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Monomer Concentration Effects of Poly (3-methylthiopene) on Electrochemical Impedance Spectroscopy

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Poly(3-methylthiophene) (PMT) doped with perchlorate anion was prepared electrochemically in the presence of sodium perchlorate (ClO_4^-) salt as the supporting electrolyte. The effect of current density, various initial monomer concentrations (0.1, 0.2, 0.5 M) and electrochemical impedance spectroscopy (EIS) on polymer films has been investigated. Cyclic voltammetry of PMT has been examined on carbon fiber microelectrode (~7 µm radius) in 0.1 M acetonitrile medium containing $NaClO_4$ in the range of 0.0 to 2.0 V versus Ag in the presence and absence of 3-methylthiophene. Thin films were characterized by Fourier transform infrared - attenuated transmission reflectance (FTIR-ATR) spectroscopy and scanning electron microscopy (SEM). SEM revealed a globular, branched and fibrous morphology of poly(3-methylthiophene). After surface modification of carbon fiber microelectrode (CFME), capacitance properties were checked by using electrochemical impedance spectroscopy. Capacitive behaviors of coated CFMEs were defined via Nyquist plot, Bode – magnitude plot, Bode – phase definitions; besides, conductance of modified microelectrodes was studied with Admittance plot. PMT / CFME exhibits high specific capacitance of ~ 4.12 F g^{-1} in the initial monomer concentration of 0.1 M, in comparison with a value of ~ 3.75 F g^{-1} for 0.2 M and ~ 2.32 F g^{-1} for 0.5 M.

Keywords: Poly(3-methylthiophene), Electrochemical impedance spectroscopy, Equivalent-electrical circuit, Carbon fiber microelectrode, Scanning electrode microscopy.

1. INTRODUCTION

The majority of electrochemical investigations of poly(3-methylthiophene) (PMT) have been carried out in organic solvents [1-4]. The electrochemical properties of PMT are very dependent on the electrolyte salts used [5]. This effect is attributed to the open structure of polythiophenes, facilitating the transport of counter ions in and out of the films. Hagen et al [6]., Zhang and Dong [7] have shown that the voltammograms of PMT has been demonstrated by cyclic voltammetry (CV) to show sensitivity towards the dopant ion when doped from aqueous solutions of different inorganic salts [8]. Cyclic voltammetry is often used as a standard method for characteristic the electrochemical doping of conducting polymers [9-12].

Among conducting polymers, PMT has been received a significant share of attention. PMT, as an important derivative of polythiophene, has led to numerous applications in the fields of microelectronics, optoelectronics, and sensors [13, 14] owing to its high conductivity and high tensile strength and flexibility. Although poly(3-methylthiophene) exhibits distinct electrochromism, the insolubility of this material is a disadvantage for its technological application [15]. Poly(3-octylthiophene) was electrochemically synthesized by galvanostat method via using air and moisture stable ionic liquid (1-butyl-3-methylimidozolium hexafluorophosphate) [BMIMPF$_6$] as the growth medium and the supporting electrolyte [16]. These conducting polymers with various nanostructures can be prepared through either chemical or electrochemical oxidation of the monomer with or without the template [17-19]. Previously, there have been quite number of studies concerning the conducting polymer synthesis [20], characterization [21-23] and electrochemical impedance spectroscopy [24, 25].

