ELECTROSYNTHESIS AND PROPERTIES OF SOME SUBSTITUTED POLYANILINES IN PHOSPHATE BUFFER

Marian SIMA,[a] Mihai BUDA,[b] Eugeniu VASILE,[c] and Teodor VIŞAN[b]

[a] National Institute of Material Physics P.O. Box MG 7, Măgurele, Bucharest, Roumania
[b] Applied Physical Chemistry & Electrochemistry Dept., "Politehnica" University, Calea Griviţei 132, 78122, Bucharest, Roumania
[c] METAV S.A., Bucharest, Roumania

The electropolymerizations of 2-aminohippuric acid methyl ester and 2-aminobenzoic acid methyl ester monomers in phosphate buffer (pH = 6.5) were studied. The formation of thin films at the platinum electrode surface is observed as main product and the electrosynthesis process of the two substituted polyanilines shows the voltammetric characteristics of the polyaniline film electrosynthesis. The necessary charge to deposit 0.05 μm poly(2-aminohippuric acid methyl ester) or poly(2-aminobenzoic acid methyl ester) films is about 60 mC/cm^2. The polymer films were investigated by electrochemical impedance spectroscopy. On the basis of the obtained results we propose the equivalent circuit for these polymer films.

INTRODUCTION

Numerous experiments have been made concerning the electrochemical synthesis of conducting polymers from an aqueous buffered solution of monomer. These polymerizations are carried out in a buffered medium especially for immobilization of protein molecules, to avoid protein denaturation.[1-8] Most authors report the use of phosphate buffer at pH = 6.5 as polymerization medium. However, the polymer chain affects the protein structure and many studies[1,9,10] about entraping enzymes in polymer films describe a rapid deactivation of these biological molecules. For this reason, it is interesting to investigate other polymer matrices which may create a more "friendly" environement for protein molecules; the polyaniline structure having some functional groups which are reminiscent of polypeptides can be an example.

The main goal of the present paper is the electropolymerization of 2-aminohippuric acid methyl ester, an aniline having attached an amino-acid residue, in phosphate buffer solution, and the electrochemical characterization of the obtained polymer. Comparatively, another aniline with a simple functional group, 2-aminobenzoic acid methyl ester was electrochemically studied.

EXPERIMENTAL PART

Aniline and 2-aminobenzoic acid methyl ester (Merck) were used without further purification. 2-aminohippuric acid methyl ester was prepared in our laboratory from isatoic anhydride and aminoacetic acid methyl esther.[11] Electrochemical experiments were carried out using a one-compartment, three-electrode glass cell. The reference electrode was a saturated calomel electrode (SCE); as working and counter electrode, a platinum wire (S = 0.1cm^2) and a large platinum plate were used, respectively. The film-forming

electropolymerization of the dissolved monomers in phosphate buffer was performed in various conditions using cyclic voltammetry, constant current density and potential step techniques. For infrared absorption measurements, powder polymer material was mixed with KBr and pressed under vacuum into uniform, partly transparent pellets. Characterization of bulk properties of the substituted polyanilines layers was performed by electrochemical impedance spectroscopy and cyclic voltammetry. The film thickness was determined using a TENCOR step-profiler. Electrochemical measurements were made with a potentiostat-galvanostat PAR 173 driven by a function generator and coupled with a digital coulometer. Impedance spectra were recorded with an IM5d Zahnerelectrik device. A 5 mV constant amplitude of applied sinusoidal signal was maintained and the data were collected in the frequency range of 10^{-1}-10^5 Hz. The impedance parameter values were calculated using the complex non-linear least squares (CNLS) fitting program written by MacDonald.[12]

