PREPARATION AND PERFORMANCE OF MODIFIED ELECTRODES BASED ON CONDUCTING CO-POLYMER AND ITS COMPOSITE WITH INORGANICS

BY

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SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENT FOR THE DEGREE OF
M.PHIL IN CHEMISTRY

DEPARTMENT OF CHEMISTRY
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY (BUET)
DHAKA-1000, BANGLADESH
MAY 2007

DECLARATION

This thesis work has been done by the candidate himself and does not contain any material extracted from elsewhere or from a work published by anybody else. The work for this thesis has not been presented elsewhere by the author for any degree or diploma.

9|5|07

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CERTIFICATE

This is to certify that the research work embodying in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any University or institution.

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ACKNOWLEDGEMENT

I am extremely grateful to my esteemed supervisor Dr. AL-Nakib Chowdhury, Professor, Department of Chemistry, Bangladesh University of Engineering & Technology (BUET), Dhaka, Bangladesh, for his thoughtful suggestions, invaluable guidance, untiring efforts, sympathy, constant encouragement and inspiration at all stages of my M. Phil. research work.

I am very much thankful to Dr, Nazrul Islam, Head, Department of Chemistry, BUET, Prof. Dr. Enamul Huq, Prof. Dr. Md. Monimul Huque, Prof. Dr. Md. Manwarul Islam, Prof. Dr. Md. Rafique Ullah, and Mr. Md. Shafiul Azam, Lecturer, Department of Chemistry, BUET, for their kind help and co-operation in different stages of my research work. I am also grateful to other teachers and staff of Chemistry Department, BUET, Dhaka.

I am grateful to the authority of BUET for providing me the financial support for conducting the research.

I would like to offer thanks to my friends Saiful Islam, Razaur Rahman Razib, Abdus salam, Abdur Rahim and to all other friends who shared with me to solve the problems confronted in the whole thesis period. Special thanks to Md. Mamun - or - Rashid of Chemistry Department, BUET for his assistance in composing the thesis.

I would like to express my deep gratitude to my beloved parents for their sacrifice and continuous encouragement throughout the research work.

Above all, all thanks are due to almighty Allah for making things and situations congenial and favorable for me for the task undertaken.

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A thesis on

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has been accepted as satisfactory in partial fulfillment of the requirements for the degree of Master of Philosophy (M. Phil) in Chemistry and certify that the student has demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on May 09, 2007.

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Abstract

Modification of electrode matrices with conducting copolymer was attempted. The electrodes thus modified were examined for their performance in carrying out some standard electrochemical redox processes on their surfaces.

Pt electrode was modified with the films of
i) conducting polymers, *viz.*, PANI, CH_3-PANI, PABA and PP
ii) conducting copolymers, *viz.*, PANI/ CH_3-PANI, PANI/PP, PANI/PABA
iii) polymeric composites, *viz.*, PANI/CH_3-PANI/SiO_2, PANI/PP/SiO_2

The film of conducting polymers, copolymers and the composites were prepared by the simple one step electrochemical means. Corresponding monomer(s), inorganics were kept in electrolytic solutions and deposited a polymeric film onto the Pt substrates either by sweeping the potentials or by constant potential mode. The film thus grown onto the Pt surface were free-standing depending on the thickness of the deposit grown.

The modifier matrices were characterized by a wide range of experimental techniques including UV-Vis and IR spectroscopy, d.c. conductance and scanning electron microscopy. IR spectral analysis yielded characteristic bands confirming the presence of polymeric and inorganic components. UV-Vis optical spectra of the samples showed strong absorption maxima in ultraviolet region and another band in the visible region that are attributable for conductive polymeric component. The electrical conductivity of the samples was measured in their compressed solid state. The electrode matrices that are synthesized in this study are found to be fairly conductive and their conductivity falls in the range of conventional semiconductors. The surface morphology of the modified electrodes was examined. The matrices showed dissimilar surface morphology from granular to fibril. The dissimilar surface morphology showed different electrode activity of the matrices.

The electrode matrices thus modified were found to be electroactive both in aqueous and non-aqueous solvents. The polymeric electrodes in the appropriate electrlytic media exhibited doping-dedoping phenomenon corresponding to the polymeric oxidation-reduction processes, respectively. This result indicates the charging-discharging capacities of modified electrodes.

The electrolytic matrices were then used as modified electrode. The redox processes $Fe^{2+} \rightarrow Fe^{3+} + e^-$ and $H_2Q \rightarrow Q + 2H^+ + 2e^-$ were performed on their surfaces. The modified electrodes thus prepared in this study were found to be capable of performing the redox processes efficiently. The effects of solvent and film thickness on the performance of the modified electrodes were also investigated. The present study clearly revealed that conducting copolymer modified electrode could be a good replacement for the costly noble Pt electrode in terms of cost, availability and ease of techniques for preparation and application in a real system.

Chapter 1

INTRODUCTION

1.1 Fundamental Aspects of Electrochemical Process

A. Design of Electrochemical Techniques

Electrochemistry involves the study of spontaneous oxidation-reductions reactions that generate an electrical current and the study of non-spontaneous oxidation-reduction reactions that are forced to occur by the passage of an electrical current. In both cases, the conversion between chemical and electrical energy is carried out by electrochemical cell. The arrangement of an electrochemical cell is briefly discussed below:

i) Electrochemical cell: The electrochemical cell consists primarily of the electrodes and the electrolyte. assembled in a compartment. Commonly a glass frit, separator, or membrane may be incorporated to isolate the anolyte from the catholyte. Three electrodes are commonly employed: a working electrode that defines the interface under study, a reference electrode which maintains a constant reference potential, and a counter (or secondary) electrode which supplies the current. The cell must be designed so that the experimental data are determined by the properties of the reaction at the working electrode.

ii) Working electrode: Design of working electrodes is diverse. Most commonly the working electrode is a small sphere, small disc, or a short wire, but it could also be metal foil, a single crystal of semiconductor or metal, an evaporated thin film, or a powder as pressed discs or pellets. An essential feature is that the electrode should not react chemically with the solvent or solution components. In principle, the electrodes can be large or small, but there are commonly experimental reasons why the electrode area should be relatively small (<0.25 cm^2). Moreover, it should preferably be smooth, as the geometry and mass transport are then better defined. Wide ranges of solid materials are used as electrodes, but the most common 'inert' solid electrodes are lead, vitreous carbon, gold and platinum. In order to obtain consistent results with solid electrodes, it is important to establish a satisfactory electrode pretreatment procedure that ensures a reproducible state of oxidation, surface morphology and freedom from adsorbed impurities. Electrodes are polished on cloth pads impregnated with diamond particles down to 1 μm and then with alumina of fixed grain size down to 0.05 μm.

iii) Counter electrode: The purpose of the counter electrode is to supply the current required by the working electrode without in any way limiting the measured response of the cell. It is essential that the electrode process is decomposition of the electrolyte medium or oxidation/reduction of a component of the electrolyte so that current flows readily without the need for a large overpotential.

The counter electrode should not impose any characteristics on the measured data, and in consequence it should have a large area compared to the working electrode. Moreover, as also noted above, its shape and position are important since these determine whether the working electrode is an equipotential surface, and consequently it is preferable to avoid a separator in the cell.

iv) Reference electrodes: The role of the reference electrode is to provide a fixed potential which does not vary during the experiment (e.g. it should be independent of current density). In most cases, it will be necessary to relate the potential of the reference electrode to other scales, for example to the normal hydrogen electrode (NHE), the agreed standard for thermodynamic calculations.

In potentiostatic experiments the potential between the working electrode and reference electrode is controlled by a potentiostat, and as the reference half cell maintains a fixed potential, any change in applied potential to the cell appears directly across the working electrode-solution interface. The reference electrode serves the dual purpose of providing a thermodynamic reference and also isolates the working electrode as the system under study. In practice, however, any measuring device must draw current to perform the measurement, so a good reference electrode should be able to maintain a constant potential even if a few microamperes are passed through its surface.

In practice the main requirement of a reference electrode is that it has a stable potential and that it is not substantially polarized during the experiment. Hence it is common to use the highly convenient aqueous saturated calomel electrode (SCE) in many experiments in all solvents. Even so, a very wide range of reference electrodes have been used in non-aqueous solvents.

Potential of some common reference electrodes are listed in Table 1.1.1.

Table - 1.1.1 Potential of some typical reference electrodes in aqueous solutions at 298K

Common name	Electrode composition	Potential / V *vs* NHE
SCE	Hg/Hg_2Cl_2, sat KCl	+0.241
Calomel	Hg/Hg_2Cl_2, 1 mol dm^{-3} KCl	+0.280
Mercurous sulphate	Hg/Hg_2SO_4, sat K_2SO_4 Hg/Hg_2SO_4, 0.5 mol dm^{-3} H_2SO_4	+0.640 +0.680
Mercurous oxide	Hg/HgO, 1 mol dm^{-3} NaOH	+0.098
Silver chloride	Ag/AgCl, sat KCl	+0.197

A great deal of modern electrochemistry is carried out in non-aqueous solvent media, and often aqueous reference electrodes can be used at the expense of an unknown aqueous-non aqueous junction potential. In acetonitrile, the calomel electrode is unstable, and the most frequently used reference electrodes are Ag/AgCl or Ag/Ag^-.

v) The electrolytic solution: The electrolytic solution is the medium between the electrodes in the cell, and it will consist of solvent and a high concentration of an ionised salt as well as the electroactive species; it may also contain other materials, complexing agents, buffers, etc. The supporting electrolyte is used (a) to increase the conductivity of the solution and hence to reduce the resistance between the working and counter electrodes (to avoid undue Joule heating), to help maintain a uniform current and potential distribution, and to reduce the power requirement on the potentiostat), and also to minimise the potential error due to the uncompensated solution resistance. With appropriate precautions, electrochemical experiments are possible in almost any medium. Table 1.1.2 lists some widely used media.

Table 1.1.2. Common solvents and media for electrochemical experiments.

1 Water

Aqueous solutions of many salts and/or complexing agents at various pH Buffered and unbuffered media.

2 Other protonic solvents

e.g acetic acid, ethanol, methanol, liquid HF

3 Aprotic solvents

e.g. acetonitrile, dimethylformamide, dimethylsulphoxide, sulphur dioxide, ammonia. propylene carbonate, tetrahydrofuran. Many studies use as electrolytes $R_4N^+X^-$, R= CH_3, C_2H_5 or C_4H_9, X= ClO_4^-, BF_4^-, PF_6^-, or halide ion. Media difficult to buffer.

4 Mixed solvents

Particularly mixtures of water with ethanol, acetronitrile, etc. Again, these media may be buffered or unbuffered, contain many electrolytes, etc.

5. Molten salts

e.g. NaCl, KCl/NaCl/LiCl eutectics etc.

Electrode reactions can be extremely sensitive to impurities in the solution; for example, organic species are often strongly adsorbed even at 10^{-4} mol dm^{-3} bulk concentration from aqueous solutions. Hence salts should be of the highest available purity and/or recrystallised, solvents should be carefully purified, and solutions must be carefully deoxygenated. Purification and drying of non-aqueous solvents have been described elsewhere [1. 2] in some detail.

vi) Instrumentation: The electrochemist's armoury is based on electronic apparatus designed to control/measure the charge passed (coulostat/integrator), current (galvanostat/current follower) and potential (potentiostat/high impedance voltmeter) in an electrochemical cell.

Potentiostat: The potentiostat is a device for controlling the potential between the working electrode and the reference electrode at a fixed and selected potential (commonly we also wish to programme this potential with time).

Galvanostat: The simplest way to obtain a constant current is to apply a voltage from a low output impedance voltage sources across a large resistor in series with the cell. The current will be given by the ratio E_{in}/R (provided resistance R is very large compared with the impedance of the cell).

B. Processes at Electrode Surface

A solid conducting materials must be present to provide the site for each electrochemical reaction. These materials are called electrodes. The electrodes at which oxidation occurs is termed as the anode. The other electrode, the cathode, is the site of the reduction process.

i) Electrode reactions: An electrode reaction is a heterogeneous chemical process involving the transfer of electrons to or from a surface, generally a metal or a semiconductor. The electrode reaction may be an anodic process whereby a species is oxidised by the loss of electrons to the electrode, e.g.

$2\,H_2O - 4e^- \rightarrow O_2 + 4H^+$ 1.1.1

$Ce^{3+} - e^- \rightarrow Ce^{4+}$ 1.1.2

$2Cl^- - 2e^- \rightarrow Cl_2$ 1.1.3

$Pb + SO_4^{2-} - 2e^- \rightarrow PbSO_4$ 1.1.4

$2Al + 3H_2O - 6e^- \rightarrow Al_2O_3 + 6H^+$ 1.1.5

By convention [3], the current density, I , for an anodic process is a positive quantity. Conversely, the charge transfer may be a cathodic reaction in which a species is reduced by the gain of electrons from the electrode, e.g.

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ 1.1.6

$Cu^{2+} + 2e^- \rightarrow Cu$ 1.1.7

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ 1.1.8

$PbO_2 + 4H^+ + SO_4^{--} + 2e^- \rightarrow PbSO_4 + 2H_2O$ 1.1.9

$2CH_2 = CHCN + 2H_2O + 2e^- \rightarrow (CH_2CH_2CN)_2 + 2OH^-$ 1.1.10

and the current density for a cathodic process is a negative quantity. The diversity of electrode reactions can already be seen from Equation (1.1.1.–1.1.10): the electroactive species may be organic or inorganic, neutral or charged, a species dissolved in solution, the solvent itself, a film in the electrode surface, or indeed, the electrode materials itself.

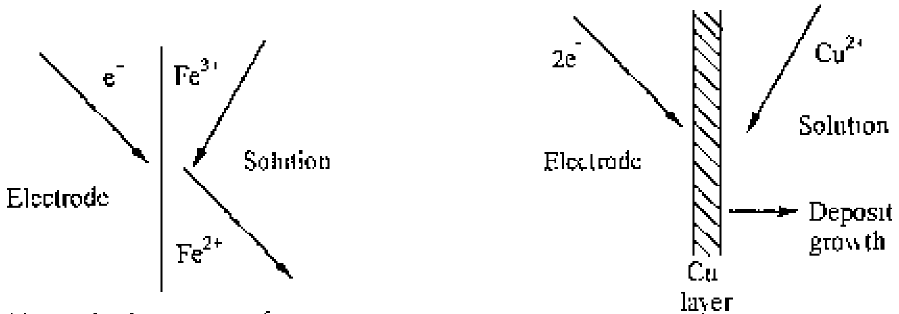
Moreover, the product may be dissolve in solution, in a gas, or a new phase on the electrode surface. The many type of electrode reactions are also illustrated in Fig. 1.1.1.

Electrolysis is only possible in a cell with both an anode and a cathode, and, because of the need to maintain an overall charge balance; the amount of reduction at the cathode and oxidation at the anode must be equal.

ii) Mass transport: In general, in electrochemical systems, it is necessary to consider three modes of mass transport; namely,

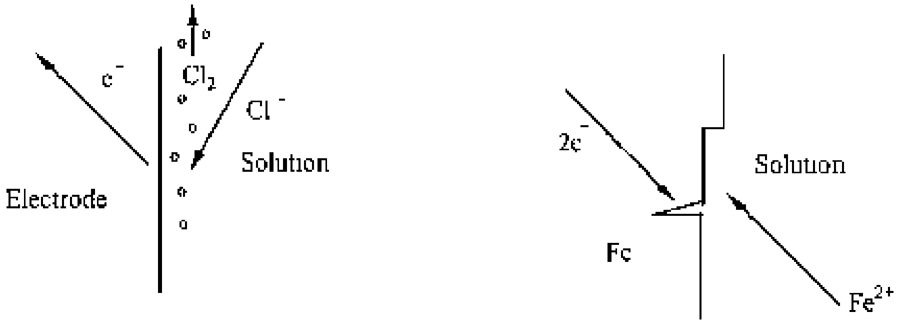
(a) Diffusion: Diffusion is the movement of a species down a concentration gradient, and it must occur whenever there is a chemical change at surface. An electrode reaction converts starting material to product (O→R), and hence close to the electrode surface there is always a boundary layer (up to 10^{-2} cm thick) in which the concentrations of O and R are a function of distance from the electrode surface. The concentration of O is lower at the surface than in the bulk, while opposite is the case for R, and hence O will diffuse towards and R away from the electrode.

(b) Migration: Migration is the moment of charged species due to a potential gradient, and it is the mechanism by which charge passes through the electrolyte; the current of electrons through the external circuit must be balanced by the passage of ions through the solution between the electrodes (cations to the cathode and anions to the anode).



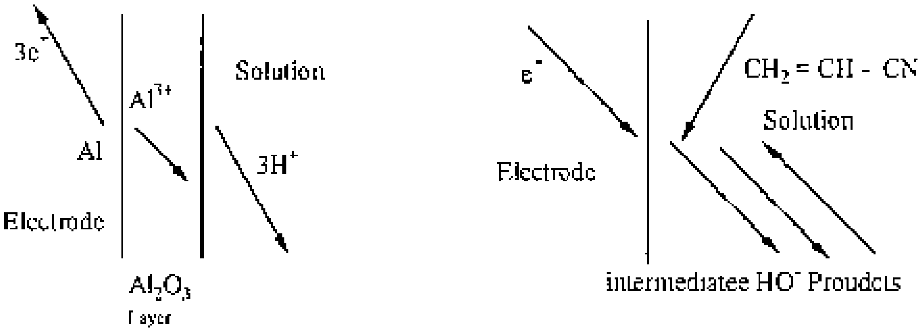
(a) simple electron transfer
$Fe^{3+} + e^- \rightarrow Fe^{2+}$

(b) metal deposition
e.g. $Cu^{2+} + 2e^- \rightarrow Cu$



(c) gas evolution
e.g. $2Cl^- - 2e^- \rightarrow Cl_2$

(d) corrosion
e.g. $Fe - 2e^- \rightarrow Fe^{2-}$



(e) oxide film formation
$2Al + 3H_2O - 6e^- \rightarrow Al_2O_3 + 6H^+$

(f) electron transfer with coupled chemistry
$2CH_2 = CH - CN + 2H_2O + 2e^-$
$\rightarrow (CH_2 - CH_2 - CN)_2 + 2OH^-$

Fig. 1.1.1: **Schematic view of some types of electrode reactions met in applied and fundamental electrochemistry.**

It is, however, not necessarily an important form of mass transport for the electroactive species even if it is charged. The forces leading to migration are purely electrostatic, and hence the charge can be carried by any ionic species in the solution. As a result, if the electrolysis is carried out with a large excess of an inert electrolyte in the solution, this carries most of the charge, and little of the electroactive species is transported by migration.

(c) Convection: Convection is the moment of a species due to mechanical forces. It can be eliminated, at least on a short timescale (it is difficult to eliminate natural convection arising from density difference on a longer time, .i.e.> 10s) by carrying out the electrolysis in a thermostat in the absence of stirring or vibration. In industrial practice, it is much more common to stir or agitate the electrolyte or to flow the electrolyte through the cell. These are all forms of forced convection and, when present, they have a very large influence on the current density.

1.2 Some Important Electrode Materials

A. Metals

Metals are crystalline solid materials consist of metal atoms distributed in a definite pattern resulting from their close packing. The types of close packing arrangement depend upon the size and electronic configuration of the atoms involved in the formation of crystal lattice. Since the metal atoms are all in direct contact with one another in the lattice and their valence electrons are in identical energy states, it is believed that the electrons are free to migrate between atoms. Metal atoms have an excess of low energy orbital vacancies. These vacancies enable valence electrons to move from near a certain nucleus to near any other nucleus where their position remains indistinguishable from the first. Thus, metals may be pictured as a collection of positive atomic cores embedded in a fluid of electrons or sea of electrons. For this fluid of electrons, metals are good conductors of electricity and heat. Metals have metallic luster; they are malleable, ductile and high melting points.

Metals have simple crystal lattices since metallic bonding envisages closest packing of atoms-one layer above another. Metals may have any system of seven common crystal systems. Fe, Cu, Al, Ag, Au etc are the most common metals which are very useful to ns.

B. Semiconductors

Semiconductors are special kind of materials which have the properties of semiconductivity, an electrical property of materials. A relatively small group of elements and compounds have an important electrical property, semiconduction, in which they are neither good electrical conductors nor good electrical insulators. Instead, their ability to conduct electricity is intermediate. Si, Ge, impure ZnO, impure NiO are some examples of semiconductors.

The magnitude of conductivity in the simple semiconductors fall within the range 10^{-6} to 10^{-1} Ω^{-1} cm^{-1}. This intermediate range corresponds to band gaps of less then 2 eV. Both conduction electrons and electron holes are charge carriers in a simple semiconductor.

In a semiconductor element, the energies of the valence electrons, which bind the crystal together, lie in the highest filled energy band, called the valence band. The empty band above, called the conduction band, is separated from the valence band by an energy gap. The magnitude of the energy gap or the width of the forbidden energy zone is characteristic of the lattice alone and varies widely for different crystals.

The transfer of an electron from the valence band to the conduction band requires high excitation energy to overcome the potential barrier of the forbidden energy zone. Consequently, such elements behave like an insulator at low temperatures. The application of heat or light energy may give enough energy to some electrons in the valence band to excite them across the forbidden zone into the conduction band. These electrons in the conduction band are now free to move and can carry electricity (Fig. 1.2.1).
Semiconductors are of two kinds such as

(i) Intrinsic semiconductor
(ii) Extrinsic semiconductor

(i) Intrinsic semiconductors : If a pure, elemental substance shows the semiconducting properties, it is called intrinsic semiconductor. Pure Si, Ge shows these semiconducting properties. For these, semiconduction results from the thermal promotion of electrons from a filled valence band to an empty conduction band . There, the electrons are negative charge carriers. The removal of electrons from the valence band produces electron holes which are positive charge carrier and identical to the conduction electrons (Fig. 1.2.1 (a). This overall conduction scheme is possible because of the relatively small energy band gap between the valence and conduction bands in silicon. If δ is the conductivity of semiconductor then for intrinsic semiconductor, we can write:

$$\delta = nq\,(\mu_e + \mu_h) \qquad 1.2.1$$

Where, n → density of conduction electron

q → charge of single carrier

μ_e → carrier mobility of electron

μ_h → carrier mobility of hole

(ii) Extrinsic semiconductors: Extrinsic semiconduction results from impurity additions known as dopants, and the process of adding these components is called doping. These types of semiconductors are extrinsic semiconductors. At room temperature, the conductivity of semiconductors results from electrons and holes introduced by impurities in the crystal. The presence of an impurity lowers considerably the activation energy necessary to transfer an electron from the valence band to the conduction band. This indicates that the ground state energies of such easily excited electrons must lie in the forbidden energy region. Two such discreate energy levels, known as donor levels and acceptor levels, may be introduced into the forbidden energy zone at a small interval of energy below the conduction band or above the valance band (Fig.1.2.1 (b)). Donor levels give rise to electrons in the conduction band, whereas acceptor levels lead to the formation of holes in the valence band. Impurity of Si. with B, P, NiO, ZnO, are the examples of extrinsic semiconductors. Extrinsic semiconductors are of two kinds such as p-type extrinsic semiconductor and n-type extrinsic semiconductor.

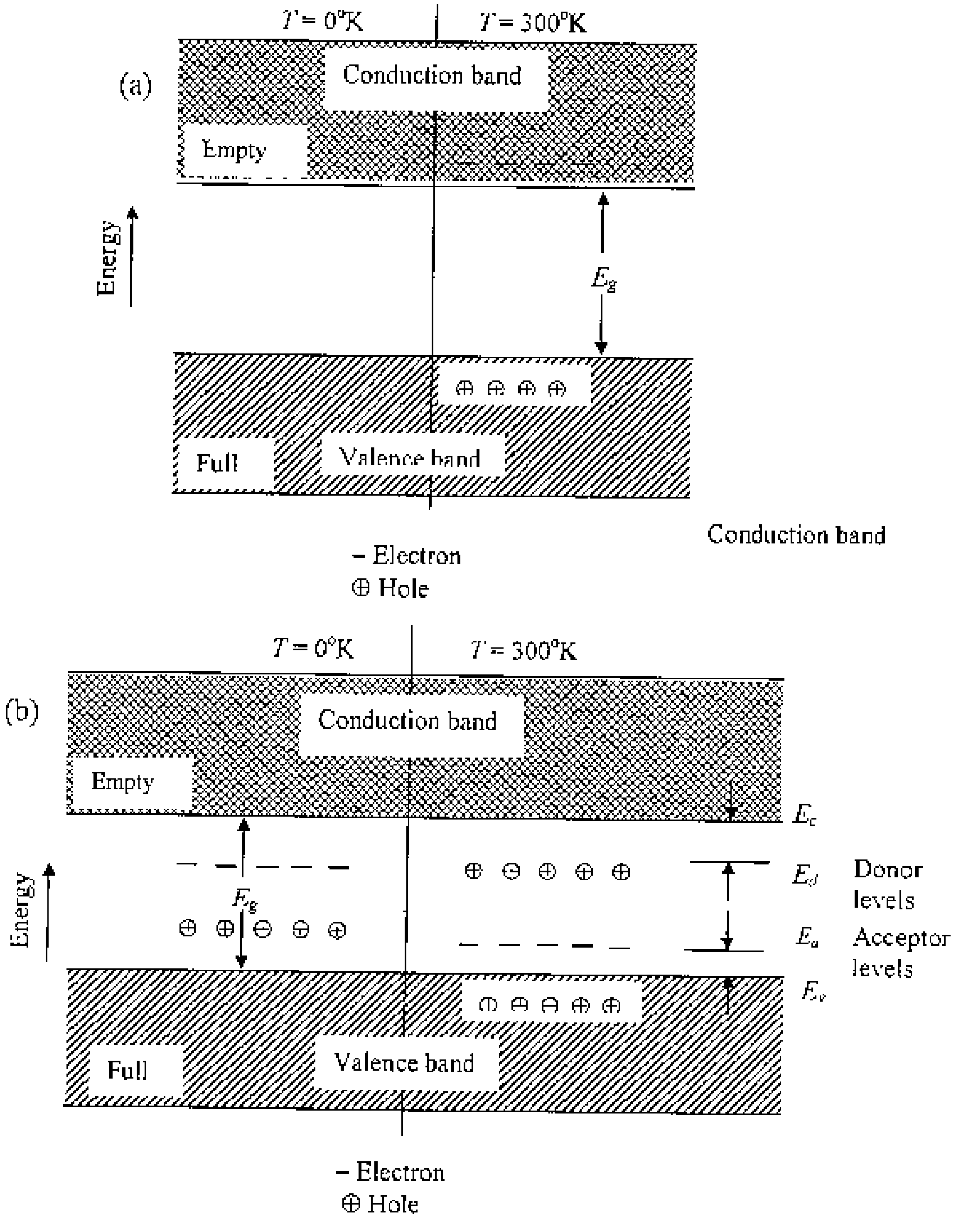


Fig. 1.2.1 A pictorial representation of an (a) intrinsic and (b) extrinsic semiconductor.

p-type extrinsic semiconductors: The p-type semiconductor is obtained when the impurity atoms have fewer valence electrons than the silicon or germanium atoms of the original crystal. When a trivalent element such as B, Al, Ga, In is substituted for Si atom, the structure will be locally incomplete and the impurity atom will acquire an extra electron from a nearly bond in the lattic to approximate the terahedral cloud distribution of the lattice. This creates a positive hole localized near the impurity, which will attempt to neutralize itself by taking an electron from another neighboring bond. Then, again a hole is formed in place of this electron and it will neutralize itself by taking another electron from the next neighboring bond. Such way the positive holes carry electricity in the extrinsic semiconductor. So it is called p (i.e. positive) type semiconductor (Fig. 1.2.2) Cu_2O also p-type semiconductor.

n-type semiconductors: The n-type semiconductor arises from substitution of impurity atoms having more valence electrons than Si or Ge atoms. Elements such as P, As, Sb, and Bi have five valence electrons. When such an element is substituted for a silicon atom, four of its five electrons will enter the inter-atomic bonds, but the fifth electron will be only slightly attracted by the excess of the positive charge on the nucleus. Thermal agitation even at room temperature is sufficient to transfer this electron to the conduction band. Since conductivity is due to the motion of electrons in the conduction band, this semiconductor is called n-type and the impurity is called the donor (Fig. 1.2.2). Titanium dioxide or titania is a non-stoichiometric transition metal oxide and behaves as n-type semiconductor [4].

There are three naturally occurring crystal phases of titanium dioxide: rutile, anatase, and brookhite. Most of the electrochemical and photocatalytic work to date have been performed on rutile or anatase, or a mixture of the two. Both rutile and anatase have tetragonal unit cells, and both structures contains slightly distorted TiO_6 octahedral. Rutile is thermodynamically more stable than anatase at room temperature; the free energy change for antatase to rutile is –5,4 kJ/mol [5].

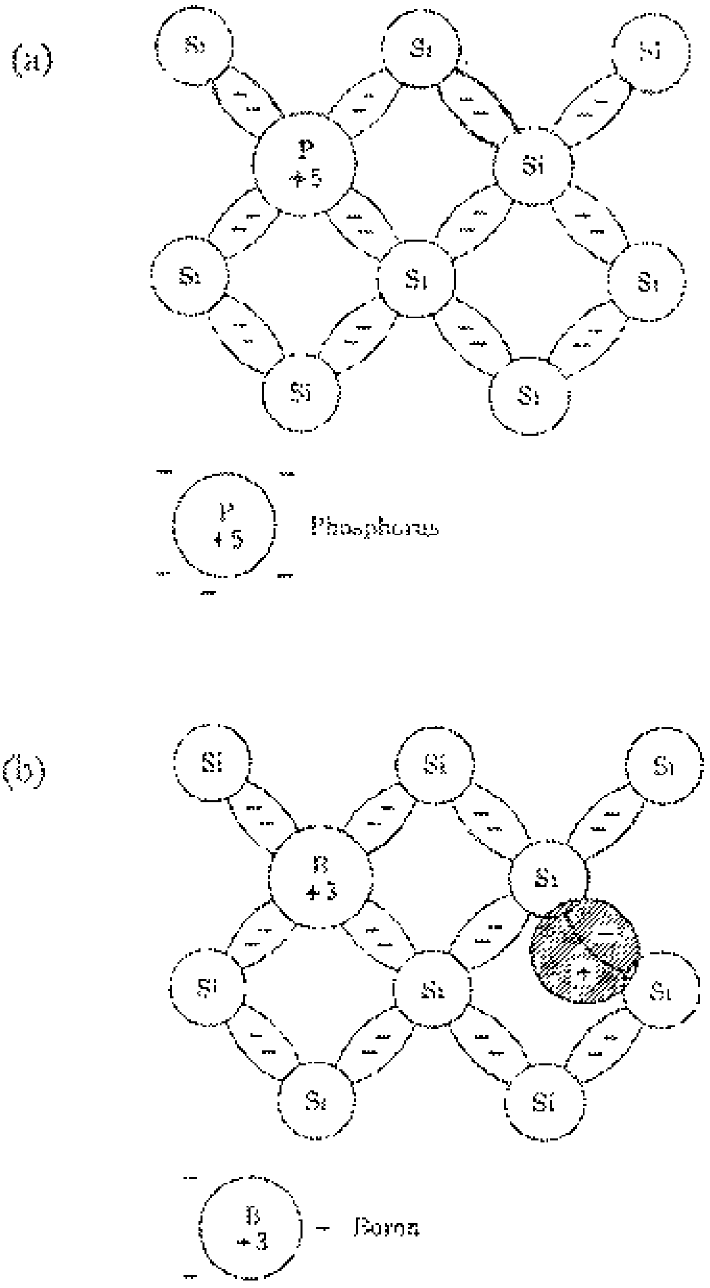


Fig. 1.2.2: Types of impurity semiconductors (a) n-type (b) p- type.

The absorption and reflection properties of rutile have been studied extensively. At 4K, the short wavelength absorption edge for rutile is 410 nm (bandgap energy = 3.05 eV) [6, 7]. The lowest energy electronic absorption at 3.05 eV is an indirect transition. On the other hand, the bandgap of anatase is reported as 3.2 eV [8]. The absorption coefficients for both crystal phases are reported as ~10^5 cm^{-1} at 340 nm [9].

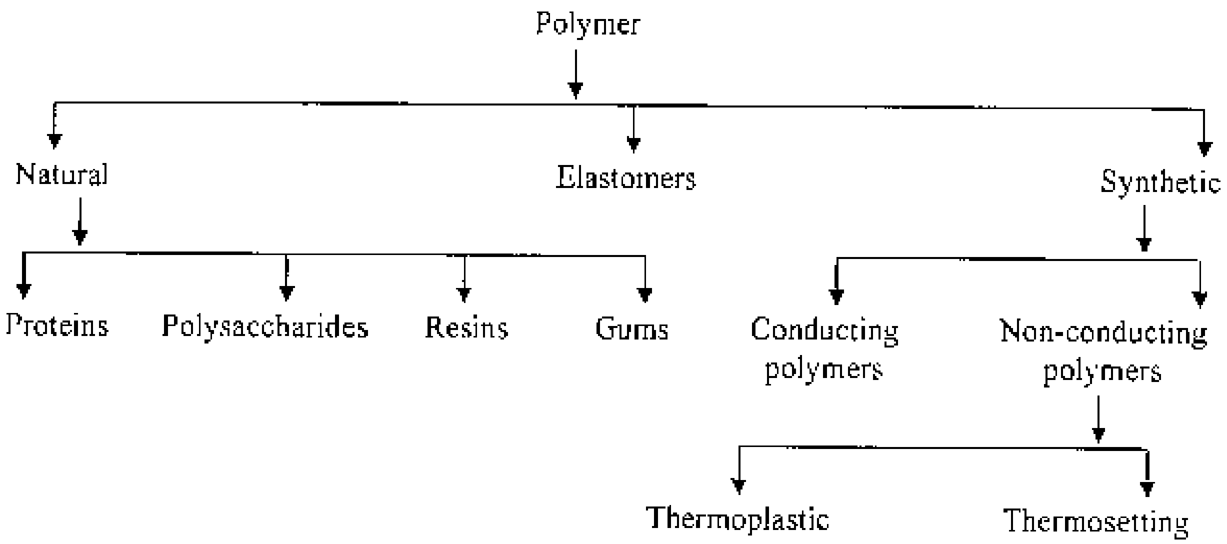
Ultraviolet radiation below ~390 nm stimulates valence-band electrons in TiO_2 particles that are suspended in contaminated water. These electrons are promoted to the conduction band (e^-_{cb}), creating holes in the valence band (h^+_{vb}). These electron / hole pairs can either recombines, producing thermal energy, or interact with the external environment to perform oxidation and reduction reactions.

$$TiO_2 \xrightarrow{h\nu} TiO_2\ (e^-_{cb}, h^+_{vb})$$

C. Polymers

Polymers are giant molecules composed of hundreds or thousands of the basic structural unit which is composed of a limited number of atoms strongly bonded together. This basic unit is called monomer. Polymers are chain like and macromolecules. The repeat unit (or basic unit) of the polymer is usually equivalent or nearly equivalent to the monomer. In some cases the repetition is linear, much as a chain is built up from its link. In other cases the chains are branched or interconnected to from three dimensional networks. The length of the polymer chain is specified by the number of repeat units in the chain. This is called the degree of polymerization. Starch, protein, lignin, cellulose, silk etc. are natural polymers and polyaniline (PANI), poly-*o*-toluidine (CH_3-PANI), polyaniline/poly-*o*-toluidine (PANI/CH_3-PANI), polyaniline/poly-*o*-toluidine/silica (PANI/CH_3-PANI/SiO_2), polypyrrole (PP), polyaniline/polypyrrole (PANI/PP), polyaniline/polypyrrole/silica (PANI/PP/SiO_2), Poly 2-amino benzoic acid (PABA), polyaniline/ poly-2-amino benzoic acid (PANI/PABA), poly-*o*-toluidine / poly-2-amino benzoic acid (CH_3-PANI/PABA), polyethylene, nylon, synthetic rubber polypropylene etc. are the example of synthetic polymers. Some polymers are conductor of electricity although most of the polymers are non-conductor or insulator.

