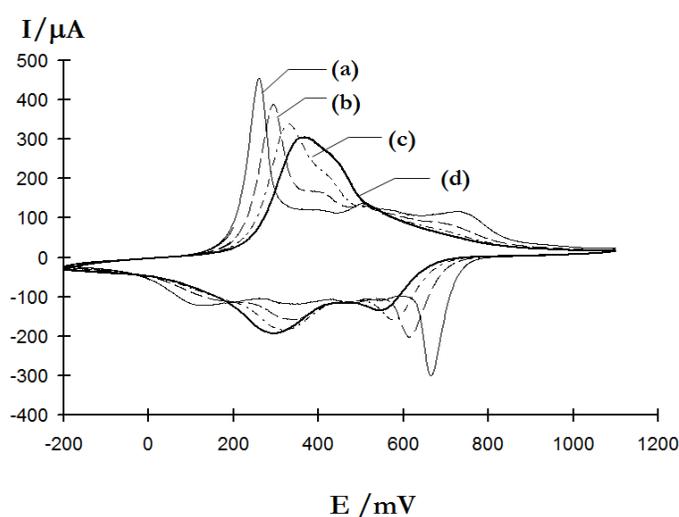


Fig. 3. Cyclic voltammograms of the 14th (a), 28th (b) 42th (c) and 56th (d) cycle of the electropolymerization of 1 mM ANS in 0.5 M H_2SO_4 , obtained onto Au/PANI electrode. The potential was scanned from -200 to 1090 mV at 100 mVs^{-1} .

From the perspectives of electrochemical applications, arguably the most important underlying process of conducting polymers is the exchange between the films and ions molecules that accompany film redox switching. In case of sulfonated polyanilines is accepted that the charge compensation is accomplished mainly by the ejection of cations (Mello et al., 2000; Varela et al., 2000a, 2000b, 2001; Cano-Márquez et al.; 2007) in contrast with the behavior of PANI, which is carried out by the incorporation of anions (Hillman & Mohamud, 2006). In order to define as is realized the charge compensation of polyANS electrochemical quartz crystal microbalance (EQCM) measurements were carried out in monomer free solution, the curves obtained were analyzed considering that the change of frequency is correlated to change of mass for the Sauerbrey equation (Donjuan-Medrano & Montes-Rojas, 2008):

$$\Delta f = -C_f \Delta m = -\left(\frac{2f_0^2}{\rho_q v_q}\right) \Delta m \quad (1)$$

Where Δf and Δm are the change of frequency and the change of mass respectively, C_f is the proportionality constant which depend of the base frequency (f_0); density of quartz (ρ_q) and the wave velocity within the quartz crystal (v_q). The negative sign in the equation indicate that when the frequency increase the mass diminishes and when the frequency decreases the mass augment. In order to use the Sauerbrey equation it is necessary probe that the film deposited in the quartz is "rigid", it is the mass loading of the quartz crystal microbalance show ideal acoustic coupling to the crystal surface (Buttry & Ward, 1992) and determinate experimentally the value of C_f (Donjuan-Medrano & Montes-Rojas, 2008). In raison that in this work only a qualitative analysis was carried out, it was not required to validate the Souerbrey equation, neither it was indispensable determinate experimentally the value of C_f , only was assumed of Sauerbrey equation that:

$$\Delta m = -C_f \Delta \quad (2)$$

It is that the change of mass is proportional to $-\Delta f$. The obtained results for H_2SO_4 are shown in Figure 4, in a first time the potentiodynamic profile of I and $-\Delta f$ was analyzed over the range -200-900 mV (Figure 4a), it was observed that when the scan begin there are not redox process, so the frequency remain constant, to 300 mV appear the oxidation peak this indicate that the polyANS is oxidate and positives charges in the polymer chain are generated, simultaneously a decrease of mass is presented, this mean that for maintain the electrical neutrality of the doped polyANS the charge compensation is carried out predominantly for ejection of cations from the polymer phase to the solution as is attain for a self-doped polymer, when it was reach the potentials for the full oxidation of polymer an increase of mass was observed, contrary to decrease of mass observed for PANI in similar conditions (Orata & Buttry, 1987). During the reverse sweep the mass decrease until finalized the reduction, it is the anion incorporated during the oxidation are ejected when the film back to netral condition, to end of scan the mass augment to until reach nearly the initial value. For the reason that the two peak of oxido-reduction of film are before 500 mV, the same experiment was repeated fixing the upper limit potential to 500 mV, as can be been in Figure 4b, the behavior is similar to those obtained for the extended range, in fact the mass of polyANS remains constant until the film commence the oxidation process in this moment the mass descend, this behavior indicate that the electroneutralization of film is achieved principally by expulsion of protons containing in the $-SO_3H$ group of polyANS, to higher potentials the mass increase, a similar behavior has

been presented for sulfonated PANI (Varela et al., 2000). After the reverse of the scan direction the mass continue increase until the process of reduction begin, in this point the mass decrease, finally the mass increase attain the value original. The experimental evidence presented above demonstrates that the charge process during the charge compensation is carried out principally by expulsion of cations of polyANS, however is not possible establish whether or not anion participation. In addition the evolution of frequency in the direct scan is completely different to those obtained in the inverted scan, it is the change of mass obtained is not reversible resulting in a broad frequency curve. This behavior is different to those obtained for sulfonated PANI (Mello et al, 2000; Varela et al. 2001) where the curves of frequency were more reversible. This behavior suggest that the electroneutralization is more complexes for the polyANS that for the films synthesized to anilines ring substituted by sulfonic groups, probably due the distance of the sulfonic group and nitrogen is much longer in polyANS that the anilines substituted directly in the ring for sulfonic groups, so in this case the electroneutralization is more easy.

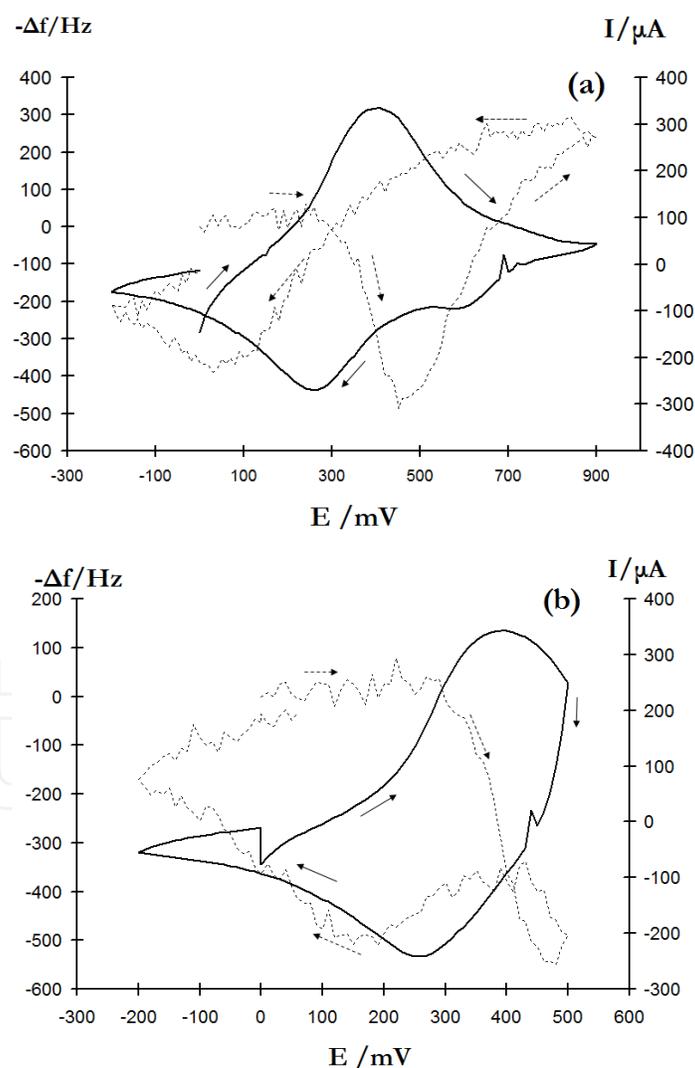


Fig. 4. Plot I/E (full line) and $-\Delta f/E$ (dotted line) potentiodynamic profile for polyANS obtained for two upper limit (a) 900 and (b) 500 mV in H_2SO_4 0.5 M electrolyte solution at 100 mVs^{-1} .

