

Electrochemical Impedance Spectroscopic Study of Electrocoated Polythiophene and poly(2-methyl thiophene) on Carbon Fiber Microelectrode for Microcapacitor

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In this study, N-thiophene (T), and N-2 methylthiophene (MT) homopolymers were electrocoated on carbon fiber microelectrodes (diameter $\sim 7 \mu\text{m}$) by cyclic voltammetry within a potential range from 0.0 to 2.0 V with well – defined parameters. All the initial monomer concentrations (from 0.1 M to 1 M) were electrodeposited in 0.1 M sodium perchlorate (NaClO_4) / acetonitrile (ACN) solution and characterized by cyclic voltammetry (CV), ex-situ FTIR attenuated total reflectance spectroscopy (FTIR – ATR), and scanning electron microscopy (SEM). The electrochemical impedance spectroscopic measurements of polythiophene (PT) and poly (2-methyl thiophene) (PMT) were given comparatively. The existence of a capacitance behavior is shown by Nyquist, Bode magnitude, Bode-phase, Admittance plots relationship. The T-deposited electrode in the initial monomer concentration of 0.5 M exhibits high specific capacitance of 1.13 F g^{-1} , in comparison with a value of 6.35 mF g^{-1} for MT modified electrode in the initial monomer concentration of 0.2 M.

Keywords: Polythiophene, modified carbon fiber microelectrodes, electrochemical impedance spectroscopy.

1. INTRODUCTION

Numerous functionalized thiophenes have been synthesized in the past due to their favorable properties [1-3]. Generally, most thiophenes with functional groups suitable for immobilization of biomolecules (such as $-\text{NH}_2$ and $-\text{COOH}$) have been difficult to electropolymerise, because such functional groups exhibit substantial nucleophilicity and attack the radical cation intermediates formed during electropolymerization, hence inhibiting the polymerization process [4]. While Albery et al. reported the electropolymerization of thiophene - 3 - acetic acid in 1991 [5], a high oxidation potential ($\sim 1.6 \text{ V vs. Ag / Ag}^+$) and high monomer concentration were necessary to obtain a conducting

polymer. At low monomer concentrations, on the other hand, the electro-oxidative homopolymerization of thiophene-3-acetate is inhibited [6]. This problem can be avoided using post-polymerization functionalization since thiophene monomers with protected carboxyl acid group can be easily electropolymerized. This approach is a widely used method for the preparation of new electroactive organic systems with tunable electronic, electrochemical and spectroscopic properties [7, 8]. For example, Li, et al. synthesized thiophene bearing an activated ester group, N-succinimido thiophene-3-acetate, and obtained its homopolymer [9]. A disadvantage of the post-polymerization functionalization process is a potentially detrimental effect on the adherence of the polymer films to the electrode surface, which is of particular importance for electrochemical biosensing. As an alternative route, copolymerization of functionalized monomers with the corresponding unsubstituted heterocyclics was developed based on a copolymer of 3-(oxyalkyl)-thiophene bearing an aryl sulfonamide group with 3-methylthiophene used to immobilize amino-end modified DNA probes [10]. Nevertheless, this approach has the disadvantage of not having well defined binding sites on the obtained film.

Functional conjugated polythiophene, in which the electronic properties inherent to the π -conjugated systems are associated with new specific properties afforded by covalently attached functional groups, have been the focus of considerable attention during the past decade [11, 12]. Due to their unique electrical properties and their environmental stability, polythiophene has shown considerable promise for materials applications [13, 17]. The electrochemical behavior of PT derivatives depends strongly on the composition of the electrolytic medium. Although electrochemistry is generally performed in acetonitrile, other solvents have been employed. Due to their hydrophobicity, PTs present only a limited electroactivity in aqueous media [18]. Propylene carbonate leads to ill-defined voltammetric waves, probably because of their high viscosity which leads to a decrease of the heterogeneous electron-transfer rate [19].

High performance carbon fibers can be combined with thermoset and thermoplastic resin systems. Polyacrylonitrile (PAN) based carbon fibers are under continual development and are used in composites in order to produce materials of low density and greater strength. They are used for weaving, braiding and filament winding applications, unidirectional tapes and prepreg tow for fiber placement having excellent creep, fatigue resistance, high tensile strength and stiffness characteristics [20]. The application of a polymeric / co-polymeric "interface", acting as a coupling agent, can improve the interfacial properties between reinforcing carbon fibers and the polymeric matrix [21-23]. Previously, there have been quite number of studies concerning the conducting polymer's synthesis [24], characterization [25-27], and their sensor applications [28, 29] and electrochemical impedance spectroscopy [30-32].

