

**ELECTROPOLYMERIZATION OF N-PYRROLE,
N -PHENYLPYRROLE, 1-(4-METHOXYPHENYL)-1H-PYRROLE ON CARBON FIBER
MICRO ELECTRODES, CHARACTERIZATIONS AND BIOSENSOR APPLICATIONS**

M.Sc. Thesis by

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**N-PIROL, N-FENİLPIROL VE 1-(4-METOKSİFENİL)-1H-PIROL'ÜN KARBON
FİBER MİKRO ELEKTROT ÜZERİNE ELEKTROPOLİMERİZASYONU,
KARAKTERİZASYONU VE BİYOSENSÖR UYGULAMALARI**

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ABBREVIATIONS

AC	: Alternating Current
ATR-FTIR	: Attenuated Total Reflectance Fourier Transform Infrared
ACN	: Acetonitrile
CP	: Conducting Polymer
CF	: Carbon Fiber
CFME	: Carbon Fiber Micro Electrode
CPE	: Constant Phase Element
CV	: Cyclic Voltammogram
DC	: Direct Current
DCM	: Dichloromethane
EIS	: Electrochemical Impedance Spectrometer
HOMO	: Highly Oriented Molecular Orbital
LiClO₄	: Lithiumperchlorate
NaClO₄	: Sodiumperchlorate
PPy	: Polypyrrole
PPPy	: Polyphenylpyrrole
PMPPy	: Poly1-(4-Methoxyphenyl)-1H-pyrrole
SEM	: Scanning Electron Microscopy
TEAP	: Tetraethylammoniumperchlorate
TEATFB	: Tetraethylammonium tetrafluoroborate
TBATFB	: Tetrabutylammonium tetrafluoroborate

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LIST OF SYMBOLS

C_{sp}	: Specific Capacitance
C_{dl}	: Double Layer Capacitance
E_g	: Band Gap
E_{eq}	: Equivalant Potential
$E_{1/2}$	: Half wave potential
$E_{a, c}$	: Oxidation, Reduction Potential
E_{onset}	: Onset potential
$I_{a, c}$	: Anodic, Catodic Peak Current
Q_{pg}	: Deposition Charge
R_p	: Polarization Resistor

ELECTROPOLYMERIZATION OF N-PYRROLE, N -PHENYLPYRROLE, 1-(4-METHOXYPHENYL)-1H-PYRROLE ON CARBON FIBER MICRO ELECTRODES, CHARACTERIZATIONS AND BIOSENSOR APPLICATIONS

SUMMARY

Electrical conductivity in a conjugated polymer (polyacetylene) in 1977 were reported by Shirakawa, Heeger and MacDiarmid [1]. Then the possibility of combining in these new conjugated materials the properties of organic polymers and the electronic properties of semiconductors has been studied for various applications. The preparation, characterization and application of electrochemically active conducting polymers are still mostly research activity in electrochemistry. Electrochemical polymerization represents a widely employed route for the synthesis of some important classes of conjugated polymer such as pyrrole (Py).

Conductive polymers can be prepared in two ways; chemical and electrochemical. Electrochemical polymerizations are mostly achieved via cyclic voltammogram by anodic oxidation onto a working electrolyte which is made from carbon based structures nowadays. Electrical conductivity is achieved for the film of conducting polymer by oxidation or reduction, followed respectively by the insertion of anionic or cationic species from supporting electrolyte solutions.

Carbon fiber is a polymer which is a form of graphite. Graphite is a form of pure carbon. In graphite the carbon atoms are arranged into big sheets of hexagonal aromatic ring. Porous carbon is the most frequently selected electrode material which offers a large surface area and very well polarization due to porosity which makes porous carbon is one of the most promising electrode material for supercapacitor application. Carbon fiber micro electrode shows superior performance in cyclovoltammetric studies due to its micron size cylindrical structure, and its disposable character having a new surface area at each time rather than cleaning the electrode surface which is necessary for Pt or Au electrodes. For many cases carbon fiber electrodes reveals better reversibilities than the metal electrodes.

The most intensively studied polymers are polypyrrole and their derivatives as well as polyphenylene. Conductive polypyrrole films are obtained directly by anodic polymerization of pyrrole in aqueous or organic electrolytes. They are black and, under suitable reaction conditions, can be detached from the anode in the form of self-supporting films.

Polypyrrole has a high mechanical and chemical stability and can be produced continuously as flexible film by electrochemical techniques. The quality of the

polymer is greatly influenced by many factors, e.g., impurities, electrode materials, pressure, concentration and temperature. By changing reaction conditions, polymers with different surface morphologies can be obtained. Variation of the monomers and their substituents yields polymers with conductivities between 10^2 and 10^{-4} S/cm. Alkyl substituents also increase the solubility of the polymers with the result that electrically conducting polymers can be applied as coatings from solutions.

In this study, N-Pyrrole, N-Phenylpyrrole and [1-(4-Methoxy Phenyl)-1H-Pyrrole] monomers were electropolymerized via cyclic voltametry and their characterizations were carried out via electrochemical impedance spectroscopy and FTIR-ATR spectrophotometer; than morphological surface analyses were performed with scanning electron microscopy and atomic force microscopy.

Cyclovoltammetric characterizations were performed with a series of combinations by differentiating the parameters. Electropolymerization process were performed in 0.05M TEAP in CH_2Cl_2 at various scan rates, scan numbers, monomer concentrations and different electrolyte solutions. CH_2Cl_2 was chosen as a standard solvent to prepare electrolyte for pyrrole derivatives during this study. Firstly, scan rate effect on polymer growth process were investigated. Cyclic voltammogram of [1-(4-Methoxy Phenyl)-1H-Pyrrole] obtained with 10, 20, 40, 60, 100 mV s^{-1} showed the broad and symmetrical redox waves. Potentiodynamic growth of [1-(4-Methoxy Phenyl)-1H-Pyrrole] obtained with different scan rates have showed different redox behavior and 60 mV s^{-1} scan rate properties were found more reversible than the others. Also the correlation with EIS was in a good agreement with the 60 mV s^{-1} .

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 transfer and charge transport processes, solution resistance etc. With impedance data a complete description of an electrochemical system is possible. For this study electrochemical impedance spectroscopy measurements were performed at open circuit potential in the range of 100 kHz-10 mHz in monomer free solutions.

On the other hand, monomer concentration effects on electropolymerization was resulted in MPPy coated electrodes showed that dilution of MPPy monomer concentration increases the charge storage from 74^0 to 85^0 Bode phase angle which is very close to 90^0 as observed in supercapacitors.

After that electrolyte effect was evaluated using multiple cycles in 0.1 M TBATFB/ACN, $\text{LiClO}_4/\text{ACN}$, TEATFB/ACN and $\text{NaClO}_4/\text{ACN}$ for 10 cycles for MPPy monomer. According to the results, TEATFB shows the best reversibility ($I_a / I_c = 1.12$). However, when we look at the $E^{1/2}$ values the conjugation length is longer for NaClO_4 because of the 0.935V half way potential. Besides ΔE (V) value of NaClO_4 is the highest (0.60V) which means it has the thicker film on CFME.

For substitution effect, characterizations for N-Pyrrole, N-Phenylpyrrole and [1-(4-Methoxy Phenyl)-1H-Pyrrole] were performed. CV of pyrrole shows different redox behaviour than N-phenylpyrrole, and 1[4H-methoxyphenyl] -1H-pyrrole. Py, PhPy, and MPPy structures were also showed differently shaped grown structures at SEM photos. Phenyl group increases the electrical properties by supplying more conjugation. Therefore, the deposition charge differences were evaluated with 1, 10

and 100 cycle numbers. While the growth charge increases than the peak current and coating thickness increases.

The electrochemical parameters of the CFME / MPPy, Ppy, Py / Electrolyte system were evaluated by employing the ZSimpWin (version 3.10) software from Princeton Applied Research. There different equivalent electrical circuit model and variation of the solution resistance, double layer capacitance and low frequency capacitance of the three monomer film investigated.

Morphology of coatings for different applied scan rates and monomer concentrations and substitutions were studied. The SEM pictures show a pronounced difference in the surface morphology. Phenylpyrrole showed the most uniformly deposition. Scan rate effect also changed the structure from thin stratified film to globular structure. AFM results were also examined the substitution effect clearly.

N-PIROL, N-FENİLPİROL VE 1-(4-METOKSİFENİL)-1H-PIROL'ÜN KARBON FİBER MİKRO ELEKTROT ÜZERİNE ELEKTROPOLİMERİZASYONU, KARAKTERİZASYONU VE BİYOSENSÖR UYGULAMALARI

ÖZET

Konjuge polimerler için elektriksel iletkenlik 1977 yılında Shirakawa, Heeger ve MacDiarmid tarafından açıklanmıştır [1]. Daha sonra bu konjuge polimerlerin bağlanması, organik polimerlerin yapıları ve yarı iletkenlerin elektriksel özellikleri yaygın olarak çalışılmaya başlamıştır. Elektrokimyasal olarak aktif olan konjuge polimerlerin sentezlenmesi, karakterizasyonu ve uygulama alanları halen günümüzde çalışılan en popüler elektrokimya konularıdır. Elektrokimyasal polimerizasyon pirol gibi önemli iletken polimerlerin sentezinde ve karakterizasyonunda kullanılan en önemli yöntemir.

İletken polimerlerin sentezi kimyasal ve elektrokimyasal olmak üzere ikiye ayrılır. Elektrokimyasal polimerizasyon genellikle döngülü voltamogram kullanılarak anodik oksidasyon ile çalışma elektrodunun üzerinde gerçekleştirilir. Son dönemlerde çalışma elektrotları karbon bazlı yapılar arasından seçilmektedir. İletken polimer filmlerde elektriksel iletkenlik anyonik ve katyonik türlerin yüklenmiş olarak yapıya girmesini takip eden yükseltgenme ve indirgenme yolu ile gerçekleşmektedir. Karbon fiber bir çeşit grafit formu olarak tanımlanırken, grafit ise saf karbon olarak adlandırılabilir. Grafit yapısında karbon atomları düzlemsel yapı üzerinde hegzagonal halkalar halinde bulunmaktadır. Porlu yapıya sahip karbon geniş yüzey alanı sağlama ve iyi polarize olması açısından süper kapasitör uygulamalarında en çok tercih edilen elektrot malzemesidir. Karbon fiber mikro elektrotlar sahip oldukları mikron boyutundaki silindirik yapıları altın ve platindeki gibi yüzey temizleme işlemi gerektirmeden tek kullanımlık olarak hazırlanmaları açısından elektrokimyasal polimerizasyon işlemlerinde tercih edilmektedir. Ayrıca birçok durumda metal elektrotlara nazaran daha iyi sonuçlar verdiği saptanmıştır.

Son zamanlarda sıklıkla çalışılan iletken polimerlerin başında polipirol ve polifenilen türevleri gelmektedir. İletken polipirol filmleri sulu ya da organik çözeltiler içerisinde anodik oksidasyon ile gerçekleştirilmektedir.

Elde edilen polimer film yapısı siyah renkte olup elektrot yüzeyinden sıyırma yöntemi ile alınabilir. Polipirol yüksek mekanik, kimyasal kararlılık ve elektrokimyasal teknikle devamlı olarak esnek film elde edilmesi nedeniyle pek çok araştırmada iyi bir maddedir. Elde edilen polimer malzemenin nitelikleri elektrot yüzeyi, safsızlıklar, basınç, sıcaklık ve konsantrasyondan çok fazla etkilenir.

Reaksiyon koşulları değiştirilerek farklı yüzey morfolojilerine sahip polimerler elde edilebilir. Monomer ve sübstütyent çeşitliliği sağlanarak 10^2 ve 10^{-4} S/cm iletkenlik aralığına sahip polimerler elde edilebilir. Ayrıca alkil grupları polimerlerin çözünürlüğünü artırır.

Bu çalışmada, N-Pirol, N-Fenilpirol ve 1-(4-Metoksi Fenil)-1H-Pirol monomerleri döngülü voltamogram kullanılarak karbon fiber mikro elektrot yüzeyleri üzerine elektropolimerizasyonu sağlanmıştır. Modifiye edilmiş mikro elektrot yüzeyleri elektrokimyasal empedans spektroskopisi ve FTIR-ATR spektrofotometresi ile karakterize edilmiştir. Son aşamada yüzey morfolojileri taramalı elektron mikroskobu ve atomik kuvvet mikroskobu ile analiz edilmiştir.

Döngülü voltamogramla yapılan kaplamalar çeşitli parametreler değiştirilerek birçok kez tekrarlanmıştır. Elektropolimerizasyon prosesi 0.05M TEAP/CH₂Cl₂ elektrolit çözeltisi içerisinde, tarama sayısı, tarama hızı, monomer konsantrasyonu ve farklı elektrolit kombinasyonları kullanılarak yapılmıştır. İlk olarak tarama hızının polimerizasyon üzerine etkisi incelenmiş, 1-(4-Metoksi Fenil)-1H-Pirol monomeri kullanılarak 10, 20, 40, 60 ve 100mV/s lik taramalarda kaplamalar gerçekleştirilmiştir. Potansiyodinamik kaplama sonucunda tüm tarama hızları için farklı redoks parametreleri elde edilmiş ancak en kararlı yapıya 60 mV/s ile kaplanan yapıda ulaşılmıştır. Bu sonuçlar empedans dataları ile aynı bulguları vermiştir.

Elektrokimyasal empedans spektroskopisi elektrokimyasal sistemlerin karakteristik özelliklerini, ara faz kapasitanslarını, difüzyon parametrelerini, yük transferini ve çözücü direncini belirlemede kullanılan ve en güvenilir sonuçlar veren yöntemdir. Elektrokimyasal empedans ölçümleri 100kHz-10mHz aralığında açık devre potansiyelinde ve monomer içermeyen elektrolit ortamında gerçekleştirilmektedir.

Bunların yanı sıra 1-(4-Metoksi Fenil)-1H-Pirol'ün farklı monomer konsantrasyonlarında alınarak elektropolimerizasyonu sağlanmış ve empedans üzerine etkileri tartışılmıştır. Alınan sonuçlarda en düşük konsantrasyon olarak belirlenen 0.001M 1-(4-Metoksi Fenil)-1H-Pirol'ün kapasitans diagramında 90⁰ lik dikliğe yaklaştığı ve faz açısı 0.1M olan polimerin 74⁰ iken 0.001M da 85⁰ dereceye ulaştığı gözlemlenmiştir. Bu durumda seyreltik çözeltideki polimerin kapasitans özelliklerini olumlu yönde etkilediğini söyleyebiliriz.

Elektrolit etkisine baktığımızda 4 farklı kombinasyon denenmiştir; 0.1 M TBATFB/ACN, LiClO₄/ACN, TEATFB/ACN ve NaClO₄/ACN. Tüm kaplamalar 10 tarama sayısı ile 40mV/s lik tarama hızlarında gerçekleştirilmiştir. Sonuç olarak NaClO₄ kullanıldığında elde edilen E_{1/2} değeri en yüksek olup (0.935V) konjugasyonun uzunluğunu ifade etmektedir. Bununla birlikte ΔE (V) anodik ve katodik pik potansiyel farkı yine en yüksek değerine NaClO₄ çözeltisinde ulaşmakta, bu da bize en kalın kaplamanın bu çözeltide olduğunu göstermektedir.

Sübstütyent etkisi incelendiğinde N-Pirol, N-Fenilpirol ve 1-(4-Metoksi Fenil)-1H-Pirol monomerleri aynı şartlar altında CV ile mikro elektrot yüzeylerine kaplanmış, Pirol'ün Fenilpirol ve 1-(4-Metoksi Fenil)-1H-Pirol'e nazaran çok daha farklı redoks davranışları gösterdiği gözlenmiş ve elektrot yüzeyindeki büyümenin farklı morfolojik şekillerde olduğu SEM fotoğrafları ile gösterilmiştir. Bu çalışmada yapılan korelasyonlar sonucunda fenil grubunun bağlı olduğu polimerlerin elektriksel

özelliklerinin konjugasyonun uzunluğundan ötürü arttığı gözlenmiştir. Bununla birlikte tarama sayısı etkisine de bakılarak 1, 10 100 tarama sayısında kaplamalar yapılmış ve kaplama sırasında açığa çıkan yük ile tarama sayısı arasında lineer bir artış olduğu gözlenmiştir.

Elektrokimyasal parametreleri KFME/MPPy,PPy,Py/elektrolit olarak bir arada değerlendirebilmek adına ZSimpWin yazılım programı kullanılarak empedans dataları sayesinde deneysel sonuçları en uygun eşdeğer elektrik devreleri simule edilmiştir. Bu çalışma yapılırken 3 farklı devre çeşidi tüm monomerler için ayrı ayrı denenmiştir.

Son olarak yüzey morfolojisi analizleri SEM fotoğrafları ile sunulmuş, tarama hızı, konsantrasyon ve sübstütyent etkisinin yapıyı yapıyı çok fazla değiştirdiği gözlemlenmiştir. AFM görüntüleri ise sadece sübstütyent etkisi içeren malzemeler için elde edilmiş ve yüzeylerinin farklı pürüzlülüklerde olduğu belirtilmiştir.

1. INTRODUCTION

1.1. Conducting Polymers

Electrical conductivity were reported in 1977 by Shirakawa, Heeger and MacDiarmid for a conjugated polymer [1], and the research on conducting polymers have been continuous for several years. Many researchers have been focused on the conducting polymers to commercialize them with applications.

Conducting polymers have been attracting a great deal of attention thanks to their potential applications to electronic devices, sensors, thin film transistors, polymer light-emitting diodes, electrochromic devices, corrosion protection and actuators. Electrical characteristics of these polymers are of central interest for their applications to the practical devices. Any appropriate molecular combination makes it possible to prepare multifunctional molecules that provide possibility for desired applications.[2-4]

The possibility of combining in these new materials the properties of organic polymers and the electronic properties of semiconductors has been the driving force for various applications [5-7]. Electronically conducting polymers, such as polypyrrole, polythiophene or polyaniline, are a class of organic semiconductors with many possible areas of application.

Conducting polymers can be prepared via chemical or electrochemical polymerization [8]. Electrochemical synthesis is rapidly becoming the general preferred method for preparing electrically conducting polymers because of its simplicity and reproducibility. Electronically conducting polymer films are obtained onto a working electrode surface by anodic oxidation of the corresponding monomer in the presence of an electrolyte solution via electropolymerization. Different electrochemical techniques can be used including potentiostatic (constant potential, chronoamperometry), galvanostatic (constant current, chronopotentiometry) and potentiodynamic (potential scanning *i.e.* cyclic voltammetry) methods [9].

Electrical conductivity is achieved in the film of conducting polymer by oxidation (p-doping) or reduction (n-doping), followed respectively by the insertion of anionic or cationic species[9]. Due to the double bond alternation in the conjugated polymer backbone, the charged species formed upon doping are able to move along the carbon chain (delocalization) allowing electron transport and thus giving an electronically conductive material [10].

The Π -electron system along the polymer backbone which confers rigidity and the crosslinking points between polymer chains, make conducting polymers insoluble, infusible and poorly processable. [5] Changing polymerization conditions and copolymerization processing of conducting polymers may offer improvements in their mechanical properties and processing.

The advantage of electrochemical polymerization is that the reactions can be carried out at room temperature and thickness of film can be controlled by varying either the potential or current.

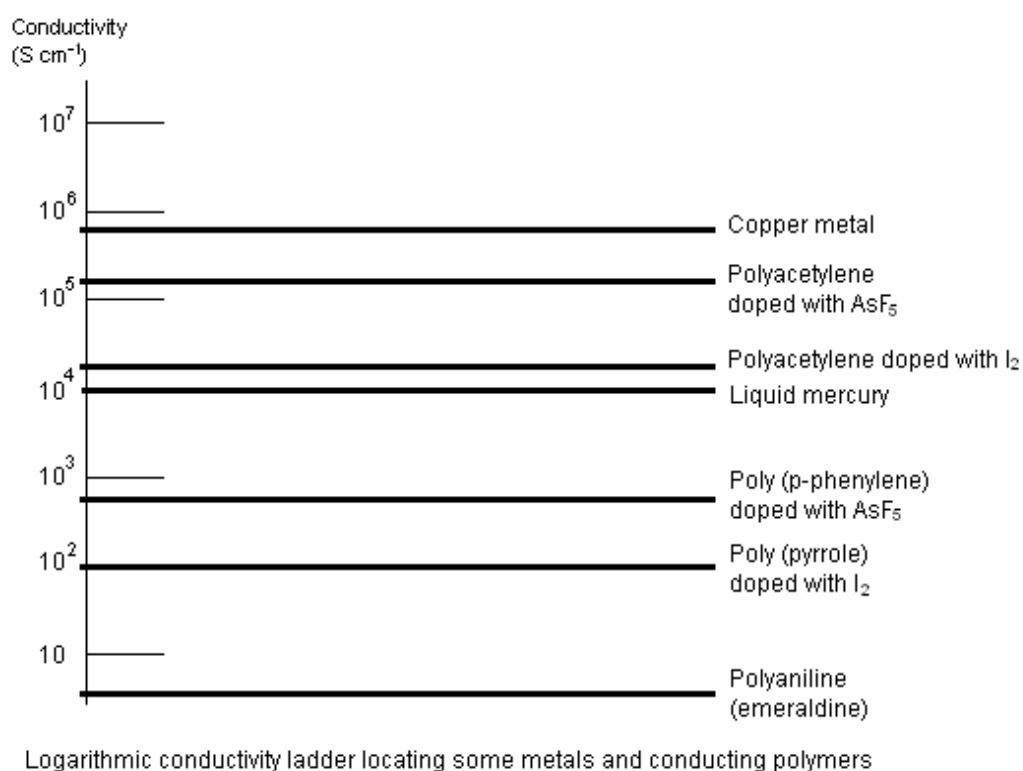


Figure 1.1: Conductivity of Some Polymers and Metals

1.1.1. Electrical conductivity for polymers

Since the discovery of Shirakawa, many other conducting polymers (CP) have been synthesized after polyacetylene (PA). The most common polymers are shown in the figure below. Their structures and electronic properties have been reviewed extensively [7]. Apart from polyaniline, all of these systems share one common structural feature, namely a rigid nature brought about by the sp^2 carbon-based backbone. The utilization of the conjugated construction affords polymer chains possessing extended π -systems, and it is this feature alone that separates CPs from their other polymeric counterparts.

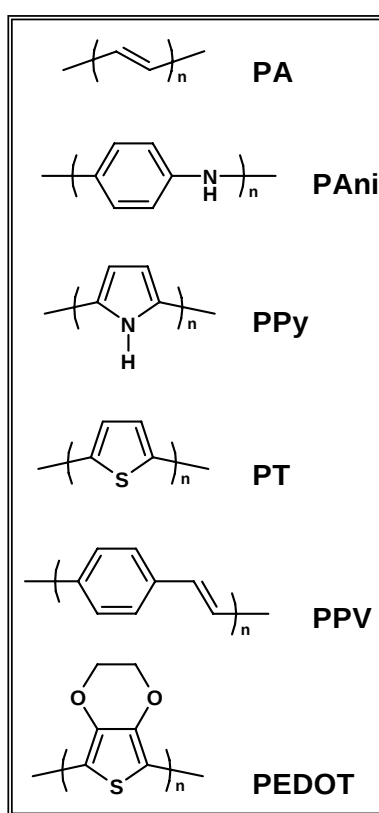


Figure1.2: The Most Common Conducting Polymer Structures

The electrical properties of any material are a result of the material's electronic structure that CP's form bands through extensive molecular orbital overlap leads to the assumption that their electronic properties can be explained by band theory. In this theory materials are classified as metals, semiconductors, or insulators indicated in Figure1.3.

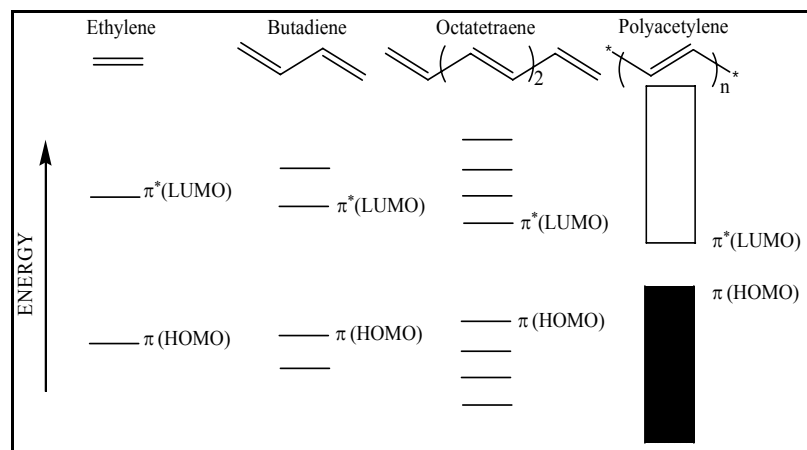


Figure 1.3: Molecular Orbital (MO) Diagram

1.1.2. Band gap theory

There is enough energy separation between the conduction and valence bands that thermal energy alone is insufficient to excite electrons across the band gap. For electrical conductivity to occur, an electron must have a vacant place to move and occupy. When bands are completely filled or empty, conduction can not occur. Metals are highly conductive because they have unfilled bands. Semiconductors have an energy gap small enough that thermal excitation of electrons from the valence to the conduction bands is sufficient for conductivity; however, the band gap in insulators is too large for thermal excitation of an electron across the band gap.

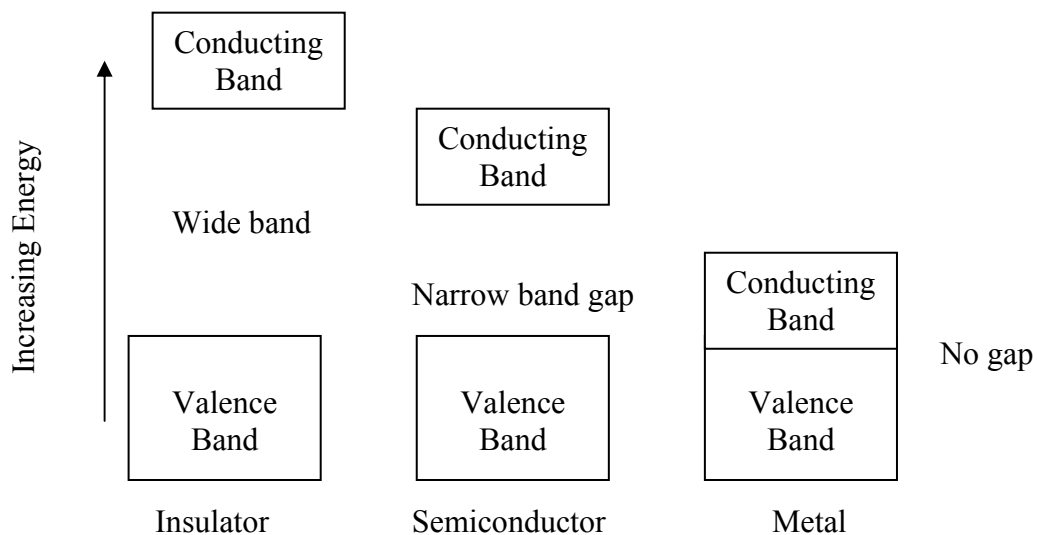


Figure 1.4: Classification of Materials, and Schematic of Valence and Conduction

1.1.3. Doping process in conducting polymers

The electrochemical switching of a conducting polymer (CP) between the doped and undoped states involves both electron and ion injection into or extraction from the polymer, concomitant with the transport of electronic and ionic charges within the CP. Consequently, the charge transport processes inside the CP bulk, as well as across the CP's interfaces, constitute crucial points in many applications and have been the object of extensive researches.

In particular, it has been reported that in most cases ion transport is the slow process, i.e. the step limiting the switching rates of, for example, displays and electronic devices based on similar materials.[11]

The diffuse nature of the extended π -system readily allows electron removal from, or injection, into the polymer. The term "doping" has been borrowed from semiconductor physics with "p-doping" and "n-doping" being used to describe polymer oxidation and reduction, respectively. Doping in regards to semiconductors is quite different as it is a very distinct process carried out at low levels ($< 1\%$) as compared to CP doping (usually 20-40%). However, the manner by which doping transforms a neutral CP into a conductor remained a mystery for many years.

When applied to CP modified electrodes, electrochemical impedance spectroscopy (EIS) has proved to be quite a useful tool for studying the charge transport inside the polymer coating and the charge transfer at the metal/polymer and polymer/solution interfaces.[12-15]

However, several problems concern both the correct execution of the measurements and the interpretation of the data obtained, due to the high complexity of the system. As to the measurements, a first, very serious though often underestimated, problem arises from the changes that the CP deposit undergoes when working on it for the long times required by the execution of a complete series of impedance measurements.[16]

1.1.4. Polaron-bipolaron

If only one electron per level is removed a radical cation is formed and is known as a "polaron". Further oxidation removes this unpaired electron yielding a dicationic species termed a "bipolaron". High dopant concentrations create bipolaron-"rich" materials and eventually lead to band formation of bipolaron levels. Such a

theoretical treatment, thereby, explains the appearance, and subsequent disappearance, of the Electron Paramagnetic Resonance signal of a CP with increased doping as the neutral polymer transitions to the polaronic form and subsequently to the spinless bipolaronic state.

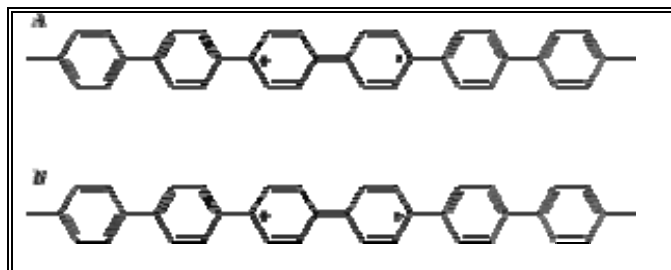


Figure 1.5: Positively Charged Defects on Poly(p-phenylene). A: Polaron B: Bipolaron

The polymer may store charge in two ways. In an oxidation process it could either lose an electron from one of the bands or it could localize the charge over a small section of the chain. Localizing the charge causes a local distortion due a change in geometry, which costs the polymer some energy.

However, the generation of this local geometry decreases the ionization energy of the polymer chain and increases its electron affinity making it more able to accommodate the newly formed charges. This method increases the energy of the polymer less than it would if the charge was delocalized and, hence, takes place in preference of charge delocalization. This is consistent with an increase in disorder detected after doping by Raman spectroscopy. A similar scenario occurs for a reductive process.

Typical oxidizing dopants used include iodine, arsenic pentachloride, iron (III) and chloride. A typical reductive dopant is sodium naphthalide.

The main criteria is its ability to oxidize or reduce the polymer without lowering its stability or whether or not they are capable of initiating side reactions that inhibit the polymers ability to conduct electricity.

The oxidative doping of polypyrrole proceeds in the following way Figure 1.6. An electron is removed from the π -system of the backbone producing free radical and a spinless positive charge. The radical and cation are coupled to each other via local resonance of the charge and the radical.

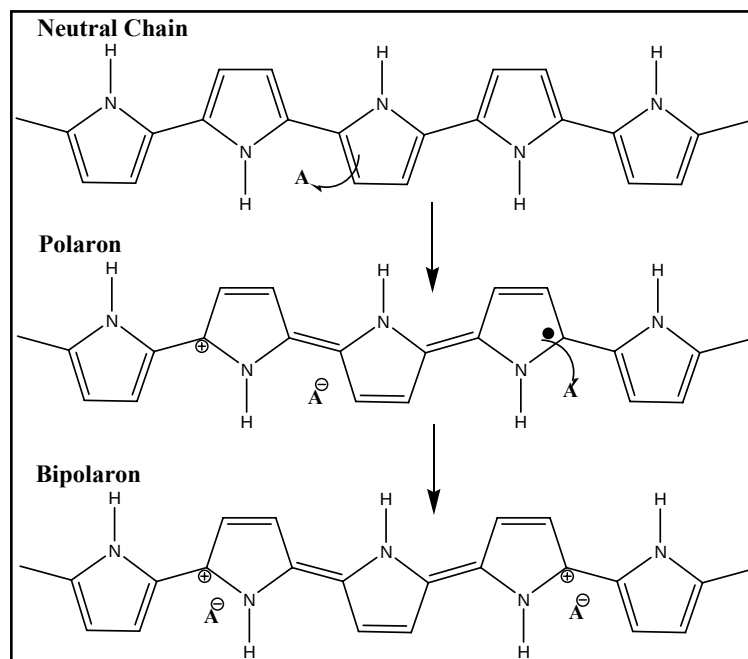


Figure 1.6: Oxidative Doping of Pyrrole. ($A^{\ominus}$: Dopant).

In the case of polypyrrole it is believed that the lattice distortion extends over four pyrrole rings. This combination of a charge site and a radical is called a polaron. This could be either a radical cation or radical anion. This creates a new localized electronic state in the gap, with the lower energy states being occupied by a single unpaired electron. The polaron state of polypyrrole is symmetrically located about 0.5 eV from the band edges.

Upon further oxidation the free radical of the polaron is removed, creating a new spinless defect called a bipolaron. This is of lower energy than the creation of two distinct polarons. At higher doping levels it becomes possible that two polarons combine to form a bipolaron. Thus at higher doping levels the polarons are replaced with bipolarons. The bipolarons are located symmetrically with a band gap of 0.75 eV for polypyrrole. This eventually, with continued doping, forms into a continuous bipolaron bands.

1.1.5. Polymer stability and processibility

Stabilities for conducting polymers can be divide into two part named as extrinsic and intrinsic. Extrinsic stability is related to sensitivity to external environmental agent such as oxygen, water, peroxides. This is determined by the polymers susceptibility of charged sites to attack by nucleophiles, electrophiles and free

radicals. If a conducting polymer is extrinsic unstable then it must be protected by a stable coating. Many conducting polymers, however, degrade over time even in dry, oxygen free environment. This intrinsic instability is thermodynamic in origin. This happens when the charge sites become unstable due to conformational changes in the polymer backbone.

Table 1.1: Stability and Processing Attributes of Some Conducting Polymers.

POLYMER	Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Stability (doped state)	Processing Possibilities
Polyacetylene	103 - 105	poor	limited
Polyphenylene	1000	poor	limited
PPS	100	poor	excellent
PPV	1000	poor	limited
Polypyrroles	100	good	good
Polythiophenes	100	good	excellent
Polyaniline	10	good	good

Electrochemical polymerization occurs by suitable monomers which are electrochemically oxidized to create an active monomeric and dimeric species which react to form a conjugated polymer backbone. The main problem with electrically conductive plastics stems from the very property that gives it its conductivity, namely the conjugated backbone. This causes many such polymers to be intractable, insoluble films or powders that cannot melt. There are, at this time, four main methods used to achieve these aims.

The first method is to manufacture a malleable polymer that can be easily converted into a conjugated polymer. This is done when the initial polymer is in the desired form and then, after conversion, is treated so that it becomes a conductor.

The second method is the synthesis of copolymers or derivatives of a parent conjugated polymer with more desirable properties. This method is the more traditional one for making improvements to a polymer. What is done is to try to modify the structure of the polymer to increase its processability without compromising its conductivity or its optical properties.

The third method is to grow the polymer into its desired shape and form. An insulating polymer impregnated with a catalyst system is fabricated into its desired form.

The final method is the use of Langmuir-Blodgett trough to manipulate the surface active molecules into a highly ordered thin films whose structure and thickness which are controllable at the molecular layer. Amphiphilic molecules with hydrophilic and hydrophobic groups produces monolayers at the air-water surface interface of a Langmuir-Blodgett trough.

1.1.6. Polypyrroles

The most intensively studied polymers are polypyrrole, polythiophene, and their derivatives as well as polyphenylenes. Polypyrrole is one of the most, widely studied organic conducting polymer due to the ease of synthesis, good redox properties, stability in the oxidized form, ability to give high electrical conductivities and useful electrical and optical properties [17, 19]. As a result of its good intrinsic properties, polypyrrole has proven promising for several applications, including batteries, supercapacitors, electrochemical (bio)sensors, conductive textiles and fabrics, mechanical actuators, electromagnetic interference (EMI) shielding, anti-static coatings and drug delivery systems [17]. Also because of its conductive properties polypyrrole has been shown to work as a protective layer against photocorrosion for photoelectrodes and its polymer coatings on electrode surface and change the catalytic activity of the electrodes [20].

Polypyrrole was shown to be a conducting polymer in 1968. Dall'Olio et al [21] prepared it by oxidation of pyrrole in sulfuric acid as a black powder with room temperature conductivity of 8 S cm^{-1} . This work was then extended by workers at IBM who showed that films of this polymer can be obtained by electrochemical polymerization. These films could be cycled electrochemically between a conducting (doped) state and an insulating state, with conductivities varying from 100 to $10^{-10} \text{ S cm}^{-1}$. Unlike the morphology of the Shirakawa's polyacetylene, which is fibrillar, polypyrrole films are dense. Thus, physically impermeable films of polypyrrole could be prepared.

Conductive polypyrrole films are obtained directly by anodic polymerization of pyrrole in aqueous or organic electrolytes (acetonitrile) [22]. They are black and,

under suitable reaction conditions, can be detached from the anode in the form of self-supporting films (minimum thickness ca. 30 μm). Some of the conducting salt used in the electrolyte solution is incorporated in the film as a counterion. In contrast to polyacetylene, polypyrrole has a high mechanical and chemical stability and can be produced continuously as flexible film (thickness 80 μm ; trade name: Lutamer, BASF) by electrochemical techniques. The quality of the polymers is greatly influenced by many factors, e.g., impurities, electrode material, pressure, concentrations, temperature, and comonomers. The most decisive, however, are the current density and the electrolyte, particularly the conducting anion X^- [23] because it is incorporated into the polymer as a counterion. The properties of the counterion (e.g., its size, geometry, charge) influence the properties of the polymer. The amount of counterion (anion) incorporated depends on the reaction conditions. In general, one anion is incorporated for every three pyrrole units.

By changing reaction conditions, polymers with different surface morphologies, (e.g., an open porous structure) can be obtained. Also variation of the monomers and their substituents yields polymers with conductivities between 10^2 and 10^{-4} S/cm. Alkyl substituents also increase the solubility of the polymers with the result that electrically conducting polymers can be applied as coatings from solutions.[24]

A crucial step in the continuing effort to develop more processable conjugated polymers has been the addition of solubilizing substituents on the monomer. However, the introduction of substituents to confer solubility and enhance processability can produce dramatic changes in the structure and electronic properties [25].

Also, the conjugated polymers composed of 5-membered heteroatomic rings present challenging problems in terms of their structural analysis and electronic properties. Among these systems, the conducting polymer of polypyrrole is still considered to be an important material for future technological applications. However, an exact determination of its structure is still not possible due to extremely low solubility and crystallinity. These experimental problems also lead to complications in understanding the growth mechanism [26].

1.1.7. Applications of conducting polymers

Until about 30 years ago all carbon based polymers were rigidly regarded as insulators. The notion that plastics could be made to conduct electricity would have

been considered to be absurd. Indeed, plastics have been extensively utilized by the electronics industry for this very property. They are used as inactive packaging and insulating material.

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes their electroactivity. The extended π -systems of conjugated polymer are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state. The two groups of applications are shown in Table 1.2.

These applications use the polymer's conductivity and electroactive property. For the first group, the polymers are used because of either their light weight, biological compatibility for ease of manufacturing or cost. By coating an insulator with a very thin layer of conducting polymer it is possible to prevent the buildup of static electricity. This is particularly important where such a discharge is undesirable. By modifying the thermoplastic used by adding a conducting plastic into the resin results in a plastic that can be used for the protection against electrostatic discharge [27].

By placing monomer between two conducting surfaces and allowing it to polymerise it is possible to stick them together. This is a conductive adhesive and is used to stick conducting objects together and allow an electric current to pass through them. Many electrical devices, particularly computers, generate electromagnetic radiation, often radio and microwave frequencies. By coating the inside of the plastic casing with a conductive surface this radiation can be absorbed.

