Int. J. Electrochem. Sci., 7 **(2012)** 1093 - 1106

International Journal of
ELECTROCHEMICAL
SCIENCE
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Scan Rate Effect of 1-(4-methoxyphenyl)-1H-Pyrrole Electro-coated on Carbon Fiber: Characterization via Cyclic Voltammetry, FTIR-ATR and Electrochemical Impedance Spectroscopy

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Received: 29 November 2011 / *Accepted:* 3 January 2012 / *Published:* 1 February 2012

Poly(1-(4-methoxyphenyl)-1H-Pyrrole) films were electrodeposited onto carbon fiber micro electrodes with different deposition rates by using cyclic voltammogram in the presence of tetraethyl ammonium perchlorate (TEAP) / dichloromethane (CH_2Cl_2) as electrolyte solution. Scan rate effect on the electropolymerization, morphology and electrochemical impedance spectroscopic behaviour of modified carbon fiber micro-electrode was investigated. Electro-growth process was achieved by applying various scan rates of 10, 20, 40, 60 and 100 mVs^{-1}. Poly(1-(4-methoxyphenyl)-1H-Pyrrole) coated CFMEs were characterized by FTIR-ATR spectroscopy. Surface morphology of the polymer films were characterized by using Scanning electron microscopy (SEM). Besides, capacitive properties were recognized by electrochemical impedance measurements. Capacitive behaviors of coated carbon fiber micro electrodes were defined via Nyquist plots, Bode-Magnitude plot and Bode-phase definitions. As a result, a good correlation was obtained between electro-growth processes, electrochemical impedance data and morphological studies.

Keywords: Carbon fiber microelectrode, Conducting polymer, Capacitor, Electrochemical impedance spectroscopy, Electropolymerization, 1-(4-methoxyphenyl)-1H-Pyrrole.

1. INTRODUCTION

Electrochemical polymerization is a simple and attractive approach for forming a polymer film on the electrode surface [1-3], the thickness of the film can be controlled and the functionality of the formed coating film can be selected through processing parameters (the current density, scan rate, scan number, temperature, etc.) and uniform coatings can be achieved [4-6].

In this study, polyacrylonitrille (PAN) based modified carbon fibers are used as micro electrodes [7, 8]. Carbon fibers present extremely high strength and modulus, good stiffness, and creep resistance etc. They have been widely employed as the reinforcing material in the high performance resin composites which have been extensively used in many industrial fields [9]. Moreover, conducting polymers offer both advantages of high charge capacity and low production cost which are necessary conditions for industrial developments [10].

The possibility of high surface area electrodes with small dimensions has been realized in several applications: for example, for higher performance and miniaturization of electrochemical devices [11]. Conducting polymers have this potential owing to their porous structure, but the electrochemical performance of polymer based electrodes has yet to be fully developed [12]. Electropolymerization of pyrrole, carbazole, thiophene and their copolymers onto CFMEs were investigated as a novel method for tailor-making CFME–polymer inter-phases to promote fiber-matrix adhesion [13-18].

In the field of energy storage systems electronically conducting polymers are promising materials due to their high specific capacitance and high conductivity values. Unlike double-layer capacitors, in which the energy storage is electrostatic in origin, ECPs are pseudo-capacitor materials with Faradaic processes due to reversible electrochemical doping-dedoping reactions. Thus, electropolymers can be interesting materials for increasing the charge storage capacity in comparison with double-layer on activated carbons. The processability of these materials for building well adapted electrodes for storage devices has been shown in literature [19, 20]. For example, polypyrrole (PPy) is an attractive polymer due to its low cost and efficient electrochemical properties and stability [21, 22]. Generally, their specific energies are greater than those of electrolytic capacitors. In this case, PPy was reported in the literature as electrode for capacitors [23, 24]. Capacitors are being considered of various applications not only coupling with batteries to provide peak power, but also replacing batteries for memory backup and electric vehicles [25-27].

PPy can be prepared by chemical and electrochemical oxidation in aqueous or non-aqueous solution. Since the first report of its synthesis by Diaz et al [28], many studies have been reported previously related to electrochemical capacitors based on PPy [29-33]. It is a well-known fact that the properties of polypyrrole and other conducting polymer films are strongly influenced by the method of preparation, counter ions and environmental conditions used during synthesis [34, 35].

Previously, electropolymerization of 1-(4-methoxyphenyl)-1H-Pyrrole was done on CFME in TEAP / CH_2Cl_2. On the contrary the previous study, in this paper, doping process was performed at different scan rates which correspond to different film thickness and features. Besides, polymer modified CFMEs were characterized via FTIR-ATR and evaluation of capacitor performance by electrochemical impedance spectroscopic (EIS) measurements. Additionaly, surface morphological analyses were achieved via scanning electron microscopy (SEM).

2. EXPERIMENTAL

2.1. Materials

1-(4-methoxyphenyl)-1H-Pyrrole (MPPy) (Fluka, 99 %), Tetraethylammonium perchlorate (TEAP) (Alfa Aesar, 97 %) and dichloromethane (CH_2Cl_2) (Merck) were used as received without further purification. A high strength (HS) carbon fibers C 320.000A (CA) (Sigri Carbon, Meitingen, Germany) containing 320000 single filaments in a roving were used as working electrodes.

2.2. Preparation of Carbon Fiber Micro Electrodes

All of the electrodes were prepared by using a brunch of CF including about 100 filaments (diameter ~ 7 μm) attached to a copper wire with a Teflon tape. The electrode area keeps up constant (~ 0.11 cm^2) by adjusting the dipping length to 1 cm and covering the rest of the fibers with the Teflon tape.

