Nanostructured Polypyrrole Impedimetric Sensors for Anthropogenic Organic Pollutants

Richard Akinyeye

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ABSTRACT

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Richard Akinleye

Polypyrrole composites of polyaromatic hydrocarbon sulphonic acids (β-naphthalene sulphonate acid (NSA) and 1, 2-naphthaquinone-4-sulphonic acid (NQS)), as well as those of transition metal oxides (tungsten (VI) oxide (WO₃) and zirconium (IV) oxide (ZrO₂)), were prepared and characterised for use as electrocatalytic sensors. The polymerization of pyrrole in β-naphthalene sulphonate acid (NSA) gave rise to nanotubules, nanomicelles or nanosheets polypyrrole (PPy) morphologies depending on the amount of NSA in the polymer and the polymerisation temperature. Scanning electron microscopy (SEM) measurements showed that the diameters of the nanostructured polypyrrole-β-naphthalene sulphonate acid (PPyNSA) composites were 150-3000 nm for the tubules, 100-150 nm for the micelles and 20 nm for the sheets. A red shift in the UV-Vis absorption spectra of PPy was observed for PPyNSA which is indicative of the involvement of bulky β-naphthalene sulphonate ion in the polymerization process. The UV-Vis also showed the existence of polaron and bipolaron in the polymer which may be responsible for the improved solubility of PPyNSA compared to PPy. All the characteristic IR bands of polypyrrole were observed in the FTIR spectra of PPyNSA, with slight variation in the absolute values. However, the absence of N–H stretching at 3400 cm⁻¹ and 1450 cm⁻¹ usually associated with neutral polypyrrole confirms that the polymer is not in the aromatic state but in the excited polaron and bipolaron defect state. Electrochemical analysis of PPyNSA reveals two redox couples: a/a′ - partly oxidized polypyrrole-naphthalene sulphonate radical cation/neutral polypyrrole naphthalene sulphonate; b/b′ - fully oxidized naphthalene sulphonate radical cation/partly reduced polypyrrole-naphthalene sulphonate radical anion. The corresponding formal potentials measured at 5 mV/s, $E_i^{°}(5\text{ mV/s})$, are 181 mV and 291 mV, respectively. Analysis of the amperometric response of GCE/PPyNSA film to phenol gave sensitivities of 3.1 mA/mole dm⁻³ with a linear correlation coefficient of 0.982 for phenol concentrations of 19.8 µM to 139.5 µM. The apparent Michaelis-Menten constant ($K_{m'}$) was estimated as 160 µM.
Novel polypyrrole thin film microelectrodes prepared from an aqueous solution of the sodium salt of 1, 2-napthaquinone-4-sulphonic acid and pyrrole in hydrochloric acid as the supporting electrolyte was characterized electrochemically for the first time and found to exhibit good electronic and spectroscopic properties. The modified PPyNQS consisted of nano micelles with diameters of 50–100 nm. It also exhibited more pronounced voltammetric redox responses, improved solubility and stronger UV-Vis absorptions at wavelengths for polarons (380 nm), bipolarons (750 nm) and overlapped bi-polarons (820 nm) compared to conventional PPy. Voltammetric investigations showed that the polymer exhibited quasi-reversible kinetics in a potential window of -400 mV to +700 mV, with a formal potential of 322 mV vs. Ag/AgCl. The diffusion coefficient was calculated to be 1.02 x 10^-6 cm^2/s for a thin film with a surface concentration of 1.83 x 10^-7 mol/cm^2 and a standard rate constant of 2.20 x 10^-3 cm/s at 5 mV/s. Substructively normalised in situ Fourier transform infrared spectroscopy (SNIFTIR) confirmed the incorporation of the surfactant into the polypyrrole film, and for the first time structural changes within the polymer were observed and used to explain the electrochemistry of the polymer. Electrochemical impedance spectroscopy (EIS) results validated the quasi-reversible kinetics observed in the voltammetric experiment. The changes in electrical properties of the polymer during electrochemical p-doping and n-doping were quantified by equivalent electrical circuit fitting. Impedimetric nanosensor systems for the determination of two anthropogenic organic pollutants, namely benzidine and naphthalene, were constructed with smart Pt/PPyNQS nanomaterials.

Analysis of sensor systems containing tungsten oxide or zirconium oxide-modified polypyrrole showed that nanohybrids of the polypyrrole were generated by the in-situ polymerisation of pyrrole in acidic solutions. Results from morphological and spectroscopic investigation confirmed the pattern of metal distribution within the nanohybrid polymers matrix. However, this class of polymers were devoid of charge carriers characteristics required for electrocatalytic sensor applications. The thesis provided justification for the preparation of nanostructured conducting polypyrrole for use as anodes for the determination of phenol, benzidine and naphthalene.

**May 2007.**
Declaration

I declare that _Nanostructured Polypyrrole Impedimetric Sensors for Anthropogenic Organic Pollutants_ is my own work, that it has not been submitted before for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged as complete references.

Richard Odunayo Akinyeye
May 2007

Signed: ...............................
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DEDICATION

This project is dedicated to

The

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 My darling wife

 Mrs Modupe Caroline Akinyeye

 and

 My loving children

 Damilola, Folakemi, Emmanuel and Isaac

 For your prayers, love, understanding and endurance during my absence from home during this period.
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Chapter One

Introduction

This chapter gives a brief introduction to intrinsically conducting polymers, the concept of doping and conductivity especially in polypyrroles. The project proposal, objectives and methodology that was adopted is presented.

1.1 Intrinsically conducting polymers and concept of doping

The current day science aims at using nanostructured-conducting polymers to boost the development of exciting opportunities in modern day science and technology. Towards achieving this objective, novel materials and technologies, new ideas, applications and techniques will always be a challenging route to explore new possibilities. The current interest in the world of conducting polymer science evolved from the discovery that the erstwhile inactive, non-conductor polymers mostly used as electrical insulators could still be obtained in a conducting state through the presence of certain additives in the polymer that enhances the conductivity [1-15]. This commonly is referred to as “doping the polymer” and it provides increase in conductivity of several orders of magnitude from the semiconductor regime. This doping terminology in conductive polymers is slightly different from its conventional use in semi-conductor physics, since considerably higher concentration (of up to 33%) are employed in the former [7].

This new class of polymer known as intrinsically conductive polymers (ICPs) or electronic (electroactive) polymers (EP) combines the mechanical and chemical properties of insulator polymers with the electrical and optical properties of inorganic semiconductors and metals [2]. This class of material is completely different from “conducting polymers” which are merely a bulk material generated from the physical mixture of a nonconductive polymer with a conducting material such as a metal or carbon powder that has been uniformly dispersed. Intrinsically conducting polymers offer a unique combination of ion exchange characteristics and optical properties that
make them distinctive. They are readily oxidized and reduced at relatively low potentials, and the redox process is reversible and accompanied by large changes in the composition, conductivity and colour of the material. In 1969, the use of electronic polymers was proposed as light emitting material, however, its first use as light emitting diode was launched in 1991 [3]. This involved the combination of carbon and metal filled polymers as mouldable semiconductors, as photoreceptors in electro photographic copying machines and some other applications.

Great publicity into the potentials in organic polymers actually came up in 1977, when the conductive properties of the alternating-bond in the conjugated polymer of trans-polyacetylene were discovered. Hideki Shirakawa et al. in 1971 had reported the enhanced conductivity of polyacetylene observed in his laboratory following an accidental addition of excess Ziegler-Natta catalyst as dopant to the pristine semi conducting polyacetylene [4]. The development generated a lot of curiosity amongst scientist like Heeger and MacDiarmid who found that the conductivity of polyacetylene could be enhanced by exposure to oxidizing agents such as iodine vapor, AsF$_5$, NOPF$_6$ (p-doping) or reducing agents such as sodium naphtide from $10^{-9}$ S cm$^{-1}$ to $10^5$ S cm$^{-1}$, an increase of well over ten million times [4]. In particular, exposure of iodine vapor to polyacetylene generated increased conductivity of about ten million times (from $10^{-3}$ S m$^{-1}$ to 3000 S m$^{-1}$) [2]. It was found that the polymer could be doped either chemically or electrochemically to the metallic state and thereby transformed into a good electrical conductor almost comparable to that of one single copper crystal. The recognition of these efforts by the world scientific community was the Nobel Prize in Chemistry awarded to Professors Heeger A, J., MacDiarmid A.G. and Shirakawa H., in 2000 for their research in that field.

Thereafter, many new conducting polymers and their derivatives were discovered and applied for different electronic applications in different fields. These include organic polymers such as polyaniline (PANI), polypyrrole (PPy) polythiophene (PTh), poly-(para-phenylene), poly-(phenylenevinyl-ene), polyfuran and other poly-(heteroaromatic vinylenes) [5]. Table 1.1 shows the idealized structure of the mostly studied conducting polymers. The structural feature common to conducting polymers is their alternating single and double bond lattice structure that allows for the transfer of charge carriers upon excitation of electron.
Table 1.1: Names and repeat units of the most widely studied conducting polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Polymer</th>
<th>Structure</th>
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<tbody>
<tr>
<td>Polyacetylene</td>
<td><img src="image" alt="Polyacetylene" /></td>
<td>Polyindole</td>
<td><img src="image" alt="Polyindole" /></td>
</tr>
<tr>
<td>Polypyrrole</td>
<td><img src="image" alt="Polypyrrole" /></td>
<td>Polyaniline</td>
<td><img src="image" alt="Polyaniline" /></td>
</tr>
<tr>
<td>Polythiophene</td>
<td><img src="image" alt="Polythiophene" /></td>
<td>Polyazulene</td>
<td><img src="image" alt="Polyazulene" /></td>
</tr>
<tr>
<td>Polyfuran</td>
<td><img src="image" alt="Polyfuran" /></td>
<td>Poly para-phenylene</td>
<td><img src="image" alt="Poly para-phenylene" /></td>
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</table>

Figure 1.1 shows the chemical structures of some conducting polymers. They are one-dimensional conductors as the electrons/holes travel mainly through the linear backbone. Doping is either the addition of electrons (reduction reaction, n-doping) or the removal of electrons (oxidation reaction, p-doping) from the polymer. The unpaired π electron per carbon atom in the conjugated polymers is only loosely bound and because they are covalently bound they have restricted span of movement. These π bonds in conjugated polymers are highly susceptible to chemical or electrochemical oxidation or reduction. Positive charges (holes) and negative charges (electrons) move to opposite directions. Once doping has occurred, the electrons in the pi-bonds are able to "jump" around the polymer chain, as they are now intrinsically mobile. During this process, the polymer, which is an insulator or semiconductor, is converted to metallic polymer, frequently called “synthetic metal” because they present electric, electronic, magnetic and optical properties of metals [5-12].
Figure 1.1: Structures of polyacetylene (PAc), polypyrrole (PPy), polyphenylene, polythiophene (PTh), polyaniline (PANi).

It was anticipated in the late 1970s to early 1980s, that synthetic conducting polymers would soon replace metals in many applications. These projected advances, expected
by chemist, for these materials have proven to be somewhat illusive to date [6]. Figure 1.2 shows the trend of conductivity in some doped conducting polymers compared with some metals and semiconductors as presented by Freund & Deore [14].

![Figure 1.2 Conductivity of some metals and doped conjugated polymers [14].](image)

The movement of electrons along the polymers molecule produce electric current. This electric current has been ascribed to the formation of non-linear defects such as solitons, polarons or bipolarons formed during doping or polymerisation of a monomer [7, 10, 16]. However the conductivity of the material is limited, as the electrons have to "jump" across molecules, so for better conductivity the molecules must be well ordered and closely packed to limit the distance "jumped" by the electrons.

Positive charges (holes) and negative charges (electrons) move to opposite electrodes. This movement of charges is actually responsible for the observed electrical
conductivity [8]. This is why small particulate and nanostructured conducting polymer materials with large surface area are desirable for good conductivity.

Doping could be achieved via chemical and electrochemical routes. Introduction of mobile carriers into the double bonds of the polymer backbone is the source of the polymers conductivity, and that is why the enumerated properties above are only intrinsic to the doped state [11, 12]. According to Wikipedia® 2007, the doping process in ICPs is similar to that of inorganic semiconductors such as silicon which could be doped with the addition of electron rich atoms such as phosphorous or electron poor atom such as boron to create an n-type or p-type semiconductor respectively [8]. This doping action could produce significant effects on the conductivity of the material, even in concentrations of one part per million. While the n-type doping is common in inorganic semiconductors, it is very rare in organic semiconductors. Most of the optical characteristics inherent to inorganic semiconductors, such as photoemission, photodetection and photocurrent have also been observed in ICPs [13]. Chemical procedure for n-doping is rarely employed because of the oxidizing nature of the atmosphere which is rich in molecular oxygen that has propensity of de-doping (oxidizing to the neutral state) an n-doped polymer once it is in contact with the atmosphere. The electrochemical route to n-doping is equally not very common in research because it is not easy to exclude oxygen completely from a solvent in a sealed cell even when burbled with argon during synthesis. Thus n-doped conducting polymer is usually not of much commercial value and thus hardly used [8].

The relatively low ionization energy and high electron affinity of the conjugated bonds readily generate changes in the electronic structure of the polymer chain. This change in electronic structure is accompanied with a change in the conductivity of the polymer. Thus the relative concentration of the charge carriers, solitons i.e. radicals with unpaired electrons, polarons i.e. couples formed from neutral or charged solitons, or bipolarons determines the polymers conductivity. The gap between the polymers valence band and the conduction band determines the relative ease with which electrons will jump across the gap. In a doped polymer, charge is removed from the highest occupied molecular orbital (HOMO) while charge is injected to the lowest unoccupied molecular orbital (LUMO) and this takes place in the mid-gap states [14].
These bands stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner reminiscent of the band structure of solid-state semiconductors (Figure 1.3). The smaller the band gap, the higher the doping level in the polymer.

![Band Structure Diagram](image)

**Figure 1.3: Band structure in an electronically conducting polymer**

The mechanism of charge propagation in conducting polymer using polypyrrole as example is discussed further in section 2.2. Other factors that influence the conductivity are impurities, folds in the chain structure, chain ends, and differences between amorphous and crystalline regions [12].

Conductivity is not only a result of charge transfer along the chain, but is also due to electron hopping between chains and between different conjugated segments of the same polymer chain. In addition to these effects that act at a molecular level, electron transfer between grain boundaries and variations in morphology also dominates bulk conductivity values. Thus, the conjugated polymers bulk conductivity may be described by Equation 1.1 [7].

\[
\sigma = \sum n_i Z_i e v_i \frac{e}{E} 
\]

**Equation 1.1**

where

- \( \sigma \) = conductivity (S/cm),
- \( n_i \) = number of charges carried by each type \( i \),
- \( Z_i \) = carrier type,
- \( e \) = electronic charge (\( 1.60 \times 10^{-19} \) C),
- \( v_i \) = drift velocity of electron (cm/s), and,
- \( E \) = electric field (V/cm)
Eq. 1.1 takes into account different types of charge carrier, which contribute to the overall observed electrical conductivity in the bulk polymer.

1.2 Some applications of intrinsically conducting polymers

The ICPs have been a big challenge to classical materials in many applications. There is however the need to temper the enthusiasm generated by the discovery of ICPs as potential competitor for classical metals and semiconductors, but rather seen as mere opportunities for new applications [1]. Polymer films of ICPs such as PPy, PTh and PANi on electrode surfaces can be switched between the oxidized conducting state and the reduced insulating state by the ingress and egress (i.e. doping and de-doping) of counter anions [15]. This change is always accompanied with a proportionate signal (e.g. current, impedance, capacitance, etc) corresponding to the concentration of the counter ion in solution and the change in conductivity of the polymer.

The oxidation-reduction processes for PANi, PPy and PTh on an electrode surface are depicted in Fig. 1.4. This reversible charging and discharging property of ICPs is a useful property employed in the production of various electronic devices, optoelectronic and biotechnological applications such as rechargeable batteries, molecular electronics, solar cells, electronic displays, electrodes, diodes, redox supercapacitors and superconductors, Electromagnetic material interference (EMI) shielding materials, ion exchange membranes in fuel cells, field effect transistors, printed circuit boards, electrochemical ionic sensors, use as ion gate membrane for drug release systems and biosensors, etc [11]. A lot of monographs and reviews have been documented for different scope of applications [7, 11, 13, 15, 16]. Some of these application ranges are already commercialised while some are still being developed. The colour changes during switching of ICPs (conducting states) enable their use in the manufacture of multichromic displays and electrochromic windows [11]. The hole-injection properties of the polymers under an applied potential or current enable their use as flexible light emitting diodes (LED) and light emitting cell (LEC) [11].
The ability of ICPs to change chemical properties by chemical, thermal or appropriate polarisation equally provides them with unique properties for easy changeable retention behaviour. This property is employed in their use for solid phase extraction (SPE) based on the sorption of analytes on the conducting polymer coated solid support. Chromatographic application using ICPs as a new stationary phase for gas and liquid systems as well as in electrochemical detectors in liquid chromatography are part of the diverse application of this novel material [16].

**Figure 1.4:** Postulated oxidation-reduction processes for (I) polypyrrole, (II) polythiophene and (III) polyaniline [15].

Another successful and important application of ICPs is in the construction of gas sensing arrays (electronic-noses) based on the use of solid contacts with ion selective electrodes [16].
Recently, use of nanostructured conducting polymers as electrode materials has received remarkable interest owing to improved electrocatalysis [17]. The production of the electrode materials must therefore take the advantage of using methods that generates nanostructured materials with good, cost effective and competitive electroanalytical applications. Section 2.1 presents the strategies for production of nanostructures such as template free, template assisted and molecular template assisted methods. These nanostructures are miniatures such as nanowires [18], nanofibres [19], nanotubes, nanoballs, and nanodots and in particular nanoparticles [17, 20, 21]. The advantages offered by nanoparticle-modified electrode when compared to a microelectrode are high effective surface area, mass transport, catalysis, and control over local environment [22].

1.2.1 Polypyrrole and its applications in sensors
Amongst the ICPs, PPy has excellent environmental stability, easy synthesis, good conductivity and other intrinsic properties that are of promising applications in various fields of science and technology [23–30]. However, its application is grossly limited because it is insoluble and infusible. Various efforts have been made to address this gross shortcoming that impairs the PPy’s processability so that the inherent electronic potentials offered by the polymer could be maximally harnessed [30 -32]. The use of conducting PPy as sensors is derived from the polymers ability to manifest different conductivities when exposed to different types and concentration of analytes. It is also well known that the mechanical, physical and chemical properties of PPy strongly depend on the nature of the dopant anion [33]. The interaction of gaseous components with deposited PPy films produces changes in colour, mass, work function or electrical conductivity. The resistance decreases with the gas of larger electron affinity [17, 34]. The factors responsible for the observed changes in resistance are ionic interactions, type of functional groups, presence of lone pairs and electron bridging species [17].

Over the last three decades, it has been known that chemiresistors with ICP layer on an electrode do respond to a variety of gases and some organic vapours [16]. The interaction of electrophilic gases attracts electrons from the polymer phase, thus causing an increase in conductivity whereas nucleophilic gases increase the resistance
of the polymer. The use of a conducting polymer modified electrode can be used for the detection of not only gaseous analytes but also for solution species. The interaction or adsorption of organic or inorganic molecular species at the polymer/solution interface may also affect the electronic charge transfer process in relation to the concentration of the gaseous or liquid analytes. Detection of ammonia in aqueous solution was reported for polypyrrole [35], and it is noteworthy that the PPy application was patented shortly thereafter [36]. A comprehensive review of different chemical sensors for electronic nose systems was reported recently by James et al. (2005) involving the use of intrinsic (doped) conducting polymers, extrinsic (composite) conducting polymers based on different transduction technologies [37].

Today, there are a lot of anthropogenic pollutants in our gaseous and aqueous environment and there is the challenge of controlling the concentration of these analytes using improved electrochemical techniques. This challenge calls for new electrochemical sensors that could be used to provide continuous information about the environment. The synthesis, characterisation and application of nanostructured PPy modified with different dopants for the determination of some anthropogenic organic pollutants found in wastewaters shall be investigated in this study. Details of the possible interfacial interaction between the various analytes and the transducer (PPy) will be undertaken based on the understanding that the molecules of analytes are first adsorbed on the surface of the sensor and finally absorbed into the matrix of the polymer [38, 39]. The research proposal which was the basis of this study is summarised and presented underneath.

1.3 Research Objectives

1.3.1 Preamble

Specialty polymers, such as native and derivatised polypyrrole (PPy), polythiophene (PTh) and polyaniline (PANI) are the most popular intrinsically conducting polymers (ICP) [40, 41]. The research and industrial interest in these ‘organic electronics’ is due to a good combination of properties, reasonable stability, low cost, ease of synthesis, and the possibility of tailoring the structures on the molecular scale. There are numerous attempts to apply high conductivity, electrochromic, catalytic, sensor,
redox and other properties of these polymers to different practical needs [41–53]. Their direct application has been however greatly limited because they suffer processability limitation because of their intractable nature. Of recent, the application of ICPs has been widened through formation of composites or blends with common polymers [41, 43-47, 54–56] and other particulate dispersants like SiO$_2$ and SnO$_2$ to form nanocomposites with better processability [52].

### 1.3.2 Background information and Motivation

The discovery of carbon nanotubes (CNTs) in 1991 by Sumio Iijima and the inherent high conductivity, high chemical stability, extremely high mechanical strength and modulus, led to a new branch of science called nanotechnology [57, 58]. Due to the ability of CNTs to promote electron transfer, they are used as electrode materials to prepare sensors and in the study of direct electrochemistry of biological molecules [59-63]. The same principle is applicable to the ICPs, otherwise called synthetic metals.

Present day material science deals with microstructures of characteristic morphology and dimensions between 1 and 100 nm. Current chip technology is also reported to produce structures with a characteristic dimension of about 100 nm [57]. In building up such nanostructures, scientist aims at structuring molecules through ingenious synthesis procedures to build functional superstructures via supramolecular self-organization. Reduction in particle size of the polymeric materials to the nanometer level imparts unique properties that make them suitable for chemical and physical sensing, and the control of the structure of sensing surfaces on the nanometer scale can be utilized to enhance sensor performance.

Inorganic, organic as well as biological materials can be integrated to functionalized systems to build up novel nanostructures for application in catalysis, electro-optics, high performance ceramics as well as chemo and gene therapy. All these will result in improvements in the areas of electronics, telecommunication and health care. For example mixing oxide nanoparticles into poly (2-methoxy-5- (2-ethyl hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) gave rise to enhancement of the current density and radiance in polymer light emitting diodes (PLEA), and the composites of conjugated
polymers and nanoparticles that exhibited useful composition for application in photonics [55, 56]. Also, in situ polymerization reactions in medium containing surfactants such as poly- (styrene sulphonic acid) (PSSA), poly-vinyl alcohol (PVA) or transition metal systems (e.g. vanadium pentoxide) do generate stable nanocomposites with properties useful for amperometric and impedimetric sensor devices [55, 56].

Delvaux et al. [56] reported the template synthesis of PANI micro and nanotubes based on oxidative polymerization of aniline within the pores of particle track-etched membranes while Wei et al. [58] suggested the possibility of preparation of PANI nanotube through a self assembly method. This opens the possibility of extending the technique of nanotube materials to other polymers. These conducting polymers can be reversibly changed between insulating and conducting states through chemical or electrochemical doping reactions [41, 48].

The present study proposes to develop novel nano-structured or nanometer scale sensor devices for environmental analysis of anthropogenic priority organic pollutants contained in industrial wastewater systems. Among the compounds of interest are benzenoids such as benzene, toluene, ethylbenzene and xylene isomers (BTEX) that are also volatile organic pollutants (VOC’s), chlorinated compounds (e.g. trichloroethylene, [TCE]), polycyclic aromatic hydrocarbons (PAHs); e.g. naphthalene, fluoroanthene, pyrene) and polychlorinated biphenyls (PCBs) and other priority organic pollutants (POP’s) such as benzidine, phenol and its derivatives. These culprit organic compounds are known to have varying degrees of toxic, mutagenic or carcinogenic activities. Chromatographic (TLC, GC, HPLC), spectroscopic (UV-Vis, IR, MS) or coupled techniques (GC-MS) are presently heavily relied upon for environmental analysis. The disadvantages are high cost, not being user friendly and failure to indicate whether the compounds are accessible for assimilation by living organisms.

The rationale for this proposed study is the need for relatively low cost, miniaturised and easy-to-use hand-held nanosensor systems for on site application, which to a great extent maintains sample integrity. Environmental impedimetric and chemosensor devices containing ICP nanotube films will be developed and applied for real-time
determination and speciation of PAHs and VOCs associated with industrial wastewater effluents.

1.3.3 Objectives

The main aim of this study is to develop a novel strategy for harnessing the properties of electroconductive polymers in sensor technology by using polymeric nanostructured blends in the preparation of high performance sensor devices. The objectives include:

i. To electrochemically and chemically prepare intrinsically conducting polymers (ICPs) of pyrrole doped with different polyaromatic hydrocarbon sulphonic acid (PAHSA) and transition metal oxides of \( \text{WO}_3 \) and \( \text{ZrO}_2 \).

ii. To characterize the intrinsically conducting polymers by instrumental, electrochemical and impedimetric techniques.

iii. To develop high performance nano-sensor devices using the polymers for determination of some priority organic pollutants (POPs) present in waste waters.

iv. To model the reactivity of the intrinsically conducting polymers sensor systems.

1.3.4 Methodology

1.3.4.1 Preparation of ICP nanomaterials and sensors

In this study processable electrically conducting PPy nanotubes was prepared by in situ oxidative polymerization of the monomer in acid solutions using PAHSA of naphthalene sulphonic acid (NSA) and the sodium salt of 1, 2-naphthaquinone-4-sulphonic acid (NQS) as stabilizing surfactants. Electrosynthetic or chemically synthesized nanostructural formats of polymer composites doped with transition metal oxides (\( \text{WO}_3 \) and \( \text{ZrO}_2 \)) were equally explored. The resulting nanotubes will subsequently be blended with polyurethane acting as a compliant, insulating host for sensor application. The oxidative polymerization will be performed either electro synthetically to produce self-assembled polymer layers on platinum, gold or glassy carbon electrode; or chemically to produce polymer pastes using ammonium peroxydisulphate as oxidant.
1.3.4.2 Characterization and application of ICP nanomaterials and sensors

Electrochemical characterization was performed in aqueous medium with the help of electrochemical workstations. The electrochemical and spectroscopic techniques used includes:

i. Cyclic voltammetry (CV).
ii. Osteryoung square wave voltammetry (OSW).
iii. Differential pulse voltammetry (DPV).
iv. UV/Vis spectroelectrochemistry.
v. Impedance spectroscopy.

Morphological and structural characterizations were performed on the prepared nanomaterials with scanning electron microscopy (SEM).

The application of ICP nanotubes sensors/electrodes was undertaken using glassy carbon, platinum or gold disc electrodes. The sensors was tested for their suitability as impedimetric and amperometric electrode materials for some anthropogenic pollutants in wastewater; namely phenol, naphthalene and benzidine. Electrochemical data generated for the various electrode materials were explored for the analysis of the pollutants in wastewaters using their reactivity in aqueous systems by EIS and voltammetry.

Modeling of the reactivities of ICP modified electrodes and sensors involved the monochromatic stimulation procedure [64-70] for the measurement of ICPs electrode impedance. The reactivity of electrochemical sensors involve slow preceding reactions, slow electrode kinetics and diffusion, all of which contribute to the impedance of electron flow and hence to lower currents. Impedance data was generated for studying the electrochemical phenomenon at the electrode’s interface by perturbations with different potentials over a broad frequency range (usually 100 kHz to 100 mHz) to determine the electrical characteristics such as resistors, capacitors and inductors of the system. The study did not only involve the Nyquist plots but also bode plots so that information on change of impedance with frequency could be obtained for the circuit elements. The electrochemical modeling of the surface properties of various ICP-modified electrodes involved search for an appropriate
equivalent circuit model in order to isolate the different contribution to the overall response during an electrochemical perturbation [64-70]. Impedance circuits tested includes:

(a) Series and parallel combination of single equivalent elements.
(b) Series and parallel combination of multiple equivalent elements.

The preparation of various impedance circuits and models for the various nanosensor systems depends on the appropriate model that fit the physical electrochemistry and equivalent circuit elements such as:

(c) Models based on purely capacitive system as Nyquist and Bode plots.
(d) Models based on randles cell for the Nyquist plots.
(e) Models based on Warburg impedance.
(f) Models based on mixed kinetic and charge transfer control circuits as Nyquist and Bode plots.
(g) Models for a failed coating.

Reliable and scalable synthetic methods for nanostructured conducting polypyrrole with interesting technological and scientific properties for both research and environmental applications are to be optimised.

1.4 Thesis layout

The thesis is structured into seven chapters. Chapter one introduces the subject of conducting polymers and how the intrinsic conductivity is generated. The research proposal, objectives, methodology and techniques used are briefly highlighted.

Chapter two gives a general literature review on the intrinsically conducting polymers and techniques for the production of nanostructurised conducting polymers. General properties of polyaniline, polypyrrole and polythiophene are discussed alongside the factors that influence their stabilities. A review of the characterisation techniques, electrocatalytic applications and challenges for the future with respect to these polymers are discussed. Introduction of dopant materials and the anthropogenic organic pollutants used as analytes is presented.
Chapter three gives a brief synopsis on the different analytical techniques and general experimental procedure for the chemical and electrochemical preparation; and characterization of the electroactive materials. This gives the necessary methodology and the applied electrochemical principles for the sensor development.

Chapter four discusses the experimental results obtained from the chemical and electrochemical preparation and characterization of naphthalene sulphonlic acid doped-polypyrrole (PPyNSA) alongside hydrochloric acid doped polypyrrole (PPyHCl). The application of the naphthalene sulphonlic acid doped-polypyrrole (PPyNSA) as amperometric sensor for phenol is presented.

Chapter five presents the experimental results obtained from the chemical and electrochemical preparation; characterization and application of naphthalene 1, 2-naphthaquinone-4-sulphonic acid doped-polypyrrole (PPyNQS) as impedimetric sensor for benzidine and naphthalene.

Chapter six presents the experimental results of the preparation and characterization of metal oxide doped-polypyrrole (PPyWO$_3$ and PPyZrO$_2$) as potential sensor material.

Chapter seven gives the summary of the main scientific contributions of the dissertation, conclusions drawn from them and recommendations for future research.

References


Chapter Two

Literature Review

In this chapter, different routes for the preparation of the intrinsically and nanostructured conducting polymers (NCP) of PANi, PPy and PTh are discussed. The preparation and blending methods, properties, factors affecting stability and characterization techniques of the NCPs together with their hybrids/composites are reviewed. Moreso, a broad review of their applications as electro catalytic sensors is presented. A review on the doping materials used in preparing modified polyprpyrrole chemical sensors is presented vis-à-vis the anthropogenic organic pollutants investigated in this study.

2. Introduction to Nanostructured Conducting Polymers

An emerging sub discipline of chemical and material science is nanomaterials. It deals with development of methods for synthesizing nanoscopic particles of a desired material and the scientific investigations of the nanomaterial obtained. Sumio Iijima introduced the terms nanotubes and nanowires to the world of science from his discovery of carbon nanotubes in 1991 [1]. During the past decade, there has been a great technological focus on the production of nanostructurised materials [1-10]. The growth of nanostructures is increasing daily because nanomaterials are not only good conductors of electricity but potential chemically inert matrix for various electron field emission characteristics [5].

A lot of research findings have been reported on nanoparticles, nanotubes, nanorods, nanobelts, nanofilms, nanowires, nanocables and nanocomposites, which are all nanomaterials [1-5, 7, 10]. Infact the number of nanoparticle-based papers published per year since 1994 to date has been on the increase [10]. It is therefore not surprising that a lot of resources are being committed to nanotechnology sector by various organizations and governments in the USA, Japan and many European countries to fund research that will help industry harness the commercial opportunities offered by
This novel technology [10]. According to a report from Lux Research entitled "Ranking the Nations: Nanotech's Shifting Global Leaders", the U.S., Japan, South Korea, and Germany dominate today, but Taiwan and China will challenge them for leadership in the next seven years [11]. The advantages derived from the use of nanoparticles or NCPs over micro/macroparticles as an electrode material includes high effective surface area, better mass transport, better catalysis and control over local microenvironment. A nanoparticle with sizes of about 100 nm has been reported to produce seventy times magnitude of current when applied in electroanalyses compared to that from a micro electrode [10].

The evolution into the world of nanomaterials came up after the scientific discovery of conducting polymers in 1970’s. The intrinsic conductivity in organic polymers, based on the utilization of the $\pi$-electrons, or electron donors or acceptors for charge propagation in the polymer matrix is significantly improved when nanostructurised materials are used [7]. Many polymers have been used as matrix materials in carbon nanotubes (CNTs) /polymer composites for various target applications. Carbon nanotubes (CNTs) are molecular scale wires with high electrical conductivity, extremely high mechanical strength, and can be divided into two categories: single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) [12]. They resemble rolled up graphite and it was found to act as conductors or semiconductors with very high tensile strength. The existence of nanotubes within nanotubes led to the distinction between multi-walled nanotubes (MWNTs) and single-walled nanotubes (SWNTs), which have been reported for potential use in photovoltaic devices [13]. Apart from its remarkable tensile strength, nanotubes exhibit varying electrical properties (depending on the way the nanostructures spirals around the tube, and other factors, such as doping), and can be superconducting, insulating, semi conducting or conducting (metallic). Usually, the MWNTs have larger diameters and better electrical properties than the SWNTs [14]. http://www.nanotech.now/nanotube reported that "one dimensional fiber (nanotube) exhibit electrical conductivity as high as copper, thermal conductivity as high as diamond and strength of 100 times greater than steel".

Present day material science and chip technology deals with microstructures of characteristic morphology with dimensions of 1 and 100 nm [13]. In building up these
nanostructures, scientist aims at structuring molecules through specialized synthesis to build functional superstructures by self-organization [13]. Inorganic, organic as well as biological materials can be integrated to functionalized systems to build up nanostructures of novel application in catalysis, electro-optics, high performance ceramics as well as chemo and gene therapy. The size dependent changes in the physical and chemical properties of the nanomaterial composite obtained makes them different from those of the bulk material. The larger surface to volume ratio provides substantial changes in the chemical, electrical and optical properties. These developments have produced significant improvements in the areas of electronics, telecommunication and health care. Recently, the electrochemistry related aspect of nanostructurised conducting polymers have attracted a great deal of interest because of their potential application as electric energy storage system, chemical-to-electric or vice versa energy conversions, sensors and biosensors, and materials for corrosion protection [8, 10].

2.1 Preparation methods for conducting polymers of PANi, PPy and PTh

Of the intrinsically conducting polymers, polyaniline, polypyrrole and polythiophene have been greatly exploited for practical applications in many areas of human needs. Other electronic polymers are poly-acetylene, poly-(para-phenylene), poly-(phenylenevinyl-ene), polyfuran, polyindole, polycarbazole and other poly-(heteroaromatic vinylenes). The structural feature common to conducting polymers is their alternating single and double bond lattice structure which allows for the transfer of charge carriers upon excitation by the use of appropriate dopants. Doping materials can include iodine, bromine, lithium, sodium, mineral acids and surfactants. The conjugated system of PANi, PPy and PTh is earlier described in Fig. 1.1.

Many publications have appeared on the preparation and blending techniques for these polymers and their substituted derivatives [15, 16, 17]. Improved solvent solubility and thermal stability for the polymers were obtained when blended with conventional polymers such as polyvinyl acetate (PVAc), polystyrene (PS) and polyvinyl acetate (PVA). However, the conductivity of the blends formed was lower than the conventional host polymers [18]. Over the years, conducting polymers are prepared by a variety of techniques including cationic, anionic, radical chain growth,
co-ordination step growth polymerization or electrochemical polymerization [17–34].

The electrochemical polymerization of conducting polymers is generally achieved by galvanostatic, potentiostatic or potential scanning voltammetry. The conductivity and yield of the polymeric product are enhanced by doping, use of oxidizing or reducing agent or a protonic acid to give a highly delocalized polycation or polyanion [18].

The preparation techniques aim at getting a product with excellent conductivity and good environmental stability. The applications of these polymers have suffered greatly because of their intractable nature and insolubility in common solvents. This limitation in post-synthesis processability is due to the chain stiffness and inter-chain interactions that render these materials insoluble in common solvents. The resulting polymers are usually cross-linked, highly branched, or electrostatically cross-linked due to polaron/bipolaron charge interactions. This chemical or ionic cross-linking is the cause of the polymer’s intractability [35]. To curtail this intractable problem which hinders processability, researchers have fashioned out some preparation procedures for synthesis of conjugated polymers that are soluble in either or both aqueous and organic solvents for a target use. Some of the approaches that have been employed include:

- Reduction of polymer to the non-conducting state so as to remove inter-chain charge interactions. For example, PANi when in the deprotonated form, emeraldine base (EB), it is readily soluble in some solvents such as N-methylpyrrolidinone, dimethyl formamide and dimethyl sulfoxide [36].

