

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**COMPERATIVE ELECTROPOLYMERIZATION AND
CHARACTERIZATION OF PYRROLE, CARBAZOLE, INDOLE AND
THIOPHENE**

M.Sc. THESIS

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Department of Polymer Science and Technology Department

Polymer Science and Technology Programme



Thesis Advisor: Prof. Dr. Belkis USTAMEHMETOĞLU

JANUARY 2012

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

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POLİMERİZASYONU VE KARAKTERİZASYONU**

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OCAK 2012

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To my mother,

FOREWORD

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Nihan AYDEMİR

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CURRICULUM VITAE	Hata! Yer işareti tanımlanmamış.

ABBREVIATIONS

ACN	: Acetonitrile
ATR-FTIR	: Attenuated Total Reflectance Fourier Transform Infrared
C_{dif}	: Differential Capacitance
C_{dl}	: Double Layer Capacitance
C_{sp}	: Specific Capacitance
CV	: Cyclic Voltammetry
Cz	: Carbazole
E_a	: Anodic Potential
E_c	: Cathodic Potential
E_g	: Band Gap
EC-QCM	: Electrochemical Quartz Micro Balance
EIS	: Electrochemical Impedance Spectroscopy
E_o	: Mean Value of E _a and E _c
F	: Faraday Constant
GS	: Galvanostatical
I_a	: Anodic Current
I_c	: Cathodic Current
IN	: Indole
Py	: Pyrrole
Th	: Thiophene
PCz	: Polycarbazole
PD	: Potentiodynamical
PS	: Potentiostatical
PIn	: Polyindole
Ppy	: Polypyrrole
PTh	: Polythiophene
R_s	: Solution Resistance
R_p	: Polymer Resistance
QCM	: Quartz Micro Balance
SEC	: Spectroelectrochemistry
SEM	: Scanning Electron Microscopy
W	: Diffusion Control Element
Z	: Impedance
Z_{im}	: Imaginary Part of Impedance
Z_{re}	: Real Part of Impedance

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COMPERATIVE ELECTROPOLYMERIZATION AND CHARACTERIZATION OF PYRROLE, CARBAZOLE, INDOLE AND THIOPHENE

SUMMARY

In this study, pyrrole (Py), carbazole (Cz), indole (IN) and thiophene (Th) were polymerized by the different electropolymerization techniques such as potentiodynamical (PD), potentiostatical (PS) and galvanostatical (GS) methods under solvent/electrolyte and the coating thickness parameters. Conductivity, impedance, capacitance were determined by electrochemical impedance spectroscopy (EIS). Conditions of best reversibility and most capacitivity were determined for each polymer, equivalent circuits of these polymerization methods were plotted. Optical bandgaps were calculated with the results of spectro electrochemistry measurements. AFM pictures were taken for the surface characterization.

Firstly, each monomer was oxidatively polymerized by PD method at 2, 4, and 8 cycles; by PS method at 30, 60 and 120 s and by GS method at 30, 60 and 120 s onto platinum button electrode under solvent/electrolyte and the coating thickness parameters separately. Ag/AgCl were chosen as the reference electrode and Pt wire was the counter electrode. Acetonitrile (ACN) was used as solvent as the polymerization media. Electrolytes were chosen as tetrabutyl ammonium tetra fluoro borate (Bu_4NBF_4) for Py, tetrabutyl ammonium perchlorate (Bu_4NClO_4) for Cz, sodium perchlorate (NaClO_4) for IN and Th. After the polymerization, voltammetric response of each polymer were plotted between 100 mV /s and 500 mV/s in monomer free solution to determine the reversibility conditions.

Secondly, in the same monomer free solution EIS measurements were obtained. Nyquist, bode phase and bode magnitude diagrams were plotted to determine the electrical parameters. At first step of measurements were done in open circuit potential. For the second step 1V constant voltage was applied to observe the semi circle behaviour of impedance to calculate experimental polymer resistance. Bode

phase diagrams were plotted to determine the phase angle which is a demonstration of capacitive behaviour. Bode magnitude diagrams showed the IZI value of polymer.

Thirdly from the voltammetric response and impedance measurements the most capacitive polymer was determined for each polymerization method and equivalent circuits were prepared by the ZSimpWin software. Behaviour of each part simulated by the classical electrical terms such as ohmic resistance (R_s), charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}), specific capacitance (C_{sp}) diffusion coefficient of electronic and ionic carriers (W). Transitions between the parameters are built in series or parallels. Capacitive, dielectrical or inductive behaviours of the polymeric films determined.

PİROL, KARBAZOL, İNDOL VE TİYOFEN' İN KARŞILAŞTIRMALI POLİMERİZASYONU VE KARAKTERİZASYONU

ÖZET

Bu çalışmada, pirol (Py), karbazol (Cz), indol (IN) ve tiyofen (Th) monomerleri elektrokimyasal olarak, potansiyeldinamik (PD), potansiyelstatik (PS) ve galvanostatik (GS) yöntemleri ile polimerleştirildi. Döngüsel voltametri (CV), elektrokimyasal empedans spektroskopisi (EIS), spektroeletrokimyasal spektroskopisi (SEC) ve atomik kuvvet mikroskobu (AFM) ile karakterizasyonları gerçekleştirildi.

Günümüzde iletken polimerlerin elektronik alet yapımında kullanılması oldukça sıklaşmıştır. Elektronik uygulamalarda polimer seçimlerinde iletken ve kapasitif özellikler ön plana çıkmaktadır. Malzemelerin iletkenlik, yarı iletkenlik, iyon transfer ortamları gibi elektriksel parametreleri elektrokimyasal empedans spektroskopisi (EIS) ölçümleri ile belirlenmektedir. Bu tarz çalışmalar iletken özelliğinin en yüksek olması açısından PPy üzerinde yoğunlaşmıştır. Ardından kapasitif özellikte en iyi olan PCz gelmektedir. İletkenlik ve kapasitifliği kısmen daha zayıf olan PTh ve PIN üzerine de az sayıda çalışma bulunmaktadır. PIN bu tarz çalışmalarda diğer elektroaktif polimerlere göre termal dayanıklılığı yüksek ve degradasyonu yavaş olduğu ve için seçilmektedir.

PD metot iletken polimerlerin sentezi konusunda en çok tercih edilen elektrokimyasal yöntemdir. Kalitatif ve kantitatif bilginin yanında gerçekçi bir karakterizasyon da sağlar. Bu çalışmada her bir monomere belli bir aralıkta değişen potansiyeller uygulandı ve her adımda hücrenin cevabı akım cinsinden kaydedildi. Monomerin oksitlenme potansiyeline ulaşıldığında, yükseltgenme gerçekleşti ve monomerler birleşerek polimeri oluşturdular.

PS metodu sabit potansiyelin uygulandığı ve karşılığında akım cevabının bir zaman fonksiyonu olarak alındığı ve polimerleşmenin gerçekleştiği bir yöntemdir. Bu akım zaman cevabı iki komponentin birleşmesi sayesinde oluşur Bunların birincisi, polimer ve çözelti arasındaki çift yüzeyin yüklenmesi, ikincisi ise elektrokimyasal

olarak aktif olan türlerin elektron transfer reaksiyonudur. Bu çalışmada her bir monomerin yükseltgenme potansiyelleri değişik zaman aralıklarında sabit olarak uygulandı ve akım cevapları kaydedildi.

GS metodu sabit akımın uygulandığı ve bu akım karşılında oluşan potansiyel cevabının bir zaman fonksiyonu olarak kaydedilerek polimerleşmenin gerçekleştiği bir yöntemdir. PS metodunun tam tersi bir işlem olarak da düşünülebilir. Bu çalışmada, uygulanan diğer metotlar gibi, bütün monomerler değişik zaman aralıklarında ve sabit akım uygulayarak polimerleştirildi.

İletkenlik, empedans, kapasitans değerleri elektrokimyasal empedans yöntemi (EIS) ile hesaplandı. Elektrokimyasal empedans spektroskopisi birçok kimyasal ve fiziksel prosesin işleyişini anlamak maksatlı kullanılan oldukça gelişmiş bir tekniktir. Elektron veya kütle transferi, redoks reaksiyonları gibi çözelti fazında ilerleyen kompleks elektrokimyasal olayları incelemek için uygundur. EIS genellikle elektrokimyasal hücre içinde AC potansiyel altında ve belli frekans aralıklarında uygulanır. Bu çalışmada EIS ölçümlerinden faydalanılarak tersinirlik ve kapasitiflik açısından en ideal koşullar tayin edildi ve bu koşullara ait eşdeğer elektriksel devre modelleri çizildi.

SEC (spektroelektrokimya) elektrokimya ve spektroskopi tekniklerinin birleştiği bir tayin metodudur. Bu çalışmada optik enerji kuşağı açıklığını SEC ölçümlerinden faydalanılarak hesaplandı. Özellikle dizayn edilmiş bir elektrokimyasal hücrede, redoks aktifliği olan bir malzemenin yükseltgenmesi ve indirgenmesi incelenir. Redoks reaksiyonlarından oluşan cevaplar, absorbans grafikleri şeklinde kaydedilir.

Atomik kuvvet mikroskobu (AFM) çok yüksek çözünürlüklü bir taramalı kuvvet mikroskobudur. Ulaşılmış çözünürlük bir kaç nanometre ölçeğinde olup alışlagelmiş optik tekniklerden en az 1000 kat fazladır. Bilgi, mekanik bir ucun yüzeyi taramasıyla toplanır. Elektronik kumanda üzerinde bulunan, küçük fakat hassas hareketleri sağlayan piezoelektrik öğeler doğruluğu kesin hassas bir tarama sağlar. İletken manivelalar kullanmak suretiyle numune yüzeyindeki elektrik potansiyeli de taranabilir. AFM uygulamaya bağlı olarak çeşitli modlarda kullanılabilir. Bu görüntüleme modları “statik” (temas) ya da “dinamik” (temassız) olabilir. Bütün monomerlerin aynı yöntemle (PS) ve aynı polimerizasyon zamanında (120 sn) elde edilmiş polimerlerinin temassız modda yüzey morfolojileri incelendi.

İlk olarak, her monomer yükseltgenerek, PD methoduyla 2, 4, 8 döngülü, PS methoduyla 30, 60, 120 sn ve GS methoduyla 30, 60 120 sn süresince platin button

elektrod üzerine çözücü/elektrolit, ve kalınlık parametrelerini değiştirerek polimerleştirildi. Çözücü ortam olarak asetonitril (ACN) kullanıldı. Elektrolit olarak, Py için tetra bütıl amonyum tetra floro borat (Bu_4NBF_4), Cz için tetra bütıl amonyum perklorat, IN ve Th için ise sodyum perklorat (NaClO_4) seçildi. Polimerizasyon işleminin ardından her polimerin tersinirlik tayini için, 100-500 mV/s aralığında döngülü voltammogram cevapları incelendi.

İkinci olarak, aynı monomersiz çözelti içinde EIS ölçümleri gerçekleştirildi. Elektriksel parametreleri belirlemek için nyquist, bode phase and bode magnitude grafikleri çizildi. İlk aşamada ölçümler açık akım-potansiyel altında, ikinci aşamada ise empedanslarda yarı daire davranışı elde edebilmek ve deneysel olarak polimer direnci hesaplayabilmek için 1V uygulanarak gerçekleştirildi. Kapasitif davranışın bir göstergesi olan faz açılarını saptamak için bode phase grafikleri incelendi. Bode magnitude grafiklerinden imajinal empedans (Z_{im}), spesifik kapasitans (C_{sp}) ve çift yüzey kapasitansı (C_{dl}) hesaplamaları yapıldı.

Üçüncü olarak, döngülü voltammogram ve empedans ölçümlerinden faydalanılarak her polimer için en kapasitif ve en tersinir koşul belirlendi, bu koşula ait eşdeğer elektrik devreleri Zsimp Win programı kullanılarak çizildi. Her bölümün davranışı ohmik resistans (R_s), yük transfer resistansı (R_{ct}), çift yönlü yüzey kapasitansı (C_{dl}), spesifik kapasitans (C_{sp}), elektronik ve iyonik taşıyıcıların difüzyon katsayısı (D) gibi klasik elektrik devre terimleri ile ifade edildi. Parametreler arasındaki geçişler paralel ve seri olarak birleştirildi. Polimerlerin kapasitif, dielektrik ve indüktif davranışları belirlendi.

Dördüncü olarak, optik band açıklığını saptamak için, her monomer ilk önce ITO cam üzerine PS metodu ile 120 sn boyunca polimerleştirildi. oluşan kaplamalar, monomersiz çözelti içine alınarak belli bir voltaj aralığındaki absorbans cevapları kaydedildi. Verilen voltaj arttıkça kromofor grupların azaldığı ve bipolaronların arttığı gözlemlendi.

Son olarak, yüzey morfolojisini saptamak için AFM mikrogafikleri çizildi. Monomerler öncelikle PS metodu ile 120 sn boyunca esnek ITO cam üzerinde polimerleştirildi. Elde edilen kaplamalar 24 saat boyunca oda sıcaklığında bekletilerek çözücünün uçması sağlandı. Ardından bütün monomerlerin temassız modda aynı nanometre aralığında AFM mikrogafikleri çekildi. Yüzey porozlukları karşılaştırıldı.

Bütün karakterizasyon yöntemlerinden elde edilen sonuçlar birlikte kullanılarak, polimerlerin elektriksel davranışları ve hangi koşullarda kapasitif, dielektrik ve tersinir özellikler gösterdikleri ve bu davranışlar arasında ne tarz geçişlerin olduğu saptandı.

1. INTRODUCTION

Almost 40 years ago all carbon based polymers were absolutely regarded as insulators. Plastics have been extensively used by the electronics industry because of their good insulating properties. Since the discovery that conjugated polymers can be made to conduct electricity through doping, a tremendous amount of research has been carried out in the field of conducting polymers [1-3] The electrically conducting polymers are able to transfer electrical charges to the same extent as an electrical conductor or a semiconductor. Due to their metal-like conductivity or semiconductivity and other fascinating properties, conducting polymers have played indispensable roles in specialized industrial applications in spite of their short history. Conducting polymers can be tailored for specific applications through the doping process such as electronic devices, bio sensors and fuel cells. Its poor mechanical and physical properties, however, prevents its application in other cases. [4,5] The most important conducting polymers are Polypyrrole (PPy), polycarbazole (PCz), Polythiophene (PTh), polyaniline (PANI) and polyindole (PIN). Studies about electro active polymers have been centered on PPy due to its high conductivity and relative processability. Next PCz can be counted as it has excellent capacity. There are some studies on relatively less conductive and capacitive PTh and PIn. PIn has been chosen for its high thermal stability in these kind of studies [11]. There are two main polymerization techniques for conducting monomers; first is electrochemical and second is chemical polymerization. Electrochemical polymerization types are potentiodynamical (PD), potentiostatical (PS) and galvanostatical (GS) method.

Electrochemical impedance spectroscopy (EIS) is an extremely powerful tool for examining a lot of chemical and physical processes in solutions. For solution phase electrochemistry a complex sequence of coupled processes such as, electron transfer, mass transport and chemical reaction can all control or influence the output from an electrochemical measurement. [36-40] Electrochemical impedance is usually

measured by applying an AC potential to an electrochemical cell and measuring the current through the cell. A sinusoidal potential is applied and the response to this potential is an AC current signal. [38].

Spectroelectrochemistry (SEC) is a combination of reaction-oriented electrochemistry with species-focused spectroscopy. This technique allows for a more complete analysis of electron transfer processes and complex redox reactions. Many researchs have been made from various sub-fields of the chemical sciences with using and developing this combined methodology. [78].

1.1 Purpose of Thesis

Purpose of this thesis is to determine the best electropolymerization techniques and conditions for Py, Cz, IN and Th by performing characterization techniques such as CV, EIS, CV-UV and AFM. Results were compared to understanding fundamental electrode processes upon electropolymerization of polymers and allow one to have a new insight into the electropolymerization reactions, thus helping electrochemists to improve the preparation of their polymers.

2. THEORY

2.1 History of Polymers

The term polymer stems from the greek roots poly (many) and meros (part). As the result of bringing them together the word means “many parts”. At the end of this new word “mer” which means the repetition of some simple unit comes so the word get its full meaning, polymers are very large molecules made up of smaller units, called monomers or repeating units which are bonded together covalently ($n \geq 10^3$) [1].

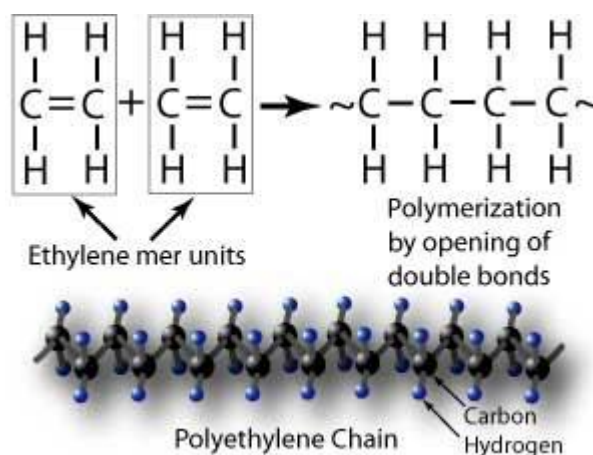


Figure 2.1 : Representaion of PE structure.

We live with polymers since beginning of time. Tortoise shell, horns and plants include natural polymers as well as tree saps that produce amber and latex. Natural polymers began to be modified during the begining of 1800s to produce differant materials. The most famous of these were vulcanized rubber, gun cotton, and celluloid. The first synthetic polymer produced was Bakelite in 1909 and was followed by the semi- synthetic fiber, rayon, which was developed in 1911 [2].

Despite significant advances and many works in polymer synthesis, the molecular structure of polymers was not understood until the work of Hermann Staudinger in 1922. Prior to Staudinger's work, polymers were understood in terms of the association theory or aggregate theory, which originated with Thomas Graham in

1861. Graham proposed that cellulose and other polymers were "colloids", aggregates of molecules small molecular mass connected by an unknown intermolecular force. Hermann Staudinger was the first to propose that polymers consisted of long chains of atoms held together by covalent bonds. It took over a decade for Staudinger's work to gain wide acceptance in the scientific community, work for which he was awarded the Nobel Prize in 1953 [2].

The World War II era marked the emergence of a strong commercial polymer industry. The limited or restricted supply of natural materials such as silk and latex necessitated the increased production of synthetic substitutes, such as rayon and neoprene in 1960's. The development of advanced polymers such as Kevlar and Teflon have continued to fuel a strong and growing polymer industry.

2.2 Molecular Structure

Polymers (or macromolecules) are very large molecules made up of smaller units, called monomers or repeating units which are bonded together covalently. This specific molecular structure (chainlike structure) of polymeric materials is responsible for their intriguing mechanical properties. Polymer architecture can vary. I three possible molecule architectures are depicted.

A *linear polymer* consists of a long chain of monomers.

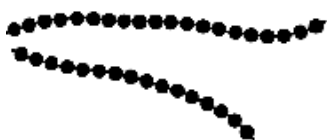


Figure 2.2 : Linear polymer structure.

A *branched polymer* has branches covalently attached to the main chain.



Figure 2.3 : Branched polymer structure.

Cross-linked polymers have monomers of one chain covalently bonded with monomers of another chain. Crosslinking results in a three-dimensional network; the whole polymer is a giant macromolecule.

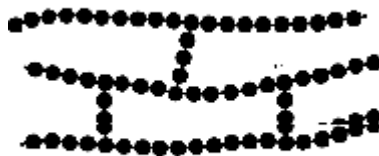


Figure 2.4 : Crosslinked polymer structure.

Elastomers are loosely cross-linked networks while *thermosets* are densely cross-linked networks [2,4].

Homopolymers consist of monomers of the same type; *copolymers* have different repeating units. Furthermore, depending on the arrangement of the types of monomers in the polymer chain, we have the following classification: In random copolymer, the two monomers may follow in any order. In alternating copolymer two monomers are arranged in an alternating fashion. In *block* copolymers long sequences of a monomer are followed by long sequences of another monomer. *Graft* copolymers consist of a chain made from one type of monomers with branches of another type [2].

2.3 Conducting Polymers

Polymers have long been thought of and applied as insulators. Indeed, not so long ago, any electrical conduction in polymers—mostly due to loosely bound ions was generally regarded as an undesirable phenomenon. Although the ionic conductivity of polymer electrolytes (macromolecular solvents containing low-molar-mass ions) and polyelectrolytes (macromolecules containing ionizable groups) have been widely utilized in electrochemical systems over the last few decades (e.g., in power sources, sensors, and the development of all-solid-state electrochemical devices), the emergence of electronically conducting polymers has resulted in a paradigmatic change in our thinking and has opened up new vistas in chemistry and physics [4].

This story began in the 1970s, when, somewhat surprisingly, a new class of polymers possessing high electronic conductivity (*electronically conducting polymers*) in the

partially oxidized (or, less frequently, in the reduced) state was discovered. Three collaborating scientists, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa, played a major role in this breakthrough, and they received the Nobel Prize in Chemistry in 2000 “for the discovery and development of electronically conductive polymers”

As in many other cases in the history of science, there were several precursors to this discovery, including theoretical predictions made by physicists and quantum chemists, and different conducting polymers that had already been prepared. For instance, as early as 1862, Henry Letheby prepared polyaniline by the anodic oxidation of aniline, which was conductive and showed electrochromic behavior . Nevertheless, the preparation of this polyacetylene by Shirakawa and coworkers and the discovery of the large increase in its conductivity after “doping” by the group led by MacDiarmid and Heeger actually launched this new field of research.

Electrochemistry has played a significant role in the preparation and characterization of these novel materials. Electrochemical techniques are especially well-suited to the controlled synthesis of these compounds and for the tuning of a well-defined oxidation state [3].

2.3.1 PPy

Among the conducting polymers PPy has a very special place due to its high conductivity as well as well processability. The structure of PPy is given in fig. 2.5.

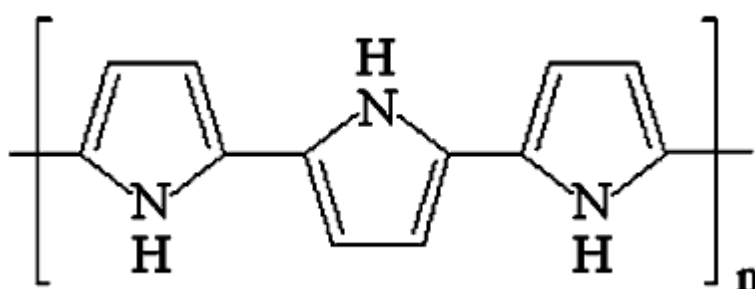


Figure 2.5 : Structure of PPy.

The most important usage area of PPy is redox super capacitors due to advantages of, fast doping and dedoping process, porous morphology, high electrical conductivity [34]. Moreover PPy is an important electrode material for redox supercapacitors and has shown advantages of porous morphology, good electrical conductivity, fast

doping and dedoping process. PPy has been successfully employed for preparation of supercapacitors, biosensors and electronics and in thin-film form it has many possible applications such as electro-chromic devices, light emitting diodes, photovoltaic cells, batteries, actuators and bio sensors [2,6].

PPy is often formed by electropolymerisation using oxidising monomer with metal salts according to the CV, CA or CP procedure [14,38,40]. The mechanism of the electropolymerization is up to the experimental conditions, especially on the solution composition and the potential applied. Furthermore, product distribution, morphology, adherence and electrochemical behaviour of the films formed are affected by the method used for the electropolymerization. Attempts have been made in the copolymerisation of Py with other heterocyclic monomers to improve the properties of the resulting product. [14]. Oxidizing mechanism of Py can be seen in Fig. 2.6 .

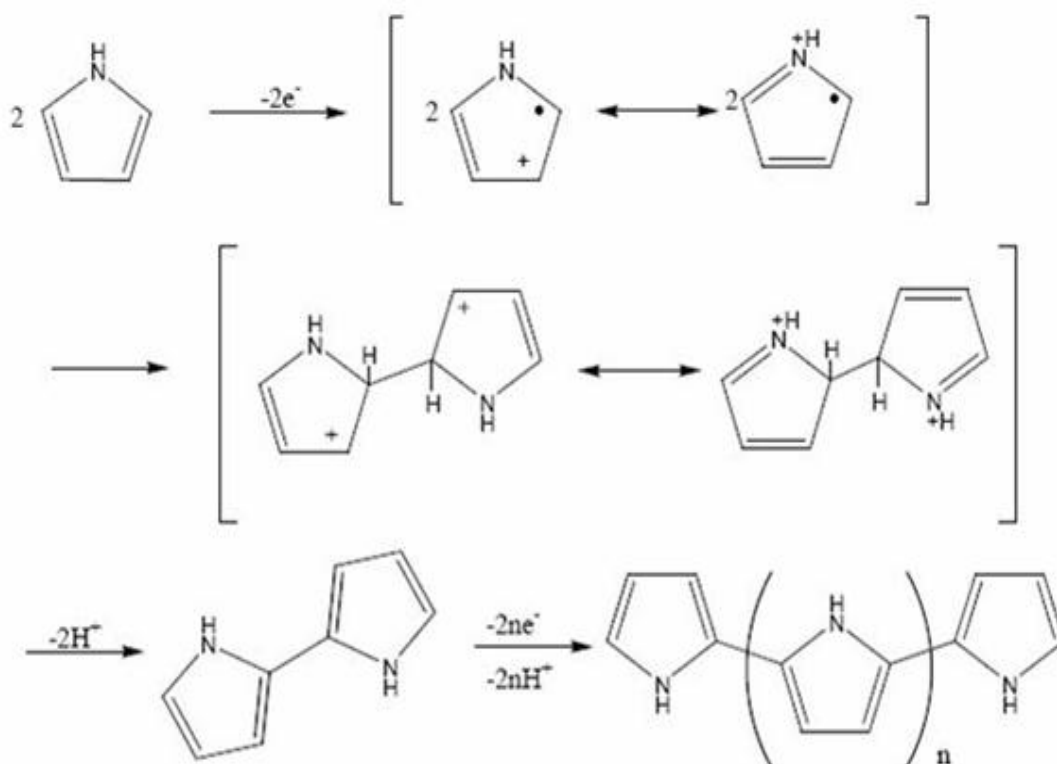


Figure 2.6 : Oxidation mechanism of PPy.

Last step is the repetition of first step, beginning oxidation followed by coupling of monomer and finally elimination of H^+ .

2.3.2 PCz

The proper increase of interest in carbazole (Fig.) containing polymers is connected mostly with its supercapacitive property besides relatively easy polymerization and processability[3,10]. Carbazole-containing polymers play an important role in the polymeric light emitting diodes, electroluminescent devices, biosensors and organic photorefractive materials photorefractive materials and photovoltaic devices. [30-34].

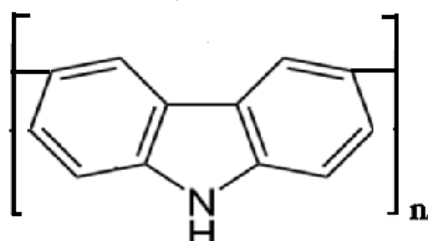


Figure 2.7 : Structure of carbazole.

Carbazole is practically insoluble in water or acidic solutions. But there are some studies that achieved soluble carbazole [7]. Consequently, carbazole oxidation can be studied only in nonaqueous or mixed electrolytes. In most cases, two different solutions have been applied, either acetonitrile containing tetrabutylammonium or Li^+ salts. [30-35]. Electrochemical polymerization of carbazole can be seen in Fig. 2.8 .

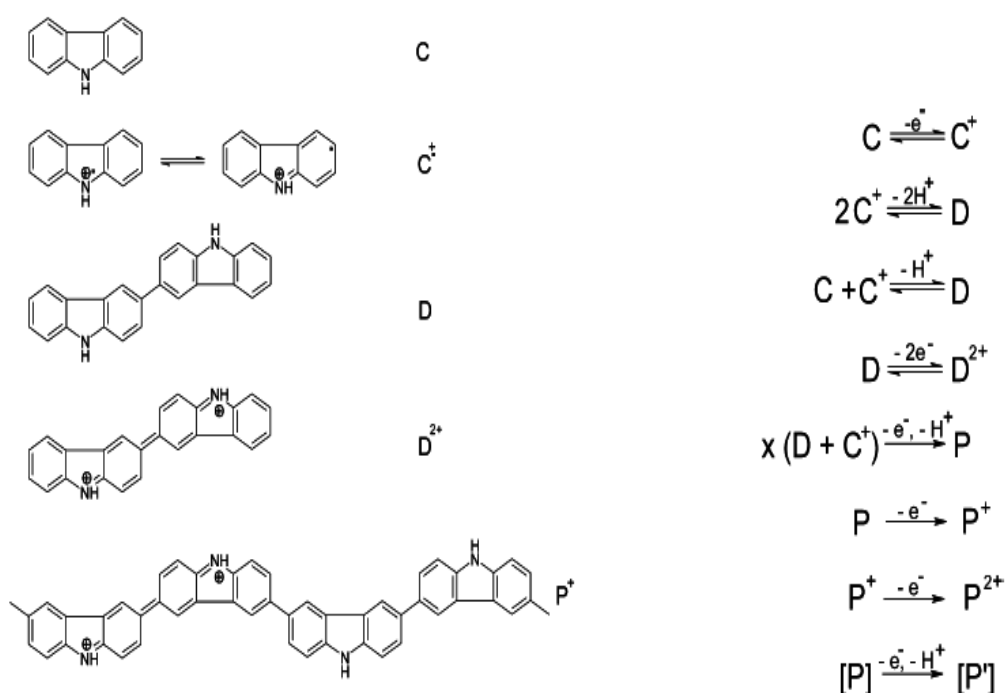


Figure 2.8 : Oxidative polymerization of carbazole.

2.3.3 PTh

Polythiophene (PTh) (Fig 2.9) has drawn much attention in recent years because of its attractive applications as conductor, electrode material, and organic semiconductor such as rechargeable batteries, corrosion protection, electrocatalysis, antistatic coatings, electromagnetic shielding, electrochromic displays, field-effect transistors. [24,26].

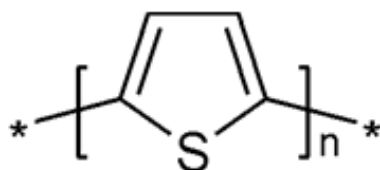


Figure 2.9 : Structure of PTh

The conducting PTh has the structure of π -electrons conjugated on the polymer backbone that allows superior electrical conductivity than the ordinary PTh molecule. The electrical conductivity can also be controlled by doping with certain kind of non-redox dopant [15,20].

Th is polymerized mostly by oxidative polymerization in organic solvents with Li^+ and Na^+ salts. [69,70]. Polymerization mechanism of Th can be seen in the Fig. 2.10 .

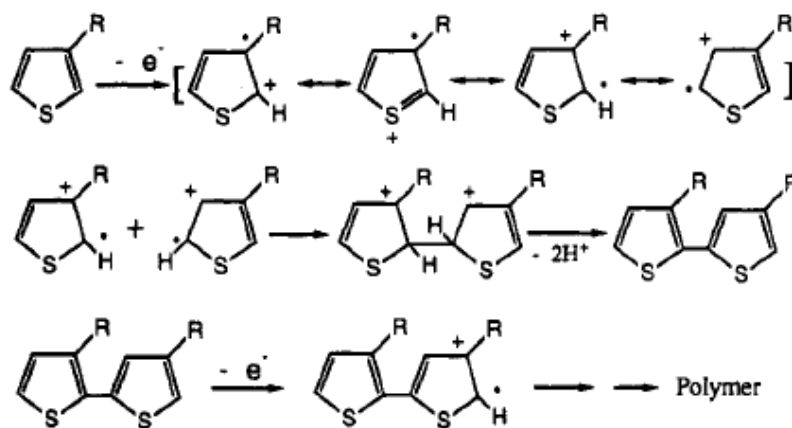


Figure 2.10 : Oxidative polymerization of Th.

2.3.4 PIn

Among polyconjugated conducting polymers, polyindoles from anodic coupling of indoles display a noticeable interest since they have been considered in applications such as sensor and because they may be model polymers for biopolymers such as melanin[16]. PIn can be obtained after anodic oxidation of indole (see in the figure)

in various electrolytes [15-19]. The qualifications of resulted polymer such as providing corrosion protection, is changed by the reaction conditions. [15,17] . Furthermore, electrochemical oxidation of indole in ACN/ LiClO₄ electrolyte medium gives an electrochromic polymer film with good air stability [15].

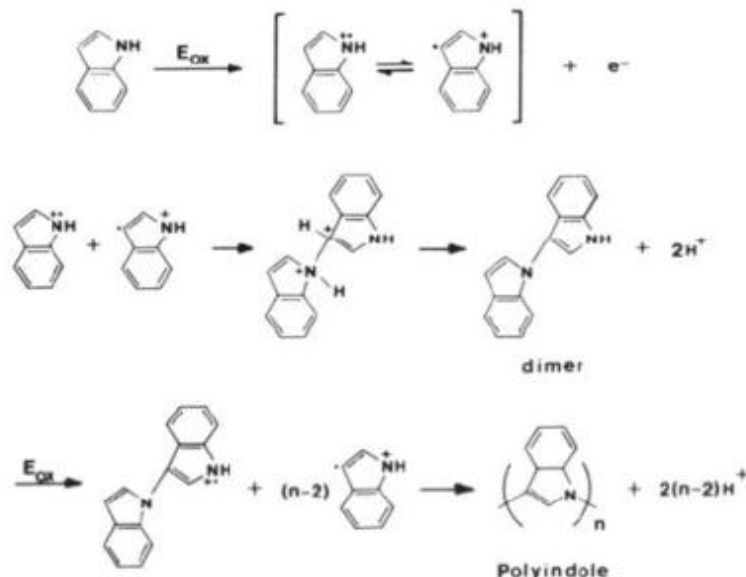


Figure 2.11 : Oxidative polymerization of Indole.

2.4 Polymerization Techniques

There are two main polymerization types for conducting monomers. First is chemical and second is electrochemical polymerization. In this thesis we will be interested in electrochemical polymerization.

Potentiodynamical method (PD) is the most popular electrochemical method in polymerization of conducting polymers. It provides both qualitative and quantitative information besides reliable characterization. A potential step profile is applied to the electrochemical cell, the response of the cell is measured at the end of each step. This technique provides to measure only the faradaic current, because the capacitive current, that appears at the beginning of the step, arising from the double layer charging, has a much higher decay rate. The rate of change of potential with time is referred to as the scan rate. [10,13,14,15]

Potentiostatical method (PS) is an electrochemical polymerization method in which a constant potential is applied and the current, I , is measured as a function of time, t .

This I-t response is comprised of two components: the current due to charging the double-layer and the other due to the electron transfer reaction with the electroactive species [11,12].

Galvanostatical method (GS) is the most basic constant current technique for polymerization of electro active monomers. In CP, a constant current step is applied across an electrochemical cell (without stirring) and the response of cell is measured as the voltage (V). It is distinguished from galvanostatics, a constant-current technique useful for the determination of heterogeneous electron-transfer rates [25].

2.5 Characterization

2.5.1 CV

The voltage is swept between two values (see below) at a fixed rate, however now when the voltage reaches V_2 the scan is reversed and the voltage is swept back to V_1 . A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is shown in below. Again the solution contains only a single electrochemical reactant. The forward sweep produces an identical response to that seen for the LSV experiment. When the scan is reversed we simply move back through the equilibrium positions gradually converting electrolysis product (Fe^{2+}) back to reactant (Fe^{3+}). The current flow is now from the solution species back to the electrode and so occurs in the opposite sense to the forward sweep but otherwise the behaviour can be explained in an identical manner. For a reversible electrochemical reaction the CV recorded has certain well defined characteristics.

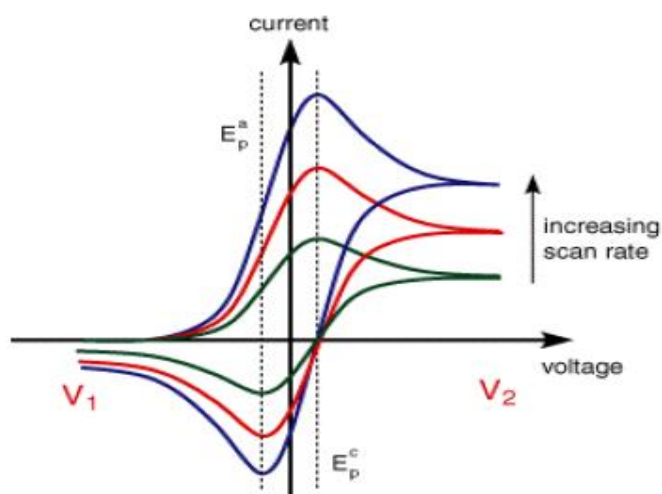


Figure 2.12 : Representation of CV.

The influence of the voltage scan rate on the current for a reversible electron transfer can be seen in Fig. 2.12 . As with LSV the influence of scan rate is explained for a reversible electron transfer reaction in terms of the diffusion layer thickness. The CV for cases where the electron transfer is not reversible show considerably different behaviour from their reversible counterparts.

By analysing the variation of peak position as a function of scan rate it is possible to gain an estimate for the electron transfer rate constants [4].

2.5.2 EIS

Electrical resistance is a concept that almost everyone is familiar. It is the ability of a circuit element to resist the flow of electrical current. Ohm's law defines resistance in terms of the ratio between voltage E and current I .

$$E = I \times R \quad (2.1)$$

This well known relationship can be used to define only one circuit element; the ideal resistor.

An ideal resistor's properties are;

- It follows Ohm's Law at all current and voltage levels.
- It's 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. Assume that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series) [41].

Electrochemical impedance spectroscopy is a power tool for examining many chemical and physical processes in solutions as well as solids. For solution phase

electrochemistry a complex sequence of coupled processes such as, electron transfer, mass transport and chemical reaction can all control or influence the output from an electrochemical measurement. [45].

Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell. Assume that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series) (3).

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" and "Bode plot". See on the Fig. 2.13 .

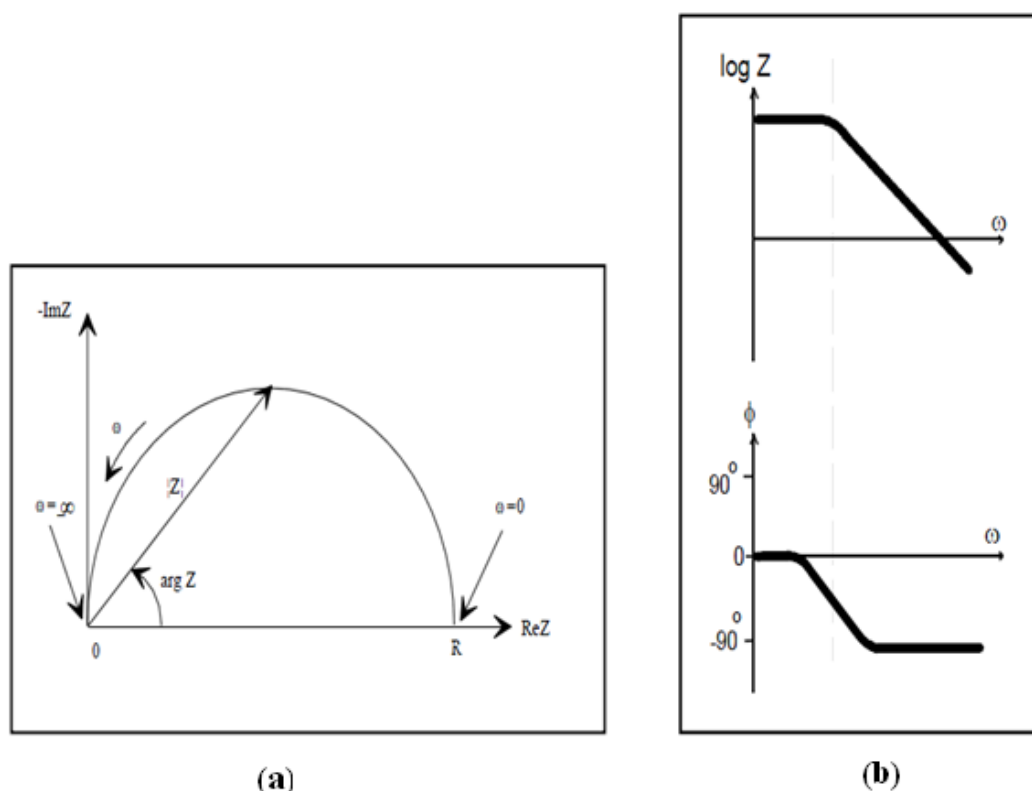


Figure 2.13 : (a) Nyquist plot (b) Bode plot.

Notice that in this plot the y-axis is negative and that each point on the Nyquist plot is the impedance at one frequency. Fig. 2.13 has been annotated to show that low frequency data are on the right side of the plot and higher frequencies are on the left.

On the Nyquist plot the impedance can be represented as an vector (arrow) of length $|Z|$. The angle between this vector and the x-axis is ϕ ($=\arg Z$) [41,45].

EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as resistors, capacitors, and inductors. To be useful, the elements in the model should have a basis in the physical electrochemistry of the system.

As an example, most models contain a resistor that models the cell's solution resistance. Addition of impedance and volt can be seen in Fig. 2.14 and in Fig. 2.15, respectively [61].

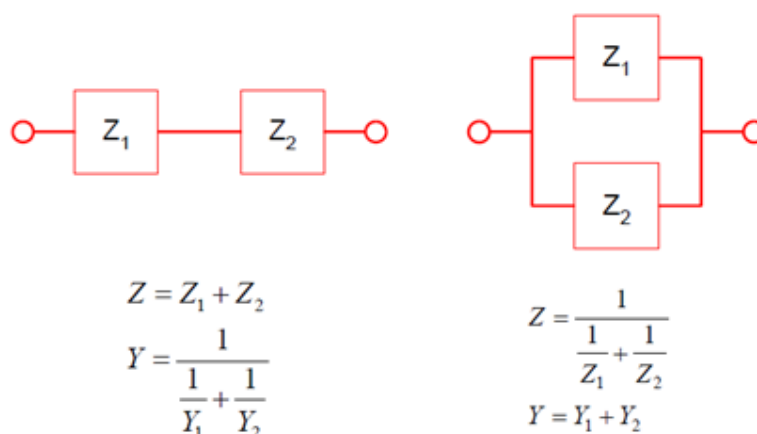


Figure 2.14 : Addition of impedance.

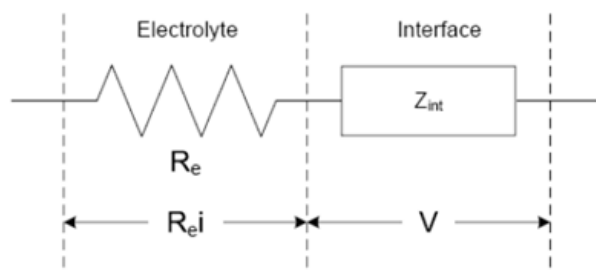


Figure 2.15 : Addition of voltage.

An equivalent circuit for a simple electrochemical reaction and a Randless circuit are given in Fig. 2.16 and Fig. 2.17, respectively.

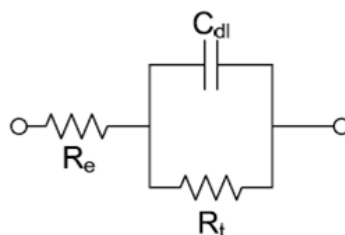


Figure 2.16 : Equivalent circuit for a simple electrochemical reaction.

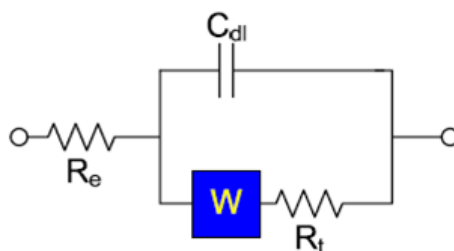


Figure 2.17 : Equivalent circuit for a simple electrochemical reaction with mass transfer. (Randless circuit).

Equivalent Circuit Elements;

- Electrolyte resistance (R_e , R_s): 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.
- Double layer capacitance (C_{dl}): A electrical double layer exists on 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 ions charges. The separation is very small, often 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 20 to 60 μF of capacitance for every cm^2 of electrode area.

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

- **Polarisation Resistance (R_p):** 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 through 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.
- **Diffusion impedance (Z_w):** Diffusion also can create an impedance called the Warburg-impedance. The 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, increasing the Warburg-impedance.
- **Charge transfer resistance (R_{ct}):** A characteristic quantity for the charge-transfer step of an electrode reaction indicative of its inherent speed: a large charge-transfer resistance indicates a slow step [38].

EIS and equivalent circuit models is a very useful combination to understand the conducting polymers' nature. In PPy case, there are a lot of reported EIS and equivalent circuit models. [46-54]. An example of PPy circuit model is seen in the Fig. 2.18 .

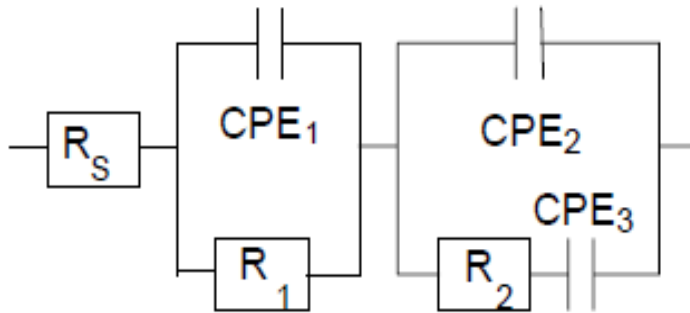


Figure 2.18 : Equivalent circuit used to fit the impedance results.

It can be assigned that; ($R_1//CPE_1$) to the polymer |electrolyte interface and ($R_2//CPE_2$) to the electrode | polymer interface. R_1 is related to an electronic charge transfer resistance during the photoelectrochemical process and/or an ionic charge transfer resistance associated to the redox process of the polymer. CPE_1 is then related to the space charge capacitance and/or to the contra-ion accumulation at the

polymer | electrolyte interface. R_2 corresponds to the electronic charge transfer at the electrode | polymer interface and the CPE2 element is associated to the double layer capacitance at this interface. The CPE3 element corresponds to a Warburg element, responsible for the diffusional control of the system [37].

There are EIS measurements and equivalent circuits models for PCz also. [55,57,58]. An example of PCz modelling is seen in the Fig. 2.19 .

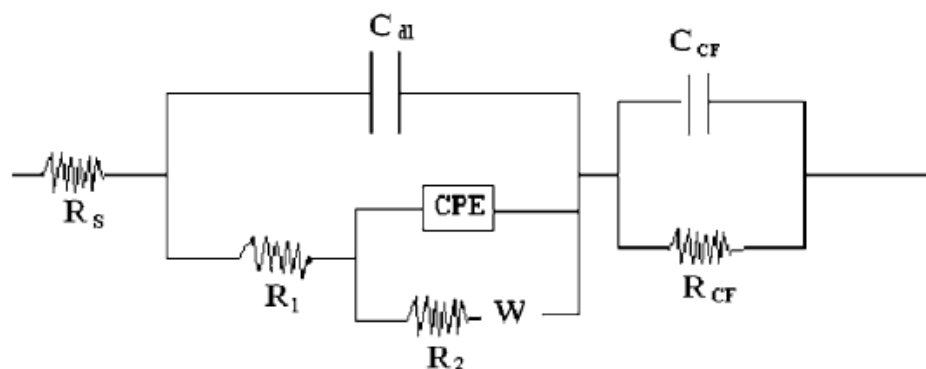


Figure 2.19 : Electrical equivalent circuit model of PCz.

In Fig. 2.19, R_s is the bulk solution resistance of the polymer and the electrolyte, C_{dl} is the parallel combination of the double layer capacitance, R_1 is electrolyte resistance. A series connection to R_1 made up from using constant phase element (CPE) in parallel with R_2 and W . R_2 is the charge transfer impedance, W is the Warburg impedance of the polymer. CPE describes the capacitor at the film |electrolyte interface considering the irregular geometry of the surface of the polymer network and the counter-ions binding to sites of different energies [61].

Since it is difficult to polymerize the indole, there are relatively less studying on PIN and its electrochemical impedance qualifications. [63-65]. There is not any characteristic equivalent circuit diagram for In polymerization.

There are less studies on PTh's electrochemical impedance behaviour [66,67]. An example of equivalent circuit modelling of PTh can be seen in the Fig. 2.20 .



Figure 2.20 : Equivalent circuit model of PTh

3.EXPRERIMENTAL

3.1. Materials:

Pyrrole (Py) was supplied from Fluka, Carbazole (Cz) from BHD Chemicals, Indole (In) from Merck and Thiophene (Th) from Sigma Aldrich and they were used as received.

Tetrabutylammoniumtetrafluoroborate (Bu_4NBF_4) Tetrabutylammonium perchlorate (Bu_4NClO_4) and Sodium perchlorate (NaClO_4) were supplied from Fluka, Acetonitrile (ACN) from Carlo Erband and they were all in electrochemical grade and used as recieved.

Electrodes; a three electrode system was employed as, platinumium button electrode (BASi stationary voltammetry electrode; diameter 1.6 mm, area 0.02 cm^2) as working electrode (WE), platinumium wire as counter electrode (CE) and Ag/ AgCl as reference electrode (RE).

3.2. Polymerizations:

Polymerization reactions were performed at room temperature ($23 \pm 2^\circ\text{C}$) by using PARSTAT 2263 model potentiostat. Solvent was selected as ACN, different electrolyte systems were used for each monomer such as; Bu_4NBF_4 for Py, Bu_4NClO_4 for Cz, NaClO_4 for Th and IN. Potentiodynamic (PD), potentiostatic (PS) and galvanostatic (GS) methods were performed on PARSTAT 2263 model potentiostat in a three electrode system with Power Suite software. Platinumium button electrode was used as the working electrode whereas platinumium wire was the counter electrode and the Ag/AgCl was reference electrode.

3.2.1. Py polymerization:

PD polymerization was permormed in the range of -0.2 and 1.2V, PS polymerization at 1.0V constant voltage and GS polymerization at 2.10^{-4} A in 5mM Py and 0.1 M Bu_4NBF_4 containing ACN solution.

3.2.2. Cz Polymerization

PD polymerization was performed in the range of 0-1.4V, PS polymerization at 1.2V constant voltage and GS polymerization at $2 \cdot 10^{-4}$ A in $5 \cdot 10^{-2}$ M Cz and 0.1 M Bu_4NClO_4 containing ACN solution.

3.2.3. IN polymerization

PD polymerization was performed in the range of 0-1.5V, PS polymerization at 1.5V constant voltage and GS polymerization at $3 \cdot 10^{-4}$ A in 0.1 M IN and 0.1 M ACN/NaClO_4 containing ACN solution.

3.2.4. Th polymerization

PD polymerization was performed in the range of 0-1.8V, PS polymerization at 1.5V constant voltage and GS polymerization at $5 \cdot 10^{-4}$ A in 0.1 M Th and 0.1 M ACN/NaClO_4 containing ACN solution.

3.3.Characterizations:

3.3.1. Cyclic Voltammetry (CV)

Experiments were performed at room temperature (23 ± 2 °C) by using PARSTAT 2263 model potentiostat. Redox behaviour of polymers were investigated by CV at different scan rates (100-500 mV/s) in monomer free supporting electrolyte. Anodic and cathodic peak potential (E_a , E_c), current (I_a , I_c), potential differences (ΔE) and current ratios (I_a/I_c) were obtained and reversibility of polymeric films were compared in order to determine the optimum conditions.

3.3.2. Electrochemical impedance Spectroscopy (EIS)

Electrical and capacitive properties were determined by the electrochemical impedance spectroscopy and experiments were performed at room temperature (23 ± 2 °C) in monomer free solution by using PARSTAT 2263 model potentiostat. A three electrode system was used as polymerization reactions. Nyquist, Bode Phase and Bode Magnitude diagrams were plotted in the absence of DC voltage and under 1V constant voltage during measurement.

Solution resistance (R_s), polymer resistance (R_p), double layer capacitance (C_{dl}) and specific capacitance (C_{sp}) values were determined for all polymerization times and methods. For the determination of C_{sp} , the Z_{im} value of nyquist plot which was corresponding to the 0.01 Hz on the bode magnitude diagram, was fitted into the

$C = 1/2\pi fZ$ equation. C_{dl} was also determined by using the same equation. The Zim value of Bode Magnitude diagram which was corresponding to the 0.169 Hz was fitted into the equation and frequency was fitted as 1 Hz. [Grija, 2006]

The impedance data were fitted utilizing equivalent electrical circuits by using the ZSimp-Win Electrochemical Impedance Spectroscopy (EIS) Data Analysis Software, delivered by EChem Software USA.

3.3.3. Spectroelectrochemistry

In-situ spectroelectrochemical measurements were performed by using CH Instruments 400 A Electrochemical analysis and Hitachi U-0080D UV spectrometer together. Each monomer were polymerized on ITO bulk electrode by application of constant voltage; 1V for Py, 1.2V for Cz, 1.5 V for both IN and Th at 120 s. The UV visible absorption spectrum at polymer film at different applied potentials were obtained in monomer free supporting electrolyte.

3.3.4. AFM measurements

AFM measurements were performed in Nanosurf Easy Scan 2 AFM-STM, between the $3.24 \times 3.24 \mu\text{m}^2$. PPy, PCz, PIN and PTh were obtained by PS method at 120 s onto ITO bulk electrode by application of constant voltage; 1V for Py, 1.2V for Cz, 1.5 V for both IN and Th.

4. RESULTS AND DISCUSSIONS

The polymer growth of Py, Th, Cz, and IN were carried out by three different methods; potentiodynamical method (PD) were performed, by scanning up to the oxidation potential of the monomer and then down to the reduction potential by applying 2, 4, and 8 cycles. Same monomers were also electrogenerated potentiostatically (PS) by applying a potential step and recording the current vs. time at 30, 60 and 120 s or galvanostatically (GS) by applying a current step and recording the potential vs. time at 30, 60 and 120 s. The optimum polymerization times were determined for each method and the redox state of the polymers generated at the electrode surface were also monitored by voltammetry at different scan rates.

On the other hand EIS measurements were also performed to gain ideas about the charge storage behaviour of polymers.

Results were compared to understanding fundamental electrode processes upon electropolymerization of monomers and allow one to have a new insight into the electropolymerization reactions, thus helping electrochemists to improve the preparation of their polymers.

4.1. Comparison of Polymerization Conditions and Characterization of Py

4.1.1. Potentiodynamically Polymerization of Py

Polymerization of Py has been performed by PD method at 2, 4 and 8 cycles. The cyclic voltammograms during polymerizations (Fig. 4.1, 4.3, 4.5) and the CV of polymer films were given (Fig. 4.2, 4.4, 4.6.). Redox parameters anodic potential (E_a), cathodic potential (E_c), anodic current (I_a), cathodic current (I_c), peak potential differences (ΔE), peak current ratios (I_a/I_c), obtained from these voltammograms were summarized in the Table 4.1- 4.3. The relation between current and the scan rates of the polymeric film obtained at different polymerization times were compared in Fig. 4.2, 4.4 and 4.6.

The PD polymerization of Py in ACN/0.1 M Bu₄NBF₄ at 2 cycles was given in Fig 4.1.

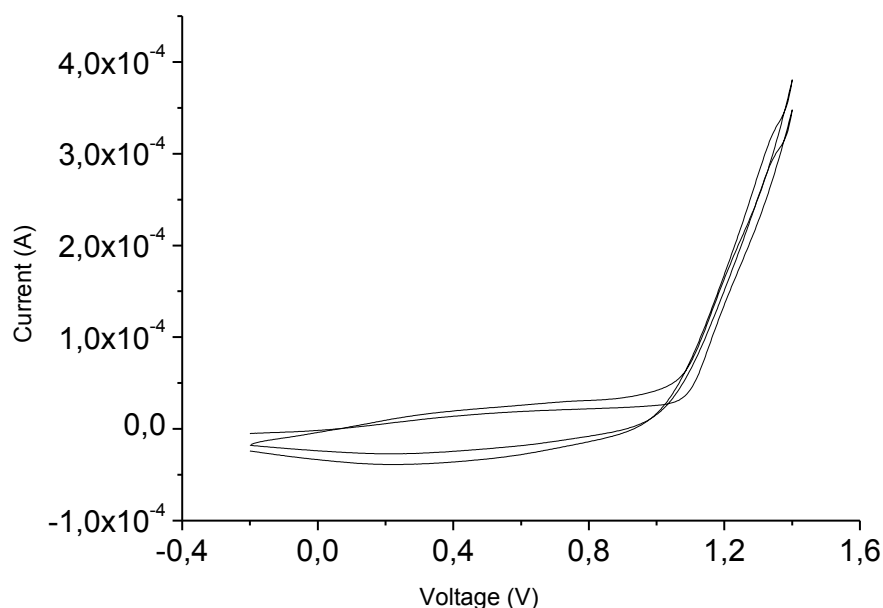


Figure 4.1 : PD electrodeposition of 5 mM Py at 2 cycles in 0.1 M Bu₄NBF₄ containing ACN at the scan rate of 50 mV/s.

As it can be seen, when the potential sweep was performed between -0.2 and 1.2 V, oxidation of Py occurred at the 1.0V. The coated electrode was then transferred into monomer free solution and the scan rate dependence of resulting film investigated and given in Fig. 4.2.

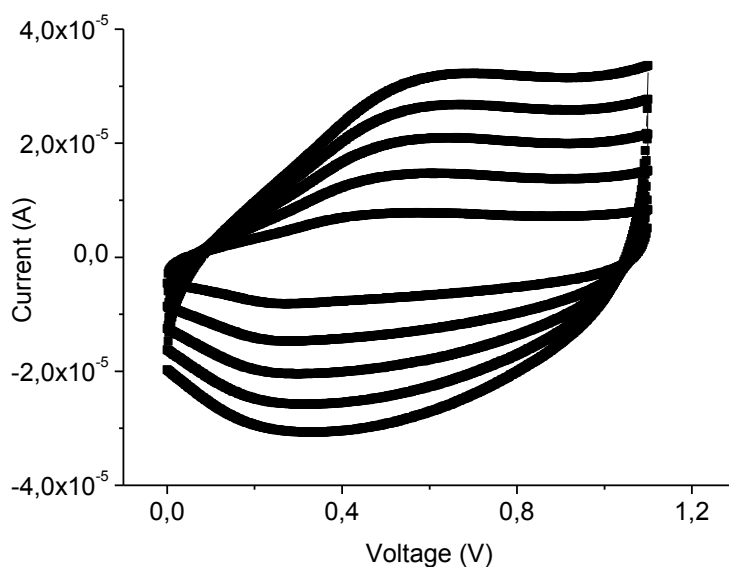


Figure 4.2 : Voltammetric response of PPy polymerized by PD method at 2 cycles in 0.1 M Bu₄NBF₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

CV of this film showed one broad wave at about + 0.4 V. Even the shifts were observed as the scan rates increased, the polymer film was still reversible. (Fig. 4.2) Results obtained from the voltammogram were presented in the Table 4.1

Table 4.1 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Py polymerized by PD method at 2 cycles

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	383	352	6.7	7.6	31	0.9
200	431	386	13.1	14.9	45	0.9
300	467	420	18.9	20.0	47	0.9
400	511	462	24.4	24.9	49	1.0
500	537	491	30.4	29.2	46	1.0

In all cases ΔE values were very small and the peak ratios were very close to unity, showing thin film behaviour and good electrochemical reversibility. As it can be seen from the Table 4.1 , the best reversibility was obtained at higher scan rates.