2.3. Polymerization and Characterization

Polymerization reactions were performed electrochemically in dichloromethane (CH_2Cl_2) solution containing 0.05 M TEAP and monomer concentration of 10 mM. Cyclic voltammogram (CV), of the polymers was performed with a Parstat 2263-1 (software; Powersuit) in a three-electrode system employing CFME as working and Ag│AgCl as reference electrode. Impedance measurements were conducted in monomer-free electrolyte solution with a perturbation amplitude of 10 mV over a frequency range 0.01 Hz-100 kHz using a Parstat 2263-1 (software; Powersuit). Additionally, polymer coated carbon fiber surfaces were analysed by FTIR reflectance spectrometer (Perkin Elmer) and the morphological features of the electrocoated carbon fiber micro electrodes were performed with SEM. The fibers were attached on copper plate by use of a double sided carbon tape. Scanning electron microscopic measurements were carried out via Jeol JSM-7000F SEM.

3. RESULTS AND DISCUSSION

3.1.Redox Behaviour and Stability of MPPy Film

The cyclic voltammograms (CV) obtained during polymer film growth on carbon fiber micro electrodes are presented in Figure 1. In previous study, monomer concentration effect of poly(1-(4-methoxyphenyl)-1H-Pyrrole) was achieved on carbon fiber microelectrode in TEAP / CH_2Cl_2 [36].

However, in this study, CV of 1-(4-methoxyphenyl)-1H-Pyrrole obtained with 10 mVs-^{1} (Fig.1a), 20 mVs^{-1} (Fig.1b), 60 mVs^{-1} (Fig.1c), 100 mVs^{-1} (Fig.1d) showed the broad and symmetrical redox waves. Electro-growth of 1-(4-methoxyphenyl)-1H-Pyrrole obtained with different scan rates -showed different redox behaviors. Polymer coated electrodes indicated that one-well defined redox systems quickly grow and correspond to the deposition of an electro-active film onto the electrode surface during successive scans. The poly(1-(4-methoxyphenyl)-1H-Pyrrole) was prepared in the initial monomer concentration of 10 mM of 1-(4-methoxyphenyl)-1H-Pyrrole monomer and the thin films were characterized by CV in 0.05M TEAP / CH_2Cl_2 monomer free solution. The influence of scan rate was investigated for electropolymerization of 1-(4-methoxyphenyl)-1H-Pyrrole.

