TITLE

STABILIZATION OF POLYANILINE FILMS BY SURFACE ATTACHMENT OF OXIDIZABLE SUBSTRATES

By

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A THESIS SUBMITTED IN PARTIAL FULFILMENT FOR THE DEGREE OF MASTER OF SCIENCE OF THE UNIVERSITY OF NAIROBI

DECLARATION

This is my original work and it has not been presented in any other University.

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DEDICATION

I dedicate this piece of work to the unborn for they, have no choice.

ABSTRACT

Cyclic Voltammetry was used to study the Electrochemical properties of P-Aminophenol on a Polyaniline modified carbon electrode surface. The resilts reveal reversible redox waves. The quinone derivatives formed frop P-Aminophenol(PAP) oxidation seem to depress the rate of degradation of Polyaniline at positive potentials.

The electrochemical properties of Phenol on a polyaniline modified electrode were also investigated. The results showed that phenol also stabilises the polyaniline film at positive potentials above 0.70 V (SCE). The effect of solution pH on the rate of degradation of the polyaniline film was also investigated. It was observed that lowering of the solution PH slows down to some extent the rate of degradation of the polyaniline film. From the degradation data an expression for calculating the pK of the polyanilne film was derived using Kinetics.

Cyclic Voltammetric analysis of the degradation of metal modified polyaniline show that Lead deposition in polyaniline suppresses the latter's electrochemical degradation at positive potentials above 0.70 V (SCE). Tin modified polyaniline appears to show improved conductivity. Modification of polyaniline by deposition of silver does not result in a substantial change in the polyaniline electrochemical characteristics.

Cyclic Voltammetry will be used as a diagnostic tool to assess film behavior in different environments.

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1.0.0 SURFACE MODIFIED ELECTRODES.

1.1.0 INTRODUCTION

The term surface modified electrode was first used in 1975 by Murray and Co-workers [1] to describe electrodes that had foreign molecules deliberately immobilised on their surfaces by adsorption as well as chemical or covalent bonding. This introduction will give a historical development, the types of modification methods that have been used, and the results obtained in their applications. Also future potential applications will be discussed.

Among the very first to study in detail surface modified electrodes were Lane and Hubbard [2,3] who took advantage of the strong adsorption of olefinic compounds on platinum and formed coated electrodes by simply soaking the electrode in a solution of the olefin. Subsequent measurement of the surface coverage showed that there was loss of p-bonds and formation of Pt-C s-bonds.

Optically active amino acids were attached to a graphite surface by Miller and co-workers . In doing this a standard procedure used in organic chemistry was employed to derivatise carboxylic acids. Surface groups were then formed on the graphite surface by air oxidation, followed by treatment with $SOCl_2$

to form acid chlorides. These were then reacted with S-(-)-phenylalanine methylester to form a modified electrode that was visually and electrochemically distinguishable from an untreated electrode. This electrode was referred to as "achiral" electrode and could be used to produce optically active alcohols as opposed to the case of an unmodified electrode which gave a racemic mixture[2]

Other early work on surface modified electrodes was performed by Murray and Co-workers[1] who attached hydrolysis sensitive trialkoxy or trichloro silanes to a SnO_2 electrode by reaction with surface hydroxy groups. They were also the first to use X-ray photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis(ESCA) to study the modified surface. The purpose of the ESCA study was two fold, firstly to confirm the presence of a Si-O-Si bond and secondly, to confirm the presence of a chemically modified surface. By observing the effects of changing the pH of the electrolytic solution, it was found that the electrically insulating silane layer was extremely stable and able to influence the double layer charging currents of the electrode. Loss of reversibility was observed with some species due to a decrease in effective electrode area by the presence of a surface silane layer. It was also shown that further reactions with the surface bound layer could be possible by complexing Cr^{2+} from solution to a pyridino silane layer on the surface.

1.2.0 GENERAL METHODS OF PREPARATION.

Three main methods used in the immobilization of reagents on to electrode surfaces are, adsorption, salinization and surface group reactions with graphite. In addition other techniques have been developed or adapted from other fields to allow the making of useful modified electrodes.

1.2.1 SALINIZATION

The modification of surfaces with different types of silane compounds was first demonstrated by Murray and Co-workers[1] who exploited the sensitivity of silanes to water. The trichloro or trialkoxy silanes are attached to the electrode material by two to three bonds by hydroxy groups formed by the action of atmospheric air or concentrated sodium hydroxide on surface oxides[5-7]. Other work,[8] has shown that an average of two surface bonds are formed with monolayers only formed under anhydrous conditions. The presence of water results in multilayers caused by polymerisation. At the same time it was observed that multilayers though much more difficult to form gave nearly ideal cyclic voltammograms than mono-layers. This is most probably due to an increased flexibility of the two dimensional layers.

Successful salinizations have been carried out on SnO_2 [1,5,6], TiO_2[6,9,10], Pt/PtO[6,8,11] Carbon[12,13] RuO_2[7,11,14] Au,[15] Si[16,17] and Ge[18] semiconductor surfaces. Pretreatment with sodium hydroxide has only been done to maximise surface hydroxy groups, but not as a necessity for coupling reactions

1.2.2 ADSORPTION

This is an important preparation method though not as widely used as salinization. It can be activated either by application of an electrodic potential (electrosorption) or by simply soaking the electrode in the species of interest. The strength of adsorption depends on the type of compound being adsorbed. For example, the adsorption of organic compounds on graphite depends on the number of aromatic rings[19]. Other reagents are adsorbed by electro-sorption, a process whereby they are adsorbed only after being electrochemically reduced or oxidised if a potential exists on the electrode.

1.2.3 POLYMER COATINGS

Polymers are coated on to electrodes by adsorption techniques. The electrode material most commonly used is platinum[20,21], but recently SnO_2[22] and carbon[23] have increasingly gained precedence. Stable surfaces have been produced by electrochemical anodic deposition[24] where the oxidised form of the polymer electrosorbs on the electrode.

1.2.4 CARBON SURFACE REACTIONS

Miller and Co-workers made the first successful modification by treating surface carboxylic acid groups generated by air oxidation at 160°) with $SOCL_2$, to form easily derivatized acid chlorides. This is the most common route now used for the modification of electrodes [25,26,27,28,29,30,31.], although direct derivatisation of the acids[25,32,33,] using dicyclohexylcarbodi-imide (DCC) as a dehydrating agent[34] has also been successful. Stable surface modified electrodes have been made by treating the acid groups with amine containing compounds to form amide bonds. Coupling with surface quinone structures[35] and surface hydroxyls[36,37] has also given stable modified electrodes.

Mazur[38] reasoning that vacuum pyrolysis of carbon surface oxides should create reaction sites, demonstrated coupling of olefins to oxide free carbon which then undergoes reaction with the p-bond of acrylyl chloride to form an immobilised acid chloride group. Oxide free surfaces have also been generated by mechanical abrasion[39] of a glassy carbon electrode under a nitrogen atmosphere, and radio frequency argon plasma treatments[40]. This introduces new functional groups to an otherwise non-functional electrode hence, opening up more modification routes.

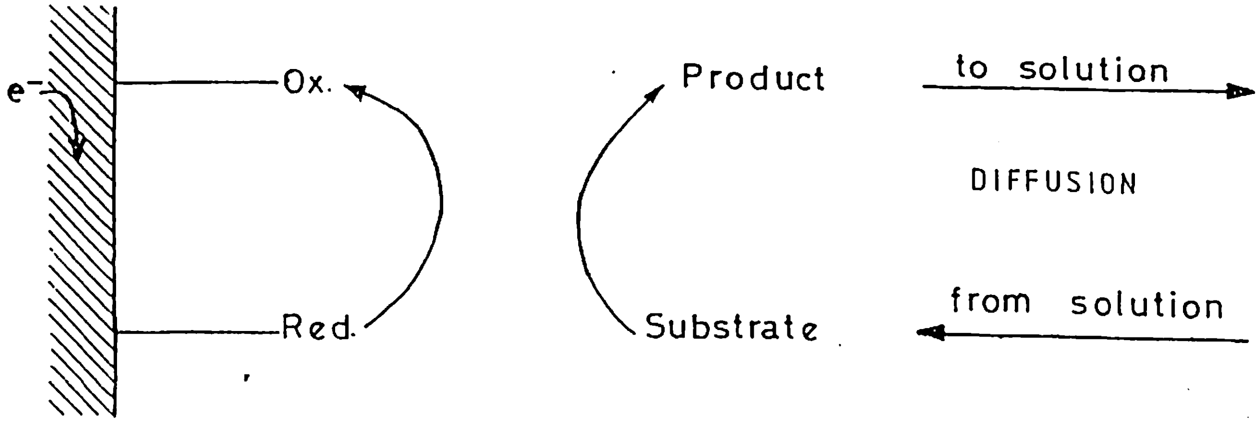
1.3.0 THE STRUCTURE OF THE SURFACE LAYER.

The study of the surface layer has focussed on three areas the bonding,the orientation and structure, and the thickness of the layer. Various electro-analytical techniques such as ESCA, Auger, Raman, and Inelastic Tunnelling Spectroscopy, have been used to probe the types and number of bonds present in a modified layer.

Trichloro or Trialkoxy silanes when used give a possible maximum of three Si-O-M (M=metal) bonds in the modification process. One major problem encountered is to determine how many surface bonds are formed in the modification process. Recent studies by ESCA[6],IETS[7] and Raman[5], have indicated that an average of two surface bonds are present. This was because the spectra contained peaks corresponding to unreacted alkoxy or chloro groups. It was then this unreacted groups that apparently reacted with 3,5-dinitrobenzoyl chloride meant to derivatise the surface silane[29], that produced voltammetric waves that were not 'cleanly' resolved as those produced by an electrode that eliminated the possibility of unreacted groups. This was made possible by using 3,5-dinitrobezoic acid by the DCC procedure[34]. ESCA has also been useful in the study of reaction Scheme 1 to graphite electrodes and establish the connection between graphitic edges and reactive carboxylic acid sites[29]. It has been shown by XPS that tetra(aminophenyl) porphyrins form on the average of two surface amide bonds[30]

Kuwana and CO-workers[78] reported on the surface coverage of the modifying layer. They estimated the Silane layer thickness on SnO_2 to be 2.4nm by use of argon sputtering with Auger spectroscopy by determining the depth at which the spectrum of the surface showed a clean Sn:O peak ratio. The coverage calculated for ethylenediamino silane surface on different electrodes was found to be in the range of 2-8 $X10^{-10}$mol /cm.This was done by White and Murray[43], who used fluorescent measurements of a cleaved surface species together with ESCA spectra. Values obtained agreed substantiantially to those calculated from ESCA, electrochemical determinations, and molecular models[1,6,12,14].

Pyrolytic graphite has shown very interesting results particularly because of the existence of two surface layers, the basal and edge plane surfaces. Studies have shown that covalent bonding primarily occurs at the plane edge[25,28] presumably because the plane edges contain most of the oxygen functions which react with the modifying species. Adsorption occurred on both surfaces [25] although smaller and cleaner backgrounds have been reported with basal planes[28]



Scheme I: Coupling of carboxylic acid functional groups on edge planes with amines

Raman spectroscopy has increasingly gained momentum as a tool for the study of modified surfaces e.g. it has been shown that in the adsorption of pyridines on silver[43,44], and platinum[44],the orientation of the surface adsorbed species depends on the electrode. Pyridine at more positive potentials was adsorbed in a parallel position to the electrode as opposed to the normal head on adsorption at lower potentials.

1.4.0 APPLICATIONS OF SURFACE MODIFIED ELECTRODES

The applications of surface modified electrodes can easily be divided into five categories as discussed below.

1.4.1 CATALYSIS

Modified electrodes have been used to catalyse different types of electrochemical reactions in solution. An obvious advantage is that the catalytic property is retained when the compound is immobilised. Electrocatalytic reactions reported so far include ascorbic acid oxidation by attached benzidine[45], $NADH^+$ oxidation by 3,4-dihydroxybenzyl amine[46],and O_2 reduction, which may find practical use in fuel cells, has been achieved by tetra-(-p-amino)porphyrin[20,47].

1.4.2 PHOTOELECTRODES

The quest for a renewable source of energy, and the possibility of harnessing solar energy has made the use of modified electrodes as photoelectrodes,a fast growing area that is being researched.

A photoelectrode can only respond to visible light if it only becomes passivated during irradiation in aqueous media. Electrodes that are more sensitive to UV wavelengths such as TiO_2 and SiO_2 are not useful as the UV wavelengths do not easily penetrate the earth atmosphere. Electrodes can be sensitized to visible light by immersing them in a solution of a highly coloured dye. An obvious extension of this would be to physically electrosorb the dye on the electrode surface.

This area has been thoroughly studied by Fujihua and Co-workers who immobilised the dye rhodamine B on the surface of a SnO_2 electrode[10,48,49],by two methods In the first method the electrodes was first salinized with amino silane and then the dye was attached using the amidization reaction[10].And in the second method the dye was attached by direct coupling with surface hydroxy groups [38] using the DCC procedure[11].

Hawn and Armstrong [50] dye sensitized SnO_2 electrode with erythrosin by electrosorption of the oxidised dye by silane linkages using amino and thiol terminal functional groups and direct coupling with surface hydroxy groups. Other workers include Wrighton and Co-workers[15,16], who made photoelectrodes with longer lives, by simply attaching a ferro silane to n-type silicon and germanium semiconductor electrodes that are normally passivated when photoanodized in aqueous solution. Similar results were obtained by Finklea and Murray[51] when they attached silanes to TiO_2 electrodes. These humble beginnings suggest a first step in the application of surface modified electrodes as photoelectrodes and most predictably this will be one of the hottest areas of research in a few years time.

1.4.3 ANALYTICAL APPLICATIONS

Surface modified electrodes have found much use in analytical chemistry. Lane and Hubbard[52] used surface modified electrodes to study the concentration of catecholamines in solution by taking advantage of the strong adsorption of I^- on platinum which prevented the passivation of the electrode. They also used the same electrode to observe the conversion of Pt^{II}/Pt^{IV} complexes in a non aqueous solvent[53]. The adsorbed I^- served to prevent solvent adsorption onto the electrode. Biological molecules such as proteins have also been used to modify electrodes. Weetal and Detal[54], developed a method that utilised cyanogen bromide for immobilization. Yamamoto and Co-workers used this method to modify titanium electrodes with antibodies and antigens, thus paving way for the sensitive detection of biologically active substances. Cheek and Nelson[55] demonstrated the use of surface modified electrodes in the measurement of picomolar concentrations. They were able to measure Ag^+ concentrations of 10^{-6} M by use of a carbon paste electrode amidized with diethylenetriamine. There are many possible analytical applications and recognition and investigation of these have only just began.

1.4.4 ELECTROCHEMICAL SYNTHESIS

One of the very first electrochemical synthesis by a surface modified electrode reported was the synthesis of optically active alcohols by an electrode which had been modified by attachment of an optically active amino acid[4]. In a similar way optically active sulphoxides from sulphides have been prepared on salinized SnO_2 and DSA(a mixture of Ta and Ir oxides) electrodes by the attachment of (-)-camphoric anhydride.

1.4.5 STUDY OF IMMOBILISED MOLECULES

Surface modified electrode have been used in the study of the electrochemical properties of molecules by making a comparison between solution and surface studies. Sharpe[56] studied the electrical activity of two isomers, 1-amino and 2-amino-9,10-anthraquinone. He observed,that only the former isomer exhibited electrical activity when immobilised, while both exhibit redox behaviour in solution. He attributed this difference to orientation which determines the efficiency of electron transfer.

Mechanistic studies have also been carried out by use of a surface modified electrode. Lenhard and Murray[8] demonstrated that the decay of ferricinium state of ferrocenylphenyl acetic acid was first order in solution but appeared to follow second order kinetics when immersed in platinum in acetonitrile solution.

1.5.0 CONDUCTING POLYMERS

A key property of most polymers, which distinguishes them from most metals is their inability to conduct electricity, thus their use as insulating materials in electrical wires. It is therefore a general consensus that polymers and electrical conductivity are mutually exclusive. However over the last two decades a new class of organic polymers has emerged with the remarkable ability to conduct electricity. These conductive polymers have been classed as synthetic metals and have found great use as rechargeable batteries, electronic capacitors and smart windows that absorb sunlight in summer. Most however remain laboratory curiosities, but with a tremendous potential for future Scientific and Technological development.

The emergence of conducting polymers as a new class of electronic materials has attracted considerable attention which has generated entirely new scientific concepts as well as potential for new technology. Conducting polymers are highly anisotropic quasi-one dimensional structures which makes them different from conventional inorganic semiconductors in two aspects,

(i) The chain like structure leads to strong coupling of the electronic states to conformational excitations or solitons peculiar to a one dimensional system.

(ii) The diffusion of dopant molecules into the structure is allowed by the relatively weak interchain binding while the strong intrachain C-C bonds maintain the integrity of the polymer.

The most extensively studied of these conductive polymers are Poly-(acetylene, aniline, pyrrole, thiophene, phenylenesulphide and phenylenevinylene). Of these polyaniline was the fist to be prepared when in 1862 H. Letherby of the college of the London Hosipital anodically oxidized aniline in sulphuric acid. A major obstacle to the rapid development of conductive polymers is the lack of understanding of how electrical current passes through them. All conducting polymers have one thing in common; they contain extended p-conjugated systems with single and double bonds alternating along the polymer chain. Also conducting polymers can be divided into two groups i.e. those with degenerate states and those without degenerate states. The mechanism of polymer conductivity can therefore be explained by considering these two cases separately.

1.5.1 POLYMERS WITH NON DEGENERATE STATES

The simple band theory has failed to explain the conductivity of polymers. The principle behind band theory is the overlap of atomic orbitals of one atom with similar orbitals of another to produce molecular orbitals. When the energies of these molecular orbitals are closely spaced together they form a continuous energy band. The energy spacing between the highest occupied and the lowest unoccupied bands is called the band gap, with the highest occupied called the valence band and the lowest unoccupied the conduction band (see Figure 1).

If the bands are filled or empty no conduction occurs. However if the band gap is narrow at room temperature thermal excitation of the valence band electrons to the conduction band gives rise to conductivity. This is what happens with classical semiconductors. For non conductors, thermal excitation at room temperature is insufficient to excite electrons across the band gap hence they are insulators.

This simple theory fails to explain the conductivity of conductive polymers as they lack a partially empty or a partially filled band. The theory also fails to explain why the charge carriers, usually electrons or holes in polyaniline and in polypyrrole are spinless.

