

Effect of *p*-Toluenesulfonate on Inhibition of Overoxidation of Polypyrrole

Amit Kumar,^{1,2} Rajiv K. Singh,¹ Khushboo Agarwal,¹ Hari K. Singh,¹ Pankaj Srivastava,² Ramadhar Singh¹

¹National Physical Laboratory, Council of Scientific and Industrial Research, New Delhi 110012, India

²Department of Chemistry, Banaras Hindu University, Varanasi 221005, India

Correspondence to: R. K. Singh (E-mail: rajivsingh@mail.nplindia.org)

ABSTRACT: Electrochemically synthesized polypyrrole (PPy) films degrade under anodic polarization in aqueous solution. PPy is irreversibly oxidized leading to subsequently to an insulating material. This article highlights the degradation behavior of electrochemically synthesized PPy films using inorganic (perchlorate, ClO_4^-), organic (*p*-toluenesulfonate, pTS^-) and mixed (inorganic-organic, $\text{ClO}_4^- + \text{pTS}^-$) anions systems in aqueous solution. The PPy films were subject to overoxidation by means of anodic polarization for a certain period of time and consecutively cyclic voltammetry and electrochemical impedance spectroscopy were employed to investigate the influence of anions used during polymerization on the stability and redox activity of the polymer. The modification in the surface morphology of PPy films due to the application of anodic polarization distinctively shows the effect of degradation at polymer/electrolyte interface. The presence of organic anion in the system (PPy/ pTS^- and PPy/mixed) has shown improved electrochemical activity and is stable to electrochemical degradation for a longer period of time than PPy/ ClO_4^- . © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 434–442, 2013

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INTRODUCTION

Polypyrrole (PPy) is one of the most extensively studied conducting polymers owing to its various advantages such as high electrical conductivity, better environmental stability, and good redox activity. It has been used in numerous technological applications for instance, supercapacitors,^{1,2} actuators,³ sensors,⁴ rechargeable batteries,^{5,6} etc. This material possesses good electrochemical activity and has a great potential for future device applications. However, the main drawback of utilizing PPy is its irreversible electrochemical degradation under anodic (oxidizing) potential. This process of degradation is an irreversible process which not only affects the electrochemical redox activity of PPy but also makes it insulator after certain redox cycles. Such kind of behavior has been often described in literature as overoxidation.^{7,8} The presence of strong nucleophiles such as OH^- leads to the formation of quinone moieties that disrupt the conjugated backbone thereby affecting the electronic and redox properties of PPy.⁹ The positive charge obtained on the polypyrrole during polymerization is often compensated by incorporation of anion in the polymer matrix. Hence the properties of PPy largely depend on the kind of dopant anion used during

synthesis. Various anions of different ionic sizes have been employed by researchers to study the mechanical, electronic and electrochemical properties of PPy. PPy films synthesized using inorganic dopant anions such as Cl^- , NO_3^- , SO_4^{2-} , ClO_4^- , etc., possess a low conductivity and are brittle. However, due to high surface area and easy transport of ions across the polymer/electrolyte interface their electrochemical activity is high. Though it lacks the flexibility and strength and the overoxidation reduces its performance after a period of time. However, PPy doped with pTS^- , SDS or PSS (organic anions) is capable of giving free standing films of good flexibility and strength with high conductivity. No doubt the bulkier anion is difficult to be removed from the polymer matrix, but they show cationic exchange characteristics. A combination of anionic and cationic exchange has also been reported in literature.^{10,11}

The overoxidation process leads to the formation of oxidized islands entrapped by cross-linkages of neighboring polymer chains making the ions difficult to diffuse during the electrochemical process and hence affects its electrochemical activity. Overoxidation of polypyrrole usually ends the polymer in dedoped state i.e., the anions are expelled out from the polymer.

The hydroxyl radical formed during the water oxidation generally react with the polymer leading to formation of carbonyl group at the β -position of the pyrrole rings.^{9,12} The degradation study on PPy has been performed using voltammetric and chronoamperometric techniques.⁸ Mostany et al.¹³ have found that the overoxidation affects the ionic and electronic transport properties of the polymer leading to irreversible degradation of the electroactive properties of the material. Recently, it has been reported that organic anions such as dodecyl sulfate and polar aromatic compounds (benzyl alcohol, benzonitrile) have effectively reduced the overoxidation of PPy.¹⁴

In view of the above consideration, the purpose of this paper is to report the detailed study of electrochemical properties (redox activity and degradation behavior) of PPy synthesized using inorganic (ClO_4^-), organic (pTS^-) and mixed ($\text{ClO}_4^- + \text{pTS}^-$) electrolyte system through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The dual channel transmission line model has been utilized to understand the system under study for their electronic and ionic behavior.

EXPERIMENTAL SECTION

All the chemicals used in the present work are of analytical grade purity. Pyrrole (Fluka Chemie) was doubly distilled prior to synthesis of PPy. Supporting electrolytes such as sodium perchlorate (NaClO_4), and sodium *p*-toluenesulfonate (NapTS) were product of Merck. All solutions in this experiment were prepared using deionized (D.I.) water (18 $\text{M}\Omega\text{ cm}$).

Electropolymerization of pyrrole was performed on a platinum (Pt) disk electrode (geometrical area = 0.07 cm^2), under galvanostatic conditions (current density = 1 mA cm^{-2}) at $\sim 2^\circ\text{C}$ for 20 min. The temperature of the electrolyte solution was maintained at $\sim 2^\circ\text{C}$ using JULABO FP 50 low temperature bath. Pt disk was polished with 0.3 μm Al_2O_3 particle suspension on a moistened polishing cloth (Metrohm) for 5 min till a mirror finish is achieved. The polished electrode is further rinsed well with D.I. water followed by sonication in acetone:isopropanol (50 : 50) and again rinsed well with D.I. water and then dried at room temperature for 20 min prior to use. Ag/AgCl (3M KCl) and Pt sheet were used as reference and auxiliary electrodes, respectively. PPy was electrochemically synthesized from aqueous solutions of 0.1M monomer (pyrrole) and 0.1M of different supporting electrolytes (NaClO_4 , NapTS, and $\text{Na}(\text{ClO}_4 + \text{pTS})$ (0.05 + 0.05 M)) separately. In all these experiments, PPy-modified Pt disk was removed from the solution and rinsed well with D.I. water and transferred to their respective electrolyte solution for further electrochemical characterizations. The synthesized polymer samples with different supporting electrolytes used i.e., NaClO_4 , NapTS and $\text{Na}(\text{ClO}_4 + \text{pTS})$ were named as PPy/ ClO_4 , PPy/pTS, and PPy/mixed, respectively. This nomenclature has been used in the following section.

