

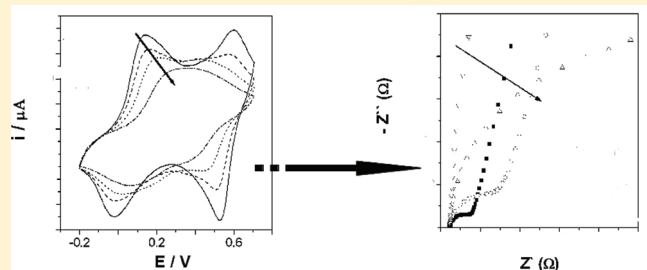
# Investigation of Electrochemical Degradation Process in Polyaniline/Polystyrene Sulfonated Self-Assembly Films by Impedance Spectroscopy

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**ABSTRACT:** In this study, the electrochemical degradation of polyaniline/polystyrene sulfonated (PANI/PSS) self-assembly films was investigated by an electrochemical impedance technique using transmission line models to fit the results. The experiments were performed by polarizing the working electrode at a fixed oxidative potential of 0.55 V. The results showed that changes in the electrochemical behavior of the oxidized PANI/PSS film occurred mainly in the polymer/solution interface by an increase in the charge transfer resistance.



## 1. INTRODUCTION

For many applications, the stability of conducting and electroactive polymers is of great importance. The limited stability of many conducting polymers has been discussed in many reports,<sup>1,2</sup> and the adequate control of the conducting polymer (CP) properties with a second polymeric material prepared by the self-assembly technique (SA) has been proposed for different applications.<sup>3–6</sup> The SA technique is widely used to prepare films due to its ease and low cost as well as the possibility of intercalating alternated layers of polyelectrolytes and CPs, allowing the modulation of the material characteristics,<sup>7–13</sup> moreover, increasing the electrochemical stability of the system.<sup>14</sup> Consequently, it is of interest for the development of sensors, once molecules assembled as alternated layers can have specific recognition sites,<sup>10,15–17</sup> or they can be used to build electrochemical devices considering the increase in the reduction/oxidation process efficiency due to the interaction between the layers.<sup>18,19</sup> To build a useful device, however, it is important to investigate their electrochemical properties, such as redox behavior and electrochemical stability.

One of the important issues regarding electrochemical devices is their stability as the number of redox cycles increases. In this sense, the main drawback in conducting polymer materials is that they undergo irreversible electrochemical degradation under anodic potentials and become an insulator after several redox cycles.<sup>20–22</sup> Considering this, electrochemical degradation represents an irreversible change that occurs upon anodic polarization, leading to an irreversible decrease in its redox activity and electronic conductivity. Such polarization is also called overoxidation.<sup>23</sup> In the case of PANI, several authors have investigated their electrochemical property changes as devices are aged by cycling between reduced and oxidized states,<sup>24–26</sup> where two pairs of anodic and cathodic peaks, corresponding to the leucoemeraldine/emeraldine

and emeraldine/permanganiline redox transitions of PANI, respectively,<sup>27–29</sup> can be easily seen.

Both the shape and the position of these peaks depend to some extent on many experimental variables, such as the film preparation conditions, the potential sweep rate, and the composition of the supporting electrolyte. Between these main pairs of peaks, small peaks can be seen that correspond to the degradation products formed during electrosynthesis of PANI film. The degradation products are usually identified as *p*-quinone/*p*-hydroquinone and *p*-quinoneimine/*p*-aminophenol redox couples.<sup>30–33</sup> By holding the working electrode for some time at a controlled potential in a supporting electrolyte, some changes in cyclic voltammetry (CV) traces are observed. Both anodic and cathodic parts of the two characteristic redox transitions diminish in height, indicating electrochemical degradation of the film.<sup>34</sup> Moreover, different techniques have been used to characterize the polymer degradation process,<sup>30,35–39</sup> with the aim of discerning an explanation for the degradation product formation.<sup>22,40</sup>

Mazeikiene and Malinauskas studied the kinetics of electropolymerized PANI layer deactivation in acid aqueous solution.<sup>41</sup> The authors observed that electrochemical degradation is strongly dependent on the most positive electrode potential applied to the system. They concluded that the mechanism of degradation is related to the electrochemical oxidative degradation of both polaronic and bipolaronic forms of polyaniline, albeit to a different extent. A fast degradation, observed at high electrode potentials, was attributed to the higher rate of degradation of the bipolaronic form, which is predominant at this potential region. At lower electrode potentials, the polaronic form of PANI dominates,