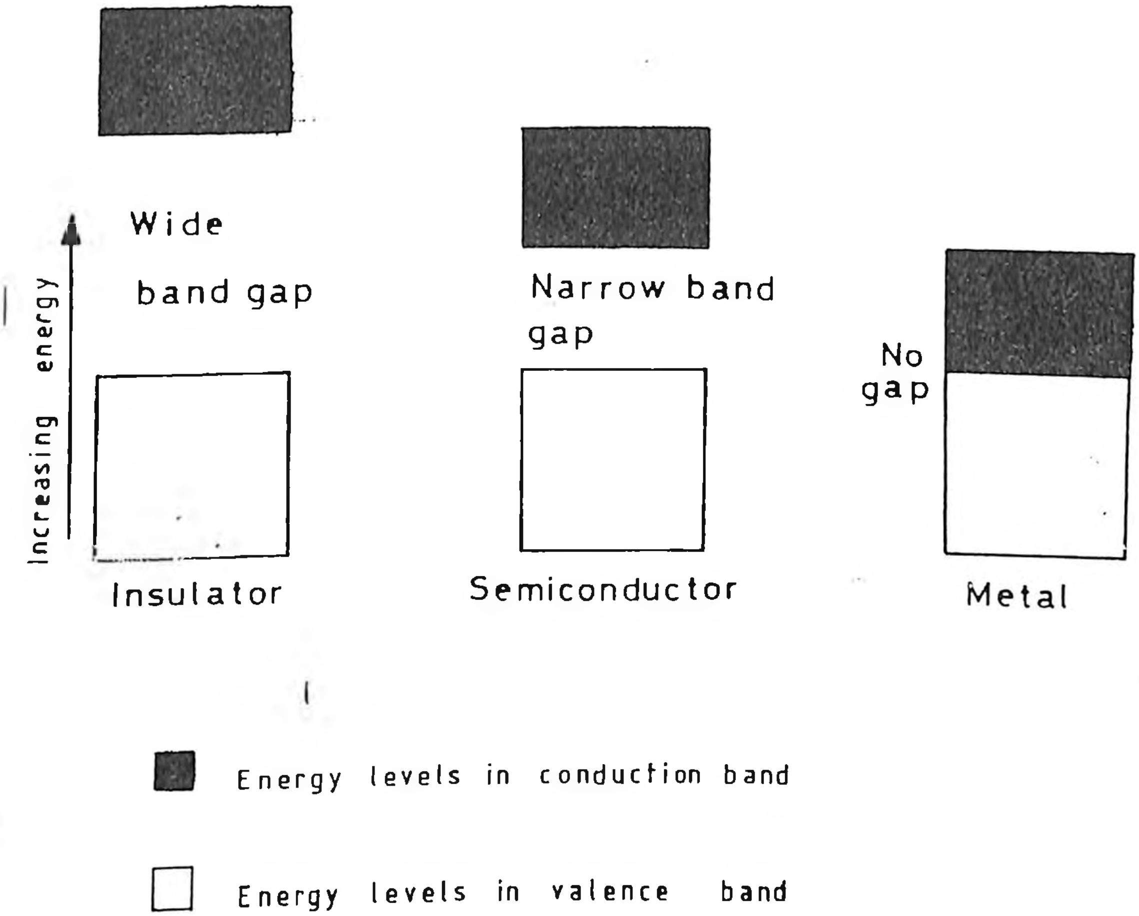


Figure 1: Band theory diagram

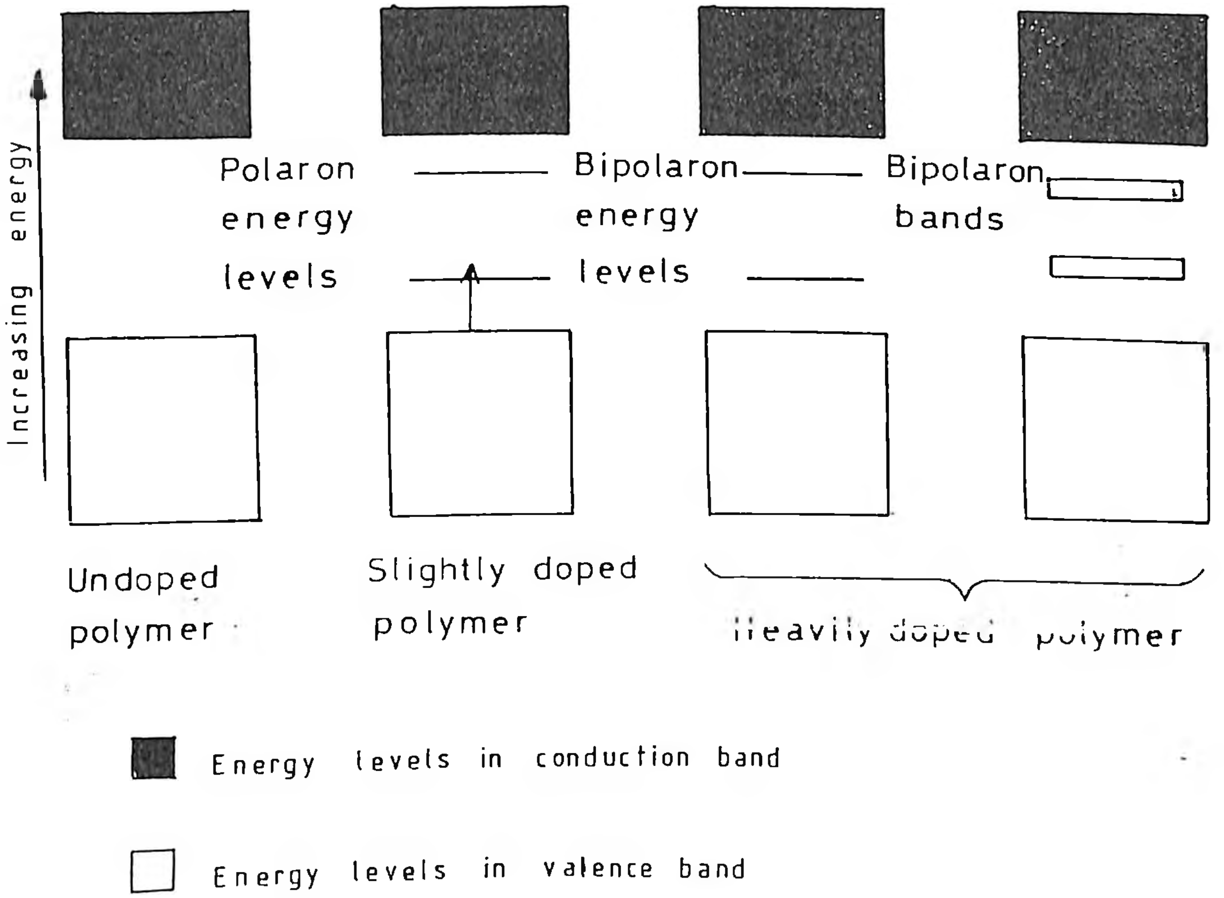


Figure 2: Diagram of a polaron and bipolaron

These electrical phenomena is explained by concepts from physics involving solitons, polarons and bipolarons. Removal of an electron from the top of the valence band of a conjugated polymer creates a vacancy (hole or radical cation) that doesn't delocalise completely as would be expected from the classical band theory. Only partial delocalisation, that extends over several monomeric units occurs causing them to deform structurally. The energy level associated with this radical cation represents a destabilised bonding orbital and thus has a higher energy than the energy of the valence band.

A radical cation that is partially delocalised over some polymer segment is called a polaron see Figure 2, which stabilises it self by polarizing the medium around it. A polaron has a spin of ½ since it is really a radical cation. Two things may happen if an electron is removed from the already oxidised polymer containing the polaron. Either the electron could come from a different segment of the polymer chain thus creating another independent polaron, or from the first polaron level(remove the unpaired electron) tocreate a special dication, which is called a bipolaron (see Figure 2). Low doping levels give rise to polarons whereas higher doping levels produce bipolarons.

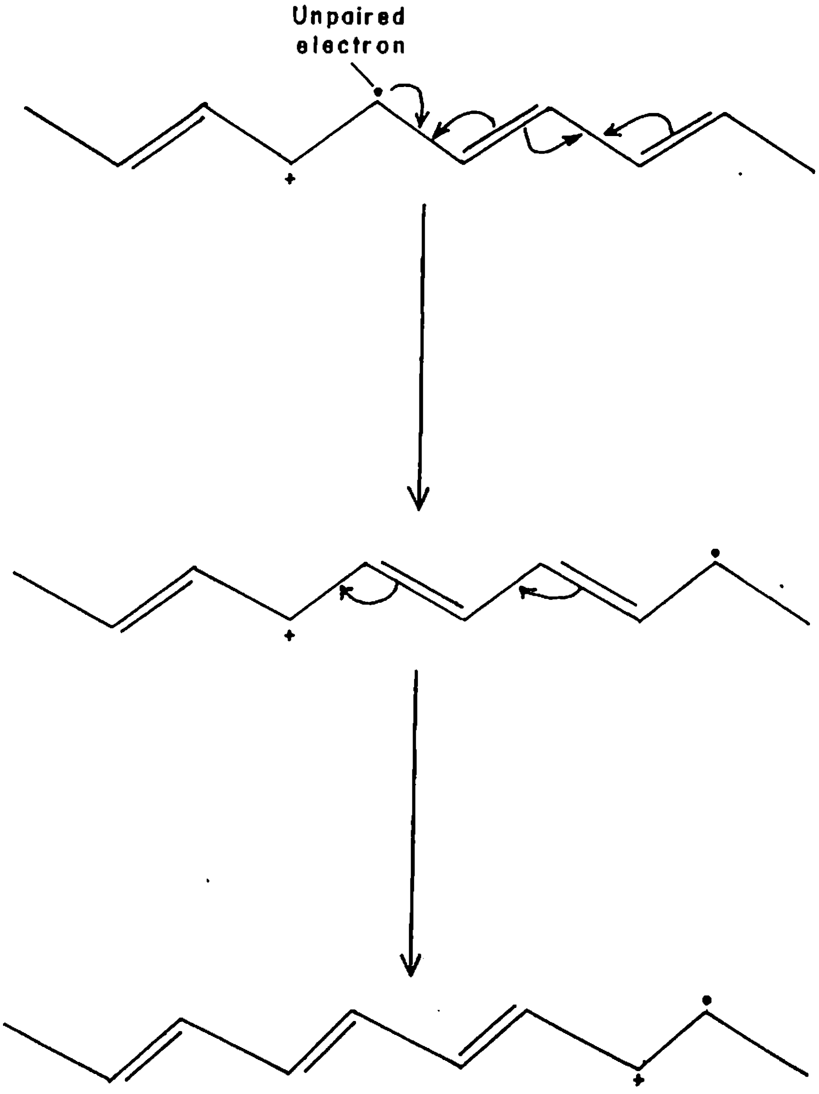


Figure 3: Movement of a polaron through a conjugated polymer chain by shifting of double bonds

Bipolarons have a characteristic structural deformation and the two positive charges act as a pair. Both polarons and bipolarons are mobile and can move along the polymer chain by the rearrangement of double and single bonds in the conjugated system that occurs in an electric field as shown in figure 3. If high doping takes place a great many bipolarons are formed and their energies start overlapping at the edges which creates narrow bipolaron bands in the band gap.

In polypyrrole, low doping concentrations create paramagnetic polarons, which as the degree of doping increases converts to spinless bipolarons which extend about four polypyrrole rings. A polaron and bipolaron in polypyrrole are shown in Figure 4.

1.5.2 POLYMERS WITH DEGENERATE STATES (POLYACETYLENE)

A well studied example that is considered a protoype of conducting polymers is polyacetylene. Polyacetylene(PA) is the simplest conjugated polymer that consists of coupled chains of -CH- forming a pseudo one dimensional lattice. The carbon atom in the monomer is SP^2 hybridized with two of the p-type bonds forming the one dimensional lattice, while a third forms a hydrogen bond with the hydrogen.

Two possible arrangements that satisfy the 120° angle cis-$(CH)_x$ and trans-$(CH)_x$ with two or four monomers per unit cell. The cis and

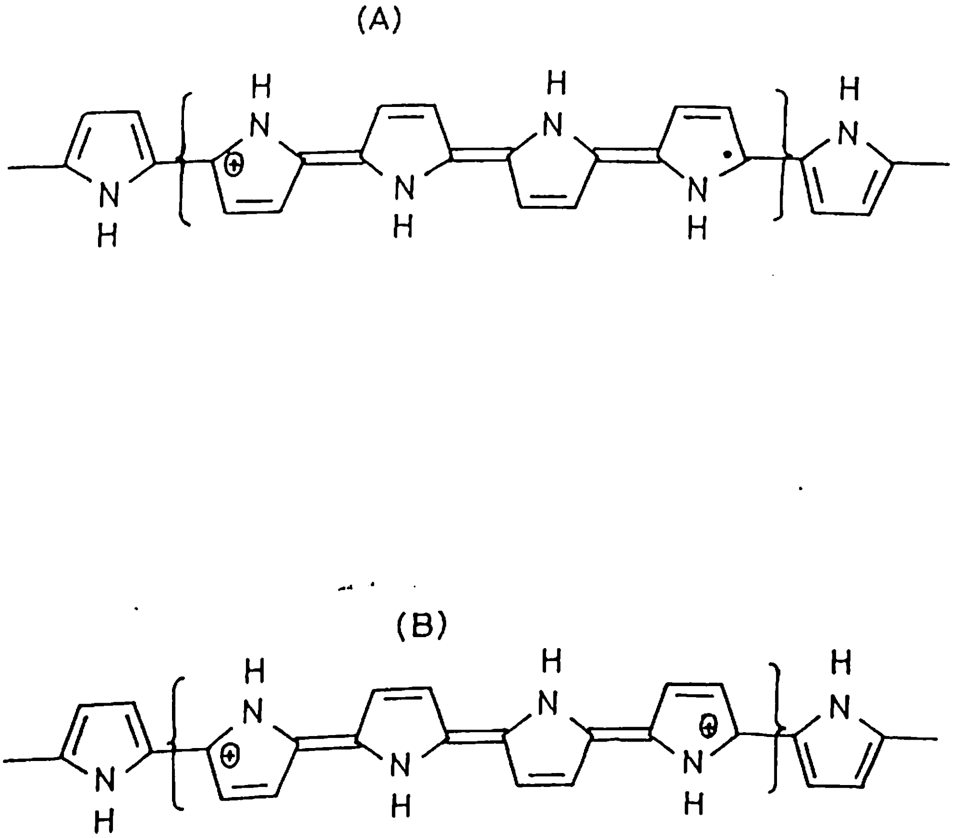
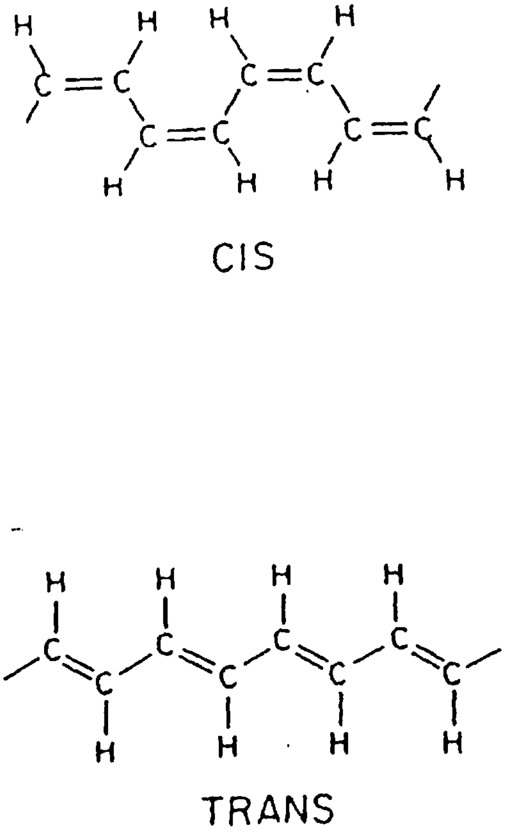


Figure 4: A polaron and bipolaron in polypyrole



CIS

TRANS

Figure 5: Cis and Trans-polyacetylene

trans forms are shown in Figure 5. The 2Pz orbital perpendicular to the molecular plane contains the remaining valence electron which overlaps with another 2Pz on a neighbouring carbon atom to form a p-bond. This p-bond leads to a partially filled orbital which is responsible for the important electronic properties observed.

Because of bond alternation i.e the single and double bonds in the trans form can be interchanged without changing the energy, there are two lowest energy states L and R having two distinct bonding structures see Figure 6. This two fold degeneracy leads to the existence of a non linear topological excitation bond alternation domain walls or solitons, which appear to be responsible for many of the remarkable properties of polyacetylene[57-62].

Both these forms can be made either free standing or on a variety of substrates e.g. on a glass or metal as flexible films of thicknesses ranging from 10^{-5}cm to 0.5cm[63]. The trans form is the thermo-dynamically stable form and total conversion of the cis-trans after synthesis is achieved by heating the film to temperatures above 150°C for a few minutes[64,65].

1.5.3 THE MECHANISM OF CONDUCTION

The conduction of electricity by polyacetylene can be explained by consideration of solitons. The understanding of the physical properties of polyacetylene results principally from two factors. Firstly, the in chain structure led to its consideration as the prototype conjugated polymer. Secondly, the thermodynamically stable trans-$(CH)_x$ has the unusual broken symmetry degenerate ground state (fig.5) which can sustain free stable solitons as natural non linear excitations. The double and single bonds in trans-$(CH)_x$ can be interchanged without changing the energy resulting in two degenerate lowest energy states L and R having two distinct bonding structures as shown in Figure 6. It is this two fold degeneracy that leads to the existence of non linear topological excitations, bond alternation domain walls or solitons. Isomerisation of a single chain of cis-(CH) can commence at any point on the chain with one part having configuration R and the other having configuration L, where these two configurations meet a free radical is produced (Figure 7).

This observation was experimentally verified when pure cis-$(CH)_x$ possessing no free spins underwent isomerisation. Approximately one in three thousand of the (CH) units in the resulting trans -$(CH)_x$ is in the form shown in Figure 7 with an unpaired spin and paramagnetic[65,66]. It has indeed been observed that if the localised state contains one electron then the soliton is neutral with spin 1/2 and hence is paramagnetic. If the localised electron is removed by an acceptor doper, the soliton is then

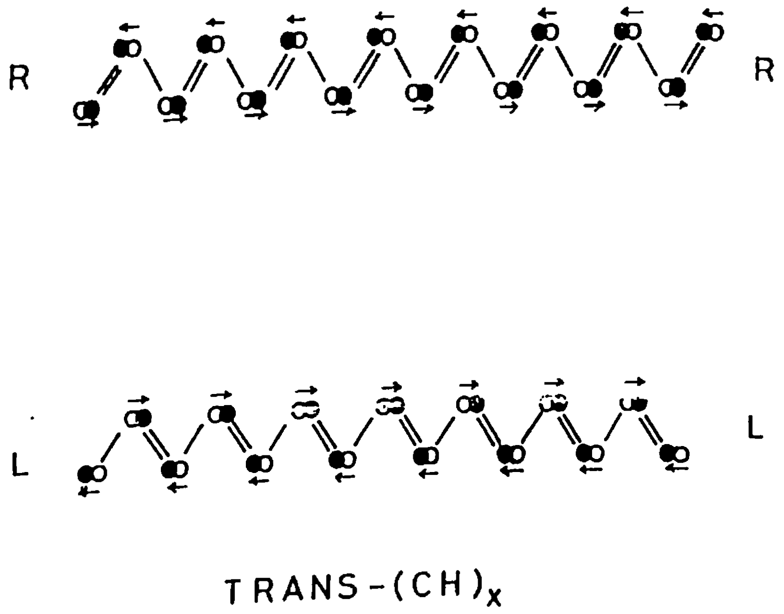


Figure 6: L and R configurations of trans-polyacetylene

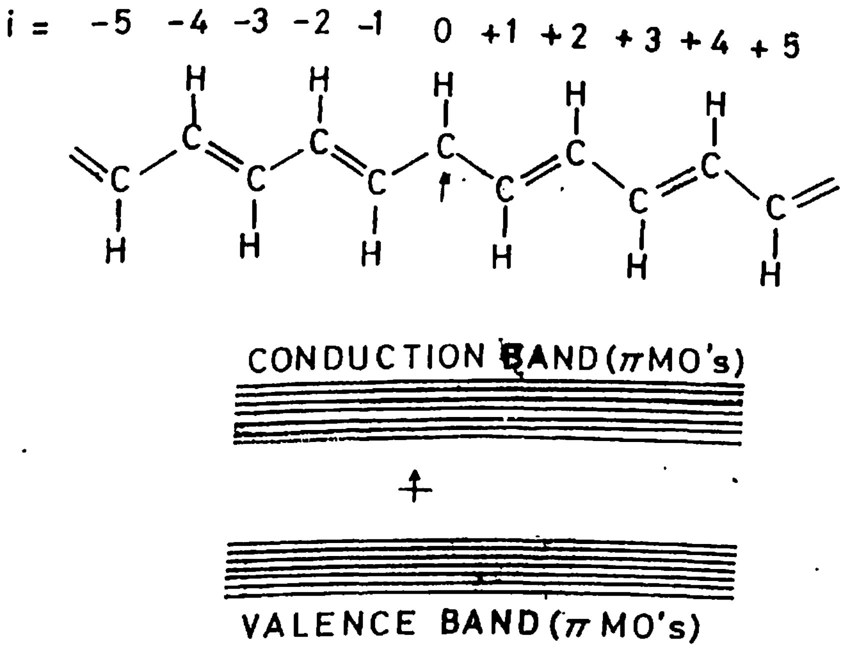


Figure 7: Diagram of a neutral Soliton

positively charged with spin zero and non magnetic. Hence the observation that careful and slow oxidation, with for example AsF_5 of $(CH)_x$ gives positive solitons[67].

