INVESTIGATION OF THE ELECTROCHEMICAL BEHAVIOUR OF PYRROLE, THIOPHENE AND ANILINE IN NITROBENZENE AT DIFFERENT ELECTRODE MATERIALS

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CONTENTS

LIST OF FIGURES

ABBREVIATIONS

Ac	Alternating current
CB	Conduction band
Dc	Direct current
E_g	Energy band gap
E_p	Peak potential
i_p	Peak current
PANI	Polyaniline
$TBuAClO_4$	Tetrabutylammonium perchlorate
VB	Valence band
v	Sweep rate
ω	Frequency

ABSTRACT

The electrochemical behaviour of the three compounds (pyrrole, thiophene and aniline) was studied by various electroanalytical techniques (dc and ac-cyclic voltammetry, linear sweep voltammetry, chronoamperometry, chronocoulometry). The influence of sweep rate on the voltammetric behaviour of pyrrole and 3-methylthiophene in nitrobenzene is discussed. The effect of anoding switching potential on the voltammetric behavior of pyrrole is also discussed. An attempt was made to prepare polythiophene film in nitrobenzene using various supporting electrolytes (lithium perchlorate, tetrabutylammonium perchlorate, tetraethylammonium tetrafluoroborate) on different electrodes. But no polymer was formed.

The ac-cyclic and impedance measurement techniques were used to characterize aniline oxidation in sulfuric acid. The variation of the peak current with frequency is discussed. Also the cyclic voltammograms of polyaniline film coated Pt electrode obtained in sulfuric acid were studied. The impedance spectroscopy of polyaniline film in the direction of the potential scan from positive to negative and from negative to positive has also been studied.

1. INTRODUCTION

The term polymer is a designation for synthetic or natural macromolecular compounds characterized by the fact that some atoms or groups of atoms in their molecules are repeated with more or less regular intervals. During the previous 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, whilst being organic polymers, have the unusual property of possessing high electrical conductivity, and can exhibit a range of properties from semiconducting to near-metallic behaviour.

The major breakthrough for conducting polymers occurred in two steps: in the early 1970s, films of the silvery polymer, polyacetylene, were synthesized by Shirakawa [2] via a Ziegler-Natta-type polymerization. Despite their metallic (silvery) appearance, these films were insulators. In 1977, Shirakawa and his co-workers Heeger and MacDiarmid [3] reported that partial oxidation with iodine or other oxidizing agents of polyacetylene films could give a value of conductivity up to 1000 S/cm at room temperature. This value of conductivity is high and just about in the range of metallic behaviour (metals: 10^4-10^6 S/cm). This was the first demonstration of metallic behaviour within the intra-molecular π-electron system along the polymer chain, and the significance of these results was quickly picked up by other groups and led to the synthesis of many other conjugated polymers. Typical conjugated polymers include straight chain units, five and six membered rings, and all combinations of these. The addition of heteroatoms and side chains allows for an even large variety of members of the class. Important examples are polypyrrole, polythiophene, polyfuran, poyaniline, polyphenylene, etc. Neutral conjugated organic polymers are generally insulating materials or sometimes semiconductors. Electrons cannot move along the polymer chains and through materials because of the lack of charge carriers. To make these polymers electrically conductive, one must introduce charge carriers. This is typically done by a reaction with small quantities of electron-accepting or electron-donating species. These oxidations or reductions are commonly termed "doping", in analogy to the similar changes that occur in the electrical properties of inorganic semiconductors. The term "p-doping" is used for an oxidation reaction of the polymer and "n-doping" for the reduction reaction of the polymer. The concept of doping is the unique, central, underlying, and unifying theme which distinguishes conducting polymers from all other type of polymers. The positive and negative charges on the polymer chains are compensated by counter-ions (dopants) which constitute from a few percents to several tenths of the bulk materials and play an important role on the bulk properties of the conducting polymers. Doping may be carried out chemically or electrochemically to attain different levels of conductivity.

The electrochemistry of conducting polymers is described in relation to electrosynthesis and charge storage properties. The electropolymerization of aniline, pyrrole and thiophene has been studied extensively during recent years. The combination of their metal-like conductivity and other properties plus the attributes of polymers (i.e., processability, flexibility, strength, and relative ease of modifications of the structures) make the polymer films promising materials for a number of applications including the construction of electro-optical cells and secondary batteries [4]. Although a great deal of research has been done on the electrochemical oxidation of these compounds at different electrode materials in different solvents with various supporting electrolytes, there are no reports (except thiophene) about their electropolymerization and electrochemical behaviour in nitrobenzene. Thus, it is the aim of this research project to investigate the influence of the solvent on the electrochemistry of the three compounds.

2. LITERATURE REVIEW

2.1. Historical Background

2.1.1. Polypyrrole

Among the conducting heterocycles, the most intensively studied polymer is polypyrrole. Polypyrrole was shown to be a conducting polymer in 1968. Dall'Olio *et al.* [5] prepared it by oxidation of pyrrole in sulphuric acid as a black powder called "pyrrole black", which formed an insoluble precipitate on a platinum electrode with conductivity of 8 S/cm. But it was not until subsequent experiments [6,7] in 1979 that the importance of electrochemical approach to the synthesis of conducting polymers become apparent. Diaz *et al.* [6,7] reported that the anodic oxidation of pyrrole using a tetraethylammonium tetrafluoroborate/acetonitrile electrolyte containing 1% water led to stable films which had a metal like conductivity. The key difference between the two experiments was that continuous films, which could be removed from the platinum electrode to yield free standing, easily manageable films that were stable in air and had much higher electrical conductivity (about 100 S/cm) than achieved before were obtained in the latter case. The availability of free standing films gave an access to a variety of electrical and modern analytical tests, which the well known chemical oxidation product of pyrrole, the amorphous, insoluble "pyrrole black" powders, had not permitted. Polymerization from aqueous solution was successful, but films grown from acetonitrile were of a higher quality, although pure acetonitrile containing no water at all gave non uniform films which adhered poorly to the electrode surface. Increasing the water content in aprotic solvents gave better adhesion of the film [8].

Polypyrrole is only a moderate conductor in the neutral or reduced form but becomes a good conductor when oxidized and hence doped with anions. There are no reports of doping with cation by reduction of the neutral film. In the neutral form, polypyrrole films are yellow/green and are sensitive to air and oxygen. The electrochemically prepared fresh films are in their oxidized form and are copper-bronze when viewed in reflection. The effect of oxygen on the neutral film of polypyrrole was studied by Downard *et al.* [9].

2.1.2. Polythiophene

The electrochemical synthesis of polythiophene was reported in 1981 [10] using conditions similar to those employed for the polymerization of pyrrole. The electrical conductivity of the resulting material was found to be in the range 10^{-3} to 10^{-1} S/cm. Polythiophene and its derivatives are the first examples of conducting polymers that are stable toward oxygen and moisture both in their undoped and doped states. They can be synthesized chemically or electrochemically. A chemically synthesized polymer is produced in its undoped insulating state and can be doped chemically or electrochemically to its conducting state. The electrochemically synthesized polymer is, however, obtained in the oxidized (doped) conducting state and can be electrochemically undoped to its insulating state.

The most important aspect of this heterocycle is the ease of 3-substitution, which can be used to prepare new polymers with exciting properties. To be potentially useful in electronic applications, a material must be environmentally stable, have excellent electronic and mechanical properties, and be solution or melt processible. The delocalized electronic structures of π-conjugated polymers which are responsible for their unusual electronic properties tend to yield relatively stiff chains with little flexibility and with relatively strong interchain attractive interaction which make them insoluble and non-processible. By substituting long flexible chains in the 3-positions, one can decrease the interchain interaction and achieve high solubility (and processibility) with some sacrifice in conductivity. Thus, whereas neither polythiophene (PT) nor poly(3-methylthiophene) (P3MT) is soluble, the addition of relatively long, flexible, hydrocarbon chain to the thiophene ring has increased the solubility and processibility of this conjugated polyheterocycle without significantly changing the π-electronic structure. It has been reported [11] that certain substituted polythiophenes with conductivities above 1000 S/cm can be prepared. The parent polythiophene has a room temperature conductivity of 50-100 S/cm.

2.1.3. Polyaniline

In 1862 Letheby [12] reported the anodic oxidation of aniline in a solution of dilute sulphuric acid, and that the blue-black, shiny powder deposited on a platinum electrode was insoluble in water, alcohol, and other organic solvents. Further experiments, including analytical studies, led Goppelsroeder [13] to postulate in 1876 that "oligomers" were formed by the oxidation of aniline. Polyaniline has been known in a variety of forms for over a century, and as such must be considered the oldest of the conducting polymers. Aniline blacks have subsequently been produced under a variety of conditions via both chemical and electrochemical routes with a low level of interest being maintained over the years up to the 1960s, but did not arouse wide-spread interest until relatively recently, when high quality films of polyaniline have been prepared [14-16]. Polyaniline, whose structure was first described by English and German chemists at the turn of the century, consists of up to 1000 or more repeating units. It exists in several oxidation states with electrical conductivities varying progressively from 10^{-11} S/cm to more than 10 S/cm. Different compositions of polyaniline have different colours and electrical properties. However, only one form called the emeraldine is electrically conducting.

2.2. Electropolymerization

2.2.1. A technique to prepare conducting polymers

Most of the polymers known today were firstly chemically synthesized as insulating powder or film. The interest in organic conducting polymers increase when one becomes able to synthesize a polymer directly under its conductive doped form by an electrochemical way. Since then, the electrochemical synthesis has made great strides and polymers can be synthesized by anodic or cathodic reactions from their monomers at the working electrode. The anodic polymerization is however the most commonly used process. The electrochemical polymerization requires generally a classical three-electrode cell (working anode, auxiliary and reference electrodes) immersed in a solution containing the monomer and a supporting electrolyte. The nature of the working electrode is a critical consideration for the preparation of these films. Since the films are produced by an oxidative process, it is important that the electrode does not oxidize concurrently with the aromatic monomer. For this reason, most of the available films have been prepared using a platinum or a gold electrode. Following an applied potential, a voltage is reached at which in sequence the polymerization takes place, and the doping of the polymer by the anion (p-doping) of the supporting electrolyte occurs, and finally, a film of the conducting polymer is deposited on the anode substrate (working electrode) of the cell.

The major advantages of the electrochemical approach to manufacturing conducting polymers over standard chemical methods are:

(i) a clear, one step production of the polymeric material directly onto the electrode surface, from which self supporting films can be peeled off,

(ii) there is no need for a catalyst, therefore, the electrodeposited polymer is essentially purer,

(iii) by controlling the time of the electrodeposition, the thickness of the polymer film may be varied from a few angstroms to many microns, and

(iv) by changing the nature of the counteranions in solution, the electrical and physicochemical properties of the polymer may be greatly changed for any suitable purpose.

2.2.2. Mechanism of Film Formation

The mechanism of electropolymerization is still not fully understood. The one certainty is that in the very first step the neutral monomer is oxidized to a radical cation. It must have an oxidation potential which is accessible via a suitable solvent-electrolyte system, and should react more quickly with other monomers than with other nucleophiles in the electrolyte solution. By analogy to the long-known coupling reactions of radical cations in aromatic compounds, Diaz suggested in 1982 [17] that in the polymerization of pyrrole the monomers dimerize after the oxidation at the electrode, and that protons are eliminated from the doubly charged dihydrodimer, forming the neutral species. As the dimer, on account of its greater conjugation is more easily oxidized than the monomer under the given experimental conditions, it is immediately reoxidized to the cation. Chain growth is accompanied by the addition of new cations of the monomeric pyrrole to the already charged oligomers. This is in turn followed by another proton elimination and the oxidation of the propagated oligomeric unit to a cation (Fig. 1: a→ b→ c→ f→ g).

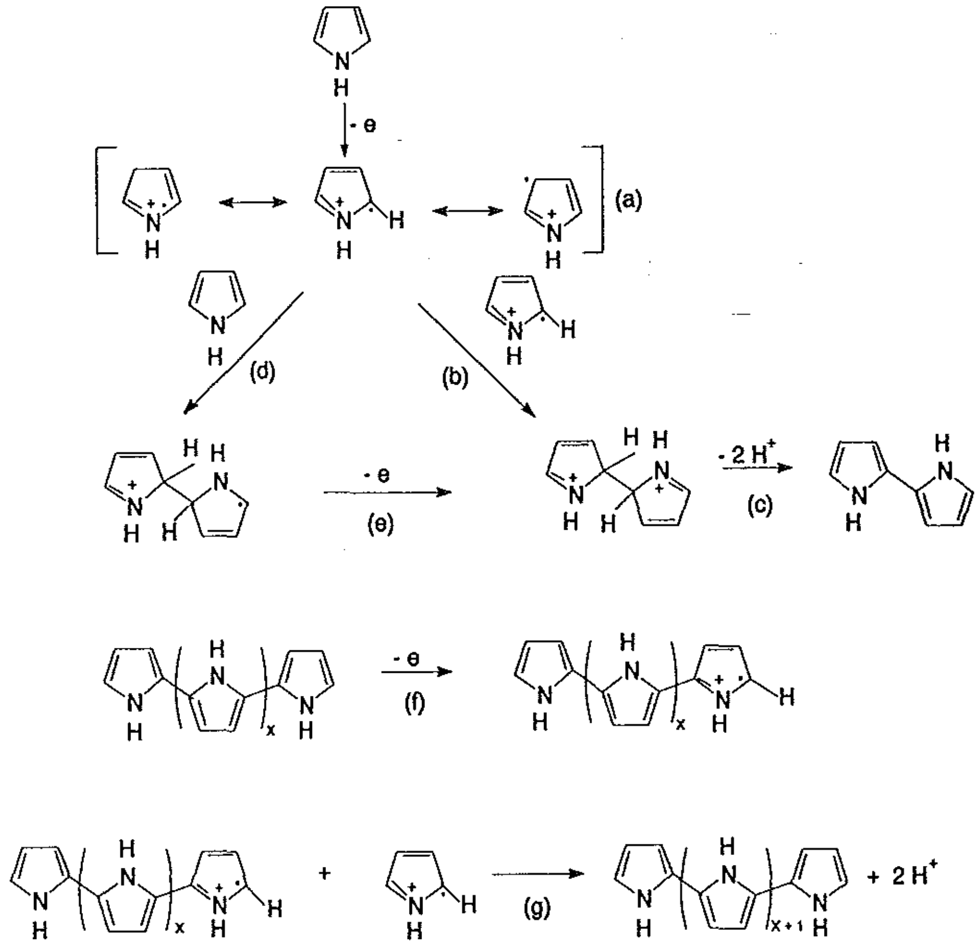


Fig. 1. A possible polymerization mechanism scheme for five membered heterocycle showing the two alternative reaction pathways of radical-radical and radical-monomer coupling [18].

Some authors [18,19] have questioned this mechanism on the ground that the strong coulombic repulsion between small cation radicals renders a direct dimerization of such particles improbable. Instead, they postulate a radical substrate coupling, whereby a single-charged dihydroderivative is formed that eliminates its protons only after a further charge transfer (Fig.1: a→ d→ e→ c→ f→ g). However, this suggestion is insufficient to characterize the chain propagation process, as growth is observed experimentally only when the oxidation of the monomer occurs parallel to the oxidation of the polymer [20].