- Use of alkyl substituted monomer for the polymerisation of PANi, PPy and PTh produces polymers which are rendered soluble in common organic solvents (chloroform, toluene, etc.) through reduced interchain interactions and favourable substituent–solvent interactions. Examples include the synthesis of soluble and conducting poly (3-alkylthiophene) [37, 38] and the introduction of N-substituent [39, 40] or alkoxy substituent [41, 42] on Polyaniline. This approach however poses some steric hindrance on the polymer with a resulting effect of lower conductivity.

- Use of large protonic acid with counter ion that is soluble in organic solvents such as camphor sulphonic or dodecyl benzene sulphonic acid during synthesis of these polymers [43, 44]. The most successful approach for increasing the solubility of conductive polymers in aqueous solution is ‘self-
doping’. This involves use of ionizable functional groups that form negatively charged sites in solution which are invariably attached to the polymer chain to make the polymer conducting. This approach avoids the use of many organic solvents which have many environmental restrictions. This approach have been found to produce conducting polymers which are environmental friendly, good water solubility and good electroactivity and conductivity over a wider pH range (in the case of polyaniline), and also good thermal stability. According to http://www.wikipatents.com/5002700.html review, different permanently doped PANi have been invented and patented using electrically polymerized polyaniline in covalent combination with an organic dopant having at least one sulphonic acid functional group (United States Patent 50002700) [45].

Other approaches of producing soluble polymers includes in-situ polymerisation with a monomer/oxidant mixture involving a chemical oxidizing agent with a formal potential which is slightly lower than the oxidation potential of the monomer. This results in a metastable reaction mixture that polymerizes upon solvent evaporation [46, 47]. Use of template guided enzymatic approach in strong acid polyelectrolyte e.g. polystyrene sulfonate also provides a lower local pH environment for the formation of soluble conducting polyaniline [48], polypyrrole [49] and polythiophene [50]. Using horseradish peroxidase (HRP), Nabib and Entezami (2004) prepared polypyrrole in the presence of sulphonated polystyrene, as a polyanionic template [49]. The HRP is an effective catalyst for the oxidative polymerization of pyrrole in the presence of hydrogen peroxide at room temperature. The reaction is sensitive to solution pH and it is performed in pH 2 aqueous solutions. Polymerization of pyrrole by this biological route produced a conducting water-soluble polypyrrole for the first time. Alternatively, a colloidal dispersion of the polyelectrolyte, polymeric stabilisers and anionic surfactants could be used [51, 52]. Simmons et al. reported for the first time the synthesis of colloidal polypyrrole particles using reactive polymeric stabilizers of poly (2-(dimethylamino)ethyl methacrylate-stat-3-vinylthiophenes) in 1995 [53]. Since then different efforts have been made in the utilisation of other organic based stabilisers.
2.2 Strategies for production of ‘nanostructurised conducting polymers/Polymer composites’

The drive for modern technologies and new materials in the past decade aroused movement from the erstwhile conducting polymers to generation of nanostructurised materials with enhanced conductivity for many areas of technology. It is therefore important that special materials and technologies should be employed that will generate the requisite metallization in the new material or target application. The attainment of this objective demands that both bifunctional additives and reaction conditions that will enhance the efficiency of oxidative polymerization should be employed. The cationic radicals and other reactive species, after oxidation forms oligomers, which agglomerate depending on the synthesis conditions to form nano, micro or macrostructures [8].

According to the 2005 Winner of the IUPAC Prize for young Chemists, Jiaxing Huang, the nanofibres that form the basic unit for polyaniline is naturally formed at the early stage of the polymerization reaction and are much smaller in diameter than most templated or electrospun fibres [54]. The nanofibrilar morphology does not require any template or surfactant, and appears to be intrinsic to polyaniline synthesized in water. Two approaches; namely interfacial polymerization and rapidly-mixed reactions were developed to prepare pure nanofibers. The trick was to suppress the secondary growth that leads to agglomerated particles. Different dopant acid was used to tune the diameters of the nanofibers between about 30 and 120 nm while changing the organic solvent in interfacial polymerization reactions has little effect on the product [54].

There are three broad strategies for obtaining nanostructured-conducting polymers:

- Template-free approach: The growth of nanostructured conducting polymers could be ordered through template-less synthesis by choosing optimum conditions of electrosynthesis at simple chemically inert electrodes or chemically via optimized and well specified synthesis conditions. It is well known that the nature of the anion present in the electropolymerization solution determines the morphology and properties of the generated conducting polymers. In their conducting form, these polymers are usually proton and anion doped, whereas reversible
expulsion and bonding of anions occurs during reduction and oxidation processes. It has been shown recently that the presence of suitable dopant anions leads to the formation of well-defined nanostructures of conducting polymers. Tubules of polypyrrole with diameter range 0.8 – 2.0 µm and length of 5 – 30 µm were synthesized by the electrochemical template-free technique in the presence of β-naphthalene sulphonylic acid (dopant) and stainless steel electrode [55]. Shortly after this, polypyrrole nanotubules with diameter ranging from 50 nm to 2 µm were synthesized electrochemically in the presence of β-naphthalene sulphonylic acid or p-toluene sulphonylic acid as dopant [19]. The micelles of dopant or dopant-monomer clusters act like a template to orchestrate tubular growth of the polypyrrole. Using this approach but varying the chemical synthesis conditions, various nanostructures of modified polypyrrole doped with β-naphthalene sulphonylic acid with particle diameters of 20 – 3000 nm were reported recently [56, 57].

- **Template assisted:** This approach involves use of an electrically insulating template possessing nanosized pores. Two common architectures are employed, one is the track-etched polymer membranes and the other is the alumina template which is used to house the nanosized structures of conducting polymers [8, 22]. Track-etched template was used by Pra et al. to prepare electrochemically assembled copper nanowires and polypyrrole nanotubules [58]. Demoustier and Stavaux used nanoporous polycarbonate track-etched membrane to prepare polypyrrole doped with poly (sodium 4-styrenesulphonate) with thickness that is dependent on the pore sizes and type of electrolyte used [8]. Duvail et al. reported the electrochemical polymerization of poly (3, 4-ethylenedioxythiophene) within the pores of a track-etched porous membranes [23]. Polymers generated using this technique is associated with increased electric conductivity because the polymerization is confined to the pore spaces and electrostatic interactions between the ionic species allow alignment on the walls of the pores [8]. Alumina template is very popular in the synthesis of conducting polymers and copolymers. Polypyrrole nanowires was electro synthesised by direct oxidation of pyrrole in a medium of 75% isopropyl alcohol + 20% boron trifluoride diethyl etherate + 5% poly (ethylene glycol) (by volume) using
porous alumina membranes as the templates. The as-prepared nanowires is composed of smooth surface, uniform diameter, and highly ordered tip array. The SEM and TEM images of the nanowires are shown in Fig. 2.1. The conductivity of polypyrrole wires is better than that from flat films and a single polypyrrole nanowire was measured to be 23.4 S cm$^{-1}$ at room temperature [59]. The field emission properties of the polypyrrole nanowire arrays prove positive for its use as emission device nanotips.

![SEM images of PPy nanowires](image)

Figure 2.1: SEM (a–c) images and TEM image (d) of PPy nanowires [59].

- Molecular template assisted electrosynthesis. This approach is similar to the template-free method described earlier. The major difference is that the electrode is physically modified with specialized kind of adsorbate that directs electropolymerisation to proceed in template-like manner. Nanosized fibres of polypyrrole films have been grown galvanostatically.
in acetonitrile solution at a gold electrode modified with thiolated β-
cyclodextrin self-assembled monolayer [60].

Other approaches that have been used to make nanostructured conducting polymer composites are the chemical or electrochemical reaction of nanosized metal ions from their salt solution at the polymer/solution interface [8]. The high metal surface area of the generated polymer composite confers a higher degree of electrocatalysis on the metal-conducting polymer nanocomposite. Different polyaniline fibre with gold nanoparticles, have been demonstrated for use as memory devices for data storage (e.g. flash memory) [54]. High catalytic nano-sized gold-polypyrrole complex was electrochemically prepared from gold complexes of Au(ClO₄)⁺ with less than 100 nm particle sizes have been reported [21]. Use of nano-sized inorganic materials such V₂O₅, TiO₂, Fe₂O₃ have also been reported to produce metal-oxide based polymer composites [8]. Clay-based nanocomposites have also been explored under this category. Some organic materials such as Nafion membranes, DNA and porphyrin derivatives have been used to produce nanocomposites of polypyrrole and polythiophenes for different applications [8].

2.3 Polyaniline (PANi) blends/composites

The polyaniline’s is a very important class of ICP with varieties based on the type of substituent on the aniline monomer. The synthesis of the conducting polymer “aniline black” was first published in the 19th century as a product of the anodic oxidation of aniline, but its electronic properties was not established for many years [61]. PANi is novel due to its relative facile processability, electrical conductivity and environmental stability [62, 17]. In acid solution, it is protonated to form an organic metal, which is easily deprotonated in alkaline medium to form a semiconductor. It generates a conductivity of about 10⁵ S/cm comparable to copper. These inherent advantages make PANi to qualify as a synthetic metal. PANi exists in three well-defined oxidation states: the electrically insulating leucomeraldine (LM), electrically conducting emeraldine (EM) and the electrically insulating pernigraniline (PE) as shown in Fig. 2.2.
Figure 2.2: Schematic diagram of PANi in different oxidation states namely, LM (insulator) as (A), EM-base (insulator) as (B) and PE (insulating) as (C).

The LM and PE states are the fully reduced (i.e. all the nitrogen atoms are amine) and the fully oxidized (all the nitrogen atoms are imines) forms respectively. In the EM state, the ratio of amine to imine is 0.5. This explains the adopted general formula:

\[
[(-B-NH-B-NH)_y (-B-N=Q=N-)_{1-y}]_x
\]

showing PANi as a continuum of oxidation states. ‘B’ and ‘Q’ denote benzene rings in the benzoid and quinoid forms respectively. Letter ‘y’ is a measure of amine to imine forms; when \( y = 1 \), it implies PANi in the Leucomeraldine form, \( y = 0.5 \) implies PANi in the Emeraldine form and \( y = 0 \) implies PANi in the Pernigraniline form. The imine’s sites of the half oxidized EM base form are easily protonated in strong acid solutions to produce the conductive EM salt form of PANi [62].

Strafstrom et al. was reported to have proposed the polaronic lattice structure for the EM salt showing the positive charges without any change in the number of pi-electrons. The combination of charged sites and electro neutral radicals (i.e. solitons) form polarons; at higher doping levels, two polarons could combine to form bipolarons [63]. In the review work of Gospodinova and Terlemezyan, the mechanism of the oxidative polymerization of PANi was reported and discussed [63]. The
chemistry of the dopant used and the polymerization mechanism determines the properties, morphology, and molecular weight distribution of the PANi product.

In the last two decades, a lot of effort has been made on the search for improved and processable PANi having good mechanical and solubility properties. This involves preparation of conducting PANi blends and composites, which possess the mechanical properties of an insulating host matrix and also the electrical properties of the PANi Guest within the matrix. Polymeric composites of conducting polymers offers the combination of the good processability of a polymer like poly-(phenylensulfide-phenylenediamine) PPDA with the conductivity and ease of synthesis of another polymer like PANi [62].

Two general methods are being adopted, one was to introduce flexible substituent to the benzene rings or nitrogen atoms of PANi [64]; the other is doping PANi with functionalised organic acid such as camphor sulphonic acid (CSA), naphthalene sulphonic acid (NSA) and dodecyl benzene sulphonic acid (DBSA) [24, 25, 26, 27]. These processes produce a soluble and more conductive product that could be blended with PANi or used to form PANi composite with materials such as poly vinyl alcohol (PVA) or polyurethane [28]. In the solid phase, the protonation of the imine sites of PANi or its blend/composites is limited by the diffusion of the dopant (acid) [17]. This also depends on the dopant anion size and the polymer matrix morphology. The more the degree of dispersion of dopants, the more the redistribution of polarons along PANi macromolecular chains and the more conductive the PANi blend or composite. Over the years, the following broad synthetic methods have been employed in preparing PANi blends or composites:

- Polymerization of aniline in dispersion systems involving the use of dopants, surfactants and suitable oxidant [17, 25, 26, 27].
- Chemical or electrolytic in situ polymerization of aniline in the presence of a polymer matrix or by incorporation of polymer/metal nanocomposites like H₂PtCl₆ at a liquid | liquid interface [6, 7, 17, 34]. This method could involve use of reverse micelles, during which polymerisable surfactants were used or incorporation of metal nanoparticles that could enhance the conductivity of polymers. The principle is based on the reduction of metal ions (clusters) that are dispersed in polymer matrices, or the
polymerization of the monomer dispersed with the metal nanoparticles followed by electrodeposition of the strongly embedded metal/polymer composites by either pulse or potential cycle program [34].

- Use of electrolytic method to polymerize aniline in suitable electrolyte at an electrode (anode) [17, 61, 62, 65, 66]. The conductive form of polyaniline was synthesized by the anodic and chemical oxidation of aniline in malonic acid medium [66]. The conductivity of polyaniline doped with malonic acid changed from $1.62 \times 10^{-6}$ to $2.5 \times 10^{-5}$ S cm$^{-1}$ depending on the way it was synthesized. The polymer growth rate was observed to be very slow in malonic acid compared with $\text{H}_2\text{SO}_4$. According to Li et al. [62], electropolymerised PANi has many advantages over the chemically polymerized PANi. These includes better adhesion and good mechanical strength, ease of control of film thickness based on the applied potential and number of cycles to give a more stable electronic property for a longer duration. Also the product is purer as there are no residual oxidants or reduced specie adhering to the polymer matrix thus providing a more ordered nanostructure.

- Grafting of the polymer on a PANi surface or copolymerized with another polymer surface [17, 67, 68]. This offers production of polymeric systems that are copolymers, composites, bilayers or blends with improved properties of the corresponding homopolymer. Free standing-grafted polymer films of PPy and PANi prepared electrolytically showed varying amounts of polyaniline and polypyrrole depending on the electrolysis time. The Raman spectra of the films taken from the electrode side were similar to those of pure polyaniline, whereas the spectra of the solution side were identical to those of pure polypyrrole [67].

### 2.4 Polypyrrole blends/composites

Polypyrrole (PPy), known as “polypyrrole black” since early 20$^{th}$ century, is one of the most studied COPs. PPy is an extensively studied CP with its monomer pyrrole being easily oxidisable, water soluble, commercially available and the PPy and its derivatives possess good environmental stability, good redox properties, high
electrical conductivity and simplicity of synthetic procedures. The main hindrance of its processability is in its insolubility in any organic solvents. PPy is usually a black powder and could be prepared by chemical or electrochemical synthesis. Various approaches have been used for the chemical synthesis of polypyrrole nanofibres and nanotubes such as soft (organic) and hard (inorganic) template approach and of recent nanofibre seeding, in which narrow pore nanotubes with an average inner diameter of 6 nm and an outer diameter of 60 – 80 nm respectively are formed [69, 70]. The new approach involved the use of reactive seed templates that chemically react with the monomer prior to the addition of oxidant. This pre-polymerization reaction on the surface of fibrilar seed templates helps direct the evolution of bulk fibrilar morphology when oxidant is subsequently added.

The mechanism of polymerization for both chemical and electrochemical methods follows an initial generation of radical cation while subsequent steps depend on the type of polymerization being adopted. In the chemical case, the radical cation attacks another monomer to form a dimer radical cation, while in the electrochemical synthesis a neutral dimer is formed by the dication of the large concentration of radical cations in the vicinity of the electrodes. The general scheme for the formation of the dimers and subsequent chain growth for both methods is shown in Fig. 2.3. The number of electrons involved in the polymerization process for each monomer is approximately 2.25, one for each of the two α positions to form the polymer and another one for every four monomer units to form the doped polymer. Similarly, one anion per four monomer units is incorporated during doping to maintain charge neutrality [71]. The chemical synthesis is used when large quantities of material are required but electrochemical synthesis is preferred for research purposes due to the simplicity of the technique, control over material thickness, geometry and location, the facility for doping during synthesis, the wide choice of available dopant ions and the generation of good quality. The electro-deposition of polypyrrole on the positively polarized working electrode proceeds via a condensation reaction between the pyrrole-monomer units, and the concomitant balance of charge (electroneutrality) along the polypyrrole backbone by the anions present in solution [32].
Figure 2.3: Generalized scheme for the polymerization of polypyrrole from monomer (a) and dimer (b) [71].

Figure 2.4 shows the scheme for the electropolymerisation of polypyrrole which is typical for other aromatic five-membered heterocycles with NH, S and O as the heteroatom. Monomer units are adsorbed onto the surface of the working electrode resulting in one-electron oxidation to form a pyrrole radical cation. These radical cations then couple with themselves, or with other cations or with neutral monomers from solution. In each case, this leads to the formation of a dimer dication, which undergoes a double deprotonation to give a neutral molecule. These more stable dimer radicals have a lower oxidation potential compared with the monomer units and chain growth then occurs by preferential coupling between the dimers and monomers [32, 71]. Anions called ‘dopants’ are incorporated into the film to maintain electrical neutrality as polymerisation progresses.
In the undoped state (pristine), neutral PPy is generally non-conducting having the aromatic and quinoid structures of which the latter possesses a higher energy configuration. In the presence of a Lewis acid, the doped form (oxidized) is formed which manifest as either a polaron and/or bipolaron depending on the doping level as follows:

$$\text{PPy} + X^- \rightarrow \text{PPy}^+X^- + e^- \quad \text{polaron}$$

$$\text{PPy}^+ + 2X^- \rightarrow \text{PPy}^{2+}(X^-)_2 + e^- \quad \text{bipolaron}$$
where $X$ are anions, (the subscript $(s)$ indicates that they are in solution phase), and PPy represents a segment of the polypyrrole chain.

The various structures of PPy are shown in Fig. 2.5. The chemical oxidations of pyrrole monomer using aqueous or anhydrous iron III chloride ($\text{FeCl}_3$), other salts of iron (III) and copper (II) and other Lewis acids and halogens have been reviewed [71]. The yield from the reactions is dependent on the choice of solvents and oxidants, initial monomer/oxidant ratio, duration and temperature of the reaction.

![Scheme for the structures of polypyrrole showing the non-degenerate: aromatic (a) and quinoid (b) configurations; and degenerate (oxidised forms): a polaron defect (c), and a bipolaron defect (d) configurations.](image)

A yield of almost 100% is obtained with $\text{Fe}$ (III)/monomer ratio of 2.4 [71]. The use of different concentrations of dopant materials has also been employed to modulate the yield and morphology of polypyrrole in aqueous medium [56]. Details of the various micro/nanotubes reported in [56] using different dopant/monomer ($d/m$) ratios and temperature settings are discussed further in Chapter four.

$\text{FeCl}_3$ have been used to chemically synthesis PPy in various solvents (water, alcohols, benzene, tetrahydrofuran, chloroform, acetone, acetonitrile and dimethyl-
formamide) [72]. The highest conductivity was obtained from PPy prepared in methanol solution [71]. Rapi et al. [72] reported improved chemical yield using shorter times of polymerization and lower temperatures (0 – 5 °C). Improved film or coatings of PPy was prepared through the use of gaseous pyrrole on FeCl₃. Persulfates (Na₂S₂O₈, (NH₄)₂S₂O₈) and H₂O₂ have also been applied as oxidant in the synthesis of PPy [71 - 73]. The use of peroxide as oxidant can be via a hydrogen peroxide based chemical or biological material. Recently, self-assembled conducting PPy micro/nanotubes and films using β-naphthalene sulphonic acid were chemically and electrochemically prepared [19, 55]. Micelllic clusters of the dopant of NSA and its complex with the pyrrole served as template for this tubular growth.

Composites of PPy with different organic and inorganic compounds having improved mechanical performance have also been reported. Omastova et al. prepared net-work like PPy composites with poly (methyl methacrylate (PMMA/PPy) [74] while Cairns et al. studied the structure of PPy composite with polystyrene and reported that pyrrole was present as discrete 20 – 30 nm nanoparticles adsorbed into the PST matrix [75]. Lu et al. [76] chemically synthesized and characterized nanometer sized PPy composites using styrene and butyl acrylate. Also, polypyrrole/poly (methyl methacrylate) coaxial nanocable was prepared through the sequential polymerization of methyl methacrylate and pyrrole monomers inside the channels of mesoporous silica template, followed by the removal of the silica template [77]. Similarly, thermoplastic polyurethane (TPU-PPy) composites on electrode [78] and PPy- poly (vinyl alcohol or chloride) blends [79] have been reported.

Although PPy can be chemically synthesized especially for large-scale preparation, electropolymerisation is easily achieved and is the most common preparative method because of the ease of oxidizing the polypyrrole compared to the pyrrole monomer. Electropolymerisation could be achieved with different electrodes such as platinum, carbon and metal oxides. The earliest electropolymerised film was prepared on platinum electrode by the oxidation of the monomer in sulphuric acid solutions. The polymer obtained was found to be brittle, conductivity of 8 Scm⁻¹ and one positive charge per three pyrrole monomer units. Subsequently, improved electrochemically synthesized PPy have been prepared by variations in conditions of preparation.
(solvent, temperature, anions, current/potential) used and on the composition of the solution used during electrochemical investigations [80-87].

Tamm et al. [80, 81] and Yuan et al. [86] had respectively reported an elaborate in-situ electrochemical study on the redox properties of polypyrrole in aqueous solutions using different anions and polymerization conditions to show the concepts of *electroneutrality coupling* and *electron hopping* which are useful for the functionalization of the polymer and its electron transportation ability. They found out that the polymer differs with respect to the extent of oxidation, doping anions, and also reduction, doping cations. Even though polymerization efficiency improves as the positive potential limit becomes more positive, however, polypyrrole films becomes over-oxidized at potentials in excess of 700 mV versus Ag/AgCl [86]. The overoxidation, which is entirely irreversible, results in the dedoping of conducting polypyrrole and the formation of carboxyl group. Overoxidation of PPy, leads to loss of conductivity and de-doping.

Study on the potentials at which the overoxidation of polypyrrole occurs have shown a strong dependence on the pH values of the aqueous solutions [87]. At higher pH values, the occurrence of the overoxidation was easier, thus occurring at lower overoxidation potential. This is coincident with the electrolysis reaction of water to give out oxygen. It was supposed that the oxygen produced in the electrolysis of water results in the overoxidation of the conducting polypyrrole films.

The polypyrrole redox scheme (Figure 2.6) is accompanied with three processes, namely, mass and resistance changes as well as electron transitions unlike other systems in electrochemistry in which only electrons are involved during the reduction and oxidation processes [88, 89]. Using cyclic voltammetry, oxidation of pyrrole yields a positive charged polymer film on an electrode surface, which is balanced by anions incorporated during synthesis. During the following reduction scan, electroneutrality can be maintained either by expulsion of these anions or by incorporation of cations. When a sufficient negative potential is applied to the polymer, the anions are expelled (undyoping), thus reducing it to the neutral state.
Conversely, when a positive potential is applied to oxidize the neutral film (doping), the anions are taken up. Therefore, the reduction/oxidation of PPy films involves the transport of ions in and out of the polymer in order to compensate the cationic nature of oxidized polymer. The dopant anions (small size) in the PPy film can be exchanged relatively easily with electrolyte anions in aqueous solutions during potential sweeping. The anion exchange processes offer an alternative chemical route for the preparation of some conductive and anion specific PPy complexes. However, the anion exchange processes do not result in any significant alteration of the basic structure of the polymer.

In the investigation of the effect of solution temperature on electroactivity of polypyrrole using cyclic voltammetry technique by Khalkhali & Wallace, thermal treatment at elevated temperatures in solutions was found to affect the electroactivity of PPy, and the changes are mostly irreversible [89]. The temperature, time of exposure, the switching potential and the nature of electrolyte in which the polymer is switched all have important effects in determining thermal stability of the polymers in solutions. The nature of the effect was greatly dependent on the nature of the counter-ion incorporated during synthesis. Large surfactants and immobilized polymeric dopants such as polyelectrolytes counterions were not released during reduction process and become trapped within the polymer matrix due to their large size and entanglement with the PPy chain; this consequently increased their solution stability at elevated temperatures. Smaller inorganic ions dopants such as chlorides gave a less stable polymer. The loss of electroactivity of PPy films when exposed to elevated solution temperatures in aqueous media was attributed to the loss of conjugation in polymer due to the nucleophilic attack by water or dissolved oxygen, which occurs more rapidly at higher temperatures [89].
2.5 Polythiophene blends and composites

The property of PTh shows much resemblance to those of PPy. The monomer, thiophene is quite cheaper than pyrrole and its redox potential is quite higher. It shows remarkable stability in both air and water. PTh usually appears as a stable infusible black powder, which is insoluble in common solvents. The chemistry of PTh is based on its conjugated $\pi$ electrons. Its conductivities in the neutral (undoped) form could be as low as $10^{-11}$ Scm$^{-1}$ while in the oxidized (p-doped form) it could be as high as $10^2$ Scm$^{-1}$, although on exposure to air this value decreases [90]. The electropolymerisation of most conductive polythiophenes is done in non-aqueous solvents [30]. Unsubstituted thiophene is insoluble in water and can thus not be polymerized in aqueous medium. This is due to the electro-oxidation potential of thiophene, which is higher than the decomposition potential of water coupled with the fact that the reaction between thiophene cation with water prevents cationic polymerization and this becomes a competing reaction [30]. The electrosynthesis of PTh could be done galvanostatically, potentiostatically or by sweeping potential voltammetry [29, 30, 33]. P-doped PTh has a characteristic blue colour, highly air sensitive and its conductivity decreases on exposure to the atmosphere. N-doping is less studied but cathodically doped PTh have been reported with lower conductivity as compared to the p-doped polythiophene [91]. The processes of p- and n- doping in PTh compounds and their effect on conductivity have been described by the ‘generalized transmission line circuit’ model using electrochemical impedance spectroscopy [91, 92].

The mechanism of polymerization of PTh and many substituted PTh’s is similar to those of PPy discussed earlier occurring via a radical – monomer coupling or radical – radical coupling intermediate to form the polymer [90]. In the process, radical cations (polarons), or dications (bipolarons) are formed. Substituted thiophene polymerizes at 1.7 V vs. SCE. This value is lower than the oxidation potential of the corresponding polymer and thus over-oxidation readily sets in which causes degradation of the polymeric film. The problem of over-oxidation is usually minimized in different ways [30]. This could be done by the addition of bithiophene to the thiophene solutions or converting the thiophene to its oligomers before electrolysis. The resulting extension of the conjugation length and lowering of the oxidation potential produces a polymer
with high conductivity and good electrochemical and thermal stability. Cho et al. have reported that substitution of the hydrogen on the monomer with electron donating groups do significantly reduce the potential at which oxidation occurs [33]. The longer the length of this substituent, the lower is the oxidation potential of the monomer. Various substituents such as long alky chain, sulfonate groups, carboxylic acids, amino acids and urethanes have been used to improve the polymers solubility [29]. The sulfonate substituent group (-SO$_3$H) acts as a counter ion and produces self doped conducting polymer.

Ballav and Biswas reported a simple procedure for the preparation of PTh in high yield using FeCl$_3$ as the oxidant and using the same method they were able to prepare PTh-Al$_2$O$_3$ nanocomposites [93]. Cyclic voltammetric experiments have shown that the electrode reactions taking place depends on the conditions used, the type and length of electron donating substituent and type of solvent used [90, 94]. Slowly polymerized PTh has more conductive states and relatively higher molecular weight than those from faster chemical reactions [95]. The positive mechanical properties exhibited by PTh over PPy coupled with its larger positive working window makes copolymers of PPy and PTh as potential better positive electrodes in lithium batteries.

Yigit et al. [96] electrochemically prepared composites of PTh with natural and synthetic rubber as the insulating polymer host. Various regio-regular PTh’s with pendant carboxylic acid functionality have been prepared as water soluble conducting polymer which produced distinct color changes when applied on divalent cations and some acting as solid state chemo sensors for acid vapors [97]. It appears that PTh films give more electro catalytic response even though the preparation procedure appears more cumbersome and must be done in totally anhydrous solvent to get good reproducibility. However, a wider application of PANi and PPy is practiced.

2.6 General properties and factors affecting processability of nanostructured polyaniline, polypyrroles and polythiophenes.

The properties and stability of nanomaterials determines the final application to which the conducting polymer is put. Some of the intrinsic properties that characterize NCPs
do originate from the preparation procedure. Understanding of the chemistry, electrochemistry, structure, electrical and optical phenomena, processing and applications of NCPs has been employed in improving the processability limitations of PANi, PPy and PTh. The effect of temperature and ageing process, nature of solvent, pH and redox potential of the polymerization liquor, and the nature of dopants on their preparation and stability are discussed below.

### 2.6.1 Temperature and ageing process

Zhang et al. [27] reported the temperature dependence of conductivity for PANi doped with various types of NSA showing decrease in conductivity with decrease in temperature, thus exhibiting semiconductor behavior. Kassim et al. [98] studied the effect of preparation temperature on conductivity of PPy films prepared by electrochemical synthesis in aqueous medium using camphor sulphonates as the dopant and temperature range of 1 – 60ºC. It was discovered that the film’s conductivity decreases with increase in temperature, the optimum conductivity was obtained between 10 - 30ºC. They established that PPy formed at low temperature is stronger and more conductive than those formed at higher temperatures. SEM analysis for the PPy films prepared at lower temperature attested to its smoother, more coherent, and stronger mechanical strength when compared with that prepared at higher temperatures. The X- ray analysis also showed that the PPy film obtained by low temperature preparation is more compact with higher conductivity. Many researchers have established that the polymerization of thiophene and its derivatives is temperature dependent. The highest quality material was obtainable at 5ºC, with rate increasing up to 16ºC after which there is decrease [90].

### 2.6.2 Nature of solvent

Many researchers have shown that the electrochemical behavior of a polymer is determined by the nature of the electrolyte used for polymerization [99-103]. Monomers with lower oxidation potentials (aniline and pyrrole) can be polymerized in aqueous electrolytes. For monomers with higher oxidation potentials such as thiophene, aprotic solvents like acetonitrile, propylene carbonate, dichloromethane etc. must be used. This is why the aqueous synthesis of polythiophene is highly
problematic. The use of acidic solvents for polymerization of PTh have been reported to substantially lower the oxidation potential of the monomer from about 1.6 V to 0.9 V vs. SCE [99]. The solvent composition used in the preparation of a conducting polymer alongside the film thickness and morphology have been reported to determine the biosensing efficiency [100].

2.6.3 pH and redox potential of the environment

The electronic conductivity of conducting polymers changes over several orders of magnitude in response to changes in pH and redox potential of their environment [104]. Unlike aniline and pyrrole, which could be electropolymerised at low potential, thiophene requires much higher oxidation potential [90, 94]. The effect of pH, oxidation potential and nature of electrolyte on conductivity of PPy films synthesized therein have been extensively studied and reviewed [104]. In alkaline media, thin insulating films are formed [105], while optimum conductivity was obtained around the synthesis potential of 0.6V (vs. saturated calomel electrode) in aqueous solutions [106]. The absence of a protonic dopant ion during electropolymerisation reaction of conducting polymers do limit the rate determining step of proton abstraction from the monomer molecule (H-M-H), and thus terminating the polymerization at the dimer or trimer stage. A reasonable level of doping is thus critical for the formation of higher oligomers. Lower oligomers are soluble in nucleophilic environment just as the monomer, but with increasing polymerization an insoluble film is formed at the electrode. This trend increases from aniline to pyrrole and to thiophene [107, 108].

2.6.4 Nature of dopants

The solubility and conductivity of the polymer could be tuned by the nature and concentration of the dopant. Use of specialized dopants during polymerization plays a major role in tuning electronic properties in conducting polymers. It helps to create a more stable polymer whose work function (work of extraction of an electron from an uncharged metal) and resistivity can be electrochemically adjusted [15, 107]. While a particular dopant may produce nanostructurised polymer from a particular monomer, it may form completely different morphology when another monomer is used. Nanofibres of PANi which could readily be produced using the surfactant-mediated
synthesis with naphthalene sulphonic acid become greatly problematic with PPy. Rather than nanofibres, different fibrilar and tubular morphology with diameters of 50 – 2000 nm range are formed [19, 55]. However, with different naphthalene sulphonie acid derivatives and depending on the dopant structure and concentration, nanotubes of PPy with average diameter of 130 to 250nm could be produced [27, 73]. Similarly, the polymeric yield of conducting polymers is greatly influenced by the relative concentration of the dopant used [15, 56, 57, 95].

2.6.5 Other factors

Amongst other factors that could affect the stability of conducting polymers is the nature of the working electrode. This determines its relative catalytic property and lifespan before fouling sets in. Del-Valle et al. have reported on the comparative performance of modified electrodes using PANi, PPy, and PTh in dispersion system of Pt or Pt – Pb respectively to monitor the catalytic oxidation of formic acid [109]. The modified system of PTh had the longest electro catalytic activity while systems with PANi and PPy were fouled within a shorter time. This informed their recommendation of the use of PTh as a better electro catalyst in fuel cells and sensors.

2.7 Characterization of nanostructured PANi, PPy’s and PTh’s

The use of physical and chemical methods for the characterization of NCPs is critical for the confirmation of the electronic species involved vis-à-vis the understanding of the electrochemical processes taking place and for fashioning procedures for development of appropriate application for the polymer. The major characterization techniques often employed are morphology, electrochemical and spectroscopic examination of the nanotube or polymer film produced depending on the potential application that is of interest.

2.7.1 Morphology characterization

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray diffraction measurement (XRD) have been severally used to characterize polymers of intrinsically conducting polymers and
their composites [25, 26, 27, 73, 51, 93, 98] The polymer could have different morphology ranging from grain-like, sponge-like, fibrous, porous-structured to tubular (hollow or closed) morphology. SEM and TEM studies of PTP-Al$_2$O$_3$ composite particles showed globular morphology with uniform particle size for polymers prepared in CHCl$_3$ while those prepared in the absence of any solvent showed relatively irregular particle formation. The morphology studies of screen-printed carbon electrode (SPCE) modified with PANi showed sponge-like high surface area suitable for enzyme immobilization, which changed to a speckled, grainy image after immobilization. Changing the chemical structure of the dopant and synthesis conditions leads to formation of different morphologies for PANi/NSA nanotubes [25, 27]. This varies from hollow to solid micro/nanotubes and fibres depending on the type of NSA used and oxidant concentrations [56, 57].

Also, Zhang and Manohar reported the synthesis of narrow pore-diameter PPy nanotubes by the chemical oxidation of pyrrole with FeCl$_3$ as oxidant, and V$_2$O$_5$ as the sacrificial seed template to orchestrate fibrilar polymer growth [69]. This seed template has the catalytic ability of oxidizing the monomer prior to the oxidation with the oxidant. The same authors also reported fibrilar and tubular morphology when large organic dopant anions such as naphthalene sulphonic acid are used to during the synthesis. Very thin nanofibres were obtained when the reaction is carried out in ethanol using FeCl$_3$ as the oxidant and V$_2$O$_5$ as seed template [70]. The SEM of the as-synthesized polymer nanotube showed that fiber diameter can be controlled by stirring the seed template in ethanol for a limited time before initiation of the oxidation of the monomer. Figure 2.7 (A) shows SEM for polypyrrole-Cl nanofibers of 30 nm diameters obtained by stirring the seed template foe 30 min, (B) is the nanofiber of 100 nm diameters obtained upon extended stirring in ethanol for 12 h. There is the need to activate the seed template to ensure fibrillar polymer growth in polypyrrole whereas some polyaniline nanofibres are readily produced in the unseeded polyaniline system which was interpreted as a peculiar feature intrinsic to polyaniline. The similarity or contrast in morphology could further be investigated using the XRD measurements. PANi indicated four sharp characteristic peaks at $2\theta = 4.6^\circ$, $9.2^\circ$, $13.8^\circ$ and $23.0^\circ$ for the crystalline tubes while amorphous PANi had only two characteristic broad peaks at $20 = 20^\circ$ and $26^\circ$. 

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While PPy/NSA tubes were amorphous, the polypyrrole doped with p- toluene sulfonate acid (PPy/TsOH) was partially crystalline [19, 55]. XRD is also employed to discriminate the compactness of a polymer film synthesized at different temperatures. The peak values for polypyrrole doped with p- toluene sulfonate acid (PPy/CSA) film were greater at lower temperatures than at higher temperatures [98].

2.7.2 Electrochemical characterization

Various voltammetric techniques are being used to study the redox activity and electrochemistry of conducting polymers of PPy and PTh tubes and films. While cyclic voltammetry (CV) is the most versatile for characterization of electrochemical systems, other techniques such as Oster-Young square wave and differential pulse voltammetric techniques (OSWV and DPV) have been severally used for both qualitative and quantitative analyses [68, 91, 92].
Polypyrrole prepared from aqueous medium has poor/ill formed oxidation and reduction peaks. However when it is modified with suitable dopants, the electroactivity is enhanced. Similarly, electrochemical impedance spectroscopy (EIS) offers a platform for a deeper intuitive study of interfacial properties of conducting polymers at electrode surfaces. The changes in the electrochemical parameters during the course of switching through the oxidation and reduction waves is dependent on the properties of the polymer, the electrolyte and the external force applied through the electrode surface.

