ELECTROCHEMICAL CHARACTERIZATION OF POLYPYRROLE MODIFIED ELECTRODES DOPED WITH LARGE ORGANIC ANIONS

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Polypyrrole modified platinum electrodes doped with of 2,7- Bis (2-sulfophenylazo)-1,8 dihydroxy-3, 6-naphthalenedisulfonic acid, tetrasodium salt and with KCl were prepared by electrochemical oxidation of pyrrole in the presence of these species using the galvanostatic method. Homogenous, regular adhesive and thick polypyrrole films doped with these large organic anions on Pt could be electrosynthesized in these conditions. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical properties of electrodes. The results indicate that the large organic anions favor redox processes, which are faster and more reversible than those associated to usual polypyrrole electrodes. In fact, while in polypyrrole 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 polypyrrole films prepared in the presence of large organic anions, the charge compensation appears to involve incorporation of cations since the large anions are not easily released from polymer matrix. The frequency response of polypyrrole films was studied in the presence of Cl− in the potential region of interest for the study of the insulator – conductor transition. The impedance spectra have been interpreted using the Randles equivalent circuit modified with a constant phase element (CPE), using nonlinear least squares fitting of the parameters of the circuit to experimental data. The results show that the distribution of relaxation times widnes with oxidation of the polymer, indicating the presence of domains with different electrical properties, consistent with hopping of charge carriers in the oxidized state. It is also shown that in Cl− solution and at moderate potentials, overoxidation leads to irreversible degradation of the electroactive properties, affecting the electronic conductivity and diffusion coefficients of ionic species within the film.

INTRODUCTION

In the last decades somewhat surprisingly a new class of polymers possessing high electronic conductivity (electronically conducting polymers) in partially oxidized (or less frequently reduced) state has been discovered. Electrochemistry has played a significant role in the preparation and characterization of these novel materials. Electrochemical techniques are especially suitable for controlled synthesis of these compounds and for tuning of a well-defined oxidation state.

The preparation, characterization and application of electrochemically active, electronically conducting polymeric systems are still in the forefront of research activity in electrochemistry. There are at least two major reasons for this intense interest. First is the curiosity of researchers that focuses on understanding the behaviour of these systems, in particular on the mechanism of charge transfer and charge transport processes occurring in the course of redox reactions of conducting polymeric materials. Second is the wide range of promising applications in the field of energy storage, electrocatalysis, organic electrochemistry, bioelectrochemistry, photoelectrochemistry, electroanalysis, sensors, electrochromic displays, electronic devices, microsystem technologies and corrosion protection.

It is well known that the electrical and mechanical properties of electronically conducting polymers strongly depend upon the synthesis conditions, for example, the type of substrate,
electropolymerization potential, current density and in particular the nature and the concentration of the synthesis solution.

Generally, adherent pyrrole films are deposited on inert anodes like Pt, Au, glassy carbon or stainless steel. Several authors have reported that, the synthesis of polypyrrole (PPY) in the presence of large amphiphilic surfactant anions results in the formation of films with improved mechanical and electrochemical properties.1-14

This fact has been recently confirmed by showing that PPY films obtained by galvanostatic polymerization in aqueous electrolytes using the large amphiphilic SDS have high electrical conductivity, enhanced electroactivity, polystyrene – like mechanical properties and sharp electrochromic contrast.5-9

In this work we extended the study by describing the electrochemical properties of PPY films deposited from aqueous solution containing 2,7- Bis(2-sulfophenylazo)-1,8 dihydroxy-3,6-naphthalenedisulfonic acid tetrasodium salt (Sulfonazo III) and KCl as “doping” electrolytes. The study has been focused on the evaluation of the effects of electrosynthesis conditions (i.e. organic compound concentration and current density) on the electroresponse of the PPY (polypyrrole) films as well as on the role of the electrolyte nature on the doping process and on the interface properties of the polymer electrode. This investigation has been carried out by cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

