1 INTRODUCTION

1.1. Electrochemistry as a way to synthesis polymers

Polymers can be prepared by electrochemical reactions, especially conducting polymers. Electrochemical transformations of non-conducting polymers (e.g. polyphenylene vinylene [1], polymer from monomers acrylamide, acrylonitrile and N, N-methylenebisacrylamide [2]) at a cathode have been carried out sucessfully. There has been rapid development of research in electrochemically synthesized polymers and polymer properties modification. A lot of research on electropolymerization of conducting polymers such as polyaniline, polypyrrole and their composites has been reported [3-31].

The reactions involved in the electropolymerization of conducting and non-conducting polymers are different[32]. Cathode reduction reactions are mainly required for non-conducting polymers and these can lead to direct or indirect transformations of polymers. The direct transformations proceed as a result of electrochemical reduction and subsequent transformations of electroactive macromolecules. The indirect transformations involved the charged nucleophilic molecules obtained by reduction of the solvent electrochemically, e.g. polyethylene terephthalate [32].

Electropolymerization of conducting polymers involves mainly reactions at the anode. Polypyrrole and polyaniline are electrosynthesized from solutions containing their respective monomers at positive (oxidative) potentials relative to Ag/AgCl or Calomel.

The advantages of electropolymerization are:

(i) uniform coatings can be obtained,

(ii) very thin and highly adherent film,

(iii) economical and easy to prepare.

Only a small current is needed to initiate chain growth, which can continue without further passage of current. Reaction mechanisms are varied (can be anionic, cationic or free radical) depending on the monomer type, the solvent and the added electrolyte used[32].

1.2. **Conducting Polymers**

The discovery of conducting polymers brought much initial excitement because of their potential as new materials with valuable applications. The very first kind of conducting polymers appeared with discouraging properties, including insolubility, poor mechanical properties and non-melting. As the development of conducting polymers progresses better understanding of the fundamentals of formation led to a remarkable improvement in such properties [33].

In the 1990s, the field of conducting polymers of interest can be broadly divided into four areas. 37% of all research was carried out in the application area; 33% in properties; 16% in processing and 14% in synthesis [33].

1.2.1. *Applications of conducting polymers*

Much research in this area pertains to new applications. Among the new applications are batteries[34, 35, 36], sensors[37], displays, electrochromic devices [38, 39, 40], solar cell, reference electrode [41] and etc. The production of plastic rechargeable batteries is one of the applications that attract much interest. The high precision reproducible control over doping levels by electrochemical synthesis of conducting polymers lead to polymers, which can reversibly store charge and energy and possess high energy density.

A number of potentially useful conducting polymers have been reported such as polyaniline, polypyrrole, polyether, polyacetylene-polyisoprene [42], poly(N-vinylimidazole) [43] and etc..

The advantages of conducting or semi-conducting polymers lie in their lightweight and ease of preparation. But most of the electrical conducting polymers, which have been described to date, have undesirable characteristics such as insolubility, poor processibility and poor atmospheric stability. For example, polypyrrole is insoluble in common organic solvents and doesn't melt, making it not technologically useful; and polyaniline appeared in powdery form, which is difficult to handle. Soluble conducting polymers can be processed[44, 45] but still only at laboratory scale.

Compositing with other materials is a means of improving the mechanical properties of the conducting films because the original conducting polymers are very brittle. Large polymeric additive are commonly inserted into the conducting polymer matrixes in order to increase the physical strength of the film. For example, polyaniline-poly(methyl methacrylate) blends[12, 13].

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1.3. **Conducting polymers and their composites**

A lot of compositions of conducting polymers with other materials have been investigated [12, 13]. The composite properties result from intrinsic properties of both conducting polymer and the inserted polyelectrolyte. Introducing the polyelectrolyte into a conducting polymer matrix may improve its processability, electrical conductivity, solubility and other mechanical properties [12-31, 41, 46-50].

1.3.1 *Polypyrrole and their composites*

Polypyrrole when incorporated with excess electrolyte possesses a higher conductivity. The results presented (Table 1) showed that the electrolyte and solvent uptake by polypyrrole played a major role in the determination of the ion transportation properties [50].

Soluble polypyrrole has been successfully produced. The use of dodecylbenzene sulphonic acid as dopant and ammonium persulphate as oxidant into polypyrrole matrix makes it soluble in m-cresol and chloroform [45, 51].