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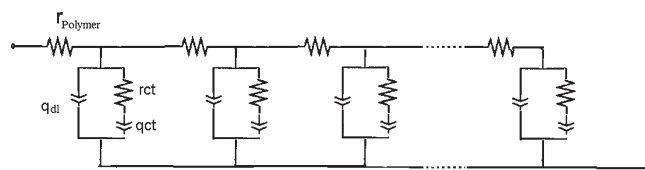
resulting in a slower degradation, probably due to the higher electrochemical stability of this form charge carrier.

The degradation of electrodeposited PANI films on optically transparent gold electrodes was studied by thin-layer bidimensional spectroelectrochemistry.<sup>38</sup> The authors have observed that, depending on the applied potential, three different degradation processes occur: (a) release of soluble compounds retained during electropolymerization, which is accompanied by a slight bathochromic shift of the PANI film absorption band; (b) breaking of polymer chains and the concomitant generation of soluble species, leading to a significant loss of polymer mass; and (c) finally, a deep transformation of PANI film, resulting in an unexpected electrochromic behavior, important morphological changes, and an intense decrease in the conducting properties of the polymer. In this sense, one could propose two different degradation possible mechanisms for a conductive polymer: electronic conductivity degradation with the bond breaking in the polymer chains and concomitant generation of soluble species, leading to a significant loss of polymer mass and appearance of C–OH and C=O functional groups in the polymer backbone as well as formation of CO<sub>2</sub> at sufficiently positive potentials;<sup>20</sup> and an electrochemical degradation, in which the change in the properties is related to an increase in the energy necessary for ion intercalation, as proposed by Palacios.<sup>38</sup>

Electrochemical impedance spectroscopy (EIS) has been highlighted as a technique that is suitable to study the interfacial process.<sup>42</sup> In most of the papers published, the results are analyzed using an electrical equivalent circuit.<sup>27,43–45</sup> However, modeling impedance data using an equivalent circuit is to assume that the material behaves as a flat or even rough surface. Although this approach is convenient for many electrodes, this is not the case of porous materials. An alternative to describe the obtained data is to analyze them using a transmission line model, which is used to investigate CPs<sup>46–54</sup> and oxide films.<sup>55–57</sup> This approach highlights the porous nature of these films and, that is, distributes the polymer/electrolyte interface within the electrode matrix.

In this paper, for example, the polymer resistance is distributed into infinitesimal elements ( $r_{\text{pol}}$ ), representing the potential drop in the polymer backbone, and the faradaic process, distributed into an infinitesimal charge transfer resistance ( $r_{\text{ct}}$ ) in parallel with the double-layer constant phase element ( $q_{\text{dl}}$ ) regarding the nonideal behavior of the double-layer capacitance, representing the potential drop in the polymer/solution interface (see Figure 1). Garcia-Belmonte and Bisquert<sup>48</sup> have offered a detailed description of this approach. The impedance measurements of the films were reported at different stages during oxidation, when varying the stationary applied potential. Rossberg et al.<sup>58</sup> studied polyaniline films on gold electrodes using a macrohomogeneous model in which all parameters are defined microscopically and the pore geometry is not restricted. The authors concluded that the porosity and the electronic and ionic conductivities are in parallel with the conducting polymer backbone, and the rate of the charge transfer process also increases as the oxidation degree of the polymer increases.

In a recent paper, we studied the electrochemical degradation of polypyrrole films by EIS technique using the transmission line model to interpret the results. As the degradation process took place, we observed no variation in the polymer backbone resistance, suggesting that the polymeric conductivity does not change. Otherwise, a huge change in the interface elements was observed as, for example, an increase in the charge transfer resistance. Such was interpreted as a hindering of the ion



**Figure 1.** Schematic presentation of the proposed transmission line model for the analyzed self-assembly PANI/PSS film.

intercalation process. This proposition was supported by electrochemical quartz crystal microbalance results that show an important decrease in the intercalated mass. In addition, a decrease in the double-layer capacitance, occasioned by a decrease in the polymer active surface area, which was supported by SEM images, was observed. Finally, an increase in the charge transfer capacitance occurred, which was interpreted as a delay between the ion intercalation process and the period of time to reach a stable site.<sup>59</sup> The model used in this paper is basically the same, differing in the pore elements, once in this case the PSS acts as a layer-by-layer doping effect, meaning that ion transport inside the polymer pore decreases substantially or is even completely absent.<sup>18</sup>

To our knowledge, in the literature, there is no investigation of the electrochemical degradation of polyaniline/polystyrene sulfonated (PANI/PSS) SA films. And considering the exposed above, the purpose of this study is to use the transmission line model to explore the process of irreversible electrochemical degradation of PANI/PSS SA films by EIS and CV analysis to understand the stability loss of such material.