Due to the biocompatibility of some conducting polymers they may be used to transport small electrical signals through the body, i.e. act as artificial nerves. Perhaps modifications to the brain might eventually be contemplated [28]. Modern planes are often made with light weight composites. This makes them vulnerable to damage from lightning bolts. By coating aircraft with a conducting polymer the electricity can be directed away from the vulnerable internals of the aircraft.

Table 1.2: Applications of Conducting Polymer According to Their Specialities.

GROUP1 / CONDUCTIVITY	GROUP2 / ELECTROACTIVITY
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Drug release systems
Printed circuit boards	Electromechanical actuators
Artificial nerves	'Smart' structures
Antistatic clothing	Optical computers
Aircraft structures	Rechargeable batterie, solid electrolytes
Active electronics (diodes, transistors)	Ion exchange membranes
Piezoceramics	Chemical, biochemical, thermal sensors

For the second group electroactive conducting polymers are used for several materials. An example for electroactive conducting polymer is a modified polyacetylene with an electron accepting group at one end and a withdrawing group at the other. A short section of the chain is saturated in order to decouple the functional groups. This section is known as a 'spacer' or a 'modulable barrier'. This can be used to create a logic device. There are two inputs, one light pulse which excites one end and another which excites the modulable barrier. There is one output, a light pulse to see if the other end has become excited [29]

The chemical properties of conducting polymers make them very useful for use in sensors. This utilizes the ability of such materials to change their electrical properties during reaction with various redox agents (dopants) or via their instability to moisture and heat. An example of this is the development of gas sensors. It has been shown that polypyrrole behaves as a quasi 'p' type material. Its resistance increases in the presence of a reducing gas such as ammonia, and decreases in the presence of an oxidizing gas such as nitrogen dioxide. The gases cause a change in the near surface charge carrier (here electron holes) density by reacting with surface adsorbed oxygen ions [30].

Probably the most publicized and promising of the current applications are light weight rechargeable batteries. The polymer battery, such as a polypyrrole- lithium cell operates by the oxidation and reduction of the polymer backbone. During charging the polymer oxidizes anions in the electrolyte enter the porous polymer to balance the charge created [31].

Conducting polymers can be used to directly convert electrical energy into mechanical energy. Electrochemical actuators can function by using changes in a dimension of a conducting polymer, changes in the relative dimensions of a conducting polymer and a counter electrode and changes in total volume of a conducting polymer electrode, electrolyte and counter electrode [32].

One of the most futuristic applications for conducting polymers are 'smart' structures. These are items which alter themselves to make themselves better. An example is a golf club which adapt in real time to a persons tendency to slice or undercut their shots. A more realizable application is vibration control .

Smart skis have recently been developed which do not vibrate during skiing. This is achieved by using the force of the vibration to apply a force opposite to the vibration. Other applications of smart structures include active suspension systems on cars, trucks and train; traffic control in tunnels and on roads and bridges; damage assessment on boats; automatic damping of buildings and programmable floors for robotics and AGV's [33].

Polypyrrole has been tested as microwave-absorbing “stealth” (radar-invisible) screen coatings and also as the active thin layer of various sensing devices. The conductivity of polypyrrole film suggests applications such as flexible conductive paths in printed circuits, heating films, and film keyboards. Polypyrrole films show good electromagnetic shielding effects of about 40 dB over a wide range of frequencies (0 – 1500 MHz).

Poly(3,4-ethylenedioxy-thiophene) doped with polystyrenesulfonic acid is manufactured as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and also serves as a hole injecting electrode material in polymer light-emitting devices.

Poly(phenylene vinylidene) derivatives have been major candidates for the active layer in pilot production of electroluminescent displays (mobile telephone displays).

Polythiophenes have been studied extensively for use in light-emitting diodes, among other applications, due to the chemical variability offered by substitution at the 3- and 4- positions. [34]. Polyaniline is also manufactured as a corrosion inhibitor.

1.1.8. Electrochemical capacitors

The most common electrical energy storage device is the battery. Batteries have been the technology of choice for most applications, because they can store large amounts of energy in a relatively small volume and weight and provide suitable levels of power for many applications. Shelf and cycle life has been a problem with most types of batteries, but people have learned to tolerate this shortcoming due to the lack of an alternative. In recent times, the power requirements in a number of applications have increased markedly and have exceeded the capability of batteries of standard design. This has led to the design of special high power, pulse batteries often with the sacrifice of energy density and cycle life.

Ultracapacitors (electrochemical capacitors) are being developed as an alternative to pulse batteries. To be an attractive alternative, ultracapacitors must have much higher power and much longer shelf and cycle life than batteries. By ‘‘much’’ is meant at least one order of magnitude higher. ECs have much lower energy density than batteries and their low energy density is in most cases the factor that determines the feasibility of their use in a particular high power application. For ECs, the trade-off between the energy density and the RC time constant of the device is an important design consideration. In general, for a particular set of materials, a sacrifice in energy density is required to get a large reduction in the time constant and thus a large increase in power capability.

During the last years, electrode materials for electrochemical capacitors (EC) have been extensively developed [36,37] due to the increasing demand for a new kind of accumulators of electrical energy with a high specific power of more than 10 kW/kg and a long durability (over 10^6 cycles).

The main advantage of this storage device is the ability of a high dynamic of charge propagation (shortterm pulse) that can be useful in the hybrid power sources for; electrical vehicles, digital telecommunication systems, UPS (uninterruptible power supply) for computers and pulse laser technique. The other profits of the EC system is a possibility of full discharge and a short-circuit between the two electrodes is also not harmful.

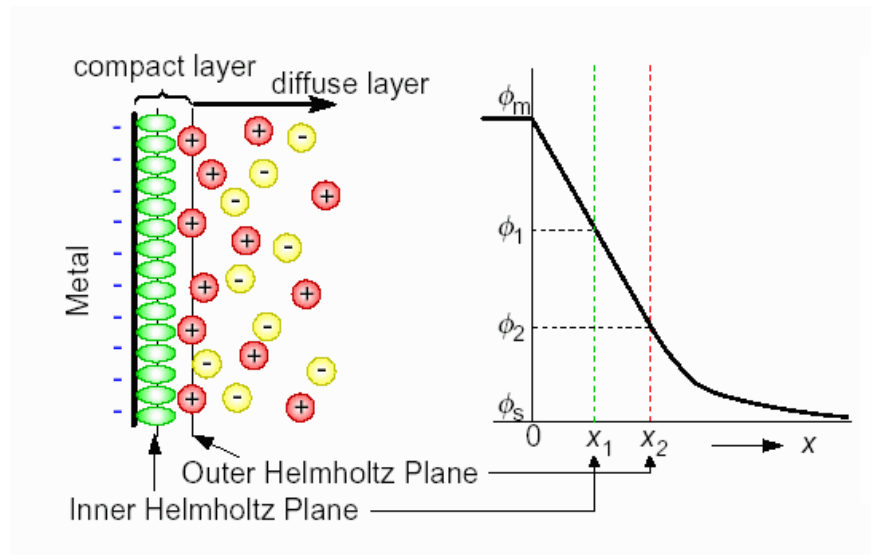


Figure 1.7: Scheme of the Electrochemical Double Layer

In the electrochemical capacitors, the electrical charge is accumulated in the double layer mainly by electrostatic forces without phase transformation in the electrode materials. The stored electrical energy is based on the separation of charged species in an electrical double layer across the electrode / solution interface illustrated in Figure 1.7. The charge density is accumulated at the distance of outer Helmholtz plane, i.e. at the centre of electrostatically attracted solvated ions. The electrochemical capacitor contains one positive electrode with electron deficiency electrodes being built from the same material

1.1.9. Supercapacitors or ultracapacitors

Supercapacitors, also known as ultracapacitors or electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors.

Performance of a supercapacitor (or ultracapacitor) combines simultaneously two kinds of energy storage i.e. an electrostatic attraction as in electric double layer capacitors (EDLC) and faradaic reactions similar to processes proceeding in accumulators. Pseudocapacitance arises when, for thermodynamic reasons, the charge q required for the progression of an electrochemical process is a continuously changing function of potential U . Then the derivative $C = dq/dU$ corresponds to a faradaic kind of capacitance.

The term *pseudo* originates from the fact that the double layer capacitance arises from quick faradaic charge transfer reactions and not only from electrostatic

charging. An ideal double layer capacitance behavior of an electrode material is expressed in the form of a rectangular shape of the voltametry characteristic behavior of supercapacitors. In this type of energy storage, the phenomenon is purely electrostatic and current is independent on potential. On the other hand, electrode materials with pseudocapacitance properties point out a deviation from such a rectangular shape and reversible redox peaks connected with pseudofaradaic reactions are remarkable. In this case charge accumulated in the capacitor is strongly dependent on the electrode material. This observed delay of potential during reversing the potential sweep is related with a kinetically slow process involved during charging pseudocapacitance.

1.1.10. Generalized transmission line circuit model

Equivalent circuit models employ mathematical or computer models of fundamental electric circuit components, such as resistors and capacitors, to model complex electrochemical processes. Simple equivalent circuits have long been used to predict the performance characteristics of porous electrodes.

These equivalent circuits primarily have been applied to attempt to capture the behavior of the double-layer at the interface between the electrode pores and electrolyte solution.

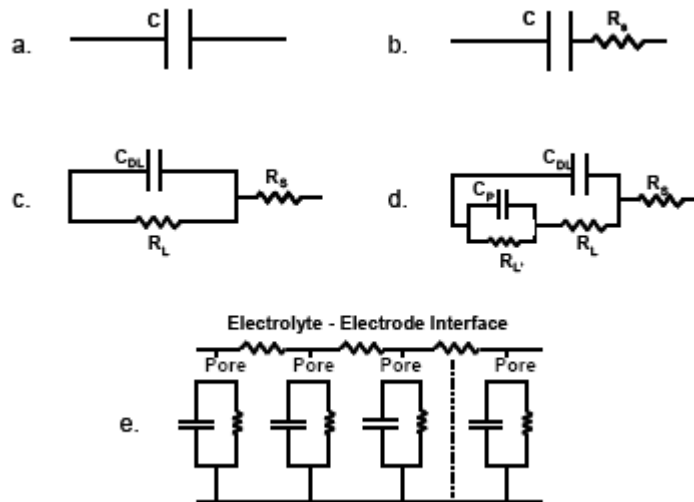


Figure1.8: Hierarchy of Equivalent Circuits For Porous Electrodes: (a) Capacitor; (b) Capacitor With Series Resistance; (c) Simple Double-Layer Pore Circuit: Capacitor and Leakage Resistance in Parallel, With Series Resistance; (d) Simple Pseudocapacitor Pore Circuit that Builds on (c) By Adding a Parallel Circuit Consisting of Capacitor in Parallel With Leakage Resistor; (e) Transmission Line Model For a Porous Electrode That Consists of a Line of Circuits Like (c) in Parallel.

Note that, alternatively, circuits like (d) could be used to model a pseudocapacitor model proposes that, because of unique electrosorption behavior found in micropores, the capacitance per micropore surface area and capacitance per external surface area must be calculated separately. The second model, which is now widely accepted, suggests that electrolyte ions cannot diffuse into pores beneath a size threshold and therefore the surface area of those pores cannot contribute to the capacitance. In considering the second model, there have been efforts to determine the optimal pore size and size distribution needed to maximize ion accessibility. As a corollary result, an inverse relationship between pore size and ESR has also been demonstrated.

Table 1.3: Circuit Elements Used in the Models

Equivalent element	Admittance	Impedance
R	$1/R$	$j\omega C$
C	$j\omega C$	$1/j\omega C$
L	$1/j\omega L$	$j\omega L$
W (infinite Warburg)	$Y_0 \sqrt{j\omega}$	$1/Y_0 \sqrt{j\omega}$
O (finite Warburg)	$\left[Y_0 \sqrt{j\omega} \right] \coth \left(B \sqrt{j\omega} \right)$	$\tanh \left(B \sqrt{j\omega} \right) / \left[Y_0 \sqrt{j\omega} \right]$
Q (CPE)	$Y_0 (j\omega)^\alpha$	$1/Y_0 (j\omega)^\alpha$

Looking at the electrode/polymer/electrolyte system from the viewpoint of the impedance characteristics, at variance with an electrified membrane inside an electrolytic solution, it constitutes a so-called ‘asymmetrical’ configuration [38], the current flow requiring the transport of electrons across the metal/polymer interface and of ions through the polymer/electrolyte interface; the charge percolation inside the polymer bulk should be additionally considered.

The generalised transmission line circuit model predicts the relevant impedance features of such a system in terms of a Nyquist plot, 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; at other times, 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 [39] Furthermore, they can also overlap to the mid-frequency Warburg impedance quasi-45°-slope segment that reflects the diffusion–migration of ions at the boundary surface between solution and polymer, inside the latter medium. Finally, the 90°-trend at the lowest frequencies, due to a capacitive impedance, accounts for the charge transport process inside the bulk of the film.

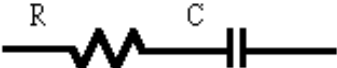
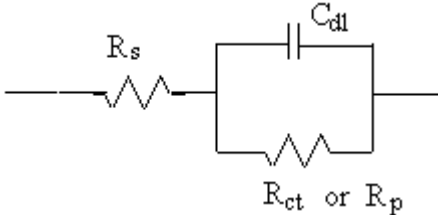
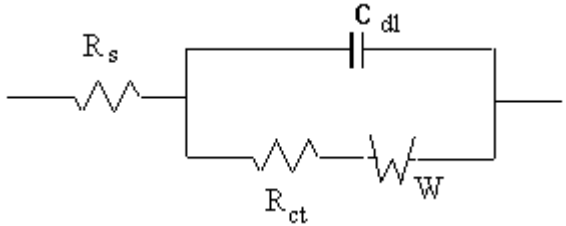
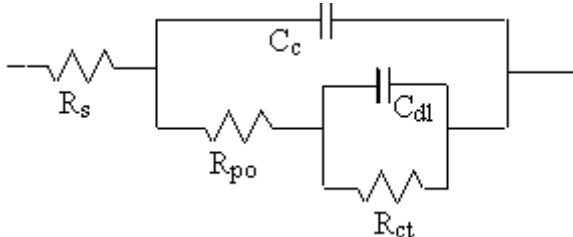
An ionic conductivity often constitutes the slow step in the overall charge percolation process through the CP-modified electrode system [40]. When the ionic conductivity is definitely very low, so that a very thin diffusion layer accounts for the transport of ions inside the polymer, the generalised transmission line circuit can be considered infinitely extended, simulating a semi-infinite diffusion–migration, the boundary surface being the polymer/solution one.

Therefore, the trend attributable to a Warburg impedance extends so much down to low frequencies that the capacitive impedance 90°-slope trend may not be observed. In this case the generalised transmission line circuit can be simplified into the classical Randles circuit.

On the opposite side, when the ionic conductivity is relatively high, the impedance value of the polymer bulk is correspondingly low, both ions being present in the bulk of the permselective polymer. The study of this situation for the case of polypyrrole, carried out by Duffitt and Pickup [41,42], has led the authors to define a condition they call ‘enhanced ionic conductivity’: for polypyrrole, electrolyte concentrations as high as 3 M are proposed.

For intermediate situations the whole generalised transmission line circuit has to be considered. In the impedance plot of such a circuit the presence of an additional semi-circle at the highest frequencies is also predictable, which is ascribed to the impedance of the polymer bulk but cannot, however, be generally observed using instrumentation with non-extraordinary performances. If one is mainly interested in the study of ionic conductivity, the generalised transmission line circuit can then be simplified into the circuit proposed by Alberly and Mount [43].

Table 1.4: Mostly Applied Equivalent Circuit Types

EQUIVALENT CIRCUIT MODELS	TYPES OF CIRCUITS
	Purely Capacitive Coating
	Randles Cell Schematic Diagram
	Equivalent Circuit with Mixed Kinetic and Charge Transfer Control
	Equivalent Circuit for a Failed Coating

1.2. Electropolymerization

Electrochemical polymerization is recognized as an effective technique for the synthesis of conducting polymers. It is widely used, because it is simple and can be used as a one step method [44]. The electropolymerization procedure offers the advantage of controlling the thickness, and functionality of such a ‘reactive’ coating through selective process parameters (i.e. current density and monomer concentration, etc.) and uniform coatings can be achieved [45].

At the beginning of the electrochemical reaction the monomer, dissolved in an appropriate solvent containing the desired anionic doping salt, is oxidized at the surface of an electrode by application of an anodic potential (oxidation). The anode can be made of a variety of materials including platinum, carbon fiber, gold, glassy carbon, and tin or indium-tin oxide (ITO) coated glass.

During the process, the monomer is electrochemically oxidized at a polymerization potential giving rise to free radicals. These radicals are adsorbed onto the electrode surface and undergo subsequently a wide variety of reactions leading to the polymer network [46]. As a result of the initial oxidation, the radical cation of the monomer is formed and reacts with other monomers present in solution to form oligomeric products and then the polymer.

The extended conjugation in the polymer results in a lowering of the oxidation potential compared to the monomer. Therefore, the synthesis and doping of the polymer are generally done simultaneously.

In Figure 1.9. electrochemical polymerization mechanism of heterocyclic compounds is shown. The growth of this polymer depends on its electrical character. If the polymer is electrically nonconducting, its growth is self-limited. Such films are very thin (10 - 100 nm). In contrast, the growth of conductive polymers is virtually unlimited.

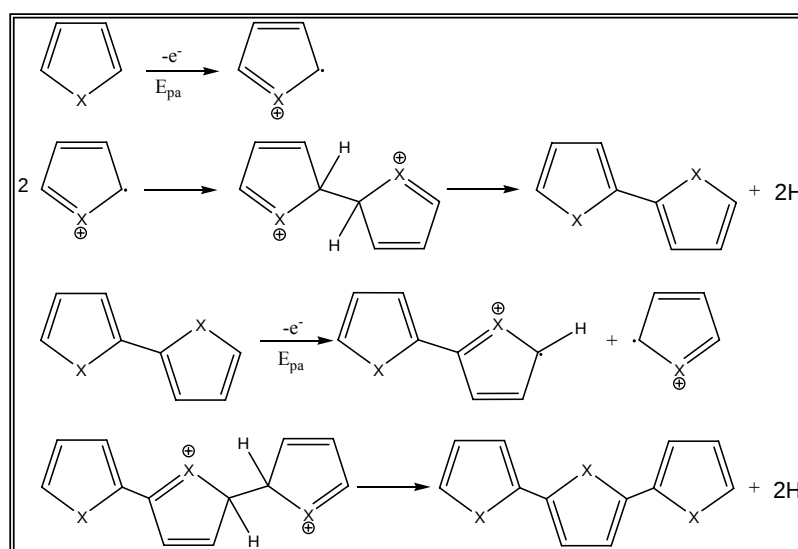


Figure 1.9: Generic Electropolymerization Pathway Valid for Heterocyclic Compounds.

The process is governed by the electrode potential and by the reaction time, which allows us to control the thickness of the resulting film [46]. In order to have uniform and reproducible results, the process parameters of electrochemical polymerization have to be optimized. The parameters; type of electrolyte, concentration ratio of monomer and electrolyte, pH of the electrolyte, monomer substitution, scan rate, solvent, temperature and current density affect the conductivity and morphology of the synthesized polymer film [44].

There are mainly 3 types of electropolymerization techniques. These are:

1. Potentiodynamic by cyclic voltammetry
2. chronoamperometry (constant potential)
3. chronopotentiometry (constant current)

These techniques are easier to describe quantitatively and have been therefore commonly utilized to investigate the nucleation mechanism and the macroscopic growth.

1.2.1. Cyclic voltammetry

Potentiodynamic techniques such as cyclic voltammetry corresponds to a repetitive triangular potential waveform applied at the surface of the electrode. Electrochemistry deals with the transfer of electrons from one substance to another. This transfer creates a current, the magnitude of which can give us clues about our substances. Cyclic voltammetry is an important electrochemical technique used in electrochemistry.

Cyclic voltammetry (CV) is very often used to characterize conducting polymer films. This is the method of choice for studying the reversibility of electron transfer because the oxidation and reduction can be monitored in the form of a current-potential diagram. Intermediate species of very short lifetimes can be observed with microelectrodes using high scanning speeds [47].

Cyclic Voltammograms trace the transfer of electrons during an oxidation-reduction (redox) reaction. The reaction begins at a certain potential (voltage). As the potential changes, it controls the point at which the redox reaction will take place. Electrodes are placed in an electrolyte solution. The electrolyte contains analyte that will undergo the redox reaction. At the negative electrode, the cathode, electrons are

given off, and reduction takes place. At the positive electrode, the anode, the excess electrons are collected, and oxidation occurs. This giving-and-taking of electrons creates an electric current.

In CV, three types of electrodes are generally used. The most important electrode in CV is the working electrode. Electrochemical reactions being studied occur at the working electrode and polymer coating is formed on it.

The working electrode can be made from a variety of materials including: platinum, gold, silver, glassy carbon, nickel and palladium. Counter (auxiliary) electrode conduct the electricity from the signal source into the solution, maintaining the correct current. It is usually inert conductor like platinum or graphite. A reference electrode is used in measuring the working electrode potential. A reference electrode should have a constant electrochemical potential as long as no current flows through it. The potential that is cycled is the potential difference between the working electrode and the reference electrode. It is usually made from silver/silver chloride (Ag/AgCl) or saturated calomel (SCE).

For cyclic voltammetry studies, the current in the cell is measured as a function of potential. The potential of an electrode in solution is linearly cycled from a starting potential to the final potential and back to the starting potential. This process, in turn, cycles the redox reaction. Multiple cycles can take place. During the CV process, first the system starts off with an initial potential at which no redox can take place. Then, at a critical potential during the forward scan, the electroactive species will begin to be reduced.

After reversal of potential scan direction and depletion of the oxidized species the reverse reaction, oxidation, takes place. Then a plot of potential versus current is produced [44]. The knowledge of the initial charge used to polymerize the monomer, and the charge involved in the doping process allows the estimation of the doping level in the conducting polymer.

1.2.2. Chronoamperometry

Chronoamperometric method is used to measure the current as a function of time, is a method of choice to study the kinetic of polymerization and especially the first steps [48]. As a potential step is large enough to cause an electrochemical reaction is applied to an electrode, the current changes with time. The study of this current

response as a function of time is called chronoamperometry (CA). CA is a useful tool for determining diffusion coefficients and for investigating kinetics and mechanisms. Unlike CV, CA can yield this information in a single experiment.

In Chronoamperometry, the current is monitored as a function of time. It is important to note that the basic potential step experiment is Chronoamperometry; that is, *during* the experiment, the *current* is recorded as a function of time. However, *after* the experiment, the data can also be displayed as *charge* as a function of time (the charge is calculated by integrating the current). Hence, chronocoulometry data can be obtained.

Chronoamperometry is an electrochemical technique in which the potential of working electrode is stepped, and the resulting current from faradaic processes occurring at the electrode is monitored as a function of time.

The current-time curve is described as Cottrell equation.

$$i = nFACD^{1/2}\pi^{-1/2}t^{-1/2}$$

where: n = number of electrons transferred/molecule

F = Faraday's constant (96,500 C mol⁻¹)

A = electrode area (cm²)

D = diffusion coefficient (cm² s⁻¹)

C = concentration (mol cm⁻³)

1.2.3. Chronopotentiometry

Chronopotentiometry is the most basic constant current experiment. In chronopotentiometry, a current step is applied across an electrochemical cell. In double step chronopotentiometry a second current step is applied. It should be noted that the time scale of a DSCP experiment is typically shorter than that of chronopotentiometry experiment (minutes or seconds). The protocol for defining the sampling rate is therefore different for the two techniques. Chronopotentiometry is a standard technique, whereas DSCP is only available as an optional addition.

Chronopotentiometric method is used to measure the potential as a function of time. For this technique constant current is applied for elapsed time, then uniformity of coated structure could be decided by checking the linearity of the potential difference with the time. Chronopotentiometry is also named as galvanostatic method and reaction could either be done via galvanostat. Common applications of the

galvanostat include constant current stripping potentiometry and constant current electrolysis. One advantage of all constant current techniques is that the ohmic drop due to solution resistance is also constant, as it is equal to the product of the current and the solution resistance.

1.3. Effectual Parameters for Electropolymerization

1.3.1. Monomer substitution effects

Presence of alkyl groups gives solubility to copolymers obtained both chemically and electrochemically [49]. N-Substituted pyrroles are known to exhibit a conductivity three orders of magnitude lower than that of polypyrrole as demonstrated by Diaz and coworkers for poly(N-methylpyrrole) [50]. These results were further confirmed by monitoring the conductivity of poly(3,4-dimethoxy-N-methylpyrrole) which was found to be three orders magnitude lower than poly(3,4-dimethoxypyrrole) [51].

The substituent of the nitrogen atom, the greater the steric interaction between repeat units, and subsequently the weaker the conductivity. The influence of N-substitution on electropolymerization characteristics was examined by Waltman [52]. The polymer yield and the rate of oxidation were found to decrease as the size of the alkyl group increases. Bonding large substituents to the nitrogen atom or to the β -carbon stabilizes the cation radical without stopping the polymerization [53]. If this intermediate is too stable it can diffuse into the solution and soluble products. As a result, the yield and the molecular weight of the polymer will be low.

An alkyl substituted conducting polymer, however, usually shows lower conductivity than the original unsubstituted polymer. Diaz et al. Measured the conductivity of poly(1-alkylpyrrole) polymer films and found that the conductivity decreased as the size of the substituent increased [54]. They also found that the oxidation potential of poly(1-alkylpyrrole) films depends on the size of the substituent.

Electroconducting polymer has a p -conjugation system along the polymer chain, and the nature of the conjugation system is reflected on the oxidation potential of the polymer [55]. The electronic and steric structure of a substituent both contribute to the polymer p -conjugation system [56]. However, the steric factor of n -alkyls is usually not so different from each other [57-59]. On the other hand, the packing and

orientation of polymer molecules in a solid are the important factors in understanding its electric conductivity [60,61]. Substituents on the polymer chain may change these factors.

1.3.2. Scan rate effects

One of the first characteristics of a CV of a conducting polymer film that one searches for is the dependence of the peak current (I_p) on the scan rate (v). According to well established

electrochemical treatments, for a behaviour dominated by diffusion effects, I_p is proportional to $v^{1/2}$, whilst for a material localized on an electrode surface, such as a conducting polymer film, I_p is proportional to v .

$$i_p = (2.69 \times 10^5) n^{3/2} v^{1/2} D^{1/2} A C \quad \text{Randles Sevcik Equation}$$

i_p : peak current, **c** : concentration, **n** : number of electrons, **v** scan rate (V / sec), **A** : electrode area (cm²), **D** is the analyte's diffusion coefficient (cm²/sec).

For most conducting polymer films obtained from the latter type electropolymerization, thus indicating surface localized electroactive species. For the copolymer system I_p is proportional to v . As more detailed analysis shows, however, this is only for conducting polymer films that are not mostly thick, not inordinately compact and not doped with very large or sluggish dopant ions which have inordinately small diffusion coefficients. If any of the latter conditions prevail, however i.e. wherever dopant diffusion effects can predominate I_p can be proportional to $v^{1/2}$, as the case of copolymer.

1.3.3. Electrolyte effects

The choice of electrolyte is made by considering its solubility and nucleophilicity. Moreover, the anion water, one of roles played by these organic anions is to orient polymer chain paralel to the electrode surface. This chain orientation increases the order in the polymer structure oxidation potential should be higher than the monomer.

The nature of the anion has an impact on the quality of the film produced which depends on the hydrophobic character of the anion and the interactions between the polymer and the anion. For instance Kassim at al.[62] have shown that in aqueous

solution, the utilization of a large aromatic sulphate anion gives stable conducting polymers with better mechanical properties than when a perchlorate anion is used because of their hydrophobic interaction with polymer [63].

One important parameter affecting the physical characteristics and morphology of PPy is the nature and the concentration of the dopant that represents about 30% of the weight of the polymer film. The size of the anion controls the microstructure and the porosity of the polymer. Indeed, this determines the ability of the polymer to undergo an easier diffusion of the dopants during the redox process [64].

The higher the basicity of the anion yields the lower the conductivity of the polymer. This phenomenon is due to an increase in the interactions between the positive charges of the polymer and the anions. Inversely, anion acidity leads to an increase in the conductivity of PPy [65]. On another hand, anion nucleophilicity interferes with the reaction by increasing the formation of soluble products. The polymers of the highest conductivity are produced when elevated concentrations of electrolyte are used.

1.3.4. Monomer concentration effects

For both chemical and electrochemical processes monomer concentration have affect on resultant product. For electropolymerization, since the oxidation of the monomer occurs at a higher potential than that of the redox processes of the polymer, side reactions including crosslinking and/or over-oxidation of the polymer could take place.

Merz et al. have studied the effect of substitution in the 3,4-dimethoxypyrrole and showed that the electron donating effect of the methoxy groups results in a 350 mV decrease of the monomer oxidation potential. Thus, polymerization occurs exclusively through the alpha-positions and is likely to proceed without crosslinking and over-oxidation of the deposited polymer because of the lower potential required for the electropolymerization [66].

The larger the substituent on the nitrogen atom result in the greater the steric interaction between repeating units and subsequently causes the weaker the conductivity. This drop in conductivity is due to fact that the pyrrole units are not totally coplanar in the polymer, as demonstrated by the X-ray studies performed by Street on the alpha-alpha-substituted tetramer of N-methylpyrrole [7]

The polymer yield and the rate of oxidation were found to decrease as the size of the alkyl group increases.

Bonding large substituents to the nitrogen atom or to the beta-carbon stabilizes the cation radical without stopping the polymerization. If this intermediate is too stable it can diffuse into the solution and form soluble products. As a result, the yield and the molecular weight of the polymer will be low.

It should also be noted that some specific N-substituent inhibit the polymerization because of their basicity, as observed for N-pyrrolidic pyrrole [67].

1.4. Biosensor Applications

A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. Chemical sensors contain usually two basic components connected in series: a chemical molecular recognition system and a physico-chemical transducer.

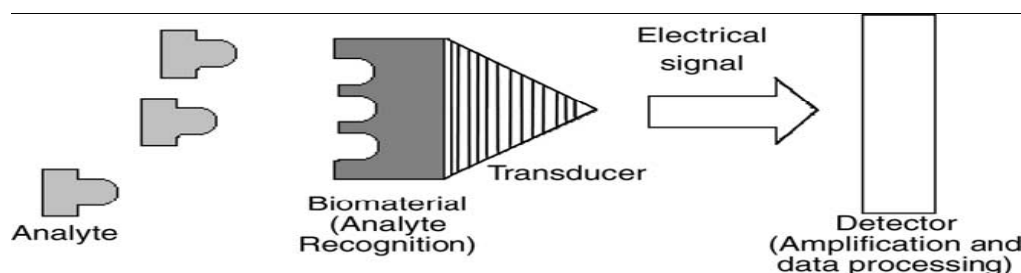


Figure 1.10: Schematic Representation of Biosensor.

Biosensors are chemical sensors in which the recognition system utilises a biochemical mechanism. The biological recognition system translates information from the biochemical domain, usually an analyte concentration, into a chemical or physical output signal with a defined sensitivity. The main purpose of the recognition system is to provide the sensor with a high degree of selectivity for the analyte to be measured.

While all biosensors are more or less selective for a particular analyte, some are, by design and construction, only class-specific, since they use class enzymes, e.g. phenolic compound biosensors, or whole cells, e.g. used to measure biological oxygen demand. Because in sensing systems present in living organisms: systems, such as olfaction, and taste, as well as neurotransmission pathways, the actual

recognition is performed by cell receptor, the word receptor or bioreceptor is also often used for the recognition system of a chemical biosensor.

The transducer part of the sensor serves to transfer the signal from the output domain of the recognition system, mostly to the electrical domain. Because of the general significance of the word, a transducer provides bi-directional signal transfer ; the transducer part of a sensor is also called a detector, sensor or electrode, but the term transducer is preferred to avoid confusion.

An electrochemical biosensor is a biosensor with an electrochemical transducer. It is considered a chemically modified electrode (CME) Durst et al., 1997; Kutner et al., 1998 since electronic conducting, semiconducting or ionic conducting material is coated with a biochemical film. A biosensor is an integrated receptor-transducer device, which is capable of providing selective quantitative or semi-quantitative analytical information using a biological recognition element.

A biosensor can be used to monitor either biological or non-biological matrixes. Chemical sensors, which incorporate a non-biological specificity-conferring part or receptor, although used for monitoring biological processes, as the in vivo pH or oxygen sensors, are not biosensors. [68,69]

A range of nanoparticles including nanotubes and nanowires, prepared from metals, semiconductor, carbon or polymeric species, have been widely investigated for their ability to enhance the response of biosensors. Nanoparticles can be used in a variety of ways, such as modification of electrode surfaces, or to modify biological receptor molecules such as enzymes, antibodies or oligonucleotides. Their use in electrochemical biosensors has been reviewed recently [70,71]. In particular, they have proved extremely useful in the preparation of electrochemical DNA sensors [72,73]. There are also many reports of the direct electrochemistry of enzymes and proteins at nanoparticle-modified electrodes. The enhanced electrochemistry is due to the ability of the small nanoparticles to reduce the distance between the redox site of a protein and the electrode, since the rate of electron transfer is inversely dependent on the exponential distance between them.

1.4.1. Epinephrine

Epinephrine is one of the most important neurotransmitters in mammalian central nervous systems, existing in the nervous tissue and body fluid in the form of large organic cations, and controlling the nervous system in the performance of a series of biological reactions and nervous chemical processes. Epinephrine or adrenaline [1-(3,4-dihydroxyphenyl)-2-methyloamino-ethanol] belongs to the catecholamine family and plays an important role as neurotransmitters and hormones. It is biosynthesized in the adrenal medulla and sympathetic nerve terminals, as well as is secreted by the suprarenal gland along with norepinephrine. It was first isolated in 1901 by Takamine and Aldrich, and was synthesized in 1904 by Stolz and Dalkin. It is used in medicine in the treatment of heart attack, bronchial asthma and cardiac surgery. Air oxidation is a major problem for epinephrine in samples.

The addition of antioxidants in pharmaceutical formulations, for example, sodium metabisulfite, serves to minimize the analyte oxidation. Several methods have been applied to determine epinephrine. However, some of these methods are very expensive or complicated and need extraction or derivatization. Biosensors developed using plant tissue materials in combination with transducers offer a good alternative compared with biosensors based on isolated enzymes as well as others analytical techniques for catecholamines determination. These biosensors have some advantages, such as low cost, simplicity of construction and needlessness of a co-factor for enzyme regeneration.[74-75]

Catecholamines, such as dopamine and epinephrine, are kinds of important compounds for the message transfer in the mammalian central nervous system, which exist as an organic cation in the nervous tissue and biological body fluid [76]. Many diseases are related to changes of their concentration.

Quantitative determinations of them are significant method for developing nerve physiology, making diagnosis and controlling medicine [77].

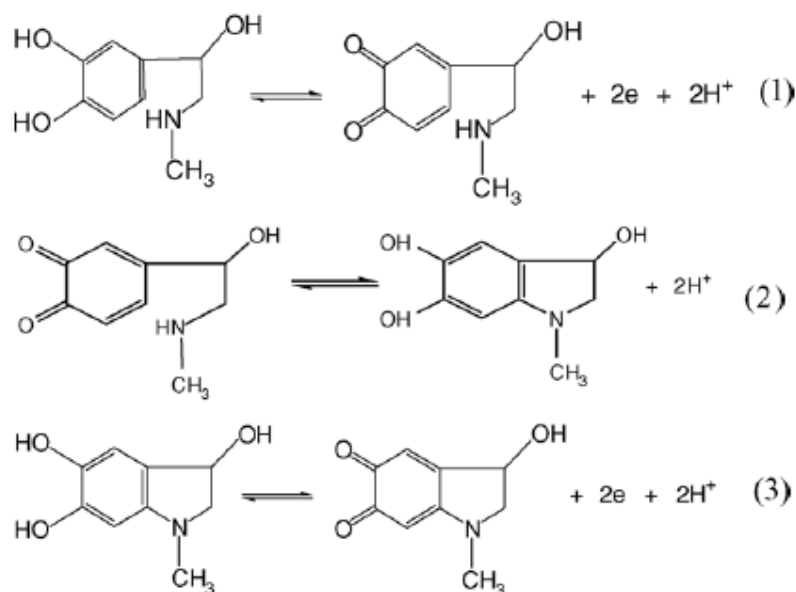


Figure 1.11: The Redox Peaks *Ep1* and *Ep2* of EP Are Consistent With Combination of The Electron Transfer Processes of Eqs. (1) and (3), Respectively.

The methods for epinephrine (EP) analysis are based on the native fluorescence of original amines. The trihidroxiindol method requires prior separation in a weak cationic resin for subsequent determination by fluorescence.

Present methods focus on electrochemical detection [78]. The electron transfer rate of EP at bare electrode is slow, because it is often adsorbed on the surface of bare electrode for subsequent passivation. Recently, an enormous amount of research has been devoted to the development of new modified electrode for monitoring EP [79–81]. EP and ascorbic acid (AA) always exist together in biological environment, at most solid electrodes; AA is oxidized at potentials close to that of the EP, resulting in an overlapping voltammetric response. Therefore, a lot of chemically modified electrodes have been developed to eliminate the interference of AA to EP determination [82] or separate the electrochemical response of EP and AA [83].

1.5. Electrochemical Impedance Spectroscopy (EIS)

Electrical resistance is the ability of a circuit element to resist the flow of electrical current. With impedance data a complete description of an electrochemical system is possible. Representations of the electrified interface have gradually evolved from repeated modifications of the model first proposed by Helmholtz. [84,85] Ohm's law (Equ.1.1) defines resistance in terms of the ratio between voltage *E* and current *I*.

$$R = \frac{E}{I} \quad (1.1)$$

While this is a well known relationship, its use is limited to only one circuit element, the ideal resistor. An ideal resistor has several simplifying properties:

- It follows Ohm's Law at all current and voltage levels.
- Its resistance value is independent of frequency.
- AC current and voltage signals through a resistor are in phase with each other.

The real world contains circuit elements that exhibit much more complex behavior. These elements force us to abandon the simple concept of resistance. In its place we use impedance, which is a more general circuit parameter. Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current. Unlike resistance, impedance is not limited by the simplifying properties listed above. Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell. Suppose that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal, containing the excitation frequency and its harmonics. This current signal can be analyzed as a sum of sinusoidal functions.

Electrochemical Impedance is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.

Impedance is a totally complex resistance encountered when a current flows through a circuit made of resistors, capacitors, or inductors, or any combination of these. Depending on how the electronic components are configured, both the magnitude and the phase shift of an ac can be determined. Because an inductive effect is not usually encountered in electrochemistry, we consider only the simple equivalent circuit, in which no inductor is present.

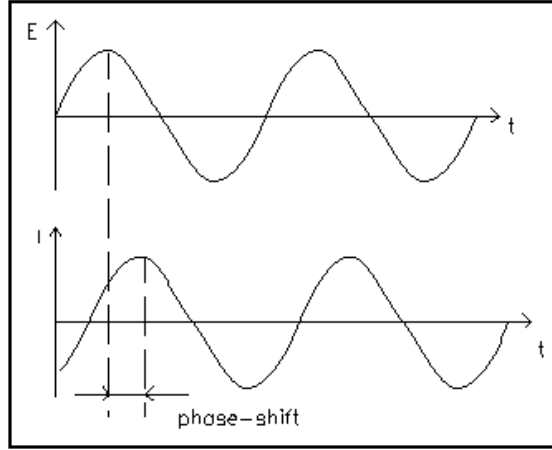


Figure 1.12: Sinusoidal Current Response in a Linear System

The excitation signal, expressed as a function of time, has the form

$$E(t) = E_0 \cos(\omega t) \quad (1.2)$$

$E(t)$ is the potential at time t , E_0 is the amplitude of the signal, and ω is the radial frequency. The relationship between radial frequency ω (expressed in radians/second) and frequency f (expressed in hertz) is:

$$\omega = 2\pi f \quad (1.3)$$

In a linear system, the response signal, I_t , is shifted in phase (ϕ) and has a different amplitude, I_0 :

$$I(t) = I_0 \cos(\omega t - \phi) \quad (1.4)$$

An expression analogous to Ohm's Law allows us to calculate the impedance of the system as:

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)} \quad (1.5)$$

The impedance is therefore expressed in terms of a magnitude, Z_0 , and phase shift, ϕ .

