

Synthesis of Poly(3-methylthiophene) in the Presence of 1-(2-Pyrrolyl)-2-(2-thienyl) Ethylene by Electropolymerization

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In this study, the electropolymerization of 3-methylthiophene (3-MT) was performed in the presence of a catalytic amount 1-(2-pyrrolyl)-2-(2-thienyl) ethylene (PTE) by cyclic voltammetry in acetonitrile as a solvent and lithium perchlorate as the electrolyte on a glassy carbon (GC) electrode. First, PTE was synthesized *via* the Wittig reaction. The addition of a catalytic amount of PTE during the electropolymerization of 3-MT changes the cyclic voltammograms such that the analysis of cyclic voltammograms of poly(3-MT) shows a considerable increase in the electroactivity and redoxability. Furthermore, the presence of PTE during the electropolymerization of 3-MT increases the polymerization rate. The CV measurement of the electron transfer ferro/ferricyanide redox system using different modified GC electrodes shows that the rate of charge transfer for poly(3-MT) in the presence of PTE is greater than that of poly(3-MT) alone. The conductivity of the obtained polymers was determined by electrochemical impedance spectroscopy (EIS) in 3.5% NaCl (w/v) solutions. With the application of Zview(II) software to the EIS, we estimate the parameters of the proposed equivalent circuit, based on a physical model for the electrochemical behavior of coatings on the GC electrode, to be 15739 ohm cm² for the charge transfer resistance (R_{ct}) for poly(3-MT) alone and 9700 ohm cm² for poly(3-MT) in the presence of PTE. Thus, the film of poly(3-MT) formed in the presence of PTE is more conductive.

Keywords: Electropolymerization, Poly(3-methylthiophene), Conducting polymer, Cyclic voltammetry, Impedance technique

INTRODUCTION

In recent years, heterocycle-based conjugated polymers such as polythiophenes (PThs), polypyrroles (PPys), and their derivatives have attracted significant attention as an important class of electrically conductive polymers due to their good stability, high conductivity, and easy preparation [1]. Application of these polymers include light-emitting diodes [2], electrochromic [3] and electronic devices, battery

electrodes [4-6], field-effect transistors [7], sensors [8,9], plastic photovoltaic devices [10] and metal protection against corrosion [11-13].

The discovery of soluble and fusible poly(3-alkylthiophenes) in 1987 has further promoted interest in these materials for their promising technological application. Most of the previous work regarding PThs has been devoted to the study of the physicochemical and electrical properties of these polymers and to the exploration of new monomers. The chemistry of the polymerization of thiophene and its derivatives has, however, received little attention. PThs and

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poly(3-alkylthiophenes) can be prepared by chemical or electrochemical methods. Among these methods, electrochemical techniques are particularly appropriate for controlled synthesis of these compounds and for the isolation of a well-defined oxidation state [14]. The preparation, characterization and application of electrochemically active, electronically conjugated polymeric systems are still in the foreground of research activity in electrochemistry [15].

However, these polymers decompose readily at high potentials, which may result in poor polymer quality [16]. Therefore, one of the most important challenges in this area is lowering the required potential for the preparation of conductive polymers by the electropolymerization method [14,17]. In our previous work, the electropolymerization of pyrrole and N-methyl pyrrole was investigated in the presence of 1-(2-pyrrolyl)-2-(2-thienyl) ethylene (PTE) and 2-(2-thienyl) pyrrole (TP) as a derivative of pyrrole and thiophene by cyclic voltammetry under different conditions. That study showed a considerable increase in the electroactivity and redoxability of pyrrole and N-methyl pyrrole [17-19].

In the present research, we investigate the effect of PTE on the electropolymerization of 3-methylthiophene (3-MT). In order to observe this effect, at first we performed separately the electropolymerization of 3-MT and PTE, then we studied the influence of a catalytic amount of PTE on poly(3-MT). For complementary experiments and confirmation of the obtained results from cyclic voltammograms of the electropolymerization, the conductivity was measured using electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

Materials

Solvents were purified and dried as previously described [20]. 3-MT was purchased from Merck and purified prior to use. Pyrrole-2-carbaldehyde was purchased from Fluka and recrystallized in petroleum ether (50-70 °C). 2-Chloromethyl thiophene was prepared according to previously published methods [21].

