Enhancement Using
Electrically Conducting Membranes

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PREFACE

The synthesis of conducting polymers and the development of conducting polymer-based sensors has been the focal point of the research activity in the modern material science. The main objectives is to understand the relationship between the chemical structure of the repeating unit of the conducting polymer (Polyaniline) and its conducting properties. Similarly, to understand the influence of the electrochemical process parameters viz. type of electrolyte, concentration ratio of monomer and electrolyte, applied current density, pH, temp, deposition time etc on the synthesis of PANI film and use of synthesized PANI for the development of sensors. The present work deals with the optimization of process parameters viz. concentration of monomer and various supporting electrolytes (dopant) viz. nitric acid, hydrochloric acid, potassium chloride, PVS, etc., pH of the electrolyte, current density etc. We have optimized process parameters for the synthesis of PANI film. We have synthesized PANI-H2SO4, PANI-PVS, films by electrochemical polymerization system (Galvanostat). These synthesized conducting polymer films have been used to develop various Chemical and Biosensors. Conducting polymers have attracted much interest in the development of Electrochemical sensors. The electrically conducting polymers are known to possess numerous features, which allow them to act as excellent materials for immobilization of biomolecules and rapid electron transfer for the fabrication of efficient biosensors. it is possible to develop novel enzyme-based bioelectronic devices.

ACKNOWLEDGEMENT

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INTRODUCTION

Membrane science developed continuously as an interdisciplinary science in which polymers have a central role. With the progress of research works dedicated to conductive polymers, researches on conductive polymers membranes preparation and their application were also initiated and developed. Membrane Technology.

1.1. Membranes Classification and Applications

Due to membrane technology's rapid growth in the past 3-4 decades, it has become a very important and unique method used for a variety of applications. Currently, commercially available membranes include reverse osmosis membranes (RO), nanofiltration membranes (NF), ultrafiltration membranes (UF) and microfiltration membranes (MF). The main differences between these membranes are their pore size properties and removal mechanisms. MF membranes have the largest pore size and use , which allows only water molecules and, occasionally, small uncharged molecules to diffuse through (Figure 1).
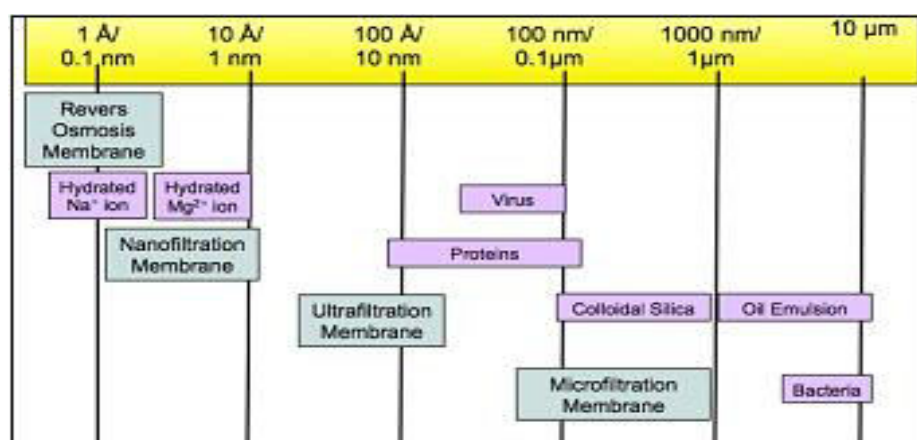

Figure 1: Membrane cut-off characteristics

1.1.2. Reverse Osmosis Membranes

RO membranes are semi-permeable membranes used to remove monovalent ions (i.e. NaCl) and small charged organic molecules. The typical rejection of NaCl is usually more than 99% (Table 1) [3,5,6]. In the RO process, an external pressure is applied to overcome the osmotic pressure caused by the concentration difference of the solute on both sides of the membrane. The typical pressure for driving seawater desalination ranges from 100-1300 psi [1,2,7]. There are two types of RO membranes on the market: asymmetric cellulose acetate (CA) RO membranes and thin film composite (TFC) polyamide (PA) membranes. The PA membranes dominate the RO membrane market sales with 91% share, with CA membrane representing most of the remaining sales. Although the CA based RO membranes are mildly chlorine resistant, which allows for chemical cleaning, the PA based RO membranes have higher salt rejection and higher pressure tolerance which serve the practical needs of seawater desalination better [3].

Table 1: Overview of membrane processes and their characteristics [6].

MembraneType	Operation Pressure (psi)	Salt Rejection(%)	MWCO (Da)	Permeability $(Lh^{-1}m^{-2}psi^{-1})$
Reverse Osmosis Membrane	100-1800	>99 (NaCl)	100	0.003-0.1
Nanofiltration Membrane	40-300	>60 (NaCl)	>200	0.1-2
Ultrafiltration Membrane	1.5-72.5	0	>10K	0.7-70
Microfiltration Membrane	1.5-30	0	>1000K	>70

1.1.3. Nanofiltration Membranes

NF membranes are also semi-permeable membranes with the pore sizes (0.1 nm to 10 nm, Figure 1) in between UF and RO. Unlike RO membranes which remove all the ions in the water, these membranes only remove divalent ions, and let the majority of monovalent ions pass through, leading to several advantages for NF membranes: low operational pressure, high flux and greater than 90% divalent ion rejection (Table 1) [8].

NF membranes are fabricated via an interfacial polymerization (IP) technique like RO membranes with a less compact thin film composition structure. They are often used for groundwater softening，RO feed pretreatment and removal of small organic dyes from textile wastewater [6].

1.1.4. Ultrafiltration Membranes

UF membranes are membranes with a pore size of 10-100 nm (Figure 1). Due to this large pore size, UF membranes typically cannot reject salts, but operate with a significantly lower operational pressure. UF membranes are commonly made by a phase inversion technique. The commonly used polymers include polyvinylidene fluoride (PVDF), polysulfone (PS), polyethersulfone (PES) and polyacrylonitrile (PAN). These polymer are chemically and mechanically robust as well as easy to process [9]. UF membranes are an alternative method for integrating coagulation, sedimentation, clarification, disinfection and sand filtration processes [10–11], because they can remove suspended particles, colloids, turbidity, algae, bacteria and viruses [12]. They are also used as pretreatment for other advanced membrane applications to reduce membrane fouling in following stages (*e.g.* NF and RO).

1.1.5. Microfiltration Membranes

MF membranes are membranes with a pore size of 100 nm to 10 μm. These membranes operate similarly to UF membranes, but with the highest permeability among four types of pressure driven membranes. The most commonly used materials are hydrophobic materials, polytetrafluoroethylene (PTFE), poly (vinylidene flouride) (PVDF) polypropylene (PP), polyethylene (PE), and hydrophilic materials, cellulose esters, polysulfone (PS) polycarbonate (PC) [6]. Microfiltration membranes are prepared by sintering, track-etching, stretching, or phase inversion techniques. Due to the robust materials used to manufacture the membranes, MF membranes have fairly good chemical stability and excellent mechanical strength. They are often used as feed pretreatment to reduce fouling for other smaller pore membranes [6].

1.2. Classification of Polymers

Polymers can be having different chemical structures, physical properties, mechanical behavior, thermal characteristics etc. Depending upon their origin, it is possible to classify polymers as natural, synthetic and conducting polymers [13.14].

1.2.1. Natural Polymers

Natural polymers such as rubber, wool, cellulose, starch etc are produced from natural materials. These materials are extremely important in our daily life. Their physical properties are fixed by nature of the particular material and cannot normally be varied. Their supplies are limited by agricultural considerations. Thus, this material is often expensive and subject to rapid fluctuations in price.

1.2.2. Synthetic Polymers

These are manufactured from cheap and readily available petroleum fractions and the physical properties may be 'tailor made' for almost any desired application. The examples of synthetic polymers are Polyethylene, PVC, Nylon and Terylene. When we talk about polymers, conventionally it means synthetic or man-made polymeric substances. The first purely synthetic polymer was the Phenol formaldehyde family of synthetic resins [15, 16].

1.2.3. Conducting Polymers

In the present era, polymers have been extensively investigated, and being used in the daily life. Polymers are generally known for their insulating property. However, in the mid-1970s, the first polymer capable of conducting electricity, polyacetylene was accidentally prepared by Shirakawa [17]. The subsequent discovery by Heeger and MacDiarmid that the polymer undergoes an increase in conductivity of 12 orders of magnitude by oxidative doping [18]. This quickly reverberated around the polymer and electrochemistry communities, and an intensive search for other conducting polymers soon followed. The product is a conducting polymer known as 'aniline Black' [19] produced coherent films of PANI with conductivity in the order of 100 $S.cm^{-1}$ and exhibited excellent air stability. However, the main hindrance of its processibility is in its insolubility in any organic solvents.

In 1976, Alan MacDiarmid, Hideki Shirakawa, and Alan Heeger, along with a group of young students started research in the field of conducting polymers and explore the possibility of doping these polymers over the full range from insulator to metal [20]. This was particularly exciting because they were able to create a new field of research and provide a number of opportunities to reduce the boundary between chemistry and condensed-matter physics [21-23]. As the commonly known polymers are in general saturated and so insulators, these were viewed as uninteresting from the point of view of electronic materials. In conjugated polymers, the electronic configuration is fundamentally different, where the chemical bonding leads to one unpaired electron per carbon atom. Professor Bengt Ranby, in his lecture at the Nobel Symposium in the year 1991, designated it as electrically conducting polymers [24]. Electrically conducting polymers are extensively conjugated in nature and therefore it is believed that they possess a spatially delocalized band-like electronic structure. 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. It is generally agreed that the mechanism of conductivity in these polymers is based on the motion of charged defects within the conjugated framework. The charge carriers, either positive p-type or negative n-type, are the products of oxidizing or reducing the polymer respectively. Since late seventies, a large number of polymers have been added to the list of conducting polymers such as polypyrrole [25], polythiophene [26], polyparaphenylene [27], polyphenylene sulphide [28], polyaniline [29], polyphenylene vinylene [30] etc.

Among known conducting polymers polyaniline and its family is most frequently used in the commercial applications due to the high conductivity, long term stability of its conductivity and the possibility of forming homo-polymers or composites with optimal mechanical properties. It is known for its stability in the oxidized state and interesting redox properties. Conducting PANI can be prepared by various methods such as chemical, electrochemical, vapor phase etc.
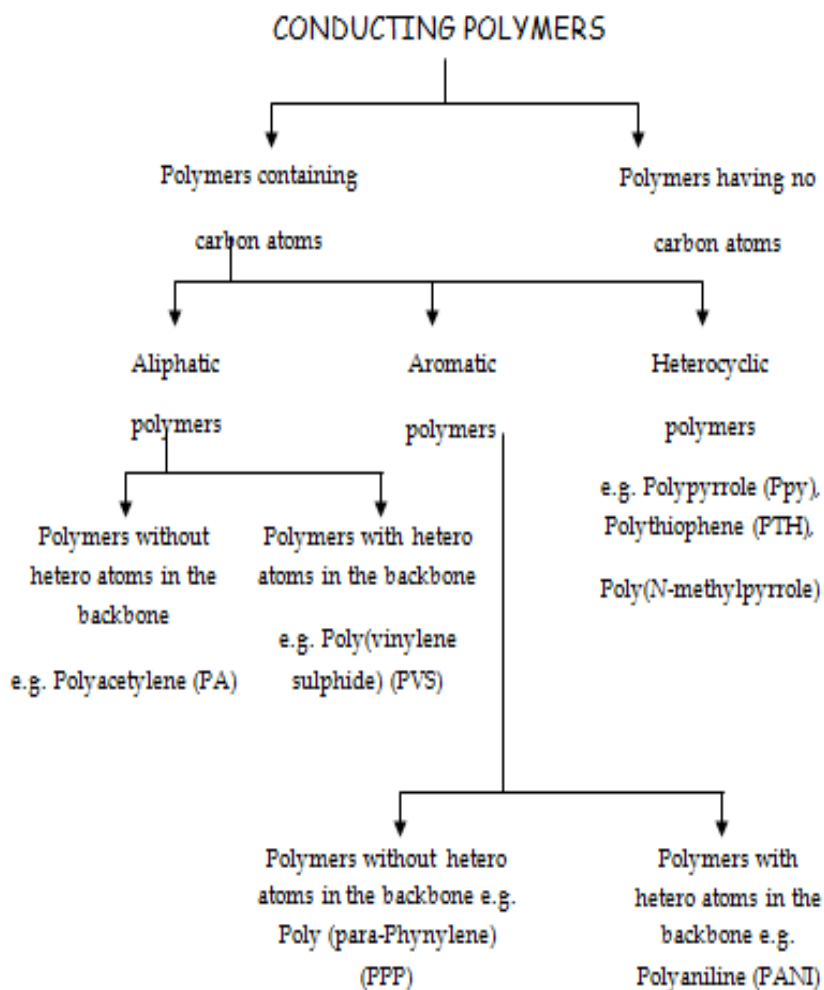
Conducting polymers have recently emerged as a new class of electroactive materials and are interesting subjects for research and development. The remarkable switching capability of these electroactive materials between the conducting oxidized (doped) and

the insulating-reduced (undoped) state is the basis of many applications. Among others, the poly-conjugated conducting polymers have been recently proposed for Environmental applications because of a number of favorable characteristics, such as (1) direct and easy deposition on sensor electrode by electrochemical oxidation of monomer, (2) control of thickness and (3) redox conductivity [31].

Conducting polymers contain π-electron backbone responsible for their unusual electronic properties such as electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity. This extended π-conjugated system of the conducting polymers has single and double bonds alternating along the polymer chain. Many applications of conducting polymers including analytical chemistry and biosensing devices have been reviewed by various researchers [32-36].

They have widened the possibility of modification of surface of conventional electrodes providing new and interesting properties. They have been applied in electrocatalysis, membrane separations and chromatography. They also create new technological possibilities in the design of chemical and biochemical sensors [37.38].

A simple classification of conducting polymer on the basis of chain composition is representing in Tree 1.1.

CONDUCTING POLYMERS

```
                          Polymers containing              Polymers having no
                            carbon atoms                     carbon atoms

         Aliphatic                 Aromatic                   Heterocyclic
         polymers                  polymers                    polymers

                                                       e.g. Polypyrrole (Ppy),
                                                       Polythiophene (PTH),

    Polymers without    Polymers with hetero            Poly(N-methylpyrrole)
    hetero atoms in the  atoms in the backbone
    backbone
                         e.g. Poly(vinylene
    e.g. Polyacetylene (PA)  sulphide) (PVS)


                     Polymers without hetero        Polymers with
                     atoms in the backbone e.g.     hetero atoms in the
                     Poly (para-Phynylene)          backbone e.g.
                     (PPP)                          Polyaniline (PANI)
```

Tree 1.1 Classification of conducting polymers

Polyaniline and its family are promising material for commercial applications because of its good environmental stability, electrochemical preparation and biocompatibility. Aqueous electrochemical process is an environment friendly and efficient technique being used for synthesis of conducting polymers. PANI and its family can often be used for biosensors, gas sensors, microactuators, antielectrostatic coatings, solid electrolytic capacitor, electrochromic windows, displays, packaging, polymeric batteries, electronic devices and functional membranes, etc [37, 39-43].

It is well known that the dopant (i.e. anion or cation) used during synthesis causes the changes in the electrochemical, structural, morphological, optical, electrical and mechanical properties of the film [43,44]

1.2.4. Conduction Mechanism

The electrical properties of any material are determined by its electronic structure. The theory that most reasonably explains the electronic structure of materials is band theory. However, it is difficult to explain the band theory of conducting polymers. In the solid state, the atomic orbital of each atom overlap with same orbital of their neighboring atoms in all directions to produce molecular orbital similar to those in small molecules. When this many orbital are spaced together in a given range of energies, they form continuous energy bands [45-49].

