Sequential Electrochemical Polymerization of Aniline and Their Derivatives Showing Electrochemical Activity at Neutral pH

Jorge Yánez-Heras,[a] *Gabriel A. Planes,*[b] *Federico Williams,*[a] *César A. Barbero,*[b] *Fernando Battaglini**[a]

[a] INQUIMAE – Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón 2, C1428EHA Buenos Aires, Argentina
phone: 54-11-45763358, fax : 54-11-45763341
[b] Departamento de Química, Universidad Nacional de Río Cuarto, Ruta Nac. 36 – Km. 601 – X5804BYA, Río Cuarto, Argentina
*e-mail: battagli@qi.fcen.uba.ar

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Abstract
Sequential electropolymerization of aniline followed by an aniline derivative bearing an ion moiety is presented. The studied derivatives contain sulfonic, carboxylate or amino groups. Its electrochemical behavior at acid and neutral pH is studied by cyclic voltammetry combined with quartz crystal microbalance or probe beam deflection in order to assess the mass transfer process involved in these new modified electrodes. All of them show a stable and quasi-reversible electrochemical behavior at neutral pH that can be attributed to a self-doping process. These new modified electrodes can be further modified due to the presence of functional groups.

Keywords: Polyaniline, Aniline derivatives, Electroactivity, Neutral pH, Mass transfer

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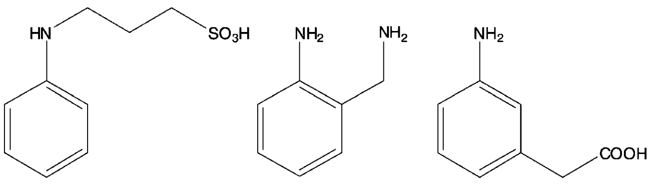
1. Introduction

The electron transfer processes between conducting polymers films and electrode surfaces is accompanied by movement of ions through the polymer film. This movement of ions is needed to maintain electroneutrality in the film and depends on the electron transfer reaction on the electrode. In turn, this movement of ions and redox state change of the polymer may be accompanied by the movement of solvent into or out of the film caused by a change in the configuration of the polymer chain [1]. As a result of these changes, the physical characteristics of the conducting polymer film can be modified significantly by the electrochemical reaction [2–4].

In particular, the properties of polyaniline (PANI) films have been found to depend on the redox and the protonation state of the films. PANI has very interesting characteristics, its polymerization is highly reproducible, it is an inexpensive, and the change in conductivity at different oxidation states has generated a new type of chemical sensor, the microelectrochemical transistor [5], however the pH dependence has been a drawback regarding its applications in biosensing. The influence of pH on the oxidation and reduction of PANI films has been widely studied; PANI films have been reported to become electroinactivated at pH higher than 3–4 [6] due to the film deprotonation. A way to avoid this is, if instead of electropolymerize aniline in the presence of mobile counter ions, long chain polymeric anions are used; they become trapped within the poly(aniline) film, and the overall process changes. As a consequence of this change, the conductivity of polyaniline can be maintained at a much higher pH [5]. This strategy has been used with several negatively charged polymers [7–11], showing application to the detection of NADH [7], glucose [8], ascorbate[9], hydrogen peroxide[10] and oligonucleotides [11] at neutral pH.

Our group has taken another strategy introducing to the system a derivative of aniline containing an ion moiety that affect as less as possible the electroactivity of polyaniline in acid media, and it is able to maintain these features at neutral pH. Our approach has been the copolymerization of aniline with derivatives like 2-aminobenzylamine (2ABA) [12], the modification of PANI with 1,3-propanesultone [13], or the sequential polymerization of aniline followed by a derivative, *N*-(3-propane sulfonic acid)aniline (PSA) [14]. The last method has the advantage of a better control of the modified electrode final structure, as both polymers grow electrochemically, and from two different solutions. This modified electrode has shown excellent electrocatalytical properties for the detection of ascorbate at low concentrations. Another advantage of this method is the ability to modify a specific electrode in an array by simply addressing the potential to the electrode that it has to be modified, especially useful in the case of microdevices.

In this work we present the analysis of the electrochemical and mass transfer process in sequential grown PANI/PSA co-polymer. Also, due to the simplicity of its construction, other aniline derivatives bearing ion moiet-



Scheme 1. Chemical structure of the monomers used in this work from left to right: *N*-(3-propane sulfonic acid)aniline (PSA), 2-aminobenzylamine (2ABA), and 3-aminophenylacetic acid (3APA).

ies are used to produce sequential copolymers and its behavior is analyzed; they are 2-aminobenzylamine (2ABA) and 3-aminophenylacetic acid (3APA). In all cases the polymerization of these aniline derivatives onto the PANI structure allows the generation of electroactive copolymers at neutral pH suggesting that the method can be extended to other aniline derivatives providing they bare an ionizable function group.