Among the numerous conducting polymers (CPs), polythiophene has rapidly become the subject of considerable interest. From a theoretical viewpoint, PT has been often considered as a model for the study of charge transport in CPs with a non degenerate ground state, while on the other hand, the high environmental stability of both its doped and undoped states together with its structural versatility have led to multiple developments aimed at applications such as conductors, electrode materials, and organic semiconductors [33, 34]. It is, in fact, quite difficult to take into account all the direct and indirect effects on the properties of the resulting product, exerted by the steric and electronic

characteristics of the substituent group (s) at the monomer thiophene ring. Challenging tasks can be identified, in this respect, in the investigation of the relations between, on the one side, monomer formulation and electropolymerization conditions and, on the other side, molar mass distribution and electrical properties of the resulting polymer [35-37]. The most stable PT film which also show slow relaxation (lowest relaxation time) was obtained using a galvanostatic technique in acetonitrile solvent with tetra butyl ammonium hexafluoro phosphate (TBAPF₆) as supporting electrolyte at 5 °C [38].

Electrochemical impedance spectroscopy (EIS) is an effective tool to validate the capacitance behavior. EIS has a well-developed theoretical background and established experimental procedures so that it serves as a convenient and readily available technique for obtaining important electrochemical information, such as electrolyte resistance, charge transfer resistance, and Faradaic capacitance [39-41].

All these features give reasons for our interest to study the comparison of electrochemistry of PT and PMT thin films by EIS, which is a powerful tool to study charge transfer, ion diffusion and capacitance of conducting polymer-modified electrodes [42]. EIS has been used to study polyoctylthiophene [43, 44] and poly (2, 5-di-(2-thienyl)-thiophene) [45] films in organic media, polybithiophene [46], poly(3,4-ethylenedioxythiophene) [47, 48], polythiophene [49] and more recently, poly(3-methylthiophene) [50] films in aqueous media. In this work, the effect of monomer concentration on the electrochemical properties of PT and PMT thin films were analyzed using EIS techniques.

2. EXPERIMENTAL PART

2.1. Materials

All chemicals were high grade reagents and were used as received. Thiophene (T, >99%), was obtained from Fluka. Sodium perchlorate (NaClO₄) and acetonitrile (ACN) were from Riedel-De Haen. PAN based Carbon fibers, Sigrafil HM 48 A 48K (Sigri Carbon, Meitingen, Germany) containing 320.000 single filaments in a roving were used as the working electrodes (Modulus of elasticity: 350000 MPa, tensile strength: 3200 MPa, Elongation at Break: 0.94 % and filament diameter: 6.63065 μm). A branch CFME was used as a working electrode. All electrodes were prepared using about 50 fibers (diameter ~7 μm) attached to a copper wire with a Teflon tape. Only 0.8 ± 0.2 cm of the carbon fiber was dipped length (~1 cm) into the solution to keep the electrode area constant (~0.11 cm²).

2.2. Instrumentations

Electrochemical impedance spectroscopy (with supplied Power Sine software package) and cyclic voltammograms of the polymer coated CFMEs were performed on a Princeton Applied Research (PAR) Parstat 2263-1 potentiostat, which is a self – contained unit that combines potentiostatic circuitry with phase sensitive detection.

The potentiostat was connected to a Faraday cage (BAS Cell Stand C₃). A three - electrode system employing CFME as the working electrode, platinum wire as counter electrode, and Ag wire as a reference electrode (calibrated against ferrocene). Thin films of homopolymers, electrocoated onto carbon fiber surface were analyzed by FT-IR reflectance spectrophotometry (Perkin-Elmer, Spectrum One, with Universal ATR attachment with a diamond and ZnSe crystal C70951). Electrocoated fibers were analyzed by Scanning electron microscopy using a SNE-3000M Mini-SEM, Scanning electron microscope (SEC GmbH, South Korea). Average values of the increase in thickness were obtained from SEM images taking into account the diameter of the uncoated fiber.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetric investigations: Electropolymerization of T and MT on CFME

Multisweep cyclic voltammogram of 0.5 M T in 0.1 M NaClO₄ / ACN on CFME show an increasing current density with each cycle ($E_{pa} = 1.25$ V, $E_{pc} = 0.49$ V at 10th cycle), resulting in the formation of thin film of conducting polymer on CFME at a scan rate of 50 mV s⁻¹ and 10 cycle (charge density $q = 5.9$ C cm⁻²) (Fig.1a). Cyclic voltammogram (CV) of a polymer coated PT / CFME in monomer – free solution with different scan rates (0.1 M NaClO₄ / ACN) shows one oxidation peak at lower scan rate (25 mV s⁻¹) and corresponding reduction peak ($E_{pc} = 0.99$ V) (weak at higher scan rates) (Fig. 1b).