RESULTS AND DISCUSSION

1. Growth of polymer films in phosphate buffer, pH = 6.5

When using phosphate buffer solution as electropolymerization medium, it was observed that during the electrosynthesis of polyaniline film the current values were very low (Fig. 1) compared to the classical synthesis (with the same concentration of aniline monomer) in inorganic acid solutions (pH < 1). In phosphate solutions, the voltammetric current is also affected by the reduced mobility of phosphate anions
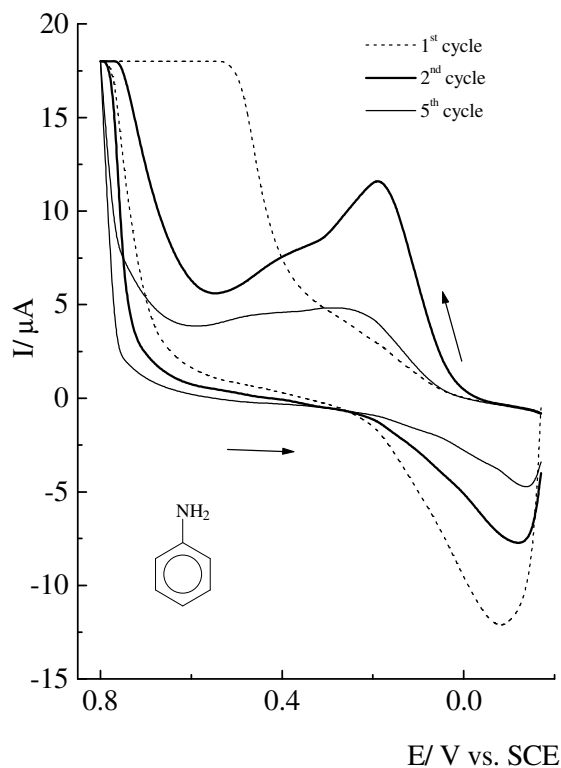

Fig. 1 – Cyclic voltammograms for the electrosynthesis of a polyaniline film from 0.015 M
aniline in phosphate buffer (0.1 M, pH = 6.5). Sweep rate = 200 mV/s.

which are present in the buffer solution.[13] The electrosynthesis process of the two substituted polyanilines, poly (2-aminobenzoic acid methyl ester) (P2ABA-ME) and poly(2-aminohippuric acid methyl ester) (P2AHA-ME), from phosphate buffer containing 2-aminobenzoic acid methyl ester and 2-aminohippuric acid methyl ester, respectively, as monomers (Fig. 2) shows the voltammetric characteristics of the polyaniline film electrosynthesis.
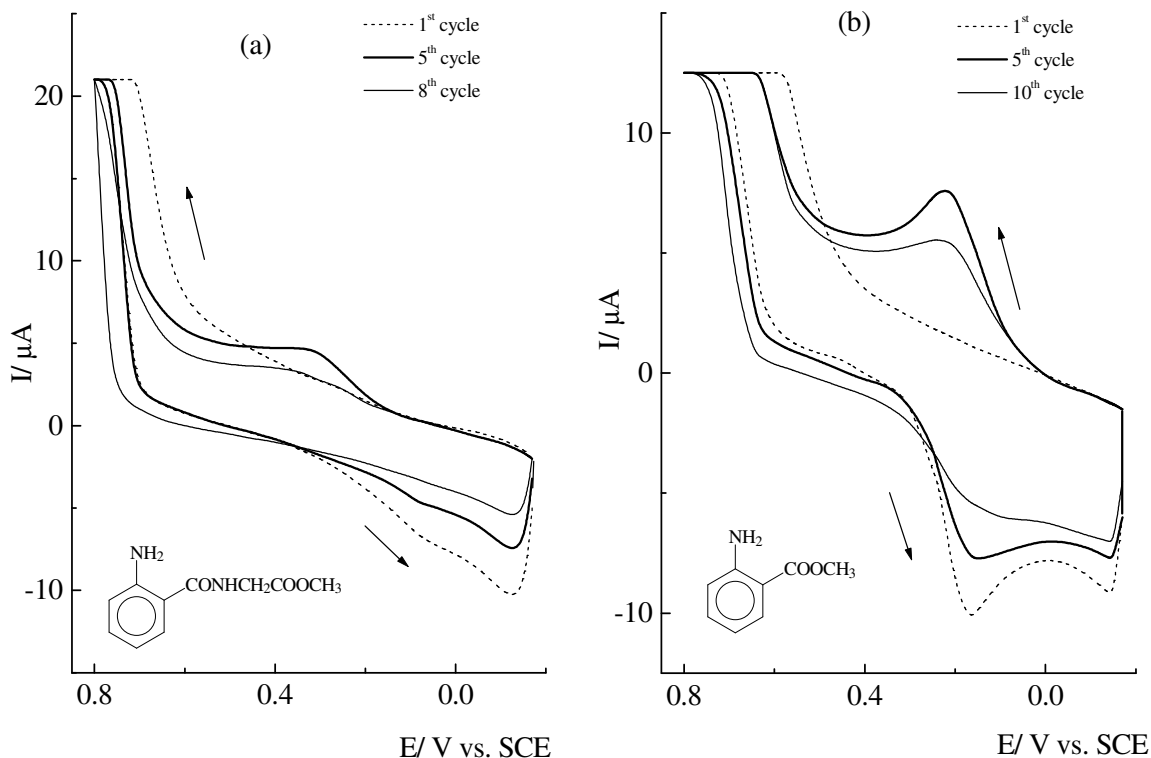
Fig. 2 – Cyclic voltammograms for the electropolymerization of 2-aminohippuric acid methyl ester (a)
and 2-aminobenzoic acid methyl ester (b), in phosphate buffer (0.1M, pH = 6.5)
solutions containing 0.015 M monomer. Sweep rate = 200 mV/s.