PD cally polymerization of Py by applying 4 cycles was given in the Fig. 4.3. Monomer concentration, voltage interval and electrodes were kept same with the polymerization conditions of Py at 2 cycles and similar investigations were done. The voltammetric response of polymeric film was given in Fig 4.4

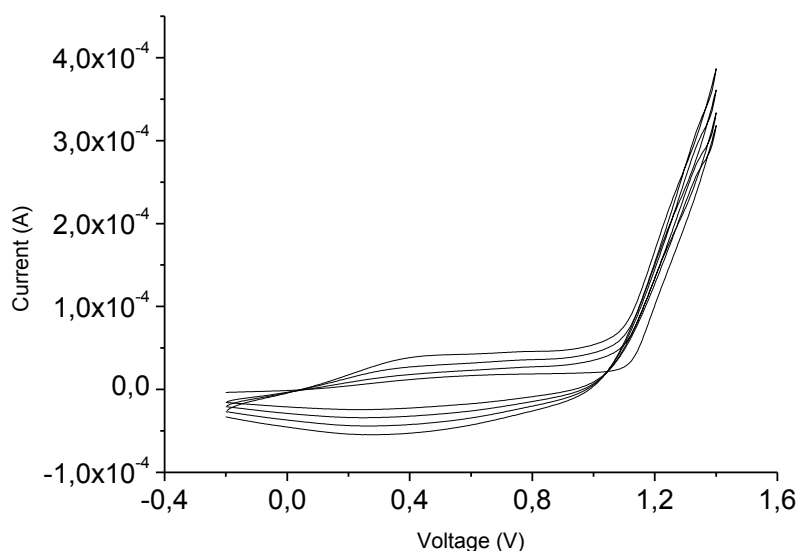


Figure 4.3 : PD electrodeposition of 5 mM Py at 4 cycles in 0.1 M Bu_4NBF_4 containing ACN at the scan rate of 50 mV/s.

Fig. 4.3 presents the PD growth of the PPy at 4 successive cycles. Broad peak at 0.4 V, increase in current by increase in cycle numbers indicated the polymer growth on the electrode surface.

The CV of resulting polymeric film in monomer free solution was given in the Fig 4.4 As the polymerization time increased, the sharper shifts on the E_a and E_c were observed which indicated the decrease of reversibility of the film. The reversibility of film decreased due to increases in thicknesses and due to the limiting diffusion.

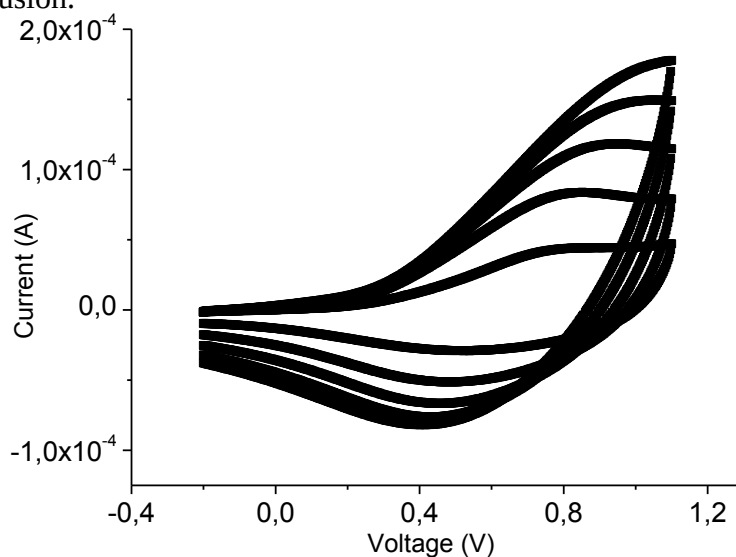


Figure 4.4 : Voltammetric response of PPy polymerized by PD method at 4 cycles in 0.1 M Bu_4NBF_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Results obtained from the voltammograms at different scan rates were summarized in the Table 4.2

Table 4.2 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Py polymerized by PD method at 4 cycles

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	628	532	3.3	2.9	96	1.1
200	679	557	7.3	5.1	122	1.4
300	781	561	1.7	6.2	220	1.7
400	845	564	13.2	6.9	281	1.9
500	880	580	15.2	7.2	300	2.1

As it can be seen from the Table 4.2 , at high scan rates, limited diffusion current became more pronounced, ΔE and peak ratio increased.

PD polymerization of Py at 8 cycles was given in the Figure 4.5. Monomer concentration, voltage interval and electrodes were kept same with previous measurements and similar investigations were done.

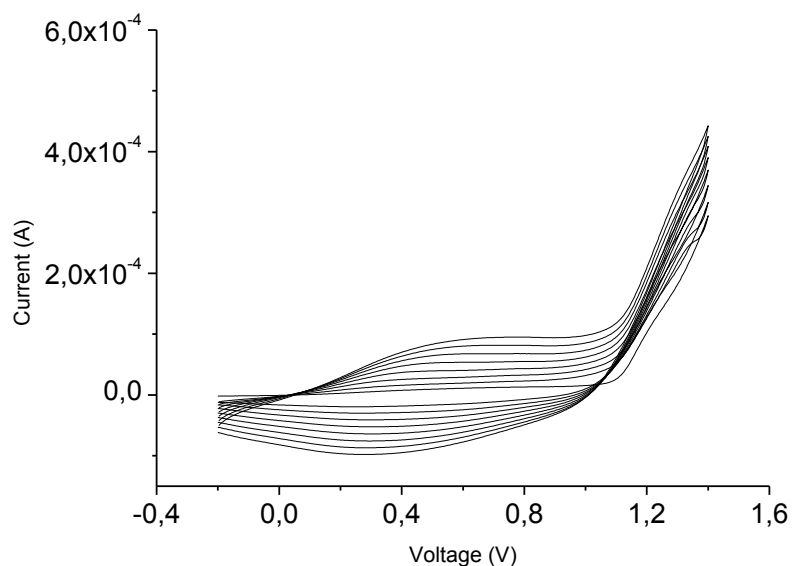


Figure 4.5 : PD electrodeposition of 5 mM Py at 8 cycle in 0.1 M Bu_4NBF_4 containing ACN at the scan rate of 50 mV/s.

Figure 4.5 presented the electrochemical growth of the PPy film by PD method at 8 cycles. Voltammetric response of PPy film was given below (Fig 4.6). The current intensity of the broad peak at 0.4 V showed increase in the regular deposition of polymeric film.

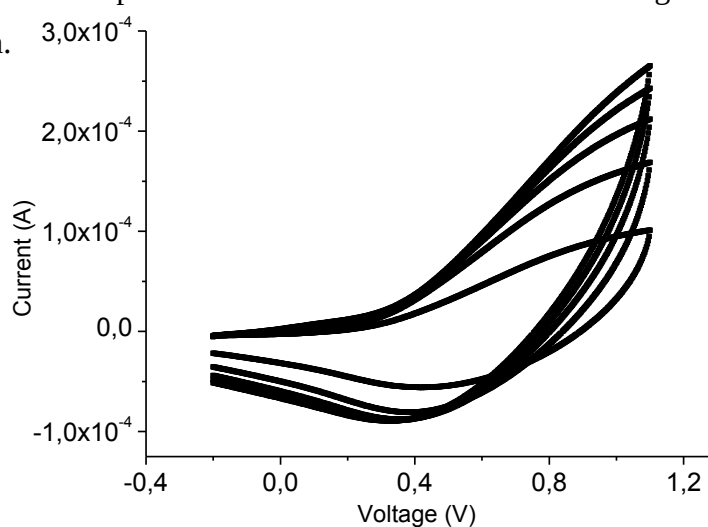


Figure 4.6 : Voltammetric response of PPy polymerized by PD method at 8 cycles in 0,1 M Bu_4NBF_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Further increase in thickness resulted a deformation of the shape of reversible voltammogram. Results obtained from these voltammograms were summarized in Table 4.3.

Table 4.3 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Py polymerized by PD method at 8 cycles.

Scan rate (mV/s)	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	768	392	7.1	5.7	376	1.2
200	794	398	12.7	8.0	398	1.6
300	858	430	16.3	8.6	428	1.9
400	889	446	19.2	8.3	443	2.3
500	928	458	21.9	8.7	458	2.5

Increase in polymerization time resulted thicker and more resistive film on the electrode surface. Potential differences and peak ratios increased with increasing scan rate due to limited diffusion.(Table 4.3)

Comparasion of current densities vs scan rates of PPy were given in the Fig. 4.7.

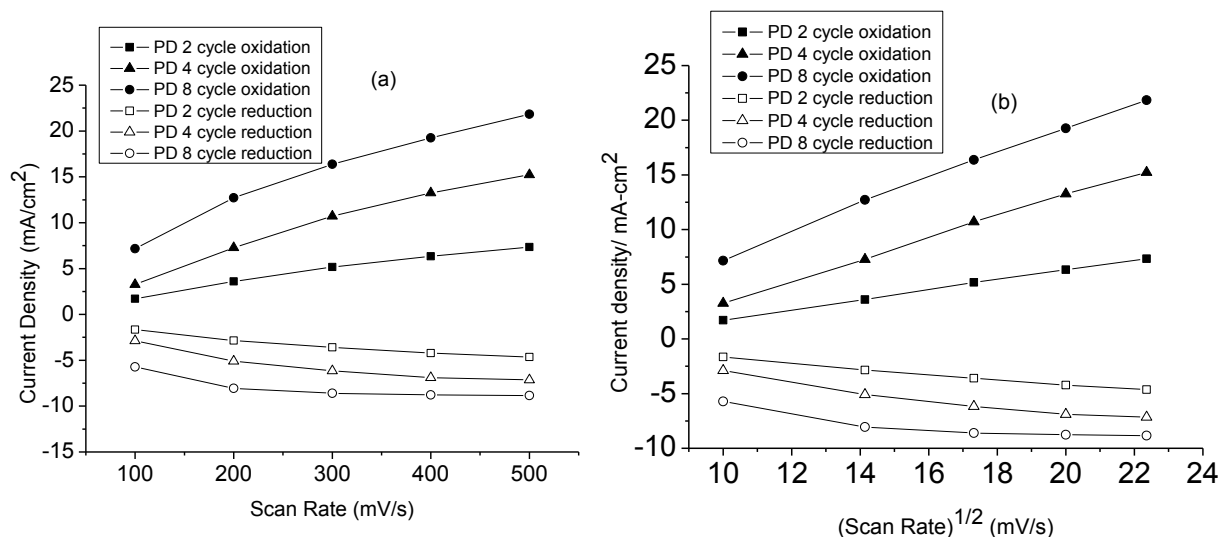


Figure 4.7 : (a)Current density versus scan rate, (b) Current density versus square root of scann rate plot of PPy films obtained by PD method at different cycle numbers (2, 4 and 8 cycles)

In the case of PD, short polymerization time (2cycles) contributed thin film character whereas the long polymerization times (4 and 8 cycles) caused diffusion control. (Fig 4.7)

For the PPy obtained at 2 cycles, at low scan rate, peak currents vary linearly with the scan rate, which is characteristic of the behaviour of a thin layer material deposited on the electrode. Conversely, at higher scan rates, linear variation with the square root of the scan rate was frequently observed, corresponding to diffusion limited currents, arising either from charge transfer process (hopping mechanism) or from an ionic contribution (diffusion of counterions). This idea also supported by increase in peak potential differences (ΔE) and peak current ratios with increasing scan rates (Table 4.1-4.3).

4.1.2 Potentiostatic Polymerization of Py.

The polymerization of Py by PS method at 30 s in ACN/ 0.1 M Bu_4NBF_4 was given in Fig 4.8 and the voltammetric response of polymer film was presented in Fig 4.9.

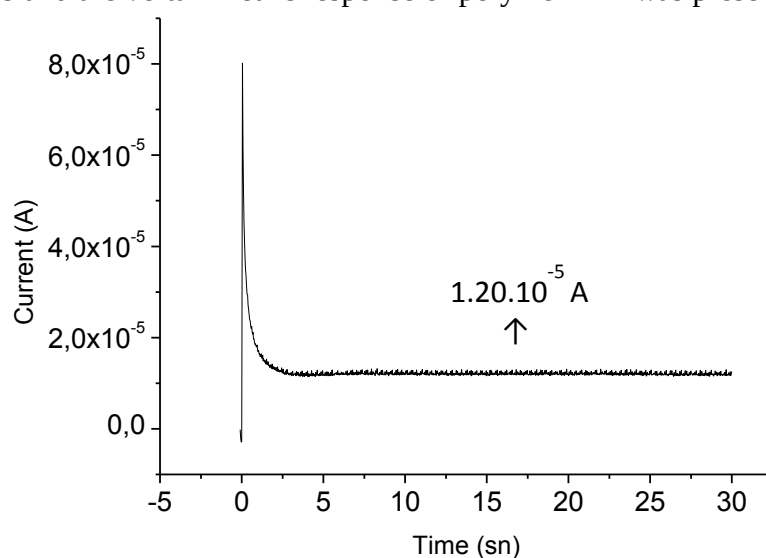


Figure 4.8 : PS electrodeposition of 5 mM Py at 30 s in 0.1 M Bu_4NBF_4 containing ACN.

While the constant voltage was applied, a decrease in current was seen after the first 5 s of polymeric growth and after it was stabilized at $1.20 \cdot 10^{-5}$ A.(Fig. 4.8)

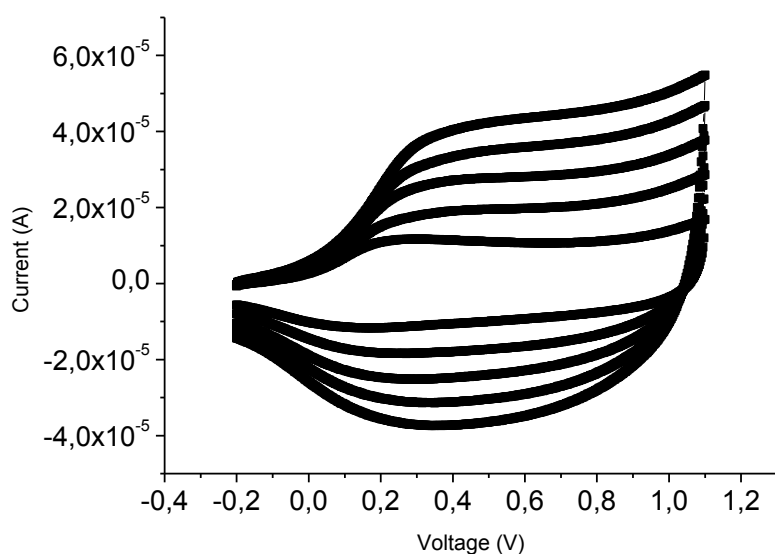


Figure 4.9 : Voltammetric response of PPy polymerized by PS method at 30 s in 0.1 M Bu_4NBF_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

The CV of the polymer film growth by PS at 30 s, showed one broad wave at +0.25 V and a peak at +0.3 V which were smaller than the ones observed from film obtained by PD method at 2 cycles. Besides shifts were not observed at oxidation and reduction peaks. These results demonstrated that the film obtained by PS method was more electroactive and reversible than the film obtained by PD method. (Fig. 4.9) The parameters obtained from voltammetric response at different scan rates demonstrated in Table 4.4.

Table 4.4 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Py polymerized by PS at 30 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	332	293	0.6	0.7	39	0.8
200	356	309	1.2	1.2	47	0.9
300	395	344	1.6	1.6	51	1.0
400	414	369	2.1	1.9	45	1.1
500	433	392	2.6	2.3	41	1.1

Similarly to PD method, in all cases ΔE values were very small and peak ratios were very close to unity, showing thin film behaviour and good electrochemical reversibility. The best reversibility was obtained at 300 mV/s.

PS polymerization of Py at 60 s was given in the Fig. 4.10. Monomer concentration, applied voltage and electrodes were kept same with previous measurements and similar investigations were done. The voltammetric response of the film was given in Fig. 4.11.

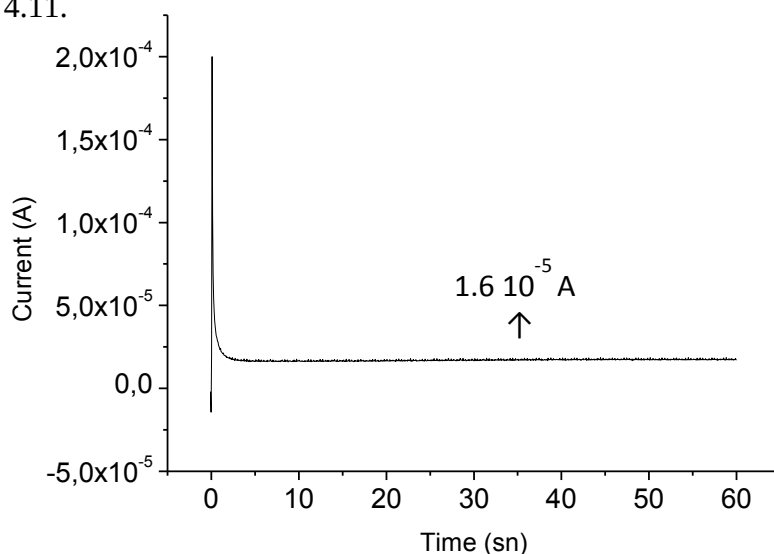


Figure 4.10 : PS electrodeposition of 5 mM Py at 60 s in 0.1 M Bu_4NBF_4 containing ACN.

As it can be seen from the Fig 4.10 a sharp decrease on current was observed after the first 5 s of polymerization, then it was stabilized at $1,6 \cdot 10^{-5}$ A which was similar to the polymerization of Py at 30 s. The CV of PPy film growth by PS method at 60 s showed one broad wave at 0.25 V and a peak at 0.30 V which were higher than the ones obtained at 30 s. (Fig. 4.9, 4.11)

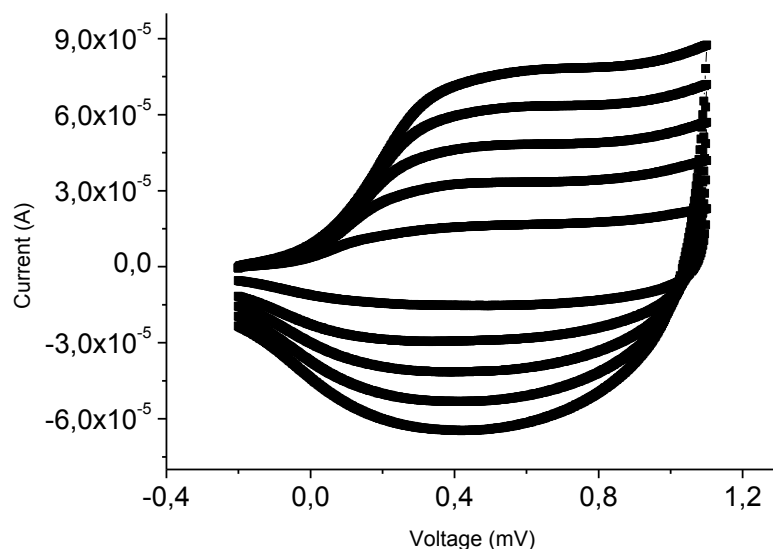


Figure 4.11 : Voltammetric response of PPy polymerized by PS method at 60 s in 0.1 M Bu₄NBF₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

The results obtained from these measurements were summarized in Table 4.5.

Table 4.5 : E_a, E_c, I_a, I_c, ΔE, I_a/I_c values of PPy polymerized by PS method at 60 s.

Scan rate m V/s	E _a (mV)	E _c (mV)	I _a (μA)	I _c (μa)	ΔE (m V)	I _a /I _c
100	299	321	1.4	1.5	22	0.9
200	350	305	3.1	2.9	45	1.0
300	385	372	4.5	4.3	13	1.1
400	443	401	6.0	5.3	42	1.1
500	484	411	7.8	6.3	73	1.2

At all scan rates, electrochemical reversibility of film obtained by PS method at 60 s, seems better than the film obtained by PD method at 4 cycles. The best reversibility was obtained at 200 mV/s. (Table 4.5)

Polymerization of Py by PS method at 120 s was given in the Fig. 4.12.

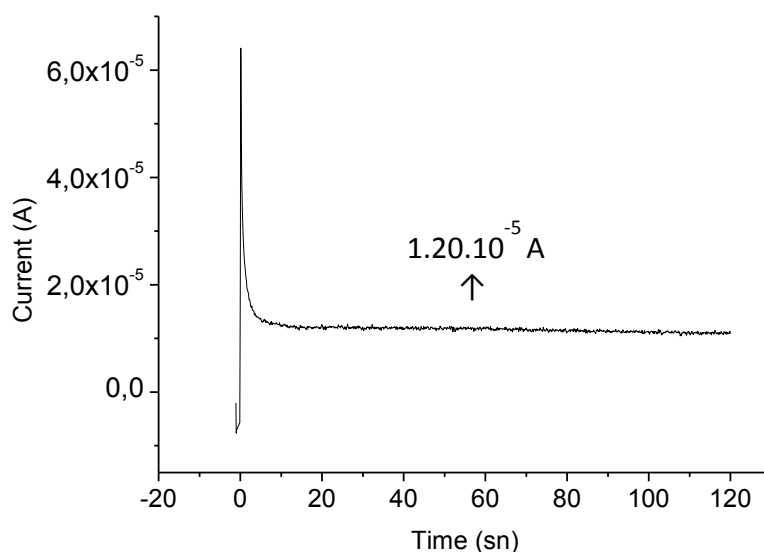


Figure 4.12 : PS electrodeposition of 5 mM Py at 120 s in 0.1 M Bu_4NBF_4 containing ACN.

In this case the current value stayed constant at $1.20 \cdot 10^{-5}$ A which was lower than the film obtained at 60 s. (Fig 4.12). The voltammetric response of the film was given in Fig 4.13

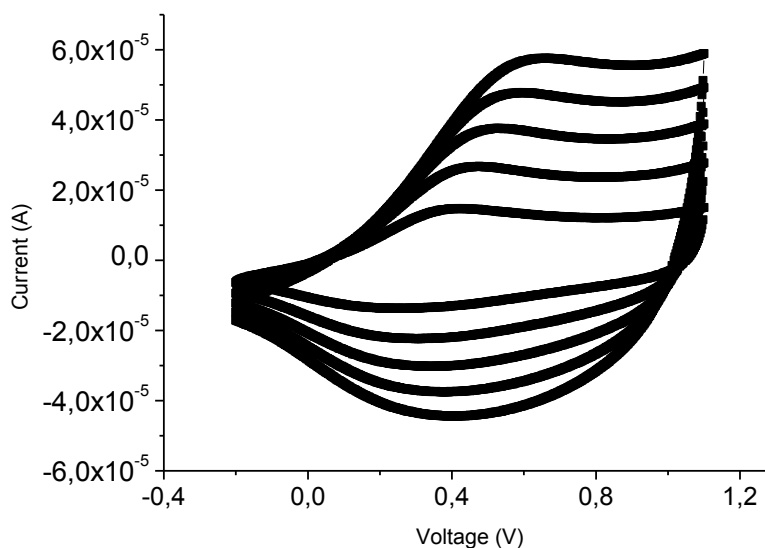


Figure 4.13 : Voltammetric response of PPy polymerized by PS method at 120 s in 0.1 M Bu_4NBF_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

The results obtained from these measurements were summarized in Table 4.6. As it can be seen from the Fig 4.13 and the Table 4.6 the reversibility of the polymeric film decreased. As the polymerization time increased, a thicker and more resistive

polymeric layer occurred on the electrode surface which made the charge/discharge process more difficult.

Table 4.6 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PPy polymerized with PS at 120 s.

Scan rate (mV/s)	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	318	330	2.3	1.8	12	1.3
200	388	369	3.9	2.8	19	1.4
300	452	414	5.6	3.9	38	1.4
400	503	475	6.9	5.1	28	1.4
500	554	516	8.6	6.2	38	1.4

In contrast to PD method, PPy films showed still reversible behaviour even at higher scan rates. (Table 4.6). This might be due to the decrease in current after 5 s and because of the resistivity of polymeric film formed on the electrode surface. Small current intensities contributed to the polymer growth after 5 s unlike the film obtained by PD method.

Comparasion of current intensities vs scan rates of polymer films obtained by PS was given in the Fig. 4.14

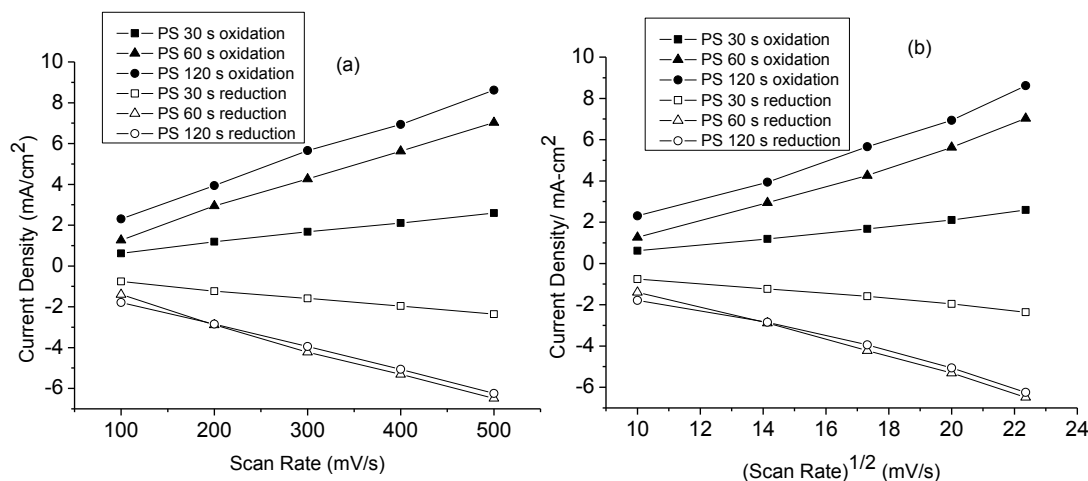


Figure 4.14 : (a) Current density versus scan rate, (b) Current density versus square root of scan rate plot of PPy films obtained by PS method at different polymerization times (30, 60 and 120 s).

In the case of films obtained by PS method at 30 and 60 s showed the thin film character where as increasing of the polymerization time to 120 s caused the diffusion controlled process. (Fig. 4.14)

4.1.3. Galvanostatic Polymerization of Py

GS polymerization of Py in ACN/0.1 M Bu₄NBF₄ at 30 s was given in Fig 4.15. Voltammetric response of polymer film was presented in Fig. 4.16.

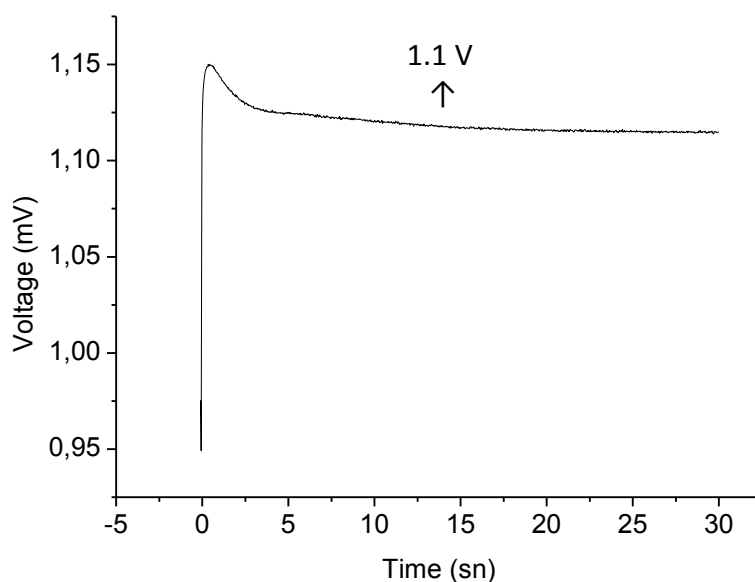


Figure 4.15 : GS electrodeposition of 5 mM Py at 30 s in 0.1 M Bu₄NBF₄ containing ACN.

After a sharp increase and a small decrease on the voltage during 5 s, the voltage was stabilized at 1.12 V and kept constant during the polymerization. (Fig. 4.15)

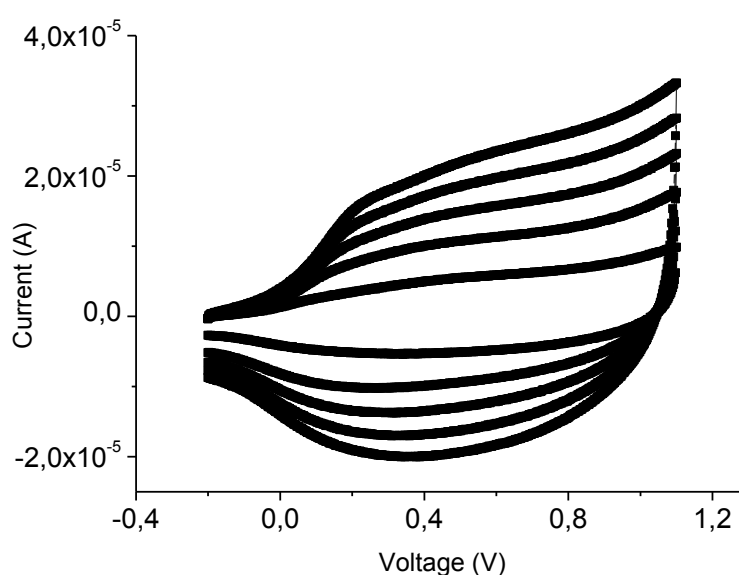


Figure 4.16 : Voltammetric response of PPy polymerized by GS method at 30 s in 0.1 M Bu₄NBF₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

The CV of the polymer film growth by GS method at 30 s, showed one broad peak at +0.3 V which was approximately similar to the PD and PS polymerizations. Since the onset of oxidation potential of polymer film shifted to lower potential value (0.1V), it can be said that the charge/discharge process of polymer film obtained by GS method was more easier than the ones obtained by PD and PS methods. (Fig 4.16) The parameters obtained from voltammogram at different scan rates demonstrated in Table 4.7.

Table 4.7 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PPy polymerized by GS method at 30 s.

Scan rate (mV /s)	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	328	296	0.4	0.5	32	0.8
200	347	309	0.9	1.0	38	0.9
300	382	331	1.3	1.3	51	1.0
400	392	350	1.7	1.7	42	1.0
500	420	382	2.0	2.0	38	1.0

As it can be seen from the Table 4.7, similarly to PD and PS methods in all cases ΔE values were very small and peak ratios were very close to unity, showing thin film behaviour and good electrochemical reversibility.

GS cally polymerization of Py at 60 s was given in the Fig. 4.17. Monomer concentration, applied voltage and electrodes were kept same and similar investigations were done. The voltammetric response of the film was in Fig. 4.18

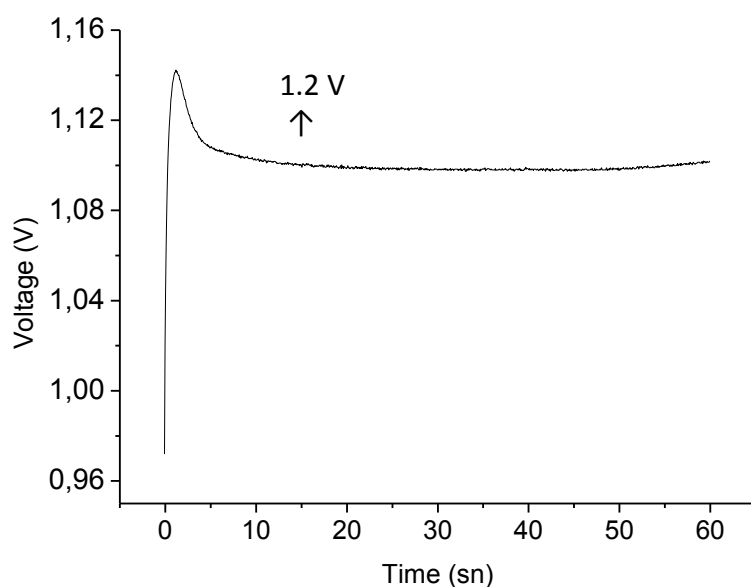


Figure 4.17 : GS electrodeposition of 5 mM Py at 60 s in 0.1 M Bu₄NBF₄ containing ACN.

After a sharp increase and a small decrease on the voltage during 5 s , the voltage stabilized at 1.1 V and kept constant during the polymerization. (Fig 4.17)

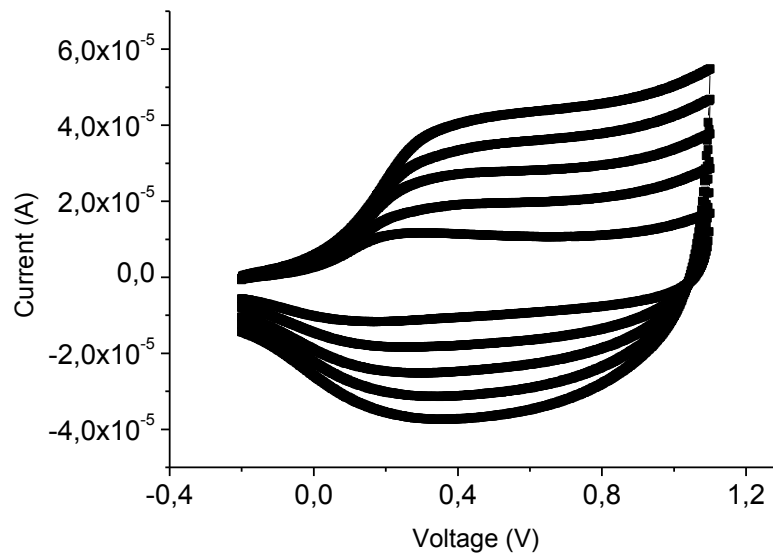


Figure 4.18 : Voltammetric response of PPy polymerized by GS method at 60s 0.M Bu₄NBF₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

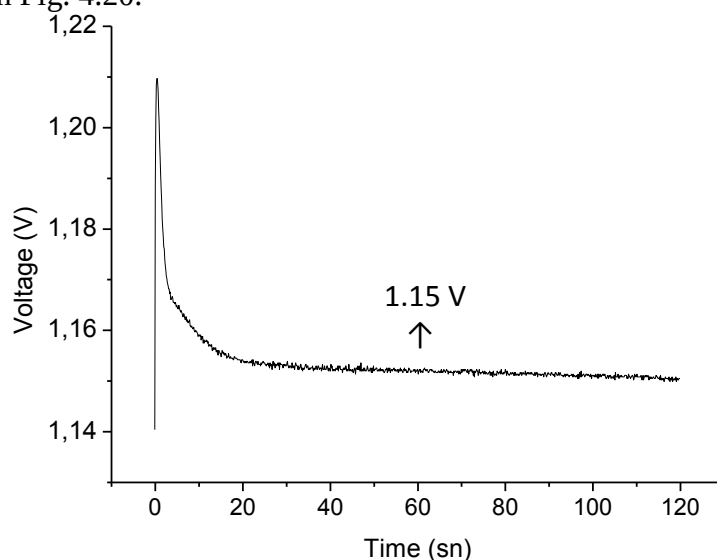
The CV of the polymer film obtained by GS method at 30 s, showed one broad wave at +0.3 V and a peak at +0.4 V as it can be seen in the Fig. 4.18. The results obtained from these measurements were summarized in Table 4.8.

Table 4.8 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PPy polymerized by GS method at 60 s.

Scan rate (mV/s)	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	324	344	1.1	1.0	20	1.1
200	341	363	1.8	1.8	22	1.0
300	347	379	2.6	2.5	32	1.0
400	376	395	3.3	3.0	19	1.1
500	411	411	4.1	3.7	23	1.1

In all cases ΔE values were very small and peak ratios very close to unity, showing thin film behaviour and good electrochemical reversibility. The best reversibility was observed at 200 and 300 mV/s. (Table 4.8) The reversibility of the films were better than the films obtained at 30 s.

GS polymerization of Py during 120 s was given in the Fig. 4.19 . Monomer concentration, applied current and polymerization media were kept the same with previous measurements. The voltammetric response of the PPy at different scan rates was given in Fig. 4.20.

**Figure 4.19** : GS electrodeposition of 5 mM Py at 120 s in 0.1 M Bu_4NBF_4 containing ACN.

After a sharp increase and a small decrease on the voltage during 5 s, the voltage stabilized at 1.15 V and kept constant during the polymerization.(Fig. 4.19) . The CV of the polymer film obtained by GS method at 120 s showed a broad peak at +0.4V as it can be seen in the Fig. 4.20

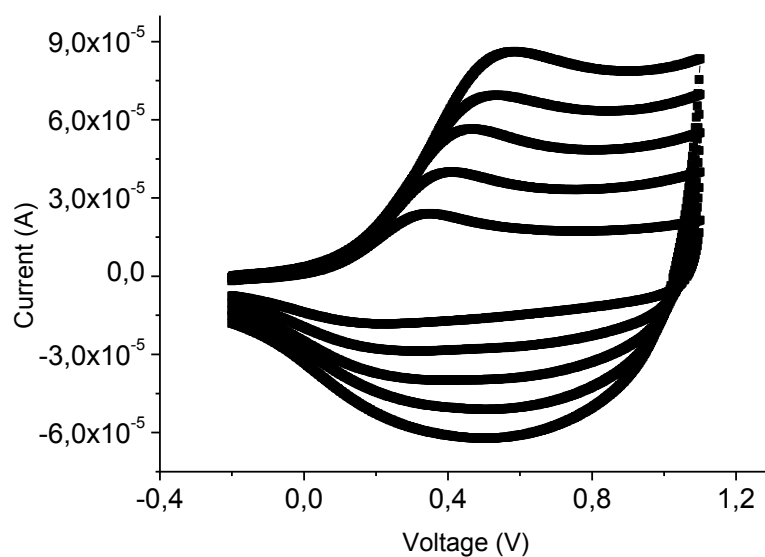


Figure 4.20 : Voltammetric response of PPy polymerized by GS method at 120 s in 0.1 M Bu_4NBF_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Results obtained from measurements were summarized in the Table 4.9.

Table 4.9 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PPy polymerized by GS method at 120 s.

Scan rate (mV/s)	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	330	372	2.3	1.7	42	1.4
200	401	437	3.9	2.8	36	1.4
300	468	443	5.7	3.9	25	1.4
400	506	478	6.9	5.2	28	1.3
500	551	506	8.6	6.2	45	1.4

As the polymerization time increased, the reversibility of the polymer films decreased as expected (Table 4.9)

Comparasion of current densities vs scan rates of PPy film obtained by GS method was given in Fig. 4.21

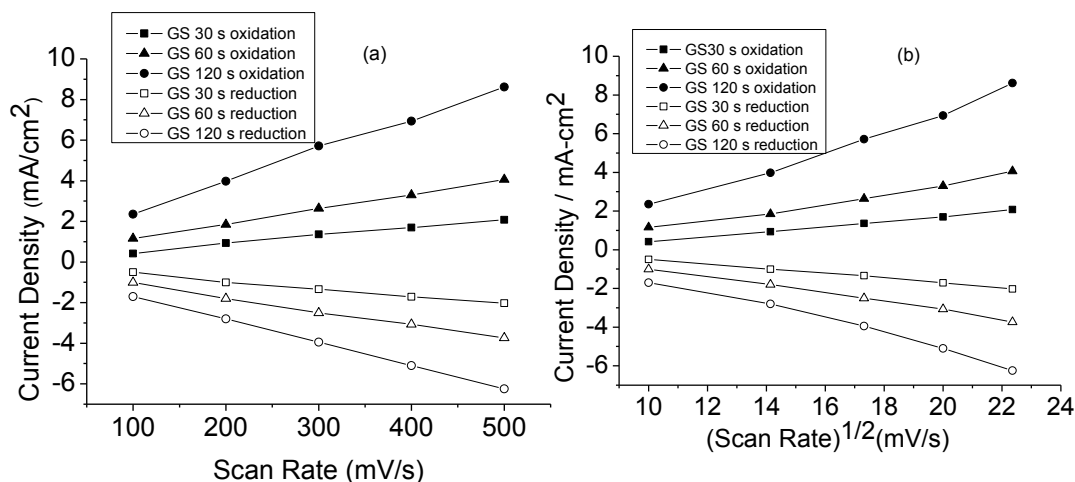


Figure 4.21 : (a)Current density versus scan rate, (b) Current density versus square root of scan rate plot PPy films obtained by GS method at different polymerization times(30, 60 and 120 s)

Current densities for all polymerization times were changed more linear with scan rate than square root of the scan rate showing thin film behaviour. (Fig. 4.21)

Comparasion of redox behaviour of PPy obtained by PD, PS and GS methods at different polymerization times was given in the Fig. 4.22.

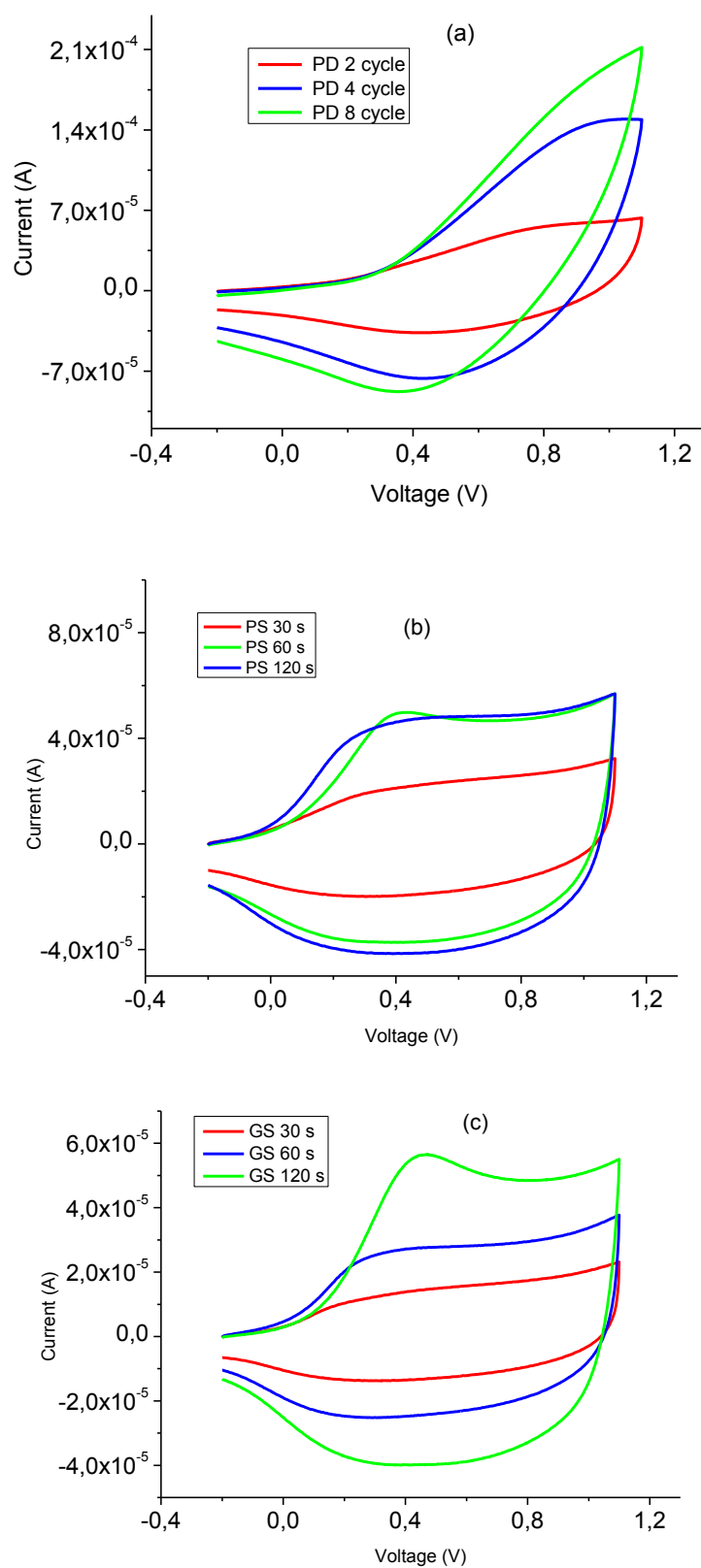


Figure 4.22 : Comparison of redox behaviour of PPy films obtained by PD (a), PS (b) and GS (c) methods depending on polymerization time at 300 mV/s in monomer free solution.

As it can be seen in Fig 4.22.a and Fig. 4.22.b for PD and PS methods respectively, the current intensities increased as the polymerization time increased due to the increase in thickness and the area of electrode. However, electrochemical reversibility of the PPy film decreased due to limiting diffusion for PD cally obtained film. On the other hand anodic peak around 0,4 V became more pronounced for PS cally obtained film. During PS polymerizations the current decreased and almost stayed constant after 5 s. (Fig. 4.22.b) . Application of further voltage contributed to further oxidation and increase in doping of the PPy film rather than further deposition of the new polymer layer. Increase in current intensities by increase in polymerization time might be due to increase in doping degree

For GS cally polymerization after 60 s, current intensities of PPy film became constant (Fig. 4.22.c) as the polymerization time increased and polymer growth on electrode surface a resistive layer occurred. In order to obtained constant current, the potential needs to be increased. This caused the overoxidation of polymer film and decreased the electroactivity. This explained why the low current intensities were observed at longer polymerization time. Three methods were compared with each other depending on polymerization time (Fig. 4.23)

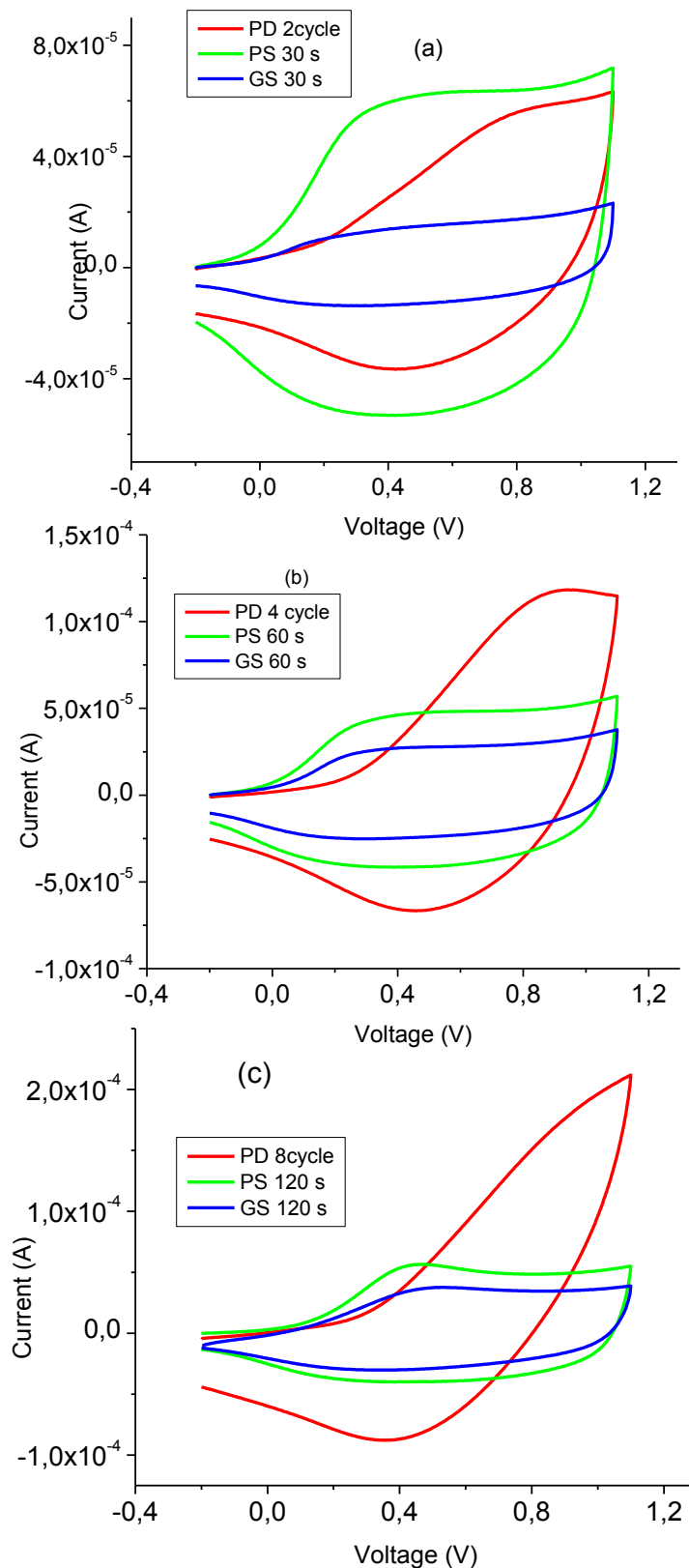


Figure 4.23 : Comparison of redox behaviour of PPy films obtained by PD , PS and GS methods depending on polymerization method. [(a), PD 2 cycles, PS 30 s, GS 30 s; (b), PD 4 cycles, PS 60 s, GS 60 s; (c), PD 8 cycles, PS 120 s, GS 120 s] at 300 mV/s in monomer free .

When the thin films obtained at 2 cycles and 30 s by three different methods were compared it can be seen that, high current intensity was observed in the case of PS method. Application of constant current might overoxidize the film and this may be the reason of lowest current intensity in the case of GS method. (Fig. 4.23. c)

In the case of PD method , it was possible to obtain more regular growing film. But in reverse scan, some of deposition removes from the electrode surface and thinner film can be obtained as compared to the other methods. The lower current in comparasion of PS might be due to this. (Fig. 4.23.a)

As the time increases, thickness and resistance increases in the case of PS and GS methods , while the in the case of PD method removal of some deposition result more regular and electroactive films. So the highest current was obtained by PD method. (Fig. 4.23. a,b)

4.1.4. Comparasion of Electrochemical Impedance Spectroscopy Measurements of PPy films

Impedance properties were investigated between 10 mHz-100 kHz range at the absence of voltage and with 1V direct voltages to the polymer film in 5ml 0.1 M ACN/ Bu_4NBF_4 monomer free solution. Nyquist, Bode phase and Bode magnitude diagrams resulting PPy films were compared for each polymerization method and time.

4.1.4.1. EIS results of potentiodynamically obtained PPy film

PPy films obtained by PD method applying 2, 4, 8 cycles were characterized with EIS. Measurements and results were given in (Fig. 4.24- 4.29)

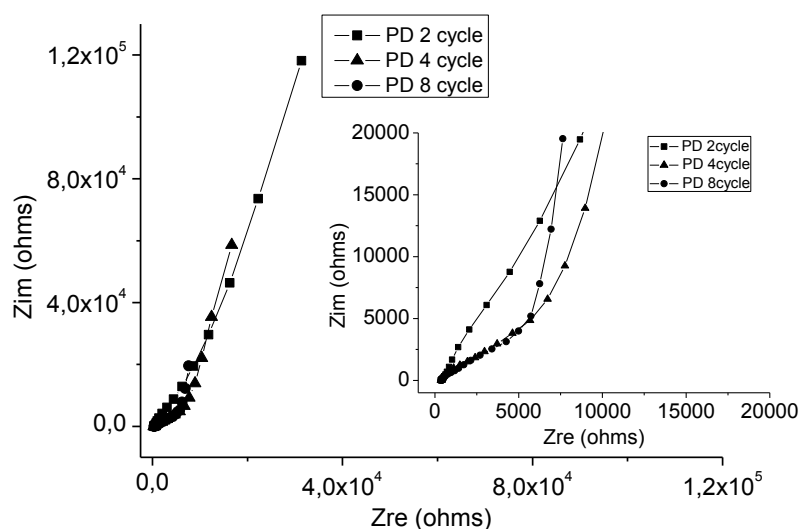


Figure 4.24 : Nyquist diagram of PPy obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

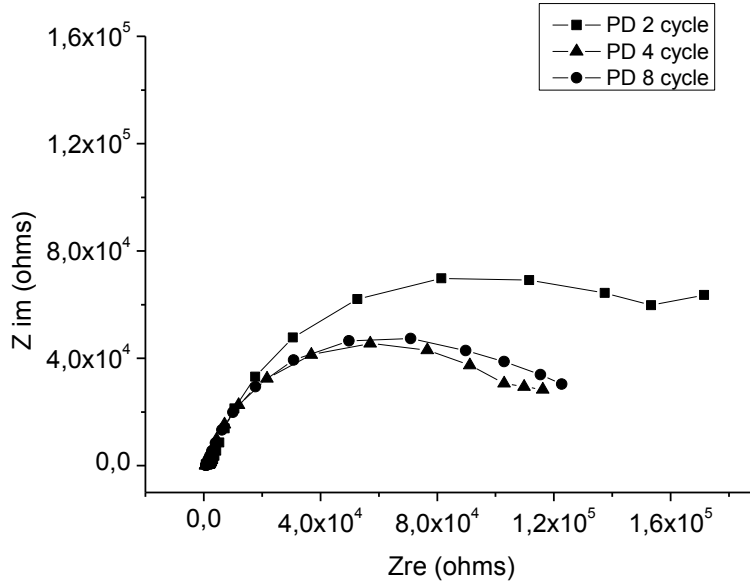


Figure 4.25 : Nyquist diagram of PPy obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

At low frequency and open circuit potential, the imaginary part of the impedance sharply increased and plot tend to a vertical line which is a characteristic of capacitive behaviour as suggested in literature [59] (Fig. 4.25) Real value of impedance showed a semi circle character under constant 1V potential. (Fig. 4.26)

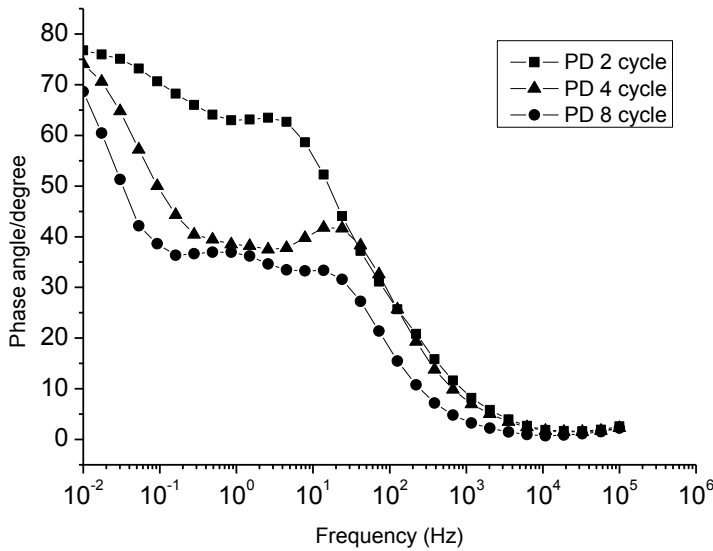


Figure 4.26 : Bode phase diagram of PPy obtained by at PD method 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

At frequencies > 1 kHz, the phase angle approached a plateau, and the electric signal reaches maximum penetration in the pores of the PPy as suggested in literature [62].

The highest phase angle was observed at the film polymerized by PD method at 2 cycles. (Fig. 4.26)

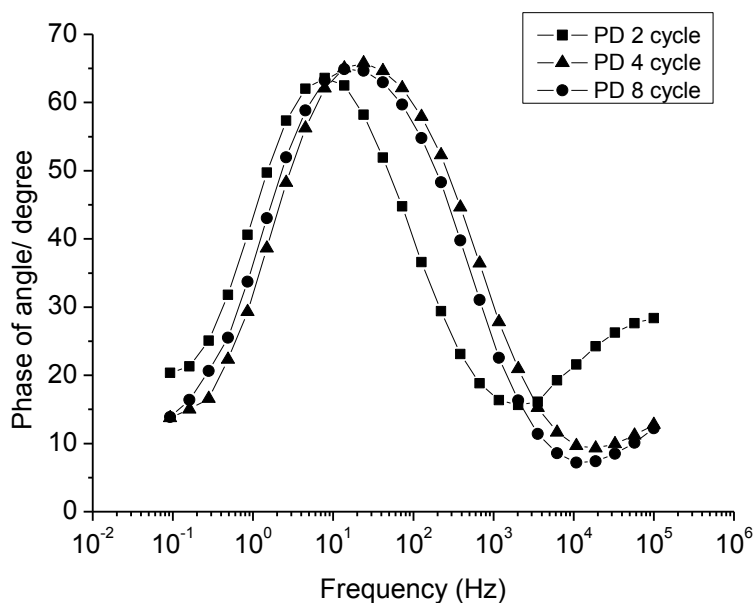


Figure 4.27 : Bode phase diagram of PPy obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Phase angles became lower and shifted to higher frequencies with increasing cycle numbers under the 1V constant voltage as the constant voltage led to the overoxidation of the polymer film surface. (Fig. 4.27)

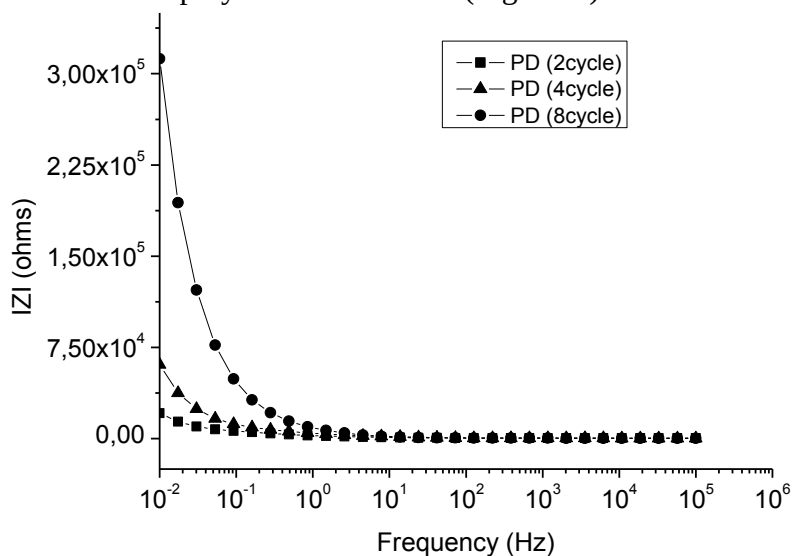


Figure 4.28 : Bode magnitude diagram of PPy obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

As it can be seen in the Fig. 4.28 at low frequencies, as the polymerization time increased the absolute value of impedance (IZI) increased also as a result of

deposition polymer on the electrode. For the frequencies >10 Hz , IZI reached a constant value for all polymerization times.