The energy spacing between the highest occupied and lowest uncoupled bands is called the band gap. The highest occupied band is called the valance band, and the lowest unoccupied band is the conduction band. The electrical properties of conventional materials depend on how the bands are filled. When the bands are filled or empty, no conduction occurs. If the band gap is narrow, at room temperature thermal excitation of electrons from the valance band to the conduction band gives rise to conductivity. This is what happens in classical semiconductors (Fig. 1.1).
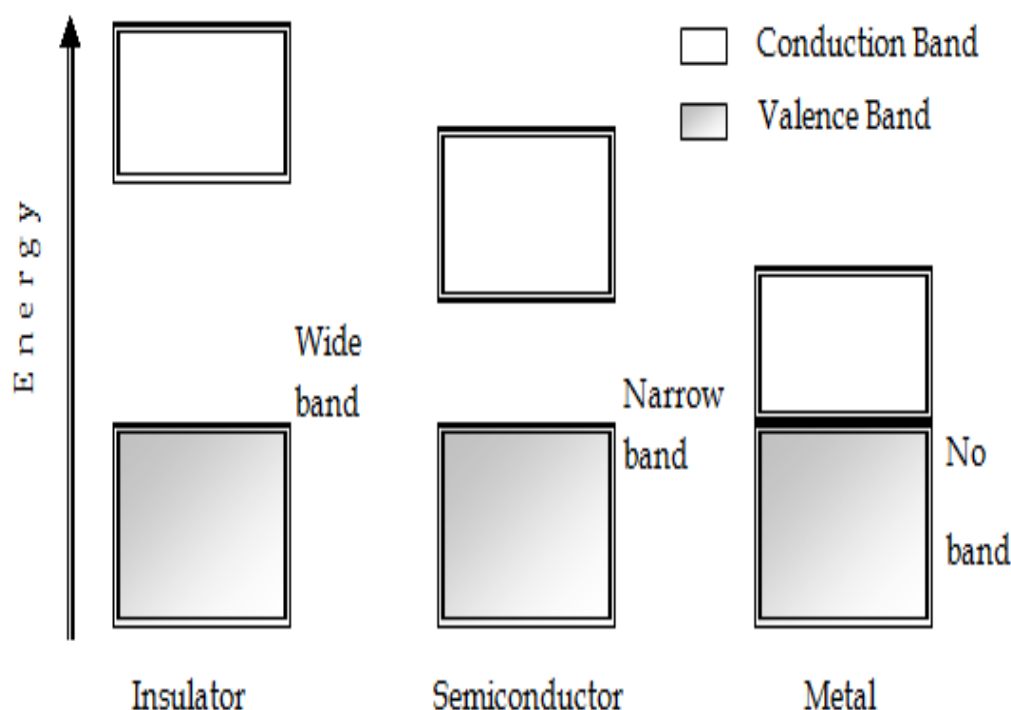

Fig. 1.1: Schematic of energy band diagram of metal, semiconductor and insulator
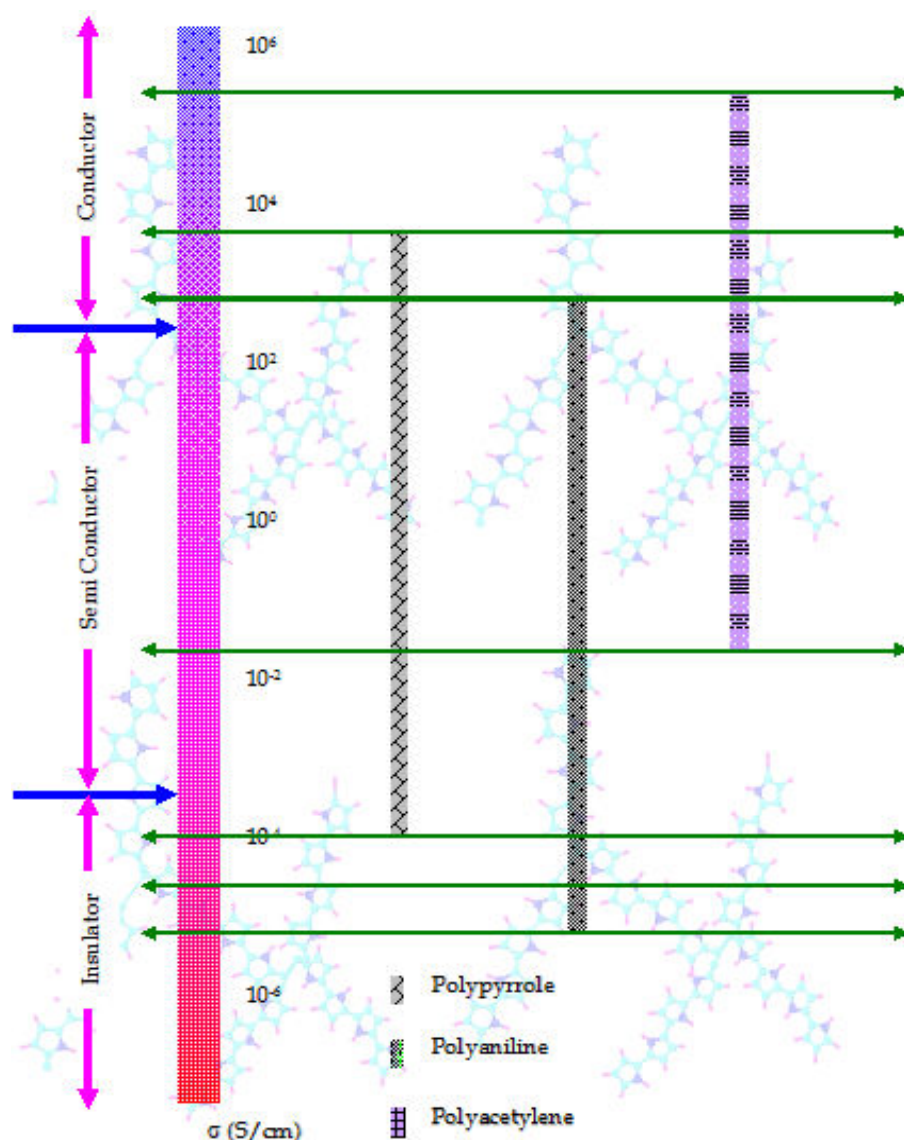
Fig. 1.2: Electrical conductivity ranges of conducting polymers 1) Polypyrrole 2) Polyaniline 3) Polyacetylene

When the band gap is too wide, thermal excitation at room temperature is insufficient to excite electrons across the gap and become an insulator. The high conductivity of metals is due to partially occupied bands, a partially filled conduction band, a partially empty valance band, or a zero-band gap. Conductive polymers are peculiar in that they conduct current without having a partially empty or partially filled band. Typical conductive ranges of some conducting polymers are as shown in Fig. 1.2. The mechanism of conduction in such polymers is very complex since such a material exhibits conductivity

across a range of about fifteen orders of magnitude and many involve different mechanisms within different regimes.

Conducting polymers show enhanced electrical conductivity by several orders of magnitude of doping. Conductivity in conducting polymers is influenced by a variety of factors including polaron length, the conjugation length, and overall chain length and by the charge transfer to adjacent molecules [50].

These are explained by large number of models based on inter soliton hopping, hopping between localized states assisted by lattice vibrations, intra-chain hopping of bipolarons, variable range hopping in 3-dimensions and charging energy limited tunneling between conducting domains. To explain some of the electronic phenomena in these organic polymers, concepts from physics that are new for chemists, including solitons, polarons, and bipolarons [51] have been applied to conducting polymers since early 1980s. When an electron is removed from the top of the valance band of a conjugated polymer, such as polyacetylene or polyaniline, a vacancy (hole or radical cation) is created that does not delocalize completely, as would be expected from classical band theory. Only partial delocalization occurs, extending over several monomeric units and causing them to deform structurally. Moreover, π-bonding, in which the carbon orbitals are in the sp^2pz configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization. This electronic delocalization provides the highway for charge mobility of the polymer chain. Therefore, the electronic structure in conducting polymers is determined by the chain symmetry, i.e. the number and kind of atoms within the repeat unit, with the result that such polymers can exhibit semi-conducting or even metallic properties. The energy level associated with this radical cation represents a destabilized bonding orbital and thus has a higher energy than the energies in the valance band.

In solid-state physics, a radical cation that is partially delocalized over some polymer segment is called a polaron. The increased distance between the two positive charges results in the polaron structure, which has a lower energy level than the bipolaron structure.

Once protonation of the imine nitrogen atoms has occurred, geometrical relaxation quickly follows, resulting in a quinoid to benzenoid transition yielding is known as a bipolaron. The bipolaron charge carrier is of relatively high energy, and thus is short-lived. Redistribution of charge and spin yields a polaron as the more stable charge carrier [52]. The relative stability of the polaronic structure is attributed to a number of factors including charge separation (reduction in Coulombic repulsions), [53] and gain of resonance energy [54]. According to MacDiarmid, the most accurate depiction of doped polyaniline is a polysemiquinone radical cation, which consists of resonance forms of two separate polarons, such that the polaron wave function is delocalized [55].
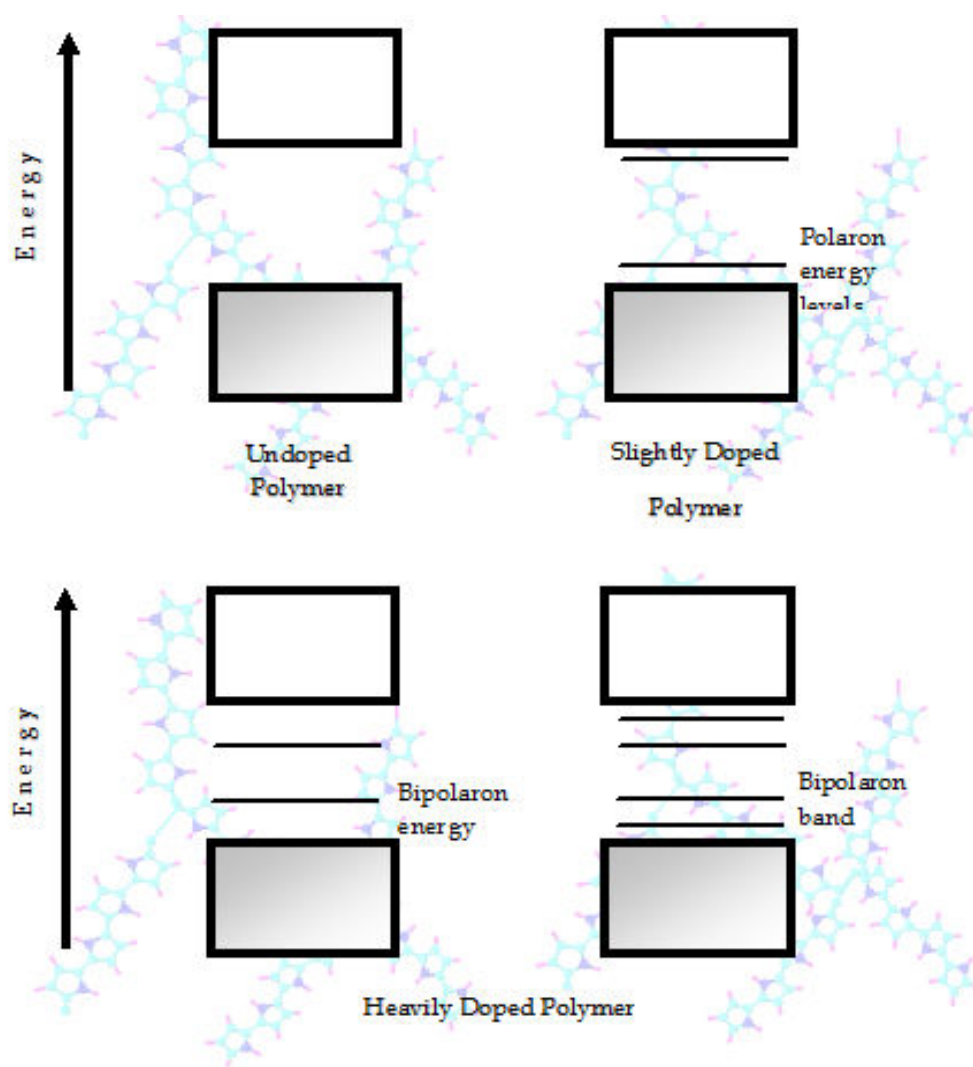

Fig. 1.3: Energy band diagram showing polaron and bipolaron states in slightly and heavily doped polymers

Geometrical Relaxation

Bipolaron

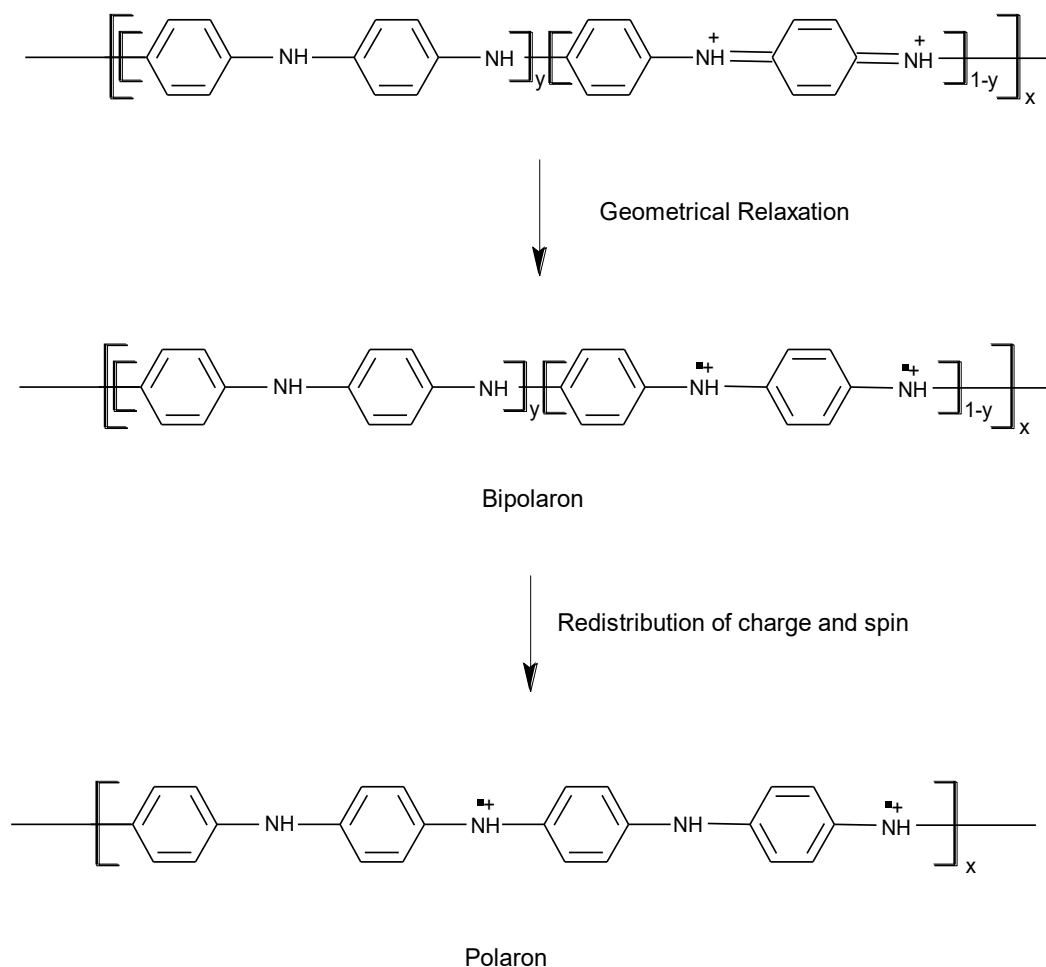Redistribution of charge and spin

Polaron

Fig. 1.4: Formation of a polaron and a bipolaron in PANI

MacDiarmid states that magnetic studies indicate that polyaniline is paramagnetic, thus the bipolaronic structure, which is diamagnetic, does not dominate. MacDiarmid, contends that the protonated polymer is a polysemiquinone radical cation. Overall, there is extensive spin and charge delocalization the polaron wave function is spread onto neighboring rings, resulting in delocalized half-filled polaron band. Energy band diagram and structure showing polaron and bipolaron in polyaniline are shown in Fig.1.3 and Fig.1.4.

1.2.5. Mechanism for PANI Formation

Let us now consider in detail the most generalized mechanism of aniline polymerization suggested by Wei et al [66-69] which is mainly based on kinetic studies of the electrochemical polymerization of aniline Fig. 1.5.
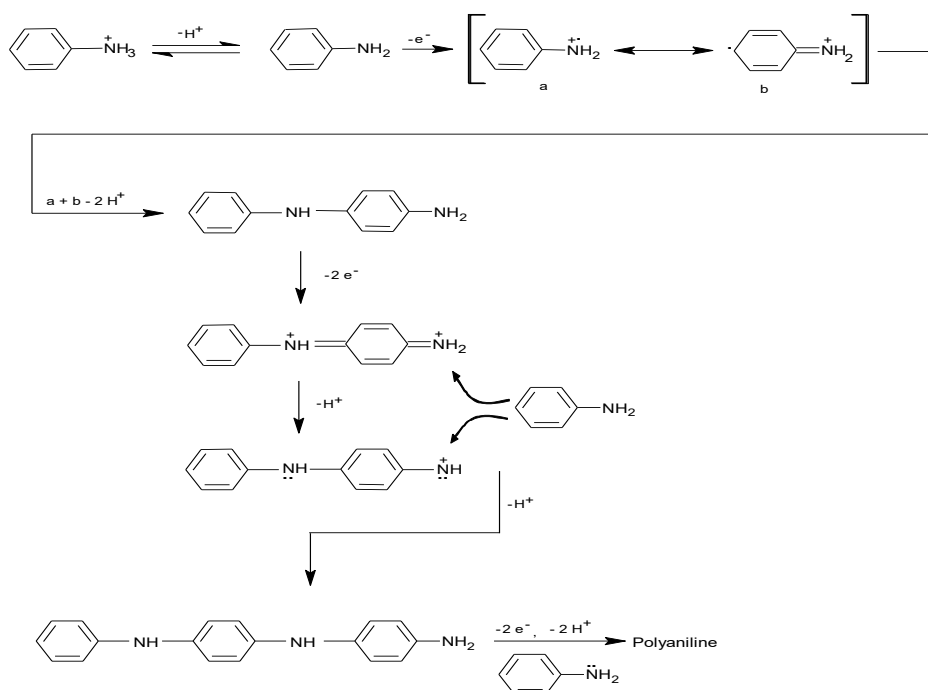
Fig.1.5: Mechanism of the polymerization of aniline

The slowest step in the polymerization of aniline is the oxidation of aniline monomer to form dimeric species, because the oxidation potential of aniline is higher than those of dimers, subsequently formed oligomers and polymer. Upon formation, the dimers are immediately oxidized and then react with an aniline monomer via an electrophilic aromatic substitution, followed by further oxidation and deprotonation to afford the trimers. This process is repeated, leading eventually to the formation of PANI.
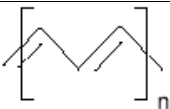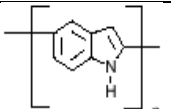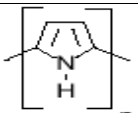
1.2.6. Aromatic Polymers
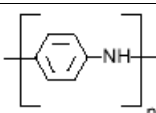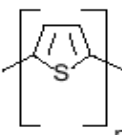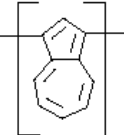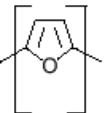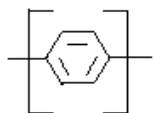
Electrodeposition of freestanding films of PANI from organic media [60] opened the way to intensive research into polyheterocyclic and polyaromatic conducting polymers [61]. The synthesis of polyacetylene in the high conducting doped form was a starting point for a considerable number of studies. The electrochemical oxidation of these resonance-stabilized aromatic molecules has become one of the principal methods of preparing conjugated, electronically conducting polymers. Names and idealized structures of the most widely studied conducting polymers are listed in Table 1.1

This table include, thiophene [62, 63], furan and indole, aniline [64-67], azulene [68, 69], *p*-phenylene [70], as well as many substituted, multi-ring and polynuclear aromatic

hydrocarbon systems. All the resulting polymers have a conjugated backbone, which is essential for electro-activity. In addition, the polymers are electrochemically oxidized to their doped states as they are formed. This oxidation necessitates the incorporation of charge compensating anions, also known as dopants, into the oxidized film to maintain electro neutrality.