By using euler equation;

$$\exp(j\phi) = \cos \phi + j \sin \phi \quad (1.6)$$

it is possible to express the impedance as a complex function. The potential is described as,

$$E(t) = E_0 \exp(j\omega t) \quad (1.7)$$

and the current response as,

$$I(t) = I_0 \exp(j\omega t - j\phi) \quad (1.8)$$

The impedance is then represented as a complex number,

$$Z = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0 (\cos \phi + j \sin \phi) \quad (1.9)$$

The expression for $Z(\omega)$ is composed of a real and an imaginary part. If the real part is plotted on the Z axis and the imaginary part on the Y axis of a chart, we get a "Nyquist plot". Notice that in this plot the y -axis is negative and that each point on the Nyquist plot is the impedance at one frequency.

By treating the impedance data in such a frequency range, system characteristics for an electrochemical reaction (i.e., R_s , R_p , and C_d) can be obtained. R_p is a function of potential; however, at $\eta = 0$, it becomes the charge-transfer resistance R_{CT} . Two convenient ways of treating the impedance data are the Nyquist plot, in which imaginary numbers $Z''(\omega)$ are plotted against real numbers $Z'(\omega)$, and the Bode plot, in which absolute values of impedance or phase angle are plotted against the frequency. Extraction of the system characteristics requires interpreting the Nyquist plot. At high frequencies, $Z(\omega) = Z'(\omega) = R_s$, which is an intercept on the $Z'(\omega)$ axis on the high-frequency side ($\phi = 0$ or $Z''(\omega) = 0$). For $\omega \rightarrow 0$, it becomes $Z(\omega) = R_s + R_p$, which is an intercept on the $Z'(\omega)$ axis on the low frequency side.

At the frequency where a maximum $Z''(\omega)$ is observed, the straightforward relationship which is the time constant of the electrochemical reaction, can be shown and indicates how fast the reaction takes place. Also, if $R_p \parallel C_d$ is known, C_d can be obtained because R_p is already known from the low-frequency intercept on the $Z'(\omega)$ axis.

$$R_p \parallel C_d = 1/\omega_{\max} = 1/(2\pi f_{\max}) = \tau_{rxn} \quad (1.10)$$

The Nyquist plot gives all the necessary information about the electrode–electrolyte interface and the reaction. Similar information is obtained by examining the Bode diagram. $\log R_s$ and $\log (R_p + R_s)$ are obtained straightforwardly from the $Z(\omega)$ versus $\log \omega$ plot at high and low frequencies from the same argument as the Nyquist plot. In the intermediate frequency region, an almost straight line with a slope of ~ -1.0 can be seen. On the other hand, contribution and the effect of the Warburg

impedance can be important at low frequencies because the mass transport of the electroactive species may limit the electron-transfer process.

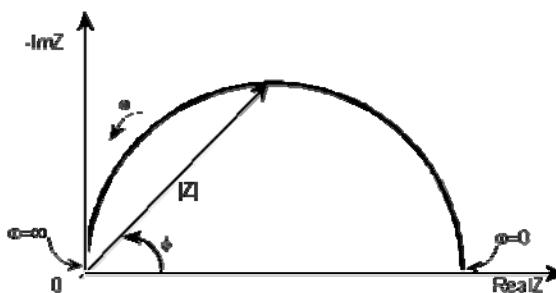


Figure 1.13: Nyquist Plot with Impedance Vector

Nyquist plot has been annotated to show that low frequency data are on the right side of the plot and higher frequencies are on the left. This is true for EIS data where impedance usually falls as frequency rises (this is not true of all circuits). On the Nyquist plot the impedance can be represented as a vector of length $|Z|$. The angle between this vector and the x-axis is ϕ .

Nyquist plots have one major shortcoming. When you look at any data point on the plot, you cannot tell what frequency was used to record that point. The semicircle is characteristic of a single "time constant". Electrochemical Impedance plots often contain several time constants. Often only a portion of one or more of their semicircles is seen. Another popular presentation method is the "Bode plot". The impedance is plotted with log frequency on the x-axis and both the absolute value of the impedance ($|Z| = Z_0$) and phase-shift on the y-axis. Unlike the Nyquist plot, the Bode plot explicitly shows frequency information.

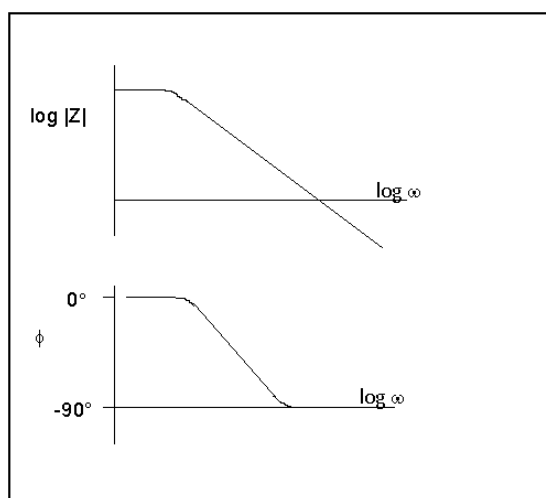


Figure 1.14: Bode Plot with One Time Constant

Impedance of a resistor is independent of frequency and has only a real component. Because there is no imaginary impedance, the current through a resistor is always in phase with the voltage. The impedance of an inductor increases as frequency increases. Inductors have only an imaginary impedance component. As a result, an inductor's current is phase shifted 90 degrees with respect to the voltage.

The impedance versus frequency behavior of a capacitor is opposite to that of an inductor. A capacitor's impedance decreases as the frequency is raised. Capacitors also have only an imaginary impedance component. The current through a capacitor is phase shifted -90 degrees with respect to the voltage.

Table 1.5: Common Electrical Elements

Component	Current Vs.Voltage	Impedance
resistor	$E = IR$	$Z = R$
inductor	$E = L \, di/dt$	$Z = j\omega L$
capacitor	$I = C \, dE/dt$	$Z = 1/j\omega C$

1.5.1. Electrolyte resistance

Solution resistance is often a significant factor in the impedance of an electrochemical cell. A modern 3 electrode potentiostat compensates for the solution resistance between the counter and reference electrodes. However, any solution resistance between the reference electrode and the working electrode must be considered when you model your cell.

The resistance of an ionic solution depends on the ionic concentration, type of ions, temperature and the geometry of the area in which current is carried. In a bounded area with area A and length l carrying a uniform current the resistance is defined as:

$$R = \rho \frac{l}{A} \quad (1.11)$$

where ρ is the solution resistivity. The conductivity of the solution, k , is more commonly used in solution resistance calculations. Its relationship with solution resistance is:

$$R = \frac{1}{\kappa} \cdot \frac{l}{A} \Rightarrow \kappa = \frac{l}{RA} \quad (1.12)$$

Standard chemical handbooks list κ values for specific solutions. For other solutions, you can calculate κ from specific ion conductances. The units for κ are siemens per meter (S/m). The siemens is the reciprocal of the ohm, so $1 \text{ S} = 1/\text{ohm}$.

Unfortunately, most electrochemical cells do not have uniform current distribution through a definite electrolyte area. The major problem in calculating solution resistance therefore concerns determination of the current flow path and the geometry of the electrolyte that carries the current.

A comprehensive discussion of the approaches used to calculate practical resistances from ionic conductances is well beyond the scope of this manual. Fortunately, you don't usually calculate solution resistance from ionic conductances. Instead, it is found when you fit a model to experimental EIS data.

1.5.2. Double layer capacitance

A electrical double layer exists at the interface between an electrode and its surrounding electrolyte. This double layer is formed as ions from the solution "stick on" the electrode surface. Charges in the electrode are separated from the charges of these ions. The separation is very small, on the order of angstroms. Charges separated by an insulator form a capacitor. On a bare metal immersed in an electrolyte, you can estimate that there will be approximately $30 \mu\text{F}$ of capacitance for every cm^2 of electrode area.

The value of the double layer capacitance depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

1.5.3. Polarization resistance

Whenever the potential of an electrode is forced away from its value at open circuit, that is referred to as polarizing the electrode. When an electrode is polarized, it can cause current to flow via electrochemical reactions that occur at the electrode surface. The amount of current is controlled by the kinetics of the reactions and the diffusion of reactants both towards and away from the electrode.

In cells where an electrode undergoes uniform corrosion at open circuit, the open circuit potential is controlled by the equilibrium between two different electrochemical reactions. One of the reactions generates cathodic current and the other anodic current. The open circuit potential ends up at the potential where the cathodic and anodic currents are equal. It is referred to as a mixed potential. The value of the current for either of the reactions is known as the corrosion current.

Mixed potential control also occurs in cells where the electrode is not corroding. While this section discusses corrosion reactions, modification of the terminology makes it applicable in non-corrosion cases as well.

1.5.4. Charge transfer resistance

A similar resistance is formed by a single kinetically controlled electrochemical reaction. In this case we do not have a mixed potential, but rather a single reaction at equilibrium. Consider a metal substrate in contact with an electrolyte. The metal molecules can electrolytically dissolve into the electrolyte, according to:



or more generally:



In the forward reaction in the first equation, electrons enter the metal and metal ions diffuse into the electrolyte. Charge is being transferred.

This charge transfer reaction has a certain speed. The speed depends on the kind of reaction, the temperature, the concentration of the reaction products and the potential.

When the overpotential, h , is very small and the electrochemical system is at equilibrium, the expression for the charge transfer resistance changes into:

$$R_{ct} = \frac{RT}{nFi_0} \quad (1.15)$$

From this equation the current density can be calculated when R_{ct} is known.

1.5.5. Warburg impedance

Diffusion can create an impedance known as the Warburg impedance. This impedance depends on the frequency of the potential perturbation. At high frequencies the Warburg impedance is small since diffusing reactants don't have to move very far. At low frequencies the reactants have to diffuse farther, thereby increasing the Warburg impedance.

The equation for the "infinite" Warburg impedance is:

$$Z = \sigma(\omega)^{-1/2} (1 - j) \quad (1.16)$$

On a Nyquist plot the infinite Warburg impedance appears as a diagonal line with a slope of 0.5. On a Bode plot, the Warburg impedance exhibits a phase shift of 45°.

This form of the Warburg impedance is only valid if the diffusion layer has an infinite thickness. Quite often this is not the case. If the diffusion layer is bounded, the impedance at lower frequencies no longer obeys the equation above. Instead, we get the form:

$$Z_O = \sigma\omega^{-1/2} (1 - j) \tanh\left(\sigma\left(\frac{j\omega}{D}\right)^{1/2}\right) \quad (1.17)$$

d = Nernst diffusion layer thickness

D = an average value of the diffusion coefficients of the diffusing species

1.5.6. Coating capacitance

A capacitor is formed when two conducting plates are separated by a non-conducting media, called the dielectric. The value of the capacitance depends on the size of the plates, the distance between the plates and the properties of the dielectric. The relationship is:

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (1.18)$$

ϵ_0 = electrical permittivity,

ϵ_r = relative electrical permittivity,

A = surface of one plate,

d = distances between two plates

Whereas the electrical permittivity is a physical constant, the relative electrical permittivity depends on the material. Table 1.6. gives you a few useful ϵ_r values.

Table 1.6: Typical Relative Electrical Permittivities

Material	ϵ_r
vacuum	1
water	80.1 (20° C)
organic coating	4 - 8

The capacitance of a coated substrate changes as it absorbs water. EIS can be used to measure that change.

1.5.7. Constant phase element

Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element (CPE) as defined below. The impedance of a capacitor has the form:

$$Z = A(j\omega)^{-\alpha} \quad (1.19)$$

When this equation describes a capacitor, the constant $A = 1/C$ (the inverse of the capacitance) and the exponent $\alpha = 1$. For a constant phase element, the exponent α is less than one. The "double layer capacitor" on real cells often behaves like a CPE instead of like a capacitor. Several theories have been proposed to account for the non-ideal behavior of the double layer but none has been universally accepted.

1.6. FTIR-ATR (Attenuated Total Reflectance-Infrared) Spectroscopy

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control, and dynamic measurement. The instruments are now small, and can be transported, even for use in field trials. Attenuated total reflectance (ATR) spectroscopy, also known as internal reflection spectroscopy or multiple internal reflectances (MIR), is a versatile, nondestructive technique for obtaining the infrared spectrum of the surface of a material or the spectrum of materials either too thick or too strongly absorbing to be analyzed by standard transmission spectroscopy.

In this technique, the sample is placed in contact with the internal reflection element (IRE), the light is totally reflected, generally several times, and the sample interacts with the evanescent wave resulting in the absorption of radiation by the sample at each point of reflection. The internal reflection element is made from a material with a high refractive index; zinc selenide (ZnSe), thallium iodide – thallium bromide (KRS-5), and germanium (Ge) are the most commonly used.

By measuring at a specific frequency over time, changes in the character or quantity of a particular bond can be measured. This is especially useful in measuring the degree of polymerization in polymer manufacture. Modern research machines can take infrared measurements across the whole range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.

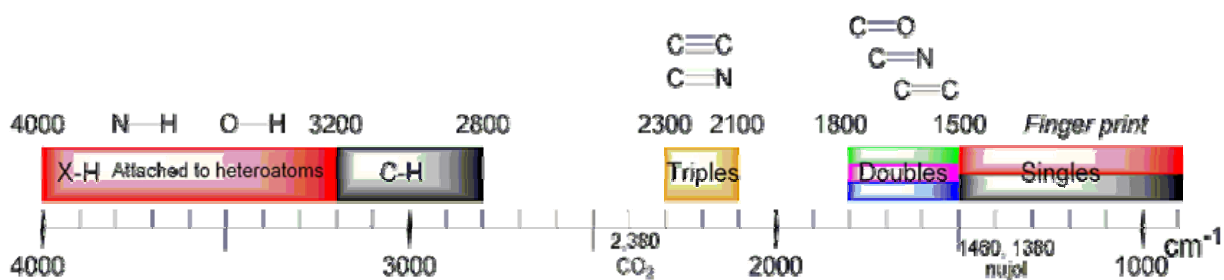


Figure 1.15: Infrared Spectrum Bands for General Substitutions

1.7. SEM (scanning electron microscopy)

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.

The scanning electron microscope generates a beam of electrons in a vacuum. That beam is collimated by electromagnetic condensor lenses, focussed by an objective lens, and scanned across the surface of the sample by electromagnetic deflection coils. The primary imaging method is by collecting secondary electrons that are released by the sample. The secondary electrons are detected by a scintillation

material that produces flashes of light from the electrons. The light flashes are then detected and amplified by a photomultiplier tube.

By correlating the sample scan position with the resulting signal, an image can be formed that is strikingly similar to what would be seen through an optical microscope. The illumination and shadowing show a quite natural looking surface topography.

In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB_6) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 50 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface.

The size of the interaction volume depends on the beam accelerating voltage, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation which can be detected to produce an image.

1.8. AFM (atomic force microscopy)

The AFM consists of a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The basic objective of the operation of the AFM is to measure the forces (at the atomic level) between a sharp probing tip (which is attached to a cantilever spring) and a sample surface. Images are taken by scanning the sample relative to the probing tip and measuring the deflection of the cantilever as a function of lateral position. Typical spring constants are between 0.001 to 100 N/m and motions from microns to $\sim 0.1 \text{ \AA}$ are measured by the deflection sensor. The

cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law.

Traditionally, the sample is mounted on a piezoelectric tube, that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Alternately a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x,y and z directions. This eliminates some of the distortion effects seen with a tube scanner. The resulting map of the area $s = f(x,y)$ represents the topography of the sample.

The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (contact) modes and a variety of dynamic modes.

The AFM has several advantages over the scanning electron microscope (SEM). Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a true three-dimensional surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms.

A disadvantage of AFM compared with the scanning electron microscope (SEM) is the image size. The SEM can image an area on the order of millimetres by millimetres with a depth of field on the order of millimetres. The AFM can only image a maximum height on the order of micrometres and a maximum scanning area of around 150 by 150 micrometres. Another inconvenience is that at high resolution, the quality of an image is limited by the radius of curvature of the probe tip, and an incorrect choice of tip for the required resolution can lead to image artifacts.

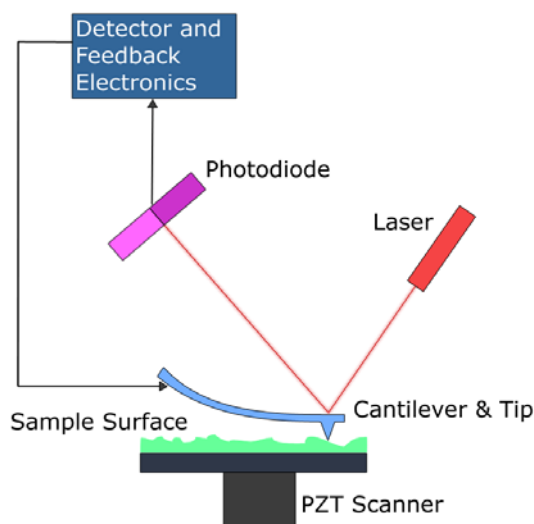


Figure 1.16:Block Diagram of Atomic Force Microscope

1.9. Carbon Fibers

Carbon fiber can refer to carbon filament thread, or to felt or woven cloth made from those carbon filaments. By extension, it is also used informally to mean any composite material made with carbon filament. Carbon fiber is a polymer which is a form of graphite. Graphite is a form of pure carbon. In graphite the carbon atoms are arranged into big sheets of hexagonal aromatic ring.

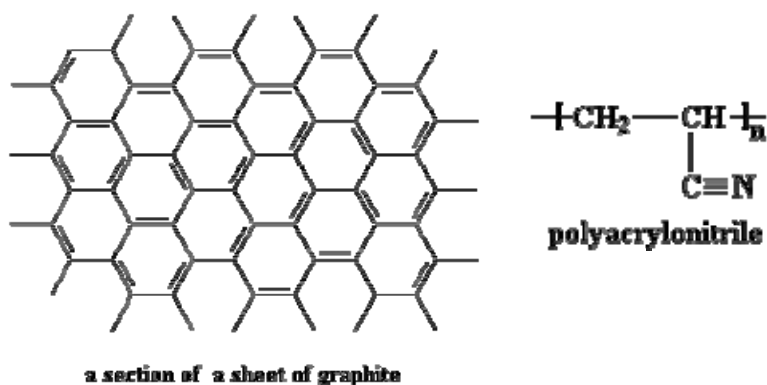


Figure 1.17: Sheet Type of Graphite and Molecular Formula of PAN

Carbon fiber is a form of graphite in which these sheets are long and thin. It could be thought as ribbons of graphite. Bunches of these ribbons like to pack together to form fibers, hence the name carbon fiber. These fibers aren't used by themselves. Instead,

they're used to reinforce materials like epoxy resins and other thermosetting materials which are called *composites* because they have more than one component.

Carbon fiber reinforced composites are very strong for their weight. They're often stronger than steel, but a whole lot lighter. Because of this, they can be used to replace metals in many uses, from parts for airplanes and the space shuttle to tennis rackets and golf clubs. Carbon fiber is made from another polymer, called polyacrylonitrile, by a complicated heating process.

Carbon fibers, which are a new breed of high-strength materials, are mainly used as reinforcements in composite materials such as carbon fiber reinforced plastics, carbon-carbon composite, carbon fiber reinforced materials, and carbon fiber reinforced cement. Carbon fibers offer the highest specific modulus and highest specific strength of all reinforcing fibers. The fibers do not suffer from stress corrosion or stress rupture failures at room temperatures, as glass and organic polymer fibers do. Especially at high temperatures, the strength and modulus are outstanding compared to other materials [86]. Carbon fiber composites are ideally suited to applications where strength, stiffness, lower weight, and outstanding fatigue characteristics are critical requirements. They are also finding applications where high temperature, chemical inertness, and high damping are important. Carbon fibers also have good electrical conductivity, thermal conductivity, and low linear coefficient of thermal expansion [87].

The two main sectors of carbon fiber applications are high technology sector, which includes aerospace and nuclear engineering, and the general engineering and transportation sector, which includes engineering components such as bearings, gears, cams, fan blades, etc., and automobile bodies. However, the requirements of two sectors are fundamentally different. The large scale use of carbon fibers in aircraft and aerospace is driven by maximum performance and fuel efficiency, while the cost factor and the production requirements are not critical.

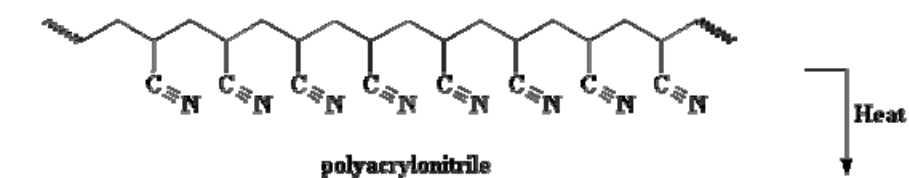
Table 1.7: Axial Tensile Properties of Carbon Fibers [88].

CARBON FIBERS	TENSILE STRENGTH (GPA)	TENSILE MODULUS E, (GPA)	ELONGATION AT BREAK (%)	DENSITY KG/M³
Polyacrylonitrile	2.5–7.0	250–400	0.6–2.5	~1800
Mesophase pitch	1.5–3.5	200–800	0.3–0.9	~2100
Rayon	~1.0	~50	~2.5	-
Metals				
Aluminum	0.172	73	-	2720
Titanium	0.324	110	-	4500
Steel	0.414	199	-	7860

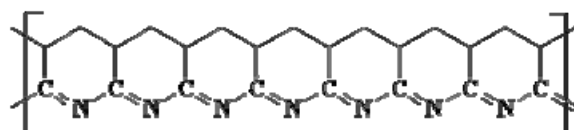
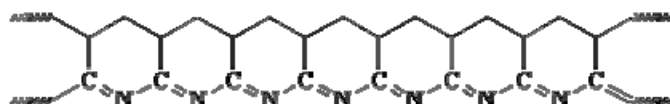
The most important mechanical and physical properties exhibited by carbon fibers are the elastic modulus, tensile strength and the electrical and thermal conductivities. These properties are sensitive to the crystallite size and perfection of the graphene layers developed within the carbon fiber and depends for the most part on the degree of molecular alignment with respect to the fiber axis. Growth and alignment of such layers occur within the precursor and within the solid carbon fiber when it is heated to high temperature.

Carbon fiber composites are ideally suited to applications where strength, stiffness, lower weight, and outstanding fatigue characteristics are critical requirements. They are also finding applications where high temperature, chemical inertness, and high damping are important. Carbon fibers also have good electrical conductivity, thermal conductivity, and low linear coefficient of thermal expansion [87].

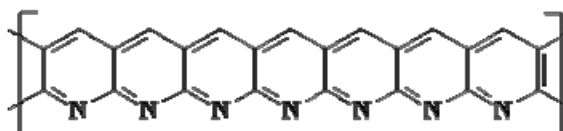
Carbon fibers when used without surface treatment produce composites with low interlaminar shear strength . This has been attributed to weak adhesion and poor bonding between the fiber and matrix. All the carbon fibers are thus given a surface treatment, the exact nature of which is a trade secret. These treatments increase the surface area and surface acidic functional groups and thus improve bonding between the fiber and the resin matrix [89]. This tends to increase the wettability of the carbon fiber and enhances the ILSS.



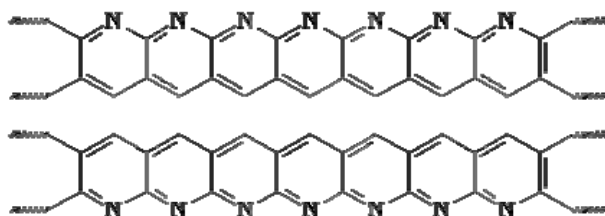
Heat



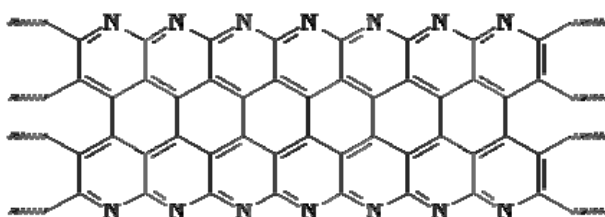
Heat, this time
to 700 °C



+ H₂ gas



More heat,
400-600 °C



+ H₂ gas

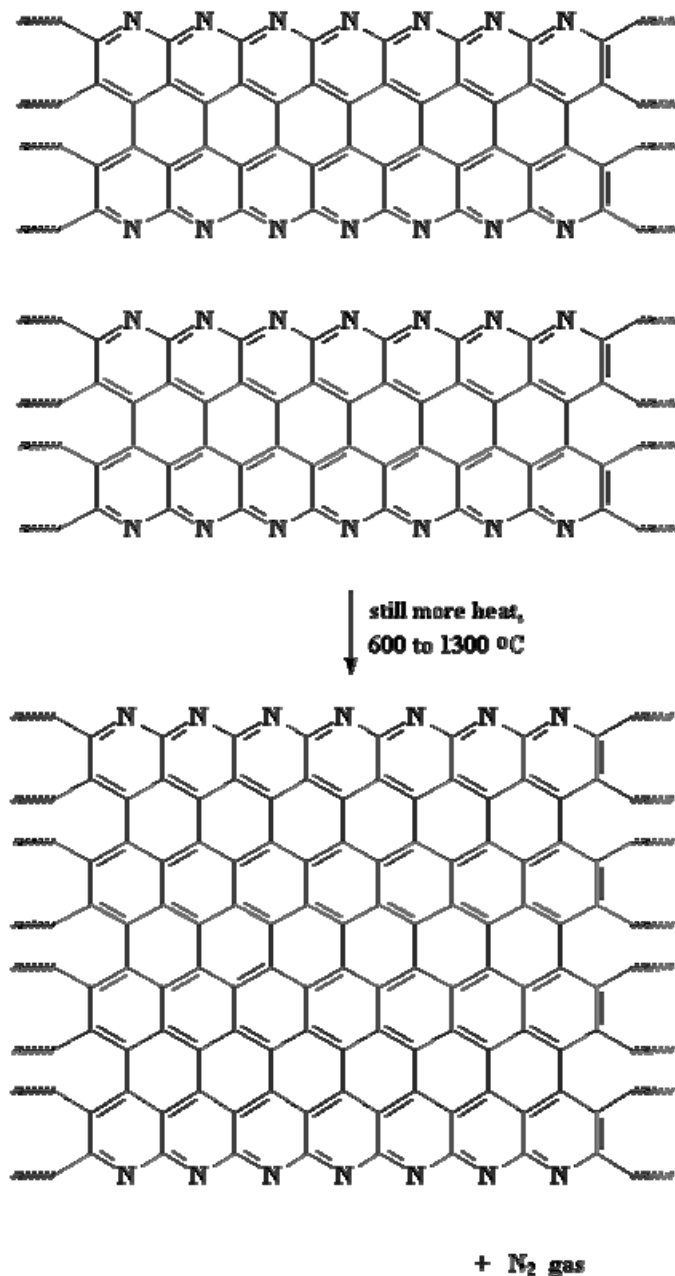


Figure 1.18: Reaction Mechanism of PAN Based Carbon Fiber Synthesis

Surface treatments may be classified into oxidative and non-oxidative treatments. Oxidation treatments involve gas-phase oxidation, liquid-phase oxidation carried out chemically [90] or electrochemically [91], and catalytic oxidation. The non-oxidative treatments involve deposition of more active forms of carbon, such as the highly effective whiskerization, the deposition of pyrolytic carbon, or the grafting of the polymers on the carbon fiber surface. Carbon fibers can also be plasma treated to improve bonding between the fiber and matrix. Liquid phase oxidation treatments are milder, very effective and are preferred.

2. EXPERIMENTAL

2.1. Materials

1-(4-methoxyphenyl)-1H-Pyrrole (MPPy) (FLUKA,%99), Phenylpyrrole (PPy) (FLUKA, %99), Pyrrole (Py) FLUKA, %99) monomers were used as received. Tetraethylammoniumperchlorate (TEAP) (Alfa Aesar, %97), Tetrabutylammoniumperchlorate (TBAP) (Sigma-Aldrich, %98), Tetramethylammoniumperchlorate (TMAP) (Sigma-Aldrich, %98) Tetraethylammonium tetrafluoroborate (TEATFB) (Fluka, %99), Tetrabutylammonium tetrafluoroborate (TBATFB) (Fluka, %99), lithiumperchlorate (LiClO_4)(Fluka, %98), sodiumperchlorate (NaClO_4) (Fluka, %98), were used as electrolytes, dichloromethane(CH_2Cl_2) (MERCK, %98) was used as solvent without further purification. Phosphate buffer solution pH-7 was from Riedel-de Haen ($\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$). These were all the highest reagent grade chemicals and were used as obtained.

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

The electrodes were prepared from by using a high strength (HS) carbon fibers C 320.000A containing 320000 single filaments in a roving. A bunch of CF including nearly 100 filaments (diameter $\sim 7\text{ }\mu\text{m}$) attached to a copper wire with a Teflon tape. Only 1 cm of the carbon fiber was dipped into the solution to keep the electrode area almost constant. The electrode area keeps up constant ($\sim 0.11\text{ cm}^2$). All prepared electrodes were washed with acetone firstly, and dried before the experiments

2.3. Electropolymerization and Characterization

2.3.1. Electropolymerization

Electropolymerization reactions were performed potentiodynamically via cyclic voltammetry at room temperature (25⁰C) in dichloromethane (CH₂Cl₂) solution containing 5.10⁻² M different supporting electrolytes as TEAP, TMAP, TEATFB, TBATFB, LiClO₄ and NaClO₄ for observation of electrolyte effect on reactions. Additionally, scan rate effect, monomer concentration effect, scan number effect and monomer substitution effect on electropolymerization were carried out.

CV is a potential controlled reversal electrochemical experiment. A cyclic potential sweep is imposed on an electrode and the current response is observed. Analysis of the current response can give information about the thermodynamics and kinetics of electron transfer at electrode-solution interface.

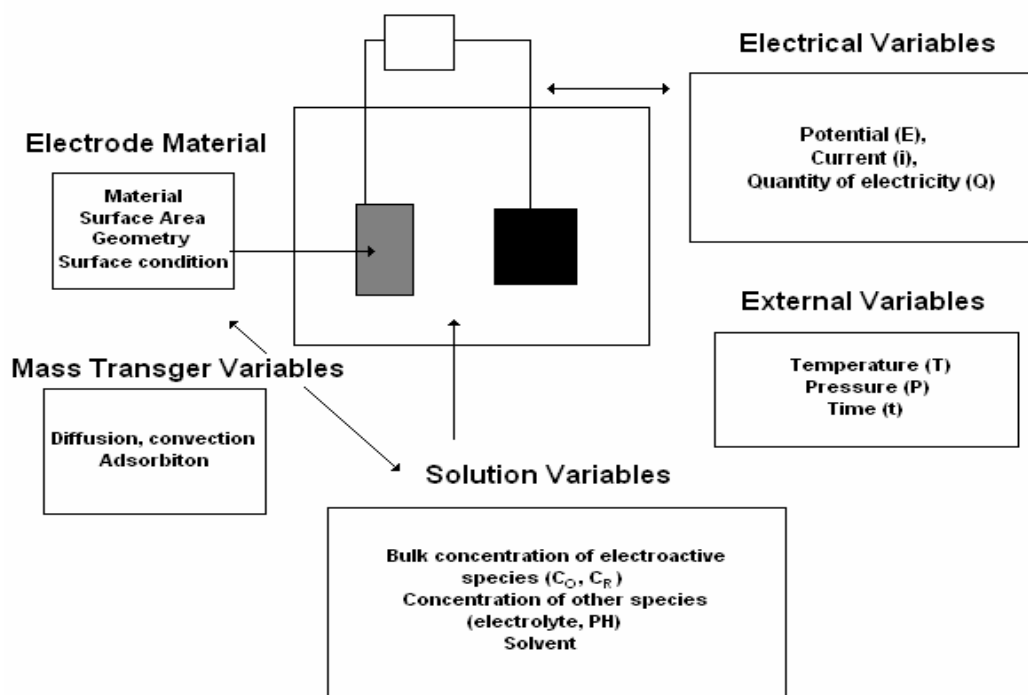


Figure 2.1: Schematic Representation of Electropolymerization Reaction

Cyclic voltammogram (CV), of the polymers were performed via Parstat 2263-1 (software; powersuit) model potentiostat which is a self contained unit that combines potentiostat circuitry with phase sensitive detection.

Electropolymerizations were carried out in a three-electrode cell system employing carbon fiber micro electrode as working, Ag|AgCl stocked in 3M NaCl as reference and Pt wire as a counter electrode. For some cases Ag wire was used as a pseudo reference electrode. These three electrodes were dipped into the cell where they are placed about 1 cm far from each other containing 5ml electrolyte solution and monomer together.

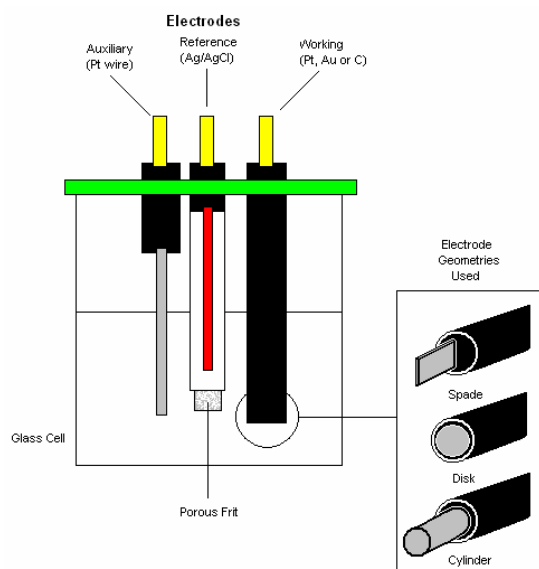


Figure 2.2: Electropolymerization Reaction Cell With Three Electrode System

2.3.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical Impedance measurements were carried out at room temperature in monomer free electrolyte solution with a perturbation amplitude of 10mV over a frequency range 0.01Hz-100kHz with Parstat 2263-1 (software; powersuit). The electrochemical cell was connected to a potentiostat. EIS measurements were also performed with Parstat 2263 Potentiostat with PowerSine software package. EIS can carry out impedance measurements between 10 mHz and 16 kHz. The impedance spectra were analyzed using ZSimpWin V3.10.

2.3.3. Bisensor response to epinephrine

A three electrode cell consisting of a saturated Ag/AgCl reference electrode and a platinum counter electrode was used for electrochemical measurements. The working electrode was either a modified carbon fiber micro electrode. While measurements, polymer modified electrodes were taken to 7 ml Ph 7 buffer solution containing 10^{-3} M epinephrine by applying potential between $[(-0,5) - (+0,3)]$ V.

2.3.4. FTIR-ATR spectroscopy

FTIR-ATR Reflectance Measurements of polymer electrografted carbon fiber surface were analysed by FTIR Reflectance Spectrometer (Perkin Elmer with an ATR attachment of spectrum one Universal ATR- with diamond and ZnSe).



Figure 2.3 : Perkin Elmer FTIR Reflectance Spectrometer

2.3.5. Morphological analysis (SEM & AFM)

Scanning Electron Microscopy: The morphological features of the coated 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 ZELMI-TUB (Germany) and Jeol JSM-7000F SEM (ITU).

Atomic Force Microscopy: Nanosurf branded easyscan 2 model AFM was used to analyze the morphological aspects by means of area and height. Analysis were applied at dynamic (noncontact) mode.

3. RESULTS AND DISCUSSION

3.1. Substrate Effect on Electropolymerization

Electropolymerization of [1-(4-Methoxy Phenyl)-1H-Pyrrole] was the mainly studied monomer for this thesis. Electropolymerization processes for three working electrodes were coated with 10^{-2} M monomer dissolved in 0.05M TEAP/ CH_2Cl_2 electrolyte solution by applying potential between $[0 - 1.4]\text{V}$ via cyclic voltammetry. CFME, button electrode and Pt electrode were used as working electrodes. According to the cyclovoltammetric results carbon fiber micro electrode showed better reversibility than the Pt button electrode and Pt wire electrode.

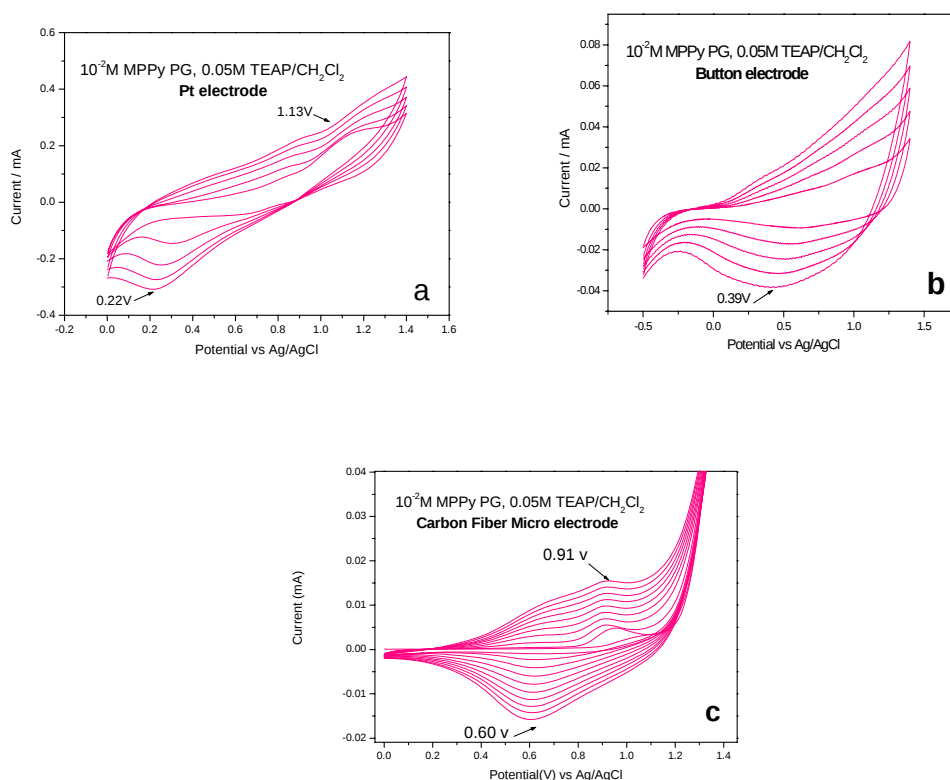


Figure 3.1: Electropolymerization of 10^{-2} M [1-(4-Methoxy Phenyl)-1H-Pyrrole] in TEAP/ CH_2Cl_2 Electrolyte Solution on a) pt Electrode, b) Button Electrode, c) CFME.

3.2. Scan Rate Effect on Electropolymerization of [1-(4-Methoxy Phenyl)-1H-Pyrrole]

3.2.1. Redox behaviour and stability of PMPPy film

The cyclic voltammograms obtained during polymer film growth on carbon fiber micro electrodes are presented in Figure 3.2 [1-(4-Methoxy Phenyl)-1H-Pyrrole] was achieved on carbon fiber microelectrode in TEAP/ CH_2Cl_2 potentiodynamically. Cyclic voltammogram of [1-(4-Methoxy Phenyl)-1H-Pyrrole] obtained with 10, 20, 40, 60, 100 mV.s^{-1} showed the broad and symmetrical redox waves. Potentiodynamic growth of [1-(4-Methoxy Phenyl)-1H-Pyrrole] obtained with different scan rates have showed different redox behavior.

Electropolymerized electrodes indicated that, one-well defined redox systems quickly grow and correspond to the deposition of an electroactive film onto the electrode surface during successive scans. The polymer electrodeposited on CFME from 10^{-3} M [1-(4-Methoxy Phenyl)-1H-Pyrrole] monomer and electrolyte, than thin films were characterized by cyclic voltametry in 0.05M TEAP/ CH_2Cl_2 monomer free solution. The influence of scan rate was investigated for electropolymerization of [1-(4-Methoxy Phenyl)-1H-Pyrrole].