2.7.3 Spectroscopic characterization
UV-Vis, FTIR and $^1$H NMR spectroscopic techniques are widely used for the characterization of NCPs. The UV-Vis absorption spectra are often used to diagnose the presence of charge carriers within the polymer structure or the existence of various oxidation state(s) of the NCPs. While the emeraldine salt form of PANi is characterized with two absorption bands at about 346 nm and 636 nm for the \( \pi - \pi^* \) excitation band and the polaron bands respectively, the higher doped PANi may have multiple polarons and bipolarons depending on the synthesis condition, type of dopant used and the level of doping [25, 26, 34]. The same trend applies to PPy and PTh in the doped state, however the relative position and intensity of the polaron and bipolaron bands changes depending on the synthesis conditions [19, 55].

In the study of Massari et al., the unique light absorbing behavior of PANi at various redox states under a modulated electrochemical oxidation was explored for illustrating the interplay of the index of refraction and absorptivity of the material [110]. In investigating the electrochemistry of polyaniline or polypyrrole synthesized via surfactant dopant, FTIR spectroscopy is a viable tool to monitor the presence or absence of surfactants as well as the level of over-oxidation attained at different electronic states [15, 17]. In-situ study using substructively normalised in-situ Fourier transform infra-red spectroscopy (SNIFTIR) on the structural changes during oxidation and reduction of the polymer at different stepping potential will manifest slight shifts in the vibrational peak positions depending on the extent of doping. The reproducibility of the peak positions during repeated oxidation and reduction is an attestation of a polymer’s high electroactivity and suitability for use in batteries and actuator applications. The sulphonated polypyrrole spectral region between 1000 and
1700 cm$^{-1}$ contains information on the relative populations of charge defects as a function of potential, and the results confirm that electronic charge transport at moderate potentials is due to formation of radical cations, which oxidize further or recombine to form dications at higher potentials. At more positive potentials the polymer degrades with formation of carbonyl, hydroxyl groups and also CO$_2$ [15, 17].

The electrochemical overoxidation of conducting polypyrrole nitrate film in aqueous solutions was studied by a combination of cyclic voltammetry, in-situ spectro-electrochemical measurement and FTIR spectroscopy [87]. The overoxidation, which is entirely irreversible, results in the dedoping of conducting polypyrrole and the formation of carboxyl group. The combination of spectroscopic techniques with electrochemical and morphological methods is indeed a vital force for characterizing and probing of structural and kinetic reactivities of nanostructured conducting polymer systems and significant breakthrough is expected from this within the next decade.

### 2.8 Application of NCPs in sensors

The application of NCPs is being greatly exploited in bioelectrochemistry, bioelectronics and voltammetric chemical sensing. The applications of ‘NCP’ could be generalized under two major groups; namely those derived from its conductivity and those derived from its electro activity. There are many publications on the prospect and usage of ‘NCPs’ based on its conductivity in electrostatic materials, conducting adhesives, electromagnetic shielding devices, artificial nerves, antistatic clothing, piezoceramics, diodes, transistors and aircraft structures [17, 61]. Salient features of conducting polymers and their wide biosensor application in health care, food industries, environmental monitoring was reviewed by Gerard at al. [111]. The electroactivity properties equally find applications in molecular electronics, interdigitated microelectrodes (IME), chemically sensitive field effect transistors (chemFET), electrical displays, biosensor and chemical sensors, thermal sensors, rechargeable batteries and solid electrolytes, ion exchange and drug release systems, optical computers and electromechanical actuators or switches [17, 61, 62, 110, 111, 112].
Conducting polymers such as polypyrrole (PPy) is unique in its ability to be used in tailoring specific bulk and surface properties of materials to provide novel solutions for tissue engineered systems. This includes controlled cell assembly (micro and nano-patterned surfaces), drug release (degradable polymers), tissue release (thermo-responsive polymers) and integrated biosensing (electroactive polymers). In addition, such materials provide a platform for the study of the fundamental science relating to tissue-material surface interactions. It is in recognition of these special requirements that researchers have engaged the use of polypyrrole in particular, for trial use in biological applications [32]. The electric conductivity of NCPs is sensitive to changes in chemical environment; this provides possibility of developing various sensors. For example, spectroelectrochemical studies have shown that the change in absorptivity with effective index of refractive of PANi could be employed to develop diffraction based chemical sensor [110]. PPy has been used as sensor material for certain components in gas mixtures, for both inorganic (NO\textsubscript{2}, CO\textsubscript{2}, CO, NH\textsubscript{3}, H\textsubscript{2}S) and organic (acetone, methanol, ethanol) compounds [71, 111].

The widespread interest of electrochemists in these polymers has been spurred by their applicability in the area of chemically modified electrodes. Coating the electrodes with electroactive polymers helps in the development of new materials with very active catalytic properties. In most electrocatalytic systems, the polymer itself is inert and serves only as a support for the electrocatalytic metal sites. The electrocatalyst site functions as a mediator, facilitating the transfer of electrons between the electrode and the substrate.

Electrocatalysis in general is of great economic importance and the aim of these modified electrodes is to drive electrochemical reactions selectively and/or at modest potentials, and with better control than could be possible by the direct interaction between the substrate and the electrode. Fig. 2.8 shows the scheme for a conducting polypyrrole based sensor in an electrolyte medium of dilute hydrochloric acid undergoing oxidation and reduction processes.
Catalysis of electrochemical reactions are determined by the availability of reactive sites at the working electrodes coupled with other hydrodynamic conditions that promotes attainment of balance between adsorption of reactants and desorption of products from the electrodes. The electrostatic binding of electroactive ions into ionomeric polymer films generates nanoscopic electrocatalytic layers. This has a concomitant effect of shifting the electrode kinetics to a region of lower formal potential at the operating potential window. Through such shifts in the formal potential, problems of electroactive interferences are reduced. Many metals such as tin, bismuth, tungsten, palladium, lead, antimony, selenium and carbonaceous inert material have been used to modify electrodes for increased reactivity [108].

Optimum preparation conditions for modified electrodes of PANi, PPy and PTh on Pt have been reported [109]. The immobilization of catalytically active compounds on
the conducting polymer film produced by electrochemical polymerization is an efficient method for production of electrode surface with high stability and catalytic stability. Processable and nanostructured conducting polymers of PANi, PPy, PTh stabilized with appropriate surfactants and other hydrogelic polymer composites are attractive raw materials in building electro catalytic chemical and biological sensors. This is readily achieved by encapsulating enzymes on the polymeric nanotubes or films, thus providing ‘wiring’ for electron transfer between the analyte and the biosensor [111, 113]. The process usually involves any of these; diffusion of substrate to the film; substrate partition and diffusion into the layer; charge transportation within the polymer modified electrode and the electrode surface or a mediation kinetics [114]. Figure 2.9 shows the scheme for a typical mediation process of a redox couple O/R \( (O + ne^- \rightarrow R) \), for the reduction of electroactive analyte. At nanoscopic level, NCPs offer enough binding sites that are readily immobilized to convey sufficient signals, while at the same time being thin enough to obtain quick and fast response. Using cyclic voltammetry such electro catalytic reactions take place at lower potentials with or without peak currents amplification [115].

**Figure 2.9**: Scheme for the mediation process of an immobilized polymeric film at an electrode surface for electroactive analyte (Y).

In the review by Wilson et al., an exhaustive report on recent research efforts and technology on chemical sensors for portable, handheld, field instrument was given [116]. Generally, large polymeric anions are more firmly fixed than small inorganic
anions on the film and consequently increase the rate of electro deposition at the electrode. X-ray microanalysis has shown that porphyrin doped PPy films were firmly fixed and were not expelled even during extensive potential cycling [117].

Electrodes formed from PTh polymeric matrix do show higher current densities and are more stable towards successive potentiodynamic cycles in formic acid oxidation than their PANi and PPy counterparts [108, 111]. This has been traced to the greater affinity for electrons by the sulphur atoms of the thiophene rings [118]. The catalytic effects of the conducting poly (3-methylthiophene)-film electrode on the redox behaviour of catecol compounds have been reported. It was established that the redox electron transfer step is taking place at the polymer/solution interface involving the heteroatom of the thiophene ring at the interface [118].

Applications of NCPs as suitable matrix for the entrapment of biological components such as enzymes for use as a medium for rapid electron transfer at electrode surfaces have attracted much interest in electrocatalysis. The advantages derived through this are enhanced speed, sensitivity and versatility of biosensors in diagnostics to measure vital analytes. The review of Aduloju and Wallace gave a concise report of earlier work on this [119].

Mathebe et al. [120] have been reported the fabrication and characterization of PANi-based amperometric biosensor incorporating Horseradish peroxidase (HRP) for the detection of hydrogen peroxide (H₂O₂) in aqueous medium. The catalytic cathodic reduction of H₂O₂ was studied amperometrically and also by cyclic voltammetry, both cases showed a positive correlation between the peak currents and increasing concentration of H₂O₂. The sensitivity of the catalytic sensor was found to be dependent on the concentration of the immobilized enzyme. A range of 0.6 and 0.7 g/l was recommended as optimum enzyme concentration. Higher concentrations generate a lower response due to a sterically hindered surface for electron transfer while at lower concentration a lower sensor response is obtained. Similar improved electro catalytic response was obtained when functionalized poly (pyrrole/cyclo dextrin) electrode was used to investigate the detection of some neuro transmitters [121].
Catalytic accumulations of analytical signals (by over five orders of magnitude) based on gold nanoparticle substrates have been used to generate high sensitivity and high selectivity in nucleic acid determinations [122]. High sensitivity polythiophene based transducer for the fluorimetric determination of nucleic acid hybridization based on the electrostatic bonding between positively charged polythiophene and a single stranded oligonucleotide probe have been reported [123]. The principle involved is based on monitoring changes in electrical/optical properties of PTh when associated with the single- or double- stranded nucleic acids.

Recently, Yokoyama et al. [124] reported a digital simulation of the cyclic voltammetry of reversible electrochemical reactions coupled with enzyme-mediated reactions. The model is applicable to any substrate and mediator system and the voltammogram changes with changes in the concentration of the enzyme or the mediator. As the substrate concentration is depleted in the vicinity of the electrode, the catalytic current is reduced. Similarly, Temsamani et al. [125] reported the use of conducting polymer film of polypyrrole doped with sulphonated-β- cyclodextrin (PPy-SβCD) for the solid phase micro extraction of cationic analytes. In another application, β-cyclodextrin doped polypyrrole was employed to fabricate an electrochemical sensor for the selective, simultaneous and quantitative detection of some polyhydroxyl phenyls and neurotransmitters derived from pyrogallol and catechol [126].

Generally, the scope of application of nanostructured conducting polymers is grossly dependent on the intrinsic conductivity, thermal stability and morphology of the doped polymer. The conductivity of PPy films doped with dopant mixtures of naphthalene sulphonic acid and HCl was reported to show more thermal stability than those from single dopants. Similarly, NCPs physical structure is radically different between different monomer starting groups with the same counter ion, or between the same monomer groups and with the different counter ions. These physical changes are useful in chemical sensing as small changes in the polymer synthesis conditions can lead to differing sensor responses and selectivity [127, 128]. PPy doped polymer with fibrilar morphology was found to show better conductivity than those with globular morphology because the former offers a better interaction between polymer chains [129, 130].
Recently, glassy carbon electrode immobilized with conducting nanostructured polypyrrole doped with naphthalene sulphonic acid is reported to electrocatalyse the oxidation of phenol at a potential of about 80 mV [56], as against about 850 mV vs. Ag/AgCl for its normal oxidation on unmodified glassy carbon electrode. In another report, when exfoliated graphite electrode was used for phenol oxidation, the irreversible conversion to quinone compounds occurred at 420 mV [131]. The electrocatalysis of conducting polymers could be further enhanced when modified with dispersed particles of platinum. A thin film of nanoparticles of polyaniline/platinum composite electrode showed significant electrocatalysis for the oxidation of hydrazine and the reduction of dichromate [132]. Similar electrocatalysis is expected for metal nanoparticle/PPy and PTh polymer composites.

A comprehensive review on the applications of electropolymerized conducting polymers in amperometric biosensors as well as current tendencies and the advances made in the field was published recently [133]. Special attention was paid to novel applications, which have opened up new possibilities and lines of research with regard to NCPs. The review covered applications in areas of imprinted electrosynthesised film, screen printing technology, immunoassay analysis, immobilization of enzymes on conducting polymer surfaces, multi-enzyme systems, miniaturization of electrodes for ‘in vivo applications, liquid chromatography electrochemical detection, organic phase biosensors and other miscellaneous applications for food and environmental applications. A lot of analytical and technological development is expected in these areas in the next few years.

2.9 Future challenges in the scope of conducting polymer applications

The development of novel and improved sensor devices with good electro catalytic properties is a major challenge for scientists in the next few decades. Improved processability for existing nanomaterials in appropriate medium, the production of new materials (synthetic metals) through doping of hitherto insulating polymers and development of terrific methods that are highly selective must be harnessed. Sensor materials with good electro catalytic property, reversible and reproducible electrochemistry must be assembled in portable and cost effective fashion. This
should cover all forms of biosensors for health, immunosensors, DNA biosensors, environmental monitoring biosensors and chemosensors for food and allied industries.

Reproducibility of nanoparticles with desirable morphology and properties for electrocatalytic application should be of utmost concern to synthetic chemists. It was reported recently that the process of stirring during the bulk synthesis of polyaniline leads to the formation of highly dispersible nanofibres [134]. The authors reasoned that homogenous nucleation of nanoparticles of PANi results in nanofibres while heterogeneous nucleation leads to granular particulates. They submitted that avoiding stirring during the oxidation of the monomers could enhance the processability problem of PANi. In the same manner, the effect of agitation on nanoparticles of polypyrrole and polythiophene should be more critically investigated.

There is the challenge of developing new electrode systems from the combination of separate chemical sensors having different transducer technologies to produce new hybrid electronic nose (E–noses) systems for various quality control applications. The problem of electrode surface fouling at high temperature by sulphur compounds in calorimetric sensors should be curtailed. Likewise the humidity levels should be optimized in polymer-based biosensors for optimal analyte discrimination in sensor assemblies. There is also the challenge of developing greater photovoltaic applications for nanostructured conducting polymers. In the near future, more photovoltaic coatings that gather and emit electricity should be developed to power and/or protect our houses and vehicles. This will be environmentally friendly and possibly cheaper than petroleum products. Conductive polymeric coatings that can fight corrosion will be more stable when applied as car paints. There is equally the need to rapidly revolutionalise the world with an accelerated commercialization of the research findings of material science so that the potential benefits therein could be tapped. In this respect, Analytical Chemist and Engineers have the challenge of producing microsystems of nanostructured conducting polymers through simplification, automation and miniaturization of electro analytical processes such that the analytical problems of selectivity and sensitivity are solved and more so that the final sensor material is cost effective [135].
2.10 Chemical sensors for anthropogenic organic pollutants.

A chemical sensor can be described as a device, which upon exposure to a gaseous or liquid chemical compound or mixture of chemical compounds alters one or more of its physical properties (e.g. mass, electrical conductivity, or capacitance) in a way that can be measured and quantified directly or indirectly. Sensors can be classified according to their operating principle, each class having a different sensitivity and selectivity. The sensor signal may be due to a change in the resistance (conductometry), a change in potential difference across the polymer interface (potentiometry), or to generation of oxidation or reduction of the analyte (voltammetric/amperometric).

The working principle of a typical electrochemical sensor is illustrated in Figure 2.10. Different sensors could be used singly or in an array to generate patterned recognition and identification of various analytes.

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Figure 2.10: Scheme for the working principle of an electrochemical sensor e.g. electronic nose, (EN).
The analyte molecules interact with the polymer interface in a lock and key mechanism to generate an electrical signal through the chosen transducer. The generated signal is amplified and monitored with an artificial intelligence such as computer hardware/software to produce measurable analytical signal. Furthermore, it is possible to change the properties of the sensor by changing parameters (e.g. sensing material or temperature) during manufacturing or operation of the sensor in order to improve selectivity and sensitivity. For example, by an inclusion of different metal ions into the polymer, the sensor can be adjusted for various chemical species. It is well known that electron conducting polymers can be used as chemical sensors by measuring the conductivity changes as a function of secondary doping or undoping of detected species [136]. In order to improve the characteristics of PPy based composites as chemical sensors; the sensitivity could be tuned by modifying the nature of the interacting polymer site with the analyte of interest.

Hwang et al. had proposed a microscopic gas-sensing model indicating that the sensitivity of the ethanol-based PPy-PEO composite film sensor depends on the site number of a monolayer, the thickness of the sensing film, the adsorption equilibrium constant as well as the change of site resistance [137, 138]. It was also found out that the ethanol sensing abilities of the PPy-PEO sensor are better at lower polymerisation charge [139]. The design of gas sensors was based on determining the sorption properties on the polymers surface. Chehimi et al. [140] had reported that conducting polymer surface is amphoteric with polar molecules (Lewis acids and bases) being adsorbed to a greater degree than non-polar molecules. The polymers surface morphology thus plays important role in surface thermodynamics of the polymer. Conducting polypyrrole based electronic sensor arrays have been developed for toxic and non-toxic substances, such as ammonia, nitrogen, nitrogen oxides, carbon monoxide, sulphur dioxide, hydrogen sulphide, methane, oxygen, hydrogen, alcohols, phenols, benzene and water vapour in materials ranging from water and beverages to waste waters and sewage effluents [139].

The conductivity of an intrinsically conducting polymer like pyrrole is simply measured at a constant current or voltage over a resistor. Sorption of gases or liquid (containing the analyte) into the polymer matrix and the interaction with the matrix
causes a change in the conductivity of the polymer. The sensor response is not 
necessarily a linear relationship between the analyte concentration and conductivity. 
Responses are typically measured as the relative differential resistance \( \frac{R_2-R_1}{R_1} \), 
where \( R_1 \) is the baseline resistance in clean air or electrolyte and \( R_2 \) the resistance in 
analyte atmosphere. In the study by Lin et al. [136], on the responses of PPyCl sensor 
to BTEX compounds, o-xylene caused increase in conductivity being an electron-
donating compound. The resistance change (\( \Delta R \)) increases linearly with o-xylene 
concentration from 20 to 60 ppm in \( N_2 \). The sensitivity was 0.8 m\( \Omega \)/ppm. The 
sensitivities obtained for BTEX compounds were in the following order o-xylene \( \succ \) m-
xylene being \( \approx p \)-xylene \( \succ \) ethylbenzene \( \succ \) toluene \( \succ \) benzene. This shows decrease from 
the polar to non-polar compounds.

Hydrogen bonding and dipole-dipole interactions are also reported to play important 
roles in sensing process [141]. The infrared spectra of a PPy film after exposing to 
acetone indicated the formation of hydrogen bonds (H-bonds) between C=O groups of 
acetone molecules and N–H groups of pyrrole units [141]. Also, the conductivities of 
conducting polymers are directly determined by the doping levels and the properties 
of counter ions. For example, the conductivity of ClO\(_4\)– doped PPy is higher than that 
of p-toluenesulphonate (TsO–) doped PPy [141].

Change in the morphology of conducting polymer’s sensing layer can strongly 
influence the performances of chemresistors and diodes. This is attributable to the 
results of changing the ratio of surface area to volume \( \frac{rA}{V} \) [143]. A film with higher 
\( \frac{rA}{V} \) makes analyte molecules diffuse and interact with the sensing layer more easily, 
which lead to a higher sensitivity and shorter response time. The exposure of 
conducting polymer samples to the vapour of volatile substances can have their 
conductivity altered in a reproducible manner. The combined pattern of variation of 
the individual conductivities of slightly different polymeric substances in an assembly 
could be used to give a specific ‘signature’ of the volatile compound. This is the 
operating principle of the conducting polymer based “electronic noses” currently in 
developmental stages in different laboratories [20, 139, 144, 145]. A comprehensive 
review of the achievements from the various research efforts from 1994 to 2005 on 
PPy-based E-Noses for environmental and industrial analysis is contained in [139].
Nanofibers (wires, tubes etc) have huge $R_A/V$ values, so they are perfect candidates for preparing polypyrrole sensors with high sensitivities and fast responses. In this study, careful control of the polypyrrole morphology have been done using surfactant dopants of naphthalene sulphonic acid and 1,2-naphthaquinone-4-sulphonic acid; and transition metal oxides of tungsten oxide and zirconium oxide to tune the interaction of polypyrrole to some anthropogenic organic pollutants.

2.10.1 Surfactant modified polypyrrole chemical sensors

Surfactants are water-soluble agents made up of hydrophilic heads and hydrophobic tails. They are widely used in soaps, detergents, pharmaceuticals and biotechnology and can also be used in the modification of conducting polymer. Improved processability of polypyrrole is usually obtainable by modification of the polymer’s structure through the use of substituted monomer, variation in the type of oxidant and also that of the doping material. However, the mostly studied approach to structural variation of a conducting polymer like PPy is to modulate the properties through the incorporation of sulphonic acid group (surfactants) which helps to improve the polymers solubility in water, and allows the possibility of self doping. Selection of a particular surfactant for a particular application is dependent on the critical micelle concentration (CMC), i.e. the concentration at which it starts to form micelles. CMC decreases as the carbon chain length and molecular weight increases, and the addition of surfactants into aqueous solutions increase the conductance of the solution [146].

Different approaches have been explored such as use of aliphatic or aromatic organic acids. In the study by Yasuo Kudoh [147], highly conducting and environmentally stable PPy was prepared by chemical polymerization using aqueous solution containing $\text{Fe}_2(\text{SO}_4)_3$ as oxidant and an anionic surfactant of either sodium dodecylbenzenesulfonate (NaDBS), sodium alkylnaphthalenesulfonate (NaANS) or sodium alkylsulfonate (NaAS). In the study, aromatic sulfonate was found to have a stronger tendency to increase the moisture and thermal stabilities of the polymer than alkylsulfonate. The improved thermal and environmental properties of the aromatic sulphonated polypyrroles were ascribed to the large-sized surfactant anions that were effectively incorporated into PPy as dopant. Evidence of the incorporation of the monovalent sulfonate anions as dopant into PPy was monitored by the increase in the
S/N ratio. The doping ratio of each dopant was calculated by the following simultaneous equations:

\[
x + y = \text{S/N ratio} \\
2x + y = \text{total doping ratio (constant)}
\]

where \(x\) and \(y\) are the doping ratios of sulfate (oxidant) and sulfonate (dopant), respectively. A yield in excess of 100 % was reported when excess DBS was adsorbed on the PPy surface.

Furthermore, the addition of the surfactant into the pyrrole-monomer solution was reported to have accelerated the polymerization reaction [147]. It was reported that the yield of the modified PPy is proportional to the surfactant concentration until near the maximal dopable concentration after which a lower constant conductivity value was maintained. The lower conductivity at the higher surfactant concentration region was ascribed to the presence of surfactant anion adsorbed on the PPy surface [147]. The effectiveness of the surfactant modified PPy was dependent on the electron withdrawing nature of the -SO\(_3\)H dopant moiety, the choice of dopants and steric effect from the dopant being used, the choice of oxidant and its relative ratio to the monomer mass concentration.

In order to improve selectivity of polypyrrole-based sensors towards acetone and toluene which are flammable components of lacquer over the non-flammable acetic acid and water, Ruangchuay et al. used blends of \(\alpha\)-naphthalene sulfonate (PPy/\(\alpha\)-NS') with common insulating polymers to create differences in surface composition and wetting ability [148]. The PPy/\(\alpha\)-NS' was more sensitive to acetone and toluene but less sensitive towards water, relative to pure PPy/\(\alpha\)-NS'. The sensitivity towards acetic acid was not significantly different from that of pure PPy/\(\alpha\)-NS'. Similarly, Jun et al. used different pre-treatment procedure to use dodecylbenzenesulphonic acid (DBSA) doped polypyrrole to generate different response times of the polymer to different alcohol gases and volatile organic compounds such as acetone and chloroform [149]. Using an array of different sensors based on polypyrrole, eight different sulfonated polypyrroles were identified by Barisci et al. to detect and quantify benzene, toluene, ethylbenzene, xylene i.e. (BTEX) compounds [150]. The uses of PPy gas sensors ENs
for various industrial and environmental materials have been critically reviewed [139].

Generally the sensing principle of chemical sensors is that it transforms the concentrations of analytes to other detectable physical signals, such as currents, absorbance, mass or acoustic variables. After exposing to the vapour of an analyte, the active sensing material of the sensor will interact with the analyte, which causes the observed change in the physical property of the sensing material. The interactions between the analytes and sensing materials are multiform, according to different analytes and different active materials [141].

2.10.2 Transition metal oxide modified polypyrrole sensors

Another approach in improving the processability and application of polypyrrole is to prepare the polymer composite using metal oxide template. The ability of transition metals to exhibit multiple oxidation states makes metal-oxide doped conducting polymers as suitable intermediate material for the catalytic exchange of electrons in many heterogeneous electrochemical systems. This also is aimed at synergistically improving selectivity and stability. Metal oxide doped polypyrrole is the hybrid polymer obtained from the chemical or electrochemical coupling of electrically conducting metal oxides with polypyrrole. These polymers find potential applications in electrochemical systems such as sensors, batteries and fuel cells [151].

The basic components of a metal oxide semiconductor (MOS) are shown in Fig. 2.11.

Figure 2.11: Scheme for the metal oxide semiconductor sensor.
Rocco et al. fabricated an electrochromic device combining PPy and WO$_3$ in 1996 [152]. The device consisted of tin doped indium oxide (ITO) coated with PPy/dodecylsulfate, an ITO electrode coated with WO$_3$ and a liquid junction. The light filtering capacity and stability of the solid-state device was dependent on the thickness of the PPy film. The chromatic contrast was stable after 15,000 double potential chromatographic steps [153].

Many Metal Oxide Semiconductor sensors (MOS) from materials such as TiO$_2$, WO$_3$, In$_2$O$_3$ and other oxides have been used in the assembly of the different chemical sensor systems, metal field effect transistors (MOFSET) and as gas sensing elements in E-noses [151]. While conducting polymer based chemical sensors could be used at ambient temperature, MOS sensors are used at elevated temperatures. Doping the metal oxide with noble catalytic metals can be used to modify the selectivity of the MOS devices through the changing of working temperature of the sensing element (250-400 °C), or by modifying the grain size [153]. Figure 2.12 shows conducting polymer sensor used to measure changes in conductance/resistance at different operating conditions. It does not require the use of a reference electrode.

![Figure 2.12: Scheme of a conductometric based sensor using a conducting polymer material.](image)

2.10.3 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants that originate from diverse anthropogenic sources. They are usually common in the vicinity of gas manufacturing plants as a result of incomplete combustion processes of organic carbon-based material [155]. PAHs are hydrophobic compounds with low
water solubility. They are of increasing interest because of their toxic, mutagenic and carcinogenic properties [156].

PAHs do accumulate in the environment because they are thermodynamically stable compounds, due to their large negative resonance energies; they have low aqueous solubilities, and they adsorb to soil particles. Because of these reasons, PAHs do not readily undergo natural environmental processes including biodegradation. Therefore, PAHs persist for long periods under many natural conditions in the contaminated environment [157]. The major natural source of PAHs in the environment is combustion of biomass. Other significant sources are petroleum and fossil fuels, coal and lignite, and coal tar residue from coal gasification processes. The major industrial sites polluted with PAHs are coal gasification and wood-preserving plants. Some PAHs such as naphthalene are also obtained from the concentration of the high boiling residual oil (and asphalt) derived from crude petroleum refinery processing. These PAHs are mostly used as intermediaries in pharmaceuticals, agricultural products, photographic products, thermosetting plastics, lubricating materials, and other chemical industries [158].

PAHs exist in various combinations that manifest various functions. They are made up of two or more fused benzene rings and some "pentacyclic moieties" in linear, angular, and/or cluster arrangements. The simplest example is naphthalene having two benzene rings side by side while others could vary from 2, 3 and more fused aromatic rings. The United States (US) Environmental Protecting Agency (EPA) proposed a list of 16 PAHs in 1984 as carcinogenic or mutagenic compounds [159], which was adopted by the US government in 1988. Some of these PAHs are shown in Figure 2.13. Further concern on PAHs necessitated the European Union to adopt a legislation in 2005 [160] that provided a list of 15 PAHs (8 in common with US EPA and 7 new compounds) which were of major concern for human health due to their toxic properties (Table 2.1). The general characteristics of PAH includes high melting- and boiling points (they are solid), low vapour pressure, and very low water solubility, decreasing with increasing molecular weight. However, resistance to oxidation, reduction, and vaporization increases with increasing molecular weight. Vapour pressure tends to decrease with increasing molecular weight. PAHs are highly lipophilic and readily soluble in organic solvents. The lower molecular weight PAHs
of 2 or 3 ring groups such as naphthalenes, fluorenes, phenanthrenes, and anthracenes have toxicity that tends to decrease with increasing molecular weight [159].

![Diagram of PAHs](image)

**Figure 2.13:** Structural representations of some PAHs included in the USEPA list [158].
Table 2.1 Chemical structure of the 15 European Union (EU) priority PAHs

<table>
<thead>
<tr>
<th>15 EU priority PAHs</th>
<th>Cyclopenta[c,d]pyrene</th>
<th>Benz[a]anthracene</th>
<th>Chrysene</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-Methylchrysene</td>
<td>Benzo[b]fluoranthene</td>
<td>Benzo[j]fluoranthene</td>
<td></td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>Benzo[a]pyrene</td>
<td>Indeno[1,2,3-c,d]pyrene</td>
<td></td>
</tr>
<tr>
<td>Dibenz[a,h]anthracene</td>
<td>Benzo[g,h,i]perylene</td>
<td>Dibenzo[a,l]pyrene</td>
<td></td>
</tr>
<tr>
<td>Dibenzo[a,e]pyrene</td>
<td>Dibenzo[a,i]pyrene</td>
<td>Dibenzo[a,h]pyrene</td>
<td></td>
</tr>
</tbody>
</table>
The main environmental impact of PAHs relates to their health effects, focusing on their carcinogenic properties. The semi-volatile property of PAHs makes them highly mobile throughout the environment via deposition and re-volatilisation between air, soil and water bodies. Most of the PAHs released in the environment end up being deposited in the oceans and/or subject to long range transport making them a widespread environmental problem. Although PAHs may undergo chemical oxidation, photolysis and volatilization, microbial degradation is the major process affecting PAH persistence in nature [157].

It is therefore desirable in order to put in place adequate clean up programmes for the prevention and remediation of PAHs pollution in the environment to avoid public health hazards. Consequently, companies prone to generate these materials for installation of abatement equipment at factory locations and also at old sites for the purposes of monitoring control and remediation of PAHs are committing a lot of investment. There are limits for workplace exposure for chemicals that contain PAHs such as coal tar and mineral oil. The Occupational Safety and Health Administration (OSHA) has set a limit of 0.2 milligrams of PAHs per cubic meter of air (0.2 mg/m³). The OSHA Permissible Exposure Limit (PEL) for mineral oil mist that contains PAHs is 5 mg/m³ averaged over an 8-hour exposure period. Likewise, the National Institute for Occupational Safety and Health (NIOSH) recommends that the average workplace air levels for coal tar products should not exceed 0.1 mg/m³ for a 10-hour workday, within a 40-hour workweek. There are other limits for workplace exposure for things that contain PAHs, such as coal, coal tar, and mineral oil [158].

Therefore, there is an ever-increasing demand for the determination of trace amounts of these substances at plant sites, water bodies and air. So far, mostly chromatographic methods such as GC-MS or HPLC with fluorimetric detection are used for these purposes [161]. However, these methods are characterized by high investment and running costs. Modern electroanalytical methods are required for the determination of these dangerous chemical carcinogens. The main advantage derivable from this electroanalytical method is a much lower investment and running costs. A study of voltammetric determination of trace amounts of carcinogenic 1-nitropyrene and 1-aminopyrene using a glassy carbon paste electrode by Barek et al. was described recently [162]. A fiber coating from polyaniline (PANI) was
electrochemically prepared and employed for solid phase microextraction (SPME) of some polycyclic aromatic hydrocarbons (PAHs) from water samples. The study revealed that this polymer is a suitable SPME fiber coating for extracting the selected PAHs [156]. The development of more electrochemical devices for these anthropogenic pollutants still remains a big challenge to scientists.

References


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Chapter Three

Analytical Techniques and Experimental Procedures

This chapter gives a synopsis on the different analytical techniques employed, detailed research methodology and general experimental procedures for the chemical and electrochemical preparation, characterization and application of the modified polypyrrole electroactive materials.

3.1 Analytical techniques

The analytical techniques used in this study are electrochemical techniques namely, cyclic voltammetry (CV), Oyster-young square wave voltammetry (OSWV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS); spectroscopic techniques namely Ultra Violet-Visible spectroscopy (UV-Vis), Fourier transform infra red spectroscopy (FTIR), subtractively normalised in-situ Fourier transform infra red spectroscopy (SNIFTIRS); and morphological technique which was mainly scanning electron microscopy (SEM).

3.1.1 Electrochemical techniques

Two broad electrochemical techniques were used in these studies namely: voltammetric and impedimetric techniques. The merits derivable from the techniques used are discussed below.

3.1.1.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is the most widely used electrochemical technique for the characterisation of redox systems. It provides information about the number of oxidation states, as well as qualitative information about the stability of these oxidation states and quantitative information about the rates, mechanisms and the electron transfer kinetics [1]. Modern electroanalytical measurements are normally
performed with software driven potentiostats, two examples of which are shown in Fig. 3.1.

(a) AUTOLAB Voltammetric instrument

(b) CV 50 Voltammetric instrument.

Figure 3.1: Typical electroanalytical instrument used for cyclic voltammetry [2].
In a CV experiment, as in other controlled potential experiments, a potential is applied to the system, and the faradaic current response, resulting from a redox reaction is measured. The potential is cycled between a pre-determined potential window from an initial potential, $E_i$, to a final (switching) potential, $E_f$, at a constant scan rate (ca. from 1 mV/s to a few thousand mV/s). By varying the potential limits, the reactivity of the electrochemical system is probed over a large range of potentials in a single sweep. Also by varying the sweep rate, the kinetics of the reactions and/or mass transfer processes is probed [3]. The potential scan may be terminated at the end of the first cycle or continued for any number of cycles leading to a multisegment voltammogram. The cycling could be done oxidatively (increasing potential) or reductively (decreasing potential) [4]. The forward half of the CV is identical to a linear-sweep voltammogram. When the potential is scanned in a positive direction, the electroactive species at the surface of the electrode is oxidised and if it is scanned in the negative direction, they are reduced. The oxidation generates a current response as a result of the depletion of species at the electrode surface. The plot of the applied potential vs. the resulting currents provides characteristic peak potentials for both oxidation ($E_{p,a}$) and reduction ($E_{p,c}$), and their corresponding peak currents ($I_{p,a}$ and $I_{p,c}$) respectively. The peak width at half the peak current ($E_{p1/2}$) is also sometimes measured. This characteristic feature of the voltammogram provides information about the redox (formal) potential of a system denoted as $E^{o}$ [4].

The chemical processes involved in redox cycling are complicated, thus, the CV could be reversible (limited by diffusion); irreversible (completely limited by kinetics) i.e. the reverse reaction is so slow at electrode potentials larger than the redox potential; or quasi-reversible (partially limited by kinetics) [3]. A redox couple in which both species rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. Figure 3.2 shows typical cyclic voltammogram for the electrochemical oxidation and reduction process. The formal reduction potential ($E^{o}$) for a reversible or quasi-reversible couple is at the mid-point of $E_{p,a}$ and $E_{p,c}$ on the voltammogram and it is commonly determined from equation 3.1 [1, 4].

$$E^{o} = \frac{(E_{p,a} + E_{p,c})}{2} \text{ equation 3.1}$$
The number of electron transferred ($n$) can be determined from the separation between $E_{p,a}$ and $E_{p,c}$ ($\Delta E_p$) using equation 3.2 [1, 4].

$$\Delta E_p = (E_{p,a} - E_{p,c}) = 0.059 / n \quad \text{equation 3.2}$$

Thus, for a one electron process, a $\Delta E_p$ of 0.059 V will be expected.

The number of electrons transferred ($n$) can also be determined via Tafel plots. This plot relates the generated current to the overpotential, $\eta$, in an exponential manner similar to the Arrhenius and Eyring equations. At a fixed temperature, $T$, the Tafel equation is:

$$I = a + b \exp \eta \quad \text{equation 3.3} \quad [1].$$

A plot of $\log_{10} I$ (as ‘y’) against overpotential, $\eta$, (as ‘x’), called Tafel plot is usually linear over a narrow range of potentials and only valid for high overpotential. As a general rule it is stated that the Tafel equation is valid for $\eta > 118/n \text{ mV}$, where $n$ is the number of electrons exchanged [5].
For low overpotentials, the Buttler Volmer approach is applied whereby the net current \( I_{\text{net}} \) from the oxidation and reduction is given by equation 3.4 [1, 4].

\[
I_{\text{net}} = I_o [\exp (\alpha n F \eta/RT) - \exp (\{1-\alpha\} n F \eta/RT)] \quad \text{equation 3.4}
\]

Where \( I_o \) is the exchange current representing the rate constant of electron transfer at zero overpotential, \( \alpha \) is the transfer coefficient, \( F \) is the Faraday's constant, \( R \) is the molar gas constant and \( T \) is the operating temperature in Kelvin. The actual value of this current \( I_{\text{net}} \) is affected by many additional factors, most importantly the concentration of the redox species, the size, shape, and material of the electrode, the solution resistance, the cell volume, and the number of electrons transferred.