The electrochemical performance of PPy was investigated using CV at a scan rate of 10 mV s^{-1} from -1.0 to 0.6 V versus Ag/AgCl electrode. To avoid the problem caused by "slow relaxation,"¹⁵ the CV was performed on each PPy-modified Pt electrode after 10 initial conditioning cycles. The CV was performed

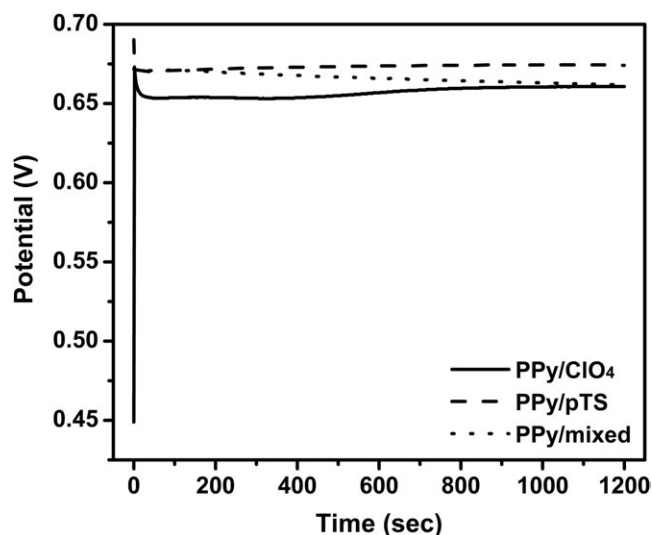


Figure 1. Typical potential transients recorded during the electrochemical synthesis of polypyrrole in various electrolytes (NaClO_4 , NapTS, and $\text{Na}(\text{ClO}_4 + \text{pTS})$) at constant current density ($\sim 1 \text{ mA cm}^{-2}$).

in 0.1M aqueous solution of respective electrolytes wherein the pyrrole monomer was absent and also in NaCl solution. To investigate the polypyrrole degradation behavior another set of experiment was performed wherein the procedure as described by Marchesi et al.¹⁶ was utilized. The EIS measurement was carried out at 0.3 V in aqueous solution of 0.1M NaCl at different time of overoxidation. The frequency range was varied from 100 kHz to 10 mHz with an applied ac potential 0.01 V rms. At 0.3 V the polymer is in oxidized (conducting) state but there is negligible effect of overoxidation during the course of measurement. The overoxidation process was carried out by applying a constant potential (0.7 V) on working electrode over a time period in the range 5–60 min. Before recording the data, a CV was performed after every overoxidation step for 10 cycles. Thereafter, the system was allowed to reach a steady state by

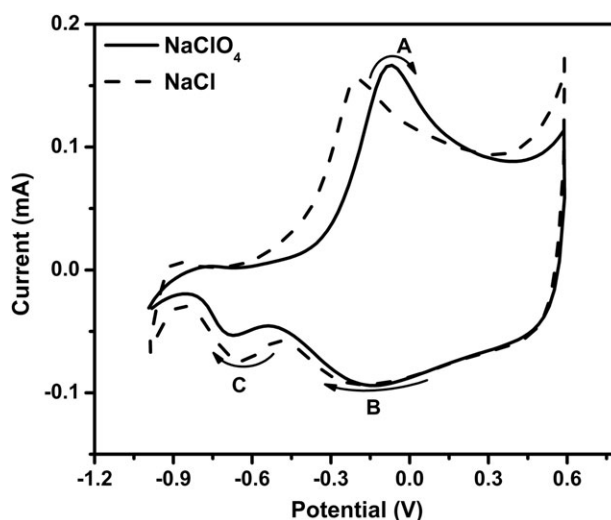


Figure 2. Cyclic voltammogram of the PPy/ ClO_4 film in 0.1M NaClO_4 (—) and NaCl (---) at a scan rate of 10 mV s^{-1} .

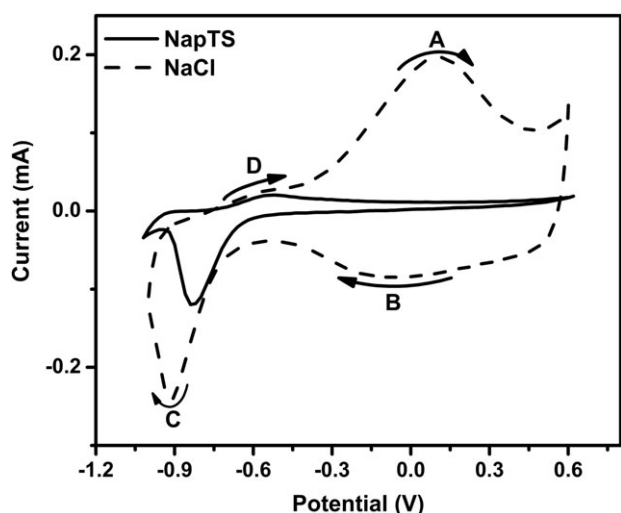


Figure 3. Cyclic voltammogram of the PPy/pTS film in 0.1M NapTS (—) and NaCl (---) at a scan rate of 10 mV s⁻¹.

taking an equilibrating time of 15 min. All the electrochemical experiments were performed in a three electrode one compartment cell using AUTOLAB PGSTAT 302N (Eco Chemie, The Netherlands) operating with computer controlled software NOVA 1.7 at room temperature. The electrolyte solutions were deaerated using dry nitrogen (N₂) for 15 min prior to experiment and a slight N₂ overpressure was maintained during the experiment.

