

Short Communication

The Overoxidation of poly(3-hexylthiophene) (P3HT) Thin Film: CV and EIS measurements

Roger Gonçalves², Ernesto C. Pereira² and Luís F. Marchesi^{1,*}

¹ Universidade Tecnológica Federal do Paraná, Av. Monteiro Lobato s/n Km 04, CEP 84016-210, Ponta Grossa, PR, Brazil

² Departamento de Química, Universidade Federal de São Carlos, CP 676, CEP 13565-905, São Carlos, SP, Brazil

*E-mail: luismarchesi@utfpr.edu.br

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In this study the electrochemical degradation of electropolymerized poly (3-hexylthiophene) (P3HT) thin film electrode was carried out by mild overoxidation conditions. Cyclic voltammetry (CV) showed the material electrochemical response lost by change in the intensity and position of the oxidation/reduction peak. Electrochemical impedance spectroscopy (EIS) showed an increase in the charge-transfer resistance (R_{ct}) and a decrease of the low-frequency capacitance related to the load of the intercalated charge in the polymeric film. Such behavior was assigned to a hindering in the ionic intercalation/deintercalation process across the polymer/electrolyte interface, which was also corroborated by the dielectric relaxation time (τ_0) analysis.

Keywords: poly (3-hexylthiophene); degradation process; electrochemical impedance spectroscopy

1. INTRODUCTION

Conducting polymers (CP) are the subject of many scientific publications in the last years because of its interesting optical, magnetic and electrochemical properties, easy preparation and unique redox behavior [1-3]. In this way, conducting polymers can find several applications as in solar cells [4], supercapacitors [5], artificial muscles [6] and others [7,8]. Nevertheless, one of the main drawback regarding such material is its stability that somehow hinders the use of CP in day life. Thus, there are many papers in literature where the CP stability is the main subject to be understood [9-11].

Our group recently published some papers regarding the CP electrochemical degradation by overoxidation conditions assisted by electrochemical impedance spectroscopy (EIS) using transmission line model [12-14]. Such model was considered in those papers taking into account the complex porous nature presented by thicker CP films. The results showed that independent on the CP studied,

the loss of the electrochemical properties of the material was assigned by a change in the film morphology, where the well-established process of ion intercalation in the CP matrix in order to maintain the polymeric film neutrality was hindered. Otero *et al.* also presented the same interpretation using different techniques [15]. In addition, the EIS technique showed to be a powerful tool in elucidating the overoxidation process in CP by the evaluation of the complex-plane impedance diagram (Nyquist plots), where an increase in the charge-transfer resistance takes place as the degradation process occurs. This is possible because EIS is a frequency-resolved and steady-state technique, once the perturbation in voltage is small, which guarantee the response linearity, and is applied in stationary conditions. By this way, tuning the frequency of the voltage perturbation one can evaluate the relative contribution of all elements (resistance, capacitance and inductor) to the overall impedance. Nevertheless, evaluate parameters such as double-layer capacitance and the low-frequency capacitance that is related to the intercalated ions in the polymer matrix upon oxidation in order to maintain charge neutrality is not straightforward when the Nyquist plot is considered. Such additional parameters are commonly evaluated by fitting the experimental EIS data to a model, being the equivalent circuit model the most used [16-18]. Moreover, depending on the complexity of the film such as the porosity, an even more complete model should be considered [19,20].

The capacitance $C^*(\omega)$ can be represented in many ways as well as the impedance $Z^*(\omega)$. One way is to represent the imaginary component of the capacitance (C'') versus the real component (C'), obtaining the complex-plane capacitance diagram. In addition, is possible to plot separated both, C' and C'' , versus the logarithmic of the frequency. It was established in the literature that the C'' could be directly related to the charge-transfer kinetics at the polymer/electrolyte interface, which a characteristic time required for ion intercalation process can be evaluated [21]. Considering this idea, Kim *et al.* studied the influence of the temperature on the supercapacitor performance through the relaxation time constant (τ_0), which is derived from the imaginary capacitance. The authors found that as the temperature increased, the maximum frequency peak shifted toward higher values, in other words, decreasing the relaxation time, which means that the ion transport through the polymer/electrolyte interface became faster [22]. Recently, another application of the imaginary capacitance has been in elucidating the quantum capacitance [23,24].

In this way, considering the exposed above, the main goal of this paper is to study the electrochemical degradation process of electropolymerized poly(3-hexylthiophene) (P3HT) thin film electrode by mild overoxidation conditions performing electrochemical measurements. An equivalent circuit model and, for the first time in literature, the qualitative analysis of the complex-capacitance will be considered to better understand the effect of the overoxidation process of a conducting polymer.