Synthesis of 1-(2-Pyrrolyl)-2-(2-thienyl) Ethylene

PTE was prepared by the Wittig reaction as previously published [17]. In summary, 2-(thienyl) methyltriphenyl

phosphonium chloride (2.92 g, 22 mmol) was added under nitrogen to a stirred suspension of sodium hydride in oil 60% (0.88 g, 22 mmol) and 150 ml toluene and the mixture was stirred at room temperature for 5 min. Pyrrole-2-carbaldehyde (1.9 g, 20 mmol) was then added to the solution of the ylide, the reaction mixture was heated at 80-85 °C for 6 h, then cooled to the room temperature and filtered. The organic layer was washed with water, dried over magnesium sulfate and evaporated under reduced pressure to leave a solid.

The obtained crude compound was purified by chromatography from Merck Kieselgel 60 using dichloromethane-petroleum ether (50-70 °C, 2:1 v/v) as the eluent; yield (42%); m.p.: 141-143 °C; IR (KBr): 3400, 1625, 1415, 1115 cm^{-1} ; ^1H NMR (CDCl_3 , TMS), δ : 6.1-7.3 (m, 9H); MS (EI, 70 eV) m/z (%): 175 (100%), 174 (51.2%), 142 (15%), 77 (15.1%), 51 (23.1%).

Electropolymerization Method and Conductivity Measurements

The electrochemical polymerization was carried out using a digital potentiostat/galvanostat (Autolab PGSTAT 30). A glassy carbon (GC) disk (2 mm ϕ diameter) was used as the working electrode in the cyclic voltammetry experiments. In each case, a platinum wire was used as a counter electrode and Ag/AgCl was employed as a reference electrode. Acetonitrile was distilled over P_2O_5 and lithium perchlorate (0.1 M, Fluka) was used as an electrolyte directly. The electropolymerization of 3-MT (0.01 M) in 0.1 M LiClO_4 /acetonitrile electrolyte was performed over potential range of -0.3 to 1.6 V vs. Ag/AgCl at a scan rate 50 mV s^{-1} . Similar conditions were used for the electropolymerization of 3-MT (0.23 M) in the presence of PTE (0.0023 M). To study the electron transfer by cyclic voltammetry, we used 1 mM ferro/ferricyanide (Merck) in the 1 M H_2SO_4 at a 50 mV s^{-1} scan rate.

As the electropolymerization proceeded, a black polymer film appeared on the electrode surface. After 15 scans, the GC electrode containing the polymer film was taken out of the electrochemical cell and was washed with acetonitrile.

For the EIS measurements, the AC frequency range extended from 100 kHz to 10 mHz, with a 10 mV peak-to-peak sine wave for the excitation signal. The real and imaginary components of the EIS in the complex plane were analyzed using Zview software (version 2) to estimate the

parameters of the equivalent electrical circuit. A computer-controlled potentiostat (PARSTAT 2263, EG&G) was used for EIS measurements.

RESULTS AND DISCUSSION

Electrochemical Synthesis of Polymers

Figure 1 shows a typical cyclic voltammogram of the electropolymerization of 3-MT. During the electropolymerization of 3-MT, an anodic peak is observed due to the oxidation of 3-MT in the first scan at *ca.* 1350 mV *vs.* Ag/AgCl. As the electropolymerization proceeds, an anodic peak current appears due to the oxidation of poly(3-MT) in the second scan at *ca.* 600 mV *vs.* Ag/AgCl, during which the peak current also increases and the black polymer film forms on the electrode surface. After 15 scans and washing the GC electrode containing the polymer film, cyclic voltammograms of the resulting polymer in the range of -300 to 1200 mV *vs.* Ag/AgCl at various scan rates demonstrate semi-reversible behavior (Fig. 2).

The electrochemical oxidation of PTE with a potential scan range of -300 to 1000 mV *vs.* Ag/AgCl is shown in Fig. 3. During the first scan, we see two maxima for E_{pa} , 570 and 700 mV *vs.* Ag/AgCl resulting from the oxidation of PTE. However, from 1000 to 400 mV *vs.* Ag/AgCl, no maxima are observed, indicating an irreversible reaction. After the first reverse scan, the new cathodic and anodic peak currents increase continuously with successive potential scans. The build-up of the electroactive polymeric product, polyPTE, from the oxidation process on the surface of the electrode, is observed to have an ionic structure. In Fig. 4, the repetitive cyclic voltammograms of polyPTE at various scan rates are illustrated with no fluctuation in the anodic and cathodic peak currents (i_{pa} and i_{pc} , respectively) of the polymer, indicating the electroactivity and stability of polyPTE.