The electrochemical impedance spectroscopy (EIS) is one of the most effective and the reliable method to extract information about electrochemical characteristics of the electrochemical system for instance double layer capacitance, diffusion impedance, determination of the rate of the charge transfers and charge transport processes, solution resistance etc [26]. EIS was used to explain the behavior of the polymer coated electrodes by well-established theories employing two models which are known as uniform and porous medium [27]. The generalized transmission line circuit model predicts the relevant impedance features of such a system in terms of a Nyquist plot [28], based on a mathematical approach. The two semi-circles at the highest frequencies, induced by the processes at the metal / polymer and polymer / solution interfaces, are, in practice, not always detectable. Sometimes, only one or even one-half semi-circle is observed; for other cases, these two semi-circles are partially overlapped to each-other, the actual situation observed depending on the characteristics of the interfacial processes in terms of energy (resistance) to overcome at the relevant interface. Moreover, these semi-circles are very often depressed, most probably due to non-homogeneous separation surfaces [29]. Furthermore, they can also overlap to the mid-frequency Warburg impedance quasi – 45^0- slope segment that reflects the diffusion – migration of ions at the boundary surface between solution and polymer, inside the latter medium. Finally, the 90^0 – trend at the lowest frequencies, due to capacitive impedance, accounts for the charge transport process inside the bulk of the film [30]. A combination of EIS with standard electrochemical methods such as CV, provides a powerful tool to understand the properties of conducting polymers and thus to develop useful compounds for the specific applications [31]. Studies on nano - composites and electrochemical nano – and micron – sized capacitors are very attractive due to their higher energy densities through the small volume of material [32]. There is another important factor; the variation of the electrolyte concentration near the interphases (but outside the double layer) which influences both the overall accumulated interfacial parameters must also be present in the overall impedance [33]. Electric double layer capacitor (EDLC) uses carbon as the electrodes and stores charge in the electric field at the interface. It uses either aqueous or non-aqueous electrolyte. It gives high power density but low energy density [34].

Electrochemical impedance spectroscopy (EIS) technique to complement and elucidate voltammetric data is desired. In this paper, we will discuss in detail the electrochemical impedance analysis of the data. The impedance spectra of PMT of different initial monomer concentrations and the electrochemical parameters are evaluated and discussed.

2. EXPERIMENTAL PART

2.1. Material and Chemicals

All chemicals were of the highest quality commercially available: 3-methylthiophene (MT) (Aldrich, 98 %), sodium perchlorate ($NaClO_4$; Aldrich, ACS grade), acetonitrile (Aldrich, 99.9+ %). Polyacrylonitrile (PAN) based, Hexcel AS4C 12K carbon fibers (12 000 single filaments in a roving) were used for the electropolymerization (diameter of ~7 μm) [35]. The electropolymerization procedure was carried out as described previously [36-40].

2.2. General procedure

PMT / CFME thin films were synthesized by CV method. PMT films were electrocoated by electrochemical oxidation of the monomer in a three-electrode cell consisting of carbon fiber (CF) as working electrode, a Pt wire counter electrode and saturated Ag / AgCl as reference electrode. The different initial monomer concentration samples were synthesized by varying the charges (Q_p). All experiments were performed at 298 K.

2.3. Detection Method

The impedance measurements were carried out using the electrochemical impedance supplied by Parstat 2263-1 (software; Powersuit). Alternating current (ac) amplitude of 10 mV over a frequency range of 0.01 Hz -100 kHz was used. Before starting impedance measurements the steady state was reached and the observed dc current in the cell was constant. Electrocoated CFMEs were analyzed by FTIR reflectance spectroscopy (Perkin-Elmer, Spectrum One B, with an ATR attachment Universal ATR - with ZnSe crystal. The morphology of the PMT surface was examined by scanning electron microscope (SNE-3000M Mini-SEM, SEC Company, South Korea).

3. RESULTS AND DISCUSSION

3.1. Electropolymerization of 3-Methyl thiophene

Electro-growth of 3-methyl thiophene 3-MT in different initial monomer concentrations on CFME substrate using cyclic voltammetry have broad peaks as can be seen in Fig. 1. During oxidation and reduction, anodic and cathodic peak potentials were determined by 10th cycle scans. Anodic and cathodic electro-growth peak potentials of 3-MT homopolymer were determined to be 1.23 and 0.15 V (Fig.1.a.) and 1.27 and 0.03 V (Fig.1.b), respectively. The peaks are broad, which are probably due to the presence of mixed valance species, such as the cation, radical, and dication of polymer anions salts [41].