A positive soliton as shown in Figure 8 is equivalent to a carbonium ion on the polyacetylene chain stabilised by delocalisation. Also double occupancy induced by donor doping will lead to a spin zero negatively charged state as also shown in Figure 8. The resulting negative soliton is an equivalent of a stabilised carbanion. In the figures shown, solitons are drawn as if localised on one lattice site, but actual detail calculations[57-60] have shown that minimisation of the energy spread the kink over a region of 15 $(CH)_x$ units as in the case of a positive soliton the maximum charge density is adjacent to the counter ion A^- but the bulk of the charge, approximately 85% is spread out systematically on either side over 15 $(CH)_x$ units.

1.6.0 APPLICATIONS OF CONDUCTING POLYMERS

1.6.1 RECHARGEABLE BATTERIES

Batteries made from polymer electrodes are slowly gaining precedence over the conventional batteries because of two reasons; Firstly, they are light and flexible with a large capacity to reversibly accept and donate electrical charge. Secondly, they will have a higher power density,

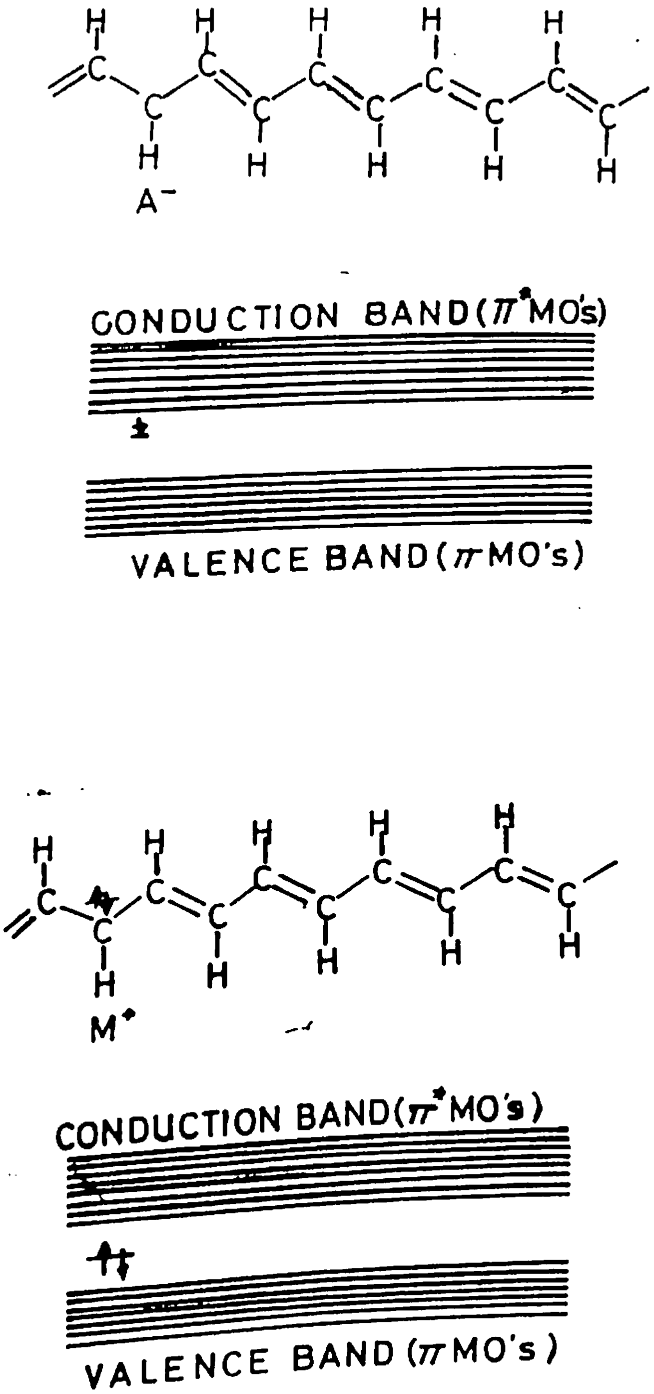


Figure 8: A positive and a negative Soliton

longer life and an energy density several times that of currently available commercial batteries.

Rechargeable batteries are among the first commercial products based on conducting polymers. The polymers usually polypyrrole, polythiophene, and polyaniline and their derivatives are the cathodes. The anodes are usually lithium or some lithium alloy e.g LiAl. Through an external load the cell discharges and electrons flow from the anode to the cathode, which reduces the P-doped polymer to its neutral (undoped) state. During this process dopant anions are ejected from the polymer into the electrolyte phase and the lithium anode dissolves into lithium ions. The cell is said to be fully discharged when all the polymer is completely undoped. To recharge the cell an opposite potential is applied to the electrodes. During the process the neutral polymer at the cathode is oxidised to the P-doped state, taking up dopant anions from the electrolyte, while lithium ion deposits as lithium metal at the anode. The electrode process occurring at the electrodes of polythiophene battery are;

Anode(negative electrode): $\mathbf{Li_{(aq)} <\!=\!=\!=\!=\!=\!> Li^{+}_{(aq)} + e^{-}_{aq)}}$.

The electrolyte can be a solution of an appropriate salt or a solid polymer electrolyte e.g, lithium salt/polyethylene oxide in which case an all solid state cell results. Conducting polymer rechargeable batteries are usually made as flat buttons or laminated rolled films .

These are excellent for application where long, life low power and reliability are of prime importance; e.g, as back up sources for static random access memory, telephones and timers for video cassette recorders and as batteries for hand held calculators, fax machines , TV remote controls and wrist watches[68].

1.6.2 ELECTROCHROMIC DEVICES.

Some conducting polymers show a whole range of colours as a result of their many protonation and oxidation forms. Hence some of them like polyaniline have been used to produce electrochromic displays and smart windows. They have an added advantage over liquid crystal displays in that electrochromic devices made of polymers can be fabricated into large areas with unlimited visual angles. Many electrochromic devices exhibit memory function (bistability) because they don't change colour after the applied voltage has been removed thus their use in storing information.

An electrochromic device is very similar to a rechargeable battery i.e, the cathode is the polymer and the anode is a metal usually aluminium. ELectrical potential is applied to cause doping and undoping and thus induce the controlled colour changes. However for this changes to be visible one of the electrodes must be optically transparent. Indium doped tin oxide glass is commonly used for this purpose.

Smart windows change colour in response to the intensity of sunlight or temperature changes . In smart windows both electrodes must be optically transparent. In the transparent (bleached state) of the device the polymer is in the neutral (undoped) state. To block sunlight a positive potential is applied causing oxidative doping of the polymer which gives the intense coloration. Table I below shows the particular colour changes for different polymers;

Table I. PARTICULAR COLOUR CHANGES FOR DIFFERENT POLYMERS

POLYMER	COLOUR UNDOPED	COLOUR DOPED
Polythiophene	Red	Blue
Polypyrrole	Yellow green	Blue black
Polyaniline	Yellow	green or blue
Polyisothianaphthene	blue	Light yellow

1.6.3 GAS SEPARATION

An unusual application for polyaniline is as a gas separator e.g O_2 from N_2 or CO_2 from CH_4 . Richard B Kaner and Howard Reiss[79] have discovered that if polyaniline is doped and undoped several times it becomes porous and can act as a gas separation membrane.

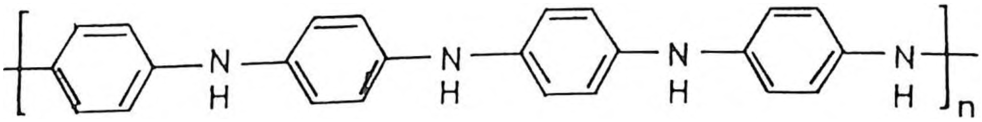
1.6.4 CONDUCTIVE FABRICS AND TEXTILES.

These are increasingly finding much use in the aircraft building industry. They are made by impregnating fabrics with polypyrrole and polyaniline without interfering with their strength and tactility. They have been considered for use in composites i.e. they can be incorporated into the plastic composites used in airframes for charge dissipation during lightning strikes, thus preventing damage to the aeroplane. Conductive fabrics have also been used in military aircraft to mislead enemy radar because such fabrics distort radar signals. Robert B. BJorklund[87] at Linkoping University in Sweden and others developed a latex composition containing poly-(pyrrole, thiophene, aniline) colloid particles. This latex when sprayed onto surfaces gave conductive coatings which provide electromagnetic shielding and may be useful as a weapon against electronic eavesdropping.

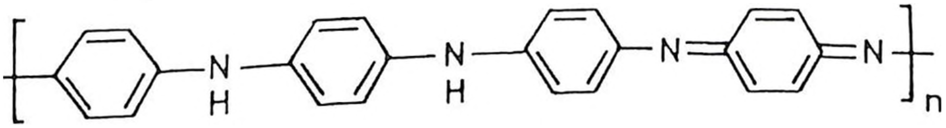
1.7.0 POLYANILINE

Polyaniline whose structure was first described by English and German scientists at the turn of the century; is a simple conjugated polymer made of 1000 or more repeating units of  It exists in several oxidation states with electrical conductivity varying progressively from 10^{-11}S per CM to more than 10 S per CM. Polyaniline occurs in four oxidation states each with a different colour and electrical property. However only one form, the emeraldine salt is conducting Figure 9.

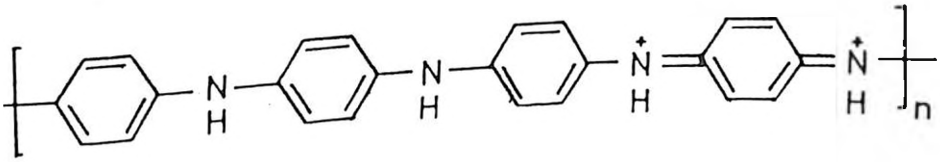
Before 1980 little research had been done on polyaniline. However Marcel Jozefowicz and coworkers[69] at the Centre National De La Recherche Scientifique in Paris found in 1968 that the conductivity of polyaniline increases by orders of magnitude as the PH of the acid it is doped with declines They also recognized that Polyaniline could serve as an excellent electrode for reversible batteries. Further studies were carried on by Eugene M. Geneis[80,81,82] at Centre 'd Etudes Nucleares in Grenohle France; and Macdiamid and coworkers[72] at Massachussests I nstitute of Technology. Thus during the 1980's Polyaniline was subjected to intense structural, physical and electrical characterisation using the latest experimental techniques. Although its structure has not been completely



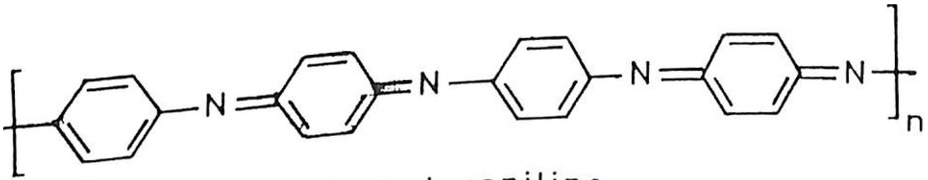
Leuco-emeraldine,
"white-emeraldine"
(Insulator)



Emeraldine
base
(Insulator)



Emeraldine salt,
conductive form
(Good conductor)



Pernigraniline
(Insulator)

Figure 9: Polyaniline oxidation states

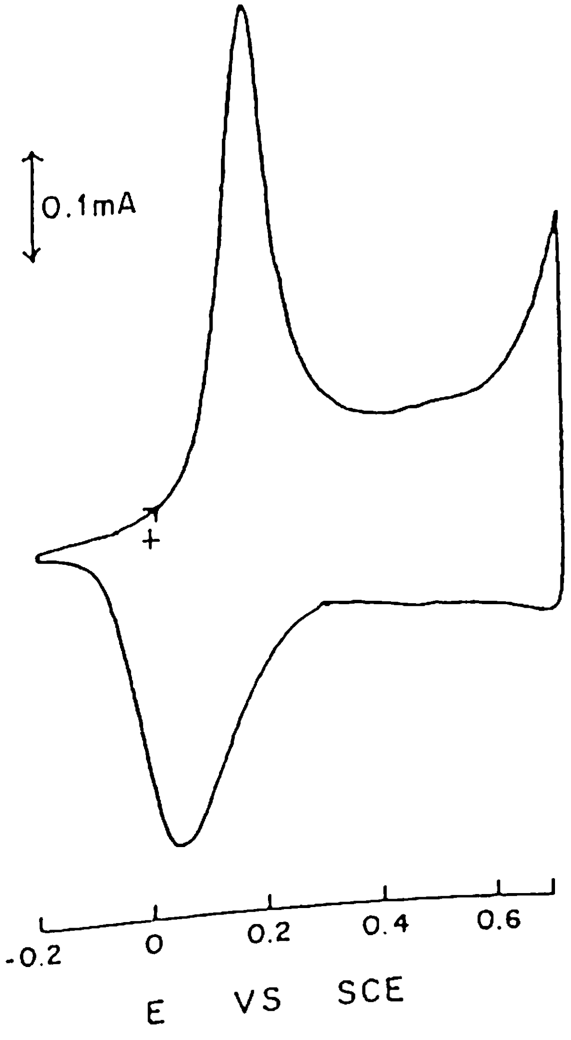
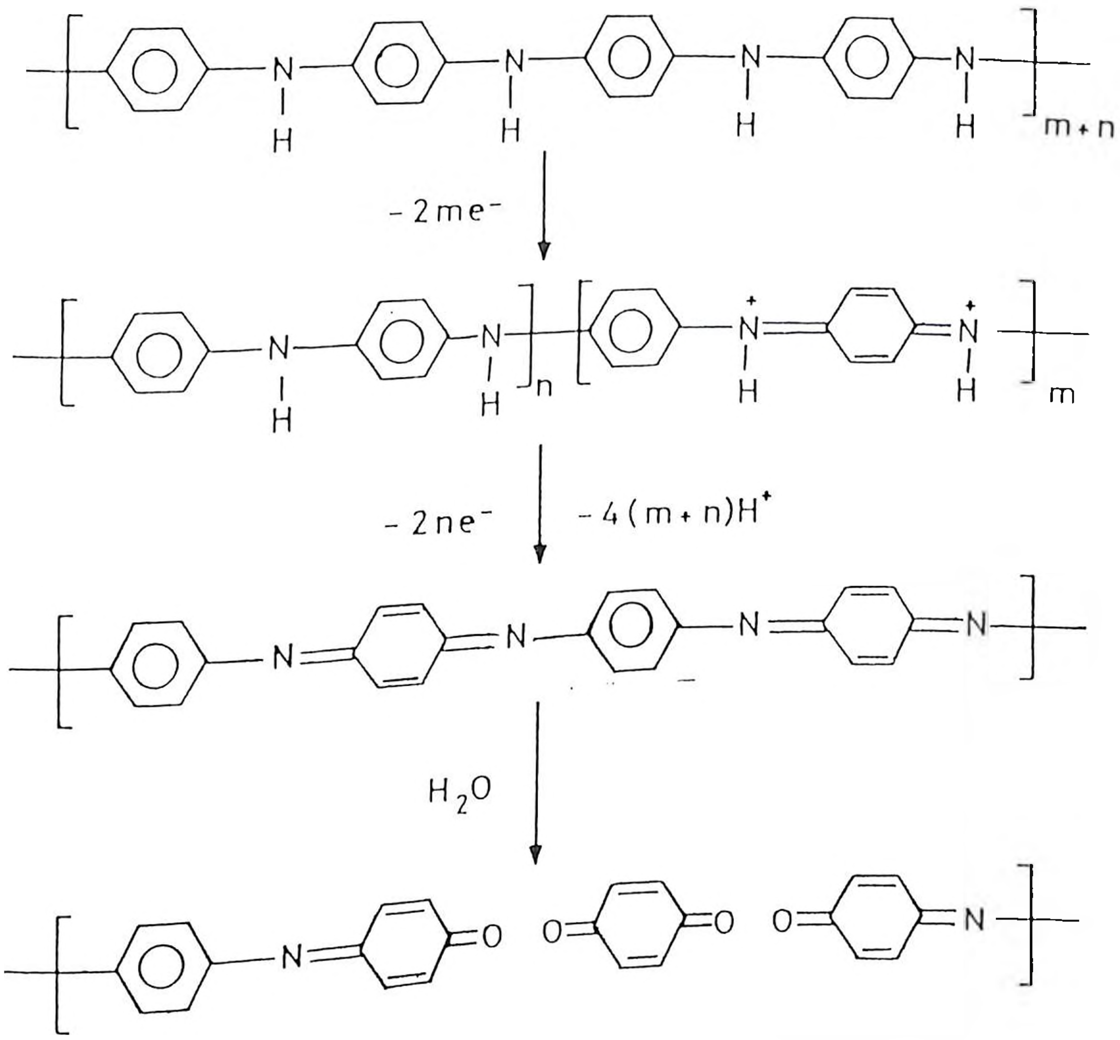


Figure 10: Cyclic Voltammogram of Polyaniline

characterised, a linear generalised formula has been developed out of the many studies

Polyaniline may be immobilised on an electrode surface by either potentiostatic or galvanostatic oxidation of the aniline monomer. The cyclic voltammogram Figure 10 of Polyaniline shows a sharp oxidation peak at 0.2V and a broad peak for the reduction at 0.04V. Polyaniline is conducting in the oxidised state and an insulator in its'reduced state. In its' conducting form Polyaniline differs from other conductive polymers because partial oxidation or reduction is not necessary to dope it. A highly conducting state is accomplished by simple protonation of the imine Nitrogen atoms in the Emeraldine base backbone. Thus the conductivity depends on the PH of the solution. The conductivity also depends on the potential; this is verified by the small charging current to the negative of the redox process and the large charging current to the positive of the redox process which is consistent with the transition from an insulator to a conductor.

Two oxidation processes occurring simultaneously are responsible for the large currents at the end of the positive scan. One is the oxidation of the film [71-75] with the subsequent loss of conductivity. The product of this oxidation process is very unstable under aqueous conditions



Scheme II: Oxidation of Polyaniline to the Quinone in acid media and this results in the degradation of the film at potentials greater than 0.8V in the absence of the aniline monomer[76], it is this problem that forms the core of this research. The second process is the oxidation of the aniline monomer to produce precursors to the Polyaniline film[76,77].

Polyaniline is known to undergo a second oxidation process at more positive potentials which leads to film degradation[75]. The structure of the hydrolytically unstable polymer is shown in scheme II[70]. In this scheme the reduced form is shown in its' deprotonated state. The imine form is a very poor base due to the nature of the imine nitrogen and it is rapidly hydrolysed to give the more stable quinone. Loss of conductivity was observed at positions positive of this wave because the charging currents drop to normal levels. They also observed that continued scanning over the second oxidation wave gave two new closely spaced reversible redox processes at 0.43 v and 0.50 v respectively, and went on to speculate that the two closely spaced waves initially observed were probably quinone and quinone immine (precursor to the quinone) which resulted from the initial hydrolysis at only one ring position as shown in scheme II. The presence of benzoquinone has been verified by spectral and electrochemical observation of a product with the same characteristics as a benzoquinone[75].

CHAPTER 2

EXPERIMENTAL SECTION

2.0.0 CYCLIC VOLTAMMETRY

Since Murray and Co-workers first ventured into surface synthesis, many electroanalytical techniques have been applied in the study of the oxidation and reduction reactions of many types of compounds. The most widely used technique is voltammetry, in particular cyclic voltammetry. Kemula and Kublik[83,84] developed the cyclic stationary electrode and applied it to studies of the mechanisms of electrode processes of organic compounds. Voltammetry provides thermodynamic and kinetic information concerning the species participating in the reaction and in this way gives insight into it's chemical properties.