## 2. EXPERIMENTAL SECTION

**2.1. Reagents.** The monomer aniline was purchased from Bayer and distilled to remove oligomers and photodegraded products. PSS (Sigma Aldrich) was used with no further purification. All reagents used were of analytical grade.

Indium tin oxide (ITO) substrates with an electrical resistance of 60  $\Omega/\text{sq}$  (Delta Technologies) were used for self-assembly film deposition. Substrates were treated prior to film deposition for 10 min in a solution of 2.5 mol L<sup>-1</sup> NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> 3.0 mol L<sup>-1</sup>; then in isopropyl alcohol; and, finally, washed with reverse osmosis water. This cleaning procedure creates negative charges at the surface.<sup>60</sup>

**2.2. Preparation of PANI/PSS SA Film.** The parameters involved in the preparation of PANI/PSS self-assembled films, such as the solubility of PANI in aqueous media, the time of deposition at each bilayer, the concentrations of polyelectrolytes, and the pH of the media, were optimized. Aniline chemical polymerization has previously been described in several studies.<sup>61–64</sup> In this study, we used a monomer/oxidant molar ratio of 4:1. The obtained PANI powder was dissolved in dimethyl formamide (DMF) (1.0 mg/mL). A 4.0 mL portion of the resulting PANI/DMF solution was diluted with 16.0 mL of water with the pH adjusted to 3.0 by the dropwise addition of 1.0 mol L<sup>-1</sup> HCl, resulting in a cationic polyelectrolyte solution. The polystyrene sulfonated powder (4.0 mg) was dissolved in 20.0 mL of aqueous solution of HCl with the pH adjusted to 3.0, resulting in an anionic polyelectrolyte solution. To wash the film between the layer depositions, an aqueous HCl solution with the pH adjusted to 3.0 was used.

Self-assembly was performed using a homemade device, which basically consists of an analogic XY recorder that has been adapted to function as an immersion and displacement robot controlled by software.<sup>65</sup> The bilayers were assembled by the subsequent immersion of ITO substrate in PANI and PSS solution, respectively, for 3 min. Before each step, the films were washed in the acidic solution (pH 3.0) for 15 s and then dried in air for 5 min. This procedure was repeated 10 times, forming a 10 bilayer film. The growth of the films by the addition of alternated polyelectrolyte layers was characterized by UV–visible spectrophotometry.

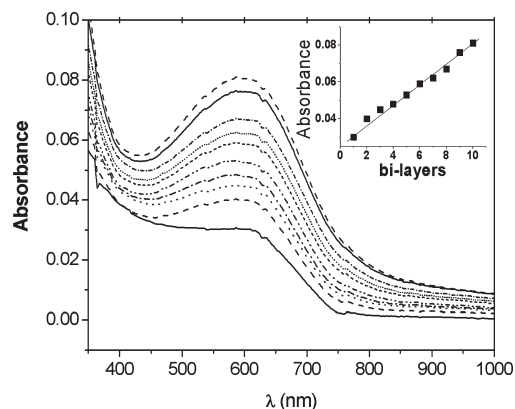
**2.3. Electrochemical Characterization of PANI/PSS Self-Assembled Films.** Films were characterized in 0.1 mol L<sup>-1</sup> HCl solution using cyclic voltammetry and impedance spectroscopy. The films were cycled voltammetrically five times at a scan rate of 100 mV s<sup>-1</sup> between -0.20 and 0.70 V versus saturated calomel electrode (SCE). Following this step, the films were polarized at 0.55 V for 300 s to promote their degradation, and then an impedance measurement was performed at the same potential in a frequency range of 10 kHz to 10 mHz with an applied ac potential of 0.01 V. After the impedance measurement, the procedure described above was repeated to promote the degradation process in the same film for different times. As described in the Introduction, the impedance data were analyzed using a transmission line model. This model allows the consideration of material porosity and the complex relationship that occurs between the polymeric chains and the solution in the pores using the model proposed by Garcia-Belmonte and Bisquert,<sup>48</sup> which is presented in Figure 1.

