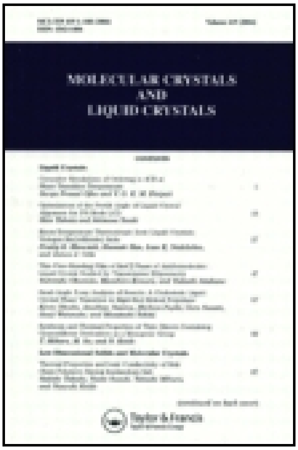

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Modified Electrodes Type Doped Polypyrrole/Pure Titanium and their Electrochemical Characterization

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Modified Electrodes Type Doped Polypyrrole/Pure Titanium and their Electrochemical Characterization

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Polypyrrole (PPY) films were electrodeposited at pure titanium from different aqueous solutions. The electropolymerization process was carried out by galvanostatic method. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical properties of electrodes. The results indicate that the surfactant anion favors redox processes which are faster and more reversible than those associated to usual polypyrrole electrodes. In fact, while in PPY films doped by conventional, small anions (e.g., Cl^-), the charge compensation is assured by uptake of the anions during oxidation and the release of the same anions during reduction, in the PPY films prepared in the presence of large-anions salts (e.g., sodium dodecylsulphate-SDS), the charge compensation appears to involve incorporation of cations since the large anions are not easily released from the polymer matrix. An equivalent circuit was proposed to successfully fit EIS data and the significant contribution of pseudocapacitance from polypyrrole was thus identified. EIS measurements on Ti/PPY film electrodes were carried out in the supporting electrolyte depending on the following parameters: PPY-film thickness, supporting electrolyte concentration c, temperature T, and polarisation potential E.

Keywords: cyclic voltammetry; electrochemical impedance spectroscopy; electropolymerization; polypyrrole; titanium

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INTRODUCTION

Electronically conductive polypyrroles are an extremely interesting class of materials that have gained popularity in the last decade. It has been accepted that the polypyrrole films have a number of potential technological applications in the areas of energy storage, solar energy, conversion and electrochromic display devices [1–6]. There is no doubt that polypyrrole is an interesting electrode material because of its good electrical conductivity, good environmental stability and relative ease of synthesis. Polypyrrole can be prepared either by electrochemical polymerization [7,8] or by chemical oxidative polymerization [9,10]. Electropolymerization of pyrrole has been attempted on many electrode substrates including noble metals and non-noble metals.

The synthesis and properties of polypyrrole (PPY) established itself as a novel material in the field of conducting polymers, have been extensively studied [1–4]. It has been shown that along with a number of other parameters, the anions incorporated in the positively charged polymer for charge compensation, influence the growth rate, the morphology of the synthesized polypyrrole films and the speed and extent of the electrochemical response. The electrochemical redox process of PPY is affected by the anions due to the motion of anions and protons in the polymer accompanying the redox of PPY. Some researchers [11–15] have detected a dependence of the electrochemical responses on the type of anions, even with no difference in the cyclic voltammograms. They have concluded that some anions tend to interact more strongly than other anions with the positive charges on the polymer chain. The anion effects are also observed in the electrochemical degradation of PPY films [16]. The rate of polymer overoxidation at relatively high electrode potentials is significantly dependent upon the nature of the anions incorporated in the positively charged polymer.

As the available explanations to the findings about the anion effects are not yet satisfactory, in the present work we investigated further the anion effects on electrosynthesis and overoxidation of PPY on pure titanium substrates in different aqueous solutions. As dopant anions, we have been used chloride (Cl^-) and dodecylsulphate anions.

EXPERIMENTAL

Polypyrrole films doped with different anions were galvanostatically deposited ($1\,mA\,cm^{-2}$ current density) onto a titanium substrate. The electrosynthesis was carried out in a one compartment cell generally using aqueous (bidistilled water) solution containing 0.1 M pyrrole (that was freshly distilled) and 0.1 M KCl as first synthesis solution. The second synthesis solution was also an aqueous solution of 0.1 M pyrrole but the dopant substance in this case was 0.1 M sodium dodecylsulphate. As cycling solution, KCl aqueous solution of different concentrations was used. A one compartment electrochemical cell with three electrodes was used. The counter electrode was a platinum gauze of large geometrical area, while as working electrode has been used a disc of titanium with its diameter of 10 mm. The reference electrode was a KCl saturated calomel electrode and all the electrode potentials were measured versus this reference electrode. A constant current density of $1\,\mathrm{mAcm^{-2}}$ was applied until the charge consumed in the electropolymerization was 868 mC corresponding to PPY layers of 2 μm thickness. All solutions were purged with dry, high purity argon, which was maintained over the solution during measurement. Prior to each experiment the working electrode was polished with abrasive paper of different granulations, then with alumina slurry (particle size 0.3 μm) on soft leather and finally washed with bidistilled water and anhydrous actonitrile. All the experiments were carried out at room temperature (20°C). Electrochemical synthesis is carried out using an EGG Princeton Applied Research (PAR) Model 173 potentiostat – galvanostat equipped with a PAR model 179 digital coulometer.

Voltammetric studies were performed using a Solartron Electrochemical Interface and current – potential responses were stored in a PC.

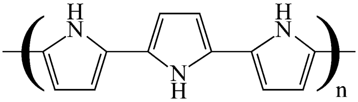
The consumed electrical charges were obtained by integration of the experimental chronoamperograms or voltamograms.

Monitoring the amount of total charge consumed during polymerization controls the film thickness, that is the film thickness is proportional to the total passed charge. Impedance spectroscopy measurements were done using a Frequency Analyzer (Solartron 1260) coupled to a potentiostat type Solartron 1287. The impedance diagrams were interpreted based on the equivalent circuits using the ZView software (version 2.4a Scribner Associates inc. Southern Pines, USA).

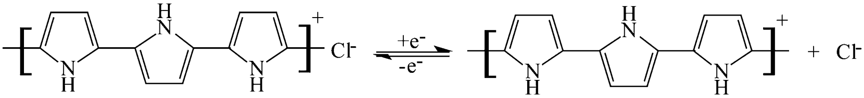
RESULTS AND DISCUSSION

Electrochemical synthesis of conductive polymers allows preparation of layers of polymers of the desired thickness, shapes and dimensions, generally not possible by chemical methods [17]. Thus, far more promising conductive polymers have been those made from the monomers of pyrrole, thiophene, aniline and benzene. These polymers can be easily prepared electrolytically in organic and aqueous solutions. Conductivities are usually in the semiconductor range. In general, the method of electrolysis affects to a great degree the electrical and physical properties of the polymer [18].

Polypyrrole is the best known of the conductive polymers. It does not require added dopants to be conductive. Its chemical structure is written as:



The polymer switches between a black conductive form and a yellow nonconductive form by changing the applied potential on the underlying electrode so as to reduce or oxidize the π-electron network of the polymer. This switching is illustrated by the following scheme:



Keeping the polypyrrole film in a massive oxidation state leads to an insulating film with no electroactivity [6].

Polypyrrole films can be very easily obtained electrooxidatively in acetonitrile or water at platinum electrodes and can be peeled off from the electrode as free-standing films for various studies. The various applications of polypyrrole films were reviewed by Moutet [19].