Cyclic voltammetry is usually performed with a small ($<1cm^2$) stationary electrode immersed in an unstirred solution of reactant in a suitable solvent and electrolyte. This electrode has two interrelated roles

(a) by controlling the current or the electrode potential a variable and precisely known amount of oxidation or reduction is caused to occur in a small volume of solution at the vicinity of the electrode.

(b) and the electrode monitors the solution reactions and gives information in the form of a current potential profile.

The potential of the electrode is varied linearly with time (scanned) from an initial potential E_i in either the positive or negative direction untill a switching potential E_f is reached at which the direction of the potential sweep is reversed, and the potential is scanned in the reverse direction[85-87].

The principal experimental variables are, the potential range from E_i - E_f and the scan rate v, which is effectively used to vary the time scale on which the electrochemistry of the reactive species is observed.The current is measured throughout the scan and he resulting current potential is called a voltammogram. The position of the peaks on the potential axis is related in a simple manner to the formal potential of the redox process, and the peak height and shape , which give information about the reactant concentration and the number of electrons in the half reaction[87].

The simplest electrode reaction is one in which an electron is transferred in a fast process to give a stable product i.e.

$$O + e \leftrightarrow R \qquad (1)$$

Such electrode processes give cyclic voltammograms such as that shown in Figure 11 [86]. Curve QR corresponds to the potential region where the ratio of the suface concentration of R to the surface concentration of O is increasing rapidly and hence the current is increasing. At R the surface concentration of the oxidised form is tending to Zero and the electrode process is purely diffusion controlled. The decrease in current over RST shows a decrease in the rate of diffusion of the oxidised form to the surface as its flux falls off with time towards a steady state value. TN is the potential region where the surface concentration of R to O decreases, this time O becoming more favourable. Finally N is the potential of R to the surface and hence the current for the reverse process, are at a maximum and beyond this peak both decrease towards zero, when there is again no electron transfer reaction taking place.[87,88]

A typical cyclic voltammogram will have the following characteristics[86].

(1) The oxidation and reduction peaks will be seperated by about 60 mv

$\Delta E_p = 60$ mv

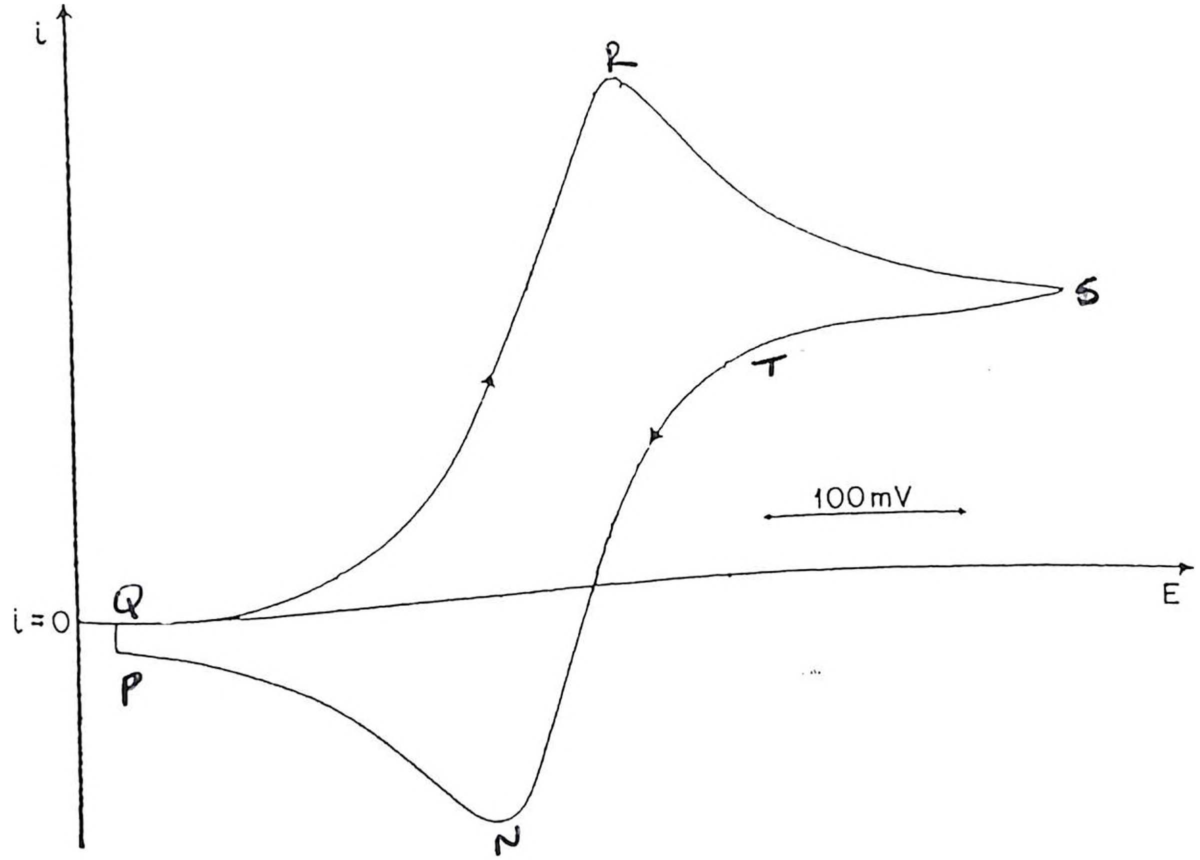


Figure 11: An example of a cyclic Voltammogram

(2) Peak potentials E_p are independent of the potential scan rate and so are $I^F_{p}/V^{½}$ and $I^B_{P}/V^{1/2}$

(3) The half peak width for the oxidation and reduction peaks are defined by $(E_p - E_p/2) = 57$ mV

(4) $I_a/I_p = 1$ where I_a and I_p are anodic and cathodic peak currents respectively.

(5) The current beyond the peaks decays according to $i\ a\ t^{½}$

(6) Peak potentials are related to the half wave potential by $E_p = E_{½} = -28.5$ mV

A pair of peaks that obeys this criteria shows that the electrode reaction involves the transfer of a single electron and the product of the electrode is stable. The ratio of I^F_a/I^F_p will be less than unity when the product of the single electron transfer is unstable. But if the scan rate is increased, the time scale of the experiment is reduced and the chemical reaction will not occur to the same extent i.e. the ratio will be higher.

2.1.0 ELECTROCHEMICAL APPARATUS

Cyclic voltammetric studies were carried out using a Princeton Applied Research model 173 Potentiostat/Galvanostat equipped with a Princeton Applied Research Model 379 Current Logarithmic converter. The potential was controlled by a Princeton Applied Research Model 175 Universal

Programmer(the triangular wave generator). Scans of 10 mv/s and above were recorded on a Princeton Applied Research Model RE0089 X - Y Recorder.

A three electrode assembly was used for the electrochemical synthesis and degradation of Polyaniline. The working electrode was a locally fabricated carbon graphite electrode with a surface area of $0.38cm^2$. The counter electrode was a platinum wire. A saturated calomel electrode (SCE) was used as the reference electrode. The working electrode was polished using alumina on a felt polishing cloth. Data was taken at room temperature (22°-25°), All potentials are quoted with reference to the saturated calomel electrode.

2.2.0 THE POTENTIOSTAT

The potentiostat is an electrochemical measuring instrument, which holds the potential between the reference and working electrode of an electrochemical cell constant, or it changes the voltage between two electrodes in a very specific, and carefully controlled manner despite large changes in the current demand by the system. The controller circuit reacts to the difference between these two potentials through a negative feedback circuit which contains the counter electrode; in such a way as to reduce the differrence to zero.

An optimum potentiostat design should;

(I). have a circuit that provides accurate potential control with no IR drops through the signal generator or current measuring resistor that leads to potential control errors;

(ii). have a stabilised amplifier (single-ended) because such a device has a lower drift;

(iii). have a circuit design that allows one grounded terminal each for the signal generator and the current measuring device, because it is more convenient to refer all signal inputs and outputs to a common ground.

A single amplifier potentiostat cannot meet all these specifications.

In order to understand qualitatively how a potentiostat operates,two factors have to be assumed,

(a). the amplifier input currents are negligibly small;

(b). the amplifier will maintain the inverting input at the same potential as the non inverting (+) input only if there is a closed feedback loop from the output to the inverting input.

The potential control operations of any potentiostat are commonly performed by an operational amplifier. An operational amplifier usually multiplies and inverts the potential passed through it by a factor known as the potential loop gain. A differential amplifier has a high loop gain and remains stable with large amounts of negative feedback from output to input.Consider the circuit diagram in Figure 12 of a simple single amplifier potentiostat.

2.2.1 THE ADDER POTENTIOSTAT

The most commonly used type of potentiostat is the adder potentiostat, which as the name suggests effectively adds up several potentials prior to passing them through the operation alamplifier. Most electrochemical wave forms are synthesis of several simpler wave functions. For example, the total wave form shown in Figure 13[88] is the sum of a ramp function, a sinusoidal perturbation, and a constant offset. The adder potentioistat thus accepts and adds several basic inputs to give a complex wave form that cannot be supplied simply. The basic adder potentiostat circuit shown in Figure 14 is the most widely used. At the summing point S the currents must add up to zero and like wise the potential here is also zero (ground or virtual potential)[88]. Resistors R_w, R_x, R_y can be replaced in a cell by the resistances due to the interphases of the liquid junctions of each of the electrodes.

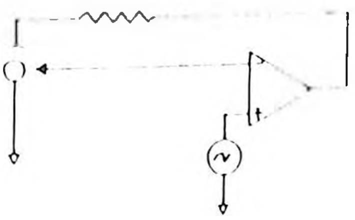


Figure 12. A single simple amplifier potentiostat

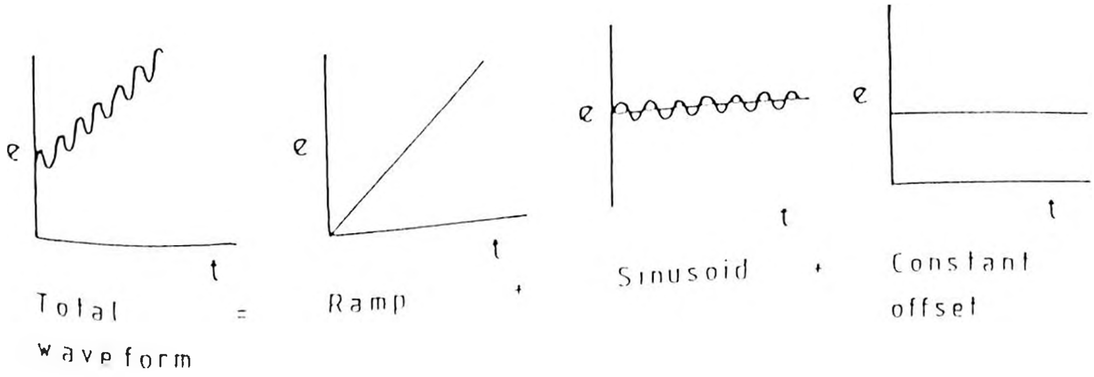


Figure 13. Basic wave forms

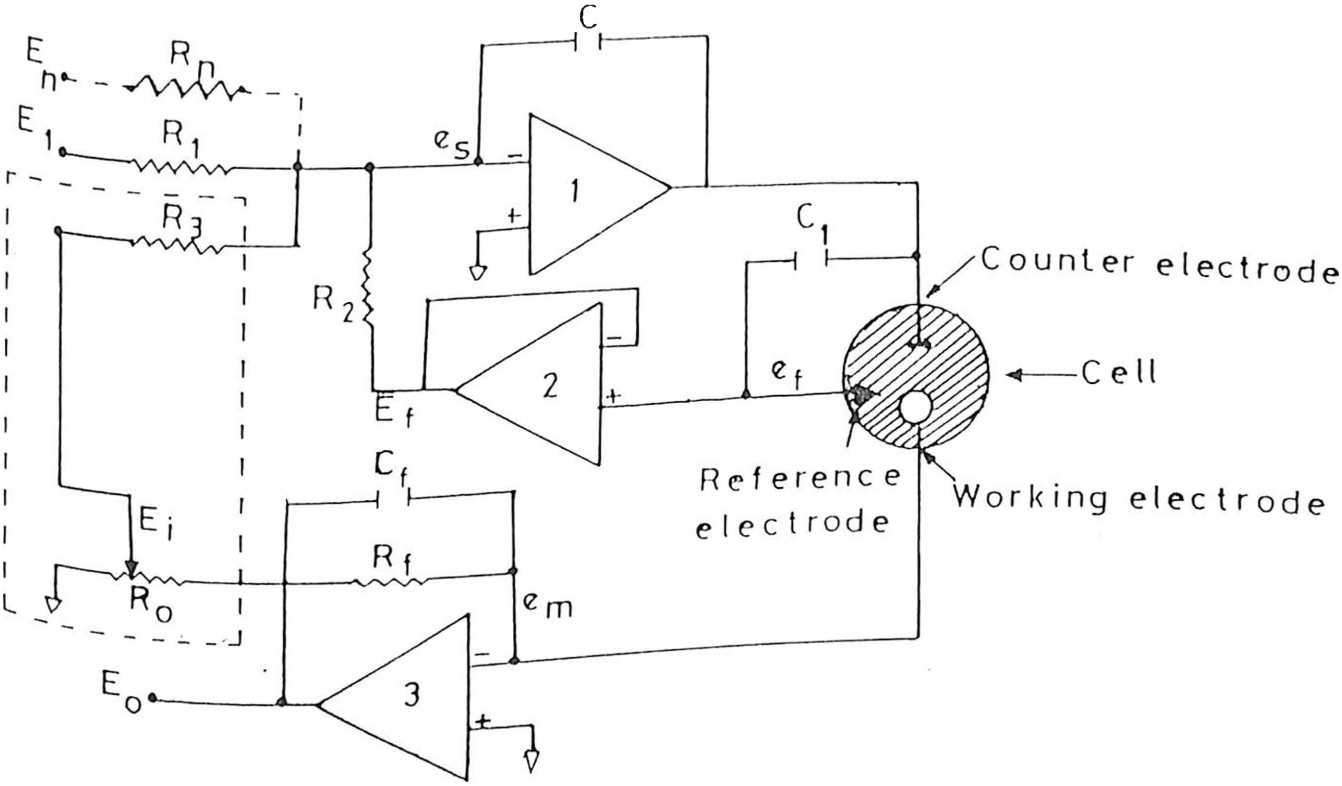


Figure 15. An Adder potentiostat

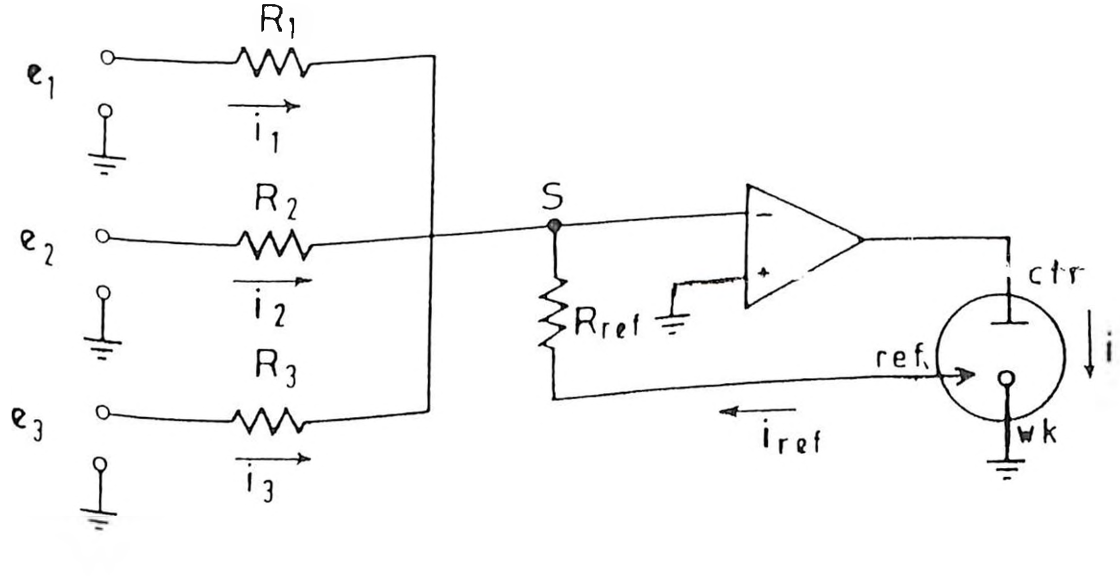


Figure 14. A basic Adder potentiostat

The adder potentiostat Figure 15 is widely popular because it's control inputs can be refered to ground as well as output voltage of the current follower (amplifier 3) which is proportional to the current. The current follower is widely used in controlled potential circuits because it maintains the working electrode at a ground potential yet still provides a single ended voltage output proportional to current.

The capacitors C_o, C_i, and C_f, which are used to stabilise the frequency response, and the components which are used for positive feedback compensation(dotted triangle) can be ignored for the time being. The working electrode is maintained at virtual ground (ground potential) by a current follower configuration by operational amplifier 3. It's output voltage is therefore given by

$$E_o = -iR_f \tag{2}$$

so that E_o is proportional to the current flowing through the working electrode.

Amplifier 2 is a voltage follower such that

$$E_f = e_f \tag{3}$$

where E_f = output potential

and e_f = input potential

The output potential is the potential of the refrence electrode measured with respect to the working electrode; because this is the reverse of the conventional defination of E_{cell}.

$$E_f = e_f = -E_{cell} = -(E_w - E_{ref}) \tag{4}$$

The IR drop in the cell due to the solution that leads to working electrode and the working electrode itself is assumed to be uncompensated for. Also the IR drops in the reference electrode are considered to be negligible since the voltage follower draws only minute current through the reference electrode. If IR drops are present in the solution or in the electrode then,

$$E_f = -E_{cell} + iR_u \tag{5}$$

where R_u = the uncompensated resistance

i = cell current

Potential of the lead from the reference electrode measured with respect to the lead from the working electrode is the only electrically measureable quantity. At zero current this quantity equal to E_{cell}.

The potential inputs E_{i-n} and E_f (the voltage follower outputs) are added or summed through separate input resistors connected to the summing point of amplifier 1 (the control amplfier). The control amplifier maintains it's summing point at ground potential ($e_s = 0$), by virtue of the feedback loop that contains counter electrode, the reference electrode and the voltage follower (amplifier 2). The currents in the summing point S must add up to zero. Such that,

$$i_n + i_f + i_2 = 0 \tag{6}$$

From Ohms law,

$$E_n = i_n R_n \tag{7}$$

and,

$$i_n = \frac{E_n}{R_n} \tag{8}$$

Hence,

$$\frac{E_n}{R_n} + \frac{E_1}{R_1} + \frac{E_f}{R_2} = 0 \tag{9}$$

Rewrite,

$$-\frac{E_f}{R_2} = \frac{E_1}{R_1} + \frac{E_n}{R_n} \tag{10}$$

Therefore,

$$-E_f = E_1\left(\frac{R_2}{R_1}\right) + E_n\left(\frac{R_2}{R_n}\right) \tag{11}$$

If $R_1 = R_2 = R_n$, then,

$$-E_f = E_1 + E_n \tag{12}$$

Since $-E_f = E_{cell}$ then

$$E_{cell} = E_1 + E_n \tag{13}$$

The control amplifier maintains a constant potential throughout the circuit as described by equation 13 by forcing current to flow through the counter and reference electrodes; e.g if the summing point tends to drift negative with respect to ground, the control amplifier (voltage follower) output and the counter electrode voltage become more positive hence E_{cell} becomes more negative and E_f more positive which then tends to cancel the negative drift at `S`, the summing point.