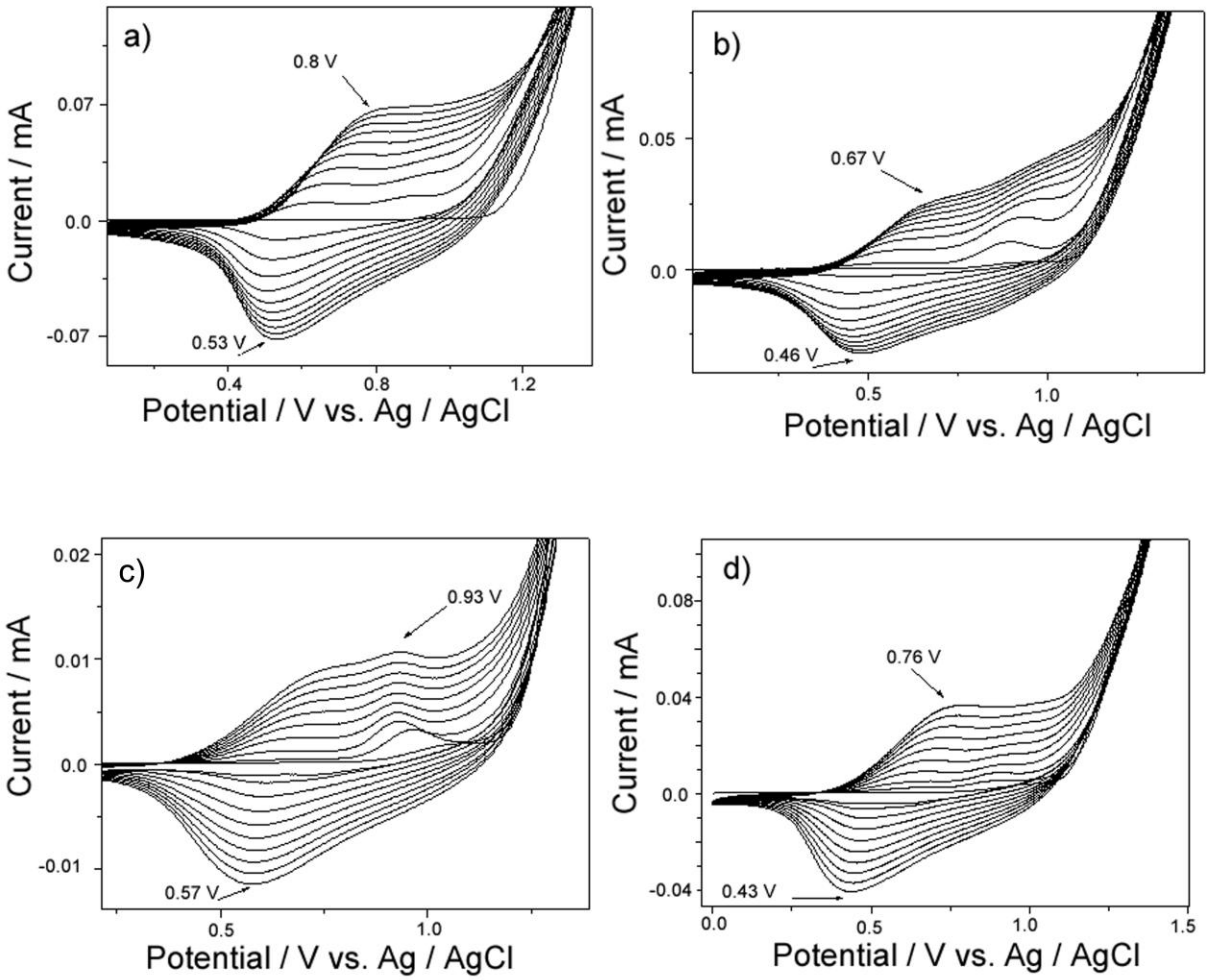

Figure 1. Cyclic voltammograms for potentiodynamic growth of 1-(4-methoxyphenyl)-1H-Pyrrole at different scan rates of a) 10 mVs-^{1} (Q=70.35 mC), b) 20 mVs-^{1} (Q=40.50 mC), c) 60 mVs^{-1} (Q=2.59 mC) and d) 100 mVs^{-1} (Q=4.42 mC). Q is the deposition charge during electropolymerization process.

The peak separation between anodic and catodic peak potentials (*ΔE*) during polymer growth was the highest for the scan rates of 60 mVs^{-1} at a potential value of 0.366 V(Fig.1c) that means ion transport resistance is much higher [37-39]. The anodic and cathodic peak current ratio is closer to the 0.955 (Ia / Ic). Therefore, these data indicate that the most reversible modified CFME is coated at a scan rate of 60 mVs^{-1}. The separation between anodic and cathodic peaks is associated with ion transport resistance involved in these redox reactions [40]. It gives information about polymer thickness that is, if polymer thickness is high, electron transfer between polymer and electrolyte will be slow. Thus, the difference between anodic and cathodic peaks (ΔE) can serve as an indication for resistance of ion migration in the electrode. The value of ΔE generally increases with the amount of polymer film on the electrode. This is expected since an increase in polymer film thickness leads to an increase in resistance for ion penetration. Electrochemically modified polymer electrodes showed linear dependency between scan rate and current density that means polymer electrode processes are thin film formation. Electroactivity of polymer electrodes is the highest for the polymer synthesized at a scan rate of 10 mVs^{-1} (Fig.1a).

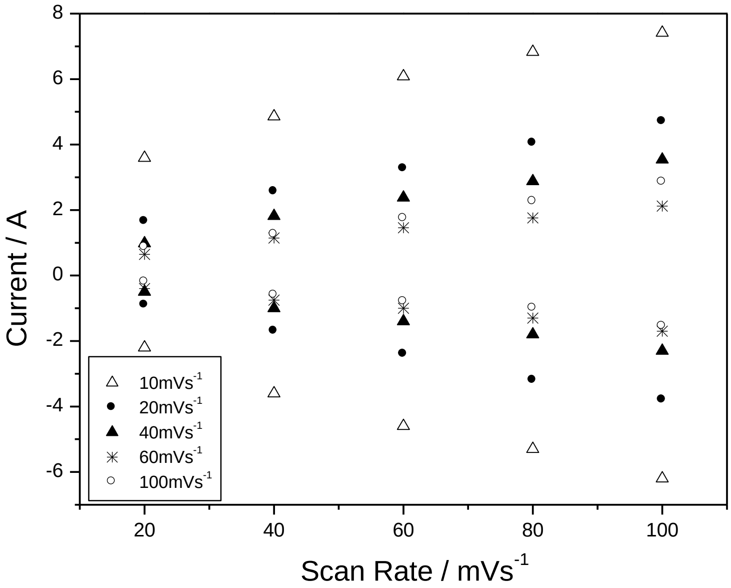

Figure 2. Change in anodic and cathodic peak currents with scan rate. Scan rate dependencies of 1-(4-methoxyphenyl)-1H-Pyrrole films that were grafted with different scan rates in monomer free solution of 0.05 M TEAP / CH_2Cl_2.

Scan rate dependencies of PMPhPy coated CFMEs were determined for each microelectrode. Figure 2 illustrates the linear proportionality of current versus scan rate, indicating all electroactive sites are electrode supported. CV of PMPhPy coated CFMEs in monomer-free electrolyte show oxidation potential in the range of 0.75 and 0.85 V.

3.2. Morphology

The morphological features of the electrocoated carbon fiber micro electrodes were performed via SEM. The fibers were attached on copper plate by use of a double sided carbon tape. The morphology of CF itself exhibits smooth surface with a surface curvature and the morphology of the polymer films are clearly dependent on the solvent type and scan rate, indicating that electron transfer to electrode at different scan rates and in different solvents is a factor which can be used to control surface morphology. The high-resolution images obtained by SEM analysis of the electro-coated CFMEs show that the electropolymerization of conductive polymers with different scan rates produces different sized grainy orientations. P(MPhPy) are illustrated in Figure 3.