The relative constancy of the current efficiency could be related to the generally accepted mechanism of polymerization: the monomer molecule is oxidized, a radical cation is generated, two radical cations dimerize, the dimmer is oxidized and the correlative radical cation interacts with a monomeric radical cation to give a trimer and so on. This mechanism needs two electrons by monomeric unit incorporated in the polymer:

$$(\mathrm{PPY})_n \rightarrow (\mathrm{PPY})_n^+ + e^-$$

$$\mathrm{PY} \rightarrow \mathrm{PY}^+ + e^-$$

$$(\mathrm{PPY})_n^+ + \mathrm{PY}^+ \xrightarrow{2e^-} (\mathrm{PPY})_{n+1}$$

Among the available electroanalytical techniques, the cyclic voltammetry technique has been widely used to understand the electroactivity and the electrochemical properties of polypyrrole films because it can better describe the characteristics of the electrochemical switching behaviour between conducting and insulating states. In this paper, both experimental and theoretical approaches are used. Experimental cyclic voltammetry is performed for electrochemically synthesized polypyrrole films doped with Cl^- and dodecylsulphate anions on titanium substrate in aqueous KCl solutions of different concentrations.

In Figure 1 is presented the cyclic voltammogram of PPY(Cl^-)/pure titanium modified electrode in 0.1 M KCl aqueous solution at 25°C and potential scan rate of $10\,mVs^{-1}$.

The broad peaks observed in the voltammogram suggest a complex redox process for PPY(Cl^-)/Ti modified electrode. A counter-ion insertion, could explain these peak systems. The Cl^- anion inserted in the polymer matrix would interact with the oxidized sites of the polymer chain. This would change the redox potential of the polymer by the formation of a mixed chain, part of it interacting with Cl^- anions that neutralize the positive charges of polypyrrole backbone and another

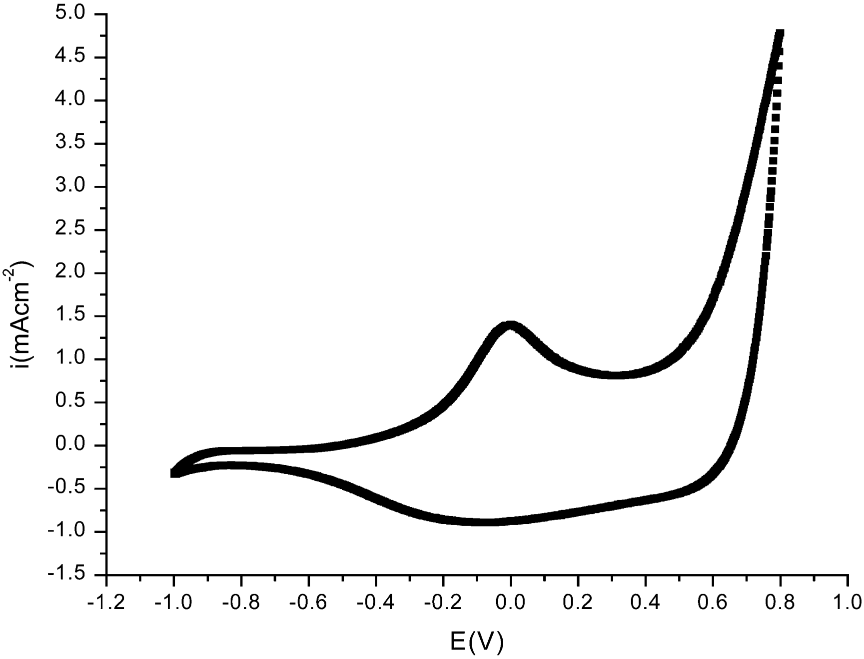


FIGURE 1 The cyclic voltammogram (1st cycle) of PPY(Cl^-)/Pt modified electrode in aqueous solution of 0.1 M KCl at 25°C and the potential scan rate of $10\,mVs^{-1}$.

part which remains positive charged. The oxidation and the reduction peaks correspond to the following equations:

$$PPY^{+}/A^{-} \underset{-e^{-}\,(\text{oxidation})}{\overset{+e^{-}\,(\text{reduction})}{\rightleftharpoons}} PPY/A^{-}$$

This equation explains the first couple redox, the following equation is related to the second couple redox thus: in this reduced state PPY/A^{-} take place insertion of the cation M^{+} from the electrolyte forming the following adduct: $PPY/A^{-}/M^{+}$ and then it follows the oxidation and reduction in the second step:

$$PPY/A^{-}/M^{+} \underset{+e^{-}\,(\text{reduction})}{\overset{-e^{-}\,(\text{oxidation})}{\rightleftharpoons}} PPY^{+}/A^{-}/M^{+}$$

As we shown above, polypyrrole films were obtained galvanostatically using an aqueous solution of 0.1 M KCl and 0.1 M pyrrole and also a solution of 0.1 M SDS (sodium dodecylsulphate) on pure titanium substrate.

Electrochemical synthesis of conductive polymers allows preparation of layers of polymers of the desired thickness, shapes and dimensions generally not possible by chemical methods [17]. Thus, far most promising conductive polymers have been those from monomers of pyrrole, thiophene, aniline and benzene. These polymers can be easily prepared electrolytically in organic and aqueous solutions. Conductivities are usually in the semiconductor range (10^{-9} to $10^{2}\,\text{Scm}^{-1}$). In general, the method of electrolysis affects to a great degree the electrical and physical properties of the polymer [18]. Polypyrrole is the best known of the conductive polymers. It does not require added dopants to be conductive.

Doping agents or dopants are either strong reducing agents or strong oxidizing agents. They may be neutral molecules and compounds or inorganic salts which can easily form ions, organic dopants and polymeric dopants. The nature of dopants plays an important role in the stability of conductive polymers. Conductivity of the polymers may be improved by the modification of the polymerization conditions. We prepared conductive polymers (in our case, polypyrrole films) from pyrrol using KCl and sodium dodecylsulphate as dopants. The resulting polymeric films are of dark colours and have short conjugated π-electrons and low electrical conductivity. However, polymer – modified electrodes prepared by direct electrochemical polymerization of pyrrole molecules at the electrode surface can provide stable wide redox couples. These couples usually exhibited a different formal potential compared to that of monomers and they were very effective to act as mediators of different compounds (organic, inorganic, biomolecules).

For such polymer-modified electrodes, not only would the proton-donor ability be decreased compared with the monomers, but they also could be used as a matrix for the immobilization of amphiphilic anions, inorganic anions (common low molecular weight), enzymes at the electrode surface simultaneously.

In Figures 2 and 3 are presented the cyclic voltammograms of PPY(Cl^-)/Pt and PPY(DS)/Pt modified electrodes in aqueous solution of 0.1 M KCl.