Although the discussion continues, numerous experimental findings and theoretical considerations would appear to favour the radical-radical mechanism. Nevertheless, the formation of conducting polymers by electropolymerization is a rather complex process, and it is very difficult to optimize all parameters in one experiment.

As might be expected, the properties of polythiophene show many similarities with those of polypyrrole. As with polypyrrole, polythiophene can be prepared via routes other than electrochemical oxidation both as the neutral material [21-23] or in the p-doped form [24].

In general the mechanism of polymerization for thiophene appears to be similar to that of pyrrole, occurring via a radical coupling mechanism [25].

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 (perhaps slightly more like nigraniline). The fact that the spectrum of the anode precipitate 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 nigraniline and emeraldine. The marked similarities in 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 [14,26].

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 as synthesized from aniline. When the electrochemical behaviour of these two compounds is compared, it was found that the electrochemical oxidation of p-aminodiphenylamine gave 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 [27].

Ever since the electrochemical oxidation of aromatic amines has been studied [14], it is generally admitted that the polymerization mechanism of aniline in acid medium is the one described in figure 2.

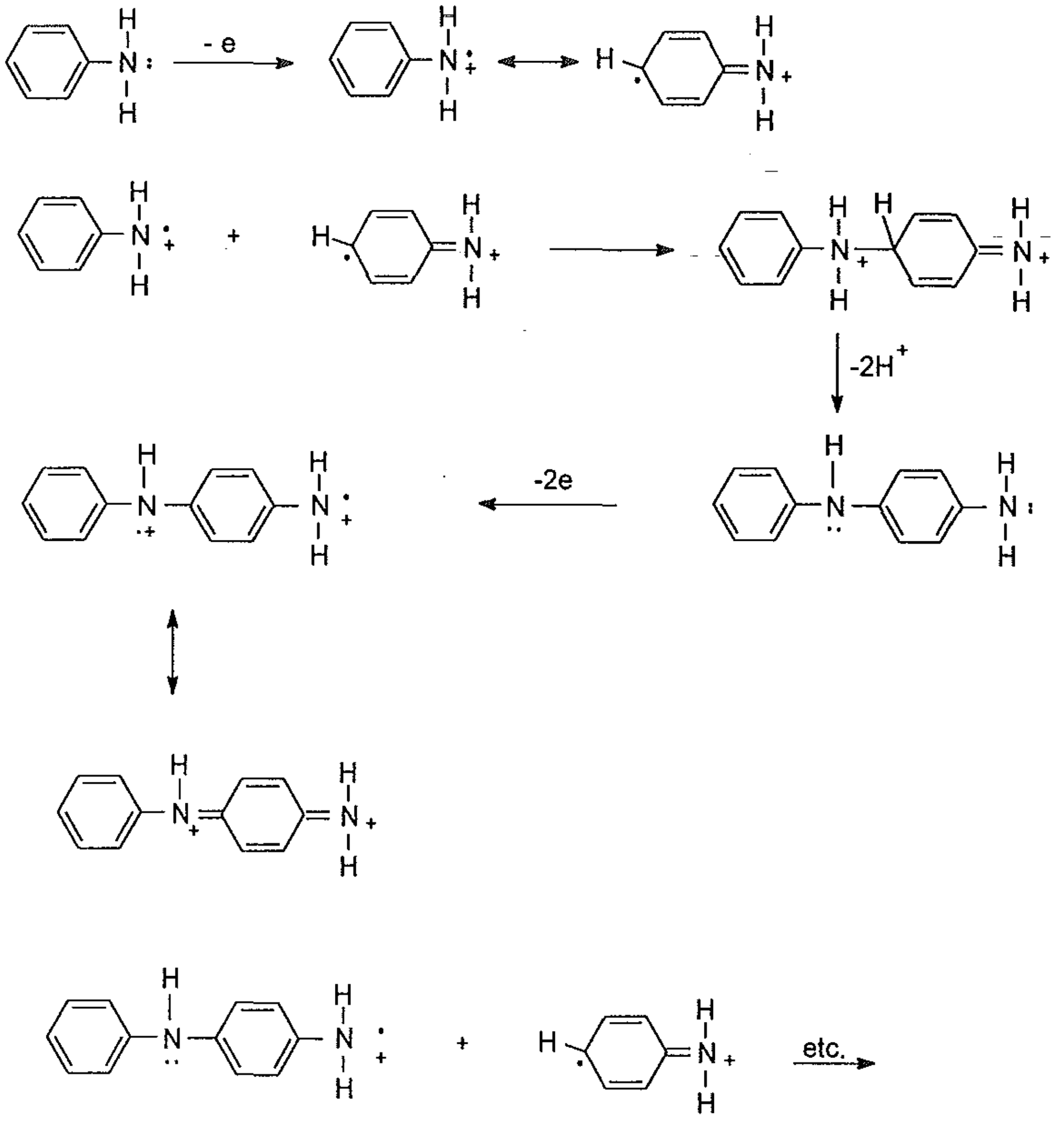


Fig. 2. General reaction scheme for the polymerization of aniline (Ref. 1, p. 23).

2.3. Effect of Counterions On the Properties of Films

The electropolymerized films of polypyrrole in the conducting form contain 25-30% anion (by weight) which is affiliated with the cationically charged polymer chains. The amount of anion found in each film is governed by_the level of oxidation of the polymer and is 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 simply by changing the electrolyte salt of the solution.

As can be seen in table 1, a wide variety of anions have been used to prepare thick free standing films of polypyrrole [28]. The anions listed in table 1 are poorly nucleophilic and permit the formation of good quality films. Tetraalkylammonium salts were used in the preparation of these films. The level of oxidation of polypyrrole is 0.25-0.32 per pyrrole units, corresponding to one anion for every four pyrrolic units. The level of oxidation is an intrinsic characteristic of the polymer and is not sensitive to the nature of the anion [29]. The anion, however, does influence both the structural properties and the electroactivities of the films. The topology of the surface is dramatically different for films containing the various perfluoride, sulfonate and carboxylate anion [17,28]. The differences observed between the surfaces is not reflected in the packing structure of the bulk material. Thus, with the exception of one or two of the anions listed in table 1, all the films have similar densities which are in the range of 1.45-1.51 g/cm^3.

Table 1: Polypyrrole Film With Different Anions

Anion	Oxidation level	Density (g/cm^3)	Conductivity (S/cm)
BF_4^- , PF_6^- , AsF_6^-	0.25-0.32	1.48	30-100
ClO_4^-	0.30	1.51	60-200
$CH_3C_6H_4SO_3^-$	0.32	1.37	20-100
$BrC_6H_4SO_3^-$	0.33	1.58	50
$CF_3CO_2^-$	0.25	1.45	12
$CF_3SO_3^-$	0.31	1.48	0.3-1.0
HSO_4^-	0.30	1.58	0.30
FSO_3^-	-	1.47	10^{-2}

The anions have a strong influence on the electroactivity and the conductivity of the films. The films with perfluoride and the perchlorate anions are more conducting (30-200 S/cm), than the films with the sulfonate and carboxylate anions (0.01-100 S/cm). The exception is the films containing the aromatic sulfonate anions (20-100 S/cm), which are as conducting as perfluoride anions.

2.4. Effect of Solvent On the Electropolymerization Process

The study of the electrochemistry of all conjugated polymers requires a suitable solvent/electrolyte system in which the experiments can be performed. Choice of the solvent is critical if side reactions such as solvent polymerization [29,30] are to be avoided.

Recognizing that the polymerization reaction proceeds via radical cation intermediates, it becomes apparent that the reaction will be sensitive to the nucleophilicity of the environment in the region near the electrode surface. This then places some restrictions on the choice of the solvent and the electrolyte. For this reason, studies have to be performed in aprotic solvents, which are poor nucleophiles.

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 an acetonitrile solution. Films are not produced in nucleophilic aprotic solvents such as dimethylformamide, dimethylsulfoxide, and hexamethylphosphoramide, unless the nucleophilicity of the solution is reduced by the addition of protic acid.

Electrochemical polymerization of pyrrole, for example, 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 aprotic solvents, such as alcohols and mixed aqueous aprotic solvent mixtures, films can be prepared with intermediate conductivity values and good physical strengths [31].

2.5. Aprotic solvents-Nitrobenzene

The use of aprotic solvents is of interest in many cases where aqueous solutions lack desired or have undesired properties. The scarcity of protons makes it generally simpler to elucidate the mechanism of an electrode reaction, as the product of the first electron transfer, a radical ion, is more stable in aprotic than in protic medium, and the same is often the case for other intermediates.

"Dry" aprotic solvents usually contain some water, which is especially of importance in voltammetric studies where the concentrations of water and substrate are about equal. The influence of a certain molar concentration of water depends on the solvent, the supporting electrolyte, and the substrate.

Electrochemical phenomena may also be simplified in organic solvents, compared to aqueous solutions, due to the less important role adsorption [32] plays in organic solvents.

Nitrobenzene has been used for electrolysis [33]; it was found that certain radicals were rather stable in this solvent. Nitrobenzene has a liquid range from 5.7 to 210.9 °C; tetraalkylammonium salts may be used as supporting electrolyte.

While it might seem strange to use nitrobenzene as a solvent system, it is highly inert in the present context and deserves further consideration as a solvent for electrochemical oxidations. Exactly why nitrobenzene is more inert in the present instance than, say, acetonitrile cannot be answered until more is known of the nature of the chemical reaction of the radical cations. The distinct advantage of nitrobenzene is that it allows observation of more clearly one-electron processes.

2.6. Charge Storage Mechanisms in Conducting polymers

Organic polymers, provided they are chemically produced, are initially insulators. Their metal like properties, i.e., their high conductivity and optical reflectivity, only become obvious after doping. Even in the earliest stages of research on these materials, it was clear that these processes were not comparable with the classical doping of typical semiconductors. Rather, they correspond to oxidation in the case of p-doping or reduction in the case of n-doping. Suitable redox reagents are either chemical electron acceptors (I, Br, AsF_5, $FeCl_3$, $LiClO_4$), or electron donors. The selection of donors, however, is limited to the alkali metals (Li, Na, K). Therefore, p-type doping is more common. It also renders higher conductivity with a better stability [34]. The process of doping may also be electrochemically induced via an electrochemical cell.

Because of the redox reaction the polymer chain is negatively charged in the case of reduction and positively charged in the case of oxidation. To maintain electroneutrality the appropriate counterions (dopants) diffuse into the polymer during charging and out of the polymer during discharging.

The charge transport phenomena in conducting polymers has been extensively investigated but still remains poorly understood. This is largely due to the complex structure and morphological forms of the conductive polymer [34].

The electrical properties of any material are determined by its electronic structure. The theory that most reasonably explains the electronic structure of materials is band theory. In the solid state, the atomic orbitals of each atom overlap with the same orbitals of their neighbouring atoms in all directions to produce molecular orbitals similar to those in small molecules. In a solid, the number of atomic orbitals is about 10^{22} per cm^3, and thus the number of molecular orbitals would also be 10^{22}. When these many orbitals are spaced together in a given range of energies, they form what looks like continuous energy bands.

The energy spacing between the highest occupied and lowest unoccupied bands is called the band gap (E_g). The highest occupied band is called the valence band (VB), and the lowest unoccupied band is the conduction band (CB).

The properties of conventional materials depend on how the bands are filled. When the bands are filled or empty, no conduction occurs. If the band gap is narrow, at room temperature thermal excitation of electrons from the valence band to the conduction band gives rise to conductivity. This is what happens in classical semiconductors. When the band gap is too wide, thermal excitation at room temperature is insufficient to excite electrons across the gap and the solid behaves as an insulator. The high conductivity of metals is due to partially occupied bands-a partially filled conduction band, a partially empty valence band, or a zero band gap.

Conductive polymers are peculiar in that they conduct current without having a partially empty or partially filled bands. Their electrical conductivity cannot be explained well by simple band theory [35,36]. To explain some of the electronic phenomena in these organic polymers, concepts from physics that are new for chemists, including solitons, polarons, and bipolarons, have been applied to conducting polymers since the early 1980s.

For the sake of clarity, the conduction mechanism of heterocyclic polymers, such as that of polypyrrole (PPY) or polythiophene (PT) will be described. In the undoped state, polypyrrole is a poorly conductive material with an energy gap of 3.2 eV between the conduction and valence bands (Fig. 3a).

The removal of an electron in a p-doping (oxidation) process leads to the formation of a positive charge localized in the polymer chain accompanied by a lattice distortion which is associated with a relaxation of the aromatic structural geometry of the polymer chains towards a quinoid form. This form extends over four pyrrolic rings [37]. The localized charge is termed a polaron and in chemical terms it represents a radical cation. The presence of polaron on the chain introduces two localized electronic levels in the gap: a singly occupied bonding polaron state above the valence band edge and an empty antibonding polaron state below the conduction band edge. For the polaron created, the lower level is half filled and the upper one is empty (Fig. 3b).

If another electron now is removed from the already oxidized polymer containing the polaron, two things can happen: This electron could come from either a different segment of the polymer chain, thus creating another independent polaron, or from the first polaron level (remove the unpaired electron) to create a special dication, which solid-state physists call a bipolaron. Low doping levels give rise to polarons, whereas higher doping levels produce bipolarons. The bipolaron again extends over four pyrrolic rings. A bipolaron introduces two states in the band gap, above the valence band edge and below the conduction band edge. Very importantly the bipolaron bonding state (VB), in contrast to the polaron case, is empty (Fig. 3c). If a great many bipolarons are formed, say as a result of high doping, their energies can start overlapping at the edges, which creates narrow bipolaron bands in the band gap (Fig. 3d).

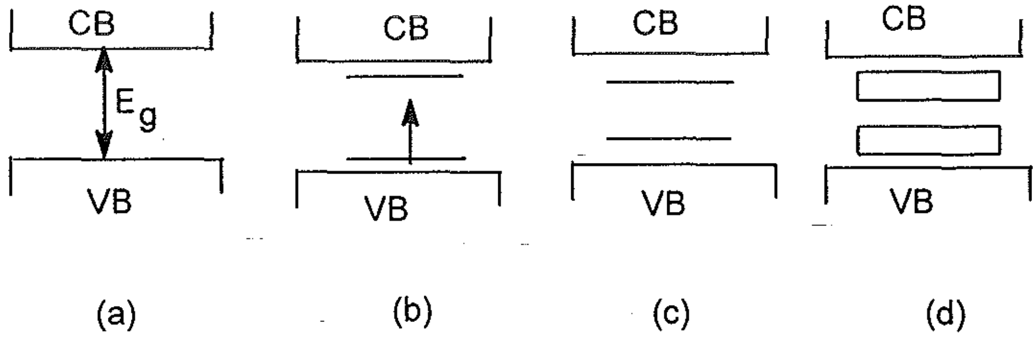


Fig. 3. Electronic band structure showing [37]

(a) neutral polymer (c) bipolaron state

(b) polaron state (d) bipolaron band.

The essence of electrical conductivity is that charges must be able to move under an applied electric field. Thus, the described band evolution accounts for the unique transport properties of the conducting polymers. 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. Conduction by polarons and bipolarons is now thought to be the dominant mechanism of charge transport in conducting polymers. This conduction mechanism, elaborated and demonstrated by Bredas and Street [38], clearly points out the basic difference between the electrical properties of conducting polymers and those of inorganic semiconductors, since in the former the conduction takes place only via mobile polarons and bipolarons while the conduction band remains totally empty and the valence band remains totally full. Such a mechanism also requires transport of the negative counterions which must migrate along the polymeric chain to compensate the transport of the positive bipolaronic charges. Therefore, unlike the situation for inorganic semiconductors, the conduction mechanism for polymers involve the movement of both ionic and electronic charges.