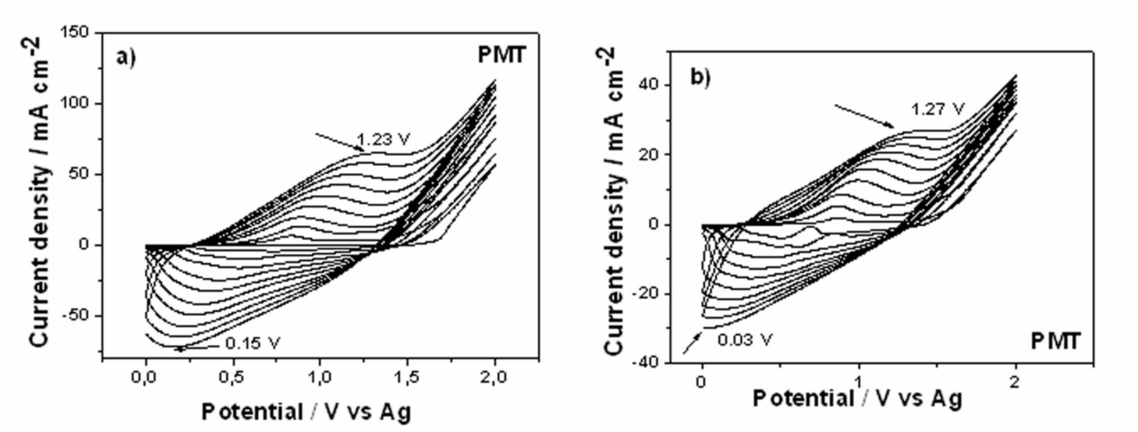
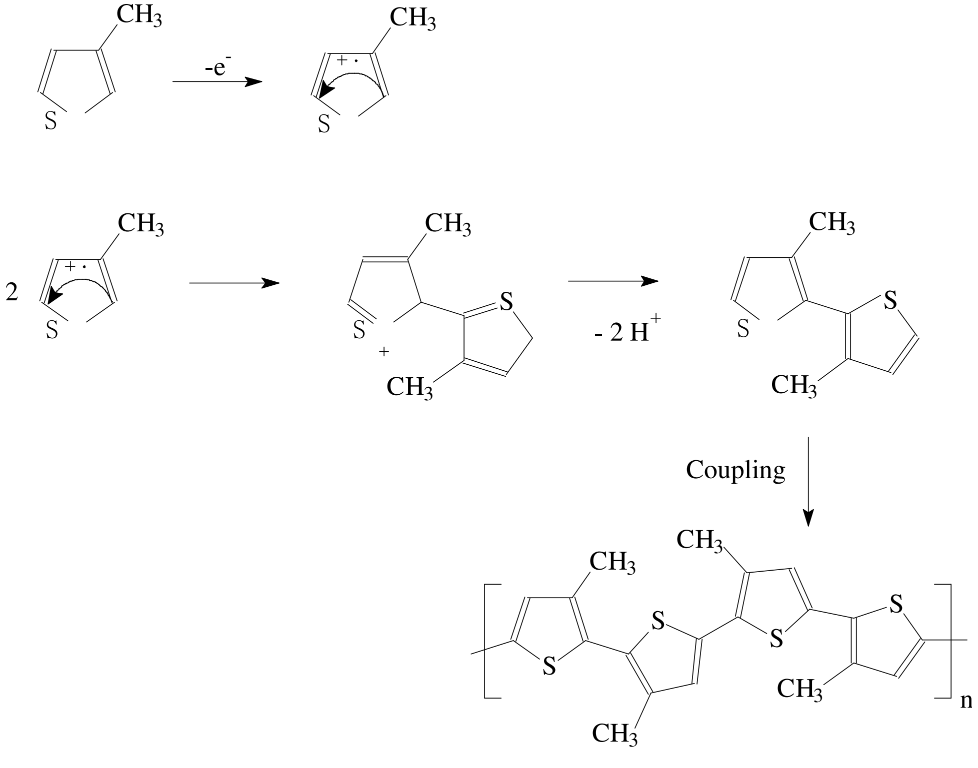


Figure 1. Electro-growth of 3-methylthiophene in 0.1 M $NaClO_4$ / ACN with 50 mV s^{-1} for ten cycles on CFME, a) $[MT]_0 = 0.2$ M, b) $[MT]_0 = 0.5$ M.



Poly (3-methylthiophene)

Figure 2. Mechanism of 3 – methylthiophene.

3.2. Mechanism part

The postulation of the mechanism of polymerization is based on the CV study and on the commonly accepted cation radical coupling mechanism [42]. The oxidation of the 3-MT monomer at the anode surface produces charged species precursors, which require the transfer of 2 electrons per molecule. In previous studies, the mechanism was proposed for the electropolymerization of 3-MT, by analogy to the already known coupling reactions of heterocyclic compounds [43]. Electropolymerization proceeds then through successive electrochemical steps according to Fig. 2.