Potential control errors are expected either if the gain or frequency response of the amplifiers is inadequate or if the control inputs change rapidly with time. An overload condition is expected if the voltage and current output of operational amplifier 1 and 3 are inadequate to meet the demand. This basic circuit is reversible and allows as many control inputs as desired to be connected to the input of the control amplifier each through it's own resistor[89].

2.3.0 REFERENCE ELECTRODE

It is important that in any electrochemical application that the half-cell and potential and reaction of one electrode be, known, constant, and completely insensitive to the composition of the solution under study. An electrode that fits this description is called a ***reference electrode***. A working electrode, whose response is dependent upon the analyte concentration is used in conjunction with a reference electrode[90].

Several criteria should be kept in mind when chooosing a reference electrode. These are

1. reproduceability without painstaking preparation or assembly.
2. a small temperature coefficient of e.m.f.
3. reversibility when fairly large currents are drawn,
4. constancy with time,
5. possibility of use with a saturated potassium bridge.

Several electrode systems fit this criteria, but the one prefered for our analysis was the saturated calomel electrode. The calomel electrode introduced by ostwald in 1890; generated outstanding interest from the historical practical and theoretical view points.

Calomel half cells may be represented as follows,

$$\cdot \| Hg_2\ Cl_2(saturated),\ KCl\ (XM) | Hg$$

where x is the molar concentration of potassium chloride in solution.

The electrode reaction is given by,

$$Hg_2Cl_2(s) + 2e^- \leftrightarrow 2Hg(l) + 2Cl^-(aq)$$

However the potential of the cell varies with the chloride concentration x and this quantity must always be specified in describing the electrode. The Table below shows the specifications of three most commonly encountered calomel electrodes.

TABLE II: SPECIFICATIONS OF THREE MOST COMMONLY ENCOUNTERED CALOMEL ELECTRODES

NAME	CONCENTRATION OF		ELECTRODE POTETIALS VS STD HYDROGEN POTENTIAL AT 25°C
	Hg_2Cl_2	KCl	
SATURATED	Sat'd	Sat'd	$+0.241 - 6.6\times10^{-4}$
Normal	Sat'd	1.0M	$+0.280 - 2.8\times10^{-4}$
Decinormal	Sat'd	0.1M	$+0.334 - 8.8\times10^{-5}$

From the table it is evident that each solution is saturated with respect to Mercury(I) chloride and that the cells only differ with respect to potassium chloride concentration. Note that also the potential of the normal calomel electrode is greater than the standard potential for the half reaction because

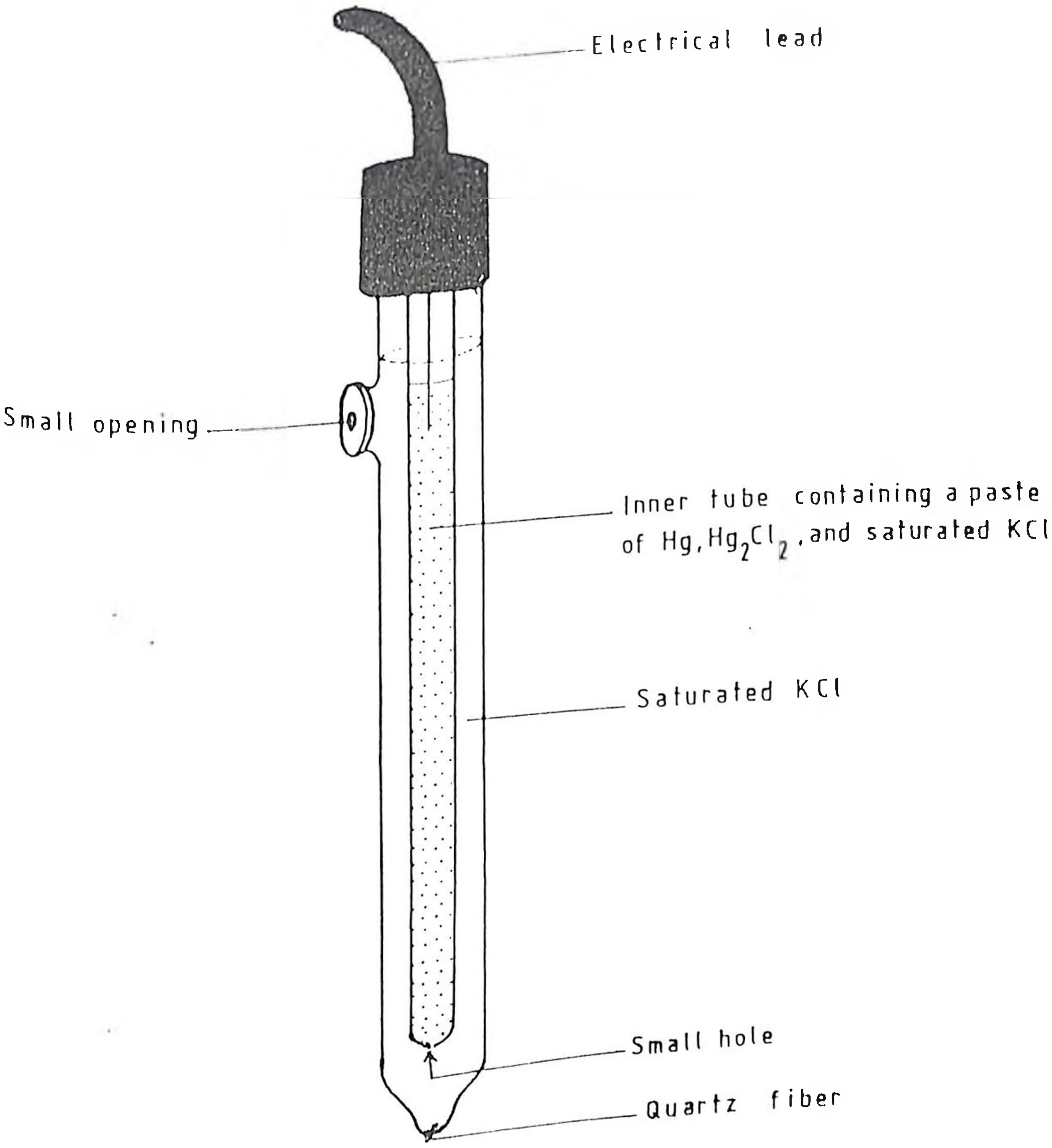


Figure 16. A saturated Calomel Electrode

the chloride ion activity in a 1.0M solution of potassium chloride is significantly smaller than unity.

Mercury has properties which are desireable for setting up well behaved electrode systems. It is a noble, liquid metal, easy to purify, and therefore easy to obtain in a standard state, with properties quite independent of its chemical, mechanical and thermal history. This is a considerable advantage over any solid metal, even a soft one such as lead.

A typical calomel electrode as shown in Figure 32, consists of a tube 5 to 15 cm in length and 0.5cm to 1.5cm in diameter. Mercury-Mercury(I) chloride paste is contained in an inner tube that is connected to the saturated potassium chloride solution in the outer tube through a small opening. Contact with the second half cell is made by means of a porous fibre sealed in the end of the outer tubing. An electrode such as this has a relatively high resistance (2000W to 3000W) and a limited current carrying capacity[91].

2.4.0 CHEMICAL REAGENTS

Reagent grade acids and chemicals were used as received. The Aniline (Aldrich) was triply distilled until a clear colourless liquid was obtained. The liquid was then purged of all oxygen by bubbling through with nitrogen. The clear aniline was then stored under a nitrogen atmosphere to prevent oxidation to a dark liquid. All solutions were prepared using triply distilled water.

The chemicals used in the various studies as were as follows,

(i) Stabilisation of polyaniline films in the presence of P-Aminophenol.

P-Aminophenol(BDH) and sulphuric acid(ALDRICH) were used as recieved without further purification.

(ii) Determination of Polyaniline PK values as a function of the external solution pH using it's degradation data.

Phenol(BDH) and Sulphuric acid (ALDRICH) were used as received without further purification.

(iii) Electrochemical degradation of metallated Polyanilne.

Potassium nitrate(BDH), Tin (II) Chloride(ALDRICH),Silver nitrate(BDH), Sulphuric acid(KOBIAN) and Hydrochloric acid(KOBIAN) were used as received without any further purification.

2.5.0 OBJECTIVES OF THE RESEARCH

The objective of the study was to investigate how Polyaniline films electrodeposited on a carbon graphite electrode could be stabilized by attachment of of surface active substrates. Accordingly the following investigations were carried out;

I) Stabilisation of the Polyaniline films in the presence of Phenol and P-aminophenol.

ii) The effect of lead modified carbon graphite electrode on the electrochemical degradation of Polyaniline.

iii) The effect of Lead, Tin and Silver modified carbon graphite electrode on the rate of degradation was also investigated

iv) The effect of solution PH on the rate of degradation was also investigated and from the degradation data an attempt was made to derive an expression for the pK of the polyanilne film from Kinetics.

It is expected that this study will be technologically relevant to the improvement of among other things, Electrochemical Energy storage systems, photoelectrodes,catalysts,electrochemical synthesis and in other areas such as in the development of new types of ion sensing Reference Electrodes.

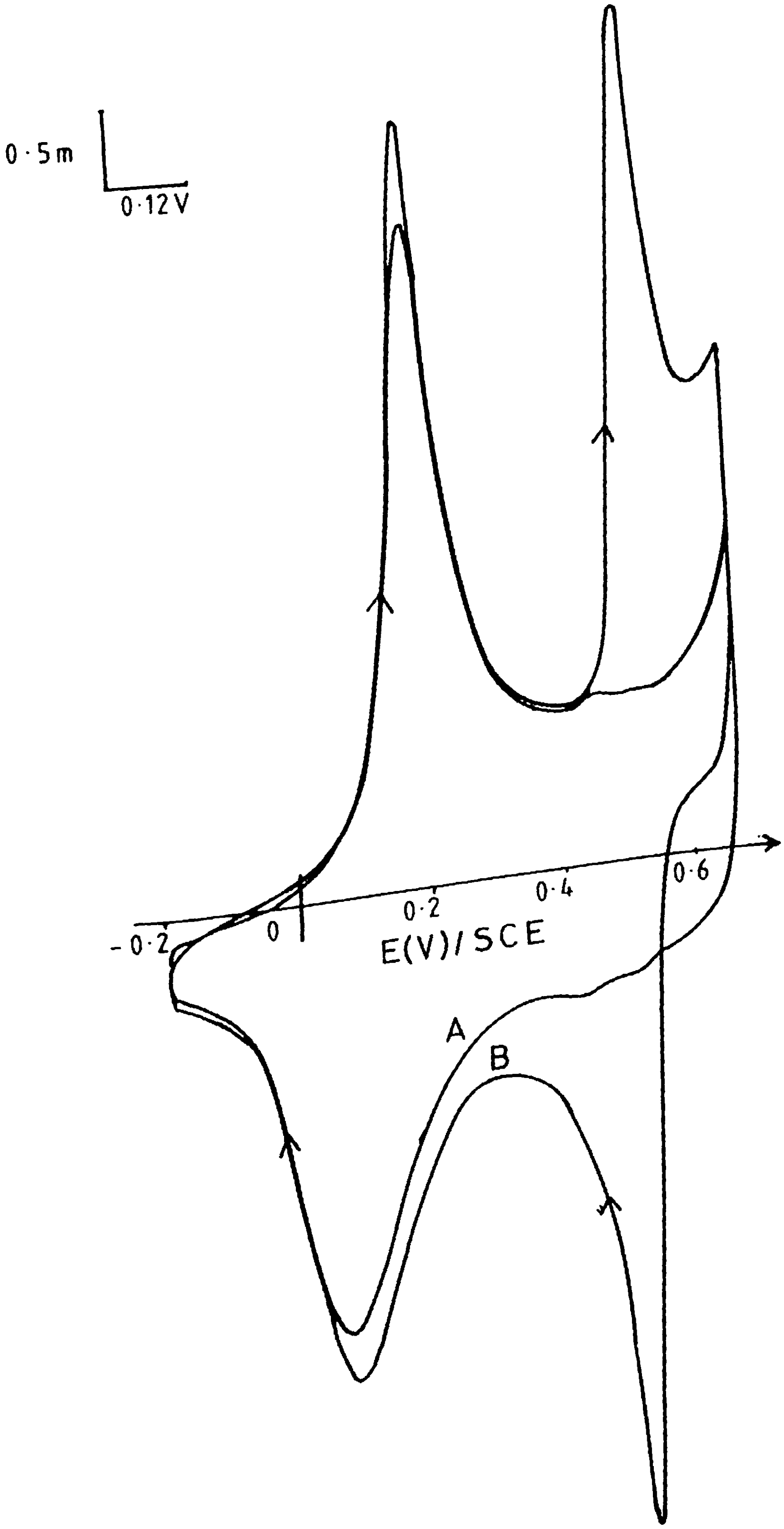
CHAPTER 3

RESULTS AND DISCUSSION

3.0.0 STABILIZATION OF POLYANILINE FILMS IN THE PRESENCE OF *P*-AMINOPHENOL

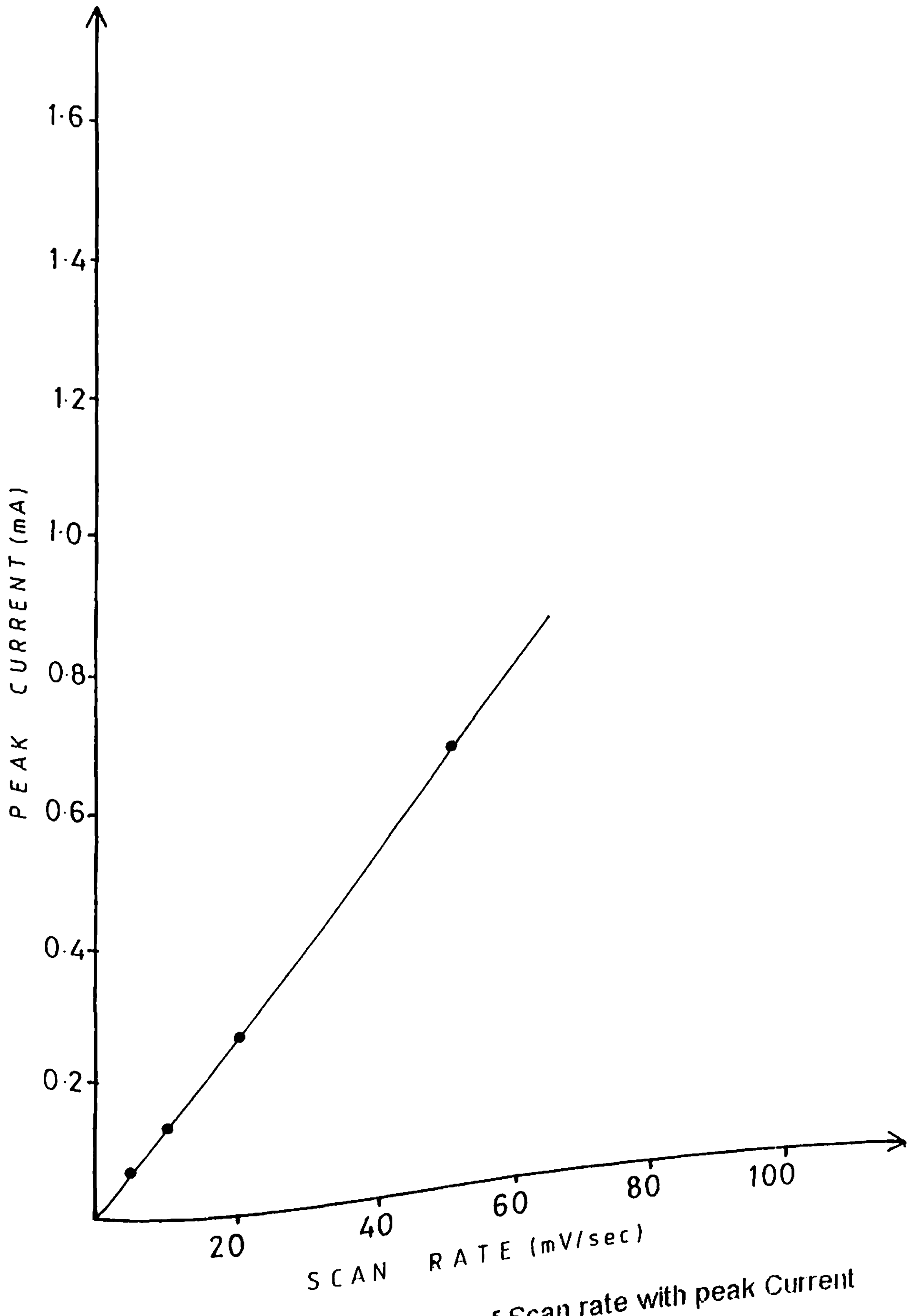
Polyaniline films were prepared by cycling the potential from -0.20 v to 0.70 v in a solution containing 0.1M aniline and 1.0M sulphuric acid. The resultant cyclic voltammogram is shown in curve A, Figure 17. The PAN oxidation and reduction peaks occur at 0.2 v and 0.04 v, respectively [93]

The PAN film(in curve A) was then transferred to a solution containing 0.01 M *P*-aminophenol and 1.0M sulphuric acid. The resulting redox waves are shown in Figure 17, curve B. The *P*-aminophenol oxidation and reduction waves both occur at 0.53 volt. Since the peak potentials for the cathodic and anodic waves are the same (ÙE$_p$=0) and scan rate dependence studies also reveal that the latter varies linearly with the peak current (see Figure 18). This suggests that we are dealing with surface waves, even though the peaks are on a sloping background which could be responsible for the apparent coincidence of the peak potentials.



ure 17.

Cyclic Voltammetric response of Polyaniline obtained in a solution (A) 0.1 M Aniline and 1.0 M Sulphuric acid and (B) 0.01 M *P*-Aminophenol and 1.0 M Sulphuric acid.



Variation of Scan rate with peak Current

Figure 18.

The oxidation peak for *P*-aminophenol has been attributed previously to a two electron process leading to the formation of a quinoneimine (QI) derivative as shown in scheme II [94]. Studies were conducted to ascertain the influence of QI on polyaniline electrochemical degradation at potentials of upto 1.0 v. Polyaniline films were transferred to solutions containing 1.0 M sulphuric acid and varying concentrations of PAP i.e.,0.01,0.02, and 0.04 M. On each occasion a freshly prepared PAN film was used. The potential was cycled from -0.2 v to 1.0 v at 20 mv/s and the resultant cyclic volt-ammograms recorded.

In all the cases, there was a decrease in the peak current with each subsequent cycle. Another fresh PAN film was prepared in a similar manner and then transferred to a solution containing only 1.0 M sulphuric acid (no PAP). The potential was then cycled between -0.2 v to 1.0 v and the resultant cyclic voltammogram recorded. A comparison of the peak currents is shown in Table 2. The successive lines correspond to peak heights measured in successive cycles.

Since the film thicknesses are not the same and also as the potential prior to oxidation can influence the first oxidation cycle (memory effect), the data for PAN and PAP (0.02 M) has been presented in the form of charge fraction, $Q_{remaining}/Q_{original}$ where, $Q_{original}$ represents the initial switching charge as shown in Table III.

TABLE III. OXIDATIVE PEAK CURRENTS (MA) OBSERVED IN VARYING CONCENTRATIONS OF PAP.

NUMBER OF CYCLES	PAN(no PAP)	PAP (0.01)	PAP (0.02)	PAP (0.04)
1	1.0	1.7	1.7	2.0
2	1.45	1.4	1.4	1.7
3	1.05	1.1	1.15	1.5
4	0.75	0.91	0.95	1.3
5	0.55	0.75	0.8	1.1
6	0.4	0.65	-	0.95
7	-	-	-	0.8

From the results shown in Table III, it is apparent that the decrease in the PAN oxidative peak current (height of peak above its apparent base) is least in case of 0.04 M PAP and greatest in the case where we have no PAP.