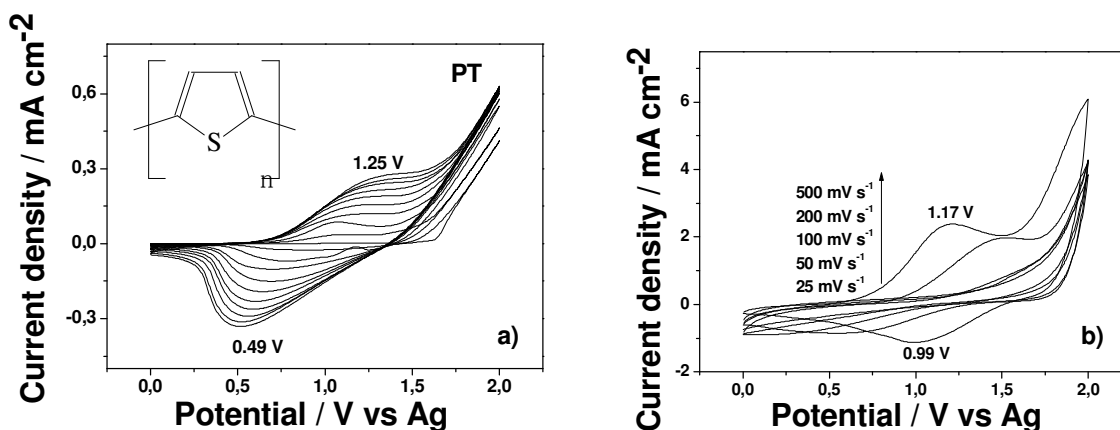


Figure 1. a) Cyclic voltammetry of electrogrowth of 0.5 M T in 0.1 M NaClO₄ / ACN; scan rate: 50 mV s⁻¹; scan number: 10 cycles on CFME (charge Q = 650.4 mC, charge density $q = 5.9$ C cm⁻²). Inset: PT: Polythiophene b) PT was obtained in monomer - free solution, cycled in different scan rates (25, 50, 100, 200 and 500 mV s⁻¹) in 0.1 M NaClO₄ / ACN.

CV of the electro - growth of 0.5 M MT in 0.1 M NaClO₄ / ACN with a scan rate of 50 mV s⁻¹ and 10 cycles on CFME is shown in Fig.2a (with a lower charge density (736.3 mC cm⁻²) compared to PT (5.9 C cm⁻²) and the CV of PMT / CFME cycled in monomer – free solution with different scan rates in 0.1 M NaClO₄ / ACN shows no clear oxidation and reduction peaks.

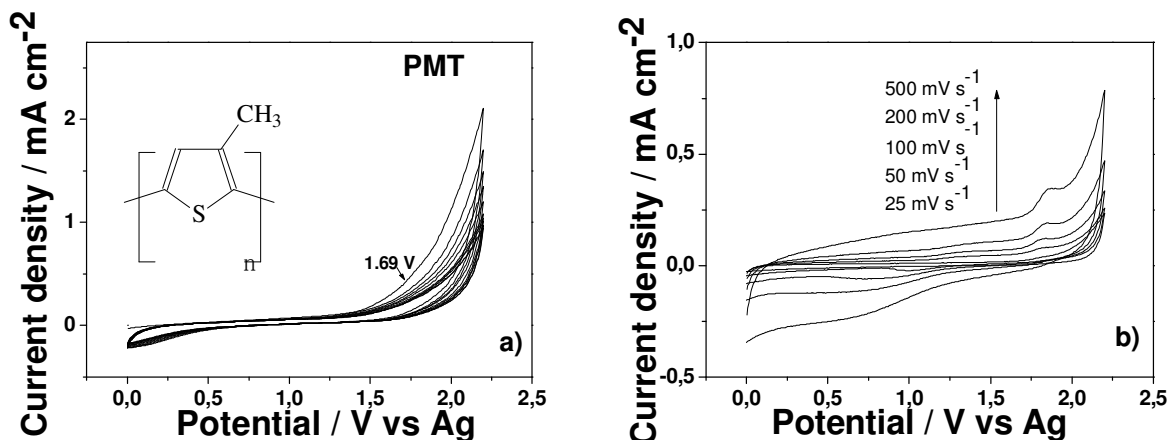


Figure 2. a) Cyclic voltammetry of electro-growth of 0.5 M MT in 0.1 M NaClO₄ / ACN; scan rate: 50 mV s⁻¹; scan number: 10 cycles on CFME (charge Q = 81.04 mC, charge density q = 736.7 mC cm⁻²) Inset: PMT: Poly(2-methyl thiophene) b) PMT was obtained in monomer - free solution, cycled in different scan rates (25, 50, 100, 200 and 500 mV s⁻¹) in 0.1 M NaClO₄ / ACN.