The comparison between the behaviour of the two types of electrodes shows some major differences. The PPY(DS)/Pt modified electrode shows much sharper peaks and lower peak separation than PPY(Cl^-)/Pt modified electrode, this indicating that the first type of the electrode is characterized by faster and more reversible electrochemical redox processes. The higher electroactivity of the PPY(DS)/Pt modified electrode, as expected based on the fact that the large amphiphilic DS (dodecylsulphate anion) surfactant anion is not easily released after its incorporation into the polymer film. This

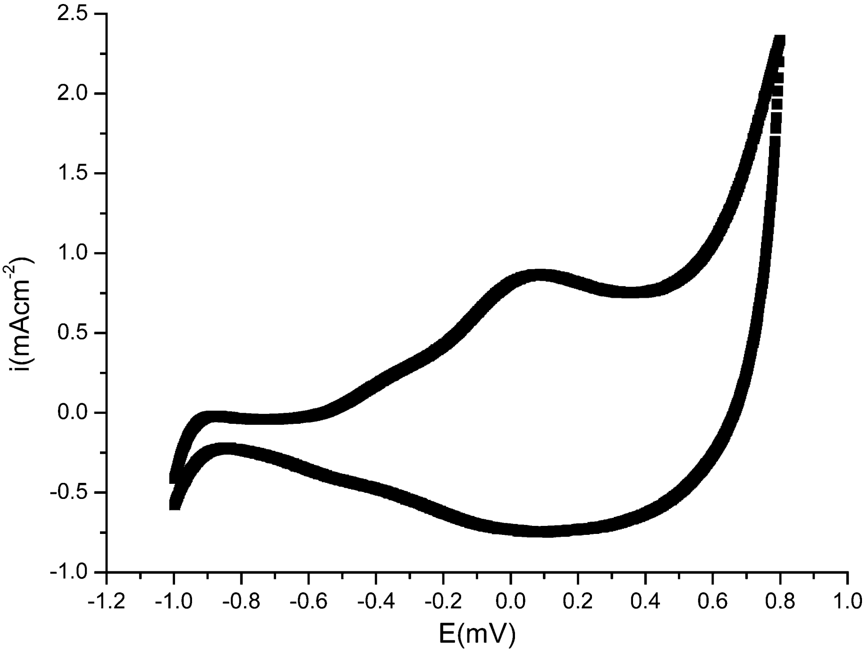


FIGURE 2 The cyclic voltammogram (5th cycle) of PPY(Cl^-)/Pt modified electrode in aqueous solution of 0.1 M KCl at 25°C and the potential scan rate of 10 mVs^{-1}.

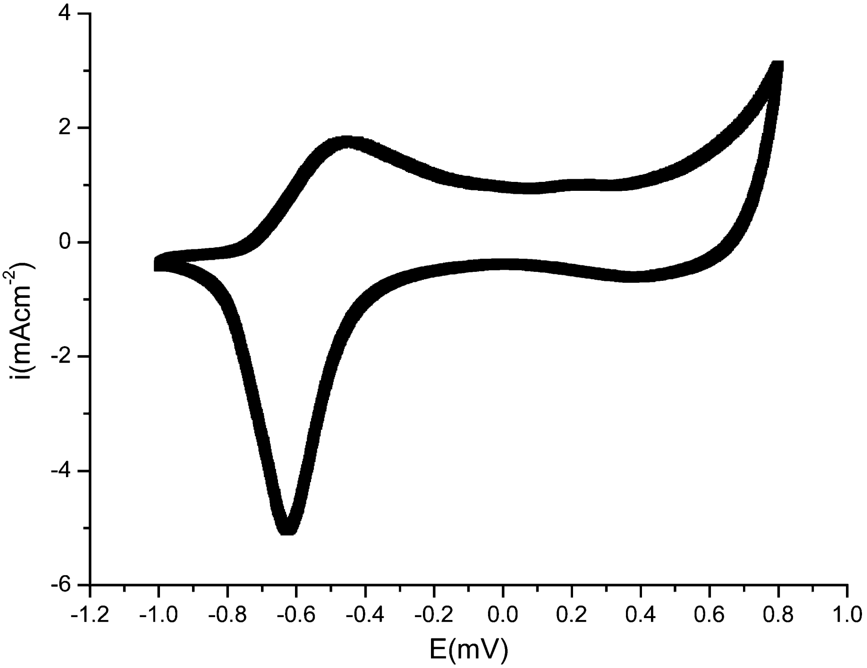


FIGURE 3 The cyclic voltammograms of PPY(DS)/Pt modified electrode in aqueous solution of 0.1 M KCl at 25°C and the potential scan rate of 10 mVs^{-1}.

fact is partially assigned to its size and partially to the compatibility of the polar end with the charged matrix and of the nonpolar end with the neutral (reduced) matrix. The same behaviour was also observed in the case of the following modified electrodes: PPY(Cl^-)/Ti and PPY(DS)/Ti in the same conditions.

In Figures 4 and 5 are shown the cyclic voltammograms of these modified electrodes in aqueous solution of 0.1 M KCl at room temperature and the potential scan rate of 10 mVs^{-1}.

We can see that, the two types of modified electrodes behave similar to the first modified electrode, which was presented above. The PPY(DS)/Ti modified electrodes show sharper peaks and lower peak separation than the PPY(Cl^-)/Ti modified electrodes and this fact was explained in the first case (presented above). Consequently, also in these electrodes, as in general family of the large-anion functionalized PPY films, the charge compensation during reduction is likely to be due to cation uptake rather than anion release. Since cations generally diffuse faster than anions, the kinetics and the reversibility of the overall redox process of the PPY(DS)/Ti modified electrodes are

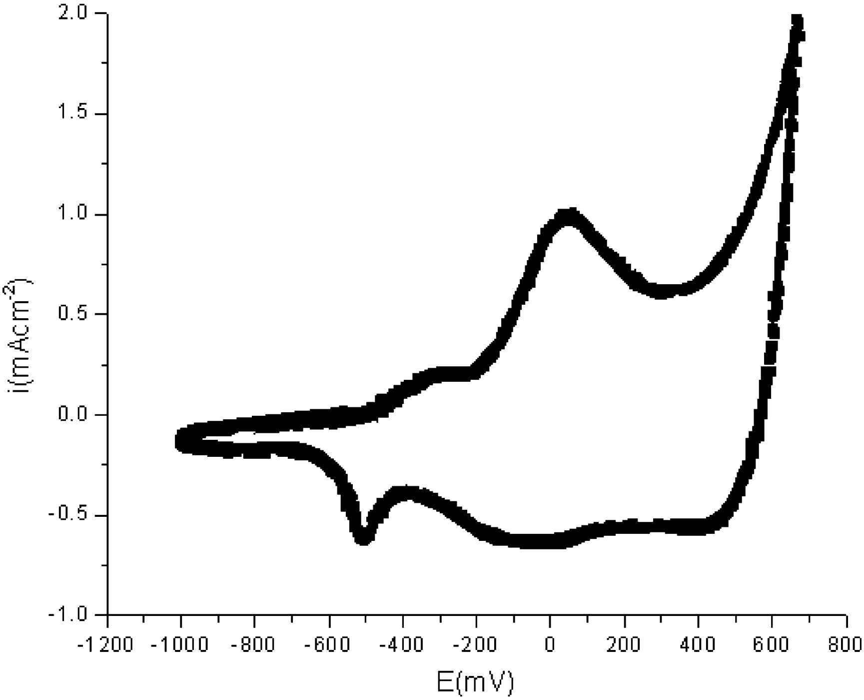


FIGURE 4 The cyclic voltammograms of PPY(Cl^-)/Ti modified electrode in aqueous solution of 0.1 M KCl at 25°C and the potential scan rate of 10 mVs^{-1}.

enhanced with respect to those of the more conventional PPY(Cl^-)/Ti modified electrodes. This fact is confirmed by the Table 1, where the voltammetric data of the two types of modified electrodes are compared and summarized.