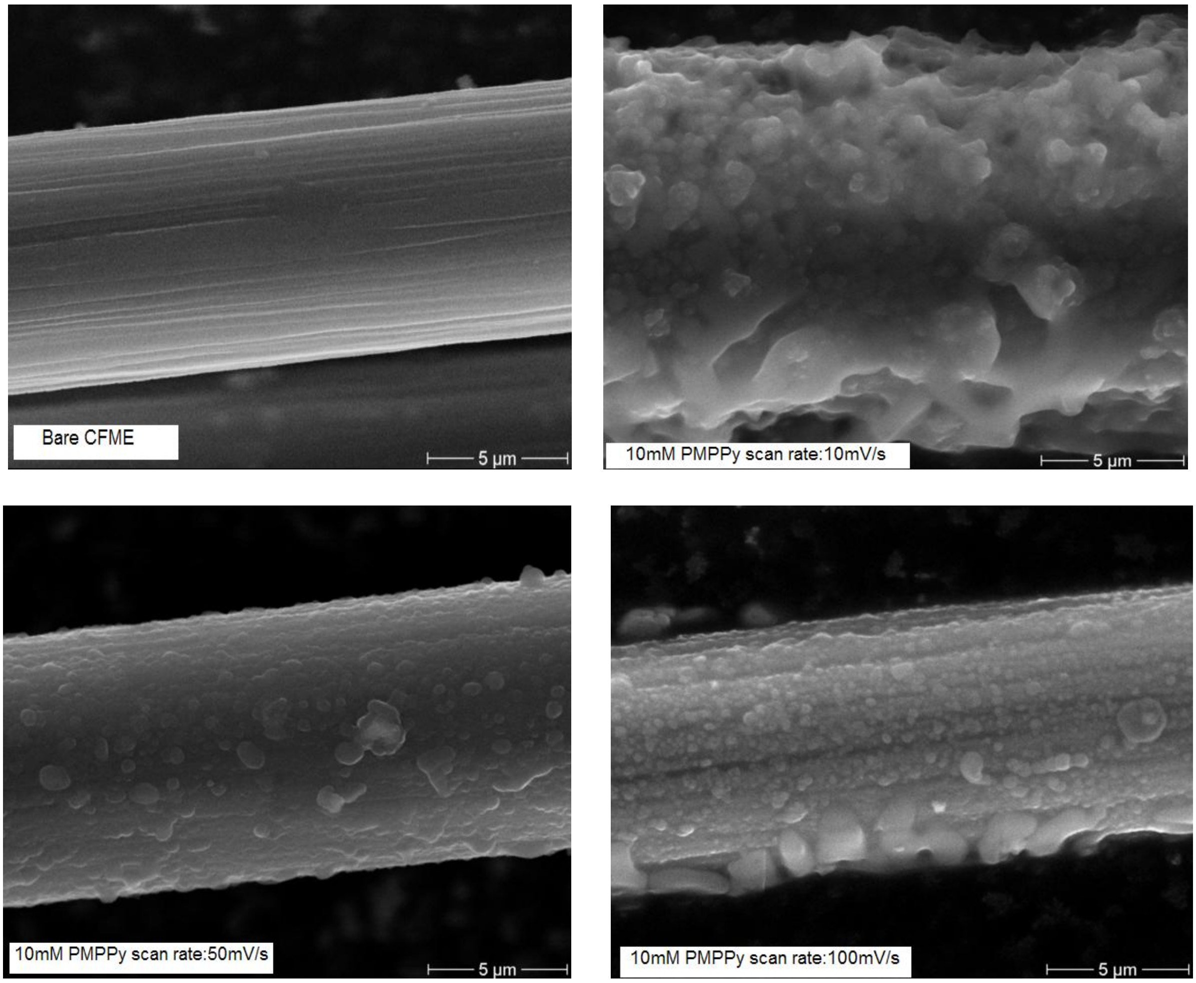

Figure 3. SEM picture of bare CFME and PMPhPy coated CFME at different scan rates of 10 mVs^{-1}, 50mVs^{-1} and 100mVs^{-1} for 10 cycles in the initial monomer concentration of 10 mM.

3.3. Effect of Scan Rates on EC Impedance Spectroscopy

The most common technique for estimating the capacitance behavior is impedance spectroscopy. It is important to mention that the real electro-active area of carbon electrodes takes part in charging of the electrical double layer only with highly conducting electrolytes and at low frequencies. Also the conductivity of the modified carbon electrode plays a crucial role for the capacitance behavior; hence, the amount of binding substance should be limited [41]. In this part of the study, electrochemical impedance spectroscopy was further employed to monitor the electrochemical behavior of the electrodes. Electrodes which were electrocoated with different scan rates, were subjected to same applied potentials and impedance characteristics were recorded. Impedance measurement was performed in monomer-free solutions after polymer growth processes on CFMEs.

Typical Nyquist diagrams of modified electrodes are indicated in Fig. 4, respectively. All impedance curves are vertical straight lines in the low frequency region. Hence, the performance of an ideal capacitive behavior (about 90^0 line at low frequency) was obviously seen in the plot. These vertical lines mean that the modified carbon fiber micro electrodes show the capacitor behavior. Moreover, the straight line observed in mid and low frequency region was giving evidence for a very good barrier property of the coating. This means that the coating has a very low porosity and exhibited very low permeability against the corrosive species [42, 43].

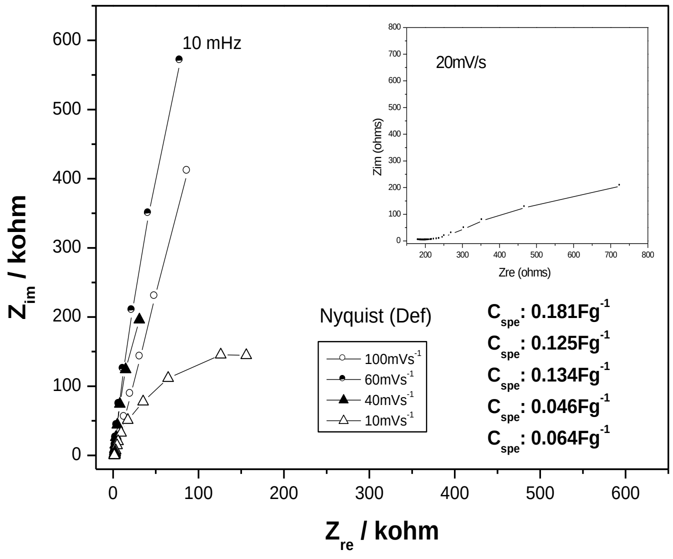

Figure 4. Nyquist-plots recorded for 1-(4-methoxyphenyl)-1H-Pyrrole electrografted CFMEs with different scan rates. Inset: for 20 mV.$^{s-1}$ and Calculated specific capacitance values.