The conduction mechanism described in the case of polypyrrole, also applies to other heterocyclic polymers, such as polythiophene and its derivatives.

2.7. Some Applications of Conducting Polymers

After many studies on the conductivity of organic materials doped with acceptors and donors, this area of materials science received a boost in 1977 with the evidence that polyacetylene doped with iodine or SbF_5 exhibited high metal like conductivity. Recent emphasis has been focused toward the development of transparent, soluble, processable, intrinsic (non-doped) conducting polymers [39-41]. In the back of many minds lies the perception and hope that such materials may also provide the technological foundation for new and/or improved electrical materials or devices. Assuming that a chemically and thermally stable polymeric conductor can be prepared and processed, a plethora of feasible applications may be considered.

A conducting polymer might be expected to have one or more of the properties listed below:

- High, metal- like electrical conductivity
- Large polarizability
- Low density
- Flexibility

-Film and/or fiber formation

-Processibility

-Transparency

-Low environmental contamination

-Compatibility with other polymers for composites

-High strength

-Redox active

-Fast optical response

One of the most promising near-future applications of conductive polymers is rechargeable batteries. The use of conducting polymers for energy storage applications stems from the fact that they can function as battery electrodes by replacing the conventional metals currently used. These batteries will have long life, usable voltage of 3 volts, and energy density several times that of the currently available commercial nickel/cadmium and lead/acid batteries [42-44]. Plastic, all solid-state batteries, are now under development in several industrial laboratories, including those of Hitachi and Bridgestone in Japan [42,43,45], Allied- Signal in the U.S. [42,46], and Varta in Germany [42,43]. Bridgestone has already commercialized a high cycle-life, button-type, 3-volt battery with a polyaniline cathode and lithium-aluminium alloy anode. Also, Varta recently commercialized a lithium-aluminium/polypyrrole, button-type, 3-volt battery developed jointly with BASF. At this stage, these batteries are excellent for applications in which long life, low-power, and reliable operation are required, such as timers for videocassette recorders, batteries for hand-held calculators, fax machines, television remote controls, and wristwatches.

Batteries that deliver high power at high rates are not yet available. Their development remains a great challenge, which, if successful, will open the way to long-range, light-weight electric vehicles.

Recently, Matsushita Research [47] developed a new aluminium electrolytic capacitor, in which electrochemically prepared polypyrrole is used as a solid electrolyte. The capacitor has excellent thermal and moisture stability and has been used in a small video camera.

Conjugated polymers that can be repeatedly driven from insulating to conductive states electrochemically with high contrast in colour are promising materials for electrochromic device technology [24,44,48-50]. Typical examples are polyaniline, polypyrrole, polythiophene and their derivatives whose electrical and optical properties may be monitored by reversible electrochemical processes. The electrochemical p-doping-undoping process, which switches conjugated polymers between insulating and conductive states and causes the colour changes, is an oxidation-reduction reaction involving ion transport into and out of the polymer matrix to balance the electronic charge. There are many applications of electrochromic materials: architectural glazing, adjustable reflectance mirrors for automobiles, electrochromic displays, sunglasses, and thermal smart windows.

Another very recent exciting development involves the use of lightly-doped polyaniline film membranes for the separation of gases [51,52]. Separations far exceed the selectivity of all known gas separation membranes for many simple gas mixtures (for example, O_2/N_2). The University of California, Los Angeles, groups of Kaner and Reiss [45] have discovered that if conductive polyaniline is doped and undoped repeatedly, it becomes porous and can act as a gas separation membrane.

Kuhn and his coworkers [39,47] at Milliken Research Corp. in Spartanburg, S.C., have invented a process to produce electrically conductive fabrics and textiles by impregnating them with polypyrrole and polyaniline. These textiles have the same strength and tactility as their regular commercially available counterparts and have been considered for use in composites. For example, the conductive fabrics could be incorporated into the plastic composites used in airframes for charge dissipation during lightning strikes, thus preventing damage to the airplanes.

Resistance changes that occur in conducting polymers when exposed to oxidants in solution can be used in specific sensor applications. One example of biosensors, under development at Ohmnicron Corporation [46] utilizes the ability of triiodide to oxidize polyacetylene as a means of measuring the concentration of glucose in solution. This technique of measuring glucose concentration begins with the glucose oxidase mediated oxidation of glucose in solution. This creates hydrogen peroxide which, in the presence of lactoperoxidase, oxidizes iodide in buffer solution to triiodide. The triiodide, being a good dopant for polyacetylene, oxidizes the polymer and causes a resistance change that is proportional to the concentration of glucose in solution. Many other potential applications of conducting polymers including indicators, electronic devices (circuits, photovoltaic cells, light emitting diodes, transistors), radar dishes, loudspeakers (electrostatic, transparent), artificial muscles and nerves are listed in Ref. 39, P. 588.

3. EXPERIMENTAL

3.1. Materials

Tetrabutylammonium Perchlorate (Fluka), Acetonitrile (Riedel-deHaen), Lithium Perchlorate (Ventron), Tetrabutylammonium Chloride (Aldrich), Thiophene (BDH Lab. Reag.), and 3-methylthiophene (Aldrich) were used without further purification. Pyrrole (Aldrich) and Aniline (Aldrich) were distilled under reduced pressure to colourless liquids. Potassium Sulphate was available in the laboratory and used as such. Nitrobenzene (Riedel-deHaen) was used after purification: First, it was washed three times with 10% (V/V) H_2SO_4, then three times with 10% (W/V) NaOH and finally with doubly distilled water until the pH was 7. The purified nitrobenzene was dried with anhydrous Sodium Sulfate. All aqueous solutions were prepared with doubly distilled water.

3.2. Instrumentation

The electrochemical investigations were performed in a one compartment three-electrode cell containing the appropriate electrolyte solution (the corresponding monomer and the supporting electrolyte in the respective solvent), Pt, Au or ITO were employed as the working electrodes. A platinum wire was used as the counter electrode. In the aqueous system, a saturated calomel electrode was used as reference electrode. In acetonitrile, an aqueous silver-silver chloride was used and in nitrobenzene a silver-silver chloride electrode in 0.01 mol/L tetrabutylammonium chloride in nitrobenzene was used as reference electrode.

The ac-cyclic voltammetry experiments were carried out with home made potentiostat. The voltammograms were recorded with an x-y/x-t recorder. All the other electrochemical investigations were performed with BAS 100W electrochemical analyzer at laboratory temperature of 22 ± 2°C.

4. RESULTS AND DISCUSSION

4.1. Characterization of Electrode Materials

The potential window of the working electrode in the solvent containing the respective supporting electrolyte is shown in Fig. 4a and Fig.4b. The cyclic voltammograms at different electrode materials (Pt, Au and GC) in acetonitrile and in nitrobenzene with 10 mmol/L tetrabutylammonium perchlorate as supporting electrolyte show a fairly wide potential window. The electrochemical area of the Pt electrode was determined by chronocoulometry utilizing equation (1).

$$Q= 2nFAD^{1/2}Ct^{1/2}\pi^{-1/2} \quad \text{..................................(1)}$$

where Q is the charge in coulomb, n is the number of electrons involved in the reaction and A is the electrode area in cm^2. Using the diffusion coefficient as 6.5×10^{-6} cm^2/sec for ferrocyanide in 0.5 mol/L potassium chloride [53] the electroactive area of the Pt electrode was found to be 0.07 cm^2, based on the slope (4×10^{-5} $Colb/sec^{1/2}$) of the plot of Q *vs.* $t^{1/2}$ (Fig.5). The electrochemical area is in very good agreement with the geometrical area of the disc electrode (0.07 cm^2).

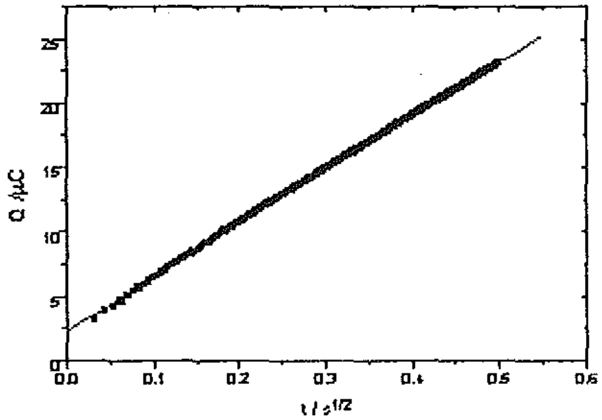


Fig. 5. Chronocoulometric response of ferrocyanide in 0.5 mol/L KCl at Pt-disc electrode.

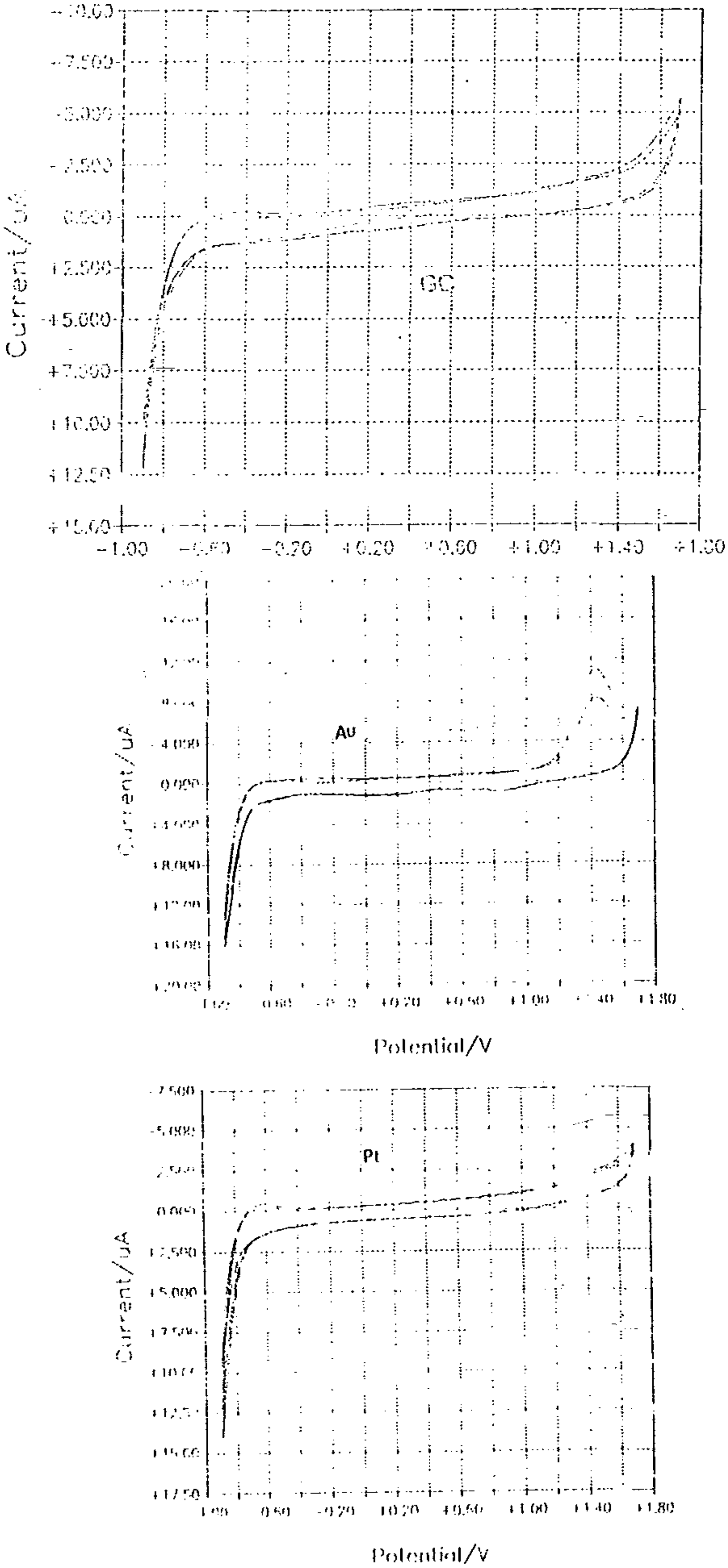

GC
Current/uA
-10.00
-7.500
-5.000
-2.500
0.000
+2.500
+5.000
+7.500
+10.00
+12.50
+15.00
-1.00
-0.60
-0.20
+0.20
+0.60
+1.00
+1.40
+1.80
Au
Current/uA
4.000
0.000
+8.000
+16.00
+20.00
+0.20
+0.60
+1.00
+1.40
+1.80
Potential/V
Pt
Current/uA
-7.500
-5.000
-2.500
0.000
+2.500
+5.000
+7.500
+10.00
+12.50
+15.00
+17.50
-1.00
-0.60
-0.20
+0.20
+0.60
+1.00
+1.40
+1.80
Potential/V

Fig. 4a

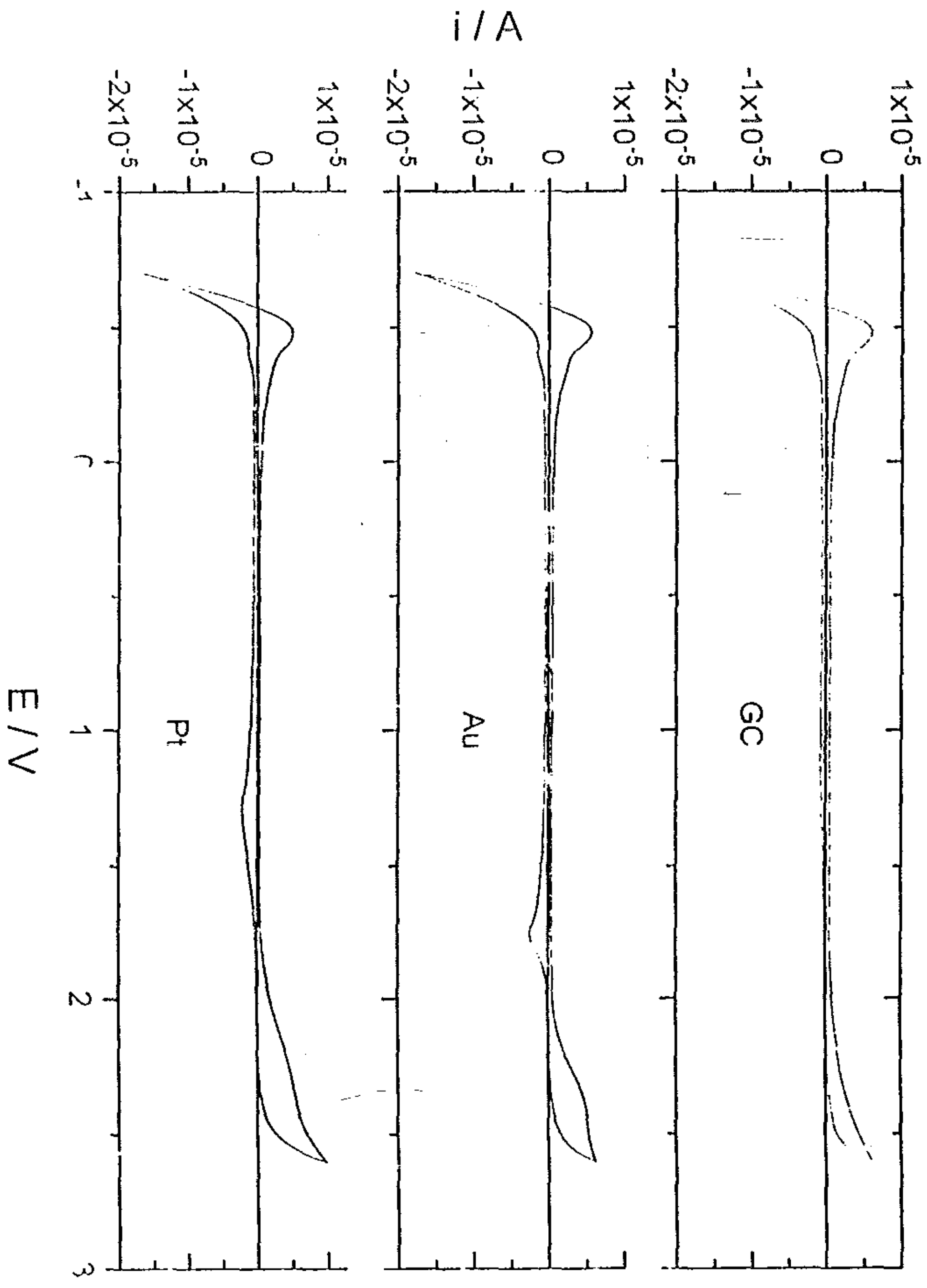


Fig. 4b

Fig. 4. The cyclic voltammograms of tetrabutylammonium perchlorate at different electrode materials in (a) acetonitrile, (b) nitrobenzene. Scan rate: 50 mV/sec.