In order to determine whether there are or not anion participation in the electroneutralization of PolyANS, EQCM measurements were carried out in solutions for acids with anions of different molar mass: H_2SO_4 (96 gmol^{-1}) (Figure 4), HCl (35.45 gmol^{-1}), HClO_4 (99.4 gmol^{-1}), HNO_3 (62 gmol^{-1}) and camphorsulfonic acid (HCS) which molar mass of anion is 231.1 gmol^{-1} (Figure 5). A decrease of mass is presented during the oxidation in H_2SO_4 , HCl , HClO_4 and HNO_3 showed that during the electroneutralization, protons are ejected to polyANS. However, a participation of anion can be proposed in reason of the marked dependence of frequency profile and cyclic voltammogram of anion of acids as is showed in Figure 4 and 5. The decrease of mass ($-\Delta f$) change with the acid used and not relation between the anion molar mass and the variation of frequency was present. These results show that the charge compensation of polyANS is carried out by both expulsion of protons and additions of anions, but the predominant process is the cation expulsion. In the HCS case also the electroneutralization is realized principally by proton expulsion despite the fact that the mass remain constant during the oxidation, in fact the change of mass registered are the sum of two contribution incorporation of anions and ejection of protons, as the frequency remains constant during the oxidation this mean that the augmentation of mass by incorporation of anions has the same value that the diminution of mass by expulsion of cations, this resultant is due to the molar mass of CS is more grand that those of the anions of other acids. Finally, it is important to note that the process of electroneutralization of polyANS is different of those of homopolymer of ortanilic acid, in

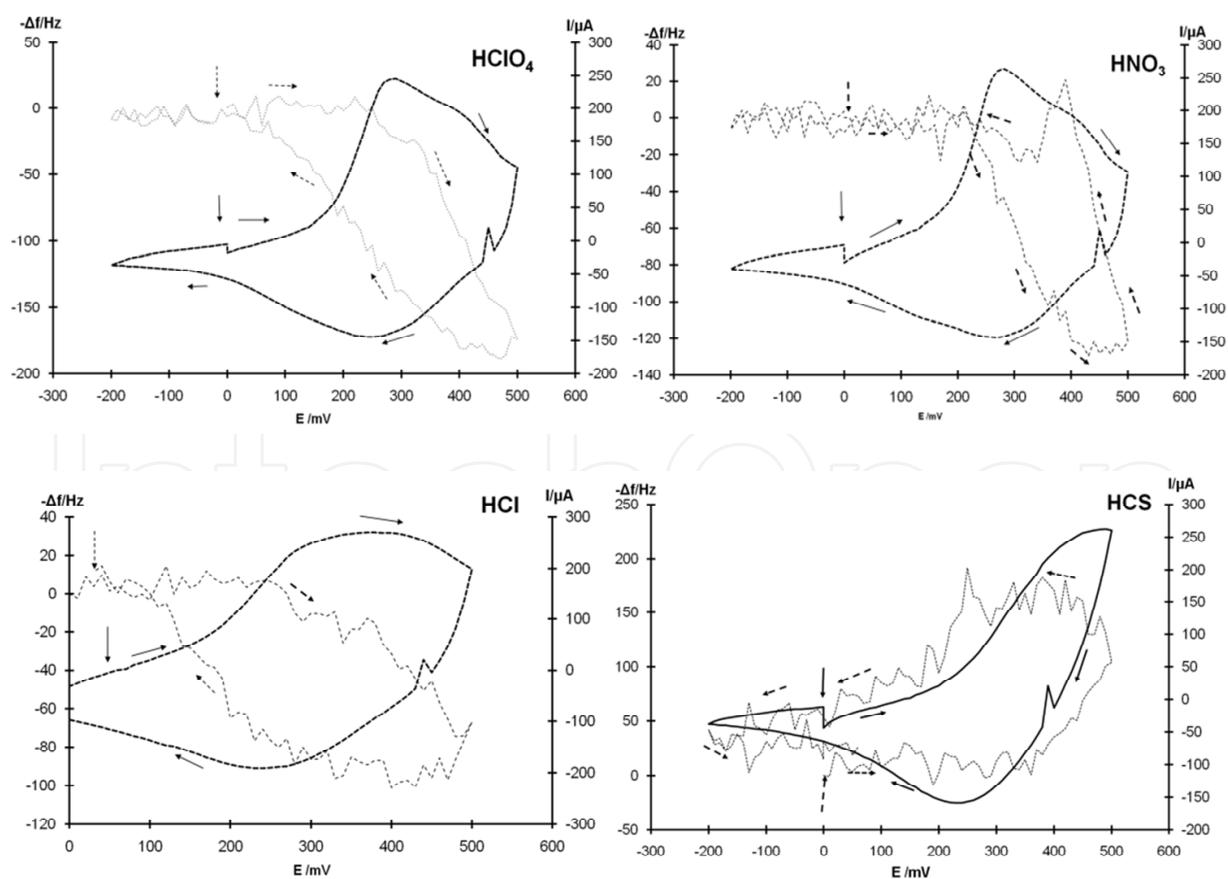


Fig. 5. Cyclic voltammograms and frequency responses recorded simultaneously of a polyANS film in different 0.5 M acids solutions. The scan rate was 100 mVs^{-1} .

fact for this polymer the compensation of charge is carried out exclusively by ejection of protons and the profiles of change of frequency are very reversible (Cano-Márquez et al, 2007), which suggest that the process is more simple. The differences between these sulfonated homopolymers proved that the distance between the sulfonic group and the nitrogen impact in the electroneutralization process, when these groups are closer the cation participation is more important.

3.1.2 Electrosyntheses of polyANS using carbon paste electrodes

The electrodeposition of polyANS was also evaluated using carbon paste electrodes, the electrosynthesis was carried out by two methods with the monomer in solution and incorporated onto the carbon paste electrode. The results found employed the first methodology are presented in a subsequent section, in the case of the second mode the electrodeposition was realized potentiodynamic in a solution containing only H_2SO_4 1 M and the working electrode was carbon paste modified with ANS, the curve registered during the successive scans are presented in the Figure 6, this cyclic voltammogram is similar to those obtained with Au/PANI electrodes, in fact the curve can be show a shoulder and a broad peak situated around 309 and 424 mV correspondingly, in the counterpart cathodic are two overlapping peak centered in 269 and 319 mV. Following an analogy to the parent polyaniline these peaks can be assigned to the leucoemeraldine to emeraldine transition and the emeraldine to perigraniline transition, respectively. Additionally a redox process appear around 100 mV, it not was possible the assignation of these peaks to an specific reaction, however it is possible that the peak correspond to the oxido-reduction of oligomers accumulate in the electrode, in fact these peaks not are observed when the response is analyzed in solutions basic. Subsequent cycles show anodic and cathodic current maxima with increasing currents, indicating progressive film formation. The electrochemical behavior of films synthetised was examined by cyclic voltametry, for this experience was necessary shift the upper limit potential to 600 mV, with the finality of avoid the oxidation of monomer and more film synthesis, it is examine only