The results shown in Table IV also show that the fractional charge left on PAN degradation is greater in the case where *P*-aminophenol is present. It is important to mention that as the film decay approaches completion computation of the charge under the voltammogram becomes less reliable.

TABLE IV. THE CHARGE FRACTIONS FOR PAN AND PAP

NUMBER OF CYCLES	PAN	PAP (0.02)
1	0.70	0.86
2	0.57	0.63
3	0.41	-
4	0.33	0.29

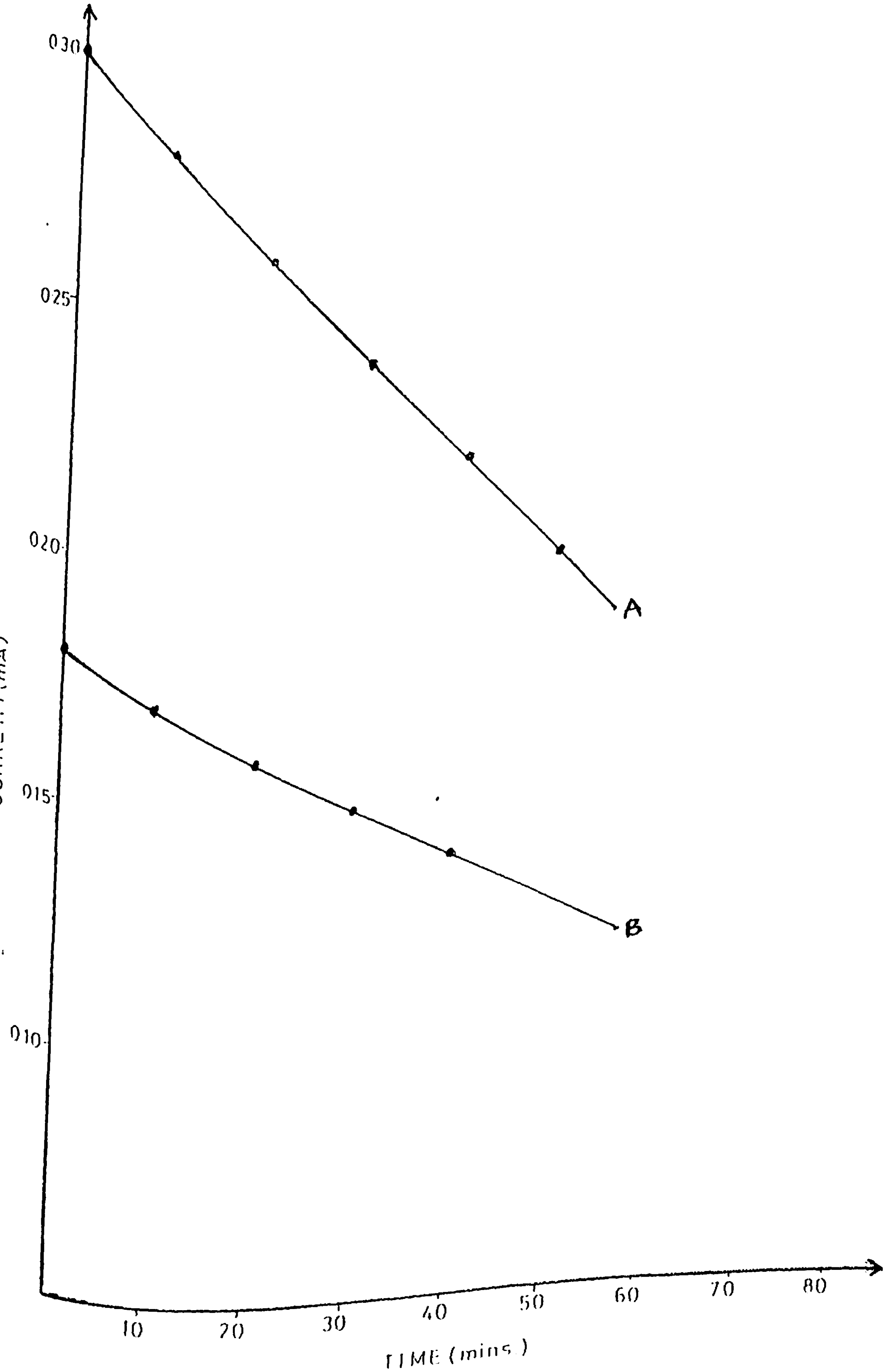
A possible explanation as to how the PAP depresses the degradation of PAN can be explained in terms of the fact that oxidation at very positive potential creates a chemical form in the polymer that is subject to irreversible degradation, even though in the presence of *P*-aminophenol, the film can relieve the "oxidative stress" by transferring the charge to PAP before the irreversible degradation occurs. For this to be achieved, the *P*-aminophenol need not be bound to the film for this effect to operate, hence any readily oxidizable substrate should show the same effect.

3.1.0 PHENOL STABILIZATION OF POLYANILINE DEGRADATION:

Polyaniline was electrodeposited on the working electrode surface by cycling the potential from -0.2 v to 0.75 v in a solution containing 0.1 M aniline and 1.0 M sulphuric acid. The polyaniline film was then transferred to a solution containing only 1.0 M sulphuric acid (no aniline monomer), and the potential cycled from -0.2 v to 0.75 v. The scan rate was 20 mV/sec. in all cases studied, there was a decrease in the oxidative and reductive peak currents with each subsequent cycle. The variation of peak current (oxidative) with time is shown in Figure 19, curve A. The electrode surface was polished and a fresh film electrodeposited as already described. The film was then transferred to a solution containing 9 mM phenol in 1.0 M sulphuric acid and the potential cycled from -0.2 v to 0.75 v at 20mv/s, and the resulting cyclic voltammogram is shown in Figure 20. The variation of oxidative peak current with time is shown in Figure 19, curve B.

It is worth noting that, the initial peak currents for film A and B are not the same even though they were grown under similar conditions, i.e film A is thicker than film B. Much emphasis was not placed on film thickness , since results obtained in our laboratory do not suggest a link between the rate of film degradation and film thickness [93]. The results depicted in Fig 19, show clearly that, the rate of decrease of the oxidative peak current is much higher in the bare polyaniline case (2 X 10^{-3} mA min^{-1}) as compared to that involving phenol (1 X 10^{-3} mA min^{-1}). Degradation of polyaniline on scanning the potential to positive end Ca. above 0.7v has been attributed by several researchers [69,86] to the formation of quinone derivatives. From the above data it's apparent that the rate of decrease of the oxidative peak current is almost half as much of that observed in the case of bare polyaniline on addition of oxidisable organic substrate phenol.

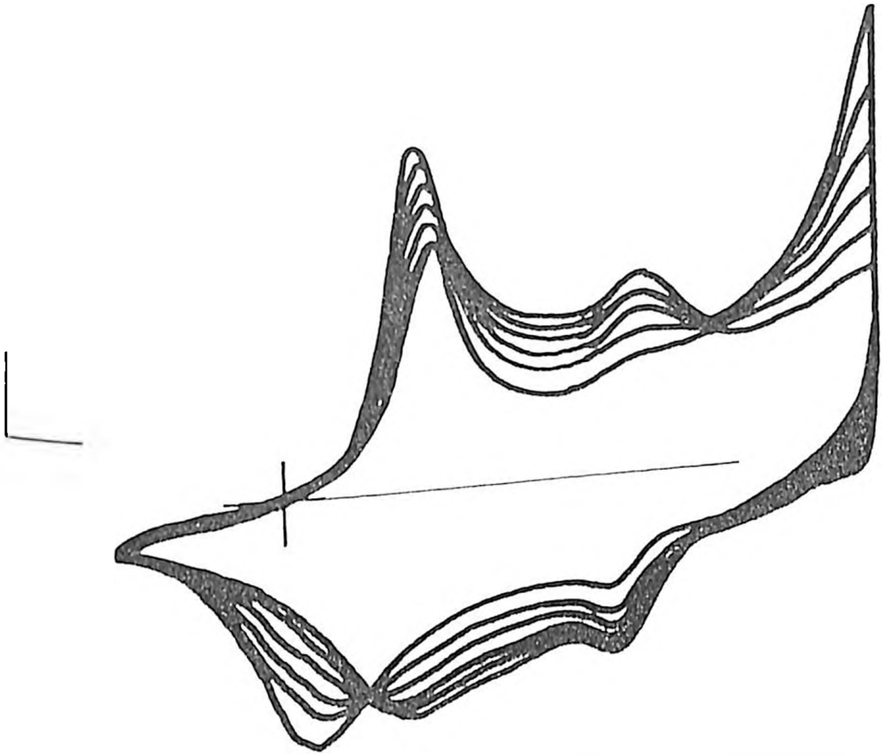
Results discussed in the previous section have shown that *P*-aminophenol also stabilises the degradation of polyaniline. It is possible that, phenol also stabilises the polyaniline film by relieving the oxidative stress on polyaniline by acting as charge sink.



ure 19.

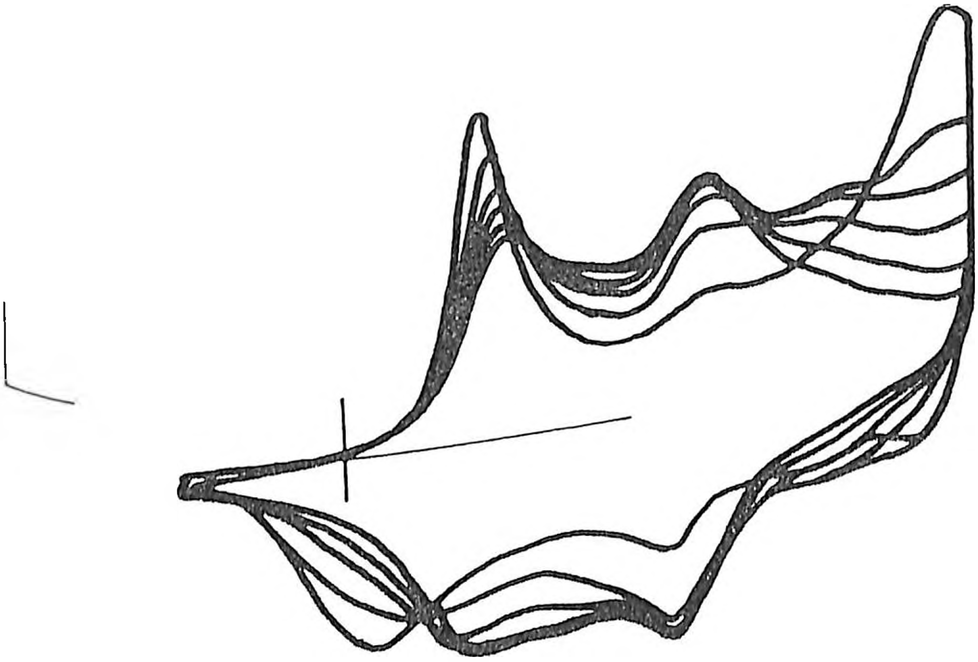
Variation of peak Current with Time for a solution containing 9 mm Phenol.

Fresh films of polyaniline were prepared as already discussed, and then degraded in solutions containing 18 mM and 27 mM phenol in 1.0 M sulphuric acid (concentration constant) and the potential cycled as described before. The resulting cyclic voltammograms are shown in Figure 21 and 22. The polyaniline film thicknesses calculation based on the assumption that a charge of 0.91 C cm^{-2} gave a thickness of 7 X 10^{-6} M[95] were 1.2 X 10^{-4} M, 1.99 X 10^{-4} M, and 1.41 X 10^{-4} M for the films used in 9 mM, 18 mM, and 27 mM phenol respectively.



gure 20.

Cyclic voltammetric response for a polyaniline coated electrode in a solution containing 9mm Phenol. Potential range -0.2v to 0.85v at a scan rate of 20mV/s.



gure 21.

Cyclic voltammetric response for a polyaniline coated electrode in a solution containing 18mm Phenol. Potential range -0.2v to 0.85v at a scan rate of 20mV/s.

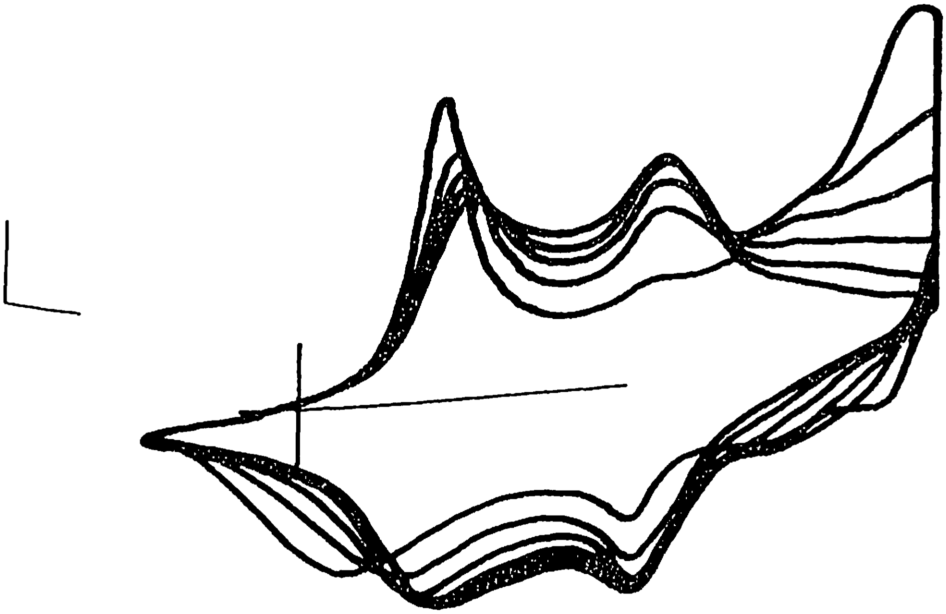


Figure 22. Cyclic voltammetric response for a polyaniline coated electrode in a solution containing 27mm Phenol. Potential range -0.2v to 0.85v at a scan rate of 20mV/s.

TABLE V: FRACTIONAL CHARGES OF A POLYANILINE FILM IN VARYING CONCENTRATIONS OF PHENOL

Cycle	9 mM phenol	18 mM phenol	27mM phenol
	Charge(X 10^{-4})		
1	5.981	9.841	6.974
2	5.904	7.915	5.134
3	2.995	6.418	4.022
4	2.096	5.562	3.423
5	1.797	4.706	2.367
6	1.069	3.679	2.353

A very significant observation from the data presented in Table V is the fact that, the fractional charge left after the first six cycles for the bare polyaniline, in 9 mM, 18 mM and 27 mM phenol, are 18%, 37%, and 34% respectively. But after the first six cycles the oxidative and reductive peak currents for mixtures containing phenol (9 mM, 18 mM and 27 mM) don't show any significant change unlike the case of bare polyaniline where the decrease in peak current, continues until when the fractional charge is less than 8%.

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3.1.1 CALCULATION OF THE PK VALUE FROM DEGRADATION DATA.

Fresh polyaniline films were electrodeposited from solutions containing 0.1 M aniline and 1.0 M sulphuric acid as already discussed. The films were then degraded by transferring them to solutions containing different sulphuric acid concentrations i.e.,no aniline monomer. The potential was cycled from -0.2 v to 0.75 v. The rate of change of oxidative peak current was then plotted as a function of acid concentration and the slope computed. The results are shown in Table VI.

TABLE VI: RATE OF CHANGE OF OXIDATIVE PEAK CURRENT (MA/MIN) VERSUS ACID CONCENTRATION $[H^{\pm}]$

Slope (mA/min)	Acid concentration Mol/L
-1.36×10^{-3}	0.1
-1.27×10^{-3}	1.0
-1.19×10^{-3}	2.0
-1.06×10^{-3}	4.0
-0.92×10^{-3}	5.0

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-1.27×10^{-3}	1.0
-1.19×10^{-3}	2.0
-1.06×10^{-3}	4.0
-0.92×10^{-3}	5.0

One obvious observation from the results depicted in Table VI is that the lowering the solution pH slows down to some extent the degradation of polyaniline. This is not suprising given the fact that as the pH is lowered the redox waves [93] which are associated with polyaniline degradation shifts to positive potentials .

The data in Table VI can be related by the equation :

$$\theta = \lambda[H^{+}]_{sol} + A \tag{14}$$

Where θ is the rate of change of peak current, $[H^{+}]_{soln}$ is the acid concentration in the external solution and A is the intercept in the plot of Q versus $[H^{+}]_{soln}$. And λ is the slope of the line. Expression (14) can be simplified by taking the logarithims of both sides of the equation leading to the following expression:

$$\text{Log}\,[H^{+}]_{soln} = \text{Log}\frac{(\theta - A)}{\lambda} \tag{15}$$

or

$$pH_{soln} = \text{Log}\left(\frac{\lambda}{\theta - A}\right) \tag{16}$$

Where pH_{soln} is the pH of the external solution.

But during the oxidation of polyaniline at very positive potentials ca. above 0.75 v, deprotonation of polyaniline nitrogens occurs as shown in Scheme II [96]. Due to the protonation/ deprotonation equilibria, the internal film pH is not the same as the external solution pH i.e., $pH_{soln} \neq pH_{PAN}$. Where pH_{soln} and pH_{PAN} represents external solution pH and pH_{PAN} the internal film pH respectively. Based on scheme III[95]; one observes that, on oxidation of the polyaniline to the imine form, we deprotonate the polyaniline nitrogens. Some of the protons will escape out of the film into the solution via the grotthus mechanism , while others will remain in the film to compensate for anionic charges resulting from anions still in the film.

Suppose p is a measure of the ratio of $[H^+]$in the film to that in the external solution, then

$$\pi[H^+]_{PAN} = [H^+]_{soln} \tag{17}$$

The value of p will range from $0 < p < 1.0$ in our case. The internal film pH will thus be given by

$$pH_{PAN} = \frac{1}{\pi} \mathrm{Log}\,(\frac{\lambda}{\theta - A}) \tag{18}$$

But by definition the pK value of an acid group MH is the negative logarithm of the equilibrium constant k(for the dissociation equilibria [97]). Therefore, the pK value for the polyaniline nitrogen will be given by:

(19)

$$pK = \frac{1}{\pi}\left[\mathrm{Log}\frac{\lambda[1-\alpha]}{\alpha[\theta-A]}\right]$$

where a is the degree of dissociation.

When a = 0.5, then

(20)

$$pK = \frac{1}{\pi}\ \mathrm{Log}\ \frac{\lambda}{\theta-A}$$

or

(21)

$$pK = \frac{1}{\pi}\ \mathrm{Log}\ |Q|$$

where

(22)

$$Q = \frac{\lambda}{\theta-A}$$

From the data expressed in Table VII; A = 1.37 X 10^{-3} mA/min and λ = 8.86 X10^{-2}. The calculated pK values for the polyaniline films in different concentrations using expression (7) are tabulated in Table VII below:

TABLE VII: POLYANILINE PK VALUES AS A FUNCTION OF EXTERNAL SOLUTION ACID CONCENTRATION.

$[H^+]$	pK (x1/p)
0.1M	3.94
1.0M	2.95
2.0M	2.70
4.0M	2.50
5.0M	2.30

If we assume an apparent pK value of 4.0 for the ionogenic group in polyaniline, similar to the value obtained for the ionogenic group -NH- in anion exchangers from pH titration curves[97], then the value of p as a function of the external solution concentration will be expressed in Table VIII.

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TABLE VIII: THE VALUE OF p AS A FUNCTION OF EXTERNAL SOLUTION CONCENTRATION FOR PK VALUE OF 4.0.

$[H^+]$	p
0.1M	0.98
1.0M	0.74
2.0M	0.68
4.0M	0.62
5.0M	0.58

Based on the previous definition of p, we observe that the internal film pH approaches that of external solution as $[H^+]$ in the external solution decreases. The continuing decrease in the value of p as $[H^+]_{soln}$ increases, suggests that $[H^+]_{PAN}$ is relatively constant. The fact that $[H^+]_{PAN}$ is significant is not suprising given the fact that the film volume is quite small.