The continuously growing interest in the study of PANI over the years is mainly because of its diverse, but unique properties of PANI, allowing its potential applications in various fields. Among the entire conducting polymer, polyaniline is known for its (i) ease of synthesis (ii) environmental stability and (iii) easy to dope by protonic acids. Polyaniline is a typical phenylene based polymer having a chemically flexible –NH-group in a polymer chain flanked either side by a phenylene ring. It can also be defined as the simple 1,4- coupling product of monomeric aniline molecule.

Table 1.1: Names and idealized structures of the most widely studied conducting polymers

Polymers	Structures	Polymers	Structures
Polyacetylene		Polyindole	
Polypyrrole		Polyaniline	
Polythiophene		Polyazulene	
Polyfuran		Poly (*p*-phenylene)	

The protonation, deprotonation and various other physico-chemical properties of polyaniline is due to the presence of the –NH group. Polyaniline is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black. There are several reports of polyaniline found in the literature over the

decades about the structure and constitutional aspect of aniline polymerization [71]. In the year 1968, Surville et al reported the proton exchange and redox properties with the influence of water on the conductivity of polyaniline [72].
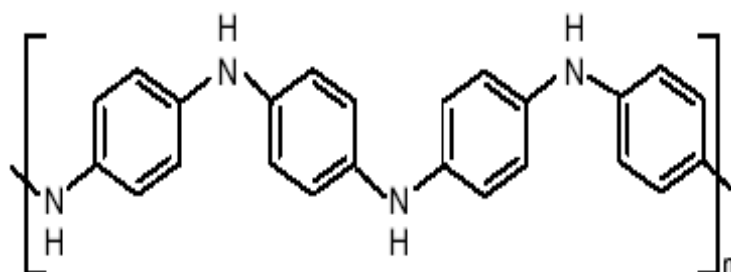
Leucoemeraldine
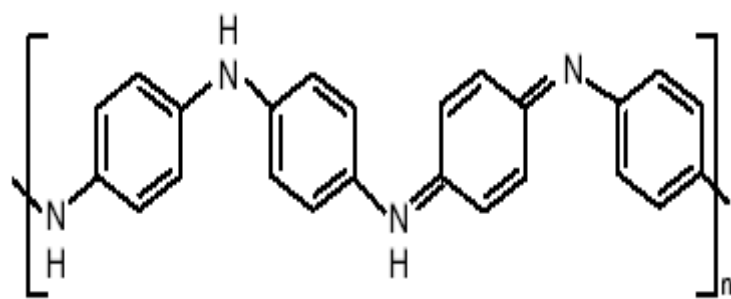
Emeraldine base
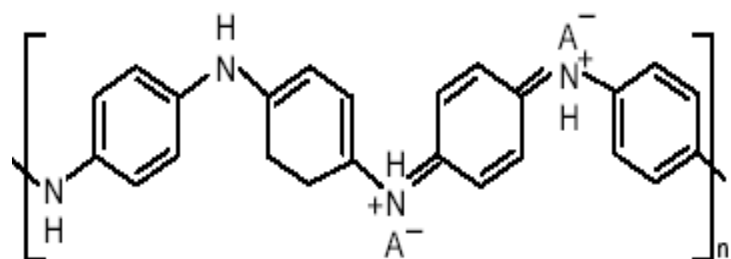
Emeraldine salt
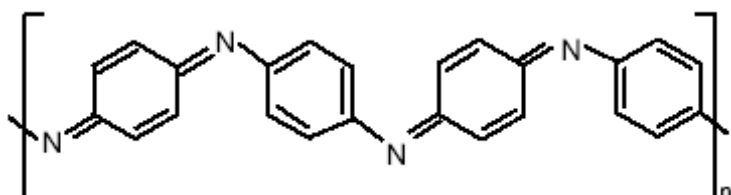
Pernigraniline

Figure 1.6: Various oxidation states of Polyaniline

However, interest in polyaniline was generated only after the fundamental discovery in 1977 that iodine doped polyacetylene gives metallic conductivity which triggered research interest in new organic conducting materials [73]. Polyaniline can be synthesized by both chemical and electrochemical oxidative polymerization [74-75]. Polyaniline exists in four main oxidation states viz. (i) Leucoemeraldine base, (ii) Emeraldine base (iii) Emeraldine salt and (iv) Pernigraniline, Schematic representations for which are shown in the Fig 1.6.

1.2.7. Applications of Conducting Polymers

An academic, governmental and industrial laboratory throughout the world involves in the basic research and assessment of possible applications of conducting polymers that makes the conducting polymers an interdisciplinary area in nature. These conducting organic molecular electronic materials have attracted much attention largely because of their many projected applications as shown in Fig. 1.7.

There are two main groups of applications. The first group utilizes their conductivity as its main property. The second group utilizes the electroactivity. They are shown in Table 1.2. An extensive research has to be done to bring many of the applications in a reality. The stability and processibility both need to be substantially improved if they are to be used commercially. The cost of such polymers must also be substantially lowered. However, one must consider that, although conventional polymers were synthesized and studied in laboratories around the world, they did not become widespread until years of research and development had been done. In a way, conducting polymers are at the center stage of development as their insulating brothers were some 50 years ago.
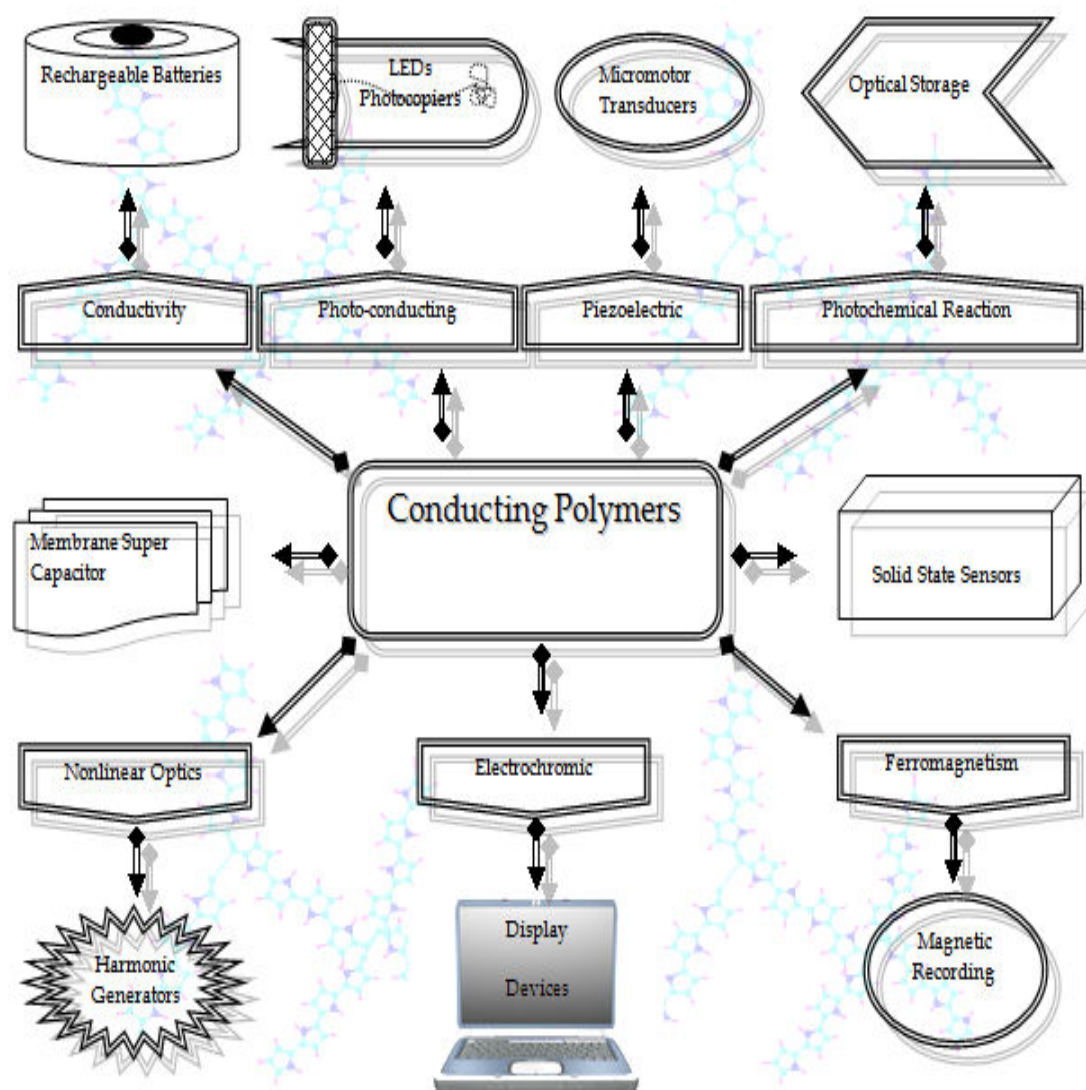
See Fig. 1.7: Applications of conducting polymers

Table 1.2: Various applications of conducting polymers

Group 1	Group 2
Electrostatic Materials	Molecular Electronics
Conducting Adhesives	Electrical Displays
Electromagnetic Shielding	Chemical, Biochemical and Thermal Sensors and Biosensors
Printed Circuit Boards	Rechargeable Batteries and Electrolytes
Artificial Nerves	Drug Release Systems

Antistatic Clothing	Optical Computers
Piezoceramics	Ion Exchange Membranes
Active Electronics (Diodes, Transistors)	Electromechanical Actuators
Aircraft Structures	'Smart' Structures

Regardless of the practical applications that are eventually developed for them, they will certainly challenge researchers in the years to come with new and unexpected phenomena. Only time will tell whether the impact of these novel plastics will be as large as their insulating relatives.

1.3. OBJECTIVES:

The main objectives is to understand the relationship between the chemical structure of the repeating unit of the conducting polymer (Polyaniline) and its conducting properties. Similarly to understand the influence of the electrochemical process parameters viz. type of electrolyte, concentration ratio of monomer and electrolyte, applied current density, pH, temp, deposition time etc

The present work deals with the optimization of process parameters viz. concentration of monomer and various supporting electrolytes (dopant) viz. hydrochloric acid, potassium chloride, sodium chloride, etc., pH of the electrolyte, current density etc. for the synthesis of conducting polymers We have optimized process parameters for the synthesis of PANI film. We have synthesized PANI-H_2SO_4, PANI-PVS, films by electrochemical polymerization system (Galvanostat). These synthesized conducting polymers initiated chemical, biological sensors and membrane technology.

REFERENCES

1. C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of everse osmosis desalination, Desalination.216(2007) 1–76.oi:10.1016/j.desal.2006.12.009.

2. L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges., Water Res. 43 (2009) 2317–48. doi: 10.1016/ j.watres.2009.03.010.

3. K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—Development to date and future potential, J. Memb. Sci. 370 (2011) 1–22. doi: 10.1016/ j.memsci.2010.12.036.

4. B. Van Der Bruggen, A Review of Pressure-Driven Membrane Processes in Wastewater Treatment and Drinking Water Production, Environ. Prog. (2003). http:// onlinelibrary. wiley. com/ doi/ 10.1002/ ep. 670220116/ abstract (accessed November 15, 2013).

5. H.K. Lonsdale, The growth of membrane technology, J. Memb. Sci. 10 (1982) 81–181. doi:http://dx.doi.org/10.1016/S0376-7388(00)81408-8.

6. M. Kurihara, H. Yamamura, T. Nakanishi, High recovery/high pressure membranes for brine conversion SWRO process development and its performance data, Desalination. 125 (1999) 9–15. doi:10.1016/S0011-9164(99)00119-8.

7. N. Hilal, H. Al-Zoubi, N.A. Darwish, A.W. Mohammad, M. Abu Arabi, A comprehensive review of nanofiltration membranes: Treatment, pretreatment, modelling, and atomic force microscopy, Desalination. 170 (2004) 281–308. doi:10.1016/j.desal.2004.01.007.

8. J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, Nat. Rev. Mater. 1 (2016) 1–15. doi:10.1038/natrevmats.2016.18.

9. P.H. Wolf, S. Siverns, S. Monti, UF membranes for RO desalination pretreatment, Desalination. 182 (2005) 293–300. doi:10.1016/j.desal.2005.05.006.

10. J. Arévaloa, G. Garralónb, F. Plazab, B. Morenoa, J. Péreza, M.Á. Gómeza*, Wastewater reuse after treatment by tertiary ultrafiltration and a membrane bioreactor (MBR): a comparative study, Desalination. 243 (2009) 32–41. doi:10.1016/j.desal.200.

11. C.-W. Jung, L.-S. Kang, Application of combined coagulation-ultrafiltration membrane process for water treatment, Korean J. Chem. Eng. 20 (2003) 855–861. doi:10.1007/BF02697288.

12. G. Tchobanoglous, J. Darby, K. Bourgeous, J. McArdle, P. Genest, M. Tylla, Ultrafiltration as an advanced tertiary treatment process for municipal wastewater, Desalination. 119 (1998) 315–322. doi:10.1016/S0011-9164(98)00175-1.

13. T A Skotheim, R L Elsenbaumer and J R Reynolds, Handbook of Conducting Polymers, (Ed. II), Marcel Dekkar, New York, 1998.

14. M G Arora and M Singh, 'Polymer chemistry', Anmol Publications Pvt. Ltd. New Delhi, India, Chap.-1, pp. 1.

15. J L Bredas and R R Chance, Conjugate Polymeric Materials: Opportunities in Electronics (NATO) ASI Series E: Applied Sciences Vol. 182, Kluwar Academic Publishers, Dorhrecht, Holland, 1990.

16. A J Heeger, Angew. Chem. Int. Ed. 40 (2001) 2591.

17. H Shirakawa, E J Louis, A G MacDiarmid, C K Chiang and A J Heeger, Chem. Commun. (1977) 578.

18. R L Greene, G B Street and L J Suter, Phys. Rev. Lett. 34 (1975) 577.

19. H Litheby, J Am. Chem. Soc. 15 (1862) 161.

20. A J Heeger, Angew. Chem. Int. Ed. 40 (2001) 2591.

21. H Shirakawa, E J Louis, A G MacDiarmid, C K Chiang and A J Heeger, Chem. Commun. (1977) 578.

22. C K Chiang, C R Fincher, Jr., Y W Park, A J Heeger, H Shirakawa and E J Louis, Phys. Rev. Lett. 39 (1977) 1098.

23. W A Little, Phys. Rev. 134 A (1964) 1416.

24. M Hatano, S Kambara and S Dkamoto, J. Polym. Sci. 51 (1961) S26.

25. A F Diaz and K K Kanazawa, 'Polypyrrole: An electrochemical approach to conducting polymers' In: J S Miller Ed., "Extended Linear Chain Compounds" Vol. 3, Plenum Publishing Corporation.

26. F Rabolt, T C Clarke, K K Kanazawa, J R Reynolds and G B Street, J. Chem. Soc. Chem. Commun. (1980) 347.

27. A F Diaz and J A Logan, J. Electroanal. Chem. 111 (1980) 111.

28. J D Capistran, D R Gagnon, S Antoun, R W Lenz and F E Karasz, Am. Chem. Soc. Div. Polym. Chem. 25 (1984) 282.

29. R Qian, Q Pei and Y Li, Synth, Met. 61 (1993) 275.

30. M Trojanowicz and T K vel Krawczyk, Mikrochim. Acta 121 (1995) 167.

31. M Situmorang, J J Gooding, D B Hibbert and D Barnett, Biosens. Bioelectron. 13 (1998) 953.

32. W Schuhmann, Mikrochim. Acta 121 (1995) 1.

33. S A Wring and J P Hart, Analyst 117 (1992) 1215.

34. A Guiseppi-Elie, G G Wallace and T Matsue, Chemical and biological sensors based on electrically conducting polymers. In: T Skotheim, R Elsenbaumer, J R Reynolds, (Eds. II), Handbook of Conducting Polymers, Marcel Dekker, New York, 1997, pp. 963.

35. G Bidan, Sens. Actuat. B 6 (1992) 45.

36. P N Bartlett and J M Cooper, J. Electroanal. Chem. 362 (1993) 1.

37. L V Lukachova, Sens. Actuat. B: Chem. 44 (1997) 356.

38. K P Vidanapathirana, Solid State Ion. 123 (1999) 287.

39. S Geetha and D C Trivedi, Mater. Chem. Phys. 88 (2004) 388.

40. A K Narula, R Singh and S Chandra, Bull. Mater. Sci. 23, 3 (2000) 227.

41. H Masuda and D K Asano, Synth. Met. 43 (2003) 135-136.

42. L X Wang, X G Li and Y L Yang, React. Funct. Polym. 47 (2001) 125.

43. M Gerard, A Chaubey and B D Malhotra, Biosens.Bioelectron.17 (2002) 345.

44. R A Khalkhali, W E Price and G G Wallace, React. Funct. Polym. 56 (2003) 141.

45. A Hallik, A Alumaa, V Sammelselg and J Tamm, J. Solid State Electrochem. 5 (2001) 265.

46. T F Otero and V Olazabal, Electrochim. Acta 41, 2 (1996) 213.

47. C Kou and T Liou, Synth. Met. 82, 3 (1996) 167.

48. G G Wallace, G M Spinks and P R Teasdale, Technomie Publishing Company USA 1997.

49. J I Kroschwitz, (Ed.), Electrical and Electronic Properties of Polymers, Wiley, New York 1988.

50. A J Heeger, In: T A Skotheim, (Ed.), Handbook of Conducting Polymers, Vol. II. Marcel Dekker, New York, 1986 p. 729.

51. A J Heeger, Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials (Nobel Lecture) Angew Chem. Int Ed Engl. 40 (2001) 2591.

52. A J Epstein and A G MacDiarmid, Polymeric Metal. Mol. Cryst. Liq. Cryst., 160 (1988) 165.

53. F Wudl, R O Angus, Jr., F L Lu, P M Allemand, D J Vachon, M Nowak, Z X Liu and A J Heeger, J. Am. Chem. Soc. 109 (1987) 3677.