Polymers can be classified in different ways depending on their use, structure, origin and property Depending on the nature of the polymers a broad classification is diagramically shown below:



(I) Natural polymers:

Natural polymers usually have more complex structure. They are classified as (a) proteins (b) polysaccharides (c) resins (d) gums.

(a) Proteins: Proteins are essential for life. All characteristics commonly attributed to living things such as reproduction, growth, movement, metabolism and sensory perception, are entirely dependent on the function of proteins. Proteins are synthesized biologically as linear polymers of twenty amino acids.

(b) Polysaccharides: Polysaccharides are carbohydrate polymer in which monosaccharides (glucose. fructose etc.) residues are linked directly through glycosidic linkages. They are found in animal, plant and microbial kingdoms, where they may serve for energy storage, as structural materials.

(c) Resins: A neutral resin in any of various solid or semi-solid amorphous, fusible, flammable natural organic substances that are usually transparent or translucent and yellowish to brown, are formed especially in plan fecretions, are electrical non-conductor and are used chiefly in medicine, varnishes, printing inks, plastics and sizes.

(d) Gums: Gums are very complex, amorphous substances of a polysaccharide nature. They contains very small amounts of Ca, Mg, K with the composition of C, H and O. They are used in pharmacy and industry.

(II) Elastomers:

Elastomers can either be natural or man made. Like fibres, elastomers are considered apart from other polymeric materials because of their special properties. Unlike fibres, elastomers do not in general lend themselves to uses. Elastomers must be amorphous when unstretched.

(III) Synthetic polymers:

Synthetic polymers are man made. They are synthesized in the laboratory by applying heat, pressure or catalyst (initiators). They are of two kinds, such as (a) conducting polymers and (b) non-conducting or insulator polymer.

(a) Conducting polymers: During the last two decades, a new class of organic polymers is synthesized which conduct electrical current. These polymers are called conducting polymers [10]. In general polymers are insulating materials having conductivities rauging from 10^{-10} Scm^{-1} for polyvinyl chloride to 10^{-18} Scm^{-1} for polytetrafluro-ethylene, which are many orders of magnitude below compare to the conductivities associated with metals ($>10^6$ Scm^{-1}). As a result, polymers have found wide spread acceptance in a myriad of insulating and structural applications through out the electronic industry. One of the earliest approaches to make polymers conducting is to prepare a composite of polymers and a conductive filler, such as metal powder, graphite powder, flake or wire etc. Conductive fillers remain embedded more or less evenly dispersed in the polymer matrix and conduct electric current. But these composites can not be regarded as conducting polymers because the polymers present in such composites are non-conducting [11-14]. When anions like Cl^-, ClO_4^-, BF_4^- etc. are doped chemically to organic polymers, their electrical conductivity increases. Again when silicon dioxide is dopped in to these plymers, their stability is increased although its electrical conductivity may be decreased.

(b) Non-conducting polymers: The polymers which cannot carry electricity are non-conducting polymers or insulation polymers, they are of two kinds, such as (i) thermoplastic (ii) thermosetting.

(i) Thermoplastic: A thermoplastic polymer is one that is capable of being repeatedly soften by heating and hardening by cooling through a characteristic temperature range, and that in the softened state can be shaped by flow into articles by molding or extrusion. Thermoplastic applies to those materials whose change upon heating is substantially physical.

(ii) Thermosetting: A thermosetting polymer is one that is capable of being changed into a substantially infusible or insoluble product when cured by heat or other means. The cured polymer may be termed thermoset.

D. Composites

Since 1965, a distinct discipline and technology of composite materials begun to emerge. That is 80% of all research and development on composites have been done since 1965 when the Air Force launched its-all out development program to make high performance fiber composites a practical reality. There are two major reasons for the revived interest in composite materials. One is that the increasing demands for higher performance in many product areas specially in the aerospace, nuclear energy and aircraft fields is taxing to the limit our conventional monolithic materials. The second reason, the most important for the long run is that the composites concept provides scientists and engineers with a promising approach to designing, rather than selecting, materials to meet the specific requirements of an application.

The term 'composite' refers to something made up of various parts or elements. In definition of composite depends on the structural level of the composite we are thinking about. At the submicroscopic level that of simple molecules and crystal cells all materials composed of two or more different atoms or elements would be regarded as composites. This would include compounds, alloys plastics and ceramics. Only the pure elements would be excluded.

At the microscopic level (or microstructural level) that of crystals, polymers, and phases a composite would be a material composed of two or more different crystals, molecular structures, or phases. By this definition, most of our traditional materials, which have always been considered monolithic, would be classified as composites. At the macro structural level which is most useful for composites, the definitions of composites is that they are a mixture of macro constituent phase composed of materials which are in a divided state and which generally differ in form and/or chemical composition. Note that, contrary to a widely held assumption, this definition does not require that a composite be composed of chemically different materials, although this usually the case. The more important distinguishing characteristics of a composite are its geomentical features and the fact that its performance is the collective behavior of the constituents of which it is composed. A composite material can vary in composition, structure, and properties from one point to the next inside the material.

The major constituents used in structuring composites are fibers, particles, laminas, flakes, filters and matrix. The matrix, which can be thought of as the body constituent, gives the composite its bulk form. The other four, which can be referred to as structural constituents determine the character of the composites internal structure. A special type of composite, fiberglass embedded in a polymer matrix is a relatively recent invention but has in a few decades, become a commonplace material. Characteristic of good composites, fiberglass, provides the 'best of both worlds', it carries along the superior properties of each component, producing a product that is superior to either of the components separately. The high strength of the small diameter glass fibers is combined with the ductility of the polymer matrix to produce a strong material capable of withstanding the normal loading required of a structural material.

1.3 Brief History of Conductive Polymers

The discovery in 1973 that poly sulfur nitride $(SN)_x$ was intrinsically conducting provided a proof that polymers could be conducting and thus greatly stimulated the search for other conducting polymer [15]. During the last two decades, a new class of organic polymers has been devised with the remarkable ability to conduct electrical current. These class of materials are called conducting polymers [16].

One of the earliest approaches to make the polymers conductive is to prepare a composite of polymers and conductive filler, such as, metal powder, graphite powder, flake or wire etc. Conductive fillers remain embedded more or less evenly dispersed in the polymer matrix and conduct electric current. But these composites cannot be regarded as conducting polymers because the polymers presents in such composites are non-conducting [17-20].

In 1964, W. A. Little [21] synthesized a superconductor at room temperature with polymeric backbone and large polarizable side groups which led the discovery of new organic compounds with high electrical conductivity.

In the early 1980s, excitement ran high when several prototype devices based on conductive polymers, such as rechargeable batteries and current rectifying *p-n* junction diodes [22] were announced. Among the many polymers known to be conductive, polyacetylene (PAT), polyaniline (PANI), polypyrrole (PP) and polythiophene (PT) have been studied most intensively [23-29]. However, the conductive polymer that actually launched this new field of research was PAT.

Research has been expanded into the studies of heteroatomic conductive polymers because of their better chemical stability and the interest in the polaron and bipolaron conduction mechanism [30, 31]. Among the heteroatomic polymers PP, PT and PANI have been studied extensively.

In 1968, Dall'Olio *et. al.* [32] published the first report of analogous electrosynthesis in other system. They had observed the formation of brittle, film like pyrrole black on a Pt electrode during the oxidation of pyrrole in dilute sulfuric acid. Conductivity measurements carried out on the isolated solid state materials gave a value of 8 Scm^{-1}. In addition, a strong ESR signal was evidenced of a high number of unpaired spin. Earlier, in 1961, H. Lund [33] had reported in a virtually unobtainable publication that PP can be produced by electrochemical polymerization.

In 1979, Diaz *et. al.* [34] produced the first flexible and stable PP film with high conductivity (100 Scm^{-1}). The substance was polymerized on a Pt electrode by anodic oxidation in acetonitrile. The known chemical methods of synthesis [35-37] usually produced low conductivity powders from the monomers. PP formed at the electrode surface and could be peeled off as a flexible, relatively dense and shiny blue-black film. This polymer is characterized not only by its high conductivity but also by its high stability.

During the 1980s, PANI was subjected to intense structural, physical, and electrical characterization, using modern experimental techniques. A brief survey, out of numerous features and studies made on PANI is presented below:

A. Structural Features

Organic conducting polymer, PANI, is being studied more and more, and up to the recent years has been the centre of considerable scientific interest. However, PANI is not really a new material and its existence has been known for the past 150 years or over, since it had already been made by Runge in 1834.

PANI has been described in many papers [38] usually as ill-defined forms such as 'aniline black' emeraldine, nigraniline, *etc.* synthesized by the chemical or electrochemical oxidation of aniline. Figure 1.3.1 shows the idealized oxidation state of PANI: leucoemeraldine, emeraldine, pernigraniline and emeraldine salt. Different structures result in different electrical behaviours of the material. Emeraldine salt is a partially oxidized compound, protonated, with electrical conducting characteristics. Leucoemeraldine is a fully reduced compound with electrical insulating characteristics. There are no double bonds between the aromatic rings and the N-H groups. Emeraldine base is an insulating compound, partially oxidized with few N-H groups in the main chain. Emeraldine changes from insulator to conductor when it is protonated with proton donor acids, such as, hydrochloric acid. This change is one of the most interesting properties of PANI.

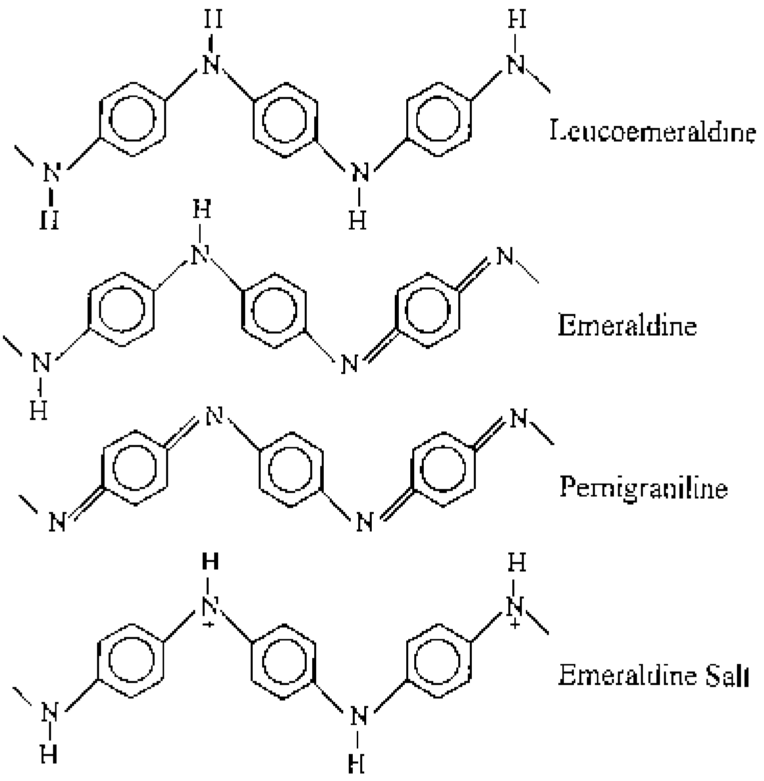
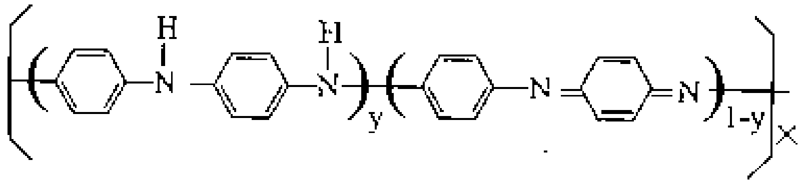
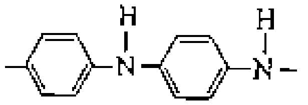
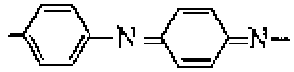


Fig. 1.3.1 Representation of idealized oxidation states of PANI.

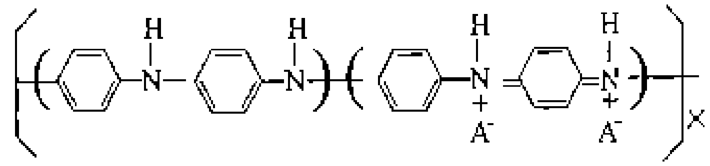
The structure of emeraldine PANI can be changed to emeraldine salt by removing an electron from the N-H group. Pernigraniline is a fully oxidized compound without conducting characteristics. There are no N-H groups in the structure. The level of protonation in the structure causes dramatic changes in the conductivity. The base form of the polymer in the emeraldine oxidation state (y = 0.5)



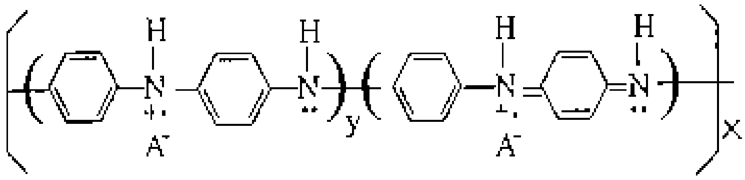
which contains equal number of alternating reduced,

 and oxidized 

repeat units can be protonated by dilute aqueous acid to produce the corresponding salt (A=anion)



which is believed to exist as polysemiquinone radical cation [39-40].



The polymer exhibits conductivities of ~ 1-5 S cm^{-1} when approximately half of its nitrogen atoms are protonated as shown above.

B. Methods of Preparation

PANI is generally prepared by direct oxidation of aniline using an appropriate chemical oxidant or by electrochemical oxidation on different electrode materials.

Various chemical oxidizing agents have been used by different authors: potassium dichromate [41, 42], ammonium persulfate or peroxydisulfate [43, 44], hydrogen peroxide, ceric nitrate and ceric sulfate [45, 46]. The reaction is mainly carried out in acid medium, in particular sulfuric acid, at a pH between 0 and 2 [41, 42]. However, MacDiarmid *et al.* [43, 44] used hydrochloric acid at pH 1. Genies *et al.* [47] used a eutectic mixture of hydrofluoric acid and ammonia, the general formula of which is NH_4F: 2.3 HF, for which the pH is probably less than 0.

When aniline is mixed with the chemical oxidant in a reaction vessel and left for a certain period of time (the duration of which depends on the temperature and the concentration of active species), the solution gradually becomes colored and a black precipitate appears [48]. The coloration of the solvent is possibly due to the formation of soluble oligomers.

Anodic oxidation of aniline on an inert metallic electrode is the most current method for the electrochemical synthesis of PANI. This method offers the possibility of coupling with physical spectroscopic technique such as visible, IR, Raman, ellipsometry and conductimetry, for *in situ* characterization.

The anodic oxidation of aniline is generally effected on an inert electrode material which is usually Pt [49, 50]. However, several studies have been carried out with other electrode materials: iron [51], copper [52], zinc and lead, chrome-gold [53], palladium [54] and different types of carbon vitreous. pyrolic or graphite [55] or on semiconductor [56, 57]. When the polymerization is carried out at constant current, a maximum current density of 10 mA cm $^{-2}$ is rarely exceeded.

The conducting polymers, CH_3-PANI, PP, and the copolymers as well as the composites can also be prepared by both chemical [58-71] and electrochemical polymerization [72-104].

C. Applications

Conducting polymeric materials prepared by electrochemical polymerization of a number of monomers have recently received considerable attention because of the large variety of their potential applications such as in energy storage [105], batteries [106,107], electrocatalysis [108,109], gas sensors [110-114], and biosensors [115-120].

PANI can be used as material for modified electrodes [55, 121], as a corrosion inhibitors for semiconductors in photoelectrochemical assemblies [122], in microelectronics [123] and as electrochromic material [124]. The application which has inspired most interest is in the area of electrochemical batteries. The possible use of PANI as active anodic material is in rechargeable batteries [38].

More recent systematic studies have been undertaken by numerous groups [24, 44, 122] on the possible use of PANI as an active electrode material. These investigations deal with the behavior of PANI in aqueous and organic media as a function of the mode of synthesis.

1.4 Theoretical Aspects of Experimental Techniques

A. Cyclic Voltammetry

Electrochemical process is widely used in the polymerization of organic polymer. Most of the system for electrochemical polymerization consists of a compartment where three electrodes are dipped into the solution containing monomer and electrolyte solution. Appropriate potential is applied to the working electrode for polymerization of the monomers. The potential of the working electrode, where deposition of the polymer film takes place, is controlled versus the reference electrode using a feed-back circuit or a potentiostat. Feed-back circuit drives the current between the working and counter electrodes while ensuring that none passed through the reference electrode circuit.

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 is not oxidized concurrently with the aromatic monomer. For this reason, most of the available films have been prepared using a platinum or a gold electrode.

Potentiostatic, galvanostatic and potential sweep techniques such as cyclic voltammetry are widely used for electrochemical polymerization of aromatic compounds. In potentiostatic technique, a constant potential is applied to the working electrode which is sufficient to oxidize the monomers to be polymerized on the electrode. In galvanostatic process, a constant current density is maintained to polymerize the monomers while film thickness can be controlled in the similar way as described for potentiostatic technique. On the other hand, cyclic voltammetry involves sweeping the potential between potential limits at a known sweep rate. On reaching the final potential limit, the sweep is reversed at the same scan rate to the initial potential and the sweep may be halted, again reversed, or alternatively continued further. In such experiments, cell current is recorded as a function of the applied potential.

B. Infra-red (IR) Spectroscopy

Emission or absorption spectra arise when molecules undergo transition between quantum states corresponding to two different internal energies. The energy difference ΔE between the states is related to the frequency of the radiation emitted or absorption by the quantum relation

$$\Delta E = h\nu \qquad 1.4.1$$

where h → planck's constant, ν → frequency. Infrared frequencies have the wave length range from 1 μm to 50 μm and are associated with molecular vibration and vibration-rotation spectra. Detection of chemical groups and bonding are done by the typical spectra.

In polymer, the IR absorption spectrum is often surprisingly simple, if one considers the number of atoms involved. This simplicity results first from the fact that many of the normal vibrations have almost the same frequency and therefore appear in the spectrum as one absorption band and second, from the strict selection rules that prevent many of the vibrations from causing absorptions. Samples were introduced as KBr pellets. A block diagram of an IR spectrophotometer is shown in Fig. 1.4.1.

C. Ultraviolet-Visible Spectroscopy (UV-Vis)

Electromagnetic radiation of suitable frequency can be passed through a sample so that photons are absorbed by the samples and changes in the electronic energies of the molecules can be brought about. So it is possible to effect the changes in a particular type of molecular energy using appropriate frequency of the incident radiation. When a beam of photons passes through a system of absorbing species, then we can write

$$-\frac{dI}{dx} = \alpha I \qquad 1.4.2$$

where, I → intensity of photon beam

dI → reduction of intensity

dx → rate of photon absorption with distance (x) traversed

α → absorption co-efficient of the material

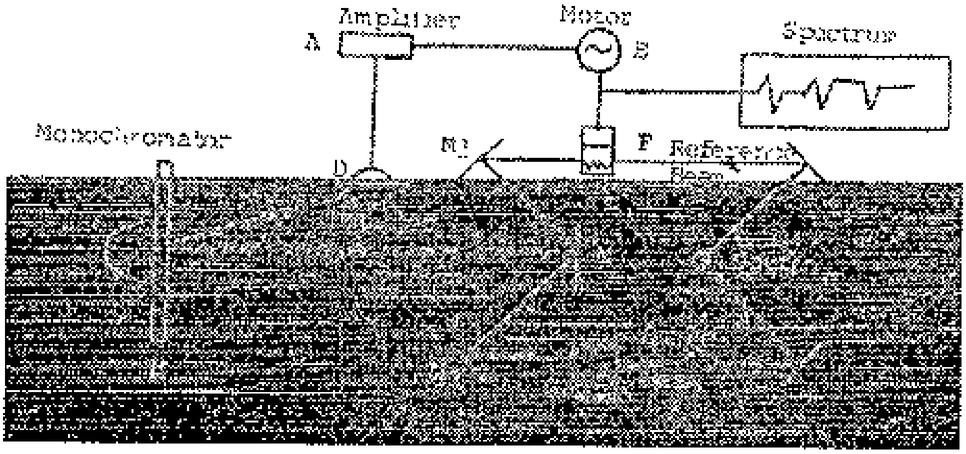


Fig. 1.4.1· A block diagram of an IR spectrophotometer.

Now if I_0 is the initial intensity at thickness $l = 0$ and I is the transmitted radiation at $x = l$, then by integration, we can write

$$ln \frac{I_0}{I} = \alpha l \qquad 1.4.3$$

For polymers and polymeric composites, UV-Vis spectrum is taken to measure the impurity level, band gap energy etc. The spectra of the present samples were recorded on a UV-Vis recording spectrophotometer in the wave length range 300-800 nm. A schematic diagram of UV-Vis spectrophotometer is shown in Fig. 1.4.2.

D. d. c. Conductivity

The conductivity of polymer or polymeric composites depends on dopant level, protonation level of an oxidized matrix and moisture content of the sample. Electrical resistivity of the polymer samples may be measured by two probe and four probe techniques. However, the electrical conductivity measurement employed the ohm's law

$$E/I = R \qquad 1.4.2$$

where I is the current in amperes, E is the potential difference in volts, R is the resistance in ohms. The reciprocal is termed the conductance, this is measured in Siemens (S) which is reciprocal of ohms (ohm^{-1}). The resistance of a samples of length L, and cross-sectional area A, is given by

$$R = \rho L/A \qquad 1.4.3$$

where ρ is a characteristic property of the material termed as resistivity. L and A will be measured respectively in cm and then ρ refers to cm cube of the material and

$$\rho = RA/L \qquad 1.4.4$$

The reciprocal of resistivity is the conductivity, (formerly specific conductance)

$$K = 1/\rho \quad \text{or} \quad K = L/RA \qquad 1.4.5$$

which is in SI units, is the conductance of a one cm cube of substance and has the units $ohm^{-1}\ cm^{-1}$ or $S\ cm^{-1}$ [60].

In this experiment, the powdered samples were pressed to rigid solid mass by pressing from the both sides of the mass. The two electrodes of microvolt were then connected with solid mass and resistivity was measured directly from the microvolt

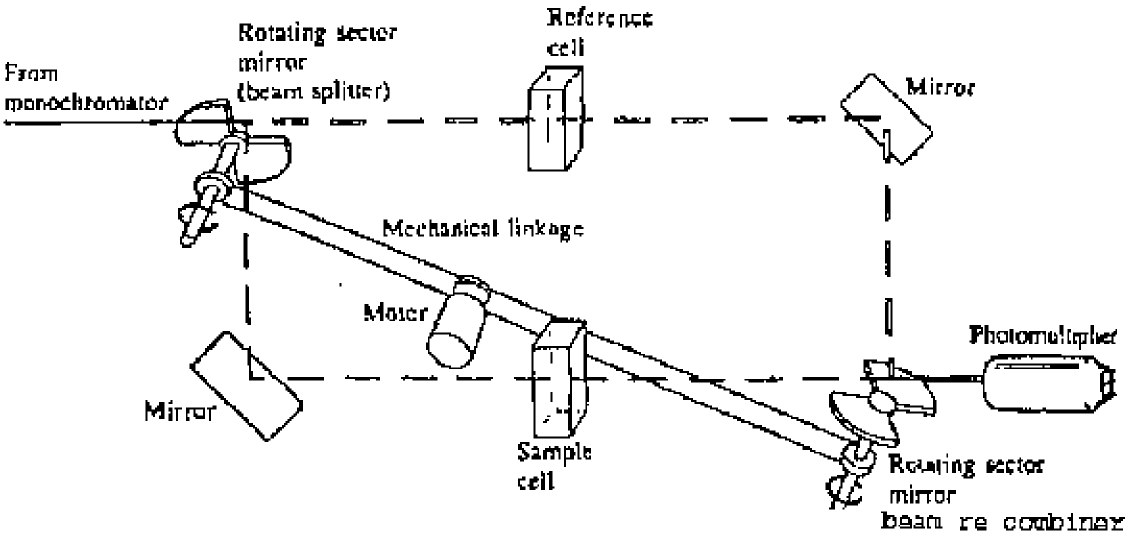


Fig. 1.4.2: A block diagram of an UV-Vis spectrophotometer.

E. SEM Technique

The scanning electron microscope (SEM) uses a finely focused beam of electrons to scan over the area of interest. The beam-specimen interaction is a complex phenomenon. The electrons actually penetrate into the sample surface, ionizing the sample and canse the release of electrons from the sample. These electrons are detected and amplified into a SEM image that consists of Back Scattered Electrons and Secondary Electrons. Since the electron beam has a specific energy and the sample has a specific atomic structure, different image will be collected from different samples, even if they have the same geometric appearance.

The specimen stage of SEM allows movement of the specimen along 5 axis. The basic stage is controlled manually by micrometers and screw-type adjusters on the stage door. The motorized stage has motors driving the X, Y, Z and rotation controls, all with manual over ride.

The stage can be tilted over 90°. The tilt axis always intersects the electron optical axis of the column at the same height (10 mm). When the specimen positioned at this height, the specimen can be tilted in the eucentric plane. This means that during tilt, almost no image displacement occurs. The tilting mechanism can be locked for more stability at high magnification.

1.5 Aim of the Present Research

A good progress has been made in preparing conducting polymers with well defined structure as addressed by the early workers. Interest in the electrical properties of highly conjugated polymers has increased rapidly. PANI is unique among the other conducting polymer that its electrical properties can be reversibly controlled both by charge-transfer doping and protonation. On the other, PP another well studied conducting polymer also show high electrical properties by charge-transfer doping. The wide range of associated electrical, electrochemical and optical properties coupled with good stability made PANI and PP potentially attractive for application as electronic materials.

Metal and semiconductor particles comprise a fundamentally and technologically interesting class of materials. These are extensively used as electrode materials both in solid and solution phase. For example, anode or cathode materials of battery are a metal or semiconductor. In the catalytic reactions, these are used to promote the reaction process. However, metals and semiconductors are very costly and rapidly exhausting from the nature. Thus, it is now a pressing need to develop alternative materials to replace these costly metals. Conductive polymers are the class of materials which exhibit excellent semiconducting properties.

Thus, in the present work, alternative electrode materials based on conducting polymeric materials are synthesized with a view for their viable application in the electrode system. Because of the superior electrical properties of the conductive polymers, it is expected that the polymeric electrodes could be a good alternative to the conventional noble metal electrodes.

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Chapter 2

EXPERIMENTAL

2.1 Materials and Devices

A. Chemicals

Analytical grade chemicals and solvents were used throughout the work and were used as received unless stated otherwise. The monomers aniline, *o*-toluidine and pyrrole were distilled prior to use in polymerization reactions. Doubly distilled water (H_2O) was used as solvent to prepare most of the solutions utilized in this work except for UV analysis where N, N–dimethyl formamide (DMF) was employed as solvent. The important chemicals and solvents utilized throughout the experiments are listed below:

i) Aniline [E. Merck, Germany]
ii) *o*-toluidine
iii) Pyrrole
iv) 2-amino benzoic acid
v) Silica
vi) Sulphuric acid (97%) [E. Merck, Germany]
vii) N, N-dimethyl formamide [E. Merck, Germany]

B. Instruments

Analysis of the samples performed in this work employed the following devices:

i) Potentiostat / Galvanostat / Coulombmeter [HABF 501, Hokuto Denko, Japan]
ii) X-Y recorder [F–5C, Riken Denshi Co. Ltd, Japan]
iii) Infra red spectrophotometer [IR–470, Shimadzu, Japan]
iv) UV-visible spectrophotometer [UV-1601 PC, Shimadzu, Japan]
v) Scanning electron microscope [Philips XL 30, Holland]
vi) Autoranging microvolt [Keithley 197 A, USA]
vii) Digital balance [FR-200, Japan]

2.2 Electrochemical Preparation of the Film Electrodes

The electrochemical synthesis and characterization of PANI, CH_3-PANI, PANI/ CH_3-PANI, PANI/CH_3-PANI/SiO_2, PP, PANI/PP, PANI/PP/SiO_2, PABA, PANI/PABA and CH_3-PANI/PABA films were carried out at room temperature in a standard three-electrode one-compartment electrolysis cell. A schematic representation of the electrochemical cell employed in this work is illustrated in Fig. 2.2.1. The cell consisted of a 0.5 cm^2 working electrode (WE) made of platinum (Pt), a 0.50 cm^2 Pt foil counter electrode (CE) and a saturated calomel electrode (SCE) as the reference (RE). Prior to each experiment, the working Pt electrode was carefully polished with fine–grained abrasive paper, followed by rinses in distilled water and 5 min immersion in concentrated nitric acid (HNO_3), before it was finally dried on clean laboratory tissues. The reproducibility of experimental results was greatly improved with this pretreatment of the working electrode. The films were grafted onto the working Pt electrode either by sweeping the potential or constant potential mode. Voltammetric sweeps were always started in the anodic direction from 0.0V at 100 mV/s, unless stated otherwise. A Hokuto Denko (HABF 501] electrochemical measurement system provided necessary potential and current control.

A. Polyaniline (PANI)

PANI film was prepared on the Pt working electrode by the ordinary anodic polarization method [1-6]. The working Pt was the anode and counter Pt foil was used as the cathode. A 0.8M sulphuric acid (H_2SO_4) in distilled H_2O containing 0.5 M aniline as well as a mixture of CH_3CN-water containin 0.5 M aniline and 0.1 M $LiClO_4$ were used as the electrolytic solutions. Electrolysis was carried out either by sweeping the potential between –0.2 V and +1.0 V *vs* SCE at a scan rate of 100 mV/sec. After polymerization, the potential of the PANI film coated Pt electrode was held at 0.0V until the cathodic current disappeared to dedoped the PANI film. The film as grown and dedoped, was washed several times in distilled water to remove any traces of monomer or any other reactants or by–products that might be produced during electrolysis.

B. Poly-*o*-toluidine (CH_3-PANI)

CH_3-PANI films were deposited on the Pt electrode from aqueous electrolytic solution containing 0.5 M *o*-toluidine and 0.8M H_2SO_4 and also from another electrolytic solution containing 0.5 M *o*-toluidine, 0.1 M $LiClO_4$ and mixture of CH_3CN-water at room temperature. The film was coated onto the Pt surface by potential sweeping method.

In the cycling method, the potential was swept from −0.2 V to +1.0 V *vs* SCE at a scan rate of 100 mV/sec. In the preparation of the film, a potentiogalvanostat (Hokuto HABF 501) with function−generating ability were used for generation of potential and supply of current. The current−potential response was recorded in a X-Y recorder (F-5C, Riken Denshi). The film grown onto the Pt electrode was dedoped and washed several times in distilled water as stated previously.

C. Copolymer: Polyaniline/Poly-*o*-toluidine (PANI/CH_3-PANI)

Electrochemical deposition of the PANI/CH_3-PANI film on the Pt substrate employed potential sweeping method. The technique involves scanning between the potential range −0.2 and +1.0 V *vs* SCE at a scan rate of 100 mV/sec. The PANI/CH_3-PANI film was grown by anodic oxidation of monomers from an aqueous electrolytic solution containing 0.8 M H_2SO_4, 0.5 M aniline and 0.5 M *o*-toluidine. A blue film appeared on the working electrode. The film thus formed was dedoped and washed carefully, according to the procedure described earlier. The potentiostat/galvanostat employed provide the necessary current and potential generation.

D. Composite: Polyaniline/Poly-*o*-toluidine/Silica (PANI/CH_3-PANI/SiO_2)

Aqueous colloidal suspension of silica was prepared by adding 2.0 g of silica particles to double distilled water (400 mL) followed by beating the mixture for two hours. The resulted dispersion was then allowed to settle for two hours. During this span of time relatively bigger silica particles were sedimented at the bottom of the container. The smaller particles remain in the system and dispersed colloidally. The colloidal solution was then decanted and used for PANI/CH_3-PANI/SiO_2 composite preparation.