**EXPERIMENTAL**

A one compartment electrochemical cell with three electrodes configuration: a platinum wire as a working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). Cyclic voltammetry experiments were performed with a PAR Programmable Potentiostat (EGG 273) interfaced to a PC-AT microcomputer. The polypyrrole (PPY) films were galvanostatically deposited onto platinum substrates at 1.0 mAcm$^{-2}$ and a total charge density of 360mCcm$^{-2}$. The synthesis electrolyte was a solution of pyrrole (freshly distilled, 0.05M) and 0.05M organic compound (sulfonazo III) in bidistilled water. A constant current density of 2mAcm$^{-2}$ was employed yielding after a sharp maximum a constant voltage near 0.78V versus reference electrode at room temperature. Polypyrrole thickness was controlled selecting electropolymerization time. Different films were grown with thickness ranging from ≈ 40nm (20mC.cm$^{-2}$) up to ≈ 1700nm (850mC.cm$^{-2}$), assuming that thickness is proportional to electopolimerization charge (approximately 2µm C cm$^{-2}$).15 Then films were removed from the synthesis solution and washed in distilled water, dried in air and transferred to an aqueous solution of 0.1 M KCl in which electrochemical experiments were performed. The electrochemical properties of polypyrrole films electrosynthesized from aqueous solutions containing sulfonazo III as doping electrolytes were studied by cyclic voltammetry using 0.1 M KCl aqueous solutions as cycling solution. The cyclic voltammograms were obtained by potential sweep rate of 10mV s$^{-1}$. Impedance experiments were performed with a Transfer Function Analyzer connected to a Programmable Potentiostat (EGG 273) and interfaced to a PC-AT microcomputer. Impedance measurements were carried out between $10^2$ and $10^5$ Hz. At this frequency range a reasonable signal to noise ratio was attained.

Impedance spectroscopy measurements were done using Frequency Analyzer (Solartron 1260) coupled to a potentiostat type Solartron 1287. The impedance diagrams were interpreted on the basis of equivalent circuit using the Z.view software (version 2.4a Scribner Associates inc. Southern Pines, USA).

**RESULTS AND DISCUSSION**

As we shown above, electrochemical synthesis of conductive polymers allows preparation of layers of polymers of the desired thickness, shapes and dimensions, generally not possible by chemical methods.16 Thus, for more promising conductive polymers have been those made 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. In general, the method of electrolysis affects to a great degree the electrical and physical properties of the polymer. However, it is widely accepted that the electropolymerization of pyrrole involves radical coupling with complex reaction kinetics at the electrode surface involving formation of an oxidized polymer.2 The electrochemical preparation of this polymer is often described as occurring to:

$$\text{H}_2\text{N}^{-} \xrightarrow{-e} \text{H}_2\text{N}^{+}$$

$$\text{H}_2\text{N}^{+} + \text{H}_2\text{N}^{-} \xrightarrow{-e} \text{H}_2\text{N}^{+}$$
The electropolymerization reaction appears to involve two electrons per molecule of pyrrole (PY) monomer and its proceeds through a radical coupling mechanism. Its chemical structure is written as:

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

Keeping the polypyrrole (PPY) film in a massive oxidation state leads to an insulating film with no electroactivity.17 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 dimer is oxidized and the correlative radical cation interacts with a monomeric radical cation to give a trimer and so on.

This mechanism needs two electron by monomeric unit incorporated in the polymer, according to the following schema:

\[
(PPY)_n \longrightarrow (PPY)_n^+ + e^- \\
PY \longrightarrow PY^+ + e^- \\
(PPY)_n^+ + PY^+ \xrightarrow{2e^-} (PPY)_{n+1}
\]

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–, sulfonazo III anions on platinum substrate in aqueous solutions of different concentrations. Reproducible behaviour of the polymer films used in this study was verified in all cases recording cyclic voltammograms of the freshly prepared films from synthesis solutions.

In figure 1 is presented the cyclic voltammogram of PPY (Cl–)/Pt modified electrode in 0.1 M KCl aqueous solution at 25°C and potential scan rate of 10mVs⁻¹.

From this figure, one can see that at the anodic potential scan a current peak (oxidation peak) is obtained, while at the reverse potential scan a cathodic current peak is obtained. The broad peaks observed in the voltammogram suggest a complex redox process for PPY (Cl–)/Pt 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 charge of polypyrrole backbone and another part, which remains positive, charged. We consider that, the oxidation and the reduction peaks correspond to the following equations:

\[ PPY^+ / A^- + e^- \xrightarrow{\text{reduction}} PPY / A^- \quad \text{insertion of the cation } M^+ \text{ from the electrolyte for min g the "adduct" } \xrightarrow{\text{release of } M^+} PPY^+ / A^- / M^+ \]

\[ PPY / A^- / M^+ - e^- \xrightarrow{\text{oxidation}} PPY^+ / A^- / M^+ \]

One or the other step may be favoured depending on the diffusion coefficient of the ionic species in the PPY film. The shape of the voltammetric curve also corroborates this redox mechanism.

Further, the cyclic voltamograms of PPY films synthesized in solutions having different amounts of sulfonazo III \([2,7-\text{Bis (2-sulfophenylazo)-1,8 dihydroxy-3, 6-naphthalenedisulfonic acid, tetrasodium salt}]\) are shown in Figure 2.