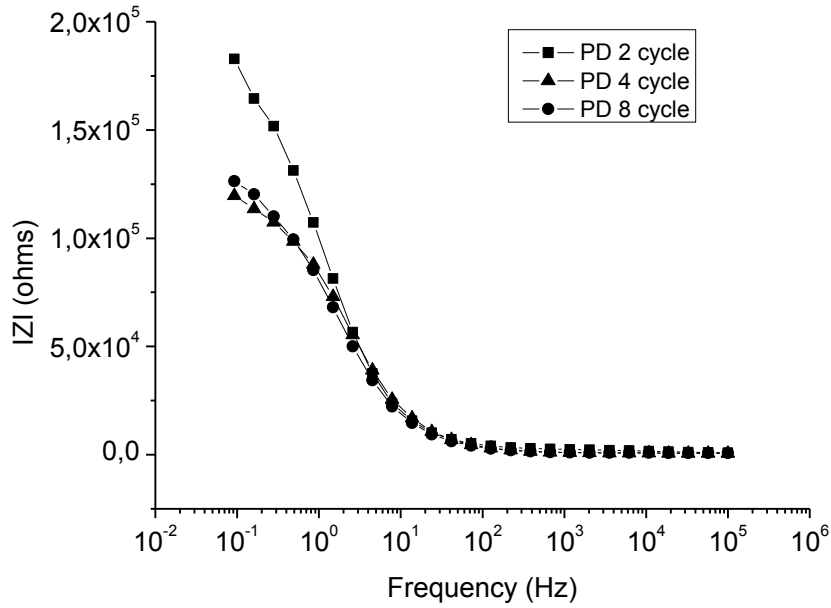


Figure 4.29 : Bode magnitude diagram of PPy obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

The results obtained from these measurements summarized in the Table 4.10.

Table 4.10 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PPy polymerized by PD method at 2, 4 and 8 cycles.

PPy ($\pm 0,5$)	PD (2 cycle)		PD (4 cycle)		PD (8 cycle)	
	Open circuit potential	1V applied	Open circuit potential	1V applied	Open circuit potential	1V applied
R_s ohm-cm ²	366	747	364	351	382	399
R_p ohm-cm ²	3402	51323	5508	78734	11062	99375
C_{dl} μF -cm ²	4.2	1	13	1.5	24	1.5
C_{sp} μF -cm ²	52	—	271	—	814	—
C_{dif} μF -cm ²	62	—	240	—	909	—
P.angle (degree)	78	18	74	14	69	14

As the short polymerization time led to the more electroactive film and the deposition on the electrode caused resistivity, highest Cdl, and phase angles were observed at the PPy obtained at 2 cycles whereas the highest Csp and Cdif were observed at long polymerization times. The most capacitive film obtained by PD 8cycles. These values were decreased in the case of 1V application showing the increase in conductivity of PPy films by applying 1V cause the decrease in capacitive behaviours of the film as expected (Table 4.10).

4.1.4.2. EIS results of potentiostatically obtained PPy film

Impedance properties were investigated in the similar conditions of PS cally polymerized PPy during 30 s. Nyquist, Bode phase and Bode magnitude diagrams (Fig. 4.30-4.35) of resulting PPy films were compared for each polymerization time.

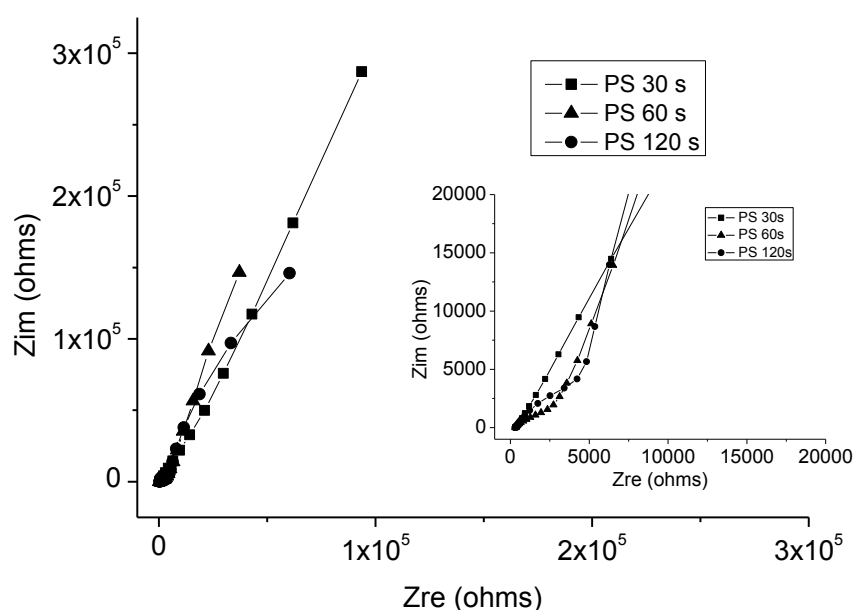


Figure 4.30 : Nyquist diagram of PPy obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

For the PPy film obtained by PS method, the imaginary part of the impedance sharply increased and plot tend to a vertical line which is a characteristic of capacitive behaviour at low frequency and open circuit potential, (Fig. 4.30). On the contrary of PD method, capacitive behaviour was still remarkable at higher polymerization times. But for the 120 s overoxidation on electrode caused a deviation from the vertical line and led to a part of semi circle, whereas it gave a full of semi circle under constant 1V (Fig. 4.31).

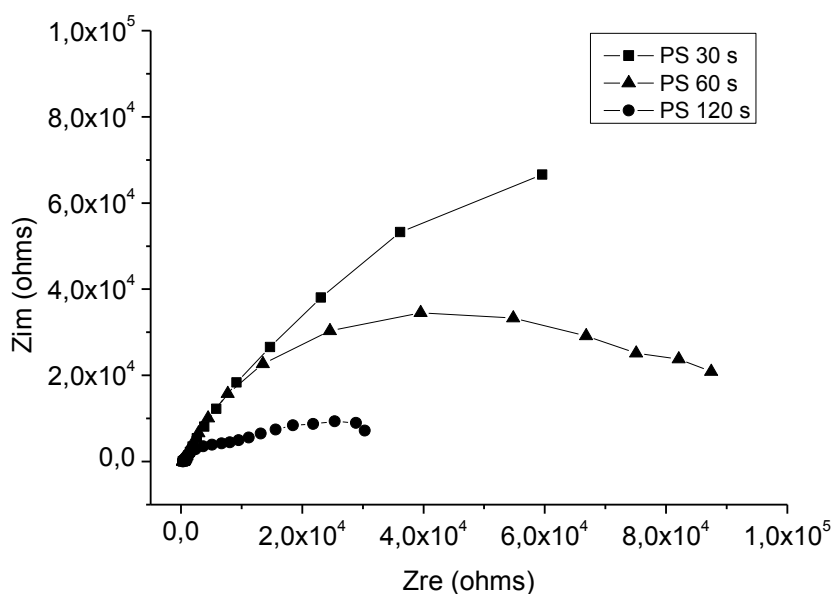


Figure 4.31 : Nyquist diagram of PPy obtained by PS method at 30, 60 and 120 s by applying 1V direct voltage.

The highest phase angle was observed for the film obtained by PS at 60 s. (Fig. 4.32)

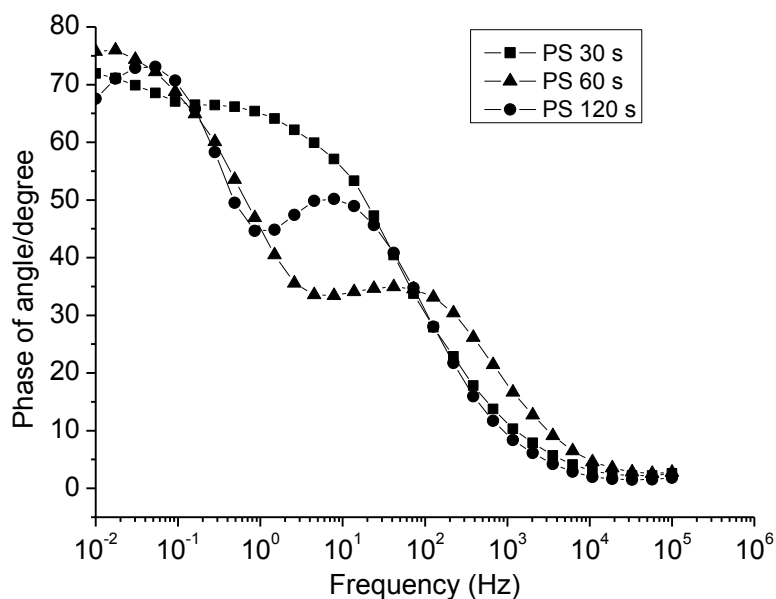


Figure 4.32 : Bode phase diagram of PPy obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency by applying 1V direct voltage.

The least shift on the frequency and the smallest decrease on the phase angle was observed for the film obtained at 30 s. (Fig. 4.33)

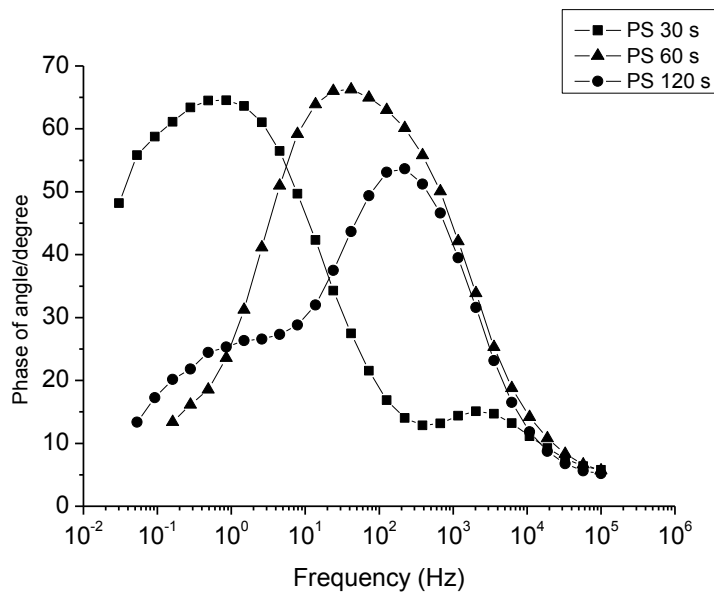


Figure 4.33 : Bode phase diagram of PPy obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

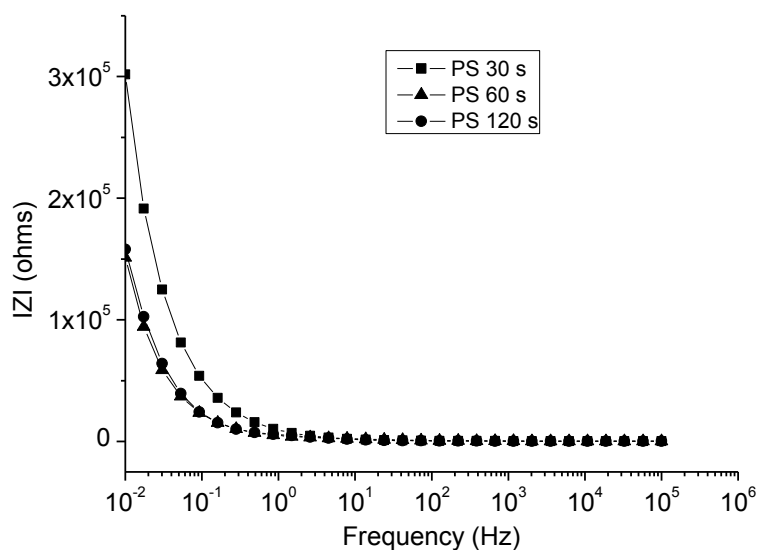


Figure 4.34 : Bode magnitude diagram of PPy obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

At low frequencies the lowest Z_{im} was observed for film obtained at 60 and 120 s. That was because of application of further charge contributed to further oxidation and doping of the PPy film rather than further deposition of the new polymer layer (Fig. 4.33). Under 1V constant voltage, similar frequency shifts with previous measurements were observed as the constant voltage led to the overoxidation of the polymer film surface. (Fig. 4.34)

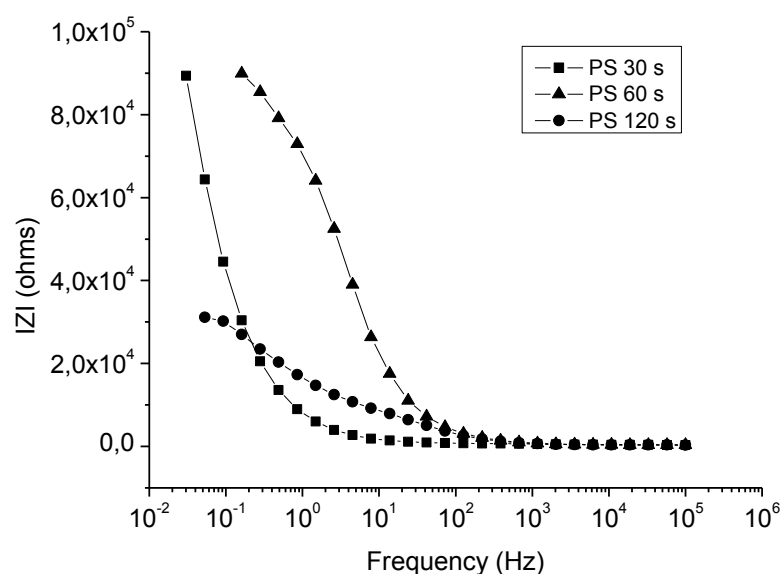


Figure 4.35 : Bode magnitude diagram of PPy obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Results obtained from these measurements were summarized in the Table 4.11

Table 4.11 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PPy polymerized by PS at 30, 60 and 120 s.

PPy ($\pm 0,5$)	PS (30s)		PS (60s)		PS (120s)	
	Open circuit potential	1V applied	Open circuit potential	1 V applied	Open circuit potential	1V applied
R_s ohm-cm ²	316	328	315	351	350	386
R_p ohm-cm ²	1948	71915	1920	79960	14242	87016
C_{dl} μF -cm ²	4.4	5.2	10.3	2	10.4	6
C_{sp} μF -cm ²	55	—	108	—	109	—
C_{dif} μF -cm ²	60	—	144	—	134	—
P.angle (degree)	72	48	76	13	73	15

As it can be seen from the Table 4.11 the most capacitive polymer films obtained by polymerization at 30 and 60 s. The highest C_{dl} and C_{sp} and C_{dif} was observed for the film obtained at 60 s. Similar behaviour of PPy film obtained by PD method were observed for the film obtained by PS method. In the case of 1V applied voltage there was a transition from capacitive behaviour of film to the resistive behaviour.

4.1.4.3 EIS results of galvanostatically obtained PPy film:

Impedance properties were investigated in the similar conditions of PD and PS polymerized PPy. Nyquist, Bode phase and Bode magnitude diagrams (Fig. 4.36 - 4.41) of resulting PPy films were compared for each polymerization time.

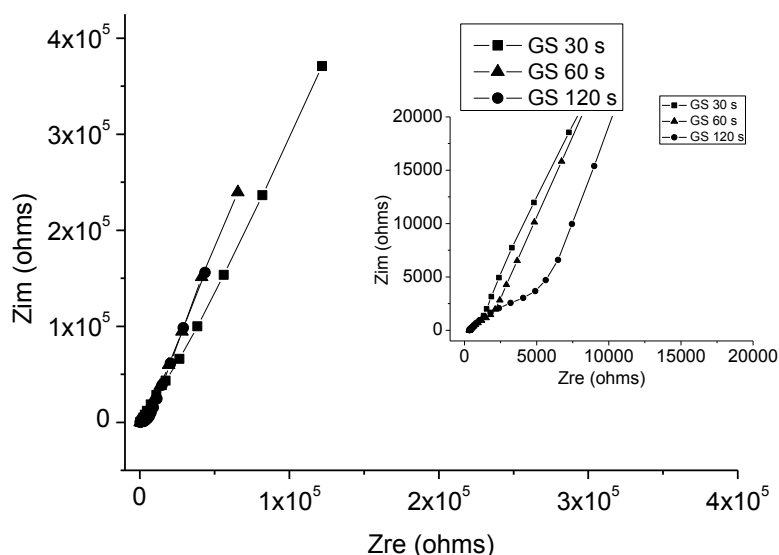


Figure 4.36 : Nyquist diagram of PPy obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

Similar with the PS method the most vertical line was observed for 60 s. And also similarly with the polymeric films obtained by PS and PD methods, after the application of 1V polymeric film behaved as resistive film. (Fig. 4.36)

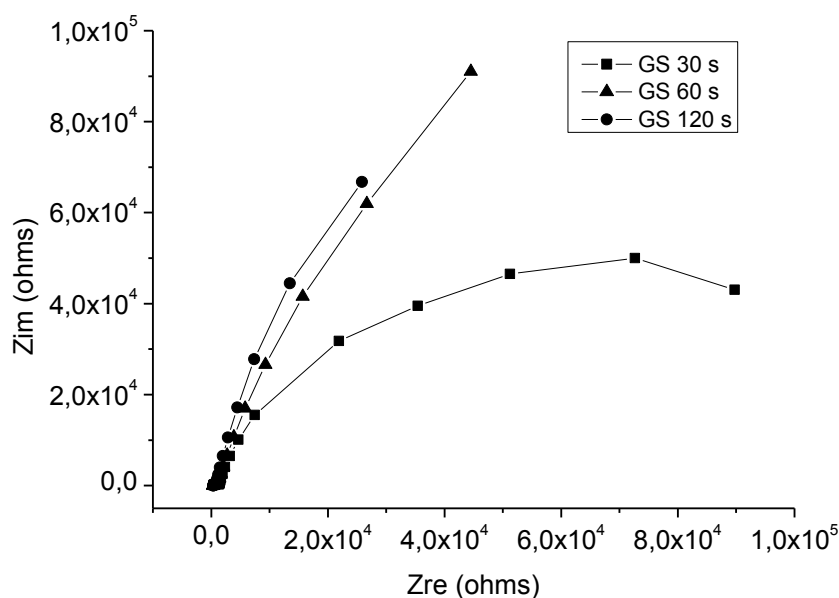


Figure 4.37 : Nyquist diagram of PPy obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Similar results were observed with the polymerized film by PS method for the Z_{im} values of GS polymerized film. Z_{im} was more vertical for high polymerization times due to the constant current contributes overoxidation instead of deposition. (Fig. 4.36) The highest phase angle was observed for the films obtained at 60 and 120 s. (Fig. 4.38) These results are well-matched with the vertical lines of Z_{im} . (Fig. 4.36)

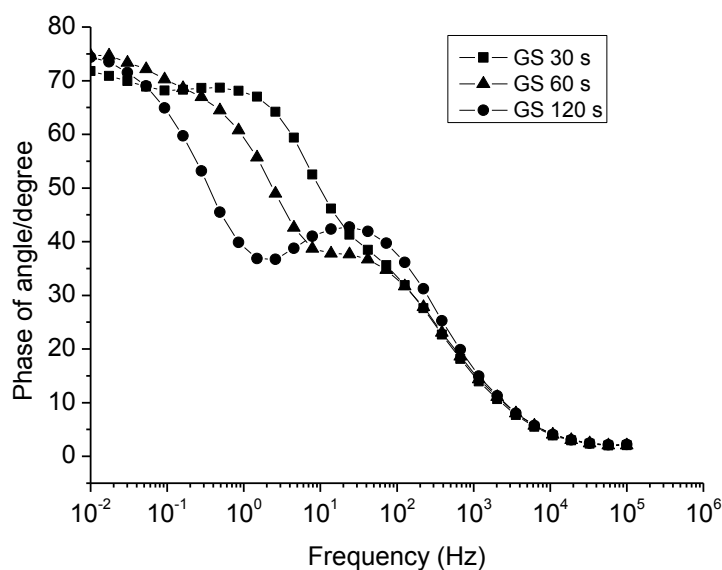


Figure 4.38 : Bode phase diagram of PPy obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range .

In the case of applying 1V, phase angles were decreased and shifted to the higher frequency ranges (Fig. 4.39)

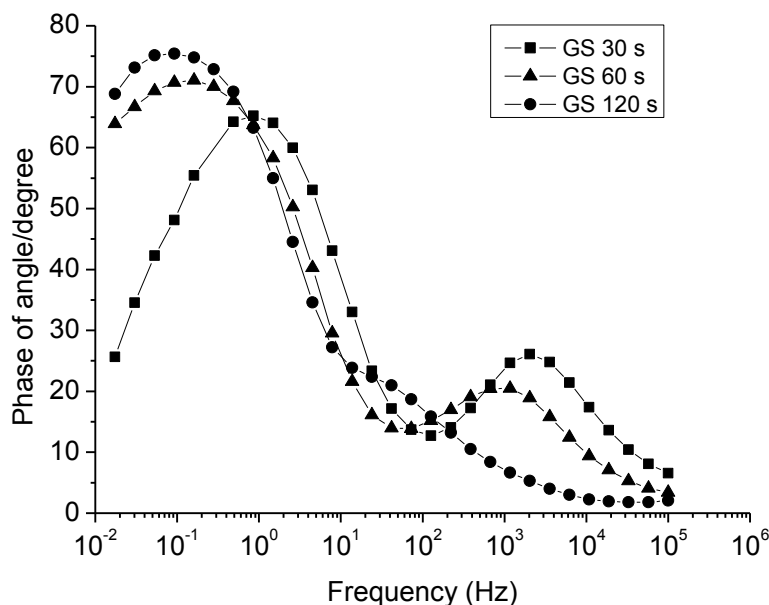


Figure 4.39 : Bode phase diagram of PPy obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

At low frequencies the lowest IZI was observed for the film obtained at 30 s. After the 10 Hz all the IZI values become constant. (Fig. 4.40)

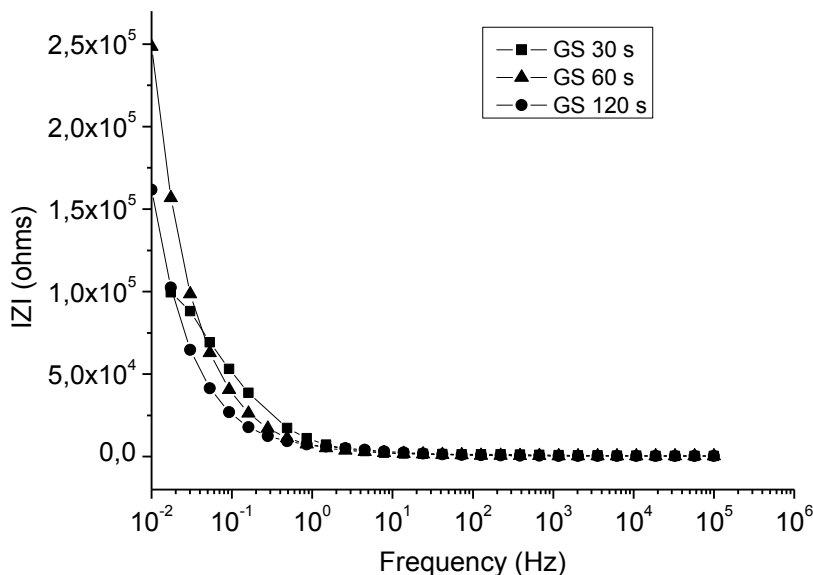


Figure 4.40 : Bode magnitude diagram of PPy obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

In the case of applying 1V, as the polymerization time increase, Z_{im} values decreased due to the degradation of the polymeric films. (Fig. 4.41)

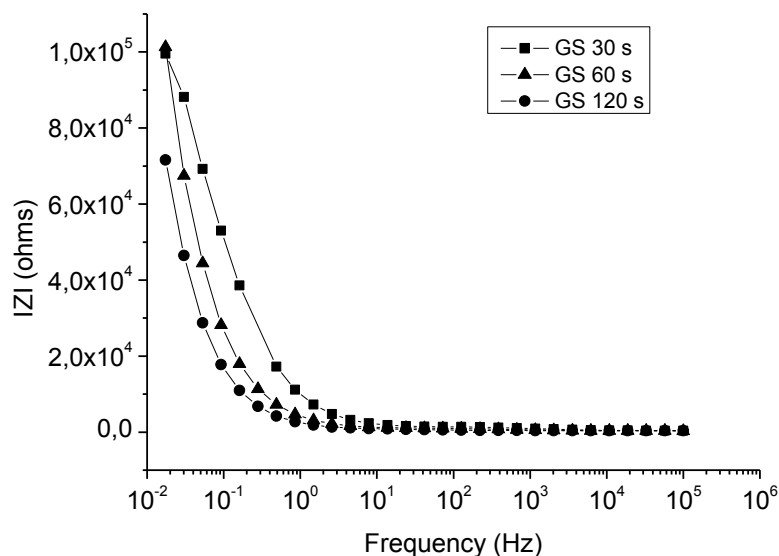


Figure 4.41 : Bode magnitude diagram of PPY obtained by GS method at 30, 60 and 120 s by applying 1V direct voltage.

Results obtained from these measurements were summarized in the Table 4.12.

Table 4.12 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PPY polymerized by GS method at 30, 60 and 120 s.

PPy ($\pm 0,5$)	GS (30s)		GS (60s)		GS (120s)	
	Open circuit potential	1V applied	Open circuit potential	1V applied	Open circuit potential	1V applied
R_s ohm-cm ²	351	366	339	340	352	351
R_p ohm-cm ²	8970	119164	8126	122455	12628	51139
C_{dl} μF -cm ²	3.4	4	6	8	9	14
C_{sp} μF -cm ²	42	—	66	—	102	—
C_{dif} μF -cm ²	47	—	70	—	108	—
P.angle (degree)	72	26	75	64	74	70

As it can be seen in the Table 4.12 the highest phase angle, C_{dl} were observed for the film obtained by GS method at 60 s whereas the highest C_{sp} and C_{dif} were observed at 120 s. Similarly to other methods, application of 1V potential caused transition from capacitive behaviour to resistive.

For the PPy films obtained by PD method, as the time increased, the C_{sp} and C_{dl} increased as well (Table 4.10) due to the polymer deposition on the electrode surface resulted thicker and more capacitive layer. This idea was also supported with the high current intensities at high polymerization times seen in the Fig. 4.22.a.

In the case of PS (Table 4.11) and GS methods (Table 4.12) C_{sp} and C_{dl} values increased as the polymerization time increased. But the increase in polymerization time for (PS) and (GS) methods contributed further oxidation of PPy film instead of further deposition which resulted less increase rates on the C_{dl} and C_{sp} when they were compared to rates seen in PD method. This was also well matched with the less increase rate of current intensities observed in the case of PS method. (Fig 4.22 b).

Phase angles stayed almost constant with the increase in polymerization times for all methods. To obtain a capacitive PPy film, PD method and longer polymerization time can be suggested. On the other hand, if reversibility is important, for all methods thinner films are favorable.

4.1.4.4. Equivalent electrical circuit diagram of PPy:

Impedance data were analyzed grafically with the use of ZSimp-Win software, the conventional equivalent circuit consists of a series of a resistor and capacitor, $(R(C(R(C(RW))))(CR)$ where R_s was the uncompasated ohmic resistance R_{ct} was the charge transfer resistance, and CPE was the constant phase element and $R_{p,s}$ was polymer resistance. R_{pt} is the resistance where as C_{pt} is capacitance of the electrode (Fig. 4.42) . CPE was the total charge accumulation at the solution/polymer interface in the outer regions of the electrode, it also might be represented by Qdl. The charge transfer resistance (R_{ct}) was a combination of resistances of solution and inner regions of polymer electrode, as the Bu_4NBF_4 was able to penetrate into the porous surface. C_{ct} was the charge accumulation at the solution/polymer interface in the inner regions of the electrode, which was also affected by the decrease on conductivity of the electrolyte. The impedance parameters obtained from these measurements were summarized in the Table 4.13.

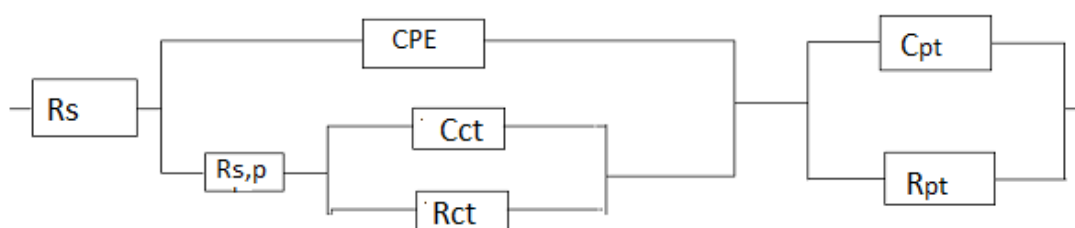


Figure 4.42 : The equivalent circuit diagram of PPy. [Chi squared: $9.048 \cdot 10^{-4}$ $n=0,6608$. Monomer:5mM Py, Method: PD at 2 cycle ,Electrolyte:0,1 M ACN/ Bu_4NBF_4 , WE: Pt (button electrode), RE: Ag/AgCl, CE: Pt (wire)]

Table 4.13 : Electrical parameters of PPy obtained by PD method at 2cycles .

R_s (ohm- cm^2)	Qdl (CPE) Y0 (S- sec^n/cm^2)	$R_{s,p}$ (ohm- cm^2)	R_{ct} (ohm- cm^2)	C_{ct} (F/ cm^2)	R_{pt} (ohm- cm^2)	C_{pt} (F/ cm^2)
346	$4.2 \cdot 10^{-5}$	2006	3340	$2 \cdot 10^{-6}$	$2.1 \cdot 10^{-5}$	$5 \cdot 10^{-5}$

4.2. Comparison of Polymerization Conditions and Characterization of Carbazole

4.2.1. Potentiodynamic Polymerization of Cz

Polymerization of Cz has been performed by PD method at 2, 4 and 8 cycles. The cyclic voltammograms during polymerizations (Fig. 4.43, 4.45, 4.47) and the CV of polymer films were given (Fig. 4.44, 4.44, 4.48.). Redox parameters such as E_a , E_c , I_a , I_c , ΔE and I_a/I_c obtained from these voltammograms were summarized in the Table 4.14- 4.16.

Polymerization of Cz by PD at 2 cycles in 0.1 M ACN/ Bu_4NClO_4 was given in Fig. 4.43

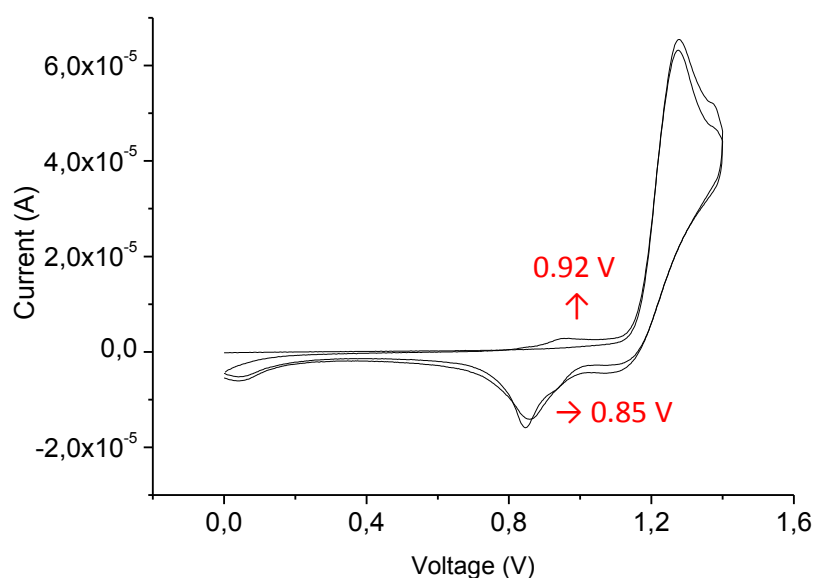


Figure 4.43: PD electrodeposition of $5 \cdot 10^{-2}$ M Cz at 2 cycles in 0.1 M Bu_4NClO_4 containing ACN at the scan rate of 50 mV/s.

Fig. 4.43 presents the polymerization of Cz by PD method at 2 cycles. On the anodic scan, the oxidation peak appeared at 0.92 V corresponding to the formation of the cation radical of Cz whereas the reduction wave was observed at 0.85 V. Since the oxidation peak of the first redox process appeared at only second and following scans, it might be due to the polymer redox activity, whereas the second oxidation peak (1.2 V), which existed for all scans, might be related to the oxidation of the neutral monomer to radical-cation as suggested in literature [62]. Then the film was washed with monomer-free electrolyte solution and its redox behaviour was

studied. Voltammetric response of the PCz film obtained by PD at 2 cycles can be seen in the Fig. 4.44.

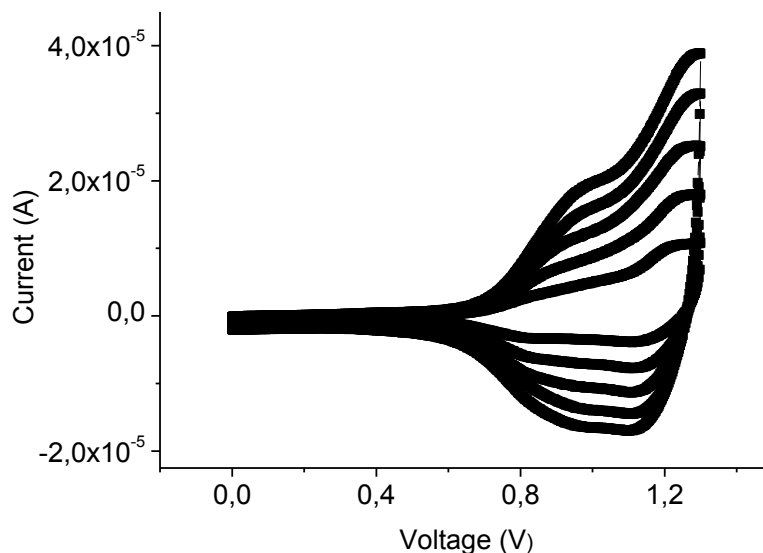


Figure 4.44 : Voltammetric response of PCz polymerized by PD method at 2 cycles in 0,1 M Bu_4NClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

As it can be seen from the Fig. 4.44 the CV of PCz showed one broad wave at +0.80 V and a peak at +0.90 V. Results obtained from these measurements were summarized in Table 4.14.

Table 4.14: E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Cz polymerized by PD method at 2 cycles

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	867	849	0.3	0.3	18	1.0
200	885	871	0.7	0.6	14	1.1
300	929	911	1.0	1.0	18	1.0
400	958	942	1.5	1.3	16	1.1
500	971	963	1.9	1.6	8	1.2

Taking into account the I_a/I_c ratio, which was close to unity and besides ΔE values were very small, it can be said that for the PCz obtained by PD at 4 cycles, the first

electronic transfer was fast and the redox process followed a quasi-reversible mechanism. The best reversibility was obtained at 300 mV/s. (Table 4.14)

PD polymerization of Cz at 4 cycles was given in the Fig. 4.45 . Monomer concentration, voltage interval and electrodes were kept same with previous measurements and similar investigations were done. The voltammetric response of polymeric film was given in Fig. 4.46.

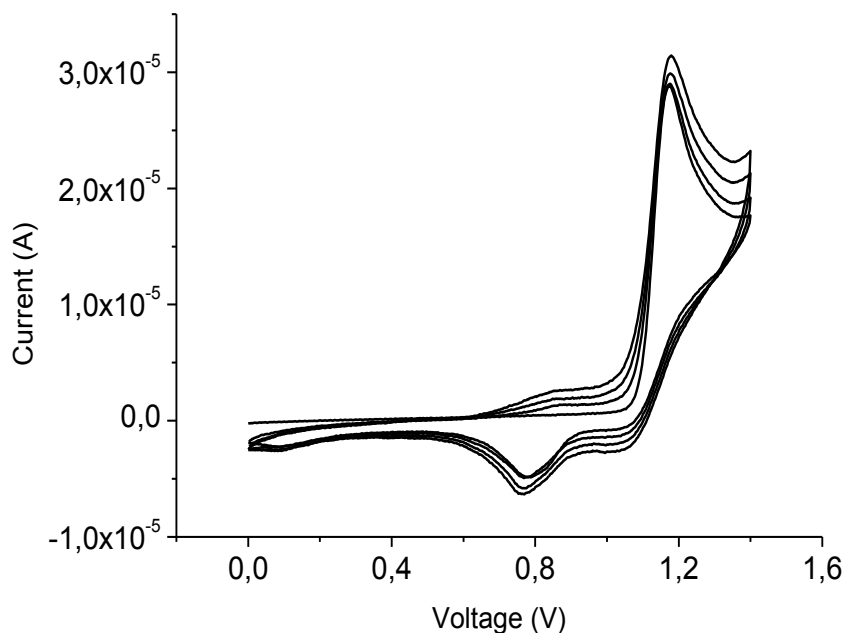


Figure 4.45 : PD electrodeposition of $5. \cdot 10^{-2}$ M Cz at 4 cycles in 0.1 M Bu_4NClO_4 containing ACN at the scan rate of 50 mV/s.

Fig. 4.45 presents the PD growth of the PCz during successive 4 cycles. Broad at 0.85 V indicated the polymer growth on the electrode. The voltammetric response was given in Fig. 4.46.

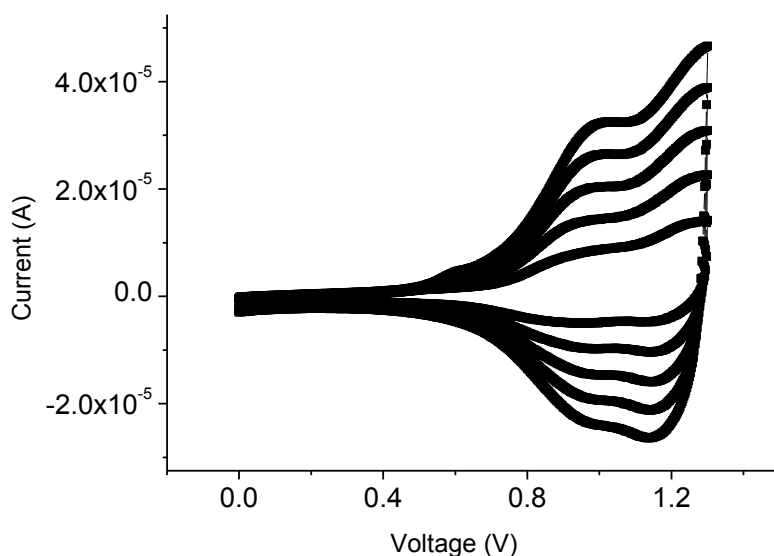


Figure 4.46 : Voltammetric response of PCz polymerized by PD method at 4 cycles in 0.1 M Bu₄NClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

As it can be seen from the Fig.4.46, the CV of PCz showed one broad wave at +0.80 V and a peak at +0.98 V which contributed that the polymerization of Cz. As the polymerization time increased E_a showed a positive shift where as the E_c showed a negative shift. Results obtained from these measurements were summarized in Table 4.15.

Table 4.15 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Cz polymerized by PD method at 4 cycles

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	879	901	0.7	0.5	22	1.3
200	901	937	1.3	1.0	36	1.3
300	939	956	2.0	1.4	17	1.3
400	965	971	2.5	1.9	6	1.3
500	981	984	3.2	2.4	3	1.3

PD polymerization of Cz at 8 cycles was given in the Fig. 4.47.

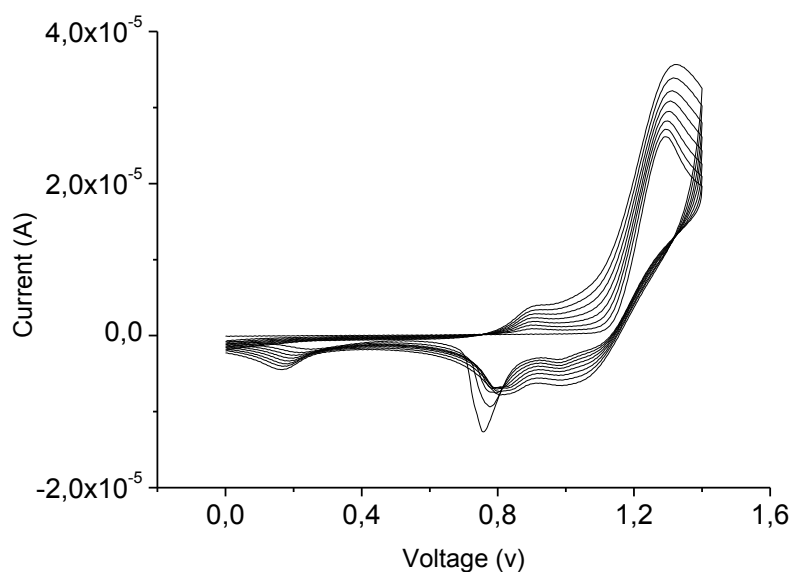


Figure 4.47 : PD electrodeposition of $5 \cdot 10^{-2}$ M Cz at 8 cycles in 0.1 M Bu_4NClO_4 containing ACN at the scan rate of 50 mV/s.

Fig. 4.47 presents the electrochemical growth of the PCz film by PD at 8 cycle. The broad which indicated the polymeric growth, was seen at 0.85V during the oxidation of monomer whereas it was seen at the 1.8 V during the reduction. The voltammetric response of the PCz was also given below (Fig. 4.48)

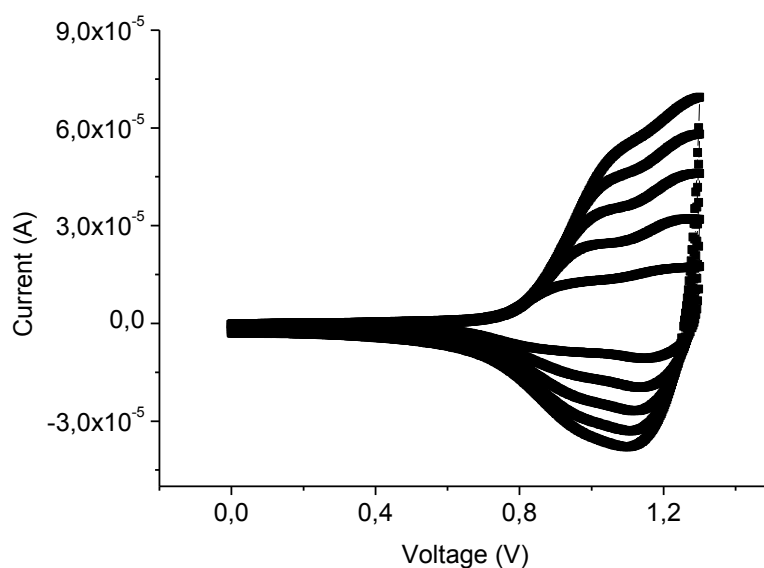


Figure 4.48 : Voltammetric response of PCz polymerized by PD method at 8 cycle in 0.1 M Bu_4NClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Results obtained from these measurements were summarized in Table 4.16.

Table 4.16 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Cz polymerized by PD method at 8 cycles

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	936	926	1.0	1.2	10	1.2
200	978	936	2.3	1.7	42	1.4
300	1020	958	3.4	2.5	45	1.4
400	1058	975	4.5	3.0	83	1.5
500	1074	990	5.4	3.5	83	1.5

As it can be seen in the Table 4.16, the polymer film was reversible for only low scan rates, due to the increase in polymerization time resulted thicker and more resistive film on electrode surface. The best reversibility was obtained at the 100 mV/s.

Comparasion of current densities vs scan rates of PCz obtained by PD can be seen in the Fig. 4.49.

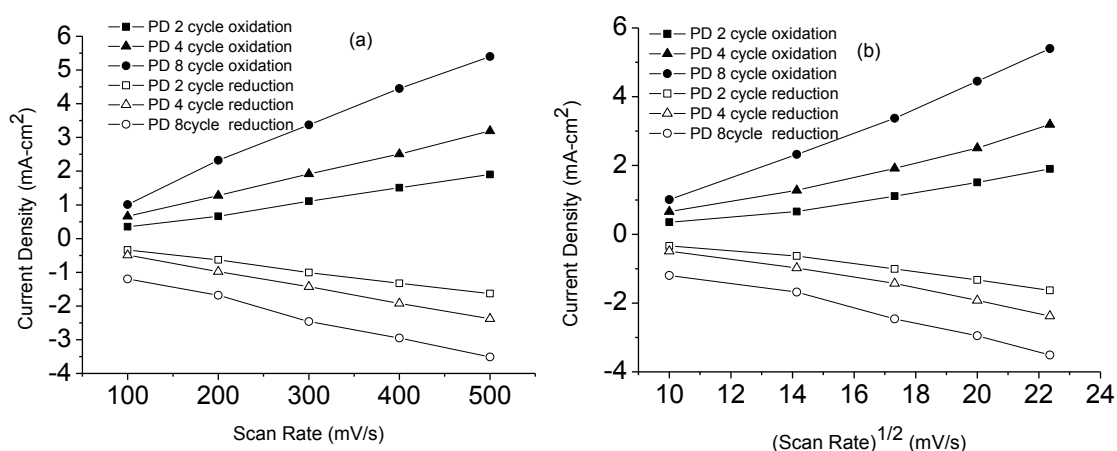


Figure 4.49 : (a)Current density versus scan rate, (b) Current density versus square root of scan rate plot of PCz films obtained by PD method at different cycle numbers (2, 4 and 8 cycles)

For PCz obtained at 2 cycles and 4 cycles, the current densities vary linearly with the scan rate which is a characteristic behaviour of thin film whereas the current intensities were linear with the square root of the scan rate in the case of long polymerization times (8 cycles) which demonstrates that the current flow through the film is diffusion controlled. (Fig. 4.49)

4.2.2. Potentiostatic Polymerization of Cz

The polymerization of Cz by PS method at 30 s in 0.1 M ACN/ Bu_4NClO_4 was given in Fig. 4.50.

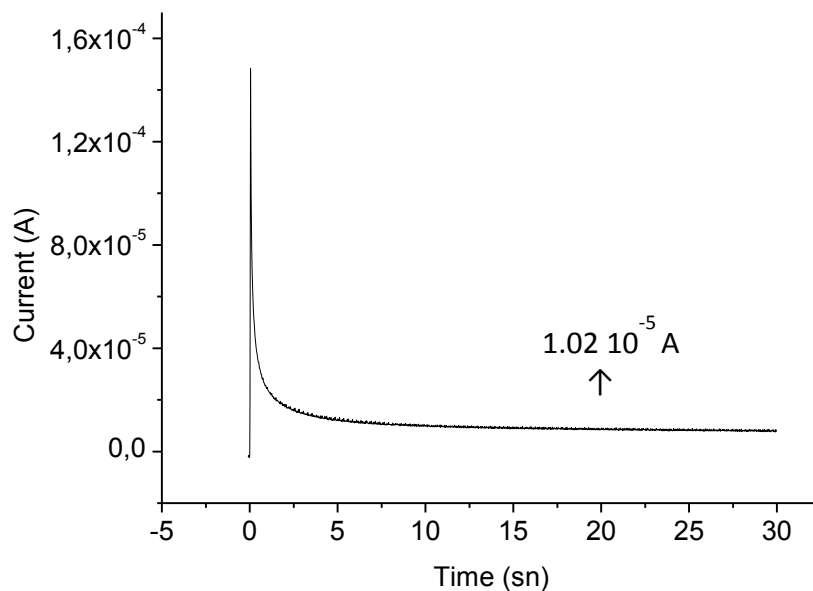


Figure 4.50 : PS electrodeposition of $5 \cdot 10^{-2}$ M Cz at 30 s in 0.1 M Bu_4NClO_4 containing ACN.

As it can be seen in the Fig. 4.50, after an increase on the current during the first 5 s of polymeric growth, it was stabilized at $1.02 \cdot 10^{-5}$ A and kept constant during the polymerization. The voltammetric response of polymer film at different scan rates was presented in Fig. 4.51.

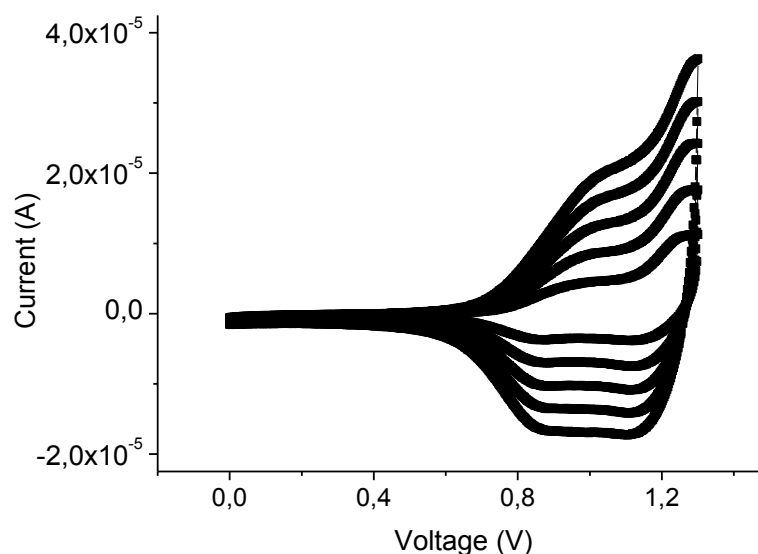


Figure 4.51 : Voltammetric response of PCz polymerized by PS method at 30 s in 0.1 M Bu_4NClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Results obtained from these measurements were summarized in Table 4.17.

Table 4.17 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Cz polymerized by PS method at 30s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	777	815	0.3	0.2	38	1.6
200	812	851	0.8	0.5	39	1.7
300	844	885	1.0	0.7	41	1.7
400	870	907	1.6	1.0	37	1.7
500	883	911	2.0	1.2	28	1.6

As it can be seen in the Table 4.17 PCz obtained by PS method at 30 s was poor about the redox reversibility. The origin of the irreversibility might be due to the partial degradation of the polymer from electrode surface.

Polymerization of Cz by PS method at 60 s was given in the Fig. 4.52. Monomer concentration, applied voltage and electrodes were kept same with previous measurements and similar investigations were done. The voltammetric response of the film was given in Fig. 4.53.

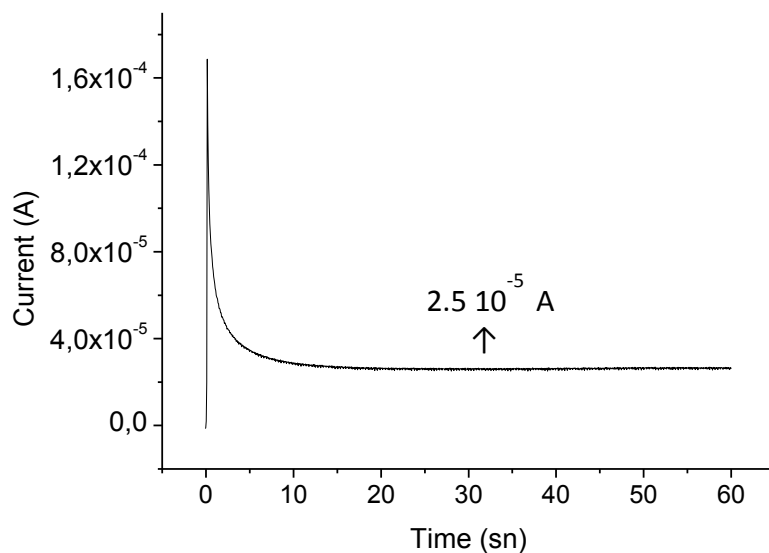


Figure 4.52 : PS electrodeposition of $5 \cdot 10^{-2}$ M Cz at 60 s in 0.1 M Bu_4NClO_4 containing ACN.

While the constant voltage was applied, a sharp decrease on current was observed during the first 5 s of polymeric growth and after that it was stabilized at $2.50 \cdot 10^{-5}$ A. (Fig. 4.52)

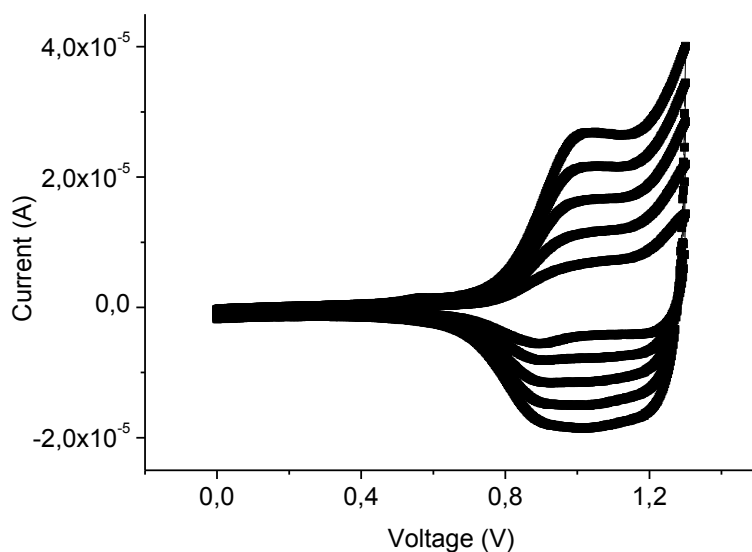


Figure 4.53 : Voltammetric response of PCz polymerized by PS method at 60 s in 0.1 M Bu_4NClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Results obtained from these measurements were summarized in Table 4.18.

Table 4.18 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PCz polymerized by PS method at 60 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	917	892	0.5	0.5	25	0.9
200	943	989	0.8	1.0	45	1.2
300	978	924	1.6	1.1	54	1.4
400	991	948	2.1	1.5	43	1.4
500	1013	981	2.7	1.8	32	1.4

As it can be seen from the table, the best reversibility was obtained at 100 mV/s.

Polymerization of Cz by PS method at 120s can be seen in the Fig. 4.54. Monomer concentration, applied voltage and electrodes were kept same with the previous measurements and similar investigations were done.

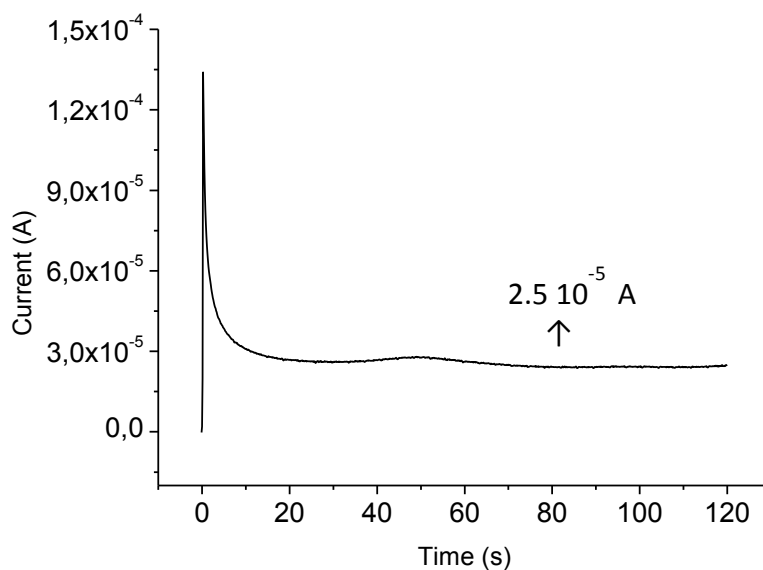


Figure 4.54 : PS electrodeposition of $5. \cdot 10^{-2}$ M Cz at 60 s in 0,1 M Bu_4NClO_4 containing ACN.

As it can be seen in the Fig. 4.54 a sharp decrease on current was observed during the first 5 s of polymeric growth and after that it was stabilized at $3.5 \cdot 10^{-5}$ A. The voltammetric response of the film at different scan rates was given in Fig. 4.55.

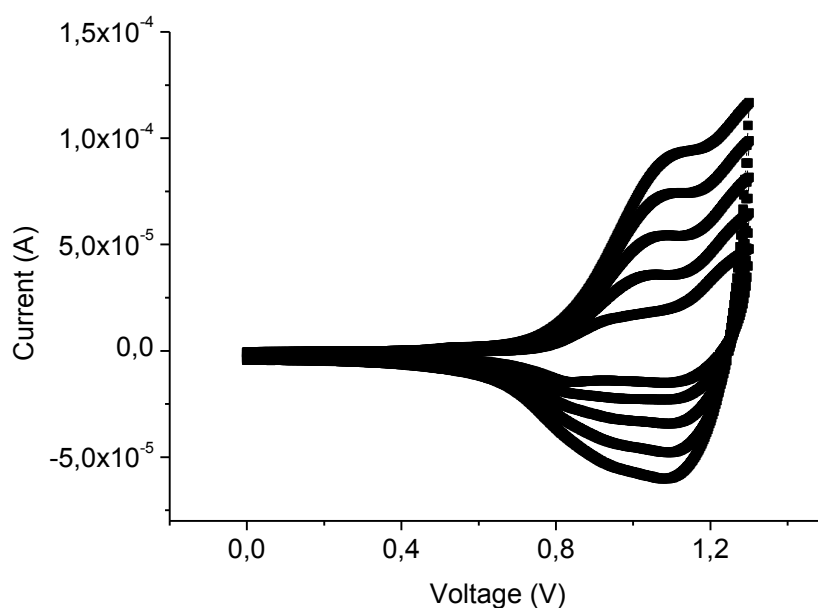


Figure 4.55 : Voltammetric response of PCz polymerized by PS method at 120 s in 0.1 M Bu_4NClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

The CV of the polymer film obtained by PS at 120 s showed a broad peak at +1.0V as it can be seen in the Fig. 4.55. Results obtained from these measurements were summarized in Table 4.19.

Table 4.19 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PCz polymerized by PS method at 120 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	997	747	2.0	2.0	250	1,0
200	1042	706	3.1	2.7	367	1,1
300	1112	675	4.7	3.9	437	1,2
400	1140	649	5.7	4.9	494	1,2
500	1160	620	6.6	5.7	496	1,2

As it can be seen from the Table 4.19, redox response of PCz obtained by PS at 120 s was poor. Reason of the irreversibility might be explained in a way that, increase on polymerization time led to thicker and more resistive film on electrode surface.

Potential differences and peak ratios increased with increasing scan rate due to limited diffusion. When the three polymerization times of PS method were compared, the best reversible film was obtained at polymerization during 60 s.

Comparison of current intensities vs scan rates of PCz films obtained by PS method was given in the Fig. 4.56.

