

THE ELECTROCHEMICAL BEHAVIOUR OF SOME COMPOSITE COATINGS OBTAINED BY ELECTROSYNTHESIS ON METALLIC SUBSTRATE

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Copolymers of aniline and pyrrole have been formed by electrochemical oxidation in acidic medium, but the composition of the polymeric chain differs from the composition of the synthesis solution. It was shown that the structure and the morphology of the obtained coatings were dependent on the feed ratio of monomers (aniline and pyrrole). The polyaniline and polypyrrole have very distinct electrochemical behaviours. The properties of those copolymers have been studied by cyclic voltammetry. The corrosion performance of composite coated aluminium was evaluated by CV and EIS. The corrosion resistance of composite coated aluminium was higher than of uncoated aluminium. The morphological structure of composite coatings was examined by metallographic microscope. It was observed the formation of a new material, namely composite coating.

INTRODUCTION

There is a lot of literature concerning the synthesis and characterisation of conducting polymers. Electrochemical synthesis of conductive polymers allows preparation of layers of polymers of desired thickness, shape and dimensions generally are not possible by chemical methods.

Thus far most promising conductive polymers have been those made from monomers of pyrrole, aniline, benzene, thiophene, acetylene.

These polymers can be easily prepared electrolytically in organic or aqueous solutions. Conductivity is usually in the semiconductor range.

The conductivity of doped polymers can be attributed to the delocalisation of Π conjugated systems.

These polymers such as polyaniline (PANI) and polypyrrole (PPY) have received great attention since its rediscovery by Shirakawa *et al.*¹ One of the key features is its wide range of proposed applications, including presently fields such as actuators, electrochromic and photovoltaic devices, secondary batteries, fuel cells, supercapacitors, ionic sensors, biosensors, electrocatalysis and corrosion protection among many other ones.²⁻²¹ Due to their potential

applications and interesting characteristics, the electrochemistry of these polymers has been intensively studied in the past years.²²⁻²⁶

Electrochemical synthesis of conductive polymers allows preparation of polymer layers of desired thickness, shape and dimensions, generally are not possible by chemical method.

Conducting polymers containing two compounds can be prepared as copolymers, composites, bilayers or blends. This is done for the improvement of the physical, chemical, mechanical and electrical proprieties of homopolymers. As we shown before, polyaniline and polypyrrole are two of the most promising conducting polymers. Both of them have a relatively high conductivity and good environmental stability.²⁷

Because the oxidation potential of aniline and pyrrole are very near, we believe that simultaneous oxidation and codeposition of polyaniline and polypyrrole is possible by changing the applied potential.

In this paper, we studied the formation of polyaniline-polypyrrole composite coatings on aluminium electrode using potentiodynamic method. The electrochemical proprieties of these composite coatings were studied by cyclic voltammetry and by

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electrochemical impedance spectroscopy. The morphological structure of composite coatings was examined by metallographic microscope. It was observed the formation of a new material, namely composite coating.

EXPERIMENTAL

A model VoltaLab 40 potentiostat/galvanostat with EIS dynamic was used for the electrochemical polymerization. Electropolymerization was carried out in a three electrodes system.

A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrode respectively. The reference electrode was placed in a separate cell and was connected to the corrosion cell via a salt bridge, which ends as a Luggin capillary in the corrosion cell. This arrangement was used to reduce the ohmic resistance of the corrosion system. The working electrode was made from pure aluminium (99.9%). Samples with 0.64 cm² geometric surface area were used. Prior to experiments, the electrodes were polished with SiC emery paper down to #4000. After polishing, the electrodes were degreased in acetone, washed with Millipore water and then introduced into the measuring cell.

Polyaniline (PANI), polypyrrole (PPY) and poly (aniline-co-pyrrole) films were electropolymerized onto an aluminium substrate by cyclic voltammetry with a scan rate of 20 mV/s. All the reactions were carried out in the scan range of -1000 up to +3000 mV versus SCE.

The electropolymerization of aniline and pyrrole monomers was carried out in a 0.1 M monomer + 0.25 M oxalic acid electrolytic solutions.

In the case of the copolymers synthesis, the concentration of aniline was maintained constant at 0.1M and the proportion in moles of pyrrole was varied from 0.1M to 0.5M. It can be observed that, the initial concentration of co-monomers (aniline and pyrrole) was varied from 1:1 to 1:5. The electrochemical characteristics of the coatings were studied by cyclic voltammetry and electrochemical impedance spectroscopy, in an aqueous solution of 0.5M K₂SO₄. The working electrode potential was cycled on the potential range of -1000 mV up to 3000 mV with scan rate of 20 mV s⁻¹.

Impedance measurements were carried out using a software program between 100 KHz and 10 mHz with an ac

wave of ± 5 mV (peak-to-peak) overlaid on a dc bias potential and the impedance data were obtained at a rate of 10 points per decade change in frequency.

All tests have been performed at 25°C under atmospheric oxygen without agitation.

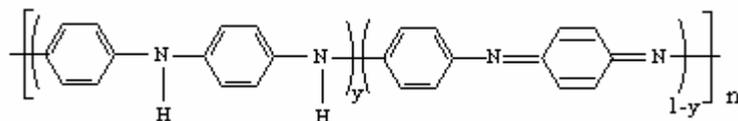
RESULTS AND DISCUSSION

Electrochemical synthesis of poly (aniline-co-pyrrole) from different precursor solutions produces homogeneous and adherent black films they show great electroactivity in the cycling solutions and the voltammetric profiles are very similar to the potential values of the current peaks being located at intermediate values of the typical electrochemical responses of homopolymers.