Cyclic voltammetry can also provide information about the rate of electron transfer between the electrode and the analyte, and the stability of the analyte in the electrolyzed oxidation states (e.g., do they undergo any chemical reactions). For a thin layer of adsorbed electro active material at the electrode surface undergoing Nerstian reaction, the plot of peak current values versus scan rates for both cathodic and anodic peaks respectively show linear dependence. This is in accordance with Brown-Anson model, equation3.5, from which the surface concentration of the various redox states could be estimated [4, 6, 7].

\[
I_p = n^2 F^2 \Gamma^* A v / 4RT \quad \text{equation 3.5}
\]

\( I_p \) = Peak current for either the oxidation or reduction peak being considered  
\( n \) = Number of electrons transferred  
\( F \) = Faraday constant (96584 C mol\(^{-1}\))  
\( \Gamma^* \) = Surface concentration of the electroactive film bound to the working electrode  
\( A \) = Surface area  
\( v \) = Scan rate (Vs\(^{-1}\))  
\( R \) = Gas constant (8.314Jmol\(^{-1}\)K\(^{-1}\))
T = Temperature of the system (K).

By varying the scan rates (Vs⁻¹) of the process, the diffusion coefficient, \(D_e\), (which tells how rapidly the electroactive species is diffusing through the solution to and from the surface of the working electrode) can be calculated using the Randles-Sevčík equation [4, 7],

\[
I_p = -0.4463 \frac{n F (nF/RT)^{1/2}}{\Gamma^* D_e^{1/2} \nu^{1/2}} \ A
\]

This reduces to equation 3.7 at 25 °C for \(A\) in cm², \(D_e\) in cm²/s, \(\Gamma^*\) in mol/L, and \(\nu\) in V/s, \(I_p\) in amperes

\[
I_p = 2.686 \times 10^5 \frac{n^{3/2} A}{\Gamma^* D_e^{1/2} \nu^{1/2}} \ A
\]

Accordingly, \(I_p\) increases with \(\nu^{1/2}\) and is directly proportional to concentration. The relationship to concentration is of particular interest in analytical applications and in studies of electrode mechanisms. A plot of \(I_p\) versus \(\nu^{1/2}\) should give a straight line from which \(D_e\) can be evaluated. For a reversible system, the values of \(I_{pa}\) and \(I_{pc}\) should be identical for a simple reversible (fast) couple. However, the ratio of the peak currents can be significantly influenced by chemical reactions coupled to the electrode process.

The standard rate constant (\(k^*\)) for electron transfer within the polymer chain could be estimated using Nicholson treatment for a quasi-reversible electrochemical system. The net shape of the voltammetric curves have been shown to depend on a kinetic parameter \(\phi\) which is given by the expression:

\[
\phi = \left[ \frac{(D_O/D_R)^{\alpha/2} k^*}{(\pi n D_e F \nu/RT)^{1/2}} \right]
\]

where for simplicity the diffusion coefficient (\(D_e\)), for the oxidized (O) and reduced (R) forms of the solution phase probe redox couple are equal, i.e. \(D_O = D_R = D_e\); This simplifies to: 

\[\]
\[ k^\circ = \varphi \left( \alpha \cdot n \cdot F \cdot v \cdot \pi \cdot D_e / RT \right)^{\frac{1}{2}} \]  

equation 3.9 \ [7].

For a typical reversible system, \( \alpha = 0.5 \). As the systems turns from reversible to irreversible, there is a transition in the magnitude of \( \alpha \) and \( \Delta E_p \). For \( 0.3 < \alpha < 0.7 \), the \( \Delta E_p \) values are nearly independent of \( \alpha \) and depend only on \( \varphi \). Thus estimates of \( k^\circ \) could be made using the tabulated values of \( \varphi \) for different values of scan rates [4].

A numerical analysis of the diffusion boundary value problem for cyclic voltammetry has established a quantitative analysis of the relationship between the kinetic parameter \( \varphi \) and the voltammetric peak separation \( \Delta E_p \). This has been plotted as a working curve and result summarised for reference purposes in different literatures [4, 7, 8]. While a \( \Delta E_p \) value of 61 mV gives a \( \varphi \) value of 20 at 25°C, the \( \varphi \) values at 63 mV and 212 mV are 7 and 0.10 respectively [4].

3.1.1.2 Oyster-young square wave voltammetry (OSWV)

The theory of SWV was invented by Ramaley and Krause in 1969 [9] but was only extensively developed by Osteryoung and co-workers in 1986 [10]. The technique involves the application of square wave modulation to a constant or nearly constant dc potential, and the current generated is sampled at the end of successive half cycles of the square wave. Three currents are generated, vis: forward current from the forward pulse (\( i_f \)), the reverse current from the reverse pulse (\( i_r \)) and that for the net current (\( I_d \)) vs. the potential on the corresponding staircase tread. The net current serves better analytical usage than the forward and reverse currents because it increases the discrimination against the charging current, since any residual charging current is subtracted out. Figure 3.3 shows the OSWV containing the forward, reverse and reverse currents. The net current is larger than that for the forward and reverse current since it is the difference between them [11]. The peak height is directly proportional to the concentration of the electroactive species and direct detection limits as low as 1 \( \times 10^{-8} \) M is possible as against 5 \( \times 10^{-8} \) M differential pulse voltammetry and 1 \( \times 10^{-5} \) M in cyclic voltammetry [1].

SWV has many advantages over other differential techniques such as much faster scan times, excellent sensitivity, the rejection of background current, high signal to
noise ratio and applicability to a wider range of electrode materials and systems. [12]. Oyster-young square wave voltammetry can play very important role in the characterization of electroactive species with poor, overlapping or ill-formed redox signals in cyclic voltammetry by producing individual, sharp peaks [11].

![Figure 3.3: Typical OSWV for PPyNSA film containing the forward, reverse and reverse currents.](image)

3.1.1.3 Differential pulse voltammetry

Differential pulse voltammetry is one of the voltammetric pulse techniques just as Oyster-young square wave voltammetry (OSWV) and normal pulse voltammetry (NPV) which are largely applicable for trace voltammetric analysis at a working electrode [1]. In DPV, a succession of differential pulses (\(dE/dt\)) of fixed, but small amplitude (10-100 mV) is superimposed on the working electrode. Two currents are generated, one taken immediately before applying the potential pulse and the second is taken late in the pulse. The differential of the two currents is displayed on the potential-current curve. At potentials, well positive of the redox potential, there is no faradaic response to the pulse, so the differential current is close to zero. At potentials
around the redox potential, the differential current reaches a maximum and decreases towards zero, as the current becomes diffusion-controlled. The current response is therefore a symmetrical curve. Figure 3.4 shows a typical differential pulse voltammogramm for a film of polypyrrole doped with 1, 2-naphthaquinone-4-sulphonate (PPyNQS) on a platinum working electrode in an undegassed 0.1 M LiClO₄ at a scan rate of 5 mV/s and 25 mV amplitude. The peaks at the positive potentials are characteristic for polypyrrole while the peaks at the negative potentials are characteristic for dissolved oxygen in the electrolyte solution.

![Figure 3.4](image.png)

**Figure 3.4:** Typical potential-current curve for the anodic and cathodic differential pulse voltammetric scan of polypyrrole in 0.1 M LiClO₄ at a scan rate of 5 mV/s and 25 mV amplitude.

Differential pulse voltammetry is widely used for the identification of any electroactive specie at the electrode surface, which will be largely used in characterising the conducting polymers used in this work. Individual redox specie generates a corresponding symmetrical peak. The potential of the peak can help identify the cation in solution in a similar manner to normal polarography. The peak area is proportional to concentration. The peak height could be used as approximation for the
estimation of an analyte’s concentration using the Osteryoung-Parry equation (equation 3.10) [1].

\[ \Delta I_p = \left( \frac{n^2 F^2 A}{4RT} \right) \left( \frac{D}{\pi t} \right)^{1/2} C_{analyte} \Delta E \] equation 3.10

Where all terms have their usual meaning and \( t \) is the time between pulses. The magnitude of \( \Delta E \) and the rooted term in brackets, \( (D/\pi t)^{1/2} \), implies that the separation of potential and diffusion of analyte to the electrode plays important role in determining the value of \( \Delta I_p \) which increases accuracy of the technique. DPV is very versatile in its scope of application just as the OSWV. Its advantages over NPV are twofold: (i) many analyte could be sampled with a single voltammogram since the analytical peaks for each analyte are well resolved, and (ii) by working with a differential current the sensitivity of the technique is improved. While the lower detection limit for DPV is \( 10^{-8} \) to \( 5 \times 10^{-8} \) M, that for NPV is only \( 10^{-7} \) to \( 10^{-8} \) M [1].

3.1.1.4 Electrochemical Impedance Spectroscopy

In cyclic voltammetry and other dynamic electroanalysis, an applied potential is either constant (potentiostatic) or changing (potentiodynamic) when ramped at a constant rate of \( V = \frac{dE}{dt} \). However, in impedance, a small perturbing potential is applied across a cell or sample that changes in a cyclic sinusoidal manner and generates a current resulting from the overpotential (\( \eta \)) caused by the small displacement of the potential from the equilibrium value. Over a time scale, the averaged over potential is zero. Because the potential is only perturbing, it has the advantage of minimising the concentration change after the experiment. The induced current alternates because the voltage changes in a cyclic manner, and hence the term alternating current (AC). The term impedance is therefore a measure of the ability of a circuit to resist the flow of an alternating current (AC). It is synonymous to resistance (R) used in direct current (DC), which is defined by Ohm’s law (equation 3.11) as the ratio between voltage (E) and current (I) [1, 4].

\[ R = \frac{E}{I} \] equation 3.11
During a controlled-potential electrochemical impedance spectroscopy (EIS) experiment, the electrochemical cell is held at equilibrium at a fixed DC potential, and a small amplitude (5–10 mV) AC wave form is superimposed on the DC potential to generate a response from the equilibrium position. The response to the applied perturbation, which is generally sinusoidal, can differ in phase and amplitude from the applied signal. This response is measured in terms of the AC impedance or the complex impedance, Z, of the system, which permits analysis of electrode process in relation to diffusion, kinetics, double layer, coupled homogeneous reactions, etc [13].

The ratio of the applied voltage (E) over measured current (I) is the impedance of the system (Z = E/I). Since an AC potential is applied to the cell, there will probably be a phase shift by an angle (\(\phi\)) between the applied AC potential waveform and the AC current response. Therefore, the impedance can be represented using a vector diagram (figure 3.5) displaying the in-phase and out-of-phase impedances, the total impedance, and the phase angle (\(\phi\)).

![Figure 3.5: Sinusoidal current response to potential perturbation as a function of time.](image)

Depending on the AC perturbation, the potential and current functions at a particular frequency could be represented by the equations 3.12 and 3.13:
\[ E(t) = E_0 \sin(\omega t) \quad \text{equation 3.12} \]

and,

\[ I(t) = I_0 \sin(\omega t + \phi) \quad \text{equation 3.13}. \]

Where \( E(t) \) is the potential at \( t \), \( E_0 \) is the amplitude of the signal, and \( \omega \) is the radial frequency (radians/second) defined as \( 2 \pi f \) with \( f \) being the frequency in hertz, \( I(t) \) and \( I_0 \) represent the response current signal and amplitude respectively. Using ohms law, an analogous expression for the impedance could be derived by substituting equations 3.12 and 3.13 into equation 3.11 as shown below:

\[ Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} \quad \text{equation 3.14} \]

\[ Z = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad \text{equation 3.15} \]

Since complex number terminology is involved when analyzing impedance spectra, the in-phase and out-of-phase impedances are often referred to as real and imaginary impedances. The complex impedance \( Z \) is made up of a resistive or real part \( Z' \), attributable to resistors (in phase with the applied voltage), and a reactive or imaginary part \( Z'' \), attributable to the contributions of capacitors (out of phase with the applied voltage by \( \pi/2 \)) and/or inductors (out of phase with the applied voltage by \( -\pi/2 \)). This is related to the resistance \( R \), reactance \( X \) and capacitance \( C \) by the equation:

\[ Z = R - j X \quad \text{equation 3.15} \]

where \( X = 1/\omega C \) and \( \omega = 2 \pi f \). \( R \) is the resistance measured in Ohms (\( \Omega \)), \( X \) the reactance, \( C \) the capacitance measured in Farads (\( F \)), \( \omega \) the applied angular frequency measured in rad/s and \( f \) is the frequency measured in Hertz (Hz) [4].

Notational representation of this in terms of \( Z' \) and \( Z'' \) is given by:
\[ Z = Z' - j Z'' \]  

where \( j = \sqrt{-1} \)  

**equation 3.16**

Because \( Z \) is defined by the complex term, \( j \), which determines the contribution of \( Z'' \) to \( Z \), the term *complex impedance* is often used. For a pure resistor that is not having any capacitance, its resistance when determined with a continuous current (DC) is \( R \) because its impedance is frequency independent, \( Z = Z' = R \).

The experimental data collated from an impedance experiment is often presented as *Nyquist plot* of \( Z' \) (usually positive x-axis corresponds to the real impedance), versus \( Z'' \) (usually, the positive y-axis correspond to -\( Z'' \)), over a wide frequency range (normally 100 kHz to 0.1 Hz). Another way of presenting impedance data is a *Bode plot* in which the logarithm of the absolute value of \( Z' \) and the phase (\( \phi \)) are plotted against the logarithm of the frequency (\( f \)) [14]. This could be plotted together or separately. Nyquist plots is more commonly displayed for historical reasons, the data is however often poorly resolved (particularly at high frequencies), and the explicit frequency dependence is not displayed. In contrast, the Bode plot directly displays the frequency dependence; in addition, the data is well resolved at all frequencies, since a logarithmic frequency scale is used.

When the frequency of the AC waveform is varied over a wide range of frequency (ca about \( 10^{-4} \) and > \( 10^6 \) Hz), the impedance obtained for the system is a function of the operating frequency. Spectrums of the resulting impedance at different frequencies do reveal the different electrochemical kinetics involved in the system. While dipolar properties are manifest at the high frequency regions, bulk and surface properties will be evident at intermediate and low frequencies respectively [14]. The total impedance of a system is determined by the impedances of the various components of the electrochemical cell; for example, electron transfer kinetics, diffusion, passivating layers, etc. The relative contribution of the various components typically varies with frequency; for example, electron transfer kinetics may dominate at high frequencies, whereas diffusion may dominate at lower frequencies.

Measuring impedance over a wide frequency range allows processes with different time scales to be detected within the same experiment. The Nyquist plot obtained for
a particular system could therefore be used for both qualitative and quantitative analysis. Some important electrochemical parameters about a NCP can be simultaneously gotten from a single experiment at a known level of charge. This includes charge transfer at the metal (electrode) /film interface, the rate of charge transfer in the film, ohmic resistance, double layer capacitance and redox capacitance of the film and even the potential dependence of the diffusion coefficient for ionic and electronic charge carriers [4, 14]. To achieve this, the practical constraint is choosing the appropriate equivalent circuit and an accurate fitting procedure to obtain the different variables.

While qualitative information could be obtained by mere inspection of the EIS spectrum, quantitative information requires proper use of appropriate software (Z-View or Z-Plot) to model the electrical components of the system to equivalent electrical circuits. One common method is based on the principle of equivalent circuit; that is, the various cell components can be modeled using electronic components (e.g., a resistor for electron transfer kinetics and solution resistance, and a capacitor for the interfacial (double layer) capacitance), and an electronic circuit can be built that gives the same impedance spectrum as the electrochemical cell. This approach requires that each equivalent circuit element corresponds to a component of the electrochemical cell and a good match must exist between the experimental impedance spectrum and the model impedance spectrum over the entire frequency range, otherwise the equivalent circuit has no meaning.

Impedance data is commonly analysed by fitting it to an equivalent circuit model. The frequently used circuit, called the Randles equivalent circuit is composed of different elements such as resistors, capacitors, and inductors joined in series and/or in parallel. Figure 3.6a shows the Nyquist plot for the real impedance (x-axis) and imaginary impedance (y-axis) with low frequency data being on the right side of the plot and higher frequencies are on the left. A typical Nyquist plot for the impedance data obtained on platinum electrode in ferricyanide solution is shown in Fig 3.6b. The semicircular shape is characteristic of a single "time constant". A representative plot of frequency as x-axis versus logarithm of real impedance as y₁-axis, and phase angle as y₂-axis called (Bode plot) is presented in Figure 3.7 for impedance spectra obtained
on the system presented in Fig. 3.6b showing the variation of phase angle and impedance with frequency.

Figure 3.6: Nyquist plot with impedance vector shown as “a” [14] and typical Nyquist plot of Ferricyanide solution on platinum electrode.
Electrochemical Impedance plots often contain several time constants, but often only a portion of one or more of their semicircles is seen. The shape varies depending on the equivalent electrical circuits for the system. Fig. 3.8 is a typical equivalent circuit of a capacitor and a resistor in parallel. This is discussed further underneath.

![Equivalent circuit of a capacitor and a resistor in parallel](image)

**Figure 3.8:** Equivalent circuit of a capacitor and a resistor in parallel (one time constant).

### 3.1.1.4.1 Electrical circuit elements

Any electrochemical cell can be represented in terms of an equivalent electrical circuit that comprises a combination of resistances and capacitances. There could also be
contribution of inductances at very high frequencies. Contributions to the resistance of a cell are the solution resistance (Rs), the charge transfer resistance (Rct), Warburg impedance (Zw) while contribution to the capacitance could be as a capacitor (C) and constant phase element (CPE) [1, 14]. These elements are described briefly underneath.

**Solution resistance (Rs):** The solution resistance is the resistance between the working electrode and the reference electrode. This is indicated as a small offset on the real impedance axis. It is measured at high frequency intercept near the origin of the Nyquist plot. The resistance of an ionic solution depends on the ionic concentration and type of ions the electrolyte is made up, temperature and the geometry of the area in which current is carried. In a bounded area with area A and length l carrying a uniform current the resistance is defined as:

\[ R = \frac{\rho l}{A} \]  

Equation 3.17

The conductivity of the solution, \( k \), is more commonly used in solution resistance calculations. Its relationship with solution resistance is:

\[ R = \frac{1}{k} = \frac{l}{kA} \]  

Equation 3.18

The units for \( k \) are siemens per meter (S/m). The siemens is the reciprocal of the ohm, (1 S = 1/ohm).

**Charge transfer resistance (Rct):** This is the resistance associated with the charge transfer mechanisms for electrode reactions. It is the resistance to electron transfer at the electrode interface. It is deduced from the kinetically controlled electrochemical reaction at low over-potentials. From the Buttler-Volmer equation (equation 3.4), the net current \( (I_{net}) \) from the oxidation and reduction reactions is:

\[ I_{net} = I_o \left[ \exp (\alpha n F \eta /RT) - \exp \left( (1-\alpha) n F \eta /RT \right) \right] \]  

Equation 3.4 [1, 4].

When \( (n F \eta /RT) \) is well below unity, the Buttler-Volmer equation could be linearised to obtain
\[ I = I_o n F \eta / RT \quad \text{equation 3.19} \quad [4] \]

And also in terms of over-potential (\( \eta \)) and concentration terms for oxidised, reduced and equilibrium states for a one electron redox process,

\[ \eta = \frac{RT}{F} \left[ \frac{C_O^{(0,t)}}{C_O^*} - \frac{C_R^{(0,t)}}{C_R^*} + \frac{i}{i_o} \right] \quad \text{equation 3.20} \quad [4]. \]

Hence, when the over-potential, \( \eta \), is very small and the electrochemical system is at equilibrium, the expression for the charge transfer resistance for an n-electron process changes into:

\[ R_{ct} = \frac{RT}{n F i_o} \quad \text{equation 3.21} \quad [3, 4]. \]

From this equation the exchange current density (\( I_o \)) can be calculated when \( R_{ct} \) is known. The charge transfer resistance is estimated from the diameter of the semicircular region on the real impedance axis of the Nyquist plot. When the chemical system is kinetically sluggish, the \( R_{ct} \) will be very large and may display a limited frequency region where mass transfer is a significant factor. However, if the system is so kinetically facile, and the mass transfer always plays a role, the semicircular region is not well formed [4].

**Warburg Impedance (\( Z_W \)):** This is the resistance associated with the diffusion of ions across the electrode/electrolyte interface. This impedance is associated with the difficulty of mass transport of electroactive species [13]. Layers of ions at the electrode interface behave like an RC element (i.e. a resistor and a capacitor in parallel) and this produces infinite sum of RC elements called the Warburg impedance. It is characterised as a linear portion at an angle of 45° and slope of unity on the Nyquist plot and a slope of -0.5 on the Bode plot [1].

**Capacitor (C):** The capacitance (\( C \)) is the ability of an electrochemical system to store or retain charge. An 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. The potential at the terminals of this double
layer (capacitor) is proportional to its charge. The impedance of a capacitor is given by the equation

\[ Z_{(C)} = Z'' = 1/j\omega C \quad \text{equation 3.22} \]

**Constant phase element (CPE):** A constant phase element is a non-intuitive circuit element that was invented while looking at the response of real-world systems. Often, a CPE is used in a model in place of a capacitor due to deviation of capacitance parameters from expected values. In some systems the Nyquist plot was expected to be a semicircle with the center on the x-axis. However, the observed plot may be an arc of a circle with the center being some distance below the x-axis. These depressed semicircles have been linked to a number of phenomena, depending on the nature of the system being investigated. This behaviour was traced to the non-homogeneity of the system or that there is some distribution (dispersion) of the value of some physical property of the system. The impedance of a CPE is represented by equation

\[ Z = A(j\omega)^{-\alpha} \quad \text{equation 3.23 [15]} \]

\[ = 1/(C j\omega)^n \quad \text{equation 3.24 [13]} \]

This is similar to that of a capacitor except that the constant \( A = 1/C \) (the inverse of the capacitance) and the exponent \( \alpha = 1 \) for a true capacitor. For a constant phase element, the exponent \( \alpha \) is less than one. When \( \alpha = 0.5 \), a 45° line is produced on the complex plane graph and could be used for an infinite length of Warburg element. During circuit fitting, the CPE is defined by two values, i.e., the capacitance, \( C \), and the CPE exponent, \( \alpha \), which has a value between 0.5 and 1 for a non-ideal capacitor. If \( n \) equals 1, the equation is identical to that of a capacitor and smaller values can be related to surface roughness and in-homogeneities, which lead to frequency dispersion.

### 3.1.1.4.2 Impedance modeling using equivalent electrical circuit

Jiri Janata [16] has identified three major points to be considered in equivalent circuit analysis for chemiresistors as follows:
(a) Description of individual physical processes by realistic electrochemical circuit elements;
(b) Arrangement of this elements in a rationally constructed equivalent circuit;
(c) Optimisation of the values of the elements in the equivalent circuit such that the overall transfer function (response) matches the response of the real cell.

The external current flowing in an electrochemical cell (voltaic cell) made up of two metal electrodes A and B (figure 3.9) serving as contact to an electrolyte solution of their salt is given by the equation

\[ I_{\text{cell}}(\omega) = \frac{E_{\text{cell}}(\omega)}{Z_{\text{cell}}(\omega)} \]

\[ \text{equation 3.25} \ [16] \]

![Figure 3.9: General representation of an electrochemical cell.](image)

The overall cell impedance is sum of the impedances in the path of the cell current,

\[ Z_{\text{cell}}(\omega) = Z_A + Z_B + Z_{\text{Electrolyte}} \]

\[ \text{equation 3.26} \ [16] \]

Considering the commonest combination of a capacitor and a resistor arranged in parallel, the flow of current will be divided into two branches, namely: \( I_R \) and \( I_C \) in line with Kirchoff’s law.

\[ I_{\text{Cell}} = I_R + I_C \]

\[ \text{equation 3.27} \]
Impedance spectrums are often modeled using an electrical circuit which produces a similar spectrum as that from the experimental data. The electrical components (resistors, capacitors, inductors, etc) and some 'components' that have no electrical analogue (constant phase elements, Warburg impedances, etc) are then matched to physical characteristics of the measured cell [13, 17]. Some of the following predefined elements are used in impedance fitting during the course of this work.

R Resistor
C Capacitor
L Inductor
CPE Constant Phase Element
Ws Warburg - Short Circuit Terminus
Wo Warburg - Open Circuit Terminus

The impedance of a resistor is constant at all frequencies. A pure resistor is usually represented as a single-point on the real impedance (Z’) axis of the Nyquist plot. However, the impedance of a capacitor decreases as the frequency is increased. The C values are infinitive at frequency of zero but having zero value at infinite frequency. Capacitors have only the imaginary component of impedance, the real impedance is zero. The impedance of an inductor increases as frequency increases.

Notational and mathematical descriptions of these behaviours are presented underneath. For all equations: \( j = \sqrt{-1} \), and \( \omega \) = angular frequency of the AC signal.

1. R – Resistor (\( Z = R \))

   \[
   Z' = R \quad Z'' = 0
   \]

2. C – Capacitor (\( Z_{(C)} = Z'' = 1/j\omega C \))

   \[
   Z' = \frac{1}{j\omega C} \quad Z'' = 0
   \]
\[ Z' = 0 \quad Z'' = 1/j\omega C \]

3. \( L = \text{Inductor} \quad (Z = j\omega L) \)

\[ Z' = 0, \quad Z'' = \omega L \]

4. \( \text{CPE} = \text{Constant Phase Element} \)

\[ Z = \frac{1}{(Cj\omega)^\alpha} \]

For kinetically favoured reactions, \( Rct \rightarrow 0 \) and \( Zw \) predominates and for difficult reactions \( Rct \rightarrow \infty \) and \( Rct \) predominates. When other steps are involved in the electrode process, homogeneous or heterogeneous, more complicated circuits are involved. A simple circuit commonly used is the Randles circuit (Figure 3.10).

**Figure 3.10**: Randles circuit for a simple electrochemical cell. \( Rs \) is the solution resistance, \( Z \) is the impedance of the electrode process and \( Cd \) is the double layer capacity.

Various combinations of appropriate circuits in series or/and parallel will be explored in modeling the reactivities at wide range of frequencies for the polypyrrole materials and sensors using Z-View software.

The impedance and capacitance generated by the perturbation of a stationary working electrode with small AC voltage (5 – 10 mV) amplitude provides bulk and interfacial electrical information on the material connected to the transducer. When this perturbation is done over a large range of frequencies (ca. \( 10^6 \) to \( 10^4 \) Hz), a spectrum
for the various electro-kinetics involved in the system will be reflected at different frequency regions [4]. While dipolar properties of solid materials will be revealed at high frequencies, bulk and surface properties becomes evident at medium and low frequencies [14]. In the production of an impedance sensor for selective hydrocarbon gas sensing, Hagen et al used a normalized impedance parameter $S_n$, to follow the interfacial reaction at a novel zeolite based electrode [18]. The methodology involved measuring deviations of the magnitude of $Z$ at a time $t$ ($Z_t$) from a value without hydrocarbon at time $t = 0$, ($Z_0$) divided by the hydrocarbon concentration at time $t = t$, ($Z_t$). The sensor effect in this work is based on similar normalized real impedance ($S_n$), and/or that of the normalized real capacitance ($K_n$) as shown in equation 3.28 and 3.29.

$$S_n = \frac{|Z_t| - |Z(t = 0)|}{|Z(t = 0)|} \quad \text{equation 3.28 [18]}$$

$$K_n = \frac{|C_t| - |C(t = 0)|}{|C(t = 0)|} \quad \text{equation 3.29 [18]}$$

### 3.1.2 Spectroscopic techniques (UV-Vis, FTIR, SNIFTIRS)

Two broad spectroscopic techniques were employed in this study, namely: Ultra Violet-Visible spectroscopy (UV-Vis) and Fourier transform infra red spectroscopy (FTIRS). In-situ FTIR studies were also carried out using substructively normalised in-situ Fourier transform infra red spectroscopy (SNIFTIRS).

#### 3.1.2.1 Ultra Violet-Visible spectroscopy (UV-Vis)

UV – Vis absorption spectra were recorded at room temperature on a GBC UV/Vis 920 spectrophotometer (GBC Scientific Instruments, Australia) between 200 and 900 nm using a 1-cm path length quartz cuvette and 99.6% dimethyl sulfoxide (DMSO) or dimethyl formamide (DMF) as reference solvent. UV-Vis measurements were made with the filtrate obtained from dispersions of the polymer materials in appropriate
solvent. Spectra obtained in each case were processed and investigated for characteristic absorptions that could be linked to the electrochemistry of the materials. The band gap peculiarities of the materials were explored using the wavelengths of maximum absorption.

3.1.2.2 Fourier Transform Infra Red (FTIR)
The Fourier Transform Infra Red (FTIR) spectra were recorded on a Perkins Elmer FT-IR Spectrometer, Paragon 1000PC. In each case, less than 0.0010 g of each polymer was ground in a medium of 0.4 g of dried KBr salt, and placed in the pallet to obtain a fairly transparent pellet. The spectra were recorded in the wavenumber region of 400 to 4000 cm\(^{-1}\). The characteristic set of absorption bands in the spectrum were used to identify various functional groups predominating in the various polymeric states.

3.1.2.3 Subtractively Normalized Interfacial Fourier Transform Infrared Spectroscopy (SNIFTIRS)\[19, 20, 21\]
Subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) measurements were performed in the staircase mode using a fully evacuated FTIR spectrometer (Bruker IFS113v) fitted with a mercury cadmium telluride (MCT) photo detector and Ge/KBr beam splitter. Thin film of polypyrrole was subjected to SNIFTIRS analysis using a three-electrode cell similar to the cyclic voltammetry set-up. The reflectance data on the film at the working electrode was collected at different applied potential using a manually controlled potentiostat. A calomel reference electrode was used and a platinum ring electrode fitted on the inside of the custom made FTIR electrochemical cell, served as counter electrode. During the in situ measurements of FTIR spectra the surface of the working electrode was positioned very close to the CaF\(_2\) window and parallel to it in order to limit the influence of solvent on the spectra.

Spectra were obtained at potentials from 0 mV to 600 mV at 100 mV intervals. Spectra were also recorded at selective potentials in the reverse direction as a check on the reversibility of the modified polymer. Spectra were obtained by Fourier transformation after averaging 200 interferograms acquired at each potential, using p-
polarised radiation. Infrared spectra have been normalized with respect to the reference spectrum collected at 0 mV and are displayed as $\Delta R/R$ difference spectra (the ratio of the signals obtained at potentials $E_i$ and $E_{ref}$ and that obtained at the reference potential $E_{ref}$) in units of reflectance, since no logarithm was applied [20]. Subtractively normalized in-situ FTIR spectra obtained in this way therefore, contain only information of the molecular changes occurring from modification of the oxidation state of the polymer. Negative bands were interpreted as indicative of absorption by species generated as the potential is changed to $E_i$, while upward peaks were interpreted as the disappearance of initial species [21].

3.1.3 Morphological technique (SEM)

Scanning electron microscopy was used for morphological investigation in this study. Polypyrrole samples were examined under a scanning electron microscope (Hitachi X650 Micro-analyzer) with interchangeable accelerating voltages of 10kV to 30kV for optimum sensitivity. In the SEM experiment, about 0.01g of the polypyrrole sample was spiked onto a carbon coated sample holder charged with gold to improve surface electrical conductivity. The charged sample is subsequently transferred into the micro-analyzer where it is transversed by electron beam. The signals produced are collected by an appropriate detector, amplified and displayed on the cathode ray tube at different magnifications. The magnification of the image is the relationship between the length of the scan line on the specimen and that on the cathode ray tube. Energy Dispersive X-ray (EDX) spectra and the elemental analysis for carbon, oxygen and sulphur were captured on the polymers micrograph by stigmation of the relevant area on the micrograph where the nanoparticles were assayed.

3.2 Chemical synthesis procedures and characterization of polypyrrole nanomaterials.

The general experimental procedure used for the chemical synthesis of polypyrrole was as described in literature [22-26]. This involved usage of different dopants, temperature, concentrations of dopant and oxidant in the mother liquor, etc. Polypyrrole was prepared from distilled water, hydrochloric acid, β-naphthalene sulphonic acid, sodium salt of 1, 2-napthaquinone-4-sulphonic acid, tungsten oxide and zirconium oxide. The characterisation techniques are as described previously.
3.2.1 Chemicals

All chemicals used in this study were purchased from Sigma – Aldrich (Pty) Ltd., South Africa. The pyrrole (98%) was re-distilled at reduced pressure and saturated with argon atmosphere and stored in 1 mL ampoules in the dark at 4 °C. β-naphthalene sulphonic acid (70%), sodium salt of 1, 2-napthaquinone-4-sulphonic acid (BDH laboratory reagent), ammonium peroxodisulfate (98%), acetone (99.8%), hydrochloric acid (32%), and methanol (99.8%) were used without further treatment. Deionised-distilled water used was prepared with Milli-Q water purification apparatus (Millipore). Solvents used for spectroscopic studies are 99.6% dimethyl sulfoxide (DMSO) or N, N-Dimethylformamide (DMF)-A.C.S spectrophotometric grade.

3.2.2 Chemical synthesis of β-naphthalene sulphonylic acid doped polypyrrole (PPyNSA); polypyrrole from distilled water (PPyDW); and polypyrrole from HCl (PPyHCl)

A series of polypyrroles was synthesized by varying the reaction conditions reported for the chemically synthesized polypyrrole doped with dodecyl-benzene sulphonylic acid (DBSA) [22, 23]. β-Naphthalene sulphonylic acid was used as surfactant and dopant [24, 25, 26]. In a typical procedure for the preparation of PPyNSA from a dopant to monomer mole concentration ratio (d/m) of 0.8 and an oxidant (APS) to monomer concentration ratio (o/m) of 0.2, 1.059 mL (0.015 mol) of pyrrole was dissolved and stirred in 20 mL aqueous solutions of 3.5696 g (0.012 mol) of NSA at 60 °C while stirring for 15 min. The reaction solution was cooled and 10 mL aqueous solution of oxidant (APS) containing 0.7607 g (0.0030 moles), was added and stirred for 24 hr at 0 °C. The beakers were rinsed with distilled water to make up the total volume of liquor to 50 mL. Similarly various polypyrroles were synthesized using d/m mole concentration ratios of 0.5 and 1 and o/m mole concentration ratios of 0.5 and 1 at 0 °C and room temperature of 25 °C. Control experiments were performed in NSA-free aqueous solutions (HCl or water) of the monomer to produce NSA-free polypyrroles tagged PPyDW or PPyHCl. Polymerization process was terminated in each case by the addition of excess methanol and the liquor allowed to age. The resulting polypyrrole precipitate was vacuum filtered and washed sequentially with excess distilled water, methanol and acetone until a colourless filtrate was obtained.
The precipitates obtained were dried in a vacuum oven at 25 °C for 12 hours. The apparent yield (g/mL) was determined by calculating the weight (g) of dry powder to initial volume (mL) of monomer.

The table showing relative amounts of materials used for the separate preparations is presented underneath (Table 3.1). The results from these syntheses were used to investigate the following:

- Effect of pH on polypyrrole synthesis
- Effect of temperature on polypyrrole synthesis
- Effect of type, presence and concentration of dopant on polypyrrole synthesis
- Effect of concentration of oxidant on polypyrrole synthesis
- Morphological examination of polypyrrole from different synthetic conditions
- Spectroscopic examination of polypyrrole from different synthetic conditions
- Electrochemistry and application of chemically synthesised polypyrrole
Table 3.1: Table of relative amounts of materials used for chemical synthesis of PPyNSA, PPyDW and PPyHCl.