The shape of the voltamograms consistently change and this indicates that the nature and the concentration of the organic compound play a very relevant role in the electrochemical responses of the PPY/sulfonazo III films. In this case, at the anodic potential sweep, two oxidation peaks are obtained while at the reverse potential sweep, respectively on the cathodic branch of the polarization curve two cathodic reduction peaks were obtained.

The comparison between the behaviour of the two types of the modified electrodes (PPY/Cl-)/Pt and PPY (anion sulfonazo III/Pt) shows major differences. The PPY (sulfonazo III)/Pt modified electrode shows two anodic and cathodic peaks which are much sharper and have a lower separation peak than PPY (Cl-)/Pt modified electrode. This fact indicates that, the first type of the modified electrode is characterized by faster and more reversible electrochemical redox processes. The higher electroactivity of the PPY (sulfonazo III)/Pt modified electrode, as expected based on the fact that the large organic anion (in

Fig. 1 – The cyclic voltammograms of PPY/Cl-/Pt modified electrode in aqueous solution of 0.1 M KCl at 25°C and the potential scan rate of 10mVs⁻¹.
our case, sulfonazo III anion) is not easily released after its incorporation into the polymer film. This fact is partially assigned to its size and partially to the compatibility of the polar end with the charged matrix and of the un polar end with the neutral (reduced) matrix. Similar behaviour was observed by Shimidzu when studying PPY doped with polyelectrolytes.18

The reduction process produces the neutral polymer chain, however, the presence of the remaining Sulfonazo III anion leads to the insertion of the cation in order to equilibrate the charge. In this way, we can presume that, in the higher oxidation step the anions from cycling solution can participate to the complex redox process. This indicates that, the mechanism of redox process may involve both the cation and the anion of the electrolyte. Taking into account these considerations, we can presume that, the oxidation and the reduction peaks correspond to the following equations:

\[
PPY^+ / A^-_{SZ} \rightarrow PPY / A^-_{SZ}
\]

Where \( A^-_{SZ} \) = the Sulfonazo III anion

This equation explains the first couple redox, the following equation is related to the second couple redox thus: in this reduced state PPY/A\(^-\)\(_{SZ}\) takes place insertion of the cation M\(^+\) (in our case K\(^+\)) from the electrolyte forming the following adduct: PPY/A\(^-\)\(_{SZ}\)/M\(^+\) and then it follows the oxidation and reduction in the second step:

\[
PPY / A^-_{SZ} / M^+ \rightarrow PPY^+ / A^-_{SZ} / M^+ / X^-\]

One or other step may be favored depending on this diffusion coefficient of the ionic species in the PPY film. The shape of the voltammetric curve also corroborates this mechanism redox.

Analyzing the cyclic voltammograms of the modified electrodes presented in figures 1-2 and also the data in the table 1 we can conclude that in the case of PPY/A\(^-\)\(_{SZ}\)/Pt modified electrode, the redox processes which take place during the potential scan are much more active than those which proceed on the PPY/Cl/Pt modified electrode.

Fig. 2 – The cyclic voltammograms of PPY/A\(^-\)\(_{SZ}\)/Pt modified electrode for different cycles in aqueous solution of 0.1 M KCl (the cycling electrolyte).
Further, we studied the influence of the number of cycles on the electrochemical responses of previous modified electrodes. In figure 2 are shown the cyclic voltammograms of PPY/A-\textsubscript{sz}/Pt modified electrode at different cycles and in tables 1 and 2 are presented all the values of the kinetics parameters which were determined from cyclic voltammograms. From analysis of these data and cyclic voltammograms one can see that the increasing the number of cycles results in all cases to the decrease of the peak surface. 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.\textsuperscript{19-20} 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 figure 2 and the values of kinetics parameters from table 1 and 2) showed that, the PPY/A-\textsubscript{sz}/Pt modified electrode has a higher stability and electroactivity than the PPY/Cl-/Pt 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/platinum substrate. Figure 3 shows the cyclic voltammograms of PPY/A-\textsubscript{sz}/Pt modified electrode obtained in synthesis solutions with different concentrations of dopant 2,7- Bis (2-sulfophenylazo)-1,8 dihydroxy-3, 6-naphthalenedisulfonic acid, tetrasodium salt. From analysis of this figure, one can see that the increasing the dopant concentrations resulted in all the cases to the increase of the anodic and cathodic peaks and also to the increase of the anodic and the cathodic currents. Hence, the increase of the dopant concentrations led to the better electroactivity of the modified electrodes and, consequently, to better electrochemical responses.