In the first scan of the electrochemical oxidation of 3-MT in the presence of the PTE (0.23 M:0.0023 M), hereafter referred to as 3-MT-PTE, an anodic peak appeared at *ca.* 570 and 700 mV *vs.* Ag/AgCl, due to the oxidation of PTE, as this anodic peak was absent without PTE (Fig. 5), and the anodic peak current, resulting from the oxidation of formed polymer, increases more rapidly in the presence of PTE than without PTE. After washing the GC electrode with the polymer film,

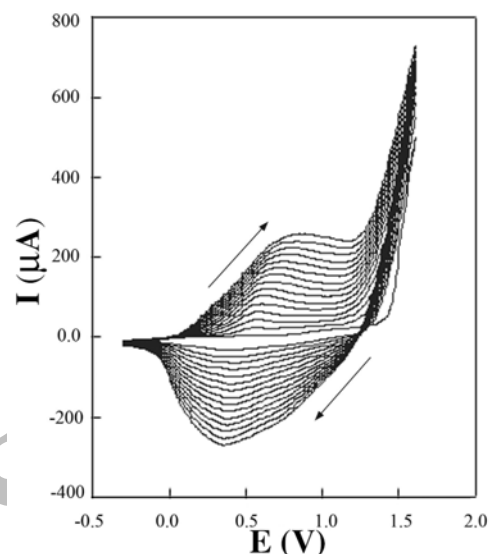


Fig. 1. Cyclic voltammograms of 0.01 M 3-MT in 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte at a scan rate of 50 mV s^{-1} *vs.* Ag/AgCl.

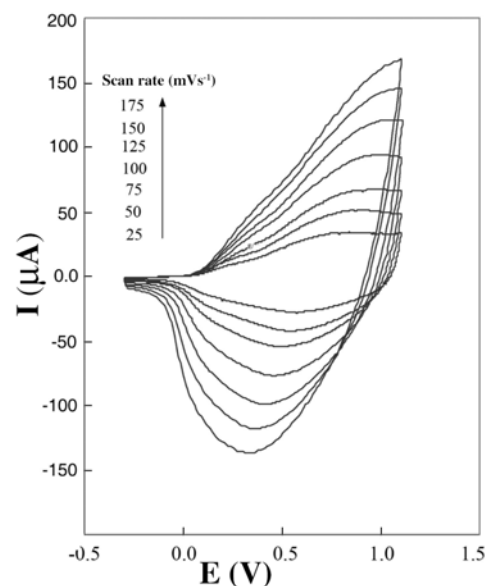


Fig. 2. Cyclic voltammograms of poly(3-MT) in 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte at various scan rates.

the cyclic voltammograms of the polymer at various scan rates show good reversible behavior (Fig. 6).

Figure 7 shows the plots of the cathodic peak currents *vs.*

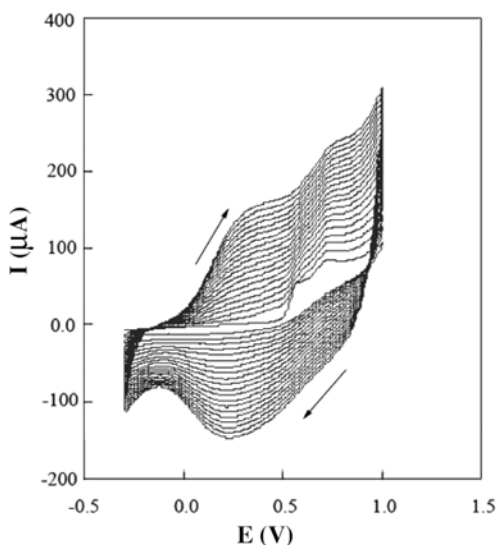


Fig. 3. Cyclic voltammograms of 0.01 M PTE in 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte at a scan rate of 50 mV s^{-1} vs. Ag/AgCl.