The peak separation between anodic and cathodic peak potentials (ΔE) during polymer growth was the highest for 60 mV.s^{-1} scan rate with the potential of 0.366V, besides, anodic and cathodic peak current ratio is closer to the one with 0.955 (I_a/I_c). Therefore these data indicate that the most reversible modified CFME is coated with 60 mV.s^{-1} scan rate. The separation between anodic and cathodic peaks is associated with ion transport resistance involved in these redox reactions. 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 polymer film coated on the electrode. This is expected since an increase in polymer film thickness leads to an increase in resistance for ion penetration. CV of polymer growth with 60 mV.s^{-1} indicates the highest ΔE (0.366 V), that means ion transport resistance is much higher.

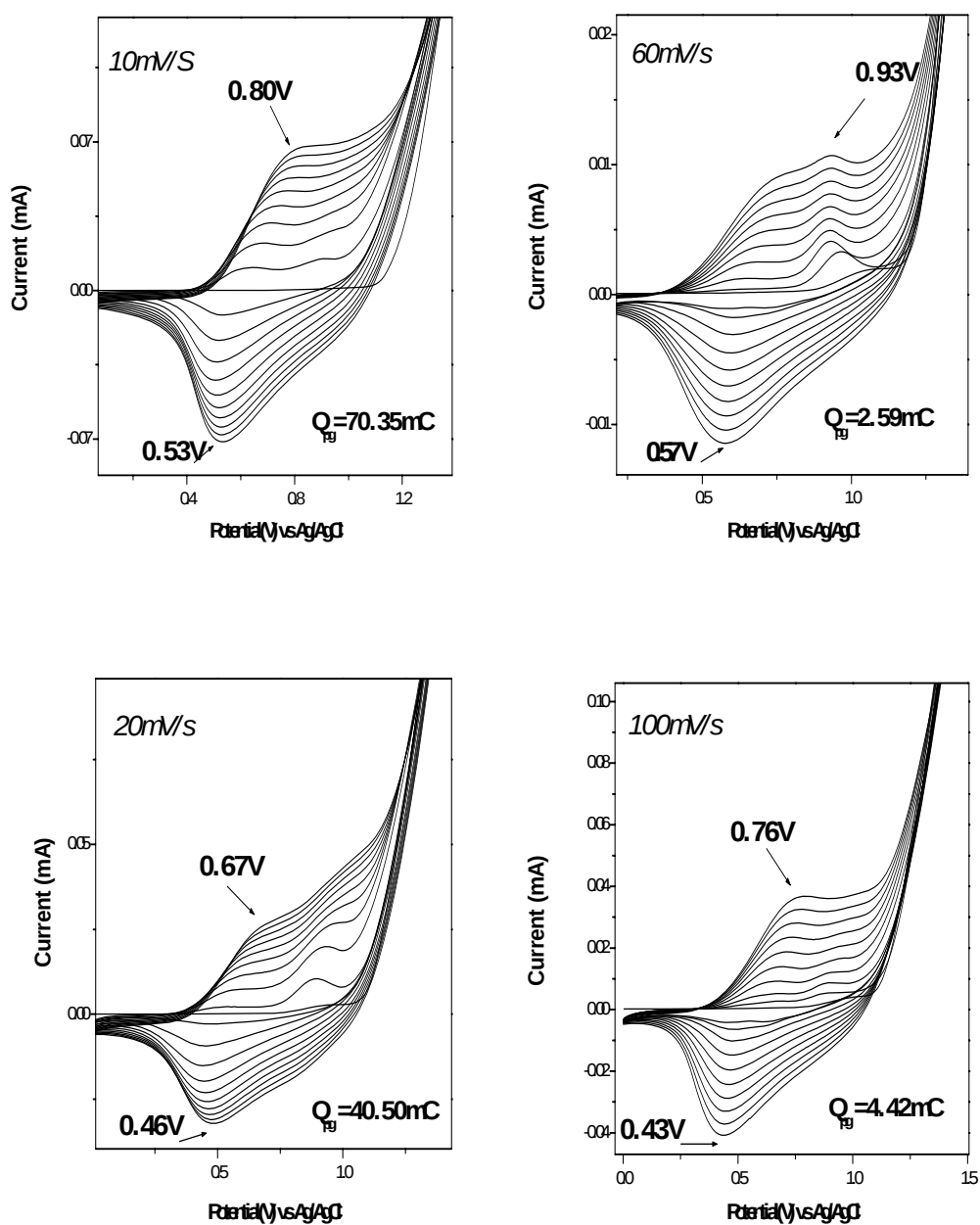


Figure 3.2: Cyclic Voltammograms For Potentiodynamic Growth of [1-(4-Methoxy Phenyl)-1H-Pyrrole] With 10,20,60 and 100 mV.s^{-1} Scan Rates.

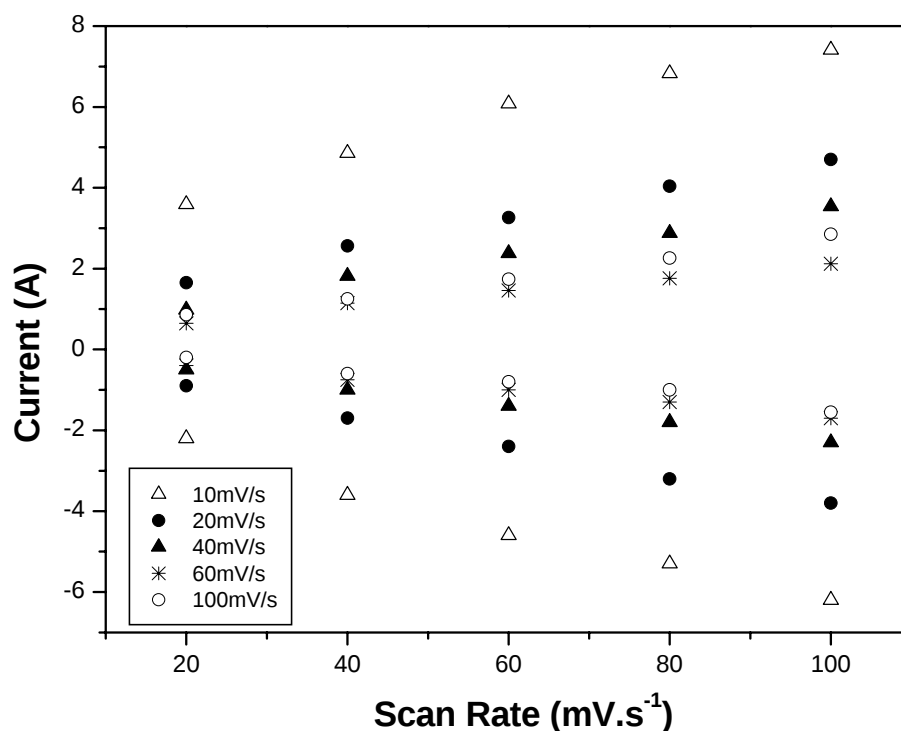


Figure 3.3: Change In Anodic and Cathodic Peak Currents With Scan Rate. Scan Rate Dependencies of [1-(4-Methoxy Phenyl)-1H-Pyrrole] Films That Were Grafted With Different Scan Rates In Monomer Free Solution of 0.05 M TEAP / CH₂Cl₂)

All polymer electrodes shows linear increase in peak current that means polymer electrode processes are thin film formation and diffusion limited according to randles-sevcik equation. (Figure 3.3.). Electroactivity of polymer electrodes is the highest for the polymer synthesized at 10mV.s⁻¹

Scan rate dependencies were determined for all homopolymers. As illustrated in Figure above the current is linearly proportional to scan rate, indicating all electroactive sites are electrode supported. CV of [1-(4-Methoxy Phenyl)-1H-Pyrrole] coated CFME in monomer free electrolyte shows oxidation potential in the range of 0.75 and 0.85 V.

3.2.2. Morphology

The CFME/PMPPy micro films was achieved in TEAP/CH₂Cl₂ solution containing 10⁻² M monomer by potentiodynamic growth. CFME includes nearly 100 single filament carbon fiber and depositions were achieved by applying 10mV.s⁻¹, 50mV.s⁻¹ and 100mV.s⁻¹ scan rate for 10 cycles. The morphology of PMPPy films are shown in figure 3.5. and figure 3.6. It looks as the CFME is uniformly coated but when the scan rate decreases the grain formation increases. (Figure 3.5, Figure 3.6)

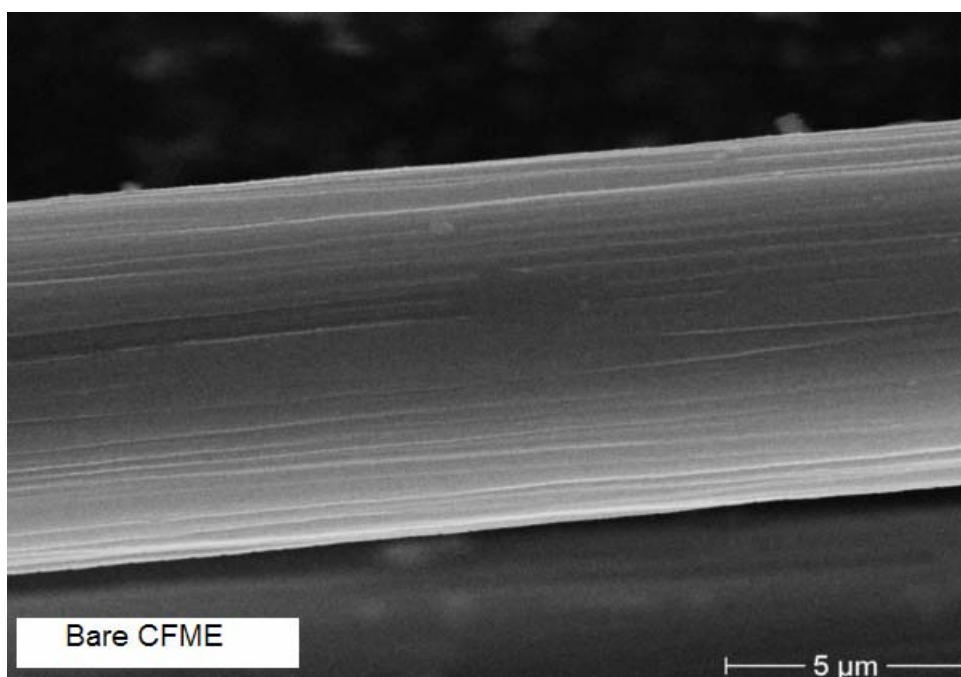


Figure3.4: SEM Picture of Bare Carbon Fiber Micro Electrode. (Uncoated CFME)

As illustrated in figure 3.4. uncoated carbon fiber micro electrode has straight strains in its structure. For morphological study CFMEs were electrocoated with three different scan rates so deposition charges decreased while the scan rate increases. Slow scan rates indicates more uniform coating than the faster rates. Porous structures were followed by filling with more compact materials at slow scan rates where polymer build up continuous inside the porous structure.

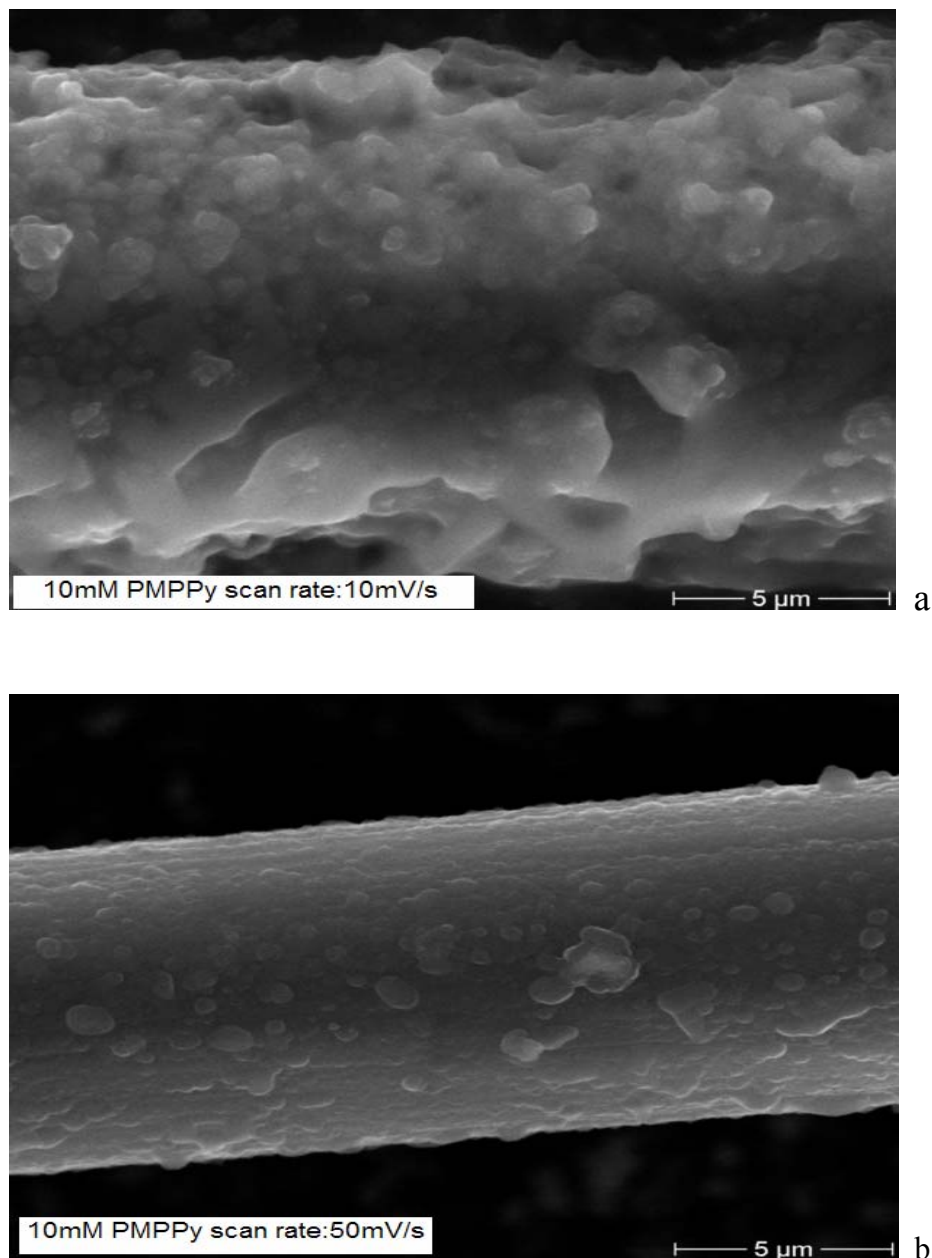


Figure 3.5: SEM Picture of Carbon Fiber Micro Electrode Modified With 10^{-2} M [1-(4-Methoxy Phenyl)-1H-Pyrrole] (10 Cycles) **a)** 10mV/s Scan Rate, **b)** 50mV/s Scan Rate

Formation of thin films on CFMEs shows huge globular structures form on the surface with 10mV/s where the deposition charge is 70.35mC. On the other hand, 50mV/s (9.59mC) and 100mV/s (4.42mC) deposition charges have resulted in more thicker film structure on CFME. In figure 3.6. cross-section area of coated CFME with 100mV/s scan rate is represented.

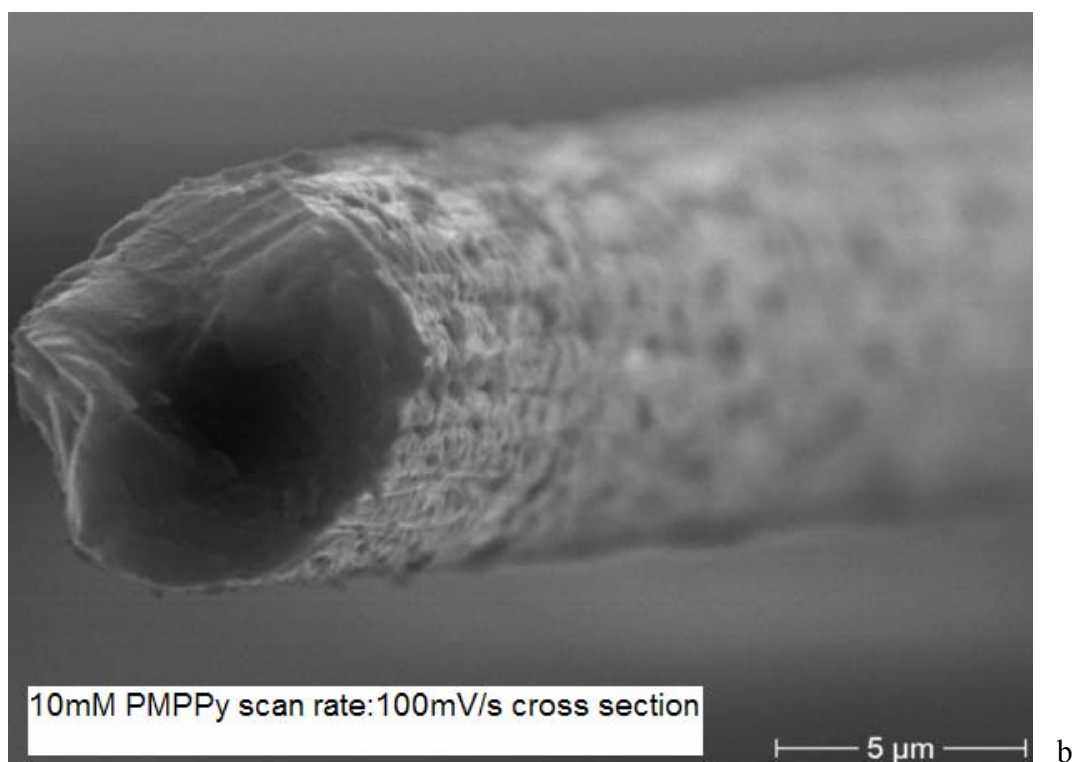
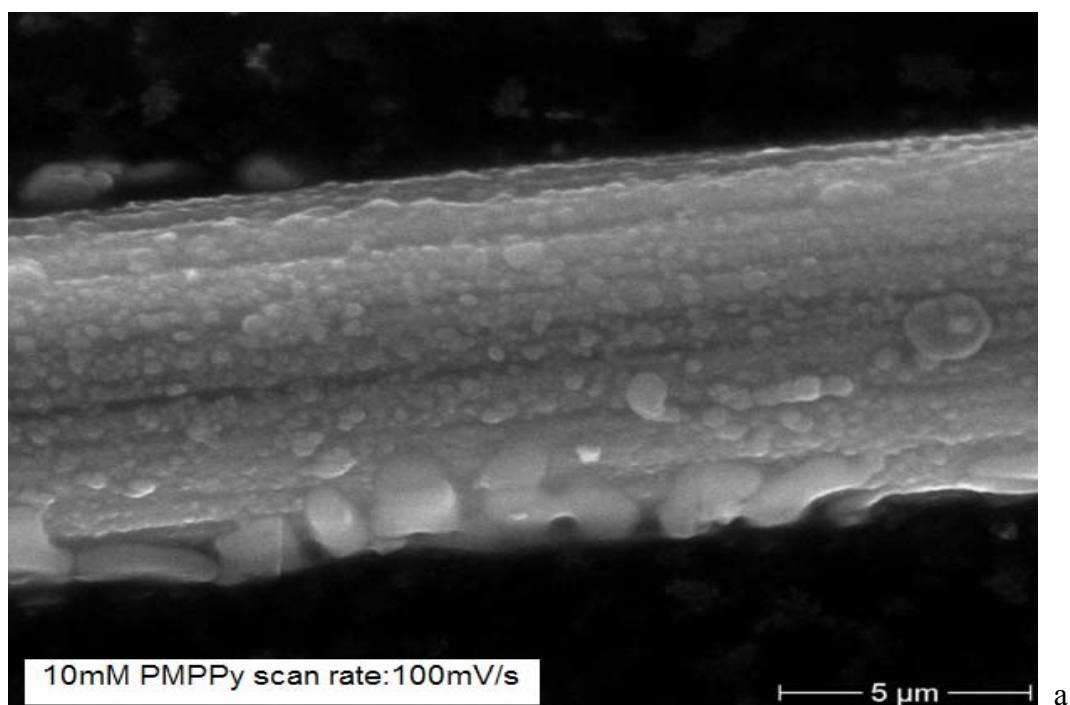


Figure 3.6: SEM Picture of Carbon Fiber Micro Electrode Modified With 10^{-2} M [1-(4-Methoxy Phenyl)-1H-Pyrrole] (10 Cycles) **a)** 100mV/s Scan Rate, **b)** 100mV/s Scan Rate Cross Section

3.2.3. Effect of scan rates on EC impedance spectroscopy

The most common technique for estimating the capacitance behaviour is impedance spectroscopy. It is important to mention that the real electroactive 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 behaviour, hence, the amount of binding substance should be limited.

On the other hand, the electric conductivity of the carbon materials is closely related to their morphology. The electrical conductivity which determines the flow of electrical carriers is another limiting factor for the power density of a capacitor, however it will not drastically influence the energy density.

In this part of the study, electrochemical impedance spectroscopy was further employed to monitor the electrochemical behaviour of the electrodes. Electrodes which were electrocoated with [1-(4-Methoxy Phenyl)-1H-Pyrrole] at different scan rates, were subjected to same applied potentials and impedance characteristics were recorded. Impedance measurement were performed in monomer free solutions after polymer growth processes on CFMEs.

Typical Nyquist diagrams of modified electrodes are indicated in figure 3.7 respectively. All impedance curves are vertical straight lines in the low frequency region. Hence, the performance of an ideal capacitive behaviour was obviously seen in the plot. These vertical lines means that the modified carbon fiber micro electrodes shows the supercapacitor behaviour. 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.

At low frequency region, polymer electrode which is electrodeposited 60, 40, 100 mV.s^{-1} behave like pure capacitors characterized by vertical line parallel 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.

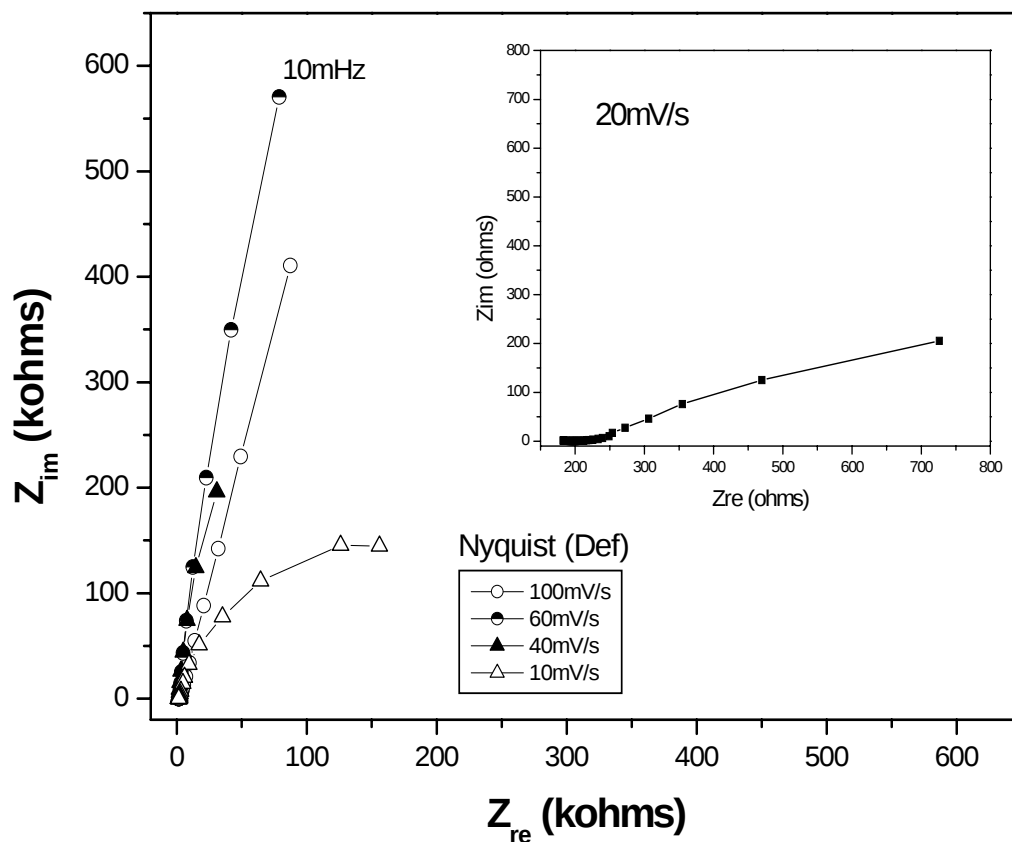


Figure 3.7: Nyquist Plots Recorded for [1-(4-Methoxy Phenyl)-1H-Pyrrole] Electrografted CFMEs With Different Scan Rates.

A drastic difference can be seen at the polymer electrode obtained with 10mV.s^{-1} scan rate, where the low frequency capacitive behaviour changed to semicircle that may be due the thicker polymer film than the others.

On the other hand the modified CFME which was coated with 20mV.s^{-1} has the lowest conductivity but it has the highest resistance because Z' axis could be named as pure resistor while the Z'' is pure capasitor. As it is seen from the Nyquist diagram 60mV.s^{-1} scan rate shows the best capacitive behaviour. On the other hand, specific capacitance values can be calculated via; $C_{spe} = 1 / 2\pi f z''$

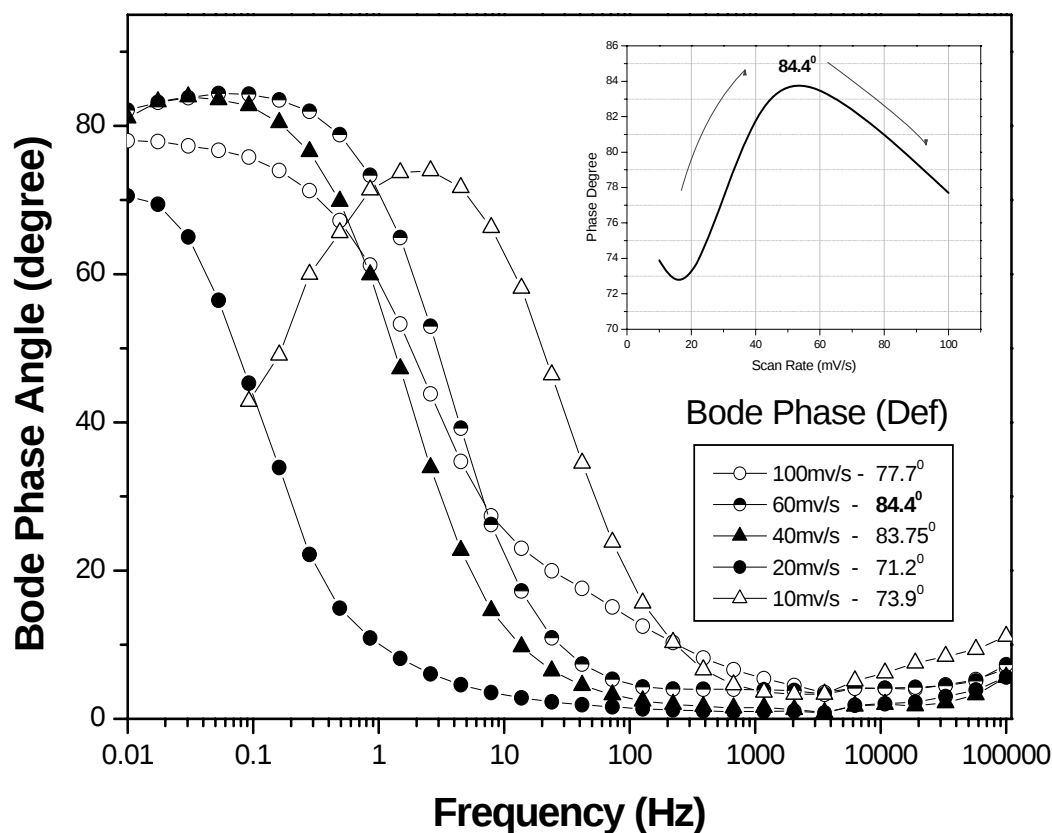


Figure 3.8: Bode Phase Definitions of [1-(4-Methoxy Phenyl)-1H-Pyrrole] Electrografted CFMEs With Different Scan Rates. In The Bode Phase Plot of PMPPy in TEAP/CH₂Cl₂, The Bode Phase Angle Approaches a Plateau (85°) Indicating Capacitor Behaviour.

In the Bode phase plot of PMPPy electrodeposited on CFME with 10 mV.s⁻¹ scan rate, the bode phase angle approaches a plateau (74°), in the frequency region 0.84Hz-4.34Hz which film indicates capacitor behavior. (Figure 3.8.) In the frequencies, 4.34Hz-697Hz, phase transition from capacitor to resistor behavior was observed.

PMPPy showed resistor behavior in the frequency region of 697Hz-100kHz. The Bode phase plot of PMPPy coated on CFME with 20 mV.s⁻¹ is indicated that in the small time interval (10mHz-17mHz) the polymer film is capacitive (71°) at low frequencies with a good supercapacitor behaviour.

The Bode phase angle plots of PMPPy electrodeposited on CFME with 40 mV.s⁻¹, 60 mV.s⁻¹ and 100 mV.s⁻¹, in the frequency region of 10mHz-1Hz, show

capacitance behavior, phase transition from capacitor to resistor is obtained in the frequency region between 0.16Hz-100Hz . The Polymer films indicated resistor behavior in the frequencies, 41Hz-100kHz.(Figure 3.8.)

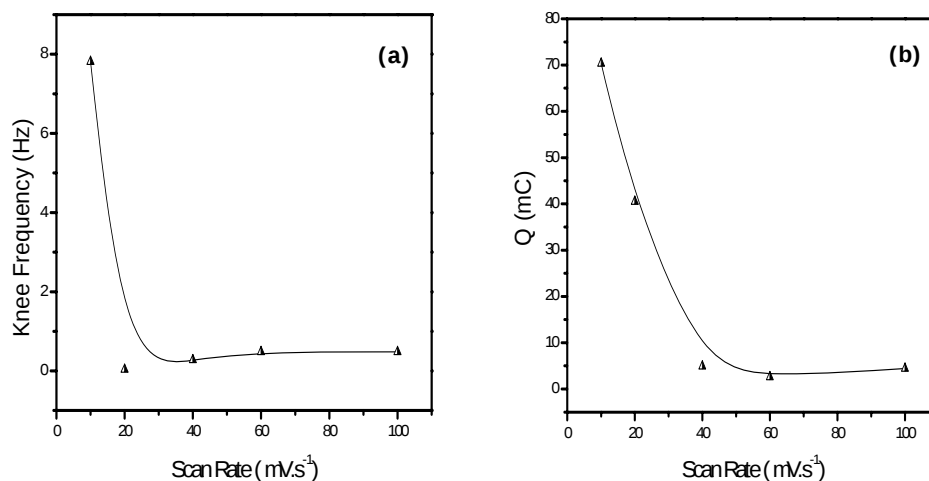


Figure 3.9: a) The Knee Frequency vs Scan Rate Graph of [1-(4-Methoxy Phenyl)-1H-Pyrrole] Obtained Different Scan Rates. **b)** Charge vs Scan Rate Graph of Poly1-(4-methoxyphenyl)-1H-Pyrrole in TEAP/ CH_2Cl_2

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 frequency of PMPPy obtained with scan rates between (20-100 mV.s^{-1}) lower than PMPPy coated with 10 mV.s^{-1} scan rate. (Figure 3.9.). The graph indicated that PMPPy electrodeposited at scan rates (20-100 mV.s^{-1}) can be more advantageous than 10 mV.s^{-1} to use supercapacitor applications.

In an other 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.

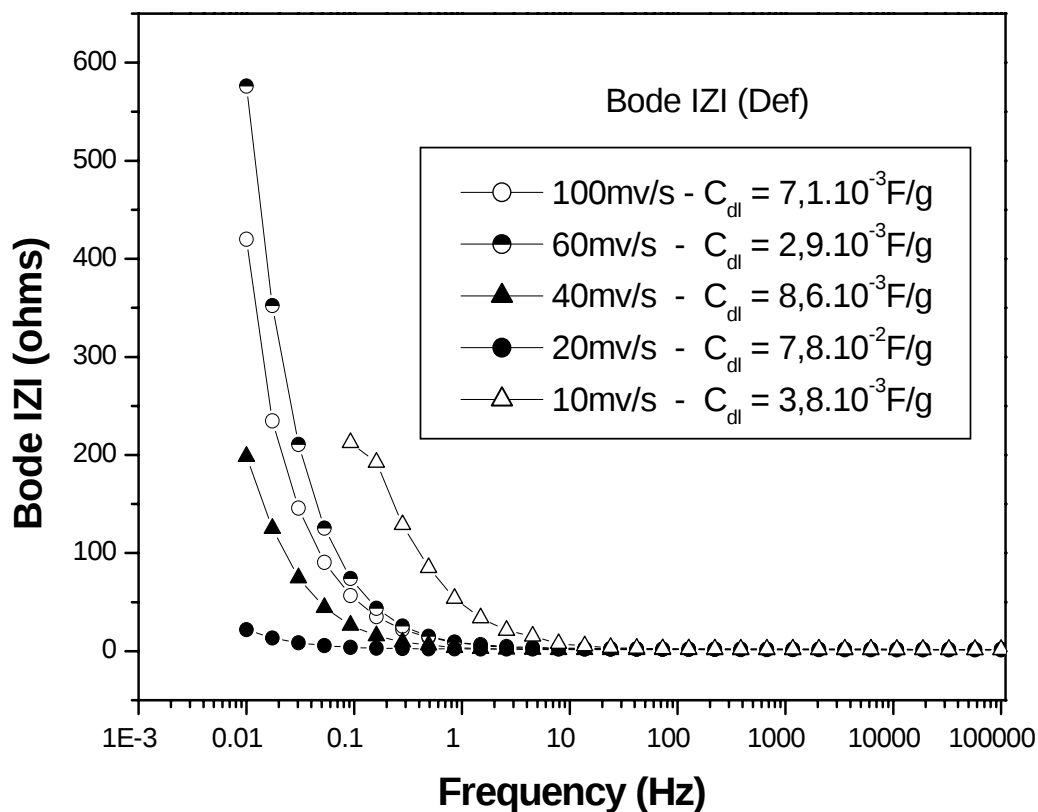


Figure 3.10: Bode Magnitude Plot of 1-(4-methoxyphenyl)-1H-Pyrrole Electrografted CFMEs With Different Scan Rates.

Bode magnitude plot gives extrapolating this line to the log Z axis at $\omega = 1$ ($\log \omega = 0$) yields the value of C_{dl} from the relationship: $|Z| = 1/C_{dl}$. Double layer capacitance value is higher for the second electrode which is coated with 20 mV.s^{-1} . The highest value determined as $7.8.10^{-2} \text{ F/g}$ could be due to the slow cycling by low potential. (Figure 3.10.)

3.2.4. Characterization with FTIR-ATR spectroscopy

FTIR-ATR Reflectance Measurements of polymer electrografted carbon fiber surface were analysed by FTIR Reflectance Spectrometer. In the spectrum doping peaks could be observed with different transmittance values. (Figure 8). Since ClO_4^- observed at 1100 cm^{-1} [42], the presence of a strong band at this wavelength poly-1-(4-Methoxy Phenyl)-1H-Pyrrole indicates that the polymer are doped with this anion. (Table 1)

The electronic properties of conductive polymers are strongly dependent on conjugation length. Defects interrupt conjugation including sp^3 carbons, carbonyl groups, crosslink etc.

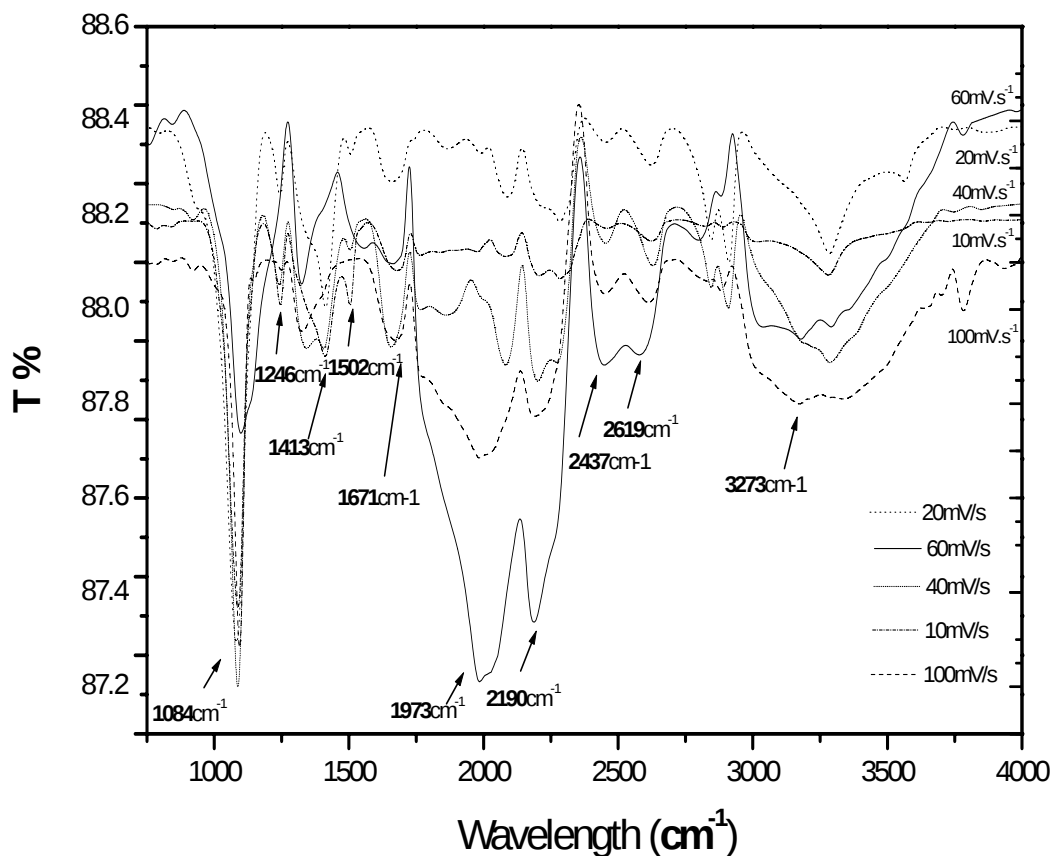


Figure 3.11: FTIR-ATR Spectrum of Poly1-(4-methoxyphenyl)-1H-Pyrrole in TEAP/ CH_2Cl_2

There are some parameters called effective conjugation coordinate to calculate IR spectra Pyrrole derivatives. This theory successfully predicts the number and position of main infrared band of poly-1-(4-Methoxy Phenyl)-1H-Pyrrole and shows that infrared spectrum strongly influenced by the conjugation length.

In particular Zerbis calculation predict that as conjugation length is increased intensity of antisymmetric ring stretching mode at around 1507cm^{-1} will decrease relative to the intensity of the symmetric mode at around 1405cm^{-1} , as a result the ratio of intensity of the 1507 and 1405 in an experimental FTIR spectrum can be used to relative measure of the conjugation length. The intensity of antisymmetric ring stretching mode at around 1507cm^{-1} will decrease relative to the intensity of the

symmetric mode at around 1405cm^{-1} with increasing deposition rate. In the FTIR of poly-1-(4-Methoxy Phenyl)-1H-Pyrrole obtained with 60 and 100 mV s^{-1} showed that antisymmetric ring stretching mode at around 1507cm^{-1} disappeared. So we can conclude that conjugation length increased with deposition rate.