On the first positive potential sweep, the monomers are oxidized exhibiting an irreversible current peak at about 0.7 V. It should be noted that even at this low concentration (0.015 M) the anodic discharge of these substituted anilines is rather a wave than a peak, which suggests some kind of kinetics control.[14,15] On the negative sweep, this wave does not show a complementary peak, indicating the existence of a very fast chemical follow-up reaction.

Only one anodic current peak has a cathodic correspondent on the cyclic voltammograms of P2ABA-ME and P2AHA-ME syntheses. The anodic current peak, attributed to the radical-cation formation[15,16] can be a growth indicator for the polymer films. At continuous cycling, only five cycle increase for the two polymer films is observed; afterwards the voltammetric current peak lowers, indicating that the obtained film has a low electroactivity. In all these cases we observe a gradual decrease of the electrodeposited rate for both P2ABA-ME and P2AHA-ME, probably because of the film resistance increase during polymerization. On the other hand, the monomers' oxidation starts with the formation of oligomers as a reddish soluble product. This process is more important for the 2-aminobenzoic acid methyl ester oxidation, for which the resulted oxidation product does not easily precipitate on the platinum electrode.

Fig. 3 shows the IR spectra of partly oxidized polymers P2ABA-ME and P2AHA-ME. For the P2ABA-ME polymer the following bands are attributed: 1243 cm^{-1} C-C stretch, 1303 cm^{-1}, C-O stretch and 1654 cm^{-1} C=N stretch, while for P2AHA-ME, 1261 cm^{-1}, C-C stretch, 1645 cm^{-1}, C=N stretch; the 1744 cm^{-1} band is attributed to the aminoacid COOR group. For both polymers, the 1161 cm^{-1} band is attributed to the phosphate anion.

Fig. 4 shows the current and charge as a function of time during potential-step electropolymerization of the two substituted anilines from 0.1 M phosphate buffer, pH = 6.5. The experiments were carried out at three
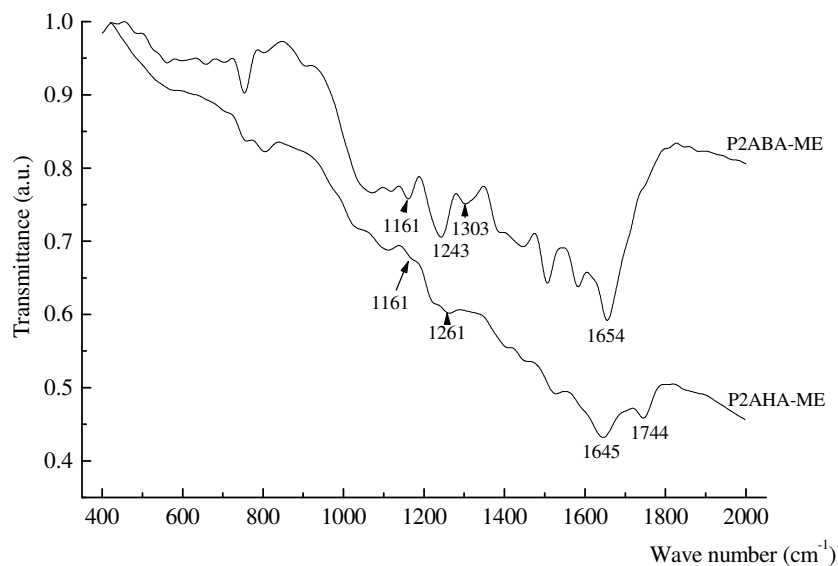
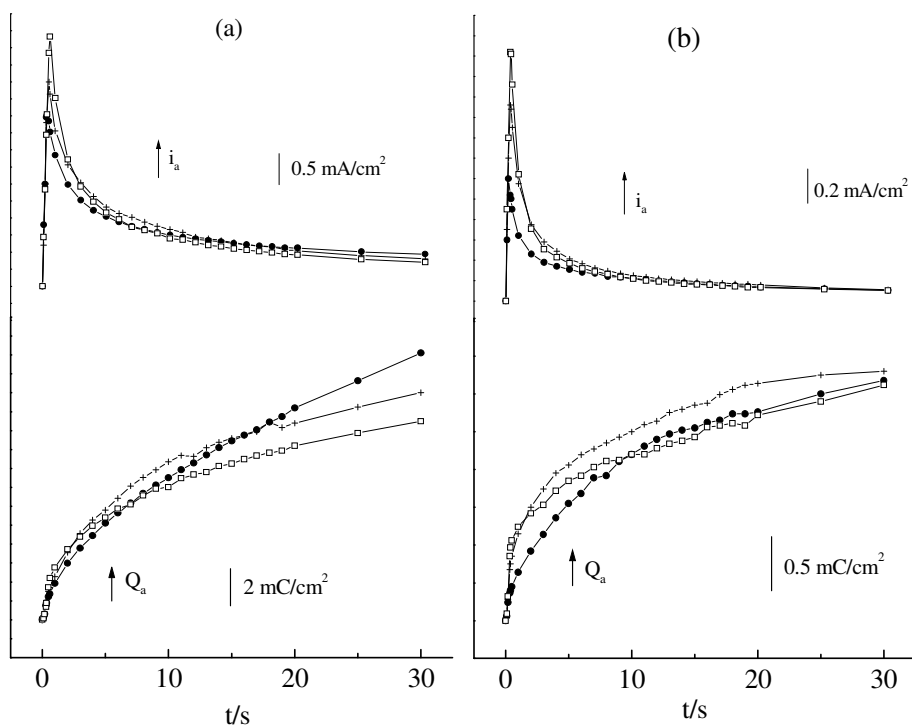Fig. 3 – IR spectra for P2AHA-ME and P2ABA-ME in KBr.