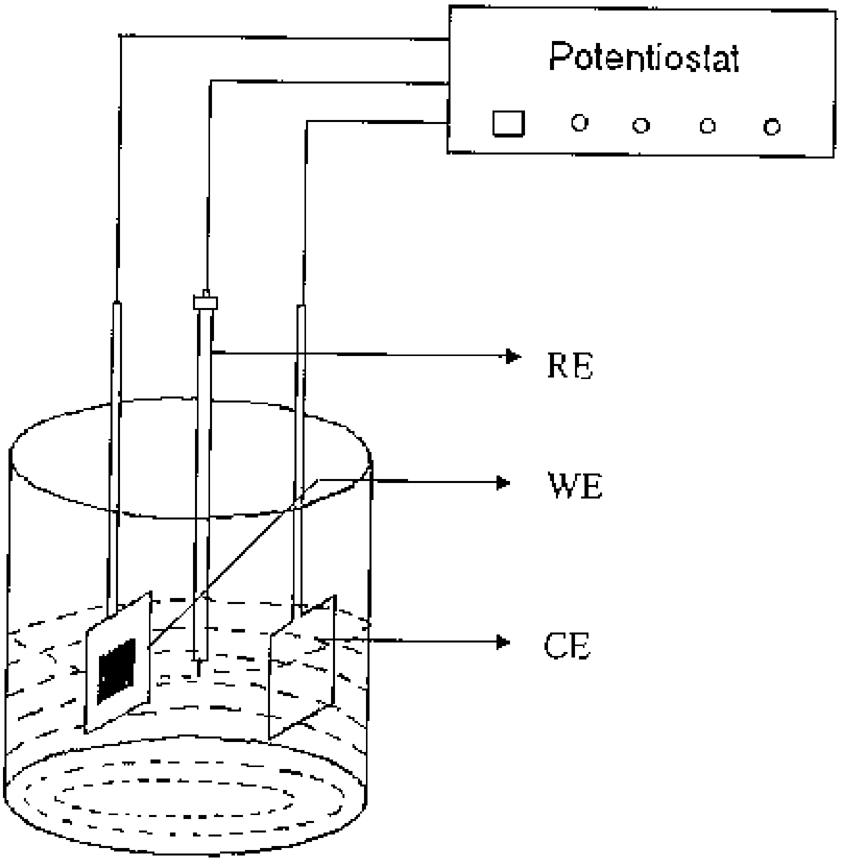

Fig. 2.2.1: Three electrode system for electrochemical measurements.

PANI/CH_3-PANI/SiO_2 films were deposited on the Pt electrode from aqueous electrolytic solution containing 0.5 M aniline, 0.5 M *o*-toluidine and 0.8M H_2SO_4 in prepared aqueous suspension of colloidal silica at room temperature. The film was coated onto the Pt surface by potential sweeping method. In the cycling method, the potential was swept from −0.2 V to +1.0 V *vs* SCE at a scan rate of 100 mV/sec. In the preparation of the film, a potentiogalvanostat (Hokuto HABF 501) with function−generating ability were used for generation of potential and supply of current. The current−potential response was recorded in a X-Y recorder (F-5C, Riken Denshi). The film grown onto the Pt electrode was dedoped and washed several times in distilled water as stated previously.

E. Polypyrrole (PP)

The electrochemical formation of the PP film employed an electrolytic aqueous solution containing 0.5 M pyrrole and 0.1 M $LiClO_4$. The content of the electrolytic solution was subjected to electrolysis in the electrochemical cell. Electrolysis was performed as before by sweeping the potential between −0.2 V and +1.0 V *vs* SCE at a scan rate of 100 mV/sec. During electrolysis, anodic polymerization of the Pt electrode in the electrolytic media results a deposition of a compact film on the electrode. The film thus formed was dedoped and washed repeatedly to remove undesired species.

F. Copolymer: Polyaniline/Polypyrrole (PANI/PP)

PANI/PP films were deposited on the Pt electrode from aqueous electrolytic solution containing 0.5 M aniline, 0.5 M pyrrole, 0.1 M $LiClO_4$ and 0.8 M H_2SO_4 at room temperature. The film was coated onto the Pt surface by potential sweeping method. In the cycling method, the potential was swept from −0.2 V to +1.0 V *vs* SCE at a scan rate of 100 mV/sec. In the preparation of the film, a potentiogalvanostat (Hokuto HABF 501) with function−generating ability were used for generation of potential and supply of current. The current−potential response was recorded in a X-Y recorder (F-5C, Riken Denshi). The film grown onto the Pt electrode was dedoped and washed several times in distilled water as stated previously.

G. Composite: Polyaniline/Polypyrrole/Silica (PANI/PP/SiO_2)

Aqueous colloidal suspension of silica was prepared as described before. PANI/PP/SiO_2 films were deposited on the Pt electrode from aqueous electrolytic solution containing 0.5 M aniline, 0.5 M pyrrole, 0.1 M $LiClO_4$ and 0.8M H_2SO_4 in prepared aqueous suspension of colloidal silica at room temperature. The film was coated onto the Pt surface by potential sweeping method. In the cycling method, the potential was swept from –0.2 V to +1.0 V *vs* SCE at a scan rate of 100 mV/sec. In the preparation of the film, a potentiogalvanostat (Hokuto HABF 501) with function–generating ability were used for generation of potential and supply of current. The current–potential response was recorded in a X-Y recorder (F-5C, Riken Denshi). The film grown onto the Pt electrode was dedoped and washed several times in distilled water as stated previously.

H. Poly-2-amino benzoic acid (PABA)

The electrochemical formation of the PABA film employed an electrolytic aqueous solution containing 0.5 M 2-amino benzoic acid and conc. H_2SO_4. The content of the electrolytic solution was subjected to electrolysis in the electrochemical cell. Electrolysis was performed as before by sweeping the potential between –0.3 V and +1.0 V *vs* SCE at a scan rate of 100 mV/sec. During electrolysis, anodic polymerization of the Pt electrode in the electrolytic media results a deposition of a compact film on the electrode. The film thus formed was dedoped and washed repeatedly to remove undesired species.

I. Copolymer: Polyaniline/ Poly-2-amino benzoic acid (PANI/PABA)

PANI/PABA films were deposited on the Pt electrode from aqueous electrolytic solution containing 0.5 M aniline, 0.5 M 2-amino benzoic acid and 0.8M H_2SO_4 at room temperature. The film was coated onto the Pt surface by potential sweeping method. In the cycling method, the potential was swept from –0.2 V to +1.0 V *vs* SCE at a scan rate of 100 mV/sec. In the preparation of the film, a potentiogalvanostat (Hokuto HABF 501) with function–generating ability were used for generation of potential and supply of current. The current–potential respouse was recorded in a X-Y recorder (F-5C, Riken Denshi). The film grown onto the Pt electrode was dedoped and washed several times in distilled water as stated previously.

J. Copolymer: Poly-*o*-toluidine / Poly-2-amino benzoic acid (CH_3-PANI/PABA)

The electrochemical formation of the CH_3-PANI/PABA film employed an electrolytic aqueous 0.8M H_2SO_4 solution containing 0.5 M *o*-toluidine and 0.5M 2-amino benzoic acid. The content of the electrolytic solution was subjected to electrolysis in the electrochemical cell. Electrolysis was performed as before by sweeping the potential between –0.2 V and +1.0 V *vs* SCE at a scan rate of 100 mV/sec. During electrolysis, anodic polymerization of the Pt electrode in the electrolytic media results a deposition of a compact film on the electrode. The film thus formed was dedoped and washed repeatedly to remove undesired species.

2.3 Spectral Analysis

A. Infra-red Spectra

The samples, PANI, CH_3-PANI, PANI/CH_3-PANI, PANI/CH_3-PANI/SiO_2, PP, PANI/PP and PANI/PP/SiO_2 were obtained electrochemically, as described in section 2.2, as thin films grafted on the Pt electrode, which can be scratched off the Pt electrode, rinsed and dried. They were crushed to powder and used for IR measurements. IR spectra of the studied solids were frequently obtained by mixing and grinding a small portion of the materials with dry and pure KBr crystals. Thorough mixing and grinding were carried out in a mortar by a pestle. The powder mixture was then compressed in a metal holder under a pressure of 8–10 tons to make a pellet. The pellet was then placed in the path of IR beam for measurements. IR spectra of all the studied samples were recorded by an IR spectrophotometer in the region of 4000–400 cm^{-1}.

B. Ultra Violet–Visible Spectra

UV-Vis spectra of the samples, PANI, CH_3-PANI, PANI/CH_3-PANI, PP and PANI/PP were recorded by dissolving the solids in DMF. The solutions were made by dissolving small amount of each solid in 50 mL of DMF. The dissolution employed 30 min sonication in an ultrasonic bath to allow appreciable extent of dissolution. The sample solutions exhibited deep color in some cases. Thus, to ensure preferred dilution of the sample solutions for this spectral measurement, the solutions were diluted with DMF to a visible extent in such a way that the optical density remains within the range 0.5 to 1.0. The sample solution was placed in the sample holder while the reference holder was filled with the DMF solvent. The UV-Vis spectral analysis of the samples employed a double beam spectrophotometer attached with a synchronized personal computer (PC) for recording the spectral data. All the optical analysis were performed at room temperature to within 30° (± 2°)C.

2.4 Electrical Conductivity Measurements

The study of electrical conductivity of the solids at room temperature was carried out by a conventional two point-probe method [7,8]. For this purpose, the dried and powdered solids were compressed mechanically in a transparent plastic tube as illustrated in Fig. 2.4.1. A few centimeters long plastic tube having diameter 1 mm was taken for loading the solids in it. One end of the tube was tightly closed with a copper (Cu) wire having the same diameter as that of the tube. The sample was then pushed gradually inside the tube and compressed mechanically from the other end of the tube by another piece of same wire. Eventually the mass become tightly compressed having a very rigid structure that on further pressing did not change the length of the compressed mass. In this position, the other end of tube was made closed by the similar wire. The two Cu wires at the two ends pressed tightly in such a way that ensures an adequate contact between the sample and the wires. The wire poles were used for electrical contact to get the voltage drop between the two ends of the sample under investigation. An auto ranging microvolt was employed for the conductivity measurements. This equipment allows reading directly the resistance of the sample. Thus, knowing the observed resistance, the specific conductance of each studied sample was calculated out by nsing the standard relation mentioned in chapter 1. The measurement was conducted at laboratory temperature (~ 30°C).

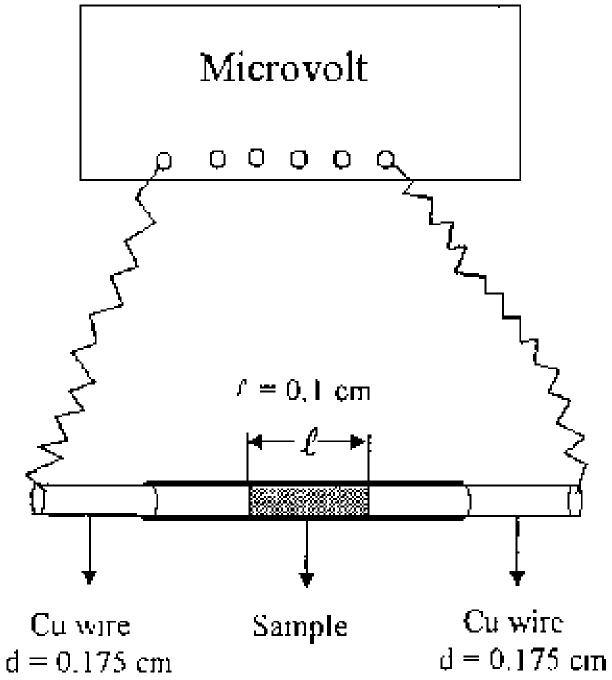

Fig. 2.4.1: The construction for the measurement of the two point-probe conductivity.

2.5 Analysis of Surface Morphology

Scanning electron microscopic technique was adapted to analyze the surface morphology of the samples. The wet mass of PANI, CH_3-PANI, PANI/CH_3-PANI, PANI/CH_3-PANI/SiO_2, PP, PANI/PP and PANI/PP/SiO_2 were coated onto the stainless steel (Fe) electrode as films. The films thus coated were then dried under vacuum before subjected to their surface analysis by SEM. The samples were loaded to the SEM chamber where these were kept under evacuation of 10^{-3} to 10^{-4} torr for about 30 min. Then a very thin layer of gold, about few nanometers thick, was sputtered onto the sample surface to ensure electrical conductivity of the sample surface under studied. The sample was then placed in the main chamber to view it surface image. A Philips XL 30 SEM arrangement was employed for this analysis. The image of the surface morphology is recorded in a PC that interfaced with the main SEM system. The operation system performed all the analysis under ambient atmospheric conditions.

2.6 Doping-Dedoping Technique

The synthesized film electrodes, *viz.*, PANI, CH_3-PANI, PANI/CH_3-PANI, PANI/CH_3-PANI/SiO_2, PP, PANI/PP and PANI/PP/SiO_2 were doped and dedoped electrochemically by the conventional anodic and cathodic treatment of the working electrode [9]. The doping-dedoping process was performed in a single compartment three-electrode cell under ambient atmosphere (Fig. 2.2.1). The films of PANI, CH_3-PANI, PANI/CH_3-PANI and PANI/CH_3-PANI/SiO_2 were grown onto the Pt electrode thick (10 cycle) deposits and the films of PP, PANI/PP and PANI/PP/SiO_2 were grown onto the Pt electrode thin (1 cycle) deposits. The film thus deposited was then rinse repeatedly to remove any traces of monomer or other by-products. To perform doping-dedoping process, the rinsed film electrode was then placed in the cell containing monomer free electrolytic solution only. A potential sweeping from –0.2 to +1.0 V was allowed with a scan rate of 100 mV/sec. Indeed, the doping and dedoping process of the films were observed to be occurred within the potential range scanned in this experiment.

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Chapter 3

RESULTS AND DISCUSSION

3.1 Electrochemical Preparation of the Modified Electrodes

A. Polyaniline (PANI)

Anodic oxidation of aniline on the inert metallic electrodes is the most current electrochemical method for the synthesis of PANI. This method is used since electrochemical methods [1-9] offer some advantages over classical chemical methods [10-15]. The anodic oxidation of aniline is generally affected on an inert material, which is generally Pt [16-22]. In the present work, electrochemical synthesis of PANI was carried out by anodic oxidation of aniline onto a Pt electrode in aqueous solution. Typical CV of electrochemical polymerization of aniline is given in Fig. 3.1.1. On sweeping the first potential cycle from –0.2 to +1.0 V *vs* SCE at a scan rate of 100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.85 V indicating the oxidation of aniline to yield PANI [23, 24]. A thin deep blue film was seen on the Pt surface.

As the sweeping repeated Fig. 3.1.2, i.e., in the second and subsequent cycles, the peak current increases further indicating the formation of more deposits of PANI on the substrate. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of PANI. The anodic peak at *ca.* +0.2 V is observed from the second scan. This peak can be assigned to the oxidation of PANI film deposited on the electrode corresponding to the conversion of amine units to radical cations in the polymer chain [25-26]. The deep blue color of the film turned to greenish-yellow when potential sweep approached to the cathodic direction at *ca.* +0.0 V or lower.

Figure 3.1.3 also represents the CV of electrochemical polymerization of aniline under similar electrolytic conditions; here polymerization was allowed to grow on the Pt upto 10 cycles. As the PANI film got thicker, the characteristic peaks seem to be less prominent or at least broadened and also their positions are shifted. However, the colour changes of the thick film also occur in the similar fashion as described for the thin PANI film. The Pt electrode thus coated with the PANI film is referred hereafter as PANI electrode.

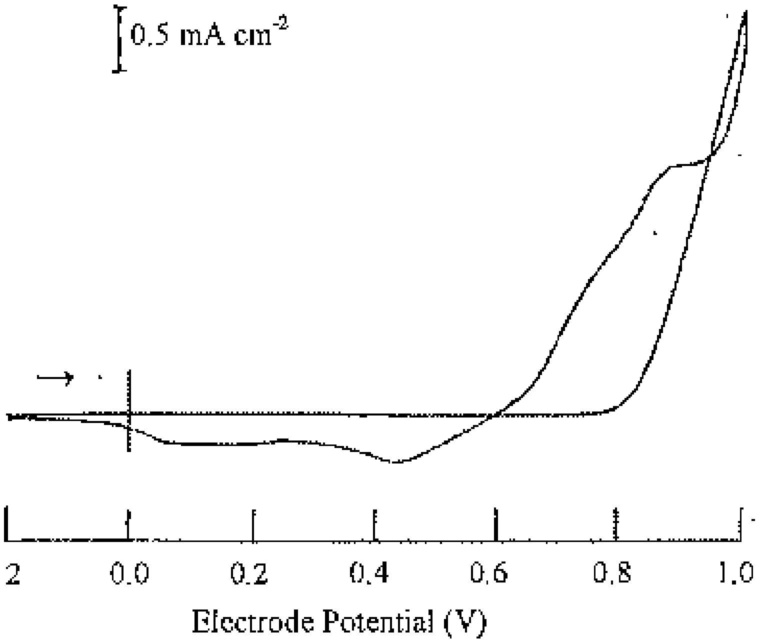


Fig. 3.1.1: CV (1 cycle) during electrochemical synthesis of PANI in aqueous solution (0.5M aniline + 0.8M H_2SO).

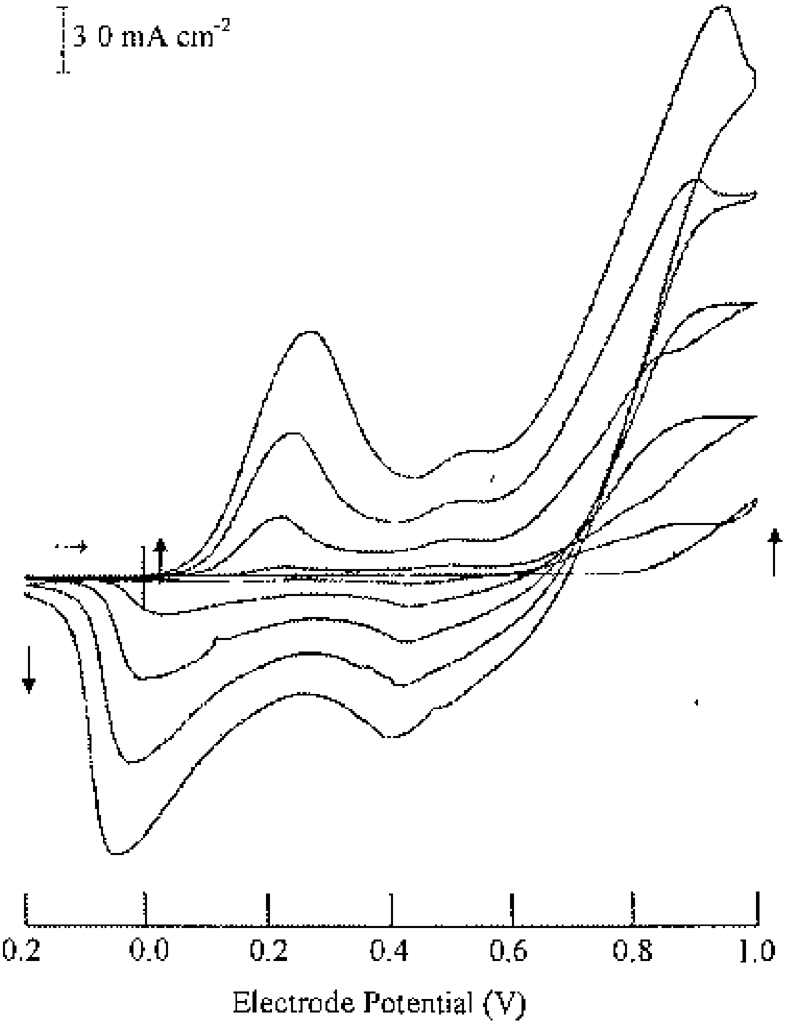


Fig. 3.1.2: CV (5 cycle) during electrochemical synthesis of PANI in aqueous solution (0.5M aniline + 0.8M H_2SO_4).

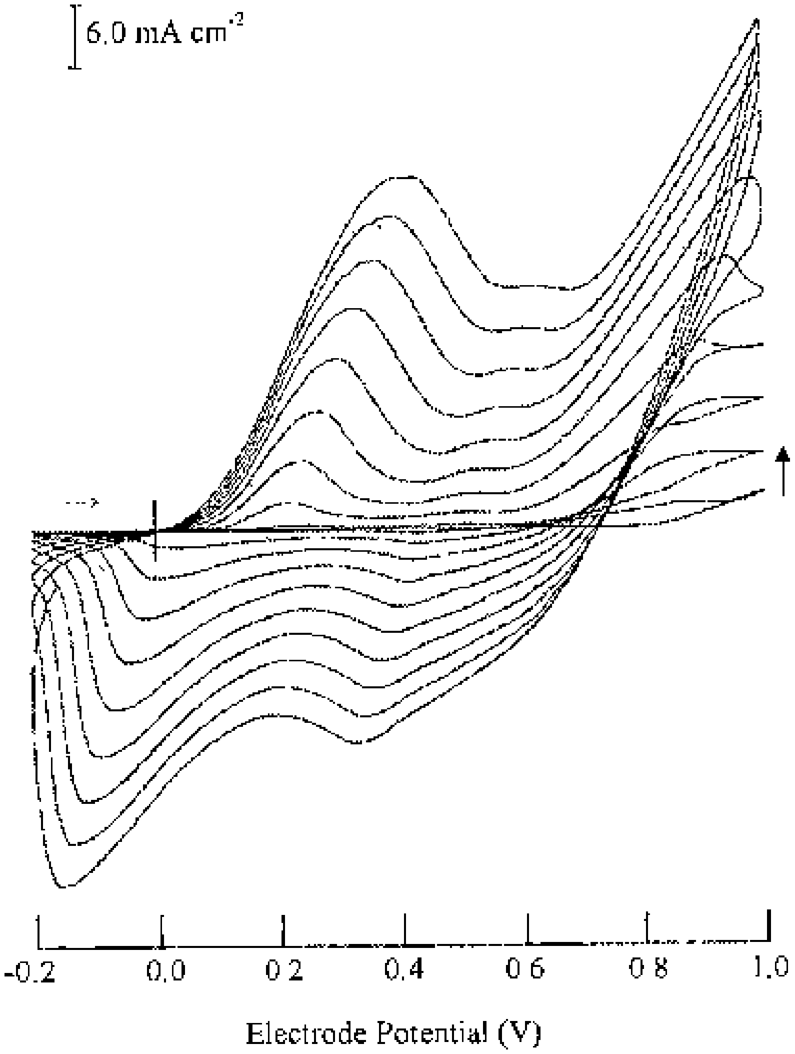


Fig. 3.1.3: CV (10 cycle) during electrochemical synthesis of PANI in aqueous solution (0.5M aniline + 0.8M H_2SO_4).

The results Figs. 3.1.1 – 3.1.3 are summarized the following table:

PANI: Prepared in H_2O media (0.5M aniline + 0.8M H_2SO_4)

3-D Matrix	Monomer oxidation potential (V)	Polymer oxidation (Doping) potential (V)	Polymer reduction (Dedoping) potential (V)	Color		Yield
				Oxid^n state	Red^n state	
PANI (1 cycle)	+0.85	–	+ 0.05	blue black	red	high
PANI (5 cycles)	+0.85 to +0.9 (shift to +ve in the subsequent cycle)	+0.2 to +0.3 (shift to +ve in the subsequent cycle)	+0.05 to -0.1 (shift to -ve in the subsequent cycle)	deep blue	greenish yellow	high
PANI (10 cycles)	+0.85 to +0.95 (shift to +ve from the second cycle)	+0.2 to +0.4 (shift to +ve from the second cycle)	+0.05 to -0.2 (shift to -ve from the second cycle)	deep blue	greenish yellow	high

If the polymer thickness increases, the polymer oxidation (doping) and reduction (dedoping) still occur indicating the electroactivity of the polymer. However, the oxidation and reduction potentials of the polymer are shifted. Potential shifting is reasonable because the reaction for the first cycle is occurred directly on the Pt surface. But after the first cycle, Pt is covered by the polymer film and the reaction for the second cycle is done on the polymer covered Pt surface. As the cycle increases, Pt surface covered with more polymer film and activity of the Pt surface may vary. As a result potential shift (for the monomer oxidation, polymer oxidation and reduction) with the increase of cycle may arise due to the dissimilar activities of the bare Pt and polymer covered Pt surface.

During electrochemical oxidation (doping), the anions in the solution become incorporated into the polymer to compensate the positive charges in the chain while in the reduction (dedoping) processes, the incorporated anions get removed out of the polymer film [27-29]. In case of PANI, most of the authors proposed that the redox processes appeared in its CV are associated to the protonation as well as to the insertion of anion in the film [1, 24, 25, 30-31].

Effect of the different solvents (e.g., propylene carbonate, γ-butyrolactone, acetonitrile etc.) on the electropolymerization of aniline was studied before by early workers [32]. In the present work, electrochemical synthesis of PANI was also carried out by anodic oxidation of aniline onto a Pt electrode in CH_3CN-water and DMF-water containing $LiClO_4$ for both cases.

Typical CV of electrochemical polymerization of aniline in CH_3CN-water is given in Fig. 3.1.4. On sweeping the first potential cycle from –0.2 to +1.0 V *vs* SCE, a sharp rise in current is seen from the potential +0.6 V indicating the oxidation of aniline to yield PANI. A thin deep blue film is seen on the Pt surface. As the sweeping repeated Fig. 3.1.5, i.e., in the second and subsequent cycles, the peak current decreases, which indicates the decrease of PANI deposition on the substrate. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of PANI. The anodic peak at *ca.* +0.2 V is observed from the second scan. This peak can be assigned to the oxidation (doping) of PANI film deposited on the electrode. The deep blue color of the film turned to greenish-yellow when potential sweep approached to the cathodic direction at *ca.* +0.0 V or lower.

CV of electrochemical polymerization of aniline in DMF-water is given in Fig. 3.1.6. On sweeping the first potential cycle from –0.2 to +1.0 V *vs* SCE, a sharp rise in current is seen at a potential *ca.* +0.5 V indicating the oxidation of aniline to yield PANI. A thin deep blue film is seen on the Pt surface. As the sweeping repeated Fig. 3.1.7, i.e., in the second and subsequent cycles, the peak current decreases, which indicates the decrease in conductivity of PANI deposition on the substrate. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of PANI. The anodic peak at *ca.* +0.2 V is observed from the second scan. This peak can be assigned to the oxidation of PANI film deposited on the electrode. The deep blue color of the film turned to greenish-yellow when potential sweep approached to the cathodic direction at *ca.* +0.0 V or lower.

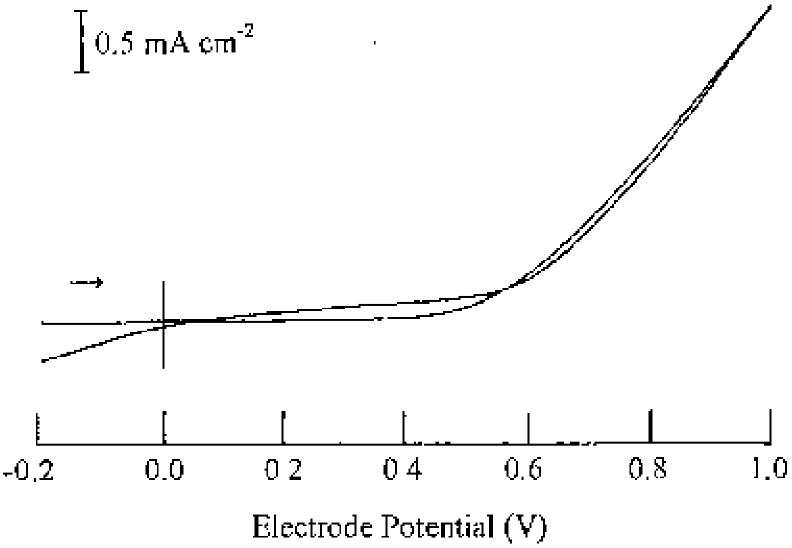


Fig. 3.1.4: CV (1 cycle) during electrochemical synthesis of PANI in CH_3CN-water solution in presence of $LiClO_4$ (0.5M aniline + 0.1M $LiClO_4$).

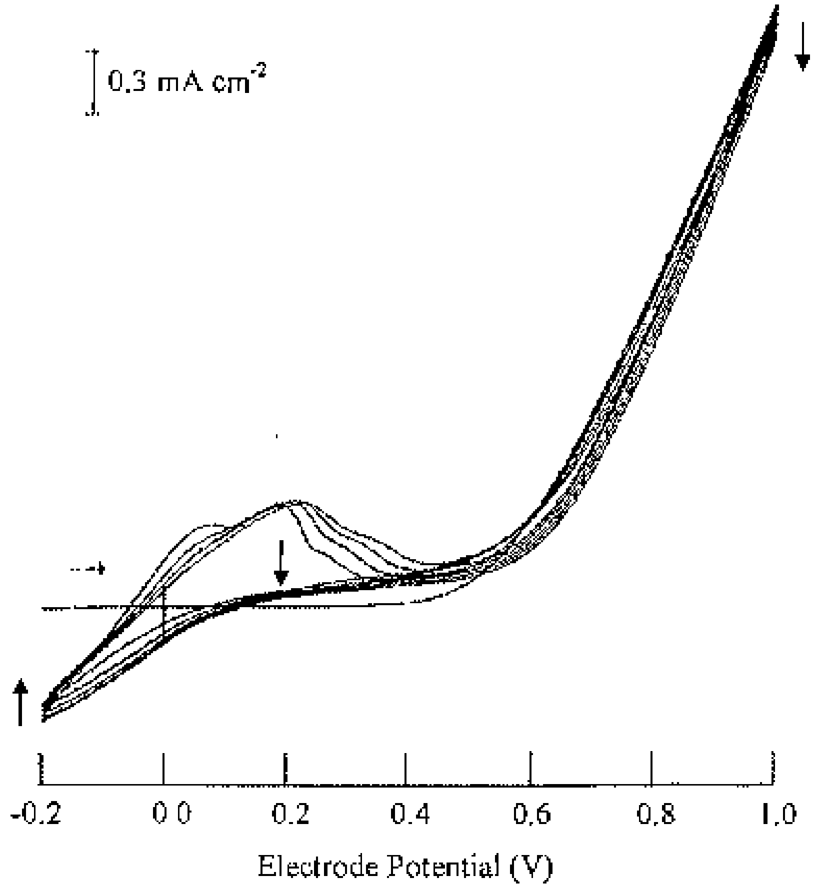


Fig. 3.1.5: CV (5 cycle) during electrochemical synthesis of PANI in CH_3CN-water solution in presence of $LiClO_4$ (0.5M aniline + 0.1M $LiClO_4$).

The results Figs. 3.1.4 – 3.1.5 are summarized the following table:

PANI: Prepared in CH_3CN - H_2O media (0.5M aniline + 0.1M $LiClO_4$)

3-D Matrix	Monomer oxidation potential (V)	Polymer oxidation (Doping) potential (V)	Polymer reduction (Dedoping) potential (V)	Color		Yield
				Oxid^n state	Red^n state	
PANI (1 cycle)	+0.55	–	-0.2	deep blue	greenish yellow	very low
PANI (5 cycles)	+0.55	+0.2 (strong peak)	-0.2	deep blue	greenish yellow	very low

The electrolytic medium influences greatly on the polymer formation (yield). Very thin film can be seen ever after several cycles during polymerization. The absence of acid in electrolytic media could be the reason for low polymerization.

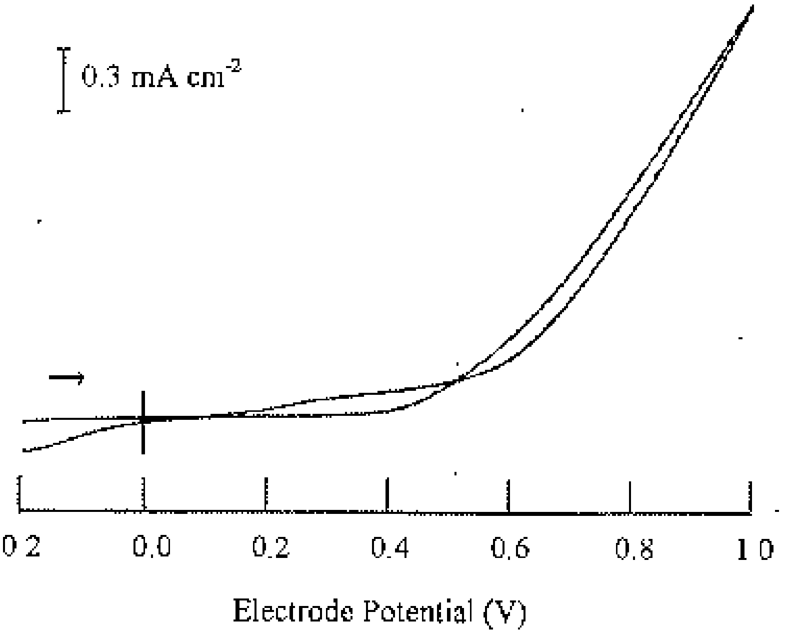


Fig. 3.1.6: CV (1 cycle) during electrochemical synthesis of PANI in DMF-water solution in presence of $LiClO_4$ (0.5M aniline + 0.1M $LiClO_4$).

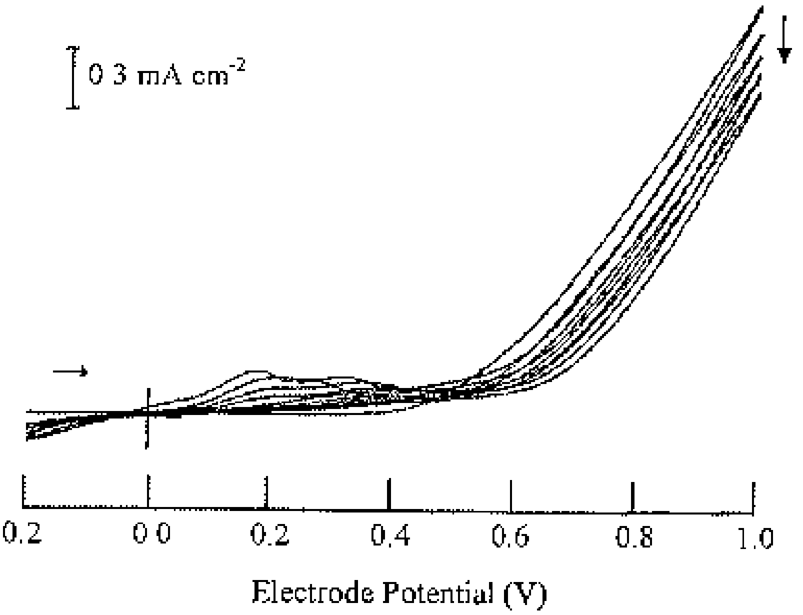


Fig. 3.1.7: CV (5 cycle) during electrochemical synthesis of PANI in DMF-water solution in presence of $LiClO_4$ (0.5M aniline + 0.1M $LiClO_4$).