In this model, for the present case, we assumed the solution resistivity to be null because the measurements were performed in an inorganic acidic medium and the film has a layer-by-layer structure in which PSS layers could partially act as a doping layer for PANI. The polymer resistance is represented by  $r_{\text{pol}}$ . The interface is described as a charge transfer resistance,  $r_{\text{ct}}$ , in series with charge transfer capacitance,  $q_{\text{ct}}$ , both in parallel with the double-layer capacitance  $q_{\text{dl}}$ .

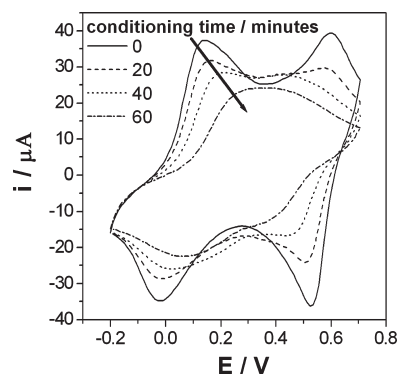
In the present case, because the capacitances present nonideal behavior, they must be represented by constant phase elements, CPE. Moreover, it is important to stress that we propose  $r_{\text{ct}}$  to be an ionic charge transference resistance of the counterions through the solution/polymer interface to neutralize the electronic charges (holes) generated by the oxidation process.  $q_{\text{dl}}$  corresponds to its well-accepted definition of the nonideal double-layer capacitance responding to the polarization process, which occurs at the polymer/solution interface inside the pores. Finally,  $q_{\text{ct}}$  could be related to the slow process of ion transport across the polymer and the time necessary to find an adequate site; that is, the ion could cross the interface at any point, but there is a finite time until it reaches an interaction site.

### 3. RESULTS AND DISCUSSION

Figure 2 shows the UV–visible spectra obtained according to the sequential deposition of each bilayer of PANI/PSS by the self-assembly technique. An absorbance band was observed that was centered at 600 nm, which according to the literature is a characteristic of SA PANI films.<sup>66,67</sup> In the inset of Figure 2, a linear increase of the absorbance as the number of bilayers deposited increases is observed. Considering each layer thickness, it was not possible to determine the film thickness using any direct measurement. However, it was observed that the increase in absorbance at each deposited bilayer was  $\sim 0.01$  absorbance units, which is in agreement with the literature data, which correspond to a thickness change of  $\sim 2.7$ – $4.2$  nm.<sup>66,67</sup>



**Figure 2.** UV–visible spectra of consecutive bilayer PANI/PSS film formation.

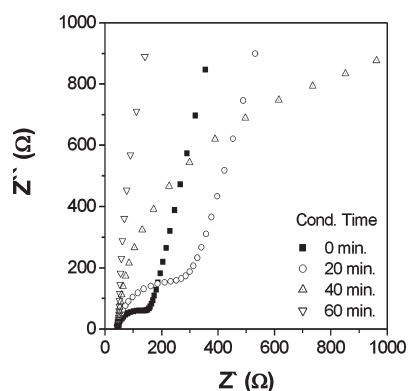


**Figure 3.** Cyclic voltammetry of PANI/PSS self-assembly films (10 bilayers) over ITO substrate. Support electrolyte of HCl 1.0 mol L<sup>-1</sup>. Conditioning times (minutes) and corresponding voltammetry/impedance measurements: 0 min = (first measurement) and 60 min corresponds to the 13th cycle of measurements.