Table 3.1: FTIR Bands of Polymethoxyphenyl 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 stretching (cm^{-1})	C=C asymmetric ring stretching (cm^{-1})	C=C Symmetric ring stretching (cm^{-1})	C-N stretching (cm^{-1})	ClO ₄ ⁻ , doping induced band
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

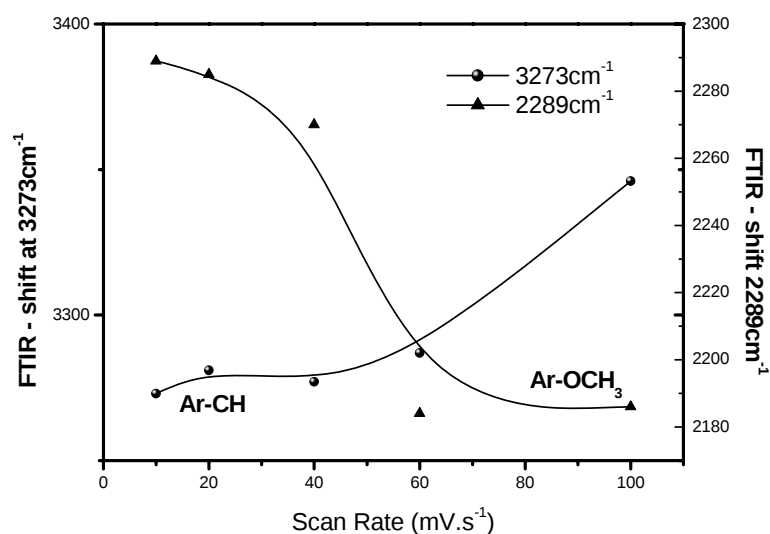


Figure 3.12: The Relationship FTIR-Shift 3273cm^{-1} and 2283cm^{-1} Between Scan Rate of PMPPy

The peak shifts increases with the electrodeposition scan rate at around 3273cm^{-1} , however the peak at 2283cm^{-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 (Figure 3.12.)

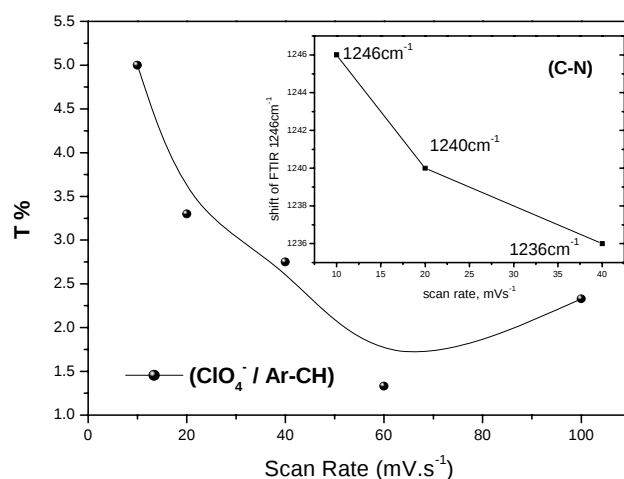


Figure 3.13: The Relationship Between %T and $\text{ClO}_4^- / \text{Ar-CH}$ Ratio. Inset: C-N Bond Shift at 1246cm^{-1} Against Scan Rate.

T% of the ratio of the bands vs scan rate graph showed that intensity of doping induced band (1086cm^{-1}) decreases with the scan rate, that may be due to changes in the oxidation levels of PMPPy film. The most oxidized PMPPy is polymer obtained at 10 mV.s^{-1} , since more charges accumulated on this polymer (Figure 3.13.)

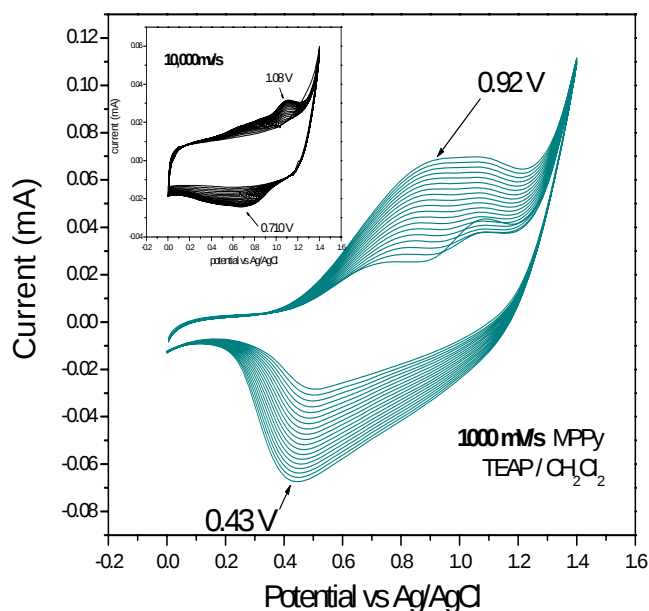
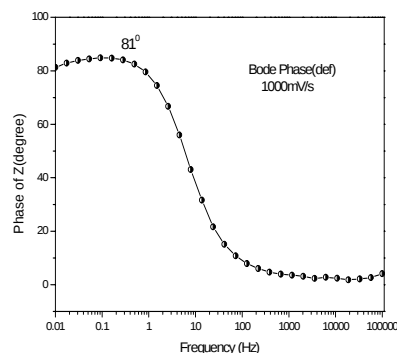
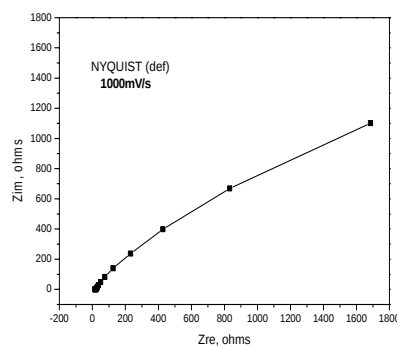


Figure 3.14: Cyclic Voltammograms For Potentiodynamic Growth of [1-(4-Methoxy Phenyl)-1H-Pyrrole] With 1000 mV.s^{-1} Scan Rates, Inset: $10,000\text{ mV.s}^{-1}$ Scan Rates.

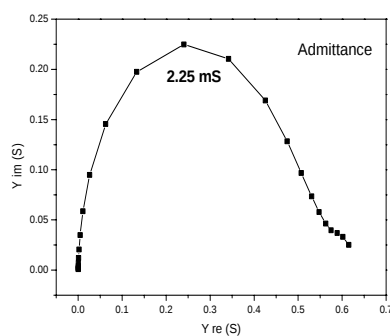
Electropolymerization of [1-(4-Methoxy Phenyl)-1H-Pyrrole] on CFME was checked for its stability against higher scan rates. For this purpose micro electrodes were coated by applying 1000mV/s and 10.000mV/s scan rates. As it is seen in the figure 3.14. even 10.000mV/s scan rate shows a very good reversibility. This result also proves that [1-(4-Methoxy Phenyl)-1H-Pyrrole] has resistive property against high scan rates and it can also be coated by fast deposition rate.



a



b



c

Figure 3.15: a)Bode Phase Definitions of [1-(4-Methoxy Phenyl)-1H-Pyrrole] Electrografted CFMEs With Different Scan Rates. In The Bode Phase Plot of PMPPy in TEAP/CH₂Cl₂, The Bode Phase Angle Approaches a Plateau (85°) Indicating Capacitor Behaviour. B)Nyquist Plots and c)Admittance Plot Recorded for [1-(4-Methoxy Phenyl)-1H-Pyrrole] Electrografted CFMEs With 1000mV/s and 10.000mV/s are Illustrated.

3.3. Monomer Concentration Effects on Electropolymerization of [1-(4-Methoxy Phenyl)-1H-Pyrrole]

For both chemical and electrochemical processes monomer concentration have affect on resultant product. For electropolymerization, since the oxidation of the monomer occurs at a higher potential than that of the redox processes of the polymer, side reactions including crosslinking and/or over-oxidation of the polymer could take place. The polymer yield and the rate of oxidation were found to decrease as the size of the alkyl group increases.

Electropolymerization of [1-(4-Methoxy Phenyl)-1H-Pyrrole] was achieved on carbon fiber micro electrodes in TEAP/CH₂Cl₂. Monomer concentration effect on electropolymerization and electrochemical impedance spectroscopy was investigated. Electropolymerization process was achieved with 40mV/s. scan rate and 10⁻¹M, 10⁻²M, 10⁻³M monomer concentrations were used.

Poly-1-(4-methoxyphenyl)-1H-Pyrrole characterization was investigated with cyclic voltammetry and FTIR-ATR spectroscopy. After surface modification of carbon fiber micro electrode, capacitance properties were checked by using electrochemical impedance spectroscopy. Capacitive behaviors of coated CFMEs were defined via Nyquist plots, Bode Plot and Bode phase definitions; besides, conductance of modified micro electrodes was studied with admittance plots.

3.3.1. Redox behaviour and stability of MPPy film

The cyclic voltammograms obtained during polymer film growth on carbon fiber micro electrodes are presented in Figure 3.16, 3.17 and 3.18. [1-(4-Methoxy Phenyl)-1H-Pyrrole] was achieved on carbon fiber microelectrode in TEAP/CH₂Cl₂ potentiodynamically. Cyclic voltammogram of [1-(4-Methoxy Phenyl)-1H-Pyrrole] obtained with 10⁻¹M, 10⁻²M, 10⁻³M monomer concentrations showed the broad and symmetrical redox waves. Potentiodynamic growth of [1-(4-Methoxy Phenyl)-1H-Pyrrole] obtained with monomer concentrations have showed different redox behavior.

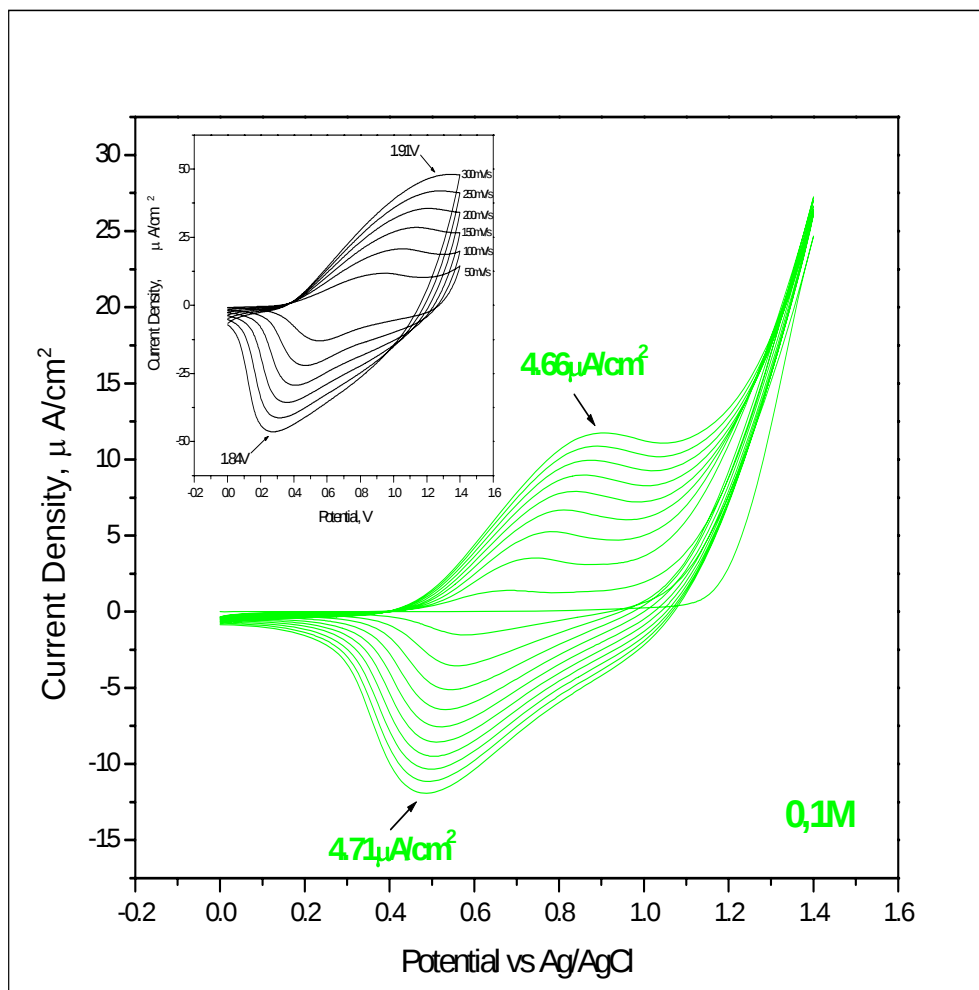


Figure 3.16: Continuous Cyclic Voltammograms in The Case of Electropolymerization of 10^{-1}M [1-(4-Methoxy Phenyl)-1H-Pyrrole] With 40mV/s Deposition Rate. Inset: Scan Rate Dependencies In Monomer Free Solution Between [100-500] mV/s.

Electropolymerization of 10^{-1}M [1-(4-Methoxy Phenyl)-1H-Pyrrole] on CFME was studied and shows better reversibility with the value of 0.989. Furthermore; monomer free diagram has a rectangular box shape which corresponds to the supercapacitive behaviour. Any increase in monomer concentration causes differences in the rectangular like shape and redox parameters.

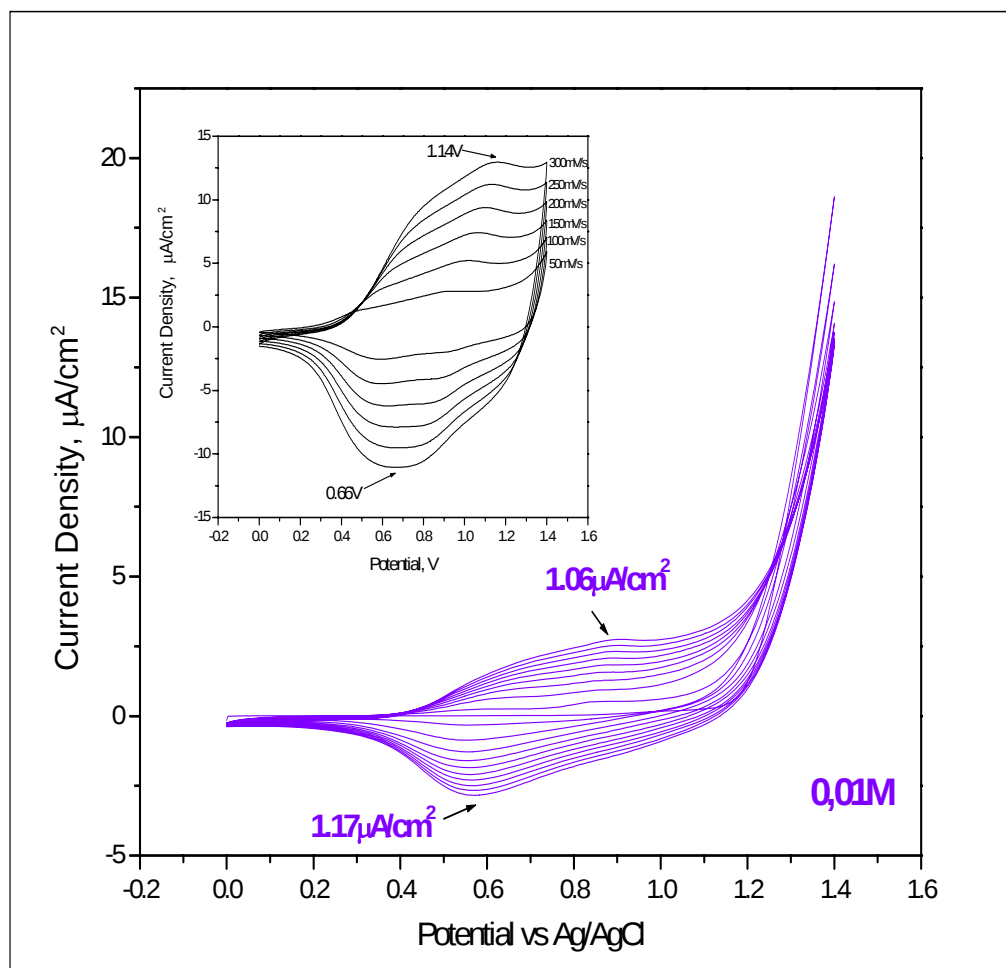


Figure 3.17: Continuous Cyclic Voltammograms in The Case of Electropolymerization of 10^{-2}M [1-(4-Methoxy Phenyl)-1H-Pyrrole] With 40mV/s Deposition Rate. Inset: Scan Rate Dependencies In Monomer Free Solution Between $[100\text{-}500] \text{ mV/s}$.

In the case of 0.01M [1-(4-Methoxy Phenyl)-1H-Pyrrole], it has the highest onset potential value (1.15V) which makes electropolymerization harder. However, $E_{1/2}$ and ΔE indicates the lowest values which predominates for conjugation and eletroactivity as well.

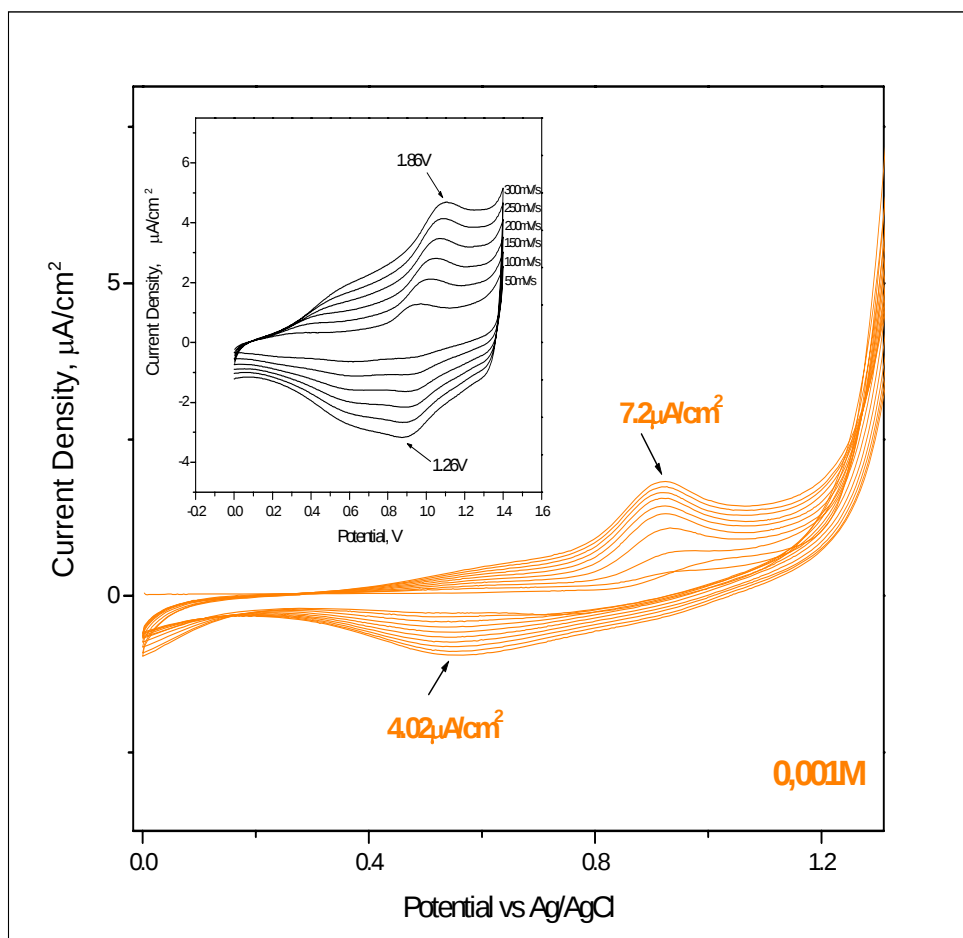


Figure 3.18: Continuous Cyclic Voltammograms in The Case of Electropolymerization of 10^{-3}M [1-(4-Methoxy Phenyl)-1H-Pyrrole] With 40mV/s Deposition Rate. Inset: Scan Rate Dependencies In Monomer Free Solution Between [100-500] mV/s.

The lowest monomer concentration in this situation stands for the lowest onset potential supplying easy polymerization. On the other hand not only the reversibility is lowest but also the film occurred is not diffusion controlled. For scan rate dependencies, anodic and cathodic peak currents are increased with the increase in scan rate.

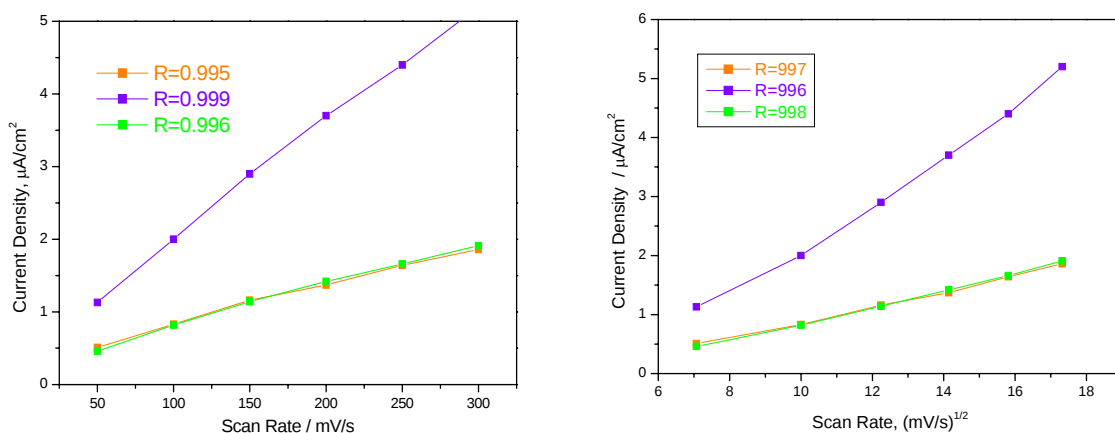


Figure 3.19: Current Densities of Electropolymerized [1-(4-Methoxy Phenyl)-1H-Pyrrole] Against a) Scan Rate b) Square Root of Scan Rate According to The Randles Sevcik Equation.

In the figure 3.19, scan rate effect on current in monomer free solution was observed. When we look at the correlation coefficient (R) values, the highest value is observed for 0.01M which corresponds to a thin film formation. Besides, square root of scan rate graph indicates that diffusion controlled film formation is observed at 0.1M and 0.001M monomers.

Table 3.2: Monomer Concentration Effects on Redox Parameters of Electrodeposited [1-(4-Methoxy Phenyl)-1H-Pyrrole]

Monomer Concentration	E _{onset} (V)	E _{1/2} (V)	ΔE (V)	I _a /I _c
0.1	1.12	0.204	0.409	0.989
0.01	1.15	0.158	0.316	0.906
0.001	0.89	0.186	0.372	0.541

The table above shows the redox parameter of polymers which are obtained from different monomer concentrations. Experimental results indicated that the lowest monomer concentration leads to the higher electroactivity and it has the lowest oxidation(onset) potential. However, the reversibility of this modified electrode was decreased. E_{1/2} gets the lowest value for 0.01M concentration, meaning that it has the longest polymer chain.

3.3.2. Morphology

The CFME/PMPPy micro films were coated in TEAP/ CH_2Cl_2 solution containing 10^{-1} M, 10^{-2} M, and 10^{-3} M monomer potentiodynamically. CFME electrodes were prepared with nearly 100 filament carbon fibers and the micro electrode coated at 40mV.s^{-1} scan rate for 10 cycles. The film formation on CFMEs were compared with three different monomer concentrations. On the other hand, the comparison of uncoated and coated fibers indicates a great difference with different structures as seen in figures.

When the concentration increases the more thicker polymer films including more grains were obtained. The charge capabilities of electrogrowth process is proportional with the film thickness. In figure 3.20. SEM images of 0.1M concentration has the most globular and thick structure with the charge capacity of 9.172mC. Besides, 0.01M is placed as second thick film with 3.817mC and the dilute solution appeared as the thinnest coating with 0.581mC charge capability.

Applying higher charges does not lead to increase in the diameter linearly but empty spaces of fibrous polymeric chain network starts to fill with more compact polymeric material.

For 0.1M monomer concentration leads to a grainy and needle type polymeric structure resulting from a three dimensional nucleation growth is observed. The SEM picture of PMPPy films shows clusters of globules without uncoated parts for 0.1M solution.

The SEM pictures show a pronounced difference in the surface morphology of the three type of different PMPPy layers. At first 0.001M concentration, after very thin film formation on CFME, where striations are still appeared somehow were disappear on the whole surface area, at high monomer concentration.

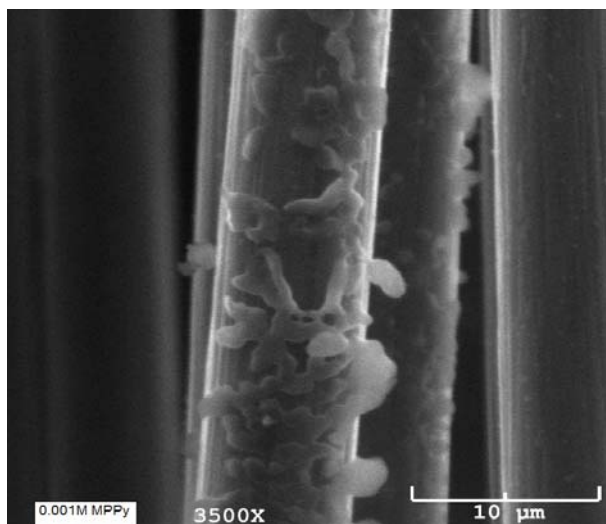
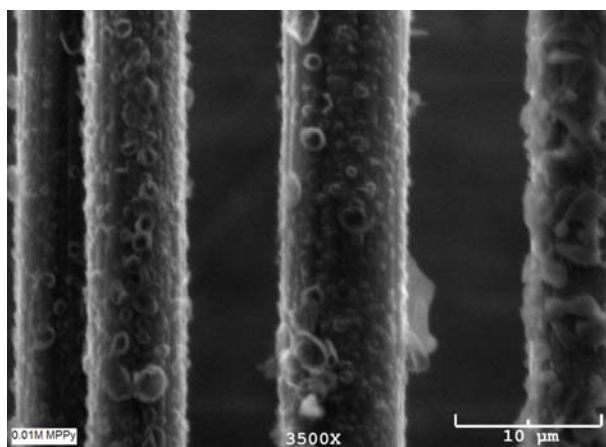
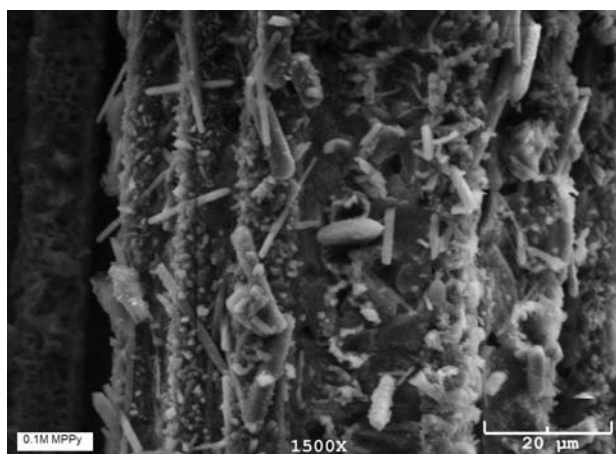


Figure 3.20: SEM Photos of [1-(4-Methoxy Phenyl)-1H-Pyrrole] Coated CFME a) 0.1m b) 0.01M c) 0.001M

3.3.3. Characterization with FTIR-ATR spectroscopy

[1-(4-Methoxy Phenyl)-1H-Pyrrole] was electrocoated onto carbon fiber micro electrodes with different concentrations. Therefore, it is observed that the obtained polymeric structures indicate different electrochemical properties compared to FTIR peak shifts. Onset potential values are increased by the increase in transmittance value.

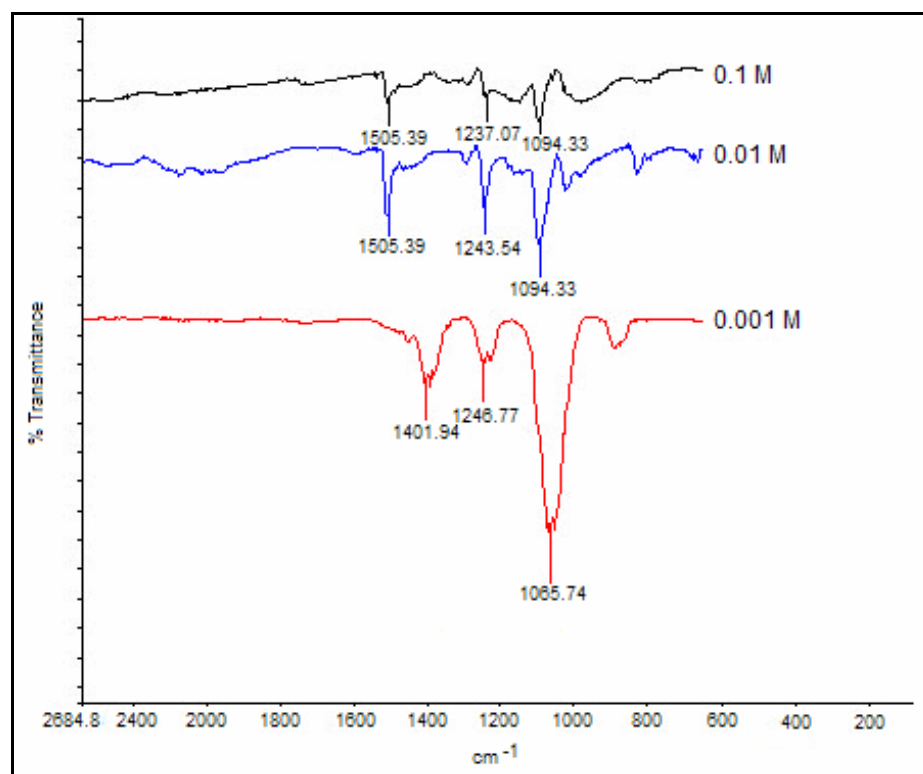


Figure 3.21: FTIR-ATR Spectrum Results of [1-(4-Methoxy Phenyl)-1H-Pyrrole] Coated CFME With 0.1M, 0.01M and 0.001M Monomer Concentration.

The peaks around 1100cm⁻¹ belong to the ClO⁻⁴ dopant anions; meaning that electrolyte was diffused into the fiber structure. The peaks at 1240cm⁻¹ indicates the C=N bonds which belongs to the pyrrole structure and the intensity is increasing with the concentration. The C=C bonds peak around 1500cm⁻¹ shifts towards 1400cm⁻¹ for 0.001M monomer concentration. These three peaks proves that the CFMEs were electrocoated and the monomer concentration effected the polymeric structure.

3.3.4. Monomer concentration effect on EC impedance spectroscopy

Electrochemical impedance spectroscopy monitor the electrochemical behavior of the modified CFME structures. All electrodes show a slight deviation from the capacitive line (y-axis), indicating fast charge transfer at the carbon fiber/polymer and polymer/solution interfaces, as well as fast charge transport in the polymer bulk. Electrocoated micro electrodes with MPPy compared with different monomer concentrations and results showed that dilution of MPPy monomer concentration increases the charge storage from 74° to 85° Bode phase angle (Fig. 3.22.(b)), which is very close to 90° as observed in supercapacitors.

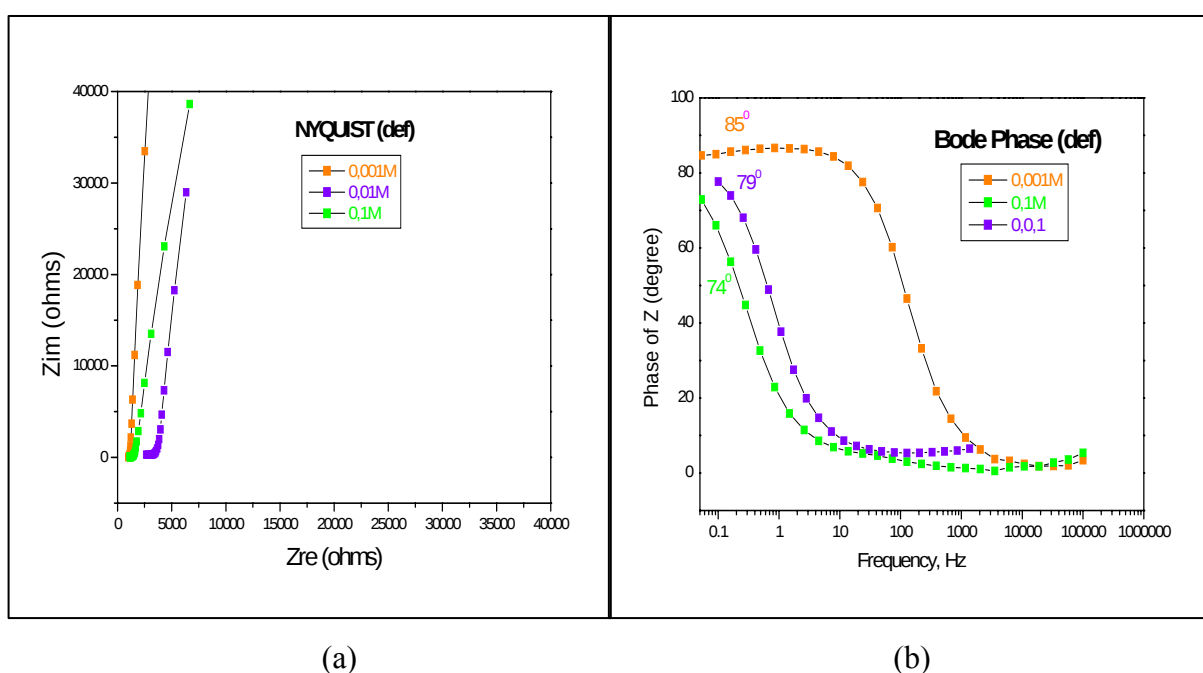


Figure 3.22: Nyquist Plots Recorded for [1-(4-Methoxy Phenyl)-1H-Pyrrole] Electrografted CFMEs With Different Concentrations. b) Bode Phase Definitions of [1-(4-Methoxy Phenyl)-1H-Pyrrole] Electrografted CFMEs With Different Concentrations. In The Bode Phase plot of PMPPy in TEAP/ CH_2Cl_2 , The Bode Phase Angle Approaches a Plateau (85°) Indicating Capacitor Behaviour.

Due to that increase Nyquist plot also correlates with the bode phase diagrams results. For nyquist graphe 0.001M monomer concentration was illustrated with the most perpendicular line to the y-axis showing the best capaitive behaviour.

SEM photos presents the globular and needle type structures for MPPy due to the monomer concentration increase, where the needle structures could be adsorbed dopant anions resulting in a lower charge storage ability and divergence from the capacitive line.

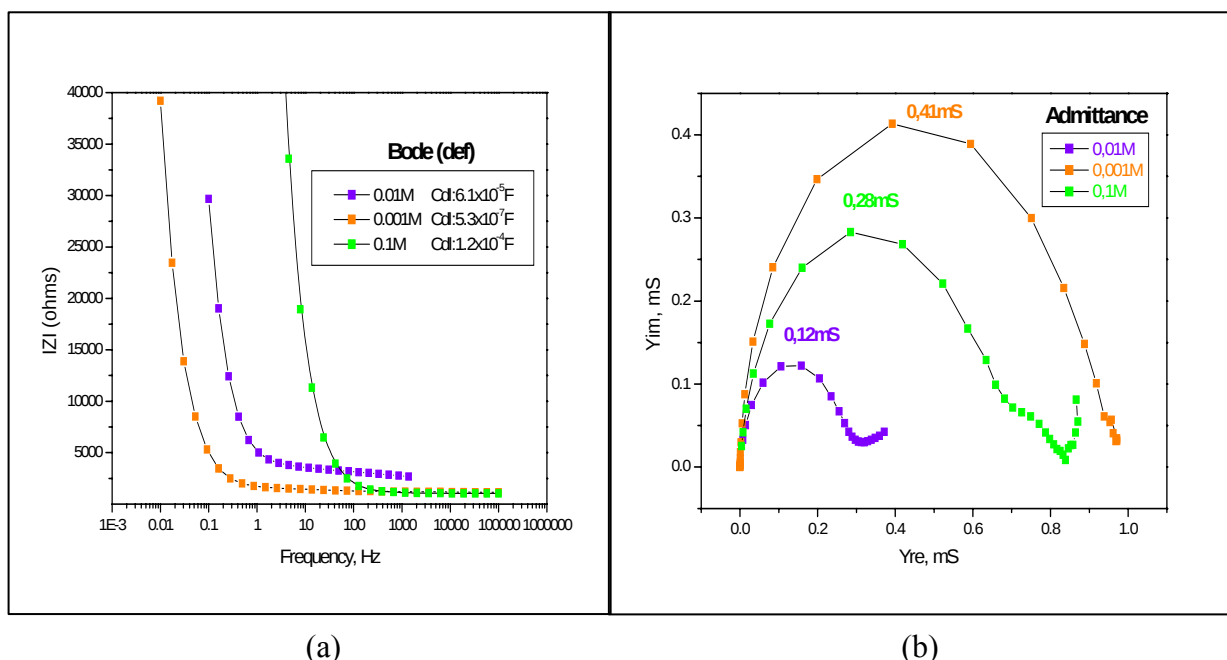


Figure 3.23: a) Bode Magnitude Plot b) Admittance Plot of [1-(4-Methoxy Phenyl)-1H-Pyrrole] Electrografted CFMEs With Different Monomer Concentrations. (0.1M, 0.01M, 0.001M)

When the bode magnitude plot results were analyzed, then double layer capacitance value can be calculated. As a result; 0.01M monomer concentration has the highest C_{dl} value with $1.2 \times 10^{-4} F$. On the other hand; admittance plot gives information about conductivity of the modified structures. Therefore; the diluted solution with 0.001M monomer concentrations conductivity has the highest value with 0.41 mS.

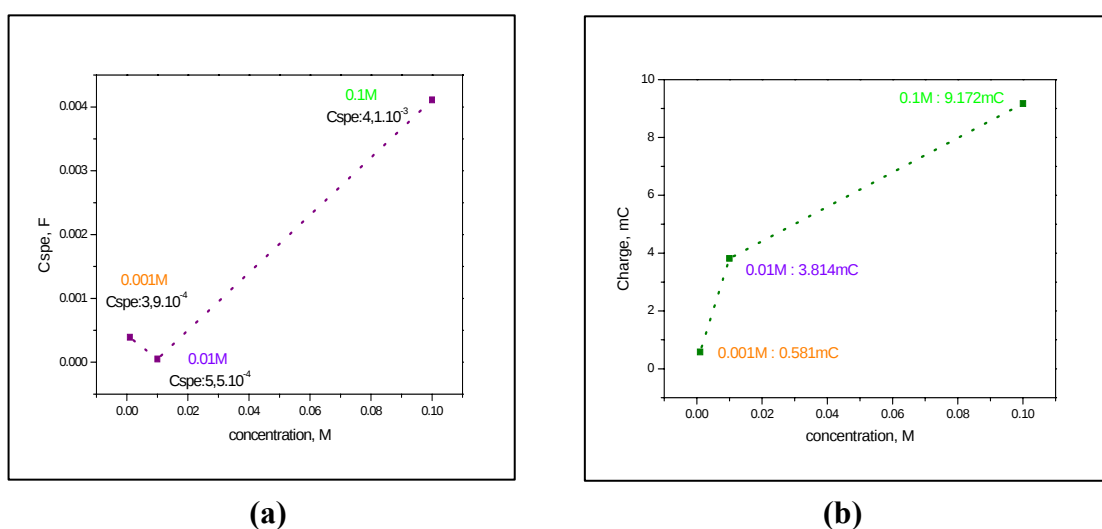


Figure 3.24: a) Specific Capacitance and b) Polymer Growth Charge Difference of [1-(4-Methoxy Phenyl)-1H-Pyrrole] With Different Monomer Concentrations. In the figure 3.24 the specific capacitance values obtained from three different concentration and the charge capabilities for electropolymerization growth process are illustrated. Cspe values have little decrease at 0.01M while the charge is proportionally increase with the concentration.