2. Experimental

2.1. Reagents

Aniline, 1,3-propanesultone, 2-aminobenzylamine (2ABA) and 3-aminophenylacetic acid (3APA) were from Sigma-Aldrich. All other reagents used were analytical grade. Aniline was distilled prior to use. N-(3-propane sulfonic acid)aniline (PSA) was synthesized from aniline and 1,3-propanesultone as previously reported [14].

2.2. Electrochemical Polymerization

Sequential polymerization was carried out by cyclic voltammetry between -0.2 and 0.85 V vs. Ag/AgCl at 10 mV s^{-1} in an Autolab type III potentisotat. The first step was carried out by cycling the electrode in a solution of 0.09 M aniline in 2 M $HClO_4$ 5 times; Then, the electrode was rinsed with water and immersed in a solution of 0.01 M of the corresponding aniline derivative in 2 M $HClO_4$ and cycled at 10 mV s^{-1}; the number of cycles for this step is indicated in each experiment. The modified electrodes are named following the polymerization sequence, for example PANI/PSA7 means an electrode modified with polyaniline and then the PSA is polymerized during seven potential cycles.

2.3. Electrochemical Quartz Crystal Microbalance (EQCM) Experiments

Electrochemical quartz crystal microbalance were carried out in a SRS, model QCM25. The mass incorporated into the surface of the quartz crystal was calculated according to the variation of the oscillation frequency of the crystal according to the equation:

$$\Delta F = -C_f\ \Delta m_f = 56.6\ \mathrm{Hz\ mg^{-1}\ cm^2}$$

Mass calculations of PANI and other derivatives of aniline can be made because the changes in resistance of the crystal are very small relative to frequency changes caused by the addition of these materials [15].

2.4. Mass Transfer During Redox Processes in Acid and Neutral pH

Once the different polymers were grown, each surface was rinsed with Milli Q water and stabilized in a solution of the working pH to make the study of mass transfer in the corresponding medium. Using the quartz crystal microbalance, the mass exchanged between the polymer film and the solutions during the redox process was followed. For the mass transfer studies, cyclic voltammetries were carried out between -0.2 and 0.6 V vs. Ag/AgCl at 10 mV s^{-1} in 2 M perchloric acid, and in 100 mM tris buffer, pH 7.0.

2.5. Probe Beam Deflection (PBD) Experiments

PBD studies were performed under the same media than EQCM experiments at a scan rate of 50 mV s^{-1}. Details regarding this technique can be found elsewhere [16]. The basic components of a PBD system is a He-Ne laser of 5 mW (Melles Griot) and a position detector (UDT model PIN-LSC/5D). All of these devices and their accessories are mounted on an optical bench (Melles Griot). The laser beam is focused through a lens of 50 mm diameter, opposite the planar electrode (working electrode). The latter is held on an internal surface of the electrochemical cell, which also includes the reference electrode (Ag/AgCl) and counter electrode. The electrochemical cell (quartz cuvette of 2 cm side) is mounted on a 3 axis tilt table (Newport) that allows movement in the three dimensions. The position is controlled by micrometer screws with a maximum resolution of 1 micron. The position detector is placed approximately 25 cm behind the electrochemical cell and has a sensitivity of 1 µrad/mV. The signal position of the detector is processed by a monitor Graserby Optronics 301-Div. To record the signal beam deflection and the electrochemical response in cyclic voltammetry experiments an Amel potentiostat 2049, a personal computer and Lab-View software were used.

2.6. XPS Studies

For XPS measurements, each surface was electropolymerized on gold plates; three modified electrodes were constructed: PANI/PSA4, PANI/PSA7 and PANI/PSA15, these were reduced by 20 minutes at a potential of -0.2 V in the same medium in which they were synthesized (2 M $HClO_4$), then they were removed from the solution and rinsed with Milli-Q water, dried with nitrogen and placed in a desiccator.

X-ray photoelectron spectroscopy (XPS) measurements were obtained using a Specs Sage 150 spectrometer equipped with a dual anode Mg/Al X-ray source and a hemispherical electron energy analyzer. Spectra were acquired using un-monochromatic MgKalpha (1253.6 eV) radiation with a 90° detection angle. The reported binding energies are based on the energy calibration of the analyzer using reference samples (Ag 3d5/2 and Au 4F7/2). No need for load compensation and there were no differential charging characteristics (tails at low binding energies) since the experiments were carried out in thin films on conductive substrates. The atomic ratios were calculated from integrated intensities of the core levels after correction of cross-section instrumental and photoionization [17]. The thickness calculation was performed considering the following equation [18]:

$$I/I_0 = \exp\{-d\ L_{\mathrm{Au}}\}$$

where I is the observed signal modified on gold, I_0 is the observed signal in the clean gold, d is the film thickness and L_{Au} is the effective attenuation length for a polymer type PANI, which has a value of 3 nm [18].