Analyzing the cyclic voltammograms of the modified electrodes presented previously [PPY(Cl^-)/Pt; PPY(DS)/Pt; PPY(Cl^-)/Ti; PPY(DS)/Ti] and also the data in the Table 1 we can conclude that in the case of platinum substrate the redox processes which take place during the potential scan are much more active than those which proceed on the modified electrodes with titanium substrate.

This behaviour can be explained by the fact that titanium is a valve metal and its corrosion resistance is due to the formation of a TiO_2 passive film. The oxide is an n type semiconductor, with a band gap of 3.1 eV. When the working electrode of titanium is anodic polarized, it is easily oxidized giving a non-conducting dielectric film (TiO_2) on the electrode surface. The TiO_2 film acts as an excellent barrier,

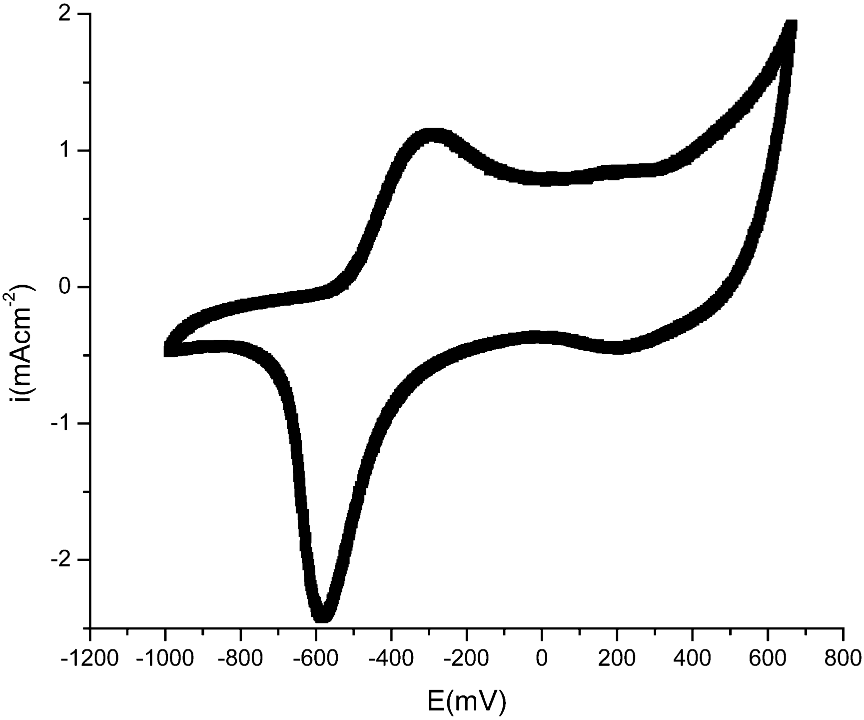


FIGURE 5 The cyclic voltammograms of PPY(DS)/Ti modified electrode in aqueous solution of 0.1 M KCl at 25°C and the potential scan rate of 10 mVs^{-1}.

inhibiting an electron transfer and thus inhibiting the redox processes which take place on it. Our experimental results are in accordance with these characteristics of TiO_2 passive film. Since the PPY polymeric film was galvanostatically electrodeposited on titanium substrate it results that the PPY doped film is formed simultaneously with TiO_2 passive film. This fact explains why the PPY(Cl$^-$)/Ti and PPY(DS)/Ti modified electrodes have an electroactivity much lower than the PPY(Cl$^-$)/Pt and PPY(DS)/Pt modified electrodes. From Figures 2–5 and Table 1, one can see that the current peaks and the average current densities of the anodic and cathodic processes are much lower in the case of the polypyrrole doped films electrodeposited on the titanium substrate.

Further we studied the influence of the number of cycles on the electrochemical responses of previous modified electrodes. In Figures 6 and 7 are presented the cyclic voltammograms of the PPY(Cl$^-$)Ti and PPY(DS)/Ti modified electrodes at different cycles.

TABLE 1 The Kinetic Parameters of [PPY(Cl^-)/Pt; PPY(DS)/Pt; PPY(Cl^-)/Ti; PPY(DS)/Ti Films for Different Cycles in Aqueous Solution of 0.1 M KCl (The Cycling Electrolyte)

Substrate	Dopant anion	Cycle number	ipa_1 ($mA \cdot cm^{-2}$)	Epa_1 (mV)	ipa_2 ($mA \cdot cm^{-2}$)	Epa_2 (mV)	ipc_1 ($mA \cdot cm^{-2}$)	Epc_1 (mV)	ipc_2 ($mA \cdot cm^{-2}$)	Epc_2 (mV)	ΔEp_1 (mV)	ΔEp_2 (mV)
Pt	Cl^-	1	1.42	0	–	–	0.92	–100	–	–	100	–
	Cl^-	5	0.87	95	–	–	0.73	110	–	–	15	–
	Cl^-	10	0.63	330	–	–	0.55	130	–	–	200	–
	DS	1	1.83	–440	1.26	400	2.64	–650	–	–	210	–
	DS	5	1.75	–440	–	–	5.04	–620	0.58	400	180	–
	DS	10	1.64	–420	–	–	1.67	–510	0.88	215	90	–
Ti	Cl^-	1	–	–	1.51	270	0.57	–460	0.74	–100	–	320
	Cl^-	5	0.19	–316	0.98	46	0.62	–500	0.63	–45	184	91
	Cl^-	10	0.44	–210	0.68	0	0.48	–360	0.53	50	150	50
	Cl^-	15	0.41	–100	0.48	150	0.4	–285	0.45	136	185	14
	Cl^-	20	0.36	–40	0.42	230	0.35	–190	0.35	0	150	230
	DS	1	1.33	–245	1.16	360	1.58	–570	0.7	–116	325	476
	DS	5	1.12	–286	0.93	356	2.41	–580	0.44	177	294	179
	DS	10	1.01	–147	–	–	1.07	–433	–	–	286	–
	DS	15	0.93	46	–	–	0.86	–425	–	–	471	–
	DS	20	0.83	80	–	–	0.79	–400	–	–	480	–

ipa, ipc = the anodic and cathodic peaks current densities.
Epa, Epc = the potentials corresponding to anodic and cathodic peaks.