The results (Fig. 3.1.6 – 3.1.7) are summarized the following table:

PANI: Prepared in the DMF - H_2O media (0.5M aniline + 0.1M $LiClO_4$)

3-D Matrix	Monomer oxidation potential (V)	Polymer oxidation (Doping) potential (V)	Polymer reduction (Dedoping) potential (V)	Color		Yield
				Oxidⁿ state	Redⁿ state	
PANI (1 cycle)	+0.55	–	-0.2 (very weak)	deep blue	greenish yellow	very low
PANI (5 cycles)	+0.55	+0.2 (weak peak)	-0.2 (very weak)	deep blue	greenish yellow	very low

Polymerization was very low due to the absence of acid. The solvents CH_3CN and DMF have also influence on the polymer oxidation and reduction processes. However, the polymerization potentials for both the solvents are seemed to be identical. The polymer seems to be less electroactive with DMF solvent.CH_3-PANI was also prepared by varying thickness and electrolytic solvent and shows similar phenomenon as that of PANI e.g., with varying thickness, potential shift of the CH_3-PANI oxidation and reduction occur. By employing different solvents in the synthesis of CH_3-PANI, electroactivity of the film found to be affected.

B. Poly-*o*-toluidine (CH_3-PANI)

The conducting polymer, CH_3-PANI, can be prepared by both chemical [33-39] and electrochemical polymerization [40-45]. In the present work, electrochemical synthesis of CH_3-PANI was carried out by anodic oxidation of *o*-toluidine onto a Pt electrode in aqueous solution. Typical CV of electrochemical polymerization of *o*-toluidine is given in Fig. (3.1.8). On sweeping the first potential cycle from –0.2 to +1.0 V *vs* SCE at a scan rate of

100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.8 V indicating the oxidation of *o*-toluidine to yield CH_3-PANI [41]. A thin deep blue film is seen on the Pt surface.

As the sweeping repeated Fig. 3.1.9, i.e.. in the second and subsequent cycles, the peak current decreases further indicating less ease of the formation of CH_3-PANI on the substrate with decreasing conductivity. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of CH_3-PANI. The anodic peak at *ca.* +0.42 V is observed from the second scan. This peak can be assigned to the oxidation of CH_3-PANI film deposited on the electrode. Whereas the cathodic peak at *ca.* +0.4 V is observed from the first scan that can be assigned to the reduction of CH_3-PANI film deposited on the electrode. The deep blue color of the film turned to greenish-yellow when potential sweep approached to the cathodic direction at *ca.* +0.4 V or lower.

Figure 3.1.10 also represents the CV of electrochemical polymerization of *o*-toluidine under similar electrolytic conditions; here polymerization was allowed to grow on the Pt upto 10 cycles. As the CH_3-PANI film got thicker, the characteristic peaks seem to be less prominent or at least broadened and also their positions are shifted. However, the colour changes of the thick film also occur in the similar fashion as described for the thin CH_3-PANI film. The Pt electrode thus coated with the CH_3-PANI film is referred hereafter as CH_3-PANI electrode.

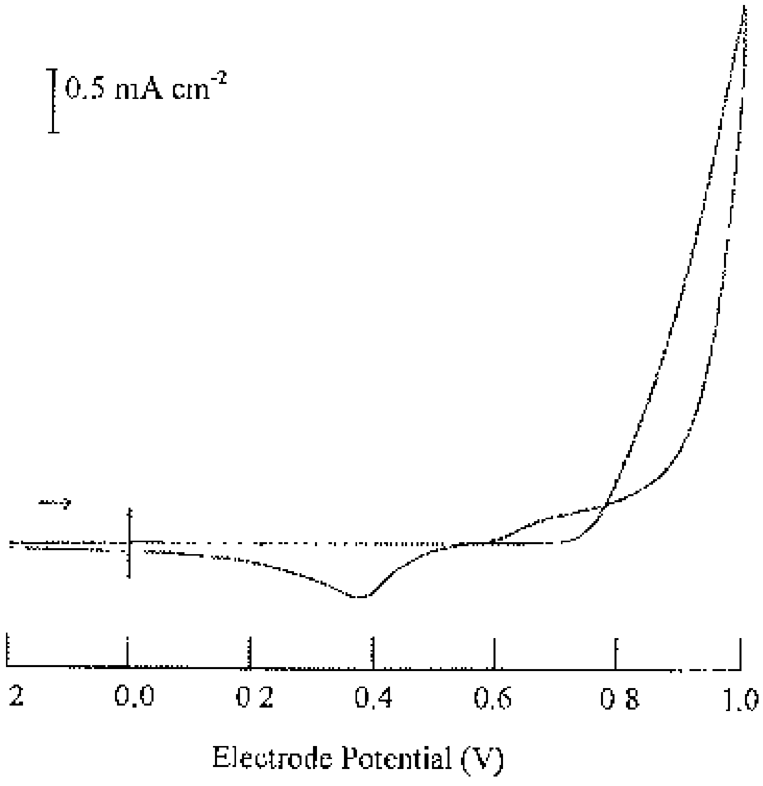


Fig. 3.1.8: CV (1 cycle) during electrochemical synthesis of CH_3-PANI in aqueous solution (0.5M o-toluidine + 0.8M H_2SO_4).

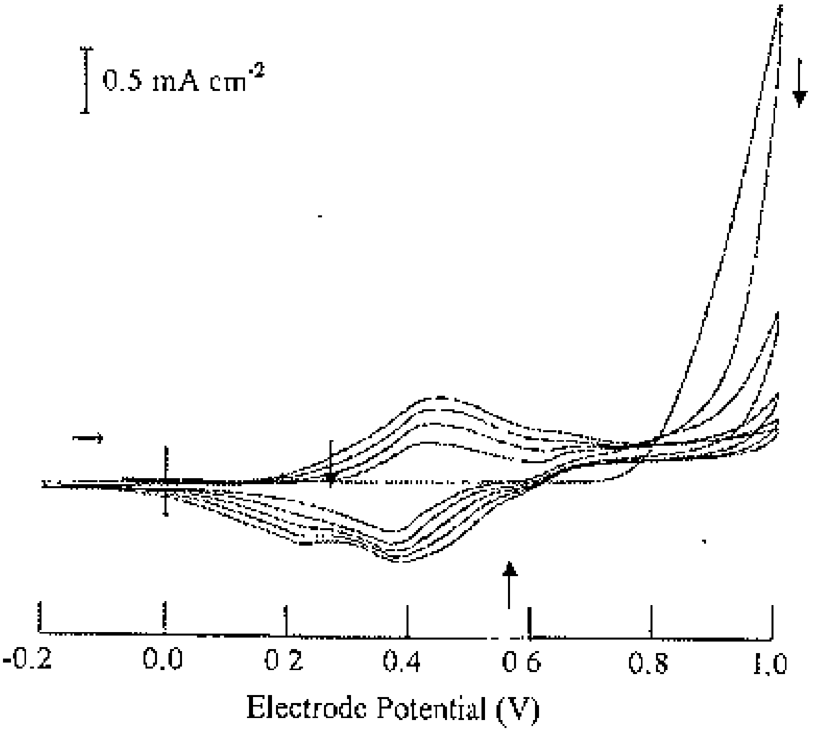


Fig. 3.1.9: CV (5 cycle) during electrochemical synthesis of CH_3-PANI in aqueous solution (0.5M o-toluidine + 0.8M H_2SO_4).

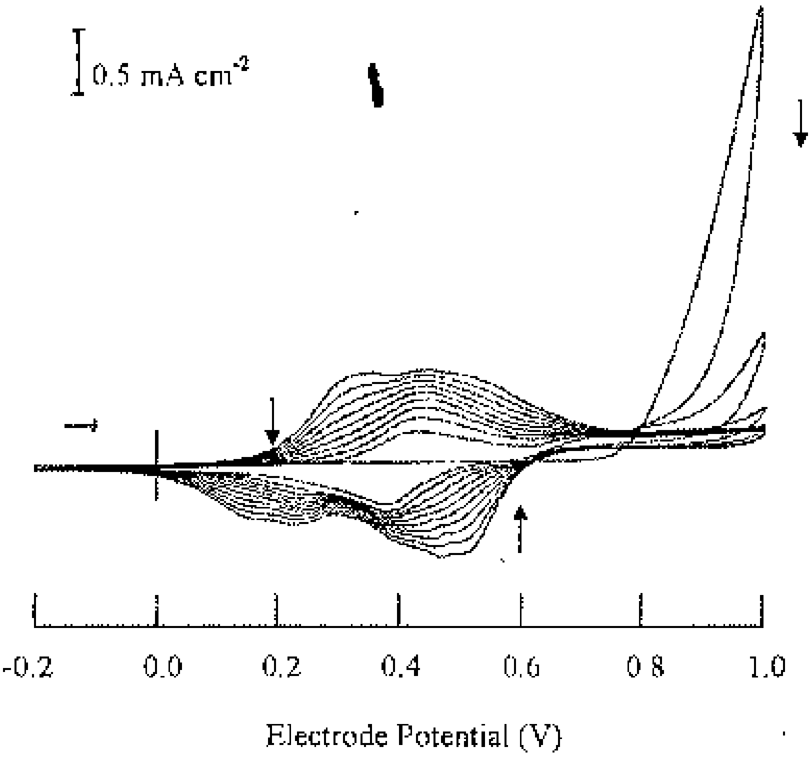


Fig. 3.1.10: CV (10 cycle) during electrochemical synthesis of CH_3-PANI in aqueous solution (0.5M o-toluidine + 0.8M H_2SO_4).

Effect of the different organic solvent on the synthesis of CH_3-PANI in both electrochemical and chemical methods were studied before [37, 40]. In the present research, electrochemical synthesis of CH_3-PANI was also carried out by anodic oxidation of *o*-toluidine onto a Pt electrode in CH_3CN-water and DMF-water containing $LiClO_4$ for both cases.

Typical CV of electrochemical polymerization of *o*-toluidine in CH_3CN-water is given in Fig. 3.1.11. On sweeping the first potential cycle from –0.2 to +1.2 V *vs* SCE, a sharp rise in current is seen at a potential *ca.* +0.6 V indicating the oxidation of *o*-toluidine to yield CH_3-PANI. As the sweeping repeated, i.e., in the second and subsequent cycles, the peak current decreases, which indicates the decrease in the formation of CH_3-PANI on the substrate. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of CH_3-PANI. A thin deep blue film is seen on the Pt surface. The anodic peak at *ca.* +0.3 V is observed from the second scan. This peak can be assigned to the oxidation of CH_3-PANI film deposited on the electrode. Whereas the cathodic peak at *ca.* -0.1 V is observed from the first scan that can be assigned to the reduction of CH_3-PANI film deposited on the electrode. The deep blue color of the film turned to greenish-yellow when potential sweep approached to the cathodic direction at *ca.* +0.0 V or lower.

CV of electrochemical polymerization of *o*-toluidine in DMF-water is given in Fig. 3.1.12. On sweeping the first potential cycle from –0.2 to +1.1 V *vs* SCE, a sharp rise in current is seen at a potential *ca.* +0.6 V indicating the oxidation of *o*-toluidine to yield CH_3-PANI. As the sweeping repeated, i.e., in the second and subsequent cycles, the peak current decreases, which indicates the decrease in the deposition of CH_3-PANI on the substrate. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of CH_3-PANI. A thin deep blue film is seen on the Pt surface. The anodic peak at *ca.* +0.3 V is observed from the second scan. This peak can be assigned to the oxidation of PANI film deposited on the electrode. Whereas the cathodic peak at *ca.* +0.0 V is observed from the first scan that can be assigned to the reduction of CH_3-PANI film deposited on the electrode. The deep blue color of the film turned to greenish-yellow when potential sweep approached to the cathodic direction at *ca.* +0.0 V or lower.

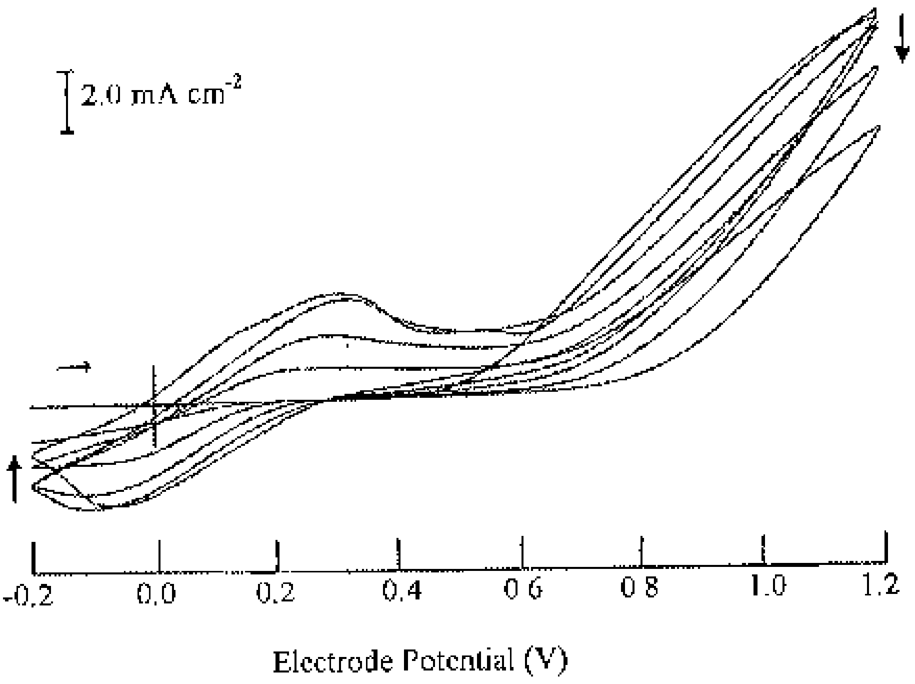


Fig. 3.1.11: CV (5 cycle) during electrochemical synthesis of CH_3-PANI in CH_3CN-water solution in presence of $LiClO_4$ (0.5M o-toluidine + 0.1M $LiClO_4$).

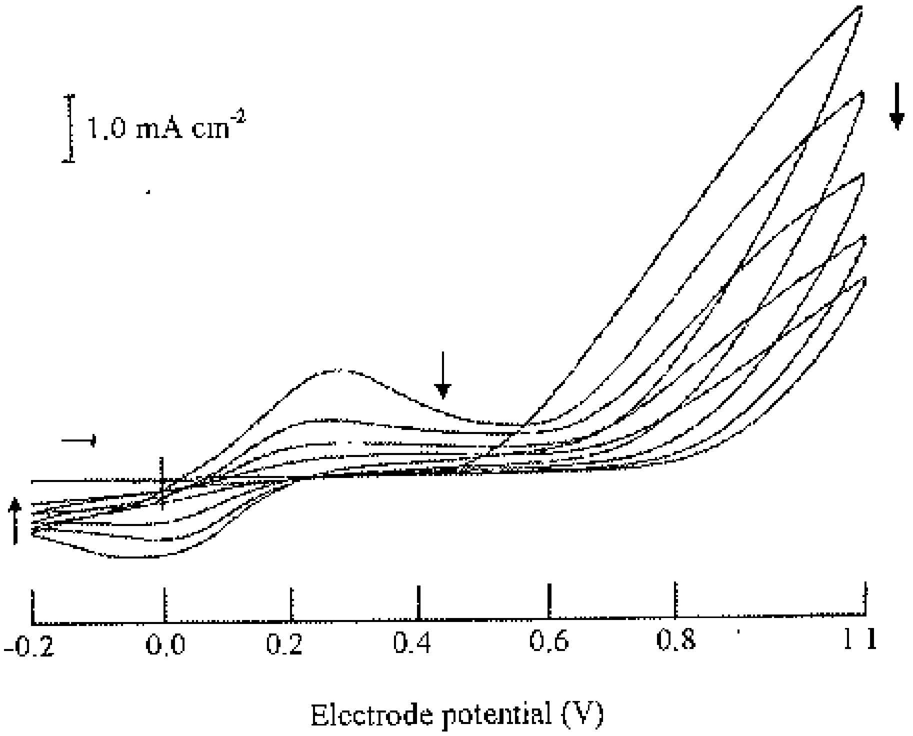


Fig. 3.1.12: CV (5 cycle) during electrochemical synthesis of CH_3-PANI in DMF-water solution in presence of $LiClO_4$ (0.5M o-toluidine + 0.1M $LiClO_4$).

C. Copolymer: Polyaniline/Poly-*o*-Toluidine (PANI/CH_3-PANI)

The large-scale application of PANI is sometimes limited by the insolubility of its protonated state and the difficulty of processing by conventional methods. This shortcoming has usually been overcome by the synthesis of various PANI copolymers [46, 47]. Copolymer of aniline with 3-aminophenyl-boric acid [48] has been reported earlier. Recently, poly-*o*-toluidine has attracted attention because it has been reported to exhibit better solubility [49] and possibility [50] than polyaniline [51, 52]. Copolymerization of aniline with toluidine is one of the best methods to modify the solubility of polyaniline and to combine the advantages of CH_3-PANI with PANI. There are only a few reports about copolymerization in the literature [53-57].

During this research, PANI/CH_3-PANI was synthesized electrochemically on platinum substrates under cyclic voltammetric conditions in aqueous solution. Typical CV of electrochemical copolymerization is given in Fig. 3.1.13. On sweeping the first potential cycle from –0.2 to +1.0 V *vs* SCE at a scan rate of 100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.8 V indicating the oxidation of monomers to yield the copolymer [7, 41]. A thin deep blue film is seen on the Pt surface.

As the sweeping repeated Fig. 3.1.14, i.e., in the second and subsequent cycles, the peak current decreases further indicating the formation of less deposits of the copolymer on the substrate with decreasing conductivity. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of PANI/CH_3-PANI. The anodic peak at *ca.* +0.45 V is observed from the second scan. This peak can be assigned to the oxidation of PANI/CH_3-PANI film deposited on the electrode. Whereas the cathodic peak at *ca.* +0.38 V is observed from the first scan that can be assigned to the reduction of PANI/CH_3-PANI film deposited on the electrode. The deep blue color of the film turned to greenish-yellow when potential sweep approached to the cathodic direction at *ca.* +0.0 V or lower.

Figure 3.1.15 also represents the CV of electrochemical polymerization of aniline/*o*-toluidine nnder similar electrolytic conditions; here polymerization was allowed to grow on the Pt upto 10 cycles. As the copolymer film got thicker, the characteristic peaks seem to be less prominent or at least broadened and also their positions are shifted.

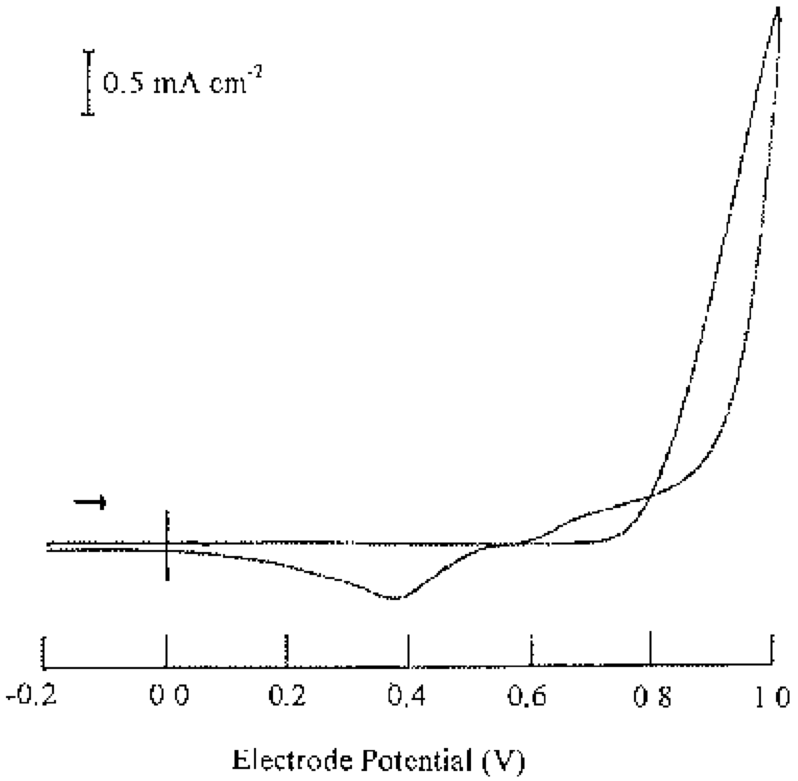


Fig. 3.1.13: CV (1 cycle) during electrochemical synthesis of PANI/CH_3-PANI in aqueous solution (0.5M aniline + 0.5M o-toluidine + 0.8M H_2SO_4).

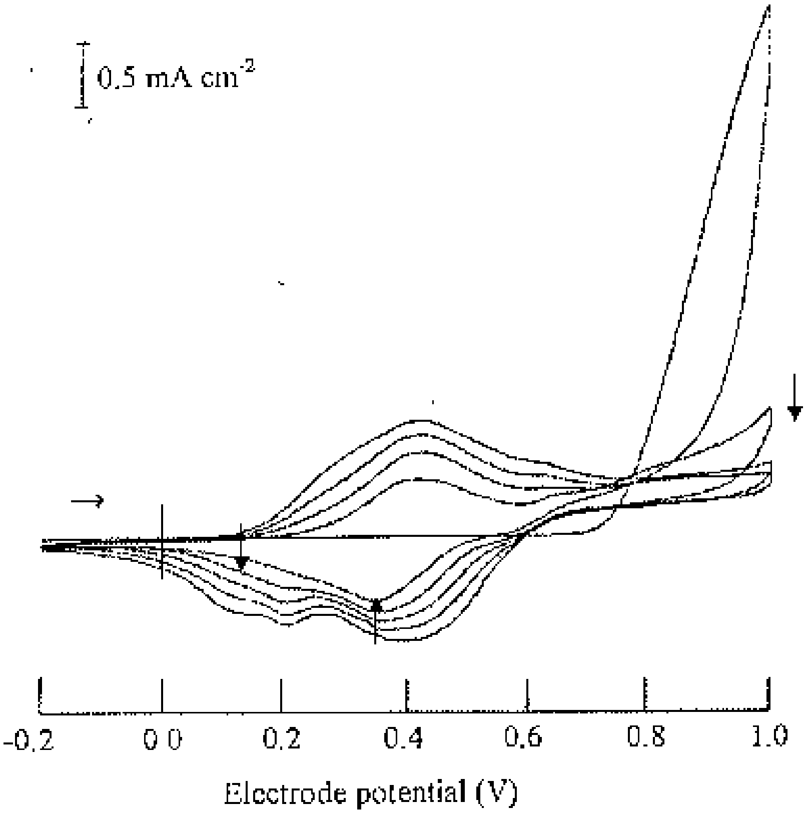


Fig. 3.1.14: CV (5 cycle) during electrochemical synthesis of PANI/CH_3-PANI in aqueous solution (0.5M aniline + 0.5M o-toluidine + 0.8M H_2SO_4).

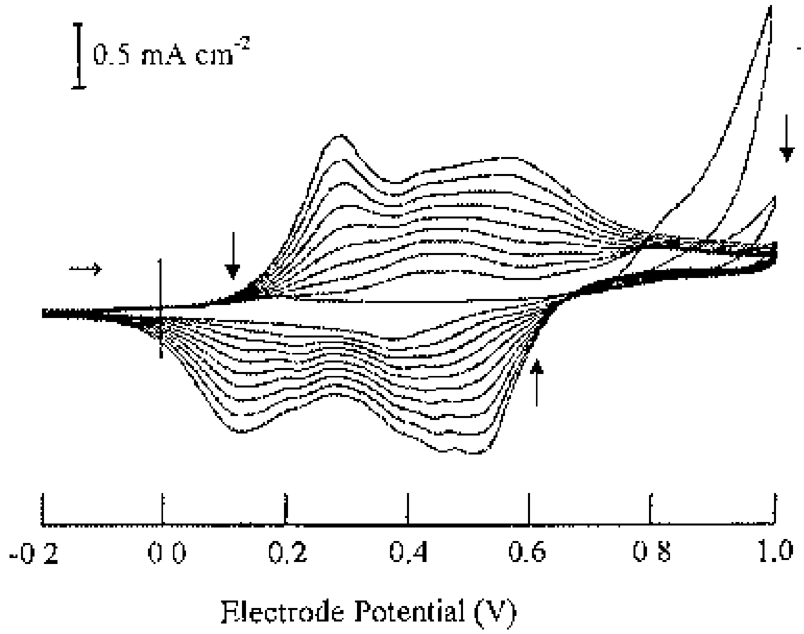


Fig. 3.1.15: CV (10 cycle) during electrochemical synthesis of PANI/CH_3-PANI in aqueous solution (0.5M aniline + 0.5M o-toluidine + 0.8M H_2SO_4).

The results (Fig. 3.1.14 and Fig. 3.1.17) are summarized the following table:

Copolymer: PANI/CH_3-PANI (Fig. 3.1.14)

prepared in aqueous solution (0.5M aniline + 0.5M o-touidine + 0.8M H_2SO_4)

Composite: PANI/CH_3-PANI/SiO_2 (Fig. 3.1.17)

prepared in aqueous solution (0.5M aniline + 0.5M o-touidine + 0.8M H_2SO_4 + colloidal SiO_2)

3-D Matrix	Monomer oxidation potential (V)	Polymer oxidation (Doping) potential (V)	Polymer reduction (Dedoping) potential (V)	Color		Yield
				Oxid^n state	Red^n state	
PANI (1 cycle)	+0.85	+0.2	+0.05	blue black	reddish	high (stand alone)
CH_3- PANI (5 cycles)	+0.80	+0.42	+0.40	deep blue	greenish yellow	high (stand alone)
PANI/CH_3-PANI (5 cycles)	+0.85	+0.40	+0.40 (strong) +0.20 (strong)	deep blue	greenish yellow	high (moderately stand alone)
PANI/CH_3-PANI/SiO_2 (5 cycles)	+0.75	+0.40	+0.35 (strong) +0.20 (less strong)	bluish	greenish	high (stand alone)

Although changing the functionality, all the four matrices show excellent electractivity exhibiting prominent oxidation-reduction process. However, their electrochemical potentials seem to be nearly identical.

D. Composite: Polyaniline/Poly-*o*-Toluidine/Silica (PANI/CH_3-PANI/SiO_2)

A number of attempts were taken previously to prepare polyaniline/silica composite by both chemical and electrochemical method [58-62]. But no attempt has yet been taken to prepare polyaniline/poly-*o*-toluidine/silica composite by any of the mentioned two methods. Electrochemical synthesis of PANI/CH_3-PANI/SiO_2 was carried out for the first time by anodic oxidation of monomers onto a Pt electrode in aqueous solution containing colloidal silica.

Typical CV of electrochemical polymerization of composite is given in Fig 3.1.16 On sweeping the first potential cycle from −0.2 to +1.0 V *vs* SCE at a scan rate of 100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.75 V indicating the oxidation of monomers to yield the composite. A thin deep blue film is seen on the Pt surface.

As the sweeping repeated Fig. 3.1.17, i.e., in the second and subsequent cycles, the peak current decreases though formation of more deposits of the copolymer on the substrate takes place. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of PANI/CH_3-PANI/SiO_2. The anodic peak at *ca.* +0.4 V is observed from the second scan. This peak can be assigned to the oxidation of PANI/CH_3-PANI/SiO_2 film as deposited on the electrode. Whereas the cathodic peak at *ca.* +0.35 V is observed from the first scan that can be assigned to the reduction of PANI/CH_3-PANI/SiO_2 film that deposited on the electrode. The deep blue color of the film turned to greenish-yellow when potential sweep approached to the cathodic direction at *ca.* +0.0 V or lower.

Figure 3.1.18 also represents the CV of electrochemical polymerization of aniline/*o*-toluidine/silica under similar electrolytic conditions; here polymerization was allowed to grow on the Pt upto 10 cycles. As the copolymer film got thicker, the characteristic peaks seem to be less prominent or at least broadened and also their positions are shifted. However, the colour changes of the thick film also occur in the similar fashion as described before. The Pt electrode thus coated with the PANI/CH_3-PANI/SiO_2 film is referred hereafter as PANI/CH_3-PANI/SiO_2 electrode.

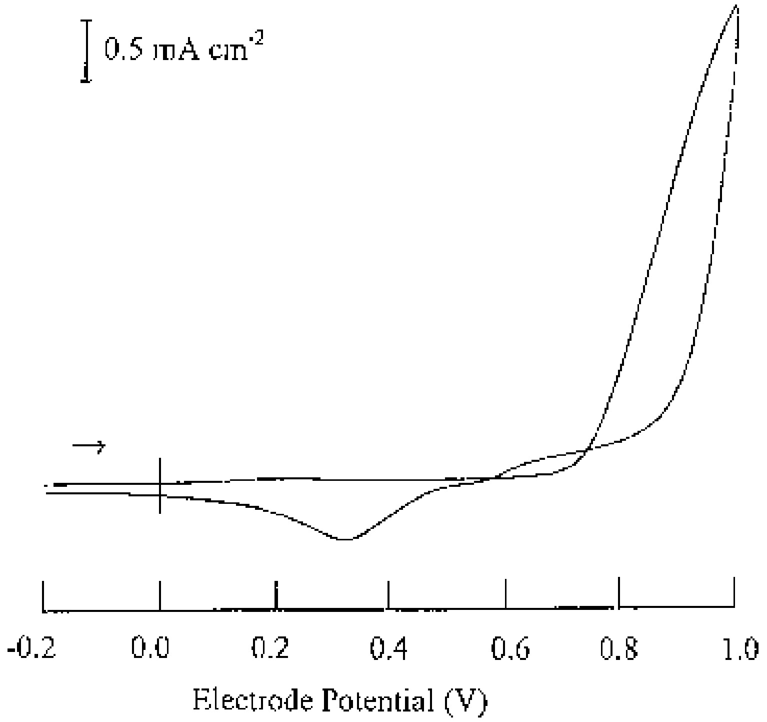


Fig. 3.1.16: CV (1 cycle) during electrochemical synthesis of PANI/CH_3-PANI/SiO_2 in aqueous solution (colloidal SiO_2 + 0.5M o-toluidine + 0.8M H_2SO_4).

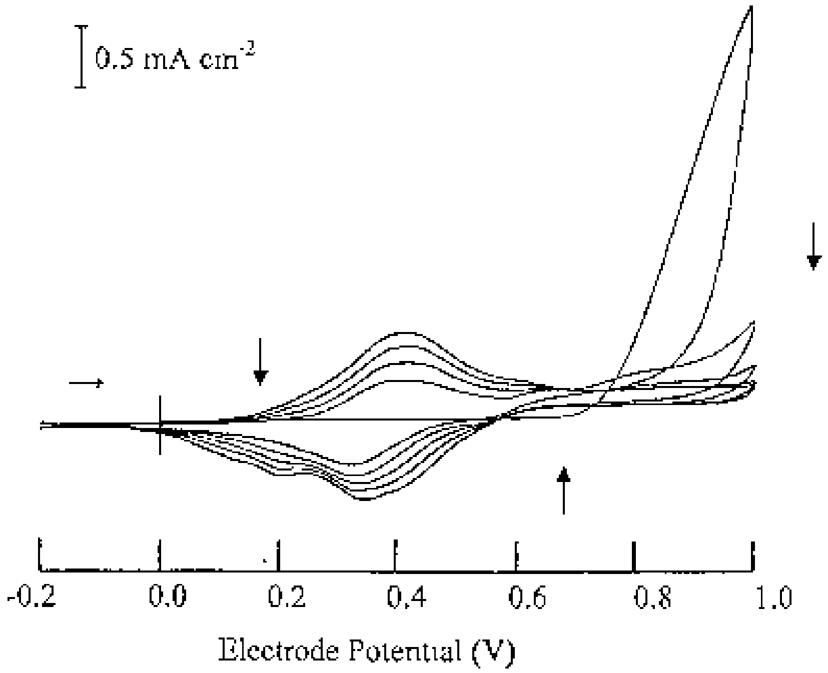


Fig. 3.1.17: CV (5 cycle) during electrochemical synthesis of PANI/CH_3-PANI/SiO_2 in aqueous solution (colloidal SiO_2 + 0.5M o-toluidine + 0.8M H_2SO_4).

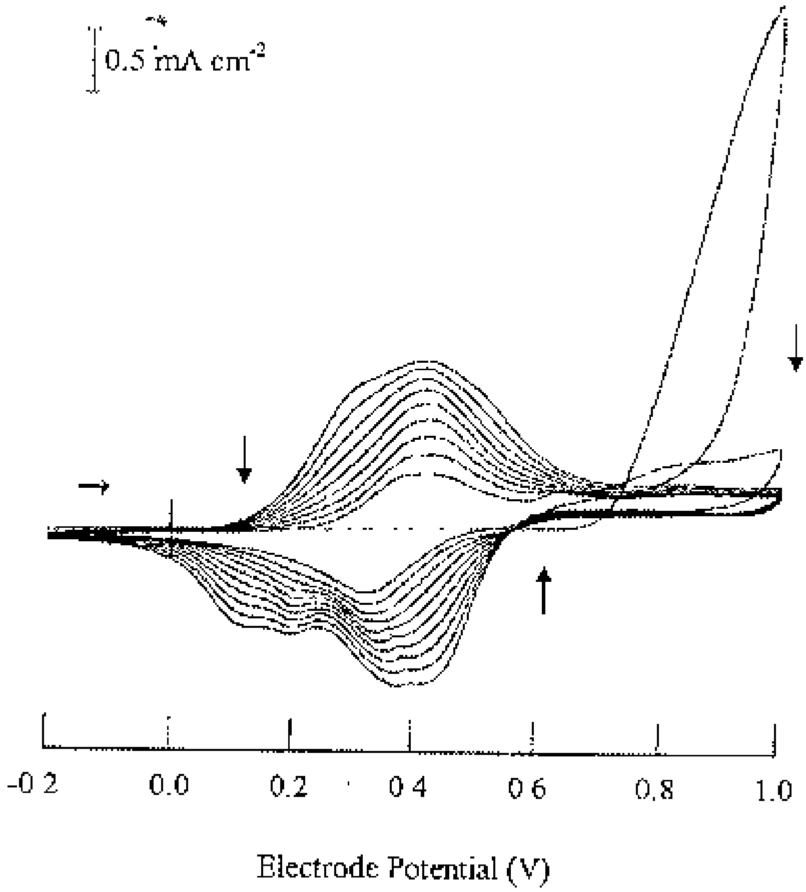


Fig. 3.1.18: CV (10 cycle) during electrochemical synthesis of PANI/CH_3-PANI/SiO_2 in aqueous solution (colloidal SiO_2 + 0.5M *o*-toluidine + 0.8M H_2SO_4).