3. Results

3.1. Polymerization Process

In a previous work [14], we have shown that the sequential polymerization of aniline followed by the polymerization of PSA yields a modified surface able to detect ascorbic acid practically at its normal redox potential and neutral pH. Also, in the same work, we observed from cyclic voltammetry experiments that the growth of the second polymer is asymptotic. In order to obtain a better insight, the growing process was simultaneously followed by cyclic voltammetry and quartz crystal microbalance. In Figure 1A, the main chart shows the frequency change as aniline polymerizes at the electrode surface, while the inset in the upper right shows the change in the cyclic voltammogram as the polymer grows. Returning to the main chart, it can be seen periodic cycles with a net drift to

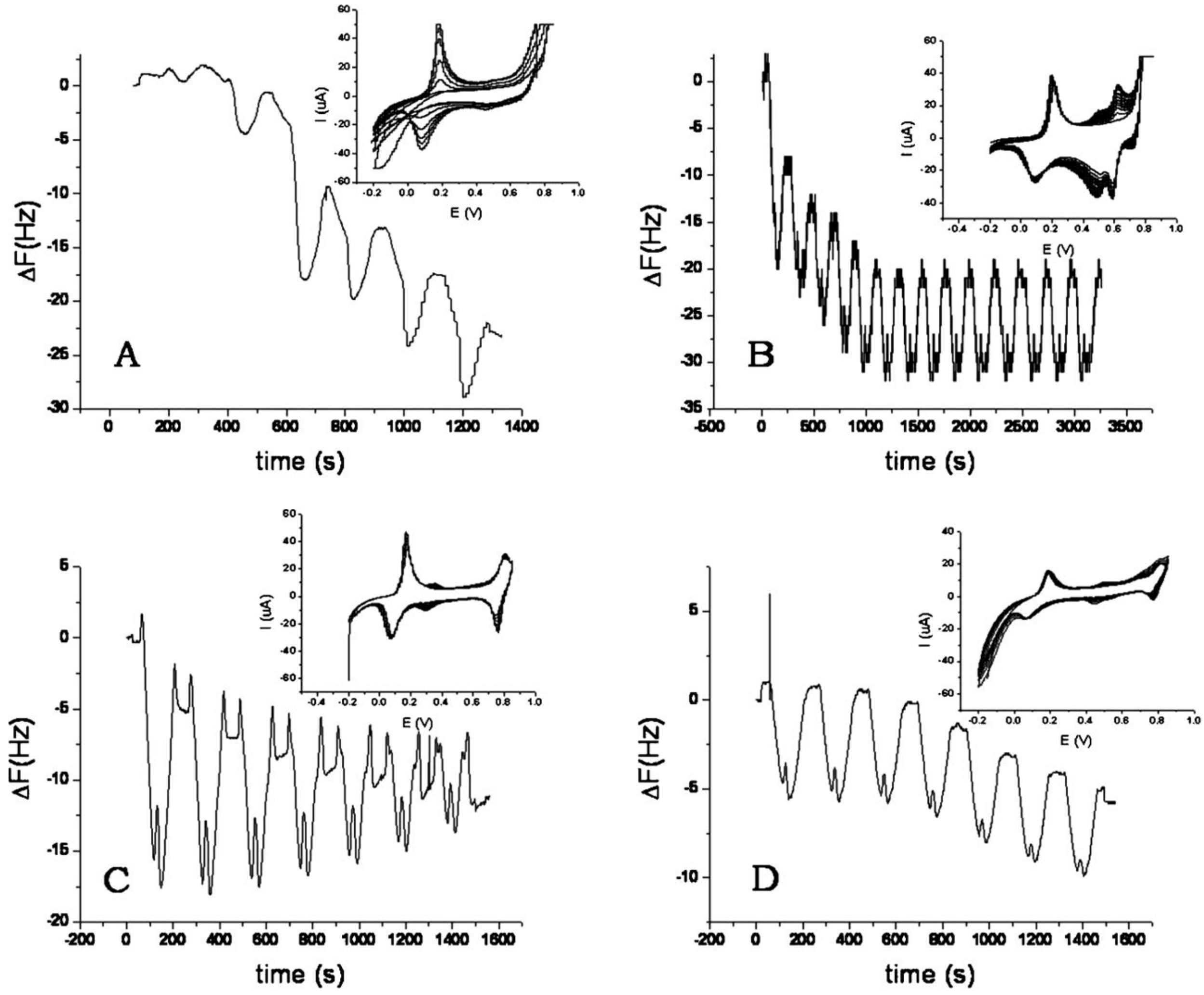


Fig. 1. Frequency change as a function of time during the electropolymerization of : A) aniline during 6 cycles; B) PSA during 15 cycles; C) 2ABA during 7 cycles; D) 3APA during 7 cycles. Insets: Current response during the electropolymerization process.

lower frequencies. In each cycle the negative slopes correspond to the aniline polymerization on the electrode plus electrolyte incorporation (positive scan), while the positive slopes correspond to the expulsion of electrolyte during the reduction process. From the net change between the first and the last cycle, it can be estimated the amount of mass incorporated on the electrode surface. This value is reported in Table 1.