RESULTS AND DISCUSSION

Figure 1 shows the chronopotentiogram obtained for the polymerization of pyrrole in various supporting electrolytes. On the application of constant current density the potential of the working electrode increases to a maximum showing oxidation of first pyrrole nuclei at the electrode interface, followed by the formation of polypyrrole at constant potential over the time pe-

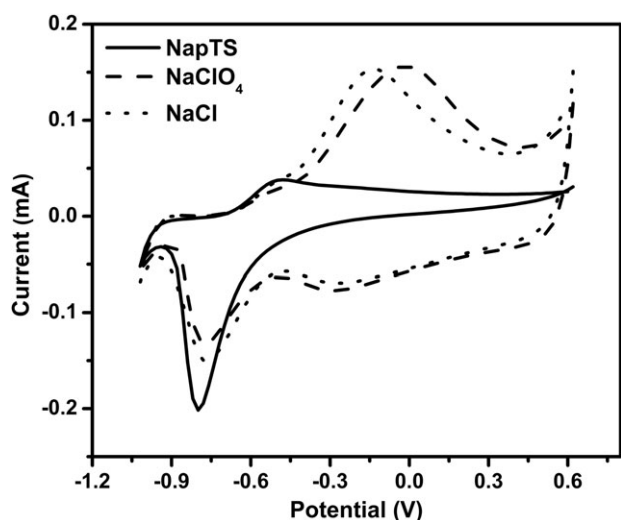


Figure 4. Cyclic voltammogram of the PPy/mixed film in 0.1M NapTS (—), NaClO₄ (---) and NaCl (· · ·) at a scan rate of 10 mV s⁻¹.

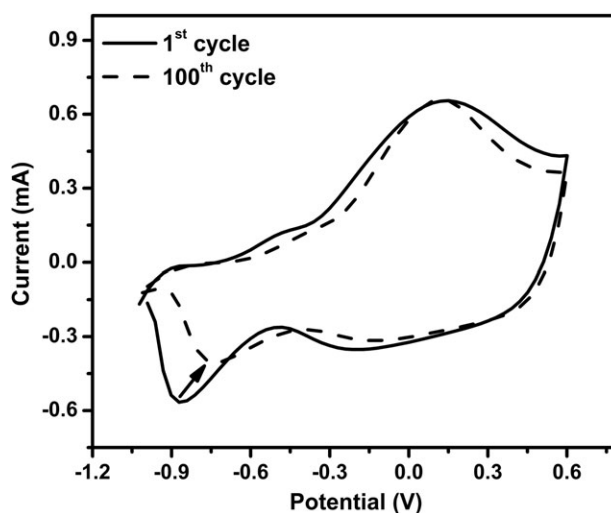


Figure 5. Cyclic voltammogram of the PPy/mixed film in 0.1M NaCl at a scan rate of 100 mV s⁻¹ for 100 consecutive cycles. Arrow represents the change in cathodic peak current after 100th cycle.

riod. It has been observed that PPy synthesized using NapTS as the supporting electrolyte requires a higher overpotential than NaClO₄. However, in mixed electrolyte system, the potential is initially at higher value similar to the potential required by pyrrole for polymerization in NapTS solution, which subsequently lowers with time and reaches to a value which is similar to the value required by pyrrole in NaClO₄ solution. This peculiar trend for PPy/mixed system could be due to the requirement of organic pTS⁻ initially at the interface which served as a template for growth of polypyrrole^{2,17} and the decrease in potential depicts the addition of ClO₄⁻ ion in polymer as well.

Cyclic Voltammetry

PPy/ClO₄. Figure 2 shows a typical cyclic voltammogram obtained during the cycling of PPy/ClO₄ in aqueous electrolyte solutions of 0.1M NaClO₄ and 0.1M NaCl at a scan rate of 10 mV s⁻¹. In the forward potential scan, there is an appearance of a single anodic peak (represented as A in Figure 2) which relates to the incorporation of anion to counter the charge generated on PPy due to oxidation. Whereas on the reverse scan the voltammogram shows two cathodic peaks corresponding to anion expulsion (B) and cation incorporation (C), sequentially. Since for PPy doped with smaller inorganic anions, the redox process has been largely governed by the anion exchange, the peak current related to cation incorporation is found to be smaller than anion expulsion during the cathodic scan. Comparing the CV of PPy/ClO₄ in electrolyte solutions of NaClO₄ and NaCl, it has been observed that there is lesser overpotential required for anion incorporation when cycled in NaCl than in NaClO₄. The reason behind this lies in the transport of ions across the polymer/solution interface, since Cl⁻ ion is smaller in size as compared to ClO₄⁻, it can easily penetrate into the polymer matrix without much need of overpotential.

PPy/pTS. Figure 3 presents the CV profile of PPy/pTS in aqueous electrolyte solutions of 0.1M NapTS and 0.1M NaCl at a scan rate of 10 mV s⁻¹. One noticeable feature observed in the