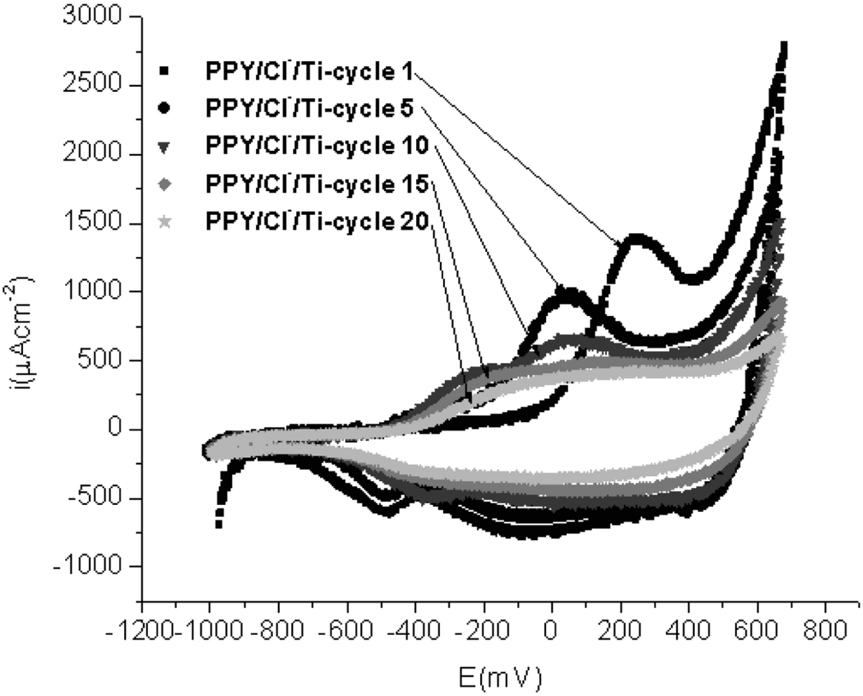


FIGURE 6 The cyclic voltammograms of PPY(Cl^-)/Ti films for different cycles in aqueous solution of 0.1 M KCl (the cycling electrolyte).

We can see that the increasing the number of cycles results in all cases to the decrease of the peak surfaces. After a number of cycles the anodic and the cathodic peaks disappear, the anodic and the cathodic current densities decrease very much and the shapes of the cyclic voltammograms are changing. The loss of polypyrrole conducting properties is probably due to the nucleophilic attack by water or anions leading to the opening of rings in the polymer backbone [8,11]. It was noticed that deactivation increased with the number of cycles and with potential. A possible explanation could be that at higher potentials a higher ratio of polypyrrole exists in the oxidized state, which is positively charged and thus attracts anions leading to nucleophilic attacks. The slowest deactivation was found for an electrode disconnected from the potentiostat.

Also the nature of the anions plays an important role in the properties of the PPY films. Repetitive cycling of the previous modified electrodes (see cyclic voltammograms from Figs. 6 and 7) showed that the

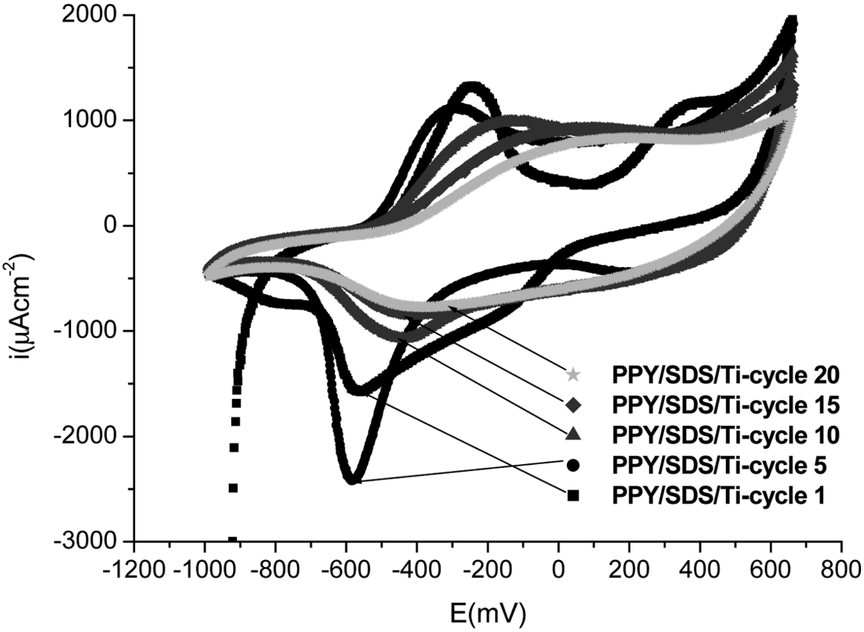


FIGURE 7 The cyclic voltammograms of PPY(DS)/Ti films for different cycles in aqueous solution of 0.1 M KCl (the cycling electrolyte).

PPY(DS)/Ti modified electrode has a higher stability and electroactivity than the PPY(Cl^-)/Ti modified electrode. In the same time, the deactivation of the first electrode is much lower for the same number of cycles.

Further, we studied the influence of dopant concentration on the electrochemical responses of the doped polymer/titanium substrate. Figures 8 and 9 show the cyclic voltammograms of PPY(Cl^-)/Ti and PPY(DS)/Ti modified electrodes obtained in synthesis solutions with different concentrations of dopant (potassium chloride and sodium dodecylsulphate).

The kinetics parameters determined from the cyclic voltammograms are given in Table 2.

From analysis of the Figures 8 and 9 and from Table 2, one can see that the increasing the dopant concentrations resulted in all cases to the increase of the height anodic and the cathodic peaks and also to the increase of the anodic and the cathodic currents. The increase of the dopant concentrations led to the better electroactivity of the modified electrodes and, consequently, to better electrochemical responses.

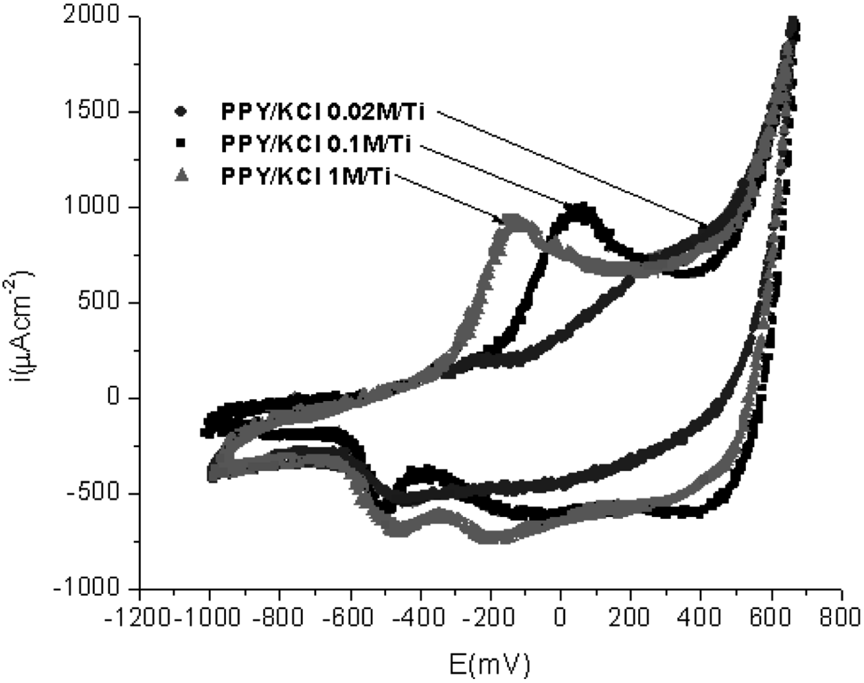


FIGURE 8 The cyclic voltammograms of PPY(Cl^-)/Ti films for different dopant anion concentrations in aqueous solution of 0.1 M KCl (the cycling electrolyte).