First we obtained the PANI films on the aluminium substrate in a synthesis solution of 0.1M aniline+0.25M oxalic acid by potentiodynamic method. The electrode potential was scanned on the range of -1000 mV up to +3000 mV with a sweep rate of 20mVs⁻¹ for a period 25 cycles.

Analyzing the cyclic voltammograms from figure 1, it can be observed that, at the first cycle on the anodic branch of the voltammograms appear two anodic oxidation peaks which point out the anodic oxidation of aniline and the formation of polyaniline (PANI) film. The formation process of PANI film was illustrated by us in a previous paper.²⁸

It is well known that, polyaniline can exist in three different oxidation states such as leucoemeraldine (fully reduced form), emeraldine form (partially oxidized form) and pernigraniline (fully oxidized form). A very important characteristic of polyaniline consists in the fact that its structural units contain two different entities with different ponderables. Taking into account this property we can write thus:



when $y = 1$, we have leucoemeraldine base, when $y = 0$ we obtained pernigraniline base and when $y = 0.5$ an intermediate state between leucoemeraldine and pernigraniline is obtained which is called emeraldine base.

These forms of polyaniline are dependent on the applied potential. At the increasing anodic potential sweep the oxidation forms of polyaniline are obtained and on the anodic branch of the

cyclovoltammogram appear the oxidation peaks (see Figure 1).

At the reverse potential sweep, no cathodic reduction peak appears up to -1000 mV, but it can be observed that, the cathodic current begins to increase at a potential value of -650 mV (see Figure 1). The increase the number of cycles led in all the cases to decrease of the height of the anodic peaks and also, to decrease of the anodic and cathodic current (see Figure 1 and Table 1).

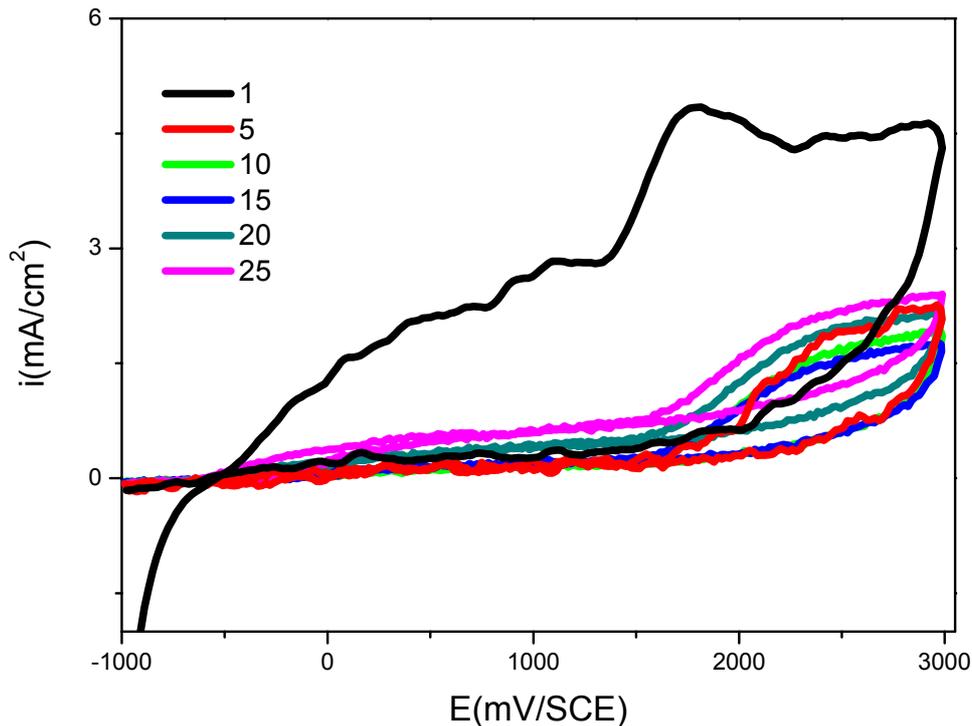


Fig. 1 – The cyclic voltammograms obtained for the aniline polymerization on the aluminium electrode surface.

Table 1

Kinetic parameters obtained from the cyclic voltammograms for aniline electropolymerisation in 0.25 M oxalic acid aqueous solutions

No. cycle	i_{pa_1} (mA/cm ²)	E_{pa_1} (mV)	i_{pa_2} (mA/cm ²)	E_{pa_2} (mV)
1	2.83	1091	7.83	1777
5	1.27	2141	1.92	2484
10	-	-	1.72	2561
15	-	-	1.83	2512
20	-	-	1.98	2508
25	-	-	2.13	2424

We can see that, after five cycles on the anodic branch of voltammogram appears only one anodic oxidation peak and its height is much lower than in the case of the first cycle. This decrease of the anodic peak height and of the anodic and cathodic current once with the increase of the cycles number is due to the formation of the Al_2O_3 passive layer which behaves as a barrier for charge transfer reaction (as we explained above in the paper).

Also, we analyzed by metallographic microscope the modified electrode PANI/Al surface and in figure 2 are given the micrographic images. Analyzing these micrographies, it can be observed very well the electrodeposited polyaniline layer and its characteristic structure formed from polymer (PANI) chains, which are uniform, distributed. These images prove once again the formation of PANI layer on the

aluminium surface by cyclic voltammetry and its characteristic structure.

Further, we studied the obtainment of the polypyrrole films on aluminium substrate by using cyclic voltammetry.