Polypyrrole doped with materials containing ion exchange functional groups (e.g. $-SO^-_3$) can be potentially applied in the wastewater treatment generally, or heavy metal removal particularly. One of the material used was polystyrene sulphonic acid (used in this project).

Table 1. Ionic conductivities (μS cm^{-1}) of electrochemically cycled polypyrrole films at 0.3 V in acetonitrile containing Et_4NClO_4 [50].

	σ / μS cm^{-1}			
	[Et_4NClO_4] / mol dm^{-3}			
Film thickness / μm	0.33	0.01	0.033	0.010
0.057		2.0±0.5		
0.11		3.2±0.7		2.5
0.17	5.5	5.5±1.8		
0.23			6.3	0.9
0.29		9.3		
0.34	7.0			5.2
0.43				4.5
0.57	10.0±1.4	9.1±2.8	5.6	
0.89		9.8		

1.3.2. *Polyaniline and their composites*

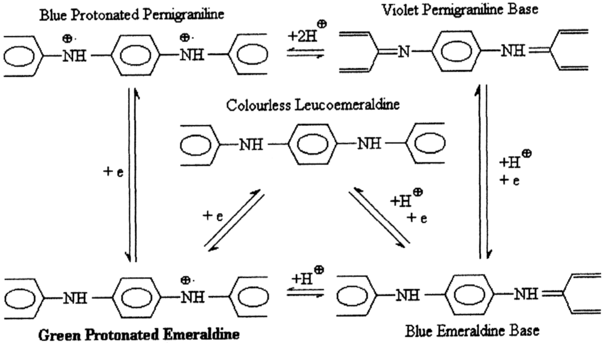
Polyaniline doped with polyvinyl acetate[10] and poly(p-vinylphenol) were found to have better miscibility. Poly(p-vinylphenol) is miscible with a large variety of polymers through hydrogen bonding interactions. Introducing such materials into the polyaniline matrix also helps to improve processability (as plasticizer).

Polyaniline/poly(methyl methacrylate) composites which are produced by electropolymerization had been reported to be flexible, free-standing, homogeneous and electrically conducting [12, 13].

Polyaniline is not soluble in most solvents (except concentrated acids which cause the polymer to break down). Composition of polyaniline with camphor sulphuric acid is soluble in common solvents, e.g. m-cresol. This feature is useful due to the ease of conducting blends preparation, e.g. polyaniline-cellulose acetate composition which is highly transparent and electrically conducting[15].

1.4. Polyaniline

Polyaniline is the most common conducting polymer due to its atmospheric stability and ease of preparation in aqueous environment. The monomer, aniline is a colourless oily liquid which is commonly used in the manufacture of dyes. Polyaniline occurs in a variety of forms with differences in colours and electrical conductivity. Some of them are non-conducting. Polyaniline is reported to have conductivities in the range from 10^{-10} to 10^{3} Scm^{-1} at room temperature [49]. Scheme 1 represents the various forms or states of oxidation of polyaniline and their colours [51-55] :

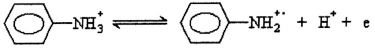


The most important form of polyaniline, protonated emeraldine which is green in colour can be easily obtained by oxidation of polyaniline in dilute acid solutions. High electrical conductivity of emeraldine is due to the presence of cation radicals (equation 1). It is powdery, stable and insoluble in any solvent except concentrated sulfuric acid.

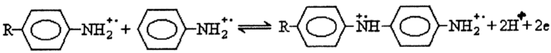
Protonated emeraldine in alkaline medium will convert to blue emeraldine base which is non-conducting and partially soluble in some organic solvents, e.g., N-methylpyrrolidone. It can also be reduced to colourless and non-conducting leucoemeraidine by hydrazine [51]. Under the strong oxidizing conditions (in presence of strong oxidizing agents, e.g., ammonium peroxydisulfate), the blue protonated pernigraniline formed is expected to be conducting. Further treatment with alkali results in formation of violet pernigraniline base[51, 52].

