PRELIMINARY INVESTIGATIONS OF THE ELECTROCHEMICAL BEHAVIOUR OF A CLASS OF CONDUCTING POLYMERS

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A Thesis Presented to the
school of Graduate studies
Addis Ababa University

In partial fulfilment
of the requirements for the
Degree Master of
Science in Chemistry

By
Gezahegn Telila

June, 1994

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

PRELIMINARY INVESTIGATION OF THE ELECTROCHEMICAL BEHAVIOUR OF A CLASS OF CONDUCTING POLYMERS

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Dedicated to the memory of

my mother,

W/o GERBA WURGESSA

ACKNOWLEDGEMENT

Profound gratitude and appreciation is expressed to my research advisor Dr. Bernd Hundhammer and Dr. Theodors Solomon for their unreserved and invaluable guidance throughout this work.

I am also grateful to Dr. Hailemichael Alemu for useful comments and suggestions from which I have benefited much. I extend my thanks to Dr. Kay Rowberg, Ato Teketel Yohannes and Ato Ghirma Moges for the very useful reprints they provided me.

I would also like to thank the Department of Chemistry, Addis Ababa University, for providing me with every assistance, facilities and other wise, at all stages of the work.

Finally, I must express my thanks to Jimma Institute of Health Sciences for sponsoring me to participate in the Graduate Studies Program.

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ABSTRACT

The electrochemical polymerization of monomers of pyrrole, thiophene, and aniline on platinum and glassy carbon electrodes was carried out with dc cyclic voltammetric technique. The oxidation peak potentials for both the monomers and the polymer films in different base electrolytes were determined by using dc cyclic voltammetry. The redox reversibility of equimolar concentrations of the $[Fe(CN)_6]^{4-/3-}$ couple in 0.1 M KCl on polymer coated electrodes has been compared with that on bare platinum and glassy carbon electrodes with dc cyclic voltammetry. The polymer coated electrodes have shown wider peak separations compared to the bare electrodes. Higher or lower peak currents were observed for the redox reaction of $[Fe(CN)_6]^{4-/3-}$ systems in 0.1 M KCl depending upon the type of polymer films and the nature of base electrolytes used in the electrochemical polymerization process.

The diffusion coefficients of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ in 0.1 M KCl were evaluated on polymer coated electrodes from rotating disk electrode experiments. The results were compared with the diffusion coefficients of these electroactive species on bare platinum and glassy carbon electrodes. These results on the bare electrodes are in good agreement with literature values. Attempts have also been made to correlate the diffusion coefficients of $[Fe(CN)_6]^{4-/3-}$ systems on polymer coated electrodes with the type of polymer film and the nature of base electrolytes.

1. INTRODUCTION

During the last ten years few other areas in polymer research could have generated as much interest among such a wide variety of disciplines as that of the so-called "Conducting polymers" [1]. These materials, whilest being organic polymers, have the unusual property of possessing high electrical conductivity, and can exhibit a range of properties from semiconducting to near metallic behavior. In view of this, these materials offer the electrochemist a whole new range of potential electrode materials and a significant body of research has been built up in recent years covering many aspects of their behavior in electrochemical systems.

The synthesis of conducting polymers can be divided into two broad areas. These are electrochemical and non-electrochemical (i.e. chemical). A major advantage of the electrochemical approach over standard chemical methods include a clean, one-step production of polymeric material directly onto the electrode surface from which continuous films can be peeled off. More importantly, a wide choice of counter ions available from different electrolytes allows facile variation of polymer film properties.

This chapter is intended to briefly present a review of some of the most important undertakings on the electrochemical polymerization of pyrrole, thiophene and aniline monomers. Moreover, the electrochemical properties of these materials as coated on to the electrode surfaces will be described. Finally, the electrical conductivity behavior of the materials

as investigated by different groups of researchers will be presented.

One of the most well investigated conductive polymers is polypyrrole. Black polypyrrole was prepared for the first time in 1916 by A. Angeli and L. Alessandri [2] in the form of a powder by chemical oxidation. In 1968 it was prepared by electrochemical method [3] with platinum electrode from sulfuric acid solution. The material obtained at that time showed a conductivity of about 8 Scm^{-1}. Little further interest was shown until pyrrole was polymerized electrochemically in the form of continuous film in 1979 [4,5]. The electrical conductivity of polypyrrole film thus obtained was much higher than achieved before with a value of 100 Scm^{-1}. Since these initial reports, the electrochemical polymerization of pyrrole has become a routine matter and films have been prepared under both potentiostatic and galvanostatic conditions on a large number of substances including semiconductors and using various electrolytes [4,6,7,8].

The polymerization reaction appears to involve radicals, although several suggestions have been made as to the initiation and propagation steps involved [8,9,10]. These include a free-radical chain polymerization and a radical-radical coupling mechanism with the coupling being the rate determining step in the film formation. It has been suggested that the initiator radical could arise from the electrolyte anion rather than the monomer. However, this is unlikely at the potentials normally employed for the reaction, and it is

not consistent with the transfer of two electrons per molecule as found by Genies et al. [9]. Furthermore, cyclic voltammetry and step potential experiments [9,11] have shown that the formation of polypyrrole on the surface of the electrolyte is via a nucleation and growth mechanism.

The polypyrrole film thus formed was believed to consist of pyrrole units coupled chiefly via their 2 and 5 positions. This conclusion was based on two pieces of information. First the oxidation degradation of polypyrrole yielded pyrrole dicarboxylic acid with the carboxylic groups in the 2-and 5 positions, plus a small fraction of pyrrole derivative with an additional carboxylic group in the 3-position [12]. Secondly, 2-5 disubstituted pyrroles don't polymerize. Monosubstituted pyrroles with the substituent in 2-position produce soluble dimeric products instead of polymer films [13].

The polypyrrole film as prepared is formed in the partially oxidized (p-doped) form due to the incorporation of anions from the electrolyte, and a wide range of anions have been used to dope the material including metallic complexes [14,15]. However, no electrochemical n-doping (with cations) has been reported [16]. The films can be repeatedly cycled between the neutral and p-doped form in the range -0.8 v to +0.4 v in acetonitrile with no change in the voltammogram [10]. If the sweep is taken positive of +1.0 v Vs SCE a large, poorly defined irreversible peak occurs which corresponds to the desintegration of the film [6], although the film is stable in the cathodic region down to -2.3 V Vs. SCE. Cyclic

Voltammograms obtained for polypyrrole in both aqueous and non-aqueous systems can be complex and show a dependence on the nature of the dopant anion [6,11,17].

Polypyrrole polymerized on platinum appears to behave essentially in the same way as bare platinum electrodes with the redox chemistry of a number of species including TCNQ [18], ferrocene, phenothiazine, chloranil, benzoquinone [19], ferricyanide, hydroquinone, catechol and p-aminophenol [20]. Santhanam and O'Brien [21] have investigated the mechanism of oxidation of organic species at polypyrrole electrodes using laser interferometry and concluded that the polymer film is porous and that redox reactions involving organic species occur within the polymer matrix.

Polyanilline has been known in a variety of forms for over a century [22]. Aniline blacks and other oligomeric forms of the material have often been produced on electrode surfaces as non-conducting passivating films [23,24]. Nearly a century ago, Letheby [22] discovered that the final product of the anodic oxidation of aniline in aqueous sulfuric acid solution on a platinum electrode is a dark green precipitate. Similar results were also reported [25,26] for hydrochloric acid solutions of aniline. In 1935, a reaction scheme for anodic oxidation of aniline at a Carbon electrode was suggested [27]. No further research on this electrode reaction was carried out until Kumutov and Gorbachev re-examined it [28].

The most extensive previous investigation of anilines was by Wawzonek and Mc Intyre [29] who found that azo-benzenes were

formed upon oxidation in acetonitrile with pyridine present. Mohilner et al. [30], whose study was restricted to only aniline in strong acids, identified emeraldine-type final products. Both groups postulated the intermediate formation of 4 - aminodiphenylamine in acidic solution and Wawzonec [29] noted that pH controls the position of the cation radicals that formed in the initial electrode reaction.

Several variations of a basic reaction mechanism have been proposed [27,30,31,32,33] for the polymerization of aniline. They differ in some details but all involve the formation of radical cation intermediates from the aniline. Substituted anilines have also been electrochemically polymerized [34]. Although initially N-substituted derivatives were though to lead to non-polymeric products via a mechanism which avoids the radical intermediates and results in tail-to-tail coupling [30], successful film formation has been reported [34,35] although with no electroactivity in the latter case [35].

The polyaniline film on platinum electrode is conducting in both the anodic and cathodic regions as evidenced by the electrolysis reaction of the electrolytic aqueous solution which occurs at -1.0 V and at +1.0 V [31]. It was found that the electrical conductivity of polyaniline can be varied between the range of 10^{-3} to 10^{-2} Scm^{-1} when oxidized and between 10^{-2} to 10^{-1} Scm^{-1} when reduced.

T.Kobayashi et al. [37] have shown that polyaniline film coated electrodes had promising properties for practical application as electrochromic display devices. Recently, redox

reactions of solution species on polyaniline coated electrodes have been investigated by Noufi et al. [32] and Oyama et al. [38]. However, redox reaction of the polyaniline film itself was only briefly discussed by Diaz and Logan [31], who regarded the redox reaction of the film as a proton addition/elimination reaction based on a report by Mohilner and coworkers [31].

It has been reported that the electrochemistry of ferrocene on polyaniline coated platinum is similar to that at a platinum electrode, although the E^0 for the reaction is shifted slightly cathodic [31]. There is also some evidence that the kinetics of the ferrocene couple are faster at polyaniline coated platinum electrodes than at bare platinum [32]. In addition to these, a system has been proposed incorporating polyaniline as a sensor for redox reagents such as $Fe(CN)_6^{3-}$ [39].

The electrochemical synthesis of polythiophene was first reported in 1981 [40] using conditions similar to those employed for the polymerization of pyrrole. The electrical conductivity of the product was found to be in the range of 10^{-3} to 10^{-1} Scm^{-1}. Other workers [14,42,43,] polymerized thiophene on to platinum-coated glass to produce thin films using acetonitrile solutions containing small amounts of water and a variety of supporting electrolytes. Similar results were achieved by Kaneto et al. [44,45] using monomer solutions in oxygen-free anhydrous solvents (acetonitrile and benzonitrile) and ITO glass substrates.

In general the mechanism of polymerization for thiophene appears to be similar to that of pyrrole, occurring via radical

coupling mechanism [46]. This mainly gives α-α linkages [47,48] and involves oligomers as well as monomer radicals, with evidence to suggest that the polymerization reaction occurs at a lower potential on existing polymer than on a bare metal [10]. Potential-step experiments [49] have shown that instantaneous nucleation occurs on a bare electrode, followed by rapid formation of a polymer monolayer. As with pyrrole, the precise nature of the electrode reaction will depend on the conditions used, with the additional possibility of nucleophilic reactions between the radical cation intermediate and other species in the cell.

Polythiophene films can be electrochemically cycled from the neutral to the conducting state with little evidence of decomposition of the material up to +1.4 V Vs. SCE in acetonitrile [42,47,50]. Unlike polypyrrole, polythiophene can be both p- and n- doped, although the n-doped material has a lower conductivity [51]. Cyclic Voltammetry shows two sets of peaks corresponding to the p- and n-doped reactions with ϵ^0 values at approximately +1.1 V and -1.4 V respectively (Vs. an Ag^+/Ag electrode). This result is in good agreement with those obtained in theoretical treatment by Bredas et al. [52].

Unlike polypyrrole, polythiophene has not been widely studied as an electrode material. However, it has been shown that the redox chemistry of ferrocene is essentially the same on thiophene polymers as on platinum [48]. Waltman et al. [47] have reported the oxidation and reduction of triphenylamine at a poly (3- methyl thiophene) electrode.

2.ELECTROCHEMICAL POLYMERIZATION

2.1. Mechanisms of the Electrochemical Polymerization Processes.

Many conducting polymers can in principle be electrochemically synthesized, the main requirement being that the monomer has an oxidation potential which is accessible via a suitable solvent system. In addition to this, it should produce a radical cation which reacts more quickly with other monomers to form the polymer than it will with other nucleophiles in the electrolyte solution. If the polymeric material is to be produced in a state which has a higher conductivity, the monomer has to produce a polymer with a lower oxidation potential than that of the monomer. In general, the polymerization method is the same for all conducting polymers. The monomer is simply dissolved in a suitable solvent and a simple cell is used to anodically polymerize the materials onto the electrode surface under either potentiostatic or galvanostatic conditions.

The polymer chains consist of linked aromatic units, which in the case of pyrrole and thiophene are primarily 2,5-coupled. For these compounds, the coupling occurs at the carbon atoms which are known to be the most reactive toward addition and substitution reactions. The polymerization reaction is a very complicated one, where the general reaction

steps are as shown in the following scheme.

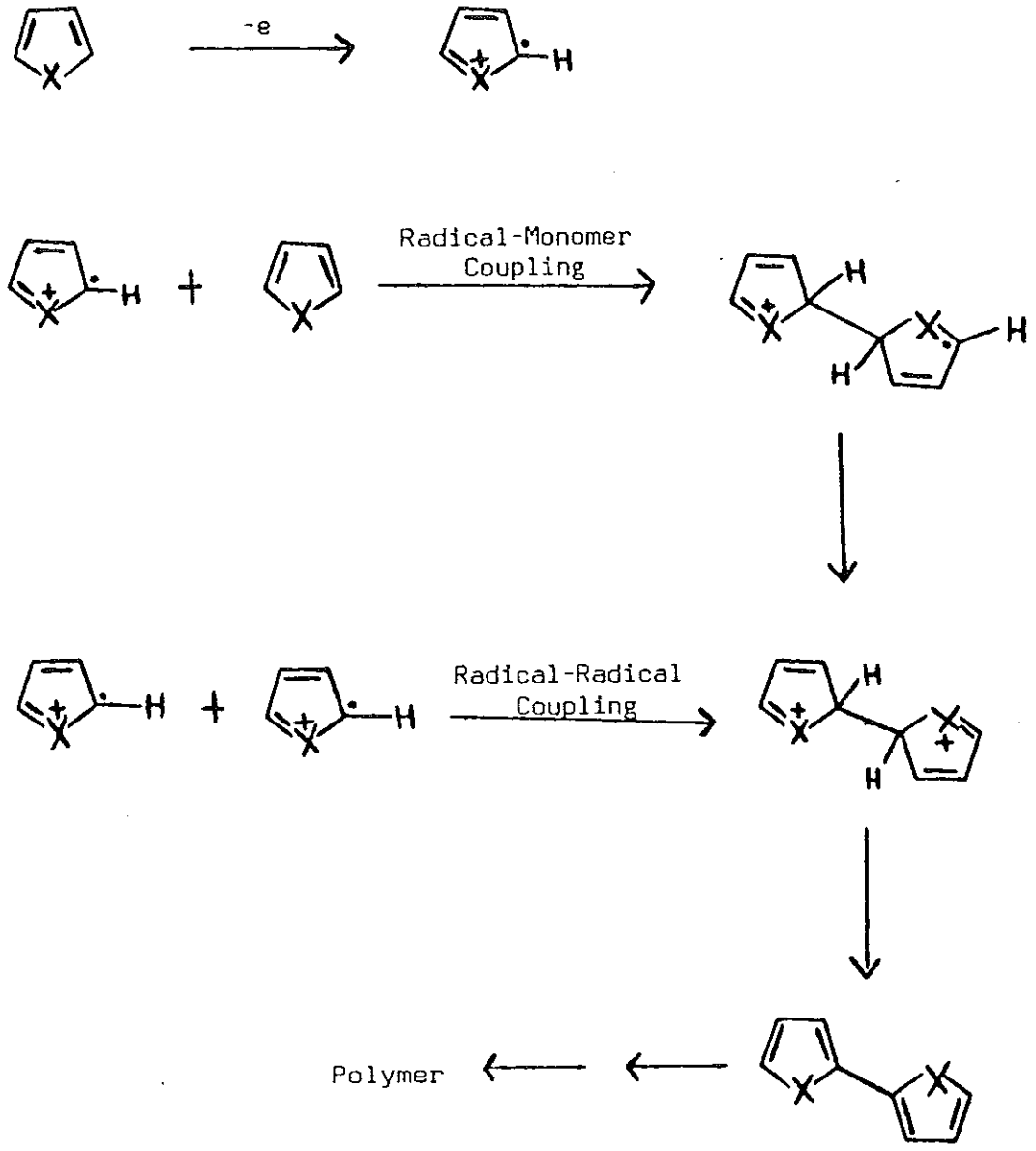


Fig. 1 A possible polymerization mechanism for pyrrole and thiophene monomers [53].