4.2. Electrochemical Oxidation of Pyrrole

The electrochemical oxidation of pyrrole has been studied in acetonitrile and in nitrobenzene. In both solvents, 10 mmol/L tetrabutylammonium perchlorate was used as supporting electrolyte. Acetonitrile was chosen as solvent for the sake of comparison of our experimental results with those obtained by other researchers. Fig. 6 shows the cyclic voltammogram of 1 mmol/L pyrrole in acetonitrile. A cross-over appears on the reverse sweep of the first cycle in the voltammogram. Pletcher *et al.* [54,55] assume the cross-over as proof of the start of the nucleation process as the first step in the formation of the polymer film. The growth of the polymer film is indicated by the increasing currents in the potential range from 0 to 1 V on successive cycles. This result is the same as that reported by J. Heinze [18].

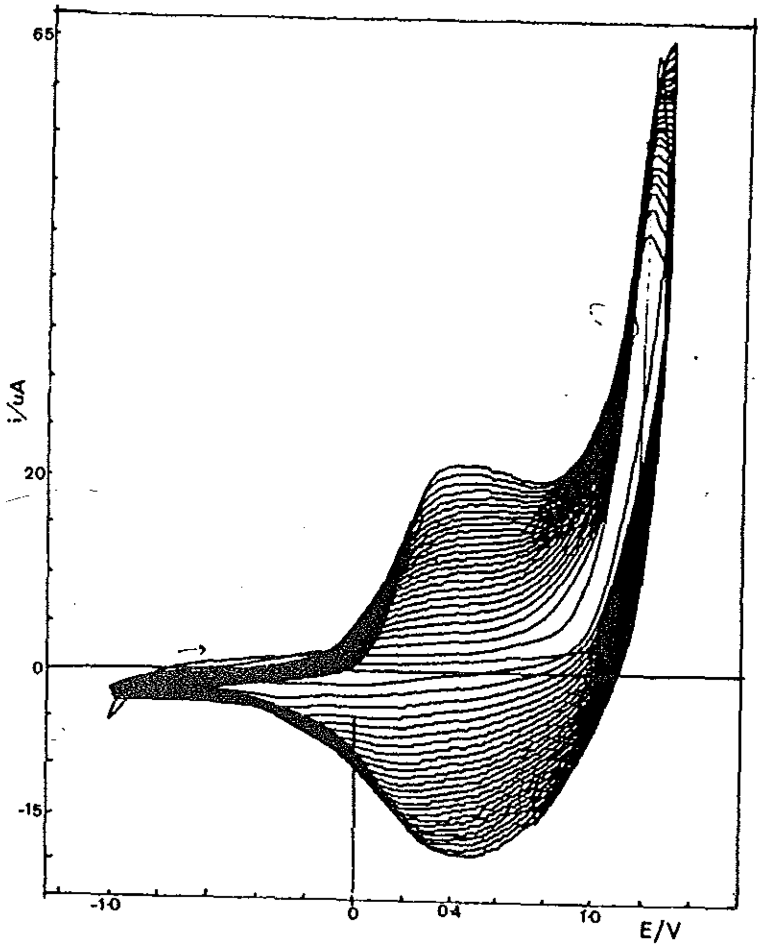


Fig. 6. Cyclic voltammogram of the oxidation of pyrrole in acetonitrile at Pt electrode (scan rate: 50 mV/sec.).

The voltammogram of the oxidation of pyrrole in nitrobenzene at a platinum electrode is shown in Fig. 7a. As observed in acetonitrile a cross-over appears on the reverse sweep of the first cycle which indicates a similar reaction mechanism as in acetonitrile in the beginning of the film formation. But unlike in acetonitrile, two reduction peaks at about 0.5 V and -0.1 V are observed.

Fig. 7b shows the cyclic voltammogram of pyrrole oxidation in nitrobenzene with a rotating disc electrode. Comparison of the negative going scan of the voltammogram in the quiet solution (Fig. 8a) with that obtained at the rotating electrode (Fig. 8b) indicates the formation of soluble oxidation products. The cathodic peak which is observed at about 0.5 V in quiet solution is not obtained at the rotating electrode. On the other hand the reduction of polypyrrole deposited at the electrode causes the cathodic current peak at about -0.1 V.

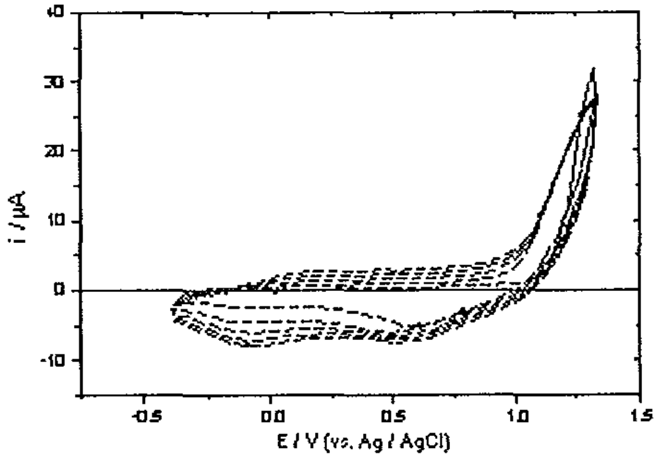


Fig. 7a

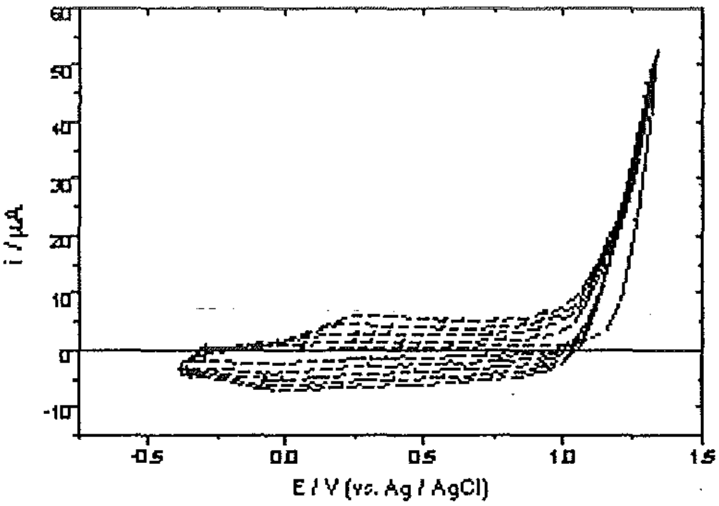


Fig. 7b

Fig. 7. Cyclic voltammograms of pyrrole oxidation in nitrobenzene at Pt electrode (a) in quiet solutions (b) at 3000 rpm.

A second piece of information that can be obtained from the cyclic voltammograms is about the growth rate of the polymer film at the electrode. Despite the fact that no direct information about the thickness of the deposit can be obtained, the relative growth of the polymer layer is reflected in the increasing current (either cathodic or anodic) with successive cycles. Results extracted from Fig. 7a are shown in Fig. 9. There is a fairly good linear relationship between current and the number of cycles at all selected potentials. This linear relationship holds up to 25 cycles.

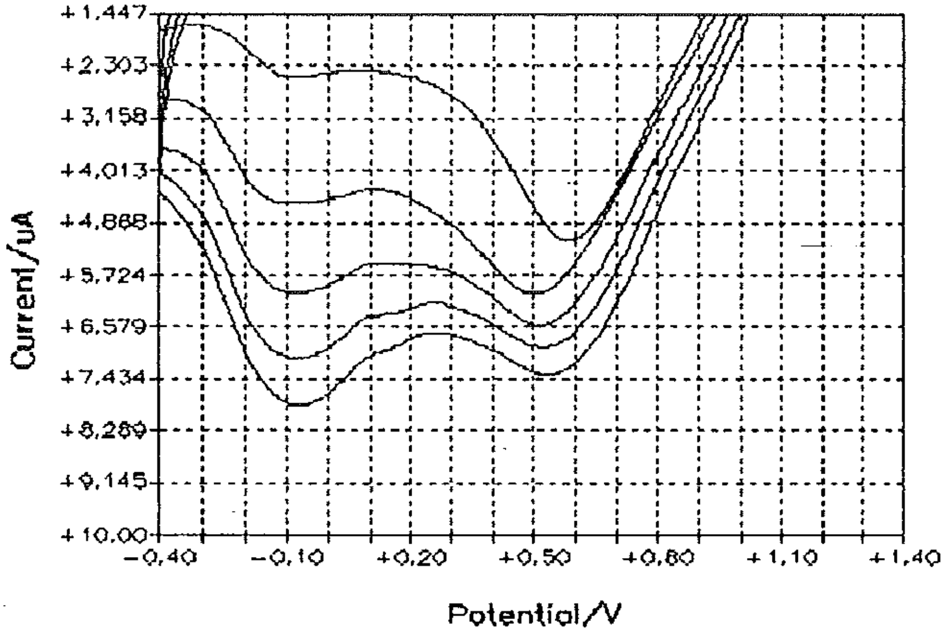


Fig. 8a

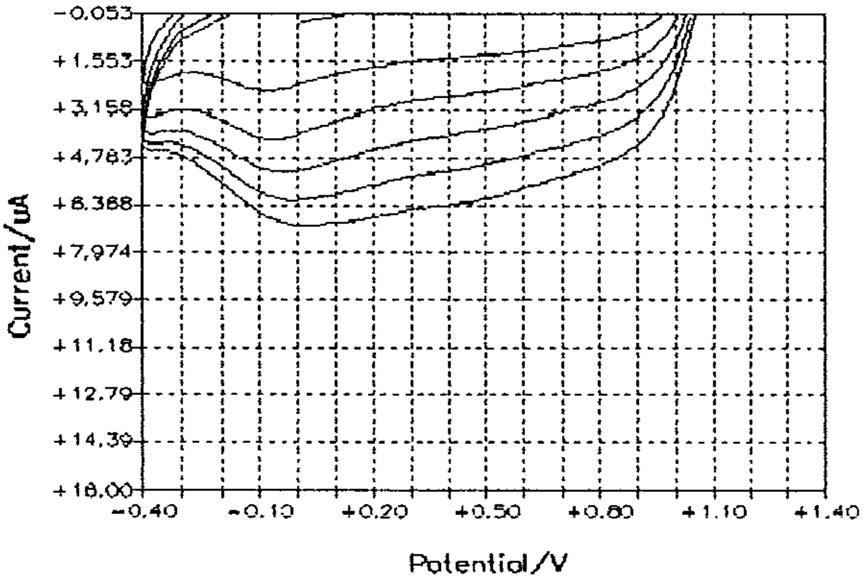


Fig. 8b

Fig. 8. Enlarged negative going scan of the voltammograms (a) and (b) in Fig. 7.

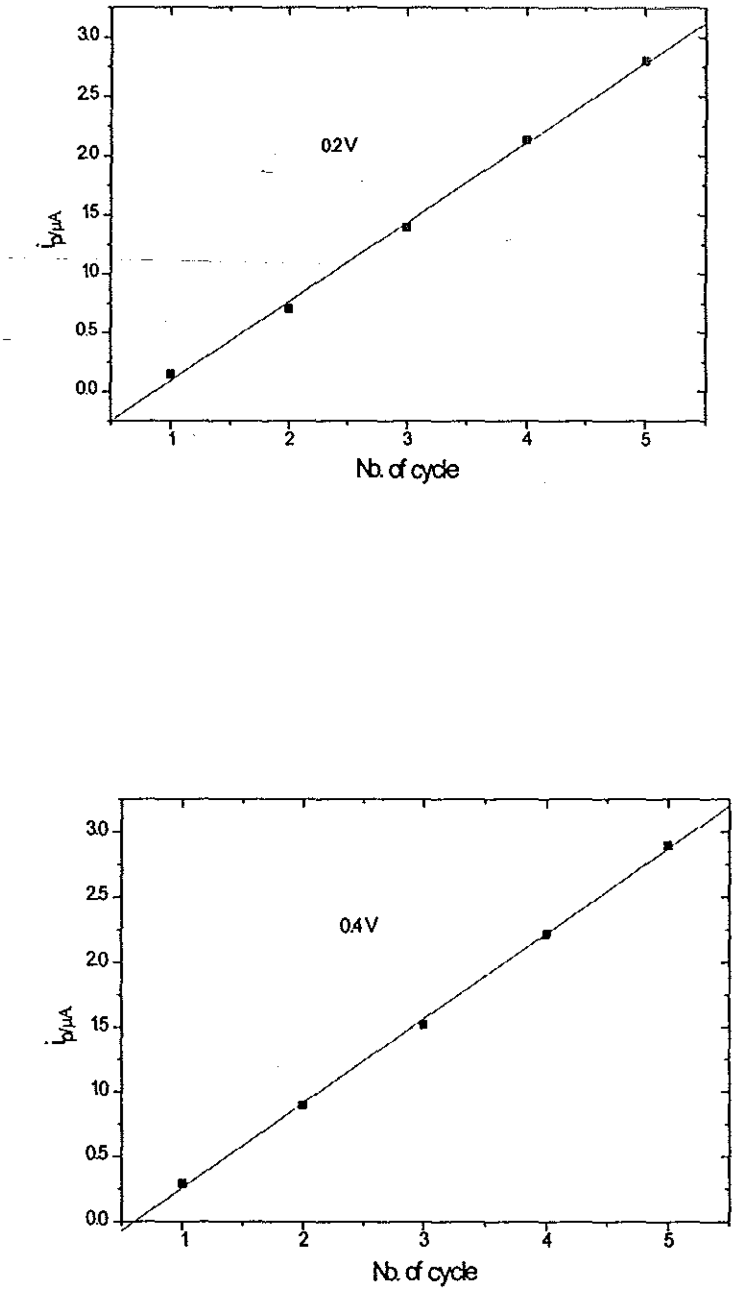

3.0
2.5
2.0
15
10
0.5
0.0
$i_{p/\mu A}$
1
2
3
4
5
Nb. of cycle
0.2V
3.0
2.5
2.0
15
10
0.5
0.0
$i_{p/\mu A}$
1
2
3
4
5
Nb. of cycle
0.4V