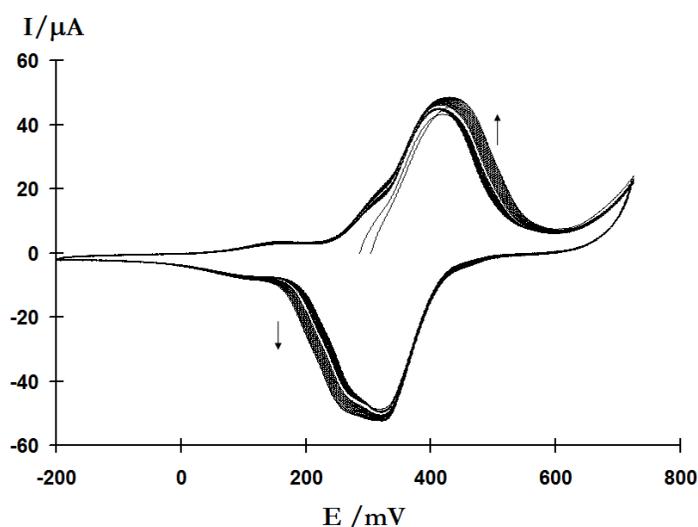


Fig. 6. Successive cyclic voltammograms of a paste carbone electrode modified with ANS (0.1452 cm^2) in H_2SO_4 (1 M). The composition of electrode was graphite powder, nujol and ANS in percentages of mass of 80, 18.5 and 1.5 respectively. Scan rate: 100 mVs^{-1} .

the response of polyANS. The polymers which dissolve very slowly, it is when are cycled repeatedly diminish slightly the current intensity. The peak heights scale linearly with the sweep rate as is expected for a surface bound species.

The electropolymerization of ANS in carbon paste electrodes not modified with this monomer in solution were carried out by chronoamperometry and cyclic voltammeter. The results obtained with potentiodynamic methods are presented in the copolymer section, in the case of chronoamperometry the electrooxidation was achieved with a solution formed only by ANS, since the monomer was used itself as an electrolyte, the potential was stepped in 1250 mV during 60 s. After the growth was terminated, the film was studied by recording cyclic voltammograms; the curves obtained are shown in figure 7. We note that the locations of the redox peak and the general appearance of the voltammogram are similar to sulfonated polyanilines (Royappa et al., 2001; Nguyen et al., 1994) and the polyANS synthesised with Au/PANI and carbon paste modified with ANS. The cyclic voltammogram obtained exhibit two broad and overlapping oxidation peak between 200 and 600 mV. The oxidation peak correspond to the oxidation of the neutral nitrogen atoms in the polymer backbone to form the radical carbon and dication and they compare well with the peaks for PANI films (Buttry & Ward, 1992). A process centered in 100, similar to those obtained with the monomer contain in the bulk paste electrode also appear when the electrodeposition is realized with the monomer in solution. A linear relationship was found between the peak current and scan rate, indicating that the electroactive polymer film is well adhered to electrode. To investigate the influence of the pH on the redox behavior of the film, cyclic voltammograms of electrochemically synthesized films prepared under the same conditions as above, were recorded in solutions of different pH values. The voltammograms obtained are shown in Figure 7. One of the most obvious changes in the voltammetric behaviour of polymer in neutral and alkaline media in comparison to pH acid is the diminution in current, which is produced by the high solubility of sulfonated polymer in pH neutral. In addition the peak attributed to polyANS shift not much to negative potentials. Thus the electroactivity of polyANS is practically independent of pH as is attain for a self-doped polymer.

The same experiments were made with glassy carbon, Au and Pt as working electrode, the chronoamperograms obtained showed no rising transients, and no evidence of a film was obtained by cyclic voltammetry, in agreement with Mažeikienė et al, 2004. These results show that the polymerization of sulfonated monomers only can be carried out in carbon paste electrodes. The reasons for this positive deposition are unknown. However physical adsorption of monomers and oligomers in the paste carbon, it may be speculated

In this part of work was showed that the ANS can be polymerized in carbon paste and Au/PANI electrodes, this result is contrary to those obtained for other amino naphthalensulfonic, in fact in this study is proved that is not possible the electrochemical homopolymerization of these type of compounds (Mažeikienė & Malinauskas, 2004). Additionally is well established that Sulphonated anilines are difficult to polymerise under conventional conditions, in fact the high solubility of film in aqueous milieu made difficult the synthesis of a film, the strategies employed for the electrodeposition of sulfonated homopolymer has been oriented to the diminution of solubility of oligomer, for this, the electropolymerization has carried out to low temperatures and the combination of organic and aqueous solvents (Krishnamoorthy et al., 2002). In other works is reported the formation of sulfonated polymers using metallic electrodes however the polymerization rate is very low (Zhang, L; 2006). The advantages of the use of Au/PANI and carbon paste

electrodes for the electrosynthesis of sulfonated polymers in relation to other strategies is the facility to obtain thick films rapidly in working to room temperatures and with aqueous solutions.

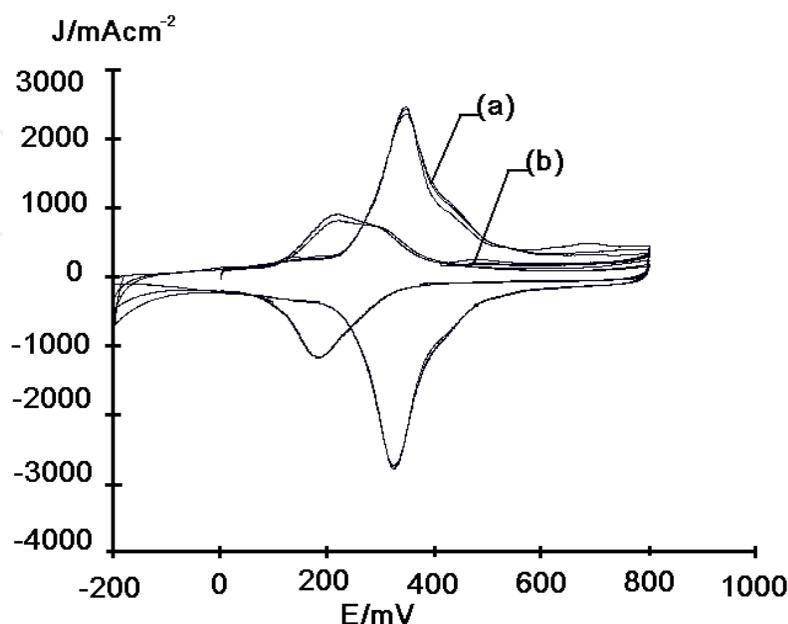


Fig. 7. Cyclic voltammograms of polyANS in: (a) H_2SO_4 0.1 M and (b) Na_2SO_4 0.1 M. Synthesis of the films was performed by potential step at 1240 mV using as working solution ANS 8 mM. Scan rate: 100 mV/s.

3.2 Electrodeposition and characterization of polyluminol

3.2.1 Electrosyntheses of polyluminol

The films obtained of electrooxidation of luminol have been denominated polyluminol. However, different works have showed that the product obtained are dimmers and no polymers (Ferreira et al., 2008; Robertis et al., 2008), the chemical composition of film has been attributed to the bass solubility of monomer in solution. In order to obtain a polymer of luminol we propose increase the monomer concentration in the interface electrode/electrolyte using paste carbon electrodes bulk modified with luminol. The curves obtained during successive scan for two different upper limit potential (E_λ) are presented in figure 8, in both cases the peaks due to the oxidation and reduction increase in intensity for each cycles as it is characteristic of growth of a film. The voltammogram acquired are different of those obtained with metallic electrodes in similar conditions, for the reason that additionally to process B_1/B_1' presented in metallic electrodes (Chang et al., 2005; Kumar et al., 2009), a second process B_2/B_2' is presented. A similar process to B_2/B_2' is obtained for the copolymers of aniline and luminol synthesised using solutions with more concentration of luminol than aniline (Roberti et al., 2008; Ferreira et al., 2008) and during the oxidation of luminol in higher potentials 1.2 V (Zhang & Chen, 2000). Additionally the aspect of voltammogram presented in Figure 8 is very similar to those of copolymer therefore probably this peak are associated to polymer formation. The current of process B_2/B_2' by rapport to B_1/B_1' is strongly dependent of upper limit potential, for $E_\lambda = 0.9$ V the intensity of current B_2/B_2' is very small in comparasion with those B_1/B_1' , while that when $E_\lambda = 0.8$ the