After the initial oxidation step, there is a coupling reaction followed by a deprotonation and a one-electron oxidation in order to regenerate the aromatic system. From a mechanistic point of view, there are two unique stages to the coupling reaction. There is the initial coupling reaction which involves the coupling of pyrrole monomers to produce the dimeric intermediates and there is steady-state coupling reaction, which involves the reaction between the pyrrole monomer and the oligomeric and polymeric intermediates. Considering the coupling reaction, in the initial stages of the reaction, the originally formed radical cation could undergo a radical coupling reaction with another radical to form a dimer, or it could react like an electrophile, and add to a neutral monomer.

Since the polymerization reaction proceeds only when the potential is sufficiently high to oxidize the monomer, the coupling reaction must involve the coupling of two radical cations. At these potentials, the concentration of the neutral aromatic species is zero at the electrode and negligible in region of the electrode.

In the initial stages of the reaction, the charge consumption which accompanies the rate of polymer formation is linearly dependent on time and independent of the concentration of pyrrole for a constant potential electrolysis [8,9]. Under the steady-state conditions, the coupling reaction must also occur between the radical cations of pyrrole and the radical cations of the oligomers, since the dimer, trimer and polymer

are more oxidized than the monomer [40]. Therefore, they will also be present in the oxidized state and not the neutral form during the polymerization reaction. Under steady-state conditions, the current depends on the rate of diffusion of pyrrole to the region of the electrode [9]. With regards to the subsequent aromatization reaction, the sequence of the various steps is not known.

Several variations have been proposed for the electrochemical polymerization reaction mechanism of aniline. Generally, the polymer consists of aniline units which are para-coupled with head-to tail linkages.

The infrared spectra of the oxidation product of aniline indicate that the anode precipitate is structurally similar to both emeraldine and nigraniline. The fact that the spectrum of this product is not identical in every detail with either of the chemically synthesized compounds may imply that the electrochemically produced material is not a single substance but, rather a mixture of emeraldine and nigraniline. The marked similarities in the other properties of the anode precipitate and emeraldine, in particular of the solutions in 80% acetic acid, argue strongly for the hypothesis that the anodically formed material is principally emeraldine [32,54].

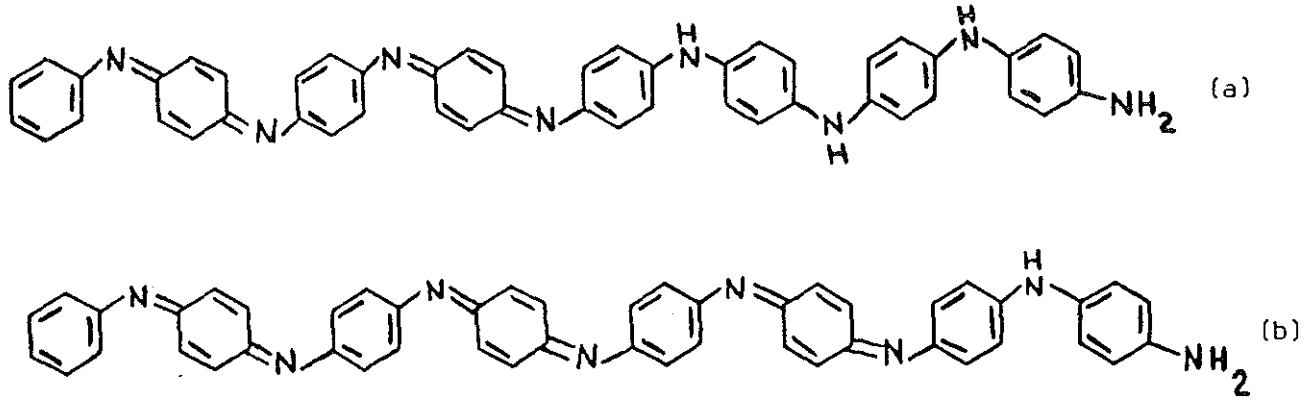


Fig. 2. Representation for the products of anodic oxidation of aniline: (a) emeraldine and (b) nigraniline.

A likely intermediate in the oxidation of aniline to emeraldine is p-aminodiphenylamine. Furthermore, emeraldine may be synthesized from this compound under the same conditions that it can be synthesized form aniline. When the electrochemical behavior of these two compounds is compared, it was found that the electrochemical oxidation of p-aminodiphenylamine give rise to a dark green precipitate which was qualitatively similar to emeraldine. Moreover, p-aminodiphenylamine was electrochemically oxidized much more easily than aniline. Thus, if p-aminodiphenylamine is one of the intermediates in the electrochemical oxidation of aniline to emeraldine, then all of the succeeding intermediates are also much more easily oxidized than aniline. This implies in the electrochemical oxidation of aniline to emeraldine, the first charge transfer step should be rate controlling [55].

Only two initial products from the first charge transfer reaction seem at all likely. These are the dipositive ion (two electron removal) or the free radical cation (one election transfer). Energetically the latter is probably more feasible and offers greater possibilities of resonance stabilization. With two electron removal and second order reaction with respect to aniline, the radical ion is the indicated intermediate. This is in marked contrast to the anodic oxidation of N,N- dimethylaniline and N-methylaniline [56], where two electrons are transferred in the rate determining step with the reaction order unity, leading to the dipositive ion intermediate. That this whole pattern is coherent is evidenced by the fact that N-methyl and N,N- dimethyl aniline lead to N-methylated benzidines (tail-to-tail coupling) upon anodic oxidation, whereas aniline gives condensation products with -NH-linkages (head-to-tail coupling).

On the basis of the foregoing facts, it is suggested that the anodic oxidation of aniline proceeds according to the steps shown in the scheme below which essentially consists of deprotonation and electron removal processes followed by the formation of chains.

2.2. Effects of Solvent and Counter ions on the Electrochemical Polymerization Process.

Recognizing that the polymerization reaction proceeds via radical cation intermediates, it became apparent that the reaction will be sensitive to the nucleophilicity of the environment in the region near the electrode surface. This then places some limitations on the choice of solvent and the electrolyte. For this reason, electrochemical studies have to be performed in aprotic solvents which are poor nucleophiles and electrolytes with high solubility and degree of dissociation as well as low nucleophilic nature.

If the nucleophilic character of the solvent is enhanced, film formation is minimized. This can be seen from the result of adding a small amount of pyridine to the acetonitrile solution containing pyrrole monomers. Films are not produced in the nucleophilic aprotic solvents such as dimethylformamide, dimethylsulfoxide, and hexamethylphosphoramide, unless the nucleophilicity of the solution is reduced by addition of the protic acid.

Electrochemical polymerization of pyrrole which was performed in aqueous media resulted in films with poor quality. They are brittle and powdery, with little physical strength and have low conductivity values. In solvents with nucleophilic character intermediate between water and the aprotic solvents, such as alcohols and mixed aqueous aprotic solvent mixtures, films can be prepared with intermediate conductivity values and

good physical strengths [57] .

The electropolymerized films of polypyrrole and poly thiophene in the conducting form contain 25-30% anion (by weight) and polythiophene contains 7-25 % anion which is affiliated with the cationically charged polymer chains [42,58]. In case of polyaniline, a maximum occupancy of one anion per two aniline units is observed [10]. The amount of anion found in each films is governed by the level of oxidation of the polymer and is a characteristic of each film. The polymer-anion compositional balance of the films actually proves to be quite useful, since the properties of the films can be conveniently altered by changing the anion. Since the anion in the film is incorporated from the electrolyte salt in the preparative solution, the modifications can be made by simply changing the electrolyte salt of the solution.

The level of oxidation is an intrinsic characteristic of the polymer and is not sensitive to the nature of the anion. The anion, however, does influence both the structural properties and electroactivity of the films. The topology of the surface is dramatically different for films containing the various perchlorate, fluorophosphate, sulfate,.....etc, anions [59]. These anions have a strong influence on the electro-activity and conductivity of the films. For instance, polypyrrole films with fluoroborate and perchlorate anions are more conducting (30-200 Scm^{-1}) than the films with the sulfonate and carboxylate anions (0.01-10 Scm^{-1}) [60].

3. CONDUCTION MECHANISM IN CONJUGATED POLYMERS.

The reactions which enhance conductivity in polymers are quite different from the well known doping processes of inorganic semiconductors. Nevertheless, the classical semiconductor terminology is commonly used in most of the papers dealing with conducting polymers. The term "p-doping" is effectively related to an oxidation reaction of the polymers, and the term " n-doping" is effectively related to a reduction reaction of the polymers.

Once the polymer is electronically charged, counter ions from solution enter the polymer fibrils to produce electrical neutrality. It is these ions which are often referred to as dopants. In semiconductors the dopant provides charge carriers. In conducting polymers the charge carriers are generated within the polymer chain. On the other hand, it is convenient to refer to the counterions in the charged polymers as dopants so this term is widely used.

Oxidation of the polymer breaks one double bond, leaving a radical and a positive charge on the polymer chain; this is the polaron. Polarons converge into dipolarons when the polaron concentration gets high enough for the polarons to " feel " each other , i.e., the radical-cation, spread out through adjacent π structure, makes contact with another radical cation. The combinations of the two radicals (one from each polaron), forms a new π bond. This π bond is more stable than the two radical-cation bonds. The result is a bipolaron which

is more stable than two polarons at the same distance apart [61].

The basic principles of the conduction mechanism in conjugated aromatic systems have been demonstrated by Yakushi, et al [51] who have recorded the optical spectra of polypyrrole (Fig. 4) at various stages of oxidation, from the as-grown highly oxidized film to the almost neutral (electrochemically reduced) film. At low levels of oxidation (lower curve, Fig. 4), there is a strong absorption maximum at 3.2 eV, associated with the interband $\pi \rightarrow \pi^*$ transition. Within the gap region there are three additional features at 0.7, 1.4 and 2.1 eV. As the level of oxidation increases, the middle 1.4 eV absorption disappears, and the interband transition weakens and shifts to higher energy. In the fully oxidized sample (upper curve, Fig. 4), two intense broad absorption bands are present at 1.0 and 2.7 eV and the interband transition appears as a shoulder at 3.6 eV.

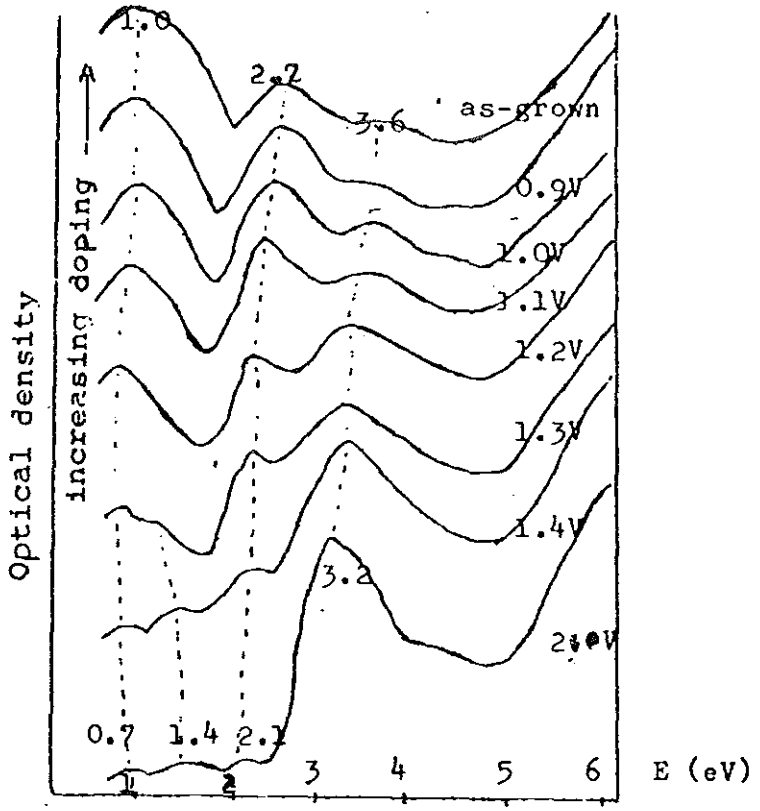


Fig.4. The optical absorption spectrum of polypyrrole as a function of doping level. The concentration of perchlorate anion increases from bottom curve (almost neutral polypyrrole) to top curve (33 mol% doping level).

In undoped state, polypyrrole has an energy gap of 3.2 eV between the conduction and valence bands. The removal of the first electron in a p-doping (oxidation) process leads to formation of a charge localized in the polypyrrole chain accompanied by a local distortion of the band. This localized charge is termed as polaron. In chemical terms it represents

The presence of a polaron on the chain introduces two localized electronic levels in the gap; a singly occupied bonding polaron state 0.49 eV above the valence band (VB) edge, and an empty antibonding polaron state 0.53 eV below the conduction band (CB) edge (Fig. 5a). The polaron states in the gap account for the three transitions observed within the gap in a very slightly oxidized polypyrrole (lower curve in Fig. 4). The first absorption peak at 0.7 ev can be related to a transition from the VB to the bonding polaron state; the peak at 1.4 eV is associated with a transition from the bonding to antibonding polaron state, and the peak at 2.1 eV corresponds to a transition from the VB to the antibonding polaron state. Exact matching of calculated transitions to peaks in the absorption spectrum should not necessarily be expected [62].

At higher oxidation levels, polaron states start interacting. Theoretical calculations indicate that two polarons, as they approach each other, become unstable with respect to the pairing of their spins and result in the formation of a doubly charged spinless bipolaron [63,64].

The above picture of polaron recombination to form bipolarons is in full agreement with ESR measurements on polypyrrole chemically doped with oxygen. An ESR signal corresponding to polarons is observed only at dopant concentrations less than 0.55%. The intensity of that signal then falls indicating that the spins pair above about 1%.

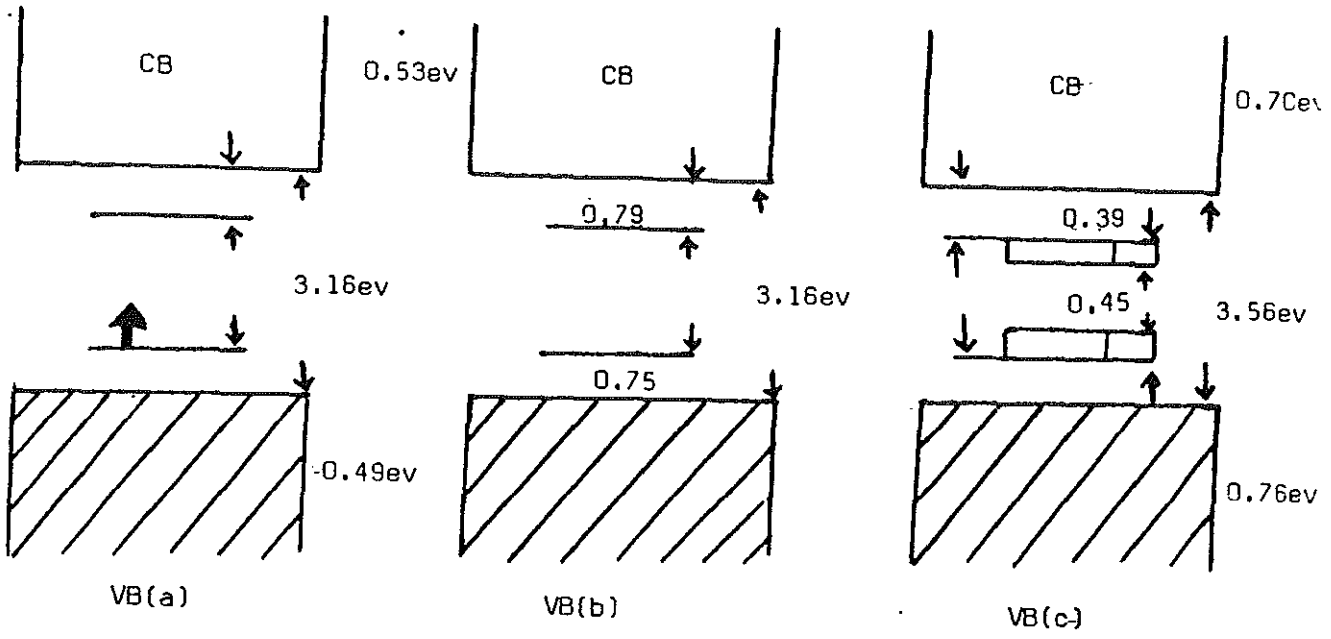


Fig. 5. Electronic structure diagrams for polypyrrole chain containing (a) polaron (b) bipolaron and (c) highly oxidized (33 mol% doping level) polypyrrole showing the presence of two broad bipolaron bands in the gap.

