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Electrochemical impedance spectroscopy of poly{pyrrole-*trans*-[(RuCl$_2$(pmp)$_4$]} copolymer films deposited on platinum electrodes

Abstract The present study focuses on the electronic and electrochemical features of a copolymer electrochemically grown from pyrrole and *trans*-[RuCl$_2$(pmp)$_4$] monomers, where pmp = 3-(pyrrol-1-ylmethyl)pyridine. The results from electrochemical impedance spectroscopy analyses revealed the redox behavior of the poly{pyrrole-*trans*-[RuCl$_2$(pmp)$_4$]} compound as well as the non-homogeneous nature of the extremely thin polymeric layers. An equivalent circuit is proposed for an optimized film produced under the scope of the work.

Key words Electrochemical impedance spectroscopy · Pyrrole copolymers · Ruthenium complex · Equivalent circuit · Electropolymerization

Introduction

Electrochemical impedance spectroscopy (EIS) has become a strategic analytical method employed in basic [1–3] and applied electrochemistry [4], as well as in the general field of materials science [5]. EIS is especially useful when applied to characterize systems whose electrical behavior is a myriad of individual processes, each one with its own relative importance [6]. As a consequence of its capabilities, the technique has drawn the attention of researchers from various areas, engaged in understanding the process of data acquisition and interpretation [6–8]. Techniques based on electrochemical impedance have been used to evaluate the performance of coated metallic surfaces owing to the versatility of the method associated with the short time required to obtain a great deal of information [5]. The results obtained from EIS can be arranged in terms of equivalent circuits that associate the components of an electronic circuit, such as resistors and capacitors, with the physical elements relevant to a coated metallic surface, i.e., resistance to charge transport (ionic and electronic resistance), solution resistance, and double layer capacitance [9]. Polyvinylferrocene films have been evaluated by EIS in an attempt to assess the effect of charge transport on the diffusion and current density changes as a function of the oxidation state of the polymer [10]. Three regions could be distinguished in the complex impedance diagram as a function of the frequency and dominant mechanism. Whereas kinetics and diffusion ruled at high and intermediate frequencies, respectively, charge saturation could be established as the dominant mechanism at low frequencies. It could also be noticed that the oxidation state of the polymer significantly influenced the current density, as well as the charge transport and redox capacitance of the film. A number of studies have been carried out to elucidate the mechanisms involved in the electronic and ionic processes taking place on conductive polymeric films, thus exploring the wide potential application of these materials in the fabrication of batteries [11, 12]. Both polymeric and copolymeric films have been studied in order to establish a relationship between film properties and deposition parameters. This work discusses the results obtained from EIS upon the characterization of pyrrole and *trans*-[RuCl$_2$(pmp)$_4$] copolymeric films electrochemically deposited on platinum electrodes [13–15].

Experimental

Reagents and synthesis

Commercially available reagents and solvents of analytical grade were employed throughout this work. RuCl$_3$·3H$_2$O (Jonhson Matthey) and 3-(pyrrol-1-ylmethyl)pyridine (Aldrich) were used without further purification, while pyrrole was freshly distilled before used. The support electrolyte, made from LiClO$_4$ solution (0.1 mol dm^{-3}), was deaerated in Ar. The resulting solid was then dried under high vacuum for 24 h. The solvents employed in

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electronic spectroscopy were reagents with spectroscopic grades, and they were also used without further purification. The synthesis of the ruthenium blue solution and *trans*-[RuCl$_2$(pmp)$_4$]) were carried out employing a method described in the literature [15].

Electrochemical measurements

Cyclic voltammetry (CV) and potentiostatic electrodeposition (PE) were carried out at 23 ± 2 °C with a 273A Princeton Applied Research potentiostat/galvanostat, interfaced with a DOS-compatible computer using a National Instrument general purpose interface board. Instrumental control, data acquisition, and processing were performed by 270 EG & G Research Electrochemistry Software. EIS tests were carried out with Solartron SI 1255 and 273A equipment controlled by an electrochemical impedance 398 computer program. The cell and instrumentation setup have been described elsewhere [13].