Once aniline was polymerized, PSA electropolymerization was carried out; fifteen cycles between −0.20 V and 0.85 V at a scan rate 10 mV s^{-1} were carried out. The incorporation of PSA was also followed by QCM (Figure 1B); in the same figure, as an inset, it is shown the amperometric response as PSA is incorporated into the electrode. The polymerization process shows a similar trend to aniline until the seventh cycle, from which the net change in frequency is practically nil (see Table 1). Moreover, the cyclic voltammogram shows a significant change when the monomer is incorporated on the PANI modified surface, showing two new oxidation peaks between 0.4–0.7 V due to oxidation of the sulfonated derivative. It is important to note that these peaks correspond in part to a soluble polymer, since they strongly decrease after the electrode is rinsed with abundant Milli-Q water and evaluated again in acid medium, remaining a slight hump around 0.5 V (see Figure $2B_2$). The modified electrodes (PANI/PSA4, PANI/PSA7 and PANI/PSA15) in $HClO_4$ show an electrochemical behavior similar to the PANI, with practically the same charge for the oxidation of leucoemeraldine (see Table 1). This indicates that although there is a net addition of PSA, this derivative does not affect the oxidation of leucoemeraldine to emeraldine in PANI.

Table 1. Charge for the leucoemeraldine oxidation process and mass incorporated during the electropolymerization.

Electrode	Q (μC cm^{-2})	PSA (μg cm^{-2})	Total (μg cm^{-2})
PANI	451	–	0.43
PANI/PSA4	435	0.39	0.82
PANI/PSA7	451	0.53	0.96
PANI/PSA15	428	0.53	0.96

To evaluate the amount of PSA bound to PANI, the different modified electrodes were analyzed by X-ray photoelectron spectroscopy (XPS). Through this technique it is possible to monitor the incorporation of PSA to the electrode surface following the signal ratios O:S and N:S. For the first one, the ratio is practically constant and close to 3, consistent with the addition of a sulfonate group; while the ratio N:S for PANI/PSA# are 6.3 (# = 4), 3.7 (# = 7) and 3.8 (# = 15). These ratios allow establish the stoichiometry between aniline and PSA. For PSA4 the ratio aniline:PSA is around 5 : 1, while for PSA7 and PSA15 is around 3 : 1. Furthermore, the film thickness is calculated by the signal attenuation in the 4f orbital of gold [19]. These results also show the asymptotic incorporation of PSA into the PANI film; a thickness of 6.7 nm was measured for the PANI film, 8.1 nm for PANI/PSA4 and 8.4 nm for PANI/PSA7 and PANI/PSA15.

In a similar way other aniline derivatives (2ABA, 3APA) were studied. 2ABA introduces an extra amino moiety, while 3APA a carboxylate moiety. These moieties introduce extra positive or negative charges, respectively, and both of them are pH dependent. Another important characteristic is that they can be easily derivatized in mild