current of B_1/B_1' is only environ three fold more grand that B_2/B_2' . This dependence show that product correspondent to peaks B_1/B_1' are produced in more quantity when E_λ is more higher. Two difference important were observed in voltammogramas obtain using two differents E_λ , first, the evolution of the intensity of current, For $E_\lambda = 0.9$ V the current of peaks B_1 and B_1' increase significantly the first cycles, after remain almost constant, while that for $E_\lambda = 0.8$ V, the current augment slowly but continually, this last evolution of current is more congruent with a polymerization. The second is relationated with the peak B_1/B_1' , for $E_\lambda = 0.8$ V, the peak is more broader that for $E_\lambda = 0.9$ V in addition in some cycles is possible to observe that the peak is the resultant of the overlap of two peaks, probably those of the dimmer or degradation oxidation and those of the bipolaron state of polymer. It is we propose that the peak B_1/B_1' and B_2/B_2' can be assigned to polaron and bipolaron states of polymer respectively; because the voltammogramas are very similar to those of copolymer formed by aniline and luminol and those of sulfonated polyanilines.

Finally the film were analysed in H_2SO_4 solution by cyclic voltammetry, for this E_λ was shifted to more negatives potentials in order to avoid the oxidation of monomer in the bulk electrode paste. Voltammogramas were carried out for different scan rates, the peak heights scale linearly with the sweep rate and the cathodic and anodic peak separation remains constant as it is attain for an electroactive specie fix to surface electrode.

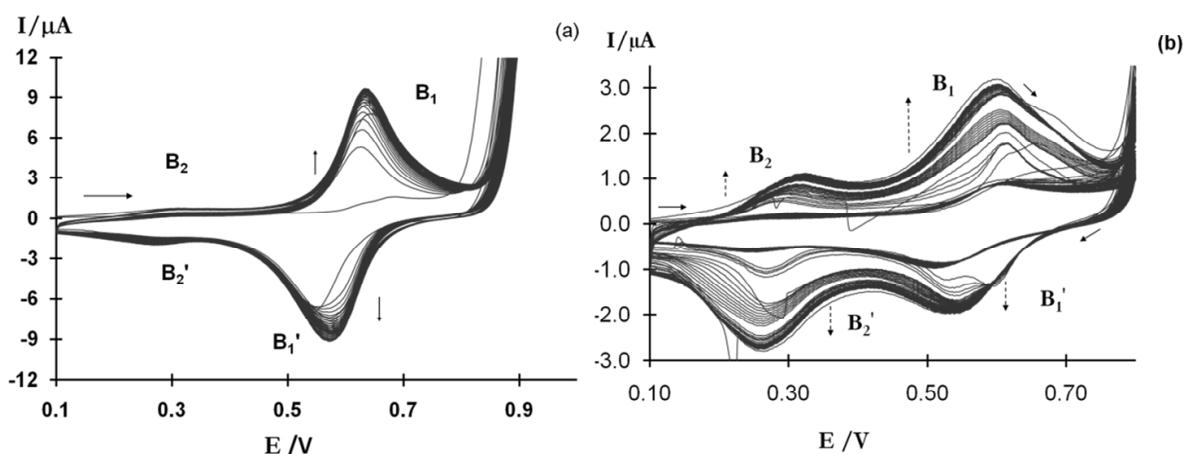


Fig. 8. Subsequent multisweep cyclic voltammograms obtained in a H_2SO_4 (0.5M), the upper limit were: (a) 0.9 and (b) 0.8 V. The working electrode was paste carbon electrodes formed by: graphite (60 %), nujol (26%) and luminol (14%). The scan rate was 100 mVs^{-1} .

In order to determinate weather the monomer concentration affect the electrosyntheses of film of polyluminol, electrodeposition were carried out employing carbon paste electrodes modified with different percentages of luminol, the results are presented in Figure 9, the voltammogramas have the same aspect, only they are differenced by the intensity in current which increase with the quantity of monomer in the bulk carbon paste electrode. This means that only the quantity of film is affected by the quantity of momomer. A similar experiment was achieved using a carbon paste electrode not modified and a solution with luminol, the curve obtained has an aspect equal to those obtained with modified electrode. It can be speculated that the curve not change with luminol concentration in the interface electrode/electrolyte, since when the monomer is in solution, the luminol is adsorbed in the electrode surface and the concentration in the interface is increase by preconcentration, so the concentration of luminol is more elevated than the metallic electrodes.

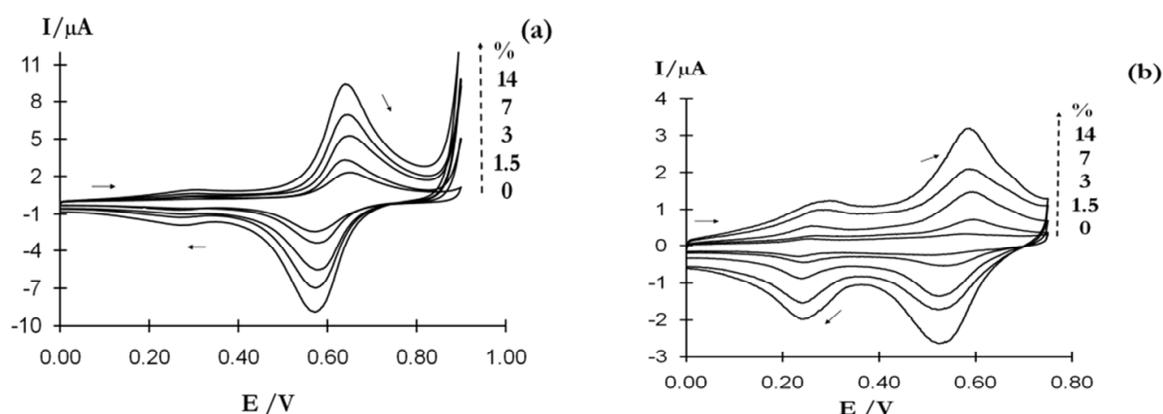


Fig. 9. Cyclic voltammograms (50 mVs^{-1}) of electrochemically synthesised polyluminol in 0.5 M aqueous H_2SO_4 . The films were synthesised with the conditions of Figure 8 with (a) $E_\lambda = 0.9$ and (b) $E_\lambda = 0.8 \text{ V}$. The composition of carbon paste was graphite (60 %), luminol (indicated in the Figure) and nujol (the necessary to reach the 100%). El 0 % indicate the film synthesised with the luminol in solution (1 mM).

3.2.2 Electrochemical activity of polyluminol to pH neutral

It is proved that the films obtained to oxidation of luminol are self-doped (Ferreira et al., 2008), this implicate that they are electroactive to $4 < \text{pH}$. Figure 10 shows the voltammograms for polyluminol synthesised with $E_\lambda = 0.8 \text{ V}$ at acid and neutral pH. It can be observed that the peaks shift slightly to lower potentials in a Na_2SO_4 aqueous solution (1 M), when the same experiment is carried out with phosphate buffers solution, $\text{pH} = 7$, (PBS) the peaks of polyluminol overlap into only one, while the current of this process remain in similar values. The difference between the voltamperometric responses at two electrolytes of a similar pH, probably is due to the charge/discharge process because the anion and cations are different. This behaviour in neutral milieu is similar to those observed in sulfonated polyanilines (Sanchís et al., 2008; Kariakin et al., 1994), and as a consequence congruent with the behaviour of a polymer. It is important note that an irreversible oxidation is observed in buffer solution (inset Figure 10), correspondent to the oxidation of monomer in the bulk electrode.