Table 3.3: Comparison Between Experimental and Theoretical Double Layer Capacitances for Different Concentrations

Concentration (M)	Cdl(experimental), F	Cdl (theoretical), F
0.1	1.2×10^{-4}	1.9×10^{-5}
0.01	6.1×10^{-5}	9.4×10^{-6}
0.001	5.3×10^{-7}	5.1×10^{-7}

3.3.5. Monomer concentrations effects on equivalent circuits

The electrochemical parameters of the CFME / MPPy / Electrolyte system were evaluated by employing The ZSimpWin (version 3.10) software from Princeton Applied Research. From the correlation results; if the chi-squared (χ^2) is observed as minimized below 10^{-4} . χ^2 is the function defined as the sum of the squares of the residuals.

Almost 10 electrical circuit model were applied for our experimental data but for the most cases the smallest χ^2 value is obtained from $R(C(R(Q(RW))))(CR)$ model for three data set. Therefore; the results from $R(C(R(Q(RW))))(CR)$ circuit model was compared for three different concentrations.

The chosen model (see Figure 3.25) was built using series components; the first one is the bulk solution resistance of the polymer and the electrolyte, R_s , second one the parallel combination of the double layer capacitance, C_{dl} , and, R_1 is the resistance of the electrolyte. A series connection to R_1 made up using CPE in parallel with R_2 and W , R_2 is the charge transfer, and W is the Warburg impedance of the polymer. The last component a capacitor element (C_{CF}) is introduced in parallel with a charge transfer resistor (R_{CF}) corresponding to the carbon fiber microelectrode polymer coating. Simulation results are given in Table 3.2 that, this electrical equivalent circuit was successfully applied to the experimental data to explain the interface between the carbon fiber microelectrode, the polymer film and electrolyte in this potential region.

The comparison between Chi Squared (χ^2) values reveals the smallest value as 1.09×10^{-4} for 0.1M monomer concentration. On the other and, 0.1M monomer concentration has the higher double layer capacitance with the value of 1.91×10^{-5} . Additionally; the correlation between experimental and theoretical C_{dl} values indicates the highest capacitances for 0.1M monomer concentration.

Table 3.4: Potential Dependence of The Parameters Calculated From The R(C(R(Q(RW))))(CR) Model Which is Given in Figure 3.25. Monomers Deposited by Electrochemically at 40 mV/s, 10 Cycle in 0.05 M TEAP/CH₂Cl₂ Solution.

R(C(R(Q(RW))))(CR)	0.1 M	0.01 M	0.001 M
R_s / Ohm	1046	2522	0.5087
C_{dl} / F	1.91x10 ⁻⁵	9.465x 10 ⁻⁶	5.084x 10 ⁻⁷
R₁ / Ohm	325.8	840.5	444.7
Q / Y₀/ S s⁻ⁿ	3.124x10 ⁻⁴	4.475x 10 ⁻⁵	6.834x 10 ⁻⁷
n	0.9116	0.96	0.948
R₂ / Ohm	1.566x10 ⁴	9.828x 10 ⁴	3.145x 10 ⁸
W / Y₀/ S s⁻ⁿ	4.521x10 ⁻²⁰	1.833x 10 ⁻²⁰	5.481x 10 ⁻⁸
C_{CF} / F	1.188x10 ⁻⁸	4.331x 10 ⁻⁷	8.86x 10 ⁻¹¹
R_{CF} / Ohm	16.92	578.5	1038
Chi Squared (χ²)	1.09x 10 ⁻⁴	4.19x 10 ⁻⁴	2.06x 10 ⁻⁴

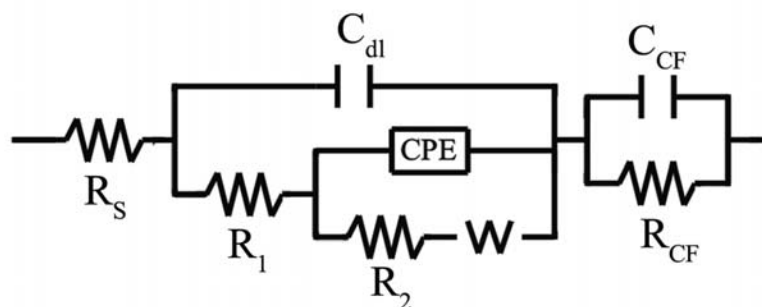
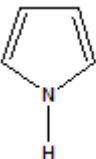
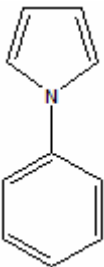
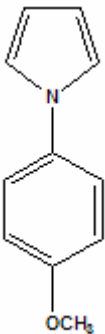


Figure 3.25: R(C(R(Q(RW))))(CR) Circuit Model

3.4. Monomer Substitution Effect on Electropolymerization

Homopolymer films of N-pyrrole (Py), N-phenylpyrrole (PhPy), and [1-(4-Methoxy Phenyl)-1H-Pyrrole] (MPhPy) were synthesized electrochemically onto a few single carbon fiber microelectrodes (CFMEs). In this study, influence of the substituent effect on electrochemical impedance spectroscopy (EIS) and correlation with electrochemical equivalent circuits were represented. All the monomers were electrodeposited in 0.05 M Tetraethyl ammonium perchlorate (TEAP) / dichloromethane (CH_2Cl_2) solution and characterized by cyclic voltammetry (CV), Fourier transform infrared reflectance spectrophotometer (FTIR-ATR), Scanning electron microscopy (SEM), and Atomic force microscopy (AFM).

Table 3.5: Monomer Structures of Py, PPy and MPPy

Monomer Structures			
Nomenclature	N-Pyrrole	N-Phenylpyrrole	[1-(4-Methoxy Phenyl)-1H-Pyrrole]

3.4.1. Electropolymerization of Py, PhPy and MPhPy by CV on CFMEs

The cyclic voltammogram of Py, PhPy, and MPhPy thin films electrochemically deposited on an CFME recorded in 0.05 M TEAP / CH_2Cl_2 as shown in Fig. 1-a, b, c, respectively. Current densities vs. potential changes were obtained from substituted monomers, Py and PhPy and MPhPy by electrochemically.

The onset potential of N-pyrrole, N-phenylpyrrole, and [1-(4-Methoxy Phenyl)-1H-Pyrrole], were obtained approximately as 0.74 V, 0.65 V and 0.63 V on CFMEs, respectively.

Table 3.6: Redox Parameters of Modified CFMEs With Py, PPy and MPPy

Polymers	Ionization Pot. (i_p / eV)	E_{pa} / V	E_{pc} / V	ΔE / V	i_a / i_c
PPy	5.14	0.74	0.66	0.08	2.93
P(PhPy)	5.05	0.65	0.43	0.22	0.72
P(MPhPy)	5.03	0.63	0.37	0.26	0.73

They are intensifying during repetitive scans and indicate the doping-dedoping of the electroactive film. Oxidation potentials of PhPy and MPhPy are obtained as 0.65 V, and 0.63 V smaller than oxidation potential of Py (0.74V) by electrogrowth mechanism. CV of pyrrole shows different redox behaviour, and oxidation potentials than N-phenylpyrrole, and [1-(4-Methoxy Phenyl)-1H-Pyrrole]. Py, PhPy, and MPhPy structures were given in Table 3.4.

Ionization potentials (i_p / eV) of Py, PhPy and MPhPy coated micro electrodes were calculated as suggested in the literature.

$$i_p = (E_{ox} + 4.4)$$

Ionization potential of P(PhPy, 5.05 eV) and P(MPhPy, 5.03 eV) have oxidation potentials similar to each other which are obtained from polymer growth (0.65 V for P(PhPy) and 0.63 V for P(MPhPy)). That is indicated that the removal of electron is easier than PPy (5.14 eV, and 0.74 V). It is shown that the polypyrrole has different cyclic voltammogram than N-phenylpyrrole, and [1-(4-Methoxy Phenyl)-1H-Pyrrole].

Table 3.5. indicated that PPy has different electrochemical redox parameters (E_{pa} , E_{pc} and ΔE , i_a / i_c and ionization potentials values than P(PhPy) and P(MPhPy). P(PhPy) and P(MPhPy) showed more reversible behavior (0.72 and 0.73 by anodic and cathodic current ratios) than PPy (i_a/i_c): 2.93). Oxidation peak potentials (E_{pa}), corresponding reverse peak potential (E_{pc}), which are obtained from cyclic voltammogram of PPy, PPhPy, and P(MPhPy).

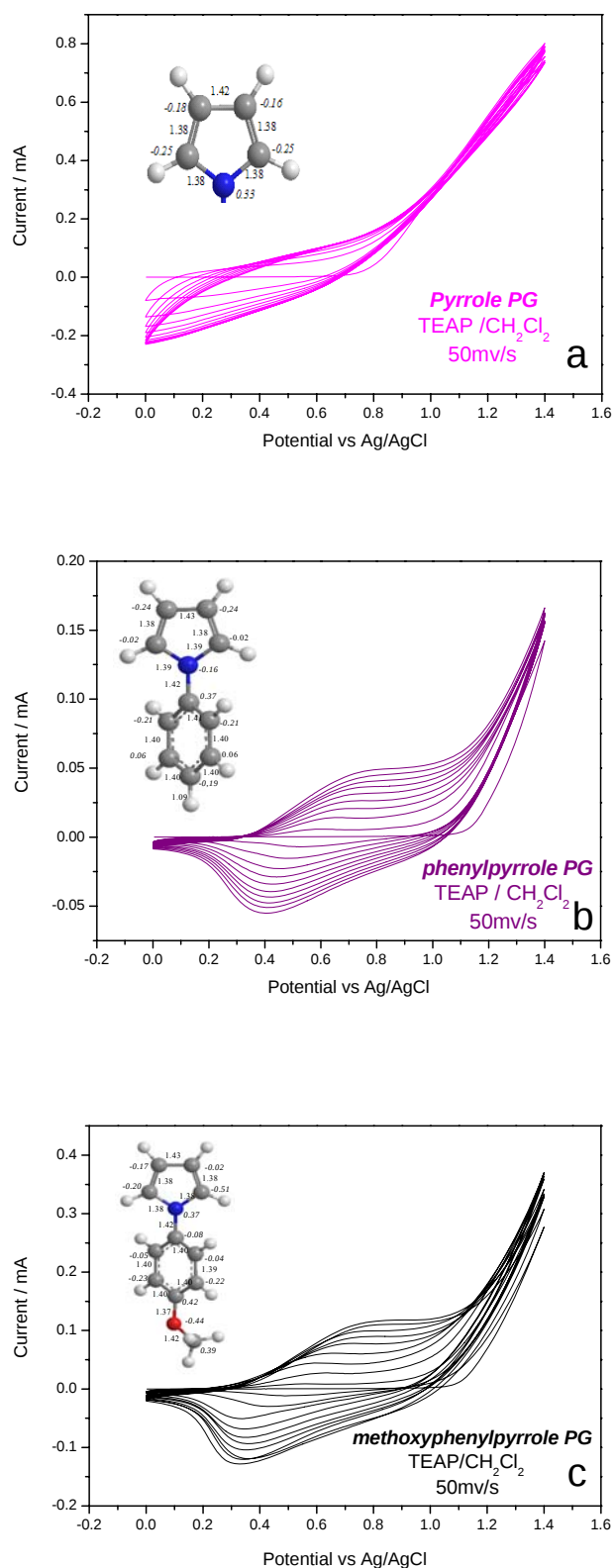


Figure 3.26: CV for The Oxidation of a) Py, b) PhPy, c) MPhPy on CFME in 0.05 M TEAP / CH₂Cl₂ at 50 mV s⁻¹. Using Multiple (10 Cycles) Potential Range: 0-1.4 V, [Py]₀=10⁻³ M, [PhPy]₀=10⁻³ M, and [MPhPy]₀=10⁻³ M.

3.4.2. Morphology

3.4.2.a. SEM

The morphological features of the coated carbon fiber micro electrodes were performed with SEM. The fibers were attached on smooth plate by use of a double sided adhesive material. Scanning electron microscopic measurements were carried out via ZELMI-TUB (Germany) and Jeol JSM-7000F SEM (ITU).

3.4.2.b. AFM

The AFM images reported in this study were obtained with Nanosurf Easy Scan 2 TM AFM. In all analysis, the non-contact mode was employed by using Al coated high resonance frequency silicon tips (190 kHz) with 7 μm thickness, 38 μm mean width, 225 μm length and 48 N/m force constant. High resolution images (1024x1024) and the raw data collected by the Easy Scan 2 SoftwareTM(version 1.5.0.0.) using left shadowing. In order to get better 3D results, raw data processed with SPIPTM software. Samples were prepared by simply using a double side sticky tape onto sample holder.

The high-resolution images obtained by AFM analysis of the electrocoated carbon fibers show that the electropolymerization of different conductive polymer onto carbon fiber produces different surfaces. In figures (5a-h) three different samples are illustrated. It is possible to see that the coating is not homogeneous for P(PhPy) as shown in Fig. 5e. Besides, in some region, coating thickness reaches approximately 200 nm. The coating is made by grains of about 150 nm radius. Some of these are of longitudinal shape and size of 150 nm - 200 nm. The uncoated and coated regions of CFME are clearly seen with both AFM and SEM measurements. The drop like poly phenyl pyrrole granules (Fig. 5c) are formed on the CFME with nano – spaces with an average roughness of 370 nm. The grains seem to be organised in rods, of size 500 nm - 50 nm. Taking into account the curvature of the carbon fiber surface, it is possible to estimate that the thickness increase in radius of the coated surface reach value of at least 0.5 μm , in agreement with SEM results. Highly oriented pyrrole molecules lessens the surface roughness with 141 nm given in Fig. 5d.

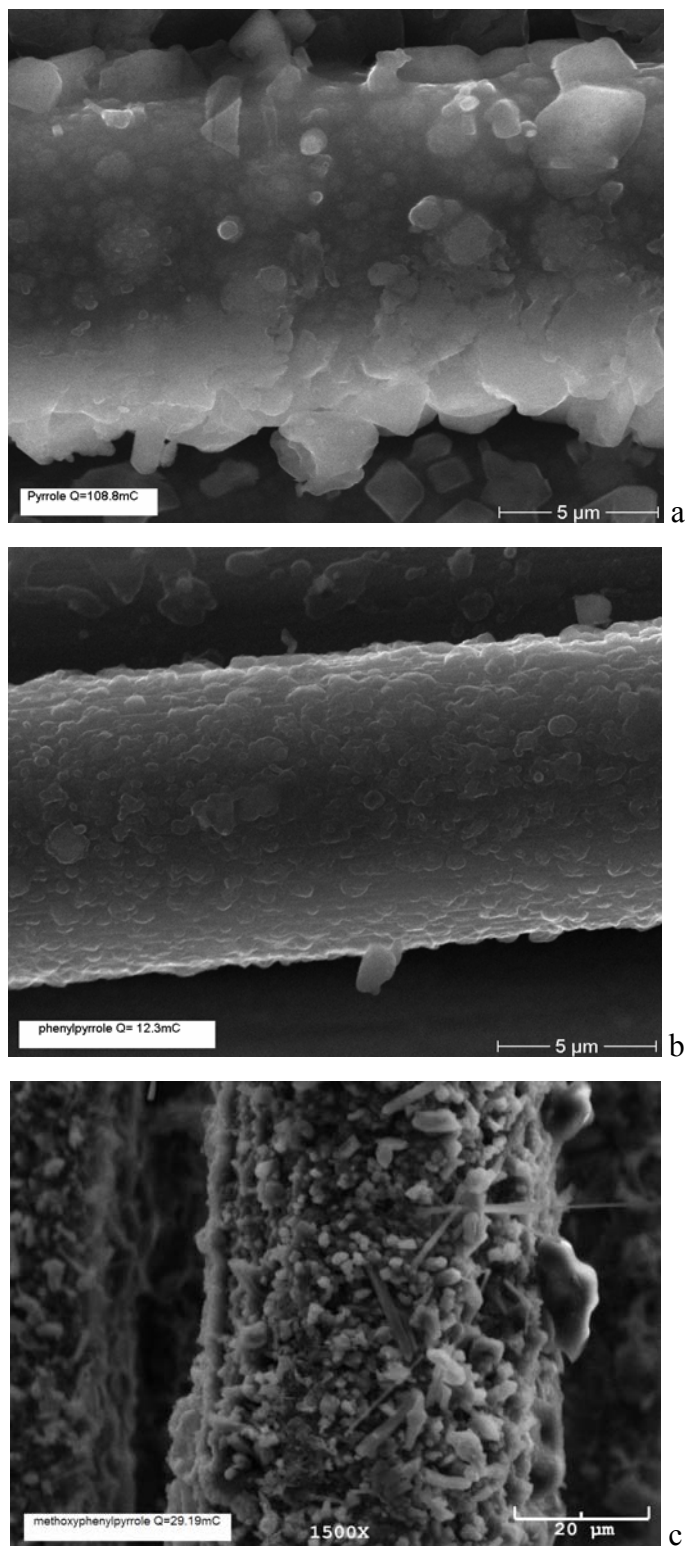


Figure3.27: SEM Images of **a)** PPy, Charge (Q): 108.8 mC; **b)** P(PhPy), Charge (Q): 12.3 mC; **c)** P(MPhPy), Charge (Q): 29.19 mC; by CV Method, 8th Cycles, Scan Rate at 50 mV s⁻¹, [Py]₀=10⁻³ M, [PhPy]₀=10⁻³ M, and [MPhPy]₀=10⁻³ M, in 0.05 M TEAP / CH₂Cl₂.

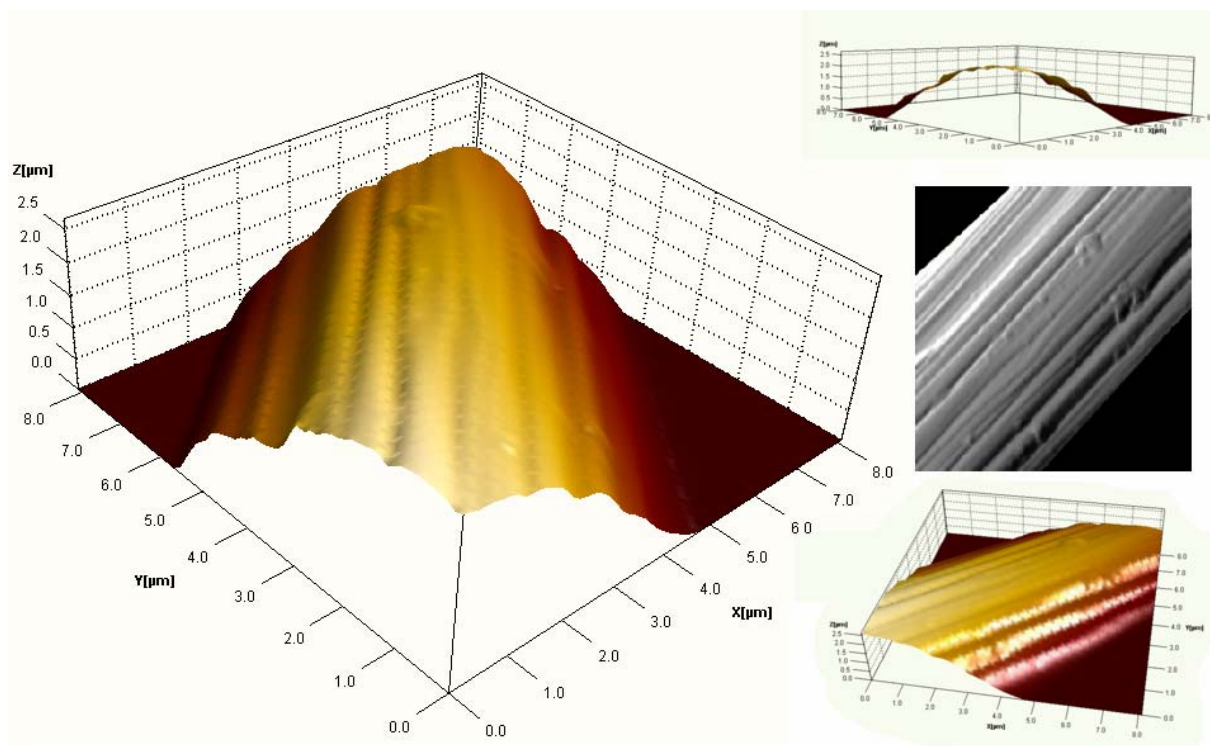


Figure 3.28: 3D(a,b,d,) and 2D(c) AFM Images of Uncoated Single CFME

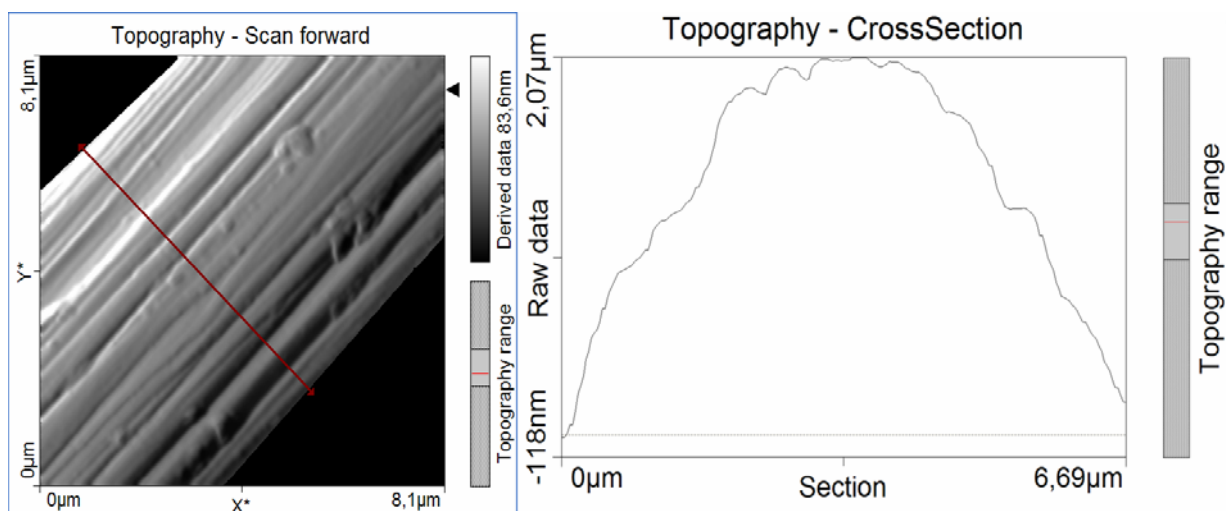


Figure 3.29: Cross Section of Uncoated CFME

The high-resolution images obtained by AFM analysis of the electrocoated carbon fibers show that the electropolymerisation of different conductive polymer onto carbon fiber produces different surfaces. In figures (3.28-3.38) are reported images of the different samples analysed in this thesis as well as an image of the uncoated Sigri 320.000 carbon fiber.

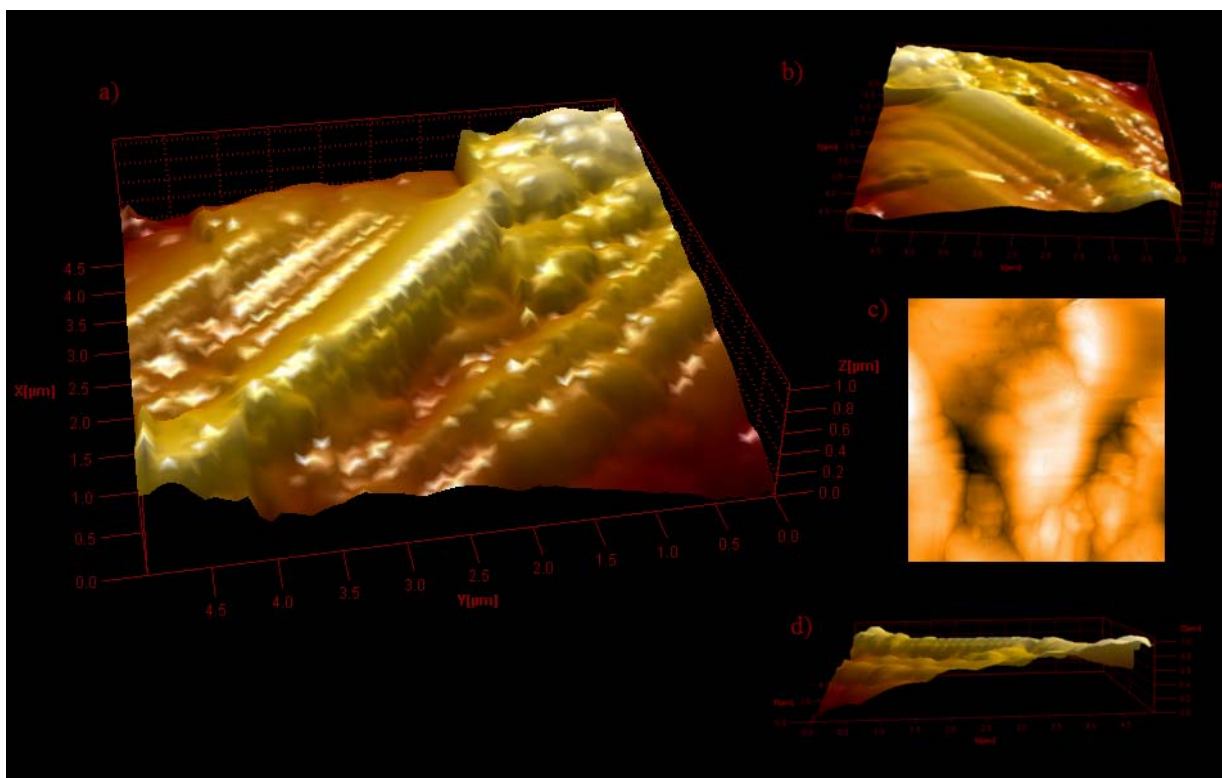


Figure 3.30: 3D(a,b,d,)and 2D(c) AFM Images of Polypyrrole Coated CFME With Image Area of $5\mu\text{m} \times 5\mu\text{m}$

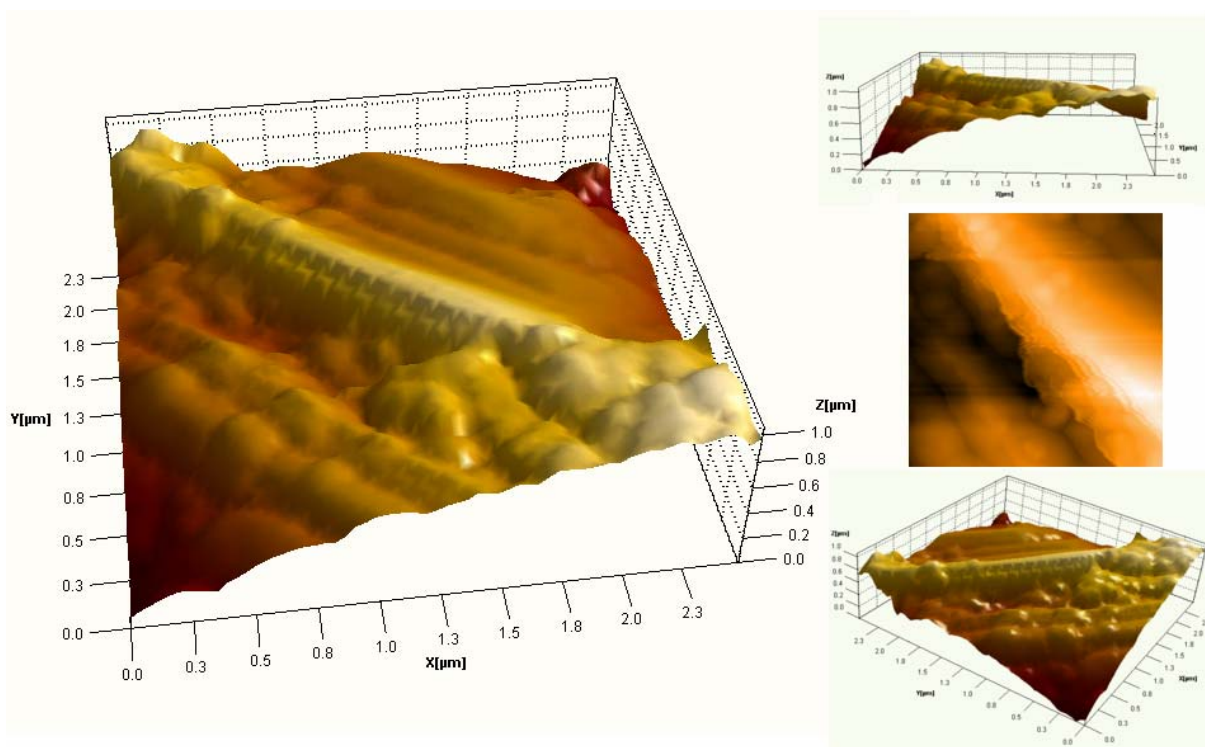


Figure 3.31: 3D(a,b,d,)and 2D(c) AFM Images of Polypyrrole Coated CFME With Image Area of $2,5\mu\text{m} \times 2,5\mu\text{m}$

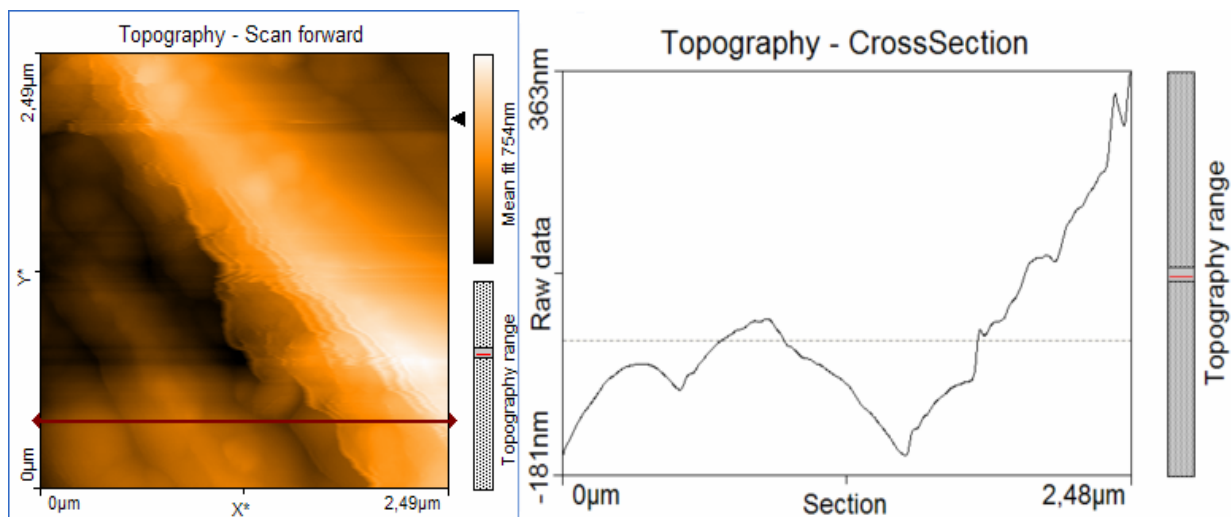


Figure 3.32: Cross-Section of Polypyrrole Coated CFME

The grains seem to be organised in rods, of size 500 nm-50 nm. Taking into account the curvature of the carbon fiber surface, it possible to estimate that the thickness of the coating reach value of at least 0.5 μm , in agreement with SEM results. Pyrrole molecules lessens the surface roughness with 141 nm in fig.3.32. Although the images of poly pyrrole molecules looks more rigid differ from the SEM micrographs. Substitution of pyrrole with a big phenyl ring imparts soft surface in view but increasases the avarage surface roughness.

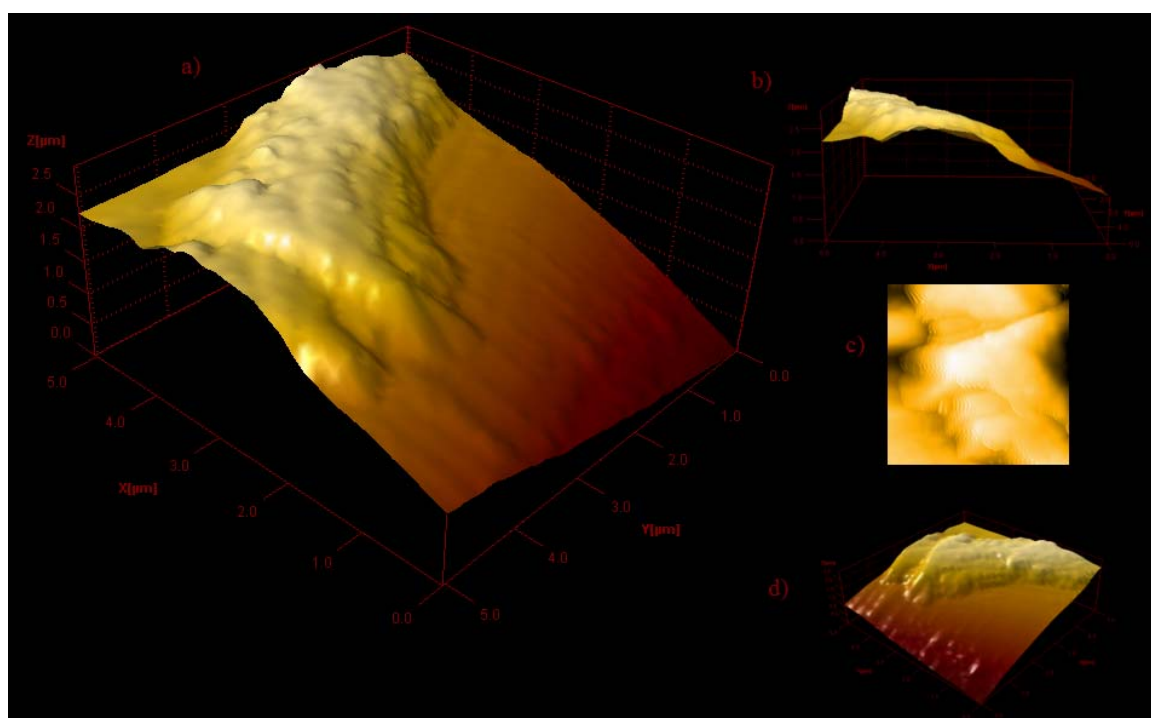


Figure 3.33: 3D(a,b,d) and 2D(c) AFM Images of Polyphenylpyrrole Coated CFME With Image Area of 5 μm x 5 μm

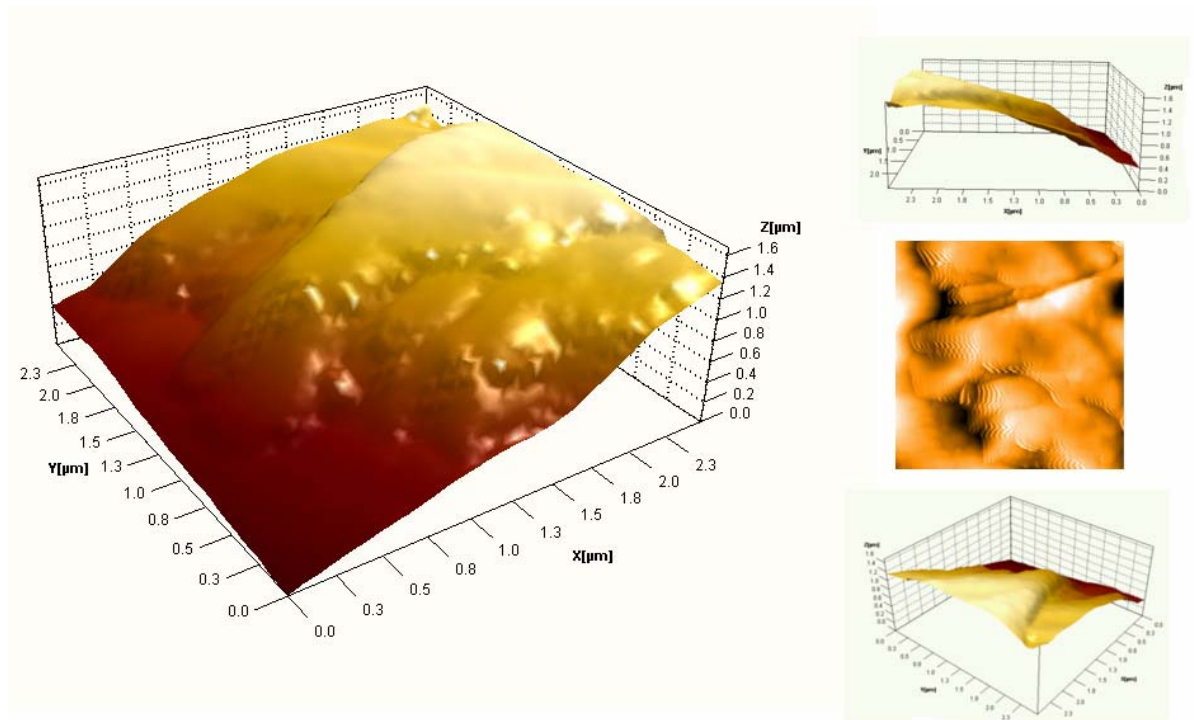


Figure 3.34: 3D(a,b,d,)and 2D(c) AFM Images of Poly-phenylpyrrole Coated CFME With Image Area of $2,5\mu\text{m} \times 2,5\mu\text{m}$

It is possible to see that the coating is not homogeneous and that, in some region, it reaches approximately a thickness of 200 nm. The coating is about 150 nm radius. Some of these are of longitudinal shape and size of 150 nm-200 nm. The uncoated and coated regions of CFME are clearly seen with both AFM and SEM measurements. The drop like poly phenyl pyrrole granules are formed on the CFME with nano-spaces with an average roughness of 370 nm.