At low frequency region, polymer electrode which is electrodeposited at different scan rates of 40 mVs-^{1}, 60 mVs-^{1} and 100 mVs^{-1} behave like pure capacitors characterized by vertical line paralel to the imaginary axis. Hence, electron transfer is going to be faster for these three electrodes, and they can store more charge than the other modified carbon fiber micro electrodes. On the contrary; the low frequency capacitive behavior changed to semicircle from vertical line for PMPhPy coated at a scan rate of 10 mVs^{-1}, which might be due the thicker polymer film formation than the others coatings with higher scan rates. Calculated specific capacitance values were illustrated as inset ~~value~~ in Figure 4.

On the other hand, the modified CFME coated at a scan rate of 20 mVs^{-1} has the lowest conductivity value. Z' axis could be named as pure resistor while the Z'' is pure capacitor. As it is seen from the Nyquist diagram at a scan rate of 60 mVs^{-1} shows the highest capacitive behavior than the other scan rates. Additionaly, specific capacitance values are another values determined from Nyquist diagrams. The lowest frequency (f) and the highest Z_{im} (z″) values are placed in the formula of; C_{spe} =

1 / 2πfz″ for specific capacitance calculations. The calculated values are represented in the Nyquist plot. The lowest specific capacitance value (0.0463 F g^{-1}) are evaluated at a scan rate of 60 mVs^{-1}. Conversly; the highest C_{spe} value belongs to the at a scan rate of 10 mVs^{-1}; it may be due to the higher thickness values.

In the Bode-phase plot of PMPhPy electrodeposited on CFME at a scan rate of 10 mVs^{-1}, the Bode-phase angle approaches a plateu (74^{o}), in the frequency region 0.84 Hz - 4.34 Hz which film indicates capacitor behavior (Fig. 5). In the frequencies, 4.34 Hz – 697 Hz, phase transition from capacitor to resistor behavior was observed. PMPhPy showed resistor behavior in the frequency region of 697 Hz-100 kHz. The Bode-phase plot of PMPhPy coated on CFME at a scan rate of 20 mVs^{-1} is indicated that in the small time interval (10 mHz – 17 mHz) the polymer film is capacitive (71^{o}) at low frequencies with a good capacitor behavior. The Bode-phase angle plots of PMPhPy electrodeposited on CFME at different scan rates of 40 mVs^{-1}, 60 mVs^{-1} and 100 mVs^{-1}, in the frequency region of 10 mHz – 1 Hz, show capacitance behavior, phase transition from capacitor to resistor is obtained in the frequency region between 0.16 Hz – 100 Hz. The Polymer films indicated resistor behavior in the frequencies, 41 Hz - 100 kHz.

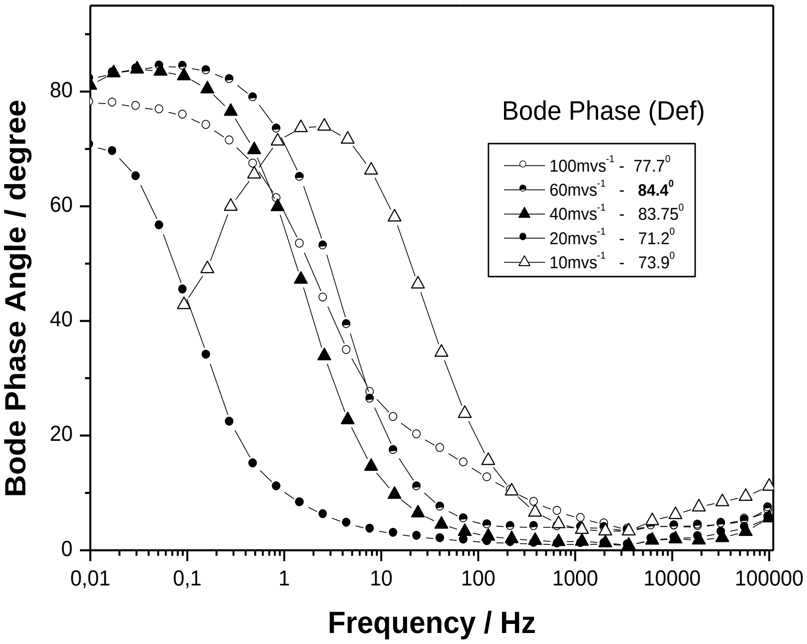

Figure 5. Bode-phase plot of 1-(4-methoxyphenyl)-1H-Pyrrole electrografted CFMEs with different scan rates in TEAP / CH_2Cl_2.

The point that divides the high frequency component of complex plane impedance plot from low frequency component referred knee frequency. The knee frequency indicates maximum frequency at which predominantly capacitive behavior maintained. The knee frequeny of PMPhPy obtained via different scan rates between (20 mVs^{-1} - 100 mVs^{-1}) lower than PMPhPy coated at a scan rate of 10 mVs^{-1} (Fig.6).