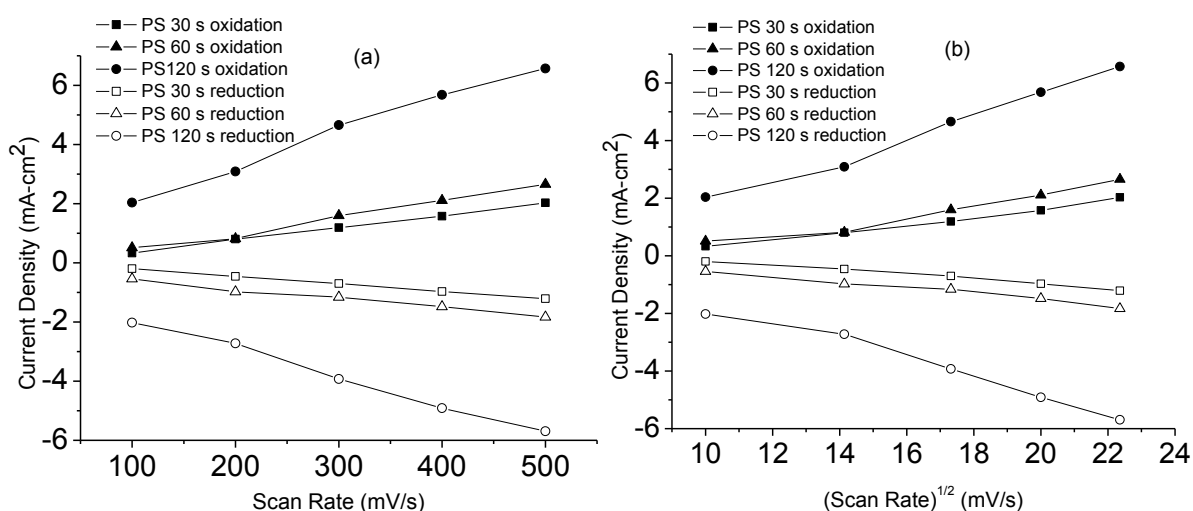


Figure 4.56 : (a)Current density versus scan rate, (b) Current density versus square root of scan rate plot of PCz films obtained by PS method at different polymerization times (30, 60 and 120 s).

In the case of PS method, short polymerization times (30 and 60 s) contributed thin film character whereas the long polymerization time (120 s) caused diffusion control. (Fig. 4.56)

In the case of PCz film obtained by PS method, reversibility was poor at high scan rates for all polymerization times even the ΔE values were very small. The main reason of irreversibility was the high value of I_a/I_c which was result of that the limiting diffusion on the current flow.

4.2.3. Galvanostatic Polymerization of Cz

Polymerization of Cz by GS method at 30 s was given in the Fig. 4.57. The voltammetric response of the film at different scan rates was given in Fig. 4.58.

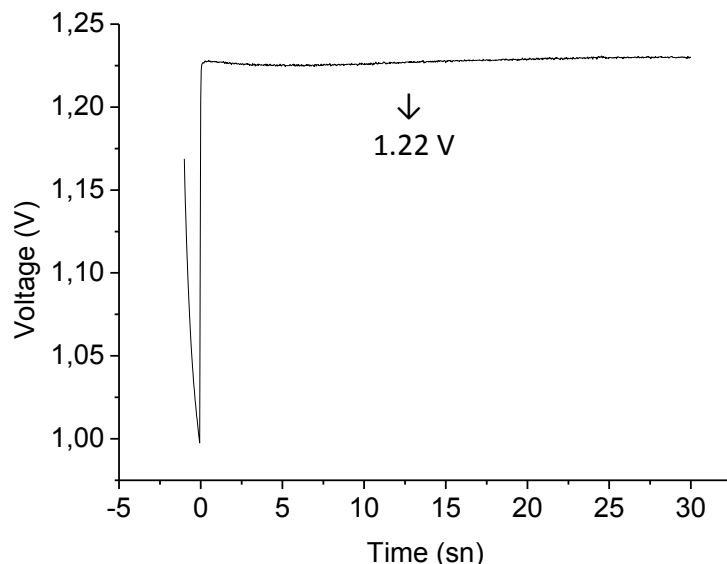


Figure 4.57 : GS electrodeposition of $5 \cdot 10^{-2}$ M Cz in 0.1 M Bu_4NClO_4 containing ACN at 30 s.

After a sharp increase on voltage was observed at the during the first 5 s of polymeric growth, it was stabilized at 1.22 V and kept constant during the polymerization. (Fig. 4.57)

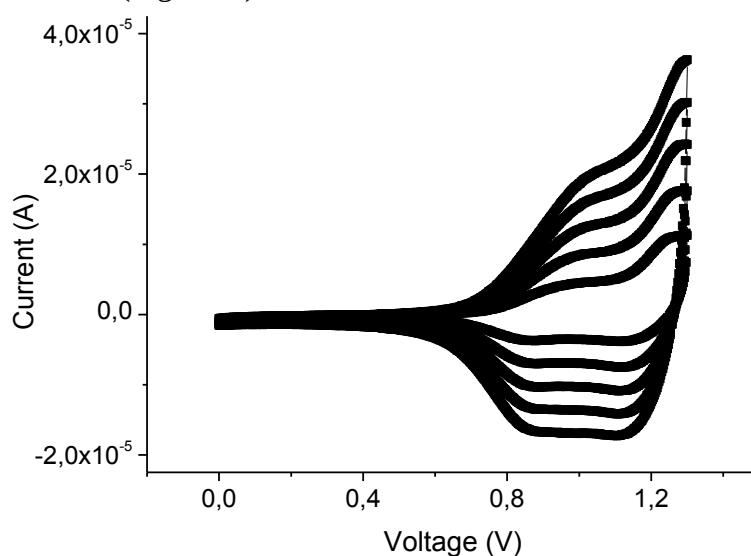


Figure 4.58: Voltammetric response of PCz polymerized by GS method at 30 s in 0.1 M Bu_4NClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

The CV of the polymer film obtained by GS at 30 s showed a broad peak at +0.9V as it can be seen in the Fig. 4.58. Results obtained from these measurements were summarized in Table 4.20.

Table 4.20 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PCz polymerized by GS method at 30 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	926	876	0.4	0.4	50	1.0
200	943	888	0.8	0.7	55	1.1
300	954	901	1.1	1.0	54	1.0
400	975	920	1.5	1.4	55	1.1
500	992	939	1.9	1.7	53	1.1

Similarly to film obtained by PD method at 2 cycles (Table 4.19) and on the contrary of film obtained by PS method at 30 s (Table 4.20), in all cases ΔE values were very small and peak ratios were very close to unity, showing thin film behaviour and good electrochemical reversibility for the film obtained by GS method at 30 s. The best reversibility was obtained at 300 mV/s.

Polymerization of Cz by GS method at 60 s was given in the Fig. 4.59. Monomer concentration, applied voltage and electrodes were kept same with previous measurements and similar investigations were done. The voltammetric response of the film at different scan rates was given in Fig. 4.61

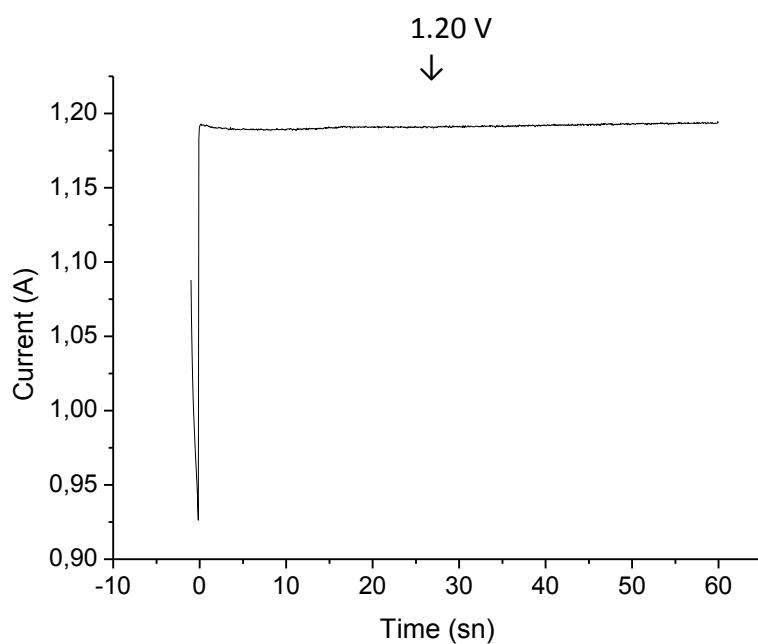


Figure 4.59 : GS electrodeposition of $5. \cdot 10^{-2}$ M Cz in 0.1 M Bu_4NClO_4 containing at 60 s.

After a sharp increase on the voltage during the first 5 s of polymeric growth, it was stabilized at 1.18V and kept constant during the polymerization. (Fig. 4.60)

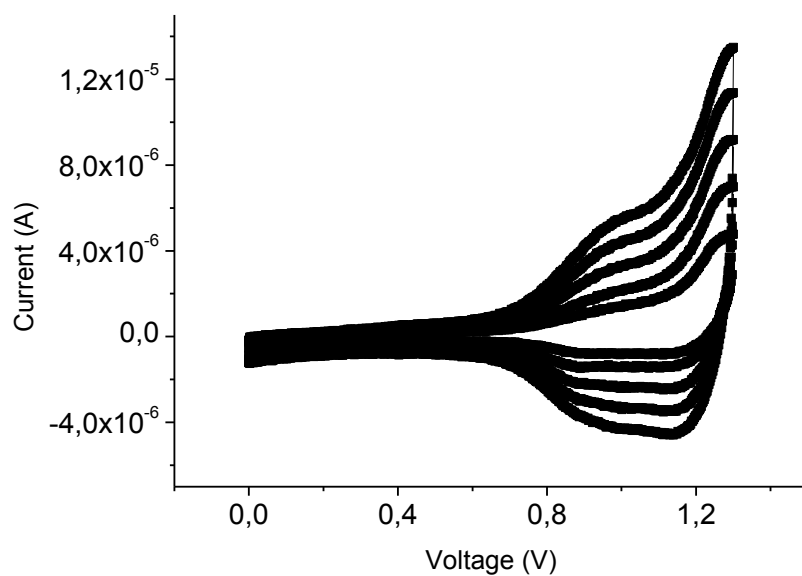


Figure 4.60 : Voltammetric response of PCz polymerized by GS method at 60 s in 0.1 M Bu_4NClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

The CV of the polymer film obtained by GS method at 60 s showed a broad peak at +0.9V as it can be seen in the Fig. 4.60. Results obtained from these measurements were summarized in Table 4.21.

Table 4.21 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PCz polymerized by GS method at 60 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	924	885	0.1	0.1	39	1.3
200	933	892	0.2	0.1	41	1.3
300	949	895	0.2	0.2	54	1.1
400	962	924	0.4	0.3	38	1.3
500	975	946	0.5	0.4	29	1.2

Similarly to PS polymerization method at 30 s, in all cases ΔE values were very small and peak ratios were very close to unity, showing good electrochemical reversibility. The best reversibility was obtained at 300 mV/s.

Polymerization of Cz by GS method at 120 s was given in the Fig. 4.61. Monomer concentration, applied voltage and electrodes were kept same and similar investigations were done. The voltammetric response of the film was given in Fig. 4.62.

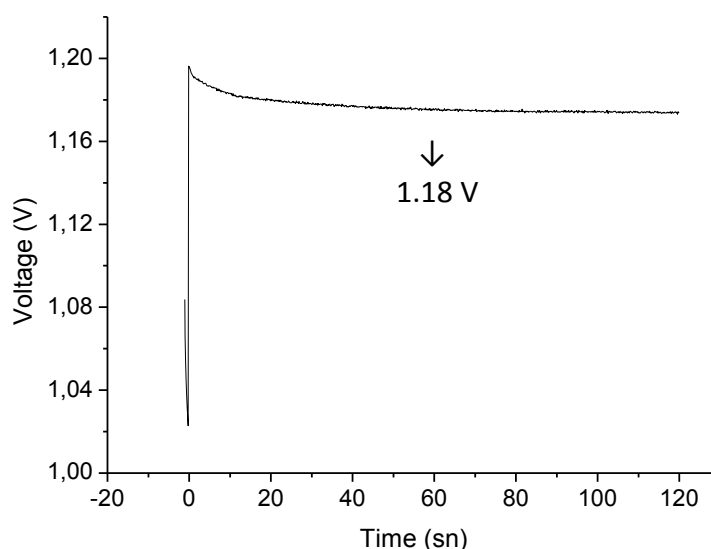


Figure 4.61 : GS electrodeposition of $5 \cdot 10^{-2}$ M Cz in 0.1 M Bu_4NClO_4 containing ACN at 120 s.

After a sharp increase and a relatively small decrease on voltage during first 5 s of polymeric growth, the voltage was stabilized at 1.18 V and stayed constant until the end of polymerization.

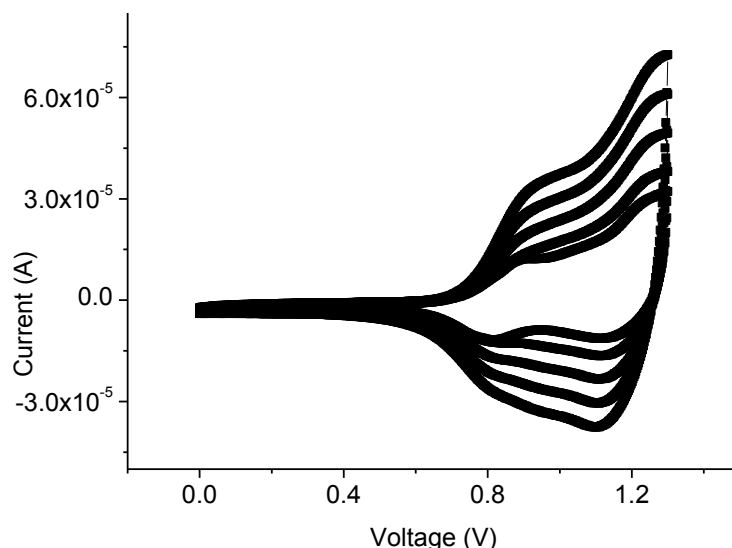


Figure 4.62 : Voltammetric response of PCz polymerized by GS method at 120 s in 0.1 M Bu_4NClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Results obtained from these measurements were summarized in Table 4.22.

Table 4.22: E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PCz polymerized by GS method at 120 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	876	825	1.04	1.17	51	0.90
200	884	840	1.37	1.34	54	0.95
300	904	850	1.88	1.86	54	1.02
400	917	871	2.70	2.40	46	1.12
500	939	888	3.45	3.08	51	1.12

Similar to films obtained by GS method at shorter polymerization times, in all cases ΔE values were very small and, peak ratios were very close to unity, showing good electrochemical reversibility. The best reversibility was obtained at 300 mV/s. (Table 4.22)

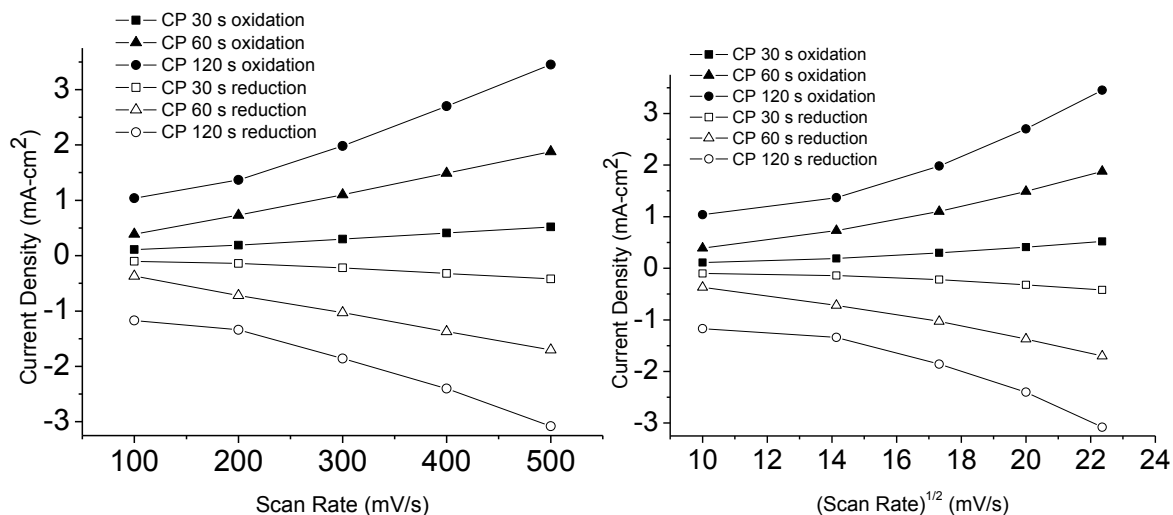


Figure 4.63: (a) Current density versus scan rate, (b) Current density versus square root of scan rate plot PCz films obtained by GS method at different polymerization times (30, 60 and 120 s)

In the case of GS method, short polymerization times (30 and 60 s) contributed thin film character whereas the long polymerization time (120 s) caused diffusion control. (Fig. 4.63 a,b)

Comparison of oxidation currents vs scan rates of PCz obtained by PD, PS and GS methods was given in the Fig. 4.64. Redox behaviour of PCz films obtained with different methods and at different polymerization times were compared.

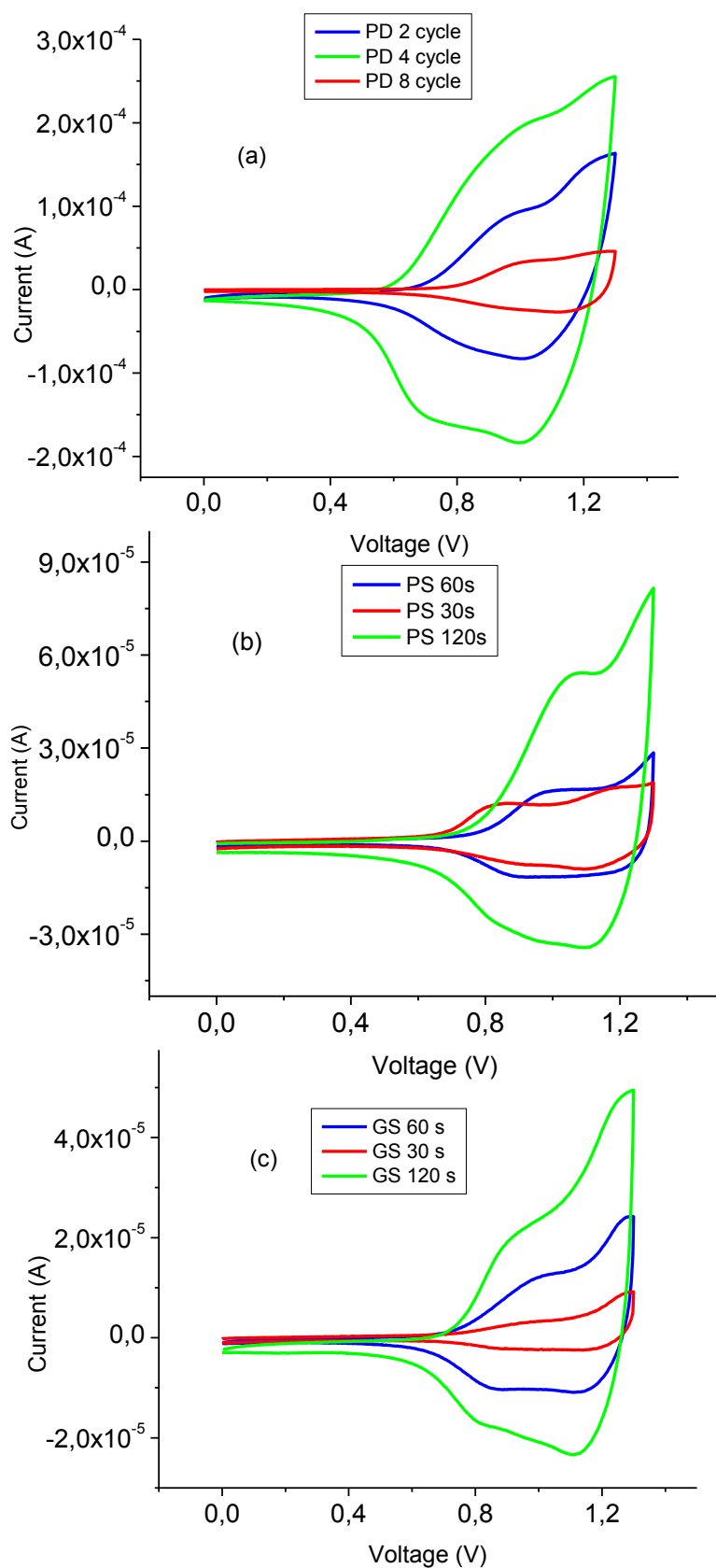


Figure 4.64: Comparison of redox behaviour of PCz films obtained by PD (a) , PS (b) and GS (c) depending on polymerization time at 300 mV/s in monomer free solution.

For PCz films obtained by PD and GS method (Fig. 4.64 a,c) , as the thickness increased the I_{ox} increased as well. In the case of PS method (Fig. 4.64 b), I_{ox} increased by polymerization time also. But for the films obtained by PS method the difference in the current intensities between 30 s and 60 s was relatively smaller and the highest I_{ox} has been achieved with the longest polymerization time

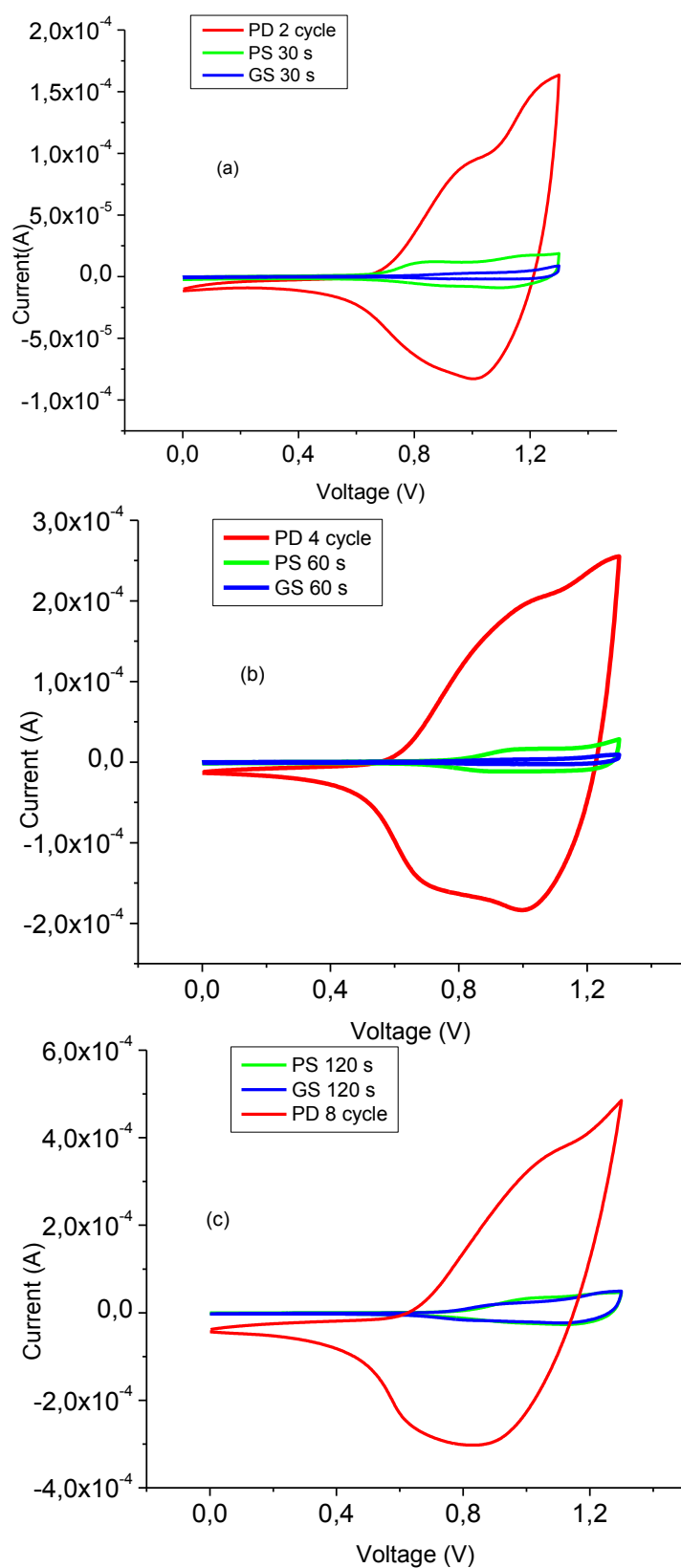


Figure 4.65 : Comparison of redox behaviour of PCz films obtained by PD , PS and GS methods depending on polymerization method. [(a), PD 2 cycles, PS 30 s, GS 30 s; (b), PD 4 cycles, PS 60 s, GS 60 s; (c), PD 8 cycles, PS 120 s, GS 120 s] at 300 mV/s in monomer free.

As it can be seen in the Fig. 4.65. in the case of all polymerization times, the highest current intensity was observed for the PCz film obtained by PD method. This might be due to the removals from the surface in reverse scan resulted thinner, more regular and electroactive film.

4.2.4. Comparasion of Electrochemical Impedance Spectroscopy Measurements of PCz films

Similar to PPy, impedance properties of the PCz films in 5ml 0.1 M ACN/ Bu_4NClO_4 monomer free solution were investigated between 10 mHz-100 kHz range, in the absence of direct voltage and under 1V constant voltage.

4.2.4.1. EIS results of potentiodynamically obtained PCz films

Nyquist, bode phase and bode magnitude diagrams resulting PCz films were compared for each polymerization time. (Fig. 4.66- 4.71). At low frequency and open circuit potential, and for short polymerization times, the imaginary part of the impedance sharply increased and plot tend to a vertical line which is a characteristic of capacitive behaviour. (Fig. 4.66)

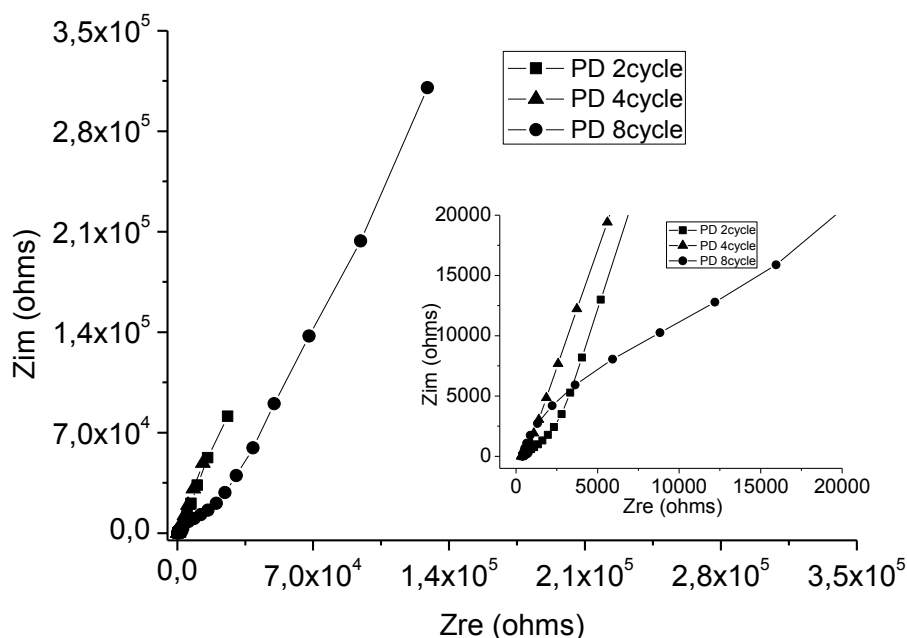


Figure 4.66: Nyquist diagram of PCz obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

At high frequency and under constant 1V voltage Z_{im} showed semi circle behaviour. Besides, as the polymerization time increased, imaginary part of impedance value increased also as expected. (Fig. 4.67)

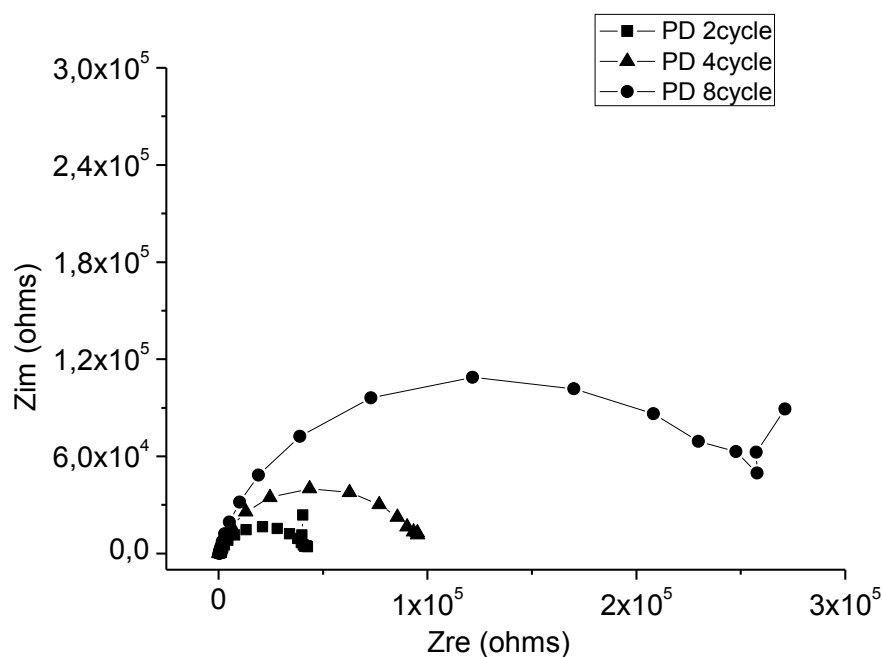


Figure 4.67: Nyquist diagram of PCz obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

At frequencies > 1 kHz, the phase angle approaches a plateau, and the electric signal reached maximum penetration in the pores of the PCz. The highest phase angle was observed at the film polymerized by PD method at 4 cycles. (Fig 4.68)

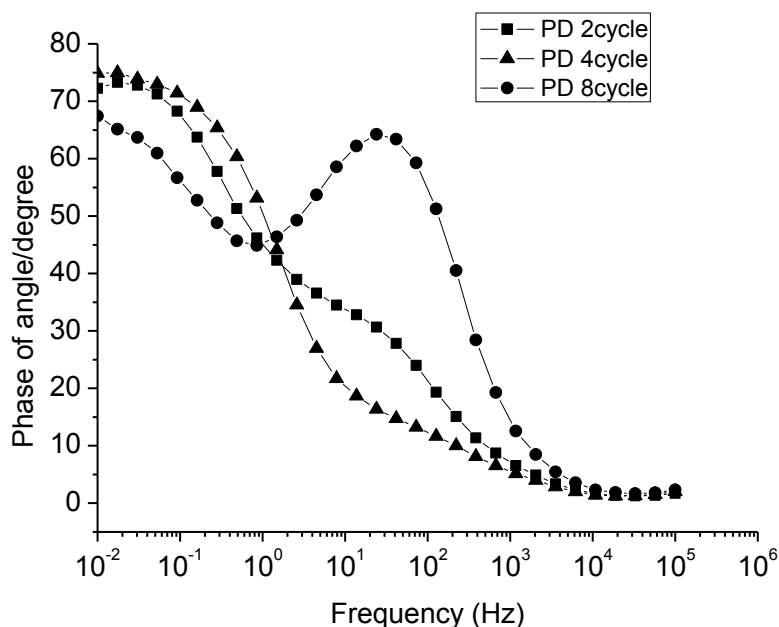


Figure 4.68: Bode phase diagram of PCz obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

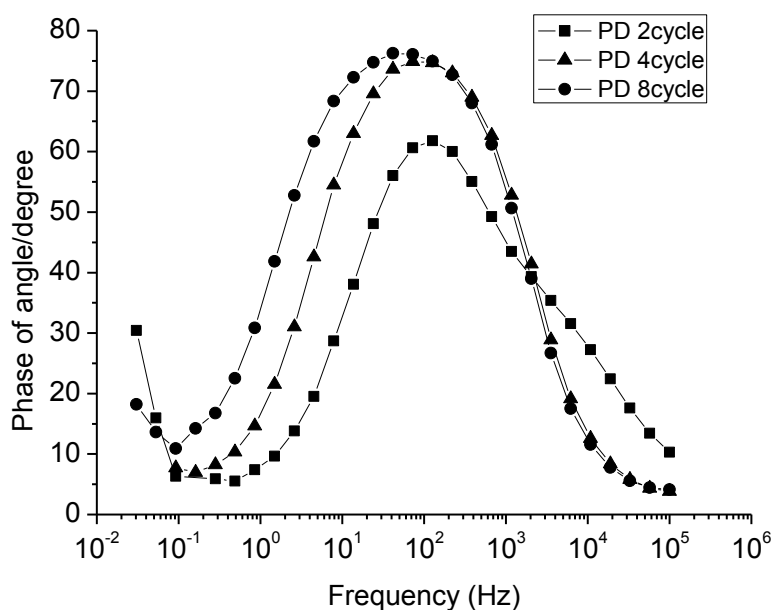


Figure 4.69 : Bode phase diagram of PCz obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Phase angles became lower and shifted to higher frequencies with increasing cycle number under the 1V constant voltage as the constant voltage led to the overoxidation of the polymer and the deposition from the film surface (Fig.4.69).

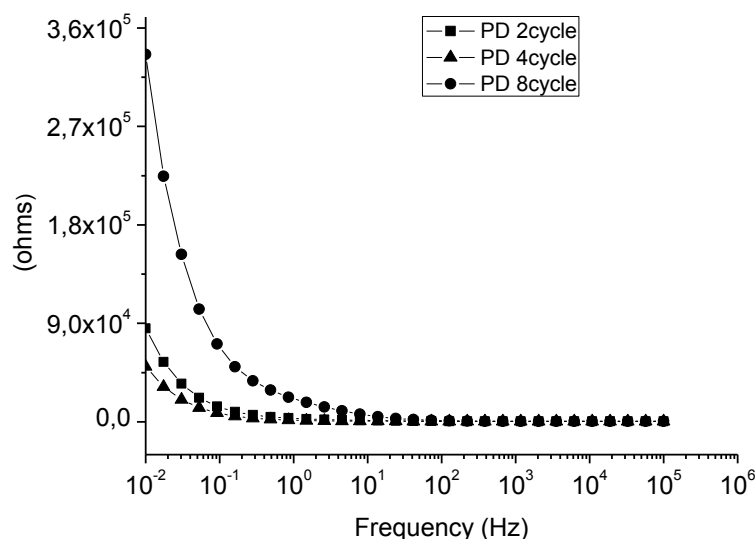


Figure 4.70 : Bode magnitude diagram of PCz obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

As it seen was in the Fig. 4.70 at low frequencies, as the polymerization time increased the imaginary value of impedance (IZI) increased due to the deposition of

polymer on the electrode. For the frequencies >10 Hz , IZI reaches a constant value for all polymerization times.

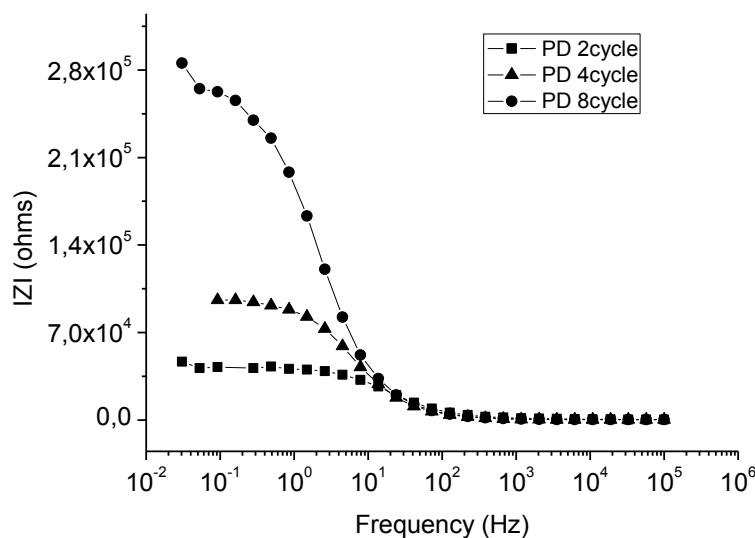


Figure 4.71 : Bode magnitude diagram of PCz obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Results obtained from the measurements were demonstrated in the Table 4.23.

Table 4.23: R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PCz polymerized by PD method at 2, 4 and 8 cycles

PCz ($\pm 0,5$)	PD (2 cycle)		PD (4 cycle)		PD (8 cycle)	
	Open circuit potential	1V applied	Open circuit potential	1 V applied	Open ircuit potential	1V applied
R_s ohm-cm ²	381	403	326	325	394	400
R_p ohm-cm ²	5071	41867	4822	12171	11456	245748
C_{dl} μF -cm ²	32	5	10	5	10	1
C_{sp} μF -cm ²	194	—	317	—	47	—
C_{dif} μF -cm ²	210	—	22	—	27	—
P. angle (degree)	72	30	75	8	68	18

As it can be seen in the Table 4.23 the best capacitive behaviour was observed for PCz obtained by PD method at 2 and 4 cycles.

4.2.4.2. EIS results of potentiostatically obtained PCz film

Impedance properties were investigated in the similar conditions of PPy obtained by PS method at 30s. Nyquist, Bode phase and Bode magnitude diagrams resulting PPy films were compared for each polymerization method and time (Fig. 4.72-4.77) As it can be seen in the Fig. 4.72, the imaginary part of the impedance sharply increased and plot tend to a vertical line which is a characteristic of capacitive behaviour for film obtained by PS method at 30 s.

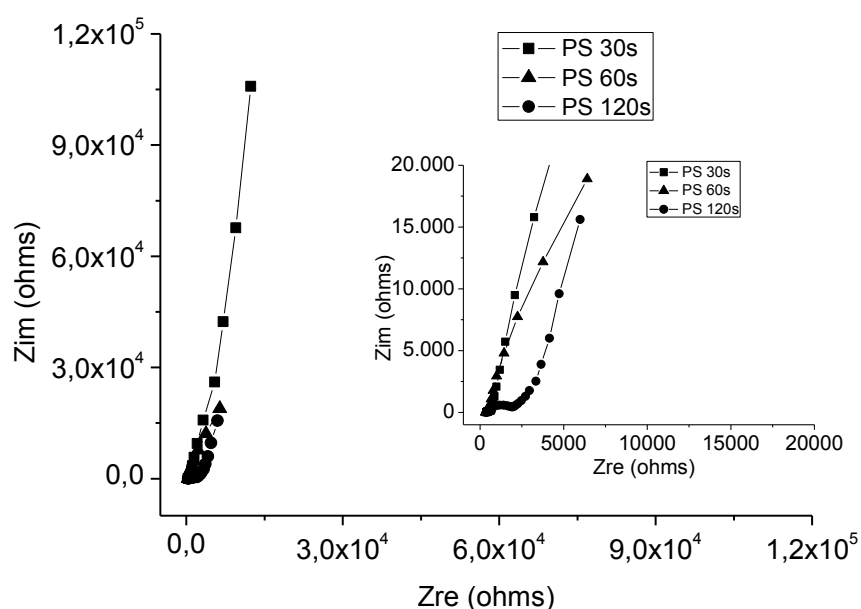


Figure 4.72 : Nyquist diagram of PCz obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

Both of real and imaginary part of impedance increased as the polymerization time increased and the imaginary part showed a semi circle character. (Fig. 4.73)

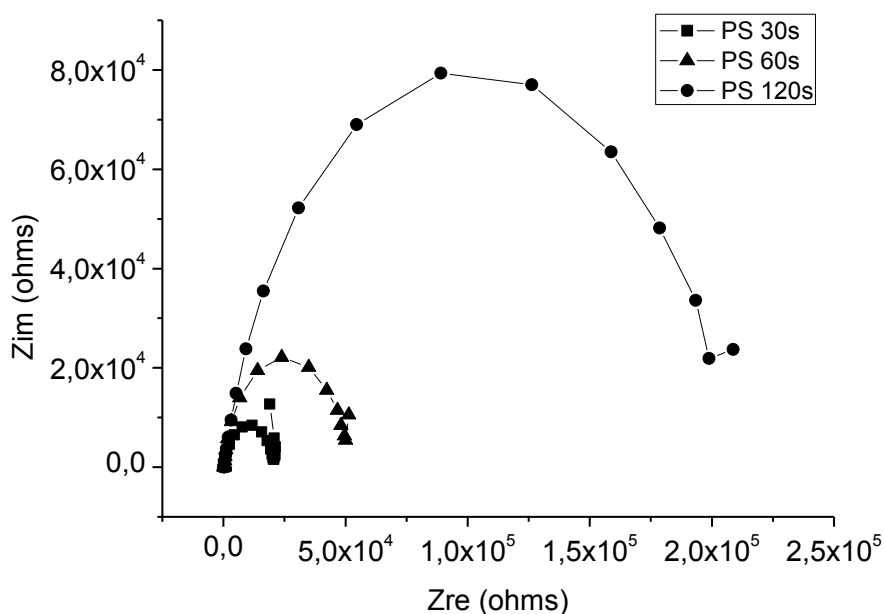


Figure 4.73 : Nyquist diagram of PCz obtained by PS method at 30, 60 and 120 s by applying 1V direct voltage.

As it can be seen in the Fig. 4.74 for PCz films obtained at 60 s, at frequencies > 10 Hz, and for PCz films obtained at 30 s, at frequencies > 1 kHz the phase angle approached a plateau, and the electric signal reached maximum penetration in the pores. The highest phase angle was observed at the film polymerized by PS method 60 s.

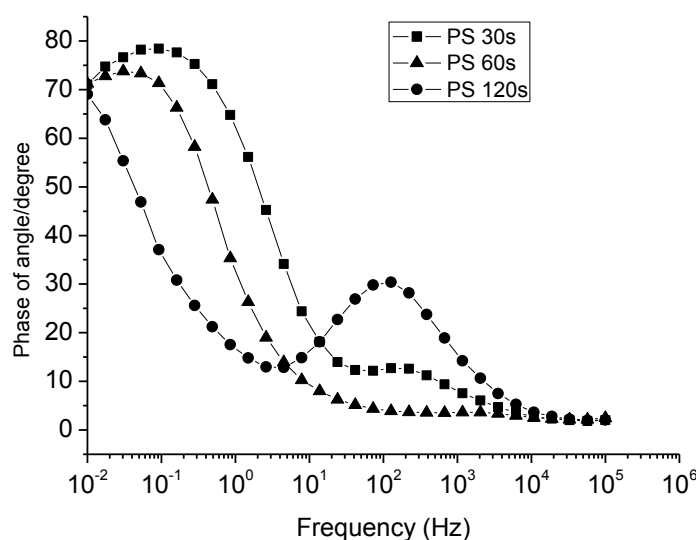


Figure 4.74 : Bode phase diagram of PCz obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency.

Similar frequency shifts with the phase angle were observed under the 1V constant voltage for the Zim value at all polymerization times. (Fig. 4.75)

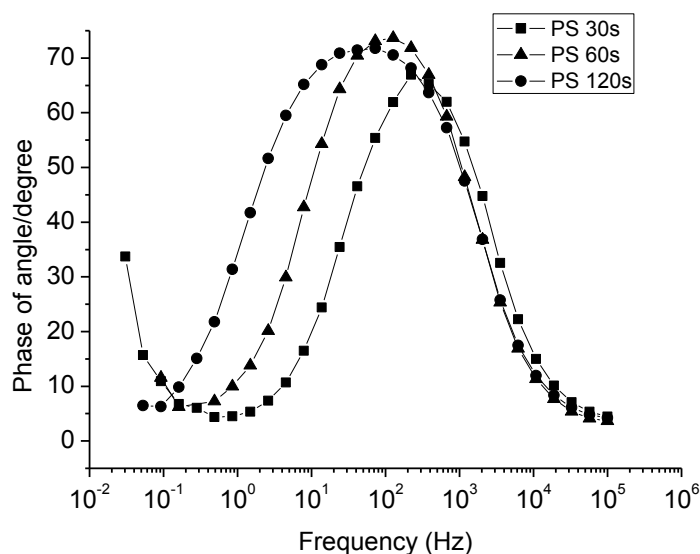


Figure 4.75 : Bode phase diagram of PCz obtained by PS method 30, 60 and 120 s between 10 mHz and 100 kHz frequency by applying 1V direct voltage.

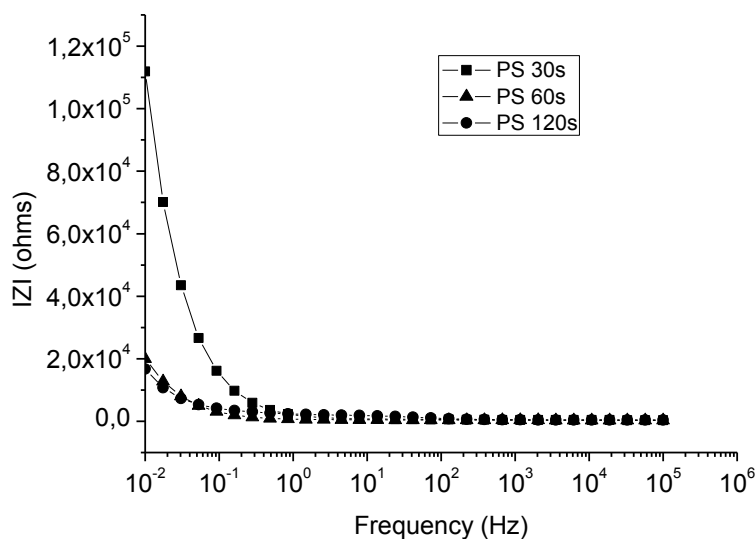


Figure 4.76 : Bode magnitude diagram of PCz obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

At low frequencies the lowest Z_{im} was observed for film obtained during 60 and 120 s. That was because of application of further charge contributed to further oxidation and doping of the PCz film rather than further deposition of the new polymer layer (Fig. 4.76). This behaviour was similar with the PPy obtained by PS method at different polymerization times, as it can be seen in the Fig. 4.34. Under 1V constant voltage, similar frequency shifts with previous measurements were observed as the

constant voltage led to the overoxidation of the polymer film surface and contributed the resistive behaviour more than capacitive character. (Fig. 4.77)

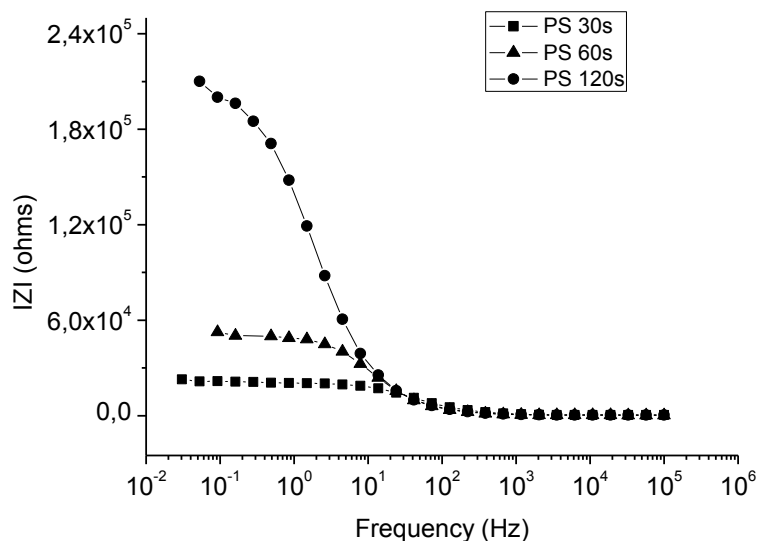


Figure 4.77 : Bode magnitude diagram of PCz obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Results obtained from the measurements were demonstrated in the Table 4.24

Table 4.24 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PCz polymerized by PS method at 30, 60 and 120 s.

PCz ($\pm 0,5$)	PS (30s)		PS (60s)		PS (120s)	
	Open circuit potential	1V applied	Open circuit potential	1 V applied	Open circuit potential	1V applied
R_s ohm-cm ²	358	368	332	330	431	382
R_p ohm-cm ²	1196	21126	2160	48050	11545	180100
C_{dl} μF -cm ²	23	3	18	4	5	1
C_{sp} μF -cm ²	143	—	964	—	832	—
C_{dif} μF -cm ²	160	—	900	—	1097	—
P. angle (degree)	71	34	71	11	69	7

As it can be seen in the Table 4.24 the best capacitive behaviour was obtained for PS method at 30 and 60 s.

4.2.4.3. EIS results of galvanostatically obtained PCz film

Impedance properties were investigated in the similar conditions of PD and PS polymerized PCz. Nyquist, Bode phase and Bode magnitude diagrams (Fig. 4.78-4.83) resulting PCz films were compared for each polymerization time.

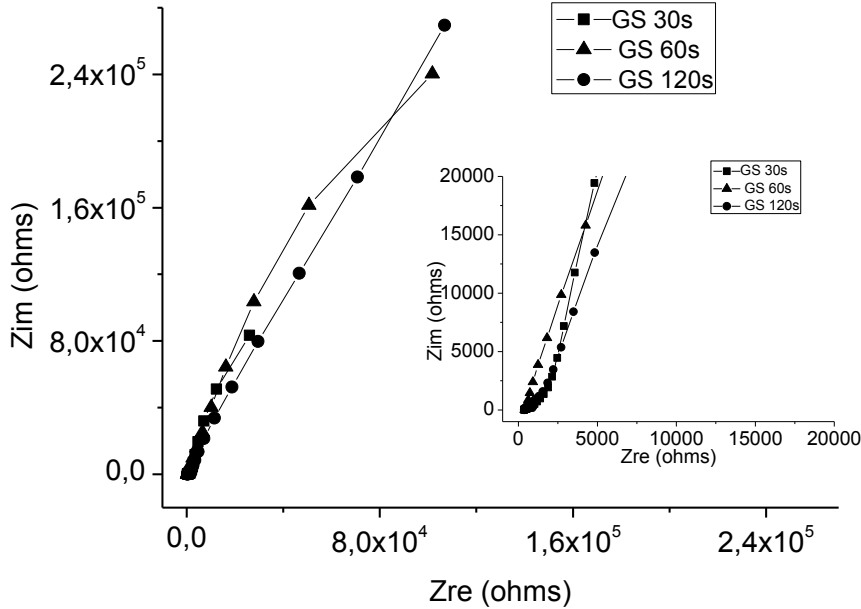


Figure 4.77 : Nyquist diagram of PCz obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

As it can be seen in the Fig 4.78 for the PCz films obtained by GS at 30 and 60 s, the imaginary part of the impedance sharply increased and plot tend to a vertical line which is a characteristic of capacitive behaviour at low frequency and open circuit potential.

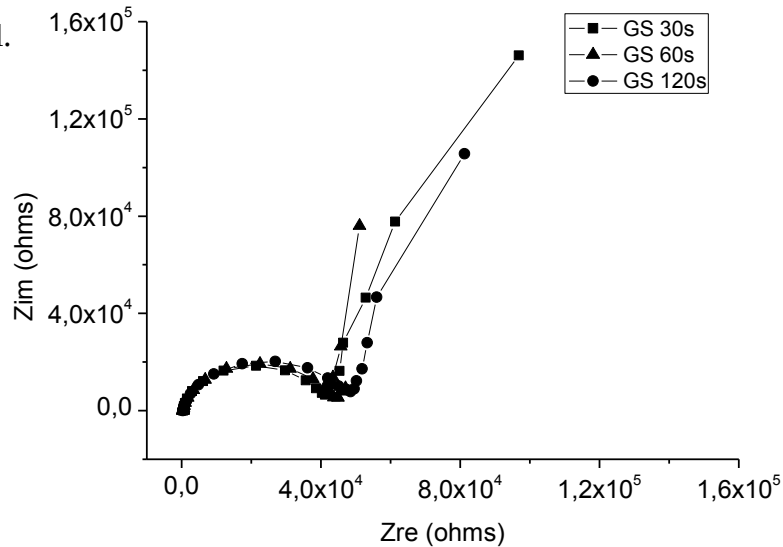


Figure 4.79 : Nyquist diagram of PCz obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

As it can be seen in the Fig. 4.79 under 1 V constant voltage, the imaginary part of the impedance gave three semi circles for all polymerization times. On the contrary of PD and PS methods, there was no increase neither imaginary nor real part of impedance as a result of increase in polymerization time.

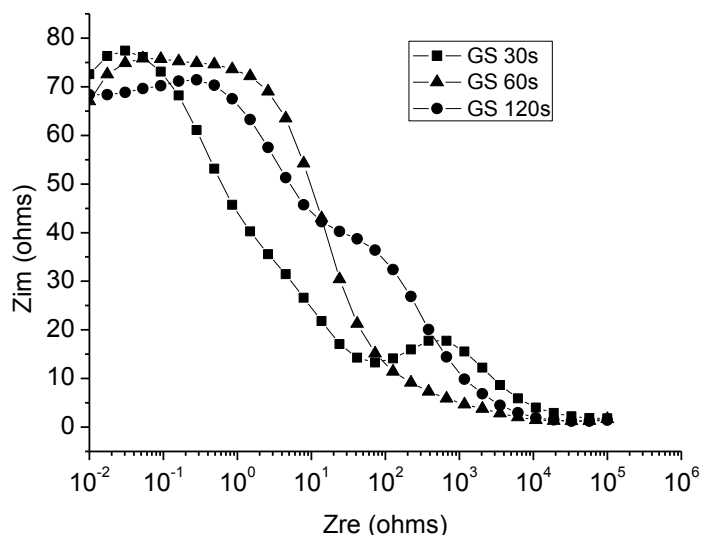


Figure 4.80 : Bode phase diagram of PCz obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

The highest phase angle was observed for PCz obtained by GS method at 30 s. (Fig. 4.80) Shifts on the phase angle were observed at the same frequencies as the impedance value was independent of polymerization time. (Fig. 4.81)

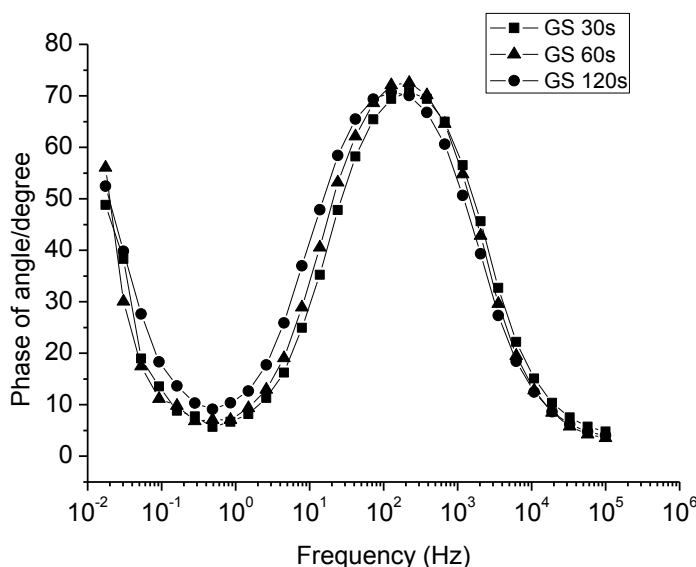


Figure 4.81 : Bode phase diagram of PCz obtained by GS method at 30, 60 and 120s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

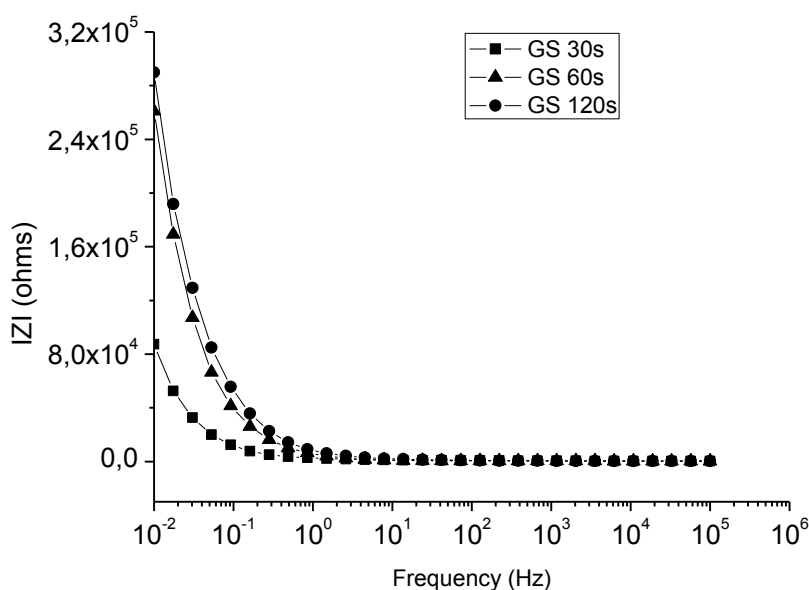


Figure 4.82 : Bode magnitude diagram of PCz obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

In the case of GS polymerization, the lowest IZI was observed for the lowest polymerization time. As the polymerization time increased to 60 s the IZI increased also. But due to the removals from the surface IZI did not increase even the polymerization time increased to 120 s. (Fig. 4.83)

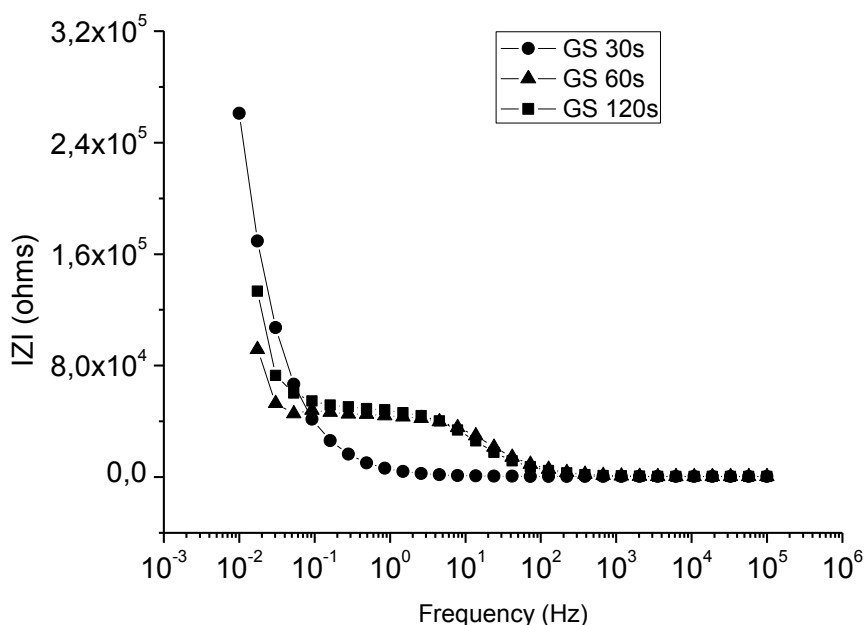


Figure 4.83 : Bode magnitude diagram of PCz obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Results obtained from the measurements were demonstrated in the Table 4.25.

Table 4.25 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PCz polymerized by GS method at 30, 60 and 120 s.

PCz (± 0.5)	GS (30s)		GS (60s)		GS (120s)	
	Open circuit potential	1V applied	Open circuit potential	1 V applied	Open circuit potential	1V applied
R_s ohm-cm^2	411	420	397	401	368	379
R_p ohm-cm^2	1018	42242	5096	44925	14084	53250
C_{dl} $\mu\text{F-cm}^2$	20	4	6	4	4	3
C_{sp} $\mu\text{F-cm}^2$	190	—	66	—	54	—
C_{dif} $\mu\text{F-cm}^2$	200	—	71	—	61	—
P. angle (degree)	71	56	67	55	68	53

As it can be seen in the Table 4.25 for the PCz films synthesized by GS method, the highest phase angle and C_{dl} and C_{sp} was observed for the film obtained at 30 s. When three polymerization methods were compared, in the case of PCz, the best reversible and the most capacitive film was obtained by PD at 2 cycles.