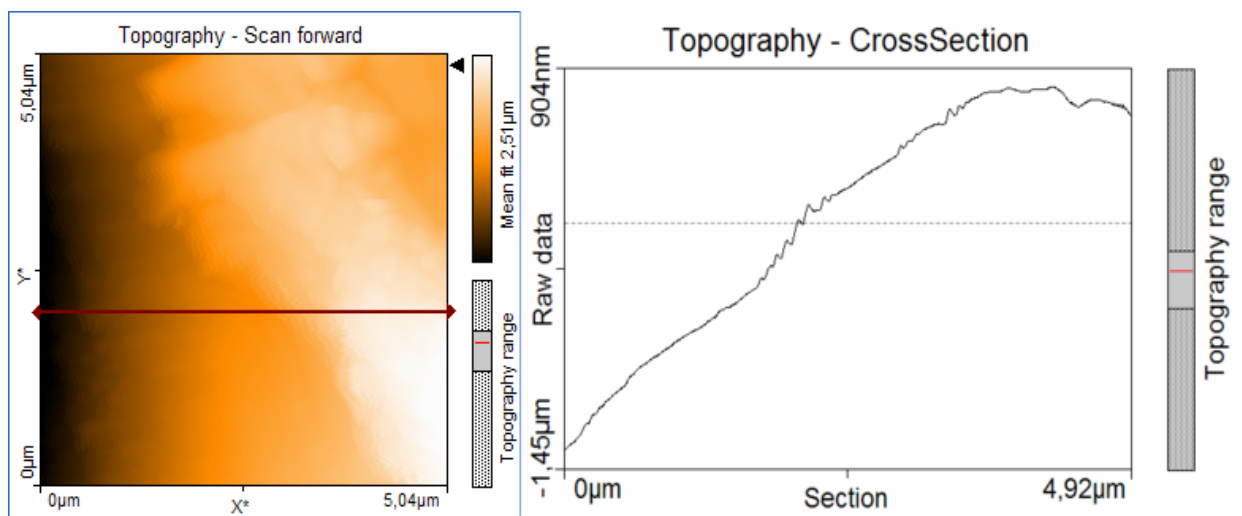


Figure 3.35: Cross-Section of Polyphenylpyrrole Coated CFME

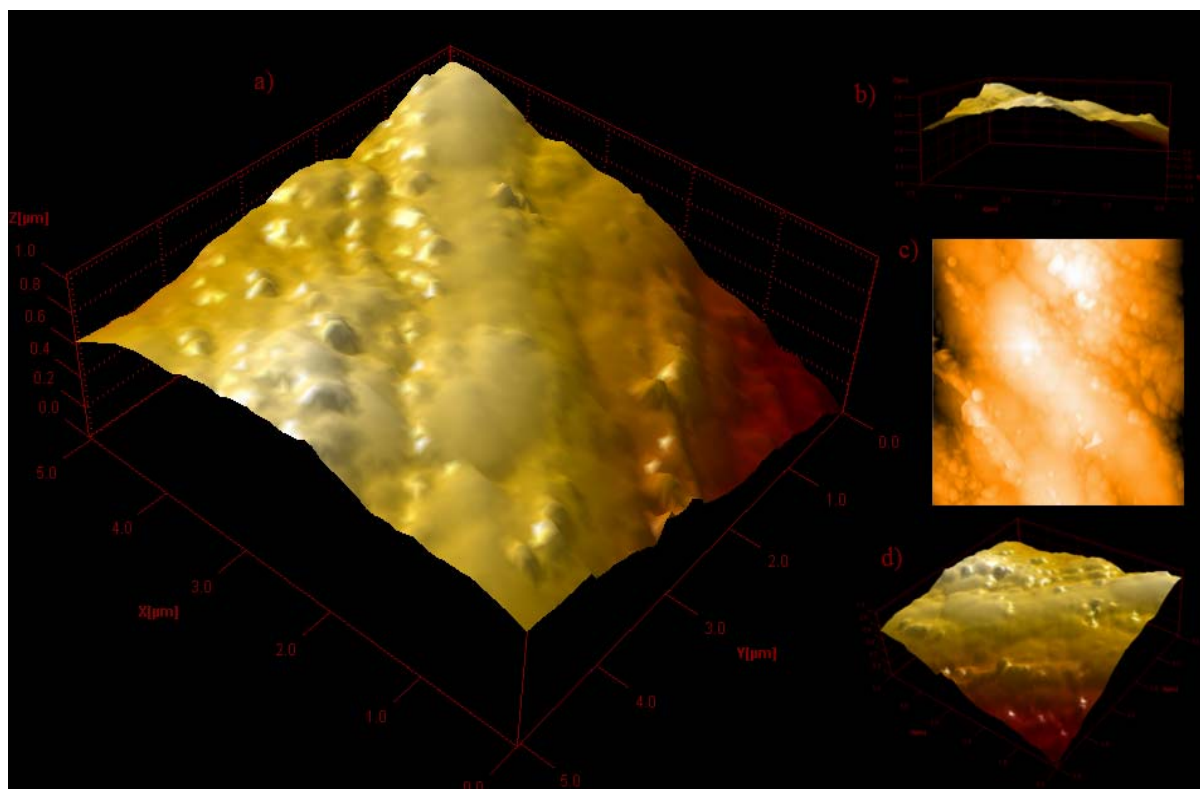


Figure 3.36: 3D(a,b,d,)and 2D(c) AFM Images of Poly-metoxypyrrole Coated CFME With Image Area of $5\mu\text{m} \times 5\mu\text{m}$

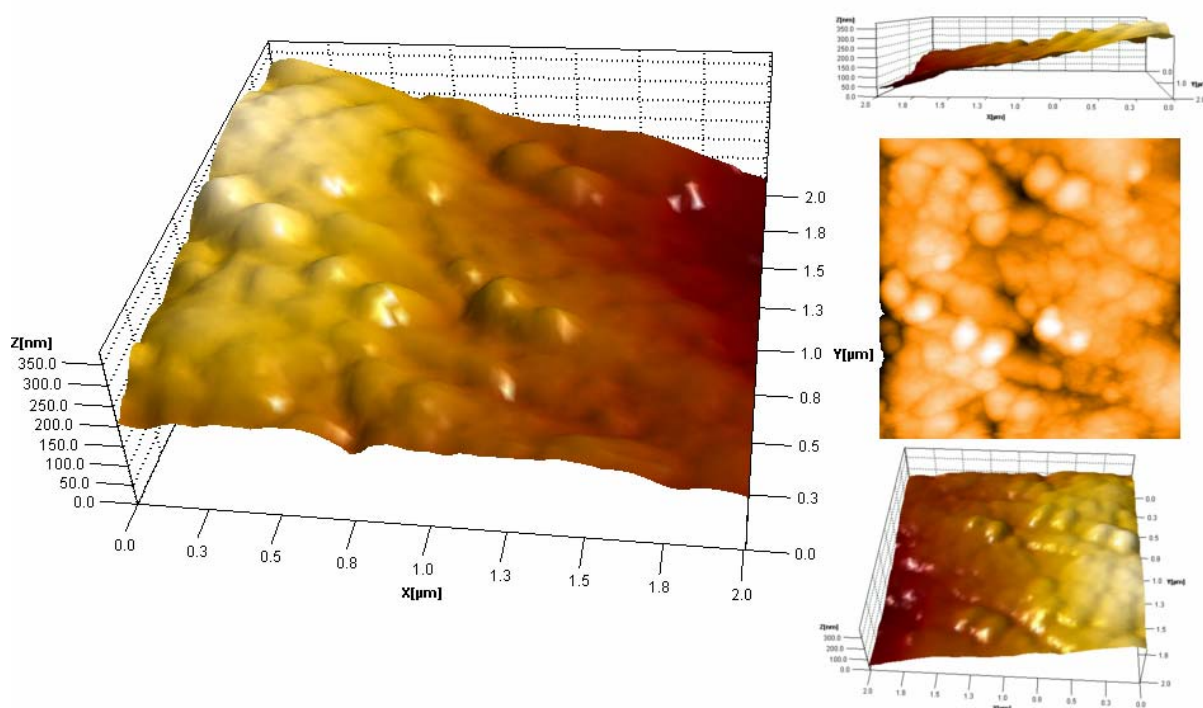


Figure 3.37: 3D(a,b,d,) and 2D(c) AFM Images of Poly-metoxyphenylpyrrole Coated CFME wWth Image Area of $2,5\mu\text{m} \times 2,5\mu\text{m}$

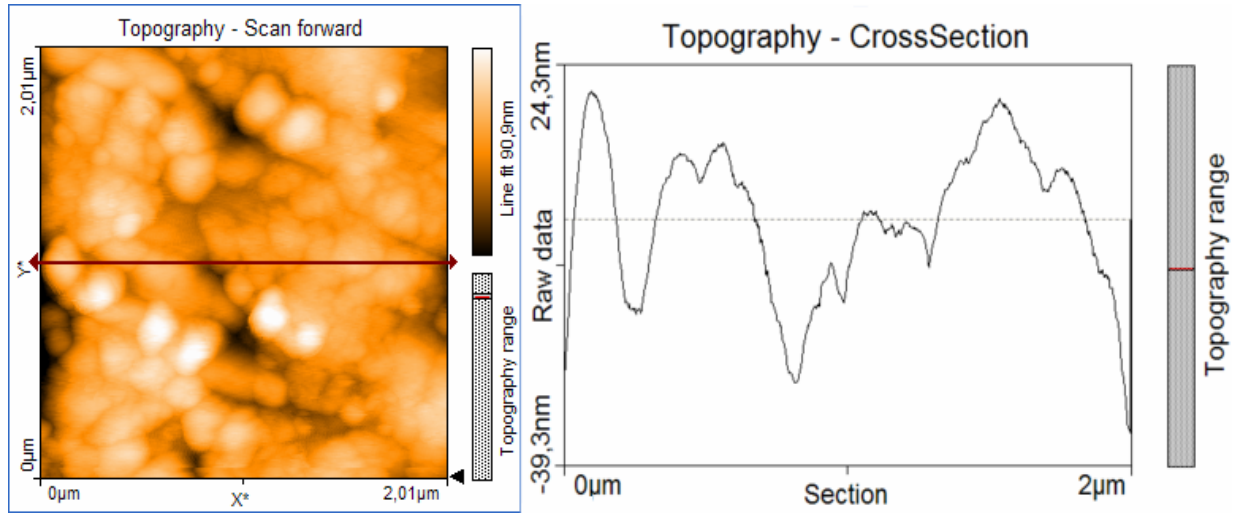


Figure 3.38: Cross-Section of Poly-metoxyphenylpyrrole Coated CFME

AFM figures indicates fully spherical formations of poly-metoxyphenylpyrrole coatings on CFME. Corresponding SEM micrographs also supports AFM images with orientations of small spherical molecules. Substitution of pyrrole both with phenyl and metoxy groups lowers the average roughness to 11,3nm which allows us to report a very smooth surface. As a result of AFM measurements, roughness arrangement is summarized as following;

$$S_{A_{PPy}} > S_{A_{Py}} > S_{A_{MPPy}}$$

When we compare the results, phenyl group included monomers show more thicker polymer films on the electrode surfaces. P(Py) shows longitudinal type of thin films while P(MPhPy) looks in drop like shape, in addition P(MPhPy) has a full spherical formation.

3.4.2.c. EDX

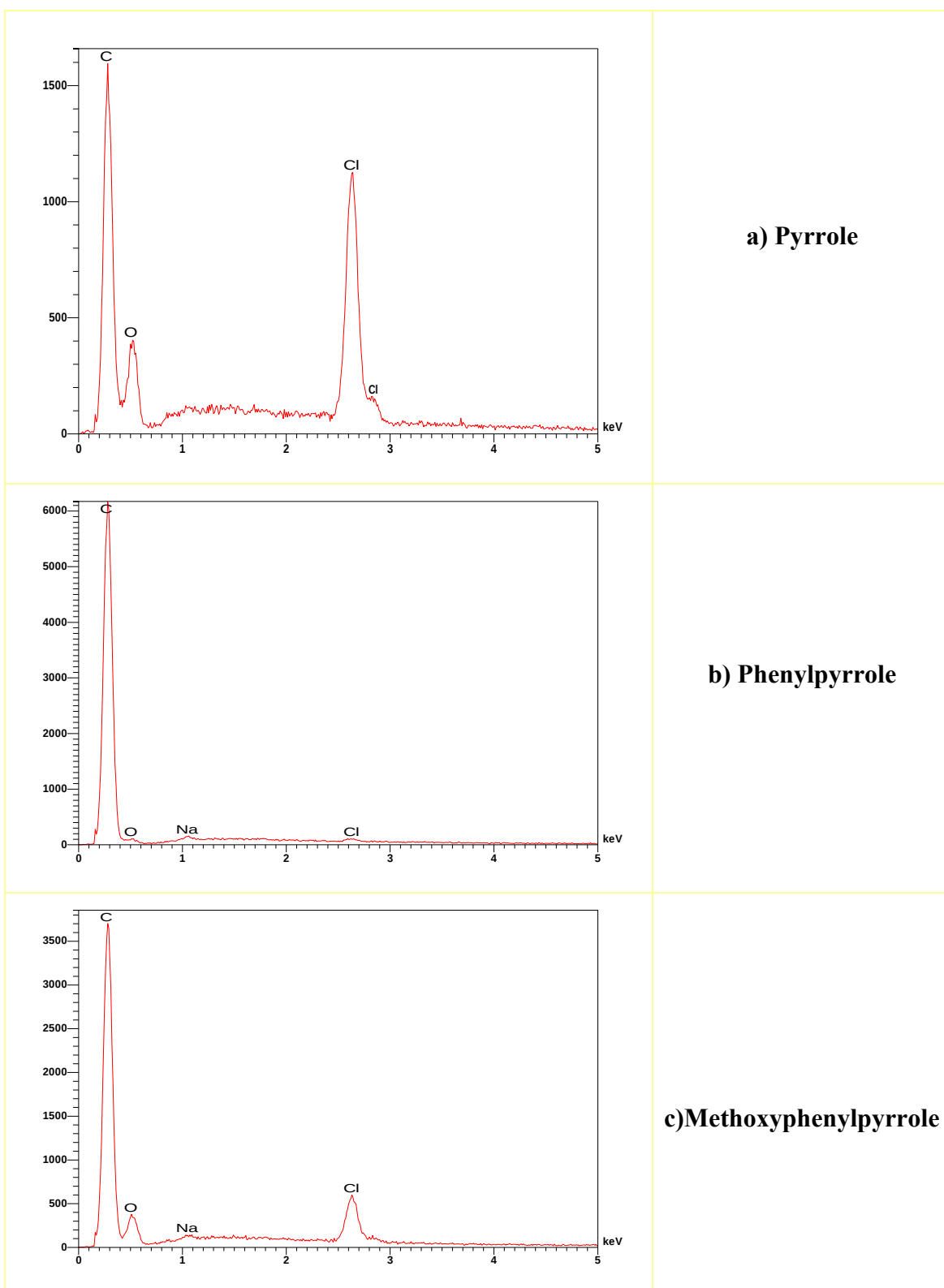


Figure 3.39: EDX Results of Modified CFMEs With a) Pyrrole, b) Phenylpyrrole, c) Methoxyphenylpyrrole.

Table 3.7: Acquisition Parameters for EDX

<i>Accelerating voltage (kV)</i>	<i>1.1.1.1. 15.0</i>
<i>Beam current (nA)</i>	<i>750.0</i>
<i>Magnification</i>	<i>50</i>
<i>Live time</i>	<i>100</i>
<i>Preset Time (s)</i>	<i>1.1.1.2. 100</i>
<i>Nb Channels</i>	<i>1.1.1.3. 2048</i>
<i>Ev / Channel</i>	<i>1.1.1.4. 10</i>
<i>Offset (keV)</i>	<i>1.1.1.5. 0</i>
<i>Width (keV)</i>	<i>1.1.1.6. 20</i>

The samples surfaces exposed to the carbon fiber micro electrode surface were analyzed by EDX to investigate their composition. EDX analyses carried out on the areas near to the coating external surface and along the coating thickness in the cross sectioned sample. In Figure 3.39 the combination of coated electrode surfaces is seen. If we look at the Cl⁻ ions ration which is coming from the dopant anion, pyrrole was doped more than phenylpyrrole and the methoxyphenylpyrrole. If we look at the carbon atoms amounts, polyphenylpyrrole structure includes nearly two times more C atom than polymethoxyphenylpyrrole.

3.4.3.Characterization with FTIR-ATR Spectroscopy

The FTIR-ATR spectra of PPy, P(PhPy), and P(MPhPy) were obtained from the surface of the electrocoated CFMEs by reflectance measurements and spectrum bands of each spectrum are given in Figure 2a, b and c. Characteristic peaks observed at 1489 cm⁻¹ (-C-N stretching of aromatic C-N bonds or vibration of disubstituted benzene ring), which is characteristic of pyrrole homopolymer. 1399 cm⁻¹ C=C symmetric ring stretching of methoxyphenyl pyrrole is obtained.

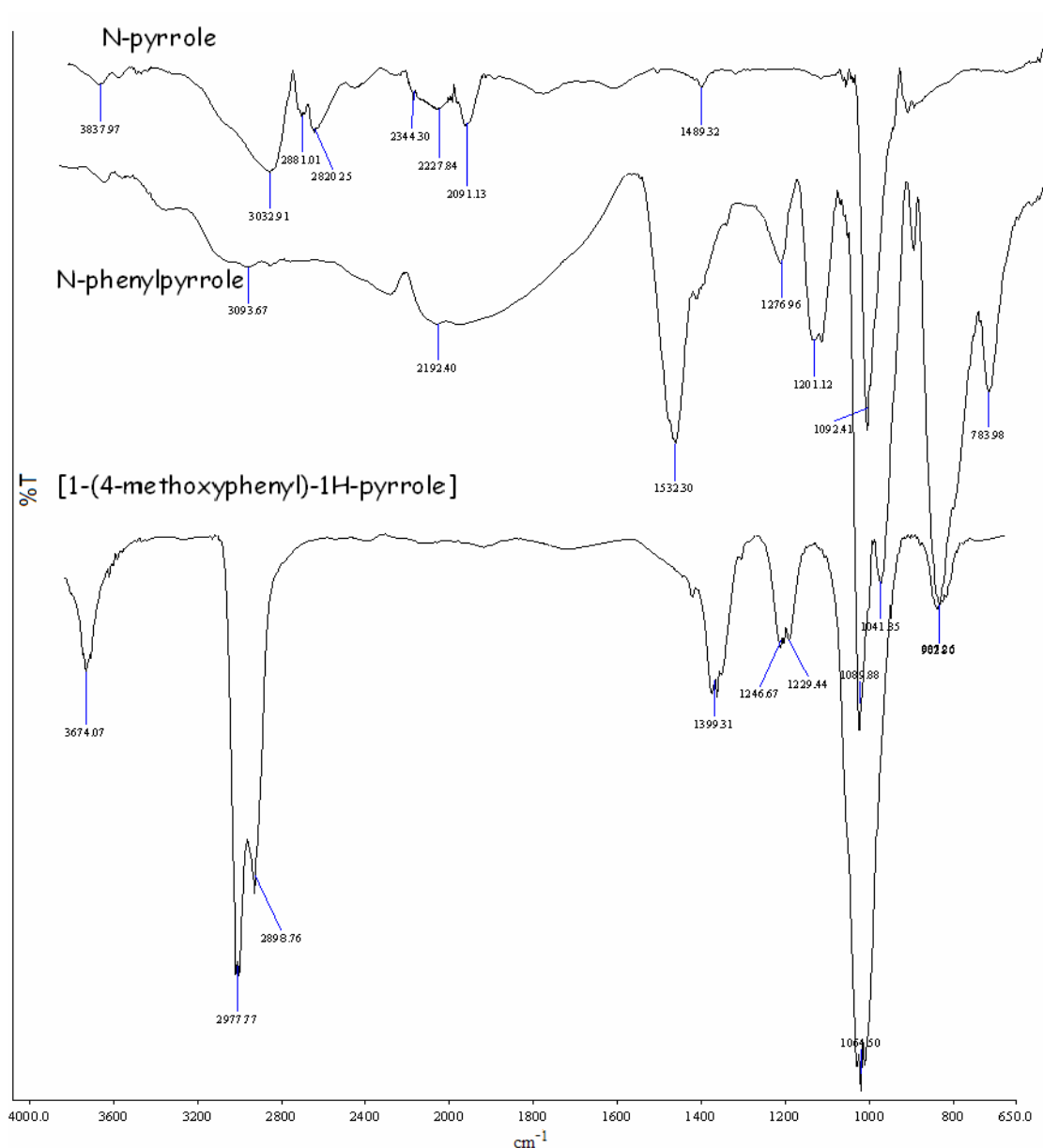


Figure 3.40: FTIR-ATR Spectrum of PPy, P(PhPy) and P(MPhPy) $[\text{Py}]_0=10^{-3} \text{ M}$, $[\text{PhPy}]_0=10^{-3} \text{ M}$ and $[\text{MPhPy}]_0=10^{-3} \text{ M}$.

The most characteristic difference in the pyrrole is the lack of bands at around 887 cm^{-1} , and 902 cm^{-1} (-C-H bending of trisubstituted aromatic rings) which corresponds to the phenyl rings. For instance, the peak around $2881\text{--}2820 \text{ cm}^{-1}$ corresponding to the aliphatic C-H bond of pyrrole, shift towards $2977\text{--}2898 \text{ cm}^{-1}$ belongs to P(MPhPy). 1229 cm^{-1} for P(MPhPy) and 1201 cm^{-1} for PhPy, which are corresponding to -C-N (stretching of aromatic C-N bonds or vibration of disubstituted benzene ring) also provide evidence of polymer formation. The peaks at $1092\text{--}1089$, and 1064 cm^{-1} which clarify ClO_4^- dopant ion, belong to PPy, P(PhPy) and P(MPhPy), respectively.

3.4.4. Substitution effect on EC impedance spectroscopy

A drastic difference can be seen at the polymer electrode obtained with 50 mV.s⁻¹ scan rate, with PPy, PPhPy and P(MPhPy). The low frequency capacitive behaviour changed to semicircle from perpendicular line to capacitive axis that may be due the thicker pyrrole film than the PPhPy and P(MPhPy).

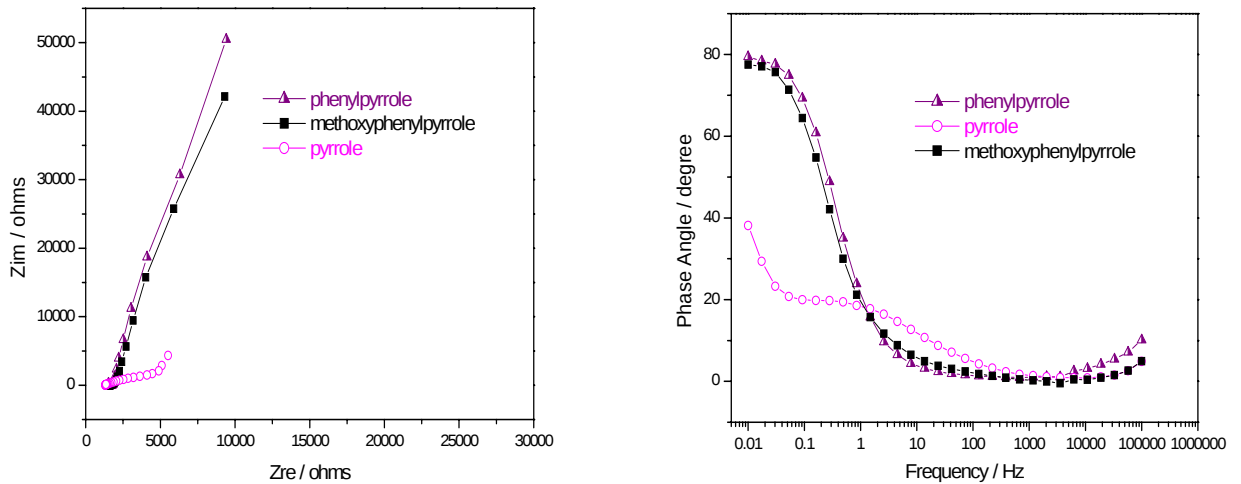


Figure 3.41: Nyquist Plots Recorded for P(Py), P(PhPy) and P(MPhPy) Electrografted CFMEs. Bode Phase Definitions of P(Py), P(PhPy) and P(MPhPy) Electrografted CFMEs.

On the other hand the modified CFME which was coated with PPy has the lowest conductivity but it has the highest resistance because Z' axis could be named as pure resistor while the Z'' is pure capacitor. As it is seen from the Nyquist diagram for P(PhPy) shows the best capacitive behaviours ($C_{sp}=3.2 \times 10^{-4}$ F for Py, $C_{sp}=3.8 \times 10^{-4}$ F for P(PhPy) and $C_{sp}=3.6 \times 10^{-3}$ F for P(MPhPy). On the other hand, specific capacitance values can be calculated via; $C_{sp} = 1 / 2\pi f z''$.

In the Bode phase plot of PMPPy and P(MPhPy) electrodeposited on CFME at 50 mV s⁻¹ scan rate, the bode phase angle approaches a plateau (80°), in the frequency region 0.01 Hz-100 kHz which film indicates capacitor behavior. However, PPy shows a phase angle around 40° in the same region.

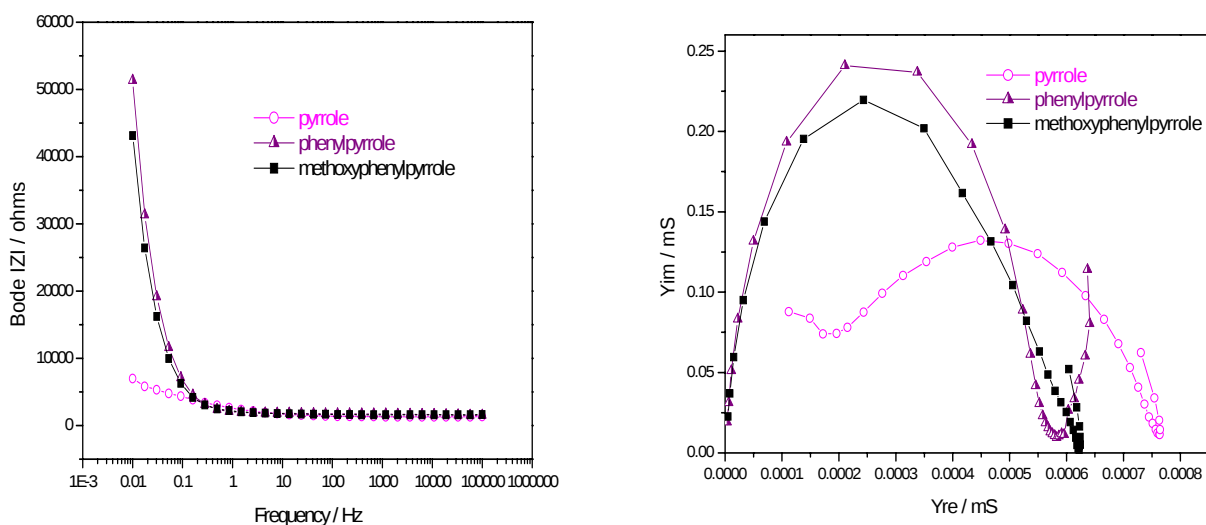


Figure 3.42: Bode Magnitude Plot of P(Py), P(PhPy) and P(MPhPy) Electrografted CFMEs. Admittance Plot for P(Py), P(PhPy) and P(MPhPy) Indicating The Conductivities.

Bode magnitude plot gives extrapolating this line to the $\log Z$ axis at $\omega = 1$ ($\log \omega = 0$) yielding the value of C_{dl} from the relationship: $|Z| = 1/C_{dl}$. Double layer capacitance value is higher $C_{dl} = 1.76 \times 10^{-4}$ F for the PPy compared to P(PhPy) $C_{dl} = 9.12 \times 10^{-5}$ F, and P(MPhPy) $C_{dl} = 8.5 \times 10^{-5}$ F.

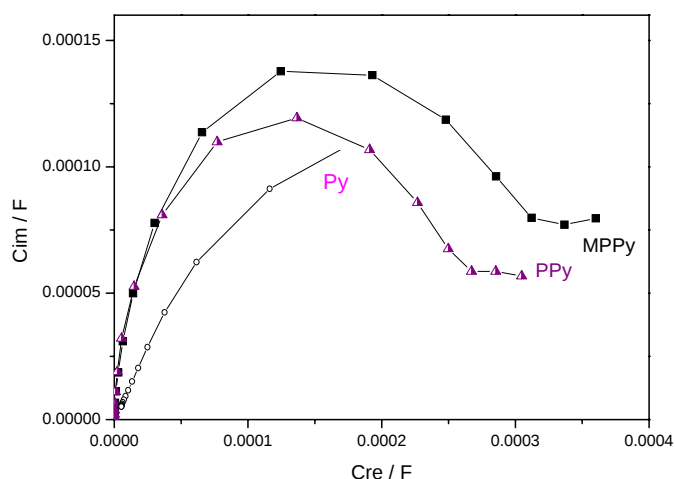


Figure 3.43: Capacitance Graph for Electropolymerized P(Py), P(PhPy) and P(MPhPy).

Capacitance plot indicates the imaginary and real capacitance values. According to the graph methoxyphenylpyrrole and phenylpyrrole have the highest capacitance values.

3.4.5. Substitution effects on equivalent circuits

The electrochemical parameters of the CFME / PPy, P(PhPy)b and P(MPhPy) / Electrolyte systems were evaluated by employing the ZSimpWin software programme. While simulating the programme it must be checked if the chi-squared (χ^2) minimized than 10^{-4} . χ^2 is the function defined as the sum of the squares of the residuals.

Three electrical equivalent circuits were used in simulation of the impedance behavior of the film from the experimentally obtained impedance data. The models was built using series components; the first one is the bulk solution resistance of the polymer and the electrolyte, R_s , second one the parallel combination of the double layer capacitance, C_{dl} , and R_1 is the resistance of the electrolyte. A series connection to R_1 made up using, constant phase element (CPE) in parallel with R_2 and W , R_2 is the charge transfer, and W is the Warburg impedance of the polymer.

The last component a capacitor element (C_{CF}) is introduced in parallel with a charge transfer resistor (R_{CF}) corresponding to the carbon fiber microelectrode of polymer coating. Simulation results for P(Py), P(PhPy) and P(MPhPy) show that this electrical equivalent circuits were successfully applied to the experimental data to explain the interface between the carbon fiber microelectrode, the polymer film and electrolyte in this potential region. Equivalent electrical circuit was constructed without the last component a capacitor element (CCF) and charge transfer resistor (RCF). Numerical results of the Model 2 are shown in Tables for P(Py), P(PhPy) and P(MPhPy). Equivalent electrical circuit was constructed for each homopolymers.

Table 3.8: Specific Capacitance Values and Comparison Between Double Layer Capacitances From Experimental and Theoretical Results P(Py), P(PhPy) and P(MPhPy)

Monomers	Cspe	Cdl (experimental)	Cdl (theoretical)
Py	3.2×10^{-4}	1.76×10^{-4}	9.6×10^{-11}
PhPy	3.8×10^{-4}	9.12×10^{-5}	7.6×10^{-11}
MPhPy	3.6×10^{-3}	8.5×10^{-5}	8.14×10^{-11}

The experimental results obtained from Bode-Magnitude plot, calculating the double layer capacitance (C_{dl}) and equivalent electrical circuits for Model, ZSimpWin (version 3.10) to find the optimum circuit conditions were compared. For Py, C_{dl} was obtained (1.76×10^{-4} F from experiments and 9.6×10^{-11} F from used circuit). Additionally, for PhPy 9.12×10^{-5} F from experiments and 7.6×10^{-11} F from used circuit. Finally; MPhPy indicates 8.5×10^{-5} F from experiments and 8.14×10^{-11} F from used circuit double layer capacitances.

Table 3.9: Theoretical Results for P(Py), P(PhPy) and P(MPhPy) Applied for R(C(R(Q(RW))))(CR) Circuit Model.

Model 1	PPy	PhPy	MPhPy
R_s / Ohm	0.012	1104	1.0×10^{-7}
C_{dl} / μF	9.26×10^{-11}	4.04×10^{-6}	7.76×10^{-11}
R_1 / Ohm	1305	137.3	1600
Q / $Y_o / S s^{-n}$	2.1×10^{-4}	2.4×10^{-4}	8.9×10^{-4}
n	0.52	0.925	0.410
R_2 / Ohm	4992	9.72×10^5	7.75×10^{11}
W / $Y_o / S s^{-n}$	23.08	7.11×10^{-6}	371.5
C_{CF} / μF	4.33×10^{-3}	2.12×10^{-9}	3.6×10^{-4}
R_{CF} / Ohm	1.72×10^5	559.6	3.19×10^5
Chi Squared (χ^2)	1.92×10^{-4}	6.7×10^{-4}	5.06×10^{-4}

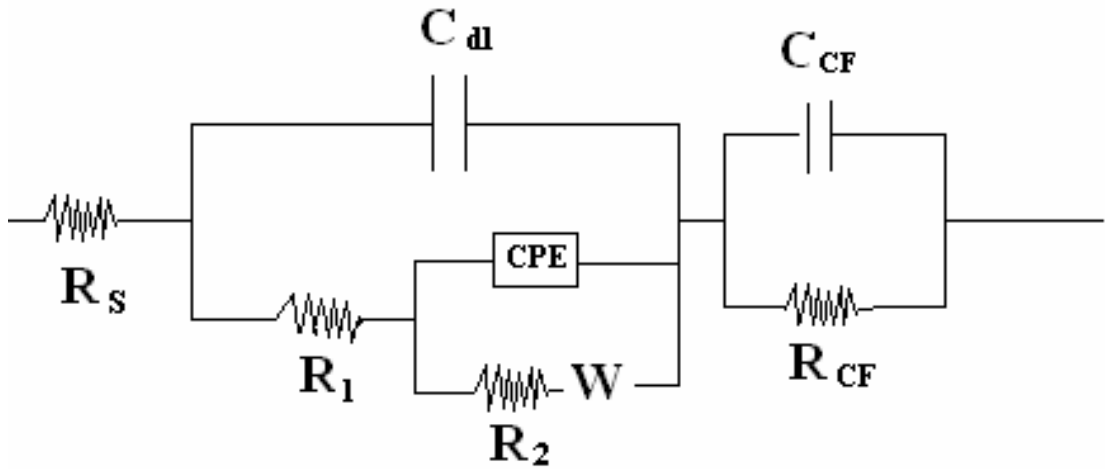


Figure 3.44: R(C(R(Q(RW))))(CR) Circuit Model

Model 1 which clarifies to R(C(R(Q(RW))))(CR) circuit model is fit for Py for this simulation with the lowest χ^2 value (1.92×10^{-4}).

Table 3.10: Theoretical Results for P(Py), P(PhPy) and P(MPhPy) Applied for R(C(R(Q(RW)))) Circuit Model.

Model 2	PPy	PhPy	MPhPy
R_s / Ohm	1.0×10^{-3}	1309	1.6×10^{-5}
$C_{dl} / \mu\text{F}$	9.58×10^{-11}	5.35×10^{-9}	4.64×10^{-11}
R_1 / Ohm	1318	433.1	1468.9
$Q / Y_o / \text{S s}^{-n}$	1.44×10^{-4}	2.4×10^{-4}	2.4×10^{-4}
n	0.59	0.916	0.897
R_2 / Ohm	2536	3.93×10^6	1.95×10^6
$W / Y_o / \text{S s}^{-n}$	7.0×10^{-4}	1.39×10^{-8}	6.22×10^{-5}
$C_{CF} / \mu\text{F}$	-----	-----	-----
R_{CF} / Ohm	-----	-----	-----
Chi Squared (χ^2)	1.93×10^{-3}	1.72×10^{-3}	9.18×10^{-4}

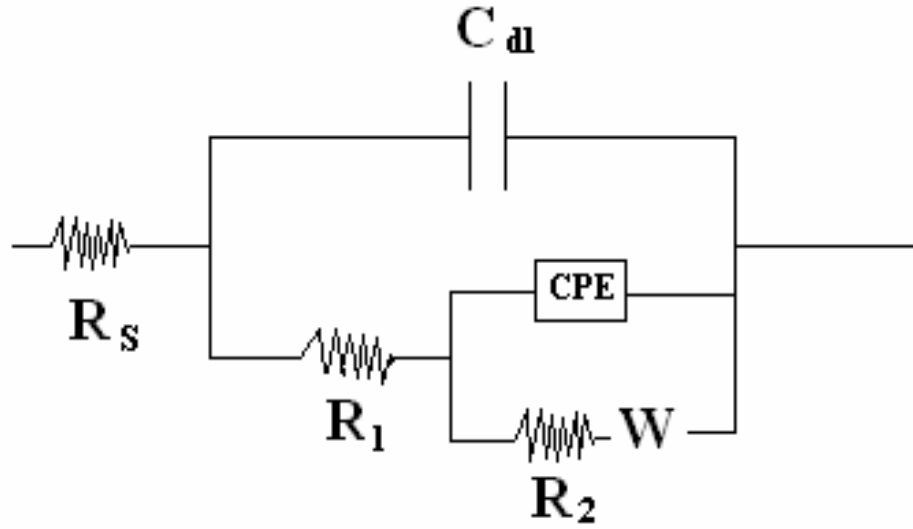


Figure 3.45: R(C(R(Q(RW)))) Circuit Model

Model 2 which corresponds to R(C(R(Q(RW))))(CR) equivalent electrical circuit, is fit for PhPy for this simulation with the lowest χ^2 value (1.72×10^{-3}).

Table 3.11: Theoretical Results for P(Py), P(PhPy) and P(MPhPy) Applied for R(C(R(QR)))(CR) Circuit Model.

Model 3	PPy	PhPy	MPhPy
R_s / Ohm	1.0×10^{-7}	1095	1.1×10^{-3}
$C_{dl} / \mu\text{F}$	9.24×10^{-11}	2.04×10^{-9}	8.14×10^{-11}
R_1 / Ohm	1305	566.3	1631
$Q / Y_o / \text{S s}^{-n}$	2.2×10^{-4}	2.4×10^{-4}	2.8×10^{-4}
n	0.51	0.92	0.91
R_2 / Ohm	5063	1.74×10^6	2.03×10^6
$W / Y_o / \text{S s}^{-n}$	-----	-----	-----
$C_{CF} / \mu\text{F}$	4.37×10^{-3}	3.56×10^{-6}	6.9×10^{-5}
R_{CF} / Ohm	1.01×10^{15}	130.6	299.1
Chi Squared (χ^2)	8.5×10^{-4}	6.49×10^{-4}	5.0×10^{-4}

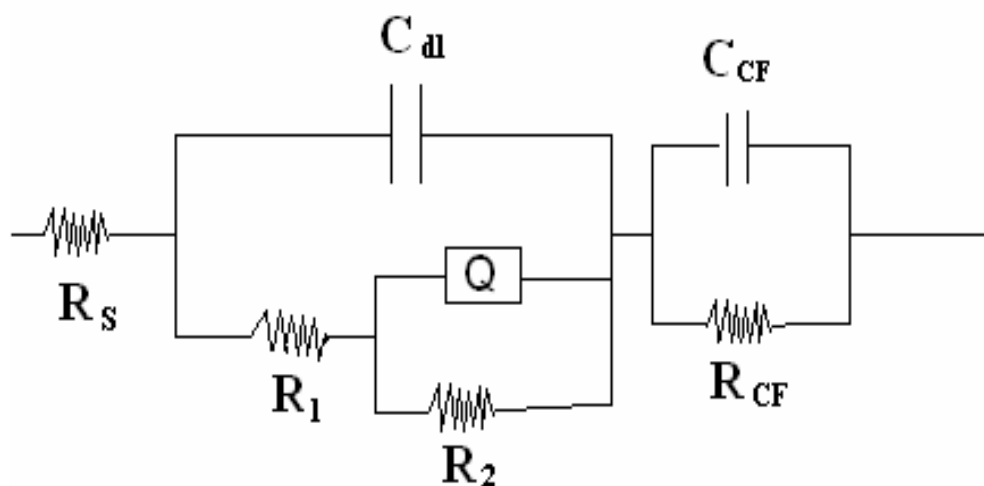


Figure 3.46: R(C(R(QR)))(CR) Circuit Model

Model 3 is defined as R(C(R(QRW)))(CR) circuit model and shows the lowest χ^2 value for MPhPy (5.0×10^{-4}).

3.5. Electrolyte Effect on Electropolymerization of [1-(4-Methoxy Phenyl)-1H-Pyrrole]

Poly [1-(4-Methoxy Phenyl)-1H-Pyrrole] films were synthesized electrochemically on carbon fiber microelectrodes (CFME). Deposition conditions on the carbon fiber and the influence of electrolyte on the polymerization, as well as the electrochemistry of the resulting polymers were studied

Electropolymerization was performed for [1-(4-Methoxy Phenyl)-1H-Pyrrole] using multiple cycles in 0.1 M TBATFB/ACN, LiClO₄/ACN, TEATFB/ACN and NaClO₄/ACN for 10 cycles. The electrodeposition of [1-(4-Methoxy Phenyl)-1H-Pyrrole] on the CFMEs by cyclic voltammetry at a scan rate of 50 mV s⁻¹ at 1.4 V. The monomer concentration was 10⁻² M. The oxidation potentials of the monomer were determined from the first cycles as shown in Table 3.11.

Table 3.12: Redox Parameters of Electrocoated CFME /MPPy Structures With Different Electrolytes

Electrolyte	E _{onset} (V)	E ^{1/2} (V)	ΔE (V)	I _a / I _c
TEATFB	0.488	0.756	0.11	1.12
TBATFB	0.607	0.899	0.37	0.6
NaClO ₄	0.527	0.935	0.60	1.95
LiClO ₄	0.401	0.826	0.46	1.5

According to the results TEATFB shows the best reversibility (I_a / I_c =1.12) while the anodic and cathodic peak potential difference (0.11V) is smaller than the other electrolytes. When we look at the E^{1/2} values the conjugation length is longer for NaClO₄ because of the 0.935V half way potential. Besides ΔE (V) value of NaClO₄ is the highest (0.60V) which means it has the thicker film on CFME.