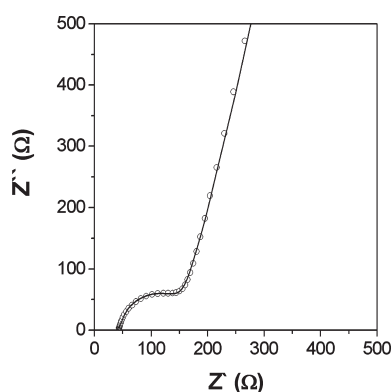
Therefore, a film with 10 bilayers, as those used in this work, should have a thickness of  $\sim 30$ – $40$  nm. About the film morphology, it is well known that SA polymer/polyelectrolyte deposition results in a globular morphology, formed by spherical globules of nanometer dimensions, as found by several authors.<sup>68–72</sup>

Figure 3 presents the cyclic voltammograms obtained cycling over the potential window from -0.20 to 0.70 V. Among the voltammograms, the working electrode was polarized at 0.55 V for 300 s to promote the electrochemical degradation. In the first cycle, the well-described PANI oxidation states<sup>27–29</sup> were observed. It was observed that after 20 cycles, the process that peaked at 0.15 V was displaced to 0.35 V, which is described as an irreversible transformation in the polymer.<sup>37,38</sup> This irreversible process can be associated with different processes, such as ortho-coupling of polymer chains generating phenazine rings;<sup>73</sup> breaking of polymer chains and cross-linking of neighboring chains;<sup>26</sup> and degradation products, such as *p*-benzoquinone, hydroquinone, *p*-aminophenol, or quinoimine.<sup>74</sup> As described by Tamm et al., the differences that appear in the voltammograms are related to the mobility of the anions because the mobility of the anions is good and they are able to leave the polymer film during reduction and enter the film during oxidation; there is no essential difference among the cycles.<sup>75</sup> However, when the differences appear





**Figure 4.** Nyquist diagrams of the self-assembly PANI/PSS films. Applied potential 0.55 V with the following polarization times: ■, 0; ○, 20; △, 40; and ▽, 60 min.



**Figure 5.** Nyquist diagrams of the self-assembly PANI/PSS films. Comparison among experimental results for 0 min conditioning and simulated data with the transmission line. Frequency range 10 mHz to 10 kHz. Support electrolyte HCl 0.1 mol L<sup>-1</sup>.

in the voltammograms, this is strong evidence that the mobility of the anions within the polymeric film is being impeded and, thus, also the electrochemical properties of the conducting polymer.

Therefore, to better understand these changes in the electrochemical process, the technique of electrochemical impedance spectroscopy was applied. Using this technique, it is possible to separate different processes occurring in the electrode, such as ionic conduction in the pore, charge transfer in the polymer/solution interface, and electronic conduction in the polymer. Figure 4 presents the Nyquist diagrams obtained for PANI/PSS film. The analysis shows the changes occurring in the material after polarization at 0.55 V for different times corresponding to the data presented in Figure 3.

Analyzing the Nyquist diagrams, it is possible to observe in the first measurement, i.e. after the first five voltammetric cycles, a well-defined semicircle (Figure 4, solid square) in the high-frequency region. After different polarization times at 0.55 V, it was observed that this high-frequency semicircle increases. This could be associated with the degradation process observed in the voltammetric curve. Figure 5 presents the experimental and fitted data using the transmission line described in Figure 1.

It is easy to observe that the experimental data can be fitted by the model used and the same kind of result was obtained for all impedance measurements. The parameters obtained from the fit

**Table 1.** Fitted Data for PANI/PSS Films Submitted to Degradation by Polarization at 0.55 V in 0.1 mol L<sup>-1</sup> HCl Solution Using the Transmission Line Described in Figure 1

polarization time (min)	0	20	40	60
$r_{\text{pol}}$ ( $\Omega \text{ cm}^{-1}$ )	12.7	15.9	18.1	20.6
$q_{\text{dl}} \times 10^{-5}$ ( $\text{F s}^{n-1} \text{ cm}^{-1}$ )	1.88	1.33	1.06	0.96
$n_{\text{dl}}$	0.91	0.94	0.97	0.98
$r_{\text{ct}}$ ( $\Omega \text{ cm}$ )	$1.31 \times 10^2$	$3.01 \times 10^2$	$1.48 \times 10^3$	$1.10 \times 10^4$
$q_{\text{ct}} \times 10^{-4}$ ( $\text{F s}^{n-1} \text{ cm}^{-1}$ )	2.73	1.82	1.03	0.52
$n_{\text{ct}}$	0.85	0.82	0.78	0.72
$\chi^2$	0.9999	0.9999	0.9999	0.9999

of the impedance data with the model presented in Figure 1 are in Table 1.