<table>
<thead>
<tr>
<th>Code</th>
<th>Pyrrole used</th>
<th>NSA/dopant used</th>
<th>APS used</th>
<th>Ratios</th>
<th>pH</th>
<th>color change</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSA-1</td>
<td>1.059 mL (1.5 x 10^{-3} mol)</td>
<td>3.4620 g (1.5 x 10^{-3} mol)</td>
<td>0.7607 g (3.0 x 10^{-3} mol)</td>
<td>d/m (1.00) o/m (0.20)</td>
<td>1.4</td>
<td>Milky white to black</td>
</tr>
<tr>
<td>NSA-2</td>
<td>1.059 mL (1.5 x 10^{-3} mol)</td>
<td>3.5696 g (1.2 x 10^{-3} mol)</td>
<td>0.7607 g (3.0 x 10^{-3} mol)</td>
<td>d/m (0.80) o/m (0.20)</td>
<td>1.50</td>
<td>Milky white to black</td>
</tr>
<tr>
<td>NSA-3</td>
<td>1.059 mL (1.5 x 10^{-3} mol)</td>
<td>2.2310 g (7.5 x 10^{-3} mol)</td>
<td>0.7607 g (3.0 x 10^{-3} mol)</td>
<td>d/m (0.50) o/m (0.20)</td>
<td>1.70</td>
<td>Milky white to black</td>
</tr>
<tr>
<td>DW</td>
<td>1.059 mL (1.5 x 10^{-3} mol)</td>
<td>(Synthesis in distilled water)</td>
<td>0.7607 g (3.0 x 10^{-3} mol)</td>
<td>d/m (0.00) o/m (0.20)</td>
<td>1.80</td>
<td>White to black</td>
</tr>
<tr>
<td>HCl-1</td>
<td>1.059 mL (1.5 x 10^{-3} mol)</td>
<td>(Synthesis in 0.1 M HCl)</td>
<td>0.7607 g (3.0 x 10^{-3} mol)</td>
<td>d/m (&lt;0.10) o/m (0.20)</td>
<td>1.69</td>
<td>White to black</td>
</tr>
<tr>
<td>HCl-2</td>
<td>0.529 mL (7.5 x 10^{-3} mol)</td>
<td>6.0 mL of 1M HCl (6.0 x 10^{-3} mol)</td>
<td>0.3457 g (1.5 x 10^{-3} mol)</td>
<td>d/m (0.80) o/m (0.20)</td>
<td>0.22</td>
<td>White to black</td>
</tr>
<tr>
<td>HCl-3</td>
<td>0.529 mL (7.5 x 10^{-3} mol)</td>
<td>3.8 mL of 1M HCl (1.5 x 10^{-3} mol)</td>
<td>0.3457 g (1.5 x 10^{-3} mol)</td>
<td>d/m (0.50) o/m (0.20)</td>
<td>0.44</td>
<td>White to black</td>
</tr>
</tbody>
</table>
3.2.3 Chemical synthesis of 1, 2-naphthaquinone-4-sulfonate doped polypyrrole (PPyNQS)

Using the same experimental procedure as in 3.2.2 above, 1,2-naphthaquinone-4-sulfonate doped polypyrrole (PPyNQS) were prepared using the sodium salt of 1, 2-naphthaquinone-4-sulphonic acid as the surfactant dopant and pyrrole monomer in aqueous solution of hydrochloric acid (acting as the supporting electrolyte). It has been observed that when a chemical material which on its own could orchestrate the oxidation of monomer is used as dopant in very small amounts, the subsequent polymerisation would be on the nanofibre seeds of the dopant and not necessarily on the surfactant acting as a polymerisation template [27]. Usage of NQS has intrinsic property of being able to pre-oxidize pyrrole to form nanofibres which generate the bulk polymer with further oxidation with the APS, or with the application of potential. Following the over-oxidation observed in the use of a d/m ratio of 0.8, and o/m ratio of 0.2, lower doping ratios were explored to arrive at an optimised d/m ratio of 0.05 and o/m ratios of 0.2 and 1. This study investigated preparations using d/m mole concentration ratios of 0.8 and 0.05; and o/m mole concentration ratios of 1.0 and 0.2 at 0 °C based on the optimised conditions established from 3.2.2. Table 3.2 presents the summary of relative amounts of materials used for the preparations.

In a typical preparation of PPyNQS using d/m mole concentration ratios of 0.8 and o/m mole concentration ratios of 1.0 at 0 °C, 0.529 mL (0.0075 mol) of pyrrole was dissolved and stirred in 20 mL aqueous solutions 1.540 g (0.0060 mol) of NQS at 60 °C while stirring for 15 min. The reaction solution was cooled and 10 mL aqueous solution of oxidant (APS) containing 1.7287 g (0.075 mol), was added and stirred for 24 hr at 0 °C. Similarly, using d/m mole concentration ratios of 0.8 and o/m mole concentration ratios of 0.2 at 0 °C, 0.529 mL (0.0075 mol) of pyrrole was dissolved and stirred in 20 mL aqueous solutions 1.540 g (0.0060 mol) of NQS at 60 °C while stirring for 15 min. After cooling, 10 mL aqueous solution of oxidant (APS) containing 0.3457 g (0.0015 mol), was added and stirred for 24 hr at 0 °C. Synthesis using d/m mole concentration ratios of 0.05 and o/m mole concentration ratios of 0.2 at 0 °C involved use of 0.529 mL (0.0075 mol) of pyrrole and 0.0982 g (3.776 x 10⁻⁴ mol) of NQS as described earlier. Control experiments were performed in NQS-free aqueous solutions of the monomer to produce NQS-free polypyrroles tagged PPyDW.
Polymerization process was terminated in each case by the addition of excess methanol and the liquor allowed to age. The resulting polypyrrole precipitate was vacuum filtered and washed sequentially with excess distilled water, methanol and acetone until a colourless filtrate was obtained. The precipitates obtained were dried in a vacuum oven at 25 °C for 12 hours. The apparent yield (g/mL) was determined by calculating the weight (g) of dry powder to initial volume (mL) of monomer.

Table 3.2: Table of relative amounts of materials used for chemical synthesis of PPyNQS.

<table>
<thead>
<tr>
<th>Code</th>
<th>Pyrrole used</th>
<th>NQS/dopant used</th>
<th>APS used</th>
<th>Ratios</th>
<th>pH</th>
<th>color change</th>
</tr>
</thead>
<tbody>
<tr>
<td>NQS</td>
<td>0.529 mL (7.5 x 10⁻³ mol)</td>
<td>1.540 g (6.0 x 10⁻³ mol)</td>
<td>0.3457 g (1.5 x 10⁻³ mol)</td>
<td>d/m (0.80) o/m (0.20)</td>
<td>1.41</td>
<td>Dark brown to black</td>
</tr>
<tr>
<td>NQS</td>
<td>0.529 mL (7.5 x 10⁻³ mol)</td>
<td>0.0982 g (3.776 x 10⁻⁴ mol)</td>
<td>0.3484 g (1.5 x 10⁻³ mol)</td>
<td>d/m (0.05) o/m (0.20)</td>
<td>1.40</td>
<td>Yellowish brown solution to black</td>
</tr>
<tr>
<td>NQS</td>
<td>0.529 mL (7.5 x 10⁻³ mol)</td>
<td>0.0982 g (3.776 x 10⁻⁴ mol)</td>
<td>1.745 g (7.5 x 10⁻³ mol)</td>
<td>d/m (0.05) o/m (1.00)</td>
<td>1.43</td>
<td>Yellowish brown solution to black</td>
</tr>
</tbody>
</table>

3.2.4. Chemical synthesis of metal oxide doped polypyrrole (PPyMO) using Tungsten oxide (WO₃) and Zirconium oxide (ZrO₂)

Similar procedure as used for PPyNSA and PPyNQS was employed in preparing polypyrrole composites using two separate metal oxides, namely tungsten (VI) oxide (WO₃) and zirconium (IV) oxide (ZrO₂). Table 3.3 and 3.4 presents the reacting materials used for the synthesis of PPyWO₃ and PPyZrO₂ respectively.
3.3 Electrochemical synthesis and characterization procedures

3.3.1 Apparatus

All voltammetric experiments (CV, OSWV, and DPV studies) were carried out with a BAS 50W electrochemical workstation (Bioanalytical Systems, Lafayate, IN, USA) at
room temperature. Electrochemical impedance spectroscopy (EIS) measurements were performed with a PGZ402 Voltalab Analyzer (Radiometer Analytical S.A, France). A conventional three-electrode cell was used. The electrodes were a 0.0201 cm² platinum disc or 0.0707 cm² glassy carbon disc as working electrode (WE), a platinum wire auxiliary electrode (AE) and a Ag/AgCl (3 M NaCl type) reference electrode (RE). The WE was cleaned by polishing on slurries of 1.0 μm, 0.3 μm and 0.05 μm alumina powders (Buehler, IL, USA) placed on individual alumina pads, and rinsed with deionised water obtained by passing distilled water through a Milli-Q water purification apparatus (Millipore). The surface of the disc WE was polished by using circular motions on the pad containing 1.0 μm followed by 0.3 μm slurry and then 0.05 μm slurry. Intermittently between usages, the electrodes were treated in hot concentrated H₂SO₄ and 30% H₂O₂ and washed with distilled deionised water. The counter electrode (AE) was cleaned between each experiment by heating in a Bunsen flame, washed and rinsed with copious amount of deionised water. The reference electrode was rinsed in deionised water between each experiment.

3.3.2 Electrochemical synthesis procedures of modified polypyrrole

While bulk quantities of intrinsically conducting polypyrrole are prepared from chemical synthesis, thin films of the polymer is preferably electrosynthesised on suitable working electrodes by careful control of the nature of electrolyte, dopants, anodes and electrochemical window. Careful control of film thickness and extent of oxidation is very crucial during processing to avoid over-oxidation of polypyrrole and subsequent loss of electroactivity. Potentiodynamic and potentiostatic polymerisation methods were used. However, the potentiodynamic approach was preferred as it gave more uniform and reproducible results during the course of the research. Potentiostatic approach was explored during the optimisation of processing conditions for PPyNSA.

3.3.3 Electrolyte and potential window for polypyrrole synthesis

An initial screening for an appropriate choice of electrolyte for the electrosynthesis and characterisation of polypyrrole involved use of different concentrations of hydrochloric acid and sulphuric acid. Films of polypyrrole were prepared from 0.1 M
solutions of freshly distilled pyrrole in an ionic solution of 0.1 M HCl with or without other dopants such as surfactants metal oxides. The choice of 0.1 M HCl was based on the clear and unambiguous potential window between -400/700 mV which allowed for characterisation of peaks resulting from polypyrrole within the same potential window. Use of sulphuric acid (H$_2$SO$_4$) as electrolyte was marred with multiple peaks resulting from the dual ionisation of the dibasic acid at low scan rates. The choice of an electrolyte concentration of 0.1 M HCl was based on the finding that higher concentration of 0.5 M and 1M HCl causes undesirable and accelerated oxidation of the pyrrole monomer before application of potential. Besides, ion transportation that is required for effective polymerisation takes place better in more dilute solutions according to Debye Huckel theory. It was the satisfactory performance of the 0.1M HCl as electrolyte/supporting electrolyte that warranted its choice as the electrolyte medium in this work. In some application stage use of 0.05 M HCl or 0.01 M HCl was used as reaction medium for sensor reaction.

Potentiodynamic polymerisation of polypyrrole using a potential limit of 500 mV or less does not generate any polymer. A minimum potential of 600 mV must be applied to initiate the polymerisation process. Care was taken to avoid over-oxidation of the polymer by growing the film at the lowest possible upper potential limit between 600 mV to a maximum of 800 mV. At about 850 mV, the irreversible oxidation of polypyrrole set in. This was in agreement with literature [28]. Further care to avoid over-oxidation of the polymer was to purge the electrolyte properly by de-gassing with a gentle flow of argon gas for 15 min prior to usage and keeping the argon atmosphere on the electrolyte during polymerisation and characterisation processes. The films were grown potentiodynamically with a scan rate of 50 mV/s. In most cases a lower and higher scan rates from this do not generate desirable quality of film. The electrosynthesised films were dried in air for about 2 min prior to characterisation in fresh hydrochloric acid solution.

3.3.4 Polypyrrole electrosynthesis from aqueous solution of HCl and product characterization.

The polypyrrole films were prepared by potentiodynamic cycling from 0.1M pyrrole in 0.1M HCl which had been properly ultrasonicated. Depending on the electrode
material, appropriate potential window were chosen for polymerization and characterization. All the electrochemical characterization (CV, OSWV, DPV, EIS) were done in an electrolyte solution of 0.1M HCl.

3.3.5 Polypyrrole electrosynthesis from aqueous solution of β-naphthalene sulphonic acid and product characterization.

The polypyrrole films modified with β-naphthalene sulphonic acid were prepared by potential cycling from a solution containing the 106-μL pyrrole-monomer (0.0015 mol) and 0.0893 g of β-naphthalene sulphonic acid -dopant (0.0003 mol) respectively in 15 mL of 0.1 M HCl or 0.05 M HCl. This d/m concentration ratio of 0.2 gave a fair trend of electropolymerisation of conductive polymer after several attempts to electropolymerise using higher ratios as used for chemical synthesis failed. The polymerization and characterization of PPyNSA were carried out separately on glassy carbon electrode (GCE) and platinum (PtE) disc electrodes at a scan rate of 50 mV/s using an optimised potential window of -600/+800 mV in 0.05 M HCl. While limited interrogation could be achieved using voltammetric techniques, more intuitive findings were obtained using EIS.

All the electrochemical characterizations (CV, OSWV, DPV, EIS) were done in an electrolyte solution of 0.1M HCl.

3.3.6 Polypyrrole electrosynthesis from aqueous solution of 1, 2-naphthaquinone-4-sulfonate and product characterization (PPyNQS)

A thin film of conducting polypyrrole was grown under potentiodynamic conditions from a solution containing the 350-μL pyrrole monomer (0.0050 mol) and 0.130 g of the sodium salt of 1, 2-naphthaquinone-4-sulphonic acid-dopant (0.0005 mol) respectively in 50 mL of 0.05 M HCl. This solution is made up of a dopant to monomer concentration ratio of 0.1. Higher d/m ratios caused over-oxidation of pyrrole. The solution from which the film was generated was then replaced with a fresh electrolyte solution of 0.05 M HCl, in which all cyclic voltammetry experiments were then performed. The potential window used for the polymerization and characterization studies was -400 mV to 700 mV vs. Ag/AgCl. OSWV were
performed at 5 Hz at 25 mV square wave amplitude, and a potential step of 4 mV from an initial potential, \( E_i \), of -400 mV to a final potential, \( E_f \), of 700 mV. DPV experiments were performed at scan rates of 5, 10 and 20 mV at pulse amplitude of 25 mV. Similarly EIS interrogation of the electrochemical behaviour of the electrosynthesised film was done at different stepping potentials.

### 3.3.7 Polypyrrole electrosynthesis from aqueous solution of metal oxide of tungsten oxide and zirconium oxide

The exploration of the electrosynthesis of polypyrrole films modified with tungsten oxide or zirconium oxide by potential cycling using platinum and glassy carbon electrodes was inconclusive. A solution containing 0.529 mL (0.0075 mol) of pyrrole and 1.391 g (0.0060 mol) of tungsten oxide in 50 mL of 0.1 M HCl was used for PPyWO\(_3\). Similarly the preparation of the PPyZrO\(_2\) was explored using a solution containing 0.529 mL (0.0075 mol) of pyrrole and 0.740 g (0.0060 mol) of zirconium oxide in 50 mL of 0.1 M HCl. The optimisation of the polymerisation conditions for the attainment of conductive polymer on the electrode surface was inconclusive.

### 3.3.8 Electrochemical characterization of chemically synthesised polypyrrole

Thin film of the chemically synthesized polypyrrole were generated from the aqueous solution of the material via adsorption at the glassy carbon electrode (GCE) being used as the working electrode. A 1- mL cell containing de-aerated saturated paste of 0.025 g of the black polypyrrole powder in 0.5 mL 0.1M HCl was cycled 20 times at 50mV/s from -500 to 1000 mV. The GCE modified with polypyrrole was characterized by multiscan rate CV, OSWV, DPV and EIS in de-aerated 0.1M HCl. OSWV was performed at 50 mV square wave amplitude, and 2 mV potential step from an initial potential, \( E_i \), of -400 mV to a final potential, \( E_f \), of 900 mV. The forward, reverse and net square wave responses were plotted for frequencies of 2, 3, 4 and 5 Hz. DPV experiments were performed at scan rates of 5 and 10 mVs\(^{-1}\) within the same potential window. EIS measurements were performed using perturbation voltage amplitude of 10 mV at different fixed potentials from -600 to 1000 mV in 100 mV or 200 mV intervals during sequential frequency scan from \( 10^5 \) to \( 10^1 \) Hz at room temperature of 25 °C.
3.4 Sensor development

The test application using some of the prepared polymers as sensor materials for some common pollutants in waste waters are presented underneath. The test applications were based on amperometric and impedimetric transduction techniques.

3.4.1 Chemicals

The chemicals used as analytes in the test application of the sensor materials are phenol (99%), benzidine (>98.0%) and naphthalene (99%) which were supplied by Sigma – Aldrich (Pty) Ltd., South Africa.

3.4.2 Phenol sensing with GCE/PPYNSA (Amperometry)

Different concentrations of phenol were analysed in acidic solution containing phenol using a thin film of β-naphthalene sulphonie acid doped polypyrrole (PPyNSA) adsorbed on a glassy carbon electrode. The GCE/PPYNSA working electrode used for phenol sensing was prepared as described in 3.3.8. The electrochemical cell was set up by placing 1 mL 0.05 HCl (pH 1.2) in a 5 mL cell. The working, reference and counter (Pt wire) electrode were placed in the solution and connected to the BAS 50 Potentiostat. The solution was degassed for 15 min with argon and an argon headspace maintained at very low gas flow rate. Square wave voltammetry of the GCE/PPYNSA working electrode was then measured at 5 Hz using 50 mV square wave amplitude, and an initial potential, \( E_i \), of -400 mV to a final potential, \( E_f \), of 900 mV. Aliquots of 2.0 mM phenol (0.0471g in 250 mL) were then added to the cell solution which was degassed (15 min) after each phenol addition, and SWV responses recorded as described before. Amperometric curve for the GCE/PPYNSA sensor to phenol addition was plotted from the square wave responses at 70 mV.

3.4.3 Benzidine sensing with Pt/PPyNQS (Impedimetry)

Stock solution of 0.001 M of benzidine was prepared by dissolving 0.0184 g of benzidine in 100 cm³ of distilled water (under continuous stirring for 3 hrs). From this
stock solution, aliquots (in μL) were drawn and added to the electrolyte in the cell and used for sensor development. Proper interaction of the analyte with the polymer surface was achieved by a gentle flow of argon being used for purging.

**Impedance measurements**

Different concentrations of benzidine in acidic aqueous solution were analysed using a thin film of 1, 2-naphthaquinone-4-sulfonate doped polypyrrole (PPyNQS) electrosynthesised on a platinum working electrode. The Pt/PPyNQS working electrode used for benzidine sensing was prepared as described in 3.3.6. A PGZ402 Voltalab Analyzer (Radiometer Analytical S.A, France) was used for all the EIS measurements using the same three-electrode cell arrangement and electrolyte as for cyclic voltammetry. An AC amplitude of 5 mV was imposed on the potential applied on the working electrode at a frequency range from 100 KHz down to 0.01 Hz at a sampling rate of 10 points per frequency decade. A voltammetric cell containing 2 cm³ of 0.05 M HCl electrolyte was used for the application tests. EIS data was first taken using 2 mL of 0.05 M HCl free of analyte and thereafter dosed with progressive aliquots (in μL) of benzidine. All electrochemical measurements were taken under an inert atmosphere of argon.

EIS data was modeled by fitting the impedance data using a simple $R_s R_1 C_1 - R_2 C_2$ circuit. These elements represent the solution resistance ($R_s$) between working and reference electrode, a $R_1 CPE_1$ parallel combination, where CPE is a constant phase element, to model movement by electron hopping through the polymer film along the polymer backbone, and a second $R_2 C_2$ component in series representing the electrode/solution interface. The CPE was modeled as a non-ideal capacitor. Thus two simultaneous kinetics are involved, one involving the bulk polymer material which is observable at high frequency and the other taking place within the electrolyte/polymer interface at the low frequency end. The capacitance and impedance values at 10 KHz for the bulk polymer data and the values obtained at 10 mHz as were used to represent the electrolyte/polymer interface. The sensor effect was based on the normalized real impedance ($S_n$), and/or that of the normalized real capacitance ($K_n$) using equations 3.28 and 3.29.
3.4.4 Naphthalene sensing with Pt/PPyNQS (Impedimetry)

The naphthalene stock solution of 0.001 M was prepared by dissolving 0.0128 g in about 5 cm$^3$ of acetonitrile (to achieve solubility) and later made up to 100 cm$^3$ solution in distilled water with continuous stirring for about 30 min. From this stock solution, aliquots (in μL) were drawn and added to the cell and used for sensor development. Proper interaction of the analyte with the polymer surface was achieved by a gentle flow of argon being used for purging.

**Impedance measurements**

The procedure adopted for the impedimetric detection of naphthalene was as described for benzidine in 3.4.2.

**References**


2. [http://www.biol.paisley.ac.uk/marco/Enzyme_Electrode/Chapter1/Ferrocene_animated_CV1.htm](http://www.biol.paisley.ac.uk/marco/Enzyme_Electrode/Chapter1/Ferrocene_animated_CV1.htm).


Chapter Four

Results and Discussion 1

Morphology, Spectroscopy, Electrochemistry and Application of nanostructured polypyrrole-β-naphthalene sulphonic acid (PPyNSA) composites

This chapter presents the results obtained on the chemical and electrochemical preparation, characterization and application of polypyrrole modified with β-naphthalene sulphonic acid (PPyNSA). The optimal synthesis conditions, spectroscopy and electrochemistry of the NSA-doped polypyrrole nanotubes, nanosheets and nanomicelles are discussed. The kinetics of the charge transfer processes, the redox properties of the polymer and its suitability for as a chemical sensor for phenol detection were also presented.

4.0 Introduction

The production of different kinds of conducting polymers in the form of nanotubes or nanowires from metallic or organic constituents inside the void spaces of nanoporous host material have received a lot of attention as a means of boosting electrical properties of intrinsically conducting polymers [1-10]. Since the initial work by Wei et al. [3] on the formation and self-assembly of Polyaniline (PANI) micro/nanotubes by the use of surfactants as against the hitherto ‘template synthesis’ method, various investigation have been made on the use of various surfactants for production of nano-structured materials of polypyrrole and other conducting polymers [1-11]. Yang (2002) [1] reported the production of self assembled micro and nanotubes of conducting PPy using protonic organic acid dopants and proposed that dopant micelles or pyrrole/dopant clusters act as template in the formation of the polymers micro/nanotubes.
Kassim et al. [2] also reported that a higher conductivity was obtained from camphor sulphonate doped PPY electrochemically synthesized at optimum temperature of 10 – 30 °C than those prepared at higher temperatures. The physical properties were equally reported to be changing with the preparation temperature. Smooth and coherent films were obtained at lower temperatures while rough and wrinkled surface was found at higher temperatures when examined under a scanning electron microscope (SEM).

Polypyrrole synthesis and electro-activity is affected by a number of experimental conditions such as type of solvent, electrolyte concentration and type of electrode material, current density, applied potential, polymerization time and temperature. The optimization of these parameters to get nanostructured and reasonably stable PPy in gaseous (air) and in aqueous media determines its potential application as electrode materials for biosensors and chemical sensors amongst other applications [13-19]. The neutral form of polypyrrole is usually insulating but this can be switched electrochemically into the conductive state by oxidative (p) or reductive (n) doping of the monomer. The property of polypyrrole to switch reversibly from one oxidation state to the other has led to a number of technological applications, including secondary rechargeable batteries, fuel cells, chemical sensors, controlled drug delivery, electrochromic and corrosion protection [11–19]. It also shows promise in the remediation of electro-active pollutants and lot of environmental control applications [20].

Despite the easy polymerization of pyrrole and the extensive π-conjugated polymer chain of PPy, the application is often limited by its insolubility in aqueous and organic solvents. Various efforts have been made to add or remove electrons from the polymer’s backbone to generate a conductive state often described as doped PPy. The use of bulky sulphonated organic acid dopants has been proposed as a means of generating the ionic form (PPy+\text{A}^{-})_x (Fig. 4.1) in which polypyrrole’s solubility is enhanced [11], where \text{A}^{-} is the bulky sulphonated organic acid anion and ‘x’ is the number of pyrrole trimers constituting the polymer sheet. The dopant ion hosted by the polymer improves the solubility of PPy in organic solvents. This is achieved by the reduction of the inter- and intra-molecular interactions of the polymer chains by the incorporation of the bulky polynuclear protonic organic acid surfactant [11].
Figure 4.1: Scheme for the ionic form of β–naphthalene sulphonic acid doped polypyrrole.

The results obtained on the nanostructured polypyrrole-β-naphthalene sulphonic acid (PPyNSA) composites prepared in this study is presented and discussed below.

4.1 Polymerization yield of PPyNSA

Preliminary investigation to ascertain the optimum conditions for the chemical synthesis of PPyNSA was carried out at room temperature of 25 °C and at 0 – 5 °C. The polymerisation yield obtained is as shown in Table 4.1 for polypyrrole doped with NSA at dopant to monomer mole concentration ratios (d/m) of 1, 0.8, 0.5 and 0 in which no dopant is involved. In all cases an oxidant to monomer mole concentration ratio (d/m) of 0.2 was used. There is a trend of higher yield from the synthesis carried out at lower temperature with the doped system having more yield.

Table 4.1: Yield/Temperature profile for doped and undoped PPy [21]

<table>
<thead>
<tr>
<th>Sample</th>
<th>d/m mole concentration ratio used</th>
<th>Yield of polypyrrole (g/ml) at 25 °C</th>
<th>Yield of polypyrrole (g/ml) at 0 - 5 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPyNSA 1</td>
<td>1.0</td>
<td>33</td>
<td>42</td>
</tr>
<tr>
<td>PPyNSA 2</td>
<td>0.8</td>
<td>35</td>
<td>44</td>
</tr>
<tr>
<td>PPyNSA 3</td>
<td>0.5</td>
<td>27</td>
<td>32</td>
</tr>
<tr>
<td>PPyDW</td>
<td>0</td>
<td>18</td>
<td>20</td>
</tr>
</tbody>
</table>
The optimum PPy yield of 44% was obtained for a d/m ratio of 0.8 while the lowest yield of 18% was obtained for the undoped polymer prepared at room temperature. This higher yield pattern observed for the doped system is due to the ability of NSA to generate enough radicals through protonation of the pyrrole monomers that initiates the cationic polymerisation of PPy. The NSA equally forms micelles in aqueous solution using its hydrophilic sulphonic acid group to combine with the hydrophobic pyrrole monomers acting as templates in the formation of micro/nanotubes [1]. The result shows that the efficiency of the polymerization reaction is highest at the d/m ratio of 0.8. Lee et al. [4] had reported optimum synthesis with an apparent PPy yield of 42% for a d/m ratio of 0.5 using dodecyl benzene sulphonic acid (DBSA) as dopant and a synthesis temperature of 0°C for the same polymerization time of 24 hours. These results are quite comparable. The lower yield value of 32% for PPyNSA-2 when a d/m ratio of 0.5 was used in comparison with the yield of 42% for PPyDBSA from similar d/m ratio of 0.5 cited above might be due to the higher steric hindrance associated with the bulkier binuclear naphthalene moiety compared to the mononuclear DBSA group.

**Optimisation of chemical synthesis conditions**

In order to further investigate the effect of processing conditions on the preparation of NSA-doped polypyrrole, a series of experiments were performed with 0.1M pyrrole using different mole-concentration ratios of dopants (HCl or NSA) and oxidant (APS). The effect of reaction medium (pH, heating, electrolyte concentration etc.) on polymerization yield was investigated for polypyrroles prepared in oxidant alone (PPyDW), HCl and oxidant (PPyHCl), and NSA and oxidant (PPyNSA) at different synthesis conditions (Table 4.2). A higher yield of polypyrrole is obtainable at low temperature synthesis of 0 – 5 °C in all cases. The yield was further increased with an initial heating of the NSA – Pyrrole solutions at 50 – 60 °C for 15 minutes and cooling before the addition of the oxidant than when there was no heating. This preparation procedure enhanced the production of higher concentration of pyrrole complexed with naphthalene sulphonate ion (Py\(^{\text{−NSA}}\)) that was subsequently oxidized to form dimeric radical cations and radical species undergoing slow cross linking as polymerization progressed in line with the mechanism in Fig. 4.2.
Figure 4.2: Scheme for the polymerization of polypyrrole via pyrrole-complex intermediates using the radical cations and the radical species that are free of naphthalene sulphonate specie [11].

The effect of o/m mole concentration ratio on polypyrrole chemical synthesis was explored by using APS – monomer concentration ratio greater than the 0.2 always reported for PPy [4, 5]. In this work, synthesis using an APS and pyrrole (o/m) of 1.0, as normally applied in polyaniline chemical synthesis [3] produced higher yields of PPyNSA: 98% at room temperature and 99% at 0 – 5 °C. Similar high polymer yields were reported for polythiophene prepared with FeCl₃ and thiophene in CHCl₃ medium [13]. The trend in PPyNSA yields in Table 4.2 could be attributed to greater interactions between the dopants and monomer species leading to formation of higher molecular weight polymers at higher concentration of APS than from lower concentration of APS [4].

The role of dopant concentration and its anionic size in the polymerization process is demonstrated in the yield results for APS only, APS with HCl, and APS with NSA. The results in Table 4.2 showed that a higher yield of PPyHCl was obtained with a
NSA – hydrochloric acid concentrations (d/m) ratio of 0.5 than with 0.8, and in case of PPyNSA, a higher yield was obtained from NSA – Pyrrole concentrations ratio of 0.8 than 0.5 or 1.0. This trend indicates that an optimal acid concentration is required for the various systems.

Table 4.2: Yield of various polypyrroles prepared under different synthesis conditions [22].

<table>
<thead>
<tr>
<th>Sample</th>
<th>d/m mixture</th>
<th>*d/m ratio</th>
<th>*o/m ratio</th>
<th>pH of mixture</th>
<th>%yield (m/v) (25 °C)</th>
<th>%yield (m/v) (0 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPyDW</td>
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<td>0.2</td>
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<td>18</td>
<td>20</td>
</tr>
<tr>
<td>PPyHCL</td>
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<td>0.1</td>
<td>0.2</td>
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<td>27</td>
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<td>PPyHCL</td>
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<td>0.2</td>
<td>0.5</td>
<td>*nd</td>
<td>47</td>
</tr>
<tr>
<td>PPyHCL</td>
<td>yes</td>
<td>0.8</td>
<td>0.2</td>
<td>0.2</td>
<td>*nd</td>
<td>27</td>
</tr>
<tr>
<td>PPyNSA</td>
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<td>0.2</td>
<td>1.4</td>
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<td>42</td>
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<tr>
<td>PPyNSA</td>
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<td>0.2</td>
<td>1.5</td>
<td>35</td>
<td>44</td>
</tr>
<tr>
<td>PPyNSA</td>
<td>no</td>
<td>0.5</td>
<td>0.2</td>
<td>1.7</td>
<td>27</td>
<td>32</td>
</tr>
<tr>
<td>PPyNSA</td>
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<td>0.5</td>
<td>0.2</td>
<td>1.7</td>
<td>*nd</td>
<td>39</td>
</tr>
<tr>
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</tr>
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<td>1.0</td>
<td>1.2</td>
<td>98</td>
<td>99</td>
</tr>
</tbody>
</table>

* defined as follows: ‘d/m’ is mole concentration ratios of dopant (NSA) to monomer (pyrrole); ‘o/m’ is mole concentration ratios of oxidant (APS) to monomer (pyrrole); and ‘nd’ are values non-determined values.

The various synthesis involved use of acidic medium with pH of less than 2. The yield of polypyrrole is optimal at a pH of about 1.0 – 1.5 while it is limited at very low pH. Yakovleva [11] reported that agitating the dopant and monomer mixture at pH less than 1.0 did dramatically decelerate electrosynthesis of polypyrrole film [11]. The
yield of the polypyrrole obtained from this study was found to increase with the size of dopant ion used for doping. Earlier work on electrochemically-synthesized polypyrrole had posited that the yield increases with the size of dopant ion used [11]. For example, the rate of electropolymerisation of polypyrrole in different electrolytes follow the trend $\text{ClO}_4^- > \text{HSO}_4^- > \text{Cl}^-$. In this study, the yield follows the trend PPyNSA >PPyHCl >PPyDW in favour of larger ionic dopants.

4.2 Morphology of PPyNSA

The physical appearance of PPyNSA obtained at $0 – 5 \, ^\circ\text{C}$ was smooth and shiny while those prepared at higher temperature appear rough and loose. This is in line with the findings of Kassim et al. that the rough physical appearance was due to greater rates of polymerization at higher temperatures that leads to faster nucleation and precipitation of nanoparticles [2]. However, even when higher yields are obtainable at higher temperatures, there is higher overlapping of micelles, which leads to surface roughness; unlike ordered and smoother nodule morphology observed at lower temperatures. From the scanning electron micrographs (Fig. 4.3) taken at magnification of 500 for PPyNSA doped in the ratio 1, 0.8 and 0.5 respectively; the trends posited above could be confirmed. The lumps (side-growth) at the sides of the identified micro/nanotubes are products from overlapped micelles, which is more probable at higher temperatures. The micrographs of similarly doped polyaniline (PANi) with NSA at $0 \, ^\circ\text{C}$ have very few lumps but more of tubes and some few flakes [3]. Wei et al. had posited an optimum d/m mole concentration ratio of 0.5 for PANiNSA [3]. At this ratio, an excess concentration of aniline is available to form NSA micelles with aniline to form nanotubes, whereas at higher ratios lesser moles of aniline are available for polymerization and bigger tubes were obtained. However, at lower d/m ratios, smaller diameter nanofibre/tubes were obtained. When the surfactant, NSA, was not used the polypyrrole featured folded sheets of fibers with tube-like morphology (Fig 4.4). The sheet-like fibers rolled up to form tubes with a hollow inner cavity. In this synthesis, APS produced both the required acid medium for the synthesis and peroxodisulfate counter ion, which served as dopant. The micrographs observed from different sides of the PPyDW could be attributed to lack of a rigid template for the formation of compact nanostructure. In alkaline media, thin
insulating films are formed from the electrochemically synthesized PPy [6]. The PPyDW synthesized from the less acidic medium of oxidant and monomer will be less conducting. The stability of the conducting cationic polypyrrole intermediate in the polymerization process is favoured in acidic medium.

![Figure 4.3](image1.png)

Figure 4.3: Typical SEM images of different polypyrrole synthesized with o/m 0.2 at 25 °C (a) PPyNSA nano/microtubes and fibers from d/m 1, (b) PPyNSA nano/microtubes from d/m 0.8, and (c) PPyNSA microfibers from d/m 0.8 [21].

![Figure 4.4](image2.png)

Figure 4.4: Typical SEM images of polypyrrole nano/micro sheets synthesized with o/m 0.2 at 25 °C in the absence of NSA dopant (PPyDW) [21] taken from different sides to show the sheet-like fibrous structures (a) hollow tubular tubes (b) and the rod-like microstructures (c).
**Morphology of polypyrrole under optimum synthesis conditions**

The SEM micrographs for PPyDW and PPyNSA synthesized under different conditions showed different morphologies including thin sheets, fibres, micro rods/tubes, nano-micelles and nano-rods/tubes (Fig. 4.5). The diameter of the tubules ranged from 150 - 3000 nm, while the sheets have a diameter of 20 nm with lengths in excess of 120 μm. More tubes were observed when heating was involved. The use of higher ratios of APS - Pyrrole mole concentrations gave honeycombed clews with smooth fibrillar surface. Figure 4.5(b), which was taken under high magnification revealed aggregations of nanostructures that appeared like micelles with fairly uniform diameter of ca. 100 – 150 nm. These are compactly joined together in chains that would afford good electron hopping. No wonder the unique electrochemistry seen during the kinetic investigation. The inter-connected porous morphology of the PPyNSA prepared from a higher ratio of o/m is different from those of PPyNSA, PPyHCl and PPyDW prepared from lower o/m ratios. The folded sheets (Fig. 4.5c) from the APS doped polypyrrole (PPyDW) have lengths of about 15 - 50 μm. The rate of polymerisation did not allow the formation of tubes, rather a highly dispersed polymer with open fibril morphology [18]. Apart from the micro/nanoscopic structures seen in the polymer micrographs, it is interesting to note that synthesis performed at low temperature of 0 °C produced polymers with smooth and coherent physical outlook, while those prepared at room temperature were coarse and rough. Kassim et al. [2] attributed this peculiarity to α – β and β – β chain bonding of the monomers during polymerization at the higher temperature, as against α – α chain bonding in low temperature synthesis.
Figure 4.5: Typical SEM images of different polypyrrole synthesized at 0 °C (a) nano/microtubes and fibers from PPyNSA (d/m 0.8; o/m 0.2), (b) nanomicelles from PPyNSA (d/m 0.8; o/m 1.0), (c) nanosheets from PPyDW (o/m 0.2) [22].
4.3 UV-Vis absorption and solubility of PPyNSA

The various PPyNSA’s were sparingly soluble in m-cresol, chloroform and dimethyl sulfoxide (DMSO). The polymer was found to be more soluble in DMSO than in other solvents. The PPyNSA prepared by pre-heating of the dopant/monomer mixture had higher solubility and more intense coloration than those prepared without preheating. Similarly, synthesis at 0 °C produced PPy with higher solubility and spectroscopic absorption than PPy prepared at room temperature synthesis. PPyHCl showed the least solubility in all solvents.