Fig. 9a

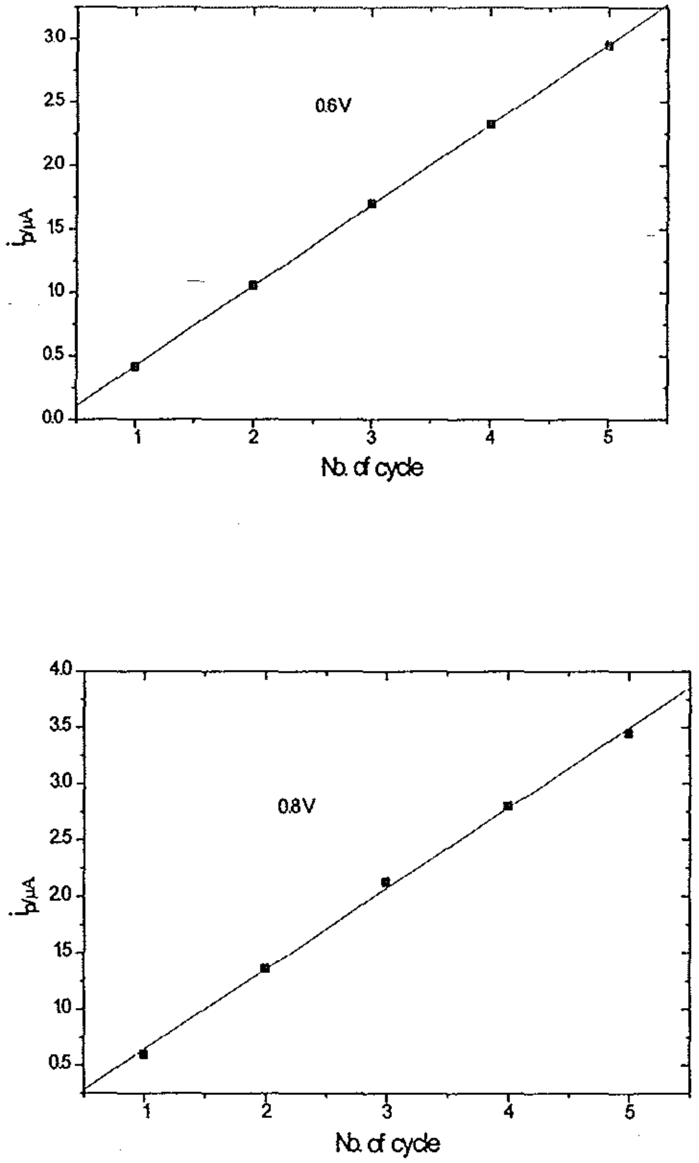


Fig. 9b

Fig. 9. Current increase with number of cycles in the anodic branch of Fig. 7a at the potentials indicated in the diagram.

In order to investigate the primary step in the polypyrrole formation and the influence of the anodic switching potential, voltammograms with varying anodic limit were recorded (Fig. 10). In all cases the crossover of anodic and cathodic branch is observed indicating the nucleation process being independent of the anodic switching potential. No additional peaks are observed in the negative going scan and thus no indication of additional reaction products due to over-oxidation of the primary oxidation product is given. The increase of the anodic current at positive potentials may be due to the formation of dications from the primary formed radical cation.

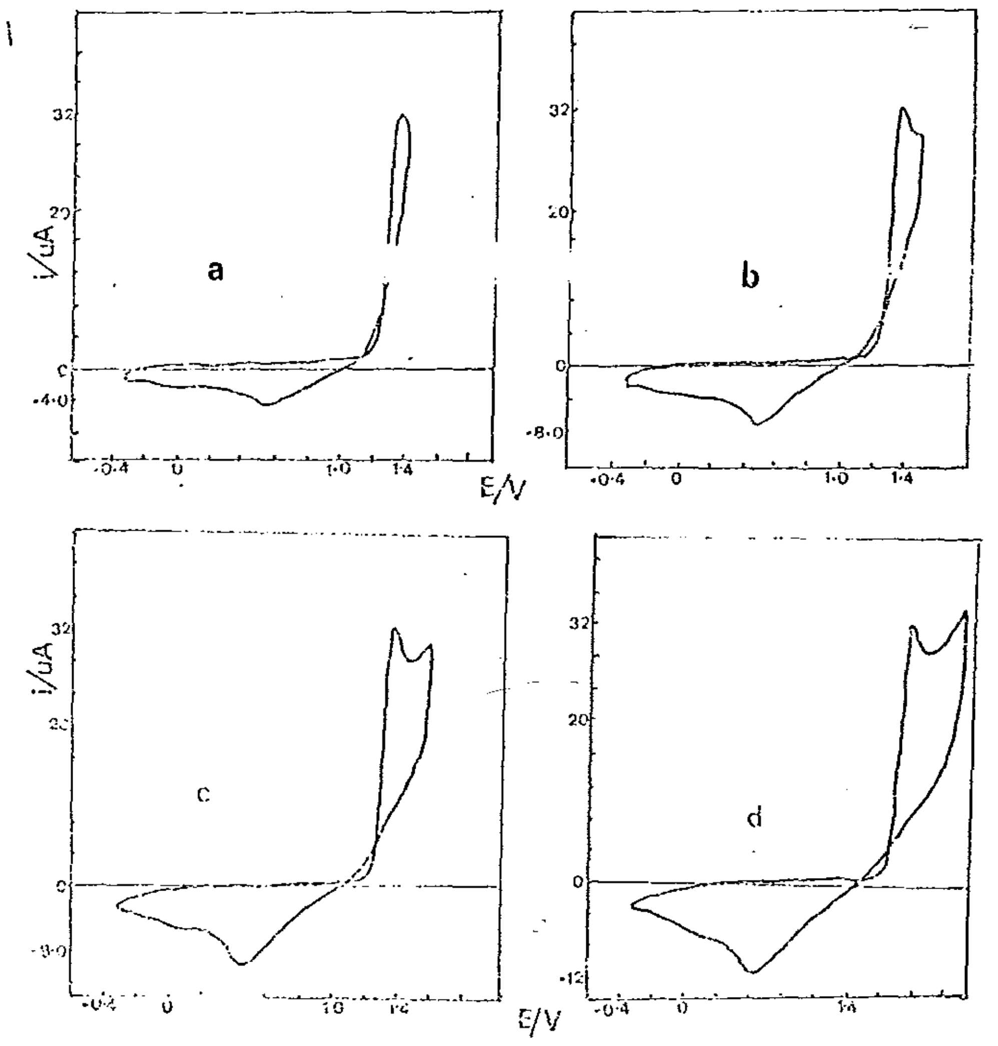


Fig. 10. First voltammetric cycle of 1 mmol/L pyrrole in nitrobenzene at different switching potentials: (a) 1.4 V (b) 1.5 V (c) 1.6 V (d) 1.7 V . Scan rate : 50 mV/sec.

The dependence of peak current and peak potential on sweep rate at a freshly polished Pt-electrode has been studied for the first oxidation step of pyrrole in order to get some information about the kinetics of this step. Fig. 11a and Fig. 11b show the experimental results.

The variation of the peak potential with sweep rate is somewhat unusual. The shift to positive values with increasing sweep rate may be interpreted by assuming a charge transfer controlled oxidation provided that the reaction product formed is soluble. But the observed invariance of the peak potential at sweep rate higher than 60 mV/s would indicate a diffusion controlled oxidation. On the other hand the linear dependence of the peak current on the square root of the sweep rate is not indicating any change in the mechanism of the pyrrole oxidation. Unfortunately this dependence does not distinguish between diffusion controlled or charge transfer controlled electrode reaction. Diffusion control can be ruled out by evaluating the apparent diffusion coefficient from the slope of the i_p *vs.* $v^{1/2}$ plot. From the slope obtained (1.447×10^{-6} $AV^{1/2}sec^{-1/2}$) the value of the diffusion coefficient would be about 6×10^{-5} cm^2sec^{-1}, a value which is at least one order higher in magnitude than the diffusion coefficient of pyrrole in nitrobenzene. The redox mechanism for the first oxidation step of pyrrole can be described by the scheme:

$Py \rightarrow Py^{\cdot +} + e^-$ (electron transfer step)

$Py^{\cdot +} + Py \rightarrow 2Py^{\cdot +}$

The anodic growth of polypyrrole is linear upon time t (and not upon $t^{1/2}$) [56], showing that the rate-limiting step is the cation radical activity itself and not the diffusion of the monomer to the electrode.

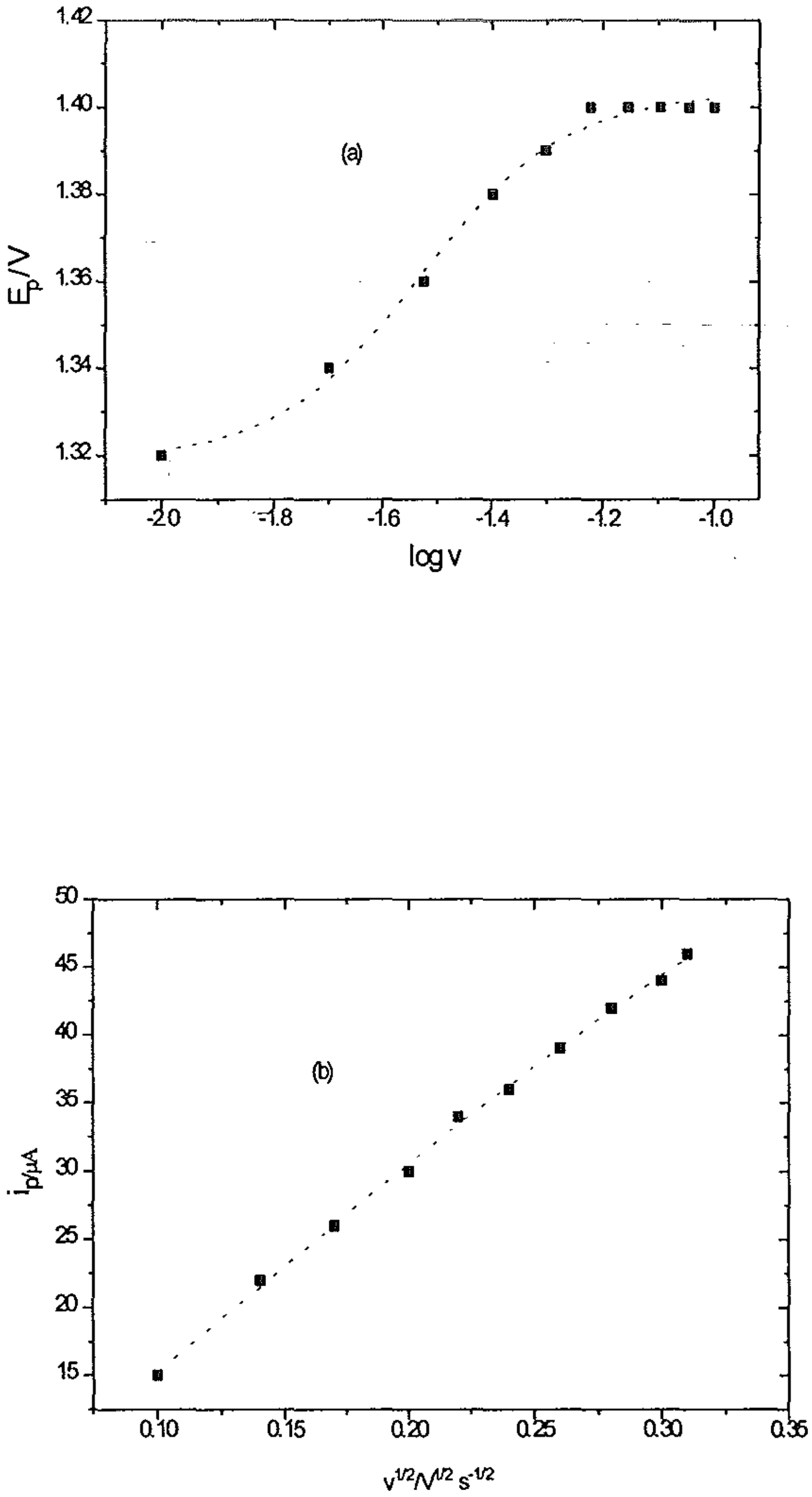


Fig. 11. Effect of sweep rate on pyrrole oxidation at a bare Pt electrode in nitrobenzene (1 mmol/L pyrrole and 10 mmol/L TBuAClO$_4$).

Fig. 12a shows the chronocoulometric curve for the oxidation of pyrrole in nitrobenzene. The charge consumed in the oxidation step becomes nearly linearly dependent on time after about 10 seconds while at short times a square root dependence is observed (Fig. 12b and Fig 12c). When the diffusion coefficient for pyrrole is evaluated from the slope at the very beginning of the experiment we obtained D = 8.8x10^{-6} cm^2/sec, which is one order of magnitude higher than the value obtained earlier. The linear dependence of the charge on time is in accordance with the observation of a linear increase of the film growth with the number of cycles in the voltammetric experiment. The time where the electrode is kept within a potential range where film formation can occur is about 8 sec per cycle thus after few cycles the condition for a linear increase of the film thickness as indicated in the chronocoulogram is given.