The equipotential hypotheses proposed here to describe the solution in the pore are compatible with an aqueous acid solution in which the conductivity is much higher than the polymer conductivity.<sup>76</sup> A second assumption for the equipotential hypothesis is that proposed by Strixino et al.<sup>18</sup> to describe self-assembly films of poly(*o*-methoxyaniline) and poly(3-thiopheneacetic acid), POMA-PTAA, samples. In that case, the authors showed using quartz crystal microbalance that the strong interaction of amine-imine groups and the carboxylic-carboxylate groups lead to a layer-by-layer doping effect, meaning that ion transport inside the polymer pores decreases substantially or is even completely absent. In this study, the interaction between amine-imine groups from PANI and sulfonated groups from PSS could also lead to a layer-by-layer doping effect.

The first important point to notice from Table 1 is that the  $\chi^2$  for all fittings is 0.9999, which is an indication of the quality of agreement between the experimental data and the proposed model. Second, considering that the cell configuration is the same for all samples, it is expected that the solution resistance,  $R_s$ , would remain constant in these experiments. Considering that the ionic solution strength is high, one can also suppose that the charge accumulated in the polymer solution (inside the pores) does not change. As such, the observed  $q_{\text{dl}}$  variation could be associated with a decrease in the surface area exposed to the solution because this element can be viewed as a capacitive-like element accounting for the double layer built on the inner surface of the electrode. Our interpretation of the nonideal charge transfer capacitance,  $q_{\text{ct}}$ , is that it represents the delay between the charge crossing to the polymer/pore solution interface, that is, the time required to reach a stable site inside the polymer structure.

An unexpected result is observed in Table 1: the polymer resistance did not change during the degradation process. This is highly noteworthy because different authors have attributed the polymer degradation to a loss of polymer chain conductivity.<sup>77,78</sup> Associated with these results, it can be observed that charge transfer resistance,  $r_{\text{ct}}$ , changes by 2 orders of magnitude during electrochemical degradation. One possible explanation for this behavior is that the ion transport through the interface polymer/solution becomes more difficult as the degradation process occurs. According to Tamm et al.,<sup>79</sup> the loss of reversibility of the conducting polymer is related to a loss of mobility of the anions inside the pores. Because they are able to leave the polymer film during reduction and enter the film during oxidation, the conducting polymer loses its conductivity when this process is hindered. The difference in the mobility of anions can be related to their different interaction strengths with the conducting polymer chains, resulting in different intercalation sites, which in some cases have

irreversible intercalation. These different interaction strengths between polymer sites and ions inside the polymer pores could occur as a result of an inhomogeneous oxidation process, that is, oxidized and reduced regions coexisting in the bulk, and charge being transferred between them. At this point, two assumptions could be made: (i) the number of intercalated ions decreases, or (ii) there is an increase in the number of stable sites accessible to these intercalated ions. It seems to us from the analysis of the  $r_{ct}$  and  $q_{ct}$  that the first option is more probable. Therefore, we conclude that degradation of the electrochemical properties could occur without polymer backbone degradation.

Considering these propositions and the data presented in this study, one can see that the electrochemical degradation of the PANI/PSS system is being caused by the damage in the ion transport across the polymer/solution interface as a consequence of the huge increase in the charge transfer resistance.

#### 4. CONCLUSIONS

The impedance results in the Nyquist diagrams showed a very well-defined semicircular curve, which is frequently associated with CPs and is generally represented by an equivalent electrical circuit constituted by capacitance in parallel with a resistor (RC parallel). However, modeling the results by transmission line, the changes in the electrochemical behavior of the oxidized PANI/PSS film was observed to occur mainly on the polymer/solution interface by the huge increase in the charge transfer resistance and the polymer bulk resistance remaining almost unaltered. Therefore, the transmission line model, which is adequate to fit porous electrodes, presented more detailed results of the electrochemical degradation of conducting polymeric films. In addition, these results reinforce the specific control of some analysis variables, such as the counterion size, which could directly influence the electrochemical degradation of the polymer in future applications of conducting polymer films.

We believe that there are two main degradation processes: electrical degradation, in which breaking of polymer chains results in carbon dioxide formation as well as C–O bonds and cross-linking between neighboring polymer chains, as related for many papers in the literature; and the electrochemical degradation, in which morphological change in the polymer matrix results in the loss of electrochemical properties of the polymer film. Both could occur in parallel, with the applied overpotential being the main key between them.

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