TABLE VIII: THE VALUE OF p AS A FUNCTION OF EXTERNAL SOLUTION CONCENTRATION FOR PK VALUE OF 4.0.

$[H^+]$	p
0.1M	0.98
1.0M	0.74
2.0M	0.68
4.0M	0.62
5.0M	0.58

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3.2.0 ELECTROCHEMICAL DEGRADATION OF METALLATED POLYANILINE.

3.2.1 ELECTRODEPOSITION OF LEAD

The carbon electrode was thorougly polished as already described and dipped into a solution containing 0.1M lead nitrate and 0.1 M Potassium nitrate. The lead was electrodeposited by cycling between -0.8 v to 0.0 v at 20mv/s. The resulting cyclic voltammogram is shown in Figure 23.

The first scan gives the highest peak but subsequent scans though much reduced are at the same peak height. This suggests that, either the stripping and depositing lead at the electrode surface is at an equilibrium or that after the first deposition the electrode becomes inactive, because the lead deposits block the electrode from `seeing' the solution[98]. The absence of a nucleation loop can be attributed to the low overpotential normally associated with the electrodeposition of lead[99]. The stripping peak (anodic) at 0.47 v is symmetrical showing that the metal is easily removed.

Polyaniline was deposited on a carbon graphite working electrode by cycling the potential from -0.2v to 0.75v in a solution

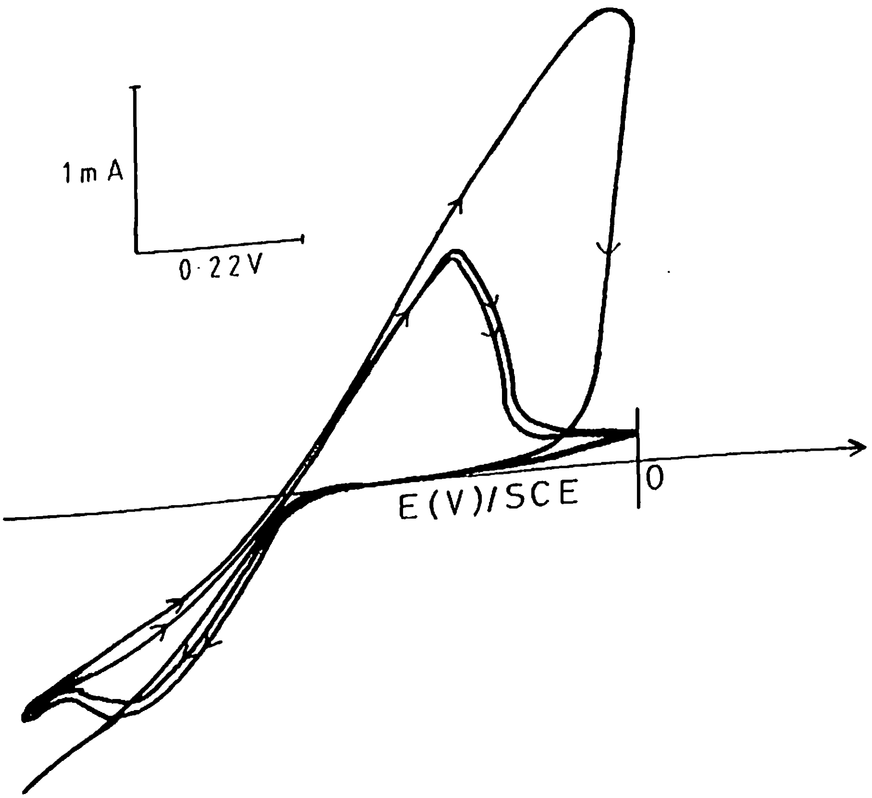

Figure 23. Cyclic voltammetric response for a bare carbon electrode in a solution containing 0.1 M Lead (II) nitrate and 0.1 M potassium Nitrate. Potential range -0.8v to 0.0v at a scan rate of 20mV/s.

containing 0.1M aniline and 1M sulphuric acid (see Figure 10). The oxidation and reduction peaks for polyaniline occurred at approximately 0.19v and 0.03v respectively. The electrochemical processes reponsible for these peaks have been discussed in detail by several researchers[71,98]. The polyaniline films used in all the analyses had the same thickness i.e., oxidative charge of approximately 3.36 X 10^{-2} Ccm^{-2},under the oxidative peak. This charge corresponds approximately to a thickness of 2.58 X10^{-7}M, based on the approximation that 0.91 Ccm^{-2} corresponds to a thickness of 7 X10^{-6}M [100]. The polyaniline modified electrode was then transferred to a solution containing 0.1M lead(II) nitrate and 0.1M potassium nitrate. The potential range was from -0.8v to 0.4v, at a scan rate of 10mv/sec (see Figure 24). The positive potential limit in this case was restricted to 0.4v to avoid degradation of polyaniline[98]. We observe commencement of lead deposition at approximately -0.52v, characterized by a large current at the cathodic limit. The large current can partly be attributed to hydrogen evolution[99]. We observe lead dissolution peak at approximately -0.1v and a polyaniline oxidation peak at 0.42v. The charges under the lead deposition/dissolution peak

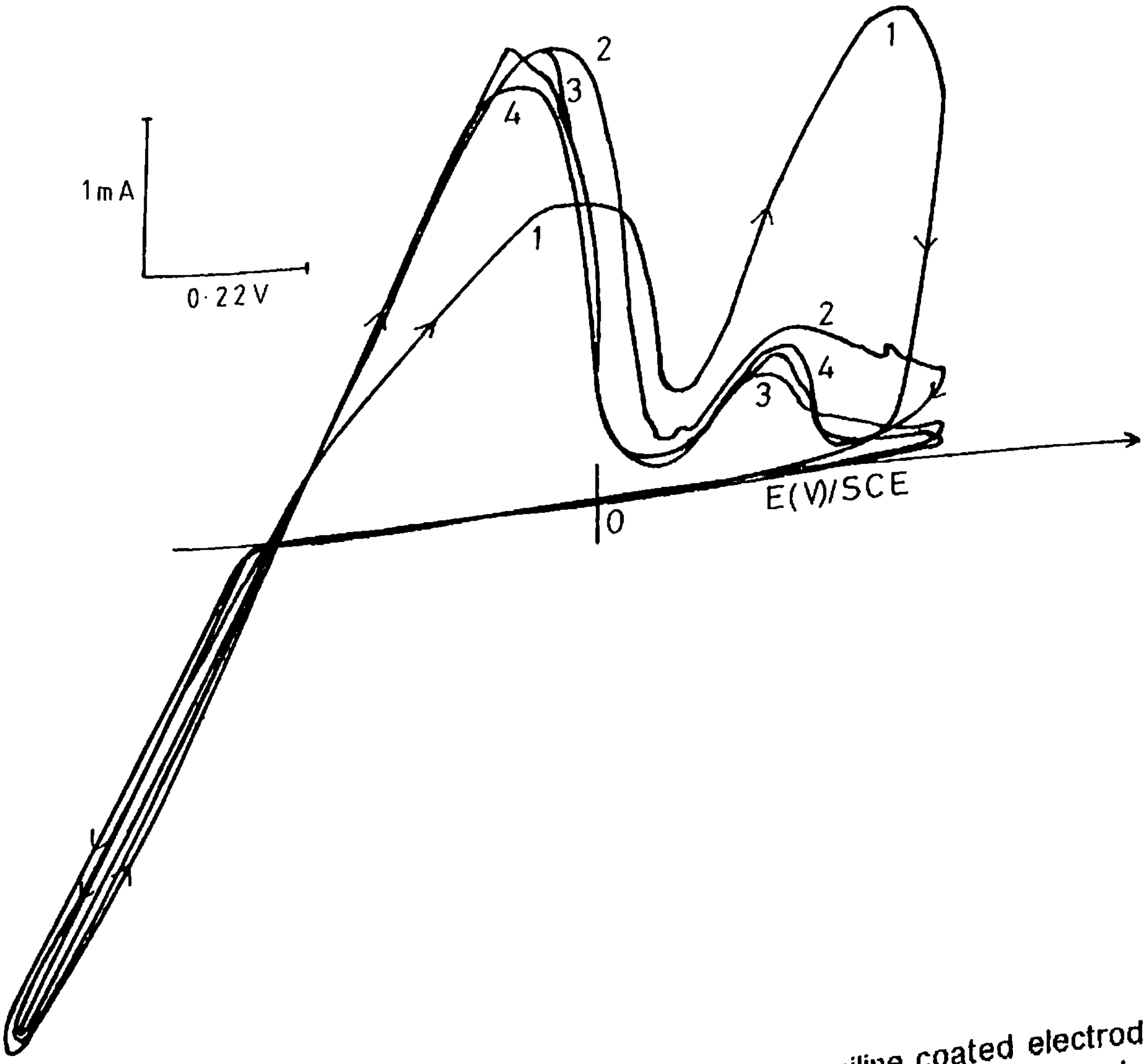

Figure 24. Cyclic voltammetric response for a Polyaniline coated electrode in a solution containing 0.1 M Lead (II) nitrate and 0.1 M potassium Nitrate. Potential range -0.8v to 0.8v at a scan rate of 10mV/s.

during the first scan are 1.85 X 10^{-7} Ccm^{-2} and 5.68 X 10^{-9} Ccm^{-2} respectively. It is apparent from the charge ratios that the dissolution of lead clearly outstrips its deposition. During the second scan the overall charge under the lead dissolution peak is 1.99 X 10^{-7} Ccm^{-2}. On subsequent scans (2nd-4th cycle), there is no substantial increase in the charge under lead dissolution/deposition peaks, suggesting a uniform deposition/dissolution process.

It is important to note that the polyaniline oxidation potential has been shifted positively by about 230 mv as compared to the unmodified polyaniline case. We also observe a decrease in the polyaniline oxidation peak on continued cycling. The decrease in the current envelope with each cycle, suggests the presence of residual lead in the polymer.

A fresh film of polaniline was electrodeposited and once again transferred into a solution similar to that discussed in figure 24. The positive potential limit was increased to 0.8v, a potential at which Polyaniline will degrade on continued cycling (see figure 25). Lead deposition commences at approximately -0.54v. We observe a large increase in current towards the cathodic limit due to hydrogen

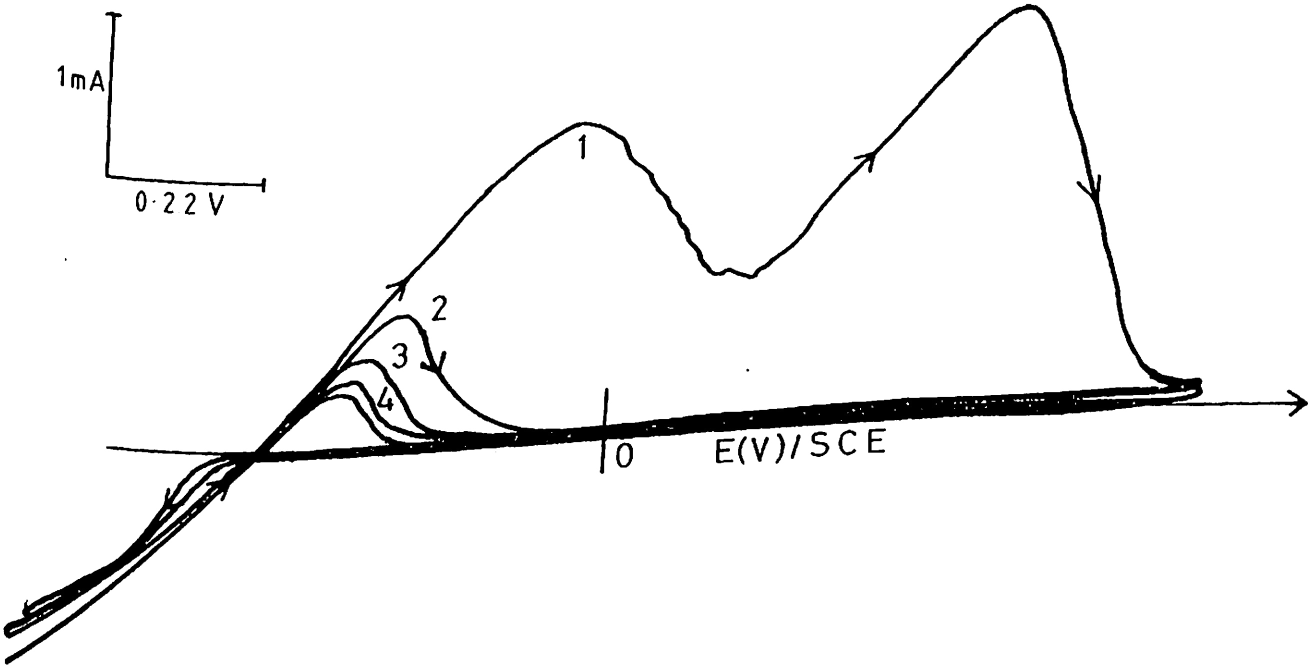

Figure 25. Cyclic voltammetric response for a Polyaniline coated electrode in a solution containing 0.1 M Lead (II) nitrate and 0.1 M potassium Nitrate. Potential range -0.8v to 0.0v at a scan rate of 10mV/s.

evolution. We observe a lead dissolution peak corresponding to a charge of 1.23 $X10^{-7}$ Ccm^{-2} at 0.1v and a broad peak in the potential region where oxidation of polyaniline occurs (at approximately 0.2v). On continous cycling the dissolution peak shifts towards negative potentials, a pointer to the fact that the electrode surface is not restored to the same state after each cycle. It is interesting to note that on subsequent scans, The polyaniline electrochemical characteristics are completely masked or absent.

Also worth noting, is the complete disappearence of the capacitative effect of the polyaniline film indicating/suggesting a possible bridging of the lead topcoat with the carbon graphite electrode by the lead deposited in the polymer matrix[93]. This probably explains why the subsequent voltammetric response approached that of lead on carbon graphite electrode. Normally in the case of unmodified polyaniline, one observes peaks attributed to quinonederivatives and also sees systematic degradation of polyaniline redox properties when the former is subjected to potentials above approximately 0.70 V[97]. In view of this, it is possible that the quinone peak is included in the broad oxidative band observed at 0.20 V and

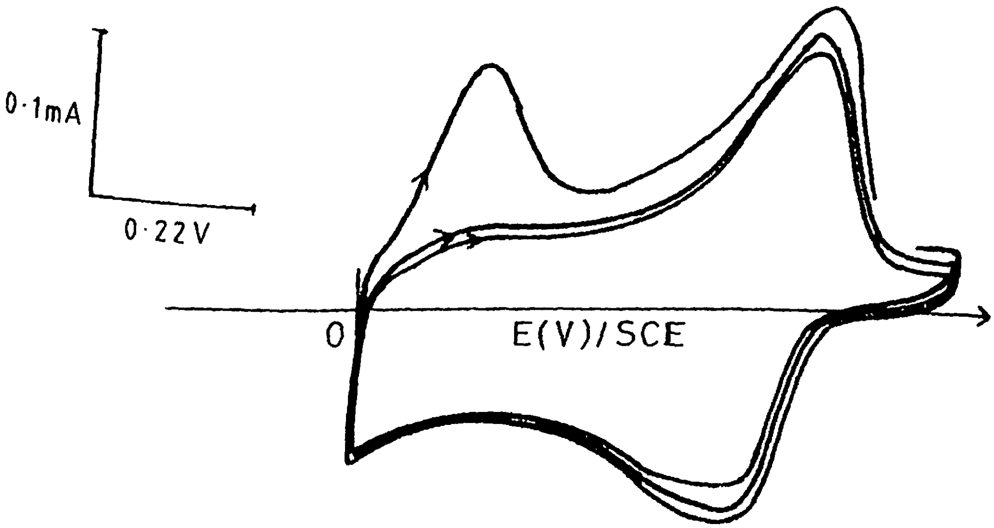

Figure 26.

Cyclic voltammetric response for a Polyaniline coated electrode in a solution containing 0.1 M Lead (II) nitrate and 0.1 M potassium Nitrate. Potential range 0.0v to 0.8v at a scan rate of 10mV/s.

its continued formation is suppressed by the lead electronegativity. To verify the latter assertion, a fresh polyaniline film was electrosynthesized and then transferred to the same solution (0.1M lead (II) nitrate and 0.1M potassium nitrate). On this occassion the potential limit did not include the range where we observe lead deposition and dissolution *i.e.,* 0.0 V to 0.8 V. The resultant cyclic voltammetric response is shown in figure 26. During the first scan, we observe polyaniline oxidation peak at 0.17 V and a quinone oxidation/reduction peak at 0.66 V / 0.55 V. Clearly this observation links lead electronegativity to the suppression quinone formation and/or electrochemical characteristics.

3.2.2 ELECTRODEPOSITION OF TIN

Tin is first electrodeposited on a bare carbon electrode from a solution of 0.1M Tin (II) chloride and 1.0m Hydrochloric acid. Voltammograms were recorded for scans between 0.0 - $^{-}$0.8 v at 20mv/s (Figure 27). Tin dissolution and deposition peaks are observed at $^{-}$0.40 v and $^{-}$0.61 v respectively with a nucleation loop[98] crossing at $^{-}$0.53 v . The stripping peak is well formed with all the scans having the same potential and peak current. For the deposition peak only the

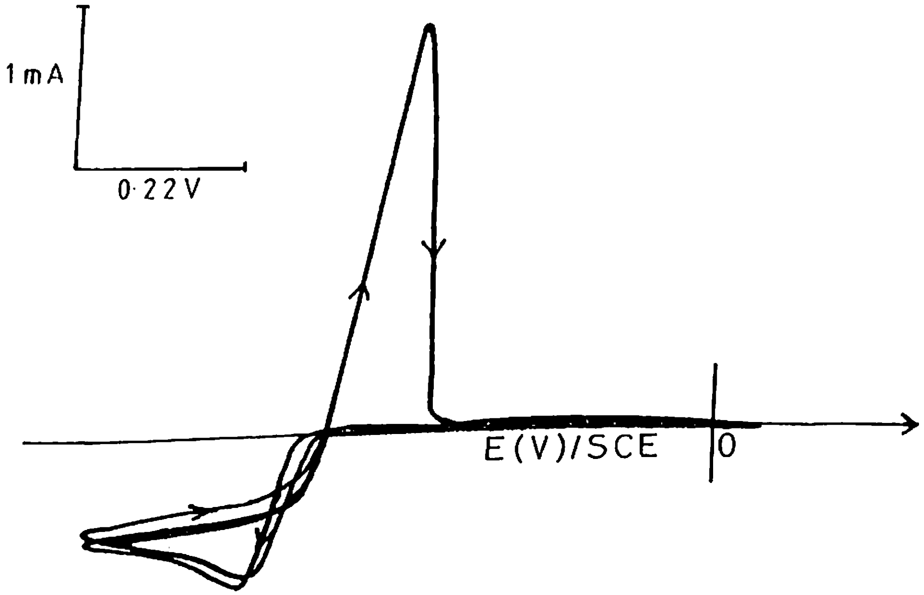

Figure 27. Cyclic voltammetric response for a bare carbon electrode in a solution containing 0.1 M Tin (II) chloride and 1.0 M Hydrochloric acid. Potential range -0.8v to 0.0v at a scan rate of 20mV/s.