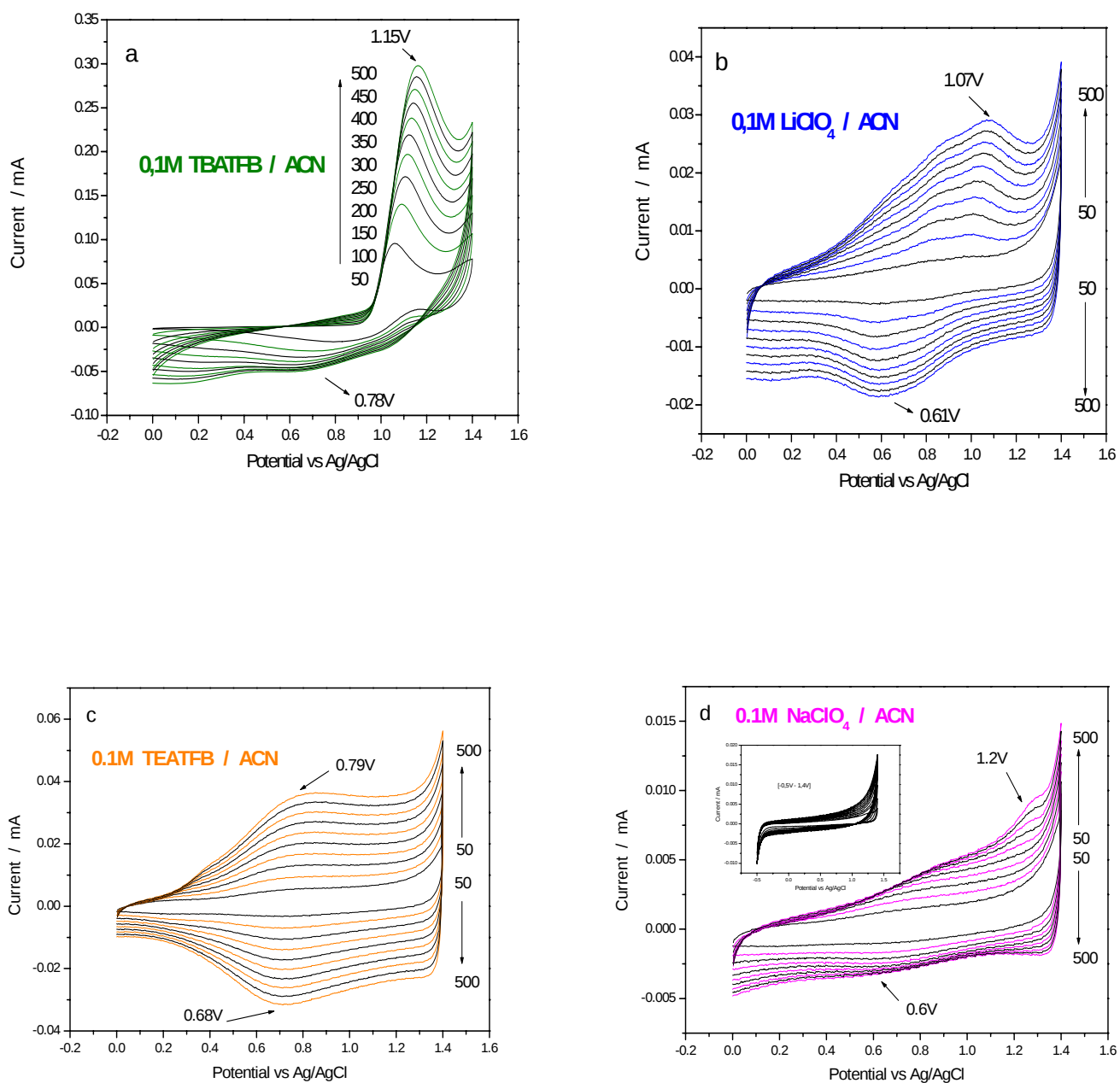


Figure 3.47: Electropolymerization of [1-(4-Methoxy Phenyl)-1H-Pyrrole] in a) TBATFB/ACN, b) LiClO₄/ACN, c) TEATFB/ACN and d) NaClO₄/ACN With 40mV/S Scan Rate for 10 Cycles.

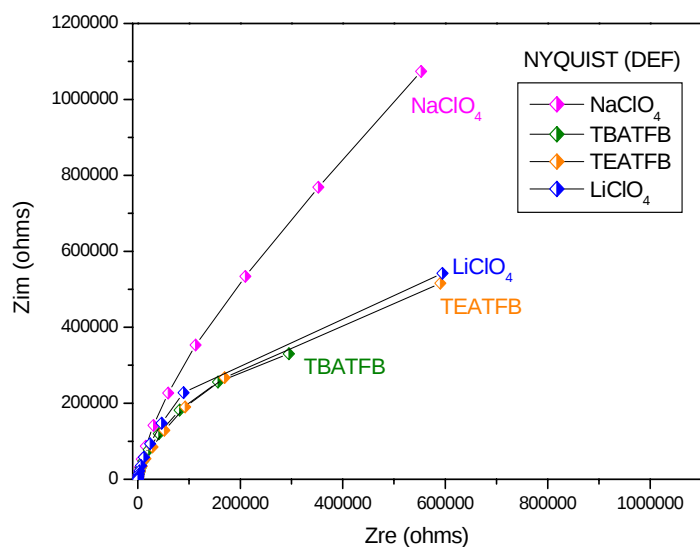


Figure3.48: Nyquist Plots Recorded for [1-(4-Methoxy Phenyl)-1H-Pyrrole] in a) TBATFB/ACN, b) LiClO₄/ACN, c) TEATFB/ACN and c) NaClO₄/ACN .

According to the Nyquist diagram e⁻ transfer rate is faster for NaClO₄ so it has more charge storage capability whereas TBATFB, LiClO₄ and TEATFB are almost in the middle range of capacitor and resistor property. Phase angle of NaClO₄ is closer to 70° that has better capacitive behaviour than the others.

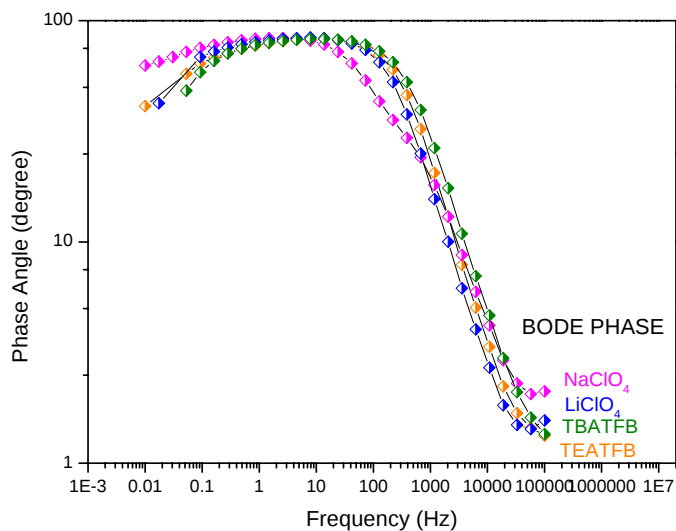


Figure 3.49: Bode Phase Definitions of [1-(4-Methoxy Phenyl)-1H-Pyrrole] in a) TBATFB/ACN, b) LiClO₄/ACN, c) TEATFB/ACN and c) NaClO₄/ACN for 10 Cycles.

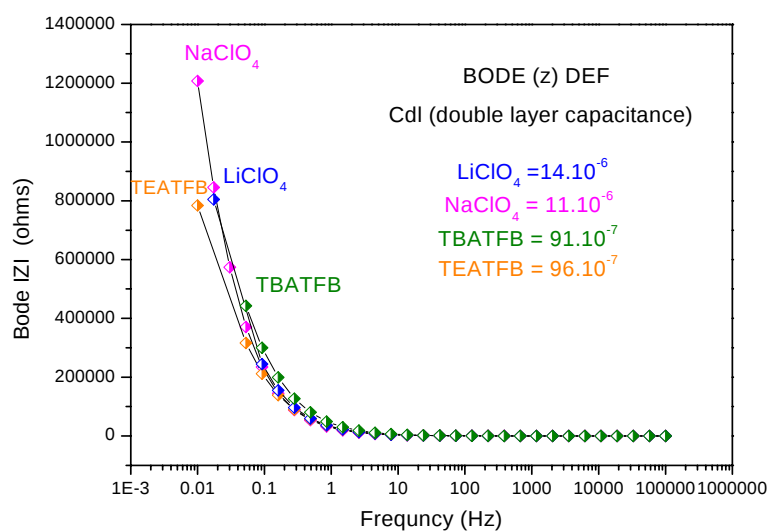


Figure 3.50: Bode Magnitude Plot of a) TBATFB/ACN, b) LiClO₄/ACN, c) TEATFB/ACN and c) NaClO₄/ACN for 10 Cycles.

NaClO₄ exhibits the highest double layer capacitance value ($11 \cdot 10^{-6}$) which is in a good agreement with nyquist data. When it is compared to ΔE (V) value of NaClO₄ has also the highest (0.60V) potential, that means thicker film. According to the admittance plot TEATFB reveals the highest conductive behaviour with 0.0046mS.

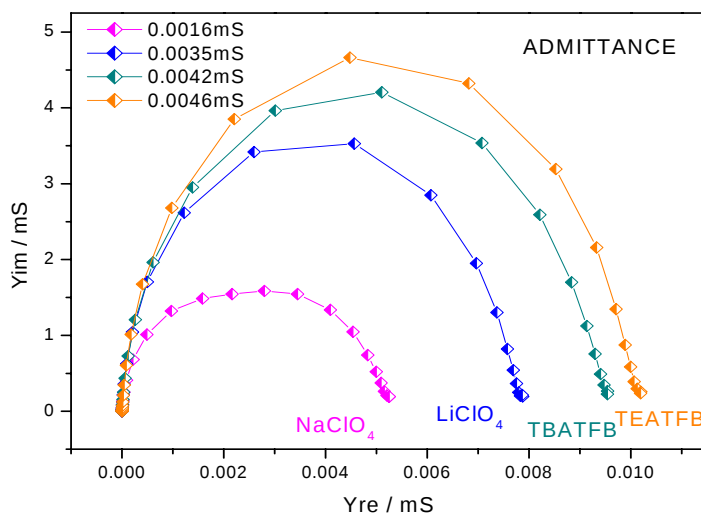


Figure 3.51: Admittance Plot a) TBATFB/ACN, b) LiClO₄/ACN, c) TEATFB/ACN and c) NaClO₄/ACN for 10 Cycles.

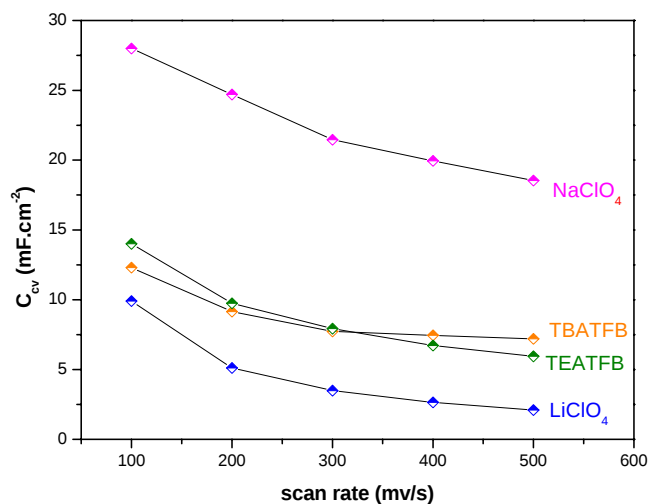


Figure 3.52: Capacitance Values Obtained from Cyclic Voltammograms Against Scan Rate.

If we compare the capacitance values from cv data and electrochemical impedance data, it is seen that NaClO₄ exhibits the highest capacitance values.

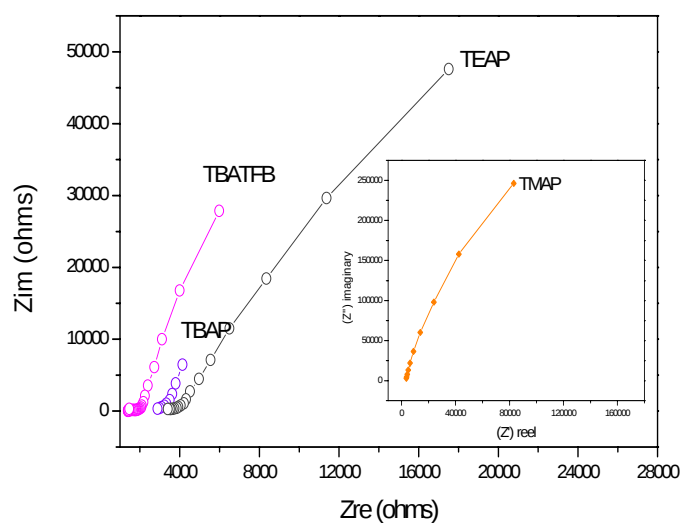


Figure 3.53: Nyquist Plot for Modified CFME Potentiodynamically With Different Electrolytes That Has Different Alkyl Groups.

On the other hand, potentiostatic conditions were used to obtain some modified electrodes that represented below by applying 0.8V. All of the polymerizations were performed in 30 minutes and capacitive behaviours were recognized as,

TBATFB > TBAP > TEAP > TMAP

The result can be explained as; long alkyl groups increase the capacitance property of the structure by supplying long chain.

3.6. Effect of Cycle Number on Electropolymerization of [1-(4-Methoxy Phenyl)-1H- Pyrrole]

In this section deposition charge effect via cycle number was studied by cyclic voltammogram. Electrogrowth process were performed via cyclic voltammetry for 1, 10 and 100 cycles. Electropolymerization reactions of [1-(4-Methoxy Phenyl)-1H- Pyrrole] was studied at the same conditions for three cases, 0.01M MPPy in TEAP/CH₂Cl₂ at 50mV/s scan rate.

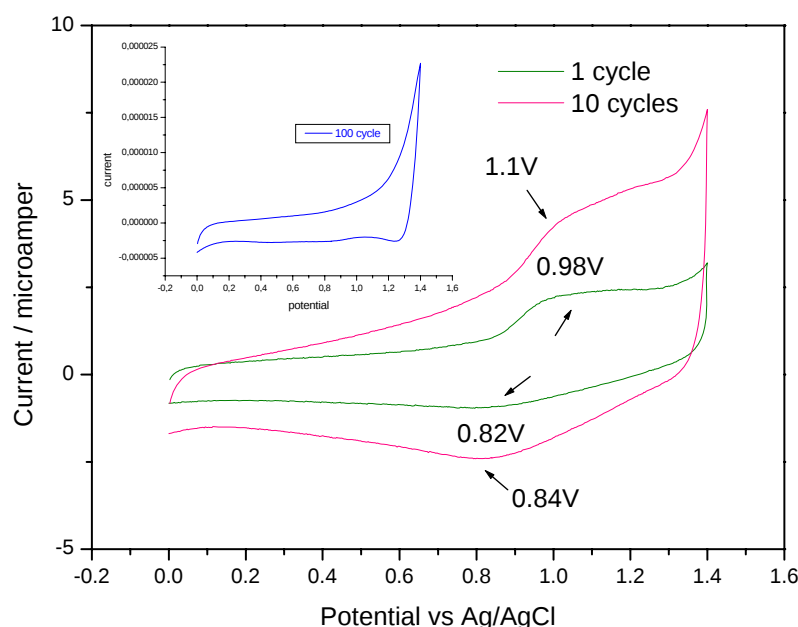
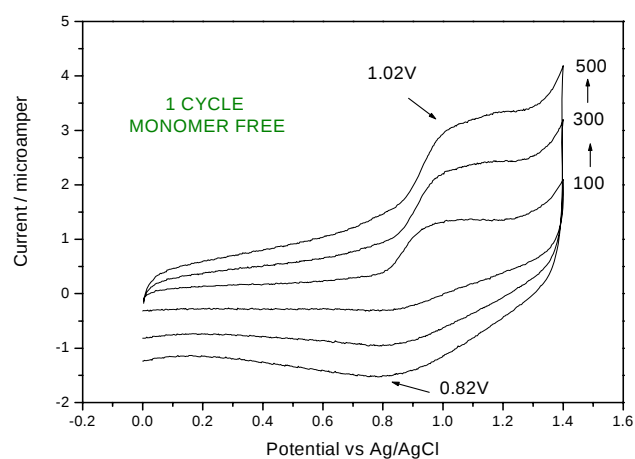
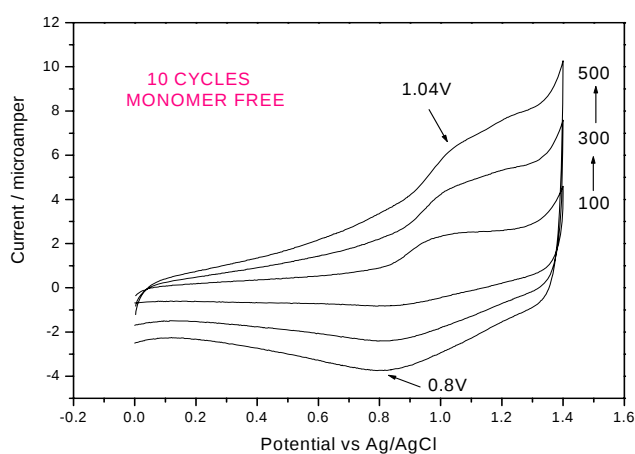


Figure 3.54: First Cycles of Three Different [1-(4-Methoxy Phenyl)-1H- Pyrrole]/ CFMEs From Scan Rate Dependencies In Monomer Free Solution.

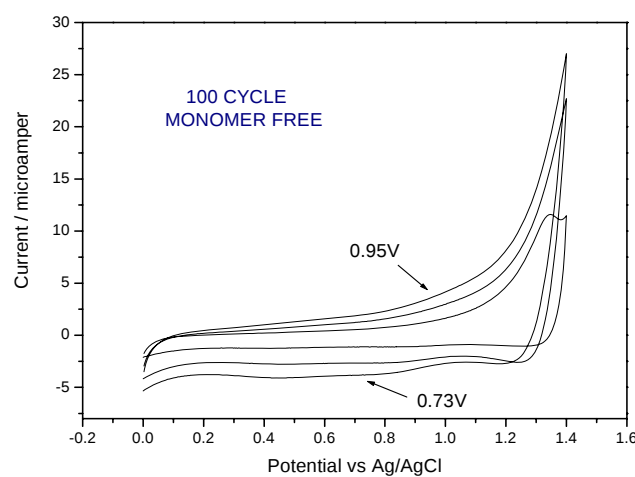
The comparison of scan numbers current and potential values, it can be said that when the scan number increases, than the deposition charge increases. Cycle number and the peak currents increase together linearly.



a



b



c

Figure 3.55: Scan Rate Dependencies of [1-(4-Methoxy Phenyl)-1H- Pyrrole] in Monomer Free Electrolyte Solution Between 100-500mV/s

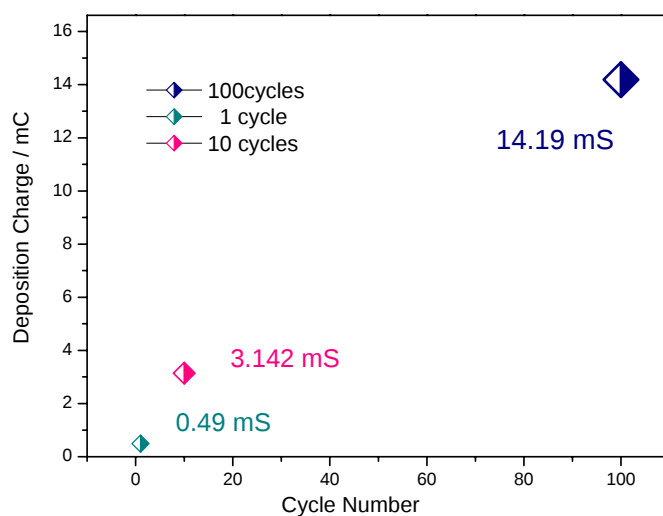


Figure 3.56 : Deposition Charge vs Cycle Number Plot.

Table 3.13: Redox Parameter Changes According to The Cycle Numbers of [1-(4-Methoxy Phenyl)-1H- Pyrrole]

Cycle number	Deposition charge, mS	Ia / Ic
1	0.49	1.93
10	3.14	1.62
100	14.19	0.92

The correlation chart reveals that the cycle number increases with the deposition charge of polymerization reaction. On the other hand; taking into account the Ia/Ic (0.92) ratio, which is close to unity and independent of the peak potential between 100 and 500 mV s⁻¹, the first electronic transfer is fast and the redox process follows a quasi-reversible mechanism for 100 cycle coated CFME.

3.6.1. Characterization with FTIR-ATR spectroscopy

The peaks around 1090cm^{-1} belong to the ClO^{-4} dopant anions; meaning that electrolyte was diffuse into the structure and the electrocoating was achieved. Scan number effect can be observed in spectrum by the shift of dopant anions peak. For instance; for 1 cycle growth, ClO^{-4} ions places at around $1092,45\text{ cm}^{-1}$ where the 10 cycles at $1091,27\text{ cm}^{-1}$ and 100 cycles at $1094,10\text{cm}^{-1}$.

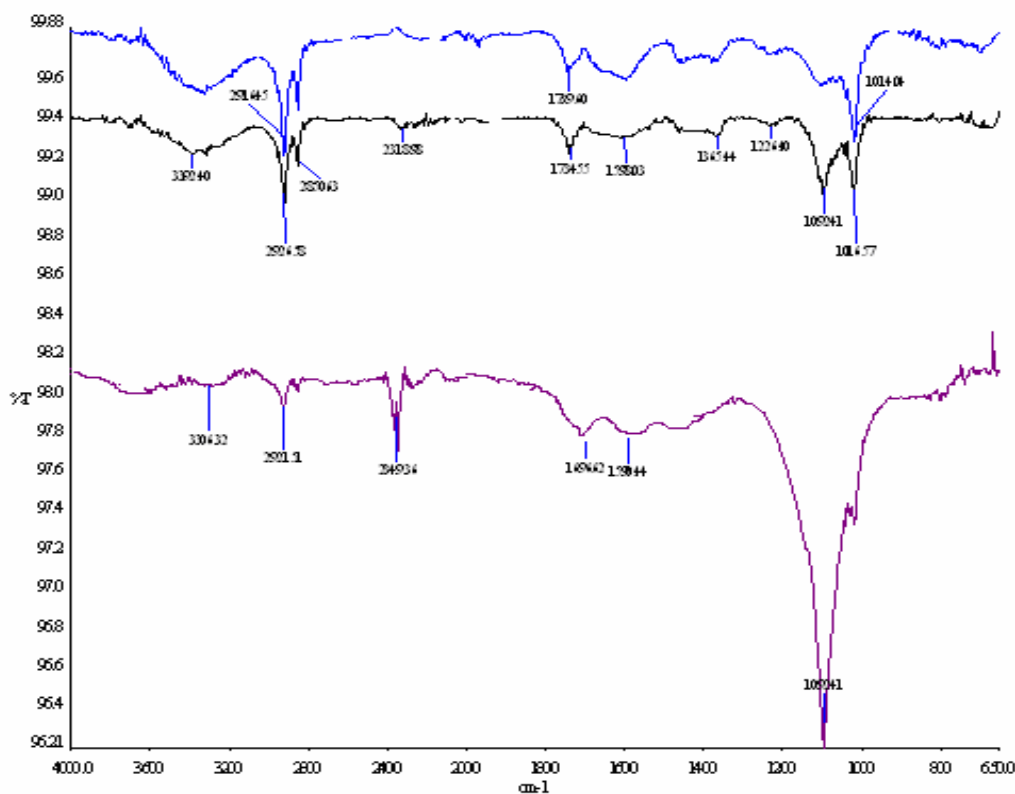
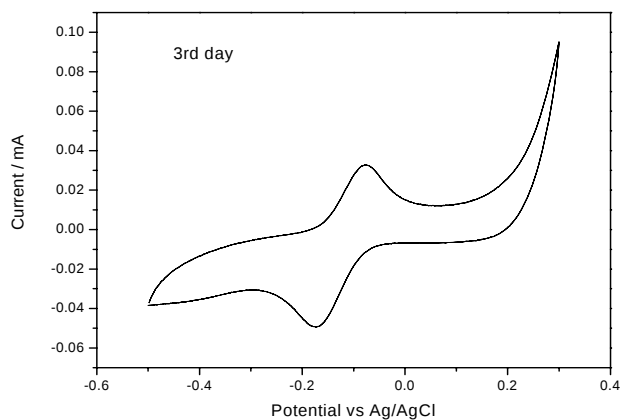
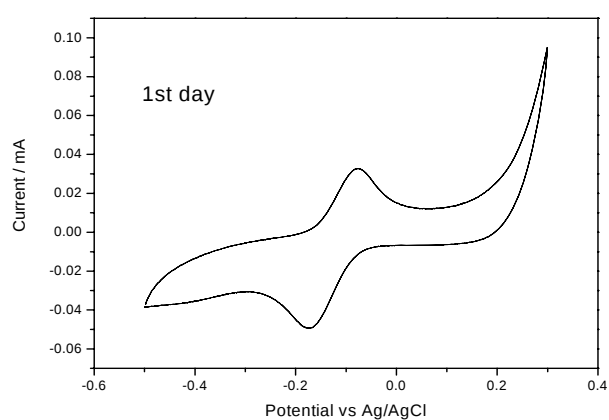


Figure 3.57: FTIR-ATR Spectrum for Electrocoated [1-(4-Methoxy Phenyl)-1H-Pyrrole] for 1, 10 and 100 Cycles.

3.7. Biosensor Application of [1-(4-Methoxy Phenyl)-1H- Pyrrole] Coated Carbon Fiber Micro Electrode For Epinephrine

Polymer modified carbon fiber micro electrode was taken to pH 7 phosphate buffer solution containing epinephrine with concentration 10^{-3} M. This micro electrode was tested for its response to epinephrine by applying potential between $[(-0,5) - (+0,3)]$ V. vs Ag/AgCl for 10 days. The electrochemical response of polymer modified CFME shows quasi-reversible peaks to epinephrine. If the redox parameter are checked, it is seen that



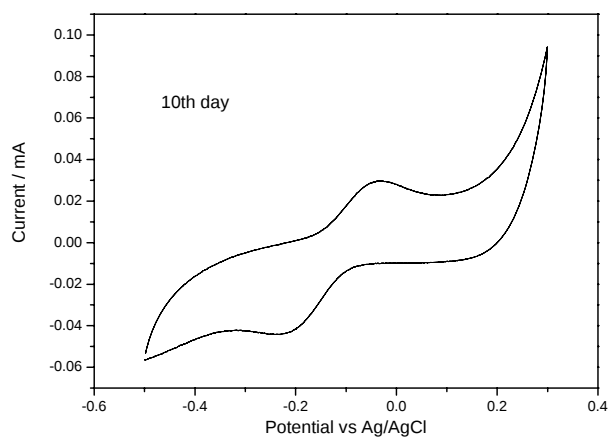
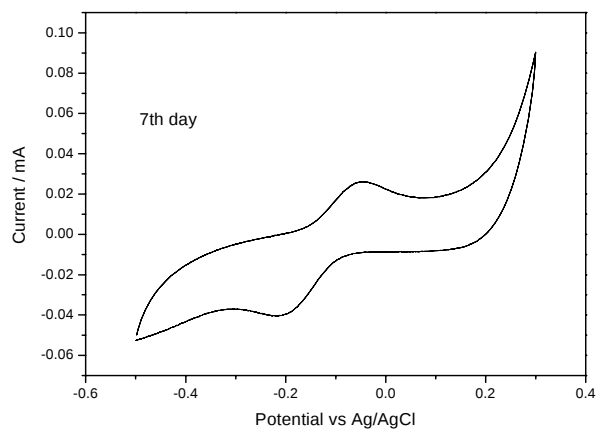
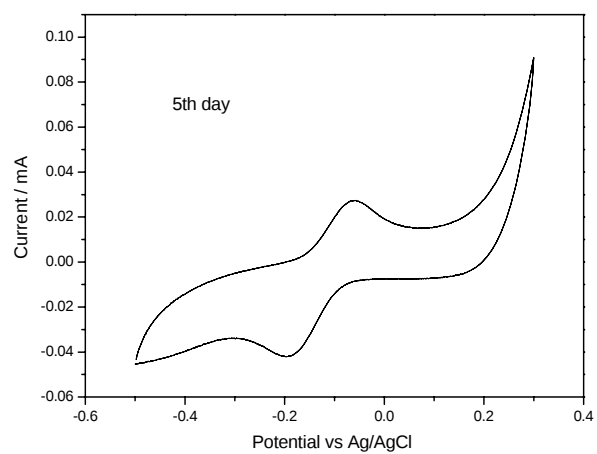


Figure 3.58: Epinephrine Response of Modified CFME for 1st, 3rd, 5th, 7th, 10th Days With the 2nd Cycle of 10.

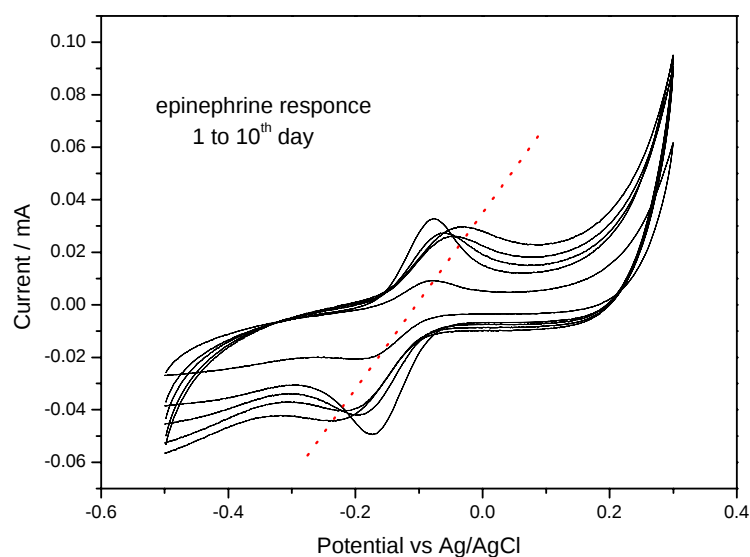


Figure 3.59: Comparison of 2nd Cycles of 1[4-methoxyphenylpyrrole] Coated CFMEs Epinephrine Response by Indicating The Shifts on Current Values.

According to results electrochemical oxidation of epinephrine and the response against 1[4-methoxyphenylpyrrole] results are quite reversible. The figure above clarifies that almost for 10 days our modified electrode is still reversible.

Table 3.14: Redox Parameter of Epinephrine Response of Modified CFME With 1[4-methoxyphenylpyrrole] for 10 Days.

Scan Rate	Eonset (V)	E ½ (V)	ΔE (V)	Ia / Ic
1 st day	-0.176	-0.249	0.095	0.703
3 rd day	-0.162	-0.254	0.096	0.695
5 th day	-0.15	-0.262	0.130	0.672
7 th day	-0.146	-0.269	0.169	0.663
10 th day	-0.142	-0.254	0.176	0.649

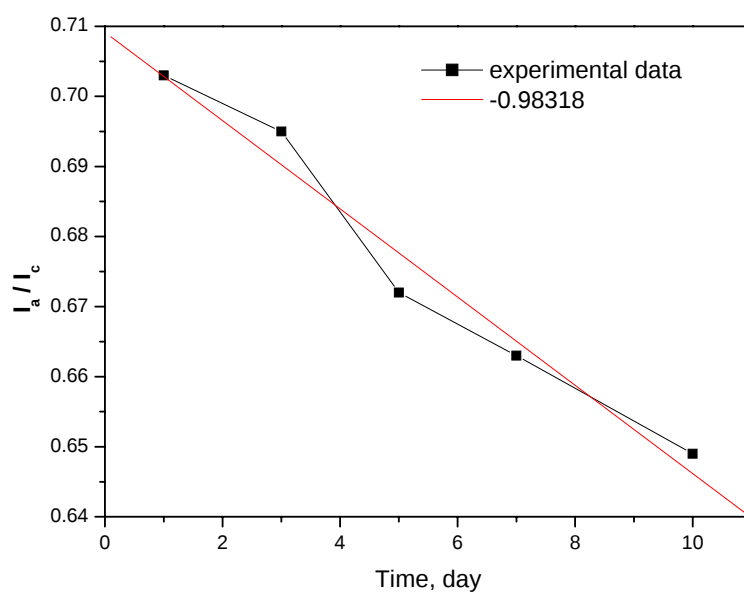


Figure 3.60: Long Term Stability Test for 1[4-methoxyphenylpyrrole] Coated CFME Against Epinephrine.

The peak current ratios according to the redox parameter are decreasing day by day. Therefore; onset potential is also decreases with the time where the monomer is begins to oxidized easily after a while. The stability test for this monomer is checked only for 10 day, and the correlation coefficient is found as 0.98318 which is a reasonable value.

4. CONCLUSION

In this thesis, homopolymer films of N-pyrrole (Py), N-phenylpyrrole (PhPy), and [1-(4-Methoxy Phenyl)-1H-Pyrrole] (MPhPy) were synthesized onto a few single carbon fiber microelectrodes (CFMEs) by electrochemical polymerization. The first scope was to determine the substitution effect, scan rate effect, scan number effect, monomer concentration effect and electrolyte effect on electropolymerization reactions and electrochemical impedance spectroscopy. Additionally, their electrochemical characterizations and morphological studies were observed.

The initial step was to determine the best substrate for electropolymerization reactions. Electropolymerization reactions were studied with a commercially new monomer onto CFME, Pt button and Pt wire electrode. The most reversible results were observed for CFME. Therefore; CFME was used in this thesis as a working electrode for all experiments.

First of all; Scan rate effect of electro growth process was studied for 1- (4-Methoxy Phenyl)-1H-Pyrrole. As a result, 60mV/s scan rate exhibited the more reversible results with the smallest deposition charge ($Q=2.59\text{mC}$) and electro activity of polymer electrodes is the highest for the polymer synthesized at 10mV.s^{-1} . Especially 1000 and 10.000mV/s scan rate was also checked for the stability monomer.

Moreover, monomer concentration effect was evaluated by using 0.1M, 0.01M and 0.001M concentrations. Monomer oxidation potentials were linearly proportional with the concentrations and conductivities as well. An increase in monomer concentration leads to an increase in the amount of radical cations; this is also increases the conjugation length of the polymer.

Substituent effect was studied with N-pyrrole, N-phenylpyrrole and [1-(4-Methoxy Phenyl)-1H-Pyrrole] monomers via cyclic voltammetry. The onset potential of N-pyrrole, N-phenylpyrrole, and [1-(4-Methoxy Phenyl)-1H-Pyrrole] , were obtained approximately as 0.74 V, 0.65 V and 0.63 V on CFMEs, respectively.

The results indicates that phenyl group included monomers indicates thin film where as the pyrrole has thicker coated surface although it has higher oxidation potential.

Electrochemical coatings of MPPy on CFME were analyzed in the presence of the different alkali cations(Li^+ , Na^+) and organic cations (tetraethylammonium) in ACN. The $E_{1/2}$ values can be correlated with the conjugation length, so it is longer for NaClO_4 because of the 0.935V half way potential. The involvement and the size of cation might have an influence on the polymer conductivity. It is shown that the larger the cation, the lower the conductivity of polymer.

Furthermore, electrogrowth process were performed via cyclic voltammetry for 1, 10 and 100 cycles for [1-(4-Methoxy Phenyl)-1H- Pyrrole] was studied at the same conditions for three case. The comparison of scan numbers, current and potential values, it can be said that when the scan number increases, than the deposition charge increases. Cycle number and the peak currents increase together linearly. We observed that the thickness of the polymer film is a function of number of cycles and increases linearly with the number of deposition charge during the electro deposition as expected.

Electrochemical impedance spectroscopy was studied to examine the electrical properties of modified micro electrodes. From impedance spectroscopy data, resistance and capacitance values of modified electrodes were explained. In the case of substitution effect, phenyl group increased the capacitance value nearly 80° where the pyrrole behaves like a resistor with 40°

Phase angle. Redox parameter changes for different scan rates is observed in the impedance data, respectively.

Additionally, ZSimpWin equivalent circuit simulation program were used to correlate the theoretical and experimental data. Several equivalent circuits were used in simulation of the impedance behavior of the polymer films from experimental data. For correlation only $R(C(R(Q(RW))))(CR)$, $R(C(R(Q(RW))))$, $R(C(R(QR)))(CR)$ circuit models were compared.

Table 4.1: Comparison of Studied Monomers Capacitance and Redox Parameters

Monomers	Eonset, V	Cspe, F	Cdl (experimental)	Cdl (theoretical)	Phase angle	Conductivity, mS
MPhPy	0.63	3.6×10^{-3}	1.76×10^{-4}	9.6×10^{-11}	78^0	0.21
PhPy	0.65	3.8×10^{-4}	9.12×10^{-5}	7.6×10^{-11}	80^0	0.24
Py	0.74	3.2×10^{-4}	1.76×10^{-4}	9.6×10^{-11}	39^0	0.13
0.1M MPhPy	1.12	4.1×10^{-3}	1.2×10^{-4}	1.9×10^{-5}	74^0	0.28
0.01M MPhPy	1.15	5.5×10^{-4}	6.1×10^{-5}	9.4×10^{-6}	79^0	0.12
0.001M MPhPy	0.89	3.9×10^{-4}	5.3×10^{-7}	5.1×10^{-7}	85^0	0.41

The surface morphology of the coated and uncoated CFMEs were studied using scanning electron microscopy for most cases and atomic force microscopy only for substitution effect study. The results indicates that more cycle number, slow scan rate, high deposition charge and high monomer concentration increases the accumulation of structures on the CFME surfaces in globular shape.

For biosensor application; the electrochemical response of polymer modified CFME was studied and quasi-reversible peaks were obtained for epinephrine. The stability test for this monomer was checked only for 10 days, and the correlation coefficient is found as 0.98318 which is a reasonable value.

In conclusion, we can say that N-phenylpyrrole (PhPy), and [1-(4-Methoxy Phenyl)-1H-Pyrrole] (MPhPy) shows very good capacitive behaviour except N-Pyrrole. Almost all phenyl group included polymers can be used for supercapacitor applications.

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PROJECTS AND SEMINARS

Polymeric drug delivery systems, smart carriers and medicine cabinets

Effects of less lithium on human body

Conducting polymers

Electropolymerization of monomers on carbon fiber micro electrodes and characterization.

GMP and GLP education at Eczacıbaşı

ISO 9002 education at Eczacıbaşı

Group Working education at Eczacıbaşı

Workman Health and Security education at Eczacıbaşı

CONGRESS

Electropolymerization of 1-(4-Methoxy Phenyl)-1H-Pyrrole on CFME, investigation of capacitance behaviour with electrochemical impedance spectroscopy, characterization with FTIR-ATR & cyclic voltammetry and epinephrine response of coated CFME.(poster presentation,) *4th ISE Spring Meeting 2006, National Singapore University, Singapore*

Effect of monomer concentration on electropolymerization and electrochemical impedance spectroscopy.(poster presentation) *1st National Polymer Congress 2006, ODTU, Ankara*

Electrolyte Effects on polymethoxyphenylpyrrole grafted Carbon Fiber Micro Electrode's Electrochemical Impedance Spectroscopy. *57th Annual Meeting of the ISE 2006, Heriot Watt University, Edinburgh*

Electropolymerization of pyrrole, phenylpyrrole and methoxyphenylpyrrole / CFME and substitution effect on electrochemical impedance and correlation with theoretical equivalent circuits. *7th Symposium of Electrochemical Impedance Spectroscopy, EIS200, Argeles-Sur Mer, France*

JOURNALS

Effect of scan rate on electropolymerization of 1-(4-methoxyphenyl)-1H- pyrrole coated carbon fiber micro electrode, and surface characterization. *S. Sezgin, E.A.Parlak, A.S.Sarac (submitted)*

Electropolymerization of pyrrole, phenylpyrrole and methoxyphenylpyrrole / carbon fiber microelectrodes and substitution effect on electrochemical impedance spectroscopy and correlation with theoretical equivalent circuits. *A.S.Sarac, S. Sezgin, M. Ates, and C. M. Turhan (will be submitted)*