54. Y Wei, G W Jang, Chan, Ch.-Ch., K F Hsuen, R Hariharan, S A Patel, and C K Whitecar, J. Phys. Chem. 94 (1990) 7716.

55. Y Wei, X Tang, Y Sun and W W Focke, J. Polym. Sci. 27 (1989) 23856

56. .Y Wei, R Hariharan and S A Patel, Macromolecules 23 (1990) 758.

57. Y Wei, K F Hsueh and G W Jang, Polymer 35 (1994) 3572.

58. A F Diaz, J. Electrochem. Soc. 123 (1989) 115.

59. R J Waltman, Can.. J. Chem. 64 (1986) 76.

60. R J Waltman, J Bargon and A F Diaz, J. Phys. Chem. 87 (1983) 1459.

61. T Yamamoto, K Sanechika and A Yamamoto, J. Polym. Sci., Polym. Lett. Ed. 18 (1980) 9.

62. A G Mc Diarmid, Polym. Prep. Am. Chem. Soc. Div. Polym. Chem. 25 (1984) 248.

63. E Genies and C Tsintavis, J. Electroanal. Chem.195 (1985) 109.

64. T Kobayashi, H Yoneyama and H Tamura, J. Electroanal. Chem.177 (1984) 281.

65. I Rubenstein, E Sabatini and J Rishpan, J. Electroanal. Chem. 134 (1987) 3078.

66. A F Diaz, J Castillo, K K Kanazawa, J A Logan, M Salmon and O Fajardo, J. Electroanal. Chem. 133 (1982) 233.

67. J Bargon, S Mohmand and R Waltman, Mol. Cryst. Liq. Cryst. 93 (1983) 279.

68. M Satoh, K Kaneto and K Yoshino, J. Chem. Soc., Chem. Commun. (1985) 1629.

69. D Y Kim, J Y Lee, C Y Kim, E T Kang and K L Tan, Synth. Met. 72 (1995) 243.

70. A C Partridge, C B Milestone, C O Too and G G Wallace, J. Membrane Sci. 152 (1999) 61.

71. M S Kiani and G R Mitchell, Synth. Met. 46 (1992) 293.

72. A Hallik, A Alumaa, V Sammelselg and J Tamm, J. Solid State Electrochem. 5 (2001) 265.

73. T F Otero and V Olazabal, Electrochim. Acta 41, 2 (1996) 213.

74. A P F Turner, I Karube and G S Wilson, Biosensors Fundamentals and Applications, Oxford University Press, Oxford 1987.

75. L C Clark Jr., Trans. Am. Soc. Artif. Intern. Organs 2 (1956) 41

76. L C Clark Jr. and C Lyons, Ann. NY Acad. Sci. 102 (1962) 29.

77. G G Guilbault and J Montalvo, J. Am. Chem. Soc. 91 (1969) 2164.

Chapter - 2

Synthesis and Characterization of Conducting Polymers

2. Synthesis of Conducting Polymers

Synthesis and characterization of conducting polymers have become most important area of the research in polymer and materials science [1-6]. In this context, major attention has been focused on synthesis of conducting polymer having

(a) New and novel structures,

(b) Good processibility,

(c) Ease of synthesis,

(d) More defined three dimensional structures,

(e) Stability,

(f) Solubility in water and

(g) Unique properties.

As conducting polymers are organic materials, there is a certain amount of flexibility in their synthesis, which allows the use of feedback from the device and allows to combine end use requirements to tailor properties of conducting polymers. This synthesis flexibility will be a key factor in successful commercialization of conducting polymers. Conducting polymers can be synthesized via chemical or electrochemical routes. The following sections describe these two different synthesis routes.

2.1. Chemical Synthesis Method

This is one of the methods for the synthesis of conducting polymers in which the reaction takes place by adding the monomer and different oxidant in an aqueous medium. The chemical reaction is carried out with time and different temperature environment. However, control over polymer morphology is extremely limited, purification can be problematic and processing is virtually impossible, there is no control over the polymerization especially on the thickness, which certainly affect on the different process parameters.

2.1.2. Electrochemical Synthesis Method

An electrochemical polymerization system for the synthesis of conducting polymer films has been indigenously developed in our laboratory. Electrochemical

polymerization of conducting polymers generally carried out by: 1) constant current or galvanostatic method, 2) constant potential or potentiostatic method and 3) potential scanning/cycling or sweeping method. Standard electrochemical technique, which employs a divided cell containing a working electrode, a counter electrode and a reference electrode generally, produces the best films [24-30].In the present research work, the conducting polymer films i.e. (PANI) with various supporting electrolytes (dopant) viz. Sulfuric acid, hydrochloric acid, potassium chloride, sodium chloride, PVS, dopants have been synthesized electrochemically on platinum and ITO coated glass substrates under galvanostatic conditions in a single compartment glass cell. Three-electrode geometry has been employed during the electrochemical polymerization. The platinum foil and ITO coated glass substrates as the working electrode, platinum foil as the counter electrode and Silver/Silver Chloride Electrode (Ag/AgCl) or Saturated Calomel Electrode (KCl) as the reference electrode. The reference electrode was kept in close proximity to the working electrode to minimize the electrolytic ohmic drop. Typical electrochemical bath consist of a monomer and a supporting electrolyte dissolved in appropriate solvent.Electrochemistry has contributed significantly to the development in the conducting polymers based biosensors. In most of the applications, it is essential to synthesize polymers into a thin film of well-defined structure, preferably with a large area. The electrochemical synthesis is a standard method for preparation of such films. The conducting polymers, which are not easily processed when prepared by chemical method, are synthesized in the form of films adhering to the electrode, so that a study of the optical and electrical properties can be carried out in-situ by using electro-analytical techniques. The electrochemical synthesis of conducting polymers is similar to the electrodeposition of metals from an electrolytic bath the polymer is deposited on the electrode surface and in the in-situ doped form. The electrochemical synthesis route/method offer many advantages over the chemical method as listed below

(a) It is simple and less expensive technique. Therefore, electrodeposition of conducting polymer on oxidizable conducting glass is extremely economical.

(b) Unlike chemical method, there is no need of catalyst and therefore, the electrodeposited polymers and co-polymers are essentially pure and homogeneous.

(c) Doping of the polymer with desired ion can be considered simultaneously by changing the nature of counter ions in the solution.

(d) The conducting polymers can be obtained directly in thin film form as coatings on electrodes and the properties of these coatings can be controlled effectively by proper choice of the electrochemical process parameters.

(e) Reduction in the possible pollution by adopting the suitable system for electropolymerization using modern sophisticated instrument.

(f) The most salient feature of this route is that polymerization, doping and processing takes place simultaneously.

(g) Opportunity to carry out various in-situ spectroscopic studies, conductivity and even determination of conducting levels at various potentials.

The detail description of three different electrodeposition method viz. 1) Potentiostatic deposition method 2) Galvanostatic deposition method and 3) Cyclic voltammetry (CV) method is as below.

2.1.3. Potentiostatic Deposition Method

In the potentiostatic deposition method, a predetermined optimum voltage is applied during synthesis with no control over the resulting current in the system. The potentiostatic deposition is generally carried out using a potentiostat to control the potential of the working electrode (WE). However, consistency is only achieved if the natures of the solutions and electrodes are rigorously controlled [7]. The reference electrode (RE) has to be kept closer to the working electrode so that it will minimize the ohmic drop within the electrolyte and reliable measurement of working electrode potential can be done.

2.1.4. Galvanostatic Deposition Method

In the galvanostatic method, a fixed oxidation current is supplied with no control over the resulting potential of the system. Galvanostatic method is more widely used because it provides more control over film thickness, and it is reproducible too. The

galvanostatic method enables a more uniform polymer film to be produced by applying constant current. The magnitude of the current density during polymerization depends upon the intended application because this can affect the morphology and the conductivity of the polymer film as well as the potential of the system during synthesis. At high potentials, the integrity of reagent to be incorporated into the film may be affected.

2.1.5. Cyclic Voltammetry (CV) Method

In CV, the voltage applied to WE is scanned linearly from an initial value to a predetermined limit of the monomer oxidation known as the switching potential where the direction of the scan is reversed. On reaching initial value again the scan may be halted/reversed alternately or continued to further value. The current response can be plotted against the applied potential. CV growth of polymer film is achieved by consecutive potential sweeps in a solution containing monomer and supporting electrolyte. However, the positive potential limit is critical since the initiation of polymerization on the electrode surface commences only above a certain potential. If the potential is too positive, the polymer can be over-oxidized, and if it is too low, the film formation can be impeded [8]. Oxidation and reduction peaks are appears during forward and reverse scan respectively. By observing the appearance and disappearance of redox peaks and variation in sweep rates, it is possible to determine the correlation between various electrochemical processes and redox peaks. However, CV polymerization is difficult to control, and the generation of reproducible polymer films is difficult to accomplish.
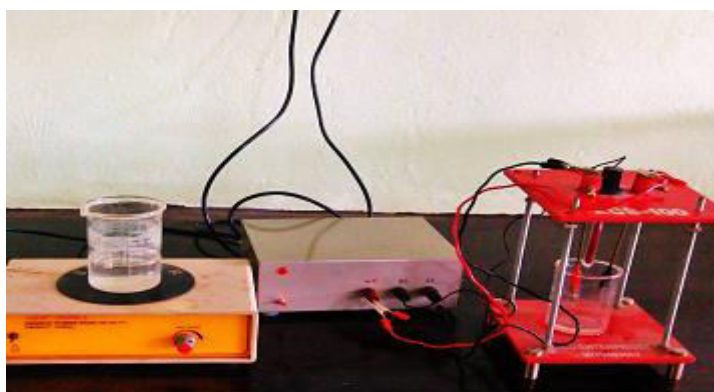

Fig. 2.1: Photographs of   Galvanostat with electrochemical cell

2.1.6. Electrochemical Synthesis Set-Up

The electrochemical synthesis setup is as shown in Fig. 2.1. It consists of indigenously developed PC based electrochemical polymerization system (Potentiostat/Galvanostat), three electrode glass cell and a constant temperature bath. The three electrode glass cell consists of working electrode, counter electrode, reference electrode and electrolyte solution.

2.2. Types of Electrodes

2.2.1. Working Electrodes (WE)

The WE is usually referred as a substrate. The material such as platinum, gold stainless steel and ITO coated glass etc are usually used for substrate.

2.2.2. Choice of Substrate (Electrode)

The electrochemical growth of polymer films can be accomplished on several substrates including gold [9], platinum [10], glassy carbon [11], indium-tin-oxide (ITO) coated glass [12], titanium, aluminium, mild steel and brass electrodes [13], as well as on mercury [14] and plastic films coated with silver and tin-oxide [15]. The choice of substrate is important for the development of conducting polymer based biosensors where the electroactive reactant or products (such as oxygen or hydrogen peroxide) are detected at the electrode metal. The platinum is being widely used as a working electrode for potentiometric detection systems. Platinum and gold substrate produces good films. The evolution of oxygen or hydrogen peroxide on Pt and Au electrodes causes the film to strip quickly from the metal substrate [16]. Mercury is not generally used because it is oxidized at less positive potentials while titanium and mild steel produce poor films. Brass forms films only under certain conditions since, at positive potentials, the copper tends to be oxidized and polymerization is retarded [17].

Broadly Speaking, the Following Criteria Should be applied for the Selection of a Substrate.

(a) It should have good conductivity,

(b) One can use insulating substrate provided a suitable conductive coating has to be applied on its surface,

(c) Good conductivity of the substrate is also beneficial to improve the carrier collection efficiency,

(d) The substrate should have good mechanical strength,

(e) In many applications cost is an important consideration, therefore it should be cost effective,

(f) It is necessary to match the lattice parameters between the single crystal substrate and the growing film for epitaxial film,

(g) The thermal expansion of the substrate should match well with that of the electro-deposition. A mismatch in the thermal expansion often leads to strains that result in cracking or packing of the film,

(h) The substrate should be stable in the electrolyte bath, for this reason, inert substrates such as platinum, gold, stainless steel and ITO coated glass are used and

(i) The substrate surface should be smooth.

2.2.3. Counter Electrode (CE)

The purpose of the CE is to supply the current required by the WE without anyway limiting the measured response of the electrochemical cell. The CE should be conductive material and chemically inert such as platinum, graphite, carbon etc.

2.2.4. Reference Electrode (RE)

The role of reference electrode is to provide fixed potential, which should not vary during the experiment. During electrochemical polymerization, it is important to have a stable and constant potential at the working electrode. In reality, the working electrode potential does not remain constant due to the continuous electrochemical reaction-taking place on the surface of the electrode. It affects the overall synthesis process. To avoid this, a reference electrode is introduced. This reference electrode is placed within the electrolyte in close proximity to the working electrode. A fixed potential is applied to the working electrode. The reference electrode maintains the value of this fixed voltage at the working electrode. Some common RE are Saturated Calomel Electrode (SCE), Silver/Silver Chloride (Ag/AgCl), Mercury/Mercurous Chloride Electrode (Hg.Hg_2Cl_2), Mercury/Mercurous Sulphate Electrode (Hg/Hg_2SO_4), Mercury/Mercurous Oxide

Electrode (Hg/Hg$_2$O), etc. In the present work, we have used saturated calomel electrode (SCE) and silver/ silver chloride electrode.

2.3. Electrolyte

The electrolyte facilitates the cell reaction and carries the ionic charge across the electrodes efficiently. It also forms a stable reference potential with the reference electrode and compatible with materials used within the working electrode. If the electrolyte evaporates too quickly, it will affect the polymerization process. The electrolyte solution is the medium between the electrodes in the cell that supplies the ions, which move upon application of an electric field. Electrolyte solution consists of monomer, supporting electrolyte and solvent. The electrolyte facilitates the cell reaction and carries the ionic charge across the electrodes efficiently. It also forms a stable reference potential with the reference electrode and compatible with materials used within the working electrode. If the electrolyte evaporates too quickly, it will affect the polymerization process. The electrolyte solution is the medium between the electrodes in the cell that supplies the ions, which move upon application of an electric field. Electrolyte solution consists of monomer, supporting electrolyte and solvent.

2.3.1. Monomer

The compound, which possess relatively lower anodic oxidation potential and are susceptible to electrophilic substitution reaction, can produce conducting polymers by electrochemical synthesis route. Table 2.1. gives peak oxidation potentials for some heterocyclic and aromatic compounds of interest. It is seen that the electrochemically polymerizable monomers generally have peak potentials below 2.1 V. Low peak potential avoids complications during polymerization arising from oxidative decomposition of the solvent and the electrolyte.

Table 2.1: Oxidation potential of some heterocyclic and aromatic monomers

Monomer	Oxidation potential (V) vs SCE
Pyrrole	1.20
Thiophene	2.07
Bithiophene	1.31

Pyrene	1.30
Aniline	0.71
O-Anisidine	0.74
m-Anisidine	0.86
N-methyl aniline	0.84

2.3.2. Supporting Electrolyte (Dopant)

One of the important parameters which affects the physical characteristics and morphology of polymer film is the nature and the concentration of the dopant that represents about 30% of the weight of the polymer film. The choice of supporting electrolyte can be made by considering its solubility and its nucleophilicity. Moreover, the anion oxidation potential should be higher than the monomer. The dopant can be organic or inorganic and can be of varying sizes (from chloride to polystyrene sulfonate). The size of the anion controls the microstructure and the porosity of the polymer. Indeed, this determines the ability of the polymer to undergo an easier diffusion of the dopants during the redox process [18]. The nature of the anion has an impact on the surface morphology of the film produced, which depends on the hydrophobic character of the anion, and the interactions between the polymer and the dopant.

The supporting electrolyte (dopants) helps to improve or increase the conductivity of the synthesized film. It reduces the electrode double layer thickness and also influences adsorption and ion pairing. It significantly eliminates the effect of migration in the mass transport. The supporting electrolytes should be soluble in the solvent. The criteria for selection of a supporting electrolyte are its solubility in the solvent and high dissociation constant yielding good electrical conductivity and the electrochemical oxidation of anion and electrochemical reduction of cation at more anodic or cathodic potentials, respectively than the electrochemical process under investigation. In aqueous media sulfuric acid, potassium nitrate, sodium nitrate, nitric acid, hydrochloric acid, potassium chloride, sodium chloride, PVS, pTS, and the composite dopant etc are used as supporting electrolytes.

2.3. Solvent

The aqueous medium is mostly used as a solvent for the synthesis of conducting polymer. The primary factors are solubility and non-reactivity. The potential at which the deposition is to be carried out should be within the working potential range of the solvent. As the morphology and growth rate depends upon the temperature, the solvent should remain in liquid form at the synthesis temperature.

Electrochemical synthesis is carried out mostly in aqueous medium. During synthesis of conducting polymer, the solvent may affect the morphology, conductivity and electrochemical activity of the resulting polymer film. Organic solvents such as, acetonitrile and propylene carbonate are often used for electropolymerization. Acetonitrile is more widely utilized because it enables the formation of highly conductive films (30-1000 $S.cm^{-1}$). However, the addition of 1 % water to the acetonitrile is necessary to improve the adhesion of the film, but the conductivities of these films are in order of magnitude lower than those grown with either acetonitrile or propylene carbonate. Unfortunately, organic solvents cannot be employed for the incorporation of biologically active material because these solvents denature the enzymes, and often do not enable solubillization of the proteins. The conformation of the enzymes may be different in organic solvents, and this affects the activity of the immobilized enzyme. In order to prevent the denaturing of the enzymes we have used the distilled water in the present research work.

2.3.1. Aqueous Solvents

Aqueous solvents are suitable for a large number of salts, complexing agents and other compounds. Barring a few hydrolysis reactions, H_2O is generally a non-reactive solvent. However, an aqueous solution necessarily contains H^+ and OH^- ions, which in extreme conditions complicate the electrodeposition process by resulting in the evolution of H_2 and/or O_2 at the electrode.

2.3.2. Non-Aqueous Solvents

Non-aqueous solvents can be classified as protic and aprotic solvents.