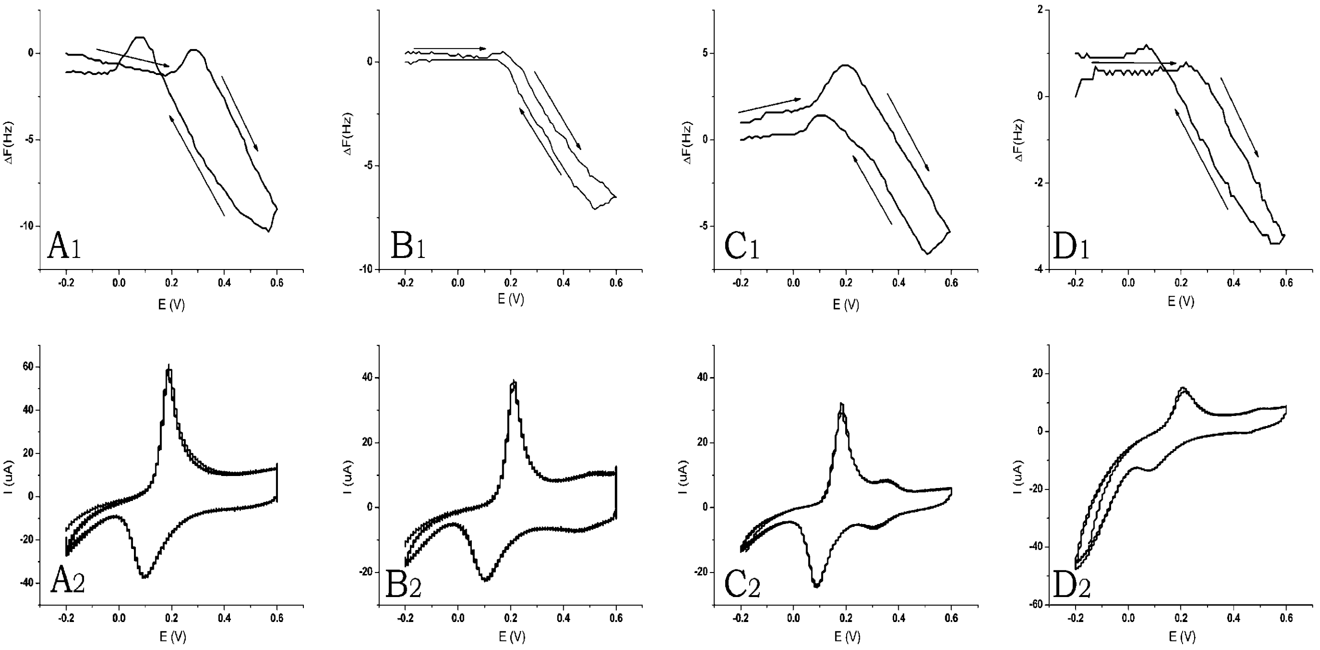


Fig. 2. Mass transfer during redox processes in acid medium for: A) PANI; B) PSA; C) 2ABA; D) 3APA. Subscript "1" corresponds to the frequency as a function of the applied potential and subscript "2" corresponds to the current as a function of the applied potential.

conditions for subsequent applications in molecular recognition devices. Figures 1C and 1D show the electropolymerization of these new monomers on a gold surface previously modified with PANI.

PANI/2ABA reveals the emergence of a new oxidation peak around 0.3 V (Figure 1C, Inset). In this case the incorporation of material is asymptotic with the number of cycles, and also the exchange of mass due to the change in oxidation state is becoming smaller. In contrast to PSA, the incorporation of 2ABA to the polymer chain hinder the charge transfer process, as it can be inferred from the significant current decrease in the redox process corresponding to the oxidation of leucoemeraldine.

In the case of 3APA, the mass incorporation present a pattern similar to the growth of PANI, even though the frequency change is considerably smaller (Figure 1D, main graph); while the cyclic voltammetry reveals the appearance of a new oxidation peak around 0.45 V (Figure 1D, Inset). As it happens with 2ABA a significant current decrease in the redox process corresponding to the oxidation of leucoemeraldine is observed.

After seven cycles, the mass incorporated of each aniline derivative presents important differences; the EQCM experiments show the addition of 0.53, 0.19 and 0.10 μg cm^{-2} for PSA, 2ABA and 3APA, respectively. These values can be attributed to the different positions where the aniline derivatization is produced; the propanesulfonate moiety on the nitrogen atom affects in a lesser extent the electron density of the aromatic ring. Instead, for the other derivatives, the presence of functional groups on the ring affects the electropolymerization; it is known that substitutions in *meta* and *ortho* positions have different effects, the fact that an *ortho* position is blocked decreases the coupling through that position, thus improving the head-to-tail polymerization [20,21]. This would explain the observed trend, a greater incorporation of PSA, followed by 2ABA and finally 3APA.

3.2. Mass Transfer

After the sequential electropolymerization, each modified electrode was rinsed with abundant MilliQ water and stabilized by cycling the electrode at least 20 times in the medium where mass transfer studies were carried out.

3.2.1. Mass Transfer in Acid Medium

Modified electrodes were evaluated in 2 M perchloric acid; mass exchange was followed by EQCM, while PBD was used to follow the egress and ingress of ions to the polymer.

In Figure 2, it can be observed the exchange of mass according to the oxidation or reduction of the different electrodes followed by EQCM. For PANI, as the polymer is oxidized, there is an increase in frequency, indicating the expulsion of protons, then an important decrease is observed. This is due to structural changes in polyaniline, from a compact to a more expanded structure when it is completely oxidized, which allows the ingress of solvent [1,22,23], in this case water accompanied by protons and perchlorate. Similar behavior is observed for PANI/2ABA7; while for PANI/3APA7, the egress of protons is less obvious since the whole mass exchange process is smaller.

In contrast to PANI, the PANI/PSA7 film presents a different behavior, and it cannot be seen a sharp expulsion of protons; however it is observed the incorporation of electrolyte as the polymer is oxidized. The mass exchanged per mole of electrons is lower than that observed for other polymers, 38.3 g per mol of electrons, while for PANI is 55.2. This effect also was reported by Mello et al. for PANI modified with sulfonic groups on the ring, noting that the process of contraction and expansion is smaller than in the case of PANI, thus reducing the exchange of material [24]. On the other hand, the mass exchanged per mol of electron by the other to derivatives is higher than the value observed for PANI (Table 2), this cannot be directly rationalize due to the presence of extra charges, since 2ABA is positively charged at that pH, while 3APA is not ionized in these conditions. The common feature for these two derivatives is the presence of a substituent in the aromatic ring that can affect the interaction between chains as it was previously reported [21].