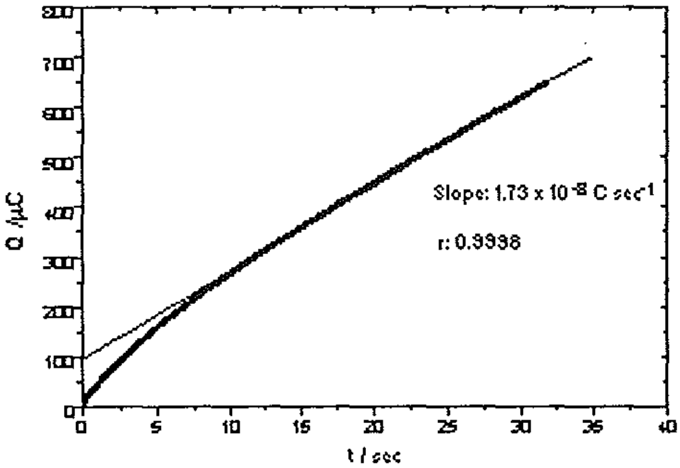


Fig. 12a

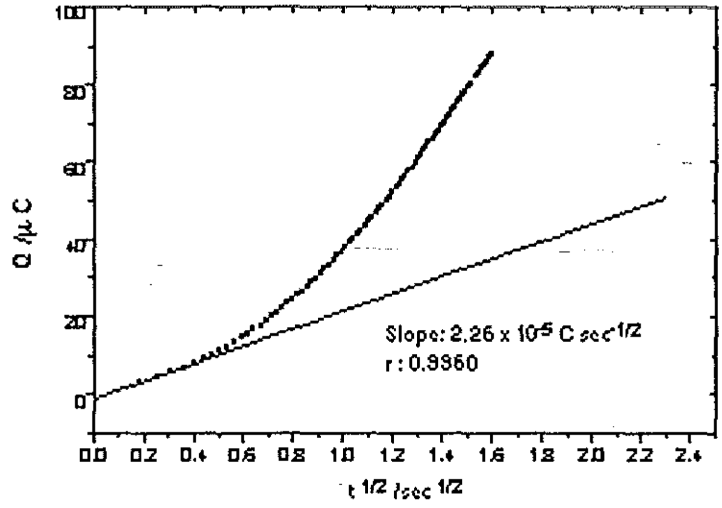


Fig. 12b

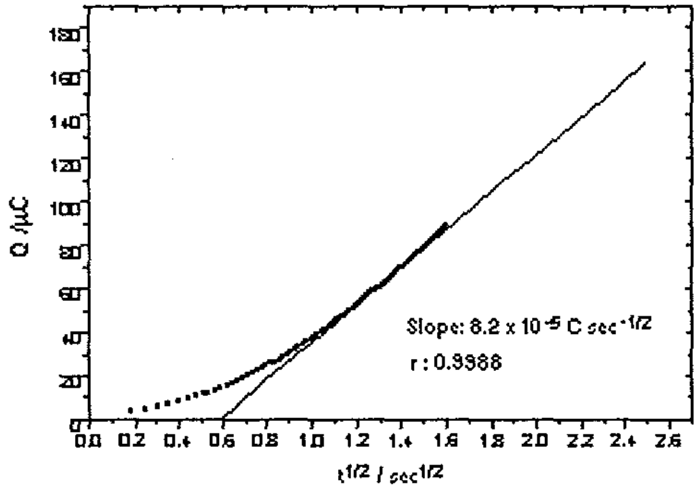


Fig. 12c

Fig. 12. Chronocoulometric response recorded during the oxidation of pyrrole in nitrobezene at Pt electrode.

The chronoamperometric response of the electrode (Fig. 13) indicates at short times a decrease in current which fits rather good to a $t^{-1/2}$ dependence with a slope of 8.5 x 10^{-6} Asec$^{1/2}$ followed by an increase in current which we attribute to the onset of the film growth at some active nuclei formed in the first period of the experiment. The following slight current decrease with time may indicate the film growth at the completely covered electrode. The evaluation of the chronoamperogram is shown in Fig. 13.

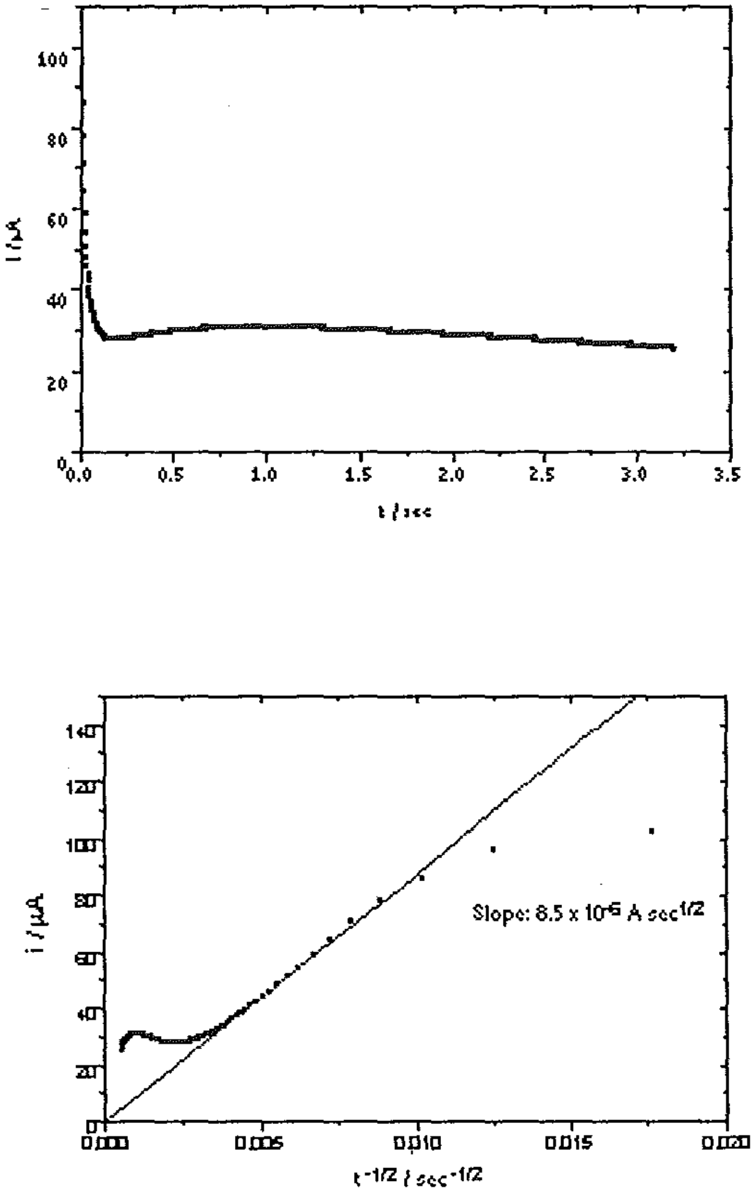


Fig. 13. Chronoamperometric response for the oxidation of pyrrole in nitrobenzene at Pt electrode.

From these experimental results we conclude that the electropolymerization of pyrrole in nitrobenzene follows a similar mechanism as in other solvents. The first step in the sequence is the oxidation to a radical cation which interacts with the monomer and forms nuclei at the electode surface which are the centres for further growth of the polymer film. After at least a mono layer of polymer has been deposited at the electrode the film thickness is linearly increasing with time.

4.3. Electrochemical Oxidation of Thiophene

The possibilities of obtaining polythiophene by the electropolymerization of the monomer using various supporting electrolytes in nitrobenzene at an indium tin oxide (ITO) [57] and at a Pt electrode [58] are reported. Fig. 14 shows the cyclic voltammogram of thiophene oxidation obtained in our experiment. A bluish colour was observed around the electrode surface. No polymer deposition at the electrode was observed. The reason for that is most probably the solubility of the oligomers formed in the course of the electrochemical oxidation. An oxidation peak at about 1.6 V with a peak current of 14 mA may correspond to the reduction peak at 0.8 V with peak current of 14 μA. Since no polymer was formed, further experiments were not carried out on thiophene.

4.4. Voltammetric Behaviour of 3-methylthiophene in Nitrobenzene

The cyclic voltammograms of 1 mmol/L 3-methylthiophene obtained on platinum electrode in nitrobenzene with 10 mmol/L tetrabutylammonium perchlorate as supporting electrolyte are shown in Fig. 15. The voltammograms compare the voltammetric behaviour of 3-methylthiophene in quiet solutions and at a rotating disc electrode. The cyclic voltammogram obtained in quiet solution shows two reduction peaks at about 0.29 V and 0.97 V. Both soluble and insoluble reaction products are formed during the potentiodynamic oxidation. The cathodic current peak obtained in the quiet solution at about 0.29 V and not being observed at the rotating electrode is attributed to the reduction of a soluble reaction product. On the contrary, the cathodic peak current at 0.97 V is assumed to be due to the reduction of an oxidation product which is deposited at the electrode surface. Similar to that of thiophene no polymer was formed.

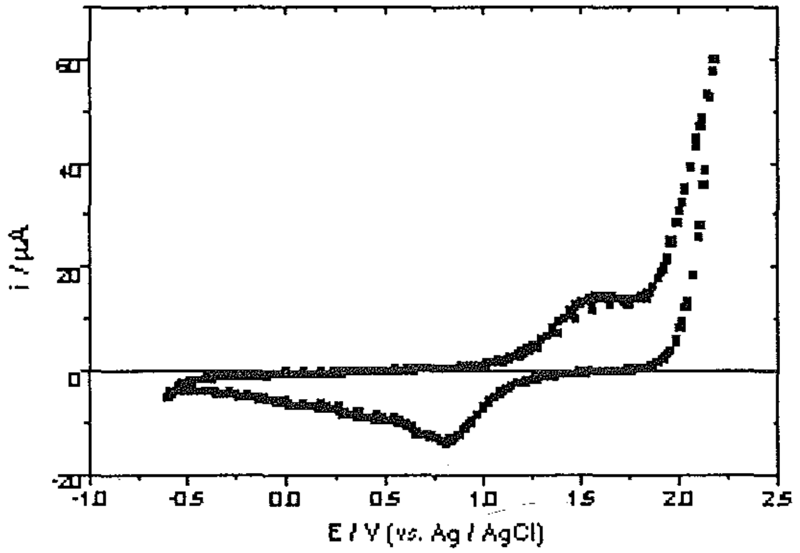


Fig. 14. Cyclic voltammogram of 0.4 mol/L thiophene in nitrobenzene at Pt electrode (scan rate: 50 mV/sec).

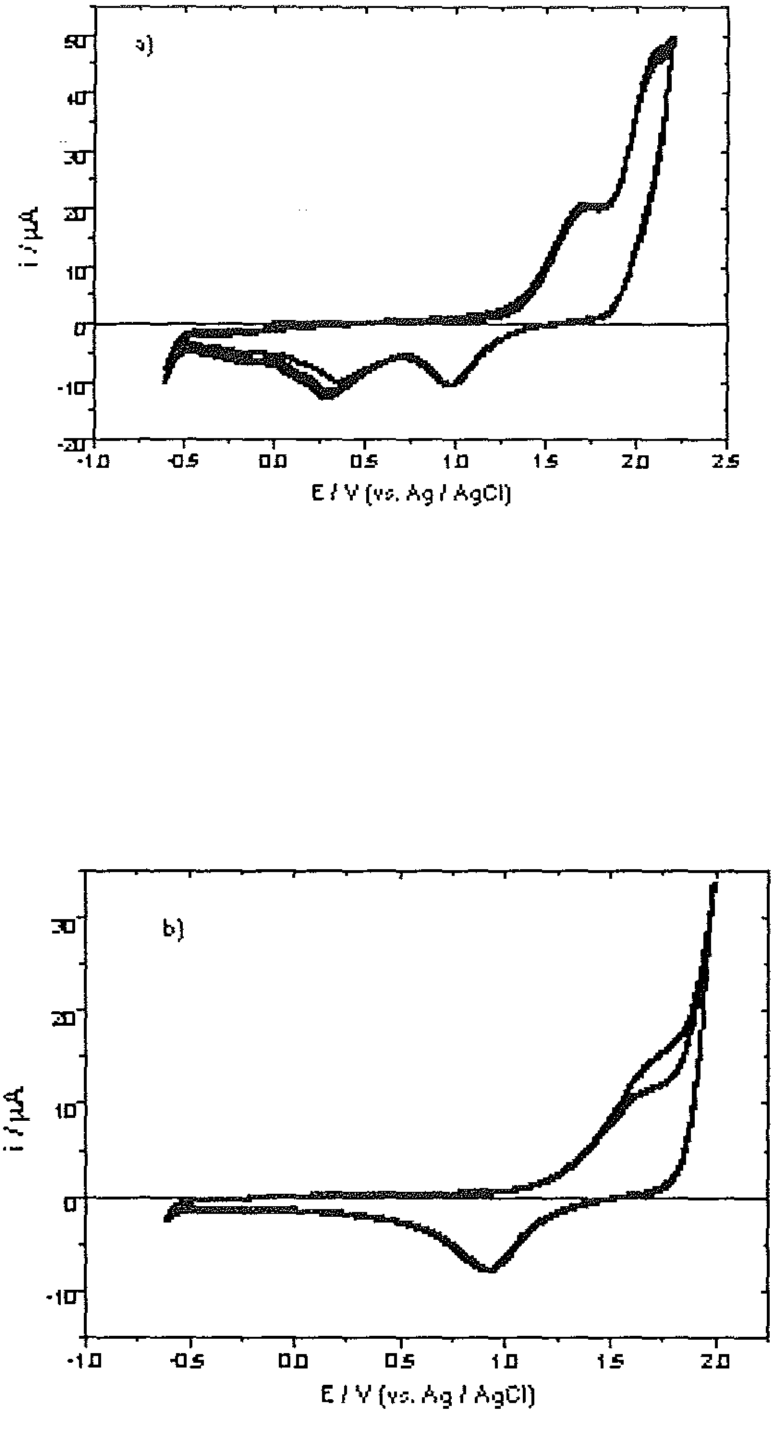


Fig. 15. Cyclic voltammograms of the oxidation of 3-methylthiophene in nitrobenzene at Pt electrode: (a) in quiet solution, (b) at 1500 rpm.

The dependence of peak current and peak potential on sweep rate has been studied for the first oxidation step of 3-methylthiophene on a freshly polished Au-disc electrode. The linear sweep voltammetry (LSV) response curve was recorded in nitrobenzene with 10 mmol/L tetrabutylammonium perchlorate and 1 mmol/L 3-methylthiophene. Fig. 16a and Fig. 16b show the experimentally obtained results.

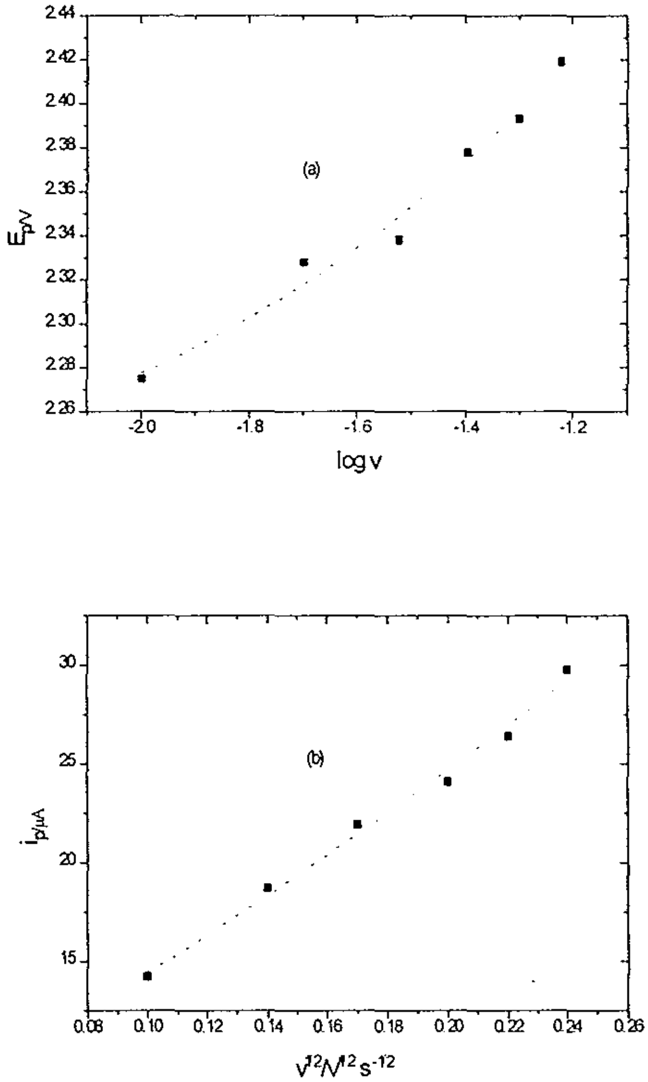


Fig. 16. Effect of scan rate on the oxidation of 3-methylthiophene at a bare Au electrode in nitrobenzene (1 mmol/L 3-methylthiophene and 10 mmol/L $TBuAClO_4$).