2.3.3. Protic Solvents

The protic solvents are generally hydrogen donor and can exchange protons rapidly. Such solvents also sometimes lead to hydrogen evolution, a problem during deposition. The examples of protic solvents are acetic acid, ethanol, methanol, etc.

2.3.4. Aprotic Solvents

The aprotic solvents contain hydrogen bounded only with carbon. The examples of aprotic solvents are dimethyl formamide, sulphur dioxide, dimethyl sulphoxide, tetrahydrofuran etc.

an exchange protons rapidly. Such solvents also sometimes lead to hydrogen evolution, a problem during deposition. The examples of protic solvents are acetic acid, ethanol, methanol, etc.

2.3.5. ph of the Electrolyte Solutions (Reaction Medium)

The pH of the electrolyte (reaction medium) has considerable influence on the reactivity and stability of the conducting polymer film formed at the electrode surface [19]. As shown by Unsworth and coworkers, [20] the optimization of the pH results in the formation of a uniform surface with very few defects of synthesized polymer film. The pH, which produces the best polymer, depends on the species chosen to serve as solution buffers [21]. A low pH or acid solution generally favors polymerization. However, a very low pH will equally be responsible for weak conductivity because the acid catalyzes the formation of nonconjugated trimers, which further react to form a partly conjugated polymer or are incorporated into the film, or even diffuse into the solution [22]. It should be noted that the pH also influences the electrochemical activity of the polymer. In acid solution, the insertion and deinsertion of the dopant is observed whereas in basic solution, the anion is replaced by hydroxy groups from the solution. The two phenomena are observed in neutral solution [23]. The stability of the polymer in aqueous solution depends equally on the pH.

2.4. Characterization Techniques of Conducting Polymers

The experimental system used in the present study has been described in earlier section of this chapter. An electrochemical synthesis of electrically conducting PANI films (with various supporting electrolytes, concentrations ratios, current densities, pH) have

been carried out. A platinum and ITO coated glass substrate have been used for all experimental investigations. The synthesized films were characterized by different characterization techniques.

2.4.1. Characterization Techniques

In order to understand the physical and chemical properties of electrically conducting polymers, and to study surface morphology, a number of characterization techniques have been employed. In the present work, synthesized PANI films were characterized by galvanostatic techniques, Electrical conductivity (Four Probe Techniques), UV-visible spectroscopy, Fourier Transform Infrared (FTIR) Spectroscopy and Scanning Electron Microscopy (SEM).

2.4.2. Galvanostatic Technique

The electrochemical synthesis of PANI films (with various supporting electrolytes, concentrations ratios, current densities and pH) on platinum or ITO coated glass substrates was carried out by galvanostatic technique using Electrochemical Polymerization System. A typical galvanostatic electropolymerized chronopotentiogram is as shown in Fig. 2.3. It shows the anodic peak (oxidation potential) at which the polymerizations process starts and the plateau (polymerization potential) at which the polymerization process reaches to the stable state with time, indicating the completion of the process. All these stages are affected by process parameter namely aniline concentration, electrolyte concentration, time of deposition, applied current density, surface pretreatment and the pH of the electrolyte. In fact, the recorded polymerization potential should be as minimum as possible so that we can have high conductivity of the synthesized film.
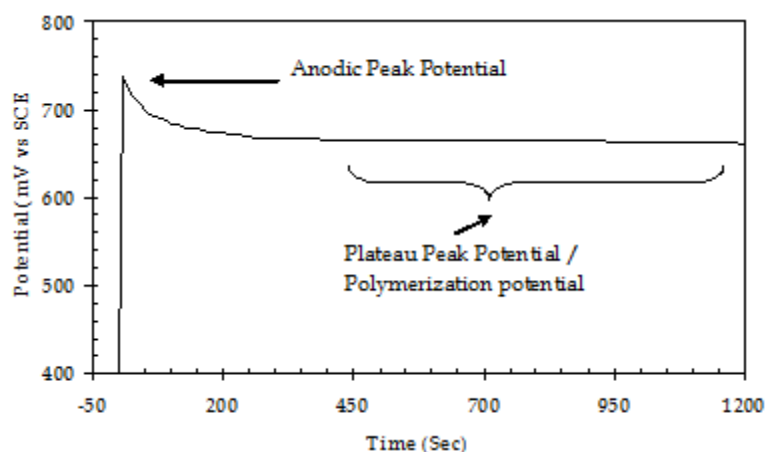
Fig. 2.3: A typical galvanostatic electropolymerized chronopotentiogram (E-t curve)

The behavior of the galvanostatic synthesis during the first few seconds probably indicates the difficult formation of dimers and oligomers. After this, the potential becomes almost constant suggesting that building up of the film proceeds according to the same reaction along the full thickness of the polymer.

2.5. Electrical Conductivity

The electrical conductivity of synthesized PANI films with various supporting electrolytes, concentrations ratios, current densities, pH were measured by two probe and four probe technique using (Model DRF-02 Owen 1038 - Optochem. International, New Delhi) on platinum and ITO-coated glass electrode.

2.6. U V Visible Studies

UV-visible spectrophotometer Shimadzu 1601 was used in the region between 300 and 900 nm for optical spectroscopic studies and the determination of oxidation state of synthesized PANI film with various dopants and composite dopants.

2.7. Fourier Transform Infrared (Ftir) Spectroscopy

FTIR spectroscopy was used for structural characterization of synthesized PANI films with various supporting electrolytes, concentrations ratios, current densities, pH. The FTIR spectrum is a plot of sample transmission of IR radiations as a function of Wavenumber. The IR spectroscopy is the physics that deals with the theory and interpretation of the spectrum and is one of the most popular techniques for identification of the molecules. The presence or absence of many chemical functional

groups usually can be established from the spectrum. The FTIR transmission spectra (Shimadzu FTIR-8400 series, University of Pune) of the synthesized PANI films were recorded in the wave number range 4000-300 cm^{-1}.

2.8. Scanning Electron Microscopy

Scanning electron microscopy (JEOL JSM-6360A SEM Machine, University of Pune) was used for morphological characterization of synthesized PANI films with various supporting electrolytes, concentrations ratios, current densities, pH. The polymer structure and morphology are greatly affected by electro-synthetic conditions, such as electrode materials, solvent and electrolyte salts, oxygen and water content of the system and the current density used for electro polymerization. Although a quantitative measure of these effects has not been established, some general observations have been made. Thin films generally appear smooth, while thicker samples have a much more uneven textured surface. Lower current densities and potentials used during electro polymerization give rise to smoother films.

The important things to pay attention to that must mention when creating any sensor are: First: the acceptable error rate of the sensor or limitation. Second: the default or standard climates used upon detection. Third: the number of times the detector can be repeated. Fourth: the shelf life of the sensor or its instant synthesis before detection.Fifth: the atmosphere that must be provide when conducting the sensor. The importance of sensors has increased rapidly in recent years. The most important aspect, which is human health in general, through vital sensors, through which disease or disorder is identified without surgical intervention, in an easy and quick manner.

REFERENCES

[1] L Alcaer, Conducting Polymers: Special Applications, Dorhrecht, Holland, 1987.

[2] M Aldissi, Intrinsically Conducting Polymers: An emerging Technology, Kluwar Academic Publishers, Dorhrecht, Holland, 1993.

[3] H S Nalwa, Handbook of Organic Conductive Molecules and Polymers, Vol. I - IV, John Wiley and Sons Ltd., 1997.

[4] P Chandrasekhar, Conducting Polymers: Fundamentals and Applications, Kluwar Academic Publishers, Dorhrecht, Holland, 1993.

[5] J H Kaufman, O R Melroy, F F Abraham, A I Nazzal and A Kapituluik, Synth. Met. 18 (1987) 19.

[6] T F Otero, R Tejada and A S Elola, Polymer 28 (1987) 651.

[7] E Beelen, J Riga and J J Verbist, Synth. Met. 41 (1991) 449.

[8] M Satoh, K Imanishi and K Yoshino, J. Electroanal. Chem. 137 (1991) 139.

[9] J Unsworth, P C Innis, B A Lunn, Z Jin and G P Norton, Synth. Met. 53 (1992) 59.

[10] E L Kupila and J Kankare, Synth. Met. 55 (1993) 1402.

[11] T F Otero and J Rodriguez, Electrochim. Acta, 39 (1994) 245.

[12] R Qian, Y F Li, B Z Yan and H M Zhang, Synth. Met. C51 (1989) 28.

[13] Q Cheng, V Pavlinek, C Li, A L Ying He and Petr Saha, Mat. Chem. Phys. 98 (2006) 504.

[14] S Radhakrishnan and A. Adhikari, Journal of Power Sources, 155 (2006) 157.

[15] S Brady, K T Lau, W Megill, G G Wallace and D Diamond, Synth. Met. 154 (2005) 25.

[16] M D Migahed , T Fahmy , M Ishra and A Barakat, Polymer Testing, 23 (2004) 361.

[17] G Han and G Shi, Sens. Actuat. B: Chemical, 99 (2004) 525.

[18] E Larraz, M I Redondo, M J González-Tejera, M A Raso, J Tortajada, E Sánchez de la Blanca and M V García, Synth. Met., 122 (2001) 413.

[19] M I Redondo, E Sánchez de la Blanca, M V García, M A Raso, J Tortajada and M J González-Tejera, Synthetic Metals, 122 (2001) 431.

[20] J Unsworth, P C Innis, B A Lunn, Z Jin and G P Norton, Synth. Met. 53 (1992) 59.

[21] E L Kupila and J Kankare, Synth. Met. 55 (1993) 1402.

[22] T F Otero and J Rodriguez, Electrochim. Acta, 39 (1994) 245.

[23] R Qian, Y F Li, B Z Yan and H M Zhang, Synth. Met. C51 (1989) 28.

Chapter - 3

Influence of Various Electrochemical Process Parameters on Conductivity and Surface Morphology of Pani Films

3.1. INTRODUCTION

Conducting polymers have been widely studied due to their many known technological applications, such as energy storage, electromagnetic interference shielding, electrochromic devices, sensors etc [1-7]. The PANI has great interest over last few years due to its potential applications in various Opto-electronic devices as well [8, 9]. The conducting polymer (PANI) resulting from oxidative polymerization of aniline has been known since 1862 [10]. The PANI is particularly challenging because of its conductive nature and solubility in polar inorganic solvents, which not only depends on the oxidation state but also on degree of protonation and dopant.

The PANI is build up from oxidized (B-N=Q=N) units, where B denotes benzeoid and Q denotes quniod ring. Thus, the ratio of amine to imine yields various structures such as LEB (reduced form) emeraldine base (50% oxidized form) and pernigraniline (Full oxidized form) (Scheme 1) [11]. Unlike other phenylene - based conducting polymers, polyaniline has reactive NH group in a polymer chain flanked on either side of phenylene ring which gives it a high chemical flexibility. It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which, having lone pair of electrons, is responsible for interesting chemistry and physics related technological applications.

The electrochemical behavior of polyaniline not only depends on the pH condition but also on the counter ion of bronsted acid used for doping [12]. It is well known that the chemistry of PANI is more complex than that of other conducting polymers. The EB form of PANI can be protonated with sufficiently strong acid to ES due to the presence of basic sites (amine and imine group) in polymer structure and the pH sensitivity.

The discovery of polymer semi-conducting film formation by electrochemical oxidation of aniline had led to the development of a new branch of fundamental and applied electrochemistry [13]. The use of conducting polymers in all solid state ion sensor applications is based on their mixed electronic and ionic conductivity. Among various matrices, conducting polymers have recently attracted much attention, since they posses, the ability to bind oppositely charged complex entities in their oxidized conducting state and to release them in their neutral insulating state [14-16]. The

synthesis of conducting polymers for the immobilization of biocomponent has been widely reported [17-22]. The conducting properties and surface morphology of the polymer (PANI) film is depends on the method of synthesis and different electrochemical process parameters viz. type of electrolyte, concentration of monomer and supporting electrolyte, applied current density, pH, deposition time etc [23-28]. Therefore, in order to improve the conducting properties of the polymer (PANI) film and to have the desirable surface morphology for a particular application (e.g. biosensor application), it is essential to optimize various process parameters, so that more stable, uniform, adhesive and porous PANI film can be synthesized on platinum which can be further used for biosensor applications.

The present investigation deals with the optimization of process parameters (mentioned above) for the synthesis of polyaniline film on platinum substrate, so that we can have PANI film with better conductivity and uniform, porous surface morphology. The resulting polymer matrix will be used for the immobilization of biocomponent, for the development of biosensor.

The synthesis of polyaniline (PANI) films in aqueous acidic media using potentiometric (Galvanostatic) method on platinum electrode has been investigated. The influence of electrochemical process parameters viz. type of electrolyte, concentration of monomer and electrolyte, pH of the electrolyte and current density on the synthesis of PANI has been studied. The changes in the conductivity of synthesized PANI film for various electrolytes were noticed by potential time curve recorded during the electropolymerization. It was found that the process parameters of electrochemical polymerization have a considerable influence on the conductivity and surface morphology of the PANI film. The electrolytes such as H_2SO_4, HNO_3, $NaNO_3$, KNO_3, KCl and HCl were used for the synthesis of PANI film. We have optimized the process parameters for better conductivity and uniform, porous surface morphology of PANI film and the optimized parameters are 0.2 M concentration of monomer, 1 M concentration of supporting electrolyte H_2SO_4, 1 mA/cm^2 applied current density and 1.0 pH of the electrolyte solution. The characterization of the PANI film was done by

electrochemical technique, conductivity measurement, UV-visible spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning electron microscopy (SEM).

3.2 EXPERIMENTAL

3.2.1. Chemicals Used During Synthesis of PANI Film

The aniline monomer was distilled twice before use and it was stored in the refrigerator to prevent UV degradation. Sulfuric acid (H_2SO_4) , potassium chloride (KCl), and hydrochloric acid (HCl) were used as supporting electrolytes. All above reagents were obtain from Rankhem, Ranbaxy, and New Delhi (INDIA). An aqueous solution of aniline (99%) and various electrolytes were prepared in distilled water.

3.2.2. Electrode Preparation for Electropolymerization

Platinum electrodes were pretreated with acetone and then washed with double distilled water. Three electrode geometry consist of counter electrode (platinum foil of area 20 mm × 40mm × 0.25 mm) working electrode (platinum foil of area 20 mm × 10mm × 0.25 mm) and the reference electrode (saturated calomel electrode (SCE)) were employed during the electropolymerization of the PANI film. Incase of working electrode, it was polished by emery paper with grit size 100, to remove any previous polymer film and then washed with acetone and double distilled water.

3.2.3. Electro Polymerization of Aniline/ Synthesis of PANI Film

The electro polymerization of aniline was carried out by galvanostatic technique in one compartment electrochemical cell with constant current density for known polymerization period. All three electrodes were placed vertically in cell. An 80 ml solution was used for each reaction. The monomer and supporting electrolytes dopants were mixed together to form the electrolyte solution. The pH of the electrolyte was measured by a calibrated pH meter (LI 120 pH meter ELICO). The pH of the electrolyte was adjusted by adding nitric acid/ or sodium hydroxide.

3.3.1 Potentiated/Galvanostat

A computer controlled   Potentiostat/Galvanostat for the electrochemical synthesis of PANI-H_2SO_4 film by using potentiometric (Galvanostatic) method.

3.3.2. UV-Visible Spectroscopy

Shimadzu UV-visible spectroscopy 1601 was used to study the oxidation state of synthesized PANI film. This facility was extended by Department of Chemistry, University of Pune (MS) India.

3. 3.3. Fourier Transform Infrared (Ftir) Spectroscopy

Test scan Shimadzu FTIR-8000 series using KBr pellets was used in the region between 500 and 4000 cm^{-1} for the study of chemical functional group of synthesized PANI film. This facility was extended by department of Chemistry, University of Pune (MS) India.

3. 3.4. Scanning Electron Microscopy (SEM)

JEOL JSM-6360 A Analytical SEM was used to study the surface morphology of synthesized PANI film. This facility was extended by department of physics, University of Pune (MS) India.

3. 3.5. Conductivity Measurement

The four-probe set up (Model DRF-02 Owen 1038- Optochem International, New Delhi) was used for the measurement of electrical conductivity of synthesized PANI-films. The conductivity measurement was done in the Optoelectronics and Sensor Research Laboratory, Department of Physics, Dr Babasaheb Ambedkar Marathwada University Aurangabad (MS) India.

Four probe setup used for conductivity measurement is shown in fig. 3.1 and 3.2.

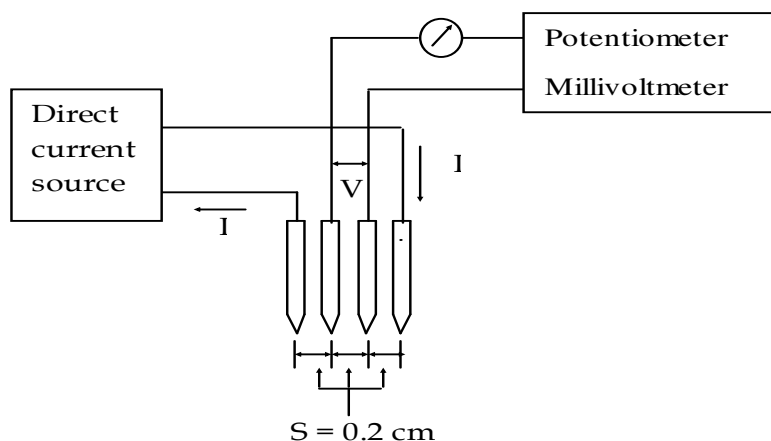**Fig. 3.1:** Photograph of four probe apparatus and its accessories

Fig. 3.2: Schematic diagram of the four probe apparatus

A nominal value of probe spacing must be 2.0 mm [10-11]. The current (I), was set to a constant value and the temperature was varied from room temperature to 110 ^{0}C. The voltage was recorded with increasing temperature with an interval of 5 ^{0}C. The resistivity was calculated at different temperatures using the following relationship

$$\rho = \frac{1}{G_7(W/S)} \times \frac{V}{I} \times 2\pi S$$

Where S is the distance between two probes, W the thickness of the sample, I the current flowing between the outer two probes, V the measured voltage between centre two probes, ρ the resistivity and G_7 the correction factor which can be written as

$$G_7(W/S) = \frac{2S}{W} \log_e 2$$

Conductivity can be computed using the relationship, $\sigma = \dfrac{1}{\rho}$

Where σ the conductivity and ρ the resistivity of the film.