3.3. FTIR-ATR investigation

The FTIR-ATR spectra of the PMT during electrocoating process (Fig.3) are comparable to those obtained for the uncoated carbon fiber microelectrodes. The C-N stretching is at about 1390 cm^{-1} for PMT (comparison with uncoated CFME) clearly indicating the inclusion of $-CH_3$ group into the polymeric structure. Although, it is probably difficult to draw conclusions about the interfacial bonding / adhesion between carbon fibers and electrocoated polymers, without having performed further experiments, there are however, some evidences of fiber / polymer interactions. There are peaks at around 1627 cm^{-1} and 3600 cm^{-1} present in PMT, but absent in the spectra of uncoated CFME. These peaks correspond to C-C and C-H stretching, which might be weakened for the coated polymer caused by fiber / coated polymer interactions [44]. The strong peaks at 1080 cm^{-1} for PMT could be due to vibration of counter ions included into the polymer from the electrolyte solution (ClO_4^-).

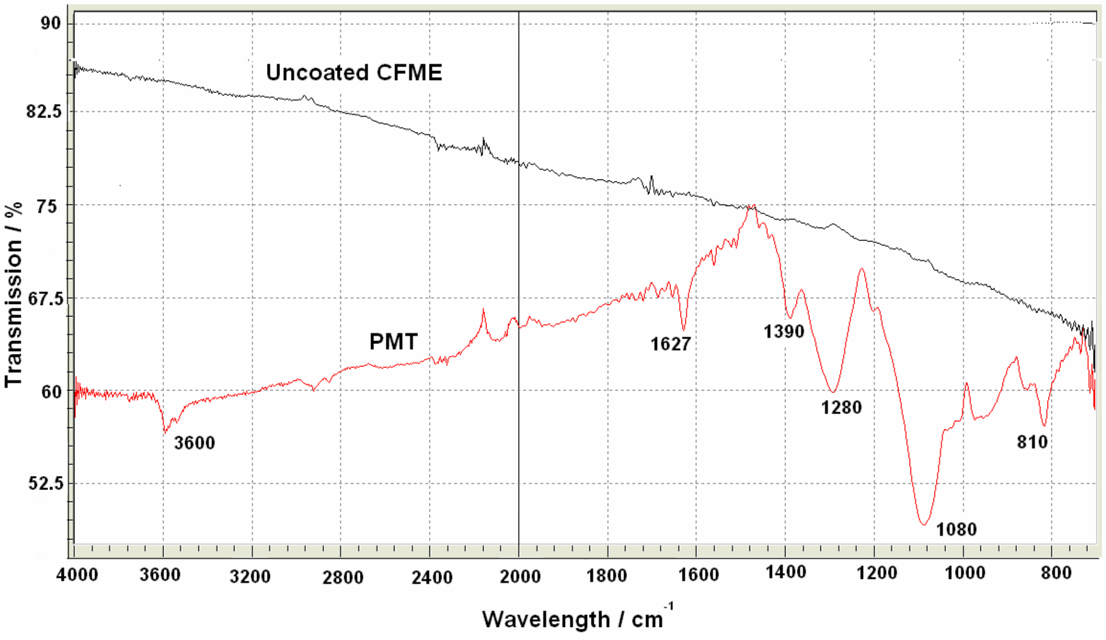


Figure 3. ATR-FTIR analysis for PMT / CFME and uncoated CFME. $[MT]_0 = 0.2$ M.

3.4. SEM images

Poly(3-methylthiophene) nanospheres with their size ranging around 50-60 nm have been synthesized by simply adding monomers into a magnetic ionic liquid [45]. SEM examination of PMT films surface after impedance measurement was carried out in presence of dopant ions. The great variation in morphology depends on the type of the doping anion used during preparation and investigation of PMT films and the size of pores formed during the doping process. By using low size electrolyte anions as ClO_4^-, a high density of pores and big pore size formed in the film was obtained (Fig.4). In previous studies in literature, a low density of pores and very small pore size formed in the film (nearly compact PMT surface) was obtained [46].