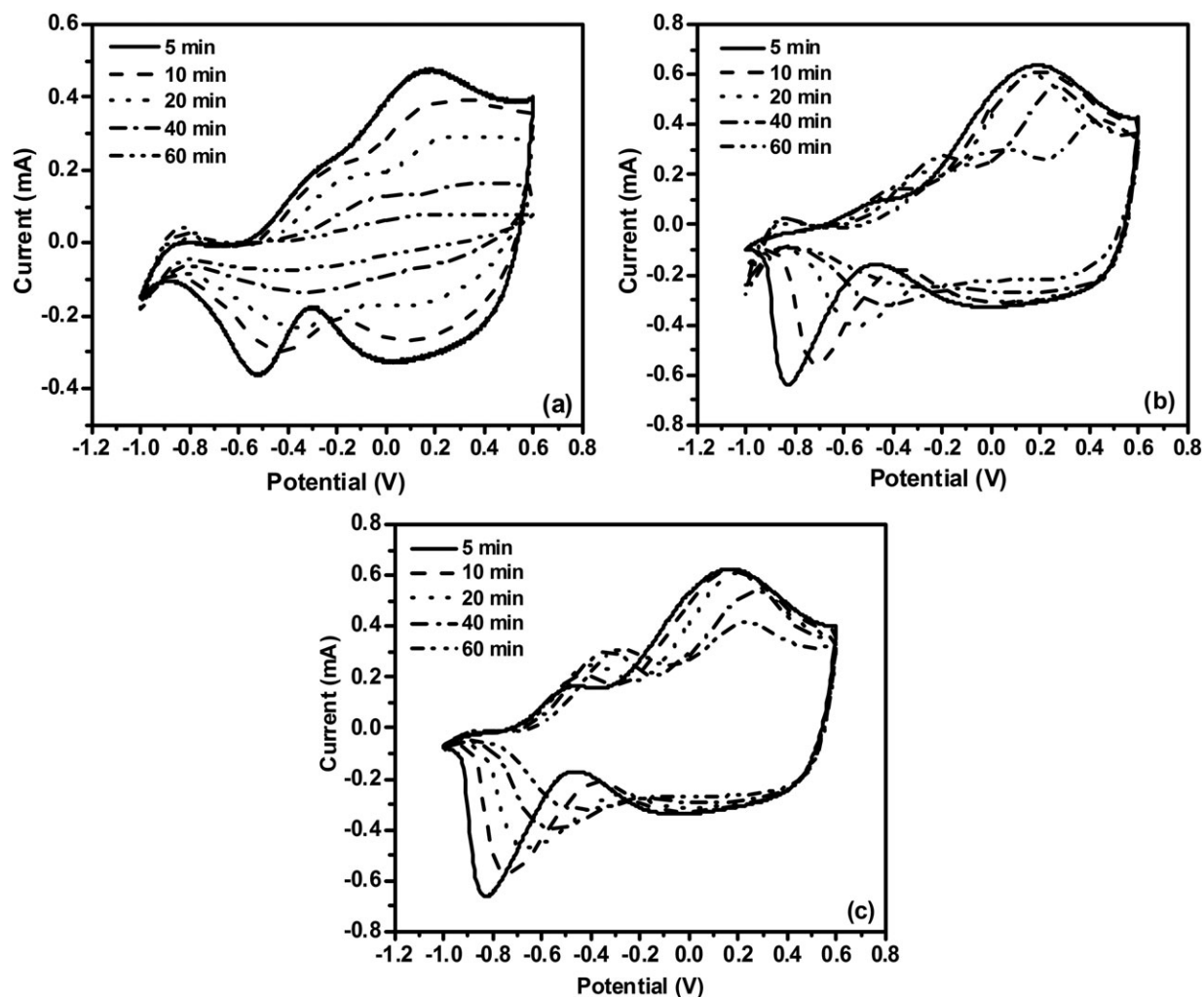


Figure 6. Cyclic voltammogram of the (a) PPy/CLO₄, (b) PPy/pTS, and (c) PPy/mixed film in 0.1M NaCl at a scan rate of 50 mV s⁻¹ after successive overoxidation at 0.7 V in the range 5–60 min.

CV is the change in the redox behavior of PPy/pTS with the change of PPy/pTS when cycled in aqueous NapTS solution, shows only one redox couple relating cation (Na⁺) incorporation and expulsion, whereas in NaCl electrolyte a combination of anion and cation exchange process is observed by the appearance of a second redox couple. This can be divided into four regions A, B, C, and D. The broad peaks in regions A and B correspond to the incorporation and expulsion of the smaller size mobile Cl⁻ anion in the polymer matrix, respectively, whereas the region C (sharp peak) and D (broad peak) contribute towards Na⁺ incorporation and expulsion in the polymer matrix. In spite of having the bulkier anion pTS⁻ in the polymer matrix, it is found that the space for smaller anion like Cl⁻ is still attainable. PPy/pTS has required higher overpotential for cation incorporation in the NaCl solution (-0.92 V) than in NapTS solution (-0.83 V). This could be a direct consequence of the simultaneous Cl⁻ ion expulsion during cathodic scan. It can be ascertained that the ion size has a bigger role to play in the transport process of ions across the polymer/solution interface. PPy synthesized using bulkier anion primarily shows cation dominant exchange processes. However, a combination of

anion and cation exchange process has been reported for electrolyte solutions where the cation and anion is of comparably smaller in size.^{10,18} Although for small size ions such as Na⁺ and Cl⁻ the amount of diffusion varies with the ionic radii, valency, structure, and its hydrophilic/hydrophobic nature, they can move in or out of PPy/pTS film easily whereas larger size ions such as pTS⁻ and (C₂H₅)₄N⁺, cannot reach the redox sites. They might block the passage of ionic transport in PPy/pTS matrix, thus inhibiting the transport of the smaller size ions coexisting in the aqueous solution.¹⁸

PPy/mixed. Figure 4 shows the CV obtained for PPy/mixed system in aqueous electrolyte solutions 0.1M NapTS, NaClO₄ and NaCl at a scan rate of 10 mV s⁻¹. As anticipated, it shows the characteristic behavior from their parent polymer systems. In NapTS electrolyte solution, the polymer shows cation governed exchange process, whereas in NaClO₄ and NaCl electrolyte solution, it shows two redox couples corresponding to simultaneous occurrence of anion and cation exchange processes, similar to that observed for PPy/pTS in NaCl solution. One distinguishing feature observed in the case of PPy/mixed system is its

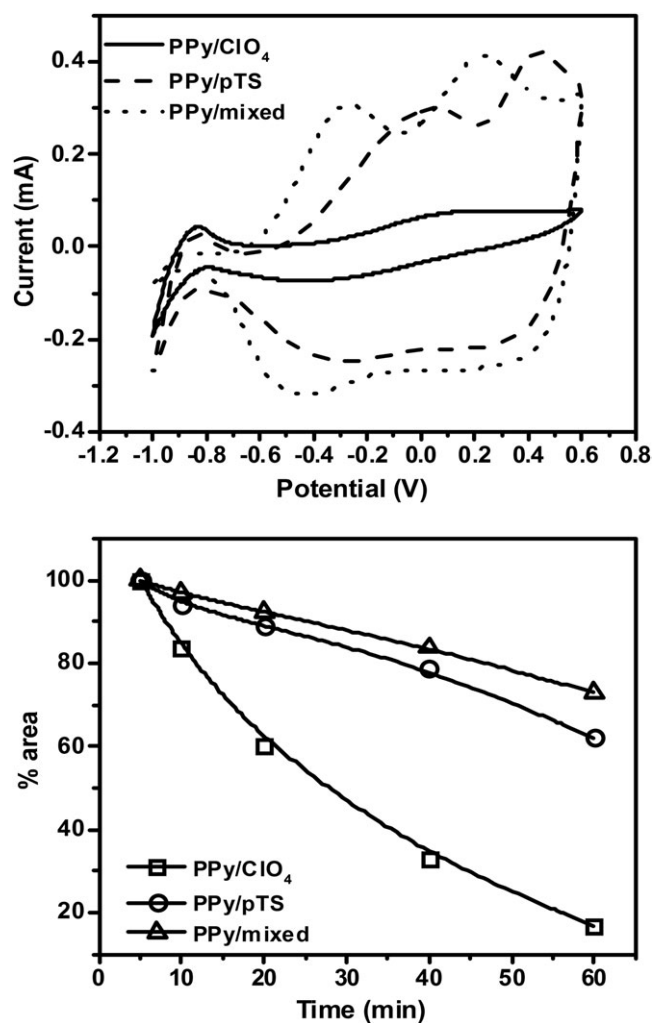


Figure 7. (a) Cyclic voltammogram of the (a) PPy/ClO₄ (—), (b) PPy/pTS (---) and (c) PPy/mixed (· · ·) film in 0.1M NaCl after 60 min of overoxidation at 0.7 V. (b) area of the voltammogram against anodic polarization time (estimated from Figure 6).