For electro-growth processes the electrodeposition charges for PT and PMT and anodic and cathodic current density ratios of PT were measured from the 10th cycles and redox parameters are summarized in Table 1. A regular and reversible growth was observed for PT and PMT homopolymers. Polymer deposition charges appeared to be more with increasing initial monomer concentrations. Reversibility of electro-growth of PT was better for 1 M concentration exhibiting I_a/I_c value of 0.92. However, irreversible oxidation of the monomer appears clearly on the 10 cycles followed by a nucleation loop for 4 different 2-methylthiophene initial monomer concentrations.

Table 1. Redox parameters of electro-growth of T and MT on CFME.

Initial monomer concentration / M	PT Charge / mC	PMT Charge / mC	I_{an} / I_{cat} (PT)
0.1	25.7	6.7	0.88
0.2	59.7	14.3	0.90
0.5	650.4	81.0	0.82
1.0	755.3	81.2	0.92

3.2. FTIR-ATR Measurements

The FTIR-ATR spectra of PT and PMT were obtained from the surface of the electrocoated CFMEs by reflectance measurements. Absorption bands of each spectrum are given in Fig. 3. There were several intensity peaks present in the range of 2800-3240 cm^{-1} , which can be attributed to the C-H stretching vibrations [51]. The peak around 1420 cm^{-1} may be ascribed to the methyl deformation of PMT. The absorption bands associated with C = C / C - C stretching vibration occurred near around 1630 cm^{-1} , which may be considered to arise predominantly from both endocyclic and exocyclic double bonds in the oxidized species of polyheterocyclics [52].

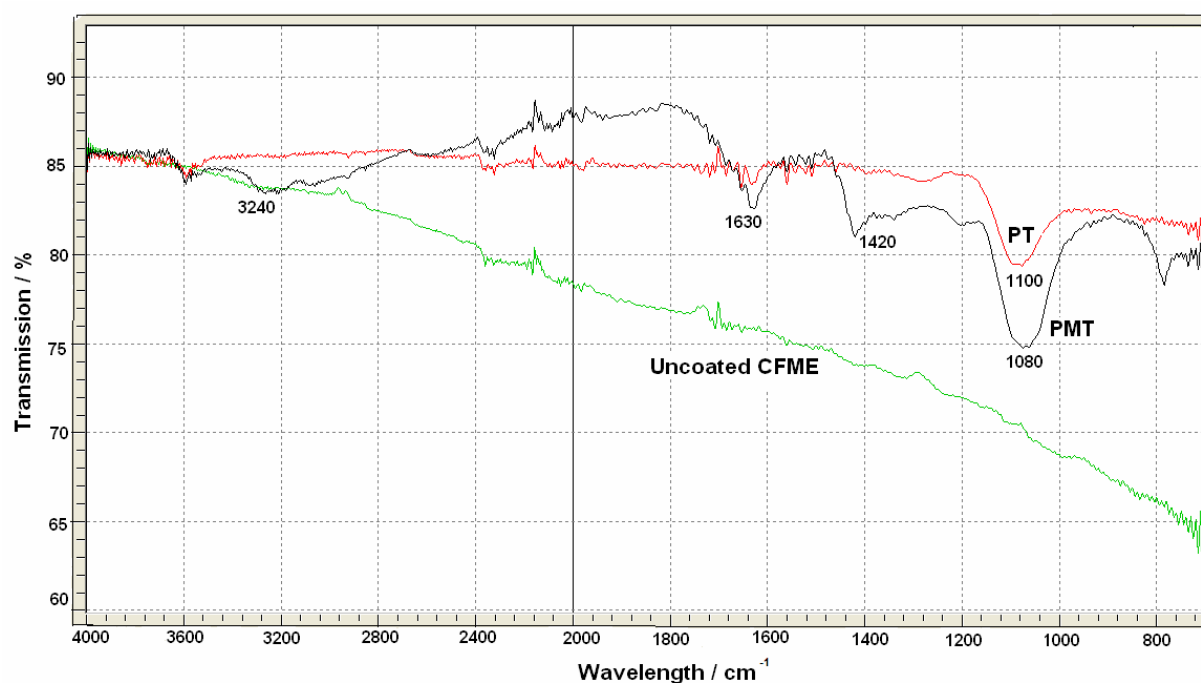


Figure 3. FTIR-ATR spectra of uncoated CFME, PT and PMT obtained in 0.1 M NaClO_4 / ACN. $[\text{T}]_0 = 0.5$ M, $[\text{MT}]_0 = 0.5$ M.