A bipolaron introduces two states in the gap, at 0.75 eV above the VB edge and 0.79 eV below the CB edge (Fig. 5). Very importantly the bipolaron bonding state, in contrast to the polaron case, is empty. As a result, only two transitions within the gap are now possible. Thus the emptying of the bonding states in the gap accounts for the loss of the middle 1.4 eV absorption peak when going from slightly oxidized to highly oxidized polypyrrole.

4. EXPERIMENTAL

4.1 Chemicals and Preparation of Reagents.

Acetone (Fluka), N-propanol (Riedel-de Haën), Acetonitrile (Fluka), Tetrabutylammonium perchlorate, $TBAClO_4$ (Ventron), Tetrabutylammonium chloride, TBACl (Fluka), Lithiumhexafluoro -phosphate, LiHFP (Aldrich), Tetraethylammonium chloride, TEACl (BDH), Potassium tetrafluoroborate, KTFB (Riedel-de Haën), H_2SO_4 (BDH), KCl (analar, BDH), $K_4[Fe(CN)_6]$ (Riedel-de Haën), and $K_3[Fe(CN)_6]$ (Merck's), were used as such without further purification. Pyrrole (Aldrich), Aniline (Aldrich), and Thiophene (Aldrich) were distilled under reduced pressure to colorless liquids. All aqueous solutions were prepared with doubly distilled water.

Tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared by mixing an aqueous solution of lithium hexafluorophosphate with a solution of tetrabutylammonium chloride in acetone. The white precipitate, tetrabutylammonium hexafluorophosphate was recrystallized twice from N-propanol. The crystal was vacuum dried at 60°C. The melting point of the crystal was found to be 244-245°C. Tetraethylammonium tetrafluoroborate (TEATFB) was prepared by mixing an aqueous solution of tetraethylammonium chloride with an aqueous solution of sodium tetrafluoroborate. The white precipitate (TEATFB) was recrystallized twice from acetone. The crystal was vacuum dried at 50°c.

reference and auxiliary electrode respectively. Prior to each experimental series the platinum and glassy carbon electrode surface was pretreated by mechanical polishing with a small quantity of aluminiumoxide powder on a polishing cloth and rinsed with plenty of distilled water. The platinum wire was soaked in chromic-sulfuric acid cleaning solution and rinsed with plenty of distilled water. The solution in the electrochemical cell was deoxygenated by purging with nitrogen gas before each experiment and N_2 was allowed to flow over the solution during the experiment.

4.3 Electronic Set-up

The block diagram of the electronic set-up used for the dc cyclic and rotating disk electrode voltammetry is shown in Figure 7.

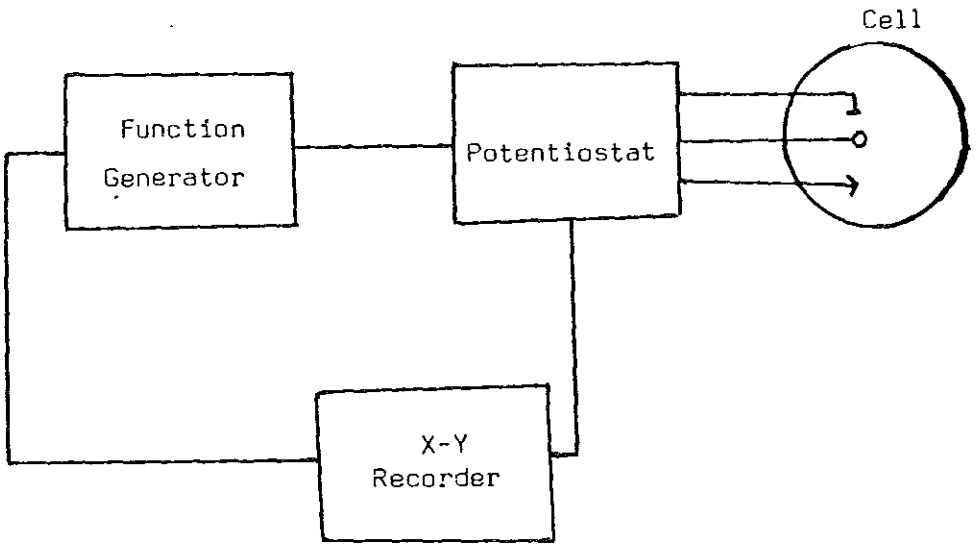


Fig. 7. Block diagram of the electronic set-up. Electrode designation: O working, ├ auxiliary, ← reference.

The set-up consisted of a Wenking VSG 83 scan generator and a PAR model 363 potentiostat /Galvanostat. The voltammograms were observed using an xy-recorder (Phillips Model PM 8041). The rotating disk electrode (Metrohm 628) consisted of a rotation speed control unit and interchangeable tips (Pt, GC).

5. RESULTS AND DISCUSSION

5.1 Determination of the Oxidation Potentials for Pyrrole, Thiopene, and Aniline Monomers as well as of the Corresponding Polymer Films in Different Base Electrolytes.

In these studies, the electrochemical polymerization of pyrrole, thiophene, and aniline have been investigated at a sweep rate of 10 mVs^{-1} using dc cyclic voltammetric technique. Prior to each experiment, the potential of the working electrode was cycled within a given range to determine the working potential range of the base electrolyte and solvent used. The oxidation peak potentials of the monomers and of the polymer films coated on the electrode surface were determined by cycling the potential within a limited range. All the potentials reported are with reference to the saturated calomel electrode (SCE).

In the cyclic voltammetery, the potential of the working electrode was changed linearly with time starting from a potential where no electrode reaction occurs and moving to potentials where reduction or oxidation of a solute occur. After traversing the potential region in which one or more electrode reactions take place, the direction of the linear sweep was reversed and the electrode reactions of intermidates and products formed during the forward and reverse scans have

been detected.

From an analytical point of view, the location of the peak potentials can be used in the qualitative identification of the electroactive species while the peak currents can be used in its quantitative determination.

Figure 8 shows the cyclic voltammogram for the electrochemical polymerization of 10 mM pyrrole with 0.1 M $TBAClO_4$ in acetonitrile containing 1% water on platinum electrode. The potential was cycled between 0.25 and 1.2V. Polypyrrole formation started at 0.8V and an anodic peak potential (E_{pa}) was observed at 1.14 V. As the number of cycles was increased, the intensities of the peak currents decreased showing that oxidation of pyrrole is an irreversible process. The potential sweep was not taken to a further anodic value to avoid oxidative degradation of the polymer film as suggested by A.F Diaz et al [6]. Previous studies [7,12] revealed that cyclic voltammograms of solutions of the pyrrole monomers show a dependence on the anion present in the electrolyte. Such voltammograms can show anodic peaks between 1.0 and 1.3V in acetonitrile whereas in aqueous solutions Epa values ranging from 0.8 to 1.1 V could be obtained.

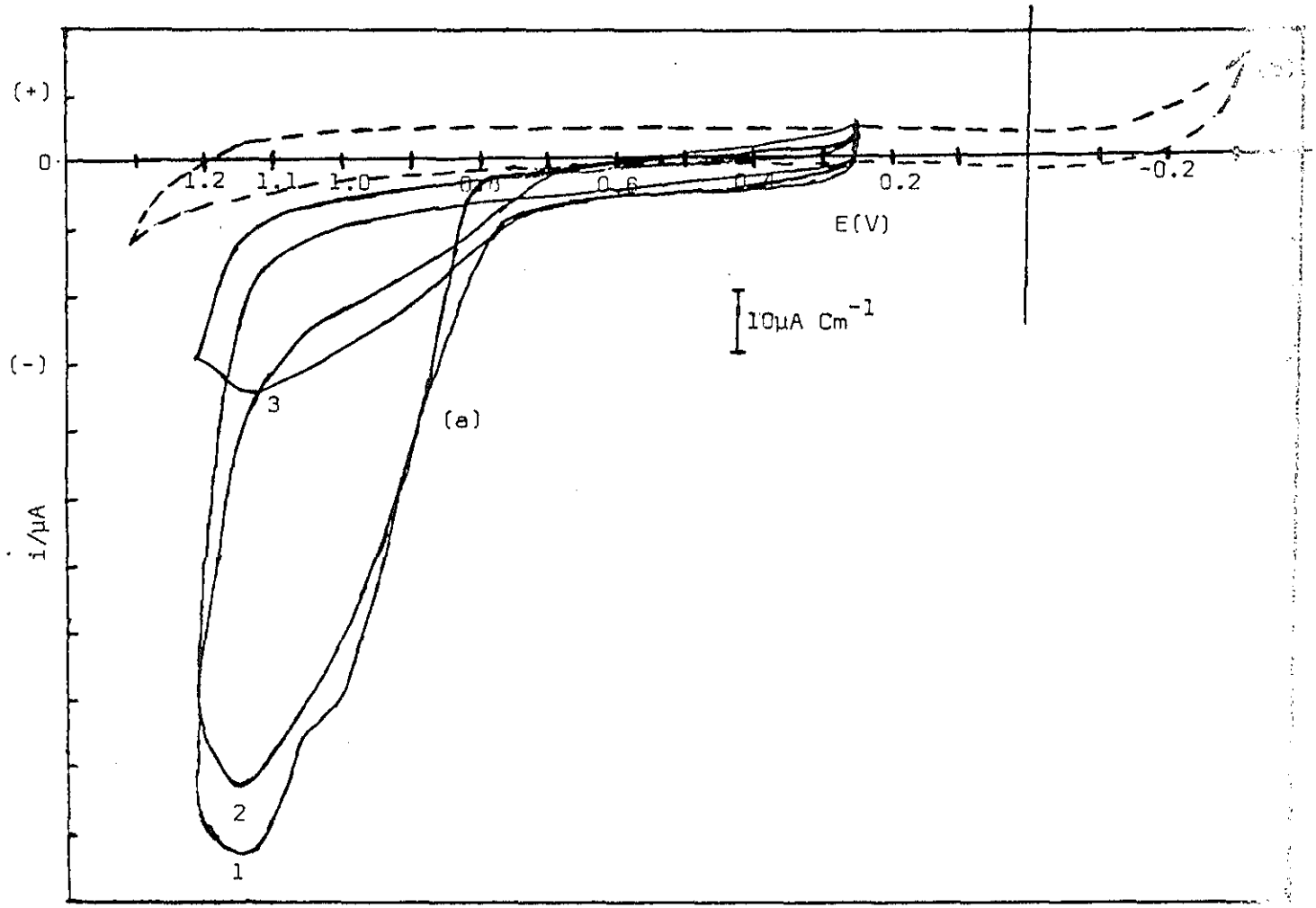


Fig. 8. Cyclic Voltammogram of 10 mM pyrole with 0.1 M TBAPCl in acetonitrile containing 1% H_2O on platinum electrode at a scan rate of 10 mVs^{-1}.

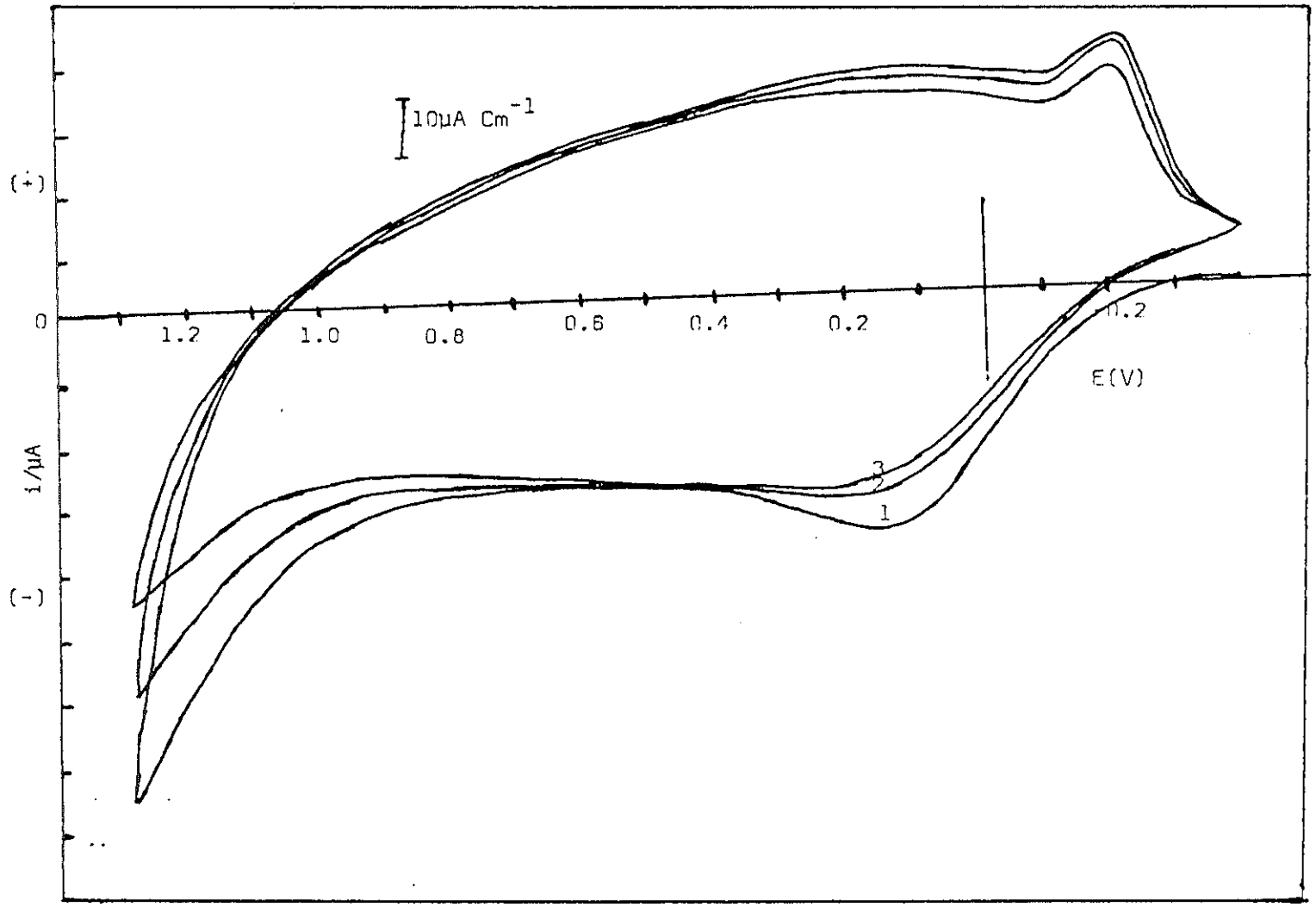


Fig. 9. Cyclic Voltammogram of polypyrrole [ClO_4^-] coated on platinum in 0.1 M TBAPCl4 in acetonitrile containing 1% H_2O at a scan rate of 10 mVs^{-1}.

Figure 9 indicates the cyclic voltammogram for polypyrrole film coated on platinum electrode with 0.1 M $TBAClO_4$ in acetonitrile containing 1% water. The potential was cycled between -0.4 and 1.3V. The voltammogram shows a sharp peak at -0.22 V and a broad peak appearing at 0.16V for the reduction and oxidation of the electroactive polypyrrole film respectively. A. F. Diaz et al [6] have obtained peak potentials for oxidation of polypyrrole in different base electrolytes ranging from -0.16 to 0.1V and reduction potentials from -0.325 to -0.195V in acetonitrile. From the peak shapes and peak separations, it is clear that the redox reaction of polypyrrole deviates from a strictly Nernstian behavior.

For a simple reversible one electron system with no chemical complications, the two peaks should be separated by 59 mV as indicated by the following equation [65].

$$E_{pa} - E_{pc} = \frac{0.059V}{n} \qquad (1)$$

The non-Nernstian behavior observed for the redox reaction of polypyrrole is believed to be partly due to the slow ion mobility in the polymer film and also partially due to repulsive interactions between the electroactive sites and/or the electrochemical non-equivalence of the sites in the polymer film [6]. In addition to these, oxidation - reduction of the polymer film involves the doping - undoping process. In such

cases when the potential is taken to positive value, anions from the electrolyte enter the polymer matrix and interact with the positive charges located on the polymer chains. On the other hand, when the potential is made more negative, the anions will be repelled out of the polymer matrix and the polymer chains assume electrical neutrality. Such a process is complicated and the resulting voltammogram is not expected to be Nernstian.