For the PCz films obtained by PD method, as the polymerization time increased, C_{sp} and C_{dl} values increased as well. Further increase in polymerization time caused a decrease in C_{sp} value which is well matched with the highest current intensity in the case of 4 cycles. (Fig. 4.64 a) C_{dl} Values stayed constant with the increase in polymerization time (Table 4.23).

In the case of PCz polymerization by PS method as the polymerization time increased the C_{sp} values increased as well.(Table 4.24). Increase in polymerization time did not contribute the increase in charge storage capacity of the PCz film.

Capacitive behaviour of polymer films decreased as the polymerization time increased in the case of GS method.(Table 4.25). Besides the C_{sp} and C_{dl} values and phase angles were less than the films obtained by PD and PS. This might be explained as, application of further voltage contributed the overoxidation and doping

of polymer films. The lowest R_p value was observed for the GS method at 30 s (Table 4.25)

Phase angles stayed constant with the polymerization time for all methods similarly with PPy.

When the three methods were compared with each other, the most capacitive films obtained by PS method at long polymerization times. The most reversible film was obtained by PD method at 4 cycles.

4.2.4.4. Equivalent electrical circuit diagram of PCz:

The experimental data was succesively well matched with the electrical equivalent circuit to explain the relation between platinum button electrode, polymer and electrode surfaces. This model can be considered as a inhomogeneous system as it was occured in different phases such as liquid (solvent) and bulk (polymer/electrode). As it can be seen in the Fig. 4.83, R_s corresponded resistance of the polymer and the electrolyte, C_{dl} was double layer capacitance. R_e was the resistance of the electrolyte. (CPE) was constant phase element in parallel with R_{ct} and W , R_{ct} was the charge transfer, and W was the Warburg impedance of the polymer. The last component a capacitor element, (C_{pt}) was introduced in parallel with a resistor (R_{pt}) corresponding resistor of platinum button electrode of polymer coating. CPE stimulated the capacitor of the film/electrode surface resulted due to the binding of counter ions in to the irregular geometry of polymer surface. C_{dl} was the electrical double layer exists on the interface between an electrode and its surrounding electrolyte. This double layer is formed as ions from the solution "stick on" the electrode surface. R_{ct} was characteristic quantity for the charge-transfer step of an electrode reaction indicative of its inherent speed: a large charge-transfer resistance indicated a slow step. Results obtained from the equivalent circuit diagram were presented in Table 4.26.



Figure 4.84 : Equivalent circuit diagram of PCz. (R(C(R(Q(RW))))(CR) [Chi squared: $4.984 \cdot 10^{-4}$, $n = 0,6627$, Monomer: $5 \cdot 10^{-2}$ M Cz, Method: PD at 2 cycles, 50 mV/s, Electrolyte: 0,1 M ACN/ Bu₄NClO₄, WE: Pt (button electrode), RE: Ag/AgCl, CE: Pt (wire)]

Table 4.26 : Potential dependence of the parameters calculated for PCz film from the equivalent circuit diagram.

$R_{p,e}$ (ohm- cm ²)	C_{dl} (F/cm ²)	R_e (ohm- cm ²)	Q (CPE) Y0 (S- sec ⁿ /cm ²)	R_{ct} (ohm- cm ²)	W Y0 (S- sec ⁿ /cm ²)	C_{pt} (F/cm ²)	R_{pt} (ohm- cm ²)
352	$23 \cdot 10^{-5}$	5245	$7.5 \cdot 10^{-5}$	415	$2.9 \cdot 10^{-20}$	$19 \cdot 10^{-5}$	$6 \cdot 10^{-5}$

4.3. Comparison of Polymerization Conditions and Characterization of IN

4.3.1. Potentiodynamic Polymerization of IN

Polymerization of IN by PD method at 2 cycles in 0.1 M ACN/ NaClO_4 was given in Fig. 4.84.

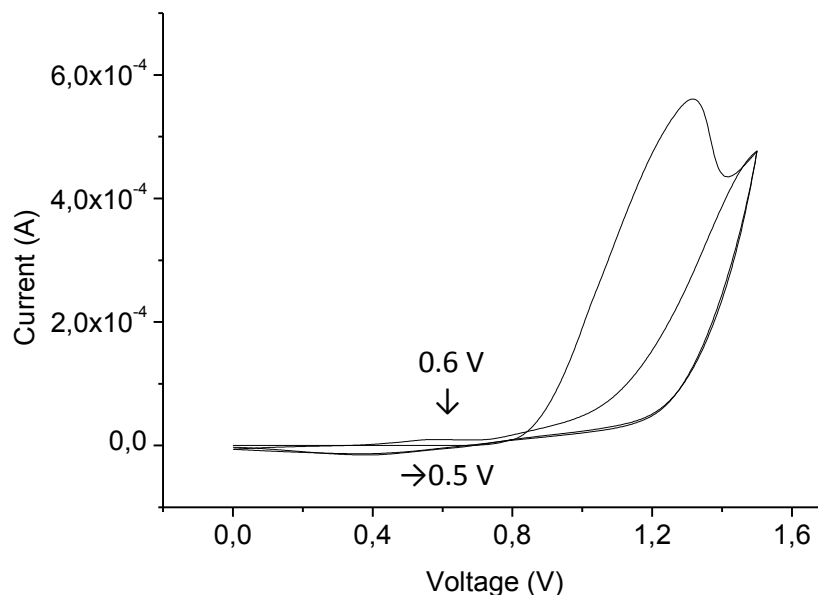


Figure 4.84 : PD electrodeposition of 0.1 M IN at 2 cycles in 0.1 M NaClO_4 containing ACN at the scan rate of 50 mV/s.

As it can be seen in the Fig. 4.84, when the potential sweep was performed between 0-1.6 V, the current value started to increase continuously at around +1.20 V due to the oxidation of monomer. At the following reverse scan, a cathodic broad appeared beyond the potential value of +0.50 V due to reduction of obtained PIN film [20,21]. In the following forward scan of second cycle, reoxidation of reduced PIN film was observed as anodic wave starting at around +0.70 V which is similar with the PD electrodeposition of Cz seen in the Fig 4.43, 4.45, 4.47) The coated electrode was then transferred into monomer free solution and the scan rate dependence of resulting film investigated and given in Fig. 4.85.

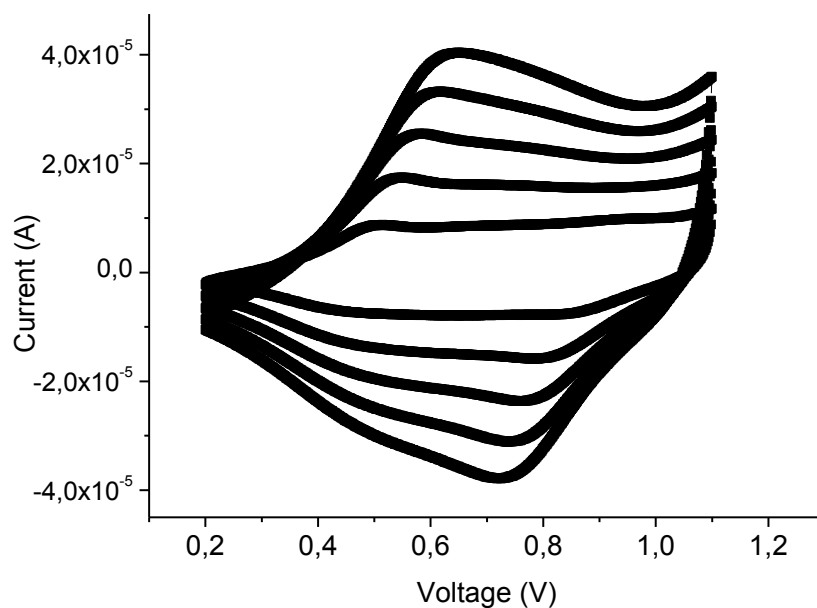


Figure 4.85 : Voltammetric response of PIN polymerized by PD method at 2 cycles in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

CV of the PIN film obtained by PD at 2 cycle showed one broad wave at about + 0.6 V (Fig. 4.85). Results obtained from the voltammogram were presented in the Table 4.27.

Table 4.27 : E_a, E_c, I_a, I_c, ΔE, I_a/I_c values of IN polymerized by PD method at 2 cycles.

Scan rate m V/s	E _a (mV)	E _c (mV)	I _a (μA)	I _c (μa)	ΔE (m V)	I _a /I _c
100	489	473	0.8	0.7	16	1.1
200	537	485	1.7	1.4	52	1.2
300	573	521	2.5	2.1	52	1.2
400	609	571	4.0	3.2	53	1.3
500	624	571	4.0	3.6	53	1.1

As it can be seen from the Table 4.27 , at high scan rates, diffusion limited current became more pronounced, ΔE and peak ratio increased. The best reversibility was obtained at 100 mV/s.

Polymerization of IN by PD at 4 cycles in 0.1 M ACN/ NaClO_4 was given in Fig. 4.86.

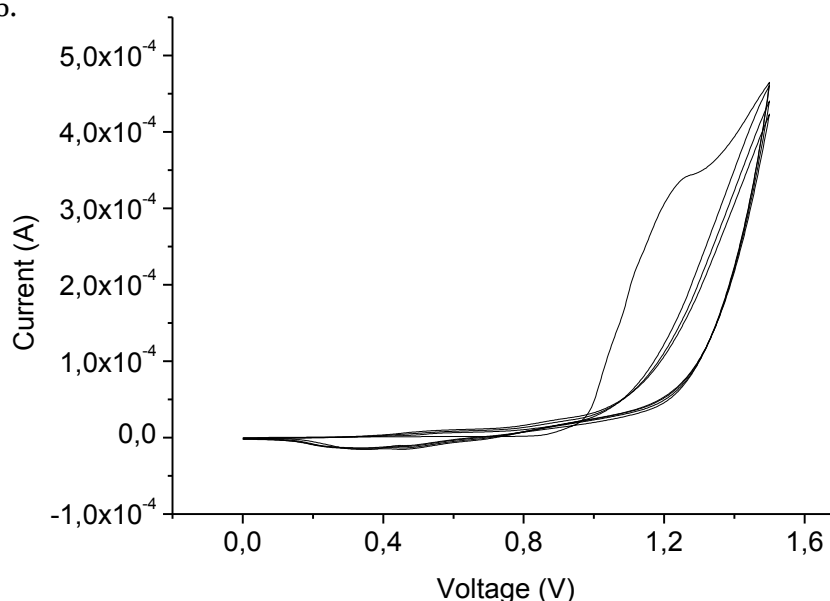


Figure 4.86 : PD electrodeposition of 0.1 M IN at 4 cycles in 0.1 M NaClO_4 containing ACN at the scan rate of 50 mV/s.

It was observed that the anodic and cathodic waves corresponding to oxidation and reduction of PIN film became greater with increasing cycle numbers which showed that the obtained PIN film was stable, and increasing cycle numbers caused a regular increase of thickness on the platinum button electrode. (Fig. 4.86). Voltammetric response of the polymer film was presented in the Fig. 4.87.

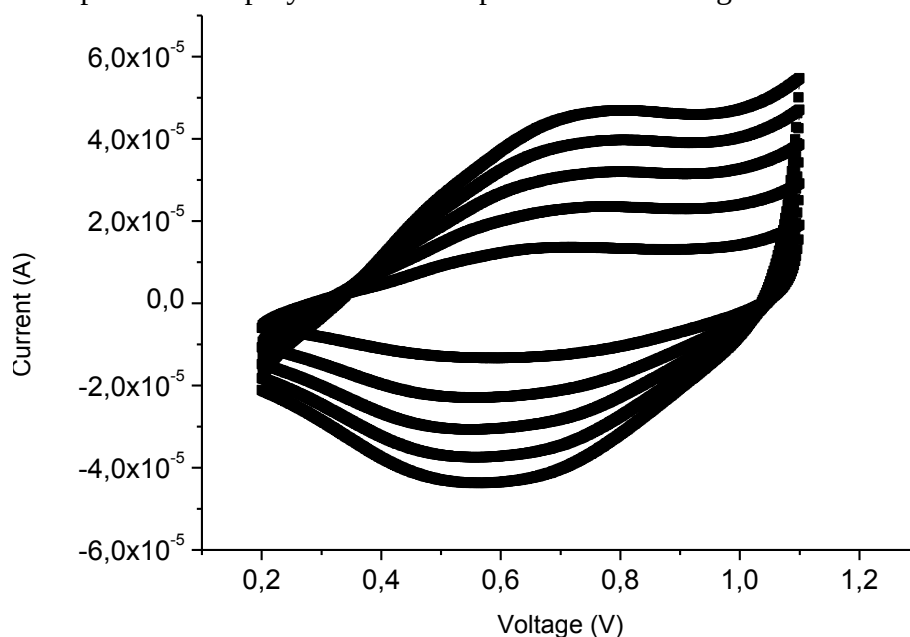


Figure 4.87 : Voltammetric response of PIN polymerized by PD method at 4 cycles in 0.1 M NaClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

As it can be seen in the Fig. 4.87, a broad was observed at about 0.4V at the 100 mV/s, as the scan rate increased, the starting potential of broad shifted to positive area whereas no shifts were observed for the reduction potentials. Results obtained from the voltammograms at different scan rates were summarized in the Table 4.28.

Table 4.28: E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of IN polymerized by PD method at 4 cycles

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	571	544	1.1	1.3	27	0.8
200	604	550	2.0	2.2	54	0.9
300	630	575	3.0	3.0	55	1.0
400	650	594	3.6	3.7	56	1.0
500	655	602	4.4	4.3	53	1.0

As it can be seen in the Table 4.28, in all cases ΔE values were very small and the peak ratios were very close to unity, showing thin film behaviour and good electrochemical reversibility. The best reversibility was obtained at 300 mV/s.

Polymerization of IN by PD method at 8 cycles was given in the Figure 4.88. Monomer concentration, potential interval and electrodes were kept same with previous measurements and similar investigations were done.

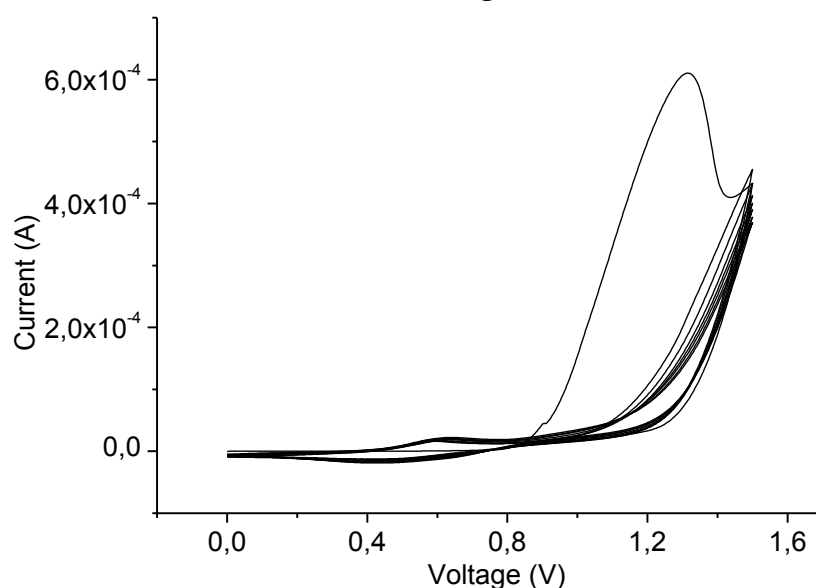


Figure 4.88 : PD electrodeposition of 0.1 M IN at 8 cycles in 0.1 M $NaClO_4$ containing ACN at the scan rate of 50 mV/s.

Similar broads and waves with the PIN films obtained by PD at 2 and 4 cycles were observed for the film obtained at 8 cycles (Fig. 4.88). The voltammetric response of the film was presented in the Fig. 4.89.

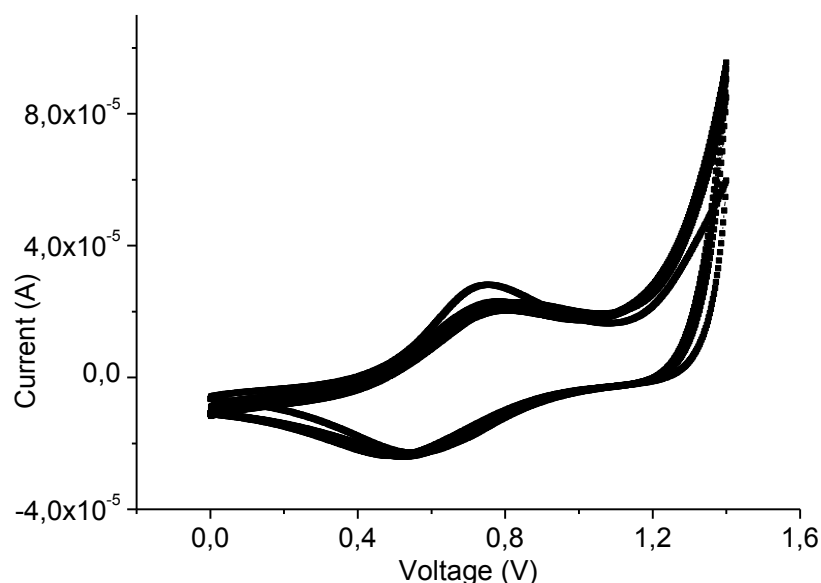


Figure 4.89 : Voltammetric response of PIN polymerized by PD at 8 cycle in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

There is a little increase on the oxidation potentials, due to the increase on the thickness led to a more resistive film. (Fig. 4.89). Results obtained from the voltammograms at different scan rates were summarized in the Table 4.29.

Table 4.29 : E_a, E_c, I_a, I_c, ΔE, I_a/I_c values of IN polymerized by PD method at 8 cycles

Scan rate m V/s	E _a (mV)	E _c (mV)	I _a (μA)	I _c (μa)	ΔE (m V)	I _a /I _c
100	716	513	17	21	203	0.8
200	726	527	20	22	199	0.90
300	743	537	21	23	206	0.92
400	753	557	22	24	196	0.91
500	760	577	28	25	183	1.12

As it can be seen in the Table 4.29, even the ratio of oxidation currents were very close to unity, the ΔE values at different scan rates were very high that corresponding the reversibility of PIN film obtained by PD at 8 cycles was quite poor.

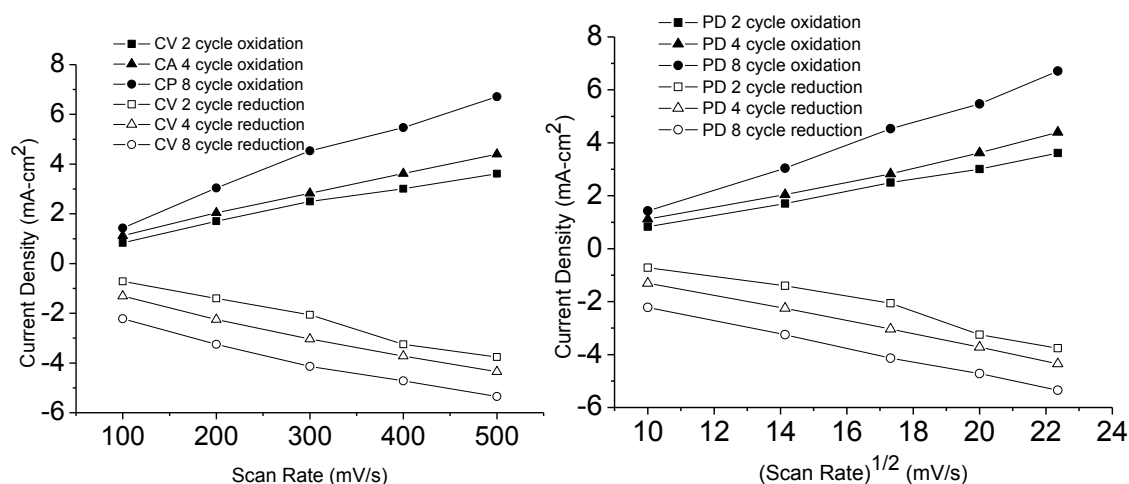


Figure 4.90 : (a)Current density versus scan rate, (b) Current density versus square root of scan rate plot of PIN films obtained by PD method at different cycle numbers (2, 4 and 8 cycles)

In the case of PD, short and middle polymerization times (2 and 4 cycles) contributed thin film character, whereas the long polymerization times (8 cycles) caused diffusion control. (Fig 4.90) For the PIN obtained at 2 and 4 cycles, at all scan rates, peak currents vary linearly with the scan rate, which is characteristic of the behaviour of a thin layer material deposited on the electrode. Conversely, for the film obtained at higher polymerization time (8 cycles), linear variation with the square root of the scan rate was frequently observed, corresponding to diffusion limited currents, arising either from charge transfer process (hopping mechanism) or from an ionic contribution (diffusion of counterions). This idea also supported by increase in peak potential differences (ΔE) and peak current ratios with increasing scan rates. (Table 4.27-4.29).

4.3.2. Potentiostatic polymerization of IN

Polymerization of IN by PS at 30 s in 0.1 M ACN/ NaClO₄ at 30 s was given in Fig. 4.91.

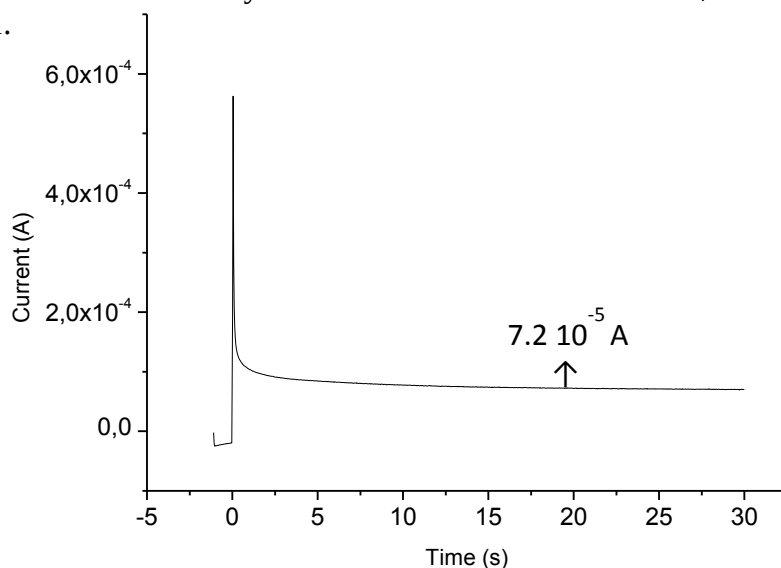


Figure 4.91 : PS electrodeposition of 0.1 M IN at 30 s in 0.1 M NaClO₄ containing ACN.

While the constant potential was applied, a decrease in current was seen after the first 5 s of polymeric growth and after it was stabilized at $7,2 \cdot 10^{-5}$ A. (Fig. 4.91)

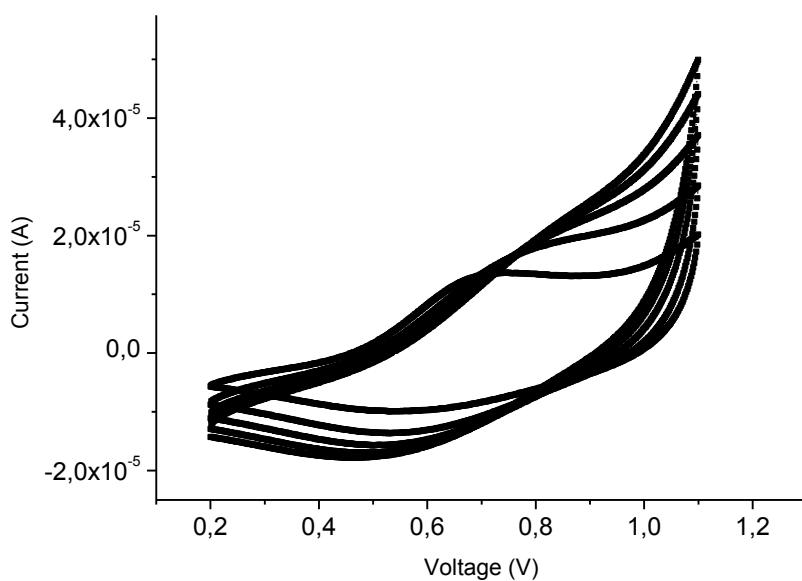


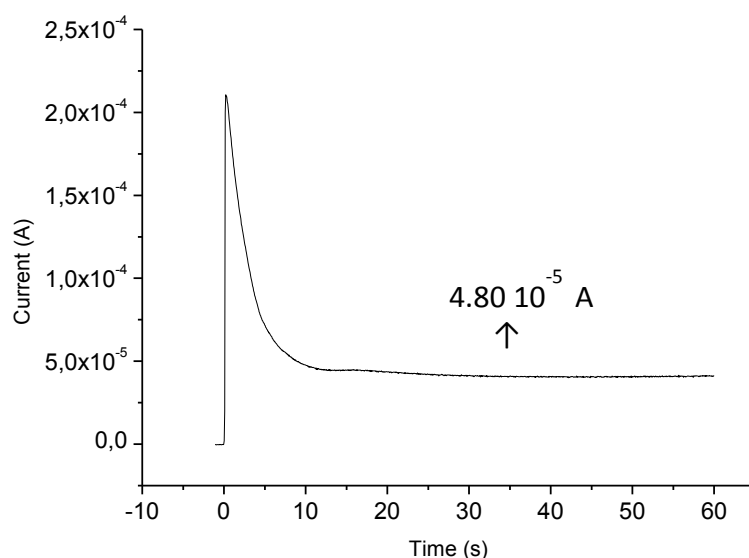
Figure 4.92 : Voltammetric response of PIN polymerized by PS at 30 s in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Table 4.30: E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of IN polymerized by PS method at 30 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	665	636	1.2	0.9	29	1.2
200	690	577	131	1.3	127	1.0
300	706	562	157	1.5	144	1.0
400	717	553	143	1.6	167	0.9
500	728	544	1.54	1.7	184	0.9

As it can be seen in the Table 4.30, at high scan rates diffusion limited current flow became more pronounced, ΔE and peak ratio increased which was similar to the PIN obtained by PD at 2cycles (Table 4.27). The best reversibility was obtained at 100 mV/s.

The PS polymerization of IN in 0.1 M ACN/ $NaClO_4$ at 60 s was given in Fig. 4.93.

**Figure 4.93 :** PS electrodeposition of 0.1 M IN at 60 s in 0.1 M $NaClO_4$ containing ACN.

In the case of PS cally polymerization of IN at 60 s, while the constant potential was applied, a decrease in current was seen after the first 5 s of polymeric growth and after it was stabilized at $4.80 \cdot 10^{-5}$ A.(Fig. 4.93) . The voltammetric response of the polymer film can be seen in the Fig. 4.94.

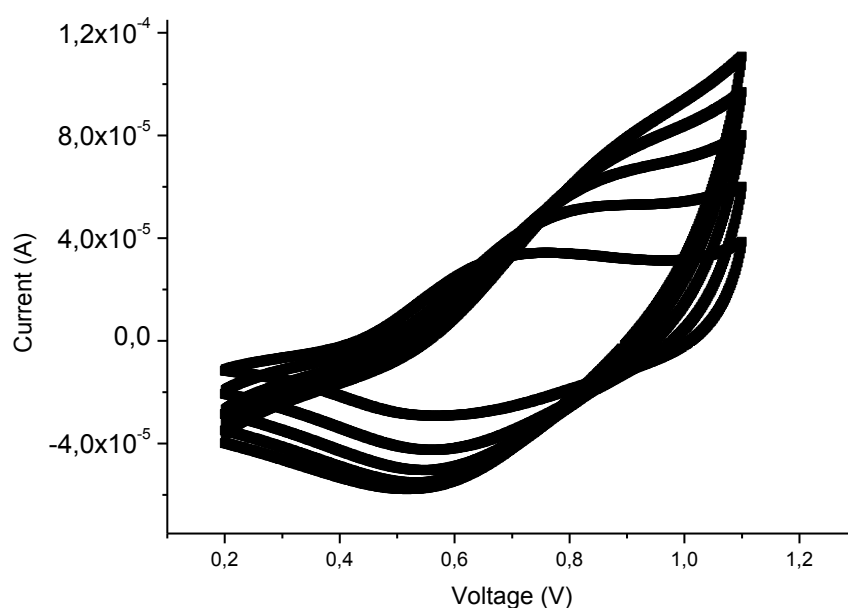


Figure 4.94 : Voltammetric response of PIN polymerized by PS at 60 s in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

As it can be seen in the Fig. 4.94, as the polymerization time increased, the sharper shifts on the E_a and E_c were observed which indicated the decrease of reversibility and electroactivity of the film.

Table 4.31: E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of IN polymerized by PS method at 60 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	652	622	3.0	2.9	30	1.0
200	787	584	4.9	4.1	203	1.2
300	850	557	6.2	4.9	293	1.2
400	895	540	7.5	5.5	355	1.3
500	913	523	8.3	5.8	390	1.4

As it can be seen from the Table 4.31 , reversibility was obtained at only lower scan rates. At high scan rates, diffusion limited current became more pronounced, ΔE and peak ratio increased. The best reversibility was obtained at 100 mV/s.

The PS polymerization of IN in 0.1 M ACN/ NaClO₄ at 120 s was given in Fig. 4.95.

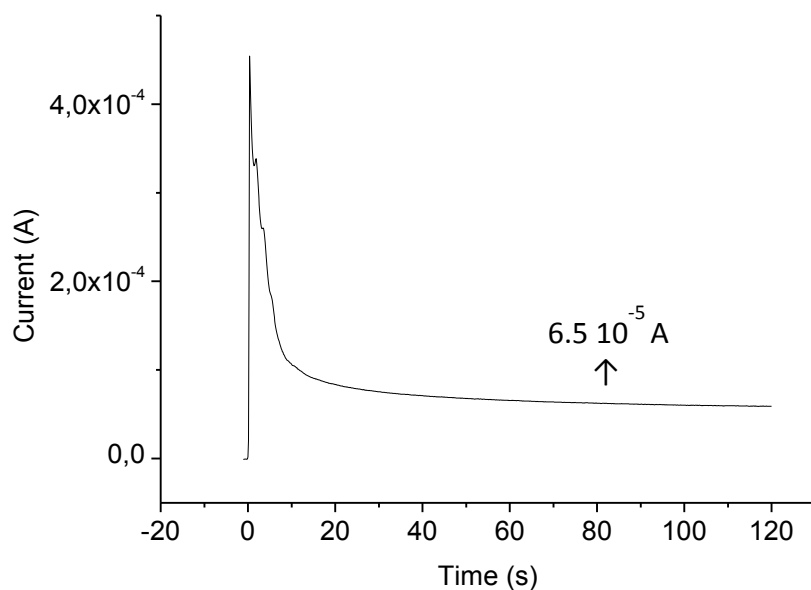


Figure 4.95 : PS electrodeposition of 0.1 M IN at 60 s in 0.1 M NaClO₄ containing ACN

As it can be seen in the Fig. 4.95 for PS polymerization of IN at 120 s, while the constant potential was applied, a decrease in current was seen after the first 5 s of polymeric growth and after it was stabilized at $6.5 \cdot 10^{-5}$ A. The voltammetric response of the polymer film can be seen in the Fig. 4.96.

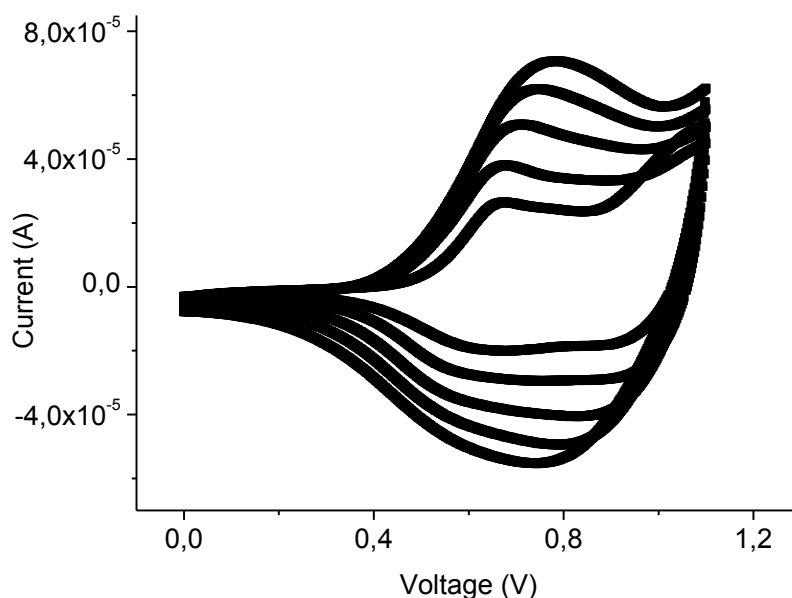


Figure 4.96 : Voltammetric response of PIN polymerized by PS at 120 s in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

As it can be seen from the Fig. 4.96, the shifts observed at the E_a and E_c was lower than the PIN film obtained at 60 s. This might be due to the application of further potential contributed to further oxidation and increase in doping of the PIN film rather than further deposition of the new polymer layer which was similar to the PPy and PCz case for the PS cally polymerization at 120 s. Results obtained from these measurements were presented in the Table 4.32.

Table 4.32 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of IN polymerized by PS method at 120 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	657	628	25	20	29	1,25
200	672	636	38	28	36	1,35
300	704	670	50	35	34	1,42
400	725	693	61	48	32	1,21
500	775	746	70	55	29	1,27

In the case of PS polymerization at 120 s, current intensities kept incercasing as the scan rate increased on the contrary of PD polymerization at 8 cycles. The best reversibility was observed at 400 mV/s.

Comparasion of current intensities vs scan rates of polymer films obtained by PS was given in Fig. 4.97.

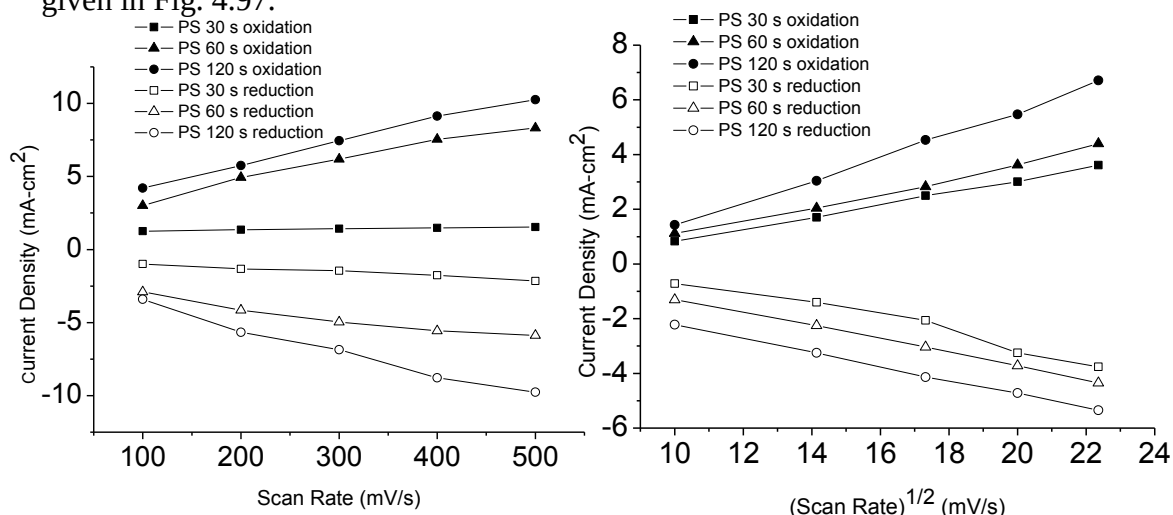


Figure 4.97 : (a)Current density versus scan rate, (b) Current density versus square root of scann rate plot PIN films obtained by PS at different polymerization times (30, 60 and 120 s)

In the case of films obtained by PS method at 30 and 60 s as the current densities were proportional to the scan rates, films showed the thin film character. But as increasing of the polymerization time to 120 s current densities became proportional to the square root of scan rates which indicated that the charge transfer process dominated by diffusion effects (Fig. 4.97)

4.3.3. Galvanostatic Polymerization of IN

Polymerization of IN by GS method at 30 s in 0.1 M ACN/ NaClO₄ was given in Fig. 4.98.

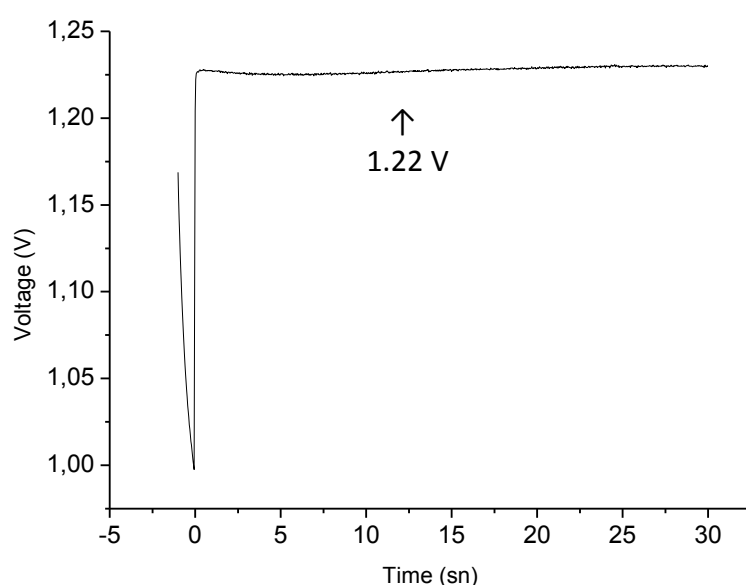


Figure 4.98 : GS electrodeposition of 0.1 M IN at 30 s in 0.1 M NaClO₄ containing ACN.

After a sharp increase observed at the beginning of polymerization, the potential stabilized at 1.22 V and kept constant during the polymerization. (Fig. 4.98) Voltammetric response of polymer film was presented in Fig. 4.99.

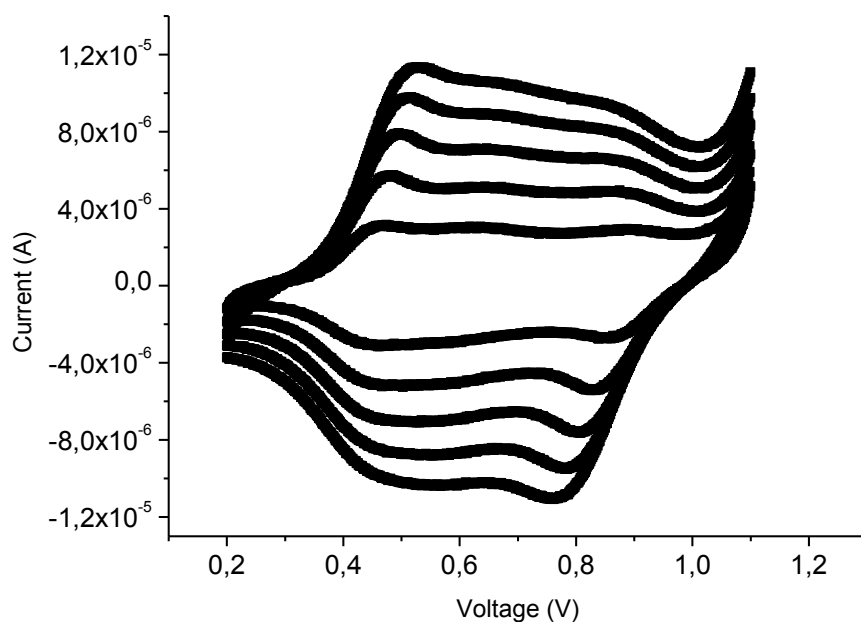


Figure 4.99 : Voltammetric response of PIN polymerized by GS at 30 s in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

The CV of the polymer film growth by GS method at 30 s, showed one broad peak at +0.5 V which was approximately similar to the PD polymerizations. Since the onset of oxidation potential of polymer film shifted to lower potential value (0.3 V), it can be said that the charge/discharge process of polymer film obtained by GS method was more easier than the ones obtained by PD and PS methods. (Fig 4.99) The parameters obtained from voltammogram at different scan rates demonstrated in Table 4.33.

Table 4.33 : E_a, E_c, I_a, I_c, ΔE, I_a/I_c values of IN polymerized by GS method at 30 s.

Scan rate m V/s	E _a (mV)	E _c (mV)	I _a (μA)	I _c (μa)	ΔE (m V)	I _a /I _c
100	458	426	0.3	0.3	32	1.0
200	478	438	0.6	0.5	40	1.1
300	496	451	0.8	0.7	45	1.2
400	512	469	1.0	0.9	43	1.1
500	526	491	1.1	1.0	35	1.1

In all cases ΔE values were very small and the peak ratios were very close to unity, showing thin film behaviour and good electrochemical reversibility. As it can be seen from the Table 4.33 , the best reversibility for the PIN obtained by GS at 30 s was observed at 100 mV/s.

Polymerization of IN by GS method at 60 s in 0.1 M ACN/ NaClO_4 was given in Fig. 4.100.

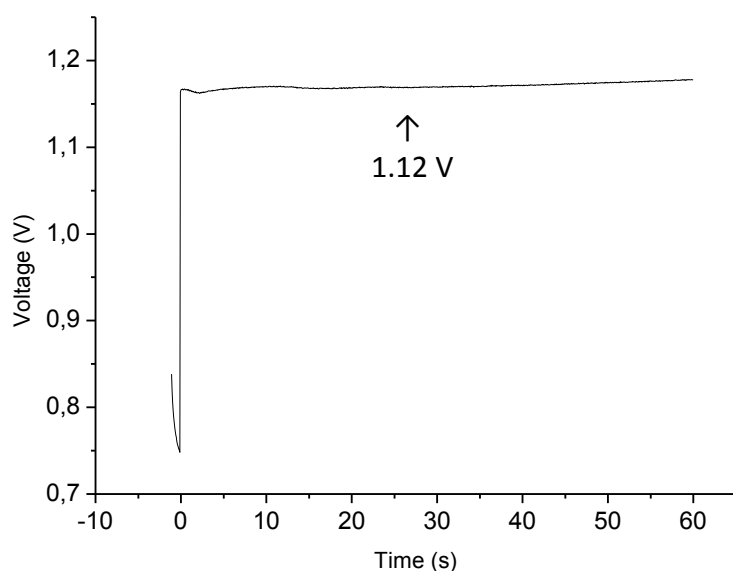


Figure 4.100 : GS electrodeposition of 0.1 M IN at 60 s in 0.1 M NaClO_4 containing ACN.

After a sharp increase observed during the first 5 s of polymeric growth, the potential stabilized at 1.15 V and kept constant during the polymerization. (Fig 4.100). The voltammetric response of PIN film obtained by PS at 60 s was given in the Fig. 4.101.

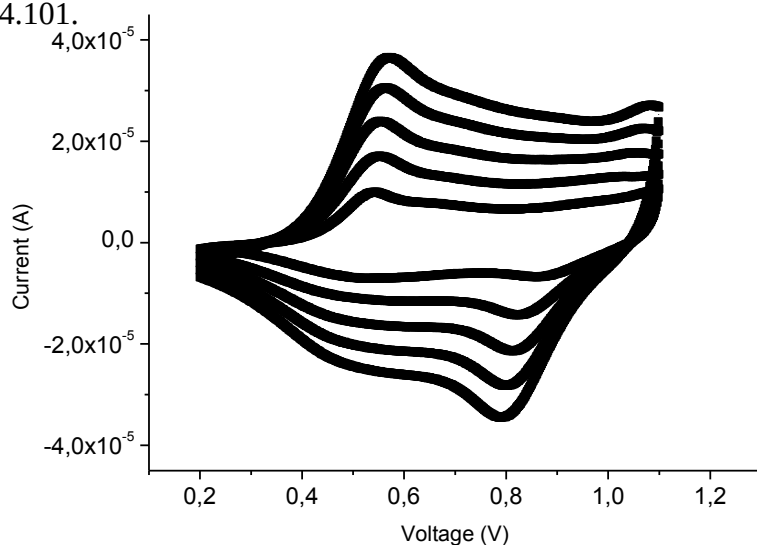


Figure 4.101 : Voltammetric response of PIN polymerized by GS method at 60 s in 0.1 M NaClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Table 4.34 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of IN polymerized by GS method at 60 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	528	514	0.9	0.8	14	1.1
200	545	530	1.7	1.1	15	1.5
300	548	535	2.4	1.8	13	1.3
400	560	541	3.0	2.1	19	1.4
500	566	546	3.7	2.6	20	1.4

As it can be seen in the Table 4.34 the best reversibility was observed at 100 mV/s.

Polymerization of IN by GS method at 120 s in 0.1 M ACN/ $NaClO_4$ was given in Fig. 4.102.

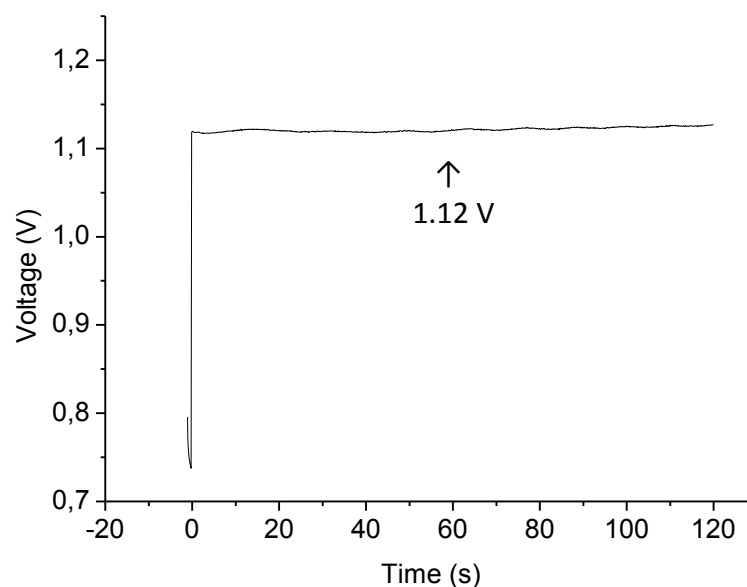


Figure 4.102 : GS electrodeposition of 0.1 M IN at 120 s in 0.1 M $NaClO_4$ containing ACN.

After a sharp increase observed during the first 5 s of polymeric growth, the potential stabilized at 1.12 V and kept constant during the polymerization. (Fig 4.102). The voltammetric response of PIN film obtained by PS at 120 s was given in the Fig. 4.103.

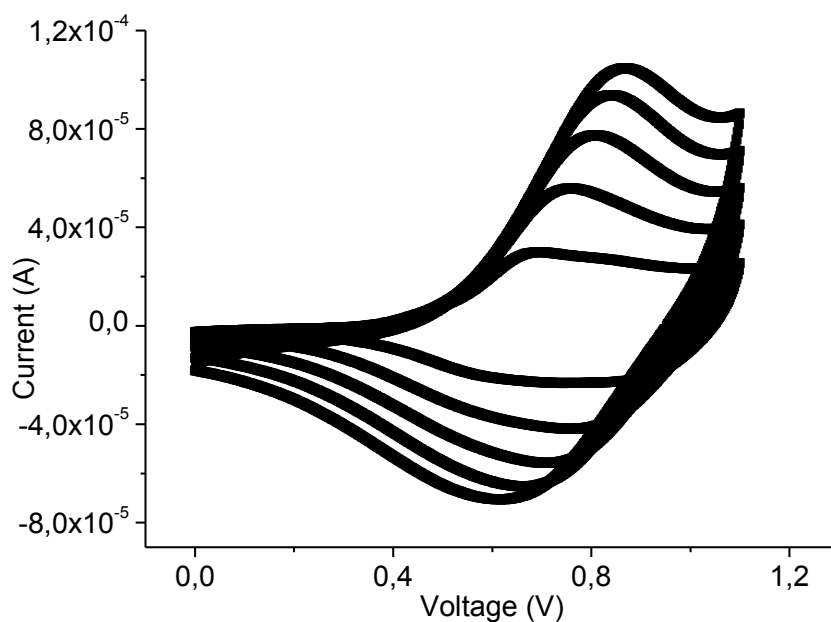


Figure 4.103 : Voltammetric response of PIN polymerized by GS at 120 s in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Table 4.35: E_a, E_c, I_a, I_c, ΔE, I_a/I_c values of IN polymerized by GS method at 120 s.

Scan rate m V/s	E _a (mV)	E _c (mV)	I _a (μA)	I _c (μa)	ΔE (m V)	I _a /I _c
100	678	657	30	21	21	1.4
200	741	693	55	40	48	1.3
300	801	760	76	61	41	1.2
400	825	700	91	64	125	1.4
500	854	636	100	71	218	1.4

Comparasion of current densities vs scan rates of PIN film obtained by GS method was given in Fig. 4.21

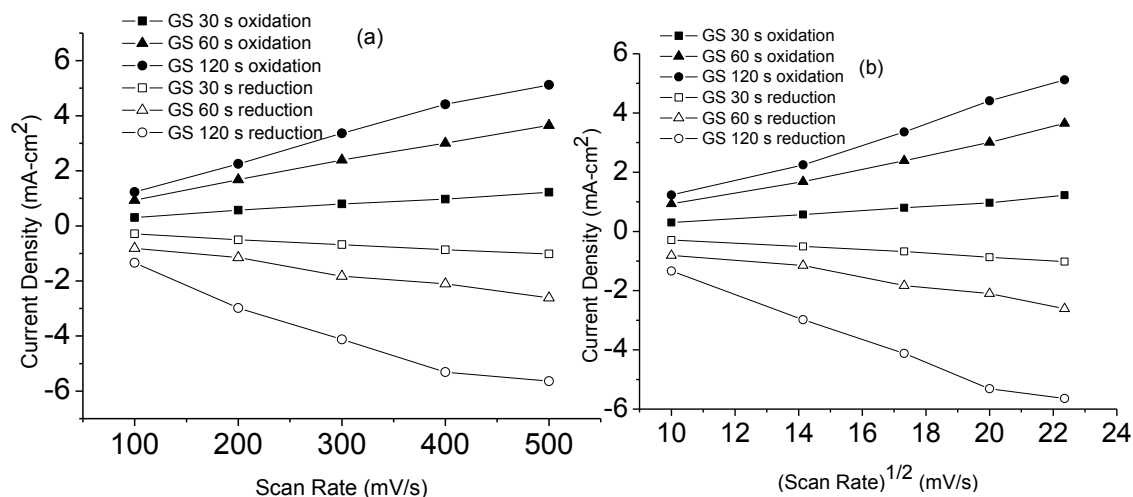


Figure 4.104 : (a) Scan rate dependence, (b) square root of scan rate of current intensities of PIN films obtained by GS at different polymerization times (30, 60 and 120 s).

In the case of films obtained by GS method, the films obtained at 30 s showed thin film character whereas the films obtained at 60 and 120 s showed diffusion control behaviour. Comparison of oxidation currents vs scan rates of PIN obtained by PD, PS and GS was studied. Redox behaviour of PIN films obtained by same methods at different polymerization times (Fig. 4.103) and by different methods at same polymerization times (Fig. 4.104) were compared.

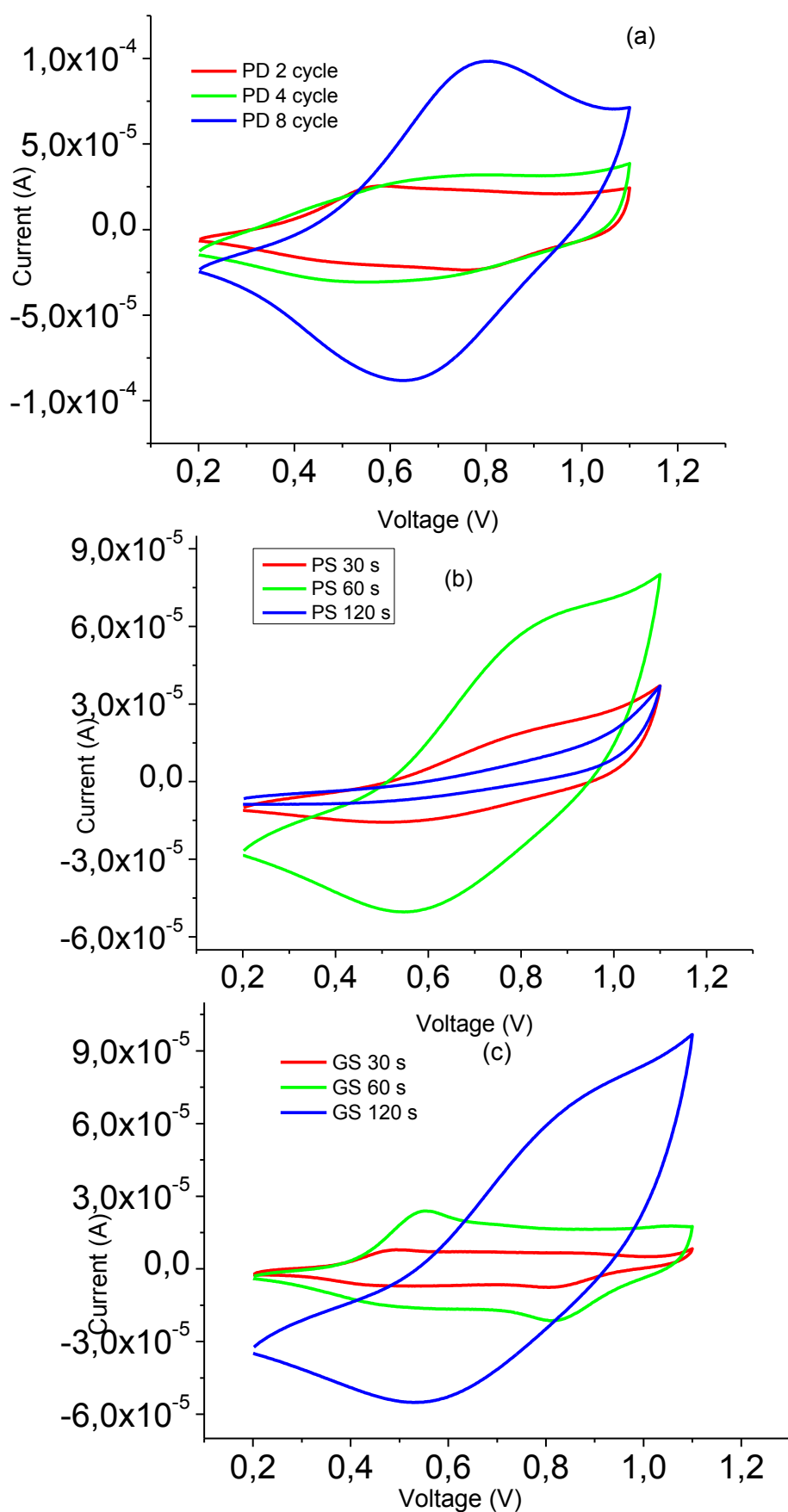


Figure 4.105 : Comparison of redox behaviour of PPy films obtained by PD (a) , PS (b) and GS (c) depending on polymerization time at 300 mV/s in monomer free solution.

As it can be seen in Fig 4.105.a and Fig. 4.22.c for PD and GS methods respectively, the current intensities increased as the polymerization time increased due to the increase in thickness and the area of electrode. In the case of PS method, as the applying of further potential resulted overoxidation instead of deposition on the film surface, current intensities did not increased for the polymer film obtained at 120 s. (Fig 4.105.b)

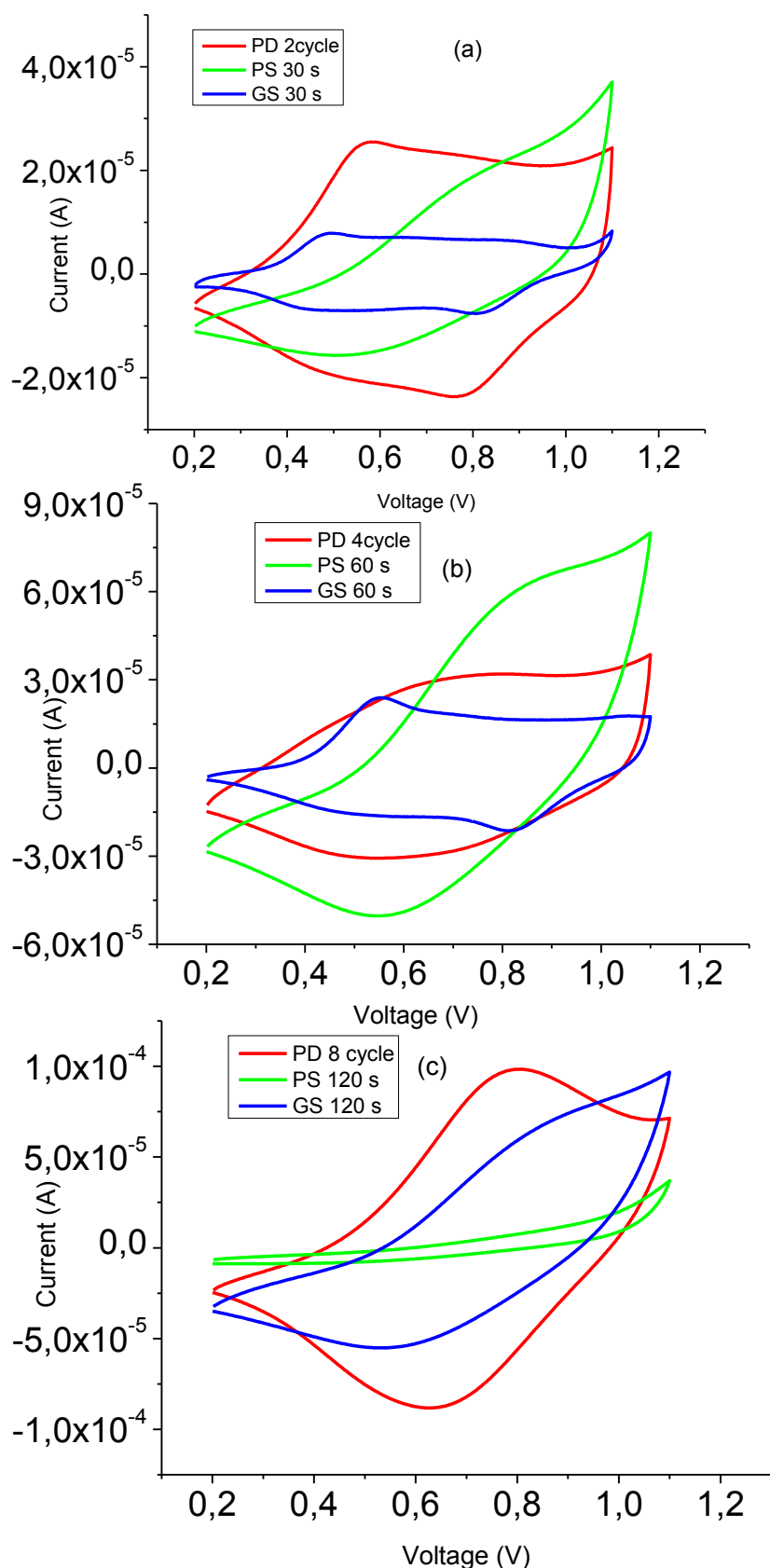


Figure 4.106 : Comparison of redox behaviour of PIN films obtained by PD , PS and GS methods depending on polymerization method. [(a), PD 2 cycles, PS 30 s, GS 30 s; (b), PD 4 cycles, PS 60 s, GS 60 s; (c), PD 8 cycles, PS 120 s, GS 120 s] at 300 mV/s in monomer free .