To compare the properties of polyluminol synthesized to monomer in solution and in the bulk carbon paste, cyclic voltammograms in supporting electrolyte solutions acid and neutral pH were investigated. Figure 11 shows voltammograms for polyluminol films obtained in acid and neutral electrolytes. The films are quite electrochemically active in both neutral solutions Na_2SO_4 and PBS, in Na_2SO_4 a shift to more positives potentials was observed and in PBS an overlap of the two peak was presented. However we note that the more defined and reversible peak in the case of films synthesised with the monomer in the bulk paste carbon electrode, in addition the relation between the anodic current peak in acid solution (I_0) respect to those obtained in milieu neuter PBS (I_{PBS}) or Na_2SO_4 (I_s), were $I_{\text{PBS}}/I_0 = 0.579$ and $I_{\text{PBS}}/I_0 = 1.249$, while that when the films were made to monomer in solution $I_{\text{PBS}}/I_0 = 0.487$ and $I_{\text{PBS}}/I_0 = 0.412$. A comparable tendance was showed for films obtained with other percentages of luminol in carbon paste 1.5, 3 and 7 %. These result demonstrate that in terms of extension of its electrochemical properties to high pH, are better the films elaborated to modified carbon paste electrodes than those carried out the monomer in solution.

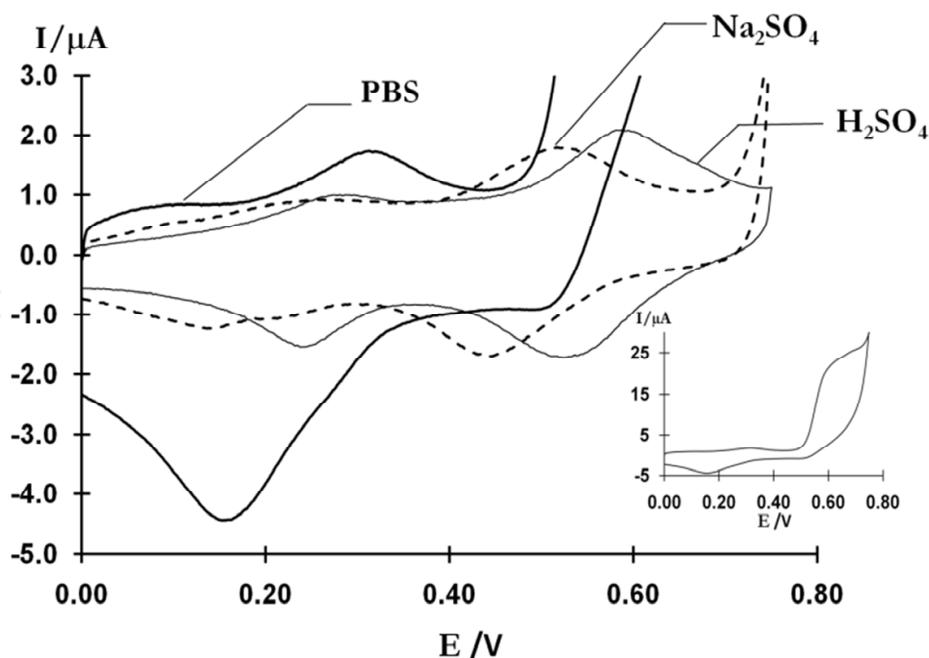


Fig. 10. Cyclic voltammograms for polyluminol synthesised using $E_\lambda = 0.8$ V and carbon paste electrode graphite (60 %), luminol (7 %) and nujol (33 %) at different electrolytes. Scan rate = 100mVs^{-1} . Inset complete cyclic voltammogram for polyluminol at PBS.

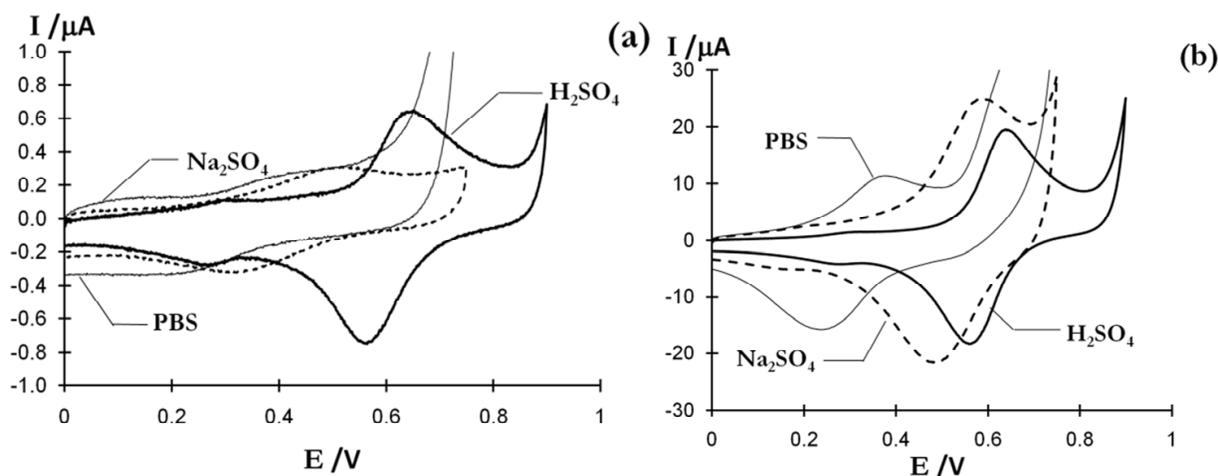


Fig. 11. Cyclic voltammetry of polyluminol, obtained in different supporting electrolytes containing: H_2SO_4 (0.5 M), Na_2SO_4 (1 M) and phosphate buffer solution (pH = 7). Synthesis of the films was performed as indicated in Figure 8a, using: (a) luminol (1 M) in H_2SO_4 (0.5 M) and (b) a modified carbon paste electrode (14%).

3.2.3 Electrochemical oxidation of ascorbic acid

A more extended application of polyluminol films and its derivatives is the electrocatalysis of ascorbic acid (Chen & Lin, 2002; Ashok et al., 2009; Ma et al., 2010; Kumar et al., 2009a; Kumar et al., 2009b). As the potentiodynamic response of films obtained using carbon paste electrodes are different to those synthesised with metallic electrodes; in fact the cyclic voltammogram is more similar to those of copolymers of aniline and luminol, we think that

the chemical composition of films in carbon paste correspond to those of a polymer, this supposition is supported by the behaviour of films in neutral solutions. In order to determinate weather the chemical composition of deposits of luminol affect or not the catalytic properties of films, the electrooxidation of ascorbic acid (aa) was studied with the films obtained and compared with those of metallic electrodes, the curves obtained are presented in Figure 12, as can be seen, the oxidation peak current augment with increasing aa concentration. The inset of Figure 12 shows that the anode peak current is linearly dependent on the aa concentration in the studied range, to slope of line was obtaining the sensibility that was $43.2 \mu\text{AmM}^{-1}$, this value is the double of those obtained using a polyluminol synthetised in a metallic electrode. This result show that the electrocatalytic activite of polyluminol film is enhanced with is obtained in carbon paste electrodes.