In figure 3 are given the cyclic voltammograms of pyrrole polymerization in a synthesis solution of 0.25 M oxalic acid + 0.1 M pyrrole. The electrode potential was scanned on the range of -1000 mV up to +3000 mV with a sweep rate of 20 mVs⁻¹ for a period of 25 cycles.

Analyzing the cyclic voltammograms from figure 3, it can be observed that, at the first cycle on the anodic branch of the voltammogram appears an anodic peak, which is very high and wide. This anodic peak points out the anodic oxidation of pyrrole and the formation of polypyrrole film. The formation process of PPY

film was illustrated by us in a previous paper²⁹ and is in according to this mechanism. The electropolymerization reaction appears to involve two electrons per molecule of pyrrole (Py) monomer, and it proceeds through a radical coupling mechanism.³⁰ During the formation a

stoichiometric amount of anions provided by the supporting electrolyte is incorporated into the polymer layer to neutralize the positive charge of the PPY chains. Therefore, the nature of the anions plays an important role in conferring the electrochemical properties of the PPY films.

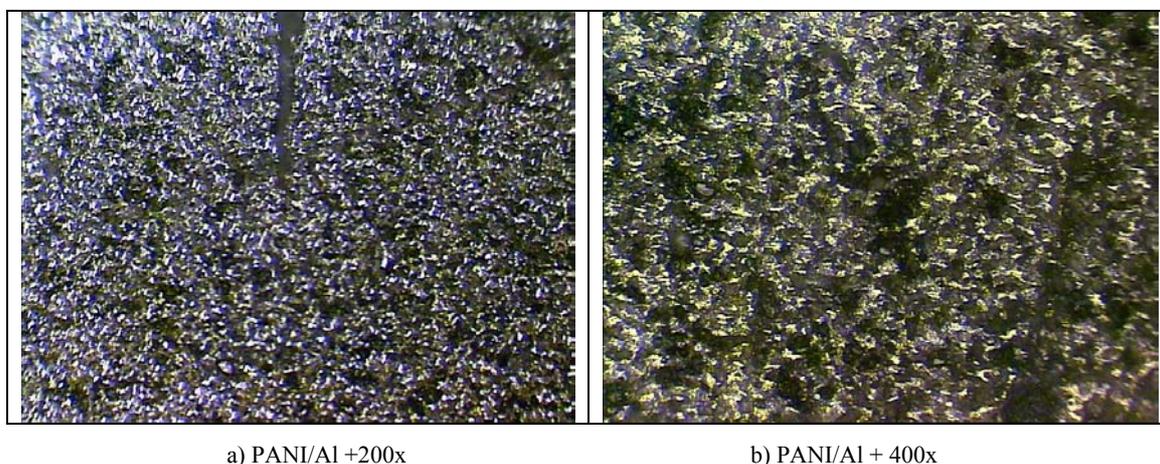


Fig. 2 – Micrographies of PANI film electrodeposited on aluminium surface after 25 cycles.

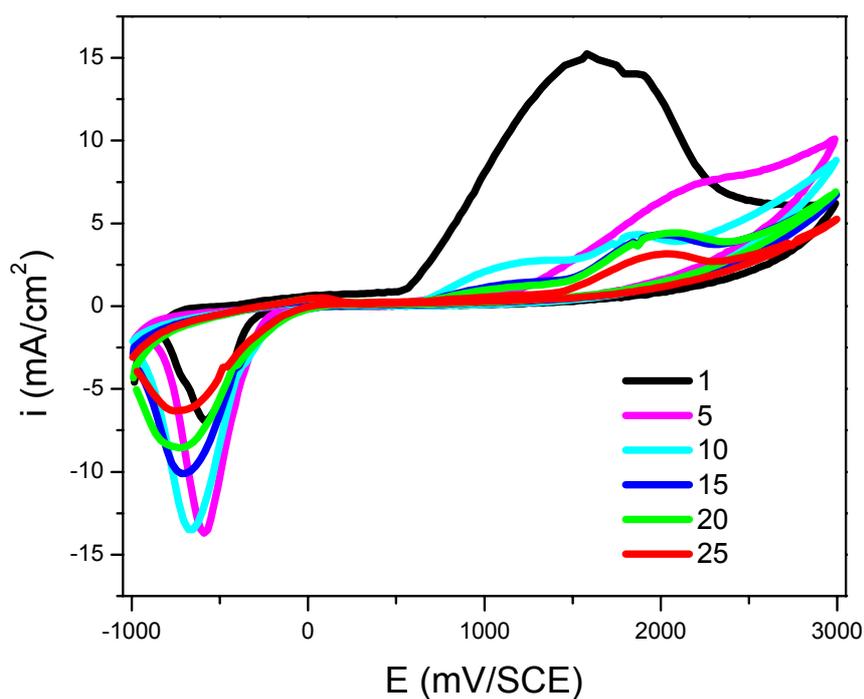


Fig. 3 – The cyclic voltammograms obtained for the pyrrole electropolymerization on the aluminium electrode surface.