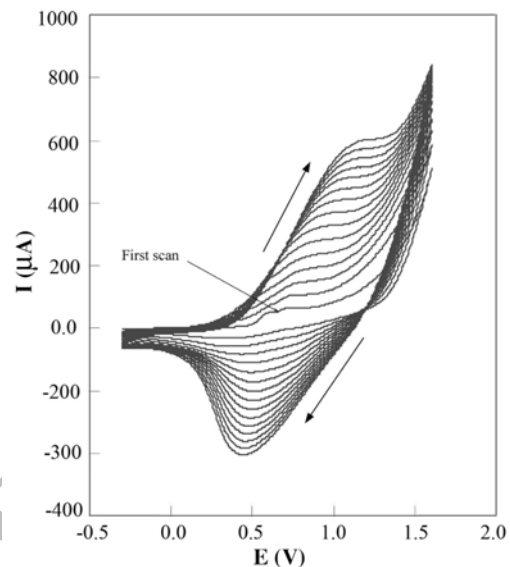


Fig. 5. Cyclic voltammograms of 3-MT-PTE (0.23 M: 0.0023 M) in 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte at a scan rate of 50 mV s^{-1} vs. Ag/AgCl.

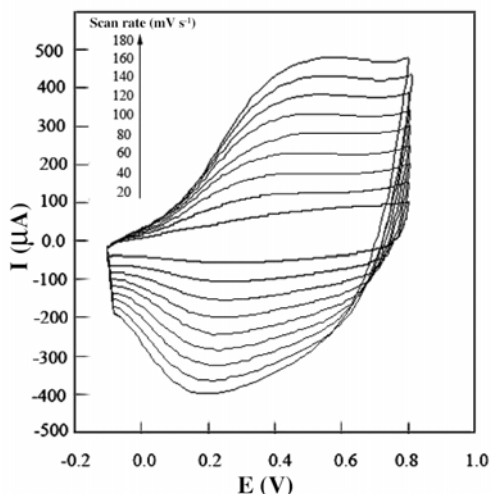


Fig. 4. Cyclic voltammograms of poly(PTE) in 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte at various scan rates.

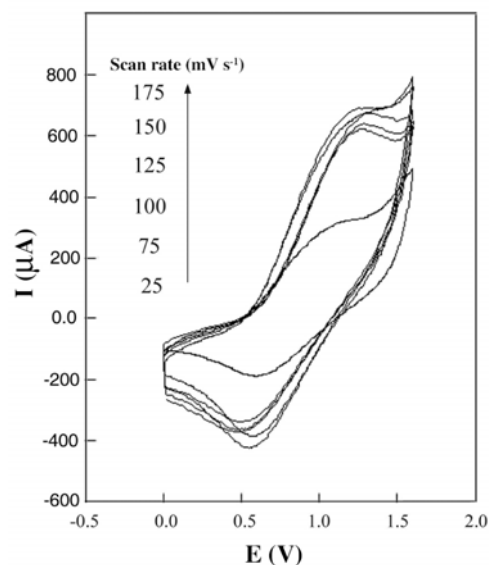


Fig. 6. Cyclic voltammograms of poly(3-MT-PTE) in 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte at various scan rates.

the number of cycles during the electropolymerization of 3-MT in the presence and absence of PTE and for the electropolymerization of PTE. Introducing this small amount of PTE to the electropolymerization system leads to a great increase in the rate of electropolymerization.

Figure 8 shows that the variation of the cathodic and anodic peaks for poly(3-MT) and polyPTE vs. the scan rate is linear, although this behavior is not observed for poly(3-MT-PTE). The ΔE_p of poly(3-MT-PTE) is calculated from Figs. 2 and 6. Because of the significant decrease in ΔE_p , from 0.77 V

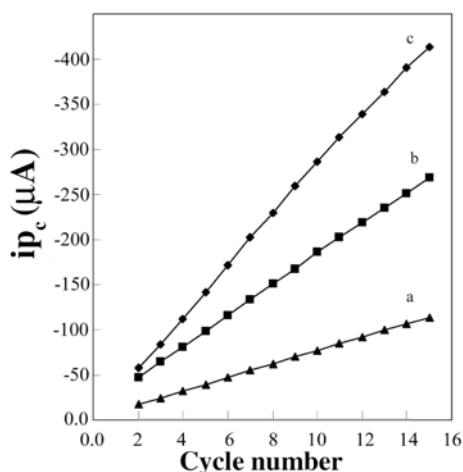


Fig. 7. Plots of cathodic peak current vs. the number of cycles for (a) PTE, (b) 3-MT and (c) 3-MT-PTE.