Figures 10 and 11 depict the cyclic voltammograms of the anodic oxidation of 0.2 M thiophene with 0.02 M TBAHFP in acetonitrile containing 1% water and of polythiophene film coated on glassy carbon in the same base electrolyte respectively. The solution containing thiophene monomer was cycled between 0.0 V and 2.25 V. The oxidation of thiophene was observed to commence at 0.6 V and the anodic peak observed at 1.32 V. In addition to this, a cathodic peak was observed at 0.4 V which corresponds to the reduction of the polymer film. F.J. Waltman et al [66] have found cyclic voltammogram of 8.9 -23 μ mol cm^{-3} thiophene in 0.1 M TEAFB/CH_3CN with a sweep rate of 50 mVs^{-1} with peak potential of 2.06 V for oxidation of the monomer and 0.96 V for oxidation of the polymer film in the same electrolyte.

Unlike polypyrrole formation, as the number of cycles increases the intensities of peak currents increase showing that the polymer film may catalyze further oxidation of thiophene monomers on the electrode. The peak potentials are

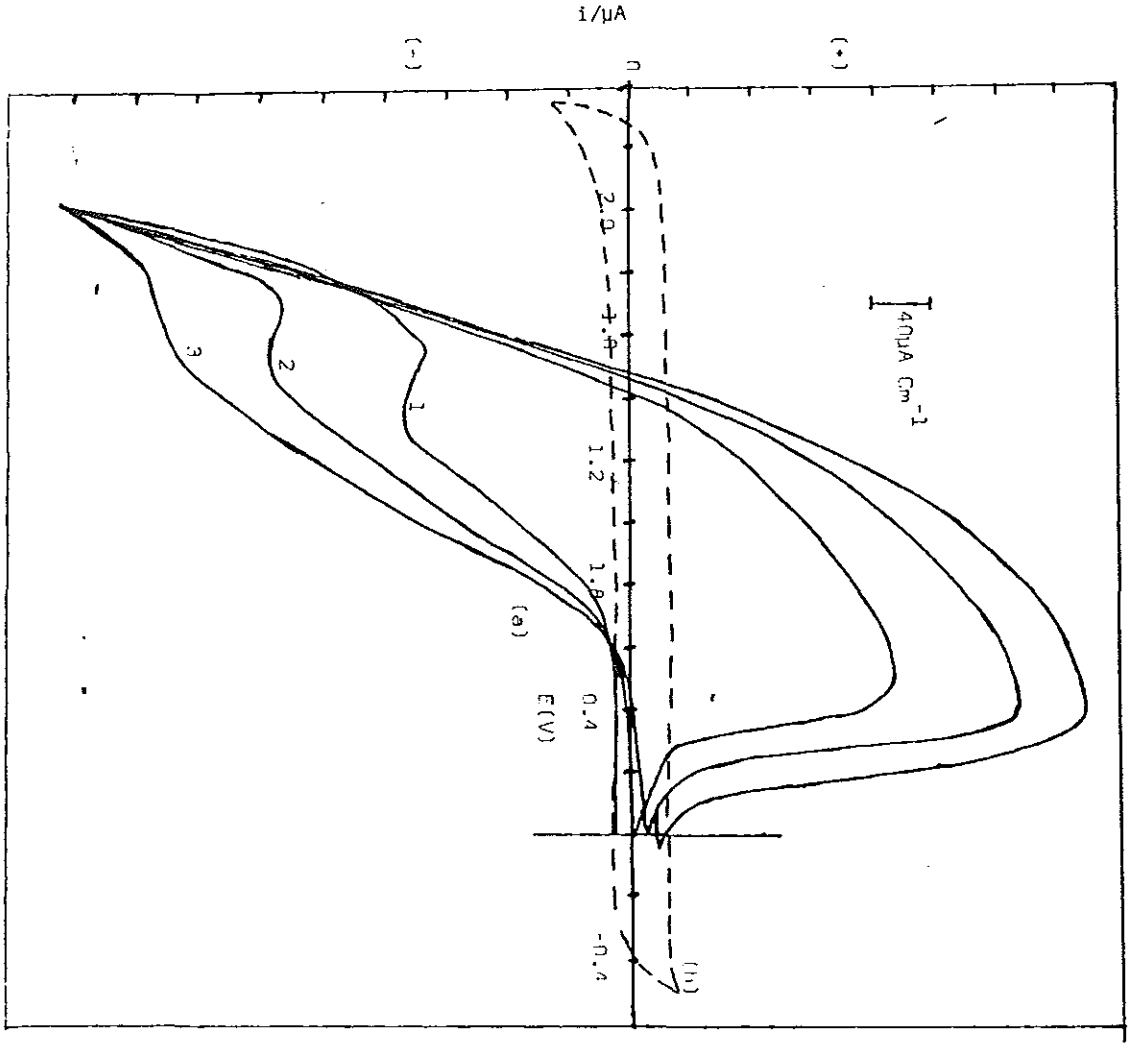


Fig. 10. Cyclic Voltammogram of 0.2 M thiophene with 0.02 M TBAHFP in acetonitrile containing 1% H_2O on glassy carbon electrode at a scan rate of 10 mVs^{-1}.

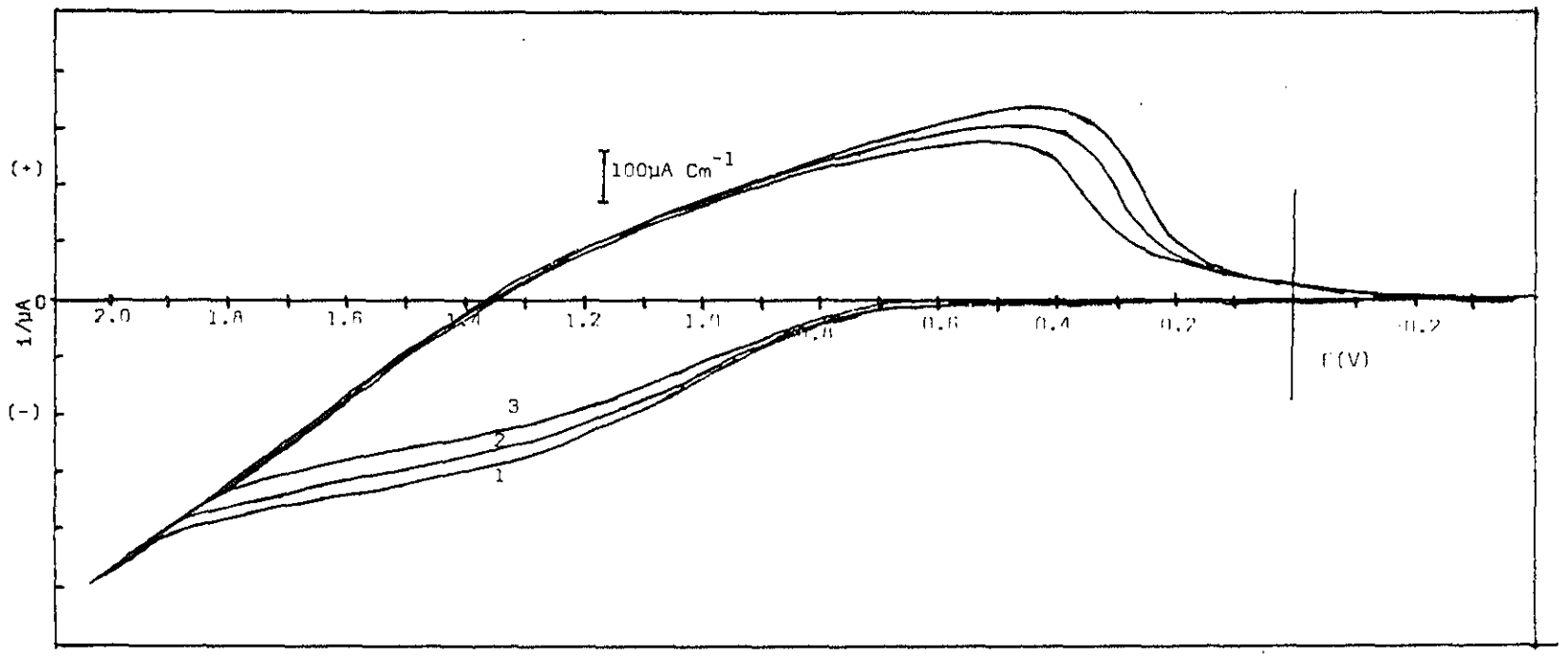


Fig. 11. Cyclic voltammogram of polythiophene [pF^-_6] coated on glassy carbon in 0.02 M TBAHFP in acetonitrile containing 1% H_2O at a scan rate of 10 mVs^{-1}.

also observed to shift to more anodic value as the number of cycles increases.

The polythiophene film thus formed was cycled between -0.4 and 2.1 V in 0.02 M TBAHFP in acetonitrile containing 1% water. Peak potentials are observed at 0.82 and 0.47 V which can be related to the oxidation and reduction of the film respectively.

Electrochemical polymerization of thiophene in solutions of $TBAClO_4$ and TEATFB in acetonitrile was not successful since the reaction require different conditions [67,68]. Thiophene is insoluble in aqueous solution of 0.1 M H_2 SO_4 and hence forms an emulsion which does not polymerize electrochemically.

The electrochemical polymerization of 0.1 M aniline with 0.1 M H_2SO_4 in water on platinum electrode is shown in the voltammogram of figure 12. The potential was cycled between 0.2 and 1.0 V. During the first cycle, only one anodic peak was observed at around 0.85 v which corresponds to the oxidation of aniline monomers. On the succeeding cycles, four significant anodic peaks are observed at 0.18, 0.47, 0.54 and 0.72 V. E.M Genies and C.Tsintavis [69] have reported that electrodeposition of polyaniline in aqueous solution of 0.1 M H_2SO_4 (PH=1) and 0.5 M Na_2SO_4 on platinum electrode at a sweep rate of 50 mVs^{-1} shows oxidation peak of aniline between 0.9 and 1.0 V from the first cycle which ranges form - 0.1 to 1.4 V. The succeeding cycles give three anodic peaks at 0.25,0.5 and 0.7 V.

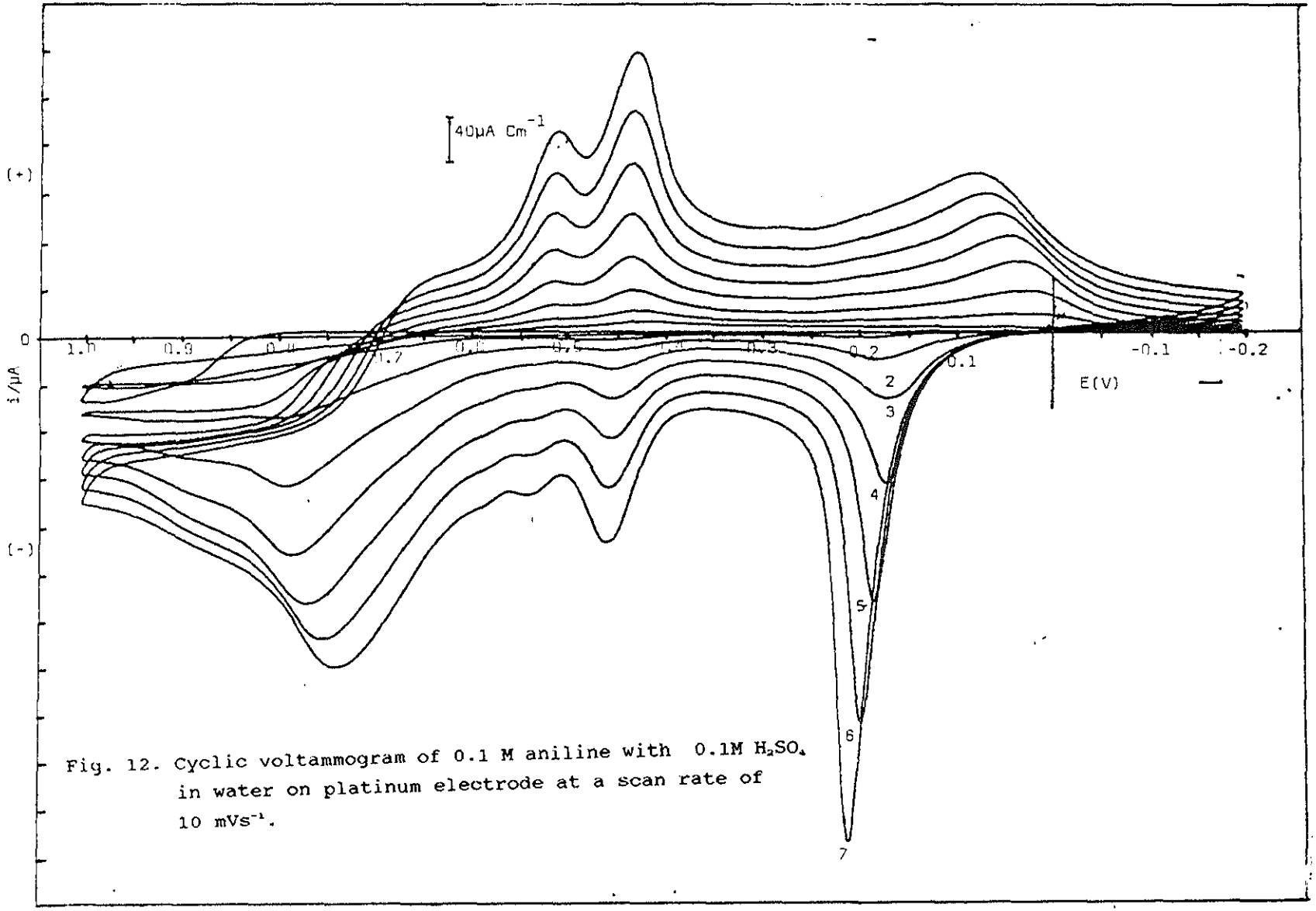


Fig. 12. Cyclic voltammogram of 0.1 M aniline with 0.1M H_2SO_4 in water on platinum electrode at a scan rate of 10 mVs^{-1}.

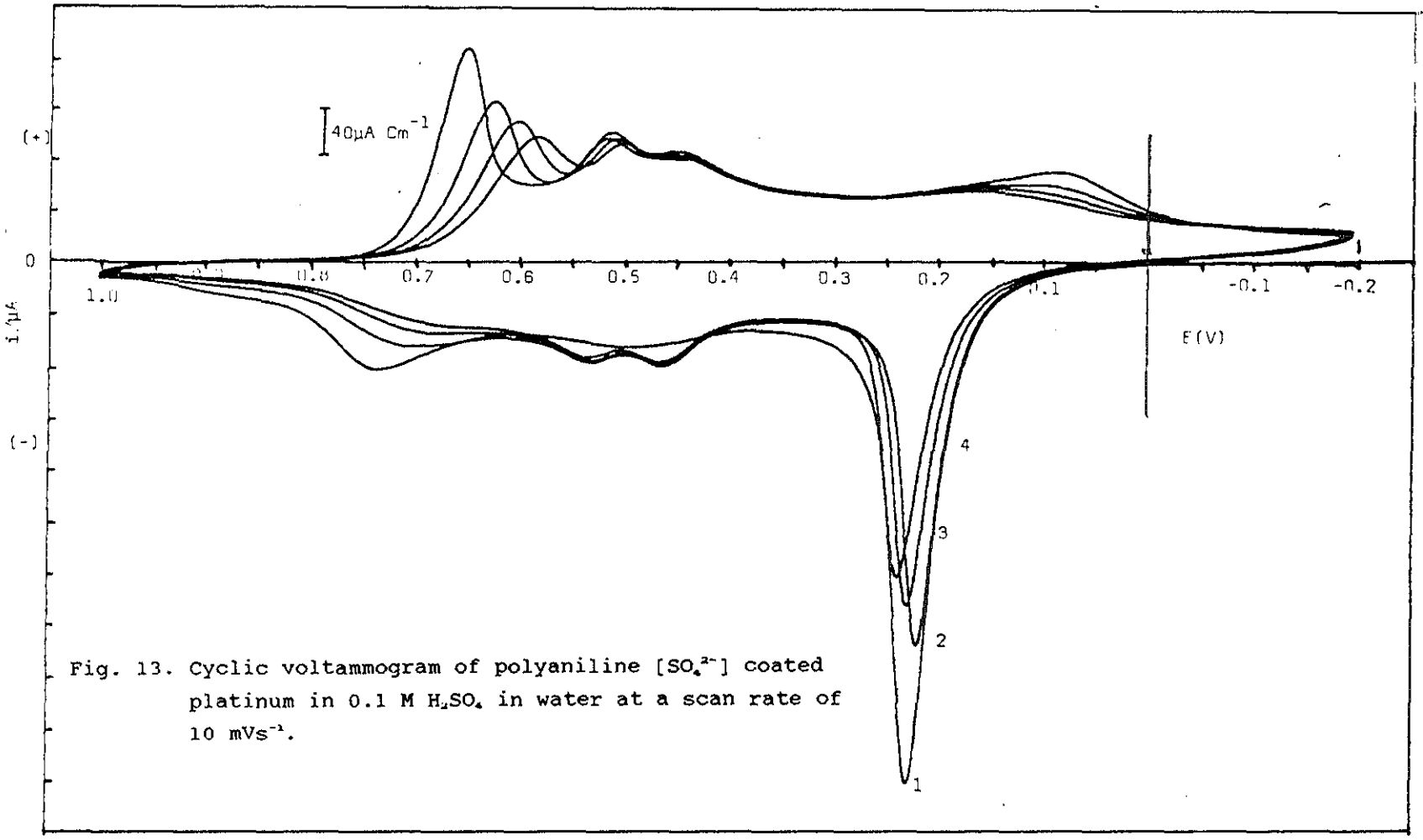


Fig. 13. Cyclic voltammogram of polyaniline [SO_4^{2-}] coated platinum in 0.1 M H_2SO_4 in water at a scan rate of 10 mVs^{-1}.