As it can be seen in the Fig. 4.106. a, 4.106. c, when the three methods were compared to each other, for the short polymerization times (2 cycle, 30 s) the maximum current intensities were observed for the films obtained by PD method which was still favorable for the long polymerization times (8 cycle, 120 s). The max current intensity for the middle polymerization times (4 cycle, 60 s) was observed in the case of PS method.

4.3.4. Comparasion of Electrochemical Impedance Spectroscopy measurements of PIN films

Similar to PPy and PCz, impedance properties of the PIN films in 5ml 0.1 M ACN/ NaClO₄ monomer free solution were investigated between 10 mHz-100 kHz range, in the absence of direct potential and under 1V constant potential.

4.3.4.1. EIS results of potentiodynamically obtained PIN films

Nyquist, bode phase and bode magnitude diagrams resulting PIN films were compared for each polymerization time. (Fig. 4.107- 4.112). At low frequency and open circuit potential, and for short polymerization times, the imaginary part of the impedance sharply increased and plot tend to a vertical line which is a characteristic of capacitive behaviour. (Fig. 4.107)

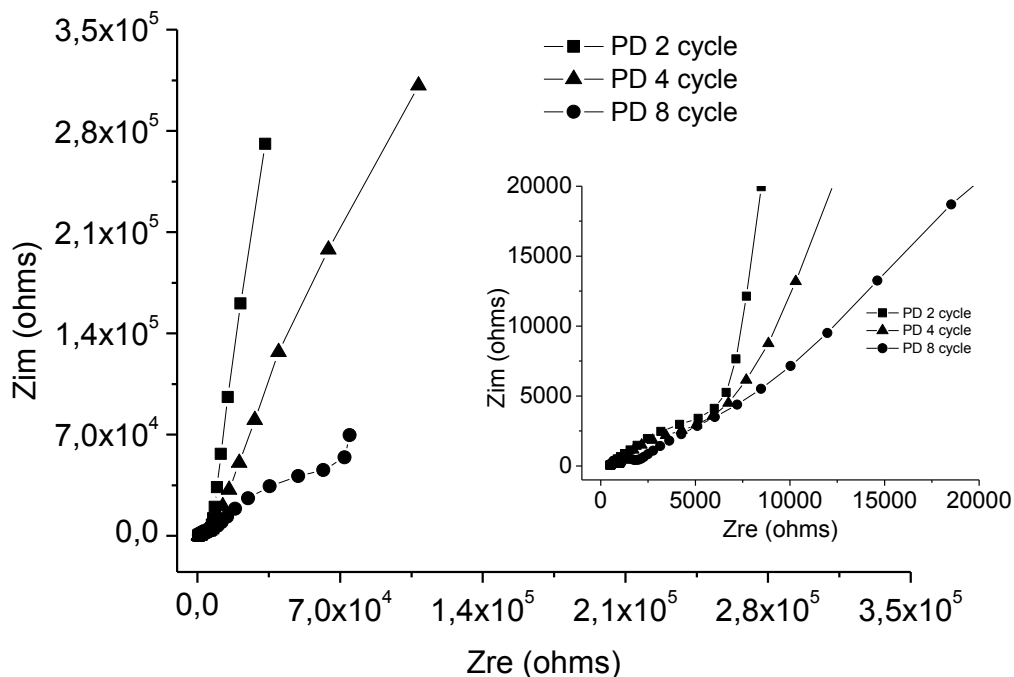


Figure 4.107 : Nyquist diagram of PIN obtained by PD at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

As it can be seen in the Fig. 4.107, for the PD method case, the imaginary part of the impedance sharply increased and plot tend to a vertical line which is a characteristic of capacitive behaviour for the the PIN film obtained at 2 cycles whereas the slope of the line decreased as the polymerization time increased.

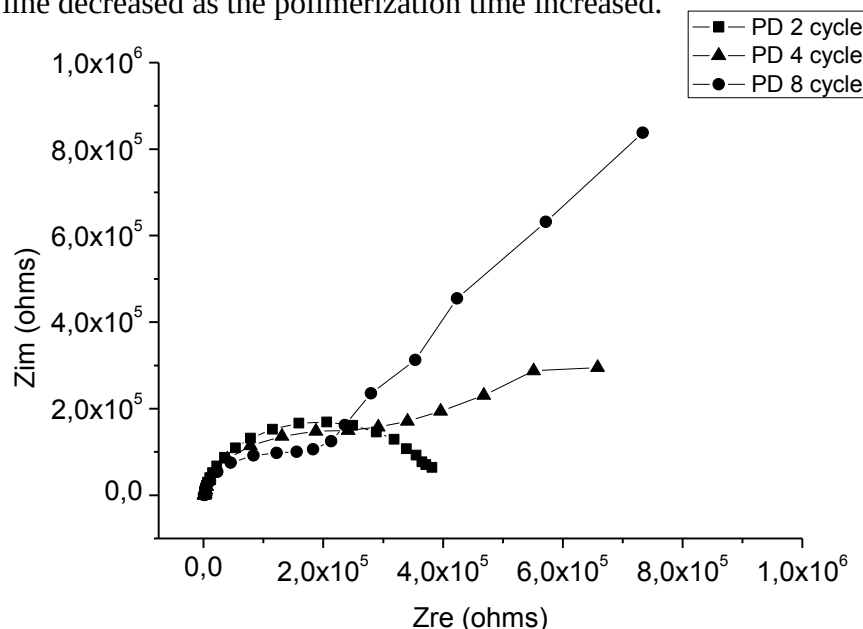


Figure 4.108 : Nyquist diagram of PIN obtained by PD 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct potential.

As it can be seen in the Fig. 4.108, a full semi circle was observed in the case of PIN obtained at 2 cycles, whereas two partial semicircles were observed for the longer polymerization times.

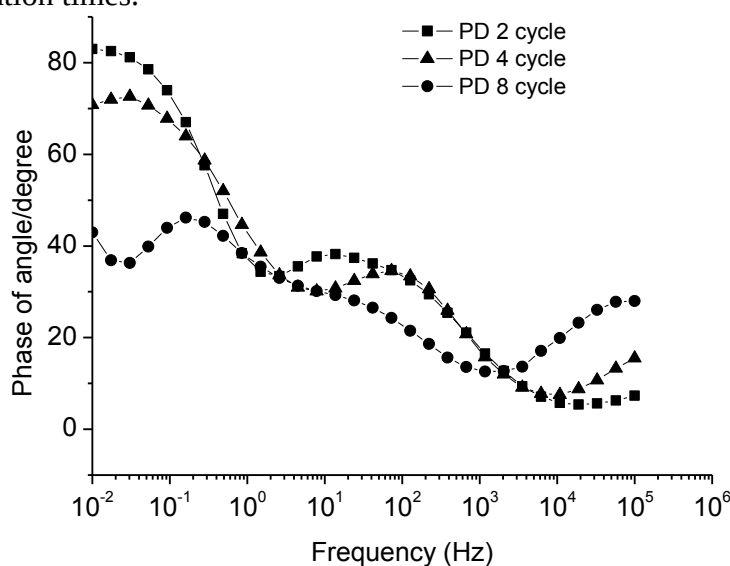


Figure 4.109 : Bode phase diagram of PIN obtained by PD 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

The highest phase angle was observed for the PIN film obtained 2 cycles as the polymerization time increased, the phase angle decreased due to the deposition of on the electrode might result decrease on the conductivity and a transition to resistive behaviour. (Fig. 4.109)

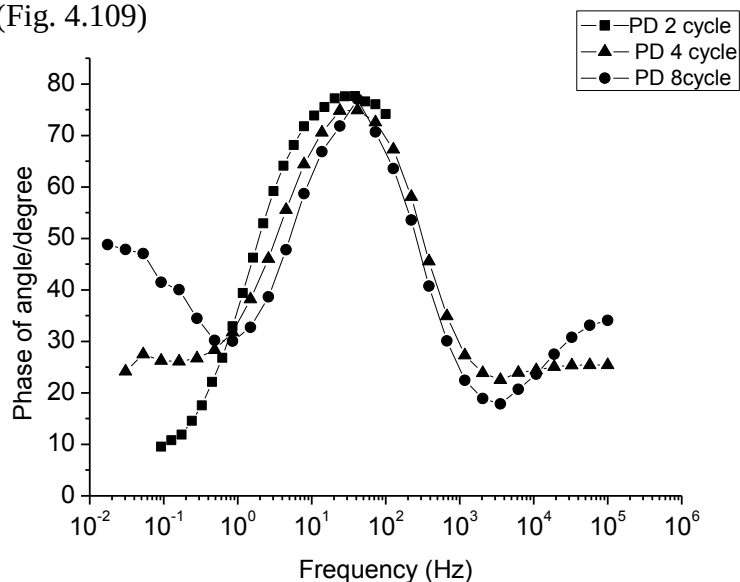


Figure 4.110 : Bode phase diagram of PIN obtained by PD at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct potential.

As it can be seen in the Fig. 4.110. , phase angles decreased and shifted to higher frequencies with increasing cycle numbers under the 1V constant potential as the constant potential led to the overoxidation which is similar to the previous measurements.

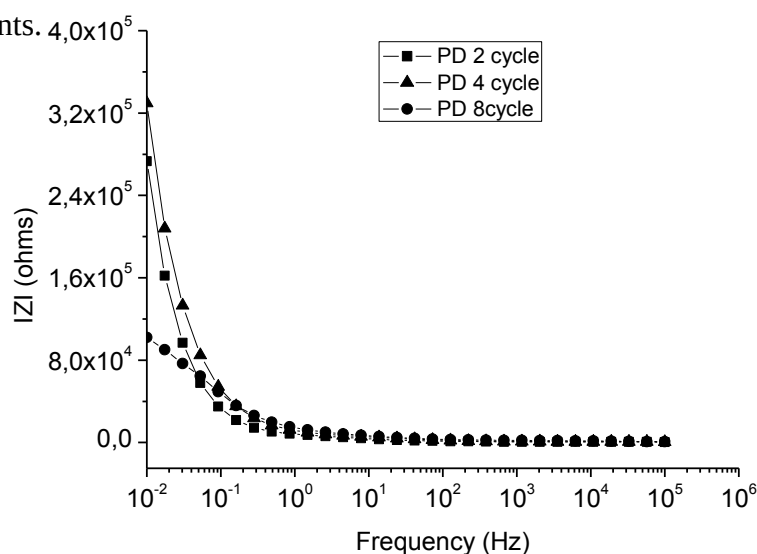


Figure 4.111 : Bode magnitude diagram of PIN obtained by PD at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

As it can be seen in the Fig. 4.111. , the lowest IZI value of PIN was observed at 2 cycles in the case of PD method. As the time increased to 4 cycles IZI increased as well, but due to the further increase on polymerization time resulted overoxidation instead of deposition on the polymer surface, the lowest IZI was observed at 8 cycles.

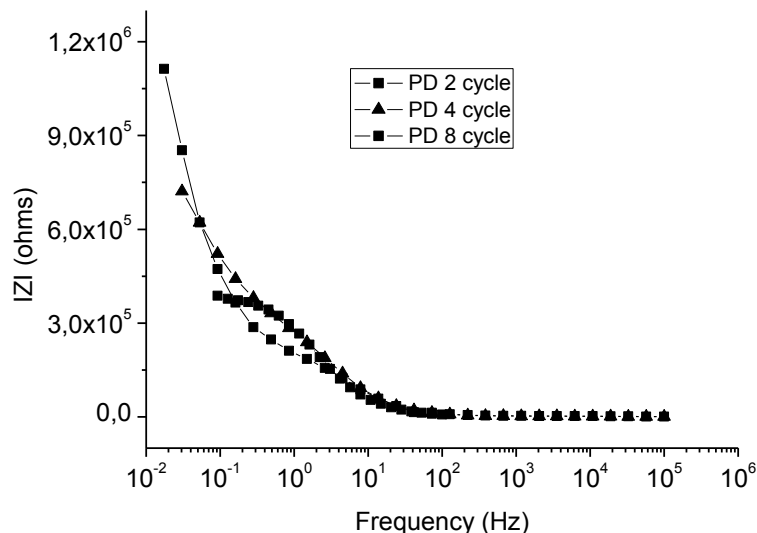


Figure 4.112 : Bode magnitude diagram of PIN obtained by PD at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct potential.

Similar frequency shifts were observed in the case of application 1V constant potential. (Fig. 4.112). Results obtained from these measurements were summarized in the Table 4.36.

Table 4.36 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PIN polymerized by PD at 30, 60 and 120 s.

PIN ($\pm 0,5$)	PD (2 cycle)		PD (4 cycle)		PD (8 cycle)	
	Open circuit potential	1V applied	Open circuit potential	1V applied	Open circuit potential	1V applied
R_s ohm-cm ²	474	496	499	497	758	759
R_p ohm-cm ²	3888	370782	3067	29555	7618	170519
C_{dl} μ F-cm ²	7	2	5	1	4	1
C_{sp} μ F-cm ²	58	—	51	—	159	—
C_{dif} μ F-cm ²	67	—	66	—	160	—
P.angle (degree)	83	9	81	5	48	45

As it can be seen in the Table 4.36. the best capacitive behaviour was observed at 8 cycles in the case of PIN films obtained by PD method.

4.3.4.2. EIS results of potentiostatically obtained PIN film

Impedance properties were investigated in the similar conditions of PS polymerized PIN during 30 s. Nyquist, Bode phase and Bode magnitude diagrams (Fig. 4.113-4.118) of resulting PIN films were compared for each polymerization time.

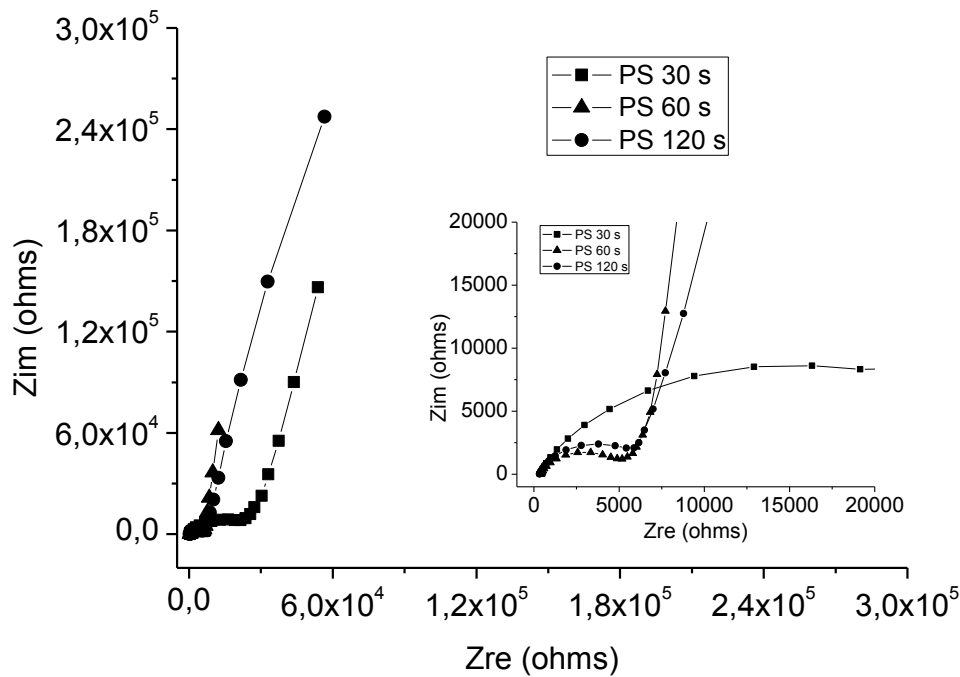


Figure 4.113 : Nyquist diagram of PIN obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

As it can be seen in the Fig. 4.113. ,at high frequencies, a partially-formed semi-circle and at lower frequencies, a linear part were observed in the case of PIN obtained by PS method. The most vertical line of Zim was observed for the film obtained at 60 s. This might be due to the partial degradation from the polymer surface resulted the less electroactive films in the case of short polymerization times. In taking account the, applying further potential might cause the overoxidation and high doping on the film surface instead of depostion, the reason of being vertical slopes of films obtained at 60 and 120 s very close to each other might be explained. This idea was supported with the very small semi circle of film obtained at 120 s when it was compared to shorter polymerimerization times. (Fig. 4.114)

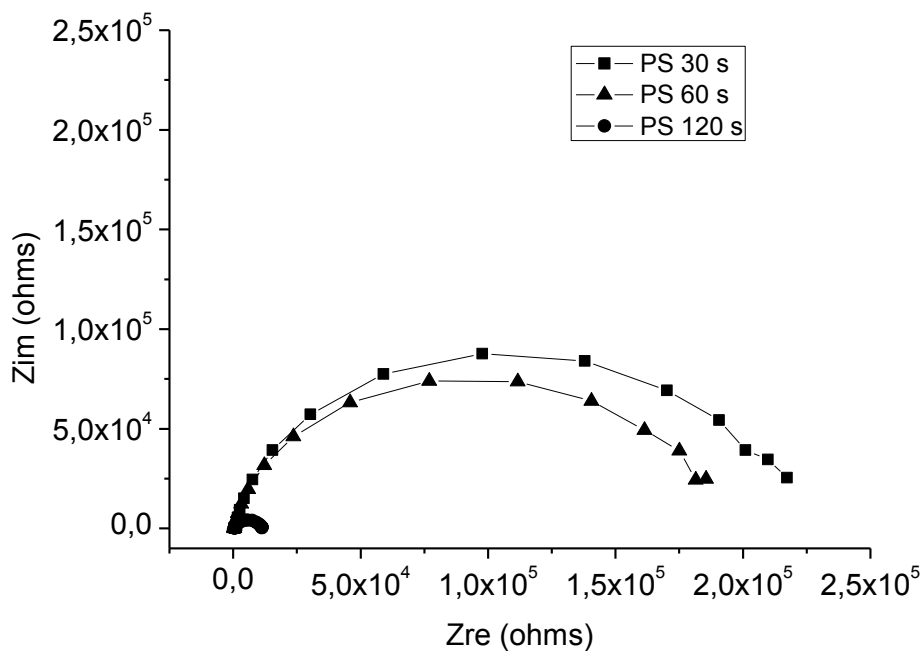


Figure 4.114 : Nyquist diagram of PIN obtained by PS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct potential.

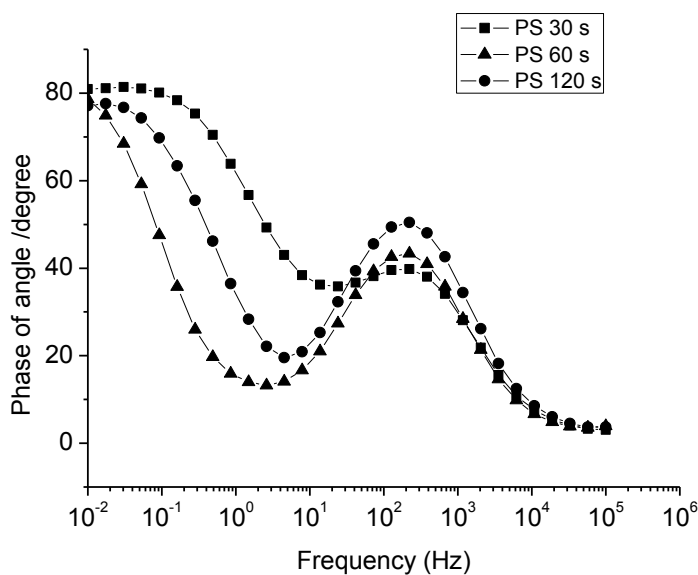


Figure 4.115 : Bode phase diagram of PIN obtained by PS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range .

As it can be seen in the Fig. 4.115, the highest phase angle was observed for the film obtained at 30 s.

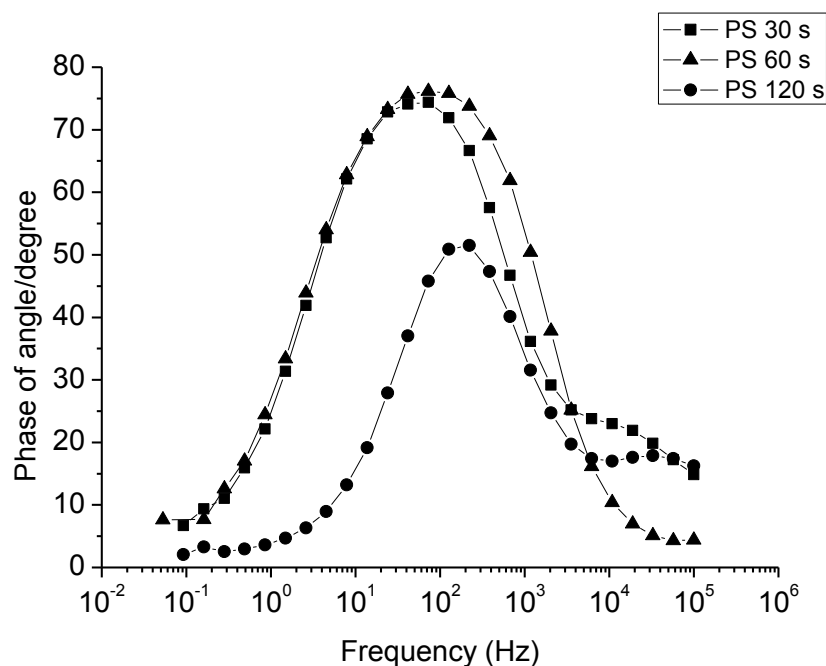


Figure 4.116 : Bode phase diagram of PIN obtained by PS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct potential.

Similar shifts on the frequency and phase angle, with the previous measurements were observed for the films obtained by PS method. (Fig. 4.116)

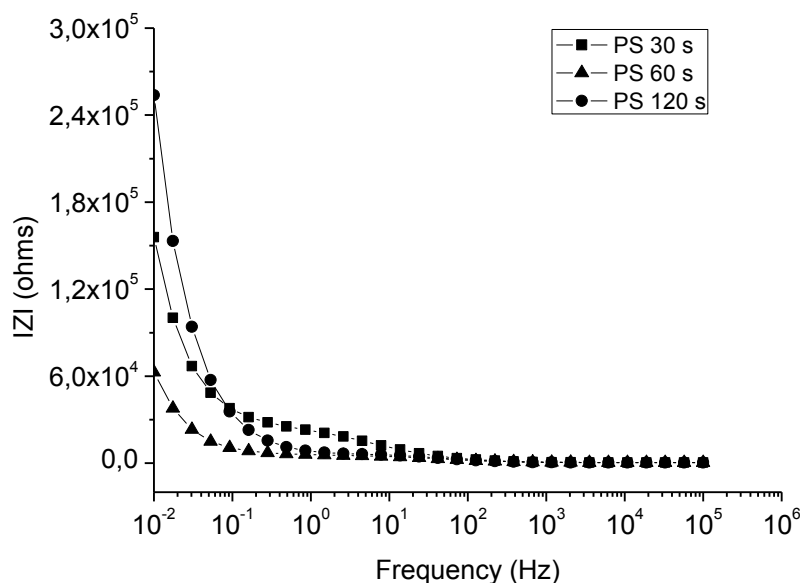


Figure 4.117 : Bode magnitude diagram of PIN obtained by PS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

The highest IZI value was observed at the highest polymerization time.(Fig. 4.117) Similar frequency shifts were observed in the case of under 1V constant potential (Fig. 4.118)

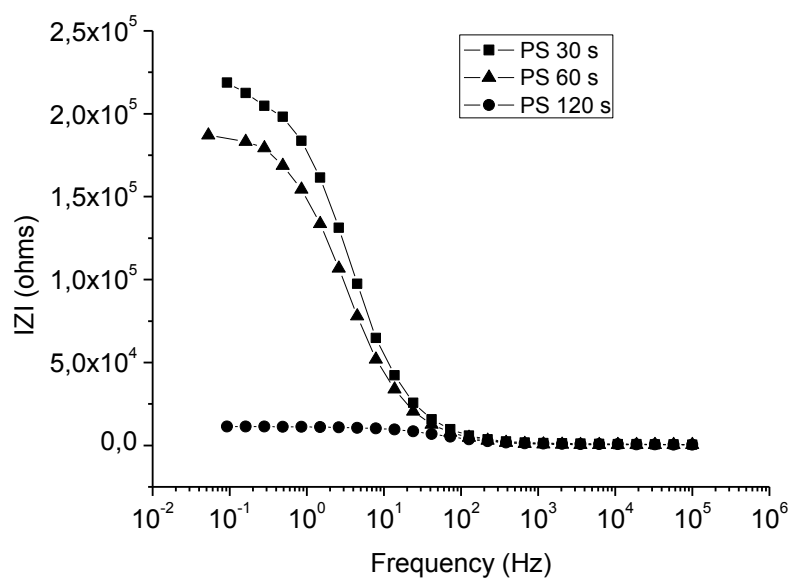


Figure 4.118 : Bode magnitude diagram of PIN obtained by PS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct potential.

Results obtained from these measurements were summarized in the Table 4.37.

Table 4.37 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PIN polymerized by PS at 30, 60 and 120 s.

PIN ($\pm 0,5$)	PS (30s)		PS (60s)		PS (120s)	
	Open circuit potential	1V applied	Open circuit potential	1 V applied	Open circuit potential	1V applied
R_s ohm-cm ²	416	470	410	413	328	420
R_p ohm-cm ²	5514	197962	4728	155853	5222	10730
C_{dl} μF -cm ²	20	1	46	1	34	19
C_{sp} μF -cm ²	103	—	260	—	62	—
C_{dif} μF -cm ²	115	—	63	—	20	—
P.angle (degree)	82	5	79	7	77	2

As it can be seen from the Table 4.37, the highest C_{dl} and C_{sp} were observed for the film obtained by PS at 60 s.

4.3.4.3 EIS results of galvanostatically obtained PIN film

Impedance properties were investigated in the similar conditions of PD and PS polymerized PIN. Nyquist, Bode phase and Bode magnitude diagrams (Fig. 4.36 - 4.41) of resulting Ppy films were compared for each polymerization time.

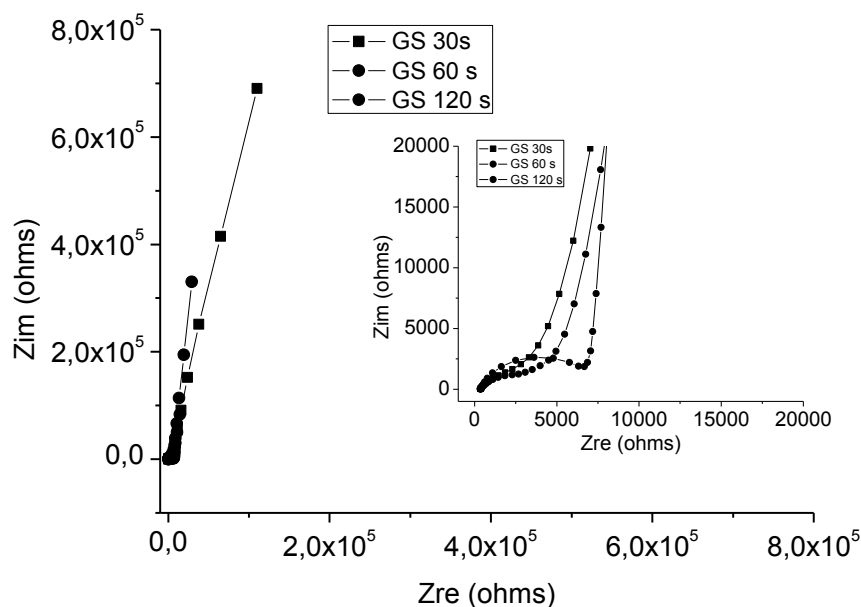


Figure 4.119 : Nyquist diagram of PIN obtained by GS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

As it can be seen in the Fig. 4.119. For the PIN film obtained by GS method, the imaginary part of the impedance sharply increased and plot tend to a vertical line characteristic which is a characteristic of capacitive behaviour at low frequency and open circuit potential. Real value of impedance showed semi circle character for all polymerization times under constant 1V potential. (Fig. 4.120)

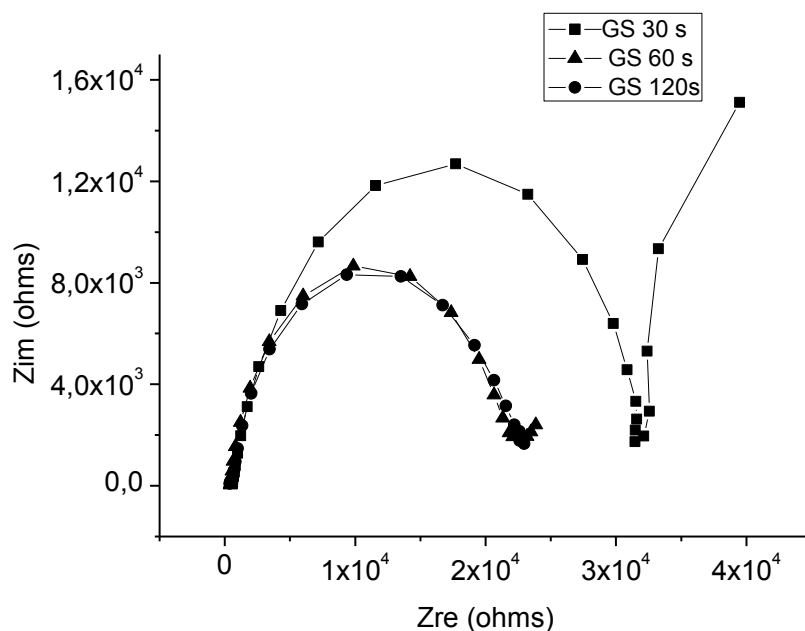


Figure 4.120 : Nyquist diagram of PIN obtained by GS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct potential.

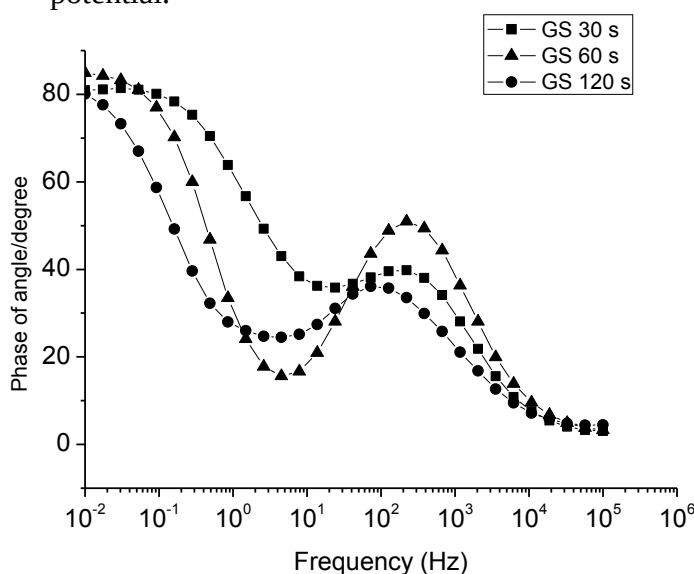


Figure 4.121 : Bode phase diagram of PIN obtained by GS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct potential.

As it can be seen in the Fig. 4.121, the highest phase angle was observed for the PIN film obtained by GS at 60 s. Same frequency shifts were observed for the all polymerization times under 1 V constant potential. (Fig. 4.122)

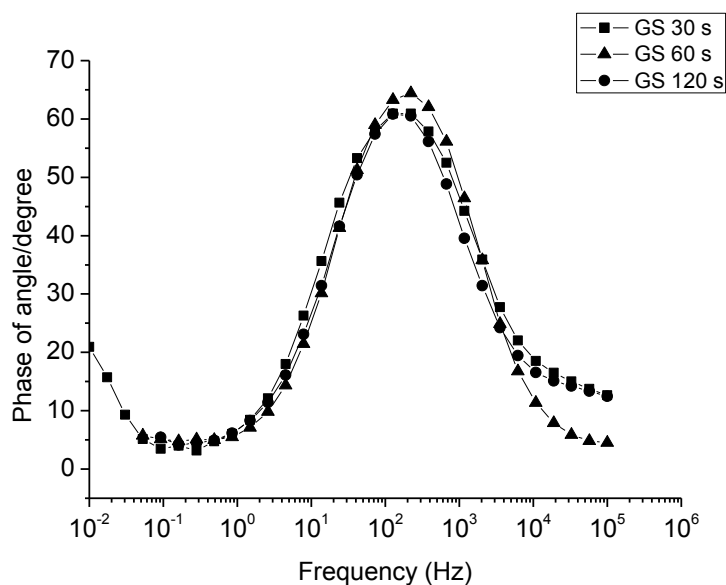


Figure 4.122 : Bode phase diagram of PIN obtained by GS at 30, 60 and 120 s by applying 1V direct potential.

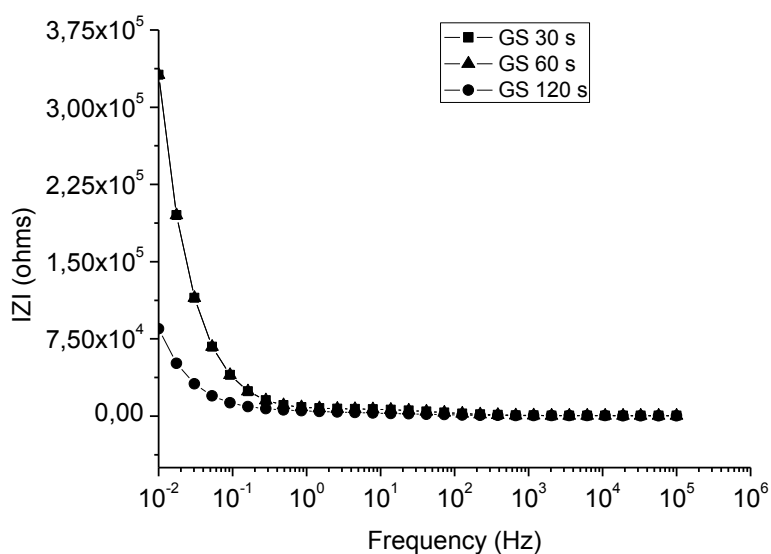


Figure 4.123 : Bode magnitude diagram of PIN obtained by GS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

As it can be seen in the Fig. 4. 123. ,similar films obtained by PD method (Fig 4.111) , the lowest IZI value was observed at the highest polymerization time (120 s).

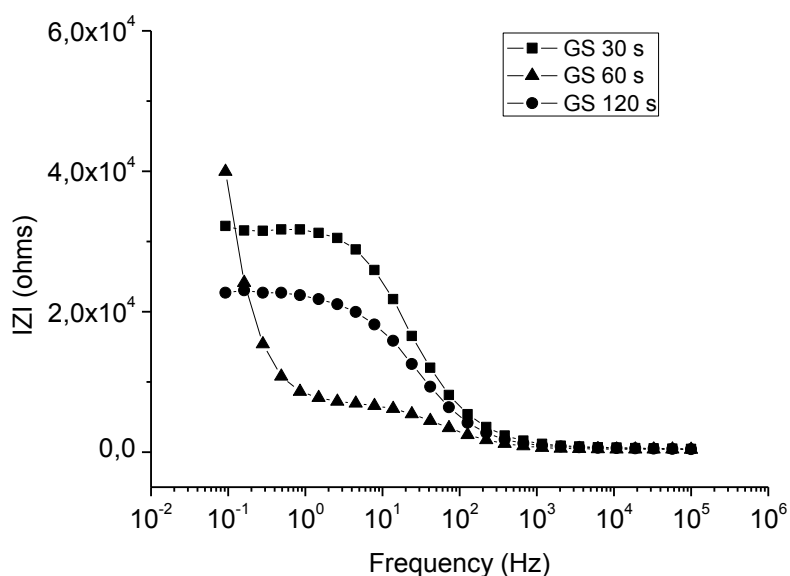


Figure 4.124 : Bode magnitude diagram of PIN obtained by GS method at 30, 60 and 120 s by applying 1V direct potential.

Results obtained from these measurements were summarized in the Table 4.12.

Table 4.38 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PIN polymerized by GS at 30, 60 and 120 s.

PIN ($\pm 0,5$)	GS (30s)		GS (60s)		GS (120s)	
	Open circuit potential	1V applied	Open circuit potential	1 V applied	Open circuit potential	1V applied
R_s ohm-cm ²	345	431	390	420	393	394
R_p ohm-cm ²	9955	34737	4608	19096	4660	18301
C_{dl} μF -cm ²	15	6	33	10	33	10
C_{sp} μF -cm ²	47	—	53	—	191	—
C_{dif} μF -cm ²	65	—	100	—	197	—
P.angle (degree)	80	21	83	8	80	6

As it can be seen in the Table 4.38, the highest phase angles and C_{dl} was obtained at 60 s whereas the highest C_{sp} was observed for film obtained by GS at 120 s.

In the case of PIN, the films obtained by PD method at 2 and 4 cycles (Table 4.36) , PS method at 60 s (Table 4.37) and GS method 120 s (Table 4.38) were quite capacitive. On the contrary of PPy and PCz, capacitive behaviour was still remarkable at high polymerization times.

Polymer growth of IN was more difficult than the other monomers such as Py, Th, Cz. This might be due to steric hindrance of the indole ring during polymerization. For the PIN films obtained by PD method, as the polymerization time increased, Csp and Cdl values decreased on the contrary of other PPy, PCz. (Table 4.36). In the case of PS method, as the polymerization time increased the Csp values increased (Table 4.37) due to the application of further current resulted further deposition which led to more charge storage on the electrode surface. In the case of GS method, as the polymerization time increased, capacitance values increased.(Table 4.38) The most capacitive film was obtained by PS method at 60 s, where as the most reversible film was obtained by PD method at 2 cycles. (Fig. 4.106 a)

4.3.4.4. Equivalent circuit diagram of PIN

As it can be seen in the Fig. 4.125, the equivalent electrical circuit of PIN was R_s corresponded resistance of the polymer and the electrolyte, C_{dl} was double layer capacitance. R_e was the resistance of the electrolyte. (CPE) was constant phase element in parallel with R_{ct} and W , R_{ct} was the charge transfer, and W was the Warburg impedance of the polymer. The last component a capacitor element, (C_{pt}) was introduced in parallel with a resistor (R_{pt}) corresponding platinum button electrode of polymer coating. CPE stimulated the capacitor of the film/electrode surface resulted due to the binding of counter ions in to the irregular geometry of polymer surface. C_{dl} was the electrical double layer exists on the interface between an electrode and its surrounding electrolyte. This double layer is formed as ions from the solution "stick on" the electrode surface. R_{ct} was characteristic quantity for the charge-transfer step of an electrode reaction indicative of its inherent speed: a large charge-transfer resistance indicated a slow step. Results obtained from the equivalent circuit diagram were presented in Table 4.39.



Figure. 4.125 : The equivalent circuit diagram of PIN. [Chi squared: $4.534 \cdot 10^{-4}$
n: 0.6008 . Monomer: 0,1M IN, Method: PD at 2 cycles, 50 mV/s,
Electrolyte: 0,1 M ACN/ NaClO₄, WE: Pt (button electrode), RE:
Ag/AgCl, CE: Pt (wire)]

Table 4.39 : Potential dependence of the parameters calculated for PIN film from the equivalent circuit diagram.

R_s (ohm-cm ²)	C_{dl} (F/cm ²)	R_p (ohm-cm ²)	Q (CPE) Y0(S-sec ⁿ /cm ²)	R_{ct} (ohm-cm ²)	C_{pt} (F/cm ²)	R_{pt} (ohm-cm ²)
345.6	$31 \cdot 10^{-5}$	149	$7.5 \cdot 10^{-5}$	8938	$54 \cdot 10^{-5}$	$25 \cdot 10^{-5}$

4.4. Comparison of Polymerization Conditions and Characterization of Th

4.4.1. Potentiodynamic Polymerization of Th

Polymerization of Th by PD method at 2 cycles in 0.1 M ACN/ NaClO_4 was given in Fig. 4.126.

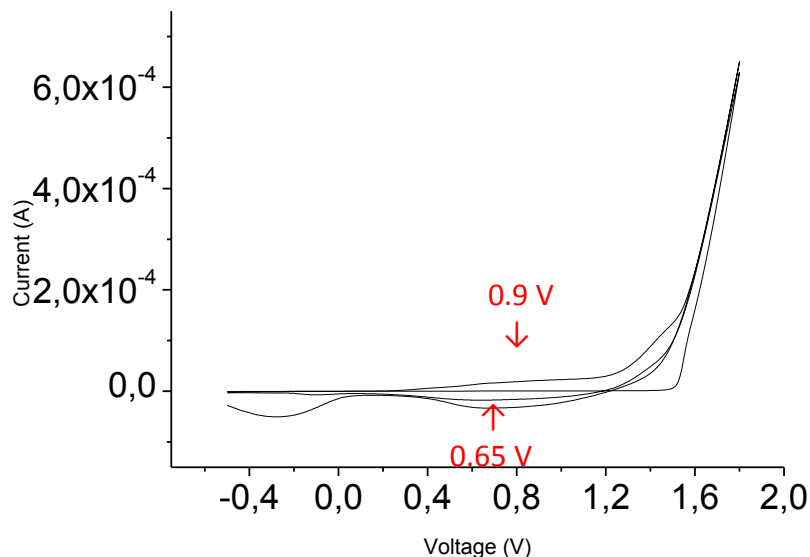


Figure 4.126 : PD electrodeposition of 0.1 M Th at 2 cycles in 0.1 M NaClO_4 containing ACN at the scan rate of 50 mV/s.

As it can be seen in the Fig. 4.126, when the potential sweep was performed between 0-1.8 V, oxidation of Th occurred at the 1.4V. The coated electrode was then transferred into monomer free solution and the scan rate dependence of resulting film investigated and given in Fig. 4.127.

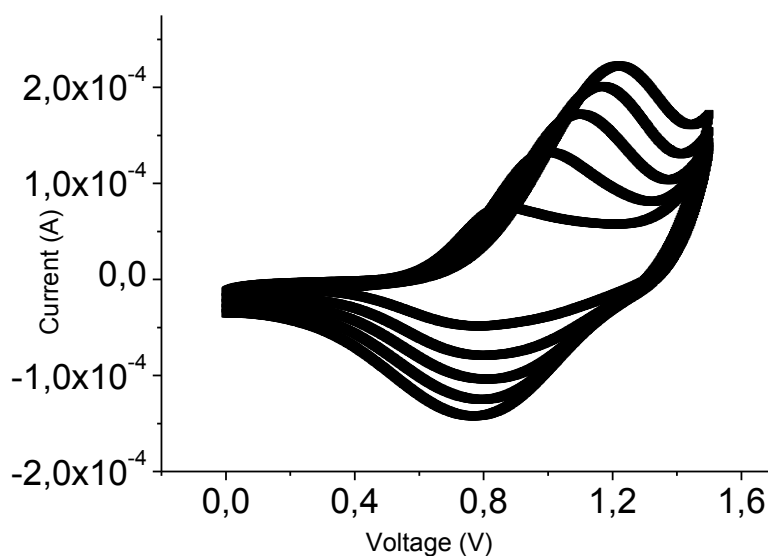


Figure 4.127 : Voltammetric response of PTh polymerized by PD method at 2 cycles in 0.1 M NaClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

CV of this film showed one broad wave at about + 0.7 V. (Fig. 4.127). Results obtained from the voltammogram were presented in the Table 4.1

Table 4.40: E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Th polymerized by PD method at 2 cycles

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	860	830	76	50	30	1.5
200	970	840	130	78	130	1.6
300	1060	810	171	102	250	1.6
400	1140	800	198	120	340	1.6
500	1190	780	220	140	410	1.5

As it can be seen from the Table 4.40 , reversibility of PTh obtained by PD at 2 cycles was poor. At high scan rates, diffusion limited current became more pronounced, ΔE and peak ratio increased.

PD polymerization of Th by applying 4 cycles was given in the Fig. 4.128. Monomer concentration, voltage interval and electrodes were kept same with the polymerization conditions of Th at 2 cycles and similar investigations were done. The voltammetric response of polymeric film was given in Fig 4.129

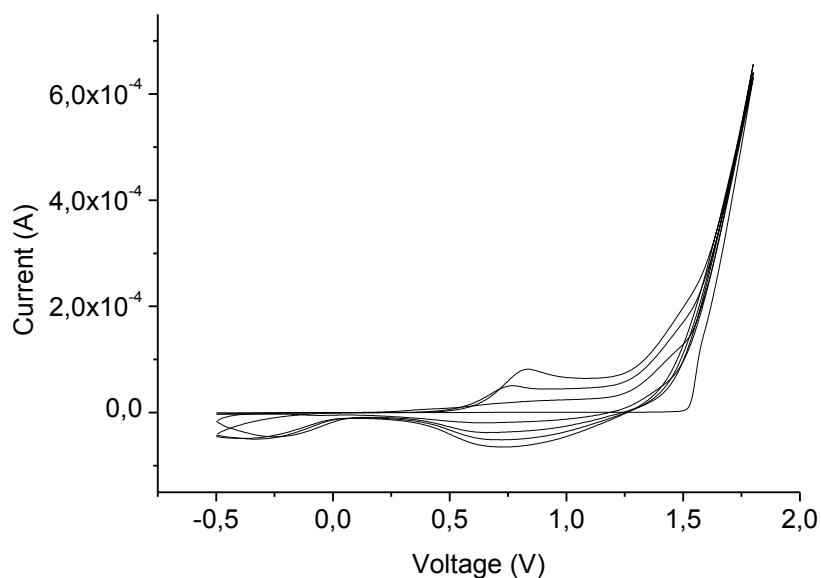


Figure 4.128 : PD electrodeposition of 0.1 M Th at 4 cycles in 0.1 M NaClO_4 containing ACN at the scan rate of 50 mV/s.

Fig. 4.128 presents the polymerization of Th by PD method at 4 cycles. On the anodic scan, the oxidation peak appeared at 0.8 V corresponding to the formation of the cation radical of Th whereas the reduction wave was observed at 0.7 V. Since the oxidation peak of the first redox process appeared at only second and following scans, it might be due to the polymer redox activity, whereas the second oxidation peak (1.4 V), which existed for all scans, might be related to the oxidation of the neutral monomer to radical-cation which is similar to Th. Then the film was transferred into the monomer-free electrolyte solution and its redox behaviour was studied. Voltammetric response of the PTh film obtained by PD at 4 cycles can be seen in the Fig. 4.129.

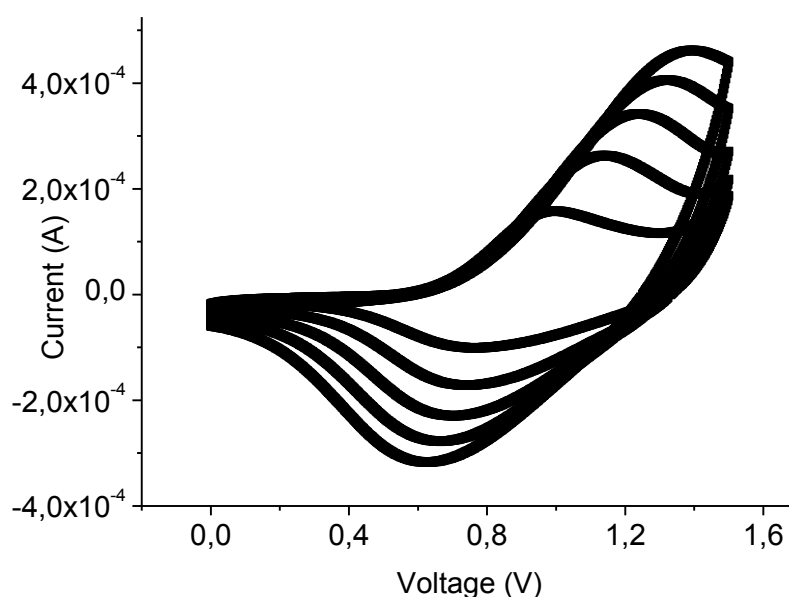


Figure 4.129 : Voltammetric response of PTh polymerized by PD method at 4 cycles in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

As it can be seen from the Fig. 4.129 the CV of PTh showed one broad wave at +0.80 V and a peak at +0.90 V which is very similar to PCz. As the scan rate increased the E_a shifted to positive area whereas the E_c shifted to negative area. Results obtained from these measurements were summarized in Table 4.41.

Table 4.41 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Th polymerized by PD method at 4 cycles

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	1010	840	158	982	170	1.6
200	1070	767	240	170	303	1.4
300	1159	724	326	231	435	1.3
400	1241	674	386	277	567	1.4
500	1284	642	433	326	642	1.3

As it can be seen in the Table 4.15, the reversibility of PTh was poor due to the I_a/I_c ratios were not close to unity and the ΔE values was very high.

PD electrodeposition of Th at 8 cycles can be seen in the Fig. 4.130.

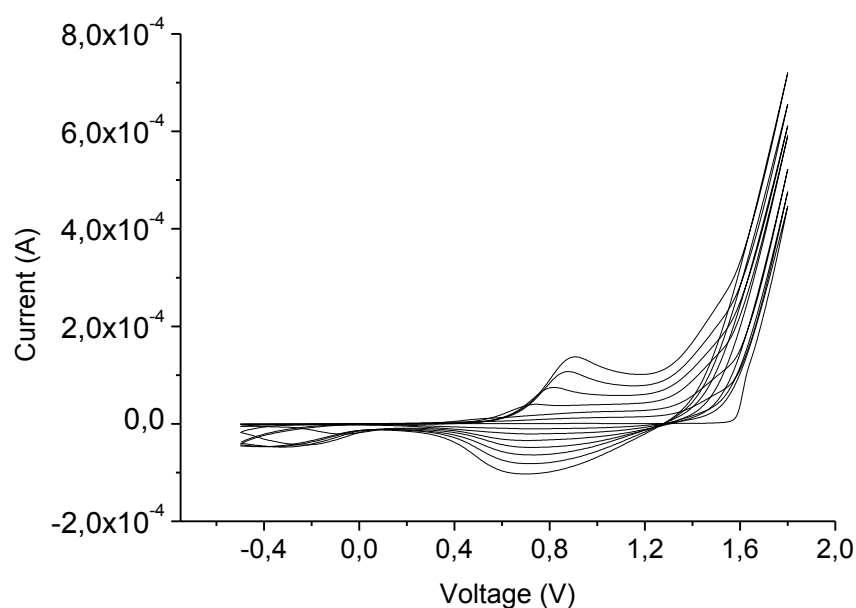


Figure 4.130 : PD electrodeposition of 0.1 M Th at 8 cycles in 0.1 M $NaClO_4$ containing ACN at the scan rate of 50 mV/s.

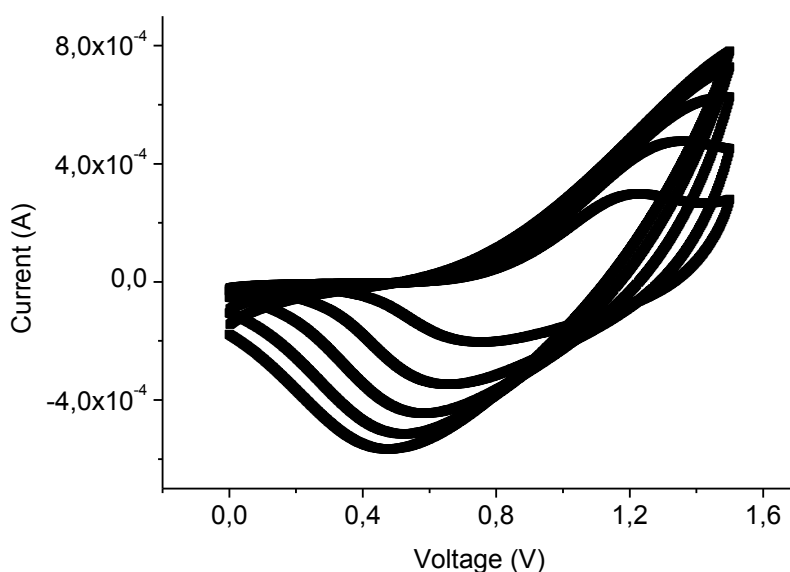


Figure 4.131 : Voltammetric response of PTh polymerized by PD method at 8 cycles in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

CV of PTh showed one broad wave at +1.0 V and a peak at +1.1 V as it can be seen in the Fig. 4.131. Results obtained from these measurements were summarized in Table 4.42.

Table 4.42 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Th polymerized by PD method at 8 cycles.

Scan rate (mV/s)	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	1099	799	250	206	300	1.2
200	1250	702	430	340	548	1.3
300	1309	616	552	430	693	1.3
400	1345	539	625	524	806	1.2
500	1374	513	693	570	861	1.2

As it can be seen in the Table 4.42. the reversibility of PTh obtained at 8 cycles, was poor similar to films obtained at 2 and 4 cycles.

Comparasion of current densities vs scan rates of PTh were given in the Fig. 4.132.

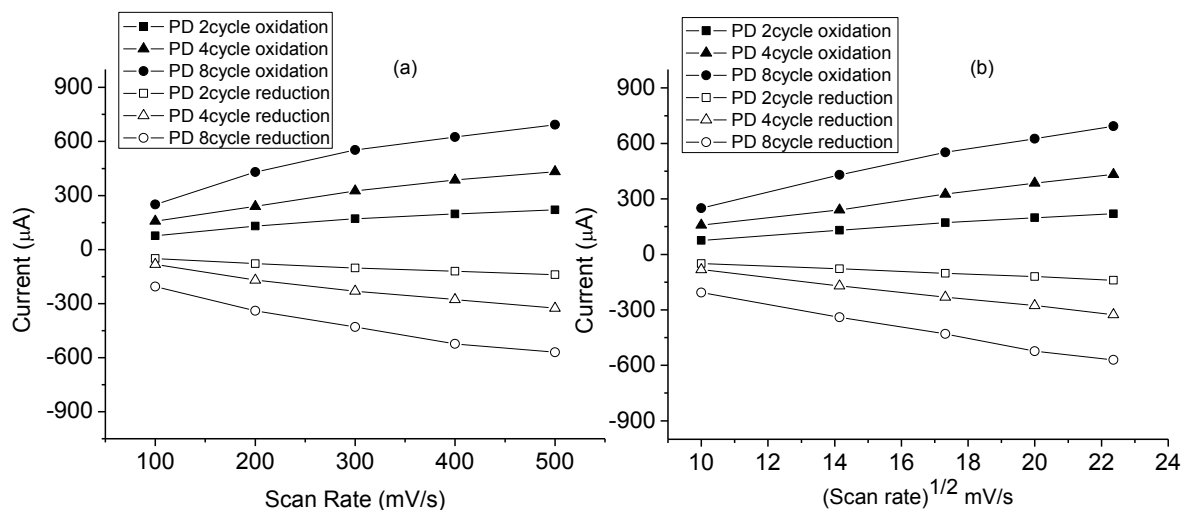


Figure 4.132 : (a)Current density versus scan rate, (b) Current density versus square root of scann rate plot of PTh films obtained by PD method at different polymerization times (2, 4 and 8 cycles)

As it can be seen in the Fig. 4.132 in the case of PD, films obtained at 2 and 4 cycles show thin film character whereas the long polymerization (8 cycles) caused diffusion control.

4.4.2. Potentiostatic Polymerization of Th

The polymerization of Th by PS method at 30 s in ACN/ 0.1 M NaClO_4 was given in Fig 4.133 and the voltammetric response of polymer film was presented in Fig 4.134.

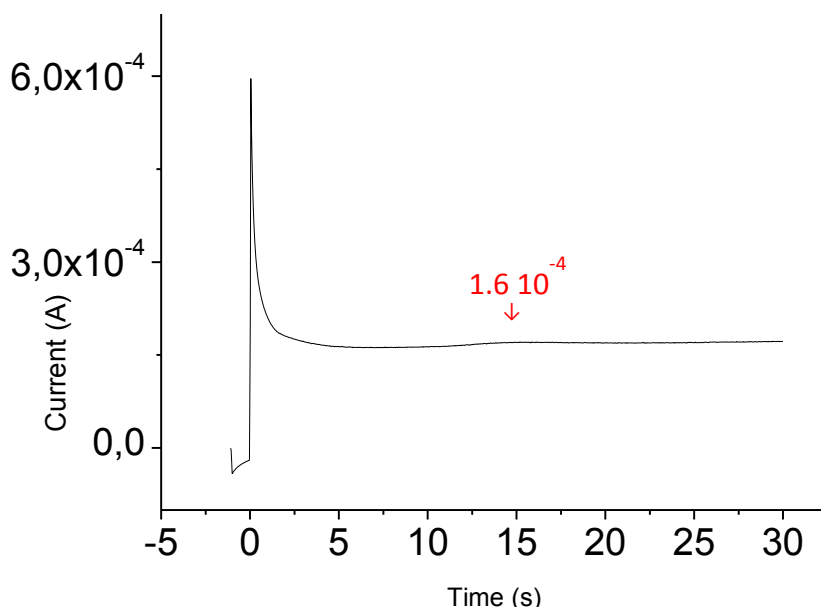


Figure 4.133 : PS electrodeposition 0.1 M Th at 60 s in 0.1 M NaClO_4 containing ACN.

As it can be seen in the Fig. 4.133, after an increase on the current during the first 5 s of polymeric growth, it was stabilized at $1.6 \cdot 10^{-4}$ A and kept constant during the polymerization. The voltammetric response of polymer film at different scan rates was presented in Fig. 4.134.