At the reverse sweep electrode potential, on the cathodic branch of the voltammogram (for the first cycle) a reduction cathodic peak appears which is much lower than the anodic peak (see figure 3 and table 2). The separation potential range (ΔE_p) between the anodic and cathodic peaks is wide enough and points out the fact that, at the electrode

surface take place quasi-reversible processes. The value of ΔE_p is very high because the formation of PPY film led to the increase of ohmic resistance of the electrochemical system and consequently the charge transfer reactions are impeded and ΔE_p increases. After five cycles, the cyclic voltammogram obtained has a modified shape in

comparison with the first cyclic voltammogram. In this case, at the anodic potential sweep appears an anodic oxidation peak which has a lower height than in the case of the first cycle and it is shifted to more anodic potential. On the cathodic branch of the cyclic voltammogram with number 5, the reduction cathodic peak appears in the same potential range, but in this case, it is more narrow and higher. Further, increasing the number of

cycles, it can be observed that, on the anodic branch appear two anodic oxidation peaks which have much lower currents density and also, on the cathodic branch of the cyclic voltammograms appears a reduction cathodic peak. The height of this peak decreases with the increase of the cycles number (see figure 3 and table 2).

Table 2
Kinetic parameters obtained from the cyclic voltammograms for pyrrole electropolymerization in 0.25 M oxalic acid aqueous solutions

No. cycle	i_{pa_1} (mA/cm ²)	E_{pa_1} (mV)	i_{pa_2} (mA/cm ²)	E_{pa_2} (mV)	i_{pc_1} (mA/cm ²)	E_{pc_1} (mV)	ΔE_{p_1} (mV)
1	16.38	1634	-	-	8.60	-578	2212
5	7.91	2235	-	-	14.51	-590	2825
10	2.70	1172	4.31	1815	13.49	-651	1823
15	1.31	1035	4.37	1896	10.08	-692	1727
20	1.18	1025	4.40	2032	8.53	-704	1729
25	0.66	1007	3.14	1970	6.29	-717	1724

The decrease of the anodic current peak height with the increase of the cycles number can be explained thus: at the anodic polarization of the aluminium electrode in synthesis solution, the formation of Al₂O₃ and PPY films proceeds simultaneously. At the first cycle the anodic oxidation of pyrrole to polypyrrole in according to the mechanism given by ²⁹ is predominant process. With the increase of the cycles number the predominant process becomes the anodic oxidation of aluminium, with formation of Al₂O₃ film, which acts as an excellent barrier inhibiting the charge transfer reactions. Hence, the formation of Al₂O₃ film inhibits the electrochemical polypyrrole formation and thus, we can explain the decreasing

of the anodic oxidation current once with the increase of the cycles number. These two films interact one with the other and it can be considered that, the bilayer film was obtained consisting from a barrier oxide film of Al₂O₃ and an electronically conducting PPY film.

Further, we analyzed by metallographic microscopy the modified PPY/Al electrode surface and in figure 4 is given a micrographic image. Analysing this micrography, it can observed very well the electrodeposited polypyrrole film and its characteristic structure like as cauliflower. This image proves once again the formation of the PPY film on the aluminium substrate by cyclic voltammetry and its characteristic structure.



Fig. 4 – Micrography of PPY film electrodeposited on aluminum surface after 25 cycles.

Further, we studied the formation of polyaniline - polypyrrole composite coatings on aluminium substrate using the cyclic voltammetry for electrodeposition of composite polymeric film. It was shown that, the yielded structure and the morphology of the coatings were dependent on the feed ratio of the monomers (aniline and pyrrole) and on the applied potential. The resulting composite also showed significant changes in electrochemical behaviour when were compared with the electrochemical behaviour of homopolymers. Because the oxidation potentials of aniline (0.8 V vs. SCE) and pyrrole (1.2V vs. SCE) are very near, we believe that simultaneously oxidation and codeposition of polyaniline and polypyrrole is possible by changing the applied potential.

Therefore, the copolymerisation of aniline and pyrrole was performed by using repeated potential cycling between -1000 mV and +3000 mV with a sweep rate of 20mVs^{-1} for a period of 25 cycles.

In figure 5 are presented the cyclic voltammograms obtained for the polymerization of a pyrrole-aniline mixture after a certain number of cycles.

As it can be seen, the voltammogram obtained after the first polymerisation cycle presents two wide and high anodic oxidation peaks which form together a very large anodic oxidation range which point out that, in this potential range takes place the active oxidation process of aniline and pyrrole with the new composite formation. For the following cycles, it can be observed that, the shape of voltammograms change, on the anodic branch of the voltammograms appears only one oxidation peak which is much lower and is shifted to more electropositive potential. At the reverse potential sweep the anodic current decreases very much and no cathodic current appears up to the very negative values of the potential.

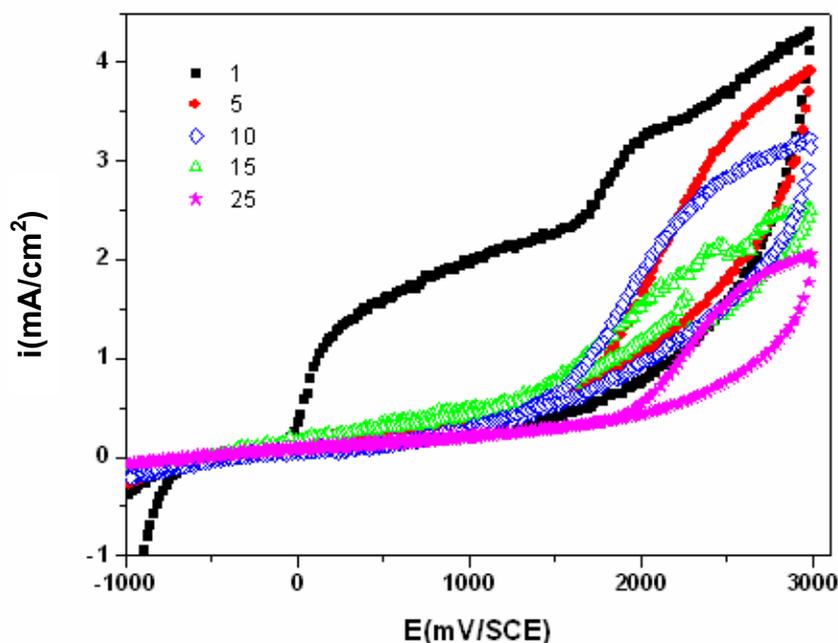


Fig. 5 – The cyclic voltammograms for polymerization of the mixture: 0.1 M pyrrole + 0.1M aniline in an aqueous solution of 0.25M oxalic acid.