The electrochemical impedance spectroscopy (EIS) was used to investigate the behaviour of the PPY(Cl^-)/Ti and PPY(DS)/Ti modified electrodes.

One of the most important applications of EIS is the evaluation of corrosion by polymer coatings. Figure 10 gives the impedance spectra in Bode coordinates for PPY(Cl^-)/Ti modified electrode after obtaining at a potential of 0 V in aqueous 0.1 M KCl solution and the range frequencies of 10^{-2}–10^5 Hz. In Figure 11 is presented Nyquist diagram for the same modified electrode in similar conditions.

Here a single semicircle for charge transfer process and a diffusion tail at low frequency region are present. The semicircle of charge transfer process is severely depressed and the slope of diffusion tail is less than 45 degrees. These could result from the porous polymer film formed on the metal surface. The diffusion impedance element suggests that the electrochemical processes might be controlled by active species diffusing to the metal surface or corrosion products diffusing away from the metal surface through the polymer film.

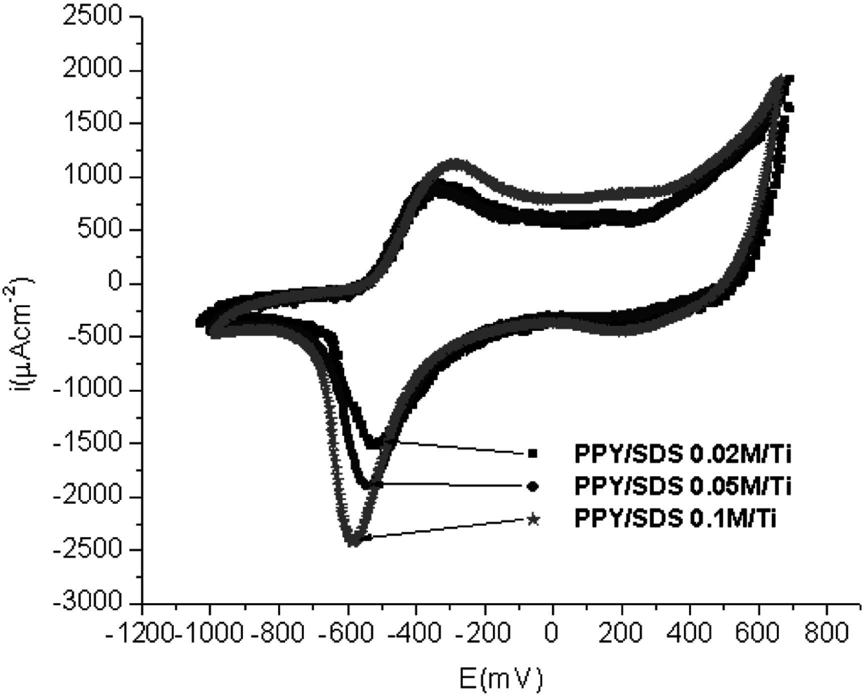


FIGURE 9 The cyclic voltammograms of PPY(DS)/Ti films for different dopant anion concentrations in aqueous solution of 0.1 M KCl (the cycling electrolyte).

Impedance spectra may be interpreted either with reference to detailed physical models or through equivalent circuits representing the different processes involved in the description of the system with discrete electric elements. In the present work the Randles equivalent circuit was used, modified by inclusion of distributed elements to take into account the finite spatial extension of the system under study, as well as inhomogeneities of the conductive medium. The latter manifests in impedance spectra as depressed semicircles, with their origin located below the real axis, Warburg slopes lower than unity and inclination (phase shift less than 90) of the low-frequency impedance. The equivalent circuit used for the interpretation of the data is shown in Figure 12.

Diffusion is represented by a Warburg element and the non-homogenous nature of the electrode material was represented by a constant phase element (CPE) with impedance given by:

TABLE 2 The Kinetic Parameters of [PPY(Cl^-)/Pt; PPY(DS)/Pt; PPY(Cl^-)/Ti; PPY(DS)/Ti Films for Different Dopant Anion Concentrations in Aqueous Solution of 0.1 M KCl (The Cycling Electrolyte)

Dopant anion	Cycle number	Concentration molL^{-1}	ipa$_1$ (mA · cm^{-2})	Epa$_1$ (mV)	ipa$_2$ (mA · cm^{-2})	Epa$_2$ (mV)	ipc$_1$ (mA · cm^{-2})	Epc$_1$ (mV)	ipc$_2$ (mA · cm^{-2})	Epc$_2$ (mV)	ΔEp$_1$ (mV)	ΔEp$_2$ (mV)
Cl^-	1	0.02	–	–	0.66	227	0.68	–455	–	–	–	–
Cl^-	1	0.1	–	–	1.51	270	0.57	–460	0.74	– 100	–	320
Cl^-	1	1	1.4	–22	–	–	0.82	–246	–	–	224	–
Cl^-	5	0.02	0.18	–270	0.67	260	0.52	–410	0.46	20	140	240
Cl^-	5	0.1	0.19	–316	0.98	46	0.62	–500	0.63	–45	184	91
Cl^-	5	1	0.97	–140	0.74	240	0.69	–430	0.72	–50	290	290
Cl^-	10	0.02	0.3	–200	0.62	186	0.46	–415	0.44	–5	215	191
Cl^-	10	0.1	0.44	–210	0.68	0	0.48	–360	0.53	50	150	50
Cl^-	10	1	0.8	–160	0.71	220	0.62	–350	0.6	–20	190	240
Cl^-	15	0.02	0.35	–90	0.53	260	0.38	–330	0.33	34	240	226
Cl^-	15	0.1	0.41	–100	0.48	150	0.4	–285	0.45	136	185	14
Cl^-	20	0.02	0.28	0	–	–	0.3	–240	–	–	240	–
Cl^-	20	0.1	0.36	–40	0.42	230	0.35	–190	0.35	0	150	230
DS	1	0.02	1.02	–150	0.98	0	1.5	–500	–	–	350	–
DS	1	0.1	1.33	–245	1.16	360	1.58	–570	0.7	–116	325	476
DS	5	0.02	0.91	–314	0.92	420	1.6	–510	0.34	225	196	195
DS	5	0.1	1.12	–286	0.93	356	2.41	–580	0.44	177	294	179
DS	10	0.02	0.78	–236	0.77	410	0.8	–386	0.41	156	150	254
DS	10	0.1	1.01	–147	–	–	1.07	–433	–	–	286	–
DS	15	0.02	0.63	–140	0.90	545	0.65	–250	0.33	347	110	198
DS	15	0.1	0.93	46	–	–	0.86	–425	–	–	471	–
DS	20	0.02	0.56	–90	0.7	500	0.55	–380	0.31	270	290	230

ipa, ipc = the anodic and cathodic peaks current densities.
Epa, Epc = the potentials corresponding to anodic and cathodic peaks.