The reactions proposed for formation of polyaniline during oxidation of aniline are [51-56]:

Aniline in acid medium exists mainly as an anilinium cation and it is oxidised to aniline cation radicals which then recombine into benzidine or N-phenyl-p-phenylene-diamine as below:



......(1)



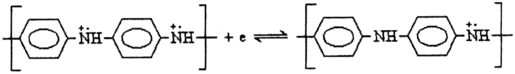
......(2)

R = H or pernigraniline chain

The electron released from aniline in the above reactions are consumed in the reduction of oxidizing agents, e.g., peroxydisulfate to sulfate:

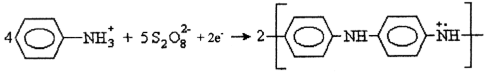
$$S_2O_8^{2-} + 2e \rightleftharpoons 2\,SO_4^{2-} \qquad ......(3)$$

If the oxidizing agent has been totally consumed and aniline is still present, pernigraniline will become oxidant and reduced to emeraldine:



......(4)

Combination of equations (1)-(4):



$$+\ \overset{10}{\cancel{12}}H^{+} + 10\,SO_4^{2-} \qquad ......(5)$$

In reactions (1) and (2), protons are released during oxidations, thus the pH of the solutions decreases at the same time. Colour and acidity changes indicates that polyaniline changes from one form to another.

1.5 Polypyrrole

Polypyrrole is one of the most conveniently prepared conducting polymers due to its stability and capability in forming a free standing conducting film. It can be easily prepared from a variety of electrolytes commonly in aqueous medium. Electropolymerization of pyrrole in aqueous solutions can produce good quality films under certain conditions.

Electropolymerization is a reliable method for polypyrrole synthesis, in which polymerization rates can be controlled precisely. Among the polymerization conditions are the rates of polymerization, temperature, concentration of monomer, ratio of the monomer to the dopant, choice of dopant and also the set-up of the polymerization. Varying the polymerization conditions on the growth of polypyrrole has been shown to have a large impact on the physical properties [46-48, 50], especially to the film thickness, conductivity, conductivity gradient and film elasticity.

The mechanism of charge transport in polypyrrole has not been fully understood because of the disordered structure of the polymer and the fact that the electrical properties exhibit both metallic and semiconducting behaviour [49]. It becomes more complicated if other composites have been introduced into the matrix of polypyrrole.

1.5.1 **Mechanism of polypyrrole formation** [57-61]

The anodic oxidation of pyrrole involves the initial formation of radical cation:-

$$C_4H_4NH\,(aq) \xrightarrow{\text{slow}} C_4H_4NH\,(aq)^{+\cdot} + e^- \qquad \ldots\ldots(1)$$

$$C_4H_4NH\,(aq)^{+\cdot} + C_4H_4NH\,(aq) \xrightarrow{\text{fast}} C_4H_3NH\text{-}C_4H_3NH\,(aq) + 2H^+ + e^- \ldots\ldots(2)$$

Further oxidation of pyrrole dimer to radical cation will then lead to reaction with pyrrole to form trimers and so on. Polypyrrole chains grow continuously by stepwise oxidation followed by reaction with pyrrole units, to form radical cations. Finally the polymer chain loses two protons by the fast electron transfer processes: -

The growth of oligomers in solution:

$$C_4H_3NH(C_4H_2NH)_n(C_4H_3NH)\,(aq) \xrightarrow{\text{slow}} C_4H_3NH(C_4H_2NH)_n(C_4H_3NH)^{\cdot+}\,(aq) + e^- \ldots(3)$$

$$\begin{aligned} &C_4H_3NH(C_4H_2NH)_n(C_4H_3NH)^{\cdot+}\,(aq) \xrightarrow{\text{fast}} C_4H_3NH(C_4H_2NH)_{n+1}(C_4H_3NH)\,(aq) \\ &\qquad + C_4H_4NH\,(aq) \qquad\qquad\qquad\qquad + 2H^+ + e^- \ldots(4) \end{aligned}$$

The oligomer form via above oxidation and reaction with pyrrole unit will further oxidise and react with pyrrole units leads to polypyrrole chains (solid) formation.

The growth of polypyrrole chains in solution:

$$C_4H_3NH(C_4H_2NH)_n(C_4H_3NH)\,(s) \xrightarrow{\text{slow}} C_4H_3NH(C_4H_2NH)_n(C_4H_3NH)^{\cdot+}\,(s) + e^- \;..(5)$$

$$\begin{aligned} &C_4H_3NH(C_4H_2NH)_n(C_4H_3NH)^{\cdot+}\,(s) \xrightarrow{\text{fast}} C_4H_3NH(C_4H_2NH)_{n+1}(C_4H_3NH)\,(s) \\ &\qquad + C_4H_4NH\,(s) \qquad\qquad\qquad\qquad + 2H^+ + e^- \quad \ldots..(6) \end{aligned}$$

1.6 Electrical properties of polymeric materials

Most polymeric materials are insulators due to their low electrical conductivities. The mechanism of electrical transportation in these materials is believed to involve free electrons but this is not well understood [62]. Understanding the mechanism of conductivity for a material, especially polymeric material, is very important in order to determine its use in certain applications. For example, materials for use as insulator require high electrical and thermal resistivity. On the other hand, materials for use as conductors must have very high conductivities for optimum performance.