The electrochemical impedance spectroscopy (EIS) was used to investigate the behaviour of the PPY/Cl-/Pt and PPY/A-\textsubscript{sz}/Pt modified electrodes.
Polypyrrrole modified electrodes

One of the most important applications of EIS is the evaluation of the corrosion by polymer coatings. Figures 4, 5 and 6 give the impedance spectra for PPY/Cl-/Pt modified electrode after obtained at potentials of the 0V and –0.1V in 0.1M KCl aqueous solution at the range frequencies of $10^2$-$10^5$ Hz. From figure 4, which presents the Nyquist diagram, one can see a single semicircle for charge transfer process and a diffusion tail at low frequency region. 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 from the metal surface diffusing away through the polymer film. 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 later 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 7.

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Fig. 5 – Bode diagrams of the PPY/Cl-/Pt modified electrode in aqueous 0.1M KCl solutions at two potentials and on the range frequencies of $10^{-2}$-$10^5$ Hz.

Fig. 6 – Bode diagrams of the PPY/Cl-/Pt modified electrode in aqueous 0.1M KCl solutions at two potentials and on the range frequencies of $10^{-2}$-$10^5$ Hz.
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: \[ Z_{CPE} = \frac{1}{\delta (j\omega)^\phi} \] where \( \delta \) and \( \phi \) are positive constants. A CPE describes a capacitor when \( \phi = 1 \), in which case \( \delta = C \) and tends to a resistor as \( \phi \rightarrow 0 \).

A similar behaviour we obtained for PPY/Az/Pt modified electrode after obtained at different potentials and in 0.1 M KCl aqueous solution. In figures 8, 9 and 10 are given Nyquist diagrams (see figure 8) and Bode diagrams (see figures 9 and 10) for PPY/Az/Pt modified electrode in different conditions.

![Equivalent Circuit](image1)

**Fig. 7 –** The equivalent circuit used for the interpretation of the data.

![Nyquist Diagrams](image2)

**Fig. 8 –** The Nyquist diagrams of the PPY/Az/Pt modified electrode after obtained in aqueous 0.1M KCl solutions, at different potentials and a frequencies range of \( 10^{-2}-10^5 \) Hz.

![Bode Diagrams](image3)

**Fig. 9 –** Bode diagrams of the PPY/Az/Pt modified electrode in aqueous 0.1M KCl solutions at three potentials and on the range frequencies of \( 10^{-2}-10^3 \) Hz.
Comparative analysis of these diagrams has shown a similar behaviour with PPY/Cl-/Pt modified electrode and hence, impedance spectra may be interpreted with the same equivalent circuit (see figure 7). 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 values in the reduced state (-500mV). Moreover, comparative analysis of the impedance data have shown that, the modified electrode PPY/A⁻₅/⁻/Pt electrode has a lower charge transfer resistance than PPY/Cl-/Pt modified electrode at the same potential. The polymer films doped with large anions have a higher electroactivity and the redox processes are more reversible and take place with higher rate.

<table>
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<th>Element of circuit</th>
<th>R₁, Ω</th>
<th>R₂, Ω</th>
<th>CPE₂, Ω⁻¹s⁰</th>
<th>R₁, Ω</th>
<th>CPE₁, Ω⁻¹s⁰</th>
<th>W₁-R, Ω</th>
<th>W₁-T, s⁰</th>
<th>χ</th>
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<tr>
<td>-100</td>
<td>17</td>
<td>9.7</td>
<td>5.55·10⁻³</td>
<td>66.1</td>
<td>2.14·10⁻⁴</td>
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<td>2.29</td>
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<tr>
<td>0</td>
<td>17</td>
<td>6.6</td>
<td>2.27·10⁻³</td>
<td>14.4</td>
<td>1.33·10⁻³</td>
<td>64.7</td>
<td>0.95</td>
<td>0.003</td>
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<td>9%</td>
<td>10%, 2%</td>
<td>7.5%</td>
<td>8%</td>
<td>7.6%</td>
<td></td>
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</table>

**CONCLUSIONS**

Polymerization of pyrrole in the presence of sulfonazo III improves both the mechanical properties associated with electrical conductivity and electroactivity of the polymer films;

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

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

The PPY/A⁻₅/Pt modified electrode shows much sharper peaks and lower peak separation than PPY/Cl-/Pt modified electrode, this indicating that the first type of electrode is characterized by faster and more reversible electrochemical redox processes;

Comparative analysis of the impedance data have shown that, the modified PPY/A⁻₅/Pt electrode has a lower charge transfer resistance than PPY/Cl-/Pt modified electrode at same potential because the polymer films doped with large anions (organic anions) have a higher electroactivity and the redox processes are more reversible and occur with higher rate.
REFERENCES