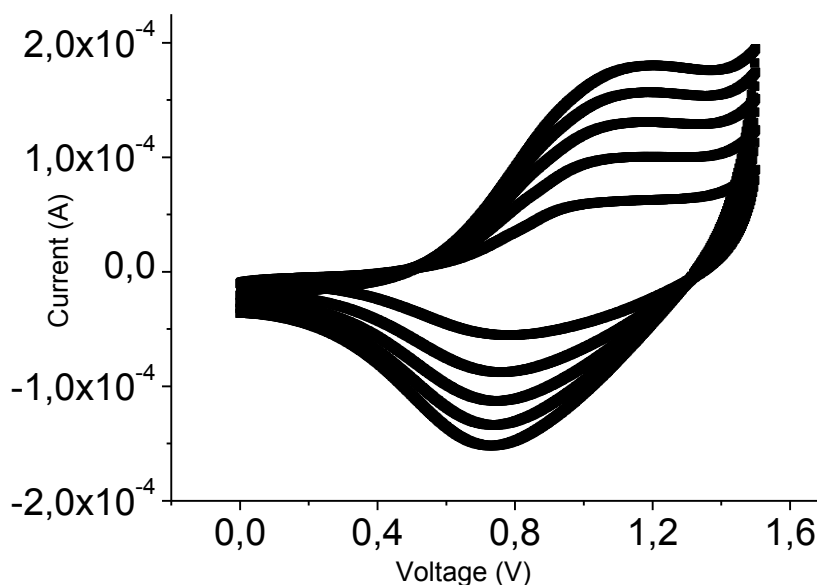


Figure 4.134 : Voltammetric response of PTh polymerized by PS method at 30 s in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

As it can be seen in the Fig. 4.134. the CV of PTh showed one broad wave at +0.80 V and a peak at +0.90 V which is similar to films obtained by PD method. Reversibility of the this film seems better than the one obtained by PD at 2 cycle. Results obtained from these measurements were summarized in Table 4.43.

Table 4.43 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of Th polymerized by PS method at 30 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	830	790	53	56	40	0.94
200	941	813	89	87	57	1.02
300	963	802	114	110	161	1.03
400	1003	764	144	134	236	1.07
500	1049	750	169	150	299	1.12

As it can be seen from the table, the film polymerized by PS method at 30 s was reversible for the low scan rates and the best reversibility was obtained at 200 mV/s.

PS polymerization of Th at 60 s was given in the Fig. 4.135. Monomer concentration, applied voltage and electrodes were kept same with previous measurements and similar investigations were done. The voltammetric response of the film was given in Fig. 4.136.

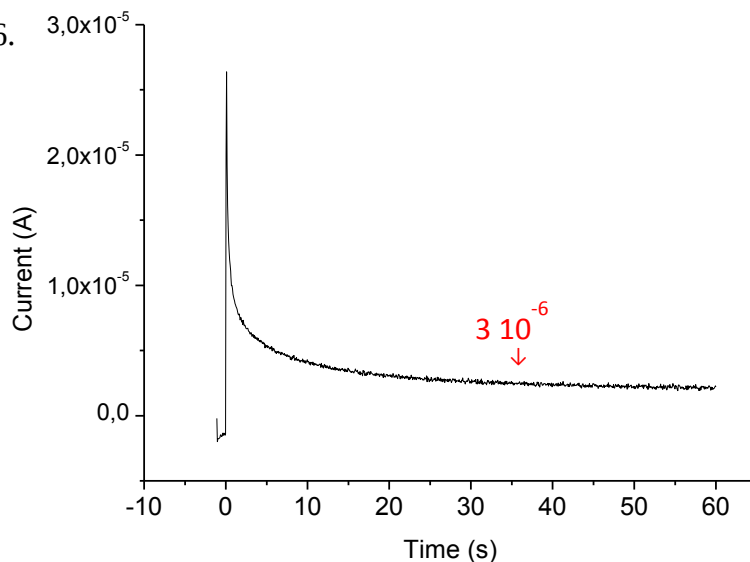


Figure 4.135 : PS electrodeposition 0.1 M Th at 60 s in 0.1 M NaClO_4 containing ACN.

As it can be seen in the Fig. 4.135, after an increase on the current during the first 5 s of polymeric growth, it was stabilized at 3.10^{-6} A and kept constant during the polymerization. The voltammetric response of polymer film at different scan rates was presented in Fig. 4.136.

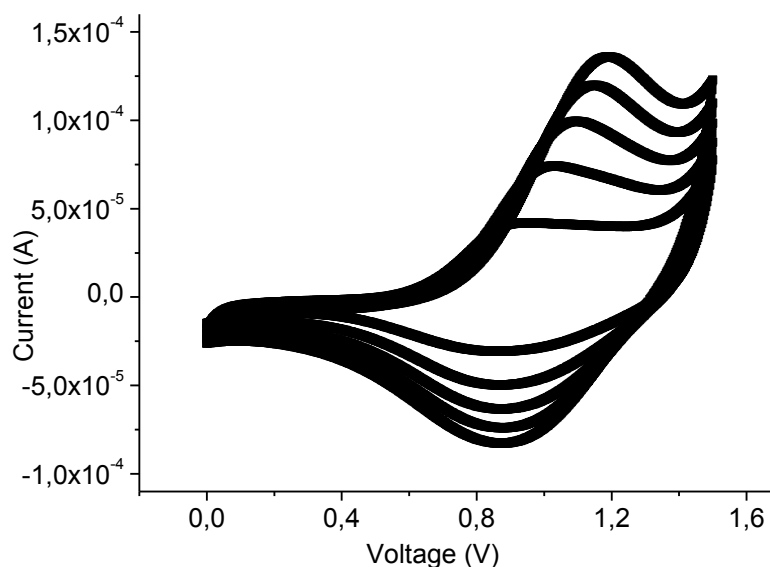


Figure 4.136 : Voltammetric response of PTh polymerized by PS method at 60 s in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Results obtained from these measurements were summarized in Table 4.44.

Table 4.44 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PTh polymerized by PS method at 60 s.

Scan rate m V/s	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	931	902	5.3	4.1	29	1.3
200	941	924	9.7	8.3	17	1.1
300	963	931	13.1	12	32	1.1
400	974	945	16.8	14.8	29	1.1
500	988	960	20.1	18	28	1.1

As it can be seen from the Table 4.44, the best reversibility was obtained at high scan rates.

Polymerization of Th by PS method at 120s can be seen in the Fig. 4.137. Monomer concentration, applied voltage and electrodes were kept same with the previous measurements and similar investigations were done.

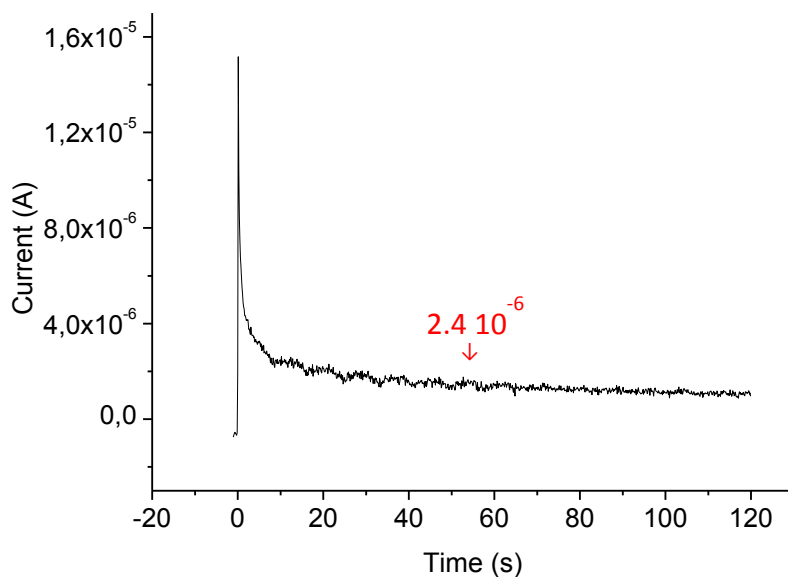


Figure 4.137 : PS electrodeposition 0.1 M Th at 120 s in 0.1 M NaClO_4 containing ACN.

As it can be seen in the Fig. 4.137 a sharp decrease on current was observed during the first 5 s of polymeric growth and after that it was stabilized at $1.3 \cdot 10^{-6}$ A. The voltammetric response of the film at different scan rates was given in Fig. 4.138.

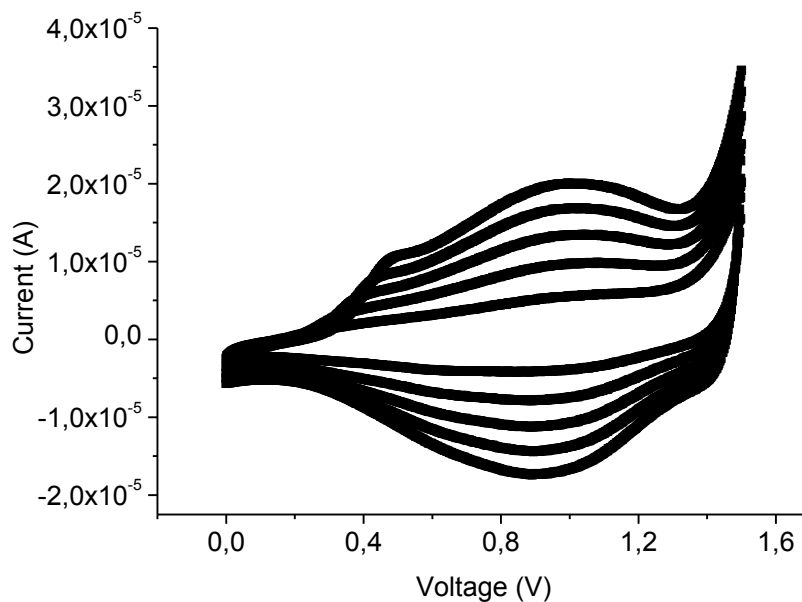


Figure 4.138 : Voltammetric response of PTh polymerized by PS method at 120 s in 0.1 M NaClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Table 4.45 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PTh polymerized by PS method at 120 s.

Scan rate (mV/s)	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	318	330	2.3	1.8	12	1.3
200	388	369	3.9	2.8	19	1.4
300	452	414	5.6	3.9	38	1.4
400	503	475	6.9	5.1	28	1.4
500	554	516	8.6	6.2	38	1.4

Reversibility of the film obtained by PS method at 120 s, seems better than the one obtained by PD method at 8 cycles. (Table 4.45)

Comparasion of current intensities vs scan rates of polymer films obtained by PS method was given in Fig 139.

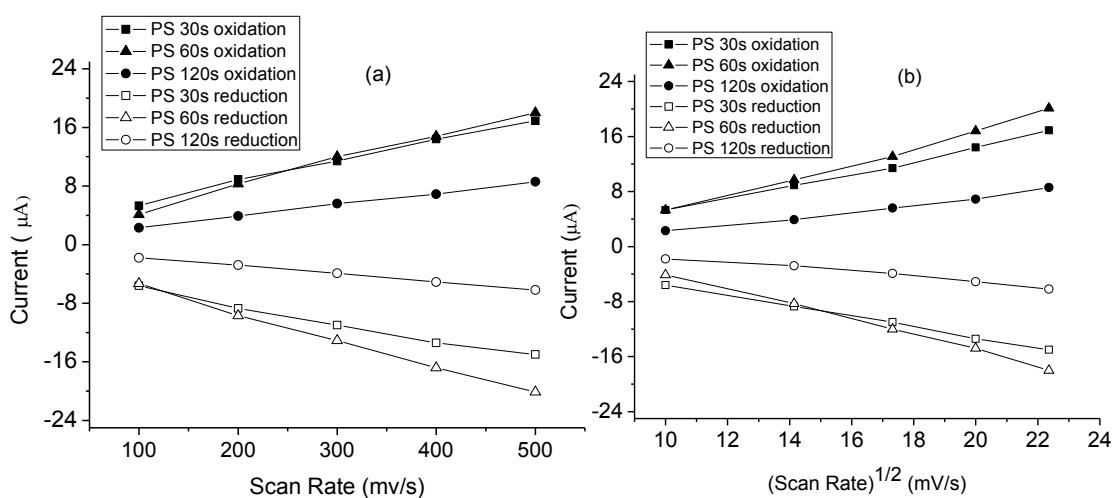


Figure 4.139 : (a)Current density versus scan rate, (b) Current density versus square root of scan rate plot of PTh films obtained by PS at different polymerization times (30, 60 and 120 s).

As it can be seen in the Fig. 4.139 in the case of PS method, films obtained at 2 cycles show thin film character whereas the longer polymerization times (4 and 8 cycles) caused diffusion control on the film surface.

4.4.3. Galvanostatic Polymerization of Th

GS polymerization of 0.1 M Th in ACN/0.1 M NaClO₄ at 30 s was given in Fig 4.140. Voltammetric response of polymer film was presented in Fig. 4.141.

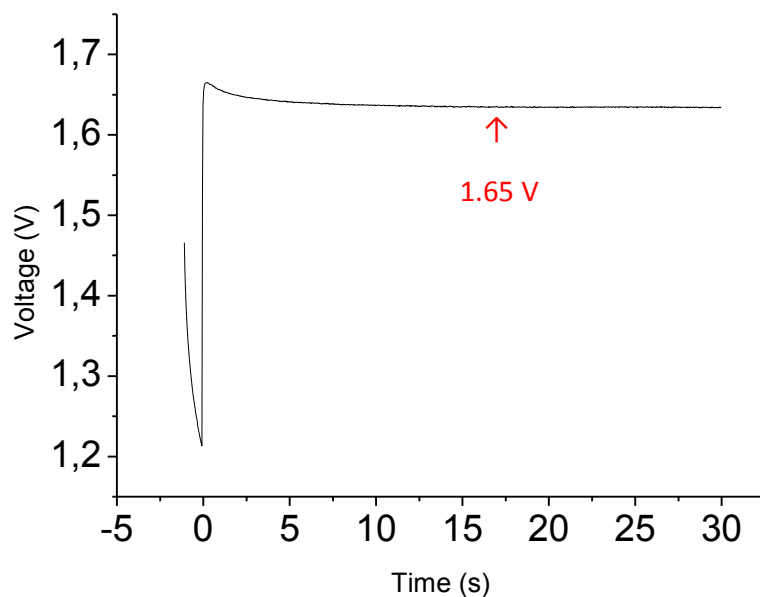


Figure 4.140 : GS electrodeposition 0.1 M Th at 30 s in 0.1 M NaClO₄ containing ACN.

After a sharp increase on voltage was observed at the during the first 5 s of polymeric growth, it was stabilized at 1.65 V and kept constant during the polymerization. (Fig. 4.140)

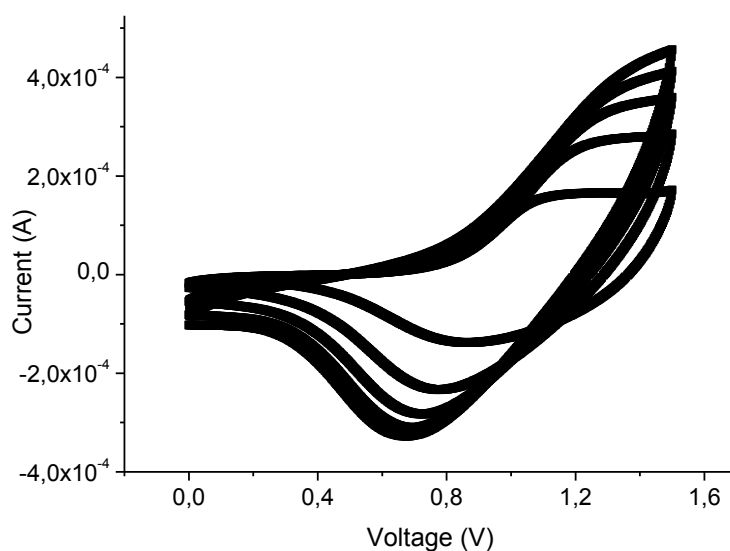


Figure 4.141 : Voltammetric response of PTh polymerized by GS method at 30 s in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

The CV of the polymer film obtained by GS at 120 s showed a broad peak at +1.0 V and as the scan rate increased the E_a shifted to positive area whereas the E_c shifted to more negative area (Fig. 4.141). Results obtained from these measurements were summarized in Table 4.46.

Table 4.46 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PTh polymerized by GS method at 30 s.

Scan rate (mV/s)	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	1102	901	156	137	201	1.1
200	1213	802	250	233	411	1.0
300	1304	731	330	280	573	1.1
400	1306	729	363	287	577	1.2
500	1363	695	417	322	668	1.3

Reversibility of the film obtained by GS method at 30 s was poor which is similar to film obtained by PD method at 2 cycles. (Table 4.45)

GS cally polymerization of Th at 60 s was given in the Fig. 4.142. Monomer concentration, applied voltage and electrodes were kept same and similar investigations were done. The voltammetric response of the film was in Fig. 4.143.

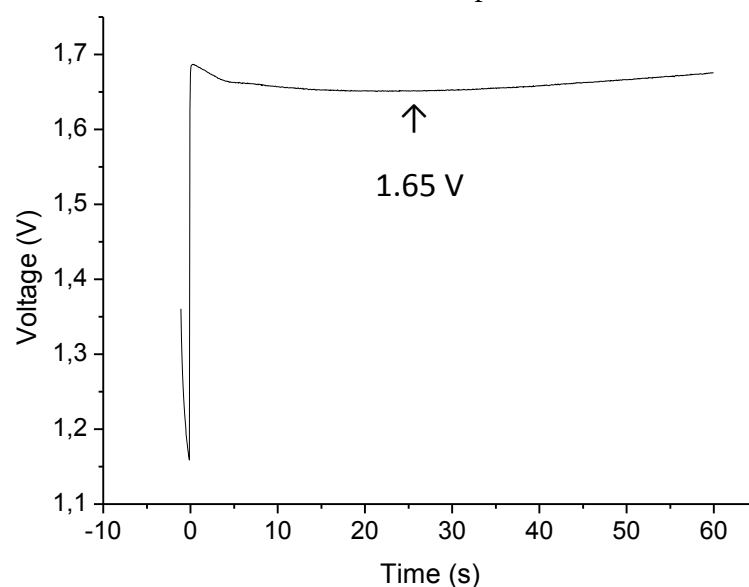


Figure 4.142 : GS electrodeposition of 0.1 M Th at 60 s in 0.1 M NaClO_4 containing ACN.

After a sharp increase on voltage was observed at the during the first 5 s of polymeric growth, it was stabilized at 1.65 V and kept constant during the polymerization. (Fig. 4.142)

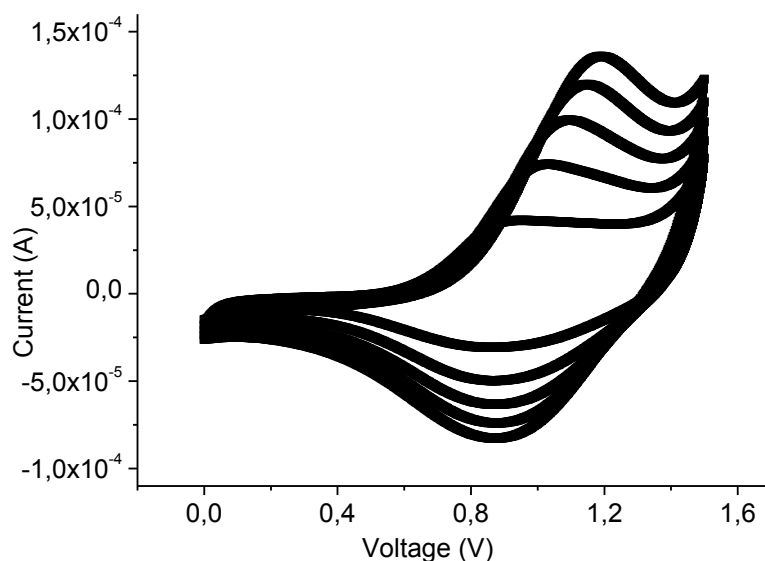


Figure 4.143 : Voltammetric response of PTh polymerized by GS method at 60 s in 0.1 M NaClO₄ containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Table 4.47 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PTh polymerized by GS method at 60 s.

Scan rate (mV/s)	E_a (mV)	E_c (mV)	I_a (μ A)	I_c (μ a)	ΔE (m V)	I_a/I_c
100	1010	840	158	98	170	1.6
200	1070	767	240	170	303	1.4
300	1159	724	326	231	435	1.3
400	1241	674	386	277	567	1.4
500	1,284	642	433	326	642	1.3

As it can be seen in the in the Fig. 143 and Table. 4.47, the reversibility of the film obtained by GS method at 120 s was poor due to the increasing polymerization time led to thicker and more resistive behaviour.

GS polymerization of Th at 120 s was given in the Fig. 4.144 . Monomer concentration, applied current and polymerization media were kept the same with previous measurements. The voltammetric response of the PTh at different scan rates was given in Fig. 4.145.

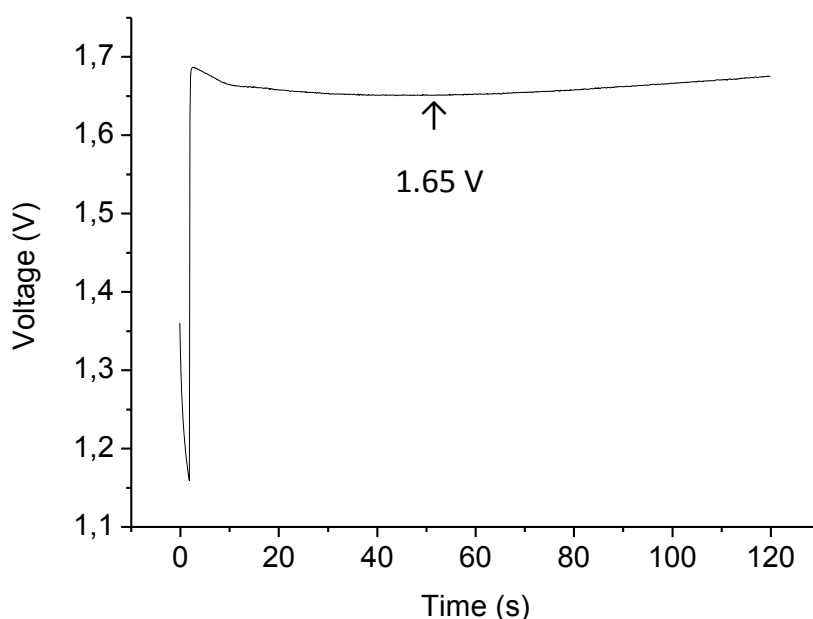


Figure 4.144 : GS electrodeposition of 0.1 M Th at 60 s in 0.1 M NaClO_4 containing ACN.

After a decrease for the first 5 seconds, the voltage stabilized at 1.65 V and kept constant until the end of the polymerization. (Fig. 4.144)

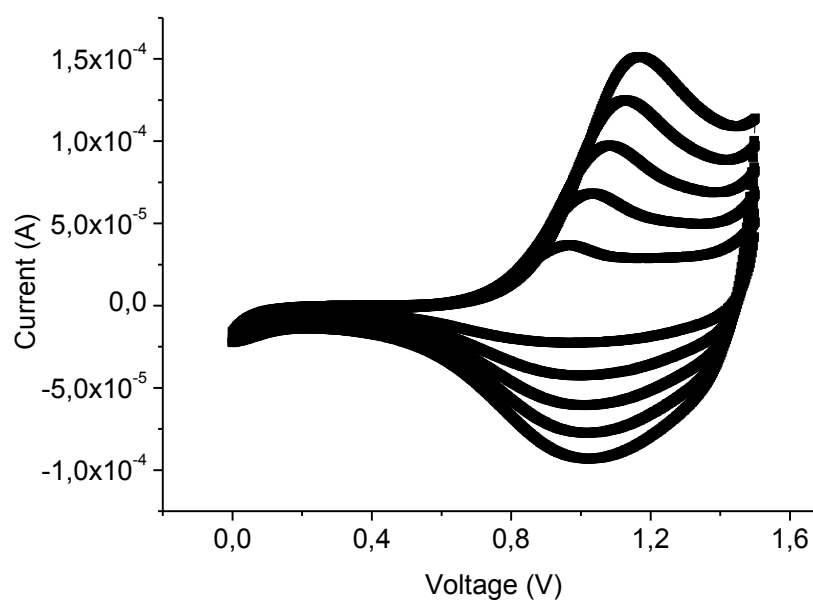


Figure 4.145 : Voltammetric response of PTh polymerized by GS method at 120 s in 0.1 M NaClO_4 containing ACN at the different scan rates between 100 mV/s and 500 mV/s.

Results obtained from these measurements were summarized in the Table 4.48.

Table 4.48 : E_a , E_c , I_a , I_c , ΔE , I_a/I_c values of PTh polymerized by GS method at 120 s.

Scan rate (mV/s)	E_a (mV)	E_c (mV)	I_a (μA)	I_c (μa)	ΔE (m V)	I_a/I_c
100	967	927	35.6	28.5	40	1.2
200	1034	994	67	54.4	40	1.2
300	1077	1030	96	60.4	47	1.6
400	1113	1045	124	78	68	1.5
500	1149	1059	149	95	90	1.5

As it can be seen in the Table 4.48, the polymer film obtained by GS method at 120 s was reversible for the low scan rates.

Comparasion of current densities vs scan rates of PTh films obtained by GS method was given in Fig. 4.146.

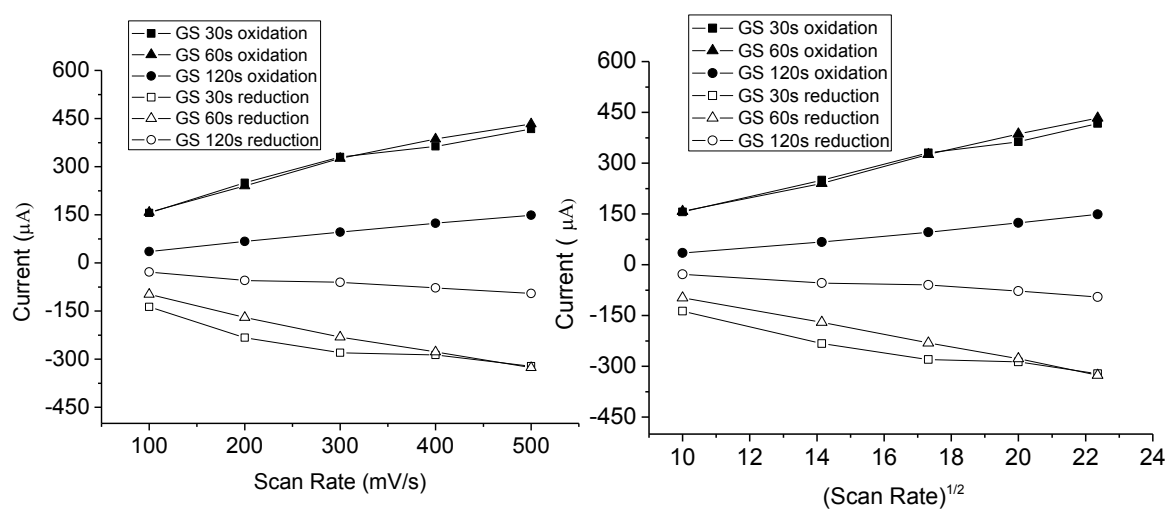


Figure 4.146 : (a)Current density versus scan rate, (b) Current density versus square root of scan rate plot PTh films obtained by GS at different polymerization times (30, 60 and 120 s)

Comparasion of redox behaviour of PTh obtained by PD, PS and GS methods at different polymerization times was given in the Fig. 4.147.

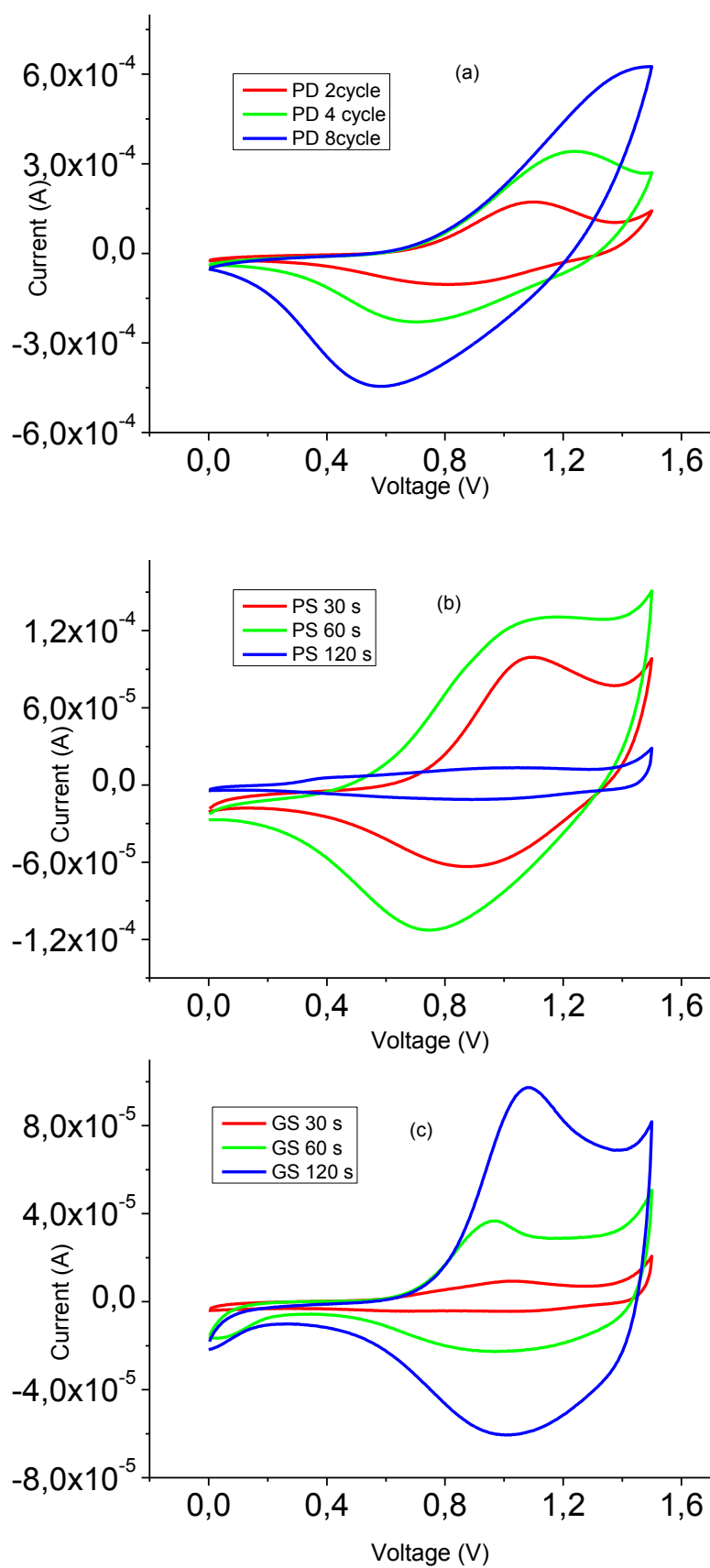


Figure 4.147 : Comparison of redox behaviour of PTh films obtained by PD (a) , PS (b) and GS (c) depending on polymerization time at 300 mV/s in monomer free solution.

For PTh films in the case of PD and GS methods as the thickness increased the the current intensities increased as well. The most reversible films were obtained by PD method at 2cycle, PS method at 30s and GS method at 30s. These results suggest that reversibility of redox behaviour is better for thin films.

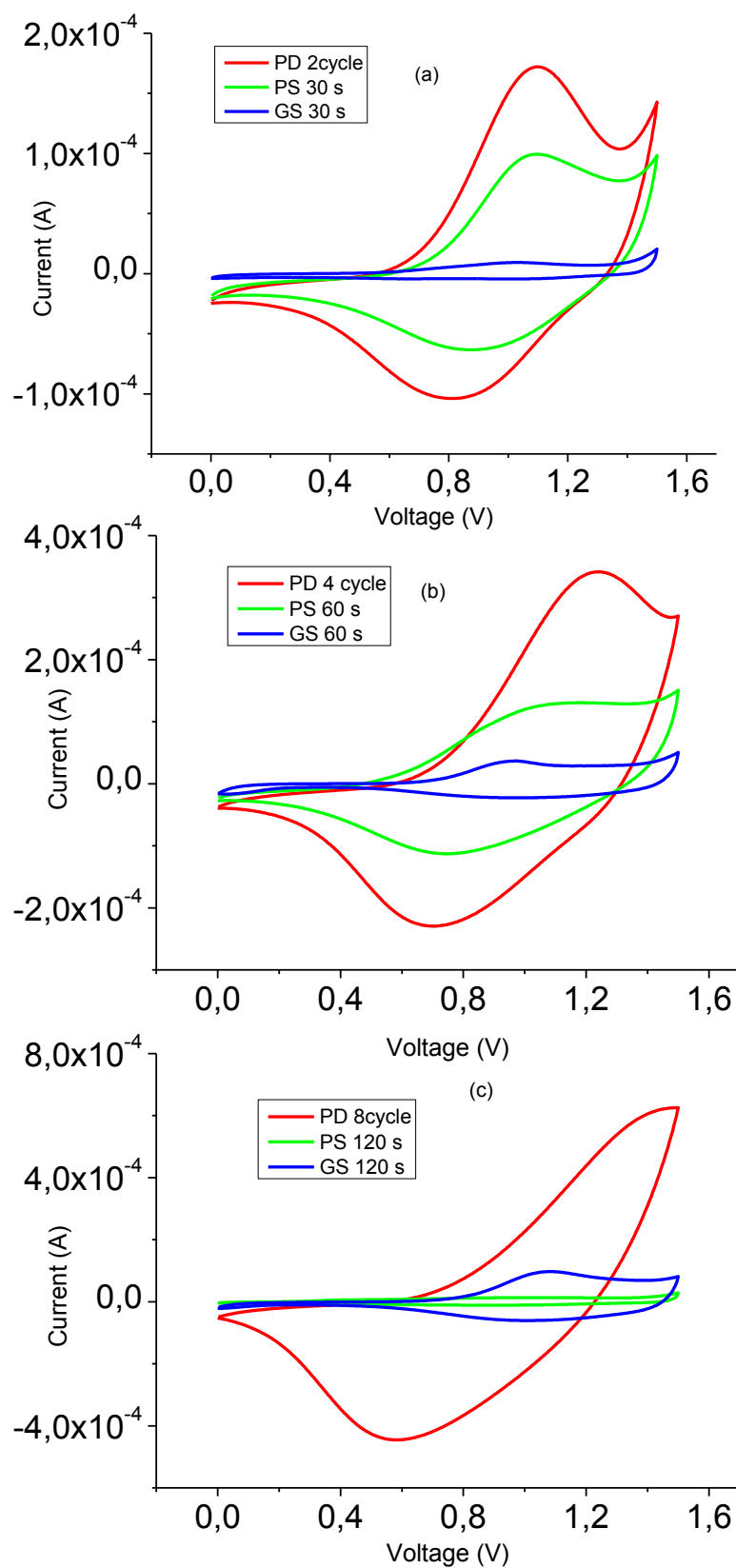


Figure 4.148 : Comparison of redox behaviour of PTh films obtained by PD , PS and GS methods depending on polymerization method. [(a), PD 2 cycles, PS 30 s, GS 30 s; (b), PD 4 cycles, PS 60 s, GS 60 s; (c), PD 8 cycles, PS 120 s, GS 120 s] at 300 mV/s in monomer free.

When the three polymerization methods were compared, it can be said that, the highest current intensities were observed for the PD method at all polymerization times due to the removals from the surface in reverse scan resulted thinner, more regular and electroactive film. (Fig. 4.145)

4.4.4. Comparasion of Electrochemical Impedance Spectroscopy Measurements of PTh films

Impedance properties were investigated between 10 mHz-100 kHz range at the absence of voltage and with 1V direct voltages to the polymer film in 5ml 0.1 M ACN/ NaClO₄ monomer free solution. Nyquist, Bode phase and Bode magnitude diagrams resulting PTh films were compared for each polymerization method and time.

4.4.4.1. EIS results of potentiodynamically obtained PTh film

PTh films obtained by PD method applying 2, 4, 8 cycles were characterized with EIS. Measurements and results were given in (Fig. 4.149- 4.154)

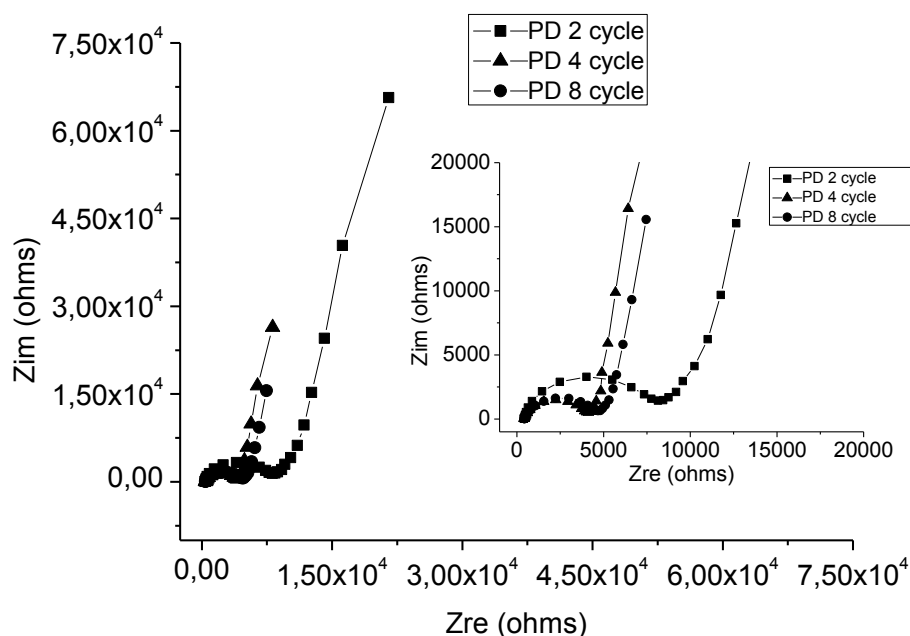


Figure 4.149 : Nyquist diagram of PTh obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

At low frequency and open circuit potential, the imaginary part of the impedance showed a semi circle behaviour which is a characteristic of resistive behaviour and well matched with the redox behaviour of films seen in the Table (4.46-4.48)

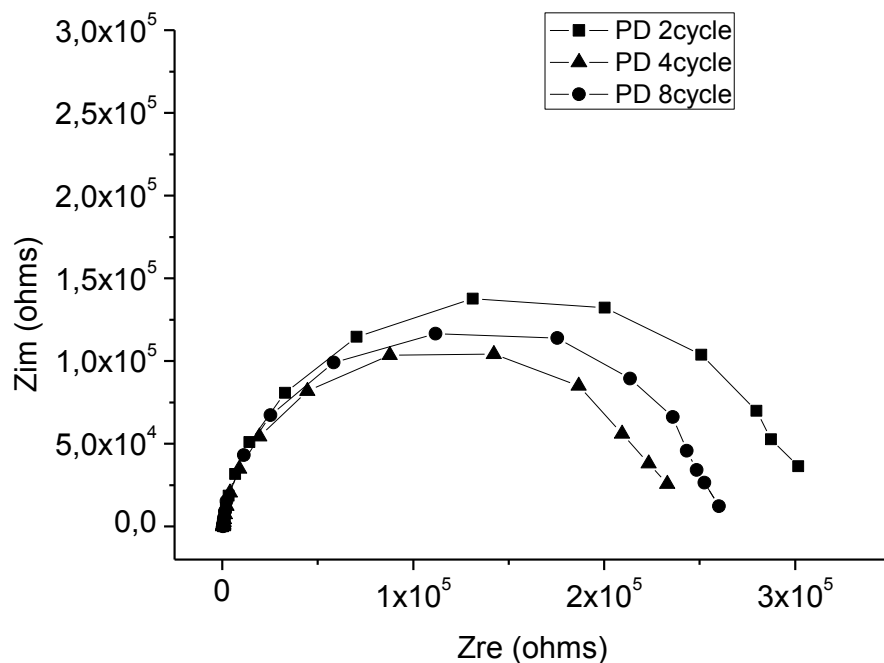


Figure 4.150 : Nyquist diagram of PTh obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

At high frequency and under constant 1V voltage Z_{im} showed semi circle behaviour.

(Fig. 4.150)

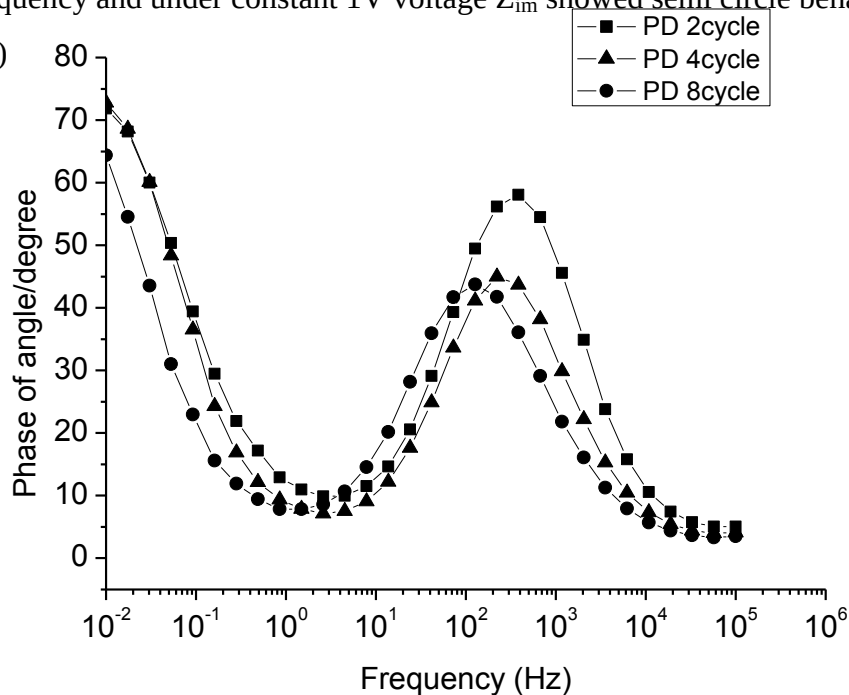


Figure 4.151 : Bode phase diagram of PTh obtained by at PD method 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

The highest phase angle was observed at the film polymerized by PD method at 2 and 4 cycles. (Fig 4.118).

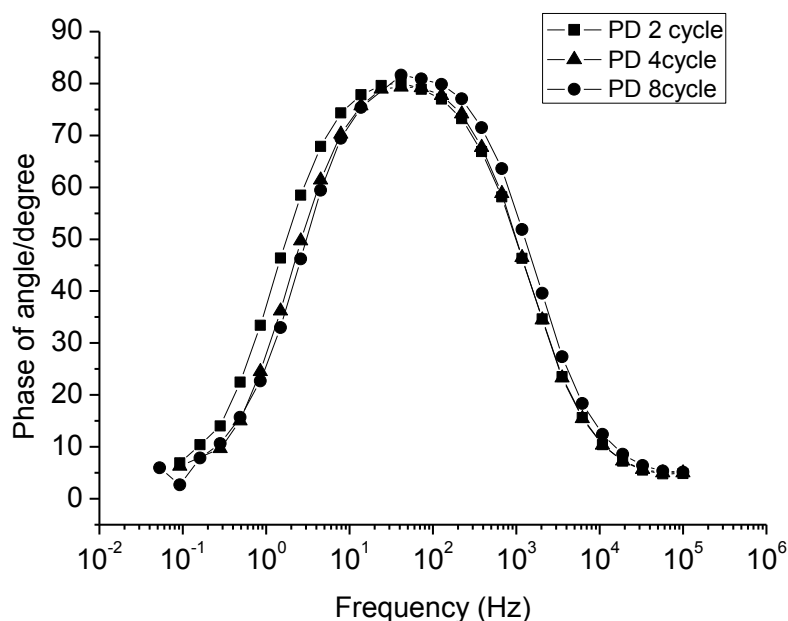


Figure 4.152 : Bode phase diagram of PTh obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Phase angles became lower and shifted to higher frequencies with increasing cycle number under the 1V constant voltage as the constant voltage led to the overoxidation of the polymer and the removals from the film surface (Fig.4.152).

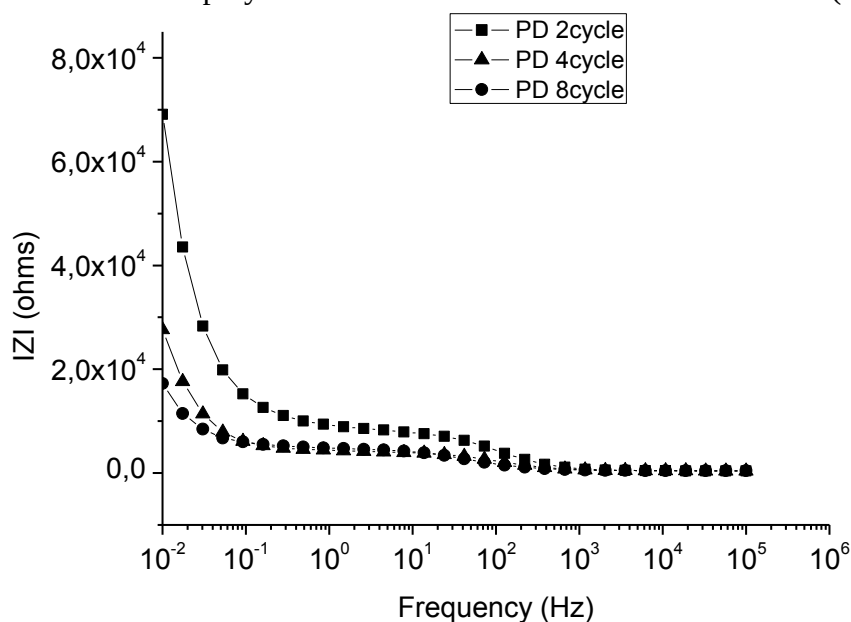


Figure 4.153 : Bode magnitude diagram of PTh obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range.

As it seen was in the Fig. 4.153 at low frequencies, as the polymerization time increased the imaginary value of impedance (IZI) decreased due to the overoxidation of polymer on the electrode. For the frequencies >1000 Hz , IZI reaches a constant value for all polymerization times.

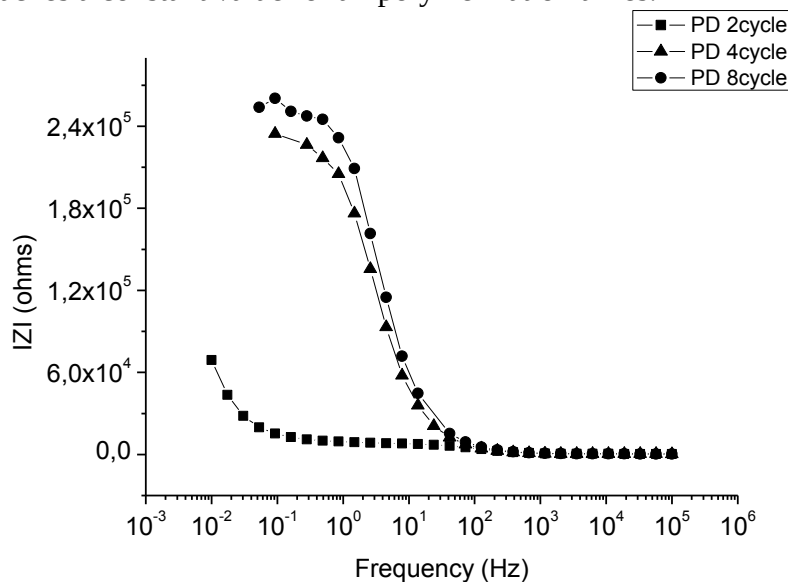


Figure 4.154 : Bode magnitude diagram of PTh obtained by PD method at 2, 4 and 8 cycles between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Table 4.49: R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PTh polymerized by PD method at 2, 4 and 8 cycles

PTh ($\pm 0,5$)	PD (2 cycle)		PD (4 cycle)		PD (8 cycle)	
	Open circuit potential	1V applied	Open circuit potential	1 V applied	Open circuit potential	1V applied
R_s ohm-cm^2	398	410	411	424	428	410
R_p ohm-cm^2	1344	263896	1703	177512	10662	221978
C_{dl} $\mu\text{F-cm}^2$	12	8	30	17	31	16
C_{sp} $\mu\text{F-cm}^2$	242	—	603	—	1022	—
C_{dl} $\mu\text{F-cm}^2$	254	—	626	—	1075	—
P. angle (degree)	71	7	70	11	65	6

As it can be seen from the table, the highest C_{sp} and C_{dl} values were observed for the film obtained PS method at 120 s.

4.4.4.2. EIS results of potentiostatically obtained PTh film

Impedance properties were investigated in the similar conditions with the previous measurements. Nyquist, Bode phase and Bode magnitude diagrams (Fig. 4.155-4.160) of resulting PTh films were compared for each polymerization time.

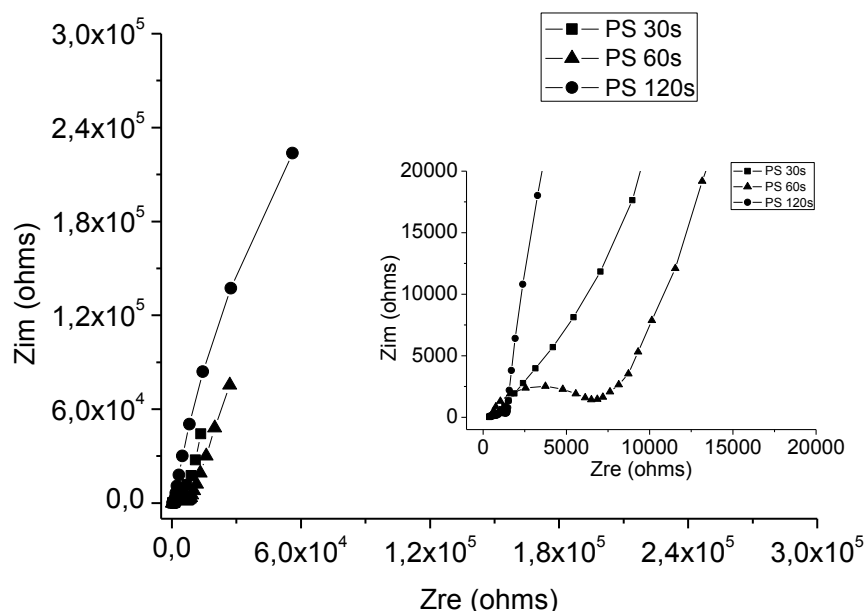


Figure 4.155 : Nyquist diagram of PTh obtained by PS at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

At open circuit potential, at low frequencies for long polymerization times, and at high frequencies for short polymerization times, the imaginary part of the impedance sharply increased and plot tend to a vertical line which is a characteristic of capacitive behaviour. (Fig. 4.155)

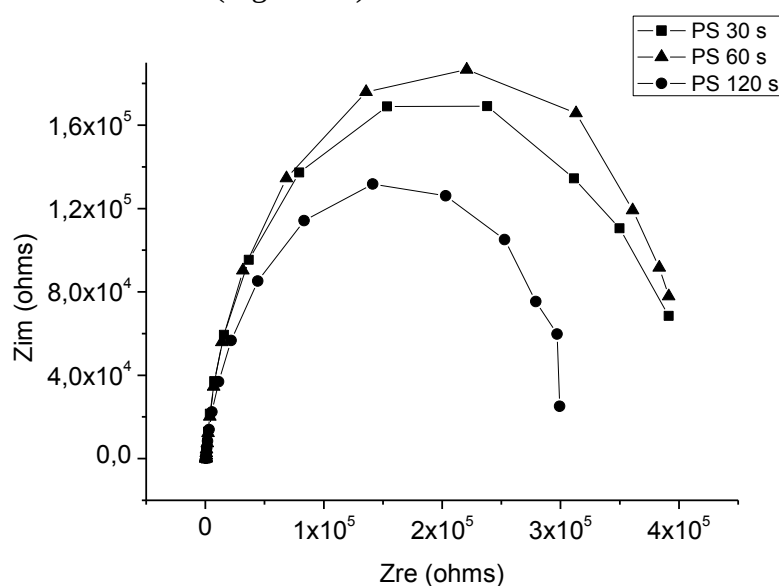


Figure 4.156 : Nyquist diagram of PTh obtained by PS method at 30, 60 and 120 s by applying 1V direct voltage.

At high frequency and under constant 1V voltage Zim showed semi circle due to the applying 1 V constant voltage led to transition from capacitive behaviour to resistive behaviour (Fig. 4.156)

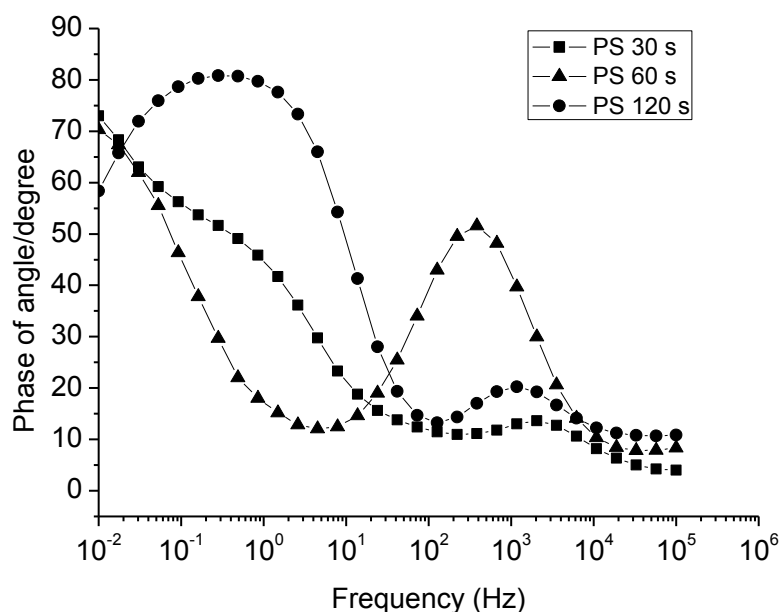


Figure 4.157 : Bode phase diagram of PTh obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency by applying 1V direct voltage.

As it can be seen in the Fig. 4.157. the highest phase angle was observed for the film obtained at 30 s.

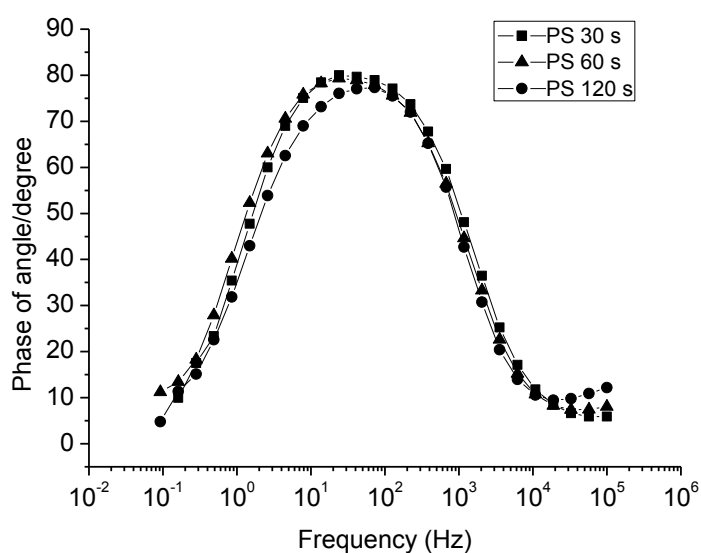


Figure 4.158 : Bode phase diagram of PTh obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

Similar frequency shifts were observed with the previous measurements. (Fig. 4.158)

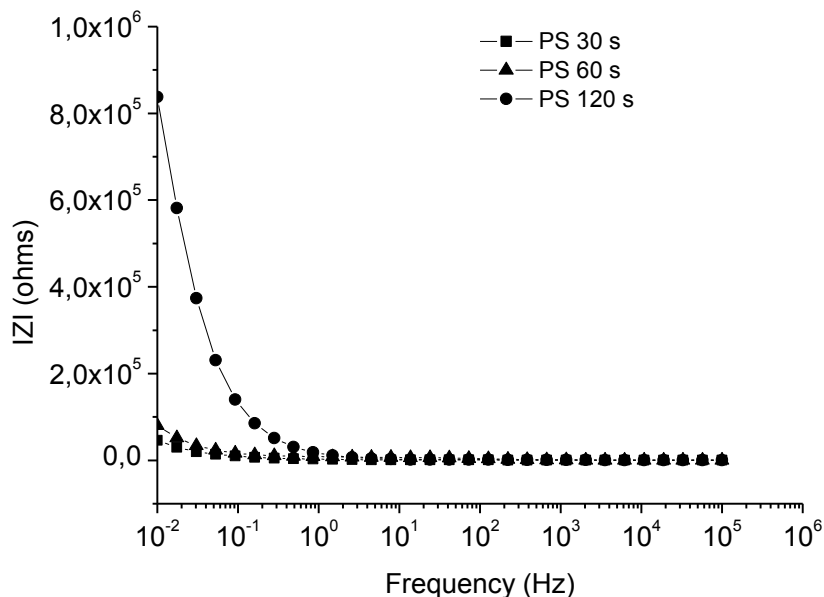


Figure 4.159 : Bode magnitude diagram of PTh obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

As it seen was in the Fig. 4.159 at low frequencies, as the polymerization time increased the imaginary value of impedance (IZI) increased due to the deposition of polymer on the electrode surface.

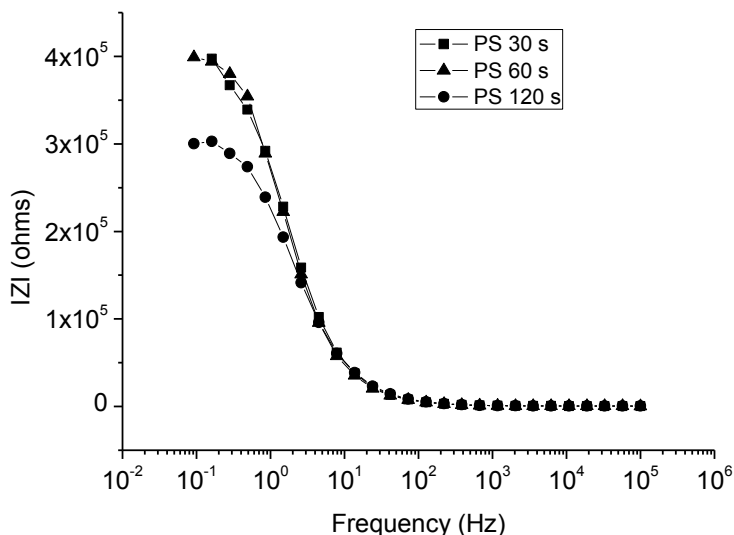


Figure 4.160 : Bode magnitude diagram of PTh obtained by PS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

As it can be seen in the Fig. 4.160. the capacitive behaviour shifted to the higher frequencies. Results obtained from the measurements were demonstrated in the Table 4.50.

Table 4.50 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PTh polymerized by PS method at 30, 60 and 120 s

PTh ($\pm 0,5$)	PS (30s)		PS (60s)		PS (120s)	
	Open circuit potential	1V applied	Open circuit potential	1 V applied	Open circuit potential	1V applied
R_s ohm-cm^2	367	419	447	452	469	506
R_p ohm-cm^2	3395	307855	2809	274220	2919	284872
C_{dl} $\mu\text{F-cm}^2$	22	13	12	4	2	1
C_{sp} $\mu\text{F-cm}^2$	360	—	580	—	655	—
C_{dif} $\mu\text{F-cm}^2$	396	—	226	—	25	—
P. angle (degree)	73	10	70	11	65	6

As it can be seen in the table for the film obtained by PS, the C_{sp} values increased but C_{dl} values decreased as the polymerization time increased.