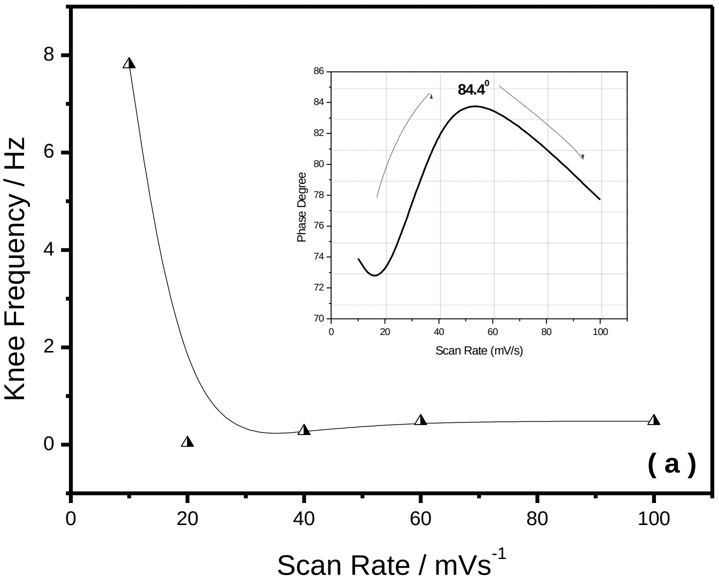

Figure 6. The knee frequency vs. scan rate graph of poly(1-(4-methoxyphenyl)-1H-Pyrrole) obtained with different scan rates.

The graph indicated that PMPhPy electrodeposited at scan rates (20 mVs^{-1} - 100 mVs^{-1}) can be more advantageous than 10 mVs^{-1} to use for capacitor applications. In another point of view, comparison of these two plots indicates that there is a correlation between knee frequency and charge values. This relation means that electrochemical impedance data is convenient with the film charge obtained from polymer growth (Fig.7).

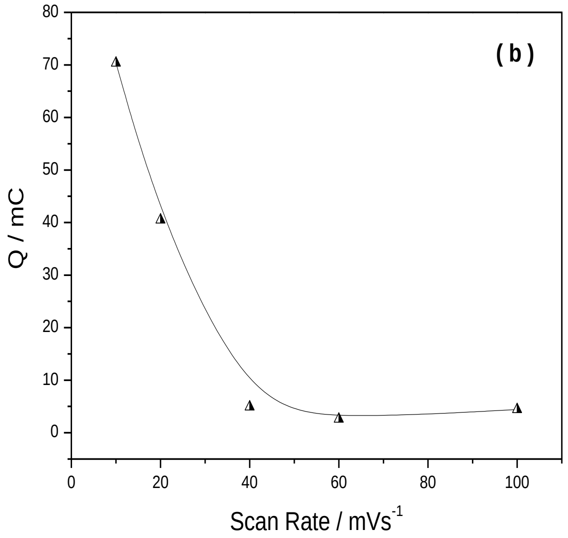

Figure 7. Charge vs. scan rate graph of poly(1-(4-methoxyphenyl)-1H-Pyrrole) in TEAP / CH_2Cl_2.

Bode-magnitude plot yields extrapolating this line to the log Z axis at w = 1 (log w = 0) the value of C_{dl} [44] from the relationship: $|Z|=1/C_{dl}$. The highest double layer capacitance value (7.8.10^{-2}

F g^{-1}) was obtained at a scan rate of 20 mVs^{-1}. It could be due to the slow cycling by low potential (Fig.8). The other results are as following: $C_{dl}=7.1x10^{-3}$ F g^{-1} for 100 mV s^{-1}; $C_{dl}=2.9x10^{-3}$ F g^{-1} for 60 mV s^{-1}; $C_{dl}=8.6x10^{-3}$ F g^{-1} for 40 mV s^{-1}; $C_{dl}=3.8x10^{-3}$ F g^{-1} for 10 mV s^{-1}.

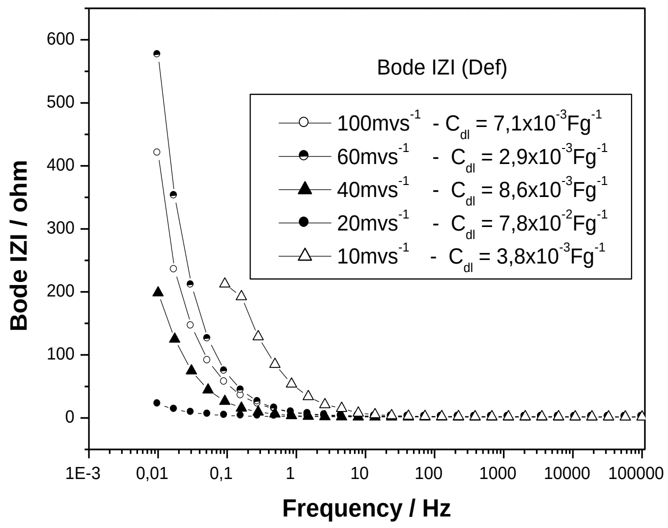

Figure 8. Bode-magnitute plot of 1-(4-methoxyphenyl)-1H-Pyrrole electrografted CFMEs with different scan rates. Inset: Calculated double layer capacitance values.