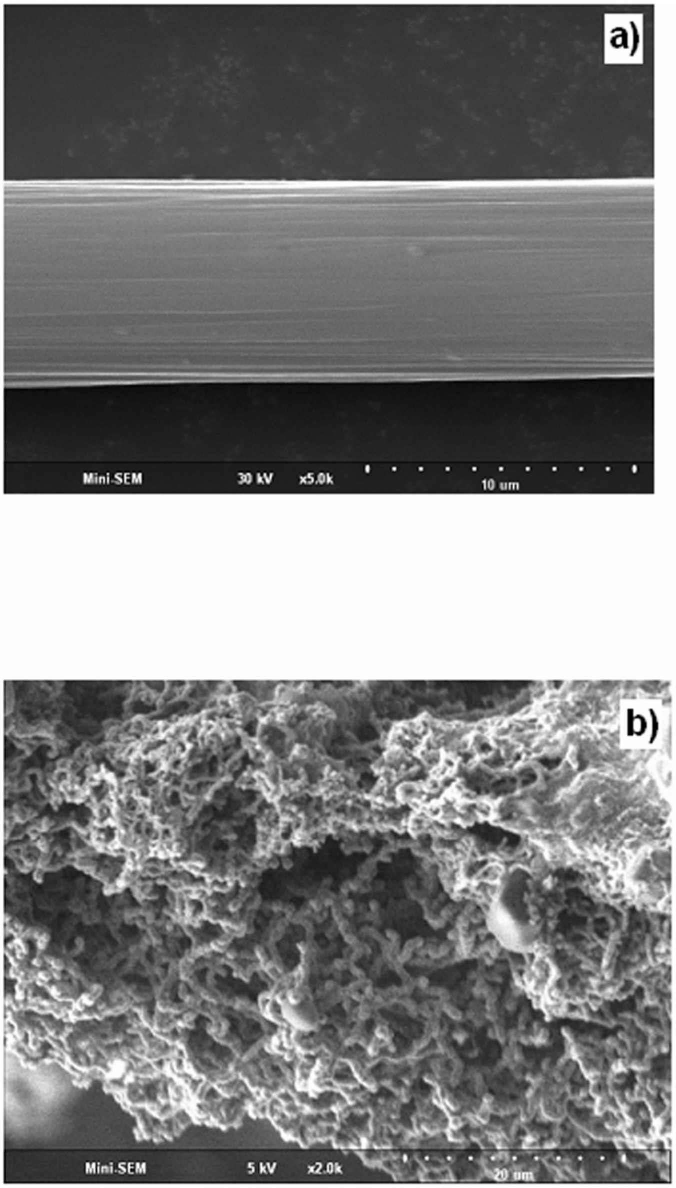


Figure 4. SEM images of a) Uncoated CFME, b) PMT / CFME.

3.4. Electrochemical impedance spectroscopic measurements

The electrochemical impedance spectroscopy (EIS) was carried out to prove the capacitive performance in the frequency range of 0.01 Hz - 100 kHz with ac-voltage amplitude of 10 mV. EIS is powerful technique to describe the surface configuration of the electrode. Among these obtained plots, Nyquist plots were the most frequently used figures to indicate the electrochemistry response; in our case, Nyquist plots were also obtained, from which the information about the double layer was hardly acquired [47]. The Nyquist plot of PMT thin films in various initial monomer concentrations (0.1, 0.2, and 0.5 M) were given in Figure 5. The observed impedance behavior is consistent with the changes induced in the CV curves upon cycling. Nyquist (complex plane impedance) plots were used to estimate the low-frequency redox capacitance of the polymer-modified CFMEs. Low frequency redox capacitance values 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) using the following equation [48]: $C_{LF} = (2\pi f Z_{im})^{-1}$. EIS study of Nyquist plot of homopolymer in various initial monomer concentrations (0.1, 0.2, and 0.5 M) showed the specific capacitance as ~ 4.12, ~ 3.75, ~2.32 F g^{-1}, respectively (Fig.5). As a result, by increasing of the initial monomer concentrations results a decrease in specific capacitance values may be due to thicker film formation. Electro-deposition charges were obtained during electro-growth process as 288 mC, 1.060 C, and 604.9 mC, respectively. The specific capacitance (C_{sp}) values were obtained in three different initial monomer concentrations and the charge capabilities for electro-growth process are correlated. C_{sp} values have little decrease from 0.1 to 0.2 M while the charge capabilities proportionally increase by initial monomer concentration. For Nyquist graph, in 0.1 M concentration was illustrated with the steepest line close to the y-axis showing the best capacitive behaviour.