PBD experiments allow establish the flow of ions (Figure 3). Looking at the deflectograms of PANI/PSA7 and PANI/2ABA7, the ion exchange in these systems can be easily explained [25]. For PANI/PSA7 (Figure 3A), when the potential departs from the fully reduced of the polymer at −0.2 V, the observed signal corresponds to the expulsion of protons (negative slope in the deflectogram). After this expulsion, and when the oxidation process begins, it is observed the incorporation of anions (positive slope), which reaches a peak value at potentials between 0.2 and 0.3 V when the oxidation to emeraldine is completed. At more anodic potentials a clear positive signal due to anion ingress is observed in accordance to the PSA oxidation process observed ca. 0.5 V (Figure $2B_2$).

In the case of PANI/2ABA7, the proton expulsion peak occurs after the current peak (egress between 0.1 and 0.3 V), suggesting that the presence of the aliphatic amino group alters the acid-base equilibrium inside the film.

The deflectogram for PANI/3APA7 shows a dominant proton expulsion during the oxidation peak. It is likely that fixed proton in the carboxylic group are expelled during oxidation while the positive charge in the nitrogen

Table 2. Mass exchanged per mol of electron.

Electrode	2 M $HClO_4$ g mol^{-1}	pH 7.0 g mol^{-1}
PANI	55.2	–
PANI/PSA7	38.3	43.6
PANI/2ABA7	90.7	91.0
PANI/3APA7	85.1	36.7

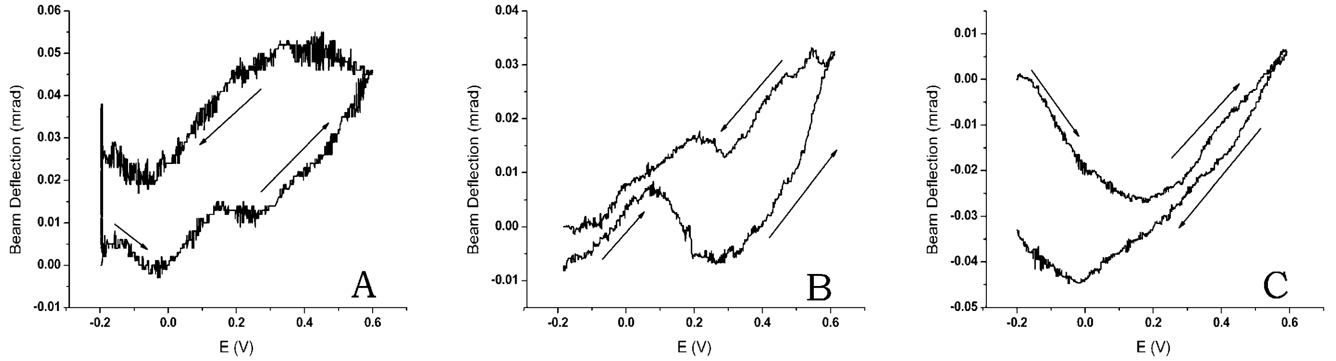


Fig. 3. Probe Beam Defection signal due to ion transfer as a function of the applied potential in acid medium for modified poly(aniline) electrodes with: A) PSA; B) 2ABA; C) 3APA.

is compensated by the carboxylate group created by deprotonation. Even in this low pH media, carboxylate moieties are stable due to ion pair formation with the neighboring positive charge. A similar situation has been previously observed in poly(aniline-co-(2-aminobenzoic acid)) [26].

3.2.2. *Mass Transfer at Neutral pH*

The mass exchange of the different modified electrode was evaluated in 100 mM Tris, pH 7.0, by performing several cyclic voltammetry between −0.2 and 0.55 V and simultaneously recording EQCM frequency variation (Figure 4).

A key difference of these copolymers with PANI is the stable and quasi-reversible behavior for the electron transfer process observed around 0.1 V (Figure 4 A_2, B_2, C_2) in all cases the voltammograms are recorded after cycling the potential until a constant pattern is obtained. The oxidation peaks are wider for all the modified electrodes respect to the observed in acid medium; this is due to the effect of the pH on the second redox couple of PANI, thus overlapping both redox processes [5], and also the redox process of the derivatives [27].