switching potential range which is nothing but the difference between the E_{pa} (anodic peak potential) for anion incorporation and E_{pc} (cathodic peak potential) for cation incorporation. The switching potential range for PPy/mixed (~ 0.64 V) is far less than PPy/pTS (~ 1.03 V). This shows that a lesser overpotential is required for the anion and cation exchange processes in PPy/mixed system. This could be due to the incorporation of ClO₄⁻ anion in the polymer matrix which enhances the surface area through its 3D growth.¹⁷

The investigation on degradation process in polypyrrole has been reported in literature,^{8,9,12,13} however, the report on interaction between the molecular structure of anions and the polymer backbone is scarce.¹⁴ In our recent work,¹⁷ we have discussed the growth mechanism of polypyrrole in different electrolytic medium. The organic dopant anion pTS⁻ contains an aromatic moiety which interacts with the aromatic pyrrole ring through π - π interaction leading to laminar growth whereas

inorganic dopant anions often leads to 3D fractal growth. The cross sectional morphology has revealed a compact film of PPy in the case of PPy/pTS whereas in the case of PPy/ClO₄ some pits and pores have been seen in which solvent can easily penetrate along with the ions. On the other hand, PPy/mixed system shows flexibility, strength, and high electrical conductivity.

Figure 5 displays CV of the PPy/mixed modified Pt electrode at a scan rate of 100 mV s⁻¹ for 100 consecutive cycles. In CV, there is no change in the anodic peak current value (~ 660 μ A) at ~ 0.12 V, however, there is a small decrease in the cathodic peak current value from ~ 568 μ A to 400 μ A at ~ -0.87 V while going towards 100th cycle. Further, the E_{pc} involving cationic incorporation shifts towards positive side (from ~ -0.87 to -0.73 V) displaying an increase in electrochemical reversibility towards ion exchange. Mainly, the cyclic voltammogram shows less decrease in the electrochemical capacity (area of the voltammogram) and retains its electrochemical activity even after cycling at a high scan rate of 100 mV s⁻¹ for 100 cycles.

Electrochemical Degradation

Figure 6(a-c) shows the CV obtained after each application of overpotential with increasing time interval for PPy/ClO₄, PPy/pTS, and PPy/mixed, respectively. PPy is known⁷ to be susceptible to overoxidation beyond 0.65 V vs. Ag/AgCl reference electrode in aqueous solution at pH ~ 6 and this process of overoxidation¹⁸ depends largely on the pH. Influence of the application of overoxidation can be seen on the subsequent cyclic voltammograms carried out on the polymer film. PPy/ClO₄ shows successive decrease in its anodic as well as cathodic peak current values. The decrease in anodic and cathodic peak current values indicates the decrease in redox competence of the material. On the contrary, PPy/pTS and PPy/mixed system show a stable anodic peak current up to 20 min of overoxidation, thereafter they start showing a decrease in both anodic and cathodic peak current. PPy/ClO₄ shows minimal or no current after 60 min of application of overpotential, whereas PPy/pTS and PPy/mixed system have a considerable electroactivity left even after 60 min of overoxidation [Figure 7(a)]. The area inside the cyclic voltammogram can be related to the charge storage capacity or the electrochemical charge stored in the polymer. Keeping this in view, a graph has been plotted [Figure 7(b)] using the area inside the voltammograms in Figure 6 and the decrease in this area with the application of anodic polarization. It is noted that this decrease is much pronounced in the case of PPy/ClO₄ left to only 20% of the electrochemical area after 60 min of overoxidation, whereas the decrease is of lesser amount for PPy/pTS and PPy/mixed system. The introduction of organic dopant anion hence gives the polymer stability towards higher anodic overpotential.

Surface Morphology

The scanning electron micrographs of as grown and overoxidized PPy films are shown in Figure 8(a-d). Organic dopant anion makes the surface smooth and homogeneous [Figure 8(a)], whereas the inorganic dopant anion generally gives a cauliflower like morphology [Figure 8(b)]. The effect of overoxidation at 0.7 V for 60 min will primarily exhibit on the polymer surface i.e., on polymer/electrolyte interface since this interface