The peak at 0.72 V from Figure 12 corresponds to oxidative degradation of the polymer film since the potential is taken positive of 0.7 V whereas the peak at 0.47 V is associated with the product of degradation process as suggested by T.Kobayashi et al [70]. They have also proposed a mechanism for the degradation process [70,71] in which benzoquinone is the main product. The appearance of the peak at 0.47 V is in accordance with the known electrochemical behavior of benzoquinone. The peak at 0.18 V is related to the oxidation of the polyaniline film coated on the electrode surface. Finally, the peak at 0.45 V is very difficult to assign to a specific process and perhaps it could be associated with another possible degradation product which may arise from the experimental conditions employed. The cathodic peaks, observed on reversing the direction of potential scan, are most likely attributed to the reverse processes of the anodic peaks.

Figure 13 refers to the cyclic voltammogram of polyaniline film coated on platinum in aqueous solution of 0.1 M H_2SO_4 Four anodic peaks are shown at 0.25, 0.47, 0.54 and 0.72v when the potential was cycled between -0.2 and 1.0v. All the peaks except the first one are at the same positions as those observed in Figure 12. The peak at 0.25 v which corresponds to oxidation of the polymer shows a decrease in current intensity as the number of cycles increases while the other peaks became more distinct . It indicates that because the monomer concentration is negligible here, there is no simultaneous

polymerization and oxidation of the polymer film. On the contrary, the polymer will be continuously degraded and the peaks associated with this degradation became more clear as the number of cycles increases.

Electrochemical polymerization of aniline in the absence of acidic media was found to be unsuccessful. In the absence of sulfuric acid, a dark brown powdery non-adhesive product which falls down from the electrode surface was observed. This confirms that the polymerization process is pH controlled.

For the purpose of comparison, cyclic voltammogram for the polymerization of aniline with 0.02 M TBAHFP and 0.01 M H_2SO_4 in acetonitrile on platinum is shown in Figure 14. During the first scan a sharp peak was observed at 1.09 v that indicates the oxidation of aniline. All the other successive scans show three significant anodic peaks at 0.25, 0.67 and 0.97 v. As the number of cycles increase, all the oxidation peaks go to further anodic potentials and all the reduction peaks to cathodic potentials. By changing the acidity of the monomer solution by one pH unit (pH 1 to 2), the oxidation potential of aniline increased by 240 mv and the peaks got broader.

Figure 15 depicts the cyclic voltammogram of polyaniline coated platinum in 0.02 M TBAHFP and 0.01 M H_2SO_4 in acetonitrile. Unlike that of Figure 13, this voltammogram shows only one important oxidation - reduction peak at 0.61 V and 0.50 V respectively A.F. Diaz and J.A Logan [31] have studied the redox reaction of polyaniline in aprotic solvents like acetonitrile. The redox reactions were found to be very

slow and a very broad and low peak appeared in the range of -0.2 to 0.7 V.

The origin of the peaks and their pH - dependence were believed to be due to a proton addition /elimination reaction of the polymer followed by anion insertion process [72]. Since polyaniline consists of aniline octamers (basically emeraldine and nigraniline) giving rise to various possible combinations of benzenoid and quinoid sequences based around aniline units, it results in different structures for the material. This complex nature of polyaniline makes it difficult to draw a specific conclusion from the observed voltammograms.

Tables 1 and 2 list the oxidation peak potentials of pyrrole, thiophene and aniline monomers in different base electrolytes and solvents on platinum and glassy carbon electrodes respectively. Moreover, the oxidation peak potentials of the corresponding polymer films as coated on the electrode surfaces are also included.

Generally, the type of base electrolyte and solvent system seem to affect the shapes and the values of oxidation reduction peaks to a small extent. The effects of type of electrode material (platinum or glassy carbon) is not pronounced as long as the base electrolytes and solvents are not changed.

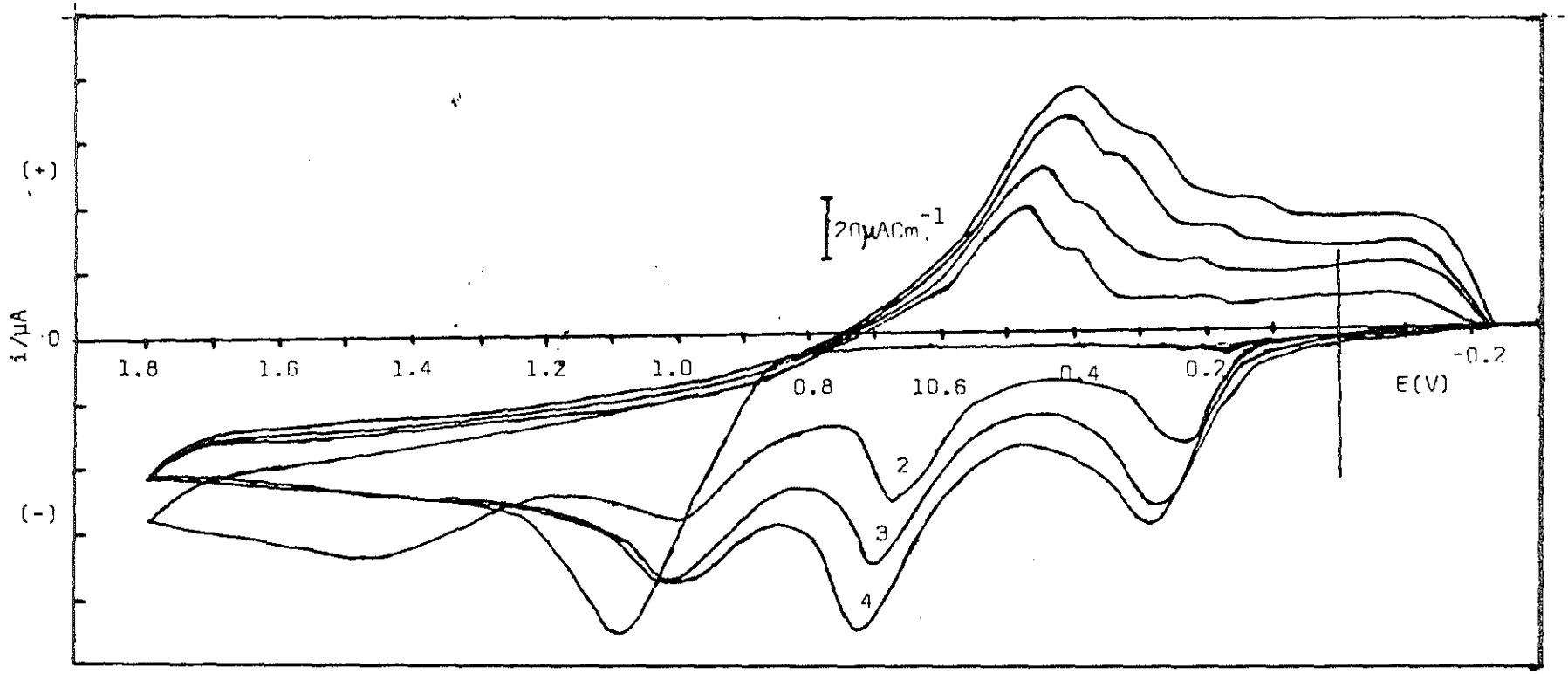


Fig. 14. Cyclic voltammogram of 0.1 M aniline with 0.02 M TBAHFP and 0.01 M H_2SO_4 in acetonitrile on platinum electode at a scan rate of 10 mVs^{-1}.

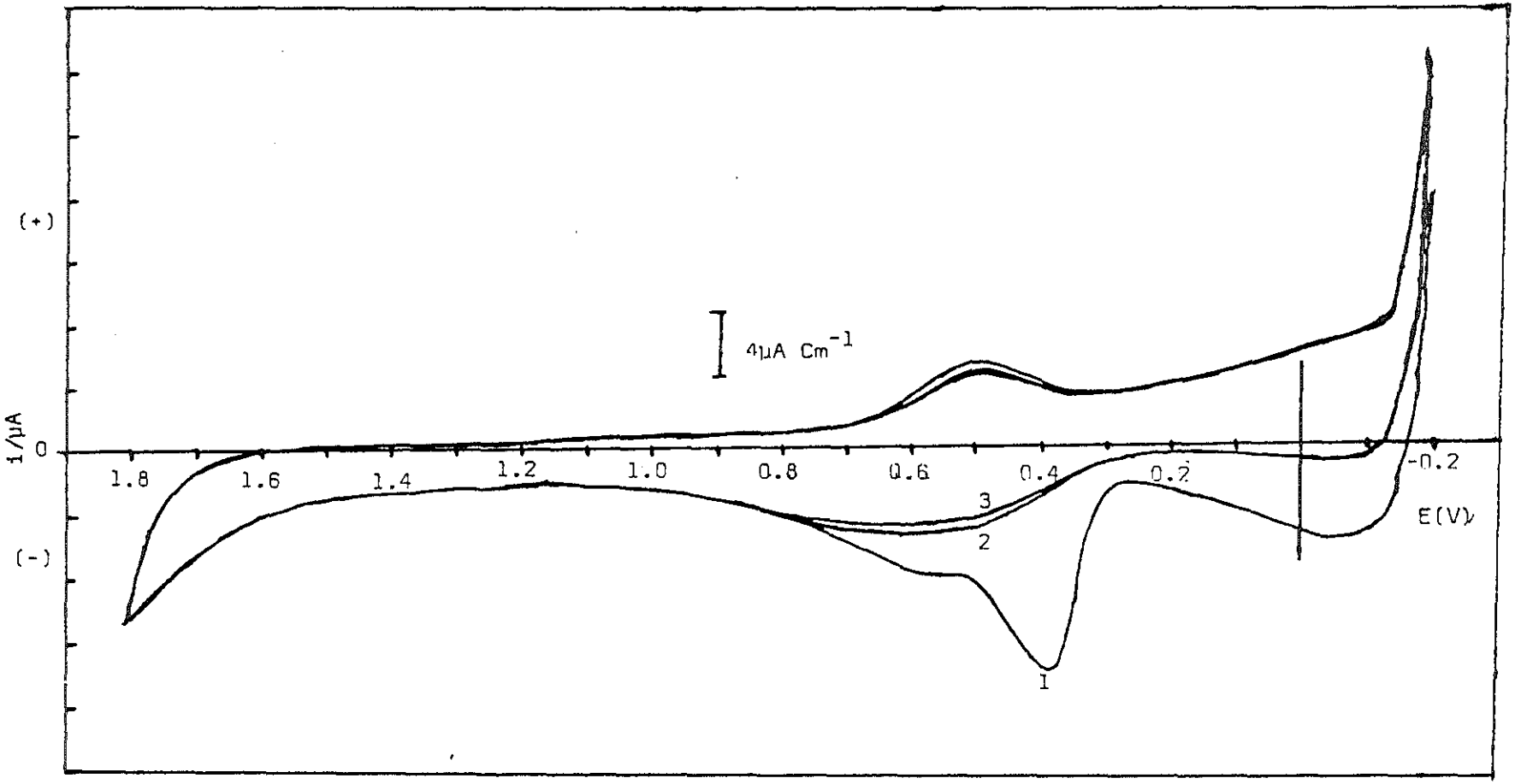


Fig. 15. Cyclic voltammogram of polyaniline [pF^-_6] coated platinum in 0.02 M TBAHFP in acetonitrile at a scan rate of 10 mVs^{-1}.

Table 1. Oxidation peak potentials for pyrrole, thiophene, and aniline monomers and polymers in different base electrolytes on platinum electrode at a scan rate of 10 mVS^{-1}

Monomer	Base electrolyte	Solvent	$E_{pa,mon}$(v)	$E_{pa,pol}$(v)
10 mM pyrrole	0.1 M $TBAClO_4$	acetonitrile/ 1%H_2O	1.14	0.16
10 mM pyrrole	0.02 M TBAHFP	acetonitrile/ 1%H_2O	1.45	0.32*
10 mM pyrrole	0.1 M H_2SO_4	acetonitrile/ 1%H_2O	0.89	0.39
10 mM pyrrole	0.1 M TEATFB	acetonitrile/ 1%H_2O	0.96*	-0.20
0.1 M aniline	0.1 M H_2SO_4	H_2O	0.85	0.18
0.1 M aniline	0.1 M $TBAClO_4$/ 0.01 M H_2SO_4	acetonitrile	1.01	0.55
0.1 M aniline	0.02 M TBAHFP/ 0.01 M H_2SO_4	acetonitrile	1.09	0.61
0.1 M aniline	0.1 M TEATFB/ 0.01 M H_2SO_4	acetonitrile	1.45	0.78
0.2 M thiophene	0.02 M TBAHFP	acetonitrile/ 1%H_2O	1.36	0.80*

* The values are reported as onset potentials for oxidation of monomers and polymers since the resulting voltammograms show broad peaks.

Table 2. Oxidation peak potentials for pyrrole, thiophene, and aniline monomers and polymers in different base electrolytes on glassy Carbon electrode at a scan rate of 10 mVS^{-1}

Monomer	Base electrolyte	Solvent	$E_{pa,mon}$(v)	$E_{pa,pol}$(v)
10 mM pyrrole	0.1 M $TBAClO_4$	acetonitrile/ 1%H_2O	1.23	0.65
10 mM pyrrole	0.02 M TBAHFP	acetonitrile/ 1%H_2O	1.50	0.29*
10 mM pyrrole	0.1 M H_2SO_4	acetonitrile/ 1%H_2O	0.90	0.45
10 mM pyrrole	0.1 M TEATFB	acetonitrile/ 1%H_2O	0.99*	-0.24
0.1 M aniline	0.1 M H_2SO_4	H_2O	0.98	0.26
0.1 M aniline	0.1 M $TBAClO_4$/ 0.01 M H_2SO_4	acetonitrile	1.12	0.71
0.1 M aniline	0.02 M TBAHFP/ 0.01 M H_2SO_4	acetonitrile	1.10	0.60
0.1 M aniline	0.1 M TEATFB/ 0.01 M H_2SO_4	acetonitrile	1.46	0.76
0.2 M thiophene	0.02 M TBAHFP	acetonitrile/ 1%H_2O	1.32	0.82*

5.2 Comparison of the Redox Reversibility of $[Fe(CN)_6]^{4-/3-}$ Systems on Bare and polymer coated Electrodes in Different Base Electrolytes.

In order to investigate the electrochemical reversibility of the redox reaction of $[Fe(CN)_6]^{4-/3-}$ couple on polymer coated electrodes using different base electrolytes, the system has been studied by dc cyclic voltammetry. Before every measurement, the working potential range of the base electrolyte (0.1 M KCl) was determined by cycling the potential between - 0.2 V and 0.55 V. The electrochemical reversibility of $[Fe(CN)_6]^{4-/3-}$ was also determined on bare platinum and glassy carbon electrodes to compare the results with that of polymer coated electrodes under similar conditions. A peak separation of 75 mv was observed on the bare electrodes. This result is in good agreement with that of 5×10^{-4}M $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl showing a peak separation ranging from 85 mv to 120 mv between sweep rates of 4.5 mvs^{-1} and 45 mvs^{-1} on a stationary carbon paste electrode [73].