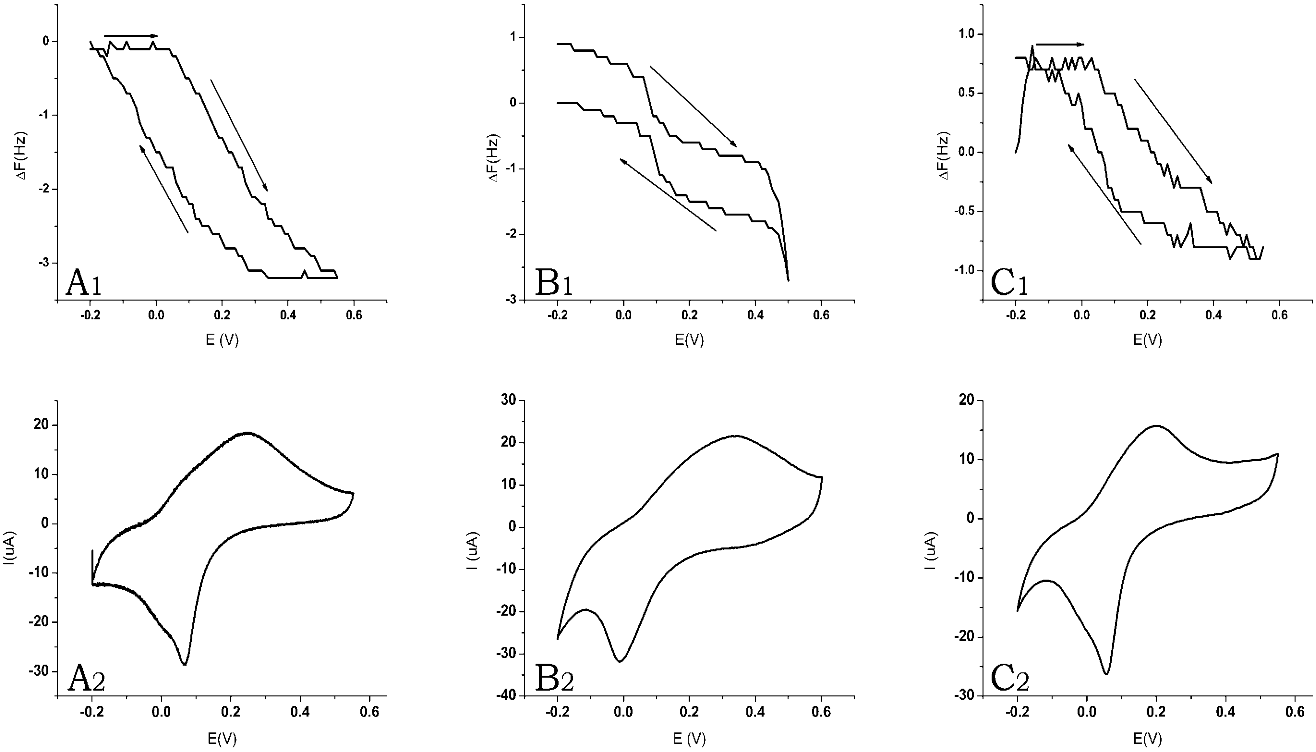


Fig. 4. Mass transfer during redox processes in neutral pH for modified poly(aniline) electrodes with: A) PSA; B) 2ABA; C) 3APA.. Subscript "1" corresponds to the frequency as a function of the applied potential and subscript "2" corresponds to the current as a function of the applied potential.

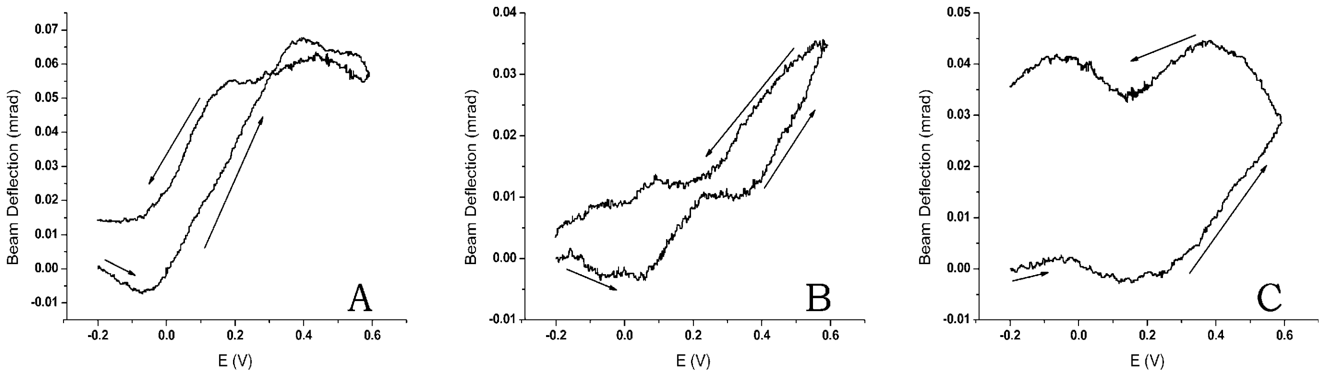


Fig. 5. Ion transfer as a function of the applied potential at neutral pH for modified poly(aniline) electrodes with: A) PSA; B) 2ABA; C) 3APA.