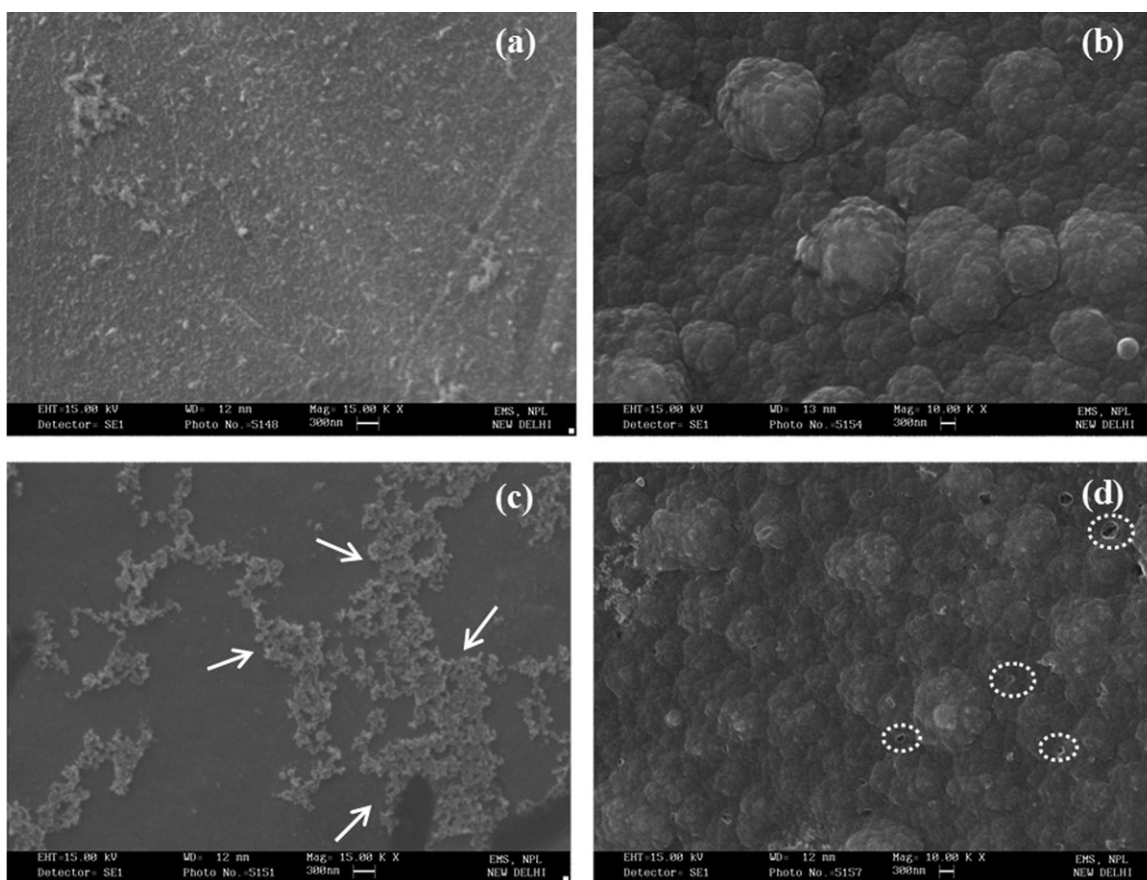


Figure 8. Scanning electron micrograph of PPY/pTS (a, c) and PPY/ClO₄ (b, d) in as synthesized (a, b) and overoxidation at 0.7 V for 60 min (c, d).

is in the plane at which the degradation of the polymer begins. It is evident from Figure 8(c,d) that the overoxidation of PPY has caused the morphological loss in the films which is due to the breakage of π -conjugated backbone of polypyrrole. As mentioned earlier, organic anions like dodecyl sulfate and polar aromatic compounds inhibit corrosion of polypyrrole and hence makes the polymer stable towards overoxidation. It is evident from Figure 8(c) that the effect of overoxidation on PPY-pTS film leads to the surface inhomogeneity wherein the domains of degraded portion are seen as patches on the polymer surface [marked by arrows in Figure 8(c)]. The organic anions incorporated in the polymer during synthesis initially counteract the overoxidation process instead of π -conjugated backbone of polypyrrole. This degradation of dopant anions provides resistance to overoxidation of the polymer. On the other hand in PPY/ClO₄, the polymer is found to be corroded due to overoxidation of π -backbone of the polymer forming pitholes [encircled in Figure 8(d)] on the surface of polymer film. On prolonged application of overoxidation potential the localization of excessive charges tear apart the surface forming pitholes. These pitholes enhance the incorporation of electrolyte deep inside the polymer matrix and thus the level of degradation in this inorganic anion (ClO₄⁻) doped polypyrrole is more pronounced in comparison to PPY/pTS. Hence, the CV obtained for polymer film (Figure 7) after 60 min of overoxidation has lost its electrochemical activity largely/completely for PPY/ClO₄. The effect of

overoxidation on polymer internal resistance and surface inhomogeneity has been further analyzed using EIS and is discussed in the following section.

EIS Studies

To interpret the impedance data, several approaches have been implemented by the authors using various impedance models. In a simple case, the impedance data has been modeled by utilizing Randles equivalent circuit,¹⁹ consisting of a double-layer capacitor in parallel with a polarization resistor described as charge transfer resistor and a Warburg impedance, connected in series with a resistor that is a measure of the resistance offered by electrolyte solution. However, authors have attempted to modify this circuit in accordance with various approaches,^{13,20} depending on the types of electrochemical reactions involved at the polymer/electrolyte interface. The charge transport and the polarization in the polymer is a highly complex interfacial phenomenon and are difficult to interpret because the conducting polymer is often considered to be a porous matrix. Hence the behavior is not limited to the polymer/electrolyte interface only because the diffusion of ions occurs inside the polymer matrix as well. To describe this authors have used distributed impedance models,^{21–24} where the total impedance is often described as the sum of impedances of metal (substrate)/polymer contact, internal impedance of the polymer and the impedance offered by polymer/electrolyte interface. The solid phase in contact with

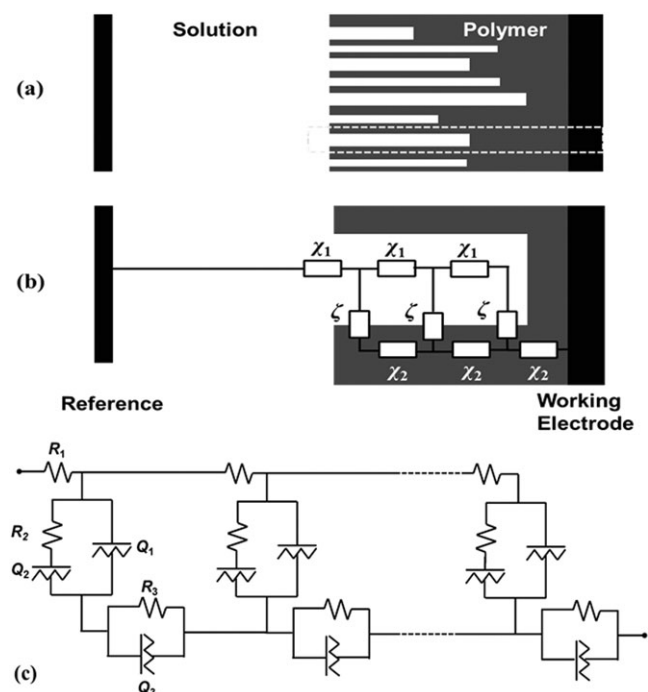


Figure 9. (a) Schematic representation of porous electrode. (b) Equivalent circuit model of the porous electrode showing distributed impedances as discussed in the text. (c) Dual channel transmission line model used for the fitting of the impedance data.

the polymer provides a path for electron transport whereas the pores provide a medium for the diffusion of electrolyte and hence contributes towards ionic conduction [Figure 9(a)]. The dual channel transmission line model has been adopted by various authors^{16,22–25} to describe the electrochemical behavior of conducting polymers. J. Bisquert^{24,25} in their study towards porous film electrodes of thickness L gives the solution of the transmission line model as:

$$Z = \frac{\chi_1 \chi_2}{\chi_1 + \chi_2} \left(L + \frac{2\lambda}{\sinh(L/\lambda)} \right) + \lambda \frac{\chi_1^2 + \chi_2^2}{\chi_1 + \chi_2} \coth(L/\lambda)$$

where

$$\lambda = \left(\frac{\zeta}{\chi_1 + \chi_2} \right)^{1/2}$$

This is schematically shown in Figure 9(b). The elements χ_1 and χ_2 describe a local ohmic drop at each point of the transport channels (the subscript 1 and 2 denotes the liquid and the solid phases, respectively) whereas the element ζ describes an exchange of electrical charge at the interface owing to faradaic currents and polarization at the pore surface.