The strong peaks at 1100 cm^{-1} for PT and 1080 cm^{-1} for PMT could be due to vibration of counter ions included into the polymer from the electrolyte solution (ClO_4^-). The FTIR-ATR data clearly shows that the thiophene and 2-methylthiophene homopolymers can be coated onto carbon fiber surfaces. Additionally, depending on the extension of further oxidation of the resulting polymers doping by counter ions from supporting electrolyte (ClO_4^-) is also detectable from FTIR measurements [53].

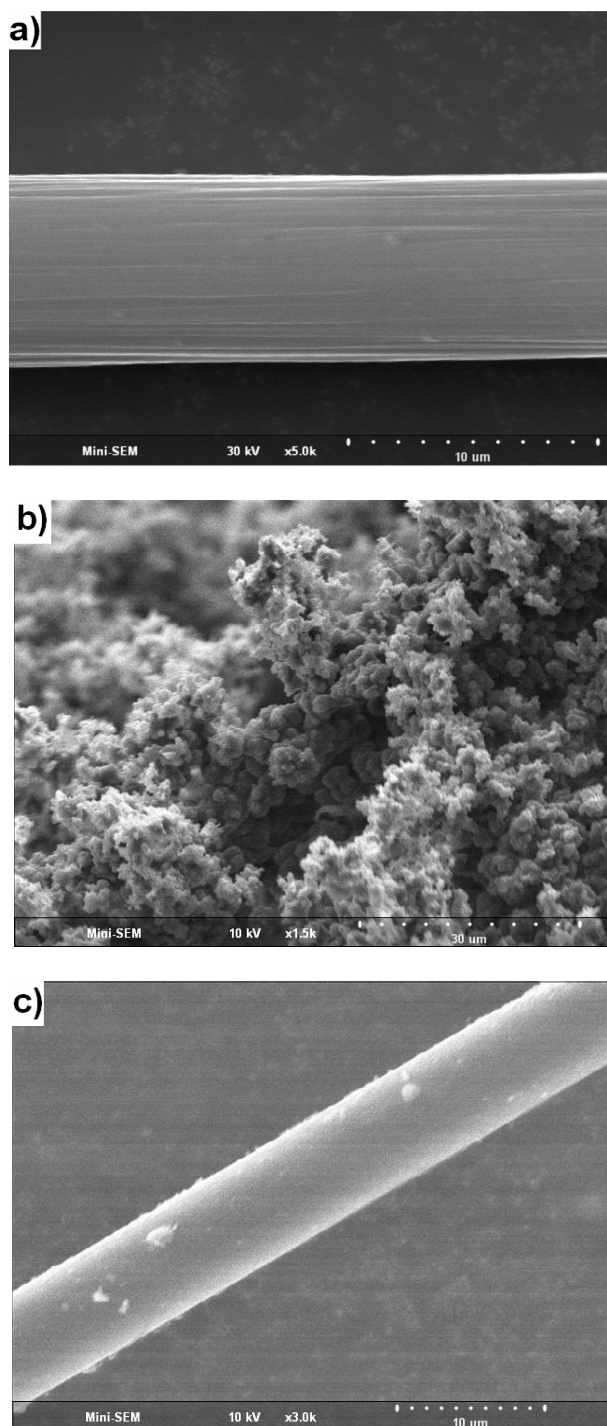


Figure 4. SEM images of a) Uncoated CFME, b) PT / CFME, c) PMT / CFME were given. Polymer films coated after 10th cycle is shown for comparison, in 0.1 M NaClO₄ / ACN at 50 mV s⁻¹. [T]₀= 0.5 M, [MT]₀= 0.5 M.

3.3. Morphological investigation by SEM

The morphology of uncoated CFME and PT and PMT electrocoated electrodes was investigated comparatively by scanning electron microscopy (SEM) for samples obtained by CV measurements with a scan rate of 50 mV s^{-1} to understand the surface structure (Fig.4). Acetonitrile leads generally to powdery deposits or to brittle films with conductivities typically comprised between 0.02 and 10 S cm^{-1} for PT and 0.1 and 50 S cm^{-1} for PMT [54, 55]. PTs are generally electrogenerated in the presence of small anions derived from strong acids such as ClO_4^- , PF_6^- , BF_4^- , and AsF_6^- , associated with sodium, lithium and tetra alkyl ammonium cations [56, 57]. The nature of the anion strongly affects the morphology [58] and electrochemical properties [59] of PTs prepared in acetonitrile. A partial crystallinity has been observed in PMT grown in acetonitrile with CF_3SO_3^- . Unlike thiophene, the electropolymerization of PMT in the presence of electrolytes containing NaClO_4 yields no or little polymer of low doping level and conductivity.