2. MATERIALS AND METHODS

All reagents were analytical grade. The monomer 3-hexylthiophene (3HT) (Sigma-Aldrich) was used as received. The poly (3-hexylthiophene) (P3HT) electropolymerization was performed under potentiostatic conditions in a three-electrode cell, where a platinum disk ($A = 0.20 \text{ cm}^2$) was the work electrode, a homemade platinum electrode as auxiliary electrode [25] and a Ag/AgNO_3 0.1 M

electrode as the reference. However, at this work, all the potentials presented were referenced to SCE using the relation ($\text{SCE} = \text{Ag}/\text{AgNO}_3 - 116 \text{ mV}$). Monomer concentration was 0.1 mol L^{-1} and the support electrolyte was LiClO_4 0.1 mol L^{-1} in acetonitrile. Before electropolymerization, the solution was purged with nitrogen for 10 minutes. The electropolymerization itself was performed applying a voltage of 1.5 V vs SCE until the passed charge of 10 mC/cm^2 . After synthesis, the electrode was removed from solution, washed with acetonitrile and placed in a solution containing only the support electrolyte, where all the electrochemical characterizations were carried out. The electropolymerization and electrochemical characterizations were performed using a potentiostat AUTOLAB model PGSTAT302N equipped with GPES and FRA module. All the experiments were carried out at 298 K in a dry chamber under nitrogen atmosphere.

Cyclic voltammetry (CV) was carried out in a potential range from 0.40 V to 1.05 V in a sweep rate of 0.05 V s^{-1} . Electrochemical impedance spectroscopy (EIS) was carried out applying a *dc* potential of 0.90 V , an *ac* potential of 0.01 V in a frequency range from 10 kHz to 10 mHz . Before the EIS measurements, the electrode was polarized at the *dc* potential for 10 minutes in order to guarantee steady-state conditions. Electrochemical overoxidation was performed polarizing the work electrode at 1.05 V at distinct times from 0 to 80 minutes, where a CV and an EIS measurements was carried out at every 10 minutes. ZView software was used to fit the EIS data. The complex capacitance data were phasorially converted from the complex impedance data using the following relation $C^*(\omega) = 1/j\omega Z^*(\omega)$.

3. RESULTS AND DISCUSSION

Figure 1 presents the cyclic voltammetry response of the P3HT film as a function of the overoxidation process. It can be observed two well-defined process concerning the oxidation/reduction process of the P3HT centered at 0.90 V and 0.83 V , respectively. As the overoxidation process takes place, a loss in the electrochemical response of the P3HT film can be observed once the oxidation and reduction peak currents are being diminished. In this way, this behavior could be an indicative that the ionic intercalation/deintercalation process at the polymeric film is being hindered with the degradation process. In addition, both oxidation and reduction peak position was also affected by the degradation process, suffering a slight shift towards more positive and negative values, respectively [12]. Such shift in peaks position could be considered a change in the energy necessary to ionic intercalation, *i.e.*, with the polymeric film degradation this process is taking more energy to occur. The P3HT overoxidation process should follow the same mechanism proposed by Barsch *et. al.* [26], where the overoxidation process of polythiophene was carried out in acetonitrile in a presence of small amount of water. The authors proposed that under overoxidation conditions, the oxygen binds the sulfur atom at the thiophene ring, producing a SO_2 molecule with concomitant break of the aromaticity.

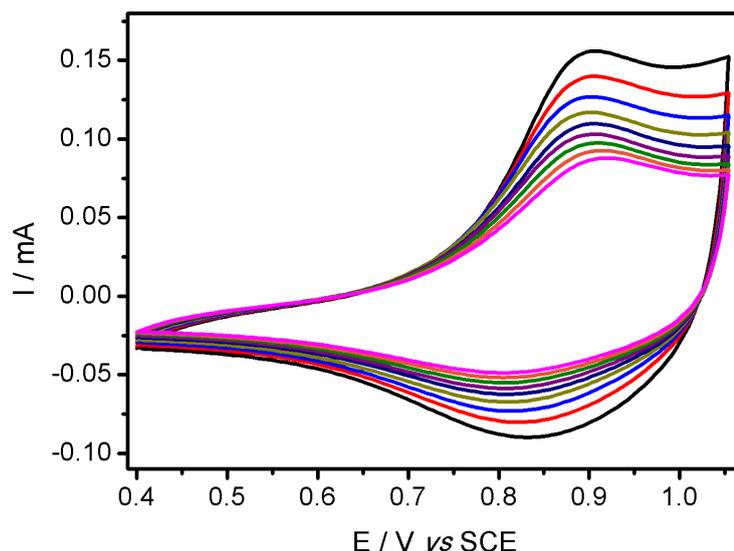


Figure 1. Cyclic voltammetry of the P3HT electrode performed in LiClO_4 0.1 mol L^{-1} at 0.05 V s^{-1} at different times of overoxidation; (–) 0 minutes, (–) 10 minutes, (–) 20 minutes, (–) 30 minutes, (–) 40 minutes, (–) 50 minutes, (–) 60 minutes, (–) 70 minutes and (–) 80 minutes.