As shown in the figure the peak current varies linearly with $v^{1/2}$. The linear dependence of the peak current on sweep rate does not distinguish between reversible and irreversible processes since in both cases i_p is directly proportional to $v^{1/2}$. However, the variation of E_p with sweep rate (Fig. 16b) may indicate that the process, i.e., the formation of the radical cation, is a slow redox process.

4.5. Electrochemical Oxidation of Aniline in Sulphuric Acid

Although it was not the aim of this investigation to study the electropolymerization of aniline in sulfuric acid some experiments were carried out in order to see the ac-voltammetric response of a polyaniline film in sulfuric acid and compare the results with those obtained by impedance spectroscopy.

The cyclic voltammogram of 10 mmol/L aniline in 0.5 mol/L aqueous sulphuric acid solution at a platinum electrode is shown in Fig. 17. The electrochemical polymerization of aniline has been carried out by cycling the potential between -0.2 V to 1.0 V. As can be seen from the voltammogram, three oxidation peaks and the corresponding reduction peaks are observed.

The growth of the polymer film is found to be exponential with the number of cycles as shown in Fig. 18. The charge obtained by integration of the anodic and cathodic branch of the voltammogram was taken as a measure of the film growth. At the sweep rate of 500 mV/sec the ratio of cathodic to anodic charges is close to unity (Fig. 19). In the chosen potential range the polyaniline is changing from its fully reduced form (leuco-emeraldine) to the polaron state (emeraldine) to the bipolaron state (nigraniline). These changes are seen by the colour changes at the electrode from yellow through green to dark blue. Since only the polaron state (emeraldine) exhibits electrical conductivity, ac-voltammetric investigations and impedance spectroscopy may be used to monitor changes in conductivity and structure as well.

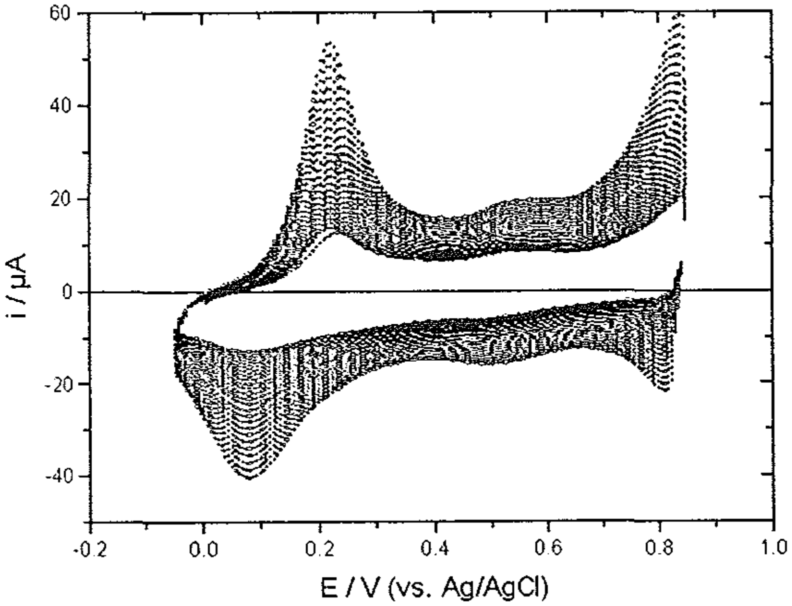


Fig. 17. Cyclic Voltammogram of aniline oxidation in 0.5 mol/L H_2SO_4 at Pt electrode at scan rate of 50 mV/sec.

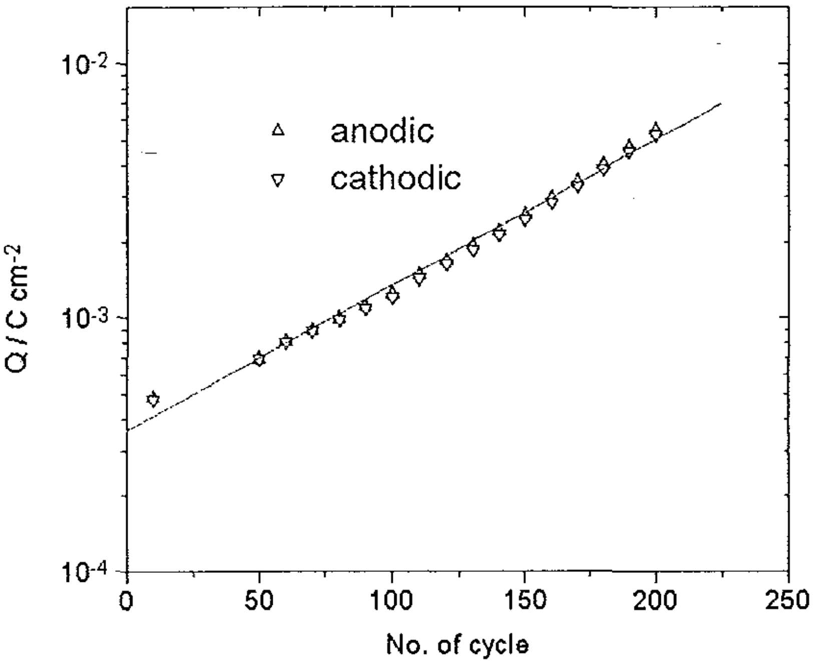


Fig. 18. The variation of charge with number of cycles in logarithmic scale for the polyaniline film shown in Fig. 17.

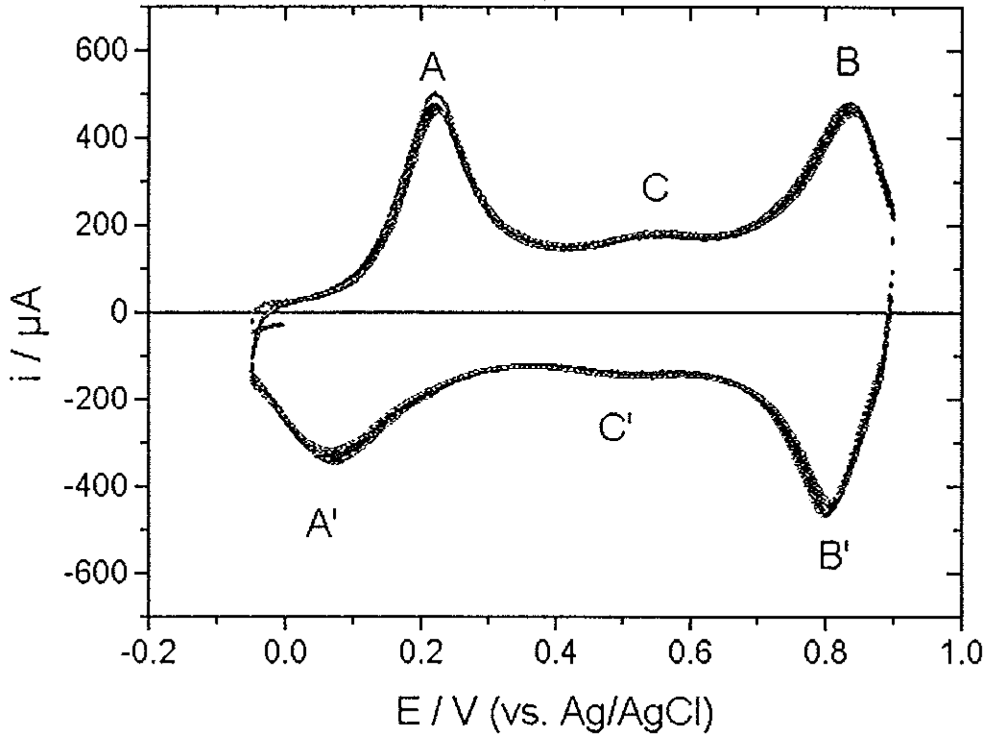


Fig. 19. Cyclic voltammogram of polyaniline at Pt-disk electrode (0.07 cm^2) in 0.5 mol/L H_2SO_4 (sweep rate : 500 mV / sec., 25 cycles).

The cyclic voltammograms of polyaniline film coated Pt-electrode obtained in 0.5 mol/L sulphuric acid at potentials between -0.1 V and 0.5 V *vs.* Ag/AgCl at different sweep rates are shown in Fig. 20. The potential range was chosen thus only the oxidation of leuco-emeraldine to emeraldine is taking place. The anodic peak currents are proportional to the sweep rate as expected for the oxidation of surface films. The variation of the anodic peak current with sweep rate is shown in Fig. 21.

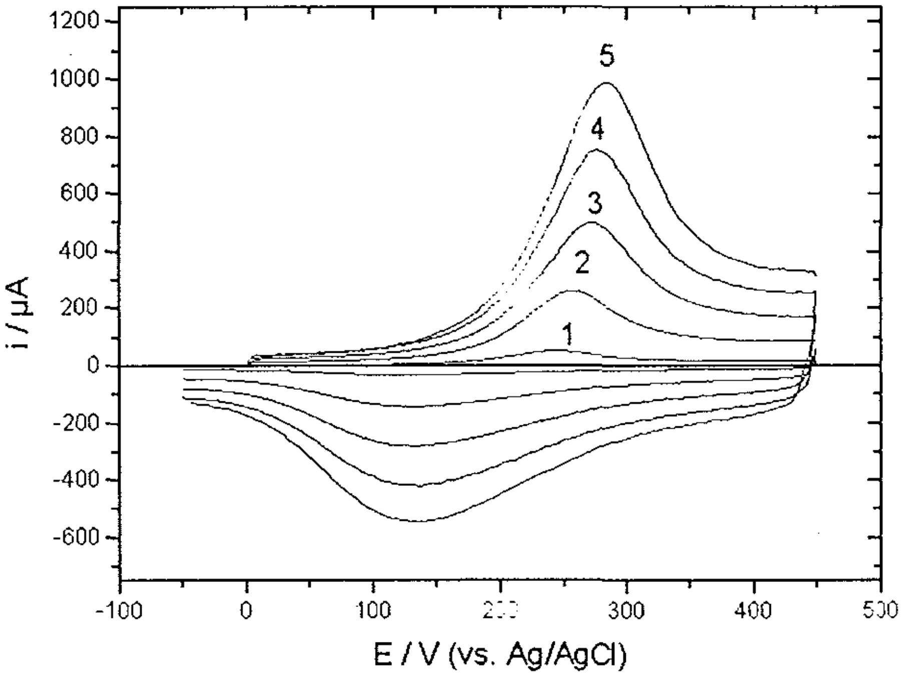


Fig. 20. Cyclic voltammogram of polyaniline film coated pt electrode at different scan rates: (1) 50 mV/sec (2) 250 mV/sec (3) 500 mV sec (4) 750 mV/sec (5) 1000 mV/sec.

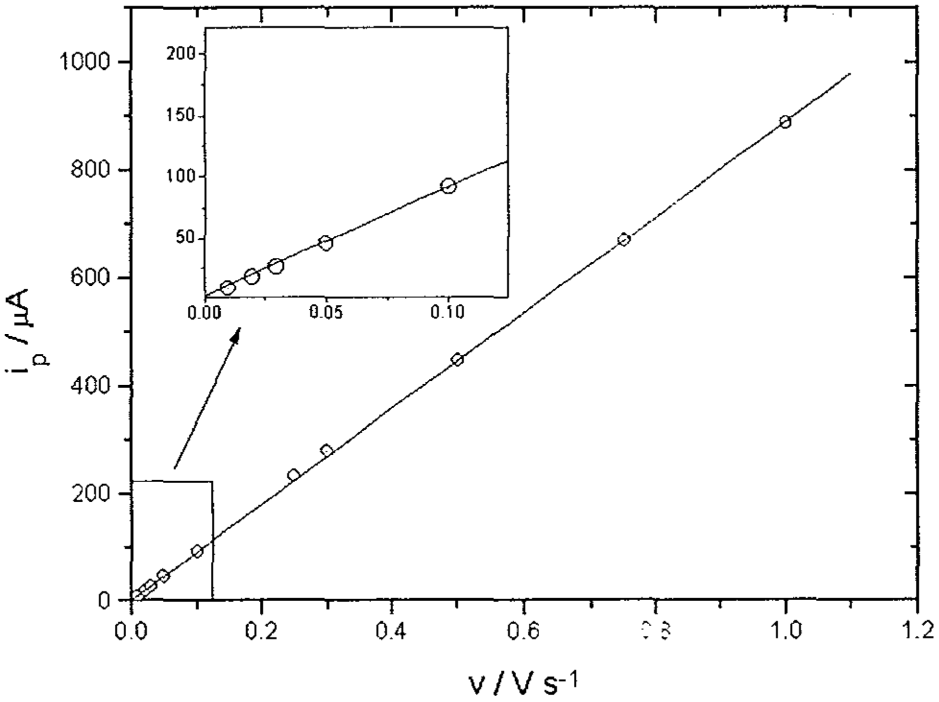


Fig. 21. The variation of anodic peak current with sweep rate for polyaniline film coated Pt electrode.

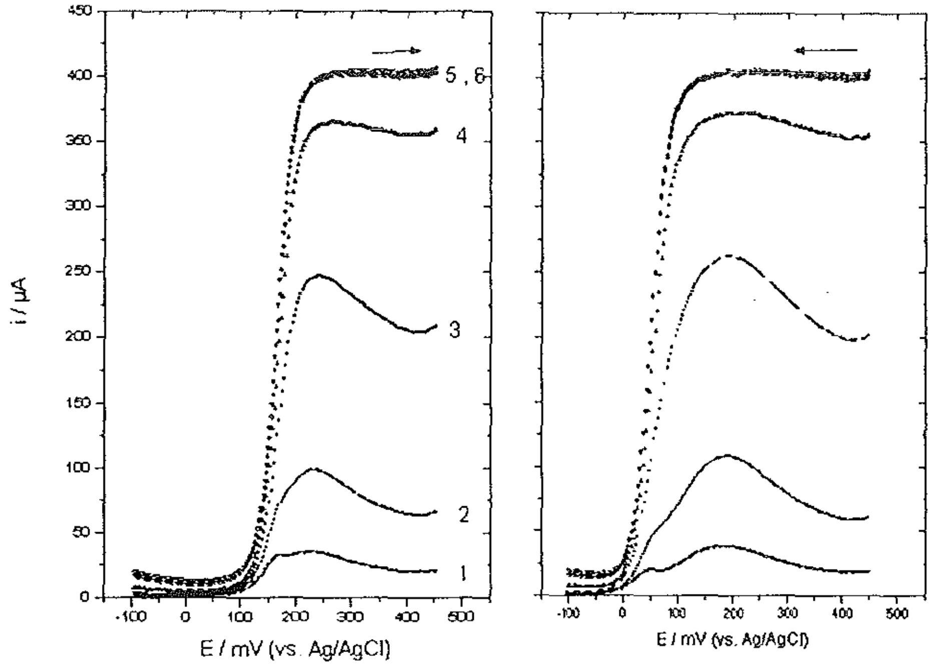


Fig. 22a. Ac cyclic response curve of polyaniline at different frequencies: (1) 5 Hz (2) 10 Hz (3) 25 Hz (4) 75 Hz (5) 175 Hz (6) 215 Hz.