E. Polypyrrole (PP)

Polypyrrole has been subject of a great number of studies due to the low oxidation potential of the respective monomer, relatively easy method of preparation from aqueous solutions, high stability and good electrical conductivity [63-65]. The electropolymerization of pyrrole has been extensively reported on noble metals such as Pt [66-68] and Au [69, 70] as well as on different forms of carbon [71-73]. Besides, polypyrrole coatings on a variety of other metals, i.e. Cu [74-76], Zn [77-79], Ti [80], Al [81] and Ni [82] have also been reported.

In the present work, electrochemical synthesis of PP was carried out by anodic oxidation of pyrrole onto a Pt electrode in aqueous solution. Typical CV of electrochemical polymerization of pyrrole is given in Fig. 3.1.19. On sweeping the first potential cycle from –0.2 to +1.0 V *vs* SCE at a scan rate of 100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.62 V indicating the oxidation of pyrrole to yield PP. A thick deep black film is seen on the Pt surface.

F. Copolymer: Polyaniline/Polypyrrole (PANI/PP)

There is very little literature on the formation of polyaniline-polypyrrole copolymers. It has been reported that the copolymer can be formed by depositing polyaniline layer chemically on the electrode followed by electropolymerization of pyrrole in the matrix [83,84]. Electrochemical copolymerization of pyrrole and aniline has also been reported [85-88]. Recently, electropolymerization of polyaniline-polypyrrole from organic acidic medium has also been reported

In this work, PANI/PP was synthesized electrochemically on a Pt substrates under cyclic voltammetric conditions in aqueous solution containing $LiClO_4$ as electrolyte. Typical CV of electrochemical copolymerization is given in Fig. 3.1.20. On sweeping the first potential cycle from –0.2 to +1.0 V *vs* SCE at a scan rate of 100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.82 V indicating the oxidation of monomers to yield the copolymer. A thin deep blue film is seen on the Pt surface.

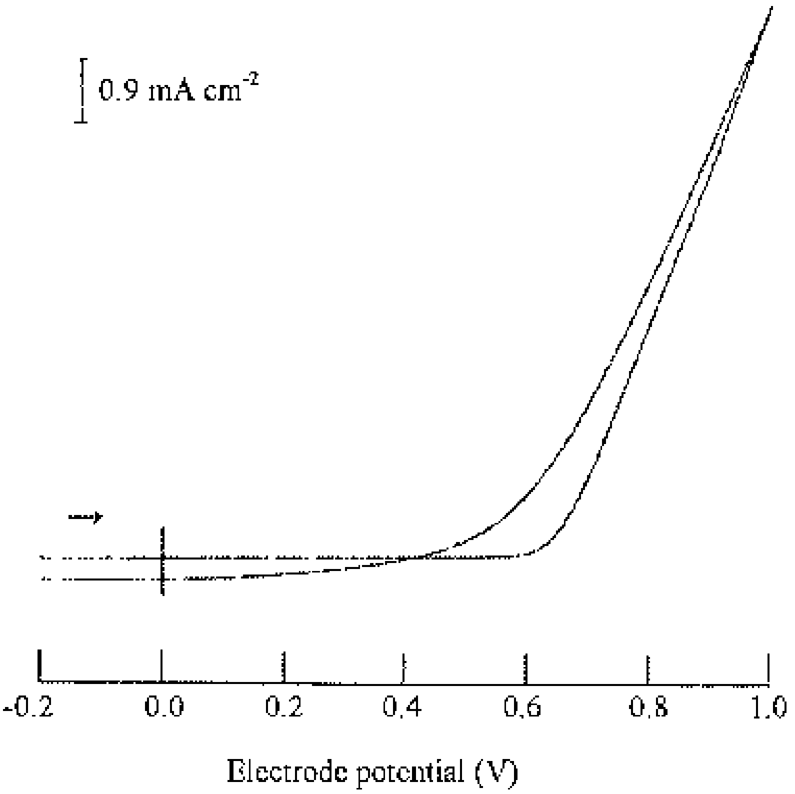


Fig. 3.1.19: CV (1 cycle) during electrochemical synthesis of PP in aqueous solution (0.5M pyrrole + 0.1M $LiClO_4$).

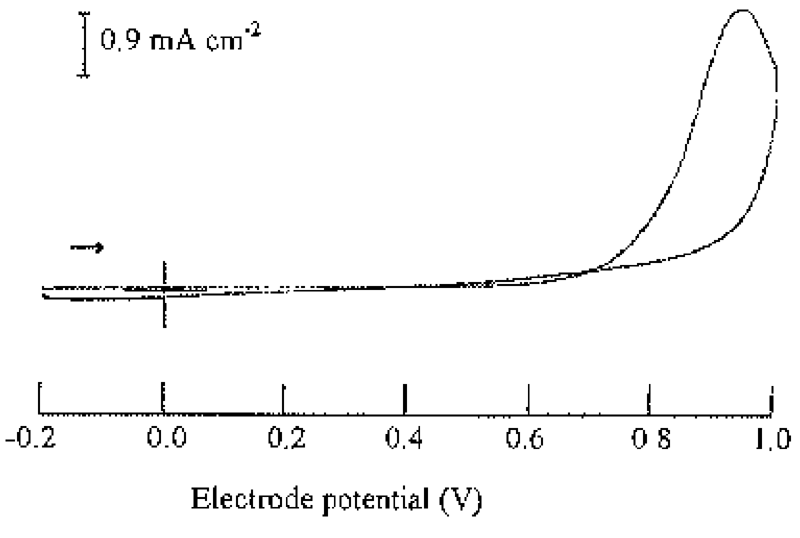


Fig. 3.1.20: CV (1 cycle) during electrochemical synthesis of PANI/PP in aqueous solution (0.5M aniline + 0.5M pyrrole + 0.1M $LiClO_4$ + 0.8M H_2SO_4).

G. Composite: Polyaniline/Polypyrrole/Silica (PANI/PP/SiO_2)

No attempt has yet been taken to prepare polyaniline/polypyrrole/silica composite by any of the mentioned two methods. Electrochemical synthesis of PANI/PP/SiO_2 was carried out for the first time by anodic oxidation of monomers onto a Pt electrode in aqueous solution containing colloidal silica.

Typical CV of electrochemical polymerization of composite is given in Fig. 3.1.21. On sweeping the first potential cycle from –0.2 to +1.0 V *vs* SCE at a scan rate of 100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.78 V indicating the oxidation of monomers to yield the composite. A thin deep blue film is seen on the Pt surface.

H. Poly-2-aminobenzoic acid (PABA)

Attempt has been taken to prepare poly 2-aminobenzoic acid by electrochemical means for the first time by anodic oxidation of monomers onto a Pt electrode in aqueous solution. Typical CV of electrochemical polymerization of *o*-toluidine is given in Fig. 3.1.22. On sweeping the first potential cycle from –0.3 to +0.9 V *vs* SCE at a scan rate of 100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.55 V indicating the oxidation of 2-aminobenzoic acid to yield PABA. A thin greenish film is seen on the Pt surface.

As the sweeping repeated Fig. 3.1.23, i.e., in the second and subsequent cycles, the peak current decreases although more deposits of PABA on the substrate was seen. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of PABA.

Figure 3.1.24 also represents the CV of electrochemical polymerization of 2-aminobenzoic acid under similar electrolytic conditions; here polymerization was allowed to grow on the Pt upto 10 cycles. As the PABA film got thicker, the characteristic peaks seem to be less prominent or at least broadened and also their positions are shifted. However, the colour changes of the thick film also occur in the similar fashion as described for the thin PABA film. The Pt electrode thus coated with the PABA film is referred as PABA electrode in the next part of the thesis.

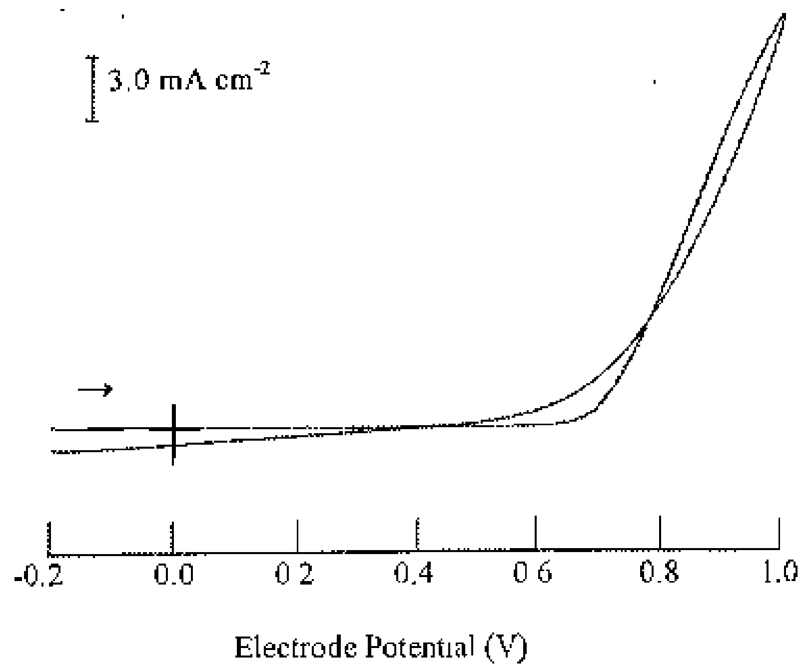


Fig. 3.1.21: CV (1 cycle) during electrochemical synthesis of PANI/PP/SiO_2 in aqueous solution (colloidal silica + 0.5M aniline + 0.5M pyrrole + 0.1M $LiClO_4$ + 0.8M H_2SO_4).

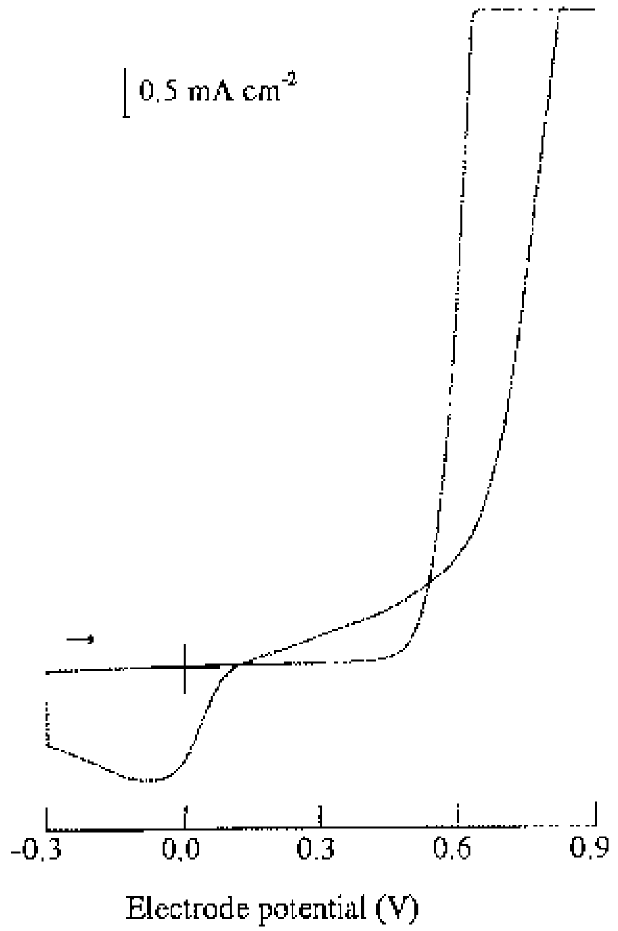


Fig. 3.1.22: CV (1 cycle) during electrochemical synthesis of PABA in aqueous solution (0.5M 2-aminobenzoic acid + 0.8M H_2SO_4).

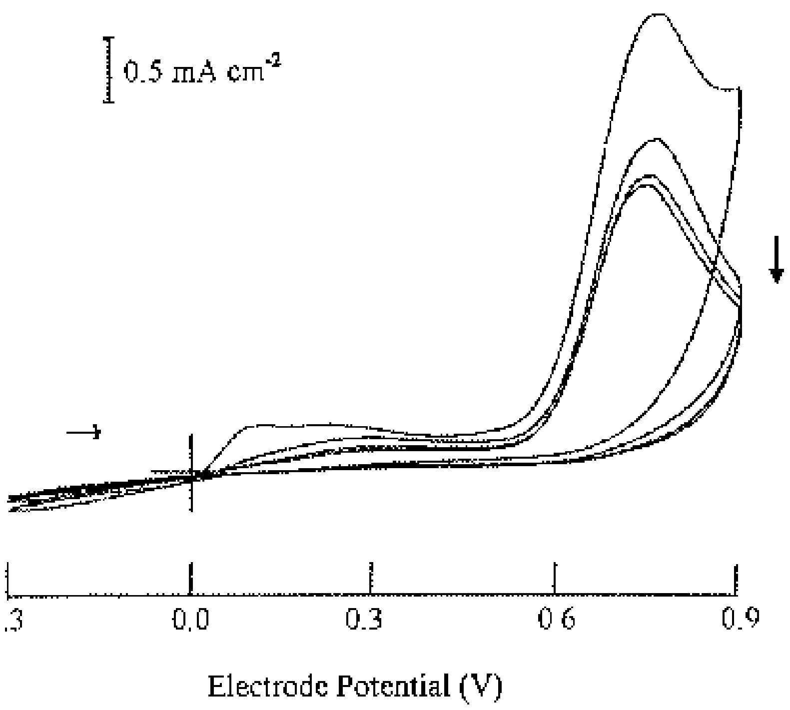


Fig. 3.1.23: CV (5 cycle) during electrochemical synthesis of PABA in aqueous solution (0.5M 2-aminobenzoic acid + 0.8M H_2SO_4).

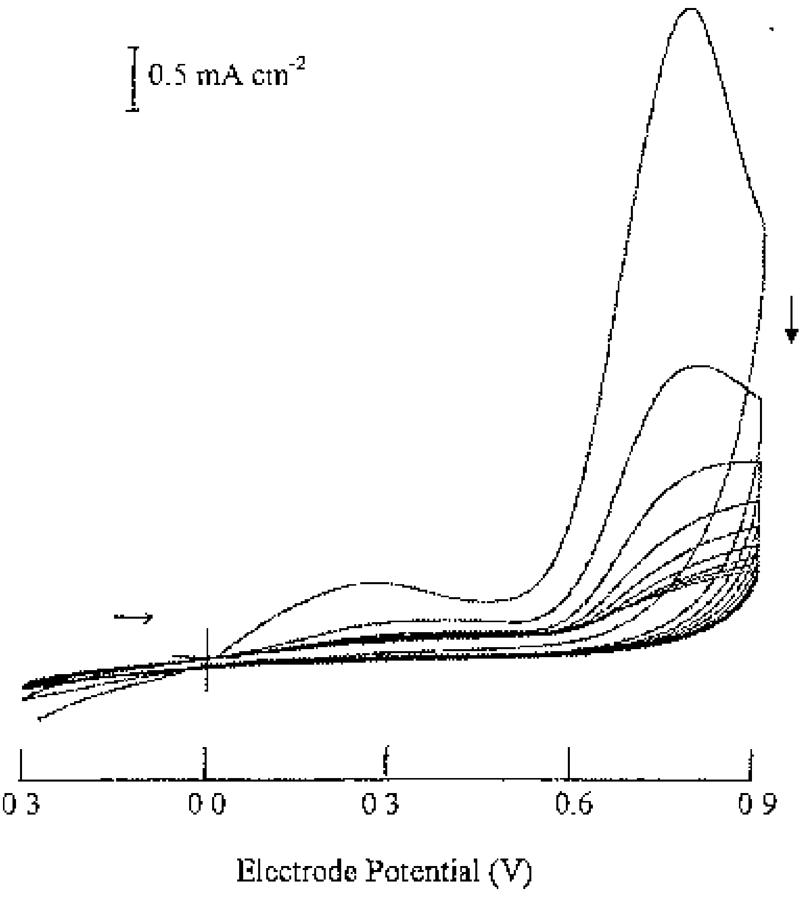


Fig. 3.1.24: CV (10 cycle) during electrochemical synthesis of PABA in aqueous solution (0.5M 2-aminobenzoic acid + 0.8M H_2SO_4).

Polypyrrole: PP (Fig. 3.1.19)

prepared in aqueous solution (0.5M pyrrole + 0.1M $LiClO_4$)

Coploymer: PANI/PP (Fig. 3.1.20)

prepared in aqueous solution (0.5M pyrrole + 0.1M $LiClO_4$ + 0.8M H_2SO_4 + 0.1M $LiClO_4$)

Composite: PANI/PP/SiO_2 (Fig. 3.1.21)

Prepared in aqueous solution (colloidal SiO_2 + 0.5M aniline + 0.5M pyrrole + 0.8M H_2SO_4 + 0.1M $LiClO_4$)

3-D Matrix	Monomer oxidation potential (V)	Polymer oxidation (Doping) potential (V)	Polymer reduction (Dedoping) potential (V)	Color		Yield
				Oxid^n state	Red^n state	
PP (1 cycle)	+0.62	Not observable	Not observable	blue black	Slightly fade	high
PANI/PP (1 cycle)	+0.82	Not observable	Not observable	deep blue	Slightly fade	high
PANI/PP/ SiO_2 (1 cycles)	+0.78	Not observable	Not observable	deep blue	Slightly fade	high

PP film is very hard compared to that of PANI and the film and the film is attached very strongly to the electrode substrate. Polymer oxidation-reduction processes are not observable. But the matrix is electrically conductive as can be seen from the CV. Because of the hard morphology, the oxidation (doping) and reduction (dedoping) processes could be slow or difficult because during oxidation and reduction, electrolyte ions are entered and rejected, respectively, from the polymer matrix. However, from analysis of the CV's, it is clear that monomer oxidation potentials of the matrices are different, though the other parameters are either "not observable" or "changed slightly".

I. Copolymer: Polyaniline/Poly-2-aminobenzoic acid (PANI/PABA)

No attempt has yet been taken to prepare polyaniline/poly-2-aminobenzoic acid copolymer by any of the earlier mentioned two methods. Electrochemical synthesis of PANI/PABA was carried out for the first time by anodic oxidation of monomers onto a Pt electrode in aqueous solution containing.

In this work, PANI/PABA was synthesized electrochemically on a Pt substrate under cyclic voltammetric conditions in aqueous solution. Typical CV of electrochemical copolymerization is given in Fig. 3.1.25. On sweeping the first potential cycle from –0.2 to +1.0 V *vs* SCE at a scan rate of 100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.9 V indicating the oxidation of monomers to yield the copolymer. A thin deep blue film was seen on the Pt surface.

As the sweeping repeated Fig. 3.1.26, i.e., in the second and subsequent cycles, the peak current increases further indicating the formation of more deposits of PANI/PABA on the substrate. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of PANI/PABA. The anodic peak at *ca.* +0.25 V is observed from the second scan. This peak can be assigned to the oxidation of PANI/PABA film deposited on the electrode corresponding to the conversion of amine units to radical cations in the polymer chain.

Figure 3.1.27 also represents the CV of electrochemical polymerization of aniline and 2-aminobenzoic acid under similar electrolytic conditions; here polymerization was allowed to grow on the Pt upto 10 cycles. As the PANI/PABA film got thicker, the characteristic peaks seem to be less prominent or at least broadened and also their positions are shifted. The Pt electrode thus coated with the PANI/PABA film is referred as PANI/PABA electrode in the rest of the thesis.

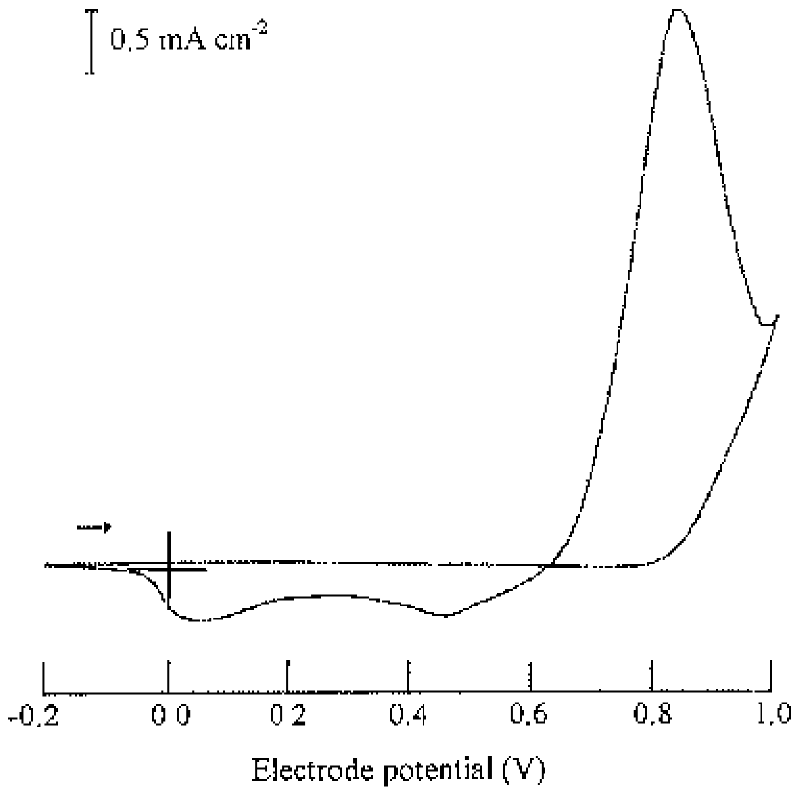


Fig. 3.1.25: CV (1 cycle) during electrochemical synthesis of PANI/PABA in aqueous solution (0.5M aniline + 0.5M 2-aminobenzoic acid + 0.8M H_2SO_4).

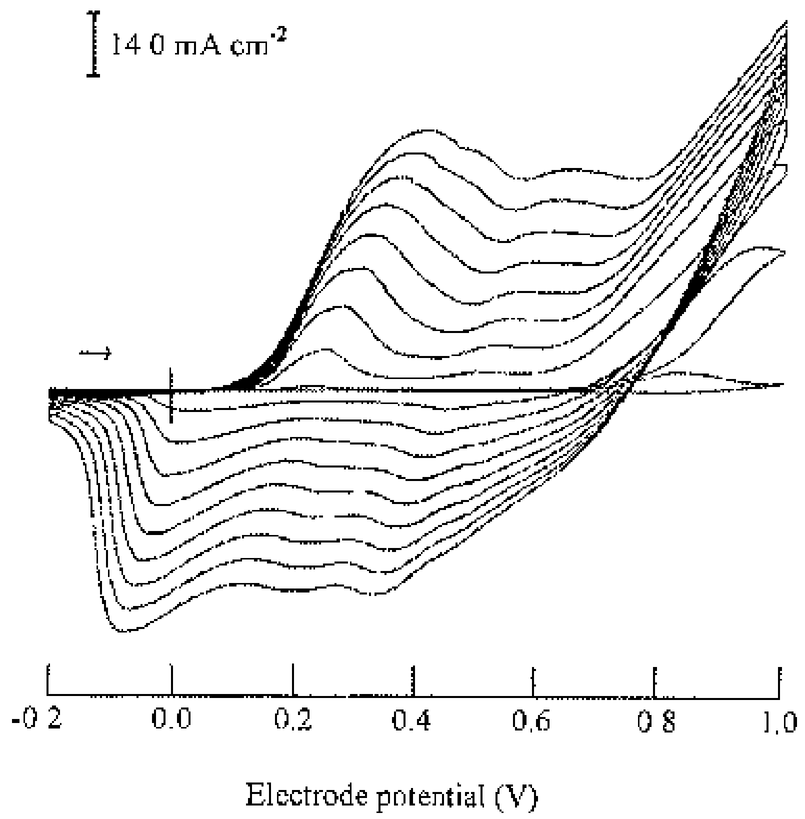


Fig. 3.1.27: CV (10 cycles) during electrochemical synthesis of PANI/PABA in aqueous solution (0.5M aniline + 0.5M 2-aminobenzoic acid + 0.8M H_2SO_4).

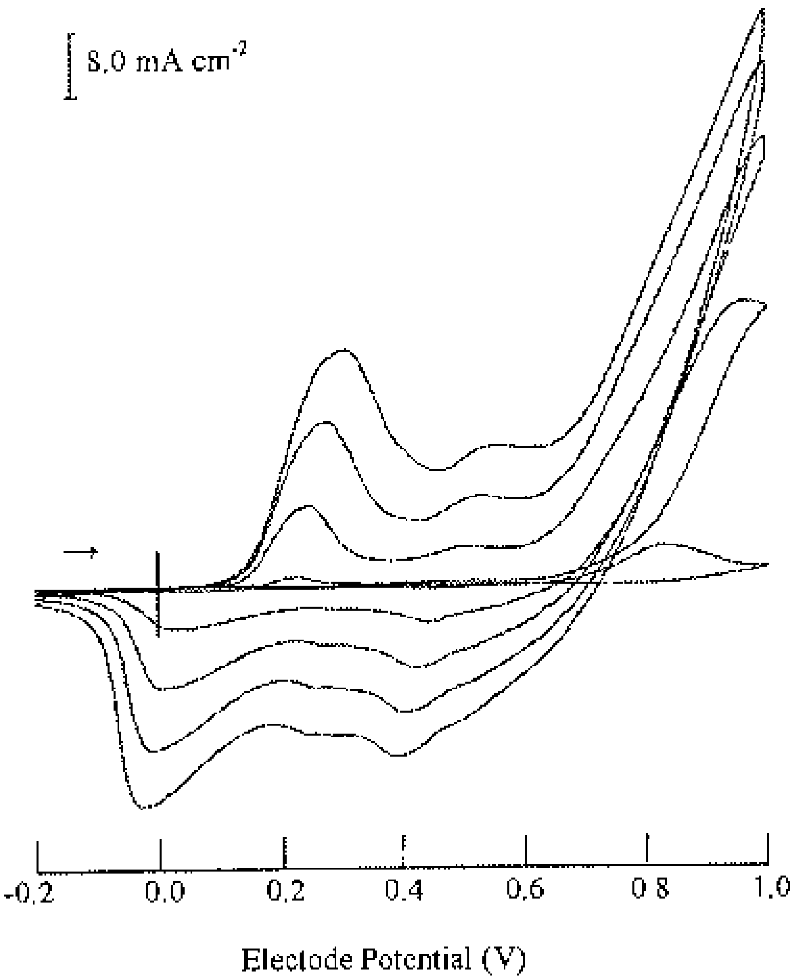


Fig. 3.1.26: CV (5 cycles) during electrochemical synthesis of PANI/PABA in aqueous solution (0.5M aniline + 0.5M 2-aminobenzoic acid + 0.8M H_2SO_4).

J. Copolymer: Poly-*o*-toluidine /Poly-2-aminobenzoic acid (CH_3-PANI/PABA)

Electrochemical synthesis of CH_3-PANI/PABA was carried out for the first time by anodic oxidation of monomers onto a Pt electrode in aqueous solution. During this research, CH_3-PANI/PABA was synthesized electrochemically on platinum substrates under cyclic voltammetric conditions in aqueous solution. Typical CV of electrochemical copolymerization is given in Fig. 3.1.28. On sweeping the first potential cycle from –0.3 to +1.0 V *vs* SCE at a scan rate of 100 mVs^{-1}, a sharp rise in current is seen at a potential *ca.* +0.8 V indicating the oxidation of monomers to yield the copolymer. A thin black film is seen on the Pt surface.

As the sweeping repeated Fig. 3.1.29, i.e., in the second and subsequent cycles, the peak current decreases however the formation of more deposits of the copolymer on the substrate took place. Potential cycling was repeated upto 5 cycles for the deposition of a thin film of CH_3-PANI/PABA. The anodic peak at *ca.* +0.3 V is observed from the second scan. This peak can be assigned to the oxidation of CH_3-PANI/PABA film deposited on the electrode. Whereas the cathodic peak at *ca.* +0.4 V is observed from the first scan that can be assigned to the reduction of CH_3-PANI/PABA film deposited on the electrode.

Figure 3.1.30 also represents the CV of electrochemical polymerization of *o*-toluidine/2-aminobenzoic acid under similar electrolytic conditions; here polymerization was allowed to grow on the Pt upto 10 cycles. As the copolymer film got thicker, the characteristic peaks seem to be prominent though they broadened and also their positions are shifted.

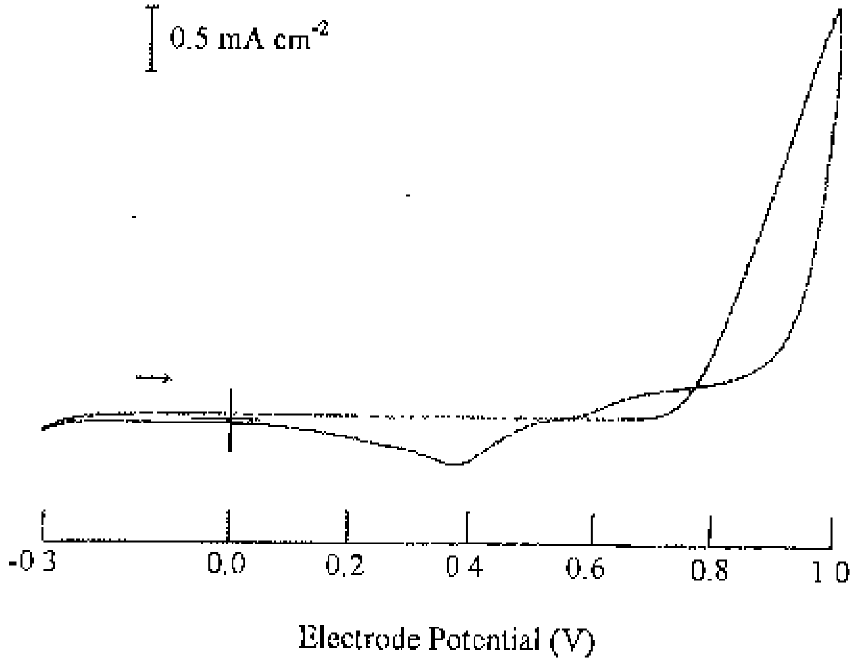


Fig. 3.1.28: CV (1 cycle) during electrochemical synthesis of CH$_3$-PANI/PABA in aqueous solution (0.5M o-toluidine + 0.5M 2-aminobenzoic acid + 0.8M H$_2$SO$_4$).

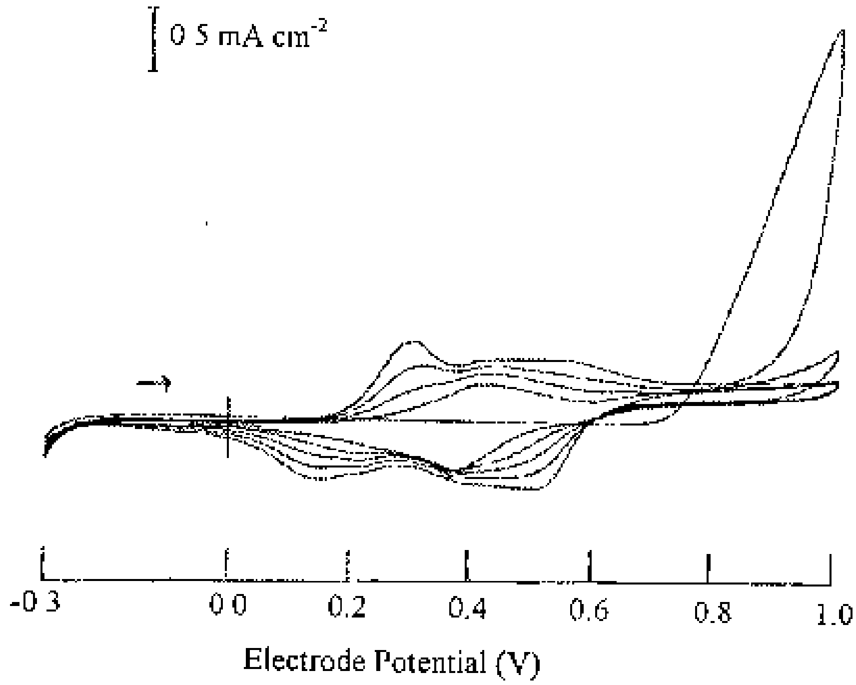


Fig. 3.1.29: CV (5 cycle) during electrochemical synthesis of CH$_3$-PANI/PABA in aqueous solution (0.5M o-toluidine + 0.5M 2-aminobenzoic acid + 0.8M H$_2$SO$_4$).

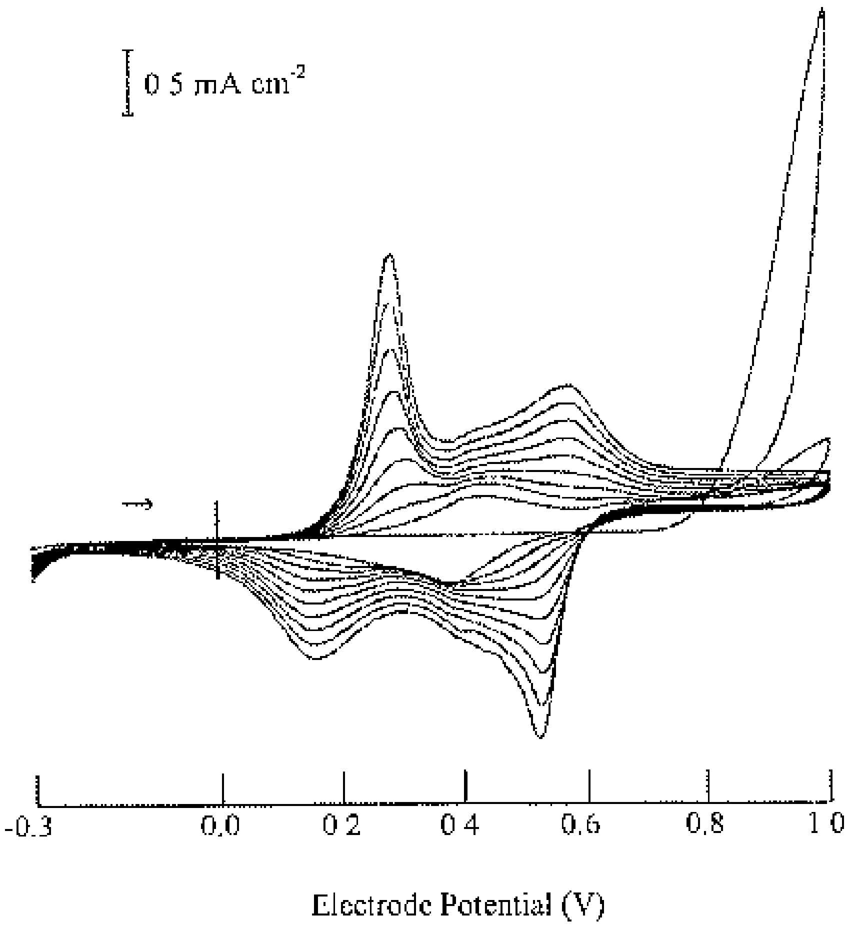


Fig. 3.1.30: CV (10 cycle) during electrochemical synthesis of CH_3-PANI/PABA in aqueous solution (0.5M *o*-toluidine + 0.5M 2-aminobenzoic acid + 0.8M H_2SO_4).