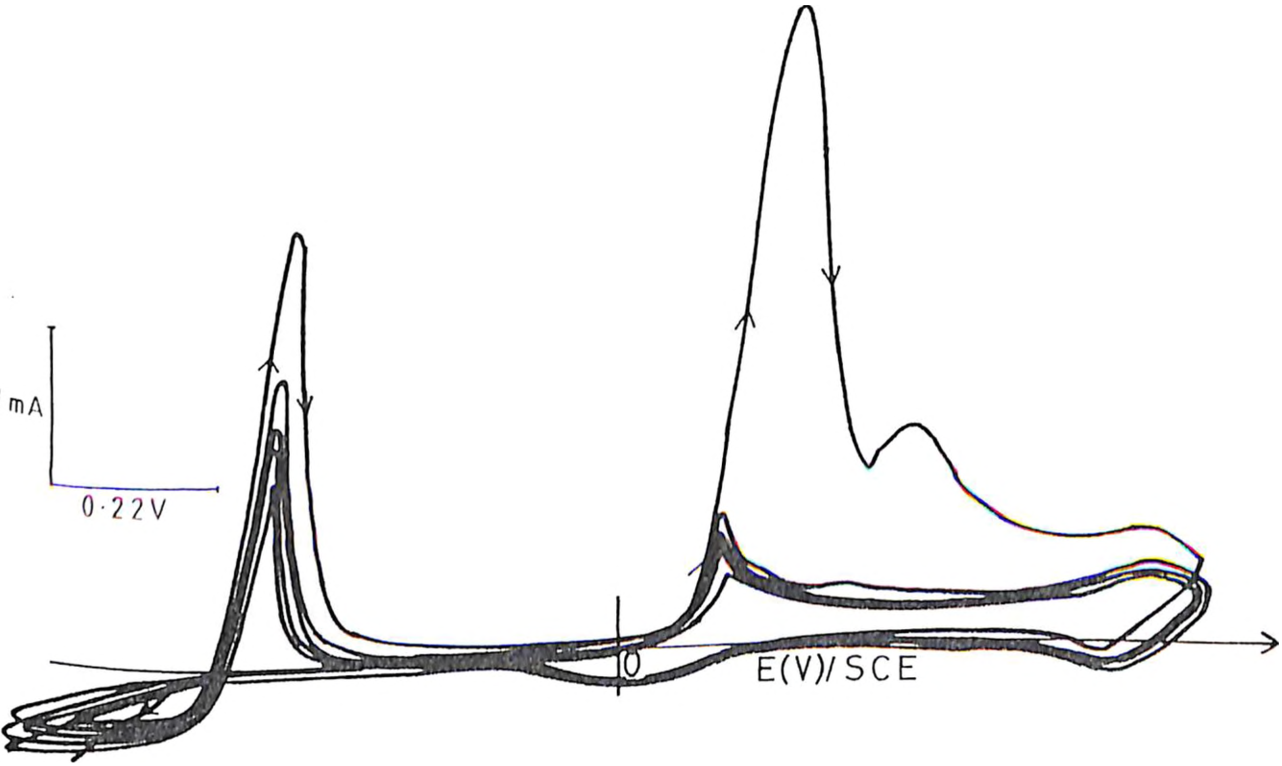

Figure 25. Cyclic voltammetric response for a Polyaniline coated electrode in a solution containing 0.1 M Tin (II) chloride and 1.0 M Hydrochloric acid. Potential range -0.8v to 0.8v at a scan rate of 20mV/s.

first scan has a higher peak current. Subsequent scans i.e 2nd to 20th are the same [98].

A fresh polyaniline film was then electrodeposited on the working electrode as already discussed. The film was then transferred to a solution containing 0.1 M Tin(II) Chloride and 1.0 M Hydrchloric acid. The potential was cycled from -0.8 v to 0.8 v. The cyclic voltammetric response is shown in Figure 28. We observe tin dissolution/deposition peaks at approximately -0.52 v/-0.64 v and a polyaniline oxidation and reduction peak at 0.22 v and 0.0 v respectively. We further observe peaks at 0.42 v, 0.74 v and 0.70 v. These peaks can be attributed to quinone derivatives[93]. One interesting aspect of this result is that,in the case of tin the latters' electrochemical activity does not suppress the formation of quinone derivatives as was the case with lead. The persistence of the capacitative effect due to the polyaniline suggests the presence of a limited amount of tin in the polymer matrix. It is also important to note the very large polyaniline oxidation peak during the first scan. This improved conductivity can only be attributed to the metal modification. It is also important to note that during the first scan

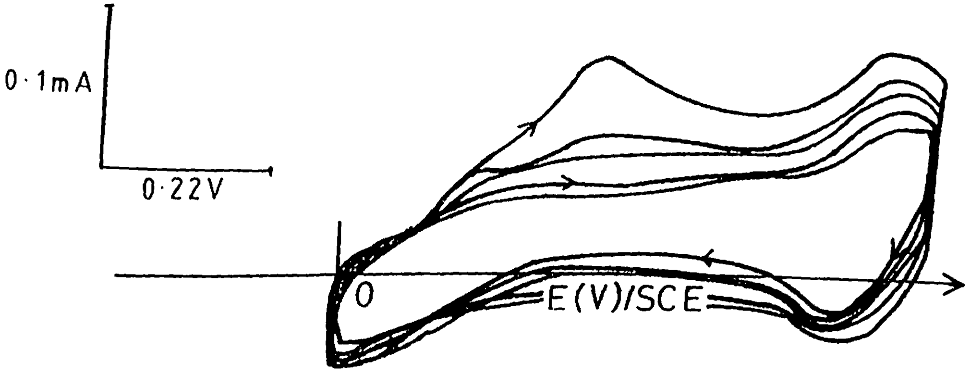

Figure 27. Cyclic voltammetric response for a Polyaniline coated electrode in a solution containing 0.1 M Tin (II) chloride and 1.0 M Hydrochloric acid. Potential range 0.0v to 0.8v at a scan rate of 20mV/s.

after holding bare polyaniline at the reduced end the peak current is usually larger than that of subsequent scans (memory effect), a phenomenon which has been attributed to the solvent population in the film [93].The very large response during the first scan cannot be attributed solely to this process.

When a fresh film of polyaniline was prepared and transferred to the same solution, and the potential cycled from 0.0 v to 0.8 v (excluding the Tin electroactive region), we no longer observe a large polyaniline oxidation peak on first scan (see figure 29). This enhances our assertion about the role of tin in relation to the polyaniline oxidation peak in Figure 28.

3.2.3 ELECTRODEPOSITION OF SILVER

A nitrate solution is used for the study of the deposition of silver. A bare carbon electrode was thoroughly polished and silver was electrodeposited by scanning in a solution containing 0.01M Silver Nitrate and 3.0M Potassium Nitrate. Scans between -0.20 v and 0.75 v were recorded as shown in Figure 30. Silver dissolution and deposition peaks occur at 0.51 v and 0.37 v respectively. The stripping peak is well formed and the deposition peak is assymetyrical with tailing. The peak current decreases after each susequent scan indicating that more silver is deposited than was dissolved.

Figure 31 and 32 show the cyclic voltammetric response for polyaniline films having oxidative charge of 3.58 X $10^{-2}Ccm^{-2}$ and 7.30 X $10^{-2}Ccm^{-2}$ respectively. The thickness of these films were thus, 7.30 X $10^{-7}M$ and 5.62 X $10^{-7}M$ respectively in both cases (i.e., for thick and thick film). The only obvious difference is that the current envelope is broader in the thick film case. It is also important to note that this current envelope due to the capacitive effect of polyaniline persists even on continuous cycling. This implies that we have very limited deposition of silver in the polyaniline matrix [98]. We also observe that the silver dissolution and deposition peak decreases on continuous cycling, probably suggesting that we are not depositing large quantities of silver and/or changing the electrode surfaces. This observation holds true for both thin and thick films.

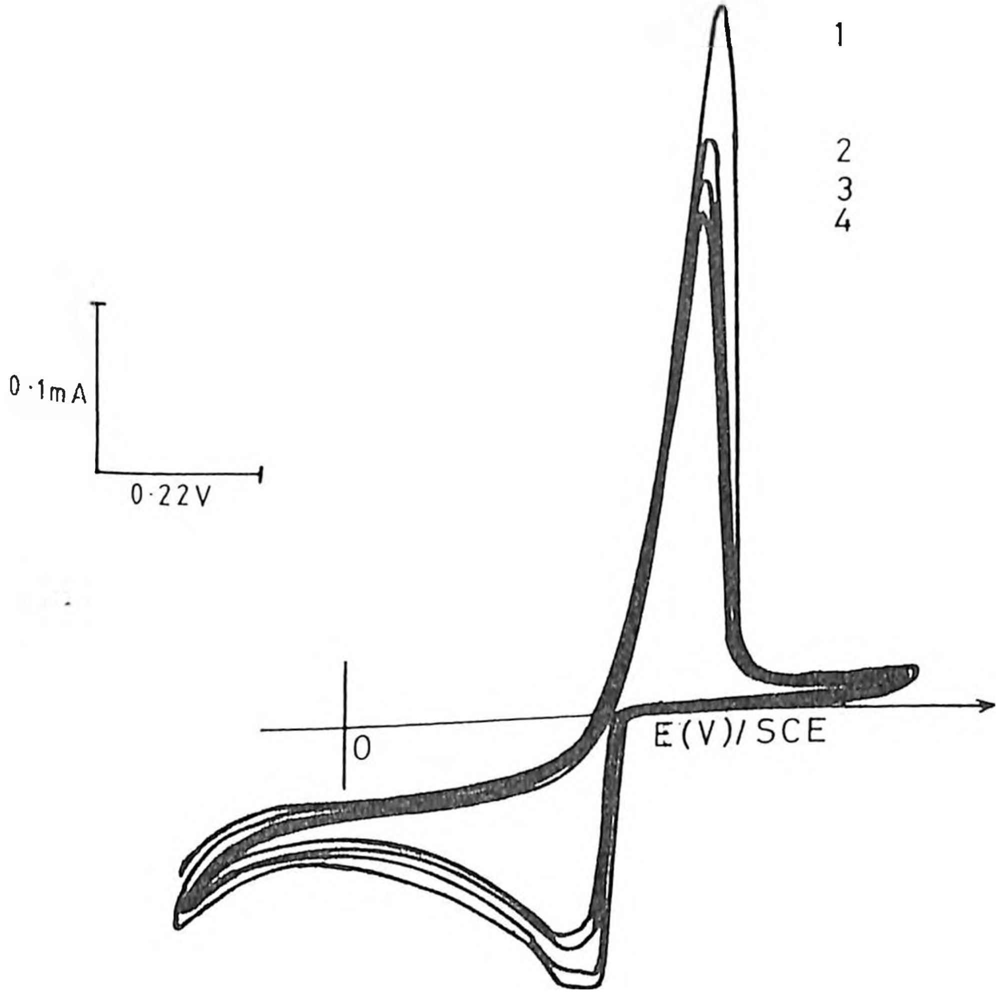

Figure 30. Cyclic voltammetric response for abare carbon electrode in a solution containing 0.01 M Silver nitrate and 3.0 M Potassium nitrate. Potential range -0.2v to 0.75v at a scan rate of 20mV/s.

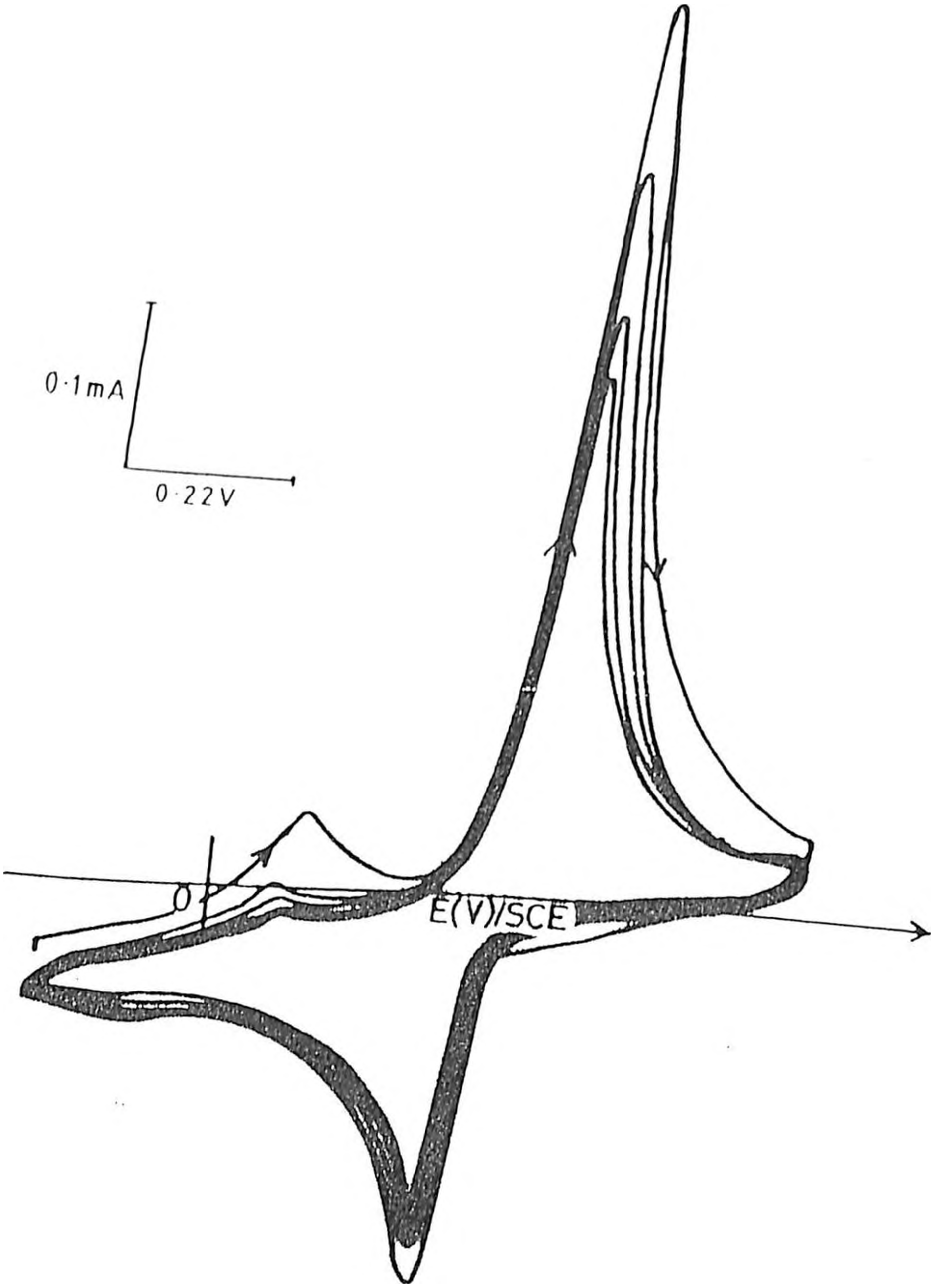

Figure 31.

Cyclic voltammetric response for Polyaniline coated electrode in a solution containing 0.01 M Silver nitrate and 0.5 M Potassium nitrate. Potential range -0.2v to 0.8v at a scan rate of 10mV/s.(THIN FILM)

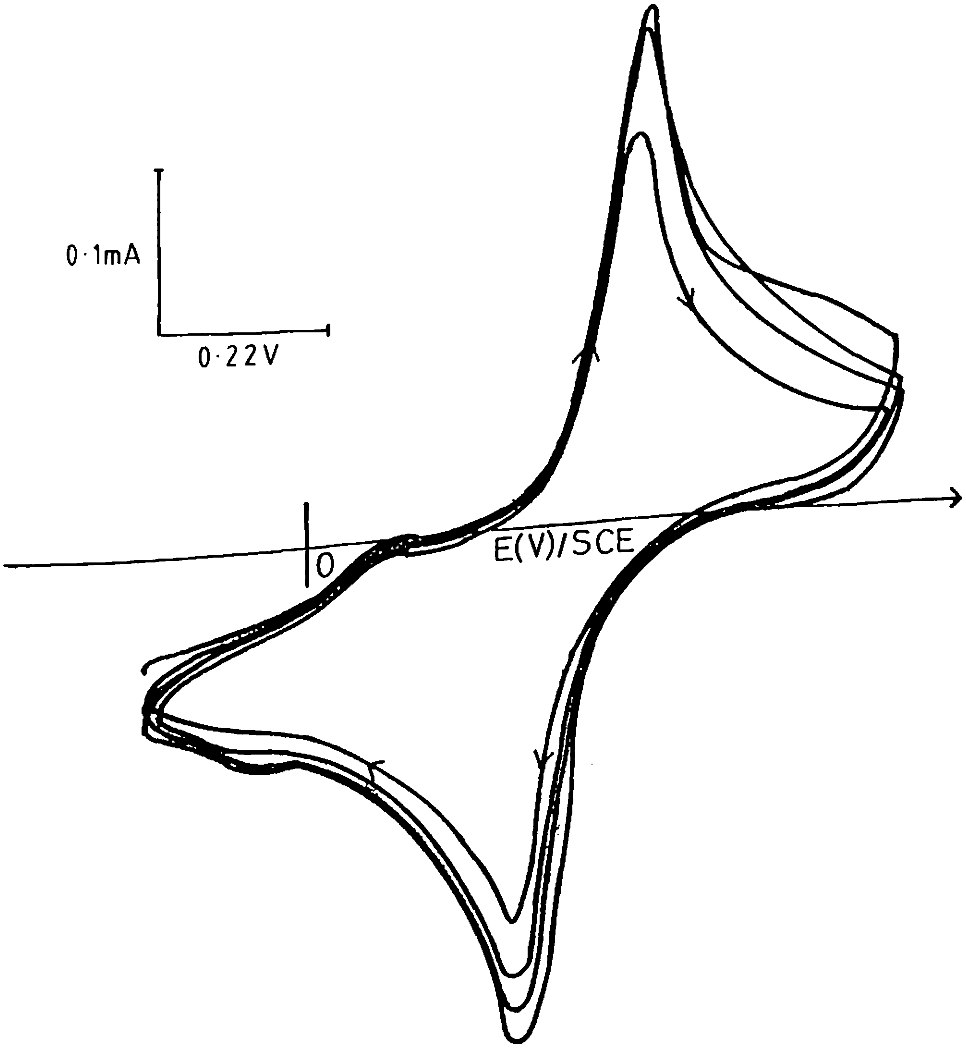

Figure 32. Cyclic voltammetric response for Polyaniline coated electrode in a solution containing 0.01 M Silver nitrate and 0.5 M Potassium nitrate. Potential range -0.2v to 0.8v at a scan rate of 10mV/s.(THICK FILM)

CHAPTER 4

4.0.0 CONCLUSIONS AND RECOMMENDATIONS.

4.1.0 CONCLUSIONS.

The results obtained suggest that there is a possibility of controlling the electrochemical degradation of Polyaniline films in the presence of P-aminophenol. This would in essence allow the use of Polyaniline at positive potentials above 0.7V.(SCE)

The results also show that readily oxidisable substrates should relieve the oxidative stress of the Polyaniline film as shown by Phenol which, stabilises it by acting as a charge sink. From the various experiments it is possible to obtain the relevant kinetic data on the degradation process which allows the determination of the order of the film reactions from the pK values.

Lead can also suppress quinone formation and hence the degradation of the Polyaniline film. Modification of the Polyaniline film with lead can thus stabilise the latter at potential s above 0.7 V(SCE). Tin, on the other hand, does not appear to suppress quinone formation, but the Tin modified Polyaniline film showed improved conductivity. Silver modified Polyaniline film does not present any new or significant characteristics from those of unmodified Polyaniline. It is apparent that the electrochemical behaviour of the unmodified Polyaniline depends on the spatial distribution of the deposited metal i.e. whether the electrode is a metal particulate composite structure, Metal /polymer/metal sandwich e.t.c..

It is therefore expected that this study will be technologically relevant to the improvement of among other things, Electrochemical Energy storage systems, as photoelectrodes, as Catalysts, in Electrochemical synthesis, to the study of the corrosion of metals and in other areas such as in the development of new types of ion sensing and reference electrodes..

4.2.0 RECOMMENDATIONS

Further work to determine a proper and complete understanding of the growth and degradation characteristics of these conducting films (e.g., the potential window at which the cyclic redox process will be more efficient), will establish an appropriate environment for the synthesis and use of such films. The structures of the metal modified Polyaniline film should be studied using XPS techniques to determine whether the electrochemical behaviour of the Polyaniline depends on the spatial distribution of the metal.

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