Fig. 4 – Current (i_a) and charge (Q_a) time dependencies during electropolymerization of P2ABA-ME (a)
and P2AHA-ME (b) at platinum electrode from 0.015 M monomer in 0.1M phosphate buffer, pH = 6.5.
Potential values: 0.75V (•), 0.8V (+) and 0.9V ( ) *vs*. SCE.

different constant potentials, 0.75, 0.8, 0.9 V/SCE, with no significant differences; however, a potential synthesis of 0.75 V/SCE may be a good choice to avoid the polymer degradation by overoxidation. In the current decay, a plateau is reached after about twenty seconds (the time for radical building before polymerization). The charge measured during the last ten seconds of the chronocoulometric experiments shows a P2AHA-ME film growth rate about ten times lower than that for P2ABA-ME film synthesis.

The growth of P2ABA-ME and P2AHA-ME films was also investigated at constant current density (Fig. 5). The values of constant current densities were selected on the basis of results obtained from potential step experiments (Fig. 4).
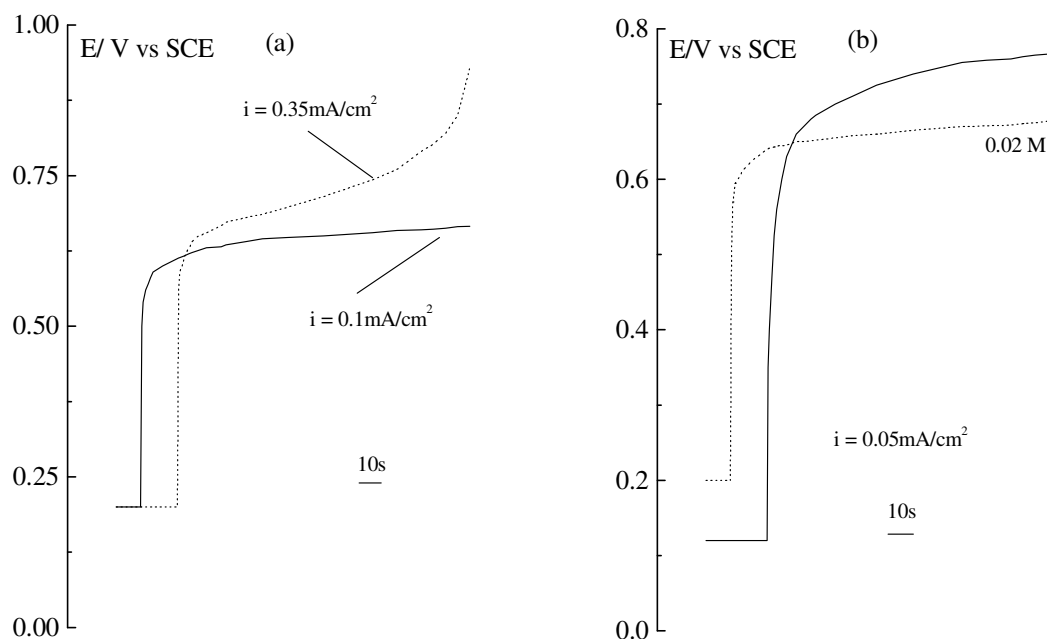

Fig. 5 – Potential-time curves for galvanostatic electrodeposition of P2ABA-ME (a)
and P2AHA-ME (b) films on platinum electrode. Electrolytes: 0.1M phosphate buffer, pH = 6.5 and 0.015 M
monomer; for case (b) (---) the monomer concentration is 0.02 M.