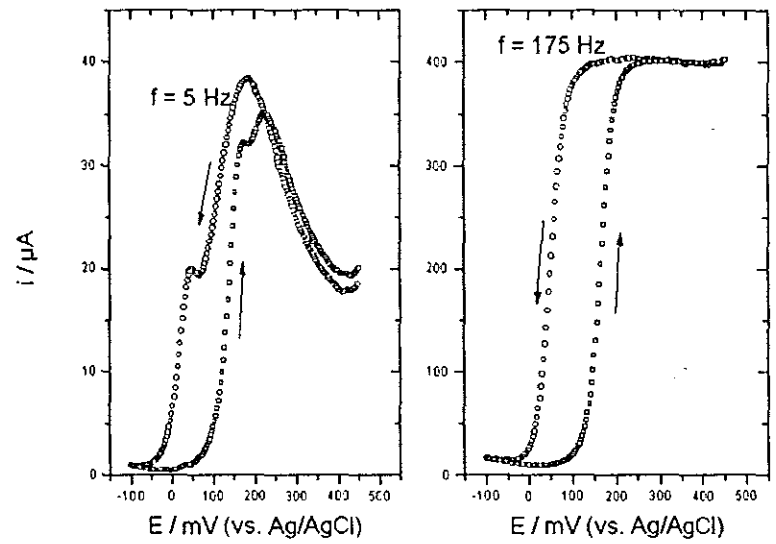


Fig. 22b. Ac cyclic response curve of polyaniline at frequencies of 5 and 175 Hz.

We suppose that ac-cyclic voltammetry is a promising tool to get a better insight of the processes during film growth and the electrochemical changes in the film. In ac voltammetric experiments, a three-electrode cell is used in the conventional manner, and the potential program imposed on the working electrode is a dc mean value, E_{dc}, which is scanned slowly with time, plus a sinusoidal component, E_{ac}, of perhaps 5-mV, peak-to-peak amplitude. The measured response is the magnitude of the ac component of the current at the frequency of E_{ac} *vs.* E_{dc}. The phase angle between the alternating current and E_{dc} is also of interest. The ac-cyclic voltammograms of polyaniline obtained at a Pt-disc electrode are shown in Fig. 22.

As can be seen from the ac-voltammogram both in the forward and reverse scan, the peak current is increasing with frequency at rather low frequencies, but at high frequency that dependence is reduced until, the ac-current becomes independent of frequency. At the same time we obtain a hysteresis between forward (positive going) and backward scan. On the other hand at very low frequencies two peaks are observed (Fig. 22b.). The appearance of the second peak may indicate the complexity of the structure.

The ac impedance technique has proved to be a powerful experimental method for the study of surface processes. The wide continuous frequency range available permits investigation of surface processes that differ widely in relaxation times.

A simple equivalent circuit for an electrochemical adsorption could be represented by a parallel combination of a double layer capacitance and a faradaic impedance (a series combination of resistance and capacitance). If it is assumed that no coupling occurs between the double layer charging and faradaic processes, then the total impedance, Z, would be:

$$Z = Z' - jZ'' \quad \text{.....................................(2)}$$

In the complex plane representation of Z, a plot is made of Z" *vs.* Z' as a function of the frequency ω. Components along the ordinate are assigned as imaginary (Z") and are multiplied by $j = (-1)^{1/2}$. Components along the abscissa are real (Z').

Fig. 22 shows the Z'-Z impedance plane plot of the polyaniline film. The results are interpreted on the basis of the equivalent circuit shown in Fig. 23. Our system can represented as:

Pt / PANI/ H_2SO_4

Thus, we have two interfaces: the first between Pt and the polyaniline film and the second between the film and the electrolyte. Since any interface can be represented by a parallel combination of resistance and capacitance, the equivalent circuit could be shown as:

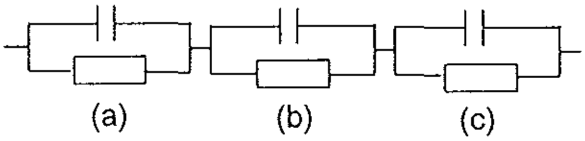
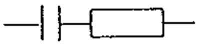


Fig. 23. Proposed equivalent circuits for polyaniline films.

Assuming no charge transfer in the interface between Pt and the film, the resistance in (a) can be neglected. Also, the capacitance in (b) can assumed to be large. Finally our equivalent circuit can be reduced to:



This model is in accordance with the impedance plane plot shown in Fig. 24. The impedance spectra were taken from positive potentials in the negative direction (a), on the other hand there is no significant change in the spectra from 0.45 V to 0.1 V. Within this potential range the spectra can be interpreted by a series circuit of capacitance and resistance. When the potential is reduced further to 0.05 V, a different pattern is obtained. This indicates the transformation of the film from one form to another (emeraldine to leuco-emeraldine) and it needs a further assignment of the equivalent circuit. Also, it indicates the complexity of the structure.

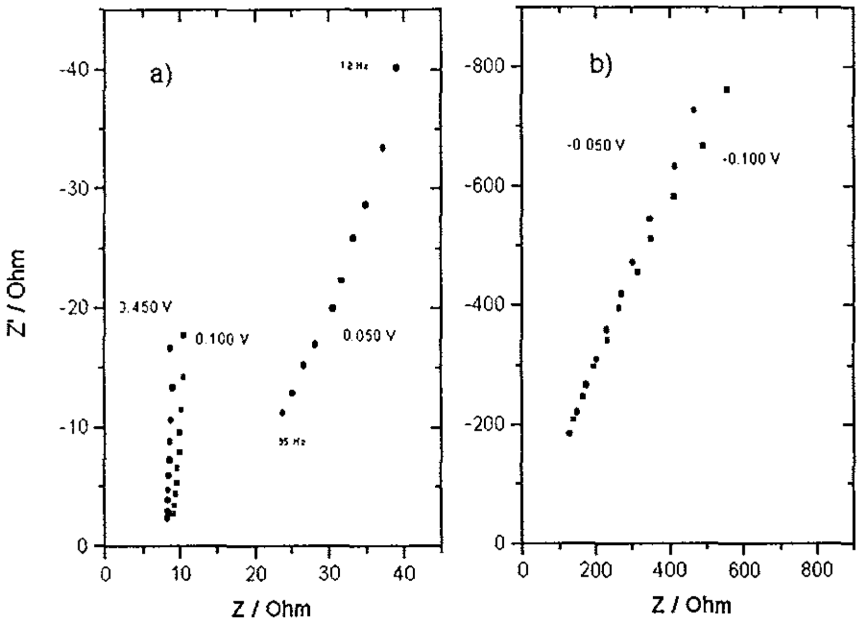


Fig. 24a

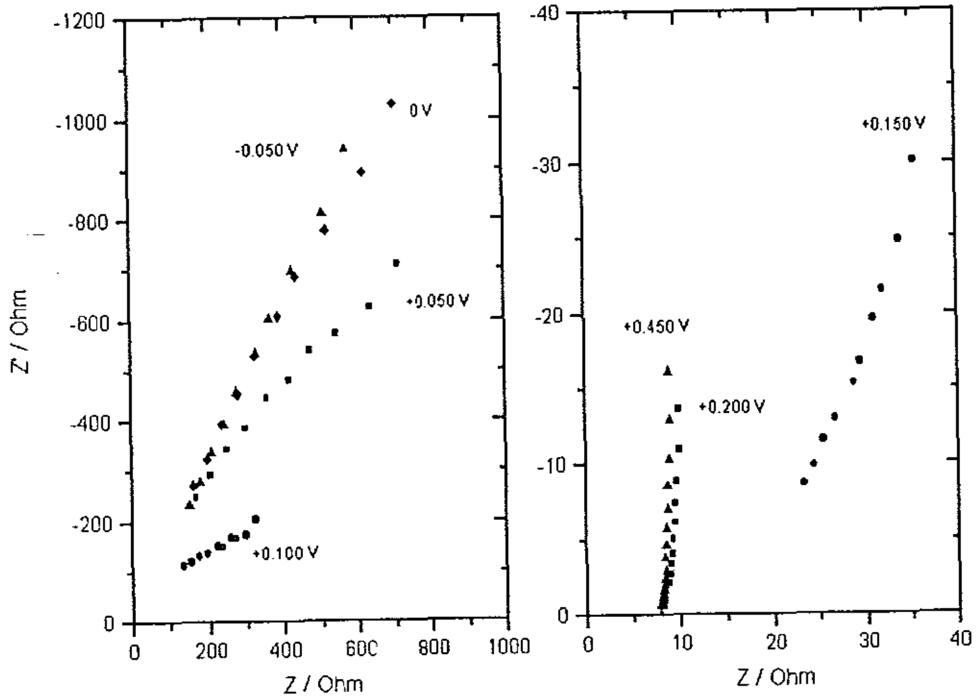


Fig. 24b

Fig. 24. Impedance plane plots of polyaniline film at Pt electrode.

6. REFERENCES

1. H. Gerischer and C.W. Tobias (Eds.), Advances in Electrochemical Sciences and Engineering, Vol.I, VCH, New York, 1990, P. 2.
2. W.R. Salaneck and J.L. Bredas, *Solid State Commun.*, **92** (1994) 31.
3. P. Baverle, *Adv. Mater.*, **5** (1993) 879.
4. A.G. MacDiarmid and A.J. Epstein, *Mat. Res. Soc. Sympo. Proc.* **328** (1994) 142.
5. A. Dall'Olio, G. Dascola, and V. Bocchi, *Chem. Abst.*, **69** (1968) 112026v.
6. A.F. Diaz, K.K. Kanazawa, and G.P. Gardini, *J. Chem. Soc. Chem. Commun.*, 635 (1979).
7. A.F. Diaz and J.I. Castillo, *J. Chem. Soc. Chem. Commun.*, 397 (1980).
8. A.F. Diaz, J.I. Castillo, J.A. Logan, and W.Y. Lee, *J. Electroanal. Chem.*, **129** (1981) 139.
9. A.J. Downard and D. Pletcher, *J. Electroanal. Chem.*, **206** (1986) 139.
10. Sato, M. Tanaka, and S. Kaeriyama, *J. Chem. Soc. Chem. Commun.*, 873 (1980).
11. S. Hotta, *Synth. Met.*, **22** (1987) 103.
12. D.M. Mohliner, R.N. Adams, and W.J. Argersinger, *J. Am. Chem. Soc.*, **84** (1962) 3618.
13. J. Heinze, *Synth. Met.*, **41** (1991) 2805.
14. R. Noufi, A.J. Nozik, J. White, and L.F. Warren, *J. Electrochem. Soc.*, **129** (1982) 2261.
15. E.W. Paul, A.J. Ricco, and M.S. Wrighton, *J. Phys. Chem.*, **89** (1985) 1441.
16. C.M. Carlin, L.J. Kepley, and A.J. Bard, *J. Electrochem. Soc.*, **132** (1985)

353.

17. E.M. Genies and J.M. Pernaut. *J. Electroanal. Chem.*, **191** (1985) 111.

18. J. Heinze, Topics in Current Chemistry, Vol.152, Springer-Verlag Berlin Heidelber, 1990, P. 8.

19. S. Asavapiriyanot, G.K. Chandler, G.A. Gunawardena, and D. Pletcher., *J. Electroanal. Chem.*, **177** (1984) 229.

20. Ref. 18, P. 7.

21. J. Prejza, I. Lundstrom, and T. Skotheim, *J. Electrochem. Soc.*, **129** (1982) 1685.

22. T. Yamamoto, K. Sanechika, and A. Yamamoto, *Bull, Chem. Soc. Jpn.*, **56** (1983) 1503.

23. M. Kobayashi, J. Chen, T.C. Chung, and F. Moraes, A.J. Heeger, F. Wudl, *Synth. Met.*, 9 (1984) 77.

24. F. Garnier, G. Yourillon, M. Gazard, and J.C. Dubois., *J. Electroanal. Chem.*, **148** (1983) 299.

25. A. Czerwinski, H. Zimmer, C. Vanpham, and H.B. Mark., *J. Electrochem. Soc.*. **132** (1985) 2669.

26. Z. Galus and R.N. Adams, *J. Am. Chem. Soc.*, **84** (1962) 2061.

27. Z. Galus, C. Olson, H.Y. Lee, and R.N. Adams, *Anal. Chem.*, **34** (1962) 164.

28. E.M. Genies and G. Bidan, *J. Electroanal. Chem.*, **149** (1983) 102.

29. K. Yakushi, L.J. Lauchlan, T.C. Clarke, and G.B. Street, *J. Chem. Phys.*, **79** (1983) 4773.

30. T. Osaka, K. Naoi, S. Ogana, and S. Nakamura, *Chem. Lett.*, 1687 (19860.

31. A.F. Diaz and J. Bargon, Handbook of Conducting Polymers, Vol.I, Marcel

Dekker Inc; New York, 1985, P. 87.

32. M.M. Baizer (Ed.), Organic Electrochemistry, Marcel Dekker, New York, 1973, P. 225.

33. L.S. Marcoux, J.M. Fritsch, and R.N. Adams, *J. Am. Chem. Soc.*, **89** (1967) 5768.

34. A.A. Moghaddam, Polymer Based Electronic Devices, Ph.D. Dissertation, Linkoping University, Sweden, 1993, P. 2.

35. A. Tager, Physical Chemistry of Polymers, Mir Publishers, Moscow, 1972, p. 319.

36. M.O. Kantazidis, *Chemical and Engineering News*, December **3** (1990) 40.

37. B. Scrosati, *Pro. Solid St. Chem.*, **18** (1988) 8.

38. J.L. Bredas and G.B. Street, *Acc. Chem. Res.*, **18** (1985) 309.

39. J.S. Miller, *Adv. Mater.*, **5** (1993) 587.

40. A.G. MacDiarmid and A.J. Epstein, *Mat. Res. Soc. Symp. Proc.* **328** (1994) 133.

41. J.R. Reynolds, *Chemtech*, July (1988) 442.

42. Ref. 36, P. 57.

43. Ref. 39, P. 672.

44. Ref. 37, P. 57.

45. S. Roth and W. Graupner, *Synth. Met.*, **57** (1993) 3623.

46. Ref. 41, P. 447.

47. Ref. 36, P. 51.

48. T. Kobayashi, H. Yoneyama, and H. Tamura, *J. Electroanal. Chem.*, **161** (1984) 419.

49. A. Kitani, J. Yano, and K. Sasaki, *J. Electroanal. chem.*, **209** (1986) 227.

50. P.C. Lacaze, J.E. Dubois, A. Desbene-Monvernay, P.L. Desbene, J.J. Basselier, and D. Richard, *J. Electroanal. Chem.*, **147** (1983) 107.

51. H. Reiss, R.B. Kaner, M.R. Anderson, and B.R. *Matts. Science*, **252** (1991) 1412.

52. Ref. 40, P. 142.

53. G. Telila, M. Sc. Theis, AAU, 1994.

54. S. Asavapiriyanont, G.K. Chandler, G.A. Gunawardena, and D. Pletcher, *J. Electroanal. Chem.*, **177** (1984) 229.

55. Ref. 54, p. 245.

56. J. Simonet and J.R. Berthelot, *Prog. Solid St. Chem.*, **21** (1991) 21.

57. S. Hotta, T. Hosaka, and W. Shimotsuma, *Synth. Met.*, **6** (1983) 69.

58. M. Ito, H. Shioda, and K. Tanaka, *J. Polymer Science.*, **24** (1986) 147.