EIS experiments

The tests were carried out at ambient temperature using a monomer-free LiClO$_4$ solution (0.1 mol dm^{-3}), deaerated in Ar. Data were gathered in the frequency range of 16×10^{-3}–100×10^3 Hz at a dc potential of 70 mV (vs. Ag/Ag$^+$). At this potential the oxidation of Ru(II) is favored, since this value is slightly higher than that of Ru(II)/Ru(III). The value of $E_{1/2}$ was estimated to be −80 mV by CV.

Copolymeric film

An electrochemical cell was formed by three electrodes: a Pt (0.115 cm^2) working electrode, a Pt auxiliary electrode, and a reference Ag/AgNO$_3$ electrode. The electrolytic solution of CH$_3$CN—CH$_2$Cl$_2$ (4 : 1) contained 0.1 mol dm^{-3} of tetrabutylammonium hexafluorophosphate and was previously deaerated with Ar. Films were produced at an optimized condition, according to literature reports [14], and were analyzed according to adherence to substrate, electrochemical and atmospheric stability, and an incorporated amount of Ru. The best films were produced by potentiostatic electropolymerization over 20 min and a 3.75 : 11 (pyrrole : Ru) ratio of monomers in solution. The thickness of the films was measured by scanning electron microscopy (SEM), and the optimized films were about 700 nm thick.

Results and discussions

EIS was employed in the study of the copolymeric films. Three regions could be distinguished in the complex impedance plot (Fig. 1a) of the platinum electrode modified by a poly{pyrrole-*trans*-[RuCl$_2$(pmp)$_4$]} film. A capacitive semicircle was present at high frequencies ($f > 16$ Hz). A detailed view of the semicircle can be seen in the magnification of the Nyquist diagram for that frequency range (Fig. 1b). At intermediate frequencies (10 Hz < f < 1000 mHz), the complex impedance plot revealed a linear behavior, whose slope changed as the frequency fell below 1000 mHz. Hunter et al. [10] pointed out that this is normal behavior for electroactive polymeric films. The electrochemical process including the oxidation and reduction of the polymeric film having an electroactive species can be expressed as:

poly{pyrrole + *trans*-[RuCl$_2$(pmp)$_4$]}

$$\rightleftharpoons \text{poly\{pyrrole} + trans\text{-[RuCl}_2\text{(pmp)}_4]\}^+ + e^- \qquad (1)$$
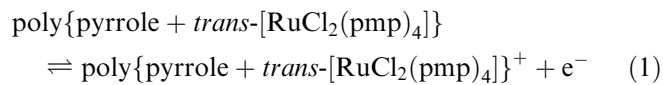
In the present study, the electroactive species is represented by the Ru(II)/Ru(III) couple.

From a macroscopic standpoint, the overall charge injection process involves electron insertion (or ejection) into the film through the metal/film interface. Charge neutrality is maintained by a concurrent insertion (or ejection) of a counter-ion (either Li$^+$ or ClO$_4^-$) through the film/solution interface. The presence of a local concentration gradient promoted the diffusion of the injected species. EIS allows individual analysis of the charge injection rate and diffusion rate. Hunter et al. [10] also point out that charge transfer is the dominant mechanism at high frequencies. Such a mechanism is represented by the presence of a semicircle, as the one observed here. At lower frequencies, charge diffusion becomes the dominant mechanism. Finally, the finite thickness of the film limits the diffusion path, leading to a redox capacitance which takes place as a result of charge saturation. Consequently, the phase angle shifts from $\pi/4$ to $\pi/2$, corresponding to a change from a diffusion-controlled region to a charge saturation region.

In summary, charge transfer across both metal/film and film/solution interfaces is the dominant mechanism at high frequencies, and is represented in the complex impedance diagram of poly{pyrrole-*trans*-(RuCl$_2$(pmp)$_4$} by a capacitive arc. The intersection of the semicircle with the real impedance axis at high frequencies represents the process of charge transfer and corresponds to the electrolyte resistance (R_s), whose value was measured to be 11.85 Ω cm^2. A similar value (12.05 Ω cm^2) was obtained for an uncoated platinum electrode. The diameter of the semicircle corresponds to the charge transfer resistance (R_{CT}), whose value was 28.04 Ω cm^2. The double layer capacitance, C_{DL}, can then be obtained from

$$C_{DL} = 1/2(\pi f R_{CT}) \qquad (2)$$

where f is frequency at the top of the semicircle, i.e., 100 Hz. The calculated value for C_{DL} was 57 μF/cm^2.