The decrease of the anodic current peak height with the increase of the cycles number can be explained thus: at the anodic polarization of the aluminium electrode in synthesis solution, the formation of Al_2O_3 and composite films proceeds simultaneously. At the first cycle the anodic oxidation of aniline and pyrrole with co-deposition of composite film is the predominant process. With the increase of the cycles number the predominant

process becomes the anodic oxidation of aluminium, with formation of Al_2O_3 film, which acts as an excellent barrier, inhibiting the charge transfer reactions. Hence, the formation of Al_2O_3 film inhibits the anodic oxidation of aniline and pyrrole and in this way, it can be explained the decreasing of the anodic and cathodic current once with the increase of the cycles number. The formation of Al_2O_3 layer proceeds two interfaces,

the first at the aluminium / Al_2O_3 layer and the second at the Al_2O_3 layer / composite film [poly(aniline-co-pyrrole) film]. It is assumed that, the species are continuously generated at metal/oxide interface. Then, they migrate through growing Al_2O_3 layer toward the solution where high electric field, while oxide ions O^{2-} migrate toward the aluminium electrode. At the interface of Al_2O_3 layer/composite film, the Al^{3+} ions encounter water species to form Al_2O_3 film. In this way, it can be explained also, the decreasing height of the oxidation and reduction peaks once with the increase of the cycles number (see Figure 5 and Table 3).

This behaviour of composite polymer is different from the homopolymers behaviour (see in comparison Figures 1, 3, 5) and this fact proved that, a new material is formed namely composite material or in our case composite coating.

Further, we studied the obtainment of composite coatings from different mixture in function of the molar feed ratio of monomers. In Figures 6 and 7 are given the cyclic voltammograms for composite electropolymerization from different mixture of aniline and pyrrole.

Analyzing in comparison these electropolymerization voltammograms, it can be observed that, the behaviour of the current-potential curves are function of the molar feed ratio of monomers and that, the composite voltammograms are very different from the homopolymers voltammograms. From analysis of these figures, we can conclude

that, in comparison with the homopolymers, the formed composite has an intermediate behaviour that proved the formation of a new material.

The EIS measurements were carried out for PPY-PANI/Al modified electrodes in 0.5M K_2SO_4 solutions in relation to the cycles number of electrodeposition and in relation to the feed ratio of the monomers (aniline and pyrrole). In figure 8 are given, for exemplification the Nyquist diagrams for PPY-PANI (5:1)/Al modified electrode in 0.5M K_2SO_4 solution in relation to the cycles number of electrodeposition.

Analysing this figure, it can be observed that in all the cases, at the high and medium frequencies the capacitive loop very well defined were obtained while at the low and very low frequencies a wide inductive region is obtained. Analysing in comparison the Nyquist diagrams obtained for different cycles of electrodeposition, it can be observed that, the capacitive loop increases with the cycles number of electrodeposition and the inductive region increases in the same mode. This behaviour can explained considering that, once with the increase of cycles number the formation of the composite coating and of Al_2O_3 layer is much more well defined and much more stable. Bode diagrams from figure 9 are in concordance with the results showed by Nyquist diagrams (see in comparison figure 8 and figure 9).

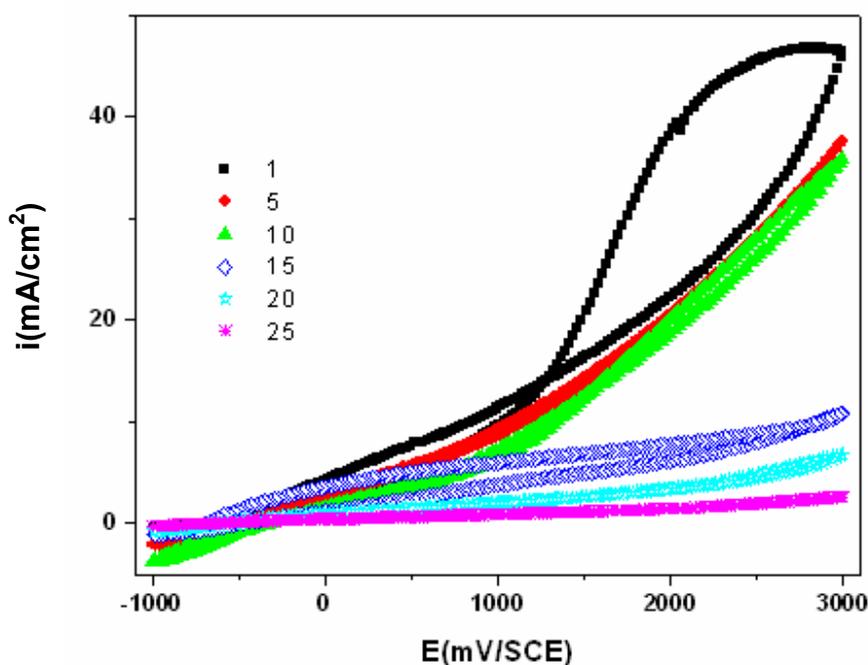


Fig. 6 – The cyclic voltammograms for polymerization of the mixture: 0.5 M pyrrole + 0.1M aniline in an aqueous solution of 0.25M oxalic acid.