The results (Fig. 3.1.22, Fig. 3.1.25 and Fig. 3.1.28) are summarized the following table:

Poly 2-aminobenzoic acid: PP (Fig. 3.1.22)

Prepared in aqueous solution (0.5M 2-aminobenzoic acid + 0.8M H_2SO_4)

Coploymer: PANI/PABA (Fig. 3.1.25)

Prepared in aqueous solution (0.5M aniline + 0.5M 2-aminobenzoic acid + 0.8M H_2SO_4)

: CH_3-PANI/PABA (Fig. 3.1.28)

Prepared in aqueous solution solution (0.5M o-toluidine + 0.5M 2-aminobenzoic acid + 0.8M H_2SO_4)

3-D Matrix	Monomer oxidation potential (V)	Polymer oxidation (Doping) potential (V)	Polymer reduction (Dedoping) potential (V)	Color		Yield
				Oxid^n state	Red^n state	
PABA (1 cycle)	+0.55	-	-0.05	Green	Yellowish green	low
PABA/PANI (1 cycle)	+0.9	-	+0.45 +0.05	Deep blue	Reddish green	high
PABA/CH_3-PANI (1 cycles)	+0.8	-	+0.38	Blue-black	-	high

PABA and its co-polymers PABA/PANI/ and PABA/CH_3-PANI have rarely been studied earlier. Although, the matrices are electrically conductive, their oxidation-reduction processes are not well evidenced, e.g. reduction process is well exhibited, while its oxidation process is not well observable. Thus, systematic study of these matrices appears to be less informative. However, in the present work, attempt has been taken to study these matrices though limited for only a few experiments.

3.2 Characterization of the Electrode Matrices

A. Infra-red Spectral Analysis

In the present study, a number of solid electrode matrices were synthesized IR spectra of a solid provide useful qualitative structural information. In order to get some insight about the structure of matrices studied, IR spectral analysis was performed. Typical IR spectra for PANI/CH_3-PANI/SiO_2 and PANI/PP/SiO_2 are presented in Figs. 3.2.1 and 3.2.2, while the observed and standard bonds assigned for different functional groups are summarized in Table-3.2.1 and 3.2.2. The assignment of the bands has been made on the basis of some standard literature [89-92] and previous studies [93-99]

Table-3.2.1: Observed and standard IR absorption bands assigned for different functional groups for the samples studied.

Functional groups	Standard absorption band range (cm^{-1})	Observed absorption bands (cm^{-1})			Probable assignment
		PANI	CH_3-PANI	PANI/CH_3-PANI/SiO_2	
Free O–H	3590-3740	3600	3710	3735	O–H stretching vibration, water may be present
N–H	3300-3500	3423	3431	3438	Aromatic secondary amine may be present
C=C	1450-1600	1520	1544	1560, 1492	C=C stretching in aromatic nuclei
C–N	1250-1350	1303, 1236	1340	1218	C–N stretching in aromatic amine
C–H	690-900	823, 850, 900	750, 890	850, 745	C–H deformation, mono substituted benzene
C=N	1640-1690	1650	1645, 1680	1655	=C=N stretching in imine
Si–O	801, 1111	-	-	1109	Presence of silica
C–H (in –CH_3)	2850-2960	-	2856, 2900	2856, 2900	C–H stretching in –CH_3
Ar–H	~3030	-	3028	3025	Ar–H stretching in *o*-toluidine

Table-3.2.2: Observed and standard IR absorption bands assigned for different functional groups for the samples studied.

Functional groups	Standard absorption band range (cm^{-1})	Observed absorption bands (cm^{-1})			Probable assignment
		PANI	PP	PANI/PP/SiO_2	
Free O–H	3590-3740	3600	3712	3649	O–H stretching vibration; water may be present
N–H	3300-3500	3423	3440	3411	N–H stretching; aromatic secondary amine may be present
C=C	1450-1600	1520	1544	1560	C=C stretching in aromatic nuclei
=C–H	1180-1300	1303, 1236	1250	1200	=C–H in plane deformation
=C–H	690-900	823	695	820	=C–H out of plane bending
Si–O	801, 1111	-	-	1109	Presence of silica

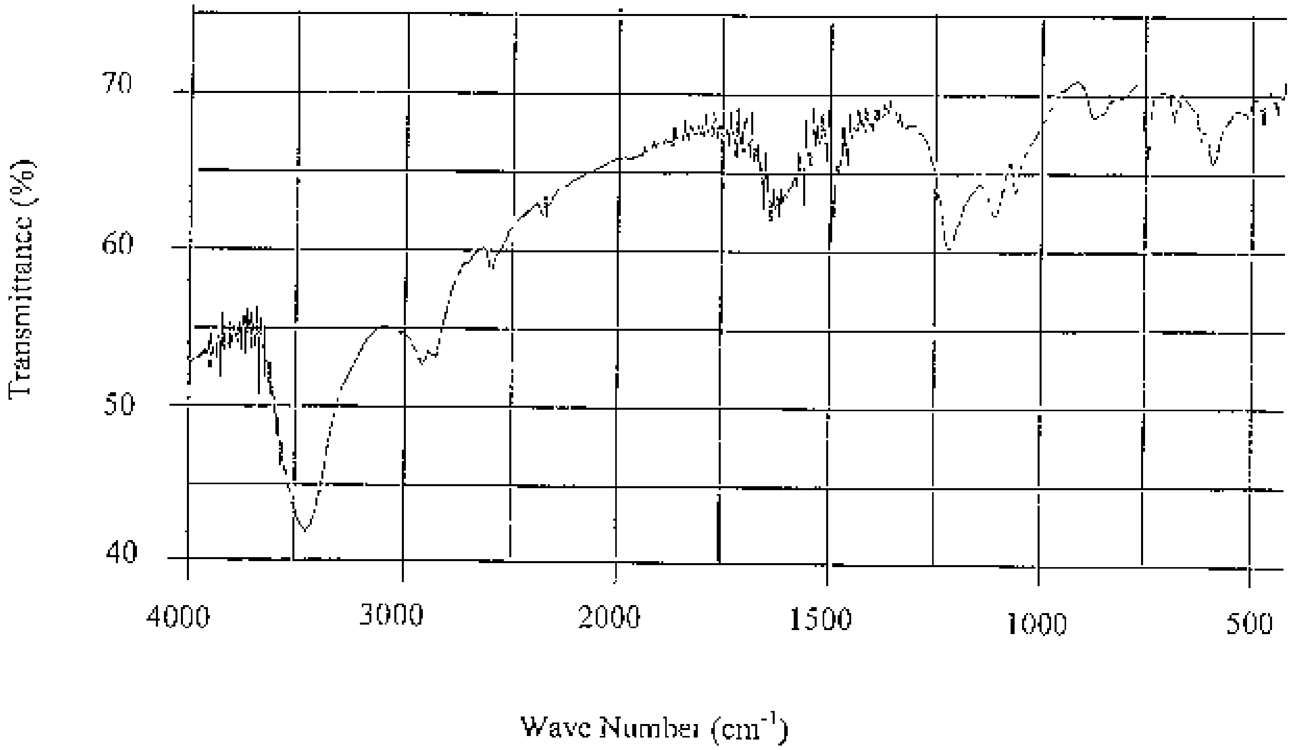


Fig. 3.2.1: IR of PANI/CH$_3$-PANI/SiO$_2$

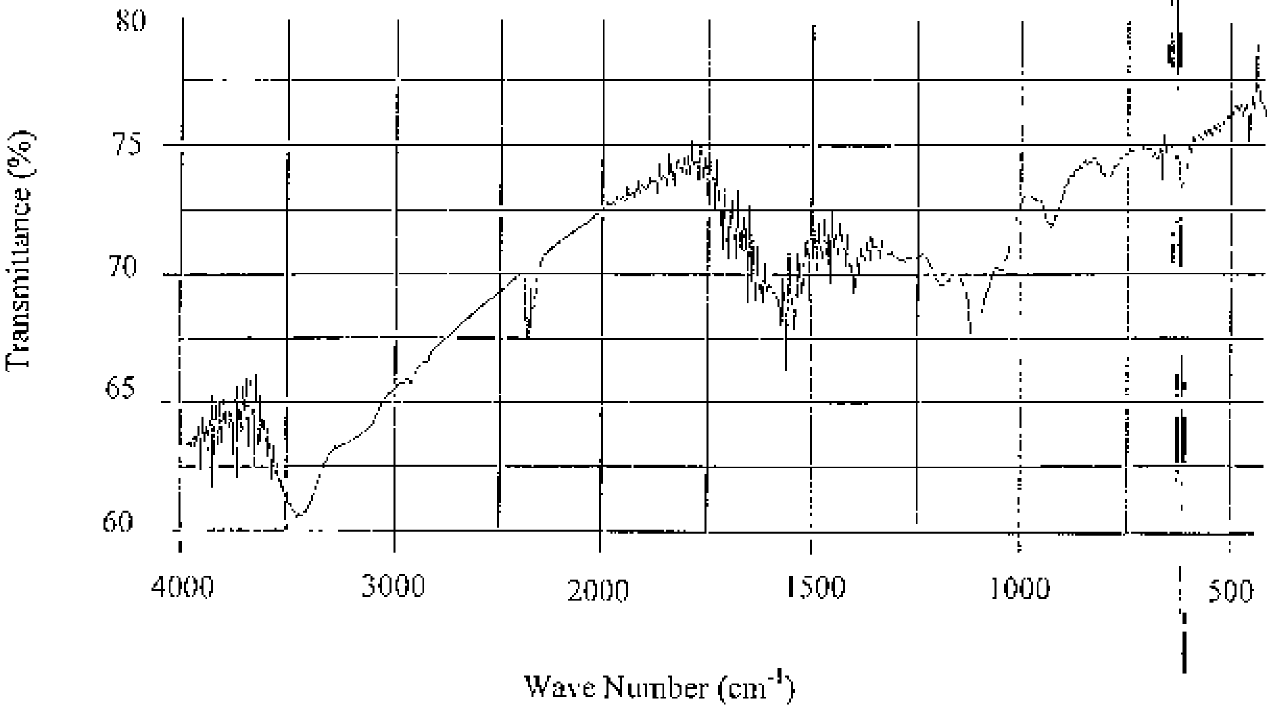


Fig. 3.2.2: IR of PANI/PP/SiO_2.

B. Ultra Violet - Visible spectroscopy

Ultraviolet -Visible (UV-Vis) spectra of doped PANI, CH_3-PANI, PANI/CH_3-PANI, PP, and PANI/PP samples in DMF solutions at room temperature are given in Fig. 3.2.3- Fig. 3.2.7. The UV-Vis spectrum of PANI is depicted in Fig. 3.2.3. From the spectrum, it can be seen a strong at absorption 271 nm. Further a shoulder at around 800 is also observed. The peak at 271 nm should correspond to the interband transition, i.e., transition between valance band and conduction band. The energy associated with this transition is the band gap energy [ ]. The shoulder may be associated with other phenomenon occured in the gap state. Similar phenomenon was also observed in fig. 3.2.4 for the spectrum of CH_3-PANI. In this case, two absorption peaks are well defined. The peaks are observed at 272 nm and 602 nm. The former peak is associated with interband transition while the other one corresponds to the mid gap state transition [ ]. This transition is responsible for polymer conductivity by forming polaron and bipolaron as mid gap gap state [ ]. In fact, polaron step is a radical cation, i.e., contains one electron whereas bipolaron is a dication, i.e., electronless. At low dopping level polaron formation takes while at highly dopped state, bipolaron formation predominates. However, because of the greater stability a bipolaron is favored over polaron.

Figure 3.2.5 shows the UV-Vis spectrum of the copolymer PANI/CH_3-PANI in DMF solvent. For this sample, the interband transition is observed at 292 nm compared to that of PANI (at 271 nm). Thus, the higher wavelength corresponds smaller band gap and hence should be more conductive than PANI matrix. Again mid gap transition occurred at 753 nm corresponding to polaronic and bipolaronic tsates. Comparing the present result with that of PANI and CH_3-PANI, it seems that absorption spectra of the PANI/CH_3-PANI sample shows a reasonable differences from PANI and CH_3-PANI suggesting different electrical property of the PANI/CH_3-PANI matrix. The spectral results are summarized in the following Table-3.2.3.

The UV-Vis spectrum of PP is shown in Fig. 3.2.6. The valence band to conduction band transition for PP was observed at 270.5 nm and other weak absorption was found to be observed at 661.5 nm which believe to be responsible for the PP conductivity by forming polaron and bipolaron as mid-gap state. It is indeed to be noted that the dissolution of PP in DMF was not satisfactory. The poor dissolution of PP may result weak absorption as observed for PP. However, further attempt was made to get spectral results for the PANI/PP copolymer. The sample in DMF results the absorption spectrum given in Fig. 3.2.7. Similar to PP and PANI spectra, two absorptions at 270.5 and 661.5 nm can be seen in this case too. Thus, it is expected that the copolymer PANI/PP should have electrical properties similar or close to that of PANI or PP. The spectral data for these samples are listed in the Table-3.2.3

Table-3.2.3: UV-Vis spectral data for the samples studied.

Sample	Wavelength (nm)	
	Interband transition	Mid gap transition
PANI	271.0	-
CH_3-PANI	272.0	292.0
PANI/CH_3-PANI	292.0	753.0
PP	270.5	661.5
PANI/PP	270.5	661.5

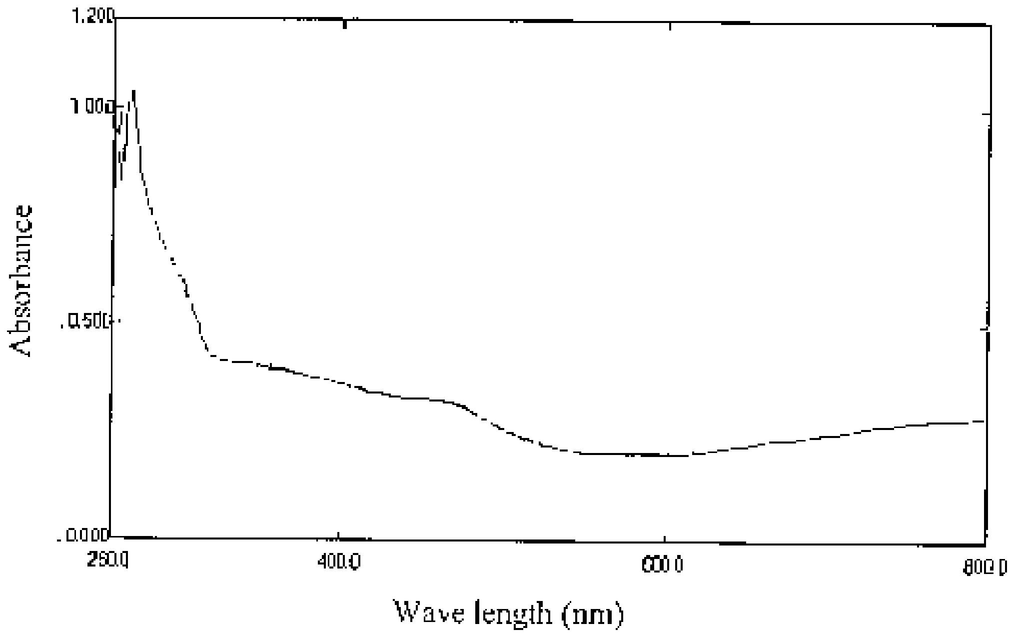


Fig. 3.2.3: UV spectrum of PANI.

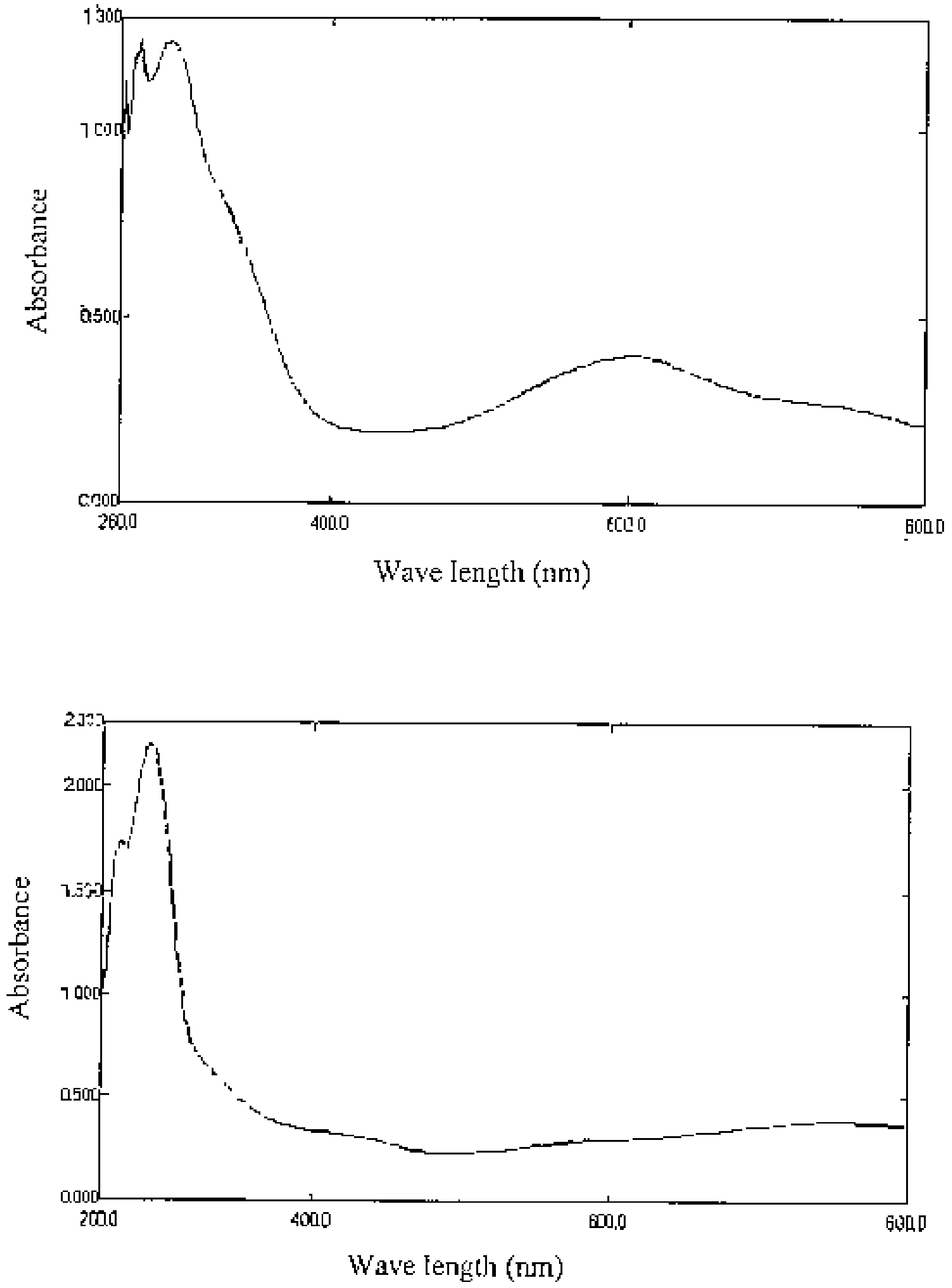


Fig. 3.2.5: UV spectrum of PANI/CH_3-PANI

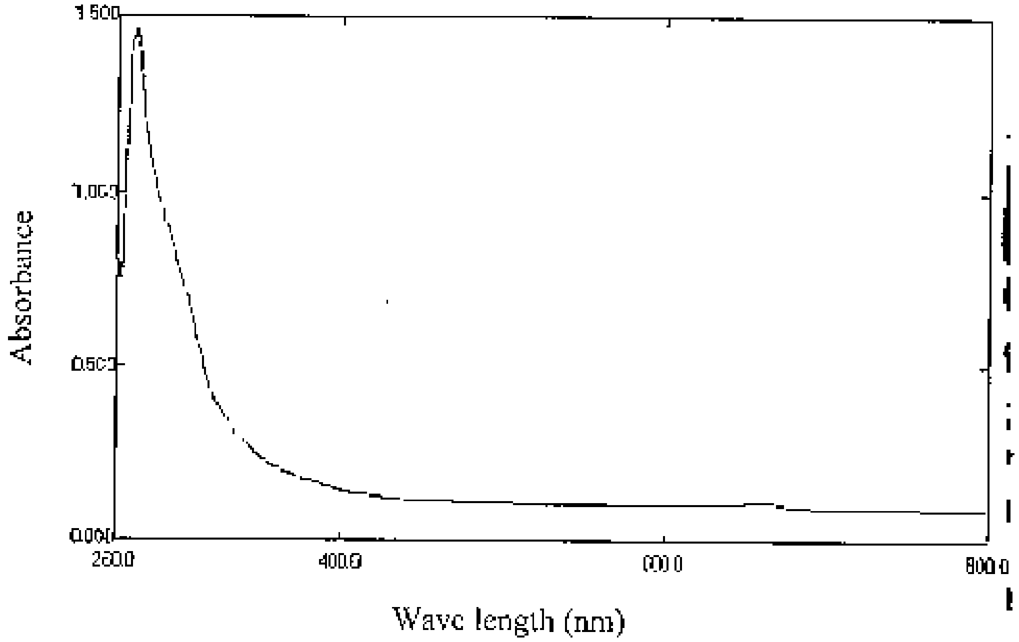


Fig. 3.2.6: UV spectrum of PP.

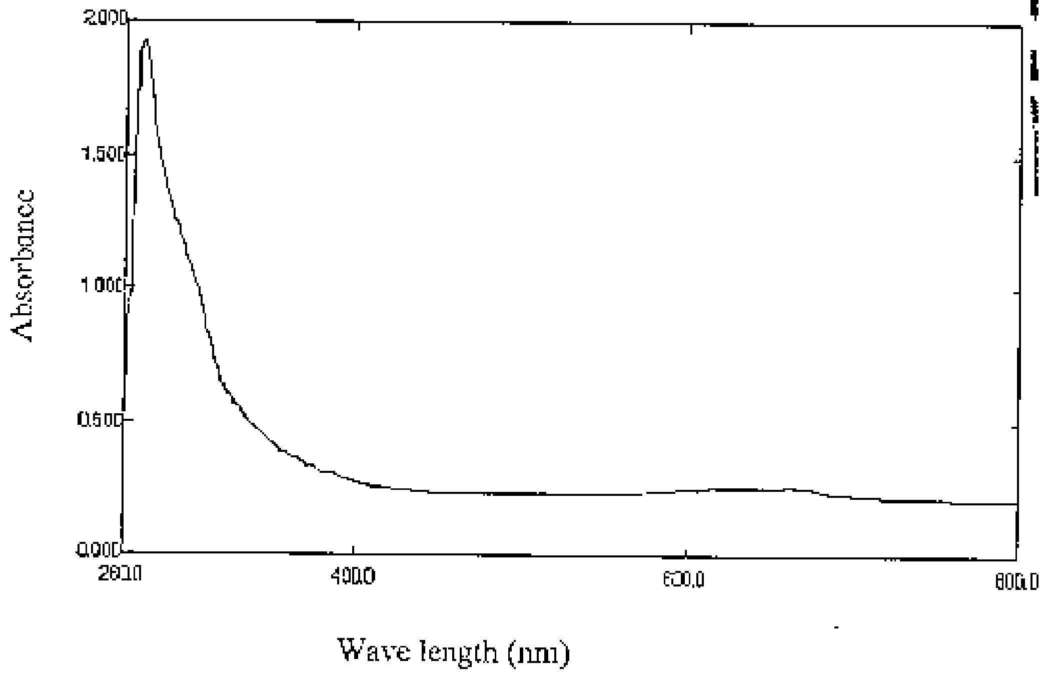


Fig. 3.2.7: UV spectrum of PANI/PP.

C. d. c. Two Point-probe Conductivity

Electrical conductivity of the samples PANI, CH_3-PANI, PANI/CH_3-PANI, PANI/CH_3-PANI/SiO_2 were measured by employing conventional two point-probe methods [100]. The vacuum dried samples were compressed to a rigid mass and stored in vacuum desiccators till the conductance measurement commenced.

The measured conductivity of PANI, CH_3-PANI, PANI/CH_3-PANI, and PANI/CH_3-PANI/SiO_2 were found to be 1.94×10^{-3} S, 3.225×10^{-3} S, 2.421×10^{-3} S and 1.29×10^{-4} S respectively. The measured conductance of CH_3-PANI seems to be higher than that of PANI. This might be due to the presence of methyl group. Methyl group can release electrons to benzene ring and thus can enhance the electron density available for transitions, resulting higher conductance of CH_3-PANI. But the conductance of the copolymer PANI/CH_3-PANI was found to be in between of the individual polymers. In the polymer matrix, conductive path for the charge carriers could be modified by the presence of the two monomeric units and thus results a different electrical conductance as observed in the present study. The conductance of PANI/CH_3-PANI/SiO_2 is again lower than that of the copolymer PANI/CH_3-PANI. This might happen due to the insertion of insulating silica particles in the copolymer matrix. The decrease in conductivity might be due to the partial blockage of conductive path by the insulating silica particles dispersed in the PANI/CH_3-PANI/SiO_2 matrix. Similar decrease in conductivity of PANI was also reported by the Zhang *et. al* [101] when Fe_3O_4 nanoparticles were embedded in the polymer.

D. Scanning Electron Microscopy

In order to examine the surface morphology, scanning electron microscopy appears to be the best choice because of its potential for precise analysis of a solid surface. Chemical composition and morphological structure of a material strongly depends on the mode of synthesis, be it chemical or electrochemical, on the synthetic conditions such as pH. concentration of reactants and products, chemical nature of oxidant, oxidation potential etc [102]. Thus, a variety of chemical structure and morphology of a material is possible. In the present work, all the polymers were synthesized electrochemically under different electrolyte conditions. Figure 3.2.8 shows the SEM images of (a) PANI, (b) CH_3-PANI, (c) PANI/CH_3-PANI, (d) PANI/CH_3-PANI/SiO_2, electrode surfaces. It can be seen that a grain-like morphology appears when PANI is prepared electrochemically from electrolytic solution containing H_2SO_4 and the surface is quite uniformly covered with the PANI fiber. Fibril morphology for PANI synthesized electrochemically was also reported previously [103]. In case of CH_3-PANI the surface morphology appears to be compact by close binding of the fibrils and grains. The surface uniformity and homogeneity seem to be different compared to that of PANI. On the other hand, when copolymer of PANI/CH_3-PANI was synthesized, its surface morphology appears to be rigid solid body like the pieces of stone. The resulting surface seems to be rather non uniform and the particles are randomly dispersed on the surface. The composite, PANI/CH_3-PANI/SiO_2, on the other hand formed flake like morphology, packed together and made the whole surface fully covered with flakes. The SEM observations thus predicted quite dissimilar surface morphologies of the studied samples. The observed dissimilar morphological features of PANI, CH_3-PANI, PANI/CH_3-PANI, PANI/CH_3-PANI/SiO_2 suggests that their electrode behavior for electrochemical processes could be different.

Figure 3.2.9 shows the SEM images of (a) PANI, (e) PP, (f) PANI/PP and (g) PANI/PP/SiO_2 electrode surfaces. In contrast to the fibril morphology of PANI it can be seen from the surface morphology of PP that the small granules formed on the surface and distributed randomly on the surface having different particle size. The present SEM observation for PP is consistent with a early work reported elsewhere [104]. On the other hand, when copolymer of PANI/PP was synthesized, the surface morphology seems to be uncovered. Only few granules stack on the different location of the surface. This observation suggests the difficulty in the formation of the copolymer PANI/PP. The surface of the composite, PANI/PP/SiO_2, shows a non-uniform but fully covered with the grains. In some places big deposits of the grains is also observed. This observation clearly suggests that incorporation of silica has modified the deposition mechanism of the matix. However, the SEM observations clearly suggest that the surface morphology of the matrices studied is quite different from each other and expected to exhibit dissimilar electrode behavior.

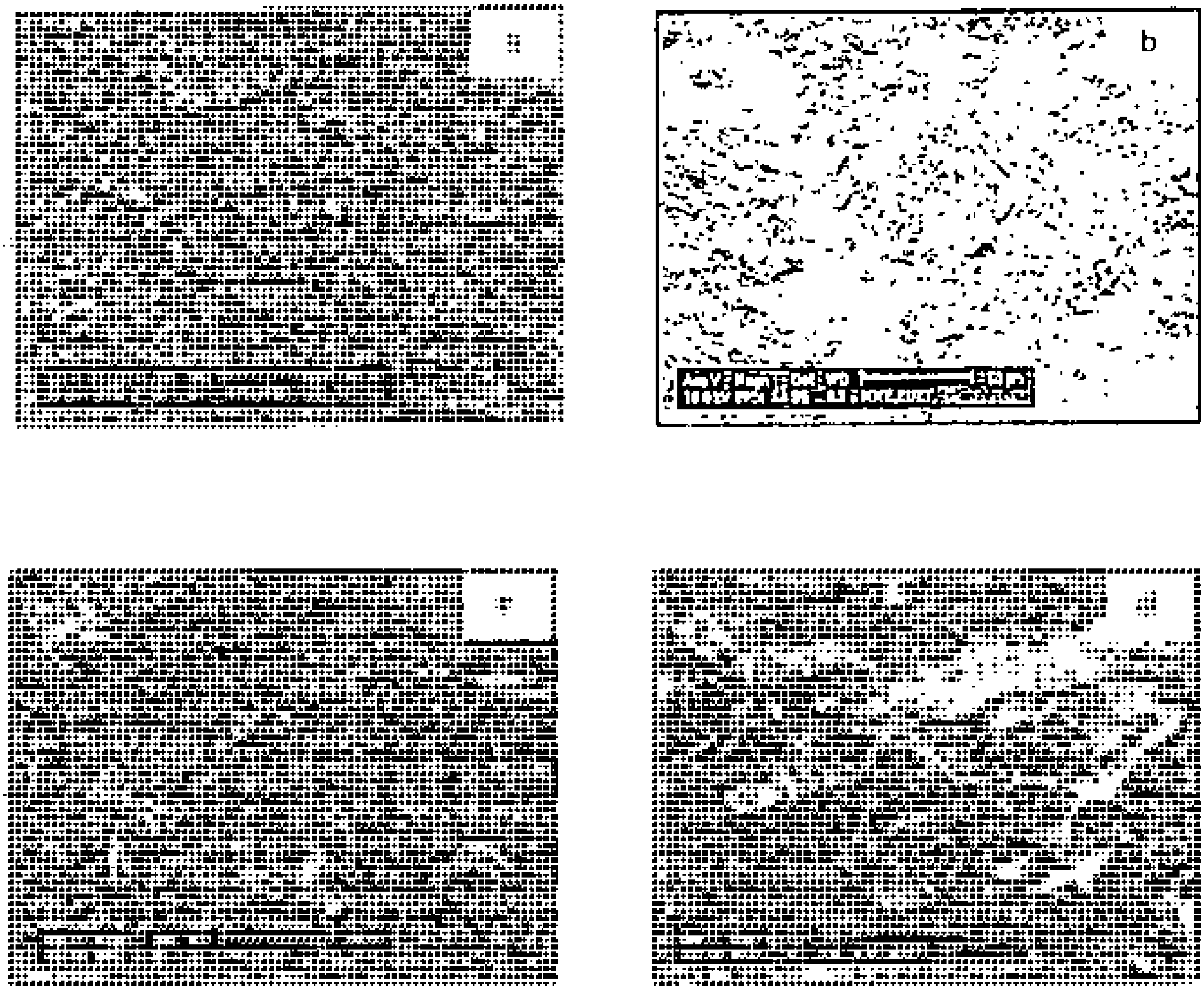


Fig. 3.2.8: SEM micrographs of (a) PANI, (b) CH_3-PANI, (c) PANI/CH_3-PANI and (d) PANI/CH_3-PANI/SiO_2

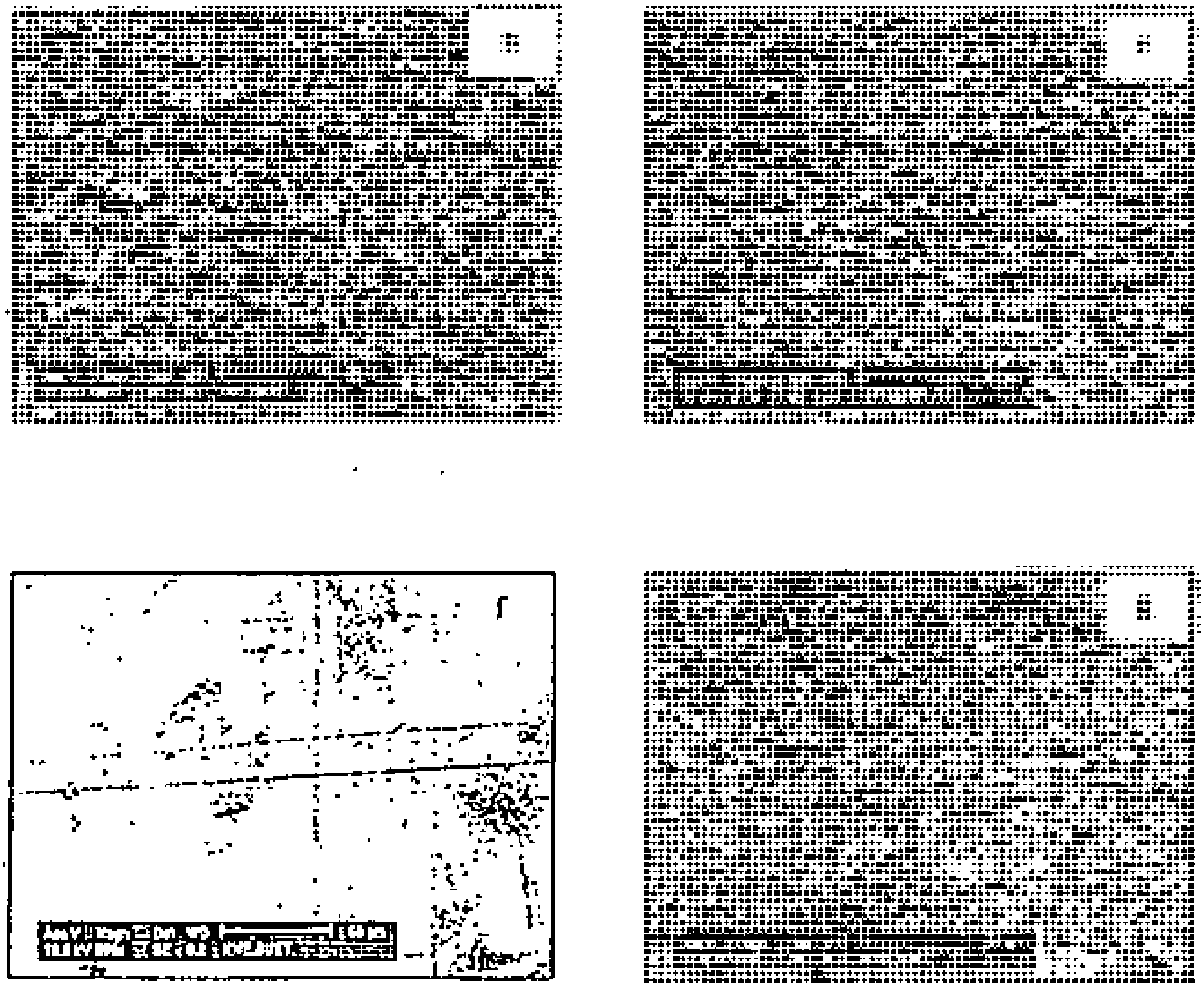


Fig. 3.2.9: SEM micrographs of of (a) PANI, (e) PP, (f) PANI/PP and (g) PANI/PP/SiO_2

3.3 Performance of the Modified Electrode

3.3.1 Electrochemical Doping – Dedoping Process

A. PANI Electrode:

The electrochemical behavior, i.e. doping–dedoping processes, of the PANI film electrode was examined by cyclic voltametry in aqueous 0.8 M H_2SO_4 solution. For this purpose PANI film was deposited on the Pt electrode by sweeping the potential three times between the potential -0.2 and 1.0 V at a scan rate of 100 mV/Sec. The film thus coated on to the Pt electrode was washed several times with distilled water and then immersed in an aniline free aqueous 0.8 M H_2SO_4 solution. A typical CV of the PANI film is shown in Fig. 3.3.1. It can be seen from the figure that the CV of the present system is composed of two redox couples. This behavior indicates the presence of variable electroactive region in the PANI film [105]. The result of present CV is identical with a previous study suggesting that the oxidation of the PANI film takes place at the potentials +0.22 V and +0.80 V at which electrolyte anion is doped into the polymer film while the corresponding reductions of the film take place at +0.03 and +0.74 V where dedoping of the electrolyte anion occurs. On sweeping the bare Pt electrode (without PANI film) from –0.2 to +1.0 V in 0.8M H_2SO_4, no such peaks are observed. The oxidation and reduction waves are not symmetrical as can be seen in the CV (Fig 3.3.1). The shape of the two peaks and the difference in the peak potentials suggest that the electrochemical reaction is quasi-reversible and that there are differences between the reduction and oxidation kinetics [106]. The redox process of PANI in aqueous H_2SO_4 electrolytic solution may be interpreted as follows:

$$(\text{Polymer}^{-}\ X^{-}) + e^{-} \leftrightarrows \text{Polymer}^{\circ} + X^{-}$$

($\text{Polymer}^{+}\ X^{-}$) is the oxidized polymer obtained through doping process and polymer° is the reduced polymer and X^{-} is the electrolyte anion (SO_4^{-2}).