At intermediate frequencies the impedance diagram depicts a linear region with a phase angle slope close to $\pi/4$. Such a region is characteristic of an electron diffusion process and the flow of counter-ions. Figure 1a,b shows that region to be rather small, which should be a consequence of the film thickness. For extremely thin films, there can be an overlap of the kinetic-dominant with the charge-saturation regions, preventing a positive identification of the diffusional region [9, 10].

At very low frequencies the diagram also shows a linear region with a phase angle close to $\pi/2$ (Fig. 1a). Its slope is a finite number and may be an outcome of the wavy aspect of the film. It can be suggested that the distribution of the copolymeric layers on the metallic surface is uneven, which implies irregular thickness and

Fig. 1 a Nyquist diagram of poly{pyrrole-*trans*-[RuCl$_2$(pmp)$_4$]} films on Pt deposited in 0.1 mol dm^{-3} LiClO$_4$ solution. E_A = 70 mV vs. Ag/Ag$^+$. **b** Magnification of the high-frequencies range

(a)

(b)
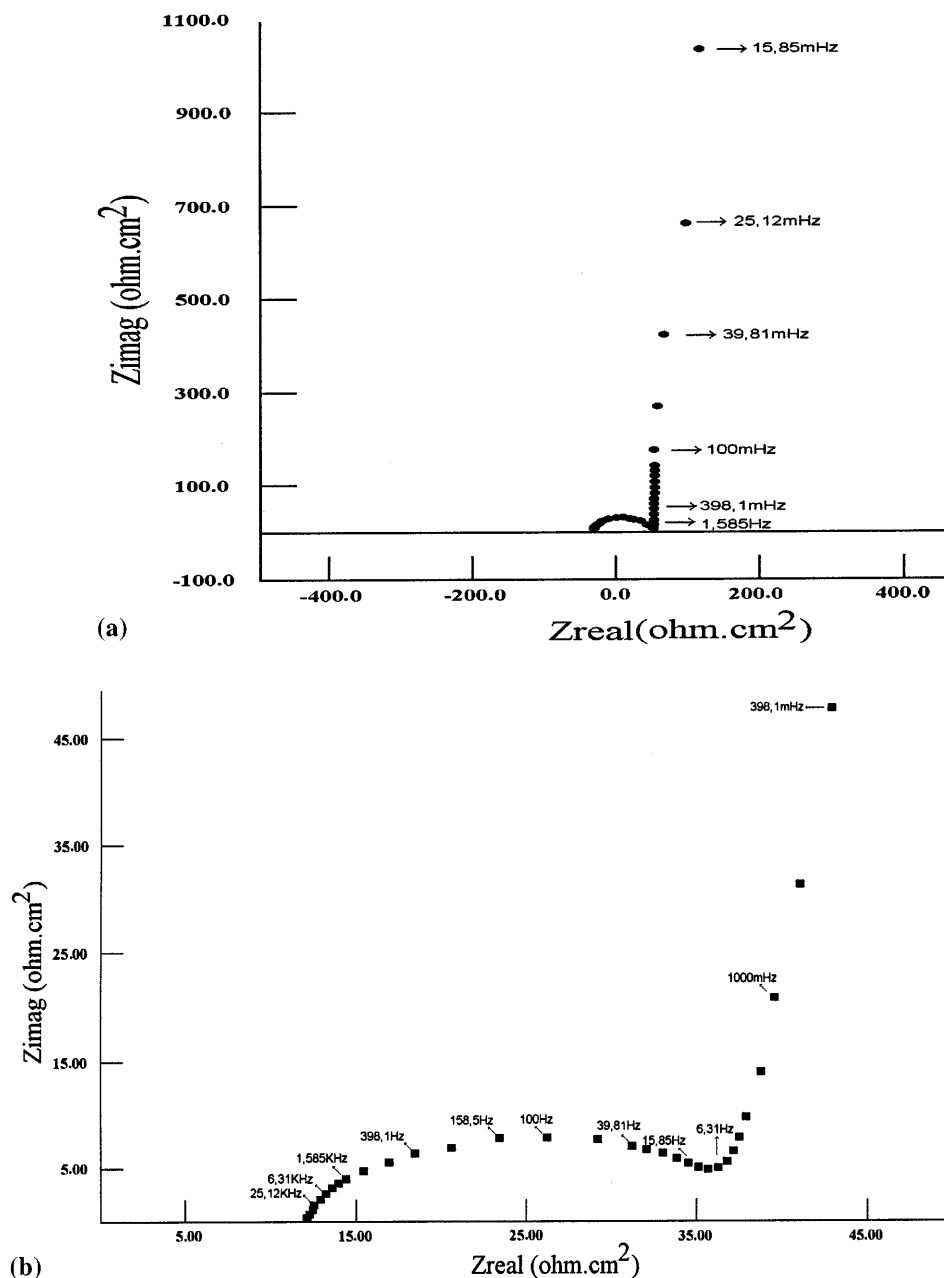
morphology in a multiphase polymeric structure. A further indication of this fact is found in the slightly flattened aspect of the high-frequency portion of the capacitive semicircle.