The distribution of capacitive elements at different types of interfaces in the system has been often expressed in terms of constant phase element (CPE). The impedance of the constant phase element is defined as:

$$Z = \frac{1}{Q} (i\omega)^{-\beta}$$

where Q and β are the frequency-independent parameters which usually depend on temperature; $\omega (=2\pi f)$ is the angular frequency. The empirical constant β can be in the range $0 < \beta < 1$ and Q is a constant with dimension $F S^{\beta-1}$. When $\beta = 0$, the CPE is an ideal resistor; when $\beta = 1$, it is an ideal capacitor ($Q = C$) and when $\beta = 0.5$, it represents homogeneous semi-infinite diffusion.

Figure 9(c) shows the equivalent circuit model used in the present investigation. On comparing it with Figure 9(b), χ_1 represents the resistance (R_1) offered by the ion diffusion in the pores along the ionic channel, χ_2 is related with the polymer resistance (R_3) in parallel with the substrate/polymer interfacial capacitance (Q_3); ζ is interfacial impedance which is described by a double layer capacitance (Q_1) in parallel with charge transfer resistance (R_2) and charge transfer capacitance (Q_2). The charge transfer capacitance (Q_2) signifies the time utilized in finding a stable site for the anion to neutralize with the oxidized polymer chain. The quality of the fitting has been checked by the chi-square value. The obtained values lie in the range $10^{-2} - 10^{-3}$ indicating towards a good fitting to the equivalent circuit model used. The corresponding parameters of the equivalent circuit obtained by fitting the experimental data with the model [Figure 9(c)] are summarized in Table I.

The values of double layer capacitance (Q_1) for PPy/ ClO_4 decreases with increasing anodic polarization time for overoxidation, whereas PPy/pTS and PPy/mixed systems show no such significant change. This shows that as the degradation of the polymer proceeds, the surface area decreases largely for PPy/ ClO_4 affecting the polymer/electrolyte interface, whereas PPy/pTS and PPy/mixed systems show resistance towards any change in the polymer surface area as is also evident from scanning electron micrographs [Figure 8(c,d)]. The charge transfer resistance (R_2) decreases for all the polymer samples with increasing polarization time. However, the change is more intense for PPy/ ClO_4 than PPy/pTS and PPy/mixed system (Table I). This indicates that the ion diffusion inside the polymer matrix has been strongly reduced in the PPy/ ClO_4 system. As described earlier,^{9,12} the formation of oxidized island by crosslinking of the polymer chains and appearance of C—OH and C=O functional groups in the polymer backbone hinders the diffusion of ions in the polymer matrix and hence their electrochemical activity. However, pTS⁻ induces a laminar growth in polypyrrole making the polymer a compact, flexible, and rigid system which is resistant to formation of any cross linkages.¹⁷ Moreover, pTS⁻ being an organic anion inhibits the PPy degradation, as hydroxyl radicals will tend to react preferentially with organic anion instead of disrupting the PPy π -conjugated backbone leading to partial protection of the latter.¹⁴

Marchesi et al.¹⁶ have discussed the variation in above mentioned impedance parameters with respect to overoxidation. The results obtained for inorganic dopant anion (ClO_4^-) system¹⁶ i.e., earlier and for the present work on PPy/ ClO_4 are similar, wherein the decrease in double layer capacitance (Q_1) and a huge increase in charge transfer resistance (R_2) are observed (Table I). This is because of the decrease in the exposed surface area between the polymer film and solution in the pores thereby hindering the process of ion insertion in the