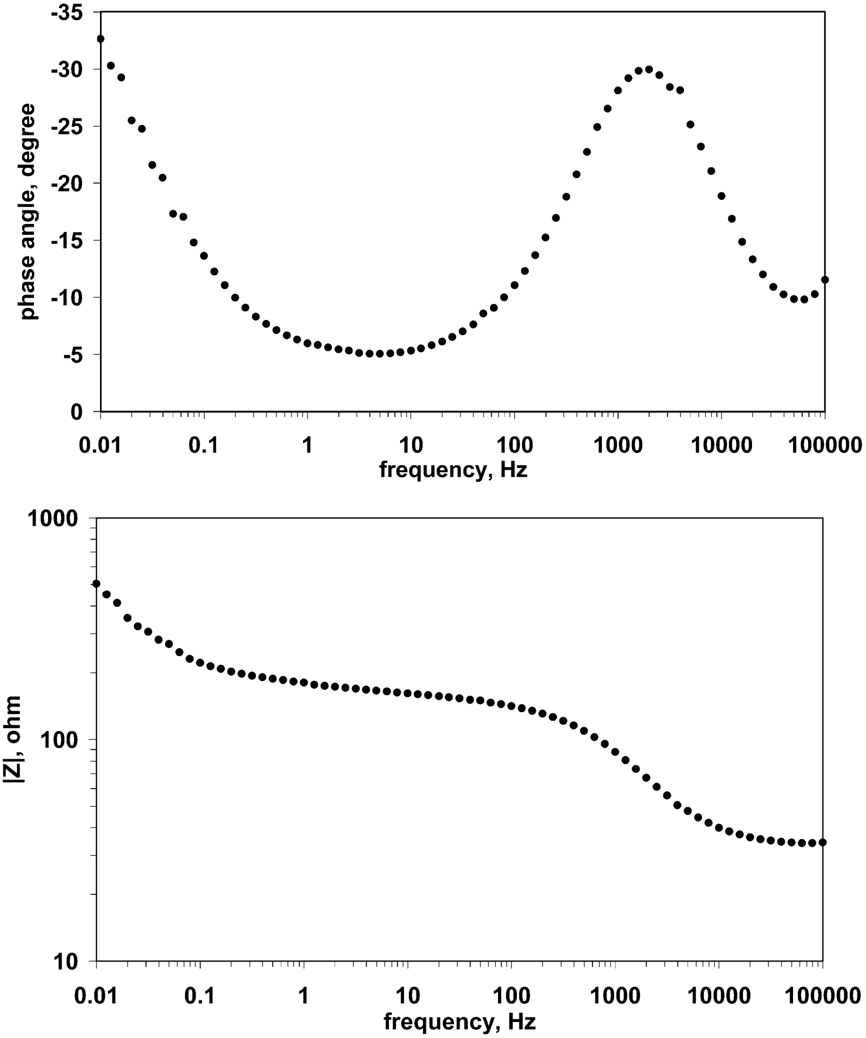


FIGURE 10 The impedance spectra in Bode coordinates for PPY(Cl^-)/Ti modified electrode after obtaining at a potential of 0 V in aqueous 0.1 M KCl solution and the range frequencies of 10^{-2}–10^5 Hz.

$Z_{CPE} = (1/\sigma)(j\omega)^{-\varphi}$, where σ and φ are positive constants. A CPE describes a capacitor when $\varphi = 1$, in which case $\sigma = C$ and tends to a resistor as $\varphi \rightarrow 0$.

A similar behaviour we obtained for modified electrodes PPY(DS)/Ti at different potentials, after 10 cycles and in 0.1 M KCl

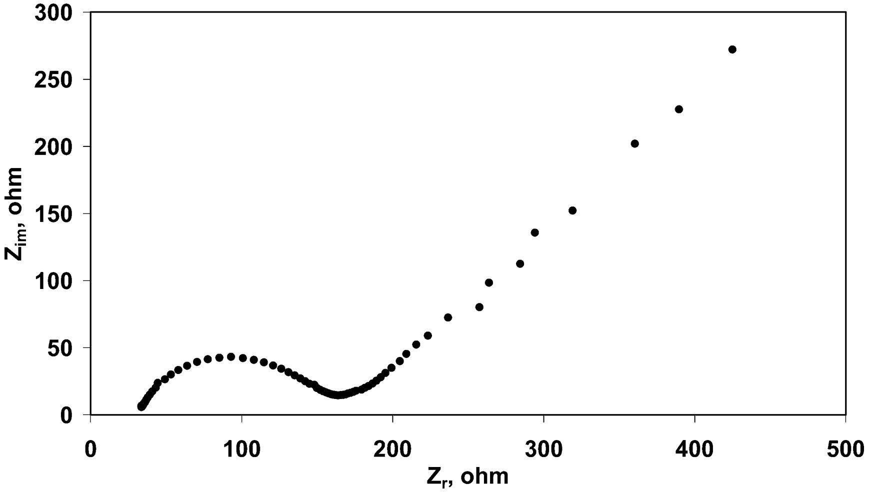


FIGURE 11 The impedance spectra in Nyquist coordinates for PPY(Cl^-)/Ti modified electrode after obtaining at a potential of 0 V in aqueous 0.1 M KCl solution and the range frequencies of 10^{-2}–10^5 Hz.

aqueous solution. In Figures 13 and 14 are given Nyquist diagrams (Fig. 13) and Bode diagrams (Fig. 14) for PPY(DS)/Ti modified electrode in different conditions.

Comparative analysis of these diagrams has shown a similar behaviour with PPY(Cl^-)/Ti modified electrode and hence, impedance spectra may be interpreted with the same equivalent circuit (see Fig. 12). In Table 3 are given the values of circuit elements obtained fitting the experimental data to the equivalent circuit proposed. From this table one can see that the charge transfer resistance has higher alues in the reduced state (–500 mV–) which decrease for increasing the oxidized states (0 mV). Moreover, comparative analysis of the impedance data have shown that, the modified PPY(DS)/Ti electrode has a lower charge transfer resistance than PPY(Cl^-)/Ti modified electrode at the same potential. The polymer films doped with large anions

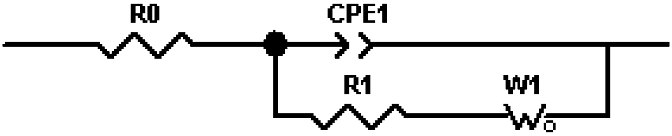


FIGURE 12 The equivalent circuit used for the interpretation of the data.