For a 0.015 M monomer concentration in buffer solution and the selected polymerization currents, 0.1 mA/cm^2 for P2ABA-ME and 0.05 mA/cm^2 for P2AHA-ME, the transition times are 1676 s and 258 s, respectively. In a 0.02 M (maximum concentration) 2-aminohippuric acid methyl ester monomer in buffer solution 0.05 mA/cm^2 polymerization current, the transition time is 558 s and the plateau potential more negative by about 0.05 V.

Changing the current density for P2ABA-ME electrosynthesis (for a 0.015 M of 2-aminobenzoic acid methyl ester – maximum concentration) has mainly two effects on the potential *vs*. time curve (see Fig. 5a). The plateau potential shifts towards positive values, while the transition time decreases with increasing current density. From profilometry measurements we estimated that the necessary charge to deposit 0.05μm of P2AHA-ME or P2ABA-ME films at constant current density (0.05 mA/cm^2) is about 60 mC/cm^2.

All these experiments show that the low monomer concentration in phosphate buffer solution does not allow to grow polymer films having a reasonable thickness (> 0.1μm). An attempt to grow thicker P2AHA-ME films was carried out from solutions containing 0.055 M 2-aminohippuric acid methyl ester in 0.1 M phosphate buffer in acetonitrile/water 1:2 vol. When using this electropolymerization medium (Fig. 6) a twenty cycle increase of the anodic current peak, used as growth indicator for the P2AHA-ME film, and also the total voltammetric current increase on the cyclic voltammogram are observed. Thus, using higher monomer concentrations in mixed water/organic solvent solutions, thicker films may be obtained. Fig. 7 shows the surface morphology of this film grown galvanostatically.

The deposit of P2AHA-ME has a poorly defined agglomerate structure. The presence of the organic solvent in the polymer synthesis solutions probably promotes the formation of this polymer structure.
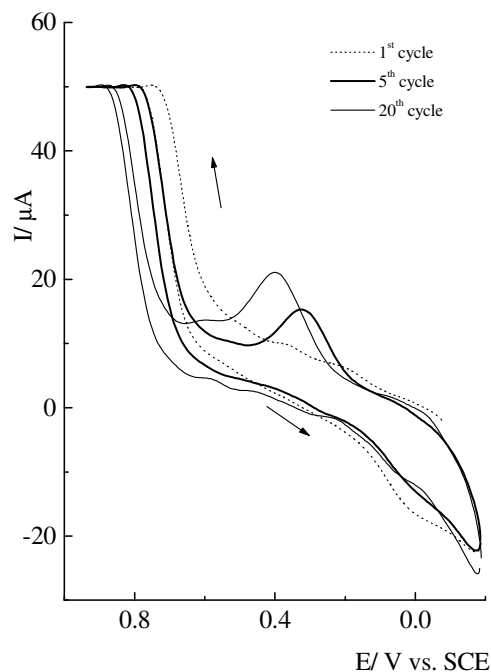
Fig. 6 – Cyclic voltammograms of P2AHA-ME synthesis from solutions containing 0.055M 2-aminohippuric acid methyl ester in 0.1M phosphate buffer in acetonitrile/water 1:2 vol. Sweep rate = 200 mV/s.
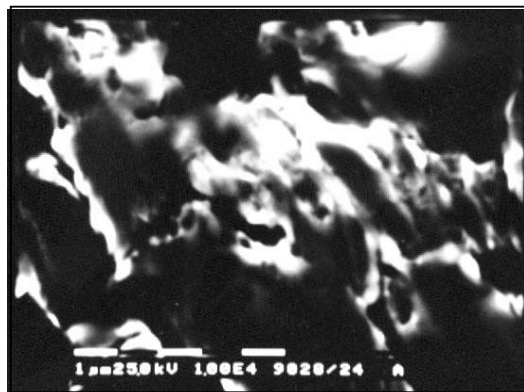

Fig. 7 – Scanning electron micrographs of P2AHA-ME film grown on Pt electrode at constant current density (0.4 mA/cm^2) from solutions containing 0.055M 2-aminohippuric acid methyl ester in 0.1M phosphate buffer in acetonitrile/water 1:2 vol.