Polyethylene with electrical conductivity in the range 10^{-13} - 10^{-17} Sm^{-1}, and polytetrafluoroethylene less than 10^{-16} Sm^{-1} are good insulators. Conducting polymers, are polymeric materials which possess high electrical conductivity. Conductivities of 1.5×10^{7} Sm^{-1}, which is very near to conductivity of copper, have been achieved [66, 67].

The essential feature of undoped conducting polymers is the existence of an extended π-conjugated system which was formed by the overlap of carbon p_z orbitals [50]. As semiconductors, conducting polymers doped with appropriate impurities can be made either p-type (oxidative doping or holes) or n-type (reductive-doping or free electron) depending on dopant used [50, 65]. The mechanism in which these large quantities of holes and free electrons are created in conducting polymers is complex and unclear.

The mechanism of electrical conduction in conducting polymers also involved the new concepts of polarons, bipolarons and their lattice structures. The studies in spectroscopy, especially Raman Spectroscopy by some researcher is to identify those polarons and bipolarons in conducting polymers [66, 67].

1.7. **Cyclic Voltammetry to characterize electropolymerization processes.**

Cyclic Voltammetry is a dynamic electrochemical method for characterizing redox reactions or to study the electrochemical behavior of species or ions at the electrode surface. It has been extensively used in the study of electropolymerization process, especially for conducting polymers [12, 68-77].

Qualitatively, the Cyclic Voltammogram gives a measure of the electroactivity of materials on the working electrode. For example the effect of thermal treatment to the electroactivity of polyaniline film had been investigated using Cyclic Voltammetry [68]. The amount of polymer coated on working electrode can be predicted by calculating the area (charge) under certain peak in the Cyclic Voltammogram while the rate of electropolymerization is related indirectly to the growth of peaks [12].

1.8. Conductivity Measurement by Method of Four-point Probe [78-82]

The "four -point Probe" method is the most convenient tool for the measurement of resistivity or conductivity for thin films. It was originally developed for measuring semiconductors, but has been also used to measure conductivity of conducting polymers[12, 14, 42, 43, 46-48, 83-85]. The "four-point probe" method requires some correction factors in resistivity measurements of rectangular and circular samples. According to Smits [84] the total voltage for the two outer points is given by:

$$V = \rho_s I \frac{1}{C\left(\frac{a}{d};\frac{d}{s}\right)}$$

$$\rho_s = \frac{V}{I} C\left(\frac{a}{d};\frac{d}{s}\right)$$

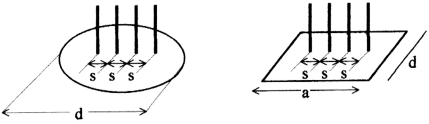


Fig. 1.1 Arrangement of four probes on circular and rectangular samples

Where s is the distance between probes, d is the diameter for the circular films and ρ_s is the resistivity of the surface. For rectangular samples, the dimension is given by a and d with distance between probes s, as shown in Figure 1.1. The values of Correction Factor C for both types of samples are given in Table 2.

Table 2 - Correction factor C for the measurement of sheet resistivities with the four-point probe [78]

	C				
	circle		rectangle		
d/s		a/d = 1	a/d = 2	a/d = 3	a/d ≥ 4
1.0				0.9988	0.9991
1.25				1.2467	1.2215
1.5			1.4788	1.4893	1.4893
1.75			1.7196	1.7238	1.7238
2.0			1.9454	1.9475	1.9175
2.5			2.3532	2.3541	2.3511
3.0	2.2662	2.4575	2.7000	2.7005	2.7005
4.0	2.9280	3.1137	3.2216	3.2248	3.2248
5.0	3.3625	3.5008	3.5749	3.5750	3.5750
7.5	3.9273	4.0095	4.0361	4.0362	4.0362
10.0	4.1716	4.2209	4.2357	4.2357	4.2357
15.0	4.3646	4.3882	4.3947	4.3947	4.3947
20.0	4.4364	4.4516	4.4553	4.4553	4.4553
40.0	4.5076	4.5120	4.5129	4.5129	4.5129
∞	4.5324	4.5324	4.5324	4.5325	4.5324

By using the "four-point probe" method, the body or bulk resistivity of thin film can be obtained with the following relation [78]:

$$\text{Bulk resistivity} = \rho = \rho_s \, w$$

where ρ_s is the surface resistivity of the film with thickness w.