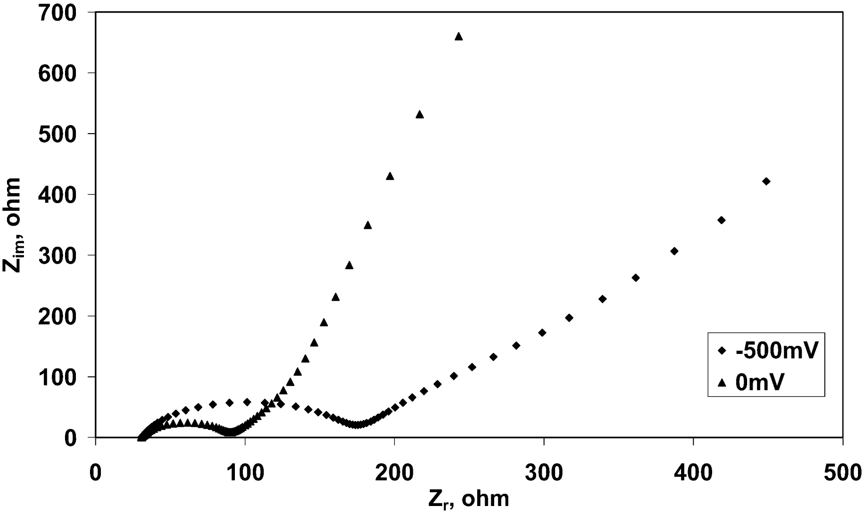


FIGURE 13 The impedance spectra in Nyquist coordinates for PPY(DS)/Ti modified electrode after obtaining at potentials of 0 V and –0.5 V in aqueous 0.1 M KCl solution and the range frequencies of 10^{-2}–10^{5} Hz.

(amphiphilic anions) have a higher electroactivity and the redox processes are more reversible and take place with higher rate.

CONCLUSIONS

The results obtained in this work suggest that a polypyrrole film should be kept disconnected from the potentiostat or at least at a reducing potential if deactivation is to be minimised.

The results indicate that the mechanism of the redox process is complex and may be governed by the diffusion of the anions and cations of the electrolyte.

The cyclic voltammograms of the PPY film synthesized in solutions having different concentrations of SDS and KCl indicate that the dopant concentration plays a relevant role in the electrochemical response of the doped polypyrrole films and respectively of the PPY(Cl^-)/Ti and PPY(DS)/Ti modified electrodes.

The increase of the dopant concentrations resulted in all cases to better electrochemical responses and hence, to activation of redox processes.

The PPY(DS)/Pt modified electrode shows much sharper peaks and lower peak separation than PPY(Cl^-)/Pt modified electrode, this

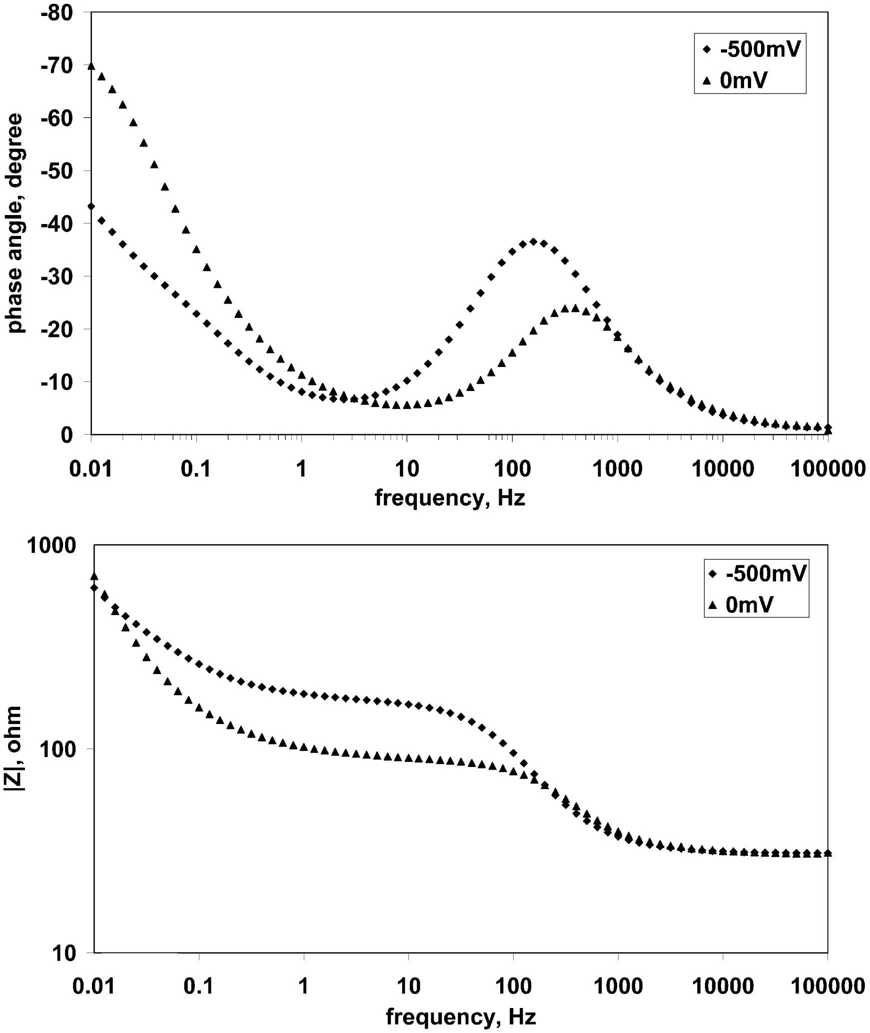


FIGURE 14 The impedance spectra in Bode coordinates for PPY(DS)/Ti modified electrode after obtaining at potentials of 0 V and –0.5 V in aqueous 0.1 M KCl solution and the range frequencies of 10^{-2}–10^{5} Hz.

indicating that the first type of the electrode is characterized by faster and more reversible electrochemical redox processes.

The PPY(DS)/Ti modified electrodes show sharper peaks and lower peak separation than the PPY(Cl^{-})/Ti modified electrodes.

TABLE 3 Values of Circuit Elements Obtained Fitting the Experimental Data for PPY(Cl^-)/Ti; PPY(DS)/Ti Films to the Proposed Equivalent Circuit

Dopant anion	Circuit element E, mV	R0, Ω	R1, Ω	CPE1, Ω^{-1} s^{φ}	W1-R, Ω	W1-T, s^{φ}	X
Cl^-	0	31.2	115	$1.36 \cdot 10^{-5}$, $\varphi = 0.77$	63.62	0.89, $\varphi = 0.28$	0.004
DS	–500	30.5	124.6	$2.94 \cdot 10^{-5}$, $\varphi = 0.90$	44.6	0.31, $\varphi = 0.31$	0.0015
DS	0	31.1	61.12	$2.47 \cdot 10^{-5}$, $\varphi = 0.90$	51.8	0.96, $\varphi = 0.42$	0.0021
	Maximum error	0.5%	1.2%	7.6%, respectively 1%	5.6%	6.4%, respectively 0.6%	

In the case of platinum substrate the redox processes which take place during the potential scan are much more active than those which proceed on the modified electrodes with titanium substrate.

Comparative analysis of the impedance data have shown that the modified PPY(DS)/Ti electrode has a lower charge transfer resistance than PPY(Cl^-)/Ti modified electrode at the same potential because the polymer films doped with large anions (amphiphilic anions) have a higher electroactivity and the redox processes are more reversible and occurs with higher rate.

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