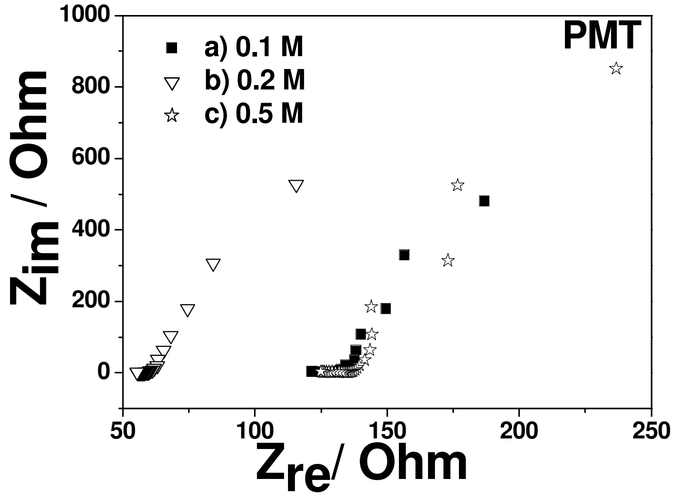


Figure 5. Nyquist plots of PMT in different initial monomer concentrations a) 0.1 M, b) 0.2 M, c) 0.5 M in 0.1 M $NaClO_4$ / ACN.

A value of double layer capacitance, C_{dl}, can be calculated from a Bode-Magnitude plot, by extrapolating the linear section to value ω = (log w = 0), employing the relationship IZI = 1 / C_{dl} [49]. The maximum double layer capacitance (~ 2.08 F g^{-1}) was obtained in the initial monomer concentration of 0.2 M compared to 0.1 M (~ 0.92 F g^{-1}) and 0.5 M (~ 0.89 F g^{-1}) (Fig.6).

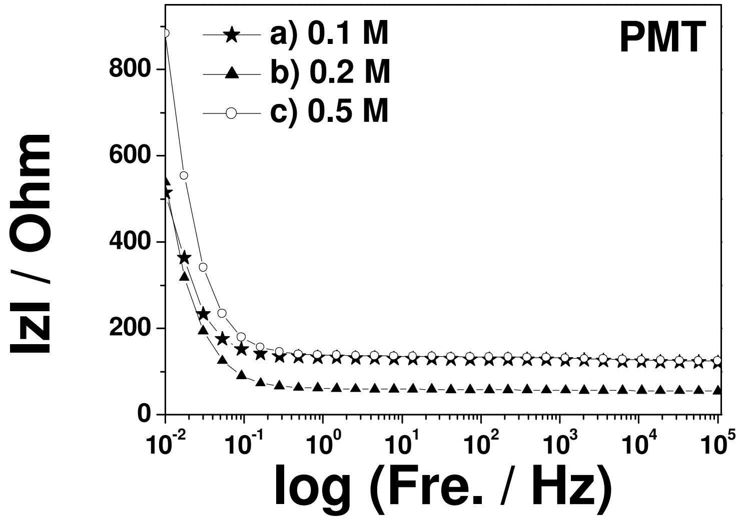


Figure 6. Bode-magnitude plots of PMT in different initial monomer concentrations a) 0.1 M, b) 0.2 M, c) 0.5 M in 0.1 M $NaClO_4$ / ACN.