Figures 16 and 17 indicate the cyclic voltammograms for equimolar (5 mM) concentration of $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl on polypyrrole $[BF_4^-]$, polyaniline $[BF_4^-]$ and polythiophene $[PF_6^-]$ coated platinum and glassy carbon electrodes respectively. The voltammograms for the same system on bare platinum and glassy carbon electrodes are also included for comparison. The peak separations on the voltammograms indicate that the redox reaction of the species is reversible as predicted by equation

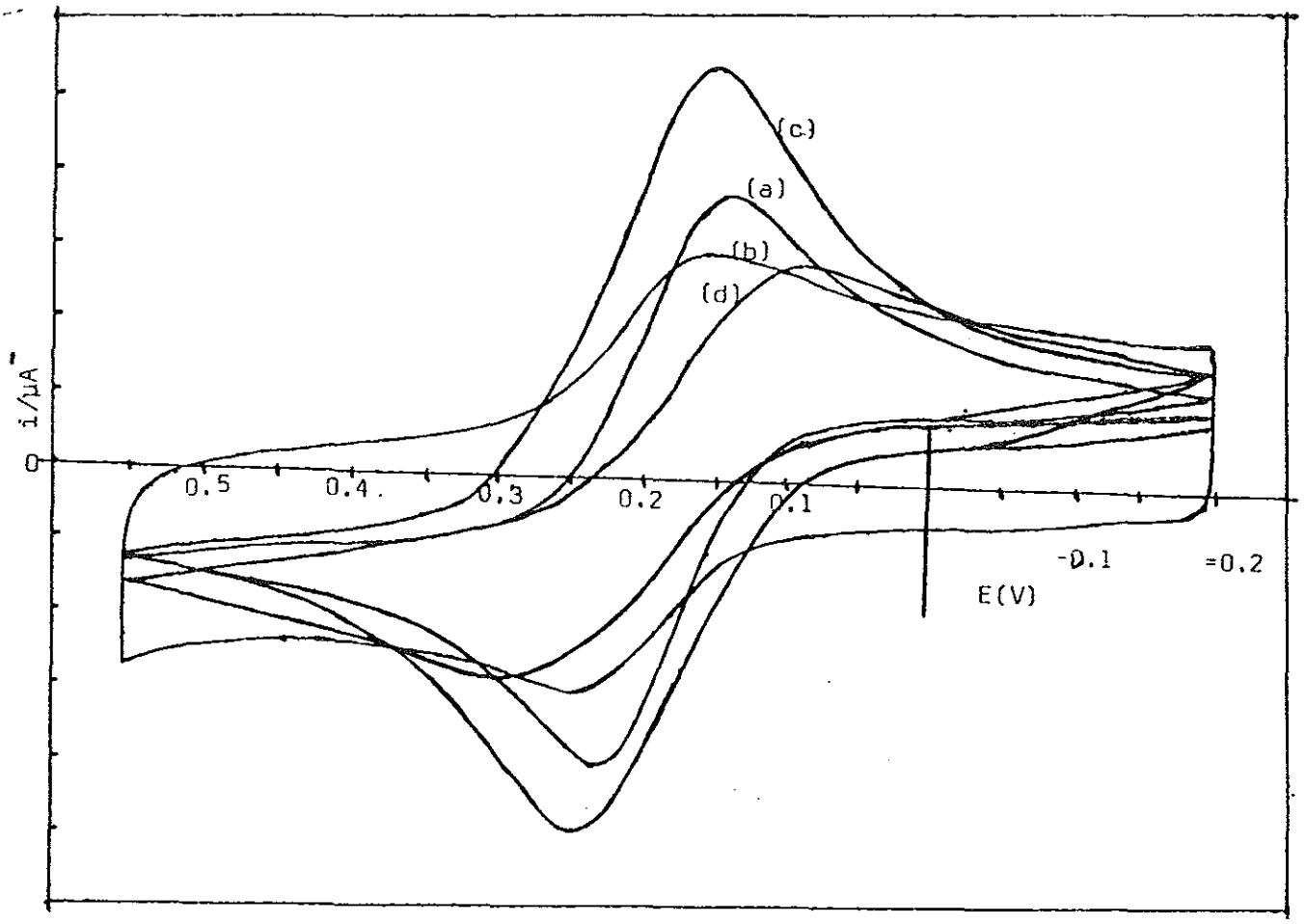


Fig. 16. Cyclic voltammogrms for equimolar (5 mM) concentrations of $[Fe(CN)_6]^{4-/3-}$ couple in 0.1 M KCl on bare platinum electrode, 2 μAcm^{-2} (a), on poly pyrrole $[BF^-_4]$ coated Pt, 4 μAcm^{-2} (b), on poly aniline $[BF^-_4]$ coated Pt, 2 μAcm^{-2} (c) and on poly thiophene $[pF_6^-]$ coated Pt, 2 $\mu A\ cm^{-2}$ (d) at a scan rate of 10 mVs^{-1}.

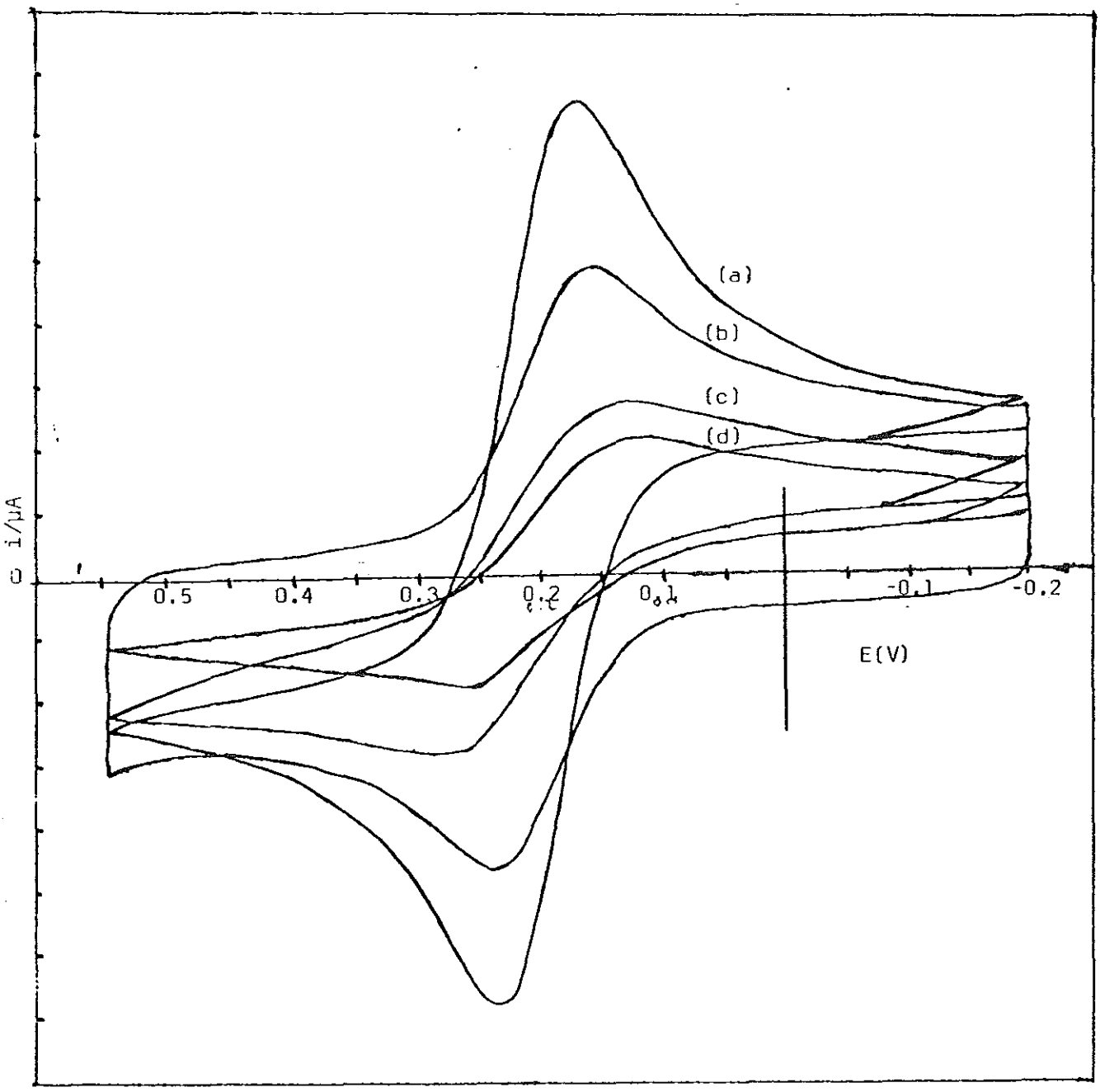


Fig. 17. Cyclic voltammogrms for equimolar (5mM) concentrations of $[Fe(CN)_6]^{4-/3-}$ couple in 0.1 M KCl on bare glassy carbon electrode, $2\mu Acm^{-2}$ (a), on polypyrrole $[BF^-_4]$ coated gc, $4\mu Acm^{-2}$ (b), on polyaniline $[BF^-_4]$ coated gc, $4\mu Acm^{-2}$ (C), and on polythiophene $[pF_6^-]$ coated gc, $4\mu Acm^{-2}$ (d) at a scan rate of 10 mVs^{-1}.

(1) in section 5.1. For irreversible processes, those with sluggish electron transfer kinetics, the individual peaks are reduced in size and widely separated.

In addition to this, for a simple system with no chemical complications, the ratio of the peak currents, ipc/ipa, is unity with the peak currents given by the following equation [74].

$$ip = 269\ n^{3/2}\ AD^{1/2}\ C^{b}\ V^{1/2} \qquad (2)$$

where A is the electrode area, D is the diffusion coefficient, C^{b} is the concentration of species in the bulk solution and V is the sweep rate.

As can be seen from Figures 16 and 17 the peak currents on polymer coated electrodes are higher than on bare electrodes in case of polypyrrole and polyaniline. When polythiophene coated electrodes are employed the peak currents are lower than those on bare electrodes.

Two factors may play important role in such cases. First the surface area of the electrode material may increase when the electrode is polymer coated. Depending upon the structure (morphology) of the polymer film, the polymer chains could be highly compact or loosely bound. Second, the diffusion coefficients of the electroactive species vary in the polymer matrix than in solution.

Based on this argument it is possible to propose two mechanisms for the charge transfer process as depicted in Figure 18.

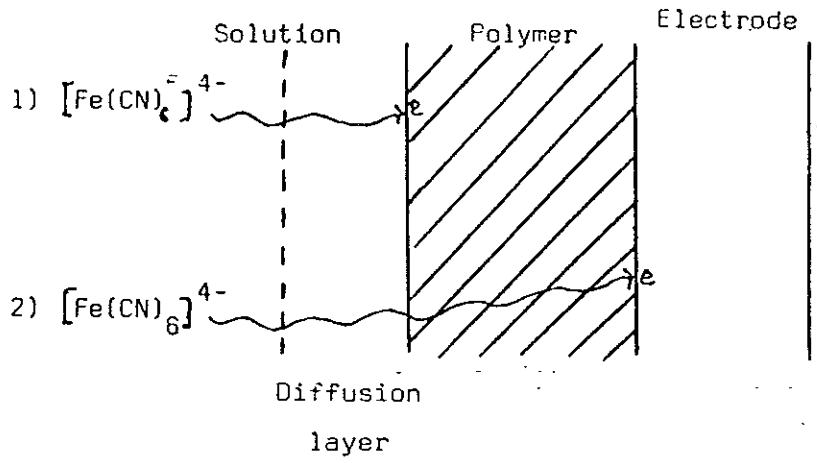


Fig. 18. A Possible mechanism for the charge transfer process of $[Fe(CN)_6]^{4-}$ on polymer coated electrode.

If charge transfer is on the polymer surface (1), then through the conduction mechanism of the polymeric material electrons may reach the electrode surface. Since the surface area of polymers depend on their morphology, it is possible to get large surface area between polymer chains and hence to observe high current response. On the other hand, the current response is also dependent on the conductivity of the particular polymer, highly conductive polymers giving high current and less conductive ones low current.

If charge transfer takes place mainly on the electrode surface (2), then the electroactive species should go all the way through the polymer matrix to reach the electrode. In such cases, the structure of the polymer matrix plays an important

cases, the structure of the polymer matrix plays an important role. Those with loose structure may allow passage of the electroactive species while those with compact structure hinder the free movement of species. Besides this, the electrical interactions between species and polymer material affect the movement of species through the polymer. Therefore, the observed results are the combination of these two processes.

Polyaniline film formed from 0.1 M H_2SO_4 in water shows a unique cyclic voltammogram for the redox reaction of $[Fe(CN)_6]^{4-/3-}$ couple in 0.1 M KCl on both platinum and glassy carbon electrodes as shown in Figure 19. The voltammograms show only cathodic current for the reduction of $[Fe(CN)_6]^{3-}$ while the reverse process is not shown. Further investigatons are necessary to explain this observation.

Among the polymer films investigated, BF_4^- doped polypyrrole and polyaniline show relatively faster electron transfer process than others for the $[Fe(CN)_6]^{4-/3-}$ redox reaction. The peak currents are also found to be higher than others. It could be said that BF_4^- doped polymers may have high surface area and higher conductivity than the other polymers. When polypyrrole and polyaniline films formed in PF_6^- and ClO_4^- are compared for the redox reaction of $[Fe(CN)_6]^{4-/3-}$ it was found that PF_6^- doped films have relatively small peak separations and high peak

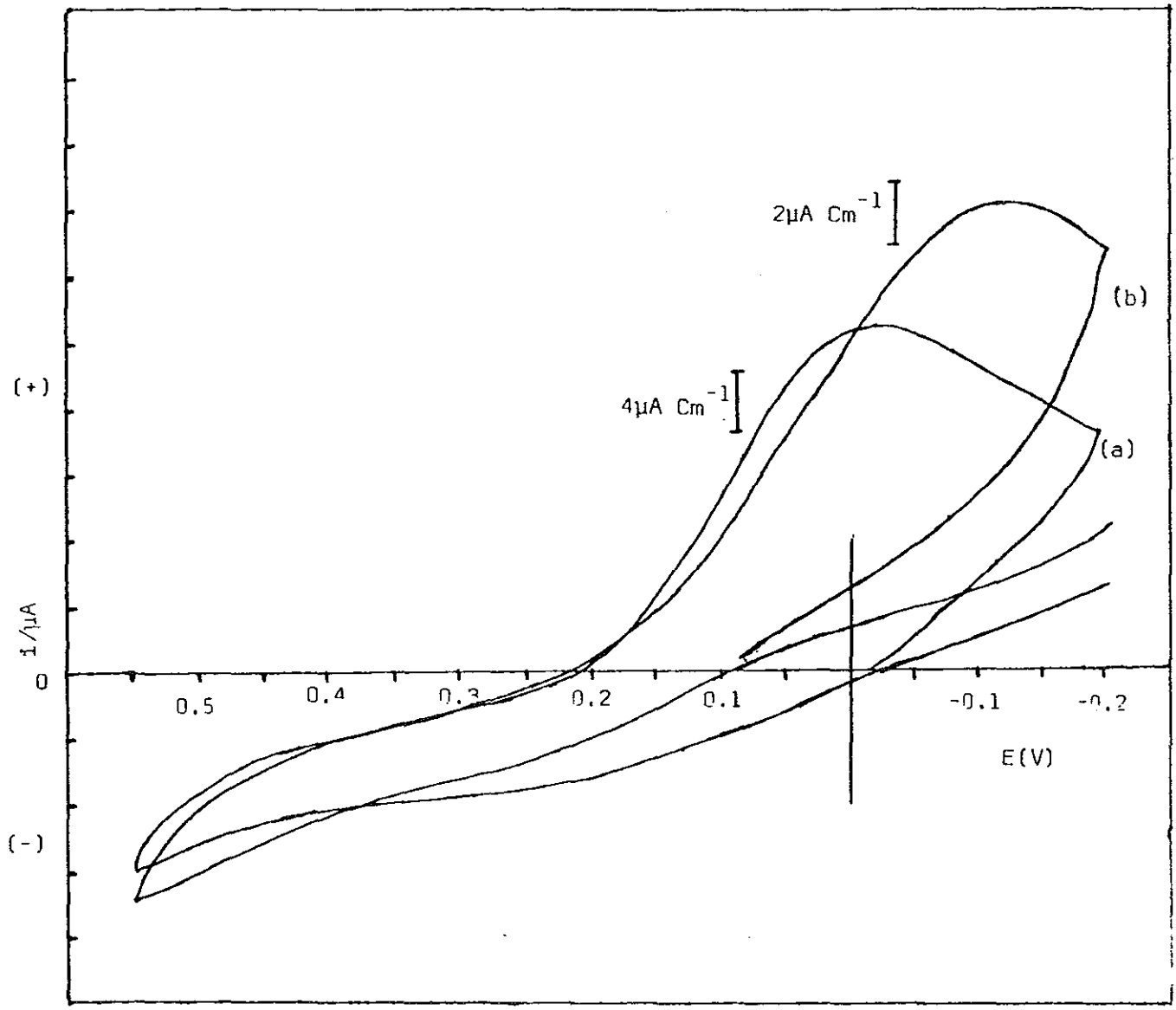


Fig. 19. Cyclic voltammogrms for equimolar (5mM) concentrations of $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl on polyaniline $[SO_4^{2-}]$ coated platinum (a), and polyaniline $[SO_4^{-2}]$ coated platinum (a), and polyaniline $[SO_4^{-2}]$ coated glassy carbon (b) at a scan rate of 10 mVs^{-1}.

currents. This observation suggests that films formed from PF_6^- are more porous than those formed from ClO_4^- as reported by T. Osaka et al. [75]

Polythiophene film which is doped with PF_6^- shows a relatively slow electron transfer for $[Fe(CN)_6]^{4-/3-}$ couple when coated on platinum and glassy carbon electrodes. The peak currents are also found to be lower. This could be related to the low conductivity of polythiophene and/or the low porosity of the polymer structure.