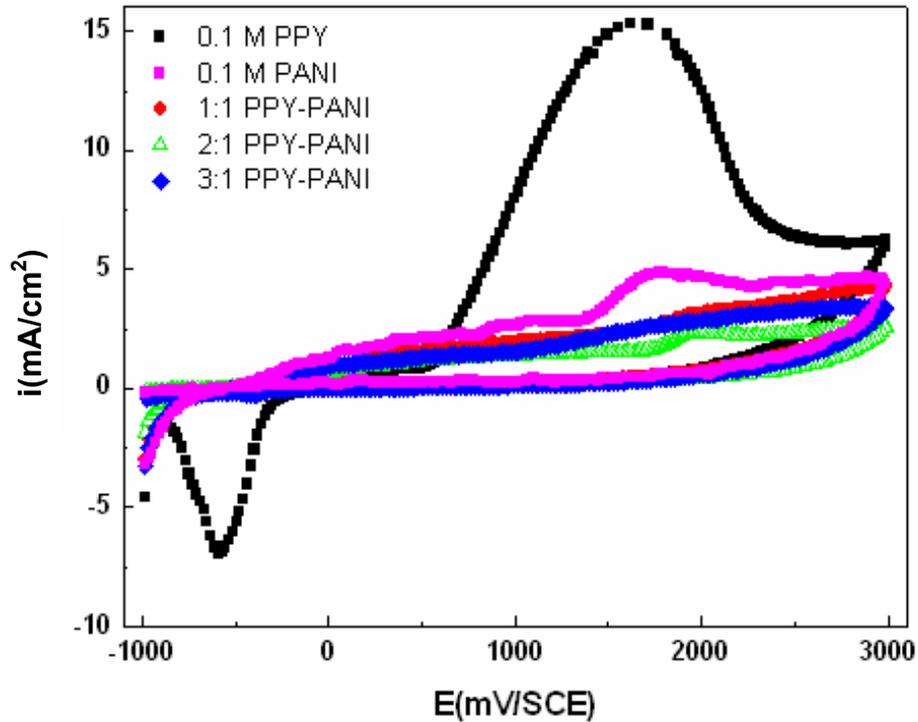


Fig. 7 – The cyclic voltammograms for PPY/Al, PANI/Al and composite PPY-PANI/Al modified electrodes in 0.25 M oxalic acid aqueous solutions.

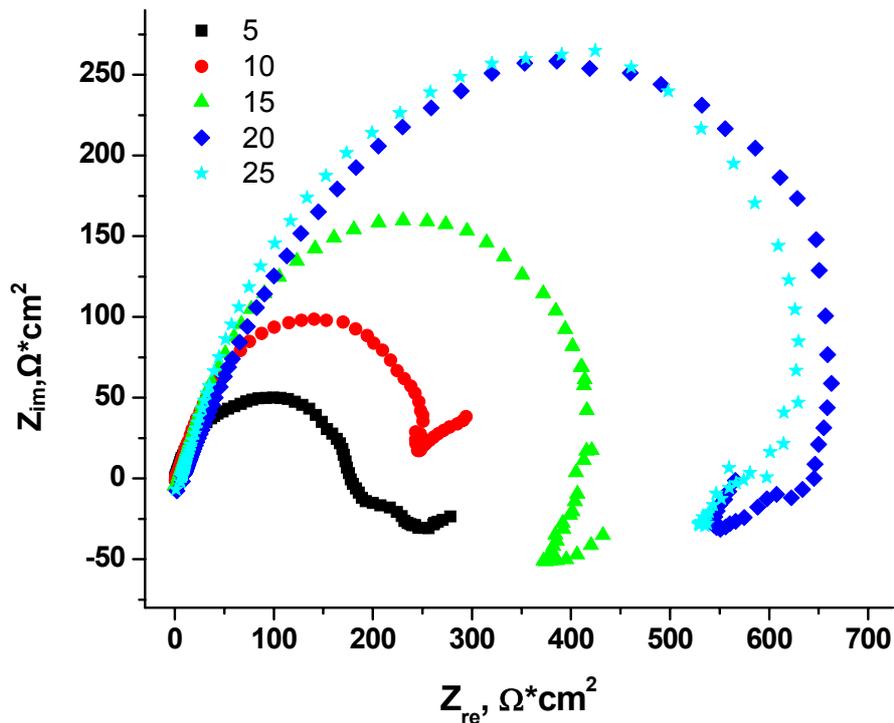


Fig. 8 – Nyquist diagrams for PPY- PANI (5:1)/Al modified electrode in 0.5 M K₂SO₄ solutions in relation to the number of electrodeposition.

Analyzing the Figure 9b, it can be observed that, on the phase angle versus logarithm frequency curve appear two maxima, respectively, two time constants. The maximum, which appears at the

high and very high frequencies, is very well defined, it is very wide and high. The phase angle for this maximum has a value of approximately 75° that means a capacitive behaviour of the

composite/Al modified electrode. This capacitive behaviour was observed for all the composite films obtained for different cycles of electrodeposition (see Figure 9b) but, the phase angle value increases once with the increase of the cycles number of electrodeposition, that means an increase of the capacitive behaviour once with the increase of the electrodeposition cycles number. The same results are pointed out by the Bode diagrams from Figure 9a. This fact is in concordance with the results pointed out by Nyquist diagrams and cyclic voltammograms.