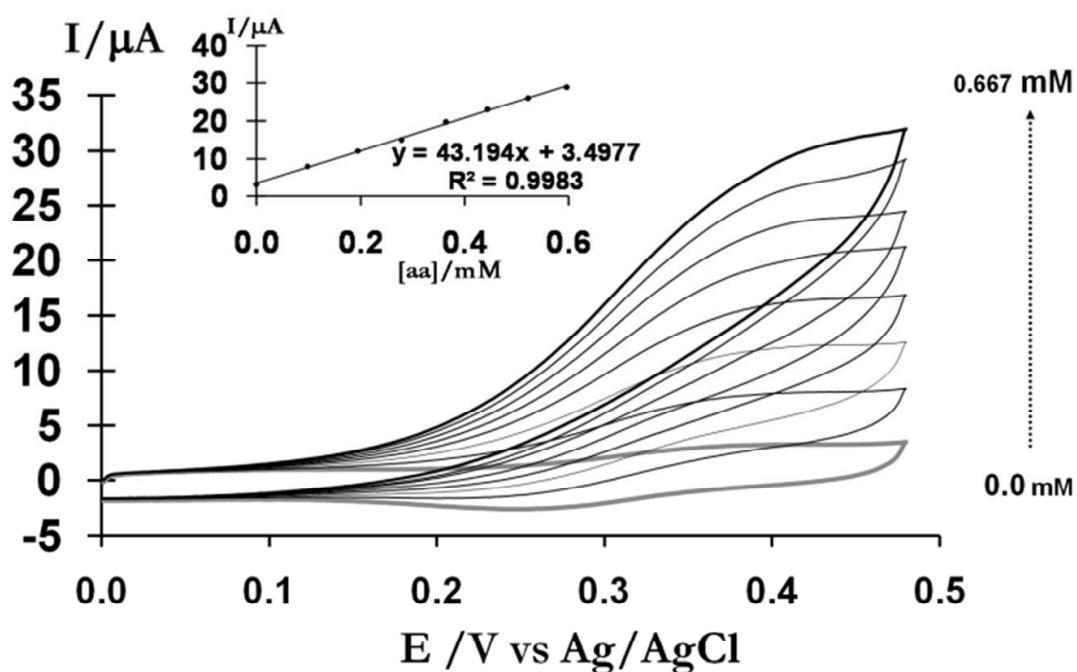


Fig. 12. Cyclic voltammetry of polyluminol in PBS containing different concentrations of aa: 0, 0.098, 0.195, 0.279, 0.364, 0.444, 0.522, 0.596 and 0.667 mM. The film was synthetised like those of Figure 8b. The scan rate was 100 mVs^{-1} .

3.3 Electrodeposition of copolymer

Finally we have tried the electrosynthesis of a novel self-doped polymer formed by ANS and luminol, in fact the electrooxidation of both compound can to produce self-doping polymers, However the polyANS is soluble in milieu neuter, this characteristic limit its use in biosensors, while the polyluminol is insoluble but the electrochemical activity is more dependent of pH in comparison with the polyANS in reason of the $-\text{SO}_3\text{H}$ is a strong acid. The combination of both monomers can be produced an insoluble polymer which present electrochemical activity in a wide pH range.

3.3.1 Electrochemical properties of monomers

In order to determinate the potential which both monomers are oxidized, potentiodynamic experiments were carried out (Figure 13a), the voltammograms exhibit a broad irreversible

anodic peak situated in the 0.7 -1.2 V and 0.9 and 1.2 V for ANS and luminol respectively. The anodic response corresponds to the irreversible oxidation of monomer entities, the potential where the oxidation of both monomers is carried out is around 0.9 V. The effect of the scan rate in the intensity of current was studied, in Figure 13b it can be observed that in the case of ANS the peak heights are linear with the square root of sweep rate in all range studied, this means that the oxidation of ANS is controlled by diffusion; while in the luminol case the peak heights scale linearly with the square root of sweep rate only in the range between 5 and 100 mVs⁻¹, in consequence for higher sweep rate, the process of oxidation can be controlled by adsorption or a combination of adsorption and diffusion. It is important to note that the slopes of both curves are essentially identical, in considering the Randles-Sevcik equation can be established that the Diffusion coefficient of both monomers should be very similar. The oxidation of both monomers is 0.9 V and in order to both monomers are in the same regime of mass transfer it is convenient working to sweep rate ≤ 100 mVs⁻¹.

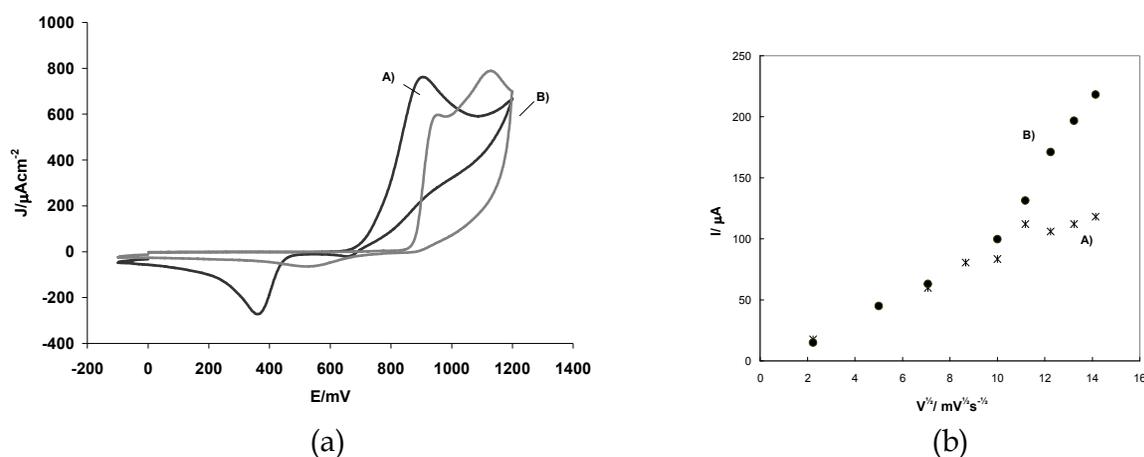


Fig. 13. (a) Cyclic voltammogram response of: (A) ANS (0.8 mM) and (B) luminol (0.8 mM) on a carbon paste electrode (0.1452 cm²) in H₂SO₄ 1 M. The carbon paste was formed by a mixture 1:1 of luminol and graphite. Potential scan rate 100 mVs⁻¹. (b) Dependence of anodic peak current with the square root of sweep rate

3.3.2 Electrochemical synthesis and characterization of copolymers

The copolymers were synthesised using a H₂SO₄ (1 M) solution contain luminol (0.8 mM) and ANS (0.8 mM) as working electrode carbon paste electrode was used, 50 potential cycles were carried out between 0 y 0.9 V. Concurrently the same experiment was repeated with a solution contain only a monomer. After their electrosynthesis, copolymers and homopolymers were characterised by cyclic voltametry in 1 M H₂SO₄ (Figure 14), in order to avoid the overoxidation of films the upper potentials were shifted to lower values. The cyclic voltammogram of copolymer was characterised by present two redox process, attributed in analogy with polyluminol and polyANS to partial and total oxidation of polymer. Comparison of the peak of copolymer with those of luminol and ANS taken under similar conditions indicate that the potential and the current of copolymers peak lies between them. This suggest that the films prepared by this procedure are indeed copolymers and not just mixtures of polyluminol and polyANS. We have tried to modulate the amount of luminol in the copolymer film. To do this, the electrosynthesis of copolymers

was performed using different ratios of luminol and ANS, in addition the potential scan rate was changed. Concerning the ratio of monomer when the amount of luminol increase in solution the cyclic voltammogram of copolymer present current and potentials mores similar to those of luminol, while that when it is augmented the amount of ANS in comparison to those of luminol in solution, the potentiodynamic response of copolymer is more near to those of polyANS. Thus, it is possible modulate the monomer proportion in the film changing the ratio of monomer in the electrosynthesis solution.