Figure 2 shows the EIS response of the P3HT electrode film as a function of the degradation process. The typical EIS response for a thin film of conducting polymer can be assigned [13,14], a semicircle at higher frequencies, related to the faradaic process and a straight line at lower frequencies related to the intercalated charge storage in the polymeric film matrix in order to maintain charge neutrality [27]. It is possible to observe an increase in the semicircle radius as the degradation process occurs, which is related to an increase in the charge-transfer resistance as consequence of the decrease in the intercalation process efficiency. In addition, a change in the low-frequency straight-line length complied with a decrease in the low-frequency capacitance could be interpreted as a decrease in the load of the intercalated charge upon the polymeric film, which is in agreement with the cyclic voltammetry discussion. To evaluate the parameters related to the faradaic process (charge-transfer resistance and double-layer capacitance) and the low-frequency capacitance, the EIS data were fitted using the equivalent circuit model showed as inset in Figure 2.

Although it is established in the literature that polymeric films present a very typical porous morphology and, in this way, the transmission line is the most indicated model to fit these EIS data; no fingerprint of transmission line model at the EIS Nyquist plots was observed herein. Probably, such behavior was not observed because of the P3HT growing charge used in this work, that was by this way very low, which resulted in a very thin film where no potential drop across it was meaningful [28].

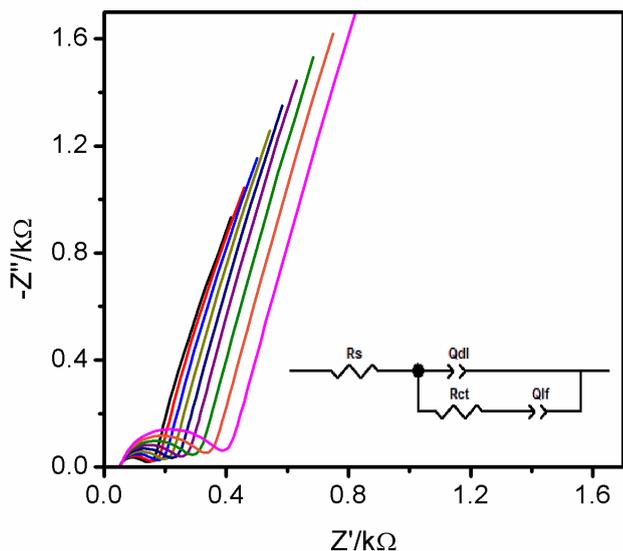


Figure 2. Nyquist diagram of the P3HT electrode performed at an *dc* potential of 0.90 V as a function of the degradation process. (–) 0 minutes, (–) 10 minutes, (–) 20 minutes, (–) 30 minutes, (–) 40 minutes, (–) 50 minutes, (–) 60 minutes, (–) 70 minutes and (–) 80 minutes.

The equivalent circuit is composed of a series resistance, (R_s), accounting for electrolyte and contacts contribution, a constant phase element (CPE) accounting for the double-layer capacitance (Q_{dl}), a charge-transfer resistance (R_{ct}), representing the interfacial faradaic process. An additional constant phase element (Q_{lf}) was used to describe the low-frequency response related to the amount of charge storage (intercalated) in the polymer matrix [16]. The non-ideality factor related to the constant phase element is taking into account by the n parameter that ranges from 0 to 1, when n assumes the unity value the constant phase element represents an ideal capacitor. These results are summarized in Table 1.

Table 1. Parameters values obtained from the EIS data fitting.