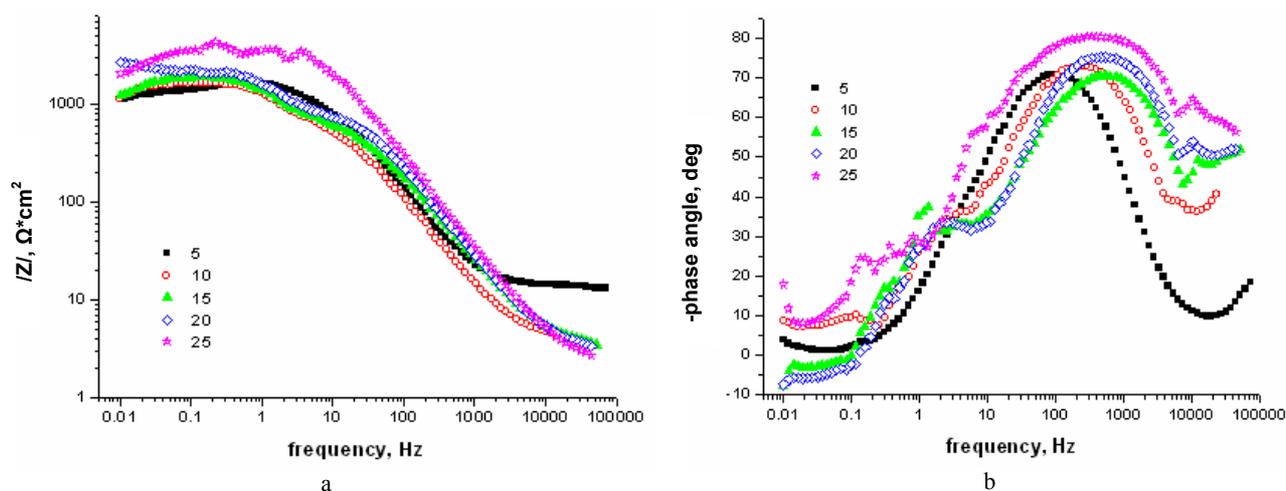


Fig. 9 – Bode diagrams for PPY-PANI(5:1)/Al modified electrode in 0.5 M K₂SO₄ solution in relation to the number of electrodeposition cycles.

Further, we studied in comparison by EIS, the electrochemical behaviour of PPY/Al, PANI/Al and composite (PANI-co-PPY)/Al modified electrodes. In figure 10 are given in comparison the Bode diagrams for PPY, PANI, Al and composite obtained from different molar feed ratios. Analyzing this figure it can be observed that, in all the cases in the high frequencies range a maximum very well defined is obtained, but the height and the diameter of this maximum differs for the each particular case. Thus, the phase angle with the highest value is obtained for composite (PANI-co-PPY) which was electrodeposited from a synthesis solution with the feed ratio of 5:1 (Py/An) and the lowest value of the phase angle was obtained for PPY film (see Figure 10).

For the PANI film, the value of the phase angle is lower than in the cases of composite coatings with the molar feed ratio of 2:1 and 5:1 (Py/An). The phase angle values for composite with other molar feed ratios were intermediates between the values for PANI film and PPY film (see Figure 10).

From Figure 9b it can also be observed that, at low and very low frequencies appears a maximum which is not well defined and the phase angle for this peak has a value of approximately 25° , that means an inductive behaviour. This value of the phase angle decreases once with the decrease of the electrodeposition cycles number. The inductive behaviour points out the fact that, on the electrode surface takes place the adsorption of the active species from electrolyte solution followed by relaxation phenomena.

This fact proves once again the formation of a new composite material with a new morphological structure in comparison with the morphological structure of PANI and PPY films.

Analyzing the phase angle values (from figure 10), it can be observed that, the composite coatings obtained from mixture with molar feed ratio changeable from 5:1 up to 1:1 have the best capacitive behaviour while the PPY film has a capacitive behaviour with diffusive tendency.

Also, we analyzed by metallographic microscopy the modified electrode PPY-PANI/Al surface and in figures 11 and 12 are given the micrographic images.

As, it can be observed, the morphological structure of the composite coatings of the PPY-PANI/Al modified electrode surfaces is different from the morphological structure of the PPY/Al and PANI/Al modified electrode surfaces (see in comparison Figures 4, 8, 11 and 12). This fact proves another one that, a new material, respectively a new composite material was formed.