The linear region observed at low frequencies and characterized by charge saturation depicts a redox capacitance, C_L, which can be estimated from the $-Z_{im}$ versus w^{-1} plot. The plot is characterized by a straight line with a correlation coefficient equal to 1.00. The slope of the line corresponds to $dE/dQ = 1/C_L$, and the value of C_L (9.74×10^{-3} F/cm^2) obtained shows a good agreement with that found in the literature [10], measured at the vicinity of $E_{1/2}$ for polyvinylferrocene films.

The resistance of the polymer at low frequencies, R_L, is related to the redox capacitance of the film and the diffusion relaxation time, L^2/D, according to the following expression:

$$R_L = 1/C_L \times L^2/3D \qquad (3)$$

where L is the film thickness and D is the charge transport coefficient of the polymeric film. The value of R_L can be estimated from the difference between the intersection of the capacitive and charge transfer regions with the real axis of the Nyquist diagram (Fig. 1b), using $R_{TOTAL} = R_S + R_{CT} + R_L$. The thickness of the film, L, was estimated by SEM to be 700 nm. D was calculated from Eq. 3, resulting in 2.15×10^{-7} cm^2/s. Although such a value is apparently high as compared to literature data for polyvinylferrocene films (1.8×10^{-9} cm^2/s) [10], it should be pointed out that D is a
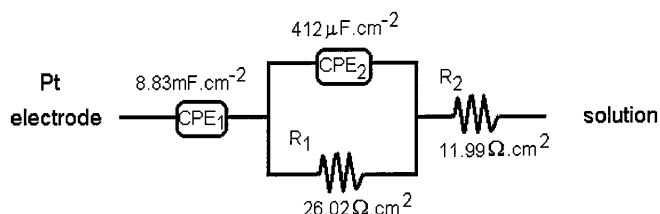
Fig. 2 Equivalent circuit proposed for poly{pyrrole-*trans*-[(RuCl$_2$(pmp)$_4$]} films

Table 1 Components of the simulated equivalent circuit

Impedance Component	Impedance	Difference (%)
CPE$_1$	8.83×10^{-3} F/cm^2	0.45
n	0.95	0.25
CPE$_2$	412 μF/cm^2	5.54
n	0.68	1.09
R$_1$	26.02 Ω cm^2	0.89
R$_2$	11.99 Ω cm^2	0.49

of the high-frequency region, showing a better visualization of the capacitive semicircle.