The redox reaction of the PANI film is accompanied by a color changes. The film appears as a deep blue color when the electrode potential is reached at +0.22 V and turns to a transparent greenish-yellow when it is switched to –0.2 V. The color changes occur evenly throughout the film with no evidence of region with different reactivity. Similar observation for color change with PANI in its redox process has also been reported previously [107].

B. CH_3-PANI Electrode:

Figure 3.3.2 shows the CV of CH_3-PANI film (3 cycles) on a platinum electrode in an aqueous solution containing 0.8 M H_2SO_4. Alike the CV of PANI, the CV of CH_3-PANI is also composed of

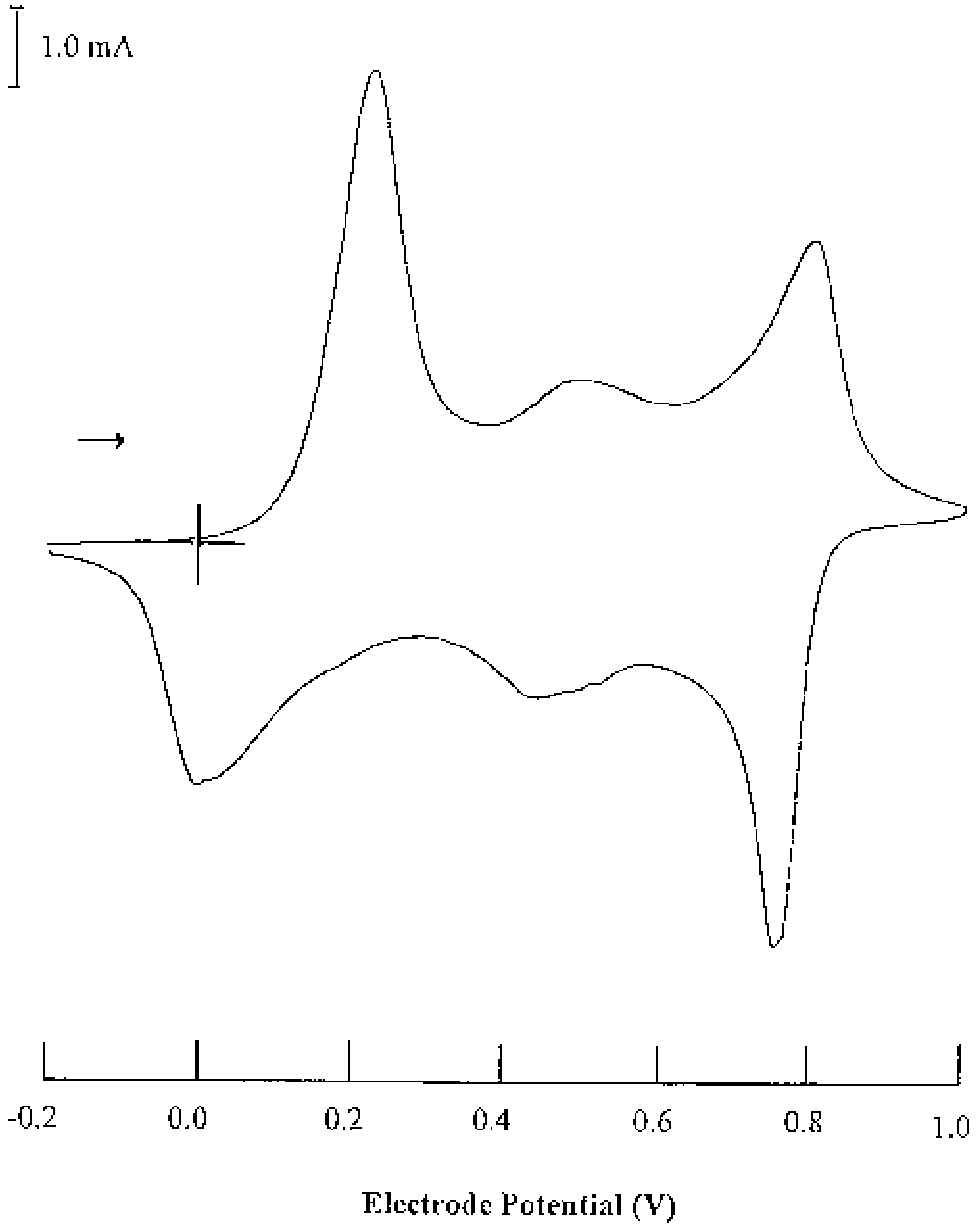
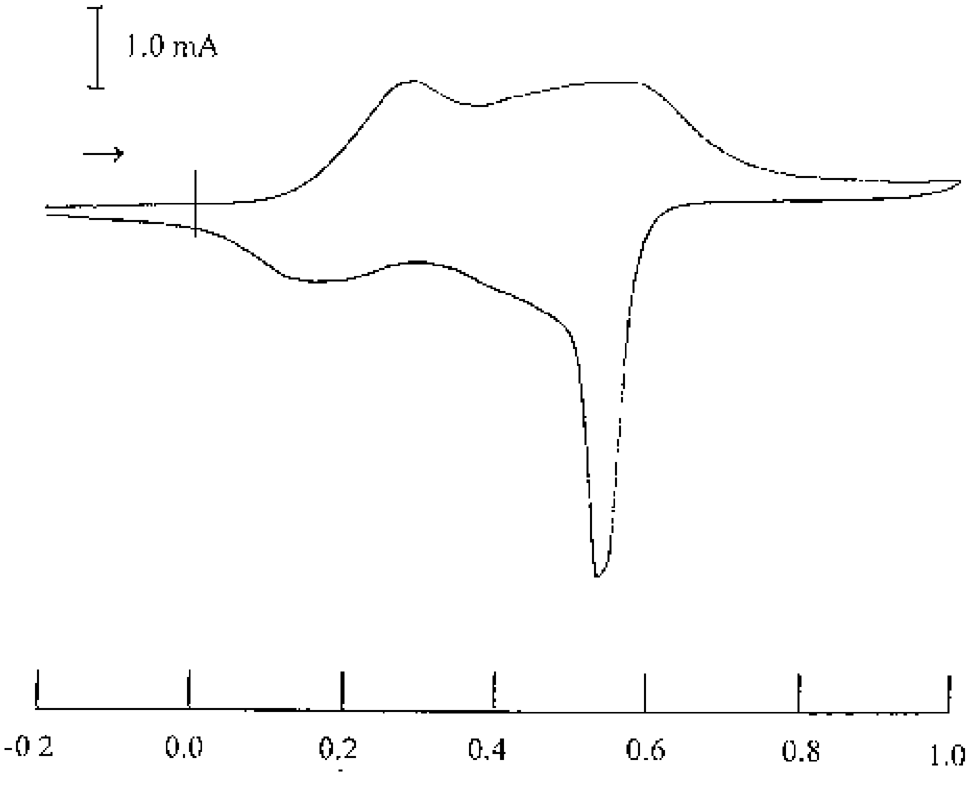


Fig. 3.3.1: CV of a PANI film (3 cycles) on a Pt electrode in aqueous solution containing 0.8 M H_2SO_4.



Electrode Potential (V)

Fig. 3.3.2: CV of a CH_3-PANI film (3 cycles) on a Pt electrode in aqueous solution containing 0.8 M H_2SO_4.

two two redox couples. This nature of CV confirms the presence of variable electroactive regions in the polymer. One couple is +0.24 V (oxidation wave) and +0.15 V (reduction wave) and other one is +0.57 V (oxidation wave) and +0.54 V (reduction wave). However, it seems from the CV's of PANI and CH_3-PANI that the shape of redox waves and their potential are not very similar. This may suggest dissimilar redox activity between the PANI and CH_3-PANI electrodes.

C. PANI/CH_3-PANI Electrode:

A copolymer compound of PANI and CH_3-PANI was prepared in order to examine its electroactivity. The electrochemical redox behavior i.e., doping-dedoping processes of PANI/CH_3-PANI film electrode in an aqueous solution containing 0 8 M H_2SO_4 is shown in Fig. 3.3.3. The CV of the PANI/CH_3-PANI film (3 cycles) is seemed to be identical with PANI and CH_3-PANI. The identical nature of the electrode is reasonable, since in its matrix both the PANI and CH_3-PANI components are present. The redox peaks correspond to polymer oxidation (doping) and reduction (dedoping).

D. PANI/CH_3-PANI/SiO_2 Electrode:

Figure 3.3.4 shows CV of the composite electrode having the structure PANI/CH_3-PANI/SiO_2 (3 cycles) in an aqueous solution containing 0.8 M H_2SO_4. A film of the composite was deposited onto a Pt electrode. The composite electrode also yielded a pair of redox couples that are identical to the CV's of PANI and CH_3-PANI. This result suggest that even after incorporating insulating silica particles in the composite matrix, it can act as an electrode matrix showing normal oxidation (doping) and reduction (dedoping) of the polymer component of the composite electrode.

E. PP Electrode:

The electrochemical behavior of a PP film deposited on the Pt electrode in an aqueous solution containing 0.1 M $LiClO_4$ was examined. A typical CV is shown in Fig. 3.3.5. The CV involved sweeping the potential between -0.2 V and +1.0 V vs SCE at a scan rate of 100 mVs^{-1}. Though any peak in the CV is not seen but gives a continuous high anodic and cathodic current suggesting that there must be some processes that gave the current. The continuous current could be due to the charging current of the PP that deposited on the Pt electrode surface. PP can be switched between its oxidized (conductive) and reduced (insulator) states [108]. The oxidation and reduction of a PP film can be explained by the following redox reaction:

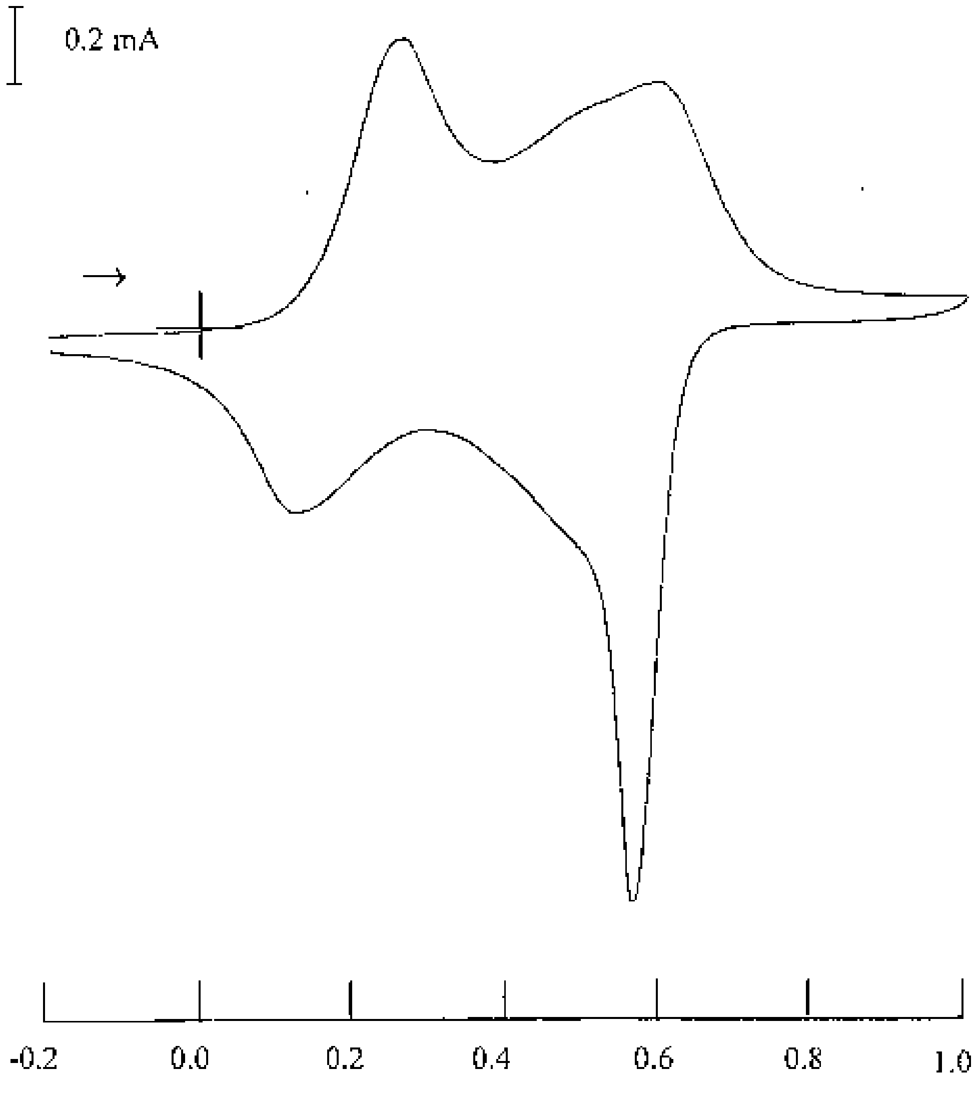


Fig. 3.3.3: CV of a PANI/CH_3-PANI film (3 cycles) on a Pt electrode in aqueous solution containing 0.8 M H_2SO_4.

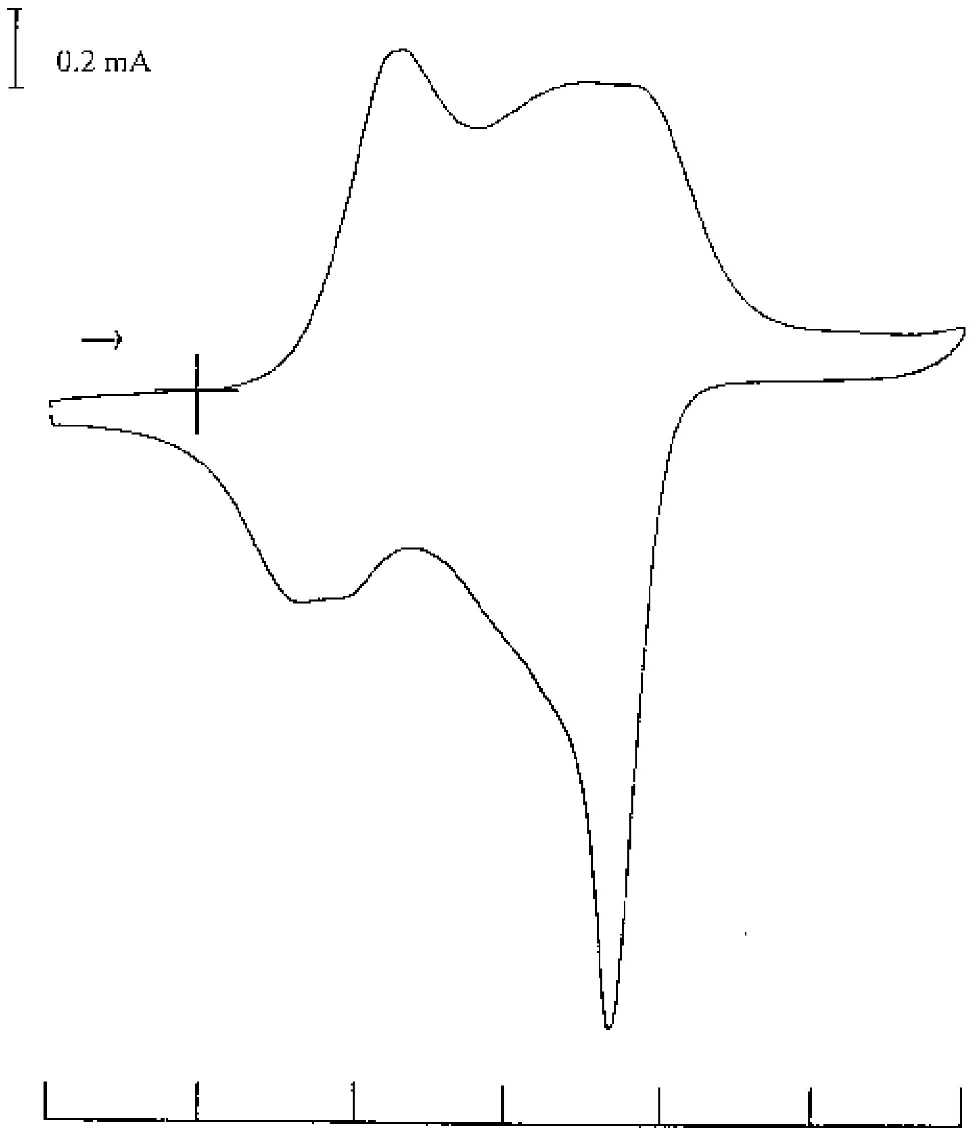


Fig. 3.3.4: CV of a PANI/CH_3-PANI/SiO_2 film (3 cycles) on a Pt electrode in aqueous solution containing 0.8 M H_2SO_4.

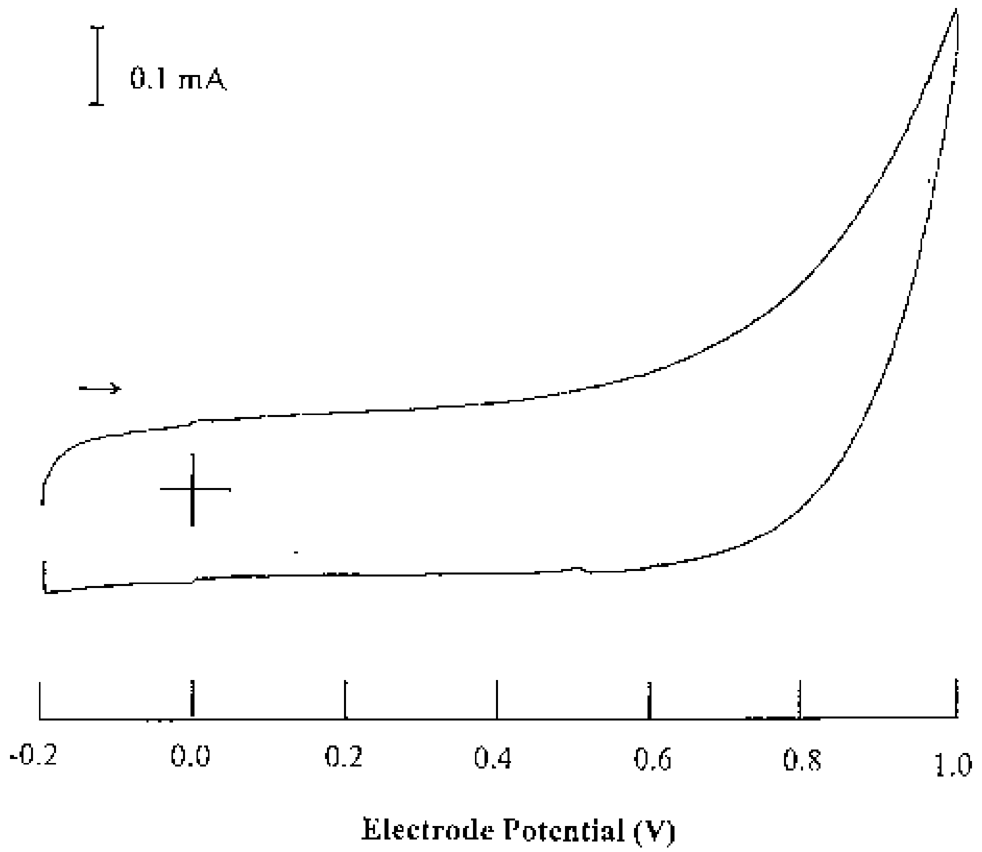
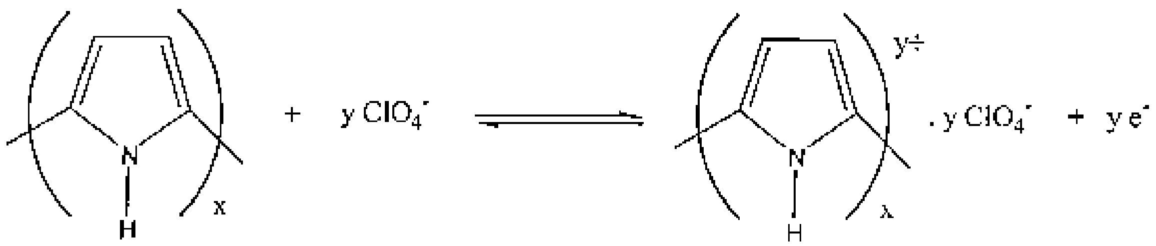


Fig. 3.3.5: CV of a PP film (1 cycle) on a Pt electrode in aqueous solution containing 0.1 M $LiClO_4$.



The oxidation is due to doping of ClO_4^- into the PP backbone while the reduction is due to dedoping of ClO_4^-. It should be noted here that the anions or cations do not behave as electron donating or accepting species. In the case of electrochemical doping, the electron acceptor or donor is the electrode itself. In other words, the oxidation or reduction of the polymer film at the electrode results in the anion or cation doping so as to achieve electrochemical neutrality in the polymer film. The observed current spectrum of the CV (Fig. 3.3.5) indicates that the PP film can be doped or dedoped with ClO_4^- at different potentials between -0.2 V to +1.0 V.

F. PANI/PP Electrode:

To examine the electrochemical doping-dedoping behaviors of the copolymer PANI/PP film electrode in an aqueous solution containing 0.1 M $LiClO_4$ and 0.8 M H_2SO_4 voltametry technique was adopted and the corresponding CV is shown in the Fig. 3.3.6. The CV of the PANI/PP film (1 cycle) is almost identical to that of PP. However, the charging current for the PANI/PP seems to be higher than that of PP. This might be due to the presence of PANI, which itself is highly conducting and thus can give current during potential sweeping as observed in the CV.

G. PANI/PP/SiO$_2$ Electrode:

Fig. 3.4.7 shows the CV of a PANI/PP/SiO_2 composite film (1 cycle) on a Pt electrode in aqueous solution containing 0.1 M $LiClO_4$ and 0.8 M H_2SO_4. The observed CV resembles to that of the PANI/PP electrode. The insertion of silica into the polymer matrix seems not to be made any change in the CV of the PANI/PP/SiO_2 composite electrode. Since SiO_2 is electroinactive and hence can not give any current to result any effect on the CV of the PANI/PP/SiO_2 electrode. Similar observation was also reported elsewhere.

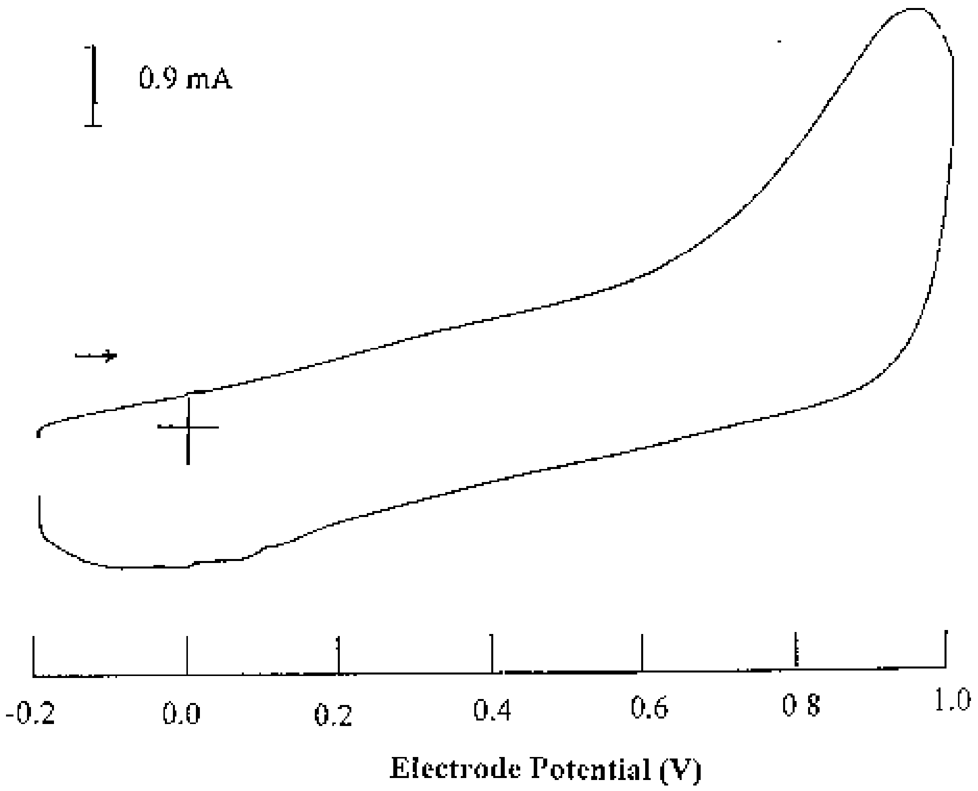


Fig. 3.3.6: CV of a PANI/PP film (1 cycle) on a Pt electrode in aqueous solution containing 0.1 M $LiClO_4$ and 0.8 M H_2SO_4.

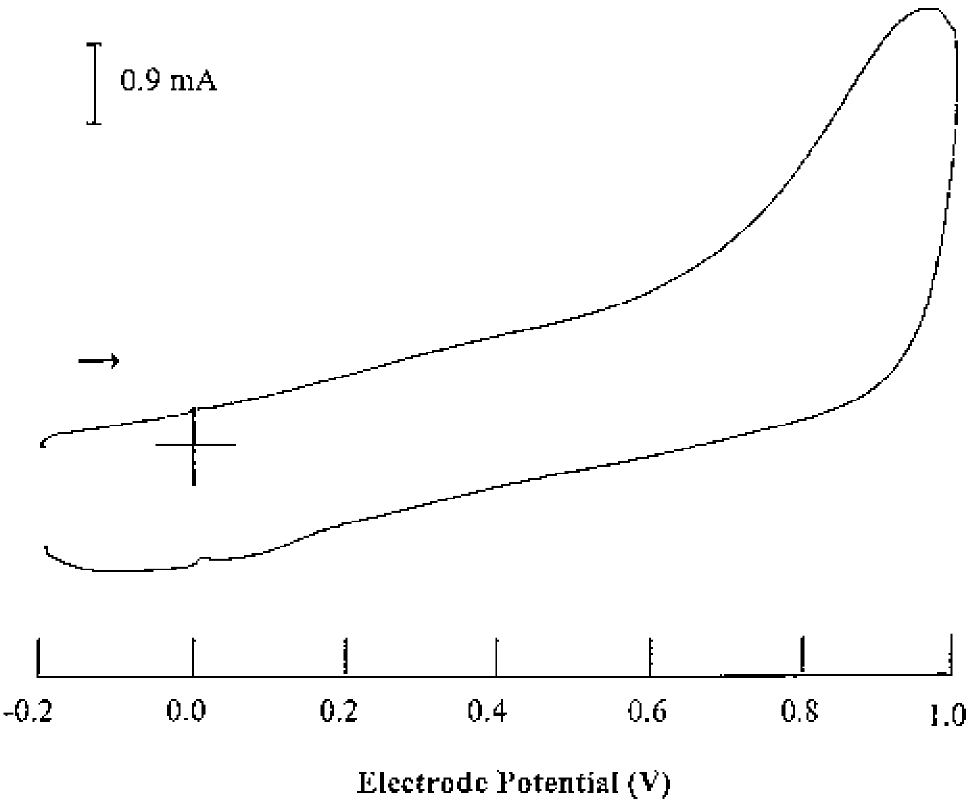


Fig. 3.3.7: CV of a PANI/PP/SiO_2 film (1 cycle) on a Pt electrode in aqueous solution containing 0.1 M $LiClO_4$ and 0.8 M H_2SO_4.

3.3.2 Electrochemical Redox Behavior

Electrodes are the sites where electrochemical oxidation and reduction take place. For the redox process, electrodes play the critical and effective role. Usually noble metals, *viz.*, Pt, Au are utilized mostly as active electrodes. However, because noble metals are costly and their abundance is limited and thus effort is given to search for new electrode materials. The conductive polymers are the class of materials which are conductive, easy to prepare and less costly and thus appeared as potentials candidates for electrode materials. In the present work, Pt electrode is coated with some polymer, copolymer and composite films and different redox processes were than studied by using redox media, such as 0.1 M $K_4Fe(CN)_6$ and 0.01M hydroquinone + 0.1 M Na_2SO_4 as electrolytes

A one electron redox reaction of ferrous (Fe^{2+}) and ferric (Fe^{3-}), shown below was studied by using $K_4Fe(CN)_6$ as an electrolyte solution of concentration 0.1 M.

$$Fe^{2+} - e = Fe^{3+}$$

On the other hand, the following two electron redox reaction of *p*-benzoquinone (Q) and hydroquinone (QH_2), was studied by using the electrolyte solution of 0.01 M hydroquinone and 0.1 M Na_2SO_4

$$Q + 2H^+ + 2e = QH_2$$

A. Pt Electrode

Figures 3.3.8 and 3.3.9 show the redox behavior of a Pt electrode when switched between two potential window in different electrolyte media. The results of two CV's as shown in Figure 3.3.8-3.3.9 are summarized in the following Table 3.3.1:

Table-3.3.1: Redox behavior of a bare Pt electrode

Electrolyte solution	Oxidation Potential (V)	Reduction Potential (V)
0.1 M $K_4Fe(CN)_6$	+0.44	+0.05
0.01M HQ + 0.1 M Na_2SO_4	+0.60	+0.09

When Pt was used as an electrode, the oxidation of Fe^{2-} to Fe^{3+} occurred at the potential of +0.44 V and reduction occurred at 0.05 V. And for the quinone/hydroquinone system the oxidation potential was found at +0.60 V whereas the reduction potential was at 0.09 V. The redox potentials observed in this study are in good agreement with previous report.