Degradation time/min	R_s/Ω	R_{ct}/Ω	$Q_{dl}/10^{-5} \cdot F s^{n-1}$	n_{dl}	$Q_{lf}/10^{-3} \cdot F s^{n-1}$	n_{lf}
0	46.33	107.51	1.93	0.75	1.53	0.83
10	47.35	120.35	1.54	0.77	1.37	0.83
20	48.47	137.66	1.22	0.80	1.25	0.83
30	49.65	157.58	0.97	0.82	1.15	0.83
40	50.73	180.72	0.82	0.84	1.07	0.83
50	51.74	209.92	0.72	0.86	1.00	0.84
60	52.53	245.74	0.65	0.87	0.95	0.84
70	53.56	287.49	0.59	0.88	0.89	0.84
80	54.44	341.67	0.55	0.88	0.85	0.84

From the parameters values showed in Table 1 it can be observed a well-established behavior of the CP overoxidation process [14]. The increase in the R_{ct} values indicates that the charge-transfer process at the polymer/electrolyte interface is being hindered, as previously discussed. Q_{dl} values decreases with de degradation process, which is related to a change in the P3HT film morphology, indicating a decrease in the polymer/electrolyte interface area, as also discussed elsewhere [12,29]. The n_{dl} parameter could be interpreted as a measurement of the film morphology homogeneity and the increase in such value represents that the morphology is getting more homogeneous. As also discussed, the Q_f parameter is related to the charge storage within the polymeric film and can be directly linked with the R_{ct} values. As the degradation process occurs, the charge-transfer process is being more hindered and the load of intercalated charge within the polymeric film is diminished. The n_{if} parameter can be interpreted as a measurement of the homogeneity of the intercalated charge distribution in the polymeric film [29]. Herein, as the n_{if} does not suffer from significant variation, one can assume that the distribution of the intercalated charge in the polymeric film is maintained at the same configuration with the degradation process. Such interpretation can be assumed regarding the mild overoxidation conditions used in this work.

The degradation process studied in this paper taking into account a thin film of P3HT follows the same behavior as the others thicker CP studied films [12,14], *i.e.*, independent on the film thickness, the degradation process occasioned by the overoxidation is directly related to a change in the polymer/electrolyte interface. This change acts in a way to difficult the charge-transfer process and consequently the charge intercalation upon the polymeric film. Considering this, in order to perform an additional discussion concerning the intercalation process, the complex capacitance analysis will be used to better analyze this process. Figure 3 presents the complex-plane capacitance diagram obtained from the complex-plane impedance diagram presented at Figure 2.

In the complex-plane capacitance diagram one can observe a semicircle that is dependent on the degradation process and is attributed to the intercalated charge in the polymer matrix. The decrease in the semicircle radius is related to a decrease in the low-frequency capacitance, it means, a decrease in the amount of intercalated charge, as discussed earlier. In this representation, no significant changes can be observed in the high frequency region even knowing that there is the double-layer capacitance under consideration. Such accomplishment is due to a large difference between the magnitude order founded for the double-layer capacitance and the low-frequency capacitance (Table 1). The real and imaginary part of the complex capacitance as a function of frequency are shown in Figure 4. The C' corresponds to the capacitive response at the P3HT film, *i.e.*, the double-layer capacitance at higher frequencies and the capacitance related to the intercalated charge in the polymeric film. In this way, a decrease in the low-frequency of C' indicates a decrease in the intercalated charge in the polymeric film matrix.

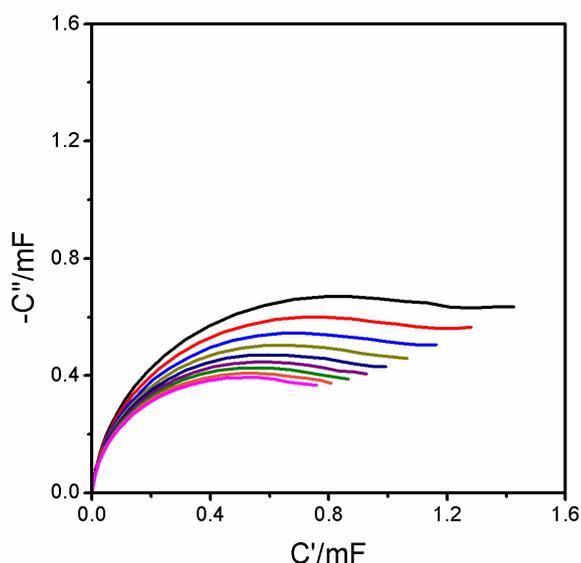


Figure 3. Complex-plane capacitance diagram of the P3HT electrode as a function of the degradation process. (—) 0 minute, (—) 10 minutes, (—) 20 minutes, (—) 30 minutes, (—) 40 minutes, (—) 50 minutes, (—) 60 minutes, (—) 70 minutes and (—) 80 minutes.