Two distinct situations can take place upon analyzing the components of an equivalent circuit representing a copolymeric film on an inert metal substrate [9]. The first possibility is that the high-frequency capacitive semicircle is associated with a resistive capacitive (RC) circuit. In this case, the resistive component (R) corresponds to the resistance to charge transfer across an interface, and the capacitive component (C) corresponds to the capacitance of the double electric layer at that interface. Alternatively, the capacitive semicircle can represent the metal/polymer interface and electron transfer across this interface, in addition to the double layer formed by the polymer and Pt substrate. Similarly, it can be attributed to the polymer/solution interface and the movement of counter-ions (either Li$^+$, during the reduction, or ClO$_4^-$,
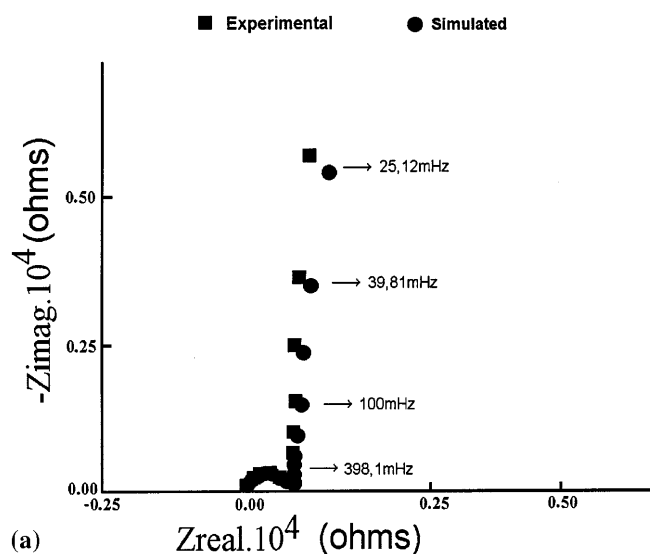
function of the oxidation state and thickness of the polymer.

Proposed equivalent circuit

The equivalent circuit 3.95 computer program was used to fit the experimental impedance data obtained for the copolymer produced at a ratio of 3.75 : 11 (pyrrole : Ru). The resulting circuit is shown in Fig. 2. Table 1 summarizes the values obtained for the different elements of the circuit, including the normalized area and the difference (in %) between experimental and fitted values. Figure 3a shows the Nyquist plot corresponding to the experimental values along with the simulated results. Figure 3b illustrates a magnification

Fig. 3 a Experimental and calculated Nyquist diagrams for poly{pyrrole-*trans*-[RuCl$_2$(pmp)$_4$]} films on Pt (in 0.1 mol dm^{-3} LiClO$_4$ solution. E_A = 70 mV vs. Ag/Ag$^+$). **b** Magnification of high-frequencies range
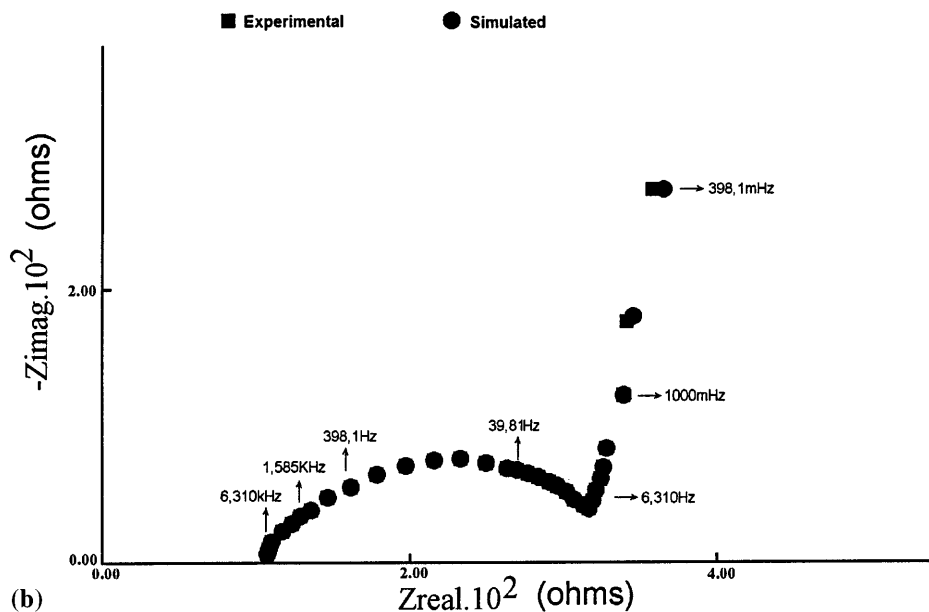
during the oxidation of the film) through the interface and the double layer formed from an alignment of the counter-ions in the solution in contact with the film. In either case, the components of the circuit are visualized at high frequencies, where the dominant mechanism is the kinetics of the process.