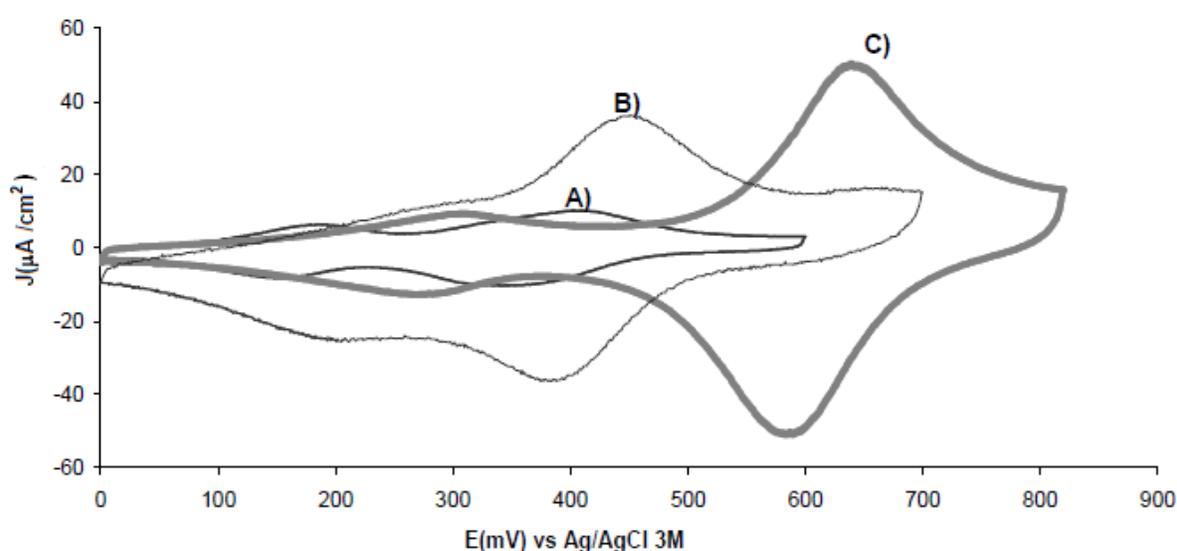


Fig. 14. Voltammograms for (A) polyANS, (B) copolymer and (C) polyluminol films obtained in H_2SO_4 (1 M). Potential scan rate 100 mVs^{-1} .

On the other hand, as can be seen in Figure 14 and Figure 15 the potentiodynamic response is dependent of the scan rate used during the electropolymerization, in the case of homopolymers the current change with this parameter in contrast the potential is the same for all scan rate studied. This indicate that only change the amount of film obtained and the chemical composition is the same, in the copolymer case both current and potential are dependent of potential scan rate Therefore the amount and composition of films synthesized are modified with the scan rate. These facts could be related with the solubility of films, because the products of oxidation of ANS are more soluble that those of luminol, since to lower scan rate the oligomers formed have time for a probable adsorption in the surface of paste carbon, since the polymerization of ANS is enhanced to low scan rate (Figure 15a). The products of luminol are insoluble and are less dependent to the scan rate, since the proportion of luminol and ANS onto the film are dependent of this variable.

The electroactivity of copolymers was analysed in neutral solutions by cyclic voltammetry, as can be showed in Figure 16, the curves obtained show process redox, this indicate that are electrochemical activity to pH neutral. This result is congruent with the behaviour of a self-doped polyaniline. The response was affected by the ratio of monomers in the films, for the films obtained to 5 mVs^{-1} the behaviour was similar to those of polyANS, while the film synthetised to 100 mVs^{-1} the cyclic voltammogram was similar to those of polyluminol.

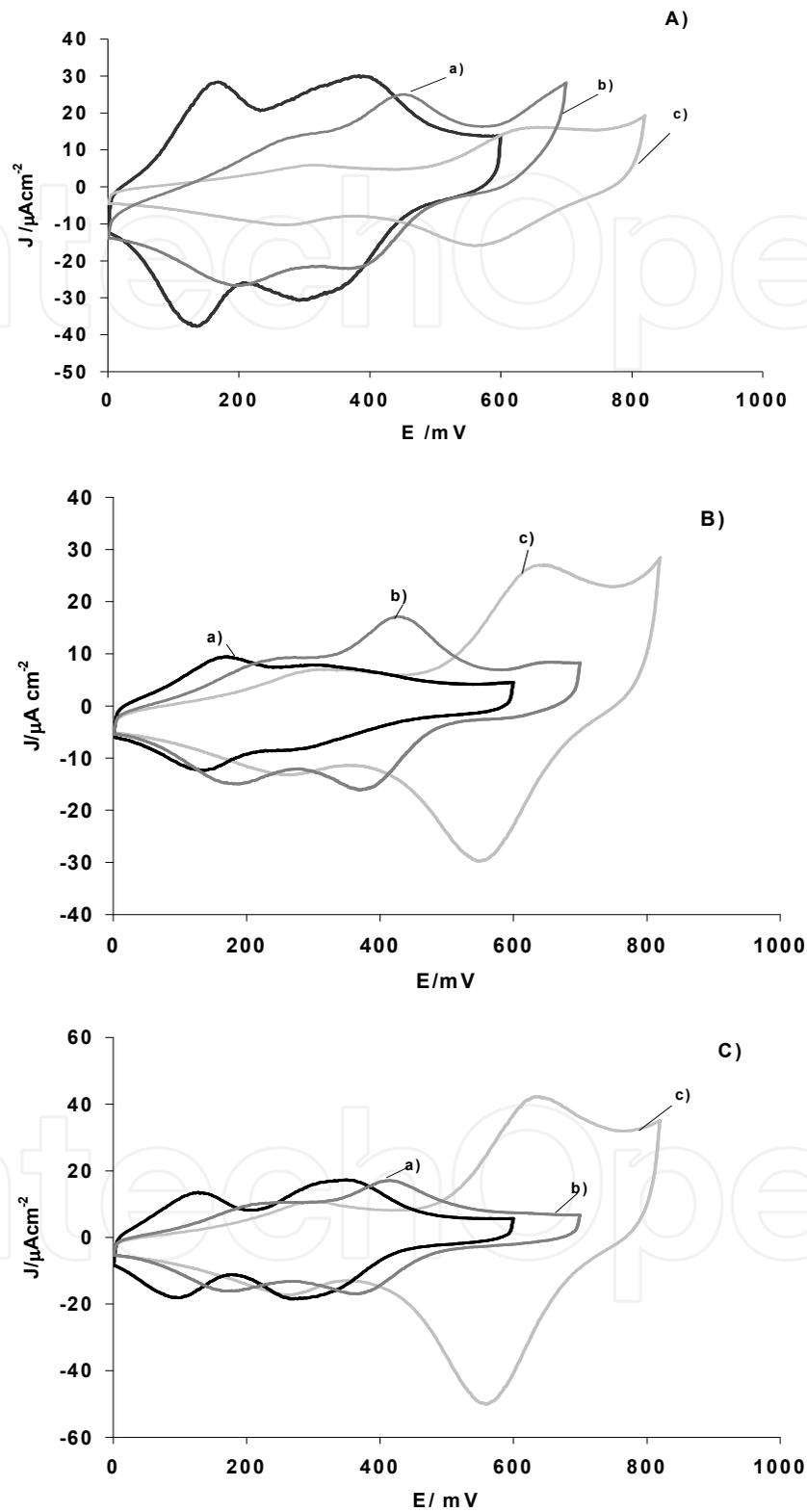


Fig. 15. Voltammograms for (a) polyANS, (b) copolymer and (c) polyluminol films obtained in H_2SO_4 (1 M). Potential scan rate 100 mVs^{-1} . The scan rates used during the electrodeposition were: (A) 5, (B) 25 and (c) 50 mVs^{-1} .