2. Impedance studies of P2ABA-ME and P2AHA-ME films

The impedance spectra (Bode plot) of polymer layers on platinum support in phosphate buffer (pH = 6.5) and 0.1 M H_3PO_4 solution (pH = 1.45) are shown in Fig. 8 a and b. The Bode plots are characterized by a capacitive region in the medium frequency range and by a resistive region (horizontal line and phase angle close to 0°) at higher frequencies. In the low frequencies region, the drop of the phase angle indicates the presence of a high parallel resistance. The polymers impedance lowers (especially for the P2AHA-ME film) in more acidic solutions. For these systems, the Nyquist plot reveals a depressed and incomplete semicircle and exhibits approximately a straight-line behaviour over a limited frequency range with $\theta \neq 45^{o}$ (Fig. 9). A constant phase element, *cpe*, in conjunction with other circuit elements was used to describe such behaviour of these polymer electrodes.
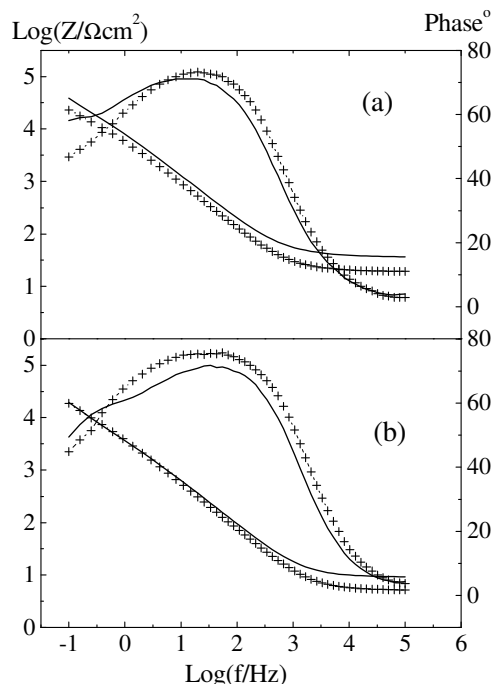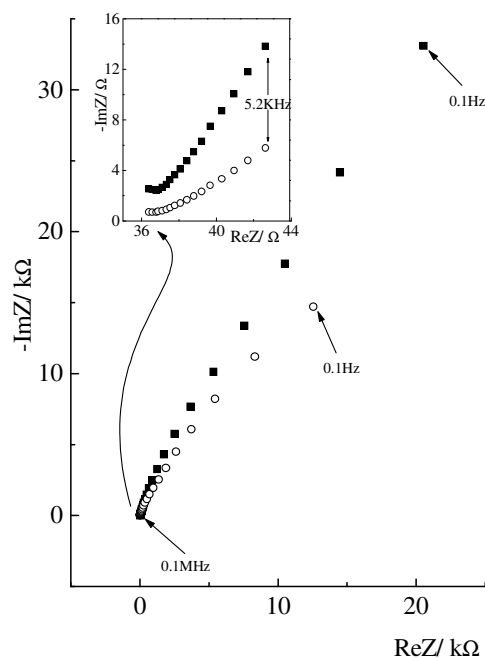
Fig. 8 – Bode plots of P2AHA-ME (a) and P2ABA-ME (b) films on Pt support in phosphate buffer pH=6.5 (——), and 0.1M H$_3$PO$_4$ pH=1.45 (++). Films thicknesses d=25 nm and surface area 1cm^2.

Fig. 9 – Nyquist plot for a Pt electrode, coated with a 25 nm P2AHA-ME (•) or P2ABA-ME (o) layer dipped in 0.1M phosphate buffer, pH=6.5. Frequency range 0.1Hz-0.1MHz. Insert: Nyquist plot in the frequency range 5.2KHz-0.1MHz.

An equivalent circuit (EQC) scheme (Fig. 10) was used to fit the impedance data. The *cpe* in parallel with a resistor, as illustrated in Fig.10, is the ZARC-Cole distributed element, used to describe the depressed arcs that can be observed when impedance data on solids are plotted in the impedance plane.[17] The mathematically equivalent version for the response of this distributed element may be written as $Z = R/[1+(i\omega\tau)^\psi]$, where Z – the overall impedance, R – the film resistance, ω – the angular frequency; τ in our case can be considered a dielectric constant[12] and $0 \leq \psi \leq 1$; the smaller ψ the more displaced the semicircle center. The exponent ψ can be regarded as a measure of the inhomogeneity of the polymer film.