From the UV-Vis spectra (Fig. 4.6), the absorption maxima for the conjugated double bonds (i.e. $\pi$ to $\pi^*$ transition) for both PPyDW and PPyHCl were seen at 291 nm. However, PPyNSA (d/m 0.5 and o/m 0.2) has an absorption maximum at 300 nm. This red shift is an indication of involvement of the bulky dopant ion (NSA) in the polymerization process [23]. From Fig. 4.6A, there are prominent polaron band at 437 nm; bipolaron band at 555 nm and over-lapped bipolaron band at 765 nm upwards for the PPyNSA prepared from NSA - pyrrole concentration ratios of 0.5 and APS – pyrrole concentration ratios of 0.2. The PPyNSA prepared from NSA - pyrrole concentration ratio of 0.8 and APS - Pyrrole concentration ratio of 0.2, 0.5 and 1.0 gave only the polaron band at 409 nm (Fig. 4.6B). The concentration of polarons and bipolaron ions along the polymer chain must have contributed to the improved solubility of the polymer in DMSO. This is evident in the higher polaronic absorption (437 – 765 nm) for PPyNSA prepared from NSA - pyrrole concentration ratios of 0.5 and APS - pyrrole concentration ratios of 0.2.
Figure 4.6: UV-Vis results for PPyNSA prepared under different synthesis conditions: Fig. 4.6A. PPyNSA (d/m, o/m): (a) [0.5, 0.2] and (b) [0.8, 0.2], Fig. 4.6B. PPyNSA [d/m 0.8] from o/m ratios: (a) 0.2, (b) 0.5 and (c) 1.0 [22].
Previous work on DBSA-doped polypyrrole by Lee et al. showed bi-polaron absorption at 480 nm and free carrier tailing in the near IR region from 750 – 1500 nm region [4]. Diffused reflectance UV-Vis-NIR spectra of doped polypyrrole by Geetha and Trivedi [24] gave indications of cation radicals at wavelength band of 400 – 600 nm for doped polypyrrole and other bands at above 800 nm associated to trapped excitons (bipolarons). Similarly, Shiigi et al. reported that the polaron and bipolaron absorption peaks at 420 nm and 860 nm respectively for overoxidised polypyrrole colloids are greatly dependent on the concentration and type of oxidant used [9]. It could therefore be postulated that the formation of the bipolaron band at 555 nm and over-lapped bipolaron bands at 765 nm upwards for PPyNSA system is feasible at an optimum concentration of d/m 0.5 and o/m 0.2 using (NH$_4$)$_2$S$_2$O$_8$ as oxidant.

It is noteworthy to mention that the PPyNSA polymer with 99% yield from a d/m of 0.8 and o/m of 1.0 did not give sharp indication of trapped polaron and bipolaron (Fig. 4.6B) within the wavelength investigated. This might be due to the facile oxidation process, which did not allow for ordered entrapment of the charge carriers. However, the polaron peak was more prominent when an o/m concentration ratio of 1.0 was used as against when 0.5 was used. The increasing order of oxidation power of some common oxidants is K$_3$Fe(CN)$_6$ < FeCl$_3$ < (NH$_4$)$_2$S$_2$O$_8$. The level of chemical oxidation could therefore be used to modulate the applicability of PPyNSA. High performance polymeric nanosensors should exhibit polaron and bipolaron bands as obtained for the PPyNSA prepared from of NSA – pyrrole concentration ratios of 0.5 and APS – pyrrole concentration ratios of 0.2 in Fig. 4.6A. The combination of other techniques is therefore necessary to further explore the properties of these polymers [15].

4.4 FTIR spectral studies

Figure 4.7 shows the IR spectra of (a) PPyDW, (b) PPyNSA (d/m 0.8; o/m 0.2) and (c) PPyNSA (d/m 0.8; o/m 1.0). Principal absorption bands observed are given in Table 4.3 together with those reported for polypyrrole by Geetha and Trivedi [24]. All the characteristic IR bands for polypyrrole were observed with slight variation in the absolute values of the absorption bands. The usual N – H stretching at 3400 cm$^{-1}$ in
neutral polypyrrole is virtually absent in all the three samples indicating that the polymer exists in doped state in PPyDW, PPyNSA (d/m 0.8, o/m 0.2) and PPyNSA (d/m 0.8, o/m 1.0).

Figure 4.7: FTIR spectra of polypyrroles in KBr medium for: (a) PPyDW, (b) PPyNSA (d/m 0.8; o/m 1.0) and (c) PPyNSA (d/m 0.8; o/m 0.2) [22].
Table 4.3: Major shifts of bands (cm$^{-1}$) in FTIR spectra of PPyDW, PPyNSA (d/m 0.8, o/m 0.2) and PPyNSA (d/m 0.8, o/m 1.0) from undoped polypyrrole major bands (Geetha & Trivedi) [24].

<table>
<thead>
<tr>
<th>Major bands (cm$^{-1}$)</th>
<th>PPyDW</th>
<th>PPyNSA (d/m 0.8, o/m 0.2)</th>
<th>PPyNSA (d/m 0.8, o/m 1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3421 (N-H str)</td>
<td>absent</td>
<td>absent</td>
<td>absent</td>
</tr>
<tr>
<td>3100 (C-H str)</td>
<td>absent</td>
<td>absent</td>
<td>3195 (sharp)</td>
</tr>
<tr>
<td>1535 (C=C &amp; C-C str)</td>
<td>1554</td>
<td>1564</td>
<td>1550</td>
</tr>
<tr>
<td>1450 (N-H str)</td>
<td>absent</td>
<td>1461</td>
<td>1400</td>
</tr>
<tr>
<td>1295 (C-H &amp; N-H def)</td>
<td>1308</td>
<td>1310</td>
<td>1299</td>
</tr>
<tr>
<td>1050 (C-H def)</td>
<td>1047</td>
<td>1048</td>
<td>1045</td>
</tr>
</tbody>
</table>

The N – H stretching band for neutral polypyrrole at 1450 cm$^{-1}$ was totally absent in PPyDW but shifted positively by 11 cm$^{-1}$ in PPyNSA (d/m 0.8, o/m 0.2) and negatively by 50 cm$^{-1}$ in the most oxidized polypyrrole PPyNSA (d/m 0.8, o/m 1.0). This is an indication that the polymer is not in the aromatic state but in the excited polaron and bipolaron defect state. The strong electronic excitations occasioned by the polypyrrole-oxidized states strongly distort the observed absorptions. The C=C and C-C stretching band at 1535 cm$^{-1}$ shifted positively by 15 – 24 cm$^{-1}$ in the three scenario investigated and is synonymous to the absorption band of 1545 cm$^{-1}$ observed for doped PPy [24]. Similarly, the C-H stretching band at 3100 cm$^{-1}$ was absent in all the three oxidized polypyrrole, though there was a new sharp and pronounced peak at 3190 cm$^{-1}$ for PPyNSA (d/m 0.8, o/m 1.0). However, the C-H deformation at 1050 cm$^{-1}$ was observed at 1047, 1048 and 1045 cm$^{-1}$ for PPyDW, PPyNSA (d/m 0.8; o/m 0.2) and PPyNSA (d/m 0.8; o/m 1.0) respectively. The new sharp peak observed at 3204 cm$^{-1}$ in the PPyNSA (d/m 0.8, o/m 1.0) spectrum might be due to hydrogen
bonded N – H or O – H bond. This is synonymous to similar sharp peak at about 3500 cm\(^{-1}\) for the undoped polypyrrole spectra by Geetha and Trivedi [24]. Similar anomalous trend was seen in the UV-Vis spectra of the polymer (Fig. 4.7b), which did not show major absorption for the existence of over-lapped cationic species (bipolarons) for the polymer at the wavelength investigated.

The relative oxidation of the polymers can be measured from the relative intensities of the band at 2340 cm\(^{-1}\). Rodriguez \textit{et al} [25] reported the possible disruption of the electronic conduction of the polymer by irreversible oxidation, leading to the formation of carbonyl groups (1720 cm\(^{-1}\)) and invariably CO\(_2\) (2340 cm\(^{-1}\)). The observed band at 2340 cm\(^{-1}\) in this study (Fig 4.7) was most prominent in PPyNSA (d/m 0.8, o/m 1.0), while the intensity is very low in PPyDW and virtually absent in the PPyNSA (d/m 0.8, o/m 0.2).

4.5 Electrochemical studies on PPyHCl and PPyNSA

4.5.1 Chemically synthesised PPyNSA

4.5.1.1 Voltammetric studies of GCE/PPyNSA systems

\textit{Cyclic voltammetry}

Cyclic voltammetry results of the PPyNSA prepared at 0 °C from NSA-pyrrole mole ratio of 0.8, indicated the existence of two redox couples a/a' and b/b'. The multiscan voltammogram is shown in Figure 4.8 for PPyNSA (d/m 0.8, o/m 0.2) and PPyNSA (d/m 0.8, o/m 1.0). These two redox couples gradually turns to single couple at scan rates above 50 mV/s. In proposing a mechanism for the polymerization of polypyrrole in aqueous medium, Yakovleva [11] predicted the probability of the formation of pyrrole complexes in acid solutions with the proton and anion in solution, in accordance with the scheme in Fig. 4.2. He opined that the discharge of pyrrole complexes with the anion and proton and their destruction yield radical-cation and radical species which could jointly interact with the active ends of pyrrole links to induce the growth and development of polymer chains. According to a scheme proposed by Yakovleva [11] (Fig. 4.2), the first anodic peak at ‘a’ represents the
oxidation of the neutral PPyNSA to the PPyNSA intermediate radical cation. This is further oxidized at a higher potential to PPyNSA radical cation at ‘b’. The cathodic voltammogram shows the reduction of PPyNSA radical cation to the partly reduced PPyNSA radical anion at ‘b’ which is further reduced to the neutral PPyNSA at ‘a’.

The voltammograms in Figure 4.8 show that as the potential scan rate increases, the anodic peak potentials (Ep,a) shifts positively, the cathodic peak potentials (Ep,c) remained unchanged and all peak currents (Ip) increase progressively. The independence of Ep,c on scan rate is characteristic of surface-bound thin film electroactive species undergoing fast electron transfer reaction at the electrode. For both redox couples a/a’ and b/b’, the peak separations ΔEp (i.e Ep,a – Ep,c) is < 65 mV even at higher scan rates (results for higher scan rates are not shown) which indicates that the shift in Ep,a values with scan rate is due to intra-molecular charge transportation. Similar peaks characterize the voltammogram of polyaniline in 1M HCl [26–29].
Figure 4.8: (a) Multi–scan rate voltammograms in 0.1 M HCl for (a) PPyNSA (d/m 0.8; o/m 0.2) at scan rates of 10, 20, 30 mV/s\(^{-1}\); (b) PPyNSA (d/m 0.8; o/m 1.0) at scan rates of 5, 10, 20 mV/s\(^{-1}\) in 0.1M HCl [22].
**Square wave and differential pulse voltammetry**

The low frequency (2, 3, 4 and 5 Hz) square wave voltammograms (SWV) of GCE/PPyNSA is presented in Fig 4.9. The voltammograms (Fig. 4.9 a and b) show two redox couples (a/a' and b/b') that are close, broad and coupling at a formal potential ($E^{o'}$) of about 241±7 mV vrs. Ag/AgCl. This agrees with the estimated $E^{o'}$ value of 241±11 mV calculated for the CV of PPyNSA (d/m 0.8; o/m 1.0) (Fig. 4.8b). The corresponding formal potentials for the emerging peak from the convolution of the two-redox couples are shown in Fig 4.9b. The SWV data show that the separation between the peak potentials ($\Delta E_p$) of redox couples a/a' and b/b' has a value of about 112 mV, which must have arisen from the overlapping of two closely related 1-electron redox processes. Similar trend was observed for the PPyNSA (d/m 0.8; o/m 0.2) shown in Figure 4.8a. The anodic differential pulse voltammograms (DPV) of the chemically doped PPyNSA [d/m 0.8, o/m 1] at low scan rates of 5 mV/s and 10 mV/s are presented in Fig. 4.10. The anodic peaks show a convolution of two-merging peaks at 195 mV and 265 mV showing that two anodic peaks may be involved. These peak potentials are close to the anodic peak points obtained for the cyclic and square wave voltammograms in Fig. 4.8 and 4.9. Similar trend was observed on the PPyNSA [d/m 0.8, o/m 0.2].
Figure 4.9: Typical anodic SWV of PPyNSA (d/m 0.8; o/m 1.0) using an amplitude of 50 mV and at frequencies of 2, 3, 4 and 5 Hz showing (a) the forward and reverse waves, (b) the net square wave responses.
4.5.1.2 Electrode kinetics of GCE/PPyNSA systems

The cyclic voltammograms of PPyNSA (Fig. 4.8) show that both the anodic and cathodic peak currents did not come to zero at the switch potentials, indicating that the polymer is neither over-oxidized nor over-reduced during potential cycling. At the potential window of -500 mV to 1000 mV, where the PPyNSA (d/m 0.8; o/m 1.0) (Fig. 4.8b) is characterised, the \( E^{\circ} \) value for couple a/a' is 184±9 mV while that of couple b/b' is 298±12 mV within the scan rates of 5 mV to 30 mV. The mid point, i.e., 1/2(\( E^{\circ}_{a'/a} - E^{\circ}_{b'/b} \)), of the two redox couples, a/a' and b/b', occur at 241±11 mV.

Kinetic evaluations based on data from the CV obtained at scan rates of 5 mV to 100 mV were used to study the electrode processes of the polymer systems. A summary of
the kinetic evaluation discussed underneath are summarised in Tables 4.4 for PPyNSA (d/m 0.8; o/m 1.0) and Table 4.5 for the PPyNSA (d/m 0.8; o/m 0.2) system. They gave peak separations of less than 60 mV at different scan rates between 5 and 100 mVs\(^{-1}\). In the GCE/ PPyNSA (d/m 0.8; o/m 1.0) system, which was evaluated based on CVs at potential window of -500 to 1000 mV, the oxidation to reduction peak current ratios \(\left|I_{pa}/I_{pc}\right|\) range was 0.8 to 0.9 for redox couple a/a’ and 1.0 to 1.3 i.e. \([1.23±0.08]\) for redox couple b/b’. The \(\Delta E_p\) ranged from 3.8 to 23.4 mV i.e. \([17.5±9.0\text{ mV}]\) for a/a’, and 11.3 to 54.1 mV i.e. \([37±14\text{ mV}]\) for b/b’. The peak current values show linear dependence on scan rates for the cathodic and anodic peaks, with slopes of 1.45 to 1.87 x 10\(^{-4}\) A.s.V\(^{-1}\) and correlation coefficient \(r^2\), of 0.997 to 0.998 for both anodic and cathodic plots. The intercept values, for the non-faradaic currents caused by the charging of the electrical double layer were close to zero being 4.6 x 10\(^{-6}\) A for the anodic plot and to 5.6 x 10\(^{-6}\) A for the cathodic plot. This is an indication of a very thin layer of adsorbed electro active material at the electrode surface undergoing near-Nernstian (quasi-reversible) reaction.

Similar trend was seen in the PPyNSA (d/m 0.8; o/m 0.2), (Fig 4.8a), studied at a potential window of –500 mV to +500 mV at scan rates between 10 mV/s and 100 mV/s. The formal potential, \(E^\circ\), was 176.3±5.4 mV with a peak separation of 48 to 61 mV i.e. \([52.4±4.4\text{ mV}]\) and \(\left|I_{pa}/I_{pc}\right|\) of 0.98 to 1.22 i.e. \([1.13±0.08]\) for a/a’. This is indicative of a quasi-reversible system. The linear relationship of the peak currents versus the scan rates featured a slope of 4.32 x 10\(^{-4}\) A.s.V\(^{-1}\) and 3.38 x 10\(^{-4}\) A.s.V\(^{-1}\) for the anodic and cathodic plots respectively. The correlation coefficient \(r^2\) for the anodic and cathodic peaks is 0.999 and 0.998, while the intercepts are 3.37 x 10\(^{-6}\) A and 4.36 x 10\(^{-6}\) A, respectively.

The surface concentration, \(\Gamma^*\), of the PPyNSA was calculated from the peak currents of the CV’s in Fig. 4.8 using the Brown-Anson method (26-29). The \(\Gamma^*\) values were 2.60 x 10\(^{-8}\) mol cm\(^{-2}\) and 5.76 x 10\(^{-9}\) mol cm\(^{-2}\) for PPyNSA (o/m 1.0) and PPyNSA (o/m 0.2) respectively. The results shows that \(\Gamma^*_{\text{PPyNSA (o/m 1.0)}} = 4.5 \text{ } \Gamma^*_{\text{PPyNSA (o/m 0.2)}}\) respectively. This agrees with the APS (oxidant) ratio in the two PPyNSA. As expected the polypyrrole prepared with higher APS ratio is expected to have more PPy.
The peak separations for the redox couple, \( \text{a/} \text{a}' \), of GCE/PPyNSA (\( \text{d/m} \) 0.8; \( \text{o/m} \) 0.2) system in Fig. 4.8a increased progressively from 49 mV at 10 mVs\(^{-1}\) to 61 mV at 100 mVs\(^{-1}\) coupled with increase in the magnitude of the peak currents with increase in scan rates. Similarly, the peak separations for the redox couple, \( \text{a/} \text{a}' \), in GCE/PPyNSA (\( \text{d/m} \) 0.8; \( \text{o/m} \) 1.0) system (Fig.4.8b) increased progressively from 4 mV at 5 mVs\(^{-1}\) to 54 mV at 100 mVs\(^{-1}\). These trends show that the peak currents are diffusion controlled. Thus the Randel- Sevčík equation (equation 3.6) was applied to determine the diffusion coefficient (\( D_e \)) for electron hopping along the polymer chain [21].

\[
\frac{I_p}{\nu^{1/2}} = 2.686 \times 10^5 \, n^{3/2} \, A \, \Gamma_{\text{PPyNSA}} \, D_e^{1/2}
\]

Figures 4.11 (a) and (b) represent plots of the absolute magnitude of the cathodic peak currents vrs. square root of scan rates for GCE/PPyNSA (\( \text{d/m} \) 0.8; \( \text{o/m} \) 0.2) and GCE/PPyNSA (\( \text{d/m} \) 0.8; \( \text{o/m} \) 1.0) systems respectively. The charge transfer coefficient, \( D_e \), of the polymers were estimated from the slopes of the graphs to be 1.81 \( \times 10^{-6} \) cm\(^2\)s\(^{-1}\) and 1.21 \( \times 10^{-6} \) cm\(^2\)s\(^{-1}\) for PPyNSA (\( \text{o/m} \) 1.0) and PPyNSA (\( \text{o/m} \) 0.2) respectively [28, 29]. Thus the PPyNSA that was prepared with higher oxidant/monomer ratio produced polymer with an enhanced charge transportion, i.e better conductivity (See Fig. 4.13). The \( D_e \) values for PPyNSA agree with the diffusion coefficient of 1.10 \( \times 10^{-6} \) cm\(^2\)s\(^{-1}\) reported for chloride ions in polypyrrole [30].
Figure 4.11: Plot showing the variation of the modulus of both the anodic and cathodic peak currents with square root of scan rates for (a) GCE/PPyNSA (d/m 0.8; o/m 0.2) system and (b) GCE/PPyNSA (d/m 0.8; o/m 1.0) in 0.1 M HCl.
The standard rate constant, $k^\circ$, {i.e. $k^\circ = \phi (\alpha \cdot n \cdot F \cdot v \cdot D_e / RT)^{1/2} [31-33]$} for the electron transfer reaction of the polymer on GCE was calculated using the Nicholson method. The $\phi$ (dimensionless parameter) value of 20 was obtained based on a peak separation, $\Delta E_p$, value of 61.1 mV [31, 33] for the voltammogram at 100 mVs$^{-1}$, which gives the number of electron transferred, n, as 1. Assuming a transfer coefficient, $\alpha$ value of 0.5, the $k^\circ$ values were calculated as 3.75 x $10^{-2}$ cm$^{-1}$s and 3.08 x $10^{-2}$ cm$^{-1}$s for PPyNSA (o/m 1.0) and PPyNSA (o/m 0.2) respectively. This is comparable with the rate constants reported for other conducting polymers, vis.: Pt/PANI electrodes with $k^\circ$ values of 0.049 to 5.4 x $10^{-3}$ cm$^{-1}$s [34] and Pt/PEDOT electrodes with $k^\circ$ values of 1.5 to 45.3 x $10^{-3}$ cm$^{-1}$s [35] under different synthesis conditions.

The conductivity in the polypyrrole film on the electrode surface arises from the electronic transfer along the conjugated $\pi$-molecular orbital coupled with the motion of charge carriers in the material. When electron is removed from the $\pi$-system of the PPy backbone, a polaronic radical cation is produced by the local distortion of charge over four pyrrole units. Further oxidation of the polaronic radicals leads to formation of the bipolarons, which are energetically more favourable [36]. The final conductivity of the polymer is determined by the combination of two processes namely; charge carrier mobility (‘hopping’) along individual polypyrrole segment and the charge transfer between the dopant and the polymer segment. More research on fuller understanding of the charge storage and transport mechanism in conducting polymers is still going on [37].
Table 4.4. Summary of estimates of kinetic parameters for PPyNSA \([d/m\ 0.8, \ o/m\ 1.0]\) on GCE based on \(n = 1\), and scan rate measurements from \(10 – 100\ mV/s\).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Couple 1 (a/ a')</th>
<th>Couple 2 (b/ b')</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anodic (a)</td>
<td>Cathodic (a')</td>
</tr>
<tr>
<td>(\Gamma^*_{PPyNSA})</td>
<td>(2.23 \times 10^{-8}\ \text{mol cm}^{-2})</td>
<td>(2.54 \times 10^{-8}\ \text{mol cm}^{-2})</td>
</tr>
<tr>
<td>(D_{e\ PPyNSA})</td>
<td>(1.81 \times 10^{-6}\ \text{cm}^{2}\text{s}^{-1})</td>
<td>(1.81 \times 10^{-6}\ \text{cm}^{2}\text{s}^{-1})</td>
</tr>
<tr>
<td>(k^° (100\text{mV/s}))</td>
<td>(3.75 \times 10^{-2}\ \text{cm}^{-1})</td>
<td>(3.75 \times 10^{-2}\ \text{cm}^{-1})</td>
</tr>
<tr>
<td>(E^{°°}) (mV)</td>
<td>187.4</td>
<td>299.5</td>
</tr>
<tr>
<td>(\Delta E_p) (mV)</td>
<td>3.8 – 23.4</td>
<td>11.3 – 54.1</td>
</tr>
<tr>
<td>(I_{p,a}/I_{p,c})</td>
<td>0.8 – 0.9</td>
<td>1.05 – 1.27</td>
</tr>
</tbody>
</table>

Table 4.5. Summary of estimates of kinetic parameters for PPyNSA \([d/m\ 0.8, \ o/m\ 0.2]\) on GCE based on \(n = 1\), and scan rate measurements from \(10 – 100\ mV/s\). NB: The second couple at \(E^{°}\) (mV) of 275 mV, was not clearly resolved at all scan rates.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Couple</th>
<th>Average</th>
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<tr>
<td></td>
<td>Anionic (a)</td>
<td>Cathodic (a')</td>
</tr>
<tr>
<td>(\Gamma^*_{PPyNSA})</td>
<td>(6.43 \times 10^{-9}\ \text{mol cm}^{-2})</td>
<td>(5.09 \times 10^{-9}\ \text{mol cm}^{-2})</td>
</tr>
<tr>
<td>(D_{e\ PPyNSA})</td>
<td>(1.22 \times 10^{-6}\ \text{cm}^{2}\text{s}^{-1})</td>
<td>(1.21 \times 10^{-6}\ \text{cm}^{2}\text{s}^{-1})</td>
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<tr>
<td>(k^° (100\text{mV/s}))</td>
<td>(3.08 \times 10^{-2}\ \text{cm}^{-1})</td>
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<tr>
<td>(E^{°°}) (mV)</td>
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<tr>
<td>(\Delta E_p) (mV)</td>
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<tr>
<td>(I_{p,a}/I_{p,c})</td>
<td>0.98 – 1.22</td>
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</table>
4.5.1.3 Impedance studies PPyNSA systems

Electrochemical impedance spectroscopy (EIS) interrogation of PPyNSA were performed with an ac amplitude of 10 mV for potentials -600 to 1000 mV over a frequency range from $10^5$ to $10^{-1}$ Hz. The behaviours of the of PPyNSA (d/m 0.8, o/m 1.0) system at different potentials in terms of conductivity vis-à-vis its charge storage capacity at a low frequency of $10^{-1}$ Hz is presented in Fig. 4.12. The potentials at which the polymer is most conductive were 100 – 300 mV with a real impedance value of about $0.30 – 0.40 \text{k}\Omega \text{ cm}^2$ based on the unfitted data. Coincidentally, the highest charge storage ability of 0.73 - 0.95 mF cm$^{-2}$ was displayed at these potentials with the highest value of 0.95 mF cm$^{-2}$ observed at 300 mV (Fig. 4.12). Low capacitance trend of $\leq 0.2$ mF cm$^{-2}$ were manifested at potentials less than -200 mV within the potential window investigated. Similar behaviour was seen with the PPyNSA (d/m 0.8, o/m 0.2) system even though it showed lower trend of conductivity as could be seen from the higher impedance values in Fig. 4.13. The trend of conductivity for the three system at the low frequency value of $10^{-1}$ Hz shows that PPyNSA (o/m 1.0) > PPyNSA (o/m 0.2) > PPyDW (Fig. 4.13). This confirms our position that the NSA-doped polypyrrole from higher oxidant to monomer ratio offers better charge transportation than that from a lower oxidant to monomer ratio. The NSA doped polypyrrole shows maximum electroactivity at lower potential (100 – 300 mV) than the polypyrrole prepared from NSA-free medium, which shows maximum charge transportation at about 400 – 600 mV (Fig. 4.13). The PPyNSA system is therefore a better electrocatalyst than the PPyDW.
Figure 4.12: Plots of the real impedance ($Z$) and capacitance ($C$) data of PPyNSA (d/m 0.8, o/m 1.0) system showing low frequency behaviours between -600 mV to 700 mV [22].
4.5.2 Electrosynthesised PPyHCl and PPyNSA

The electrosynthesis of the polypyrrole was first done in an electrolyte medium of hydrochloric acid (pH, 1.1) using glassy carbon and platinum electrodes. Subsequently, the electrosynthesis was explored with the introduction of naphthalene sulphonic acid into the electrolyte (pH, 1.6) as described in chapter 3.

4.5.2.1 Voltammetric studies on electrosynthesised PPyHCl and PPyNSA

*Electropolymerisation of PPyHCl*

The voltammogramms for the electrosynthesis and characterisation of PPyHCl at room temperature on platinum disc electrode is presented in Fig. 4.14. The polymerization wave gave sharp oxidation and reduction peaks. The PPyHCl film grown on GCE does not give similar sharp peaks but rather forming plateaus at the
maximum anodic and cathodic currents (Fig. 4.15.). The voltammograms in Fig. 4.14 (a) and (b) showed that the Pt/PPyHCl polymer film is fully in the reduced form at about –300mV and in the fully oxidized form at the switching potential of 600mV, whereas the GCE/PPyHCl was not fully in the reduced form even at the switching potential of –600mV, even though at 600mV it is fully oxidized and overoxidation setting in. This is an attestation to the different electrochemistry of polypyrrole at different electrode surfaces. The complete switching of polypyrrole from the fully reduced state to the fully oxidised state is a major advantage derivable from the Pt/PPyHCl over GCE/PPyHCl system.
Figure 4.14: (a) The polymerization voltammograms of Pt/PPyHCl (20 cycles) from 0.1 M Pyrrole in 0.1 M HCl at 50 mV/s and (b) multi-scan rate voltammograms for electropolymerized Pt/PPyNSA at 10 to 50 mV/s.
Figure 4.15: (a) The polymerization voltammograms of GCE/PPyHCl (30 cycles) from 0.1 M Pyrrole in 0.1 M HCl at 50 mV/s and (b) multi-scan rate voltammograms for electropolymerized GCE/PPyNSA at 10 to 100 mV/s.

The voltammograms for the polymerisation of Pt/PPyHCl and GCE/PPyHCl involves oxidation of the monomer units to form the radical cations as described earlier in Fig. 2.3. The coupling i.e. dimerisation of the cation radicals leads to expulsion of two hydrogen atoms from the reacting species followed by attack of the radical on a neutral monomer during the oxidative scan. This is the rate-determining step [12]. With progressive cycling the dimers are more readily re-oxidised under the operating conditions than the monomer owing to its stronger conjugation. The oxidation potential for the dimer and oligomers of pyrrole has been reported to be lower than that for the monomer. This is reflected with progressive shift in anodic peak potentials to lower values with cycling in Fig. 4.14a. The chain growth proceeds via the addition of a newly formed radical cation to an oligomeric one. Thus we have nucleation, dimerisation, adsorption and polymerization at the anode while essentially we have
polymerisation at the cathode. The shifts of anodic peak position to lower potential with cycling were due to the continuous ease of polymerization after the initiation of the polymerization process. Subsequent growth of polymer layers can only take place after the formation of conducting polymer nuclei at the electrode surface via adsorption. Electrochemical evidence of this is the nucleation loop present at the reduction switch-potential in the cyclic voltammogram in Fig. 4.14a.

**Electropolymerisation of PPyNSA**

The introduction of the surfactant (NSA) into the electrolyte medium caused a reduction in the conductivity of the medium and thus posing greater difficulty in electrolytic polymerisation. This trend is occasioned by organic nature of the NSA which is less conducting than when pure HCl solution is used. The electrosynthesis of PPyNSA on platinum disc electrode was not successful due to the high electrode resistivity preventing initiation of polymerization process at the experimented conditions. The observed trend in the electropolymerisation on GCE was however better as there was less resistance to polymer adsorption on the electrode surface (Fig 4.16a). The multi scan voltammograms of the GCE/PPyNSA featured a diffusion controlled system with peak separations ranging from 108 to 369mV while the $|I_{p,a} / I_{p,c}|$ ranged from 1.6 – 2.2 with lower values at low scan rates respectively (Fig. 4.16b). The GCE/PPyNSA redox peak potential points were unfortunately not sharp at low scan rates. Sharper peaks were seen at scan rates of over 100 mVs$^{-1}$ but they were not kinetically related (Fig. 4.16b).
Figure 4.16: Polymerization voltammograms of GCE/PPyNSA (15 cycles) from 0.1 M Pyrrole and 0.05 M NSA in 0.1 M HCl at 50 mVs\(^{-1}\) (a), and multi scan rate voltammogram for the electropolymerized GCE/PPyNSA at 5 to 400 mV/s (b).
Cyclic voltammetry (CV) of over-oxidized electrosynthesised PPyNSA

During the potentiodynamic electro-synthesis of PPyNSA at room temperature in excess of a potential higher than 800mV, I observed there was overoxidation of PPyNSA. It had been reported that the use of platinum electrode for the synthesis of metal-doped polypyrrole has the disadvantage of loss of polypyrrole activity at potentials more anodic than 700mV and activity decrease at potentials more cathodic than – 300mV [11]. This was traced to the high electrocatalytic activity of polypyrrole on platinum electrode. The electropolymerisation (10 cycles) of PPyNSA on GCE using high anodic switch potential of 1500 mV from from 0.1 M Pyrrole and 0.05 M NSA in 0.1 M HCl using a scan rate of 20 mV/s at room temperature is shown in Figure 4.17a. At the potential window of -800mV to 1500mV used, there was cathodic growth over the first four cycles of the 10 cycles of polymerization after which growth ceased. The anodic peak current showed continual decrease in peak current with cycling. Upon characterisation of the film, there was no anodic peak because of the overoxidation but the cathodic peak currents increased with scan rate from 5 to 100 mV/s (Fig. 4.17b) after which there was progressive decrease in current with increasing scan rate. The decrease in current is due to saturation of the electrode surface with poor conducting film generated at the high potentials used for polymerisation. The shifts in the anodic peak currents to lower potentials with progressive cycling was due to the high potential used, which generated less electroactive and less conducting film. Overoxidised PPy, despite its disadvantages of decreased electroactivity, has wide electro analytical applications that utilize perm-selectivity [9]. The overoxidation was however curtailed when the electrosynthesis was done using an electrolyte/monomer mixture equilibrated at 0 °C within the same potential window. Usage of higher scan rates for the polymerisation is undesirable as it saturates the electrode surface faster.
Figure 4.17: (a) Polymerization voltammograms of GCE/PPyNSA (10 cycles) from 0.1 M Pyrrole and 0.05 M NSA in 0.1 M HCl at 20 mVs$^{-1}$ showing overoxidation current pattern, (b) multiscan voltammograms.
4.5.2.2 Kinetic studies on electrosynthesised PPyHCl

Pt/PPyHCl

The dynamics of electropolymerisation of PPyHCl is as shown in Fig 4.14. Analysis of the polymerisation and the multiscan rates voltammogram displayed in Fig. 4.14 (a and b), as well as the OSWV and DPV investigation showed that about 3 electrons might be involved in the polymerisation process. The peak separation, \( \Delta E_p \), between the anodic and cathodic peaks in Fig. 4.14b is about 171 mV which suggest that there may be more than one redox couple involved in the electrochemistry as earlier discussed for PPyNSA. The formal potential, \( E^{\infty} \), of the PPyHCl system in the hydrochloride electrolyte solution of 0.1 M HCl was estimated using the CV at 5 mV/s as 86.5 mV. This was arrived at using equation 3.1,

\[
E^{\infty} = \frac{(E_{p,a} + E_{p,c})}{2} = \frac{(115.9 + 57.1)}{2} = 86.5 \text{ mV}
\]

From the CV for the polymerisation of Pt/PPyHCl, Fig 4.14a, the estimate for \( E^{\infty} \) was

\[
E^{\infty} = \frac{(E_{p,a} + E_{p,c})}{2} = \frac{(152 + 19)}{2} = 85.6 \text{ mV}.
\]

Similarly the OSWV at 15 Hz, and square wave amplitude of 25 mV gave \( E^{\infty} \) as 98.3 mV. Averaging the estimates of \( E^{\infty} \) from these three approaches gave \( E^{\infty}_{PPyHCl} \) as 90.1±7.3 mV at the operating conditions.

The ratio of \( |I_{p,a}/I_{p,c}| \) was 1.88±0.24 over different scan rates between 5 to 50mV/s. At higher scan rates, the ratio increases and thus reducing the quasireversibility of the Pt/PPyHCl. Surface concentration \( (\Gamma^*_{PPyHCl}) \) at the electrode surface was estimated from data generated at 5, 10, 20, 30, 40 and 50 mV/s using the Brown-Anson model (equation 3.5) to be \( \Gamma^*(\text{anodic}) \) of \( 1.32 \times 10^{-8} \text{ mol cm}^{-2} \) and \( \Gamma^*(\text{cathodic}) \) of \( 5.93 \times 10^{-9} \text{ mol cm}^{-2} \). The \( \Gamma^*(\text{cathodic}) \) value is a better indication of the concentration of the PPyHCl film on the platinum surface as this is the form in which the polymer is adsorbed on the electrode surface.

A plot of the peak currents versus square root of scan rates gave linear plots for both anodic and cathodic waves. The slopes for the anodic and cathodic plots (Fig. 4.18) was \( 9.4032 \times 10^{-4} \text{ A} / (\text{V/s})^{1/2} \) \( (r^2 = 0.9793) \) and \( 4.2572 \times 10^{-4} \text{ A} / (\text{V/s})^{1/2} \) \( (r^2 = 0.9928) \)
respectively. The diffusion coefficient (De) was estimated from the slope in the
Randles-Sevčík plot (Fig. 4.18) using equation (equation 3.6) to be $3.20 \times 10^{-5}$ cm$^2$ s$^{-1}$
for the cathodic and $1.30 \times 10^{-6}$ cm$^2$ s$^{-1}$ for the anodic. The average diffusion
coefficient for the PPyHCl film is estimated as $1.67 \times 10^{-5}$ cm$^2$s$^{-1}$. The polymer
showed poor reversibility between the anionic and cationic species, as seen by the
$|Ip,a / Ip,c|$ being 1.81; $\Gamma^*(\text{anodic specie})/ \Gamma^*(\text{cathodic specie})$ being 2.23; and $De
(\text{anodic specie})/ De (\text{cathodic specie})$ being 0.04. This trend attests to the poor kinetics
and lesser quasi-reversibility of the electrosynthesised PPyHCl compared to the
chemically synthesised PPyNSA discussed earlier.

Figure 4.18: Plot showing the variation of the modulus of both the anodic and
cathodic peak currents with square root of scan rates for Pt/PPyHCl system in
0.1 M HCl.

4.6 Amperometric response of GCE/PPyNSA to phenol

The square wave responses of the GCE/PPyNSA to phenol are shown in Fig 4.19. The
analytical region (0 to 139.5 µM) of the phenol calibration plot of the electrode is the
The estimated electrode sensitivity was 3.1 mA.M\(^{-1}\) and the detection limit was estimated from the noise to signal ratio of the SWV responses and found to be 0.65 µM (i.e. 2 x noise / sensitivity, where noise was estimated as 1 x 10\(^{-9}\) A). For extended phenol concentration range, the GCE/PPyNSA electrode follow typical hyperbolic Michaelis-Menten kinetics reaching \(I_{\text{Max}}\) (maximum current) of 0.5µA at phenol concentration of 333.3 µM. The apparent Michaelis-Menten constant (\(K'_M\)) was estimated as 160 µM. This \(K'_M\) value is 48% of the observed maximum substrate concentration of 333.3 µM for the PPyNSA-GCE sensor. Iwuoha et al [38] had reported that maximum biosensor catalytic response is obtainable at \(\frac{1}{2} I_{\text{Max}}\), when the \(K'_M\) value is reached. The \(K'_M\) value obtained is within the range 10\(^{-2}\) and 10\(^{-7}\) M obtainable for enzyme catalysed reactions [39].