3.4. Electrochemical impedance spectroscopy (EIS)

The low frequency capacitance values from impedance spectroscopy were obtained from the slope of a plot of the imaginary component (Z_{im}) of the impedance at low frequencies versus inverse of the reciprocal frequency (f) (where $f = 0.01 \text{ Hz}$) using following equation [60]: $C_{\text{LD}} = -1 / 2\pi f Z_{\text{im}}$

Low frequency capacitance values of PT / CFME (C_{LF}) (for the scan rate of 50 mV s^{-1} during electro growth) were calculated for the initial monomer concentrations of 0.1 M , 0.2 M , 0.5 M and 1 M are 27.7 mF g^{-1} , 5.8 mF g^{-1} , 1.13 F g^{-1} and 0.98 mF g^{-1} , respectively. In contrast, low frequency capacitance values of PMT / CFME were calculated for the same initial monomer concentrations are 3.36 mF g^{-1} , 6.35 mF g^{-1} , 2.0 mF g^{-1} and 1.25 mF g^{-1} , respectively. They are not exactly comparable results with the initial monomer concentrations to low frequency capacitance values (Fig.5).

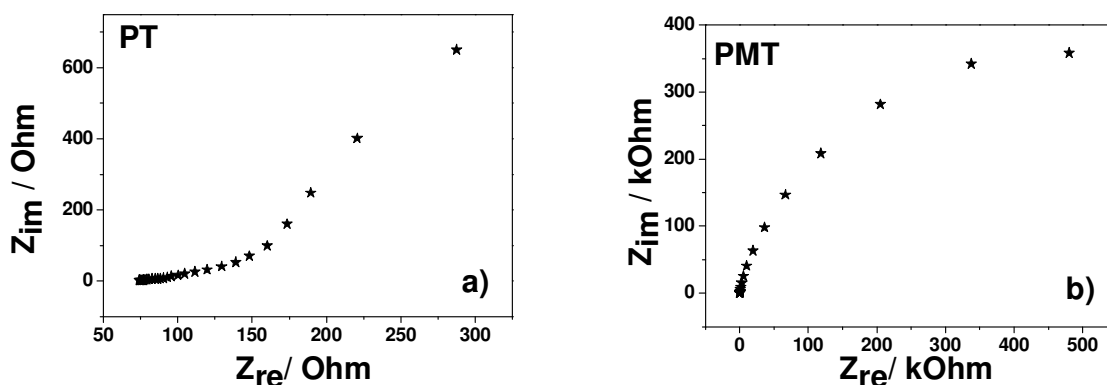


Figure 5. Nyquist plots of a) PT / CFME, and b) PMT / CFME. Polymer films coated after 10th cycle is shown for comparison. EIS measurements were made in $0.1 \text{ M NaClO}_4 / \text{ACN}$. $[\text{T}]_0 = 0.5 \text{ M}$, $[\text{MT}]_0 = 0.5 \text{ M}$.

Conducting polymers can be doped and dedoped rapidly to a high charge density; hence, they can be applied as active materials for supercapacitors. Higher energy densities can be achieved because changing occurs through very thin thickness from the nano to micro scale range. Taking into account the costs and compatibility of the materials, the modification of carbon fiber microelectrode by electrocoating of PT in 0.5 M ($C_{LF} = 1.13 \text{ F g}^{-1}$) for micro super capacitor applications seems to be a very attractive results compared to PMT in 0.2 M ($C_{LF} = 6.35 \text{ mF g}^{-1}$).

Bode-magnitude plot gives by extrapolating line to the log Z axis at $w = 1$ ($\log \omega = 0$) yielding the value of C_{dl} from the relationship: $|Z| = 1 / C_{dl}$ [61] (Fig.6).