Fig. 1.2 Measurement of bulk resistivity by "four-point probe" method

$$\rho = \rho_s \, . \, w = (V/I) \, . \, w \, . \, \pi/(\ln 2) \, . \, F[\, w/s \,]$$

Table 3 - Correction factor F for the measurement of bulk resistivities with the four-point probe [78]

w/s	**F[w/s]**
0.4	0.9995
0.5	0.9974
0.5555	0.9948
0.6250	0.9898
0.7146	0.9798
0.8333	0.9600
1.0	0.9214
1.1111	0.8907
1.25	0.8490
1.4286	0.7938
1.6666	0.7225
2.0	0.6335

1.9. **Wastewater Treatment**

Chemical pollutants in wastewaters can be broadly categorized into organic and inorganic compounds. Most organic pollutants can be removed by biological or thermal oxidation, which converts them to carbon dioxide, water and other small compounds. Unfortunately, inorganic pollutants cannot be removed in the same way [86]. Current physico-chemical methods for treating toxic inorganic contaminant involve either dispersion into the environment, conversion into another physical form, e.g. sludge, or recycling them into useful products.

The effluents from electroplating, electrorefining and electrowinning industries commonly contain very high concentrations of heavy metals like copper, lead, zinc, chromium, nickel arsenic and mercury. Table 4 shows typical metal concentrations in such wastewaters.

Table 4: Metal Concentration in Industrial Wastewater [87, 88].

	Concentration , mg/L		
Metal	Low	Typical	High
Arsenic	0.5	10	1,000
Cadmium	1.0	25	5,000
Chromium	1.0	50	50,000
Copper	1.0	25	7,500
Iron	5.0	50	5,000
Lead	0.5	10	900
Mercury	0.005	1.0	2,000
Nickel	5.0	50	900
Zinc	5.0	50	3,000

There are several well known techniques for heavy metals removal from wastewater, such as ion-exchange, precipitation-coprecipitation, and electrowinning [86].

1.10. **Ion-exchange**

The ion-exchanging process is not a chemical reaction. It is simply a rearrangement of existing species in the system to achieve the highest stability. The following equations represent the ion-exchanging process:

for cation exchanger,

$$A^-X^+ \quad + \quad Y^+ \quad = \quad A^-Y^+ \quad + \quad X^+$$

(solid) (solution) (solid) (solution)

for anion exchanger,

$$A^+X^- \quad + \quad Y^- \quad = \quad A^+Y^- \quad + \quad X^-$$

(solid) (solution) (solid) (solution)

Cation exchangers possess negatively fixed charges and positively charged counter ions. The reverse situation is found in the anion exchangers. The counter ions can be freely moved within the resin matrix and will be replaced by other ions from solution. This is the "ion-exchanging" process.

There are many types of commercial ion exchangers available in the market. For example, Zeolite (Aluminosilicate type exchanger); Dowex 50, Amberlite IR-120 (organic, sulphonic acid exchanger). Polystyrene sulphonic acid exchanger resin is so far the most commonly used cation exchanger because it is stable in strong acid or base solutions and also thermally stable up to 120°C.

The problem for most existing resins is irreversibility of exchanging processes and the associated loss of exchange capacity[86].

Conducting polymers are new materials considered for making new types of electrochemically reversible ion-exchanger. For example, polypyrrole, when incorporated with polystyrene sulphonate, was successfully established for ion-exchanging purposes [89]. The application is slightly different from that of normal ion-exchangers. Due to the electrical conductivity of conducting polymer, the ion-exchanging processes could be enhanced by an applied electric field. Metal deposition and cation exchanging can both occur at the same time. Basically, the idea is to apply a negative potential to attract cation of heavy metals to the surface of conducting polymer and exchange with H^+ from sulphonate groups. After that, the film will be transferred to a smaller volume of solution and the metal ions released by reversing the potential (positive).