**Figure 4.19:** Graph of the square wave voltammetric response of GCE/PPyNSA to different concentrations of phenol in 0.05 M HCl [22].
Conclusions

The effect of temperature, concentration of reacting species and synthesis conditions have been identified as critical factors for yield and morphology in conducting polymers of PPyNSA. This study showed that at optimal synthesis temperature of 0 °C, the highest yield of PPyNSA (99 %) is obtainable with d/m 0.8 and o/m 1.0. The morphology of the polymer varies from thin sheets to fibres, micro rods/tubes and nano micelles/rods/tubes. The diameters of the tubules range from 150 - 3000 nm while the nano-sheets have a diameter of 20 nm. Use of APS-pyrrole mole concentration ratio of 1.0 produced micelles with typical diameters of ca. 100 - 150 nm. The concentration of charge transfer species along the polymer chain through doping with the NSA improved the solubility of the polypyrrole in organic solvents.
Besides, the use of NSA as dopant gave better electrochemistry than when only HCl was used. PPyHCl was the least soluble of all the polypyrrole investigated. PPyNSA (d/m 0.5 and o/m 0.2) gave the highest solubility; and its UV-Vis revealed polaron and bipolaron concentration at 437 nm and 555 nm respectively. In dodecylbenzenesulphonic acid doped polypyrrole the best compromise between conductivity and solubility in m- cresol was found to be at o/m ratio of 0.13 [40]. FTIR result show better doping for PPyNSA (d/m 0.8, o/m 0.2) than for the PPyNSA (d/m 0.8, o/m 1.0). EIS analysis together with OSWV data shows that the β-NSA doped polypyrrole systems exhibit highest electroactivity at potentials between 200 mV and 300 mV. Test application of the GCE/PPyNSA electrode as phenol sensor showed that PPyNSA based sensor can be used in the detection of phenol in water and environmental samples. The dynamic linear range of the sensor showed that the sensor is analytically useful at phenol concentrations of 2 – 10 µM and with the extended hyperbolic curve higher concentration range of 0.65 - 139.5 µM could be determined. This translates to phenol mass concentration of 6.7 - 1500 parts per billion (ppb). This is within the range of phenol found in pharmaceutical industries and refinery effluents.

References


Chapter Five

Results and discussion 2

Morphology, Spectroscopy, Electrochemistry and Applications of novel polypyrroles-1, 2-napthaquinone-4-sulphonate (PPyNQS) composite

This chapter gives the results for the chemical and electrochemical preparation, characterization and application of polypyrrole modified with sodium salt of 1, 2-napthaquinone-4-sulphonic acid (NQS). The chemical synthesis option was based on the optimized conditions established for PPyNSA with a dopant to monomer (d/m) mole concentration ratio of 0.8 and oxidant to monomer (o/m) mole concentration ratios of 0.2 and 1. Yield, morphological and spectroscopic properties of the NQS-doped polypyrrole nanomicelles is discussed. Electrochemical synthesis option was employed for the evaluation of the redox properties and kinetics of the charge transfer processes of the polymer. SNIFTIR spectroscopic result provided information on the structural changes during oxidation and reduction and evidence of doping with NQS. The test application of the PPyNQS electrode as a chemical sensor for benzidine and naphthalene in aqueous medium is also presented.

5. Introduction

Having achieved some success in establishing optimum conditions for the synthesis of highly electroactive, soluble and processable naphthalene sulphonic acid doped polypyrrole PPyNSA via the chemical synthesis options [1, 2], which is one of the major objectives of this study, it was desirable to further explore other surfactant routes to the modification of polypyrrole. In this chapter, nanomicelles and nano-film of novel polypyrrole 1, 2-napthaquinone-4-sulphonate (PPyNQS) was self assembled with sodium salt of 1, 2-napthaquinone-4-sulphonic acid (NQS) and pyrrole (Py) in
electrolyte medium of hydrochloric acid [3]. The polymer composite in the nanostructured and conducting state is expected to produce improved catalytic effect.

It is well known that various conducting polymers can self assemble into nanostructures both in solutions [4] and at electrode surfaces [5]. The ability of surfactant mediated synthesis to give different forms of nanostructures has made its use quite versatile in the present drive for production of improved sensor materials [6]. In using 1, 2-naphthaquinone-4-sulphonate as dopant, we expect improvement in the solubility, processability and electroactivity of the modified polymer and also create an expansion in its applications to sensor measurements. The introduction of the two ketonic groups on the naphthalene sulphonate is expected to further improve the coulumbic interactions required for the production of a more electroactive, processable, ‘intelligent’, and soluble polypyrrole [7]. Within the scope of available information at our disposal, the synthesis of modified polypyrrole using the NQS dopant option is novel. The ionic form of the polymer is represented by Fig. 5.1.

![Ionic form of polypyrrole 1, 2-naphthaquinone-4-sulphonate (PPyNQS) smart nanomaterials.](image)

The polymer composite formed with the NQS will combine the properties of low dimensional material, conducting polymer and that of the functional 1, 2-naphthaquinone-4-sulphonate (PPyNQS) acting as dopant and acid electrolyte [6]. Through careful experimental control of the conditions of self assembly of this PPyNQS smart nanomaterial on platinum working electrode and stabilizing the film
through mild evaporation, a Pt/PPyNQS working electrode was formed and used as impedimetric sensor for determination of benzidine and naphthalene in aqueous medium.

The experimental results of the morphological, spectroscopic, electrochemical and test applications of the PPyNQS polymer are now presented.

5.1 Chemical synthesis and yield optimization

5.1.1 Yield and morphological properties of PPyNQS

Table 5.1 presents the yield result obtained from the chemical synthesis using a d/m mole concentration ratio of 0.80 which generated instantaneous precipitation of black polypyrrole from the black solution of pyrrole/NQS in 0.1 M HCl.

Table 5.1: Yield profile for chemically synthesised PPyNQS at different dopant and oxidant concentration ratios.

<table>
<thead>
<tr>
<th>Code</th>
<th>pyrrole used</th>
<th>NQS/dopant used</th>
<th>APS used</th>
<th>ratios</th>
<th>pH</th>
<th>color change</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NQS-1</td>
<td>0.529 mL (7.5 x 10^-3 mol)</td>
<td>1.540 g (6.0 x 10^-3 mol)</td>
<td>0.3457 g (1.5 x 10^-3 mol)</td>
<td>d/m (0.80) o/m (0.20)</td>
<td>1.41</td>
<td>Dark brown to black</td>
<td>0.1920 g (37 %)</td>
</tr>
<tr>
<td>NQS-2</td>
<td>0.529 mL (7.5 x 10^-3 mol)</td>
<td>1.540 g (6.0 x 10^-3 mol)</td>
<td>1.745 g (7.5 x 10^-3 mol)</td>
<td>d/m (0.05) o/m (1.00)</td>
<td>1.43</td>
<td>Dark brown to black</td>
<td>0.5160 g (104 %)</td>
</tr>
<tr>
<td>NQS-3</td>
<td>0.529 mL (7.5 x 10^-3 mol)</td>
<td>0.0982 g (3.776 x 10^-4 mol)</td>
<td>0.3484 g (1.5 x 10^-3 mol)</td>
<td>d/m (0.05) o/m (0.20)</td>
<td>1.40</td>
<td>Yellowish brown solution to black</td>
<td>0.1660 g (31 %)</td>
</tr>
<tr>
<td>NQS-4</td>
<td>0.529 mL (7.5 x 10^-3 mol)</td>
<td>0.0982 g (3.776 x 10^-4 mol)</td>
<td>1.745 g (7.5 x 10^-3 mol)</td>
<td>d/m (0.05) o/m (1.00)</td>
<td>1.43</td>
<td>Yellowish brown solution to black</td>
<td>0.562 g (106 %)</td>
</tr>
</tbody>
</table>
Fig. 5.2 shows the SEM micrograph of dry powder of PPyNQS at nanometer range. It displayed clusters of micelles and grains with diameters ranging from 50 – 150 nm, which are compactly joined together with helical chains of about 20 nm diameters. The cluster arrays provide large surface area for electron hopping. The existence of this morphology is derived from the micelle guided growth process at optimum conditions of dopant to monomer (d/m) mole concentration ratios of 0.05 and oxidant to monomer (o/m) mole concentration ratios of 0.2 and 1 for Fig. 5.2a and b respectively. The pyrrole molecules preferentially dissolved into the micellar assembly of the surfactant because of the monomers hydrophobic nature and through external nucleation generate networks of clusters [6]. This ordered arrangement led to the micellic clusters seen in the micrograph.

The structure of the polymer might change from spherical to rod- and lamellar-shape as the concentration of the surfactant increases. It is therefore important to ensure that the surfactant’s critical micelle concentration (CMC) is not exceeded for production of electroactive polymer. The optimized synthesis condition for the electrochemical synthesis requires a maximum d/m ratio of 0.1. At higher concentrations of surfactant the polymer is over-oxidised. The micellic clusters seen in the chemically synthesized PPyNQS was obtainable at d/m concentration ratio of 0.05.

Fig. 5.3 shows the energy dispersive X-ray (EDX) spectra and the elemental analysis for carbon, oxygen and sulphur based on the micrograph portion containing the nanostructures. The proximate % elemental composition of C:89; O:5 and S:6 for PPyNQS compares with that for PPyNSA, which was C:91; O:3 and S:3. The higher % elemental composition S for PPyNQS is an indication of better surfactant incorporation into the polymers structure via sulphonation of the polypyrrole moiity. Likewise the higher % elemental composition obtained for O in PPyNQS is traceable to the ketonic group from NQS which gave additional contribution to what is obtainable for NSA.
Figure 5.2: SEM micrographs of dry powder PPyNQS showing the typical fibrous-micellar structures obtained from (a) PPyNQS [d/m 0.05; o/m 0.2] and (b) PPyNQS [d/m 0.05; o/m 1.0].
5.1.2 Spectroscopic properties of PPyNQS

**FTIR**

Figure 5.4 shows the Fourier Transform Infra Red (FTIR) spectra of PPyNQS obtained from the two o/m mole concentration ratios of 0.2 and 1.0 compared with that where NQS was not used (PPyDW). The spectra showed the existence of all the characteristic absorption bands for polypyrrole with slight variations in the absolute values for the PPyDW, PPyNQS (d/m 0.05; o/m 0.2) and PPyNQS (d/m 0.05; o/m 1.0). The characteristic absorption bands observed were compared with those reported by Geetha and Trivedi [8] for doped polypyrrole and presented in Table 5.2. The absence of the usual N – H stretching vibration at 3400 cm\(^{-1}\) shows that the polymers are not in the neutral state just as was observed for the PPyNSA system in chapter four. The N – H stretching band for neutral polypyrrole at 1450 cm\(^{-1}\) shifted positively by 11 cm\(^{-1}\) in PPyNQS (d/m 0.05, o/m 0.2) and by 8 in the more oxidized polypyrrole PPyNQS (d/m 0.05, o/m 1.0). This is a confirmation that the polymers were not in the
aromatic states but rather in the excited polaronic states. The C=C and C-C stretching band absorption at 1542 cm$^{-1}$ in the two PPyNQS system is synonymous to the absorption band of 1545 cm$^{-1}$ characteristic of doped PPy [8]. The usual C-H deformation at 1050 cm$^{-1}$ for doped polypyrrrole was observed at 1042 cm$^{-1}$ for the PPyNQS system. The sensitivity of the instrument could not resolve clearly the doublet, asymmetric stretching of O=S=O at 1320 and 1288 cm$^{-1}$ which is expected for polypyrrrole doped with sulphonic acids. More interesting investigation was sought using SNIFTIR and the results are discussed underneath.

Figure 5.4: FTIR spectra of polypyrroles in KBr medium for: (a) PPyDW, (b) PPyNQS (d/m 0.05; o/m 0.2) and (c) PPyNQS (d/m 0.05; o/m 1.0).
Table 5.2: Major shifts of bands (cm⁻¹) in FTIR spectra of PPyDW, PPyNQS (d/m 0.05, o/m 0.2) and PPyNQS (d/m 0.05, o/m 1.0) from undoped polypyrrole major bands (Geetha & Trivedi) [8].

<table>
<thead>
<tr>
<th>Major bands (cm⁻¹)</th>
<th>PPyDW (d/m 0.05; o/m 0.2)</th>
<th>PPyNQS (d/m 0.05; o/m 0.2)</th>
<th>PPyNQS (d/m 0.05; o/m 1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3421 (N-H str)</td>
<td>absent</td>
<td>absent</td>
<td>absent</td>
</tr>
<tr>
<td>3100 (C-H str)</td>
<td>absent</td>
<td>absent</td>
<td>absent</td>
</tr>
<tr>
<td>1535 (C=C &amp; C-C str)</td>
<td>1554</td>
<td>1542</td>
<td>1542</td>
</tr>
<tr>
<td>1450 (N-H str)</td>
<td>absent</td>
<td>1461</td>
<td>1458</td>
</tr>
<tr>
<td>1295 (C-H &amp; N-H def)</td>
<td>1308</td>
<td>1307</td>
<td>1307</td>
</tr>
<tr>
<td>1050 (C-H def)</td>
<td>1047</td>
<td>1042</td>
<td>1042</td>
</tr>
</tbody>
</table>

**SNIFTIRS**

The substructively normalized FTIR spectra showed the ability of the modified polymer to switch from the oxidized state to the reduced state within reasonable potentials. A shift of the baseline was evident in the spectra obtained at potentials increasingly positive of 0mV, when the spectra were viewed over the extended scale, covering the complete wavenumber range experimentally available i.e. 5000 cm⁻¹ to 1000 cm⁻¹ (Fig. 5.5). This is related to low energy transitions within the polymer and is evidence of the conductive nature of the modified polymer. The solvent features seen at around 3500 cm⁻¹ were not expected to interfere with other absorptions. During the analysis of spectral data however emphasis was placed on the absorptions between 2400 cm⁻¹ to 1000 cm⁻¹, which covered the fingerprint region (1700 to 1000 cm⁻¹) of the spectrum (Fig. 5.6). The intensity of absorption bands present in this region is indicative of the oxidation state of the polymer.

The bands present in the region of ring stretching are particularly intense due to strong coupling between charge carriers and ring vibrational modes, facilitating movement...
of carriers within conjugated polymer chains. These enhanced signals (IRAV bands) are typical of doped conducting polymers. The vibrations occur as paired bands at very close frequencies. The downward bands at 1531 and 1586 cm$^{-1}$ were assigned to C=C and C-C vibrations. The bands at 1432 and 1380 cm$^{-1}$ are assigned to C=N vibration. The band at 1294 cm$^{-1}$ was assigned to N-H in plane contributions. Evidence of the sulphonie acid presence in the doped polymer matrix was provided by the absorption bands at 1172 and 1080 cm$^{-1}$ in Fig. 5.6 assigned to the asymmetric stretch of the O=S=O group [9-12]. An absorption band at 2340 cm$^{-1}$ which increased in intensity at potentials above 300 mV, is indicative of the presence of CO$_2$ [9, 12, 13].

![Figure 5.5: Full SNIFTIRS spectra of PPyNQS at 100 mV potential intervals from 0 to 600 mV, vs calomel electrode.](image)

Figure 5.5: Full SNIFTIRS spectra of PPyNQS at 100 mV potential intervals from 0 to 600 mV, vs calomel electrode.
Figure 5.6: Normalised SNIFTIRS spectra of PPyNQS showing the enlargement of the fingerprint region.

**UV-Vis results**

The polymer showed good solubility in DMSO and DMF. Figure 5.7 shows the UV-Vis of PPyNQS compared with that of polypyrrole prepared in distilled water in the undoped state, (PPyDW) taken in DMF. The sharp peaks at 380, 750 and 820 nm correspond to the polaron, bipolaron and overlapped bi-polaron bands within the polymeric structure [8, 14]. These absorptions are not associated with that of PPyDW. The concentration of these charge carriers lends credence to the intrinsic high electroactivity of PPyNQS through the incorporation of the surfactant dopant. The wavelength absorption bands here are similar to that of polypyrrole doped with naphthalene sulphonic acid in the optimized ratio of dopant/monomer (d/m) concentration ratio of 0.5 and oxidant/monomer (o/m) concentration ratio of 0.2 [6].
5.2 Electrochemical investigation

5.2.1 Chemically synthesized PPyNQS:

Since our subsequent sensor application was based on the electrochemically generated PPyNQS, the electrochemical investigation carried out was concentrated on the electrochemically synthesized product.

5.2.2 Electrochemically synthesized PPyNQS

The electrosynthesis of PPyNQS in the acidic aqueous electrolyte was very successive on both platinum and glassy carbon electrode. The choice of platinum electrode was made because it offers a transparent surface for comparative spectroscopic studies. Initial investigation showed that better electropolymerisation and film adherence is obtainable at 50 mVs$^{-1}$. At lower scan rates, the film formed was loosely adhered and at higher scan rates there was poor polymer growth.
5.2.2.1 Voltammetric investigation

Cyclic voltammetry (CV)

The cyclic voltammogram for the electropolymerisation of PPyNQS is shown in Fig. 5.8a, and the potentiodynamic behaviour of the modified polypyrrole is at different scan rates is shown in Fig. 5.8b. The electrochemically-polymerized film, grown at a scan rate of 50 mVs$^{-1}$ for 25 cycles, was observed to have good adhesion to the Pt electrode surface. It should be noted that the ratio of the mole concentration of the monomer/dopant mixture is critical in order to produce a conducting polymer. A potential window of –400 through 700 mV vs. Ag/AgCl was used for the polymerization and investigation after optimization of the synthesis conditions so as to eliminate/minimize interference from other peaks. Additionally, this range is required to prevent the over-oxidation and degradation of polypyrrole which normally occurs at higher positive potentials, whilst a too negative potential will result in hydrogen evolution [15].

(a)
Figure 5.8: Typical voltammograms for (a) the polymerisation of Pt/PPYNQS from 0.1 M Py + 0.01 M NQS in 0.05 M HCl. (25 cycles) at 50 mV/s and (b) multi–scan rate voltammograms of the thin film in 0.05 M HCl at scan rates of 5, 10, 15, 20, 25, 30, 40 and 50 mV/s.

The cyclic voltammograms consistently displayed one distinctive oxidation and one reduction peak. The peak separation between the anodic and cathodic peaks, increased with increase in scan rates. From our multi–scan rate voltammograms (Fig. 5.8b), the anodic/cathodic peak potentials at 5 mVs\(^{-1}\) were 364 mV and 301 mV vs. Ag/AgCl respectively. The average formal potential (\(E^\circ\)) estimated from peak potentials at 5, 10, 15, 25, 30, 40 and 50 mVs\(^{-1}\) was calculated as 322 ± 5 mV. The peak separation of 63 mV obtained on the CV at 5 mVs\(^{-1}\) was used as an indication of a one electron
process for the polymer \(n = 1\). Applying equation 3.2 gives an \(n\) value of 1.1. Similar electron transfer of unity had been reported for the electropolymerisation of polypyrrole doped with p-toluenesulphonate, [16].

**Test for reversibility**

In order to assess the degree of reversibility of the oxidation and reduction processes of PPyNQS, the following diagnostic tests attributed to Nicholson [17] and Matsunda [18] were performed:

a) The change in \(|I_p|\) vs. square root of scan rates \((\sqrt{\nu})\)

b) The \(|I_{p,a}/I_{p,c}|\) value was determined provided \((\alpha_a = \alpha_c = 0.5)\)

c) The shifts in \(E_{p,c}\) with increasing \(\nu\) was monitored

d) The change in \(\Delta E_p\) with increasing \(\nu\) was monitored and compared with \((59/n) \text{ mV}\) obtainable for reversible systems

Data from the multi scan rate voltammetry at 5, 10, 15, 20, 25, 30, 40 and 50 mVs\(^{-1}\) (Fig 5.8b) were used to perform these diagnostic tests. Figure 5.9a shows the variation of anodic and cathodic peak current with square root of the scan rates, while Fig. 5.9b shows the variation of the modulus of both the anodic and cathodic peak current with square root of the scan rates. Figure 5.9b shows that \(|I_p|\) increases for both anodic and cathodic peak currents with increases in \(\sqrt{\nu}\). However, the relationship is not proportional as \(|I_p|/\sqrt{\nu}\) is not a constant in either case. Figure 5.9b further depicts the best-fit line for all data points with a slope of \(1.0309 \times 10^{-3} \text{ A/(V/s)}^{1/2}\) (correlation coefficient of 98.1%); and a slope of \(0.8025 \times 10^{-3} \text{ A/(V/s)}^{1/2}\) (correlation coefficient of 99.1%) for the anodic and cathodic peaks, respectively. Thus the results obtained for test (a), satisfy the condition for quasi-reversibility. Based on the assumption that the anodic and cathodic transfer coefficients \((\alpha_a\) and \(\alpha_c)\) are equal to 0.5 for simple electron transfer [19], the diagnostic test (b) reveals that ratio of the modulus of the two peak currents shown in the multi plot voltammogram (Fig. 5.8b) gives \(1.30 \pm 0.05\) which is approximately 1 over the range of 5, 10, 15, 20, 25, 30, 40 and 50 mVs\(^{-1}\). This is in line with the specifications of quasi-reversible systems. Test (c) which investigates the shifts in \(E_{p,c}\) with increasing \(\nu\) is shown in Fig. 5.10a. It is seen that as the scan rate increases the cathodic peak potential shifts to lower values, thus, providing further evidence for quasi-reversibility. The final test (d) which investigates
the behavior of the peak separation ($\Delta E_p = E_{p,a} - E_{p,c}$) with increases in scan rates is shown in Fig. 5.10b. This indicates that the $\Delta E_p$ increases with increasing scan rates because the cathodic peak potentials are becoming more negative while the anodic peak potentials adopt more positive values.

It could therefore be generalized based on the compliance of the results with Nicholson/Matsunda criteria that the Pt/PPyNQS system in the 0.05 M HCl electrolyte undergoes a quasi-reversible electrochemistry under the conditions used for the investigation.
Figure 5.9: (a) Plot of variation of anodic and cathodic peak currents with square root of the scan rates and (b) plot showing the variation of the modulus of both the anodic and cathodic peak currents with square root of scan rates of Pt/PPyNQS in 0.05 M HCl.
Figure 5.10: (a) Plot showing the variation of cathodic peak potentials with scan rates and (b) plot of peak separations versus scan rates of Pt/PPyNQS in 0.05 M HCl at a 1.6 mm diameter Pt electrode at a temperature of 25 °C based on the data from Fig. 5.8b.

Pulse techniques (DPV and OSWV)
The redox properties of the Pt/PPyNQS film were investigated using pulse techniques. DPV investigation at a scan rate of 5 mVs$^{-1}$ gave both anodic and cathodic peaks at 317 mV thus indicating an $E^\theta$ estimate of 317 mV (Fig. 5.11). Also, the OSWV (Fig. 5.12) at a frequency of 15 Hz and amplitude of 25 mV gave one oxidation and one reduction peak within the potential window of -400/700 mV. The average of the peaks at 360 and 273 mV was used as an estimate for the formal potential ($E^\theta$) value, being 317 mV.
Figure 5.11: Differential pulse voltammograms for the anodic and cathodic wave difference for Pt/PPyNQS film in 0.05 M HCl using a scan rate of 5 mV/s and 50 mV pulse amplitude.
5.2.2.2 Kinetic analysis of the Pt/PPyNQS system

The Brown Anson model was used to estimate the surface concentration of the polymer ($\Gamma^*_{PPyNQS}$) using the peak currents ($I_p$) obtained at different scan rates ($\nu$) between 5 mVs$^{-1}$ and 50 mVs$^{-1}$ [20]. Thus from equation 3.5:

$$I_p = \frac{n^2 F^2 \Gamma^*_{PPyNQS} A \nu}{4RT}$$
The notations F, A, R and T are constants for the Faraday’s constant (96584 C mol⁻¹), working electrode area, molar gas constant and room temperature of 298 K respectively. The plots in Fig. 5.13 showed linear relationship with correlation coefficient (r²) of 0.994 and 0.999 respectively for the cathodic and anodic currents vs. scan rates. The ratio of anodic peak current (I_{p,a}) to cathodic peak current (I_{p,c}) ranged from 1.23 to 1.38 over the range of scan rates applied, which is not exactly unity as required for fully reversible one electron transfer, which further gave credence to the quasi-reversible electron transfer mechanism that was suggested. The plot confirms the formation of a stable film whose density is slightly lower during reduction (1.42 x 10⁻⁷ mol.cm⁻²) as compared to oxidation (1.83 x 10⁻⁷ mol.cm⁻²). This computation was based on the Brown Anson model using the cathodic slope of 2.687 x 10⁻³ A.s./V and the anodic slope of 3.478 x 10⁻³ A.s./V. The intercept values, for non-faradaic currents caused by charging of the electrical double layer at the electrode interface were close to zero being 8.50 x 10⁻⁶ A for the cathodic plot and 9.47 x 10⁻⁶ A for the anodic plotm (Fig. 5.13). This further lays credence to the quasi-reversible electrochemistry of the system.

The systems displayed progressive shift in anodic peak potential towards more positive values coupled with shift in cathodic peak potential to less positive values with increase in scan rate. The peak separations increase progressively from 63 mV at 5 mVs⁻¹ to 166 mV at 50 mVs⁻¹ coupled with increase in the magnitude of the peak currents with increase in scan rates. This shows that the peak currents are diffusion controlled. Thus the Randel-Sevčík equation (equation 3.6) was applied to determine the diffusion coefficient (D_e) for electron hopping along the polymer chain [21].

\[
I_p / \nu^{1/2} = 2.686 \times 10^5 n^{3/2} A \Gamma_{PPyNQS}^* D_e^{1/2}
\]

Ip is the peak current in A, n is the number of electron transferred, \( \nu \) is the scan rate in V s⁻¹, n is the no of electrons transferred, A is the surface area of the electrode in cm², \( \Gamma_{PPyNQS}^* \) is the surface concentration of the polymer film in mol cm⁻², \( D_e \) is the rate of charges transportation in cm².s⁻¹ along the polymer chain. The slopes of the linear plots shown in Fig. 5.9b are 1.0309 x 10⁻³ and 0.8025 x 10⁻³ A / (V/s) ½ for the oxidation and reduction scan waves with a corresponding correlation coefficient of 0.981 and 0.991 respectively.
The rate of charge transportation, $D_e$, along the polymer chain was found to be $1.02 \times 10^{-6}$ cm$^2$.s$^{-1}$, being the same for the oxidation and reduction reactions. This suggests that the deviation from full reversibility does not necessarily involve permanent electronic changes to the bulk polypyrrole film upon potential cycling, but that some other phenomenon is responsible for the kinetics observed. The cyclic voltammogram at a scan rate of 5 mVs$^{-1}$ was used to investigate the rate constant ($k^*$) for electron transfer within the polymer chain using Nicholson treatment for a quasi-reversible electrochemical system [17, 19-21]. Thus using equation 3.9, the $k^*$ was estimated.

$$k^* = \varphi (\alpha \cdot n \cdot F \cdot v \cdot D_e / RT)^{1/2}$$

The transfer coefficient, $\alpha$, of 0.5 was assumed for the PPyNQS systems and the kinetic parameter, $\varphi$ (dimensionless), was assigned a value of 7 based on the peak
separation, $\Delta_{E_p}$, of 63 mV at a scan rate of 5 mVs$^{-1}$ which indicated $n = 1.1$. The $k^*$ value of $2.20 \times 10^{-3}$ cm.s$^{-1}$ obtained for the polymer at 5 mVs$^{-1}$ shows that electron hopping along the polymer chain at the low scan rate is quite facile. This is comparable with the rate constants reported for other conducting polymers Vis. Pt/polyaniline electrodes with $k^*$ values of 0.049 to $5.4 \times 10^{-3}$ cms$^{-1}$ in different electrolytes [22] and Pt/poly(3,4-ethylenedioxythiophene) electrodes with $k^*$ values of 1.5 to $45.3 \times 10^{-3}$ cms$^{-1}$ when prepared under different conditions [23] under different synthesis conditions.

5.2.2.3 Impedance spectroscopic investigation of Pt/PPyNQS

Electrochemical impedance spectroscopy (EIS) enables the separation of interfacial electron transfer from concomitant electronic changes occurring within the bulk material of the electrode on the basis of frequency dependent electrochemical response. EIS data was collected, in consecutive 50 mV steps, in the potential range corresponding to the oxidation of the polymer film (0 mV to 600 mV) and the subsequent reduction by inversion of the steps in potential back to 0 mV. The values obtained from the fit results of the data obtained from the impedance experiment using the equivalent circuit in Fig. 5.14 is presented in tables 5.3 and 5.4. This corresponds to the oxidative and reductive potential steppings respectively.

Typical data obtained at an applied potential of +50 mV vs. Ag/AgCl are shown in the complex plane impedance plots of Fig.5.14 for a frequency range between 40,000 – 223 Hz. The data obtained over an extended frequency range of 100 KHz - 100 mHz was analyzed using an equivalent electrical circuit consisting of the solution resistance ($R_s$), an $R_1$CPE$_1$ parallel combination, where CPE is a constant phase element, to model movement by electron hopping through the polymer film along the polymer backbone, and a second $R_2C_2$ component in series representing the electrode/solution interface, as indicated in [24, 25]. The CPE was modelled as a non-ideal capacitance, according to equation 3.24

$$CPE = \frac{1}{(C_i \omega)^n} \quad \text{equation 3.24}$$
The CPE is defined by two values i.e. the capacitance, \( C \), and the CPE exponent, \( n \), which has a value between 0.5 and 1 for a non-ideal capacitor. If \( n \) equals 1, the equation is identical to that of a capacitor and smaller values can be related to surface roughness and inhomogeneities, which lead to frequency dispersion. When a CPE is placed in parallel to a resistor, a depressed semi-circle (Cole-Element) is produced.

Figure 5.14: Complex plane impedance plots of PPyNQS thin film electrode at 50 mV vs. Ag/AgCl in 0.05 M HCl during (●) step-by-step oxidation and (○) subsequent reduction, (insert is the equivalent circuit used to fit the data).
Table 5.3: Analysis of the oxidative impedance data at the conductive polymer electrode.

<table>
<thead>
<tr>
<th>Potential /mV</th>
<th>$R_s$ /Ωcm$^2$</th>
<th>CPE1-T /mFcm$^{-2}$</th>
<th>CPE1-P /mFcm$^{-2}$</th>
<th>$R_{ct}$ /Ωcm$^2$</th>
<th>$C_{dl}$ /µFcm$^{-2}$</th>
<th>$R_{it}$ /Ωcm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>10.54</td>
<td>0.98</td>
<td>0.597</td>
<td>20.88</td>
<td>28.0</td>
<td>4.22</td>
</tr>
<tr>
<td>100</td>
<td>10.11</td>
<td>1.98</td>
<td>0.553</td>
<td>17.76</td>
<td>28.8</td>
<td>3.74</td>
</tr>
<tr>
<td>150</td>
<td>10.00</td>
<td>2.58</td>
<td>0.538</td>
<td>14.81</td>
<td>32.9</td>
<td>3.13</td>
</tr>
<tr>
<td>200</td>
<td>9.67</td>
<td>2.94</td>
<td>0.543</td>
<td>11.87</td>
<td>32.9</td>
<td>3.14</td>
</tr>
<tr>
<td>250</td>
<td>9.59</td>
<td>3.40</td>
<td>0.532</td>
<td>11.19</td>
<td>34.7</td>
<td>2.87</td>
</tr>
<tr>
<td>300</td>
<td>9.68</td>
<td>3.55</td>
<td>0.529</td>
<td>10.76</td>
<td>35.5</td>
<td>2.77</td>
</tr>
<tr>
<td>350</td>
<td>9.85</td>
<td>3.14</td>
<td>0.545</td>
<td>10.88</td>
<td>34.7</td>
<td>2.74</td>
</tr>
<tr>
<td>400</td>
<td>9.55</td>
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<td>0.533</td>
<td>11.52</td>
<td>34.5</td>
<td>2.95</td>
</tr>
</tbody>
</table>

Table 5.4: Analysis of reductive impedance data at the conductive polymer electrode.

<table>
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<tr>
<th>Potential /mV</th>
<th>$R_s$ /Ωcm$^2$</th>
<th>CPE1-T /mFcm$^{-2}$</th>
<th>CPE1-P /mFcm$^{-2}$</th>
<th>$R_{ct}$ /Ωcm$^2$</th>
<th>$C_{dl}$ /µFcm$^{-2}$</th>
<th>$R_{it}$ /Ωcm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>10.19</td>
<td>1.29</td>
<td>0.58</td>
<td>16.68</td>
<td>30.7</td>
<td>4.09</td>
</tr>
<tr>
<td>350</td>
<td>10.22</td>
<td>0.48</td>
<td>0.58</td>
<td>16.2</td>
<td>31.3</td>
<td>3.76</td>
</tr>
<tr>
<td>300</td>
<td>10.23</td>
<td>1.35</td>
<td>0.59</td>
<td>14.43</td>
<td>34.8</td>
<td>3.33</td>
</tr>
<tr>
<td>250</td>
<td>10.11</td>
<td>1.78</td>
<td>0.57</td>
<td>14.35</td>
<td>39.6</td>
<td>3.17</td>
</tr>
<tr>
<td>200</td>
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<td>14.55</td>
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<td>3.12</td>
</tr>
<tr>
<td>150</td>
<td>10.12</td>
<td>1.60</td>
<td>0.58</td>
<td>13.96</td>
<td>46.9</td>
<td>2.94</td>
</tr>
<tr>
<td>100</td>
<td>10.22</td>
<td>1.23</td>
<td>0.60</td>
<td>14.32</td>
<td>47.0</td>
<td>2.91</td>
</tr>
<tr>
<td>50</td>
<td>10.37</td>
<td>0.84</td>
<td>0.63</td>
<td>16.03</td>
<td>49.5</td>
<td>2.78</td>
</tr>
<tr>
<td>0</td>
<td>10.53</td>
<td>0.54</td>
<td>0.66</td>
<td>19.19</td>
<td>52.7</td>
<td>2.86</td>
</tr>
</tbody>
</table>
The solution resistance varied from 9.6 to 11.0 Ω. The values of $R_1$ and CPE$_1$ were interpreted through the electrical characteristics of the electopolymerised PPyNQS polymer bulk material. The capacitive nature of the bulk material was substantiated by the inverse relationship between the capacitance and resistance values of the high frequency loop. The polymer material showed good conductivity (10 – 20 Ω) and in the region of the formal potential as obtained by voltammetric experiments, the conductivity of the polymer material was measured as 10.8 Ω. The average value of $n$ for all experiments was 0.56, which is indicative of a rather rough morphology and porous structure and is probably also associated with electron hopping along the polymer backbone. The interface of the polymer with the HCl electrolyte showed consistently low values of capacitance, $C_2$ (30 μF) and resistance, $R_2$ (2.7 - 4.2 Ω) during the oxidation steps, the latter reaching a minimum value at the formal oxidation potential. The electron transfer from solution to the polymer film during oxidation is thought to be direct electron transfer without mediation by any surface bound species, since the interfacial capacitance values of 16 μF hardly varied over the potential range studied.

During the subsequent reduction steps, from 600 mV to 0 mV vs. Ag/AgCl, the capacitance (2 mF) and the resistance (15.5 Ω) of the polymer bulk material remained fairly constant. The bulk capacitance (CPE$_1$) and resistance ($R_1$) values were of the same order of magnitude during the reduction steps as compared with oxidation. However, a plot of the interfacial capacitance ($C_2$) versus applied potential showed a gradual increase in capacitance as the potential became more negative, and gradual increase as it became more positive (Fig. 5.15). The capacitance values for the oxidation and reduction trend intersect in the region of the formal potential (300 mV).
Figure 5.15: Plot of interfacial capacitance versus potential for the oxidation and reduction of the PPyNQS thin film.

This trend suggests a disruption to the direct electron transfer kinetics observed during oxidation. Evidence from SNIFTIRS equally suggests degradation of surface bound polymer units by anions in solution (e.g. Cl\(^-\)) which results in ring opening of surface polymer units and eventual loss of CO\(_2\), similar to the structural degradation induced in pyrrole under strongly basic conditions [26]. This surface chemistry could explain the observed changes in EIS data and confirms the quasi-reversible oxidation kinetics predicted by the scan-rate-dependent CV. The difference between the complex plane impedance plots at 50 mV before oxidation and after reduction (Fig.5.15) is further evidence of this.

**Polymer structure and proposed mechanism for the surface chemistry**

During the first cycle of electrochemical polymerization of pyrrole an inner layer is formed upon which the polymerized polypyrrole grows. Subsequent cycling steps allow for the development of the polymer chain resulting in the main layer and the thickness thereof depends on the number of potential cycles employed. It is also the main layer that influences overall film stability. The outer layer is produced by polymer termination when the potential is turned off and is made up of mainly short
chain polypyrrole and therefore less stable than the main layer (Fig. 5.16a). When the polypyrrole film is oxidized at 315 mV (vs Ag/AgCl) the surfactant anions (A⁻) align close to the polymer surface to compensate for the positive charge caused by the formation of bipolarons under anodic potentials (Fig. 5.16b). This phenomenon is sometimes referred to as electro-neutrality coupling and results in electron hopping within the polymer main layer to accommodate the bipolaron/ anion coupling at the surface [27].