3.4. RESULTS AND DISCUSSION

3.4.1. Influence of Supporting Electrolytes

The potential - time curve for synthesis of PANI film with supporting electrolytes NaNO$_3$, KNO$_3$ and KCl for concentration ratio 0.2:1 M of monomer and supporting

electrolyte at 1 mA/cm^2 current density and 1.0 pH is shown in Fig 3.4.1. The lowest polymerization potential was recorded for electrolyte KCl
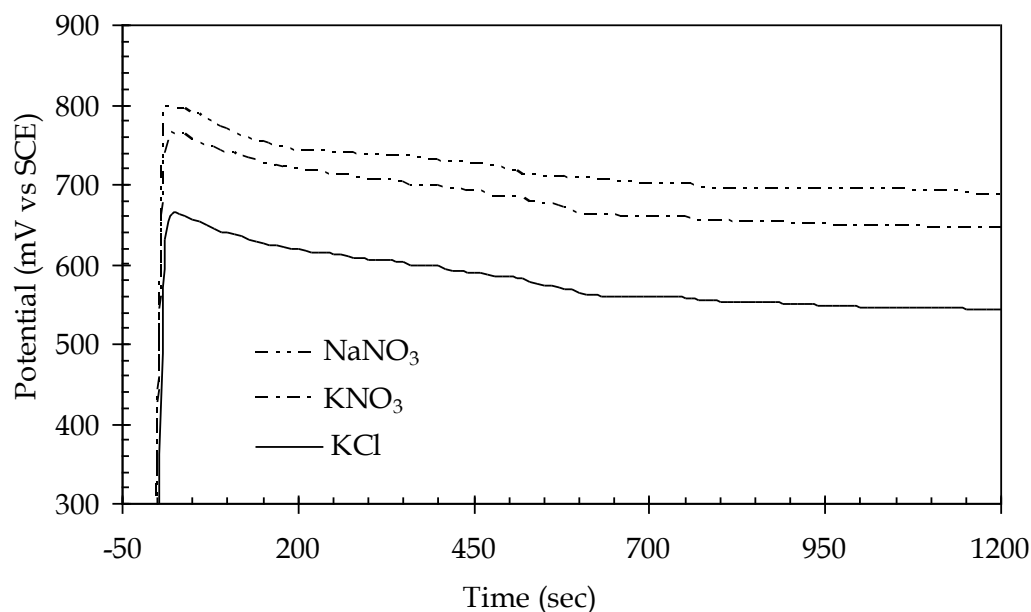

Fig.3.4.1: Potential-time curves obtained during synthesis of polyaniline film with NaNO$_3$, KNO$_3$ and KCl.

We could also synthesize more adhesive PANI with good uniformity with KCl as compared with NaNO$_3$ and KNO$_3$. The conductivity of the synthesized PANI film with NaNO$_3$, KNO$_3$ and KCl was measured. The conductivity strongly depends on the anion present in the electrolyte and follows the order KCl$^-$ >KNO$_3^-$ >NaNO$_3^-$ [29], which shows very good resemblance with the polymerization potential (Table 1). It can also be seen from table 1 that as the polymerization potential increases the conductivity decreases [30]. The conductivity strongly depends on the mobility of ion as well [31].

Table 1: Relation between the polymerization potential and conductivity of various Supporting electrolytes

Sr. No	PANI Film with Supporting Electrolytes	Polymerizations Potential (mV)	Conductivity (S/cm
1	H$_2$SO$_4$	419	0.73

2	KCl	544	0.71
3	HCl	570	0.47
4	KNO_3	644	0.35
5	HNO_3	660	0.30
6	$NaNO_3$	686	0.20

The potential - time curves recorded during synthesis of PANI film with supporting electrolyte HCl, HNO_3 and H_2SO_4 for concentration ratio 0.2 M: 1.0 M of monomer and supporting electrolyte at 1 mA/cm^2 applied current density and 1.0 pH is shown in Fig 3.4.2. The lowest polymerization potential was recorded for H_2SO_4 as compare to HCl and HNO_3. Similarly the synthesized PANI film with H_2SO_4 was more uniform, porous and adhesive as compared with HCl and HNO_3.
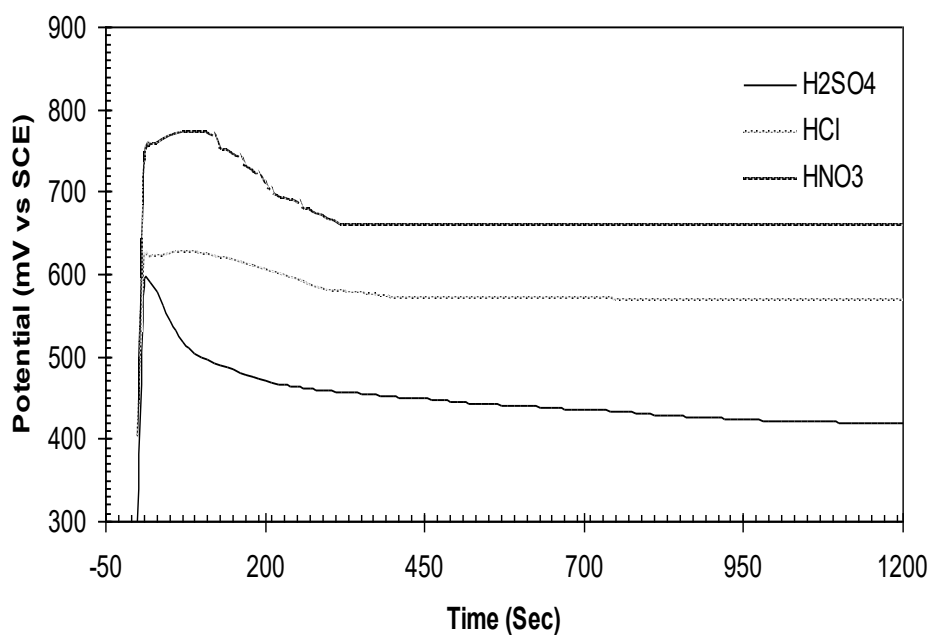
Fig.3.4.2: Potential-time curves obtained during synthesis of polyaniline film with, H_2SO_4HCL and HNO_3.

The potential-time curves recorded during synthesis of PANI with KCl and H_2SO_4 is shown in Fig 3.4.3 for comparison. It can be seen from Fig 3.4.3 that the recorded polymerization potential is lower for H_2SO_4 as compared with KCl. The conductivity of

synthesized PANI film with electrolyte H_2SO_4, KCl, HCl, KNO_3 and $NaNO_3$ is as shown in Table 1. It can be seen from Table 1 that the conductivity of synthesized PANI film with H_2SO_4 supporting electrolyte is highest as compared with other supporting electrolytes. This indicates that the mobility of H_2SO_4 ion in aqueous solution is more as compared with other supporting electrolytes ions [31].
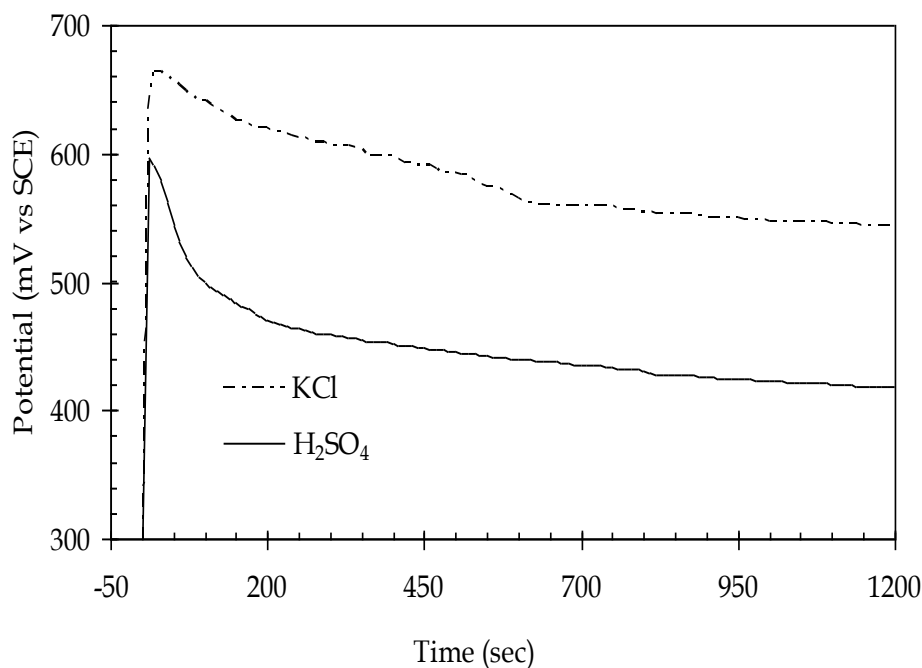

Fig. 3.4.3: Potential-time curves obtained during synthesis of polyaniline film with KCl and H_2SO_4.

Similarly the synthesized PANI film with H_2SO_4 was more uniform, adhesive and porous as compared with other supporting electrolytes.

3.4.2. Influence of Concentration of Monomer (Aniline) and Supporting Electrolyte (Sulfuric Acid).

We have studied the influence of concentration of monomer (aniline) and supporting electrolyte H_2SO_4 on the conductivity and surface morphology of the synthesized PANI film. The potential – time curve obtained during electrochemical polymerization of PANI film at different concentration of aniline (0.2 M, 0.1 M and 0.5 M) and 1 M of H_2SO_4 is shown in Fig 3.4..
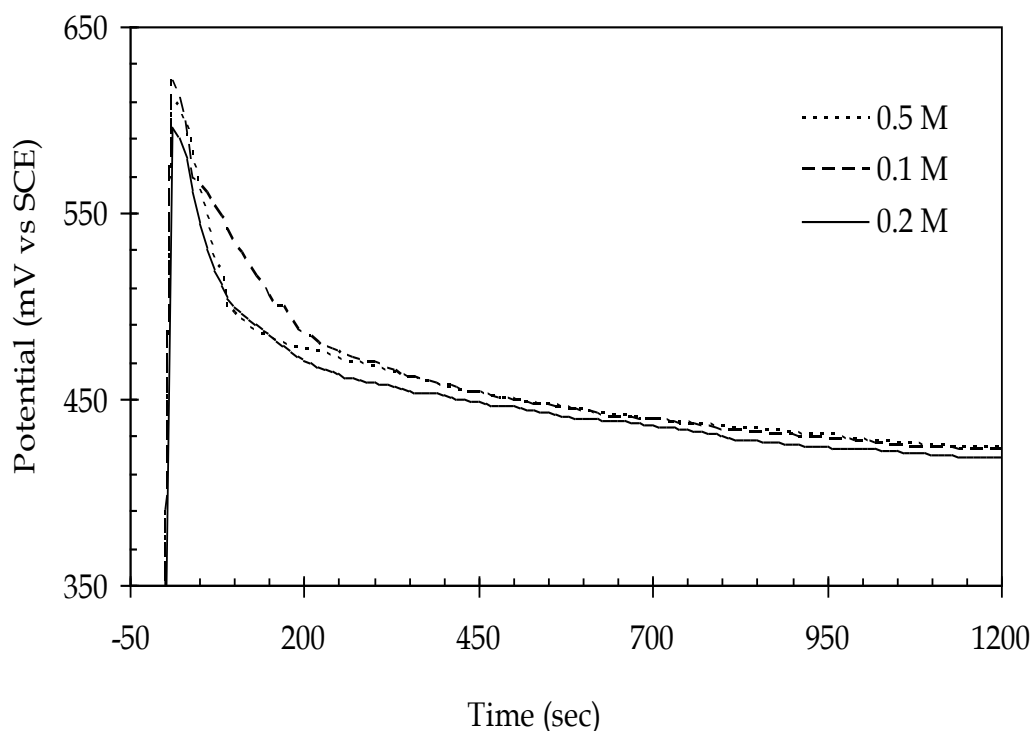
Fig. 3.4.4: Potential-time curves obtained during synthesis of polyaniline film with different Concentrations of aniline.

The synthesized PANI film was thin, uniform, porous and adhesive for 0.2 M concentration of aniline.

Similarly lowest polymerization potential was also recorded for 0.2 M concentration of aniline as compare with other concentrations. This indicates that the synthesized PANI film with 0.2 M concentration of aniline will have higher conductivity as compared to other concentrations. The potential-time curves recorded during synthesis of PANI for different concentrations of supporting electrolyte H_2SO_4 viz 0.5 M, 1 M, and 1.5 M and for 0.2 M concentration of aniline is shown in Fig 3.4.4. The lowest polymerization potential was recorded for 1 M concentration of H_2SO_4 and therefore it will have higher conductivity.

The conductivity of synthesized PANI film with different concentrations of H_2SO_4 is as shown in Table 2. It can be seen from Table 2 that the conductivity of PANI is higher for 1 M concentration of H_2SO_4.

Table 2: The conductivity of PANI films for different concentrations of H_2SO_4 and 0.2 M concentration of aniline.

Sr. No.	Electrolyte (H$_2$SO$_4$) (in Molar)	Conductivity (S/cm)
1	0.5	0.06
2	1	0.73
3	1.5	0.27

Similarly the synthesized PANI film with 1 M concentration of supporting electrolyte was more adhesive, uniform and porous as compared to other concentration of supporting electrolyte. Borole et al [29] have synthesized PANI with 0.1 M concentration of aniline and 1 M concentration of supporting electrolytes using cyclic voltammetry.
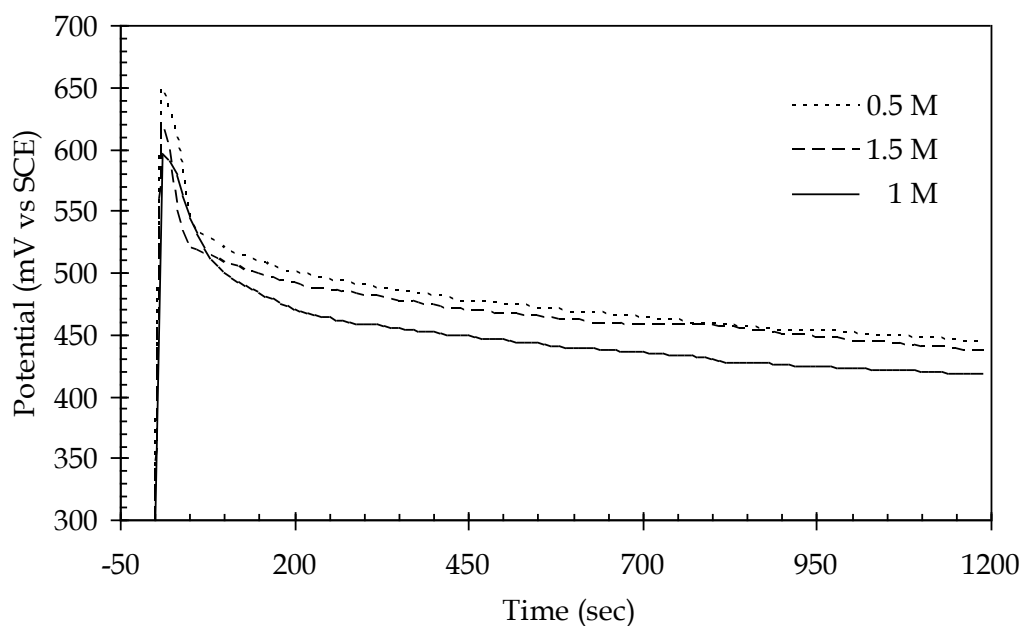

Fig. 3.4.4: Potential-time curves obtained during synthesis of Polyaniline film with different concentrations of supporting electrolyte.

However, in the present investigation we have synthesized PANI with different concentration of aniline and supporting electrolyte and found that 0.2 M concentration of aniline and 1 M concentration of supporting electrolyte have resulted into the PANI

film with higher conductivity and uniform, porous surface morphology as compared with other concentration of monomer and supporting electrolyte.

3.4.3 Influence of Current Density and Ph

The applied current density and pH of the reaction medium also has influence on the conductivity and surface morphology of the PANI film. We have also investigated the influence of current density and pH of the reaction medium on conductivity and surface morphology of the synthesized of PANI film.
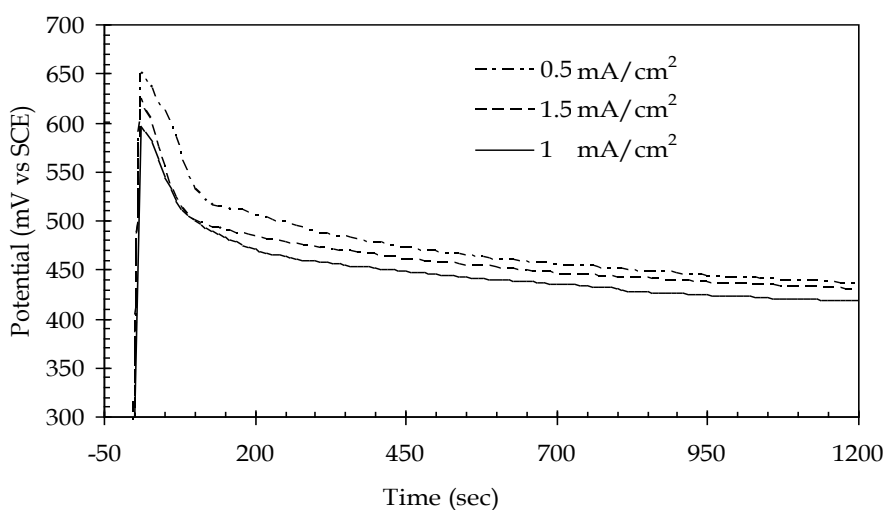
Fig. 3.8: Potential-time curves obtained during synthesis of polyaniline film with different Current densities.