The *cpe* takes into account the displacements of the doping ions in porous electrodes. Expressions such as $Z_{cpe} = 1/\tau(i\omega)^{\psi}$ are indeed currently used to describe ionic movements in porous media or fractal structures.[18, 19]

The film resistance is quite large, and is responsible for lowering the phase angle at low frequencies; this resistance is connected in series with charge transfer resistance, R_{ct} at the platinum-polymer interface. Capacitance C_d is attributed to the electrolyte-polymer interface double layer.
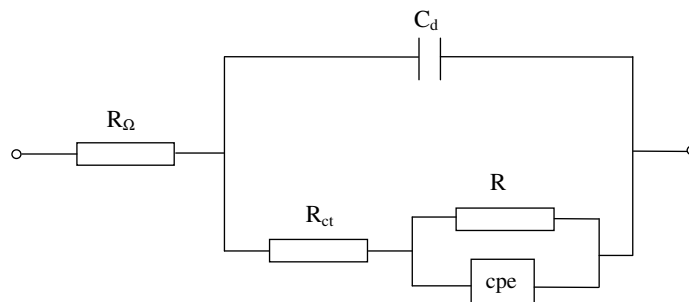
Fig. 10 – Proposed equivalent circuit (EQC) for the P2ABA-ME and P2AHA-ME layers in 0.1 M phosphate buffer pH = 6.5 and 0.1M H_3PO_4 solution. R_Ω = electrolyte resistance; R_{ct} = charge transfer resistance; R = film resistance; C_d = double layer capacity; cpe = constant phase element.

Table 1 presents the values of the elements shown in Fig. 10, corrected by substracting the electrolyte resistance term.

Table 1

Parameters of EQC (Fig.10) of the P2ABA-ME and P2AHA-ME electrodes (d = 25 nm) in 0.1M phosphate buffer pH=6.5 and 0.1M H_3PO_4 solution, pH = 1.45

Solution	Parameter	P2ABA-ME	P2AHA-ME
Phosphate buffer 0.1M, pH=6.5	R_{ct}/ohm cm^2	1.013	4.397
	C_d/μF cm^{-2}	0.947	0.344
	R /ohm cm^2	2.967×10^4	1.042×10^5
	τ	1.785	4.050
	ψ	0.816	0.796
0.1M H_3PO_4 Solution, pH=1.45	R_{ct}/ohm cm^2	0.573	1.669
	C_d/μF cm^{-2}	3.497	0.858
	R /ohm cm^2	2.579×10^4	3.258×10^4
	τ	1.368	1.195
	ψ	0.835	0.824

Data in Table 1 show:

(i)   The polymer films exhibit a large resistance not only in the phosphate buffer pH = 6.5 but also in 0.1 MH_3PO_4 solution pH = 1.45.The resistance of the P2AHA-ME is somewhat greater than for the P2ABA-ME film.

(ii) The same behaviour is observed for the charge transfer resistance, R_{ct}.

(iii) A small capacitance C_d is noticed, especially for P2AHA-ME film, as a result of a reduced active polymer surface area. In a more acidic medium this capacitance increases probably due to the increase of the number of active zones in the polymer film.

(iv) Taking the τ parameter as a dielectric constant of the polymer film, we can see that the capacitive behaviour of these electrodes in acidic solutions becomes less evident; a similar response may be observed on the cyclic voltammograms of P2ABA-ME (Fig. 11.a) and P2AHA-ME (Fig. 11.b) films which show a capacitive current decrease for these polymers dipped in a more acid solution.