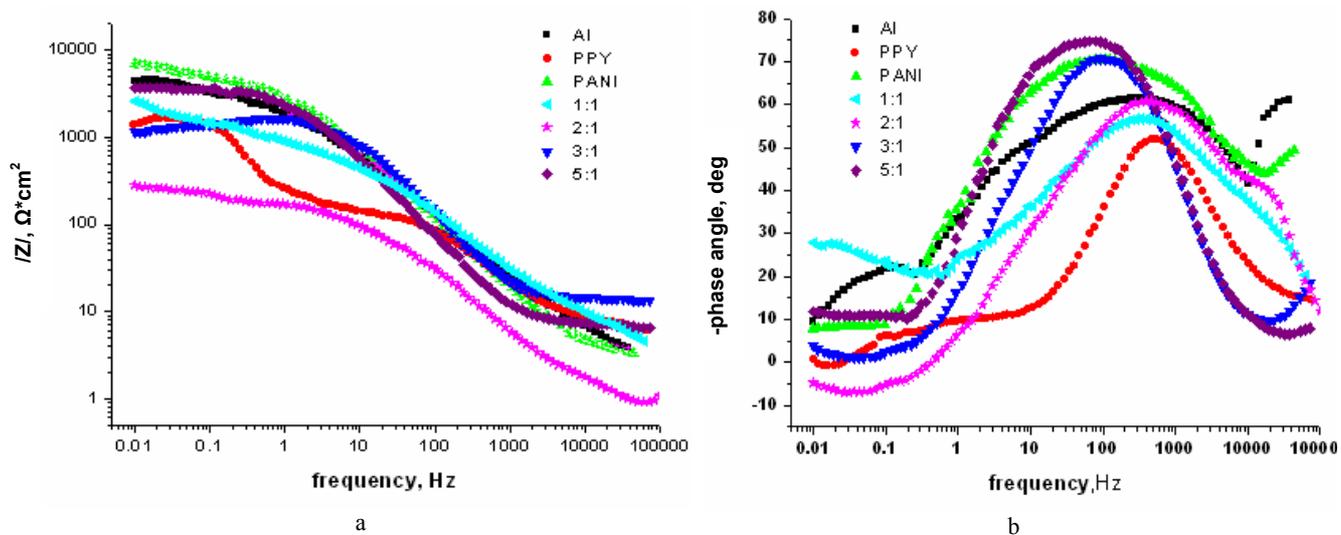


Fig. 10 – Bode diagrams for PPY/Al, PANI/Al and composite PPY-PANI/Al modified electrodes in 0.5 M K_2SO_4 aqueous solutions in relation to the number of electrodeposition cycles.

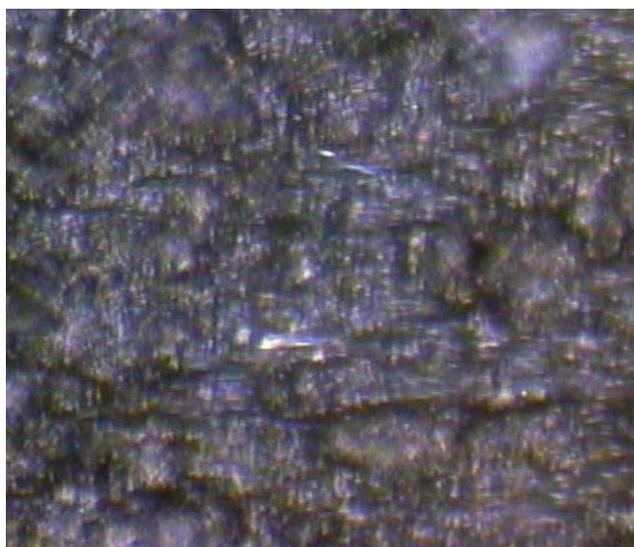


Fig. 11 – Micrographic image of pyrrole – aniline (1:1) film electrodeposited on aluminium surface after 25 cycles.

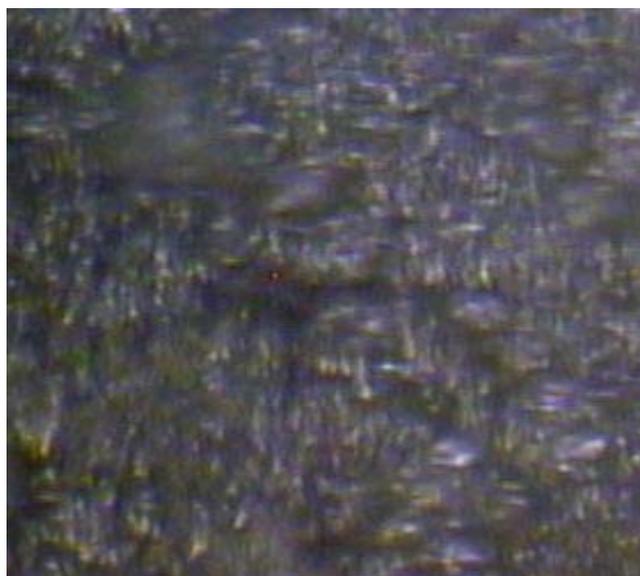


Fig. 12 – Micrographic image of pyrrole – aniline (5:1) film electrodeposited on aluminium surface after 25 cycles.

CONCLUSIONS

The electropolymerization of aniline is an anodic oxidation process.

The formation of Al_2O_3 films inhibits the electrochemical polyaniline formation and thus the decrease of the anodic oxidation current takes place.

For PANI/Al modified electrodes the increase of the number of polymerization cycles led in all the cases to decrease of the anodic peak height and to decrease of the anodic and cathodic current and in general of the average of the anodic and cathodic current.

The electropolymerization of pyrrole is also, an anodic oxidation process, which involves two electrons per molecule of monomer incorporated in the polymer chain.

The formation of Al_2O_3 film inhibits the electrochemical polypyrrole formation and thus the decrease of the anodic oxidation process takes place.

After a prolonged anodic oxidation the PPY film becomes loose and porous and the polarization resistance decreases.

The increase of the cycles number led in all the cases to decrease of the anodic peak height and of the anodic and cathodic current.

The composite coatings on aluminium substrate from pyrrole and polyaniline were obtained using the cyclic voltammetry.

The morphological structure of the composite coatings is dependent on the molar feed ratio of the monomers (aniline and pyrrole) and the applied potential.

The composite formation takes place by simultaneous oxidation and codeposition of aniline and pyrrole.

The behaviour of the composite polymer is different from the homopolymers behaviour and this fact proved that, a new material is formed, namely composite material or composite coatings.

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