For the three electrodes a decrease in frequency is observed as the polymer is oxidized, corresponding to the incorporation of electrolyte to the film. The exchange of mass per mole of electrons is higher for 2ABA respect to PSA and 3APA (Table 2). Considering the molar masses of the species present in solution, water (18), chloride (35.5) and Tris (121), the mass exchange is mostly due to the solvent, being the self-doping a very important factor for maintaining the electrochemical activity of the polymer at neutral pH.

The evaluation of the ion exchange by PBD shows in all cases that the most important process is the incorporation of anions when the surface is oxidized and their expulsion as the reduction process is carried out (Figure 5). Looking at the deflectograms in detail, it can be clearly observed the presence of two processes for PANI/2ABA7 and PANI/3APA7. These processes can be attributed to the oxidation of leucoemeraldine to emeraldine and emeraldine to pernigraniline that converge at neutral pH [26], or the first oxidation process of PANI plus an oxidation process corresponding to the derivative added. In the case of PANI/PSA7 not apparent changes in the slope is observed as if there were a single redox process involved.

4. Discussion and Conclusions

The gravimetric study shows that PSA is incorporated more easily than the other derivatives to a previously modified PANI gold surface. This can be explained based on the structure of PSA having an alkyl chain bound to the N atom of aniline; this chain contributes to the nitrogen electron density, thus making this molecule a more reactive monomer for polymerization [20,21].

On the other hand, the addition of these aniline derivatives in the polymer creates a disruption in the electron transfer process of PANI. This is clearly seen when comparing the cyclic voltammetries in acid medium for the different modified electrodes (Figure 2). For PSA the effect is small, however it becomes important in the cases of 2ABA and 3APA, where the signal corresponding to the leucoemeraldine oxidation process significantly decreases.

In acid medium, EQCM experiments show that there is substantial incorporation of electrolyte, once the polymer has been oxidized. At this point the main difference is observed in 2ABA, which shows a net egress of mass (Figure 2) confirmed by PBD as the outflow of proton. For PSA, the outflow of protons is negligible, PBD experiments show that the slope is slightly negative between 0.1 and 0.3 V and the main ion exchange is given by anions.

The most interesting process observed in these modified electrodes is the electrochemical response at pH 7.0. As it was raised by Nyholm [27], "a priori there is no connection between the loss of conductivity and electroactivity loss for PANI at pH greater than 4, provided that the solution has an adequate ion strength to supply counterions due to the generation and destruction of charge". The cyclic voltammetries conducted for the three derivatives (Figure 4) show a quasi-reversible behavior, in clear contrast to those usually obtained for PANI, even at high ionic strength[27]. EQCM experiments show the entry of solution when the polymer is oxidized (Table 2), where important differences between PSA and other derivatives are observed. This effect can be explained mainly by the type and number of charges present in each case. PSA, in both conditions, acid and neutral pH, present a number of negative charges that interact strongly with the positive charges of PANI, whereas in the case of 3APA, in acid medium is not dissociated, while at neutral pH presents negative charges as the sulfonate moiety. Finally, 2ABA, in acid medium and neutral pH is positively charged, further increasing the repulsion between the chains allowing the ingress of a higher amount of electrolyte.

The deflectograms obtained for these derivatives at neutral pH clearly show that ion exchange occurs through the incorporation and expulsion of anions. This technique also shows the presence of two redox processes for 2ABA and 3APA.

Despite the information gathered by these techniques is not easy to explain the persistence of the electrochemical response. One hypothesis could be the presence in the polymer of a number of fixed charges (not dependent on oxidation state) within the polymer, which retards or prevents the egress of protons, settling in the layers of the polymer closest to electrode; the other hypothesis, in accordance with the results of Nyholm [27], propounds that the PANI does not suffer the second redox process if the potential is swept until 0.6 V, avoiding in this way the reduction of the fully oxidized form of PANI, a very slow process at neutral pH; under this hypothesis the second process observed in 2ABA and 3APA would correspond to the oxidation of the derivative.

This study shows a new route to extend the application of poly(aniline) based sensors, overcoming an important drawback in biosensor applications. These new platforms are highly stable at neutral pH and they are completely synthesized by electrochemical means, which facilitates their miniaturization and reproducibility. The fact that all of them are able to undergo a quasi-reversible process at neutral pH suggests the method can be extended to other aniline derivatives providing they bare an ionizable function group. The derivatives tested in this work have already shown its application in bioassays, the PSA based electrode was used in the detection of ascorbate at low concentrations in physiological conditions [14]; more recently, the 3APA based electrode was used in environmental analysis for the detection of traces of metal ions in water [28] and endotoxins [29] as part of electronic tongues. In these cases, 3APA was modified with recognition elements toward the corresponding analytes, showing another feature gained by the method presented here. Work is in progress regarding their possible applications as microelectrochemical transistors.

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