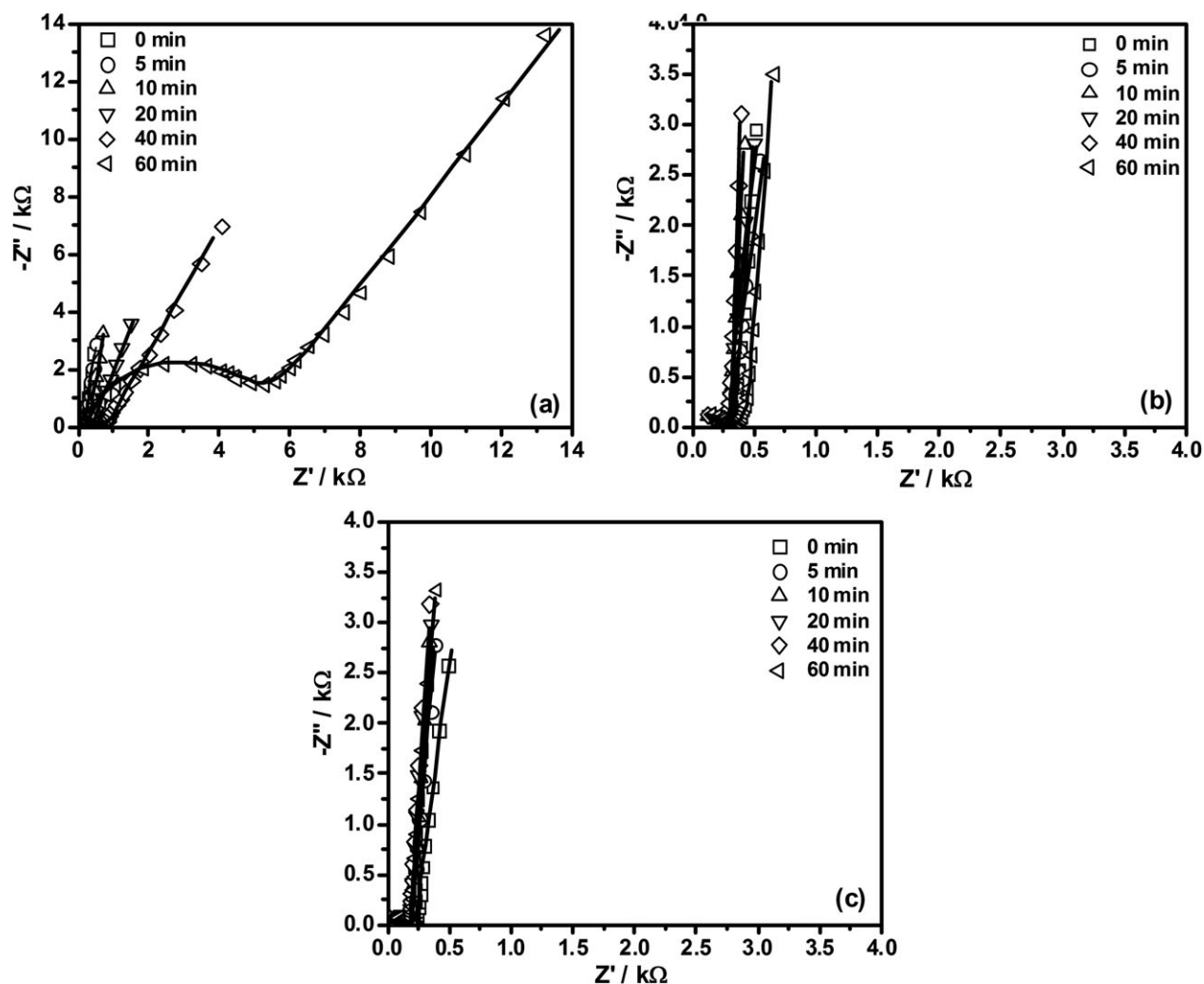


Figure 10. Nyquist plot of data (symbols) and fitted results (lines) of (a) PPy/ClO₄, (b) PPy/pTS, and (c) PPy/mixed film in 0.1M NaCl at 0.3 V measured after each CV.

polymer matrix. The effect of overoxidation has been observed on the polymer/electrolyte interface showing a decrease in double layer capacitance (Q_1). Similar decrease in the value of interfacial capacitance (Q_3) suggests the degradation of polymer/substrate (Pt) interface. The variation in the value of Q_3 is more pronounced for PPy/ClO₄ than for PPy/pTS and PPy/mixed systems, imitating the observed effect of overoxidation on polymer/electrolyte interface.

CONCLUSIONS

Polypyrrole degradation mechanism has been studied in PPy/ClO₄, PPy/pTS and PPy/mixed systems by considering the loss of electronic as well as electrochemical activity of the polymer after anodic polarization for a certain period of time. Cyclic voltammogram of the PPy samples gives the indication towards a successive loss in electrochemical activity with increasing overoxidation time for PPy/ClO₄. On the other hand, PPy/pTS and PPy/mixed system can withstand the degradation up to 20 min. After 20 min of application of overoxidation potential, the effect of degradation on electrochemical activity of PPy/pTS and PPy/

mixed system starts. The introduction of pitholes due to morphological loss on the surface of PPy/ClO₄ system gives rise to this degradation. In PPy/pTS system, the inhomogeneity of the surface is seen but is found to be resistant to overoxidation to a certain extent due to laminar stacking and tight structure. The disruption in the polymer chain is related to the formation of C—O bonds and/or the cross-linking between neighboring polymer chains due to overoxidation. The cauliflower morphology in PPy/ClO₄ system allows the nucleophile OH⁻ to readily interact with polymer chain at the surface and in the pores, however, the tight stacking in PPy/pTS system does not allow it to do so. This loss in morphological features of the PPy films is also seen in the decrease of double layer capacitance (Q_1) at the polymer/electrolyte interface and the interfacial capacitance (Q_3) at the polymer/substrate (Pt) interface. PPy/mixed system shows better redox activity than its parent counterparts because it has inherited strength from PPy/pTS and higher surface area/redox capability from PPy/ClO₄. A mixed organic-inorganic dopant anion system shows the improved stability and higher redox activity by inheriting the benefit from both counter anions.

Table I. Parameter Values Obtained from the Degradation Process of the Polypyrrole Using Equivalent Circuit as Described in Figure 9(c)

Sample	Time/min	R_1 (Ω)	Q_1 ($F S^{n-1}$)	β_1	R_2 (Ω)	Q_2 ($F S^{n-1}$)	β_2	Q_3 ($F S^{n-1}$)	β_3	R_3 (Ω)
PPy/CIO ₄	0	22.6	3.18×10^{-05}	0.672	44.2	2.66×10^{-03}	0.993	8.42×10^{-03}	0.491	50.7
	5	21.9	1.72×10^{-05}	0.447	193	4.80×10^{-03}	0.936	2.90×10^{-03}	0.786	132
	10	22.9	6.62×10^{-06}	0.936	198	4.55×10^{-03}	0.957	2.61×10^{-03}	0.885	142
	20	20.2	5.07×10^{-06}	0.641	430	2.38×10^{-03}	0.806	5.86×10^{-04}	0.852	169
	40	20.0	1.35×10^{-06}	0.769	673	9.88×10^{-04}	0.726	7.72×10^{-06}	0.526	369
	60	20.3	9.73×10^{-07}	0.776	4881	3.63×10^{-04}	0.643	7.56×10^{-07}	0.817	778
PPy/pTS	0	17.9	3.34×10^{-03}	0.540	212	5.22×10^{-03}	0.967	2.70×10^{-08}	0.867	215
	5	18.3	1.21×10^{-03}	0.818	225	3.89×10^{-03}	0.995	1.66×10^{-08}	0.920	221
	10	17.9	4.36×10^{-03}	0.422	313	5.51×10^{-03}	0.979	6.64×10^{-09}	0.990	352
	20	17.1	1.46×10^{-03}	0.841	328	3.63×10^{-03}	0.992	8.92×10^{-09}	0.968	365
	40	19.7	2.56×10^{-03}	0.227	329	5.14×10^{-03}	0.990	3.07×10^{-09}	0.991	384
	60	20.0	3.28×10^{-03}	0.148	388	4.36×10^{-03}	0.971	1.98×10^{-09}	0.991	893
PPy/mixed	0	19.0	1.25×10^{-03}	0.832	45.6	3.62×10^{-03}	0.979	2.67×10^{-06}	0.739	124
	5	18.0	1.21×10^{-03}	0.873	52.0	3.99×10^{-03}	0.987	1.55×10^{-06}	0.785	126
	10	18.0	1.13×10^{-03}	0.889	53.1	4.10×10^{-03}	0.987	1.36×10^{-06}	0.777	127
	20	20.0	1.17×10^{-03}	0.898	58.2	3.98×10^{-03}	0.990	9.69×10^{-07}	0.821	138
	40	17.0	1.19×10^{-03}	0.915	64.3	3.72×10^{-03}	0.983	9.60×10^{-07}	0.810	148
	60	19.0	1.15×10^{-03}	0.873	122	3.73×10^{-03}	0.988	3.37×10^{-07}	0.866	163

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