On the other hand, C'' versus logarithmic of frequency could be used to better understand the charge intercalation kinetics behavior upon degradation process (Figure 4B). It can be observed that the C'' plot goes through a maximum at a particular frequency (f_0) that represents the minimum time need to discharge all the energy from the polymeric film, called the dielectric relaxation time (τ_0), calculated using the following relation ($\tau_0 = 1/f_0$). As the degradation process takes place, the peak maximum frequency shifts toward lower values. The shift toward lower values indicates an increase in the τ_0 (from 2.16 s to 3.83 s for 0 and 80 minutes of overoxidation, respectively). Since the τ_0 is related to the discharge process in the polymeric film across the polymer/electrolyte film interface, the increase in such value could be related to the slow ion transport occasioned by the degradation process.

In order to compare, the overoxidation degradation process of polypyrrole (Ppy) was carried out using the same methodology studied elsewhere [14] and is showed in Figure 4C. It is important to note that the same changes presented for the P3HT degradation could be assigned, however, more pronounced. This difference could be attributed to a difference in how the film undergoes interfacial changes upon overoxidation conditions used in each study. At the Ppy degradation study, the overoxidation conditions lead to a more pronounced change, which was also reflected in a more pronounced change in the C'' plot. Nevertheless, at this point it is very important to mention that such representation plot directly relates the degradation process to the ionic intercalation kinetics, providing by this way a quantitative value (τ_0) without further treatment (equivalent circuit model). Moreover, such achievement is independent on the conducting polymer nature and the film thickness, which make such representation plot a powerful tool in elucidating the conducting polymers degradation process.

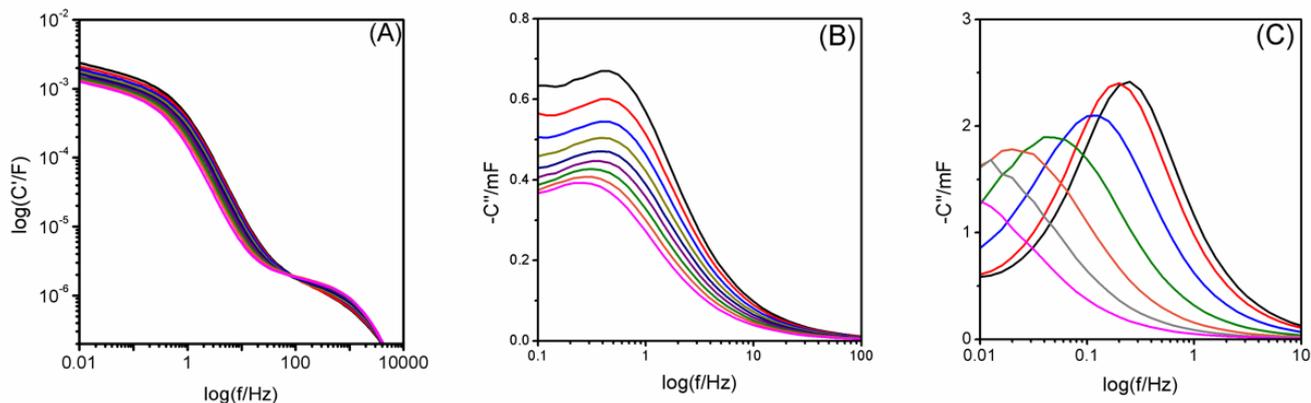


Figure 4. The real (C') and imaginary (C'') capacitance as a function of the frequency. (A) and (B) P3HT electrode; (—) 0 minutes, (—) 10 minutes, (—) 20 minutes, (—) 30 minutes, (—) 40 minutes, (—) 50 minutes, (—) 60 minutes, (—) 70 minutes and (—) 80 minutes. (C) Polypyrrole electrode; (—) 0 minute, (—) 10 minutes, (—) 20 minutes, (—) 30 minutes, (—) 40 minutes, (—) 50 minutes and (—) 60 minutes.

4. CONCLUSIONS

By the discussion made so far, the different representations of the electrochemical impedance spectroscopy (EIS) showed to be a powerful tool in order to evaluate the degradation process in the poly (3-hexylthiophene) thin film electrodes. Adjusting the EIS data to an equivalent circuit, it was possible to evaluate an increase in the charge-transfer resistance (R_{ct}) at the polymer/electrolyte interface and a decrease in the low-frequency capacitance that is related to the load of intercalated charge within the polymeric film in order to maintain charge neutrality. Such achievement corroborates the cyclic voltammogram, where a shift and a diminishment of the oxidation/reduction peak intensity was assigned to a hindering in the ionic intercalation process within the polymeric film. For the first time the dielectric relaxation time (τ_0) was evaluated from the complex-capacitance data in order to characterize the overoxidation process of a conducting polymer thin film and the increase of such value represented the slow kinetics of ionic transport across the polymeric film.

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