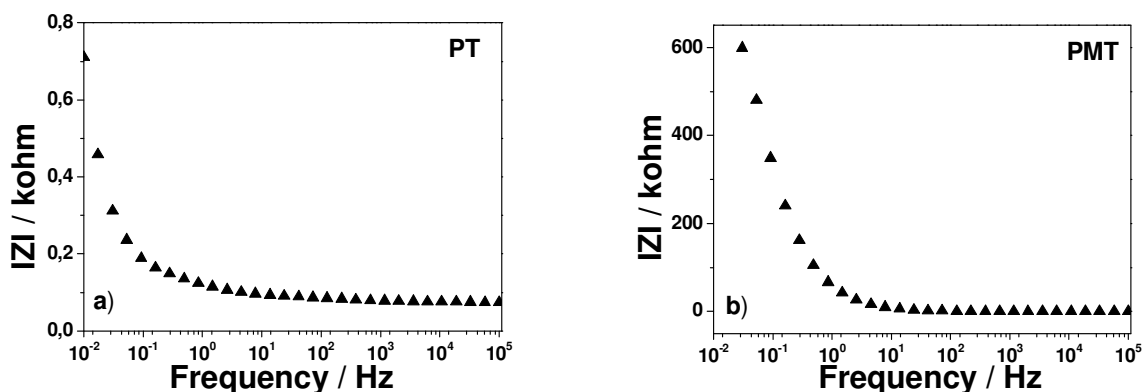


Figure 6. Bode-magnitude plot of a) PT / CFME, and b) PMT / CFME. Polymer films coated after 10th cycle is shown for comparison. EIS measurements were made in 0.1 M NaClO₄ / ACN. $[T]_0 = 0.5 \text{ M}$, $[MT]_0 = 0.5 \text{ M}$.

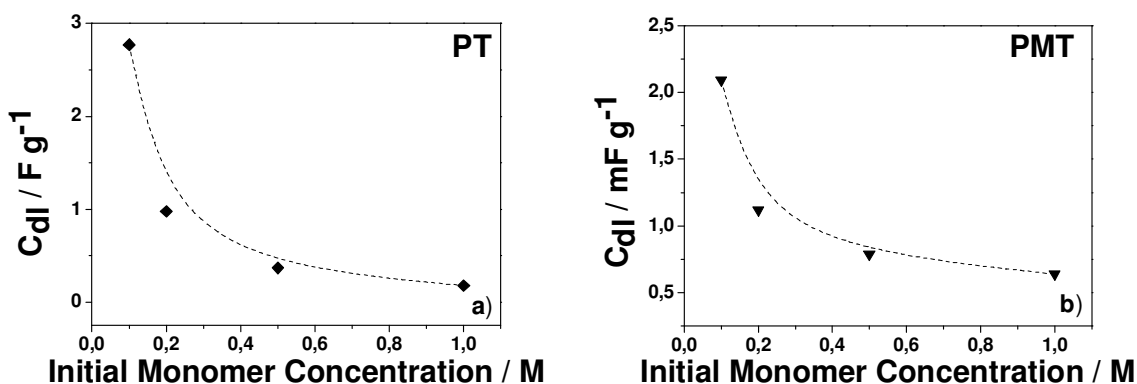


Figure 7. Initial monomer concentrations vs. Double layer capacitance (C_{dl}) for a) PT / CFME and b) PMT / CFME.

The highest C_{dl} values of 2.77 F g^{-1} for PT and 2.09 mF g^{-1} for PMT were obtained in 0.1 M NaClO₄ / ACN. These results were also performed in the lowest electrodeposition charge (25.7 mC for PT and 6.7 mC for PMT) (Fig.7).

Electrochemical impedance spectroscopy was performed to monitor the electrochemical behavior of the PT and PMT homopolymer electrodes. Bode phase angle, which is very close to 90° as observed in highly capacitive behavior (may be supercapacitors). Maximum phase angles were obtained as 78° and 79° at 10 Hz for PT and PMT, respectively (Fig.8). When the initial monomer concentration of PT / CFME increases from 0.1 to 1 M, maximum phase angles and frequency decrease gradually. For example, phase angles in the initial monomer concentration in 0.1, 0.2, 0.5 and 1 M for PT were obtained as 78° (at 10 Hz), 56° (at 1 Hz), 67° (1 mHz), 45° (1 mHz). Initial monomer concentration of PT increases from 0.1 M to 1 M, which destroys the homogeneity of electrode and therefore decreases the electron transfer resulting a lower charge storage ability and divergence from the capacitive line. That result supports the Bode-Magnitude plot since the thinner film presents a phase angle 78° for PT (electrodeposition charge, $Q = 25.7$ mC) and 79° for PMT ($Q = 6.7$ mC) at 10 Hz (near ideal capacitor) and the thick film with 10 cycles of PT shows a phase angle of 45° (smaller) ($Q = 755.3$ mC). However, the maximum phase angles are nearly constant 79° (at 10 Hz) for PMT.