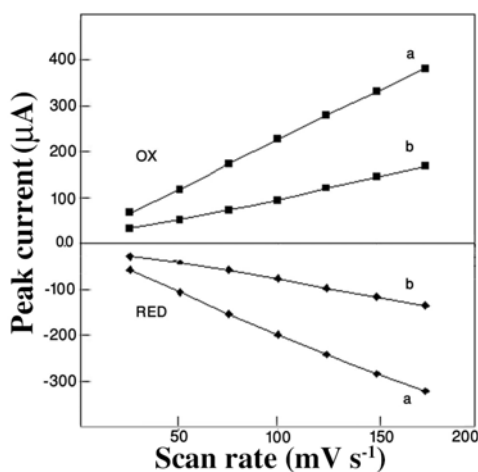


Fig. 8. Plots of anodic and cathodic peak currents vs. scan rates for (a) poly(PTE), (b) poly(3-MT).

for poly(3-MT) to 0.5 V for poly(3-MT-PTE), the electrochemical behavior of poly(3-MT-PTE) varies greatly as a result of the presence of PTE in the electropolymerization of 3-MT.

As can be seen in the cyclic voltammograms of 3-MT-PTE (Fig. 5), the oxidation potential of PTE is less than that of 3-MT. PTE is oxidized and the active sites (cation radicals) are created, causing these active sites to polymerize 3-MT. At this point, the amount of PTE is catalytic, and we can conclude

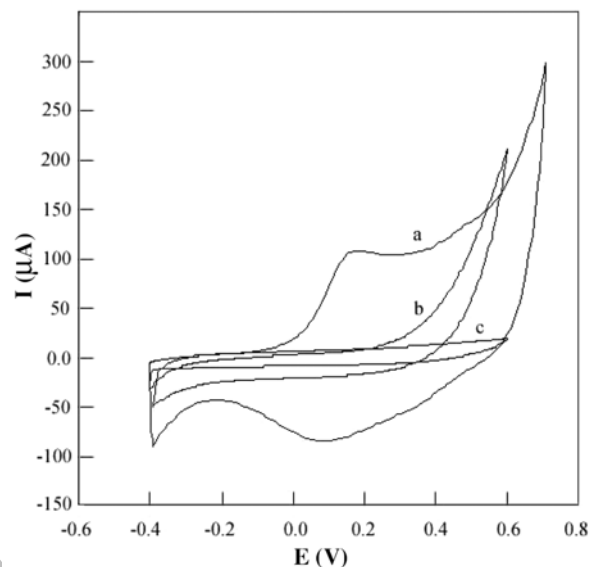


Fig. 9. Cyclic voltammograms of (a) poly(PTE), (b) poly(3-MT-PTE), and (c) poly(3-MT) using a GC electrode in 1 M H_2SO_4 and 1 mM $\text{Fe}(\text{CN})_6^{4-/3-}$ redox system at 50 mV s^{-1} scan rate.

that the resultant polymer is not a blending of two individual polymers. Thus, it seems that the chain of poly(3-MT) contains PTE in a random form.

Further cyclic voltammetry experiments were performed to assess the effect of PTE on the poly(3-MT) film in the transfer of electrons in the ferro/ferricyanide redox system. Figure 9 shows the CV of the electron transfer ferro/ferricyanide redox on different modified GC electrodes with poly(3-MT), poly PTE, and poly(3-MT-PTE). This figure indicates that the electron transfer of ferro/ferricyanide for poly(3-MT) in the presence of PTE is easier than that for poly(3-MT) alone because the conductivity of poly(3-MT) significantly increases in the presence of PTE.