![Figure 5.16](image)

(a) Neutral polymer          (b) Oxidized state

**Figure 5.16. Model illustrating the alignment of charges at different oxidation states of polypyrrole: (a) neutral polymer and (b) oxidized polymer.**

While actuating the polymer in monomer free 0.05 M HCl, the entrapped 1, 2-napthaquinone-4-sulphonate (NQS⁻¹) anion is immobile, it does not move and the hydrated small proton strictly determines ionic transport. However, with prolonged actuation or overoxidation, there is breakdown of the surface bound pyrrole and sulphonated units. The surfactant anion, NQS⁻¹, which is formed upon dissociation in the electrolyte behaves as a weak base. The surface bound pyrrole units lose the protons on the nitrogen in order for the surfactant to return to the preferred acidic state. The loss of the proton on the pyrrole rings however leads to disruption of the cyclic structure by rearrangement to form hydroxyl and carbonyl species and eventual loss of material through formation of CO₂ [28].
This suggests that some pyrrole units on the surface of modified polypyrrole chain undergoes ring opening [26]. The lone pair on the ring nitrogen combined with the four \( \pi \) electrons of the two double bonds to give pyrrole an aromatic sextet of electrons. The nitrogen is sp\(^2\)-hybridised and acquires a positive charge as its lone pair is delocalized around the ring [29, 30]. Therefore we propose a mechanism for the oxidation of the polymer, which involves adsorption of the surfactant onto the polypyrrole film on the electrode surface. The interaction of the surfactant anion with the strongly polarized surface pyrrole units on the polymer backbone leads to disruption of the induced aromaticity on the pyrrole. This results in the protonation of the surfactant to yield the sulphonic acid and deprotonation of the ring nitrogen. Further oxidation in the acid medium favors the reduction of the double bond adjacent to the nitrogen, which leads to ring opening and subsequent rearrangement to produce the more stable imine structure. The oxidation is irreversible and subsequent electronic rearrangement transforms slowly to yield the capacitive material observed under reduction conditions at around 200 mV vs. Ag/AgCl.

### 5.3 Modeling of the electrochemical and impedimetric properties of PPyNQS

In section 5.5.2.1, we established that the electrochemical behaviour of electropolymerised PPyNQS on a platinum electrode involves a one electron, quasi-reversible electrochemistry (\( \Delta E_p \approx 60 \) mV), \( E^{\circ} \) of 322 mV and \( I_{pa} / I_{pc} \) is 1.3 with a facile charge transport coefficient of \( 1.02 \times 10^{-6} \) cm\(^2\)s\(^{-1} \) [3]. Interfacial behaviour was described with the equivalent circuit in Fig. 5.17 based on the characteristic impedance profile obtainable at the potential (322 mV) where the polymer exhibits maximum electro-activity (Fig. 5.18). The circuit defines two simultaneous kinetics; one involving the bulk polymer material and the other taking place at the electrolyte/polymer interface. The observed kinetics were investigated and used to fashion out the relationship to changes in the analyte concentrations being sensed by the transducer. The first intercept on the x-axis (Fig 5.18) is, typically, due to the solution resistance Rs. It is independent from the applied potential for a given cell configuration and typically about 10 Ohms. The high frequency semicircle is not fully formed and hardly visible when the full frequency sweep is completed. However, by
expansion of the impedance data over a smaller range at the high frequency, it is obvious that it do exist even though it was not fully formed.

Figure 5.17: Equivalent electrical circuit describing the electrical components of Pt/PPyNQS in an electrolyte medium of 0.05 M HCl.
Figure 5.18: Typical Nyquist plot (top), Bode plot (bottom) for the Pt/PPyNQS system.
It has already been reported that the series combination of a resistance, $R$, and a constant phase element as in Fig. 5.17 leads to a depressed arc in the $Y$ plane [31]. The impedance transformation from high to low frequency is highlighted in the Bode plot (Fig. 5.18, bottom). The inability of the polymer to exhibit constant impedance over some frequency range at the low frequency end is a major peculiarity of this system.

The interrogation of the impedance profiles revealed that the least value of interfacial real impedance at the lowest frequency (10 mHz) was obtainable at 322 mV (Fig. 5.19), which is the potential at which the most conductive state is obtainable. This potential coincidentally gave the highest capacitance for the polymer. The interfacial impedance values as we switch to lower potentials from 322 mV are progressively higher because of the transformation from conducting polypyrrole state to the neutral state. At higher potentials to 322 mV, gradual over-oxidation of polypyrrole sets in which is accompanied with increase in interfacial impedance. Similar transformation in interfacial impedance has been reported for polyaniline as it switches through the emeraldine (conducting) and the pernigraniline and leuco-emeraldine (insulating) states [32].

![Figure 5.19: Plot of the interfacial impedance and capacitance at different perturbation potentials of the Pt/PPyNQS electrode.](image)

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Pt/PPyNQS impedimetric sensor for benzidine and naphthalene

The Pt/PPyNQS sensor was constructed using the electrochemically prepared film of PPyNQS via potentiodynamic polymerization as described earlier. At the pre-fixed potential of 322 mV, the impedance response generated by addition of the benzidine analyte to the cell shows that the reactivity proceeds at the interface, followed with that within the bulk polymer chain (Fig 5.20). The waveform of the plots in Fig. 5.20 shows that changes associated with the plot of the interfacial impedance (●) leads that for the plot of the bulk polymer impedance (▼).

Figure 5.20: Plot of changes in real impedance with increasing concentrations of benzidine at the bulk polymers region (▼) and at the interface (●).
As the benzidine concentration was added to the electrolyte from 0 to 333 μM, the impedance observed for the bulk polymer at the high frequency region (ca 10 KHz) had values of 172 – 234 Ohms. The high frequency value of 10 KHz was chosen because reproducible impedance measurements free of drift were obtainable as against that obtained at the start up frequency of 100 KHz. At the interface mapped by the low frequency region (ca 10 mHz), the impedance values were 840 - 920 Ohms. The relative change in the real impedance values at the two regions translates to 62 and 80 Ohms respectively. There is greater change in the interfacial impedance compared to that of the bulk polymer impedance. In the contrary, we observed from figures 5.21 and 5.22 that a more significant change in the capacitance values was recorded for this system at the 0 and 333 μM extremes. While the bulk polymer capacitance decreased from 72.7 to 57.1 μF, the interfacial capacitance decreased from 4.7 to 3.7 mF. This translates to a difference in absolute capacitance values by a factor of about 1000 times, with that at the interface being higher compared to that at the bulk polymer (Fig. 5.21 and 5.22). This offers us a comparative advantage to model the reactivity based on capacitance changes rather than the changes in the real impedance.

Increasing concentration of BZD is insulating and thus increases the resistance of the system. It also decreases the double layer capacitance at the electrode interface. It could therefore be hypothesized that the sensing effect is occasioned by the displacement of the double layer capacitance by the addition of the organic compound. The interaction of the analyte (polar or non-polar) with the delocalized positive charges along the polypyrrole chains induces changes in capacitance of this nanostructured material.

The Pt/PPyNQS sensor effect is based on the normalized real impedance (Sₙ), and/or that of the normalized real capacitance (Kₙ) as shown in equation 3.28 and 3.29 as used earlier by Hagen et al and described in chapter 3 [33].

\[
S_n = \frac{|Z| - |Z(t = 0)|}{|Z(t = 0)|}
\]

equation 3.28
\[
K_n = \frac{|C(t) - |C(t=0)|}{|C(t=0)|}
\]  
\text{equation 3.29}

When the \( K_n \) values (deviations of the magnitude of capacitance at a time \( t \) containing a known concentration of the analyte from a value without analyte at \( t = 0 \)) for the electrochemical set up were plotted against increasing concentrations of analytes, a hyperbolic curve defined by the equation: \( y = ax / (1 + bx) \) was followed. Fig. 5.21 shows the plot for interfacial capacitance vs. [benzidine] with a correlation coefficient, \( r^2 \) value of 0.985 (\( n = 13 \)), exhibiting a typical shape for Michaelis-Menten kinetics. This could be used to determine benzidine concentrations of 0 to 400 µM without total de-naturation of the sensor. A linear plot defined by the equation \( y = 0.059x + 1.514 \) was observed at low concentration range of 0 – 100 µM with a correlation coefficient, \( r^2 \) of 0.992, (\( n = 5 \)). From the linear plot (insert) shown in Fig. 5.21, low concentration range of 0 – 100 µM for benzidine could be determined with a sensitivity of 0.059 x 10\(^{-4}\) F/µM, i.e. 5.9 µF/µM, and detection limit of 3.407 µM. This concentration range of 0 to 100 µM for benzidine is obtainable in waste waters from contaminated environment.

When similar plots were made for the normalized capacitance vs. benzidine concentration at the bulk polymer region (Fig. 5.22), a seeming linear relationship with \( r^2 \) of 0.96 was seen as against hyperbolic trend seen for interfacial normalized capacitance plots (Fig.5.21). This confirms that different kinetics of electron transfer is taking place within the bulk polymer as well as at the interface.
Figure 5.21: Plot of changes in capacitance with increasing concentrations of benzidine at the interface with insert showing the calibration curve for the linear region.
The kinetics involved in the interfacial impedance with benzidine concentration is presented in Fig. 5.23. The normalized impedance increased gradually with small concentration of benzidine after which it decreased in a sinusoidal pattern. This transformation could be due to reaction between the polar groups of the analyte with ionic species in the electrolyte, thus altering the conductivity. A direct relationship between the impedance measurements and benzidine concentration could therefore not be made because of the coupled reactions involved.
Pt/PPyNQS impedimetric sensor for naphthalene in comparison to that for benzidine.

In the investigation of the sensor response to naphthalene, the magnitude of the real impedance was found to increase with increasing concentration of the analyte while the double layer capacitance decays hyperbolically (Fig 5.24). This is expected because the organic moiety naphthalene, is relatively insulating compared to the electrolyte medium and thus should create higher impedance. The relative change in capacitance from the naphthalene addition over the concentration range investigated is smaller compared to that from benzidine. This could be attributed to the greater electrostatic interaction at the polymer’s interface resulting from the polar benzidine compared to the non-polar naphthalene. The hyperbolic decay for the naphthalene’s capacitance plots (Fig 5.24) gave a much lower $r^2$ value of 0.886 compared with that from benzidine capacitance plots with $r^2$ value of 0.992 (Fig 5.21). However, within a
narrow concentration range of 0 – 3 µM, a linear plot defined by $y = 0.294x + 0.042$ is satisfied with $r^2 = 0.980$ (n = 3) for the naphthalene concentration vs. capacitance plot (insert of Fig 5.24). This offers room for the development of capacitance-based sensor for the determination of benzidine and naphthalene at ppm and ppb levels.

The usage of the sensor for high concentration of benzidine solutions has a fouling effect on the sensor. At concentration of 340 µM and above, there was gradual deterioration of the real impedance trend and loss of interfacial electrochemistry (Fig 5.21 and 5.23). The naphthalene based capacitance sensor showed similar saturation at naphthalene concentrations in excess of 150 µM. The naphthalene solution brought about the saturation of the sensor at a lower concentration because of its higher insulating capability compared with that of benzidine.

![Naphthalene concentration vs. capacitance plot](image)

**Figure 5.24:** Plot of changes in capacitance with increasing concentrations of naphthalene at the interface with insert showing calibration curve for the linear region.
The electroactivity of the polymer is hindered by the repulsion to the ingress/egress of counter ion at the polymers interface due to the restriction caused by the large NQS moiety. This factor is responsible for the decrease in the double layer capacitance with increase in analyte concentration. Higher concentration range of these pollutants could be determined by using the hyperbolic curve of the normalized capacitance vs. analyte concentrations. Polycyclic aromatic hydrocarbon (naphthalene) showed a higher propensity to displace the interfacial double layer capacitance than the polar benzidine moiety.

**Conclusions**

1, 2-napthaquinone–4-sulphonate have been successfully incorporated into the matrix of polypyrrole on a platinum disc electrode through potential cycling in aqueous solution of pyrrole-monomer (0.1 M) and the sodium salt of 1, 2-napthaquinone–4-sulphonic acid-dopant (0.01 M) in 0.05 M HCl. The resulting polymer showed high conductivity, optical changes, spectroscopic transitions and good electroactivity. The polypyrrole thin film microelectrode was characterized electrochemically for the first time and found to exhibit good electronic and spectroscopic properties. Voltammetric investigations showed that the polymer exhibited quasi-reversible kinetics in a potential window of -400 mV to 700 mV, with a formal potential of 322 mV vs. Ag/AgCl. The diffusion coefficient was calculated to be $1.02 \times 10^{-6}$ cm$^2$ s$^{-1}$ for a thin film with a surface concentration of $1.83 \times 10^{-7}$ mol cm$^{-2}$ having a rate constant of $2.20 \times 10^{-3}$ cm.$s^{-1}$ at 5 mVs$^{-1}$. The self-assembled film of the nanostructured-modified polypyrrole showed good adherence on platinum disc electrode (Pt/PPyNQS) and showed potential for use as anode for environmental sensor applications. The modified polypyrrole is composed of nano micelles with diameters of 50 – 100 nm. It displays high electroactivity and quasi-reversible electrochemistry. It also shows stronger electrochemical activity than conventional PPy, improved solubility and strong UV-Vis absorptions at 380, 750 and 820 nm for the polaron, bipolaron and over lapped bi-polaron bands respectively. There was good correlation of data between the electrochemical and spectro electrochemical investigation on the modified polymer using cyclic voltammetry, differential pulse voltammetry, square wave voltammetry, electrochemical impedance spectroscopy and SNIFTIRS. During SNIFTIRS investigation of Pt/PPyNQS thin film, there was smooth transition from the neutral to the polaronic and bipolaronic states as it was switched through a
potential window of –400 through 700 mV vs. Ag/AgCl. It is worth noting that the NQSA doped polypyrrole showed strong emissions in aqueous dispersion, which provides indication of potential applications in fabrication of various optometric devices. The use of the Pt/PPyNQS novel impedimetric smart sensor for the detection and quantification of benzidine and naphthalene in aqueous solutions proves promising based on our preliminary investigation. Our test application of the Pt/PPyNQS shows that sensors with good linear relationship ($r^2 > 0.98$) between capacitance and concentration for benzidine and naphthalene could be constructed using a concentration range of 0 – 100 µM and 0 – 3 µM for benzidine and naphthalene respectively.

References


Chapter Six

Results and discussion 3

Spectroscopic and morphological studies of polypyrrole composites with metal oxides (PPyWO$_3$ and PPyZrO$_2$)

This chapter presents results and discussion on the chemically synthesised metal oxide modified polypyrrole. The hybrid materials based on WO$_{3-x}$ and ZrO$_{2-y}$ and polypyrrole were prepared from the in-situ oxidation of pyrrole in acidic solution of the individual metal oxide. Results obtained from the morphological and spectroscopic investigation are discussed.

6.0 Introduction

Metal oxide modified polypyrrole have been used as organic/inorganic hybrid electrodes for increased charge storage in electrochemical storage devices such as supercapacitors and batteries [1-3]. While transition metal oxides incorporated into the matrix of double layer activated carbons are used as double layer capacitors, based on their high specific capacitance and relatively low electric conductivity, the metal oxide nanohybrid-polypyrrole offers room for increased charge storage capacity and conductivity because of the advantage of being both electroactive and conductive. The effective energy storage generated from the nanohybrid of a fairly conducting transition metal oxide with an electroactive and conducting organic polymer like polypyrrole offers room for improved technological possibilities such as electrochemical sensors and supercapacitors. In this study, in-situ reaction between pyrrole and tungsten (VI) oxide or zirconium (IV) oxide in acidic solutions are used to produce insoluble polypyrrole composites via oxidation with aqueous solution of ammonium persulfate. While the pyrrole is oxidized to polypyrrole, the metal oxide in solution also gets reduced to form insoluble particles in the process. The simultaneous reactions coupled with stirring allows for the incorporation of the insoluble metal oxide particles into the interstitial pores of the polymer. The polymer yield,
morphism and spectroscopic properties of the metal oxide polypyrroles are discussed underneath.

6.1 Chemical synthesis of (PPyWO$_3$ and PPyZrO$_2$)

The dry product of the tungsten oxide modified polypyrrole (PPyWO$_3$) and zirconium oxide modified polypyrrole (PPyZrO$_2$) obtained using the experimental procedure described in Table 3.3 and 3.4 was investigated for their morphological and spectroscopic properties.

6.1.1 Yield pattern of metal oxide modified polypyrroles

The yield obtained from the chemical synthesis in acidic solution prepared from a metal-oxide:pyrrole mole concentration ratio of 0.8 and oxidant:pyrrole mole concentration ratio of 0.2 and 1.0 for PPyWO$_3$ and PPyZrO$_2$ is presented in Table 6.1. The pH indicated was determined after the polymerization reaction in the 0.1 M HCl (pH = 1.2) is completed. The % yields represent the % of the dry polymer (g) obtained from the pyrrole used (ml). The polymerization yields of the hybrid polymers prepared from the higher o/m mole concentration ratio is higher than those from the lower o/m mole concentration ratio at a fixed d/m mole concentration ratio of 0.8. More polymer hybrid is obtained from the tungsten oxide modified polypyrroles than that from zirconium oxide. This might be due to the relatively higher mole equivalent of the tungsten oxide leading to higher weight for the precipitated polymer. The evidence for the incorporation of the metal oxides into the polymer matrix was provided by stigmation of the polymers micrograph with energy dispersive x-ray (EDX) within the scanning electron microscope chamber. The EDX spectra provided information on the proximate elemental analysis for the transition metal, carbon, oxygen and sulphur in the nanoparticles assayed. Optimisation of the chemical synthesis conditions to determine desirable maximum loading of metal oxide into the polymers matrix for the production of a highly conducting polymer composite state is still being investigated.
Table 6.1: Yield of metal-oxide modified polypyrroles prepared under different synthesis conditions.

<table>
<thead>
<tr>
<th>Code</th>
<th>PPyWO$_3$-</th>
<th>PPyWO$_3$-</th>
<th>PPyZrO$_2$-</th>
<th>PPyZrO$_2$-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>pyrrole used (ml)-m</td>
<td>0.529 mL (0.0075 mol)</td>
<td>0.529 mL (0.0075 mol)</td>
<td>0.529 mL (0.0075 mol)</td>
<td>0.529 mL (0.0075 mol)</td>
</tr>
<tr>
<td>metal-oxide used (g)-d</td>
<td>1.391 g (0.0060 mol)</td>
<td>1.391 g (0.0060 mol)</td>
<td>0.740 g (0.0060 mol)</td>
<td>0.740 g (0.0060 mol)</td>
</tr>
<tr>
<td>APS used (g) -o</td>
<td>0.3484 g (0.0015 mol)</td>
<td>1.745 g (0.0075 mol)</td>
<td>0.3484 g (0.0015 mol)</td>
<td>1.745 g (0.0075 mol)</td>
</tr>
<tr>
<td>ratios [d/m and o/m]</td>
<td>d/m (0.80) o/m (0.20)</td>
<td>d/m (0.80) o/m (1.00)</td>
<td>d/m (0.80) o/m (0.20)</td>
<td>d/m (0.80) o/m (1.00)</td>
</tr>
<tr>
<td>pH</td>
<td>1.68</td>
<td>1.36</td>
<td>1.77</td>
<td>1.37</td>
</tr>
<tr>
<td>colour change</td>
<td>Light green to black after oxidation</td>
<td>Light green to black after oxidation</td>
<td>White milky solution to black</td>
<td>White milky solution to black</td>
</tr>
<tr>
<td>polymer yield (g/ml)</td>
<td>1.138 g (210 %)</td>
<td>1.889 g (357 %)</td>
<td>0.753 g (142 %)</td>
<td>1.215 (230 %)</td>
</tr>
</tbody>
</table>

* defined as follows: ‘d/m’ is mole concentration ratios of metal oxide to monomer (pyrrole); ‘o/m’ is mole concentration ratios of oxidant (APS) to monomer (pyrrole)

6.1.2 Morphological and EDX examination

The SEM micrograph on the polypyrrole from the o/m mole concentration ratio of 0.2 was taken to see if nanohybrids were formed and to determine relative metal oxide loading in the polymer matrix. Figures 6.1 show the fibrillar morphology of the nanofibres forms of the polypyrrole hybrids. The micrograph of the dry, granular powder of the tungsten oxide modified polypyrrole (Fig. 6.1a) gave agglomerated
nanobundles with circular diameters of about 75 - 300 nm while that from zirconium oxide modified polypyrrole (Fig. 6.1b) gave islands of globular nanobundles of similar diameter as PPyWO$_3$. Similar morphology with spherical particles of particle sizes of 400-500 nm was reported for nanohybrid of PPy/Fe$_2$O$_3$ nanocomposite [3].
Figure 6.1: SEM micrographs of dry powder of metal oxide modified polypyrrole showing the typical fibrous nanostructures from (a) PPyWO₃ [d/m 0.8; o/m 0.2] and (b) PPyZrO₂ [d/m 0.8; o/m 0.2].

Table 6.3 presents the proximate elemental composition obtained from the EDX spectra of different polypyrroles. Evidence of the incorporation of the metal oxides was revealed in the respective metal oxide modified polypyrrole. The higher product yield observed from the PPyWO₃ was also corroborated by the higher metal loading of about 12 % for PPyWO₃ as against about 8 % seen in PPyZrO₂ (Table 6.3). Furthermore, the data shows lower % carbon from the metal oxide modified polymers (PPyWO₃ and PPyZrO₂) compared to the organic acid modified polymers (PPyNSA and PPyNQS). The order of decreasing % carbon is PPyNSA > PPyNQS > PPyZrO₂ > PPyWO₃. The relatively lower % sulphur in the metal oxide modified polypyrrole is attributed to the absence of surfactants whereas the sulfonated polypyrroles have higher % sulphur. The observed 1.5 % sulphur in the metal oxide modified
polypyrrole must have originated from the oxidant (APS) used in the polymers preparation. Higher values for the surfactant modified PPy is therefore not surprising.

Table 6.2: Comparative trend of elemental composition (C, S, O, W, Zr, others) in different modified polypyrroles prepared at from d/m ratio of 0.8 and o/m ratio 0.2 by EDX spectroscopic analysis.

<table>
<thead>
<tr>
<th>samples</th>
<th>C (%)</th>
<th>S (%)</th>
<th>O (%)</th>
<th>W (%)</th>
<th>Zr (%)</th>
<th>others (%)</th>
<th>total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPyNSA</td>
<td>91.84</td>
<td>5.24</td>
<td>2.66</td>
<td>-</td>
<td>-</td>
<td>0.26</td>
<td>100.00</td>
</tr>
<tr>
<td>PPyNQS</td>
<td>89.37</td>
<td>5.46</td>
<td>4.58</td>
<td>-</td>
<td>-</td>
<td>0.67</td>
<td>100.08</td>
</tr>
<tr>
<td>PPyWO3</td>
<td>82.55</td>
<td>1.47</td>
<td>4.05</td>
<td>11.77</td>
<td>-</td>
<td>0.22</td>
<td>100.06</td>
</tr>
<tr>
<td>PPyZrO2</td>
<td>87.23</td>
<td>1.15</td>
<td>3.92</td>
<td>7.55</td>
<td>-</td>
<td>0.15</td>
<td>100.00</td>
</tr>
</tbody>
</table>

6.2 Spectroscopic properties of metal oxide modified polypyrroles

6.2.1 UV-Vis Spectroscopy

Figures 6.2 present the UV-Vis spectra for the metal oxide modified polypyrrole. Similar trend of spectra were obtained on the polymer composites of PPyWO3 (Fig. 6.2A) and PPyZrO2 (Fig. 6.2B) using different o/m mole concentration ratios of 0.2 and 1. For the PPyWO3, a small absorption maxima at 325 nm for the conjugated double bonds (i.e. $\pi$ to $\pi^*$ transition) is indicated. The red shift from the normal $\pi$ to $\pi^*$ absorption at about 295 nm might be due to the inclusion of the solvated tungsten oxide along the polymers matrix [4]. The polaronic absorption is poorly formed at about 480 nm (Fig. 6.2A). Similar trend of spectra were seen for the PPyZrO2 (Fig. 6.2B). Absence of sharp polaronic absorption and bipolaronic absorption at higher
wavelengths is an indication of insignificant charge carriers in the system and further optimisation may be required to improve the polymers conductivity.
6.2.2 FTIR spectral studies

Figure 6.3 shows the IR spectra of the metal oxide modified polypyrrole. Fig. 6.3A gives spectra for PPyWO$_3$ and metal oxide free polypyrrole (PPyDW) while Fig. 6.3B gives the spectra for PPyZrO$_2$ and metal oxide free polypyrrole (PPyDW) respectively. The Tables 6.3 and 6.4 present’s data on some characteristic bands for
the polymers and compared with those reported for polypyrrole by Geetha and Trivedi [5]. All the characteristic absorption bands for the metal oxide modified polypyrrole were observed especially at the fingerprint region of 1000 – 1700 cm\(^{-1}\) with slight variation in the absolute values (Tables 6.3 and 6.4). The usual N–H stretching at 3400 cm\(^{-1}\) in neutral polypyrrole is present in both PPyWO\(_3\) and PPyZrO\(_2\) samples, though with slight variations, indicating that the polymers are not in the doped state as was observed in the earlier investigation on PPyDW, PPyNSA (d/m 0.8, o/m 0.2) and PPyNSA (d/m 0.8, o/m 1.0) [6].

The most interesting feature in the IR spectra is the lower wavelength absorption band at 822 cm\(^{-1}\) for PPyWO\(_3\) (Fig. and 558 cm\(^{-1}\) for PPyZrO\(_2\). Similar low band absorption at around 500 cm\(^{-1}\) was reported for polypyrrole-manganese (IV) oxide nanocomposite hybrids [1]. Furthermore, an extra sharp peak due to the C=\(\equiv\)C/C-C vibrational modes at 1636 – 1720 cm\(^{-1}\), depending on the metal ion and the oxidant concentration used, was seen in the spectra of the metal oxide modified polypyrroles. This peak is assigned to the shifted peak from 1540 cm\(^{-1}\) due to significant overoxidation of the polypyrrole matrix [1, 6]. The oxidising nature of the metal oxide coupled with that of the oxidant might have caused this over-oxidation. This will invariably reduce the electronic conductivity and ultimately loss or reduced electrochemical activity. These characters in the metal oxide modified polypyrrole attest to the incorporation of the metal oxide in the polypyrrole. The included inorganic component in the hybrid is a reduced metal ion resulting from the oxidative polymerisation. Thus, the reduced for in which the metal oxide precipitate could be represented as WO\(_{3-x}\) and ZrO\(_{2-y}\) respectively where x and y are integers showing the extent of oxidation in each case [1].
Figure 6.3: FTIR spectra of metal oxide modified polypyrroles in KBr medium, Fig. 6.3A: (a) PPyDW, (b) PPyWO$_3$ (d/m 0.8; o/m 0.2) and (c) PPyWO$_3$ (d/m 0.8; o/m 1.0); and Fig. 6.3B: (a) PPyDW, (b) PPyZrO$_2$ (d/m 0.8; o/m 0.2) and (c) PPyZrO$_2$ (d/m 0.8; o/m 1.0).
Table 6.3: Major shifts of bands (cm\(^{-1}\)) in FTIR spectra of PPyDW, PPyWO\(_3\) (d/m 0.8, o/m 0.2) and PPyWO\(_3\) (d/m 0.8, o/m 1.0) from undoped polypyrrole major bands (Geetha & Trivedi) [5].

<table>
<thead>
<tr>
<th>Major Bands</th>
<th>PPyDW</th>
<th>PPyWO(_3) (o/m 0.2)</th>
<th>PPyWO(_3) (o/m 1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3421 (N-H Str)</td>
<td>Absent</td>
<td>3420</td>
<td>3413</td>
</tr>
<tr>
<td>3100 (C-H Str)</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
</tr>
<tr>
<td>1535 (C=C &amp; C-C Str)</td>
<td>1554</td>
<td>1550</td>
<td>1547</td>
</tr>
<tr>
<td>1450 (N-H Str)</td>
<td>Absent</td>
<td>1461</td>
<td>1458</td>
</tr>
<tr>
<td>1295 (C-H &amp; N-H Def)</td>
<td>1308</td>
<td>1305</td>
<td>1305</td>
</tr>
<tr>
<td>1050 (C-H Def)</td>
<td>1047</td>
<td>1040</td>
<td>1040</td>
</tr>
</tbody>
</table>
Table 6.4: Major shifts of bands (cm$^{-1}$) in FTIR spectra of PPyDW, PPyZrO$_2$ (d/m 0.8, o/m 0.2) and PPyZrO$_2$ (d/m 0.8, o/m 1.0) from undoped polypyrrole major bands (Geetha & Trivedi) [5].

<table>
<thead>
<tr>
<th>Major Bands</th>
<th>PPyDW</th>
<th>PPyZrO$_2$</th>
<th>PPyZrO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cm$^{-1}$)</td>
<td>(o/m 0.2)</td>
<td>(o/m 1.0)</td>
<td></td>
</tr>
<tr>
<td>3421 (N-H str)</td>
<td>Absent</td>
<td>3461</td>
<td>3468</td>
</tr>
<tr>
<td>3100 (C-H str)</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
</tr>
<tr>
<td>1535 (C=C &amp; C-C str)</td>
<td>1554</td>
<td>1556</td>
<td>1558</td>
</tr>
<tr>
<td>1450 (N-H str)</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
</tr>
<tr>
<td>1295 (C-H &amp; N-H def)</td>
<td>1308</td>
<td>1311</td>
<td>1307</td>
</tr>
<tr>
<td>1050 (C-H def)</td>
<td>1047</td>
<td>1045</td>
<td>1045</td>
</tr>
</tbody>
</table>

Conclusions
This preliminary investigation on metal oxide modified polypyrrole has shown that significant modification of the polypyrrole matrix is generated by the in-situ polymerisation. The metal oxide nanoparticles served as a support to the polymerisation process of pyrrole and lead to a more porous structure with a higher specific surface area. Nanohybrids are readily formed via the in-situ polymerisation in acidic aqueous medium. Two simultaneous processes have been hypothesised; namely the oxidation of pyrrole to polypyrrole and the reduction of the WO$_3$ to WO$_{3-x}$ (or ZrO$_2$ to ZrO$_{2-y}$). The investigated polymers do not show significant features indicative of reasonable composition of charge carriers required for electrocatalytic application and further optimisation of synthesis conditions to come up with an ideal metal oxide loading is required. Evidence of incorporation of the metal oxide into the polymers matrix was provided by both EDX and FTIR spectroscopic analysis. Electrochemical
characterisation and test application of the nanohybrids will be looked into in future work. The likely scope of application of the hybrid polymers are in electrochromic devices and metal oxide sensors (MOS) that are operated at elevated temperatures.

References


Chapter Seven

Conclusions and Recommendations

7.1 Conclusions

This research work has investigated the aqueous synthesis, characterization and amperometric/impedimetric applications of some polypyrrole involving modification with different polyaromatic hydrocarbon sulphonic acid (PAHSA) and transition metal oxides of $\text{WO}_3$ and $\text{ZrO}_2$. The PAHSA used are $\beta$-naphthalene sulphonic acid (NSA) and the sodium salt of 1, 2-napthaquinone-4-sulphonic acid (NQS). In order to follow the transition in the properties of the modified polypyrrole with different synthesis conditions, controls synthesis were carried out as follows:

- Polypyrrole was chemically synthesized using oxidant of ammonium persulphate (APS) without the use of acidic medium of hydrochloric acid as the electrolyte (PPyDW),
- Polypyrrole was chemically synthesized using oxidant of ammonium persulphate (APS) in acidic medium of hydrochloric acid as the electrolyte (PPyHCl) otherwise referred to as polypyrrole (PPy).

The investigation involved synthesis at different temperatures, dopant to monomer mole concentrations ratios (d/m), oxidant to monomer mole concentrations ratios (o/m), use of different electrodes for electrochemical synthesis and variation of pH and electrochemical potential window. A general electrochemical characterization of the polymers was undertaking to ascertain electroactivity of the derived polymers. Morphological and spectroscopic characterizations were also used to determine the existence of nanostructures and their intrinsic properties. Test applications on the modified polypyrroles with good morphological, spectroscopic and electrochemical properties were investigated for some common pollutants in waste water. The testing was aimed at determining if there is amperometric or impedimetric response to changing concentrations of the pollutants in waste water. The study have provided a platform for the production of various chemical and biological sensors based on the
broad evaluation of the morphology, spectroscopic, electrochemical and test applications explored in this study.

7.2 Main scientific contributions of the dissertation

- Production of various nanostructures of polypyrrole using surfactant mediated synthesis was successfully carried out within the first one year of this study. The polymerization of pyrrole in β-naphthalene sulphonic acid (NSA) gave nanotubules, nanomicelles or nanosheets of polypyrrole (PPy) morphologies depending on the amount of NSA in the polymer and the temperature of the reaction. The modified polypyrrole from NQS is composed of mainly nanomicelles with diameters of 50 – 100 nm.

- Validation of the electrochemistry of the various polypyrrole transition states during cycling. Electrochemical analysis of PPyNSA reveals two redox couples: a/a’ - partly oxidized polypyrrole-naphthalene sulphonate radical cation/neutral polypyrrole naphthalene sulphonate; b/b’ - fully oxidized naphthalene sulphonate radical cation/partly reduced polypyrrole-naphthalene sulphonate radical anion which are closely associated. However, CV, SWV and EIS showed that PPyNQS had single redox couple with a quasi reversible electrochemistry at low scan rates.

- Modification of polypyrrole with NQS was carried out for the first time and conditions for the chemical and electrochemical synthesis were optimized.

- Validation of the electrochemistry of the nanostructured modified polypyrrole (PPy) self assembled with sodium salt of 1, 2-napthaquinone-4-sulphonic acid (NQSA) and pyrrole (Py) on platinum disc electrode (Pt/PPyNQS). The incorporation of the NQS dopant in the polymer matrix was validated by in-situ SNIFTIR investigation.

- The synergy of synthesis conditions, morphology of modified polypyrroles, UV-Vis and FTIR properties of the polymer materials in different solvents, and the electrochemical properties at different electrodes and potentials were used to establish optimum synthesis conditions for PPyHCl, PPyNSA, PPyNQS. Further optimizations are still required for the metal oxide modified polypyrroles.

- Kinetic study shows PPyNQS had slightly higher rate constant ($k^0$) than PPyNSA being $3.08 \times 10^{-2}$ cm s$^{-1}$ @ 100 mV/s for PPyNSA and $3.75 \times 10^{-2}$
cm s-1 @ 100 mVs-1 for PPyNQS which are close to literature values for other conducting polymers.

- Beside, the PPyNQS adhered better to the electrode surface than the PPyNSA and it is relatively more stable to many potential cycling.
- Impedimetric investigation attest to redox activities at potential between 200 - 300 mV for PPyNSA and 320 mV for PPyNQS at the polymers/electrolyte interface.
- Test application of the GCE/PPyNSA electrode as phenol sensor in aqueous acidic medium showed that PPyNSA based sensor can be used in the amperometric detection of phenol in water and environmental samples. The dynamic linear range of the sensor showed that the sensor is analytically useful at phenol concentrations of 0.65-139.5 µM. This translates to phenol mass concentration of 6.7-1500 parts per billion (ppb). This is within the range of phenol found in pharmaceutical industries and refinery effluents.
- Test application of the Pt/PPyNQS electrode as benzidine sensor in aqueous acidic medium showed that PPyNQS based sensor can be used in the impedimetric detection of phenol in water and industrial waste water effluents.
- An impedimetric transduction mechanism was proposed for the interaction of analytes of benzidine and naphthalene with a film of PPyNQS on platinum disc electrode based on the high impedimetric pattern observed at low frequency.

7.3 Recommendations for future work

The polyaromatic hydrocarbon sulphonic acid (PAHSA) and transition metal oxides evaluated in this dissertation represent only a sample of their respective groups. While more conclusive study is required on the metal oxide modified polypyrrole, further evaluation on other PAHSA should be explored for their potential use as electrocatalytic sensor devices. The developed sensor systems based on PPyNSA and PPyNQS should be explored for use as biological sensors at neutral pHs.

The morphological study on the electrochemically generated films in this study could not be carried out due to lack of instrumentation for in-situ simultaneous
electropolymerisation and morphological evaluation. It will be needful to further validate that the features observed on the chemically synthesized polymers as being readily reproducible or improved upon in electrochemically generated film.

The inability of the polypyrrole used in this study to attain a constant impedance value at low frequency is a major limitation in the development of direct impedimetric and capacitive sensor in this study. Conditions for the attainment of this desirable impedance pattern for the polymer systems should be explored.

Obviously, the ultimate objective is to have assembly of chemical sensors for determination of environmental pollutants, particularly the anthropogenic ones such as benzenoids e.g. benzene, toluene, ethylbenzene and xylene isomers –BTEX, that are also volatile organic pollutants -VOC’s; chlorinated compounds e.g. trichloroethylene, -TCE; polycyclic aromatic hydrocarbons -PAHs, e.g. naphthalene, fluoroanthene, pyrene; and polychlorinated biphenyls (PCBs) and other priority organic pollutants (POP’s) such as benzidine, phenol and its derivatives. The development of E-Noses that can determine many of these analytes simultaneously is an objective that should be met in the nearest future.

7.4 Output from the dissertation

7.4.1 Contributions at conferences


2. **Akinyeye, R.**: Chemical and Electrochemical Synthesis of Polypyrrole Impedimetric Sensors, Presentation to the Sensor Research Group, University of the Western Cape, Bellville, South Africa, 6th December, 2005.


7.4.2 Manuscripts and publications authored or co-authored from the PhD study.