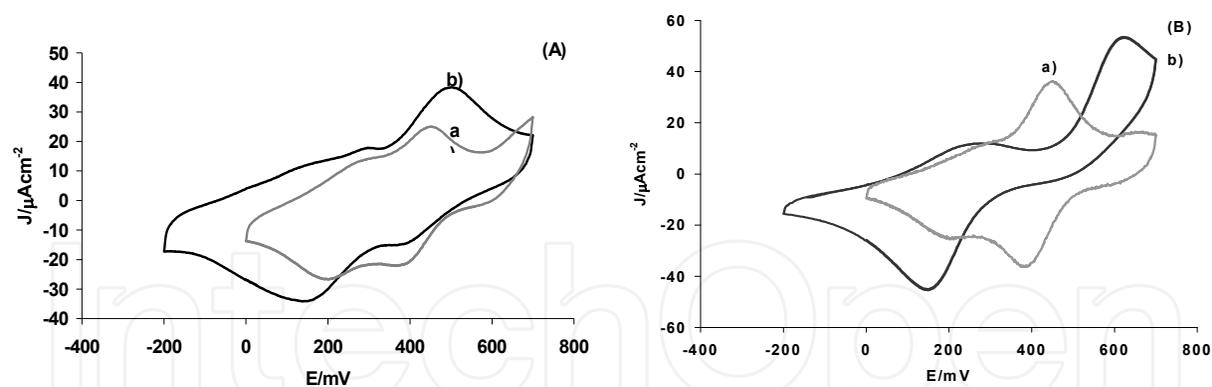


Fig. 16. Cyclic voltammograms of copolymer synthesised to (A) 5 and (B) 100 mVs^{-1} in (a) H_2SO_4 (1 M) and Na_2SO_4 (1 M). The scan rate was 100 mVs^{-1} .

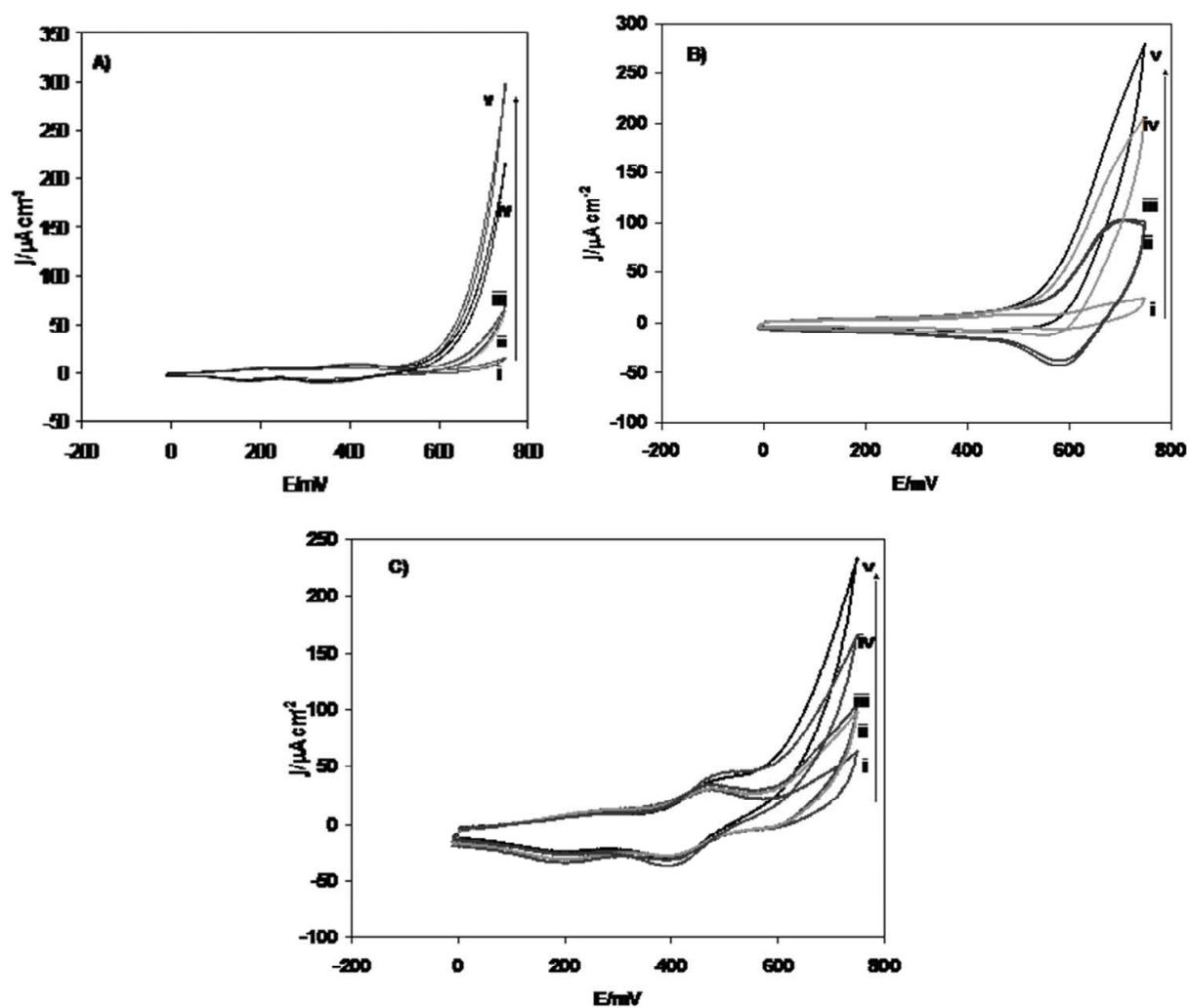


Fig. 17. Cyclic voltammograms curves for (A) polyANS, (B) polyluminol and (C) copolymer electrode in the presence of (i) 0.1, (ii) 0.2, (iii) 0.4, (iv) 0.6 and (v) 0.8 mM. Supporting electrolyte H_2SO_4 1M. The scan rate was 100 mVs^{-1} .

3.3.3 Electrocatalytic oxidation of ascorbic acid

Finally the oxidation of aa was analysed in the copolymer and compared with those of homopolymers, Figure 17 show the ascorbic acid oxidation on the different films, immersed in 1 M H₂SO₄ solution in the absence and in the presence of different concentrations of ascorbic acid. An increase in intensity of the anodic current peak, as the acid ascorbic concentration was increased is an indication of catalytic oxidation of ascorbic acid mediated for each film. The effect catalytic of polyluminol in the oxidation of aa is well established (Chen & Lin, 2002), however the electrocatalysis in polyANS and copolymer has been not reported. The current obtained for a same concentration of aa is higher in the polyANS this suggest that the catalysis is more favourable for this film.

4. Conclusion

In conclusion we have found that it is possible the formation of polymer of ANS, when the electrooxidation of monomer is carried out in PANI/Au or carbon paste electrodes. The films obtained are electrochemically active in neutral pH. The charge compensation of this film is carried out principally by ejection of cation, but anion insertion is simultaneously presented. On other hand, the electrochemical polymerization of luminol in carbon paste electrodes give a film with characteristic of a self-doped polymer contrary to the film obtained using metallic electrodes which are dimmers. A polymer was synthesised to luminol and ANS, the cyclic voltammogram obtain show peak intermediate between luminol and ANS, the film can catalyze the oxidation of aa and is electrochemically active to neutral pH, the proportion of monomers in the film can be modulate by the solution composition and the scan rate.

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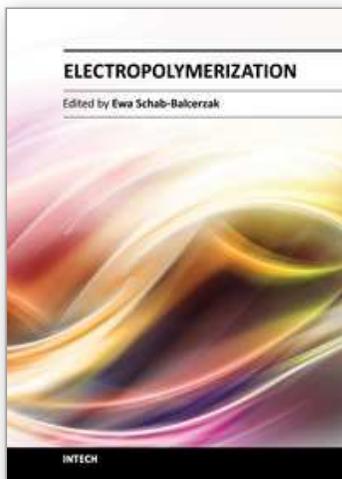
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In recent years, great focus has been placed upon polymer thin films. These polymer thin films are important in many technological applications, ranging from coatings and adhesives to organic electronic devices, including sensors and detectors. Electrochemical polymerization is preferable, especially if the polymeric product is intended for use as polymer thin films, because electrogeneration allows fine control over the film thickness, an important parameter for fabrication of devices. Moreover, it was demonstrated that it is possible to modify the material properties by parameter control of the electrodeposition process. Electrochemistry is an excellent tool, not only for synthesis, but also for characterization and application of various types of materials. This book provides a timely overview of a current state of knowledge regarding the use of electropolymerization for new materials preparation, including conducting polymers and various possibilities of applications.

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