The polymeric film itself is characterized by a single transmission line consisting of a faradaic capacitance, corresponding to charge build up, and two parallel resistances (ionic and electronic) [8, 9]. The components of the circuit corresponding to the polymeric film require low and intermediate frequencies for better definition, as those ranges demand higher relaxation times. The last circuit component is the solution resistance. Thus, R_2 of the equivalent circuit corresponds to the solution resistance, R_S. The fitted value for R_S, 11.99 Ω cm^2, is in good agreement with the experimental one of 11.85 Ω cm^2 which, in its turn, is rather similar to the value obtained for an uncoated Pt electrode (12.05 Ω cm^2), prepared under similar conditions. The parallel (CPE$_2$ R_1) subcircuit is associated with the film/solution interface. R_S is in series with this circuit. The constant phase circuit, CPE, generates an impedance that can be expressed by:

$$Z_{CPE} = A(jw)^{-n} \tag{4}$$

where $0 < n < 1$, $j = (-1)^{1/2}$, and A is a frequency-related constant. The value of CPE calculated in this fashion takes into account the deviation observed from an ideal capacitor, such as the capacitive slope and phase angles lower than $-1°$ and $90°$, respectively.

If CPE is associated with a diffusion-controlled impedance (Warburg type), n tends to 0.5. Therefore, CPE$_2$ can be seen as a combination of the capacitance of the double electric layer in the film/solution interface and the Warburg impedance, which represents the diffusion of counter-ions from that interface and through the film. This hypothesis is confirmed by the value obtained for n (0.68). In addition, it is in good agreement with the flattening effect observed in the capacitive semicircle, and the presence of a rather limited diffusion region. Those two regions combine in the Nyquist plot (Figs. 1, 2) as a consequence of the small thickness of the film, which leads to rapid charge saturation. R_1 may be related to the resistance to charge transfer which, in this case, would correspond to the flow of counter-ions in the film/solution interface. The fitted value for R_1 (26.02 Ω cm^2) is rather similar to the experimental one (28.04 Ω cm^2).

Ren and Pickup [9] state that it is not obvious to imply whether the RC subcircuit obtained from the high-frequency diagram represents the metal/film or film/solution interface. A subcircuit may represent the interface of highest impedance or a combination of the two, depending on the resistance imposed to the transfer of electrons or counter-ions. For the compound addressed in this work, it can be suggested that since the film is reduced, upon the oxidation of Ru(II) to Ru(III), the higher impedance is associated with the flow of ClO$_4^-$

into the film instead of the flow of electrons to the substrate. At low frequencies the equivalent circuit is represented by CPE$_1$, which can be associated with a combination of the faradaic capacitance, C_L, and the resistance of the film, R_L, such as in a transmission line. This hypothesis accounts for the difference observed between the experimental value measured for C_L (9.74×10^{-3} F/cm^2) and the impedance generated by CPE$_1$ (8.83×10^{-3} F/cm^2), suggesting that C_L might be associated with other elements of the circuit as well. In any event, the value of n (0.95) reveals the high capacitive nature of CPE$_1$. In the transmission line representative of the polymer, R_L is a parallel association of the film ionic and electronic resistance. It has been contended [8, 9] that the electronic resistance is more suitable to represent the resistance of highly reduced films at low potentials. Conversely, the ionic resistance promotes a better fit of the resistance of oxidized films, since electrons are easily accepted. This study used a reduced film, which was oxidized during the experiment to achieve charge saturation. In that sense, it appears that an interpretation of the results in terms of a total resistance, R_L, is more appropriate than considering separate contributions of the terms of the parallel association $1/R_{ionic} + 1/R_{electronic}$.

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