3.4. Characterization with FTIR-ATR Spectroscopy

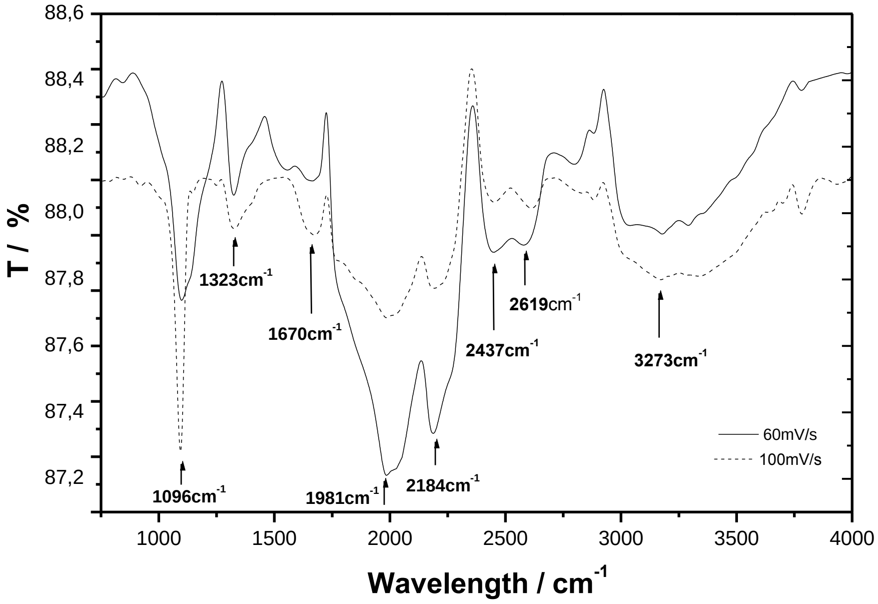

Figure 9. FTIR-ATR spectrum of poly(1-(4-methoxyphenyl)-1H-Pyrrole) in TEAP/CH_2Cl_2 . [1-(4-methoxyphenyl)-1H-Pyrrole$]_0$ = 10 mM.

The FTIR-ATR spectra of P(MPhPy) was obtained from the surface of the electrocoated CFMEs by reflectance FTIR measurements and absorption bands of each spectrum at a scan rate of 60 mV s^{-1} and 100 mV s^{-1} are given in Figure 9. The results of other modified electrode at different electrodeposition scan rates were given in Table 1.

Table 1. FTIR bands of 1-(4-methoxyphenyl)-1H-Pyrrole obtained with different electrodeposition scan rates.

Scan rate / mVs^{-1}	**Ar-CH/ cm^{-1}**	**Aliphatic C-H/ cm^{-1}**	**Ar-OCH$_3$/ cm^{-1}**	**C=C ring streching/ cm^{-1}**	**C=C asymmetric ring streching/ cm^{-1}**	**C=C Symmetric ring streching/cm^{-1}**	**C-N streching/ cm^{-1}**	**ClO$_4$, doping induced band/ cm^{-1}**
10	3273	2626	2289	1675	1502	1413	1246	1086
20	3281	2626	2295	1675	1504	1413	1240	1080
40	3277	2628	2270	1654	1504	1406	1236	1084
60	3287	2594	2186	1661	1541	-	-	1099
100	3346	2619	2437	1671	-	-	-	1091

In FTIR spectrum ClO_4^- ion observed at 1100 cm^{-1} [45], the presence of a strong band at this wave number poly(1-(4-methoxyphenyl)-1H-Pyrrole) indicates that the polymer are doped with ClO_4^- ion. The electronic properties of conductive polymers are strongly dependent on conjugation length. Defects interrupt conjugation including sp^3 carbons, carbonyl groups, crosslink etc. [46]. Tian and Zerbi [47, 48] have used a parameter called effective conjugation coordinate to calculate IR spectra of poly(1-(4-methoxyphenyl)-1H-Pyrrole). This theory successfully predicts the number and position of main infrared band of poly(1-(4-methoxyphenyl)-1H-Pyrrole) and shows that FTIR spectrum strongly influenced by the conjugation length.

In particular Zerbis calculation predict that as conjugation length is increased intensity of anti-symmetric ring stretching mode at around 1507 cm^{-1} will decrease relative to the intensity of the symmetric mode at around 1405 cm^{-1}, as a result the ratio of intensity of the 1507 and 1405 in an experimental FTIR spectrum can be used to relative measurement of the conjugation length. The intensity of anti-symmetric ring stretching mode at around 1507cm^{-1} will decrease relative to the intensity of the symmetric mode at around 1405 cm^{-1} with increasing deposition rate. The peak shifts increases with the electrodeposition scan rate at around 3273 cm^{-1}, however the peak at 2283 cm^{-1} decreases with the scan rate. The variance of the peaks in the FTIR-ATR revealed that (Table1) C=C double bond decrease might be due to the chain growth of pyrrole ring with a steric effect of phenyl ring at higher scan rates. The relationship FTIR-shift 3273 cm^{-1} and 2283 cm^{-1} between scan rate of PMPhPy was given in Figure 10.

Transmittance (%) of the ratio of the bands vs. scan rate graph showed that intensity of doping induced band (1086 cm^{-1}) decreases with the scan rate, which may be due to changes in the oxidation levels of PMPhPy film. The most oxidized PMPhPy is polymer obtained at a scan rate of 10 mVs^{-1}, since more charges accumulated on this polymer. Comparison of T % vs. scan rate and shift of C-N streching 1246 cm^{-1} vs. scan rate were given in Fig.11.