(v)   The parameter ψ has a value close to 0.8 for both polymers, having slightly higher values in acid solution; the ψ value is greater for P2ABA-ME film.
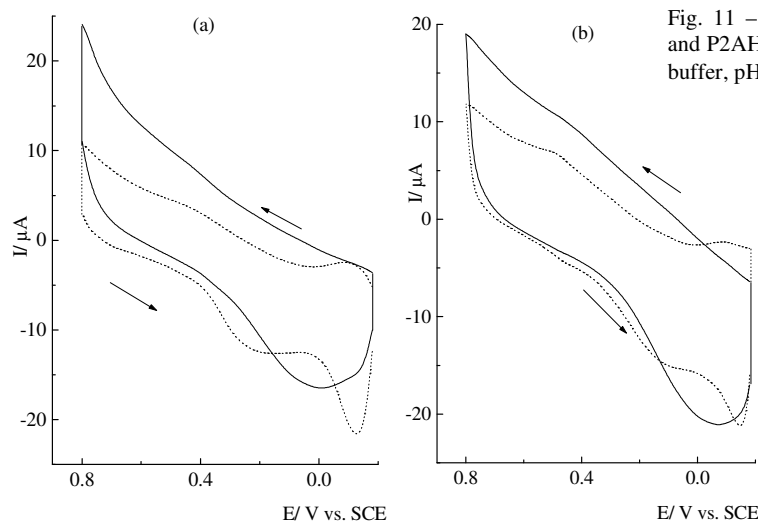
Fig. 11 – Cyclic voltammograms of the P2ABA-ME (a) and P2AHA-ME (b), Q_{synth}=20 mC/cm^2 in 0.1M phosphate buffer, pH=6.5 (——) and 0.1M H$_3$PO$_4$ solution (----). Sweep rate=200mV/s.

The parameter values of the postulated circuit are in agreement with polyaniline films behaviour dipped in a more protonated solutions: the polymer film resistance and the charge transfer resistance values decrease and the double layer capacitance increases. On the other hand, the proposed equivalent circuit is a Ladder type circuit applied also for other electroactive polymer films.[20]

CONCLUSIONS

It has been shown that P2AHA-ME and P2ABA-ME can be prepared in phosphate buffer solution, pH = 6.5 even if the monomers' solubility is low. In this case, thin polymer films (thickness < 0.1μm) were obtained having a large resistance not only in phosphate buffer, pH = 6.5 but also in 0.1 MH$_3$PO$_4$ solution pH = 1.45. The data obtained from impedance spectroscopy measurements show the important capacitive behaviour of these films, predominantly for P2AHA-ME film.

Thicker P2AHA-ME films (> 0.1μm) can be obtained from solutions containing larger concentration of monomer in mixed aqueous/organic solvent solutions. The surface morphologies of P2AHA-ME films, grown from these solutions exhibit a poorly defined agglomerate structure.

REFERENCES

1. N. C. Foulds and C. R. Lowe, *J. Chem. Soc. Faraday Trans*. **1986**, *82*, 2159.
2. P. N. Bartlett and R.G. Whitaker, *J. Electroanal. Chem.*, **1987**, *224*, 27.
3. P.N. Bartlett and J.M. Cooper, *J. Electroanal. Chem.*, **1993**, *32*, 1.
4. M. Trojanowicz and T. Krawczynski vel Krawczyk, *Mikrochim. Acta*, **1995**., *121*, 167.
5. W. Schumann, *Mikrochim. Acta*, **1995**, *121*, 1.
6. P.N. Bartlett and P.R. Birkin, *Synth. Metals*, **1993**, *61*, 15.
7. S.A.Emr and A.M. Yacyncych, *Electroanalysis*, **1995**, *7*, 913.
8. A. Q. Contractor, T. N. Sureshkumar, R. Narayanan, S. Sukeerthi, R. Lal, and R. S. Srinivasa, *Electrochim. Acta*, **1994**, *39*, 1321.
9. Z. Zhang, H. Liu and J. Deng, *Anal. Chem.*, **1996**, *68*, 1632.
10. M. B. Madaras and R. P. Buck, *Anal. Chem.*, **1996**, *68*, 3832.
11. R. H. Clark and E. C. Wagner, *J. Org. Chem.*, **1944**, *9*, 55.
12. J. R. Macdonald, *CNLS Program LEVM Manual Version 7.1.* **1999**.
13. S. Winkels and M. M. Lohrengel, *Electrochim. Acta*, **1997**, *42*, 3117.
14. J. M. Saveant and E. Vianello, *Electrochim. Acta*, **1963**, *8*, 905.
15. D. E. Stilwell and Su-Moon Park, *J. Electrochem. Soc.*, **1988** *135*, 2254.
16. Yoan-Bo Shin, Mi-Sook Won and Su-Moon Park, *J. Electrochem. Soc*. **1990**, *137*, 538.
17. J. R. MacDonald (ed.), *Impedance Spectroscopy*, J.Wiley, New York 1987 p. 17 and 93.
18. I. D. Raistrick, *Solid State Ionics*, **1986**, *18-19*, 40.
19. B. Savopol, *Solid State Ionics*, **1987**, *23*, 253.
20. J. Bobacka, M. Grzeszczuk and A. Ivaska, *Electrochim. Acta*, **1992**, *37*, 1759.