4.4.4.3. EIS results of galvanostatically obtained PTh film

Impedance properties were investigated in the similar conditions with the previous measurements. Nyquist, Bode phase and Bode magnitude diagrams (Fig. 4.161-4.166) of resulting PTh films were conducted for each polymerization time.

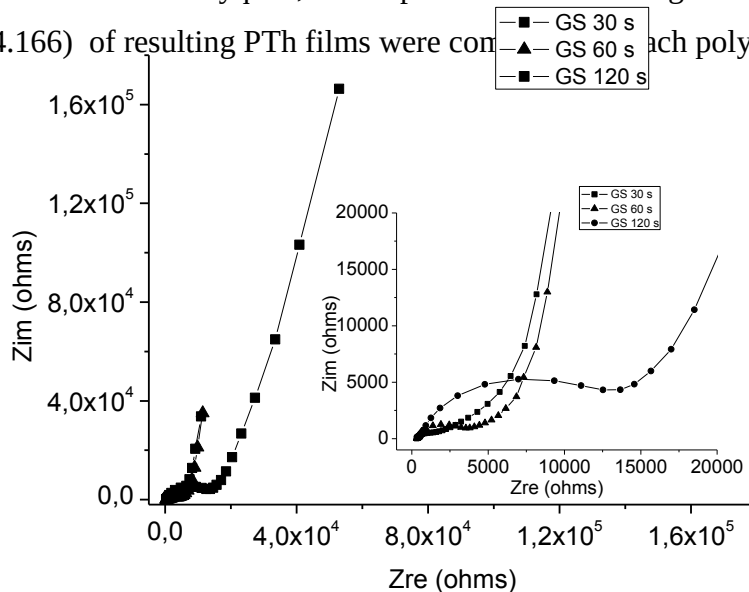


Figure 4.161 : Nyquist diagram of PTh obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

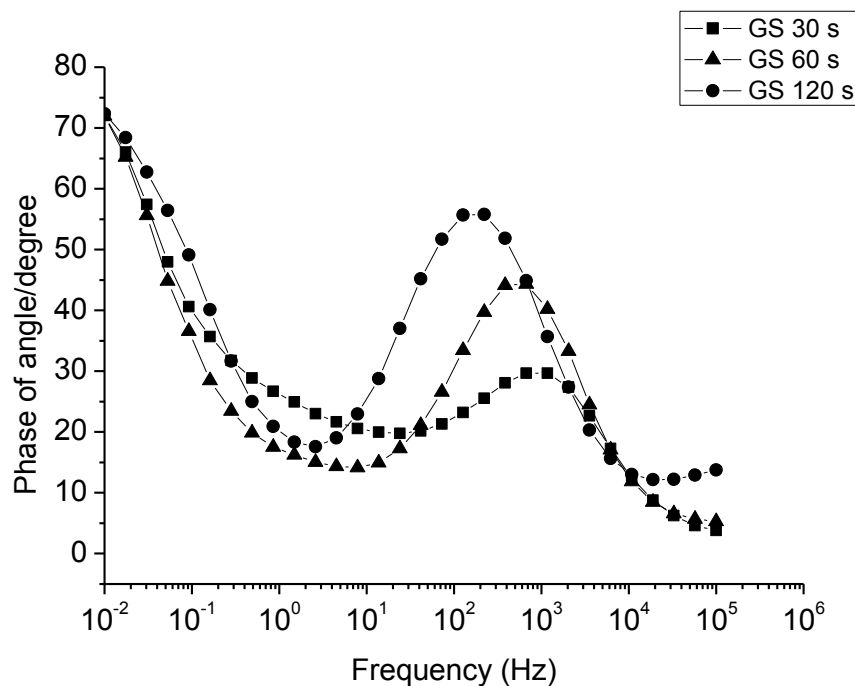


Figure 4.162 : Nyquist diagram of PTh obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

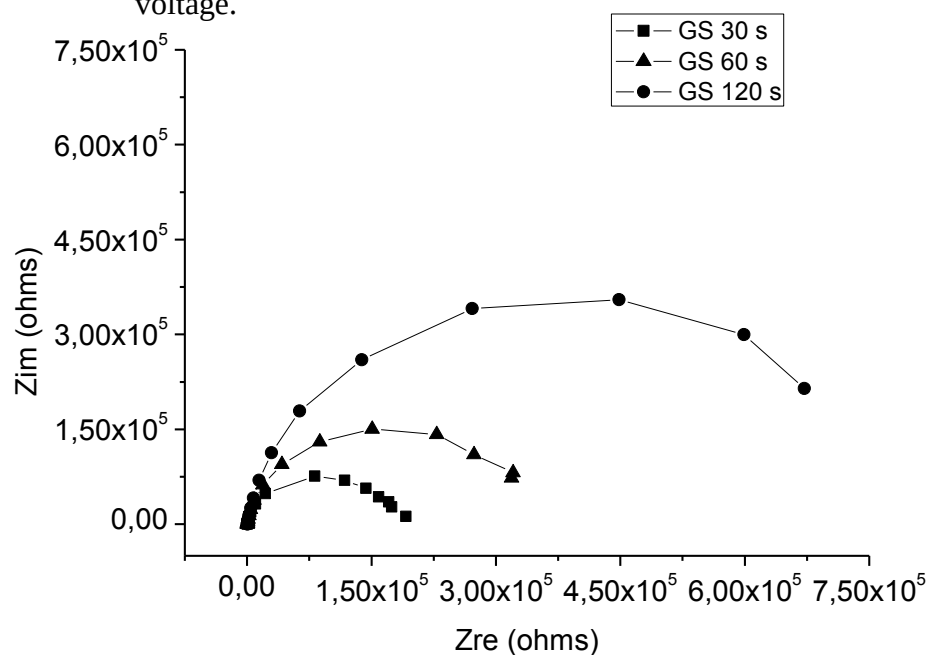


Figure 4.163 : Bode phase diagram of PTh obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

The highest phase angle was observed for PTh obtained by GS method at 30 s. (Fig. 4.163) Shifts on the phase angle were observed at the same frequencies as the impedance value was independent of polymerization time. (Fig. 4.164)

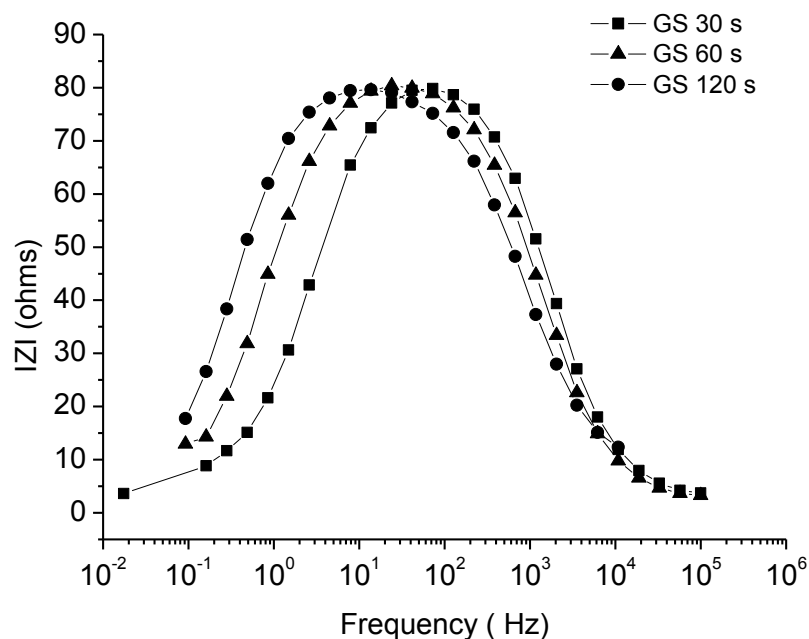


Figure 4.164 : Bode phase diagram of PTh obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range by applying 1V direct voltage.

As it can be seen in the Fig. 4.164. applying 1V constant voltage resulted to shift higher frequencies.

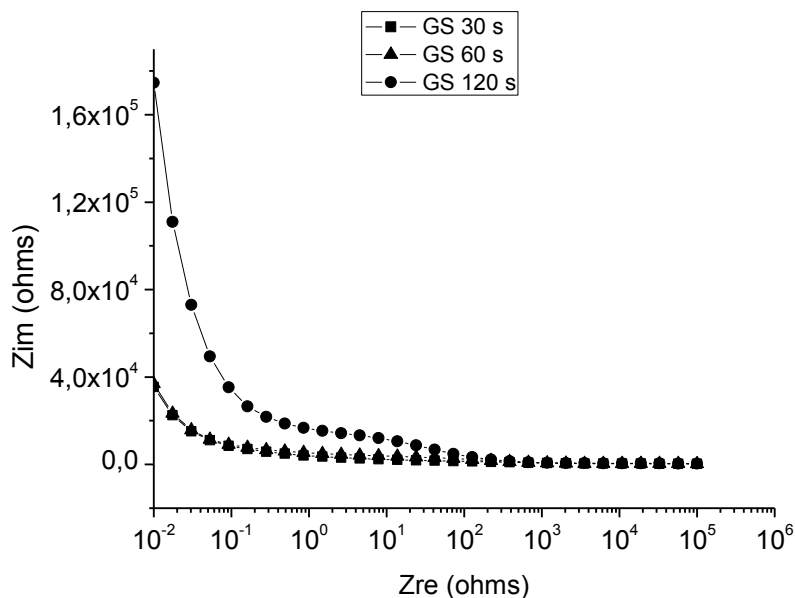


Figure 4.165 : Bode magnitude diagram of PTh obtained by GS method at 30, 60 and 120 s between 10 mHz and 100 kHz frequency range.

The highest Z_{im} value for the PTh films obtained by GS method was observed at 120 s.(Fig. 4.165).

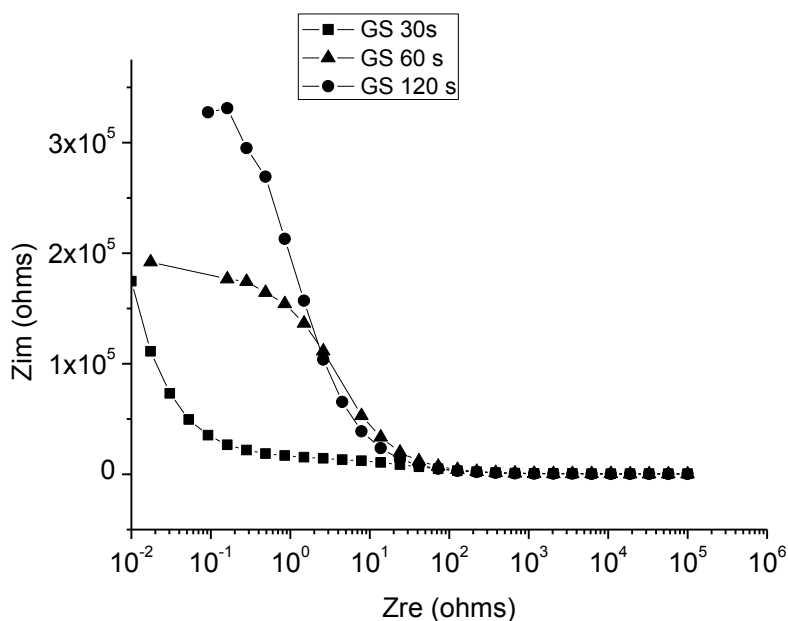


Figure 4.166 : Bode magnitude diagram of PTh obtained by GS method at 30, 60 and 120 s by applying 1V direct voltage.

Similar frequency shifts with the previous results was observed for the PTh films obtained by GS method. (Fig. 4.166) Results obtained from these measurements can be seen in the table 4.51.

Table 4.51 : R_s , R_p , C_{dl} , C_{sp} , C_{dif} and phase angles of PTh polymerized by GS method at 30, 60 and 120 s.

PTh (±0,5)	GS (30s)		GS (60s)		GS (120s)	
	Open circuit potential	1V applied	Open circuit potential	1 V applied	Open circuit potential	1V applied
R_s ohm-cm ²	443	470	430	416	400	554
R_p ohm-cm ²	6943	655286	2326	298478	2908	544016
C_{dl} μF-cm ²	22	7	12	5	8	2
C_{sp} μF-cm ²	472	—	453	—	956	—
C_{dif} μF-cm ²	482	—	479	—	102	—
P. angle (degree)	73	10	72	13	72	17

As it can be seen in the Table 4.51., Csp value increased as the time increased and the highest Csp was observed for the film obtained at 8cycle whereas a decreased on Cdl was observed as time increased.

For the PTh films obtained by all polymerization methods, as the polimerization time increased, the Csp and Cdl increased as well (Table 4.49-4.51) due to the polymer deposition on the electrode surface resulted thicker and more capacitive layer. This idea was also supported with the high current intensities at high polymerization times for PD and PS methods seen in the Fig. 4.144 (a,c). When the three polymerizations methods were compared each other, the most capacitive film was obtained by PD method at 8 cycles, (Table 4.49) where as the most reversibility was observed for PS method at 30 s. (Table 4.40).

4.4.4.4. Equivalent Circuit diagram of PTh

The most capacitive PTh film obtained by PD method a Impedance data were analyzed grafically with the use of ZSimp-Win software, the conventional equivalent circuit consists of a series of a resistor and capacitor, $(R(C(R(C(RW))))(CR)$ where Rs was the uncompasated ohmic resistance Rct was the charge transfer resistance, and CPE was the constant phase element and Rp,s was polymer resistance. Rpt is the resistance where as Cpt is capacitance of the electrode. W was the Warburg impedance of the polymer. (Fig. 4.167) . CPE was the total charge accumulation at the solution/polymer interface in the outer regions of the electrode, it also might be represented by Qdl. The charge transfer resistance (Rct) was a combination of resistances of solution and inner regions of polymer electrode, as the Bu_4NBF_4 was able to penetrate into the porous surface. Cct was the charge accumulation at the solution/polymer interface in the inner regions of the electrode, which was also affected by the decrease on conductivity of the electrolyte. The impedance parameters obtained from these measurements were summarized in the Table 4.51.

t 30 s.

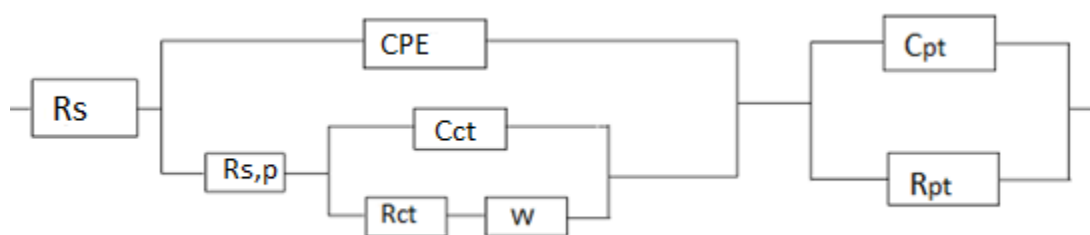


Figure 4.167 : The equivalent circuit diagram of PTh. (R(Q(R(C(RW))))(CR)
 [Chi squared: $8.345 \cdot 10^{-4}$, n: 0.5331 Monomer: 0,1M Th,
 Method: PS at 30 s, Electrolyte: 0,1 M ACN/ NaClO₄, WE:
 Pt (bottom electrode), RE: Ag/AgCl, CE: Pt (wire)]

Table 4.52 : Electrical parameters calculated for PTh film from the equivalent circuit diagram.

Rs (ohm- cm ²)	(CPE) Y0 (S- sec ⁿ /cm ²)	Rs,p (ohm- cm ²)	Rct (ohm- cm ²)	Cct (F/cm ²)	W Y0 (S- sec ⁿ /cm ²)	Cpt (F/cm ²)	Rpt (ohm- cm ²)
340	$2.5 \cdot 10^{-5}$	621	4143	222	$15 \cdot 10^{-5}$	$5.7 \cdot 10^{-3}$	5141

4.5. Spectroelectrochemistry measurements of PPy, PCz, PIN and PTh

Py, Cz, IN and Th were coated onto a ITO glass via PS method at 120 s by a potential of 1.0 V for Py, 1.2 V for Cz and 1.5 V for both IN and Th. The polymer films were then washed in monomer free solution. During the spectroelectrochemical measurements, Ag wire was used as reference electrode instead of Ag/AgCl.

UV visible absorbance spectrum of PPy obtained at different potential application was given in the Fig. 168.

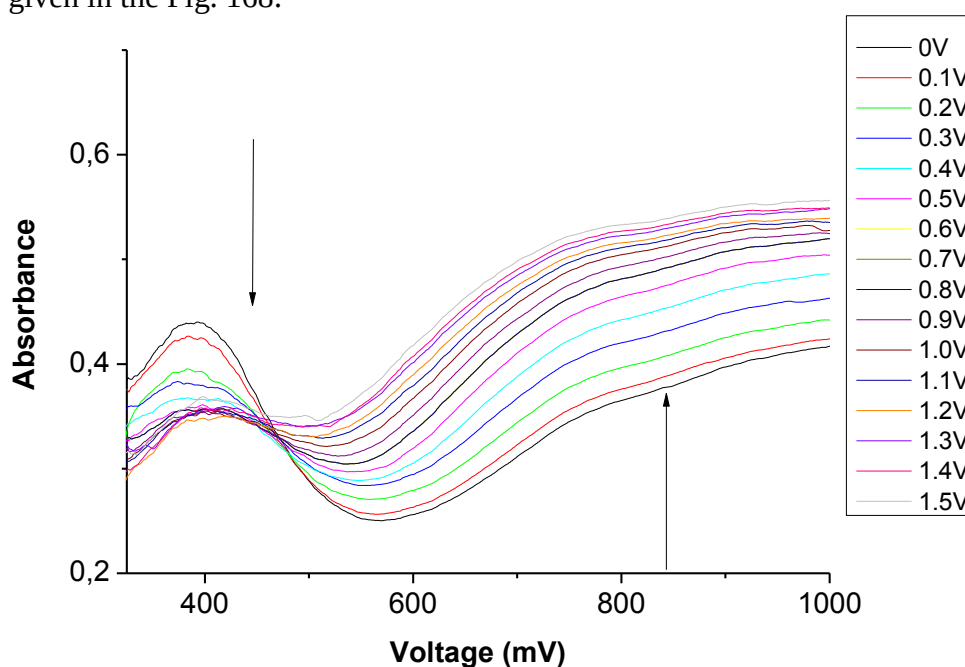


Figure 4.168 : Absorption spectra of PPy film at different potentials.

In neutral state polypyrrole had an absorbance maximum around 400 nm. During the spectroelectrochemical measurements, Ag wire was used instead Ag/AgCl electrode. By varying the potential between 0 V to 1.4 V the major peak of pyrrole band at around 400 nm decreases and the polaron and bipolaran bands above 600 nm increases as seen above. From the red edge of the neutral polypyrrole band gap found to be 2.26 eV.

UV visible absorbance spectrum of PCz obtained at different potential application was given in the Fig.169

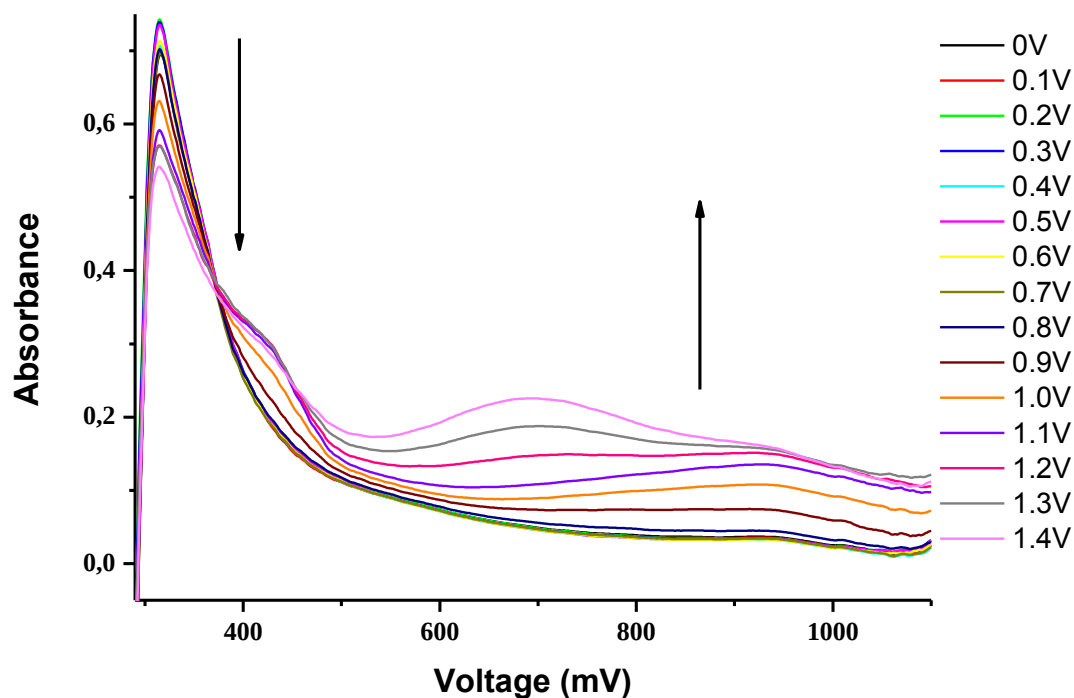


Figure 4.169 : Absorption spectra of PCz fim at different potentials.

In neutral state PCz films showed a maximum absorbance at 330 nm that belongs to $\pi \rightarrow \pi^*$ transition and its value is lower than that of PPy film (400nm) and from the minimum absorbance edge the band gap can be calculated as 2.94 eV. As the anodic potential application, this absorbance was decreased and a new absorbance at higher wavelenght occured due to polaron and bipolaron formation.

UV visible absorbance spectrum of PIN obtained at different potential application was given in the Fig.170.

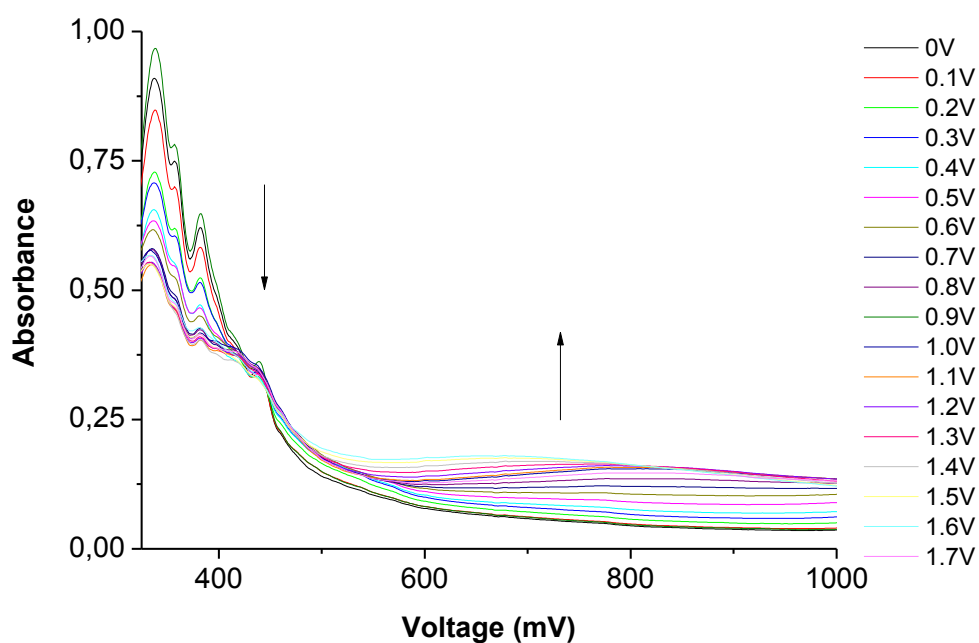


Figure 4.170 : Absorption spectra of PIN fim at different potentials.

In neutral state of the of the PIN film showed two characteristic absorbance peaks above 400 nm. Absorbances of these two bands were decreased and the slight increase above 600 nm was appeared by application of anodic potential. By using the red edge of neutral state the band gap found to be 2.53 eV.

UV visible absorbance spectrum of PTh obtained at different potential application was given in the Fig.171.

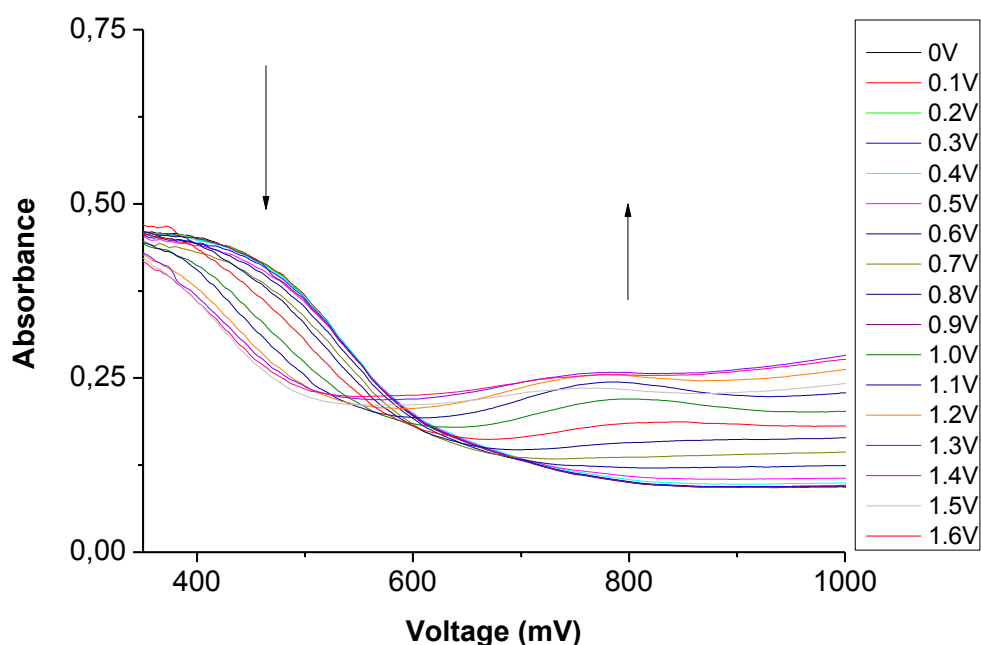


Figure 4.171 : Absorption spectra of PTh fim at different potentials.

The maximum absorbances at 425 nm that corresponds to $\pi \rightarrow \pi^*$ transition decreased with oxidation and a broad peak started to appear around 800 nm due to formation of polaronic species. The band gap was obtained as 1.89 eV which is the lowest among four polymers.

The bang gaps of polymers were summarized in the Table 4.52

Table 4.53 : Bandgap values of PPy, PCz, PIN and PTh

Polymer	PPy	PCz	PIN	PTh
E_g (eV)	2.26	2.94	2.53	1.89

As it can be seen in the Table 4.52, the highest band gap was observed for the PCz, whereas the lowest band gap was observed for the PTh.

4.6. AFM micrographs of PPy, PCz, PIN and PTh

Py, Cz, IN and Th were coated onto a ITO glass via PS method at 120 s by a potential of 1.0 V for Py, 1.2 V for Cz and 1.5 V for both IN and Th. The polymer films were dried then in room temperature (23 ± 2 °C) for 24 hours and polymer morphologies were probed using non-touch mode atomic force microscopy. All AFM images were shown in the 3D height mode. Bright colors indicated higher regions whereas darker colors demonstrated lower regions on the sample. Results can be seen in the Fig.4.172-4.175.

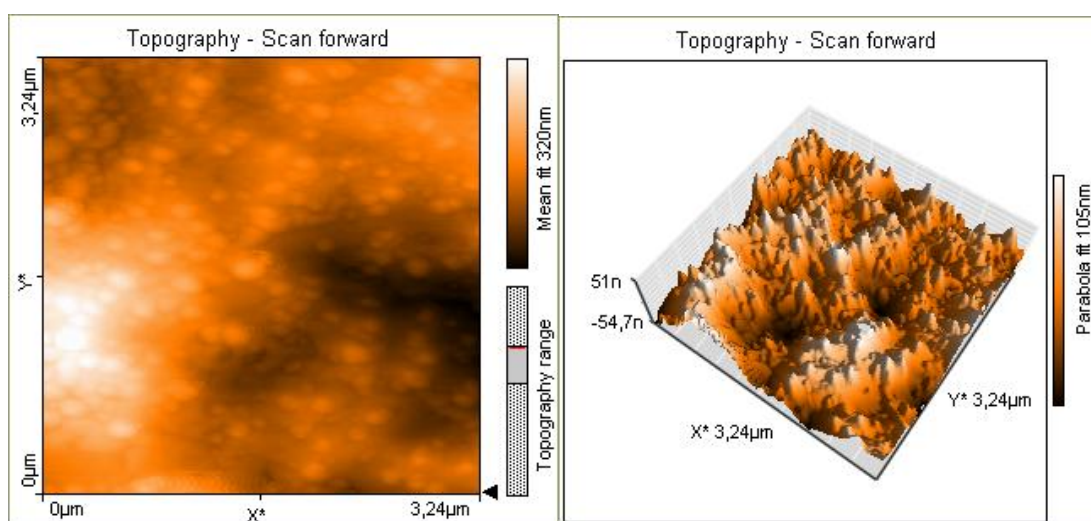


Fig.4.172 : AFM micrograph of PPy obtained by PS method at 120 s.

As shown in Fig. 4.172, the morphology of the relatively thick (>1 µm) PPy films electrosynthesized from monomer containing Bu_4NBF_4 was generally globular (left and center) and exhibited the characteristic “cauliflower-like” morphology. The mean roughness of PPy film determined as 45.4 nm.

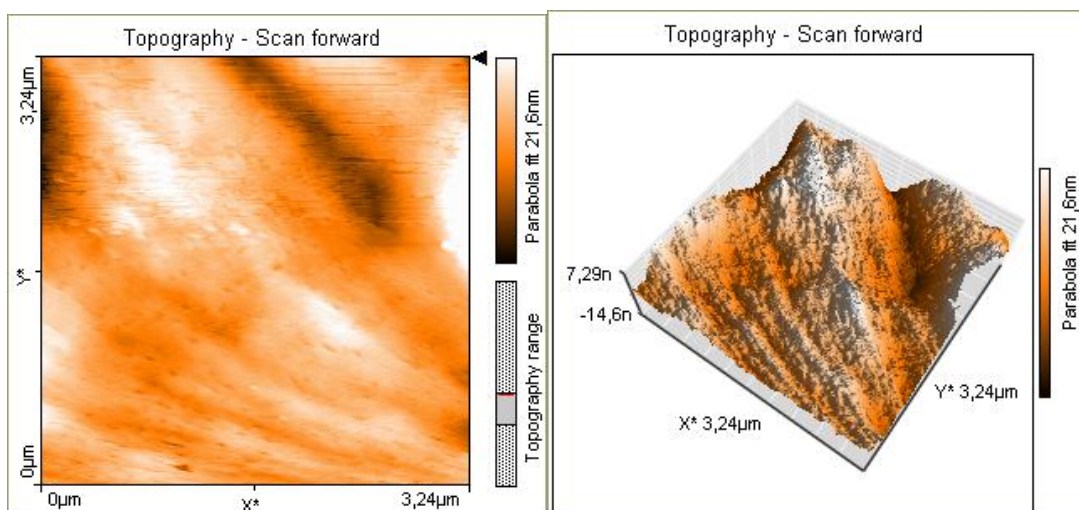


Fig.4.173 : AFM micrograph of PCz obtained by PS method at 120 s.

As it can be seen in the Fig. 4.173, the morphology of PCz film might be defined as “plateau”. The mean roughness of PCz film determined as 3 nm which one the lowest value of all polymers measured.

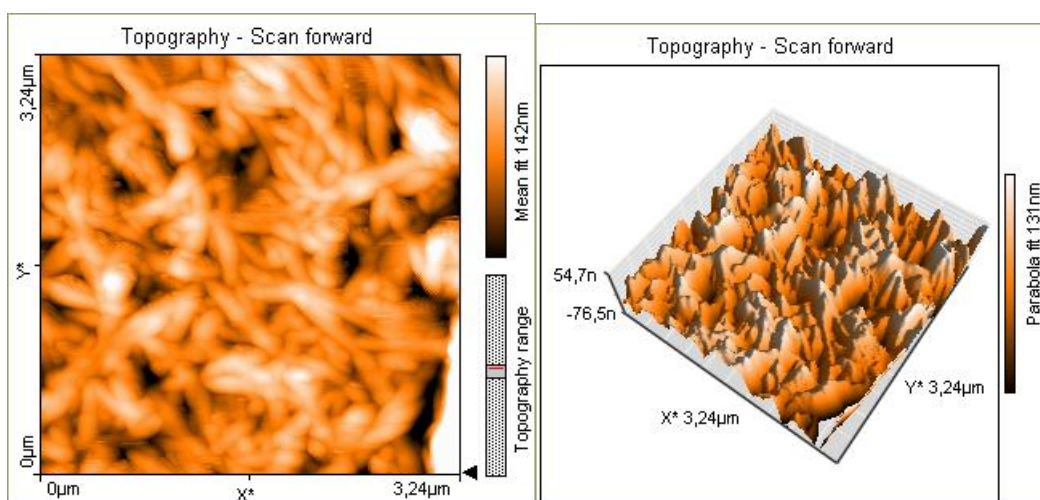


Fig.4.174 : AFM micrograph of PIN obtained by PS method at 120 s.

The PIN film showed a “tree root” like morphology. The mean roughness of the film was determined as 22 nm. (Fig. 4.174)

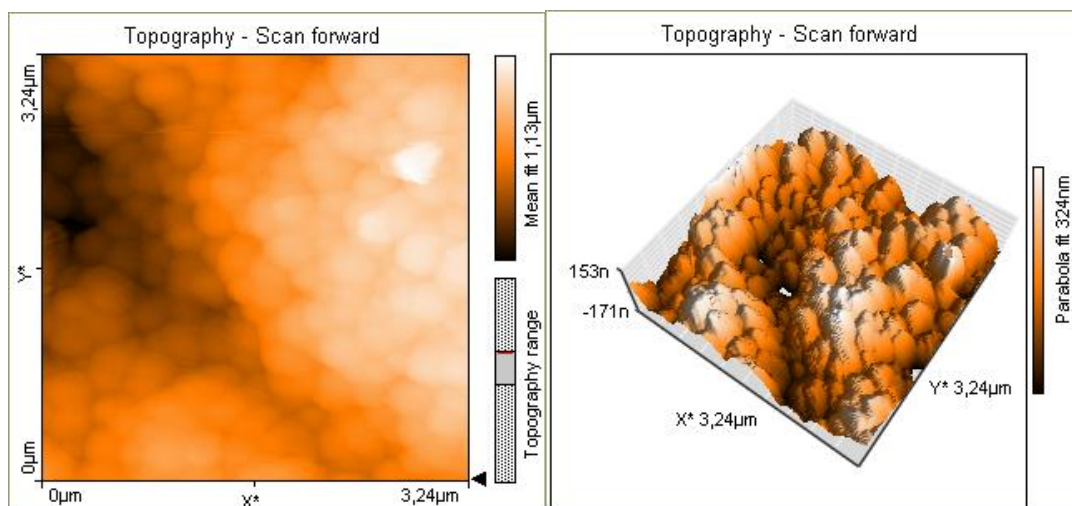


Fig.4.175 : AFM micrograph of PTh obtained by PS method at 120 s.

As shown in the Fig. 4.175. PTh film obtained by PS at 120 s exhibited the characteristic “cauliflower-like” morphology similar to PPy. The mean roughness of PTh film determined as 200 nm which was the highest value of all polymers measured.

5.CONCLUSIONS

In this thesis, Py, Cz, IN and Th monomers were succesively electropolymerized via PD, PS and GS methods and characterized by voltametry, EIS, spectroelectrochemical and AFM measurements. Electropolymerization of each monomer was performed at different polymerization times such as 2, 4 and 8 cycles for PD method, 30, 60 and 120 s for PS and GS methods respectively. Redox behaviour of polymers were investigated by CV at different scan rates, electrical parameters such as C_{dl} , C_{sp} , R_p , R_s were determined by EIS, morphological properties were studied via AFM micrographs and results were compared with each other.

In the case of PPy, to obtain a capacitive film, PD method and longer polymerization time can be suggested. On the other hand, if reversibility is important, for all methods thinner films are favorable.

In the case of PCz, PS method and long polymerization times can be suggested to obtain capacitive films. Besides the most reversible film was obtained by PD method at 4 cycles.

In the case of PIN, the if capacitive behaviour is important, PS method at 60 s is quite favorable, whereas for the reversibility film obtained by PD method at 2 cycles can be sugested.

In the case of PTh to obtain a capacitive film PD method at 8 cycles can be suggested. On the other hand, in the case of the reversibility , PS method and low polymerization time is quiet favorable.

Application of 1.0 V constant voltage during EIS measurements, resulted semi circle characater and transition from capacitive behaviour to resistive behaviour was observed for all polymers and all methods.

Table: 4.54. : The E_g and mean roughness comparasion of PPy, PCz, PIN, PTh obtained by PS method at 120 s.

Polymer	PPy	PCz	PIN	PTh
E_g (eV)	2.26	2.94	2.53	1.89
Mean Roughness(nm)	45.4	3 nm	22 nm	200 nm

When the four polymers were compared with each other, PPy showed the most reversible character whereas PCz and PTh were highly capacitive among the other polymer films. The highest current intensity was observed in the case of PTh also. The most porous surface and the lowest E_g was obtained for PTh, whereas the least porous surface and highest E_g was obtained for PCz case.

Although phase angles stayed almost constant, capacitance parameters increased with polymerization time for PPy, PCz, PTh, which demonstrates that these polymers are highly favorable for charge storage applications such as batteries and supercapacitors. Reversible behaviour of thinner films of all polymers make them for electrochromic and electronic applications such as OLED, fuel cells, sensors and actuators.

REFERENCES

- [1] Introduction to polymers. (2002). *The University of Edinburgh Division of Engineering Session 2001-2002 Materials*
- [2] **Url-1** <[http://www.americanchemistry.com/shops/intro_to_plastics/teachers.html / history](http://www.americanchemistry.com/shops/intro_to_plastics/teachers.html/history)>, date retrieved 09.09.2011
- [3] **György, I.** (2008), *Conducting Polymers A New Era in Electrochemistry*. Springer-Verlag Berlin Heidelberg
- [4] **Shirakawa, H., Louis, E.J, A.G., MacDiarmid, C.K., and Heeger, A.J.** (1977). Synthesis of electrically conducting organic polymers—Halogen derivatives of polyacetylene, *(CH)X*. *Chem Commun* 16:578–580
- [5] **Skotheim, T.J., Elsenbaumer R.L., and Reynolds, J.R.** 1998. *Handbook of Conducting Polymers*, 2nd ed. *New York: Marcel Dekker*.
- [6] **Ustamehmetoglu, B. Sezer, S. and Sarac, S.** 2001. Oxidative polymerization of N-vinylcarbazole in polymer matrix. *Polymer Int.* 50: 728-733.
- [7] **Tarushee, R. and Kumar,A.** (2009). Recent progress in the development of nano-structure conducting polymers/ nanocomposites for sensor applications. *Sensors and Actuators B* 136 (2009) 275–286
- [8] **Kalaycioglu, E., Toppare, L., Grchev T., Cvetkovska M. and Yagci, Y.** (1999). Impedance Characteristics of Conducting Polypyrrole-poly(ethylvinylether) Graft Films. *Turk J Chem* 23 , 1- 7.
- [9] **Pringle, J. M., Efthimiadis J., Howlett P.C., Douglas, R. M., Chaplin A. B., Hall S.B., Officer D.L., Wallace G.G. and Forsyth M.** (2004). Electrochemical synthesis of polypyrrole in ionic liquids. *J.M. Pringle et al. / Polymer* 45 (2004) 1447–1453.
- [10] **Paulse C.D. and Pickup P.G.** (1988). Chronoamperometry of polypyrrole: migration of counterions and effect of uncompensated solution resistance. *J. Phys.Chem.*, 1988, 92 (24), pp 7002–7006.
- [11] **Compton, R. G., Laing M. E., Ledwith A. and Abu-Abdoun I.** (1988). Polymer-coated electrodes: cyclic voltammetry and chronoamperometry of non-ideal systems the anodic oxidation of poly(4-vinyl-triphenylamine) films. *Journal of Applied Electrochemistry* Volume 18, Number 3, 431-440.
- [12] **P. Audebert, J.-M Catelb, V. Duchenetb, L. Guyarda; P. Hapiotcs, G., Le Coustume, P.** Redox chemistry of thiophene, pyrrole and thiophene-pyrrole-thiophene oligomers.(1999). *Synthetic Metals* 101 642-645.

- [13] **Sezer, E., Ustamehmetoglu, B. and Sarac, S.** (1999). Chemical and electrochemical polymerisation of pyrrole in the presence of *N*-substituted carbazoles. *Synthetic Metals* 107 -17–17.
- [14] **Dudukcu, M., Koleli, F.** (2006). Electrochemical synthesis of polyindole on 304-stainless steel in LiClO₄–acetonitrile solution and its corrosion performance. *Progress in Organic Coatings* 55- 324–329.
- [15] **Zotti, G., Zecchin S. and Schiavon G.** (1994). Structure of Polyindoles from Anodic Coupling of Indoles: An Electrochemical Approach. *Chem. Mater.* 1994,6, 1742-1748.
- [16] **Token, T., Yazici, B. and Erbil, M.** (2005). Electrochemical synthesis of polyindole on nickel-coated mild steel and its corrosion performance. *Surface & Coatings Technology* 200 (2005) 2301– 2309
- [17] **Trung, V. and Duong, N.H.** (2009). Synthesis, properties and application of polyindole/TiO₂ nanocomposites. *Journal of Physics: Conference Series* 187 (2009) 012058.
- [18] **Aleman, C., Oliver, R., Brillas E., Casanovas J., Estrany F.** (2005) A combined theoretical and experimental investigation about the influence of the dopant in the anionic electropolymerization of α -tetrathiophene. *Chemical Physics* 314 (2005) 1–7.
- [19] **Shi, J. H., Sun, X., Yang, C. H., GAO, Q. Y., Li, Y. F.** (2002). Electrochemical Synthesis of Polythiophene in an Ionic Liquid. *Chinese Chemical Letters Vol. 13, No. 4, pp* 306 -307.
- [20] **Yoo, K. S. and Woo S.B.** (2001). Studies on the Polythiophene(PT)/GC Electrode for the Determination of Some Metals by Differential Pulse Anodic Stripping Voltammetry (DPASV). *Bull. Korean Chem. Soc.* 2001, Vol. 22, No. 10.
- [21] **Chowdhury A.** (2002). Polythiophene:An Organic Polymeric Semi conductor. *Second International Conference on Electrical and Computer Engineering ICECE 2002, 26-28 December 2002, Dhaka, Bangladesh.*
- [22] **Kıralp, S., Kucukyavuz, Z., Qasrawi, A. F.** (2003) Preparation and Characterization of Conducting Polybutadiene/Polythiophene Composites. 2003. *Turk J Chem* 27, 417 - 422. *Tubitak.*
- [23] **Udum, Y. A., Pekmez, K., Yıldız, K.** (2004). Electropolymerization of self-doped polythiophene in acetonitrile containing FSO₃H. *Synthetic Metals* 142) 7–12.
- [24] **Lingane, P. J., Peters, D.** (1971) Chronopotentiometry. *Critical Reviews in Analytical Chemistry Volume 1, Issue 4, 1971, Pages* 587 – 634.
- [25] **Waenkaew, P., Taranekar, P., Phanichphant, S., Rigoberto C., Advincula, R. C.** (2007) Electro-Copolymerization of Layer-by-Layer Deposited Polythiophene and Polycarbazole Precursor Ultrathin Films. *Macromol. Rapid Commun.* 28, 1522–1527.

- [26] **Cha, S. K.** (1997). Electropolymerization Rates of Polythiophene / Polypyrrole Composite Polymer with Some Dopant Ions. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 35, 165–172.
- [27] **Sarac, S., Sonmez, G., Ustamehmetoglu, B., Mustafaev, M.** (1996). Water-Soluble Polypyrroles by Matrix Polymerization: Interpolymer Complexes. *Journal of Polymer Science: Part A Polymer Chemistry*, Val. 33, 1581-1587.
- [28] **Saraç, S., Sezer, S., Ustamehmetoglu, B.** (1997). Oxidative Polymerization of N-substituted Carbazoles. *Polymers for Advanced Technologies Volume 8*, pp. 556–562.
- [29] **Marrec, P., Dano C., Simonet, N. G., Simonet, J.** (1997). The anodic oxidation and polymerization of carbazoles and dicarbazoles N-substituted by polyether chains. *Synthetic Metals* 89 171-179.
- [30] **Tran, F., Henri, T. and Chevrot, C.** (2002). Synthesis and electrochemical properties of mixed ionic and electronic modified polycarbazole. *Electrochimica Acta* 47 2927_/2936.
- [31] **Grazulevicius, J.V., Strohriegel, P., Pielichowski, G. and Pielichowski K .** (2003). Carbazole-containing polymers: synthesis, properties and applications. *Prog. Polym. Sci.* 28 1297–1353.
- [32] **Diamant, Y., Furmanovich, E., Landau, A., Lellouche, J. and Zaban K .** (2003). Electrochemical polymerization and Characterization of a functional dicarbazole conducting polymer. *Electrochimica Acta* 48 507-/512.
- [33] **Taoudi, H., Bernede, J. C., Del Valle, M. A., Bonnet, A., Molinie, P., Morsli, M., Diaz, F., Tregouet, Y. and Bareau, A.** (1998). Polycarbazole Obtained by Electrochemical Polymerization of Monomers Either in Solution or in Thin Film Form. *Journal of Applied Polymer Science*, Vol. 75, 1561–1568
- [34] **Diamant, J., Chen, H., Han, B., Kamenev, L., Tsybeskov, H. and Grebel D.** (2005). Electrochemical polymerization, optical and electrical characterizations of polycarbazole on single wall carbon nanotubes. *Electrochimica Acta* 48 510-/425.
- [35] **Jegadesan, S., Swaminathan Sindhu, S., Rigoberto C., and Valiyaveetil, S.** (2006). Direct Electrochemical Nanopatterning of Polycarbazole Monomer and Precursor Polymer Films: Ambient Formation of Thermally Stable Conducting Nanopatterns. *Langmuir*, 22, 780-786.
- [36] **Wei, Z., Jingkun X. J., Guangming N., Yukou D. and Shouzhi P.** (2006). Low-potential electrochemical polymerization of carbazole and its alkyl derivatives. *Journal of Electroanalytical Chemistry* 589 (2006) 112–119.
- [37] **Tlili, C., Hafsa Korri-Yousoufi, H. K., Laurence Ponsonne, L., Claude Martelet, C., Nicole, J. and Renault, H.** (2006). Electrochemical impedance probing of DNA hybridisation on oligonucleotide-functionalised polypyrrole. *Talanta* 68-131–137.

- [38] **Sharma, R.K., Rastogi, A.C. and Desu, S.B.** (2007). Nano crystalline porous silicon as large-area electrode for electrochemical synthesis of polypyrrole. *Physica B* 388 -344-349.
- [39] **Ferenets, M. and Ali Harlin, A.** (2007). Chemical in situ polymerization of polypyrrole on poly(methyl metacrylate) substrate. *Thin Solid Films* 515 5324–5328.
- [40] **Dalmolin, C., Sonia, R., Biaggio, R. C., Filho, R. and Bocchi N.** (2010). Reticulated vitreous carbon/polypyrrole composites as electrodes for lithium batteries: Preparation, electrochemical characterization and charge–discharge performance. *Synthetic Metals* 160. 173–179
- [41] **Url-2** <<http://www.gamry.com/eis>> Electrochemical Impedance Spectroscopy Primer, date retrieved 11.10.2011.
- [42] **Lasia, A.** (1999) Electrochemical Impedance Spectroscopy and Its Applications, Modern Aspects of Electrochemistry, B. E. Conway, J. Bockris, and R.E. White, Edts., Kluwer Academic/Plenum Publishers, New York, , Vol. 32, p. 143-248.
- [43] **Mark E. and Orazem, F.** (2007). Electrochemical Impedance Spectroscopy lecture representation. Department of Chemical Engineering University of Florida Gainesville.
- [44] **Url-3** <<http://www.gamry.com/eis>> Basics of Electrochemical Impedance Spectroscopy, date retrieved 12.10.2011.
- [45] **Electrochemical Impedance Spectroscopy (EIS): A Powerful and Cost-Effective Tool for Fuel Cell Diagnostics.** *Scribner Associates - Tutorial.*
- [46] **Komaba, S. and Osaka., T.** (1998). Impedance analysis of electrodeposited insulating polypyrrole. *Journal of Electroanalytical Chemistry* 453 (1998) 19–23.
- [47] **Martinia, M., Matenciob, T., Vantec, N. A. and De Paoli, M. A.** (2000). Electrochemical Impedance Spectroscopy of Dodecylsulphate Doped Polypyrrole Films in the Dark and Under Illumination. *J. Braz. Chem. Soc., Vol. 11, No. 1, 50-58.*
- [48] **Iroh, J.O. and Levine, K.** (2003). Capacitance of the polypyrrole/polyimide composite by electrochemical impedance spectroscopy. *Journal of Power Sources* 117 (2003) 267–272.
- [49] **Levine, K. I. and Iroh. J.** (2004). Resistance of the polypyrrole/Polyimide Composite by Electrochemical Impedance Spectroscopy. *Journal of Porous Materials* 11: 87–95.
- [50] **Hallik, A., Alumaa, A., Tamm, J., Sammelselg, V., Vaartnou, M., Janes, A. and Lust, A.** (2006). Analysis of electrochemical impedance of polypyrrole|sulfate and polypyrrole|perchlorate films. *Synthetic Metals* 156- 488–494.

- [51] **Montserrat, C.P., Xavier, M. B., Valle, M., Munoz, F. J. and Asuncion M.** (2007). Characterization of an ion-selective polypyrrole coating and application to the joint determination of potassium, sodium and ammonium by electrochemical impedance spectroscopy and partial least squares method. *Analytica Chimica Acta* 597 231–237
- [52] **Xiao, Y., Li C.M., Y. and Liu, Y.** (2007). Electrochemical impedance characterization of antibody–antigen interaction with signal amplification based on polypyrrole–streptavidin. *Biosensors and Bioelectronics* 22- 3161–3166
- [53] **Wang, J., Youlong Xu, Y., Xi Chen, X. and Du, X.** (2007). Electrochemical supercapacitor electrode material based on poly(3,4-ethylenedioxythiophene)/polypyrrole composite. *Journal of Power Sources* 163 -1120–1125.
- [54] **Lehr, I. L. and Saidman S.B.** (2008). Electrochemical impedance study of iron electrodes covered by polypyrrole films electrosynthesized in the presence of AOT. *Reactive & Functional Polymers* 68- 1152–1158
- [55] **Cihaner, A. and Onal, A.** (2007). Impedance Spectroscopy of N-Substituted Oligo- Oxyethylene Polypyrrole Films. *Journal of Applied Polymer Science*, Vol. 108, 2373–2378.
- [56] **Bonastre, J., Garcés, P., Galván, J.C. and Cases, F.** (2009). Characterisation and corrosion studies of steel electrodes covered by polypyrrole/phosphotungstate using Electrochemical Impedance Spectroscopy. *Progress in Organic Coatings* 66- 235–241.
- [57] **Sabouri, M., Shahrabi, T., Faridi, H.R. and Hosseini, M.G.** (2009). Polypyrrole and polypyrrole–tungstate electropolymerization coatings on carbon steel and evaluating their corrosion protection performance via electrochemical impedance spectroscopy. *Synthetic Metals* 145- 658–923.
- [58] **Ramanavicius, A., Finkelsteina, A., Cesiulis, H., Ramanaviciene, A.** (2010). Electrochemical impedance spectroscopy of polypyrrole based electrochemical immunosensor. *Bioelectrochemistry* 79- 11-16.
- [59] **Sarac, S., Parlak, E., Serhatlı, E. and Cakır, T.** (2006). Microcomposite Electrochemical Capacitor: Electrocoating of Poly[N-(hydroxymethyl)carbazole]
- [60] **Sarac, S.,** (2005). Carbon Fiber, Surface Morphology, Spectroscopic Surface Characterization, Electrochemical Impedance Spectroscopy. *Journal of Applied Polymer Science*, Vol. 104, 238–246
- [61] **Sarac, S.** (2006). Nanocharacterization of electrocoated polymers on carbon fibers. *Microelectronic Engineering* 83 (2006) 1534–1537
- [62] **Ates, M. and Sarac., S.** (2009). Capacitive behavior of polycarbazole- and (N-vinylcarbazole)-coated carbon fiber microelectrodes in various solutions. *Progress in Organic Coatings* 65 281–287.

- [63] **Inzelt, G.** (2003). Formation and redox behaviour of polycarbazole prepared by electropolymerization of solid carbazole crystals immobilized on an electrode surface *J Solid State Electrochem* 7: 503–510
- [64] **Dudukcu, M. and Koleli, F.** (2006). Electrochemical synthesis of polyindole on 304-stainless steel in LiClO₄–acetonitrile solution and its corrosion performance. *Progress in Organic Coatings* .
- [65] **Sivakkumar, S. R., Angulakshmi, N., Saraswathi, R.**(2005). Characterization of Poly(Indole-5-Carboxylic Acid) in Aqueous Rechargeable Cells. *Wiley InterScience*.
- [66] **Entezaml, A. and Arsalan, N.** (1992). Electrosynthesis of Highly Conducting Polythiophene Thin Film in Perchloric Acid. *Iranian Journal of Polymer Science & Technology*.
- [67] **Kondratev, V. V., Tolstopyatova, E. G., Trofimova, Ya. V. and Malev, V. V.** (2003). Electrochemical Behavior of Polythiophene Films: Effect of Electrolyte Concentration and the Nature of the Alkyl Substituent. *Russian Journal of Electrochemistry*.
- [68] **Marco F., Herrera, S. and Feliu, J. M.** (2009). Electrochemical Properties of Thin Films of Polythiophene Polymerized on Basal Plane Platinum Electrodes in Nonaqueous Media. *J. Phys. Chem. B* .
- [69] **S. Richard Prabhu Gnanakan, M. Rajasekhar and A. Subramania.** 2009.Synthesis of Polythiophene Nanoparticles by Surfactant - Assisted Dilute Polymerization Method for High Performance Redox Supercapacitors. *Int. J. Electrochem. Sci.*, 4.
- [70] **Snook, G.** (2000). Investigation of Solid-State Reactions by Electrochemical and Quartz Crystal Microbalance Measurements, PhD thesis.
- [71] **Smith, A.** Final Draft of “The Quartz Crystal Microbalance”, a chapter for Volume 5 of the Handbook of Thermal Analysis and Calorimetry, Elsevier
- [72] **Schiavon, G., Zotti, G., Comisso N., Berlin, A. and Pagani G.** (1994). Ion Exchange in the Electrochemical Switching of Polypyrroles in Acetonitrile by the Electrochemical Quartz Crystal Microbalance. Electrolyte Incorporation by Hydrogen Bonding of Anions to Pyrrole. *J. Phys. Chem.* 98, 4861-4864.
- [73] **Yoon, S. and Kim, H.** (1997). A Stable Mercury Film on Gold Through Conducting Polypyrrole Layer for Electrochemical Quartz Crystal Microbalance. *Synthetic Metals* 84 (1997) 179-180
- [74] **Peng, X., Xiang, C., Xie, Q., Kang, Q. and Yao S.** (2006). Electrochemical quartz crystal impedance study on the electrodeposition of LiOH onto a gold electrode in acetonitrile containing LiClO₄ .3H₂O and its application in preparing a Pt-plated porous polypyrrole thin film for the catalytic electrooxidation of methanol. *Journal of Electroanalytical Chemistry* 591. 74–84

- [75] **Tu, X., Qingji Xie, Q., Jiang, S. and Yao, S.** (2007). Electrochemical quartz crystal impedance study on the overoxidation of polypyrrole–carbon nanotubes composite film for amperometric detection of dopamine. *Biosensors and Bioelectronics* 22 (2007) 2819–2826
- [76] **Sezer, E. and Heinze, J.** 2006. Voltammetric, EQCM, and in situ conductivity studies of 3,6-bis(2-thienyl)-*N*-ethyl carbazole. *Electrochimica Acta* 51 (2006) 3668–3673.
- [77] **Taranekar, P., Fulghum, T., Patton, D., Ponnappati, R., Clyde, G. and Advincula, R.** (2007). Investigating Carbazole Jacketed Precursor Dendrimers: Sonochemical Synthesis, Characterization, and Electrochemical Crosslinking Properties. *Jacks Articles. Published on Web* 09/26/2007
- [78] **Taranekar, P., Fulghum, T., Baba, A., Patton, D. and Advincula, R.** (2007). Quantitative Electrochemical and Electrochromic Behavior of Terthiophene and Carbazole Containing Conjugated Polymer Network Film Precursors: EC-QCM and EC-SPR. *Langmuir* 23, 908–917.
- [78] **Blouin, N., Michaud, A., Wakim, S., Luc P., Boudreault, T., Leclerc, M., Vercelli, B., Zecchin, S., Zotti, G.** (2005). Optical, electrochemical, Magnetic, and Conductive Properties of New Polyindolocarbazoles and Polydiindolocarbazoles. *Macromol. Chem. Phys.* 207, 166–174
- [79] **Jang, S. Y. and Gregory A. Sotzing, G. A.** 2007. Poly(thiophene)s Prepared via Electrochemical Solid-State Oxidative Cross-Linking. A Comparative Study. *Macromolecules* 37, 4351–4359
- [80] **Park, J.Y., Chang, B.Y., Nam, H. and Park. S.M.** (2008). Selective Electrochemical Sensing of Glycated Hemoglobin (HbA1c) on Thiophene-3-Boronic Acid Self-Assembled Monolayer Covered Gold Electrodes *Analytical Chemistry*, Vol. 80, No. 21
- [81] **Toribio F. and Bengoechea, M.** (1999). UV-Visible Spectroelectrochemistry of Conducting Polymers. Energy Linked to Conformational Changes. *Langmuir*, 15, 1323–1327.
- [82] **Arjomandi, J. and Holze, J.** (2007). Spectroelectrochemistry of conducting polypyrrole and poly(pyrrole–cyclodextrin) prepared in aqueous and nonaqueous solvents. *J Solid State Electrochem* 11:1093–1100.
- [83] **Pomerantz, Z., Zaban, A., Ghosh, S., Lellouche, J.P., Belmonte, G.G. and Bisquert, J.** (2008). Capacitance, spectroelectrochemistry and conductivity of polarons and bipolarons in a polydicarbazole based conducting polymer *Journal of Electroanalytical Chemistry* 614, 49–60.
- [84] **Girija, T.C. and Sangaranarayanan, M.V.** (2006). Investigation of polyaniline -coated stainless steel electrodes for electrochemical supercapacitors. *Synthetic Metals*. Elsevier Publishing.

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