Previous workers have investigated the redox behaviors of a number of species on electrodes coated with these polymeric materials. A. F. Diaz and K. K. Kanazawa [76] have observed the cyclic voltammogram of 10^{-3} M Ferrocene on polypyrrole in acetonitrile to resemble that obtained on platinum with peak separation of 90 mV at a sweep rate of 20 mVs^{-1} and i_{pc}/i_{pa} equal to unity.

A. Czerwiniski and coworkers [48] have studied the cyclic voltammograms for $[Fe(CN)_6]^{4-/3-}$ redox systems at an electrode formed with polythiophene film and it was found to be similar in shape as those obtained at a bare platinum electrode. However, the magnitude of the peak currents was much lower than that of platinum electrode having the same surface area.

Because of the uncertainty that surrounds the exact nature of the material and the mechanisms involved in its reactions, relatively little work has been done on applications of polyaniline as electrode material. However, the polyaniline

film on platinum was used as an electrode to drive the redox reaction of ferrocene when dissolved in acetonitrile containing 0.1 M TEAFB [31]. The film behaved well as an electrode and peaks for the redox reaction of ferrocene appeared superimposed on the background current with E° near 400 mV which is close to the value measured with a pt electrode (420 mV). The peak size was similar to that on bare platinum electrode of the same geometric area.

In general, the effect of the electrode material (platinum and glassy carbon) on the reversibility of the redox reaction of $[Fe(CN)_6]^{4-/3-}$ system is not significant. Glassy carbon electrode usually gives a slightly higher peak current and wider peak separation compared to platinum electrode. Some polymer coated electrodes show wider peak separations than expected. This may be attributed to the uncompensated iR drop in the measurements. Table 3 and 4 list all the results of the studies made on bare and polymer coated platinum and glassy carbon electrodes respectively.

Table 3. Values of potential differences between cathodic and anodic peaks, $E_{p,a} - E_{p,c}$, cathodic peak current, $i_{p,c}$ and the ratio of catodic current to anodic current, $i_{p,c}/i_{p,a}$ corresponding to the redox reaction of $[Fe(CN)_6]^{4-/3-}$ on bare and polymer coated platinum electrodes in 0.1 M KCl at a scan rate of 10 mVs^{-1}

Electrode Material	$E_{p,a} - E_{p,c}$	$i_{p,c}(\mu A)$	$i_{p,a}(\mu A)$	$\frac{i_{p,c}}{i_{p,a}}$
Platinum	75	8.6	8.8	0.977
Polypyrrole, ClO_4^-	150	4.0	3.0	1.333
Polyprrrole, PF_6^-	115	12.0	11.5	1.142
Polypyrrole, SO_4^{2-}	90	9.0	8.0	1.125
Polyprrole, BF_4^-	80	8.4	8.0	1.050
Polyaniline, SO_4^{2-}	-	18.0	-	-
Polyaniline, ClO_4^-	115	1.0	0.6	1.666
Polyaniline, PF_6^-	100	3.2	2.8	1.142
Polyaniline, BF_4^-	90	12.0	11.6	1.034
Polythiophene, PF_6^-	230	4.2	5.8	0.724

Table 4. Values of potential differences between cathodic and anodic peaks, $E_{p,a} - E_{p,c}$, cathodic peak current, $i_{p,c}$ and the ratio of catodic current to anodic current, $i_{p,c}/i_{p,a}$ corresponding to the redox reaction of $[Fe(CN)_6]^{4-/3-}$ on bare and polymer coated glassy carbon electrodes in 0.1 M KCl at a scan rate of 10 mVs^{-1}

Electrode Material	$E_{p,a} - E_{p,c}$	$i_{p,c}(\mu A)$	$i_{p,a}(\mu A)$	$\frac{i_{p,c}}{i_{p,a}}$
Glassy carbon	75	16.9	17.0	0.994
Polypyrrole, ClO_4^-	155	8.0	6.0	1.333
Polyprrrole, PF_6^-	114	18.0	16.0	1.125
Polypyrrole, SO_4^{2-}	115	4.9	5.2	0.942
Polyprrole, BF_4^-	85	16.4	15.6	1.051
Polyaniline, SO_4^{2-}	-	11.2	-	-
Polyaniline, ClO_4^-	150	2.3	1.8	1.277
Polyaniline, PF_6^-	145	4.6	3.0	1.533
Polyaniline, BF_4^-	110	9.2	6.4	1.437
Polythiophene, PF_6^-	165	10.8	12.4	0.871

5.3. Determination of Diffusion Coefficients for $[(Fe(CN)_6]^{4-/3-}$ Couple on Bare and Polymer coated Electrodes in Different Base Electrolytes.

To determine the diffusion coefficients of equimolar (5 mM) concentrations of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ in 0.1M KCl on polymer coated platinum and glassy carbon electrodes, rotating disk electrode (RDE) voltammetry was employed. Prior to each experiment, RDE measurement was done on the base electrolyte (0.1 M KCl). The potential of the working electrode was varied from -0.2 to 0.55v at a scan rate of $10mvs^{-1}$.

The effect of rotation speed on the anodic and cathodic limiting currents of $[Fe(CN)_6]^{4-/3-}$ systems using polypyrrole, polyaniline and polythiophene coated electrodes in 0.1 M KCl were investigated. The results are shown in Figures 20, 21 and 22 for polymers coated on platinum. Figure 23 shows the RDE voltammogram for the $[Fe(CN)_6]^{4-/3-}$ couple at platinum electrode coated with polyaniline from 0.1 M H_2SO_4 as the base electrolyte. In this case limiting currents are observed only for the reduction of $[Fe(CN)_6]^{3-}$on both platinum and glassy carbon electrodes when coated with this polymer. This is consistent with the result that was obtained for the determination of the reversibility of the $[Fe(CN)_6]^{4-/3-}$ redox reaction in section 5.2.

In all the measurements, increase in anodic and cathodic limiting currents are observed as the rotation speed increases. This implies the process is diffusion controlled and it is in agreement with the Levich equation [77].

$$i_l = 0.62\ nFA\ C^b\ D^{2/3}\ v^{-1/6}\ w^{1/2} \qquad (3)$$

where i_l is the limiting current, W is the angular frequency, v is the kinematic viscosity which is $0.01 cm^2 s^{-1}$ for aqueous solution, and the others have their usual meanings.

This equation thus applies to the totally mass - transfer limiting condition at the RDE and predicts that the limiting current is proportional to the square root of the angular frequency. If the limiting cathodic and anodic currents are plotted versus the square roots of angular frequency, straight lines are obtained as indicated in Figures 24 and 25 on polymer coated platinum and glassy carbon electrodes. The diffusion coefficients of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are determined from the slopes of these lines. It is worth noting that the shape of the wave for a totally reversible reaction is independent of ω. Thus, since i_l varies as $\omega^{1/2}$, i at any potential should vary as $\omega^{1/2}$. A deviation of a plot of i vs $\omega^{1/2}$ from a straight line that intersects the origion suggests some kinetic step involved in the electron transfer reaction. The polymer coated electrode area was assumed to be the same as that of the bare electrode in the calculations. The values are listed in tables 5 and 6. These results of the diffusion coefficients are in good agreement with the literature values ($7.63 \times 10^{-6} cm^2 s^{-1}$ for $[Fe(CN)_6]^{3-}$, and $6.5 \times 10^{-6} cm^2 s^{-1}$ for $[Fe(CN)_6]^{4-}$) at bare platinum and glassy carbon electrodes in 0.1 M KCl base electrolytes [78].

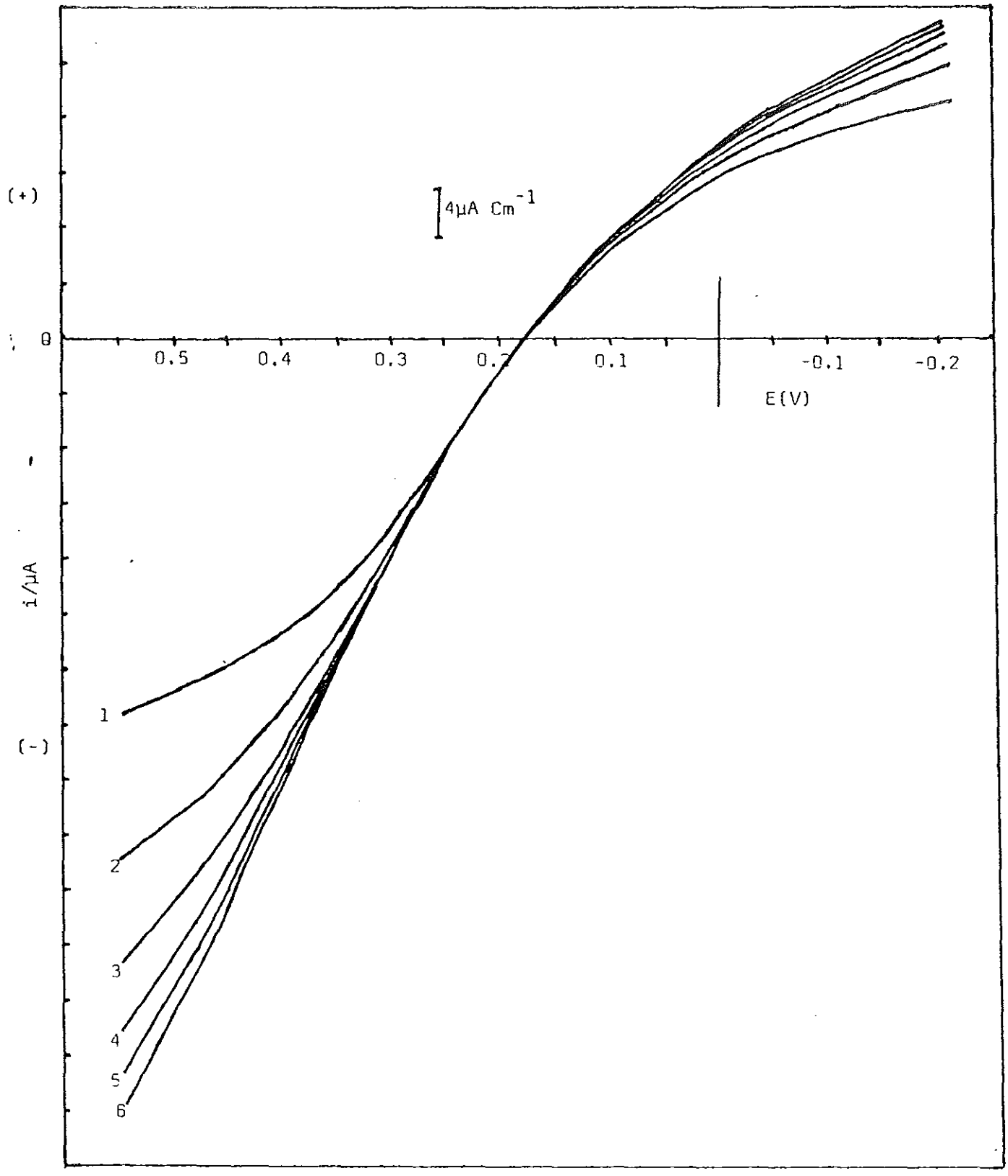


Fig. 22. RDE Voltammograms for equimolar (5mM) concentrations of $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl at rotational speed 1) 500 2) 1000 3) 1500 4) 2000 5) 2500 6) 3000 rev min^{-1} and a scan rate of 10 mVs^{-1} using polythiophene [PW.] coated platinum

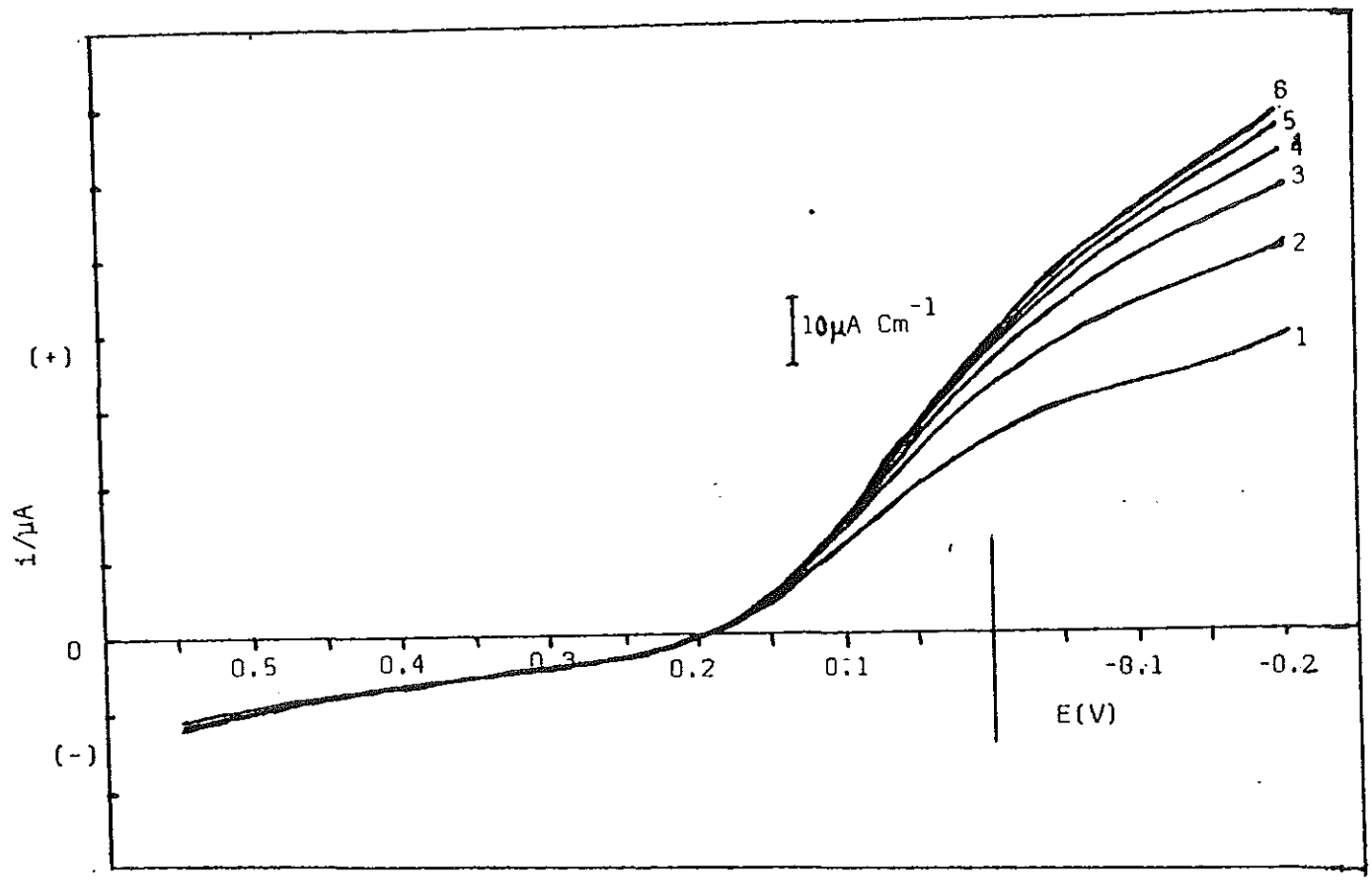


Fig. 23. RDE Voltammograms for equimolar (5mM) concentrations of $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl at rotational speed 1) 500 2) 1000 3) 1500 4) 2000 5) 2500 6) 3000 rev min^{-1} and a scan rate of 10 mVs^{-1} using polyaniline $[SO_4^{2-}]$ coated platinum electrode.