We have synthesized PANI film for various current densities (0.5, 1 and 1.5 mA/cm^2) and various pH (0.5, 1, 1.5). It was observed that the lowest polymerization potential recorded for 1 mA/cm^2 (Fig 3.8) similarly the synthesized PANI film was uniform, porous and adhesive for this current density as compared to other current densities.

The potential – time curve recorded during synthesis of PANI film for different pH of the reaction medium viz. 0.5, 1.0 and 1.5 is shown in Fig 3.9. It was found that the polymerization potential increases with increasing acidic medium of electrolyte. We have recorded lowest polymerization potential for 1.5 pH but for this pH the synthesized PANI film was not uniform and adhesive. However, it was   uniform, porous and adhesive for pH 1.0.
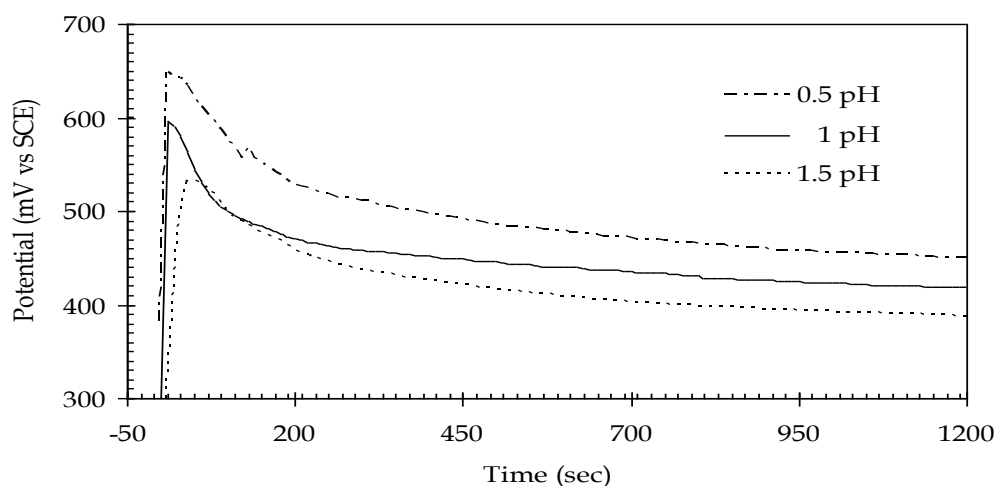
Fig 3.9: Potential-time curves obtained during synthesis of polyaniline film with different pH.

Therefore, the optimized process parameters are 0.2 M concentration of monomer, 1 M concentration of supporting electrolyte H_2SO_4, 1 mA/cm^2 applied current density and 1.0 pH of the electrolyte solution.

3.4. Characterization of the Synthesized PANI Film with Optimized Process Parameters

3. 4.1. Ohmic Behavior of H_2SO_4 Doped PANI Film

The current-voltage current relationship of PANI film with 0.2M concentration of aniline and 1M concentration of H_2SO_4 is as shown in Fig 4.1. It shows ohmic behavior.
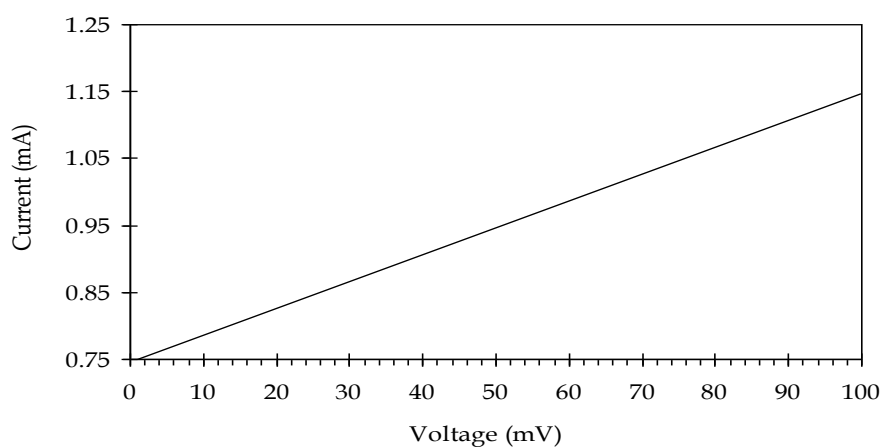

Fig. 4.1: I-V curve of H_2SO_4 doped PANI Film

3. 4.2. Conductivity   of H_2SO_4 doped PANI Film

The relationship between conductivity and temperature of H_2SO_4 doped PANI Film is illustrated in Fig. 4.2. It has been observed that as the temperature increases the conductivity increases. We have recorded higher conductivity for higher current. In order to study whether the conduction is due to the impurities induced by the dopants or due to the electrons transferred to the conduction band we have plotted the graph of log (σ) vs 1/T (Fig 4.3). It can be seen form Fig 4.3 that the conductivity directly proportional to the temperature i.e. as the temperature increases the conductivity of the film also increases. This indicates that for all applied current ((a) 0.9 mA, (b) 1.8 mA and (c) 2.0 mA)) the conduction is purely due to electrons transferred to the conduction band.

The conductivity of the polyaniline film synthesized with 0.2 M of aniline and 1 M of H_2SO_4 shows an excellent conducting behaviour for the temperature ranges from 28-110 ^{0}C. It is reported that the acidic doping of polyaniline results in partial protonation of nitrogen atom   [32-33]. However, in this case the H_2SO_4 doping does not protonate the nitrogen completely in the polymer system.
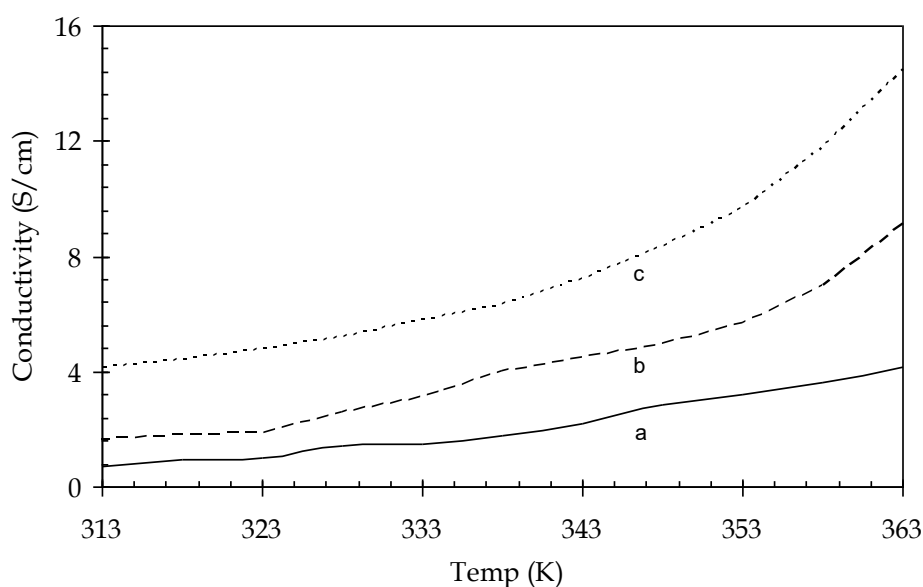

Fig. 4.2: The relationship between conductivity and temperature of H_2SO_4 doped PANI Film ((a) 0.9 mA, (b) 1.8 mA and (c) 2.0 mA).
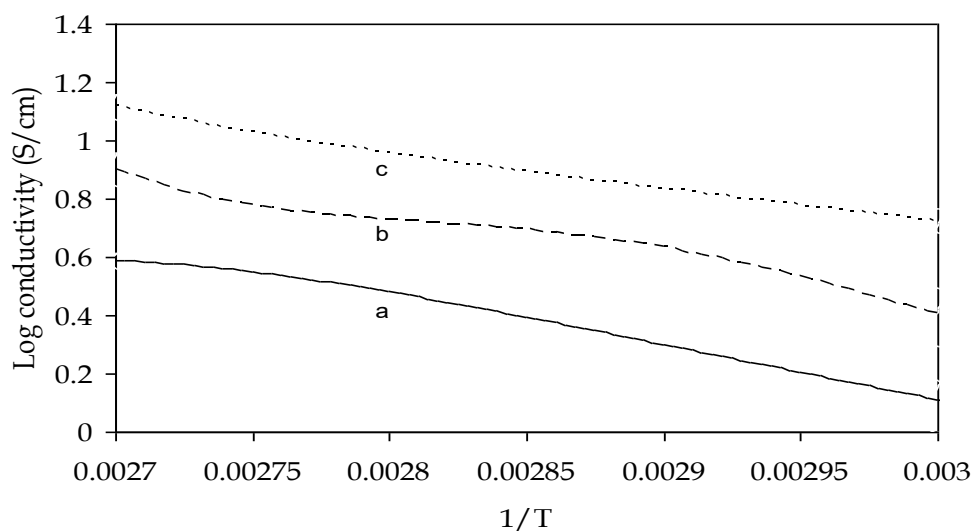
Fig. 4.3: 1/T vs Log σ (s/cm) at different applied current ((a) 0.9 mA, (b) 1.8 mA and (c) 2.0 mA).

3.4.3. UV-Visible Studies

The UV-visible spectrum of synthesized PANI film with optimized process parameters is shown in Fig 4.4. The synthesized PANI film was dissolved in DMSO solvent and its absorption spectrum was recorded. A green colored film showed two absorption peaks, peak at 338 nm is because of π-π^* transition and the peak at 629 nm is due to excitation formation of quinoid ring of polyaniline film prepared in H_2SO_4 medium [34].
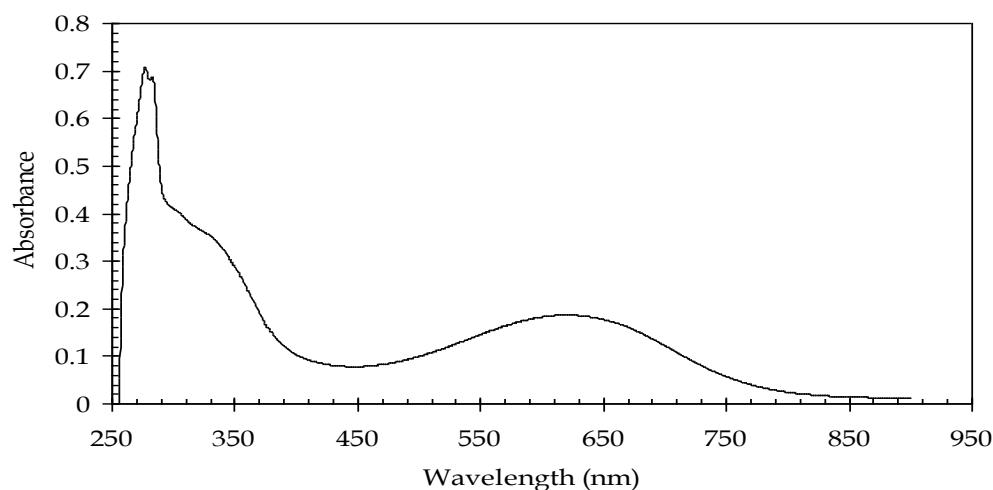

Fig 4.4: Absorption spectra of synthesized polyaniline film with optimized Process Parameters.

3. 4.4. FTIR Studies

The principal transmittance of synthesized PANI film with optimized process parameters observed in the FTIR spectrum is shown in Fig 4.5. The broad peak at 3442.7 cm^{-1} corresponding to -NH$_2$ stretching, peak observed at 2995.2 cm^{-1}due to C-H stretching and C-N stretching is observed at 1311.5 cm^{-1}. Thus, the FTIR spectral results confirm the formation of polyaniline film in H$_2$SO$_4$ medium. This shows good resemblance with the earlier reported work [35].
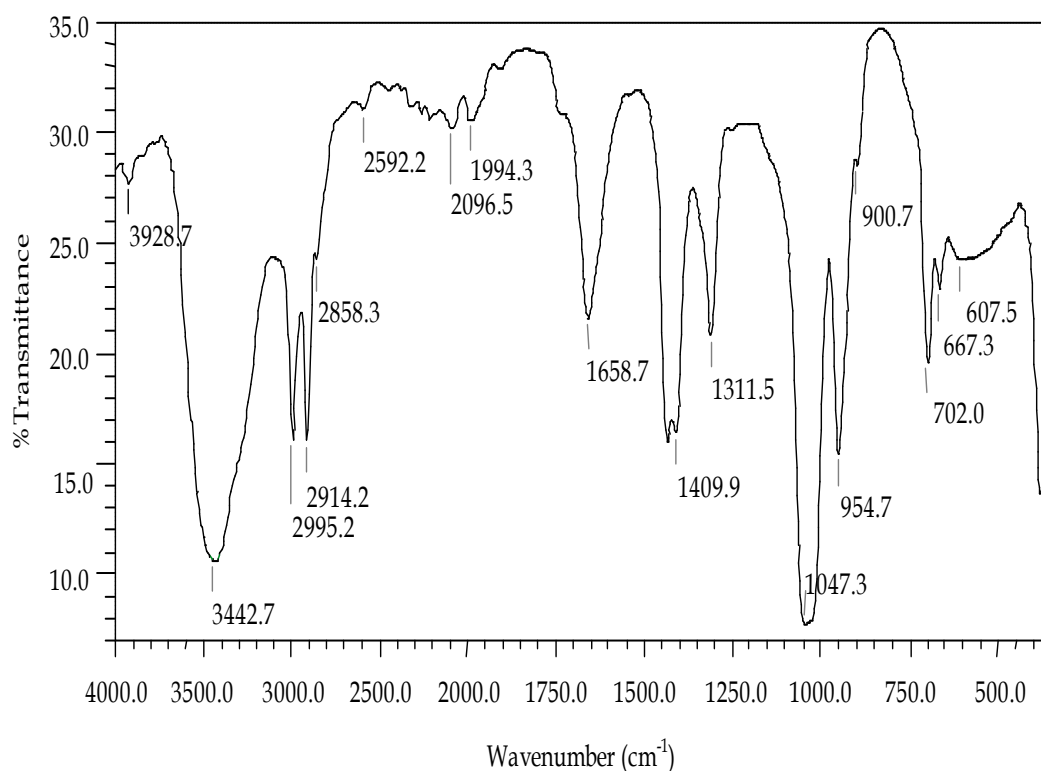

Fig. 4.5: FTIR Spectra of synthesized polyaniline film with optimized process
Parameters**.**

3. 4.5. SEM Studies

The SEM micrograph for synthesized PANI film with optimized process parameters is shown in Fig 4.6. It is   cauliflower like structure, it show very good uniformity and porosity, which is suitable for immobilization of biocomponent [36].
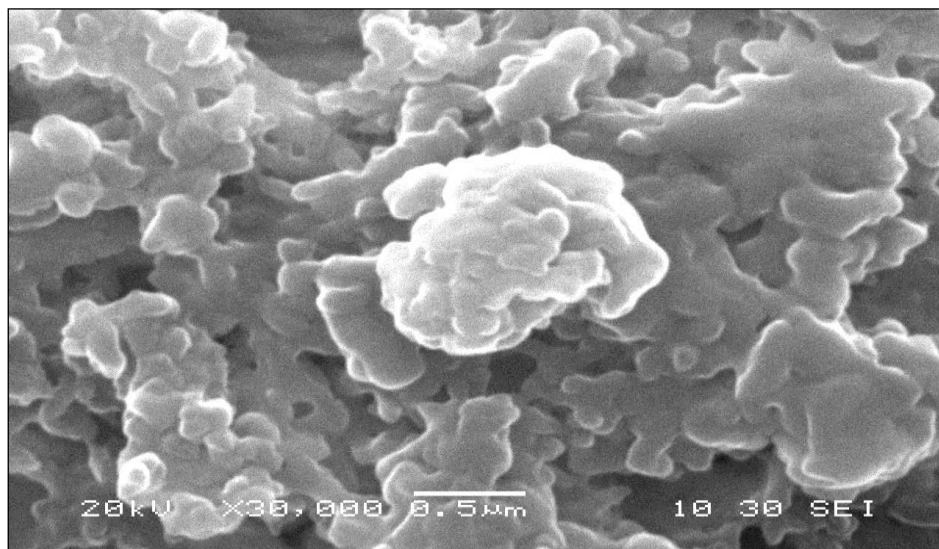
Fig. 4.6: SEM of synthesized polyaniline film with optimized process parameters.

3.5. Preparation of Polyaniline-Polyvinyl Sulphonate (PANI-PVS) Composite Film.

PANI-PVS films were synthesized in an aqueous solution of distilled 0.2 M aniline (S.D. Fine. Chem.) and 0.5 M of polyvinyl sulfonate (Aldrich) using electrochemical deposition method. It was carried out by potentiometric (Galvanostatic) technique at 27 °C in one compartment, three-electrode glass cell. The ITO coated glass plate was used a working electrode, platinum foil as counter electrode and Ag/AgCl was used as reference electrode. The electrolyte solution was prepared in distilled water. The applied current density 1 mA/cm^2 and the 1.0 pH were kept constant during synthesis of composite film. After synthesis the polymer coated electrodes were rinsed thoroughly in distilled water, dried in cold air and then use for subsequent characterization.