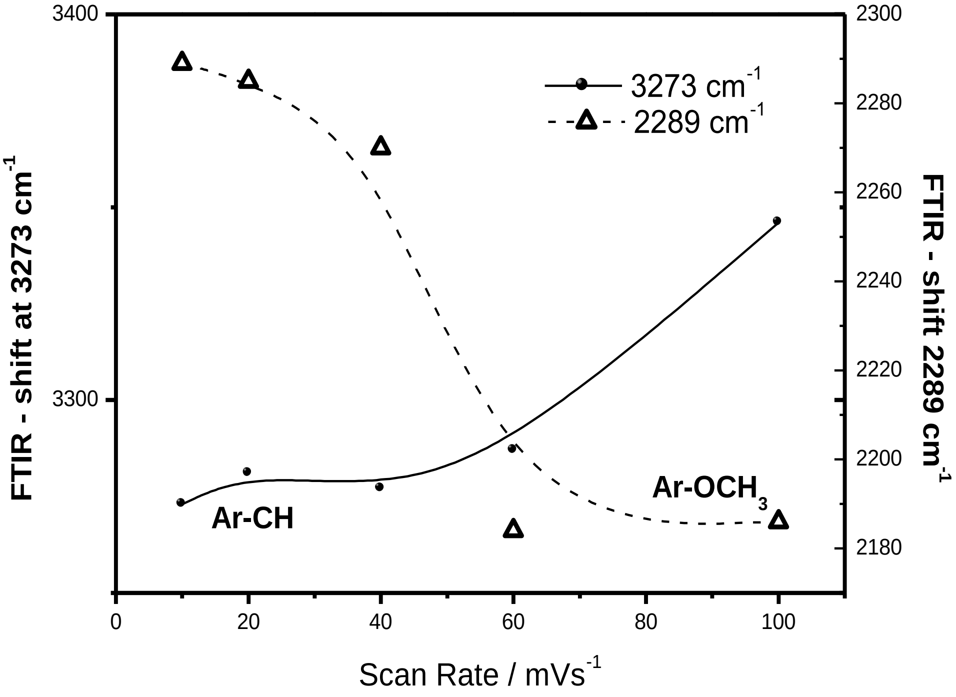

Figure 10. The relationship FTIR-shift 3273 cm^{-1} and 2283 cm^{-1} between scan rate of PMPhPy.

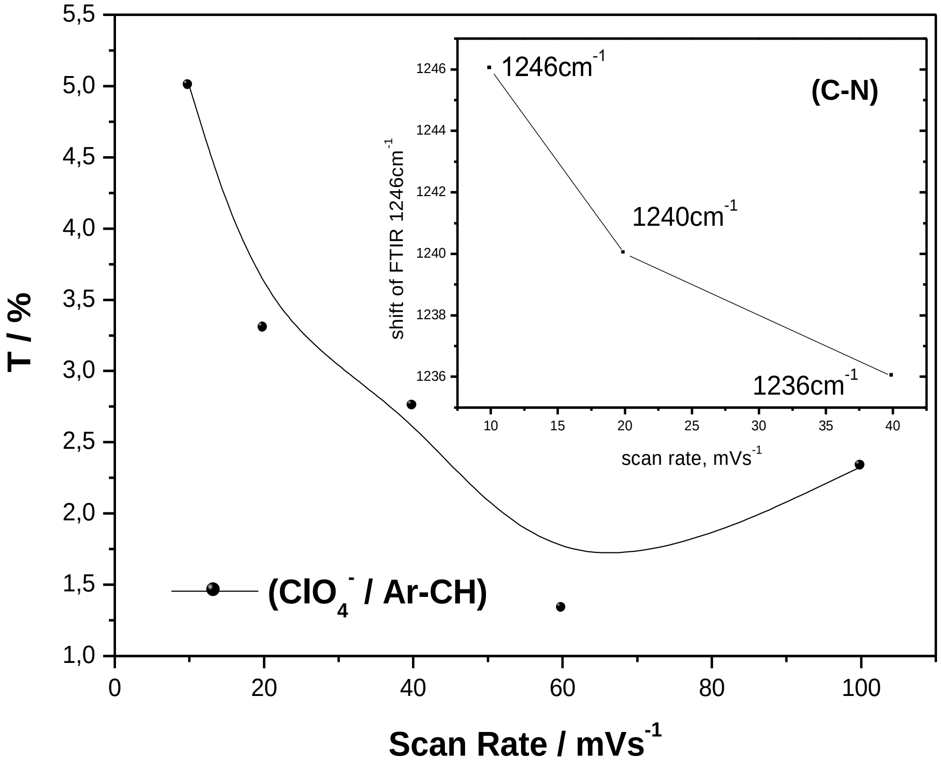

Figure 11. Comparison of T % vs. scan rate. Inset: Shift of C-N strecthing 1246 cm^{-1} vs. scan rate.

4. CONCLUSION

Carbon fiber micro electrodes were modified via electrodeposition of 1-(4-methoxyphenyl)-1H-Pyrrole. In this study electropolymerization reactions were studied with a commercially new monomer at different scan rates. Cyclic voltammogram for a modified carbon fiber electrode with the resultant polymer shows an enhanced cathodic and anodic peak current that increases linearly with different scan rate. Variant scan rates changed the redox parameters of coated micro electrodes and affected the electrochemical impedance measurement results. The comparison with the impedance and growth processes gives a reasonable correlation.

The obtained conductive polymeric films onto the carbon fiber micro electrodes denote capacitor behavior with nearly 90^0 lines at low frequency region and having very high phase angles (85^0). These results indicate that electrochemically modified carbon fiber microelectrodes can be used for the storage of energy in electrochemical capacitors and polymerization conditions have very drastic effect on modified surfaces.

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