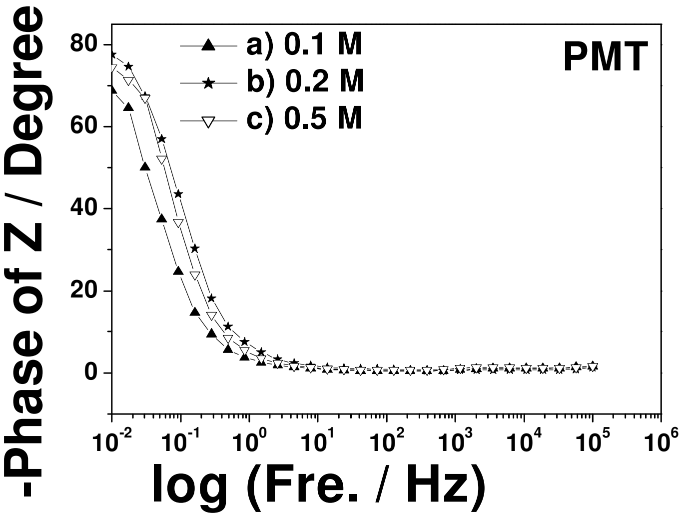


Figure 7. Bode-phase plots of PMT in different initial monomer concentrations a) 0.1 M, b) 0.2 M, c) 0.5 M in 0.1 M $NaClO_4$ / ACN.

Bode-phase plots of PMT in various initial monomer concentrations are presented in Fig. 7. At frequencies < 0.01 Hz, a Bode-phase angle approaches a maximum value and the electric signal reaches maximum penetration in the pores of the PMT. The maximum phase angle (~ 77.2^0) can be obtained for PMT in the initial monomer concentration of 0.2 M at a frequency of 0.01 Hz, which is comparable to (~ 74.8^0) for 0.5 M and (~ 68.8^0) for 0.1 M.

The admittance plot for PMT was presented in Fig.8, where the evident distinction exhibited in various initial monomer concentrations (0.1, 0.2 and 0.5 M) was showed definitely. The admittance plot supported the findings of Bode-Magnitude plots. On the other hand, admittance plot indicates the information about conductivity of the modified structures. Therefore; polymer film obtained in more concentrated solution (in 0.5 M) conductivity has the lowest value ~ 3.30 mS cm^{-2} as shown in Fig.8.

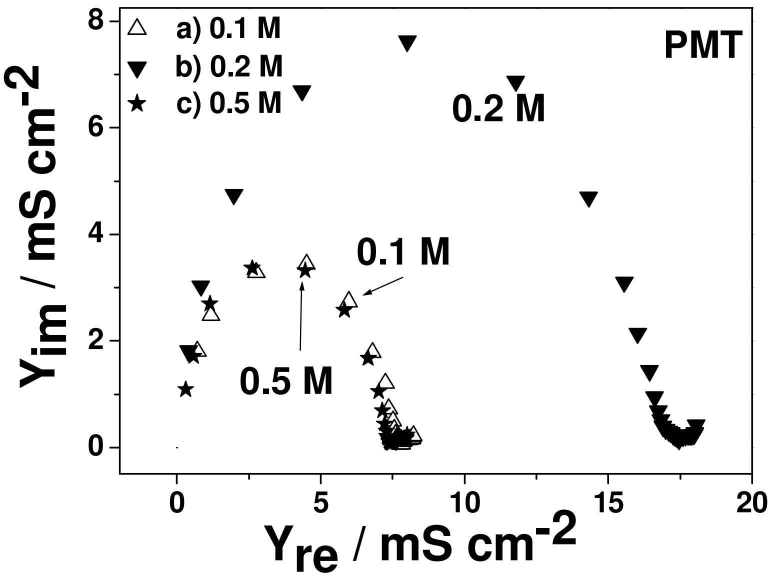


Figure 8. Admittance plots of PMT in different initial monomer concentrations a) 0.1 M, b) 0.2 M, c) 0.5 M in 0.1 M $NaClO_4$ / ACN.

4. CONCLUSIONS

The carbon fiber microelectrodes have certain electrical double capacitance and can be used as electrodes for electrochemical polymerization. PMT / CFME can be directly used as electrodes of prototype capacitors, and shows good potential application in electrochemical capacitors. Electrochemical analyses, using CV and EIS show the significant contribution of PMT to the overall capacitance due to PMT exhibiting high Faradic pseudocapacitance. The PMT / CFME exhibits a higher specific capacitance of ~ 4.12 F g^{-1} in the initial monomer concentrations of 0.1 M, obtained thin film as 288 mC during electro-growth process, higher than in the initial monomer concentrations of 0.2 and 0.5 M. The highest double layer capacitance (C_{dl} = ~ 2.08 F g^{-1}) and maximum phase angle (77.2^0) at 0.01 Hz for PMT was obtained in the initial monomer concentration of 0.2 M. The high specific capacitance of PMT / CFME was concluded as the combination of double layer capacitance and pseudo-capacitance.

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