3.5.1. Potentiometric Studies of PANI-PVS Composite Film

The chronopotentiogram of the potentiometrically synthesized PANI-PVS composite is shown in Fig.3.5.1.
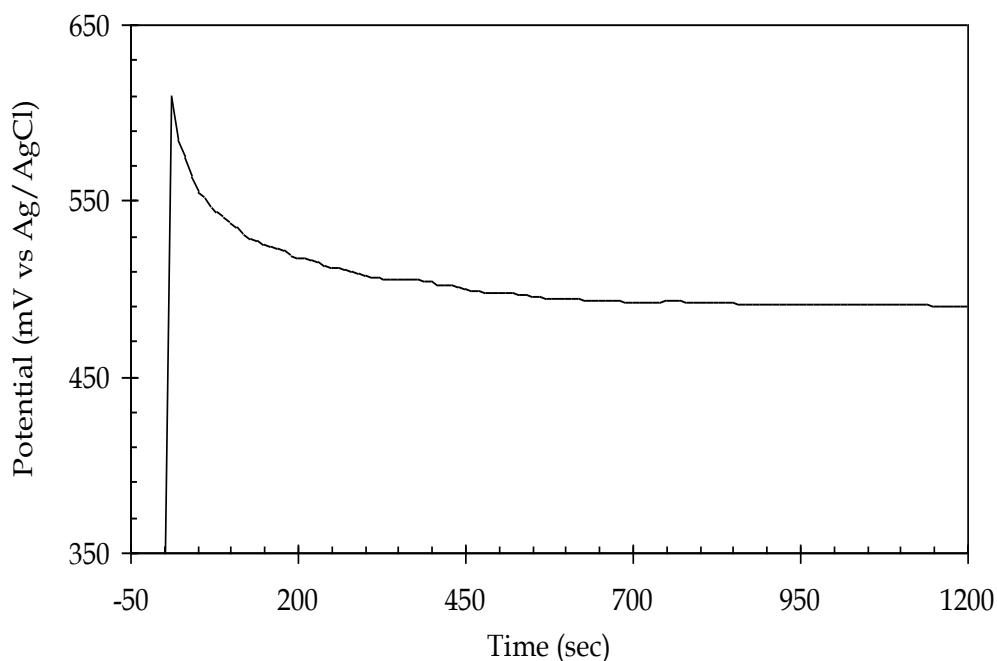
Fig.3. 5.1: Chronopotentiogram of PANI-PVS film synthesized at 1.0 pH, 0.2 M aniline, 0.5 M PVS, 1 mA/cm^2 current density and T=27 °C.

The PANI-PVS film was synthesized on ITO coated glass from 0.2 M concentration of aniline and 0.5 M of PVS with 1 mA/cm^2 current density at 1.0 pH and temp 27 °C. This has resulted conducting PANI-PVS film with uniform and porous surface morphology. The behavior of the potentiometric synthesis overshoot during first few second probably indicates difficult formation of dimmers and oligomers. After this, potential remain constant suggesting that building up of the film proceeds according to the same reaction along the full thickness of the polymer. The electrical conductivity of synthesized composite PANI-PVS film was measured by four probe technique and it was 1.6 S/cm.

3.5.2. UV-Visible Studies of PANI-PVS Composite Film

The UV-visible spectrum of synthesized PANI-PVS film recorded using UV-visible spectrophotometer 1601 is shown in Fig. 3. 5.2. A green colored film showed two absorption peaks for PANI-PVS composite film. The peak at 395 nm is because of π-π^* transition and a broad peak at 794 nm is corresponds to the conducting phase for PANI-PVS.
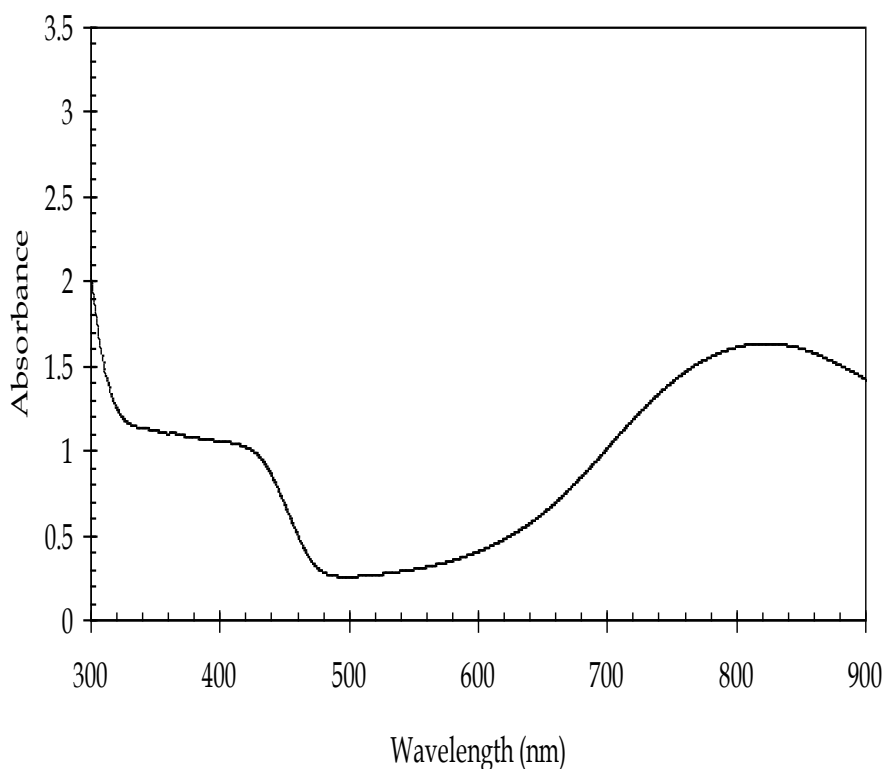
Fig.3.5.2: UV-visible spectra of PANI-PVS film synthesized at 1.0 pH, 0.2 M aniline, 0.5 M PVS, 1 mA/cm^2 current density and T=27 ℃.

3.5.3. FTIR Studies of PANI-PVS Composite Film

The broad peak at 3415.2 cm^{-1} corresponding to NH stretching peak .The peak at 1533 cm^{-1} and 1497 cm^{-1} corresponds to the quinine and benzene ring stretching deformation respectively. The C-N stretching in the quinoid ring is observed at 1378 cm^{-1}, while C-N stretching of a secondary aromatic amine is observed at peak 1038 cm^{-1}. The peak at 1093 and 1099 cm^{-1} corresponds to the C-H in plane bending mode. The C=N stretching of quinine diimine unit is observed at 1565 cm^{-1}. The peak observed at 1035 cm^{-1} and 694.3 cm^{-1} are due to the symmetric stretching of SO$_3^-$ group. Thus, the FTIR spectral results confirm the formation of polyaniline film composite with PVS medium.

The FTIR spectra of synthesized PANI-PVS film were recorded by using Testscan Shimadzu FTIR-8400 series, in the region 2000-2100 cm^{-1} is shown in Fig. 3.5.3.
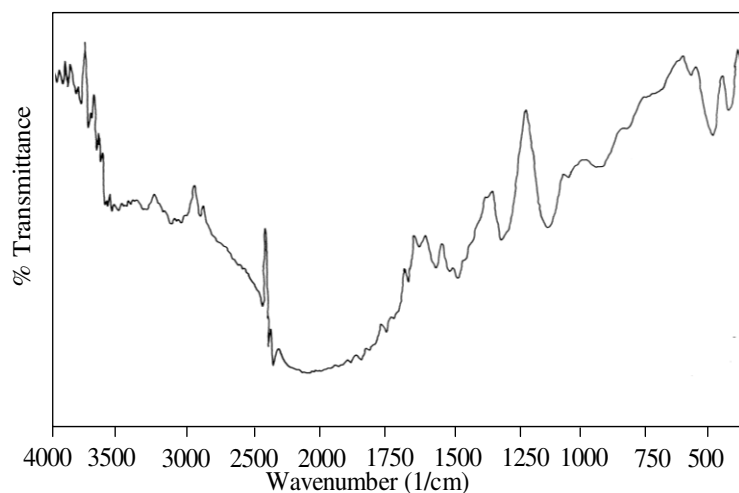
Fig. 3.5.3: FTIR spectra of PANI-PVS film synthesized at 1.0 pH, 0.2 M aniline, 0.5 M PVS, 1 mA/cm^2 current density and T=27 ºC.

3.5.4. SEM Studies of PANI-PVS Composite Film

The scanning electron micrograph of synthesized composite PANI-PVS film is as shown in Fig.3.5.4. The scanning electron micrograph was recorded using JEOL, JSM-6360A SEM machine. It can be seen that the surface morphology is porous, uniform with granular like structure, which is suitable for immobilization of biocomponent.
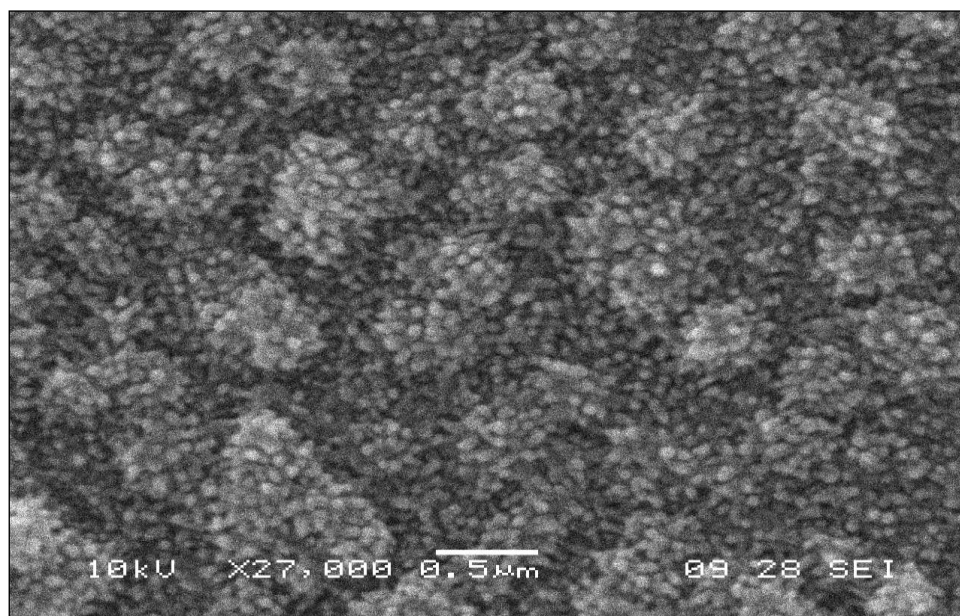

Fig.3.5.4: SEM micrograph of PANI-PVS film synthesized at 1.0 pH, 0.2 M aniline, 0.5 M PVS, 1 mA/cm^2 current density and T=27 ºC.

3.6. CONCLUSIONS

The process has been developed for the aqueous electropolymerization of polyaniline coating on platinum substrates.

1. The present study reveals that the H_2SO_4 is more suitable electrolyte (as compared to KCl, HCl, KNO_3, HNO_3 and $NaNO_3$) for the synthesis of PANI with higher conductivity, adhesive, uniform and porous surface morphology.

2. The concentration 0.2: 1 M of aniline and H_2SO_4 have resulted into the PANI film with higher conductivity, adhesive uniform and porous surface morphology.

3. The applied current density 1 mA/cm^2 and 1.0 pH of the reaction medium have resulted into the PANI film with higher conductivity, adhesive uniform and porous surface morphology.

4. The synthesized PANI- H_2SO_4 film with optimized process parameters is suitable matrix for the development of biosensors.

REFERENCES

1. D C Trivedi and S K Dhawan, J. Mater. Chem. 2 (1992) 1091.

2. D M Big and E J Bradbury, in R B Seymour (ed.), Conductive Polymers, Vol. 15, Plenum, New York, 1981. p. 13.

3. F Trinidal, M C Montemayor and E Falas, J. Electrochem. Soc., 138 (1991) 3186.

4. T Matsunaga, H Daifuku, T Nakajima and T Kawage, Polym. Adv. Technol., 1 (1990) 33.

5. A Kitani, J Yano and K Sasaki, J. Electroanal Chem. 209 (1986) 227.

6. G Gustafsson, Y Cao, G M Treay, F Klaretter, N Colaneri and A J Heeger, Nature 357 (1992) 477.

7. P N Bartlett, B M A Patricia and K L C Sin, Sens. Actuat. 19 (1989) 125.

8. E W Paul, A J Ricco and M S Wrighton, J. Phys. Chem. 89 (1985) 1441.

9. J M Andre and J Delahalle, J. Chem. Rev. 91 (1991) 843.

10. H Letheby, J. Chem. Soc. 15 (1862) 161.

11. E Lang, K G Neoh and L T Tan, Prog. polym. Soc. 23 (1998) 277.

12. D C Trivedi and S K Dhawan. Synth. Met. 38 (1993) 309.

13. A A Karyankin, A K Strakhava and A K Yatsimirsky, J. Electroanal. Chem. 371 (1994) 259.

14. D J Shirale, V K Gade, P D Gaikwad, H J Kharat, K P Kakde, P A Savale, S S Hussaini, N R Dhumane and M D Shirsat, Matter. Lett. 60 (11) (2006) 1407.

15. T Lindfors and A Ivaska, J. Electroanal. Chem. 531 (2002) 43.

16. D J Shirale, A S Bhalerao, H J Kharat, P D Gaikwad, K P Kakde, H J Kharat, P A Savale, V K Gade, S S Hussaini, N R Dhumane, M D Shirsat, in: M D Shirsat(Ed), Microwaves and Optoelectronics, Anshan Tunbridge Wells, UK, 2005, p.455.

17. M Gerard, A Chaubey and B D Malhotra, Biosens. Bioelectron. 17 (2002) 345.

18. J D Nero, D S Galvao and B Laks, Optical Materials 21 (2002) 461.

19. M Trojanowicz, O Gescheke, T Krawczynski vel Krawczck and K Cammann, Sens. Actuator. B 28 (1995) 191.

20. D J Shirale, V K Gade, P D Gaikwad, H J Kharat, K P Kakde, P A Savale, S S Hussaini, N R Dhumane and M D Shirsat, Transations of the SAEST 40 (2005) 128.

21. A Efekhari, Synth. Met. 125 (2002) 295.

22. K Ramanathan, S Annapoorm and B D Malhotra, Sens. Actuat. B21 (1994) 165.

23. P A Savale, D J Shirale, P D Gaikwad, H J Kharat, K P Kakde, H J Kharat, V K Gade and M D Shirsat, in: M D Shirsat (Ed), Microwaves and Optoelectronics, Anshan Tunbridge Wells, UK, 2005, p. 409.

24. J Lei, Z Cai and R C Martin, Synth. Met. 46 (1992) 53.

25. E L Kupila and J Kankare, Synth. Met. 55-57 (1993) 1402.

26. V K Gade, D J Shirale, P D Gaikwad, H J Kharat, K P Kakde, P A Savale and M D Shirsat, in: M D Shirsat (Ed), Microwaves and Optoelectronics, Anshan Tunbridge Wells, UK, 2005, p 459.

27. R Stankovic, O Pavlovic, M Vojnovic and S Jovanovic, Eur. Polym., J. 30 (3) (1994) 385.

28. P D Gaikwad, D J Shirale, V K Gade, H J Kharat, K P Kakde, P A Savale and M D Shirsat, in: M D Shirsat (Ed), Microwaves and Optoelectronics, Anshan Tunbridge Wells, UK, 2005, p 450.

29. D D Borole, U R Kapadi, P P Kumbhar and D G Hundiwale, Mater. Lett., 56 (2002) 685.

30. S J Shaw, Ph.D. Thesis, University of western Sydney, (1994) p.58.

31. P W Atkins (Ed.), Physical Chemistry, Vol. 4, Oxford University Press, Oxford, 1990.

32. A A Karyakin, A K Strakhova, A K Yatsimirsky, J. Electroanal. Chem 371 (1994) 259.

33. W S Huang, B D Humphery and A D MacDiarmid, J Chem Soc Faraday Trans. 1, 82 (1986) 2385.

34. T Abdiryim and Z Xiao-Gang R Jamal, Mater. Chem. Phys. 90 (2004) 367.

35. B Sari, M Talu and F Yildirim, Russian Journal of Electrochemistry, 38 (7) (2002) 707.

36. A F Diaz and J A Logan, J. Electroanal. Chem. 111 (1980) 111.

Chapter - 4

Concluding Remarks
& Future Scope

4.1. CONCLUDING REMARKS

➤ We have successfully synthesized PANI-H_2SO_4, PANI-PVS, polymer membrane by Galvanostatic method using indigenously developed computer controlled Galvanostat for the development of sensors.

➤ In the beginning, we have optimized the process parameters viz. type of supporting electrolytes/dopants, concentrations of monomer and supporting electrolytes/dopants, current density, pH of electrolyte solution etc for the synthesis of PANI membrane and following conclusions have been drawn.

1. The sulfuric acid is an excellent supporting electrolyte for the synthesis of PANI membrane as compared with hydrochloric acid, potassium chloride, sodium nitrate, sodium chloride, potassium nitrate and nitric acid.

2. The concentration ratio of monomer and supporting electrolyte H_2SO_4 (0.2: 1.0 M), the current density 1 mA/cm^2 and 1.0 pH is an excellent combination for the synthesis of PANI film with higher conductivity, uniform and porous surface morphology.

4.2. FUTURE SCOPE

The exiting experimental setup and the synthesized PANI membrane with various dopants and composite dopants can be used for the development of the various sensors for detection of CNT, Gases, Metal oxides, and Neurotransmitters etc. Efforts are also directed to develop mobile equipment for the uniquely designed biomedical Applications.

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Area of Research: Electrochemical Method Chemical sensors, Biosensors sensors, Optical fiber sensors, Bioelectronics. Remote Sensing.

ABOUT THE BOOK

The research and development in the field of sensors have greatly expanded in many ways. Here, we will focus on conjugated polymers-based chemical and biological sensors. The function of a sensor is known to detect events or changes in quantiles and generates a corresponding output, thus providing information on our physical, chemical and biological environment. A chemical sensor consists of a physical transducer and a chemically selective layer. A biosensor contains a biological entity such as enzyme, antibody, bacteria, tissue as a recognition agent. Among the materials used in sensor devices, π conjugated polymers have gained tremendous attention due to their potential of exhibiting collective properties that are very sensitive to minor perturbation compared to small molecules. CPs-based sensors can be divided into various schemes based on the kind of signal change they display in response to an analyte interaction. The changes include electrical conductivity, chemical potential, optical absorption widely used and rapidly expanding method in chemical and biological sensing.

The Book is organized as follows. Firstly, we give an overview of various classes of CPs for chemical and biological sensors. Secondly, we discuss various device structures based on two different transduction principles, i. e. Electrochemical technologies, and in particular those employing structures. Membrane science developed continuously as an interdisciplinary science in which polymers have a central role. With the progress of research works dedicated to conductive polymers, researches on conductive polymers initiated chemical, biological sensors and membrane technology d. Membrane Technology.