Evaluation of Conductivity and Electrochemical Behavior by EIS

EIS is a measurement technique that allows for a wide variety of coating evaluations and is an effective in probing the interfacial properties of surface-modified electrodes. EIS has been used to characterize the electrical properties of the electropolymerized films, as well. Nyquist plots are constructed and the appropriate equivalent circuit model is

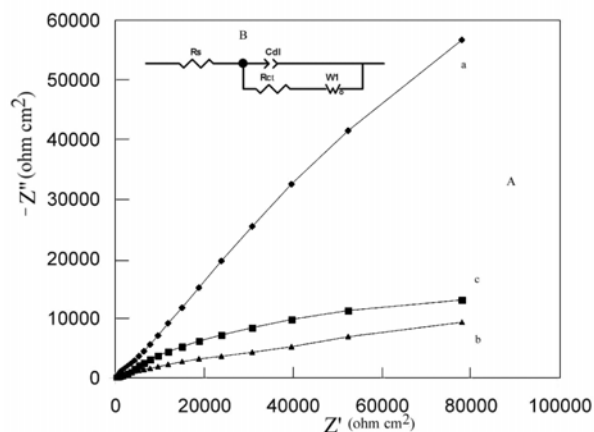


Fig. 10. A) Nyquist plots for: (a) poly(PTE), (b) poly(3-MT-PTE), and (c) poly(3-MT) in 3.5% (w/v) NaCl solution. B) Proposed equivalent circuit.

used to correlate the impedance with the capacitance and resistance of the film. Figure 10 shows Nyquist plots of (a) Pth, (b) poly(T-PTE) and (c) poly(PTE) coated on GC electrodes in 3.5% NaCl solution. These Nyquist plots are characterized by two regions: a depressed semicircle at high frequencies associated with charge transfer (R_{ct}) at the polymer/solution interface, note the decrease in the diameter.

A second region consists of a straight line, as shown in Fig. 10, indicating a diffusion-controlled process at the electrode, known as the Warburg process. The electrochemical behavior of thiophene changes in the presence of PTE. Based on Randles equivalent circuit model, with a modification that takes into account the presence of porous interfaces on the electrodes, electrical parameters were calculated using Zview software. All fitting results are presented in Table 1.

According to these results, we observe a decrease in the charge transfer resistance (R_{ct}) value for poly(3-MT) in the presence of PTE compared to poly(3-MT) alone. The R_{ct} values obtained for poly(3-MT) alone and poly(PTE) are 15739 and 3751 ohm cm^2 , respectively. However, for poly(3-MT) formed in the presence of PTE, this value decreases to 9700 ohm cm^2 , indicating that the poly(3-MT-PTE) film is more conductive. On the other hand, in the presence of PTE, the value of the capacitance of the electrical double layer (C_{dl}) goes up from 2.35 to 14.4 $\mu\text{F cm}^{-2}$, which can be attributed to an increase in the electrode surface area. This change in the capacitance strongly supports the hypothesis of the incorporation of PTE in the poly(3-MT) film. Furthermore, these results support the CV results in Fig. 9. In the presence of PTE, the conductivity of poly(3-MT) is improved. The increase C_{dl} for poly(3-MT-PTE) compared to poly(3-MT) alone confirms the improved electron transfer in the ferro/ferricyanide redox system using poly(3-MT-PTE), as shown in Fig. 10.

CONCLUSIONS

Our results show a considerable increase in the electroactivity, redoxability, and the rate of polymerization due to the addition of a catalytic amount of PTE during electropolymerization of 3-MT. In addition, CV measurement of the electron transfer ferro/ferricyanide redox system using different modified GC electrodes shows that the rate of charge transfer for poly(3-MT-PTE) is greater than that of poly(3-MT) alone.

The resistance of poly(3-MT) alone is much greater than that in the presence of PTE, indicating that the poly(3-MT-PTE) film is more conductive. Moreover, the presence of PTE

Table 1. Impedance Data Obtained by Simulation of the Various Membranes on the GC Electrode^a

Sample	C_{dl}^b ($\mu\text{F cm}^{-2}$)	n_{dl}	R_{ct}^c ($\Omega \text{ cm}^2$)	W1-R ($\Omega \text{ cm}^2$)	W1-T ($\Omega^{-1} \text{ cm}^{-2}$)	W1-P
PolyPTE	153.3	0.80578	3751	0.20393	1.7267E-8	0.31395
poly(3-MT-PTE)	14.4	0.58947	9700	7071	3.597	0.29034
Poly(3-MT)	2.35	0.56667	15739	9.228E5	243.2	0.65877

^aIn 3.5% NaCl. ^bCapacitance through the double layer. ^cCharge transfer resistance.

in this membrane increases the capacitance of the electrical double layer and probably increases the electrode surface area, as well, which is supported by the good agreement between the CV and EIS results.

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