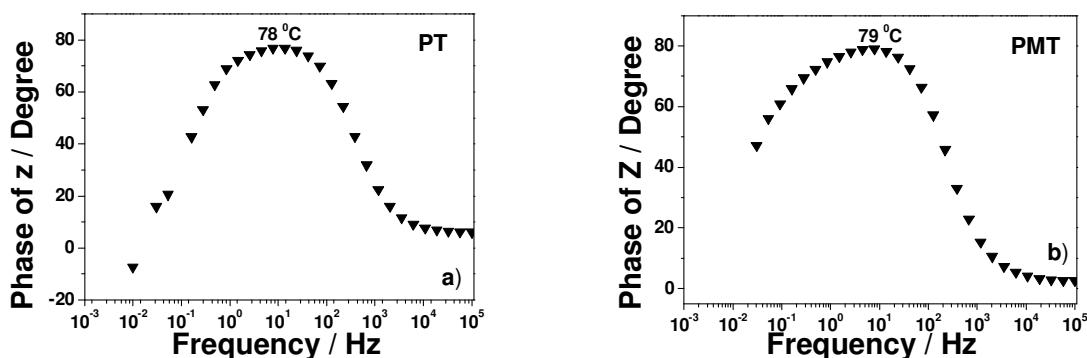


Figure 8. Bode phase plots of 0.1 M Thiophene and 2-methylthiophene electrocoated on a) PT / CFME, and b) PMT / CFME base electrode for 10 cycles in 0.1 M NaClO_4 / ACN at 50 mV s^{-1} . $[\text{T}]_0 = 0.1 \text{ M}$, $[\text{MT}]_0 = 0.1 \text{ M}$.

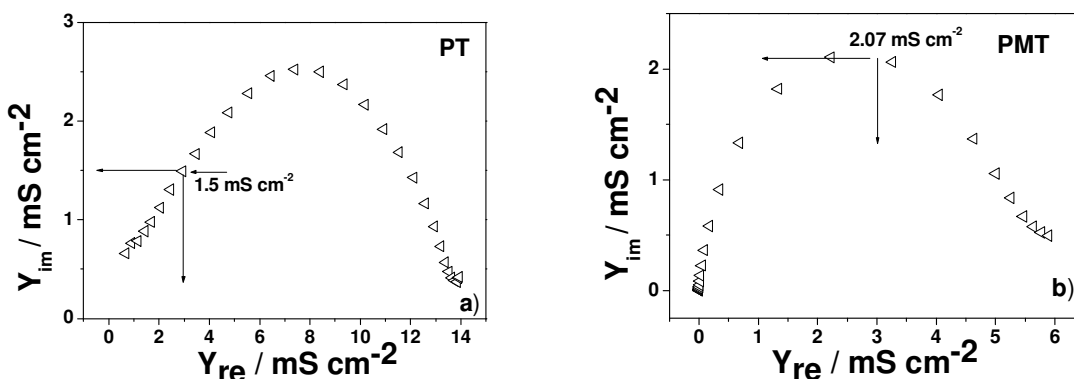


Figure 9. Admittance plots obtained from EIS measurements a) PT / CFME, and b) PMT / CFME base electrode for 10 cycles in 0.1 M NaClO_4 / ACN at 50 mV s^{-1} . $[\text{T}]_0 = 0.5 \text{ M}$, $[\text{MT}]_0 = 0.5 \text{ M}$.

PT / CF modified electrodes has the lowest conductivity according to the Admittance plot as shown in Figure 9. However, it has the highest resistance since Z' axis could be named as pure resistors while the Z'' is pure capacitor [62]. Additionally, the admittance plot supported the findings of Bode-magnitude plots.

4. CONCLUSIONS

PT and PMT were electrodeposited onto CFMEs in NaClO_4 / ACN medium using cyclic voltammetry under different applied charges by varying initial monomer concentrations at constant scan rates (50 mV s^{-1}). Cyclic voltammetric and electrochemical impedance spectroscopic studies clearly revealed the existence of high capacitive behavior for PT in the initial monomer concentration of 0.5 M ($C_{\text{LF}} = 1.13 \text{ F g}^{-1}$) compared to PMT in the initial monomer concentration of 0.2 M ($C_{\text{LF}} = 6.35 \text{ mF g}^{-1}$) thin film coating on the CFME. The electroactivity and well-defined electrochemistry of PT compared to PMT on the CFME opens the possibility of using these coated electrodes for electrochemical capacitor microelectrodes and (bio) electrochemical sensor electrodes in future studies.

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