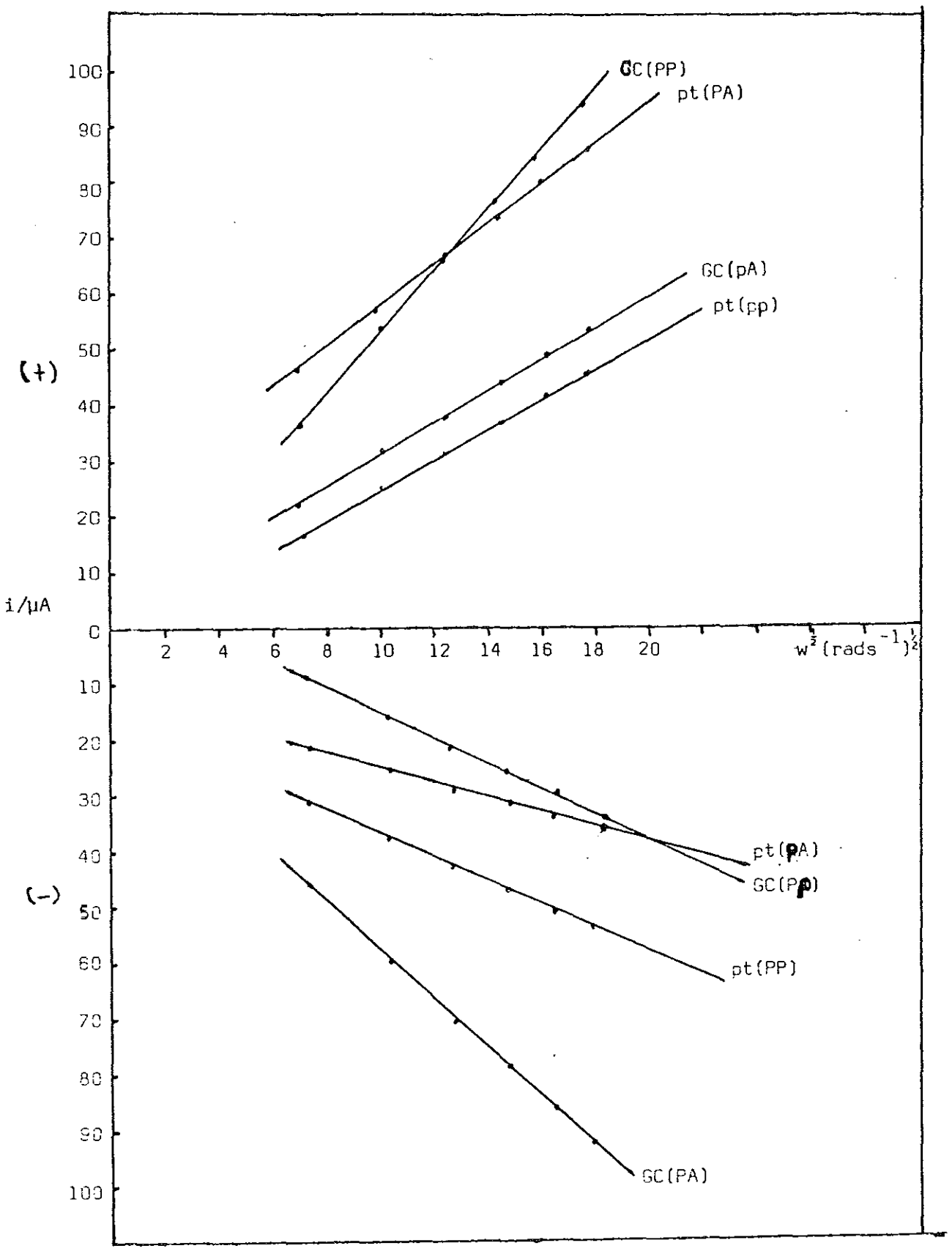


Fig. 24. Plots of $i_{L,c}$ Vs $W^{1/2}$ and $i_{L,a}$ Vs $W^{1/2}$ from RDE Voltammograms of equimolar (5mM) concentrations of $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl at different rotational speeds on polypyrrole [BF_4^-], PP, and polyaniline [BF_4^-] PA coated platinum and glassy carbon electrodes.

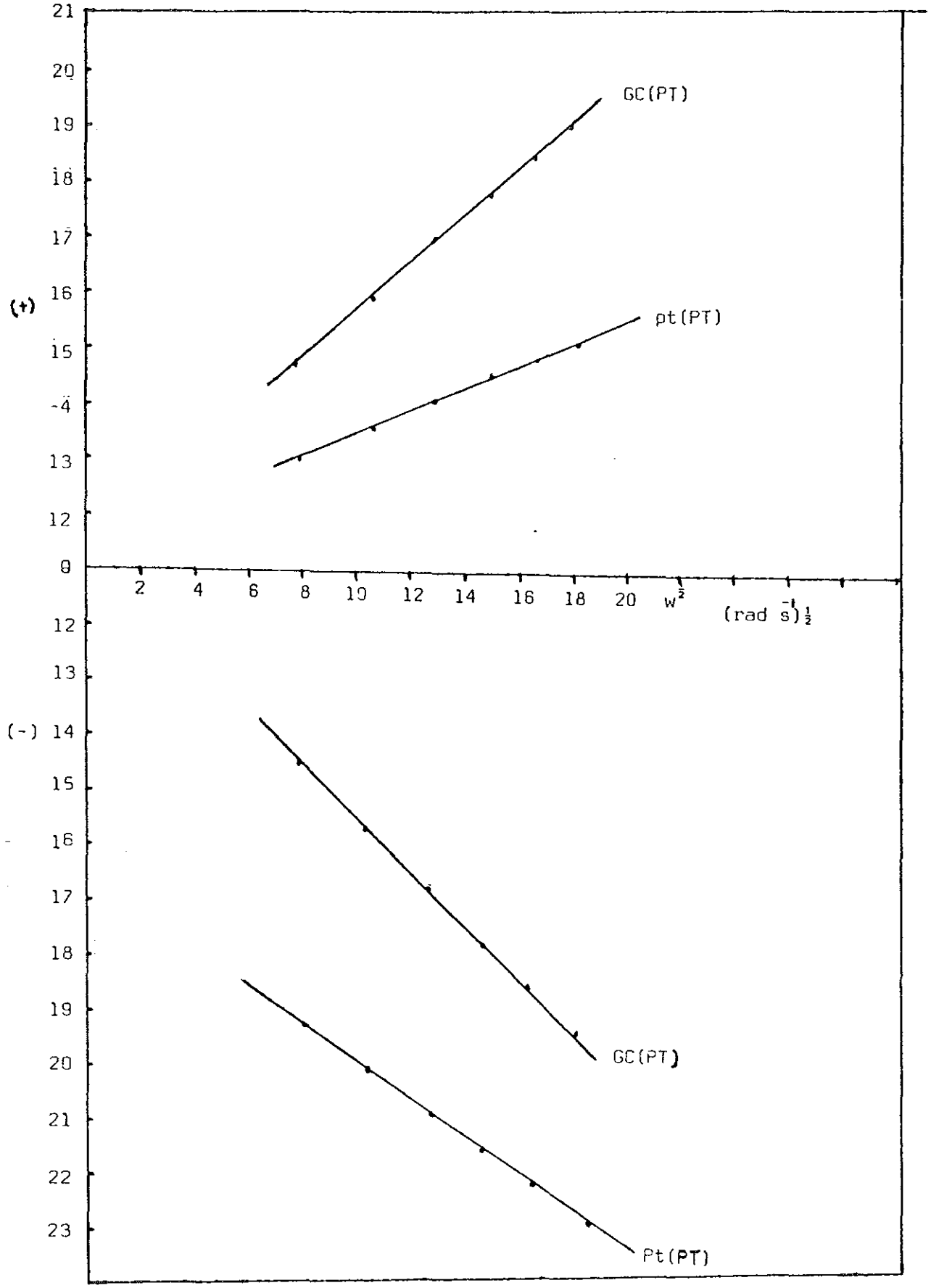


Fig. 25. Plots of $i_{L,c}$ Vs $W^{\frac{1}{2}}$ and $i_{L,a}$ Vs $W^{\frac{1}{2}}$ from RDE Voltammograms of equimolar (5mM) concentrations of $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl at different rotational [illegible] polythiophene (PT) [illegible] and glassy carbon electrodes

Table 5. Diffusion coeffficents for equimolar (5mM) concentrations of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ in 0.1 M KCl on bare and polymer coated platinum electrode from RDE voltammograms at a scan rate of 10 mVs^{-1}

Electrode Material	$D[Fe(CN)_6]^{3-}$ $x10^6$ Cm^2s^{-1}	$D[Fe(CN)_6]^{4-}$ $x10^6$ Cm^2s^{-1}	$\frac{D[Fe(CN)_6]^{3-}}{D[Fe(CN)_6]^{4-}}$
Platinum	6.7	5.2	1.3
Polypyrrole, ClO_4^-	2.5	3.0	0.81
Polyprrrole, PF_6^-	5.0	1.7	2.8
Polypyrrole, SO_4^{2-}	3.2	1.9	1.7
Polyprrole, BF_4^-	22.2	10.9	2.0
Polyaniline, SO_4^{2-}	6.5	-	-
Polyaniline, ClO_4^-	0.01	0.01	1.0
Polyaniline, PF_6^-	0.23	0.15	1.5
Polyaniline, BF_4^-	8.1	2.0	3.9
Polythiophene, PF_6^-	0.14	0.22	0.63

Table 6. Diffusion coeffficents for equimolar (5mM) concentrations of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ in 0.1 M KCl on bare and polymer coated glassy carbon elctrode from RDE voltammograms at a scan rate of 10 mVs^{-1}

Electrode Material	$D[Fe(CN)_6]^{3-}$ $x10^6$ Cm^2s^{-1}	$D[Fe(CN)_6]^{4-}$ $x10^6$ Cm^2s^{-1}	$\frac{D[Fe(CN)_6]^{3-}}{D[Fe(CN)_6]^{4-}}$
Glassy Carbon	9.8	6.7	1.4
Polypyrrole, ClO_4^-	2.5	3.0	0.81
Polyprrrole, PF_6^-	5.2	4.1	1.2
Polypyrrole, SO_4^{2-}	3.2	0.91	3.5
Polyprrole, BF_4^-	14.6	10.9	1.3
Polyaniline, SO_4^{2-}	2.4	-	-
Polyaniline, ClO_4^-	0.02	0.02	1.0
Polyaniline, PF_6^-	0.41	0.36	1.1
Polyaniline, BF_4^-	4.6	3.8	1.2
Polythiophene, PF_6^-	0.34	0.40	0.85

The calculated diffusion coefficients for $[Fe(CN)_6]^{4-/3-}$ systems are higher when bare glassy carbon electrode is employed compared to when bare platinum is used. To explain this observation, the roughness factor which is the ratio between the real area of contact between the electrode and the solution and the apparent or cross-sectional area was determined. For practically porous electrodes the roughness factor has a magnitude in the range of 10^2 to 10^4 [79].

The electrochemical area of platinum and glassy carbon electrodes is calculated by substituting the diffusion coefficients from the literature into equation (3) and the results are included in Tables 7 and 8.

Table 7. Determination of the electrochemical area of platinum electrode from RDE measurement for equimoalr (5mM) concentrations of $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl from equation (3).

NO.	i_l (μA)	$w^{\frac{1}{2}}$ (rad)$^{\frac{1}{2}}$	electrode area (cm^2)
1	24	7.23	0.132
2	33	10.23	0.129
3	40	12.53	0.128
4	46	14.47	0.127
5	51	16.18	0.126
6	56	17.72	0.126

Average area = 0.128 cm^2

Table 8. Determination of the electrochemical area of glassy carbon electrode from RDE measurement for equimoalr (5mM) concentrations of $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl from equation (3).

NO.	i_l (μA)	$w^{1/2}$ $(rad)^{1/2}$	electrode area (cm^2)
1	44	7.23	0.244
2	61	10.23	0.239
3	73	12.53	0.233
4	84	14.47	0.232
5	93	16.18	0.230
6	102	17.72	0.230

Average area = 0.234 cm^2

The roughness factors of platinum and glassy carbon electrodes were calculated from the results of tables 7 and 8, and found to be 1.9 and 3.6 respectively. The observed high diffusion coefficients of $[Fe(CN)_6]^{4-/3-}$ for glassy carbon electrodes is due to the larger surface area of the electrode than the geometrical area measured.

Among the polymer films studied, BF_4^- doped polypyrrole and polyaniline gave a higher diffusion coefficients for $[Fe(CN)_6]^{4-/3-}$ systems than the others as can be seen from Tables 5 and 6. In such cases, the surface area of the polymer coated electrodes may be higher than bare electrodes. As a consequence, the electroactive species could get larger area for charge transfer to take place in the polymer matrix that result increase in current response.

Comparison of PF_6^- and ClO_4^- doped polymers (polypyrrole and polyaniline) for the diffusion coefficients of the $[Fe(CN)_6]^{4-/3-}$ couple shows that the PF_6^- doped polymers give higher values. Similar results were obtained for the peak currents determined with cyclic voltammetry. It supports the idea that PF_6^- doped polymers are more porous than ClO_4^- doped ones and hence diffusion of species is relatively fast in the former cases if charge transfer is to take place on the electrode surface.

The diffusion coefficients of $[Fe(CN)_6]^{4-/3-}$ on polythiophene coated electrodes are found to be low. In this case if charge transfer is possible on the polymer film, polythiophene should be less conductive since it has an oxidation level of 0.06 while polypyrrole has an oxidation level ranging between 0.25 and 0.3 [42,58]. The low conductivity of polythiophene could also be explained interms of its oxidation potential which is above 0.8V as shown in tables 1 and 2. Since the $[Fe(CN)_6]^{4-/3-}$ systems are investigated in the potential range of -0.2 to 0.55V, polythiophene is not at its oxidized state at this potential interval and is expected to be less conductive. Instead, polypyrrole and polyaniline films are in their oxidized state at this potential range and hence show the expected higher conductivity.

Tables 5 and 6 do not show diffusion coefficient values for $[Fe(CN)_6]^{4-}$ oxidation similar to the cyclic voltammetric results observed in section 5.2. The possible explanation is

that the $[Fe(CN)_6]^{4-}$ is chemically oxidized by one or more products of oxidative degradation of polyaniline film at the given PH of the electrolyte solution from which the polymer was made. Hence there will be no $[Fe(CN)_6]^{4-}$ to be oxidized on the electrode surface.

The diffusion coefficients show a regular increase or decrease in value when platinum or glassy carbon electrodes are coated with identical polymeric material. This implies that once the electrode is coated with a polymer, the polymer is responsible for the observed behavior of the $[Fe(CN)_6]^{4-/3-}$ couple irrespective of the metal electrode employed. In addition to this, comparison of the ratios of diffusion coefficients for $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ were done. The results are in fair agreement with the known diffusion coefficient ratio of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ which is about 1.21 in 0.1M kcl base electrolyte [80].

6. CONCLUSION

DC Cyclic Voltammetry has been used to determine the oxidation peak potentials of pyrrole, thiophene, and aniline monomers and the corresponding polymers in different solvent systems and base electrolytes. The choice of these solvents and supporting electrolytes was based on the solubility of monomers and less nucleophilic character of solvents and base electrolytes. DC Cyclic Voltammetry has also been used to determine the redox reversibility of $[Fe(CN)_6]^{4-/3-}$ systems on bare and polymer coated platinum and glassy carbon electrodes. Studies of the redox reversibility of $[Fe(CN)_6]^{4-/3-}$ coupled had so far been made on bare electrodes and a few polymer coated electrodes. The present work has extended these studies to include a group of conducting polymers synthesized under identical experimental conditions and supporting electrolytes on a comparative basis.

Rotating disk electrode voltammetric experiments were employed to determine the diffusion coefficients of $[Fe(CN)_6]^{4-/3-}$ systems in 0.1 M KCl on bare and polymer coated platinum and glassy carbon electrodes. In all cases, the redox reaction of $[Fe(CN)_6]^{4-/3-}$ couple are diffusion controlled and found to obey the Levich equation. From the studies made on these polymers, it has been possible to infer that among the polymer films investigated, BF_4^- doped polypyrrole and polyaniline coated on platinum and glassy carbon electrodes behave more close to the bare electrodes.

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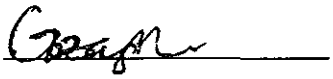
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D E C L A R A T I O N

I, the undersigned, declare that this thesis is my original work and has not been presented for a degree in any other University. All sources of materials used for the thesis have been duly acknowledged.

Name Gezahegn Telila

Signature 

Date of Submission July 4, 1994

This thesis has been submitted for examination with my approval as University advisor.

Dr. B. Hundhammer 