B. PANI Electrode

Next, Pt electrode was modified by coating its surface with PANI film of different thickness. The PANI film modified Pt electrodes were then investigated for their redox performance by studying

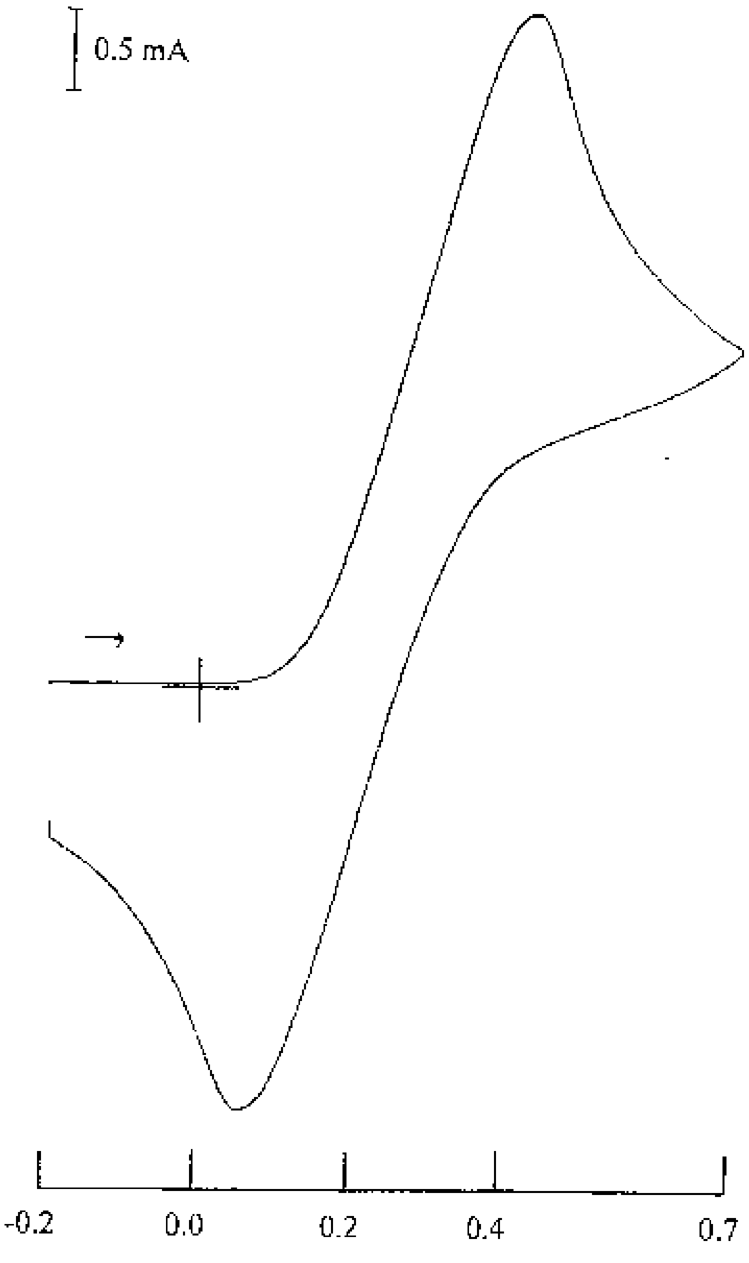


Fig. 3.3.8: CV of a bare Pt electrode in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$.

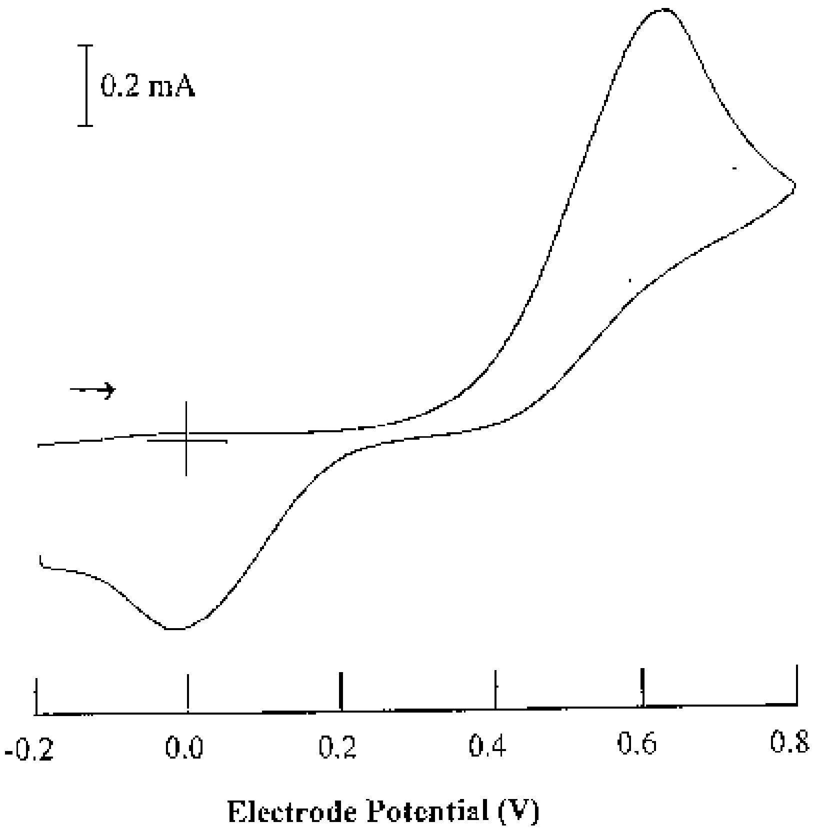


Fig. 3.3.9: CV of a bare Pt electrode in an aqueous solution containing 0.01M Hydroquinone + 0.1 M Na_2SO_4.

oxidation reduction processes on the modified surface. The same electrolytic media, $K_4Fe(CN)_6$ were also utilized in these experiments. In modifying the Pt electrodes, the PANI films were electrodeposited on the Pt surface from an electrolytic solution containing 0.5 M aniline + 0.8 M H_2SO_4 as described in the experimental section. The observed redox parameters of the PANI modified Pt electrode as obtained from the Figs. 3.3.10-3.3.15 are given in the following Table-3.3.2:

Table-3.3.2: Redox behavior of PANI electrode (PANI film was prepared from an aqueous solution containing 0.5 M aniline + 0.8 M H_2SO_4)

Electrolyte solution	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.1 M $K_4Fe(CN)_6$	1	+0.42	+0.05
	5	-	-
	10	-	-
0.01M HQ + 0.1 M Na_2SO_4	1	+0.49	+0.16
	5	-	-
	10	-	-

It can be seen from the result that the oxidation potential of the Fe^{2+}/Fe^{3+} system was slightly lower (+0.42 V) for the modified PANI electrode than that (+0.44 V) for the bare Pt electrode but the reduction potential was quite same for both the electrodes. And for the Q/QH_2 system, the oxidation potential is much smaller (+0.49 V) for PANI electrode than that (+0.60 V) for the bare Pt electrode but the reduction potential is slightly higher. These observations suggest that on the modified PANI electrode the oxidation of ferrous and hydroquinone could have been easier compared to that on the bare Pt electrode. When the thickness of the polymer on the Pt electrode was increased to 5 cycles or 10 cycles there was no such significant redox peak in the CV which could be due to the high charge carrying properties of PANI. The current density became larger and thus the redox peaks could be suppressed by that continuous current. However, the current shoulder as observed in the CV for thick PANI films clearly indicates that the coated films retained their electro conducting state though the film got thicker.

Further, PANI film was prepared from the organic solvents viz., CH_3CN and DMF. The films thus coated on the Pt electrode were thus employed for investigating the redox activity of the Fe^{2+}/Fe^{3+} and H_2Q/Q couples. The result of redox behavior of the modified PANI electrode as shown in Figs. 3.3.10-3.3.11 and Figs. 3.3.16-3.3.19 are summarized in the following Table-3.3.3:

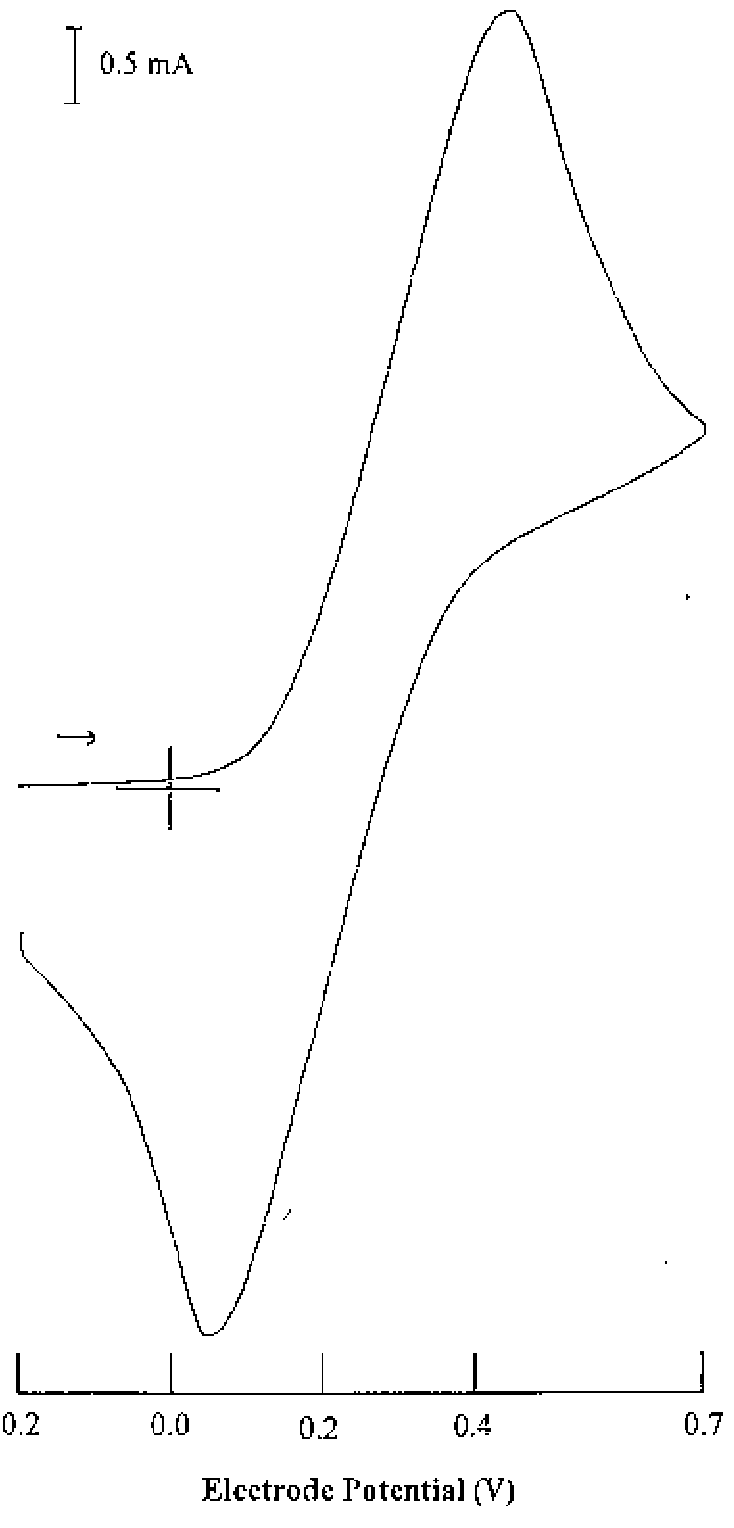


Fig. 3.3.10: CV of a PANI electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI film was prepared from an aqueous solution containing 0.5 M aniline + 0.8 M H_2SO_4.

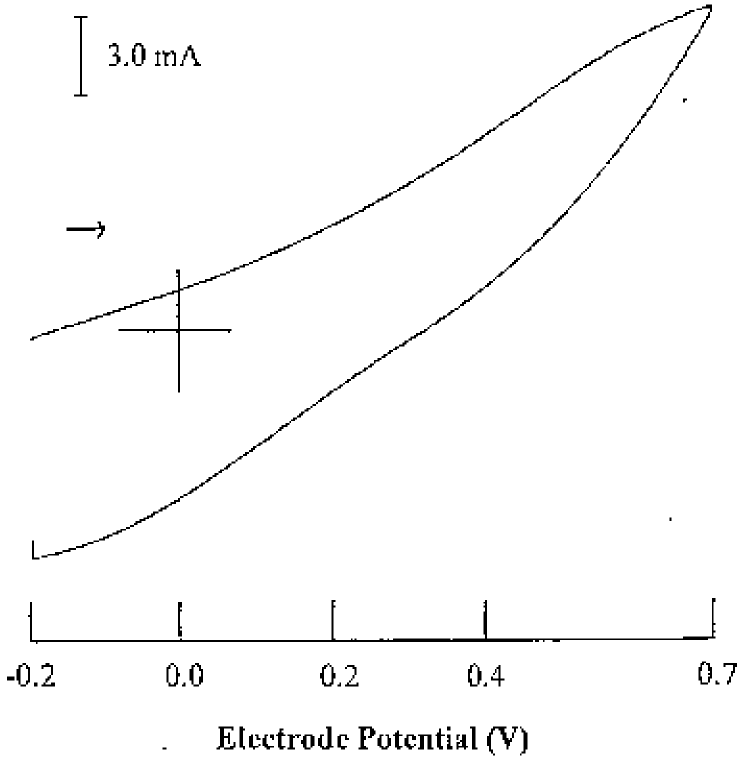


Fig. 3.3.11: CV of a PANI electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI film was prepared from an aqueous solution containing 0.5 M aniline + 0.8 M H_2SO_4.

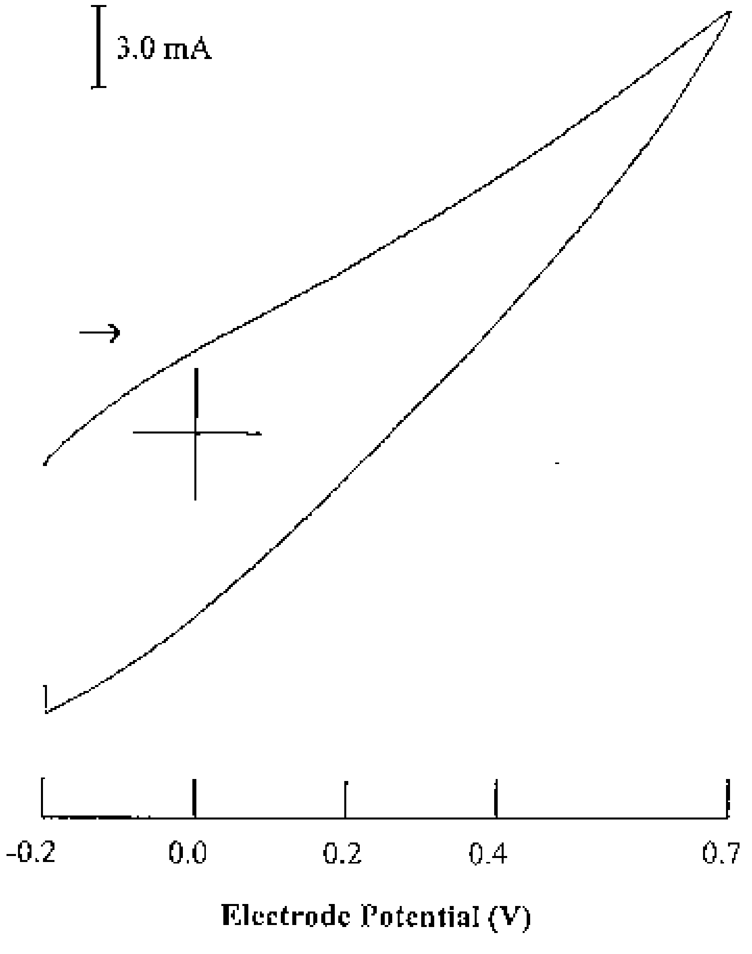


Fig. 3.3.12: CV of a PANI electrode (10 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI film was prepared from an aqueous solution containing 0.5 M aniline + 0.8 M H_2SO_4.

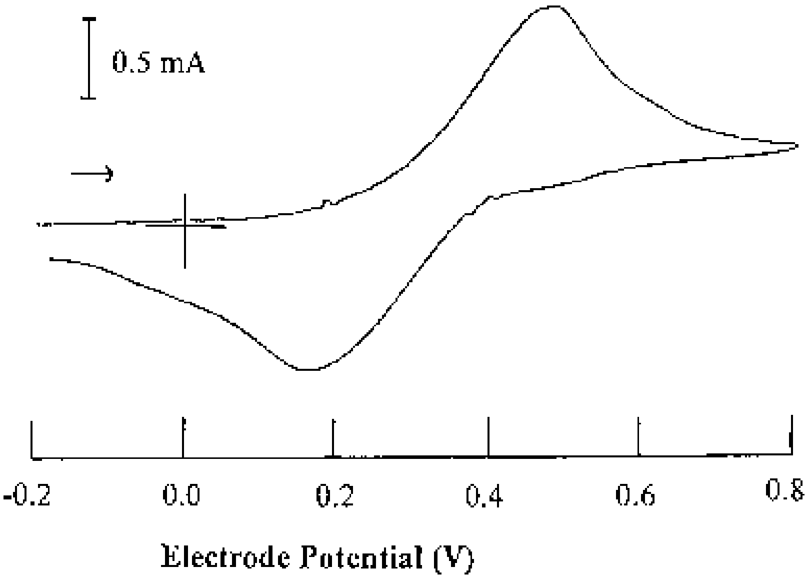


Fig. 3.3.13: CV of a PANI electrode (1 cycle) in an aqueous solution containing 0.01 M Hydroquinone + 0.1 M Na_2SO_4. PANI film was prepared from an aqueous solution containing 0.5 M aniline + 0.8 M H_2SO_4.

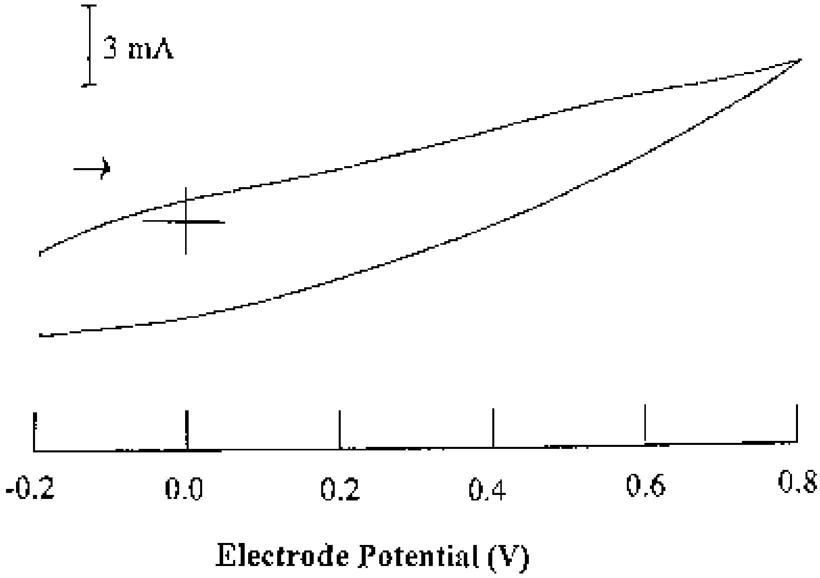


Fig. 3.3.14: CV of a PANI electrode (5 cycles) in an aqueous solution containing 0.01 M Hydroquinone + 0.1 M Na_2SO_4. PANI film was prepared from an aqueous solution containing 0.5 M aniline + 0.8 M H_2SO_4.

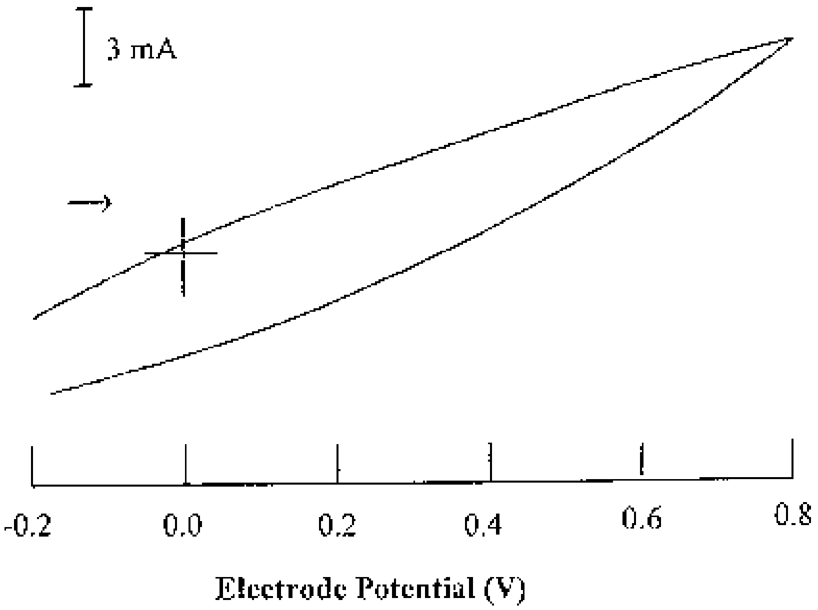


Fig. 3.3.15: CV of a PANI electrode (10 cycles) in an aqueous solution containing 0.1 M Hydroquinone + 0.1 M Na_2SO_4. PANI film was prepared from an aqueous solution containing 0.5 M aniline + 0.8 M H_2SO_4.

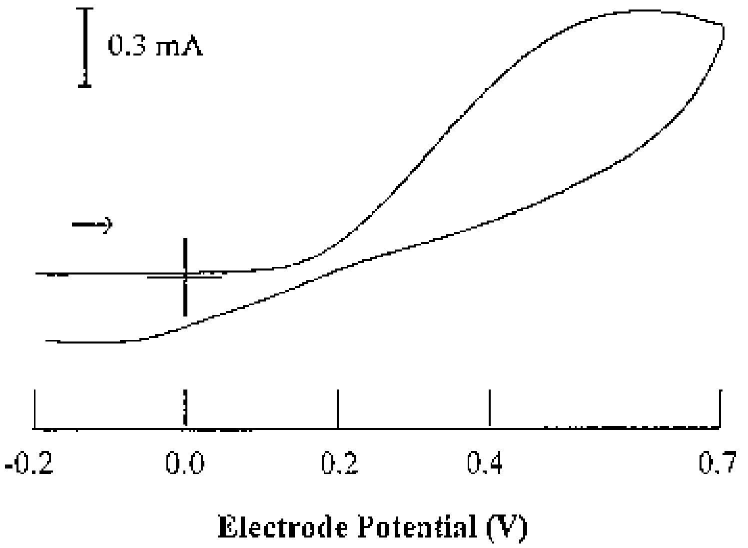


Fig. 3.3.16: CV of a PANI electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI film was prepared from a CH_3CN solution containing 0.5 M aniline + 0.1 M $LiClO_4$.

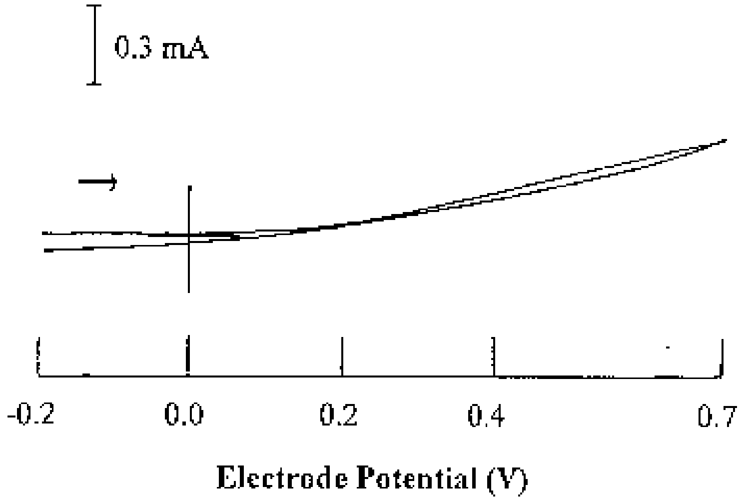


Fig. 3.3.17: CV of a PANI electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI film was prepared from a CH_3CN solution containing 0.5 M aniline + 0.1 M $LiClO_4$.

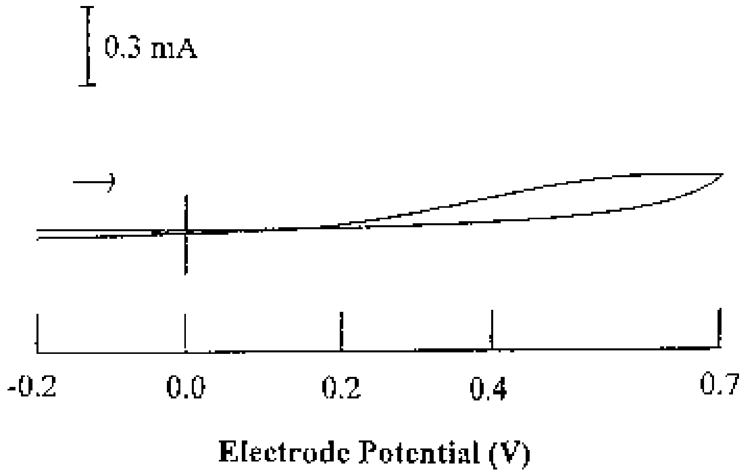


Fig. 3.3.18: CV of a PANI electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI film was prepared from a DMF solution containing 0.5 M aniline + 0.1 M $LiClO_4$.

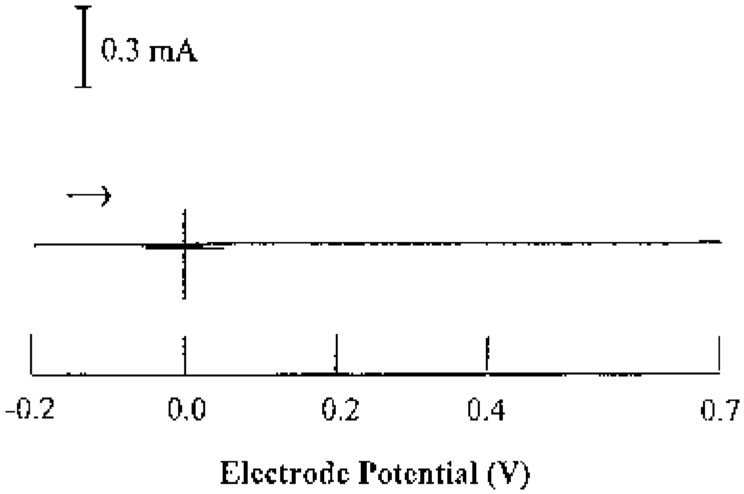


Fig. 3.3.19: CV of a PANI electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI film was prepared from a DMF solution containing 0.5 M aniline + 0.1 M $LiClO_4$.

Table-3.3.3: Redox behavior of PANI electrode (prepared from different solvents) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$

Solvent used for the preparation of PANI	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.8 M H_2SO_4 solution in H_2O	1	+0.42	+0.05
	5	-	-
0.1 M $LiClO_4$ solution in CH_3CN	1	+0.55	-0.07
	5	-	-
0.1 M $LiClO_4$ solution in DMF	1	-	-
	5	-	-

The results show that the oxidation of ferrous to ferric occurred at comparatively higher oxidation potential and reduction of ferric to ferrous occurred at lower potential when PANI was synthesized from a CH_3CN solution containing 0.1 M $LiClO_4$. It seems that the ease of the redox reaction decreased when CH_3CN is used as solvent for the synthesis of PANI. The solvent may have some role in the morphology of the PANI films. Indeed, the PANI obtained from CH_3CN looks very hard morphology compared to that obtained from aqueous medium. The hard morphology of the polymer could have effect on the electron transfer associated with the studied redox processes. When PANI was prepared from DMF solution there was no significant redox peaks observed even at low or high thickness of PANI. This may be also due to the similar solvent effect on the PANI morphology that result a difficult electron transfer between the Pt and PANI substrates. However, dull current shoulder is appeared, indicating that the coated films are electro conducting.

C. CH_3-PANI Electrode

Electrode modification was further attempted by changing the polymer to CH_3-PANI. In this case, CH_3-PANI was prepared from aqueous solution having different thickness. The CH_3-PANI film was deposited on the bare Pt electrode electrochemically following the similar procedure as mentioned for PANI. The modified CH_3-PANI electrode was thus employed for examining the redox activity of the systems as discussed bellow.

The result of the redox behavior of the modified CH_3-PANI electrode as shown in Figs. 3.3.20-3.3.25 are summarized in the following Table-3.3.4:

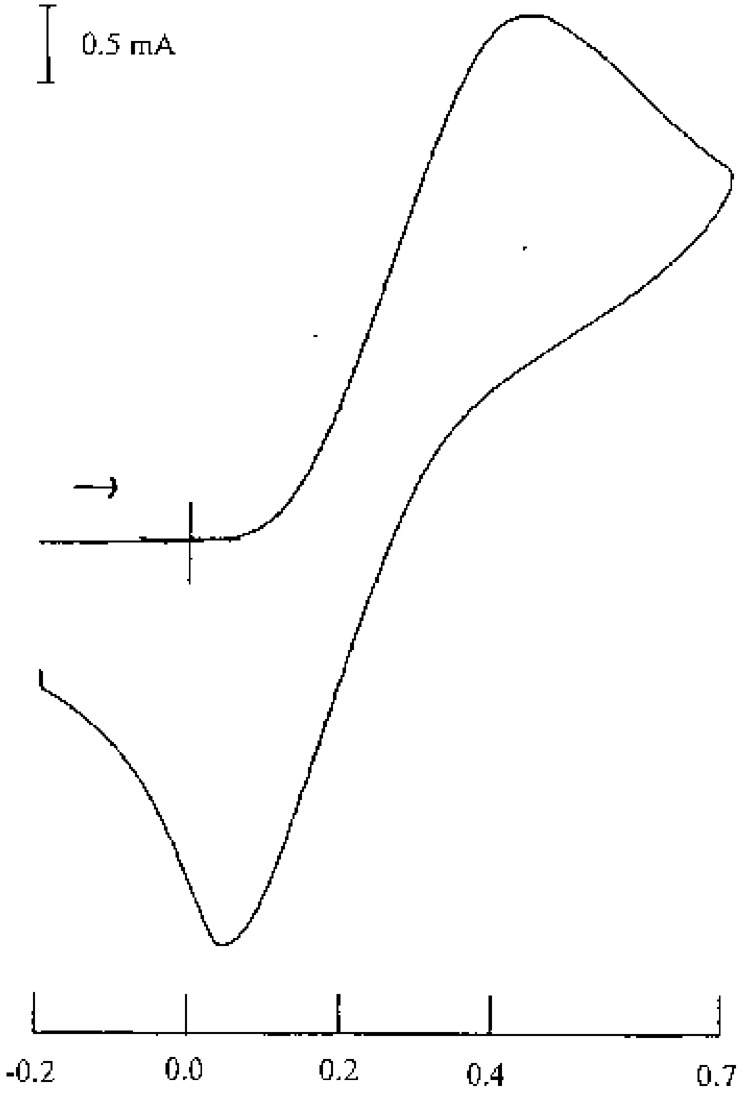


Fig. 3.3.20: CV of a CH_3-PANI electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. CH_3-PANI film was prepared from an aqueous solution containing 0.5 M toluidine + 0.8 M H_2SO_4.

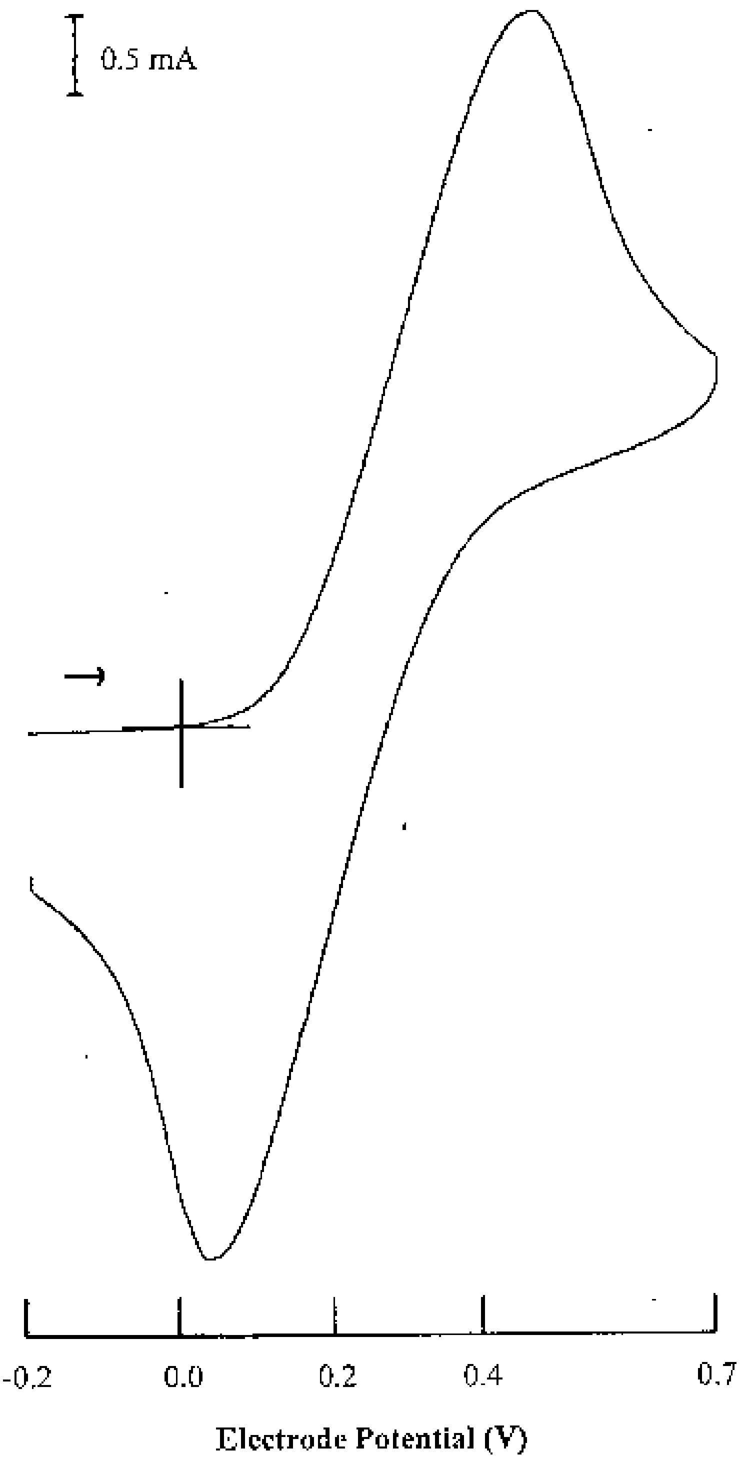


Fig. 3.3.21: CV of a CH_3-PANI electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. CH_3-PANI film was prepared from an aqueous solution containing 0.5 M toluidine + 0.8 M H_2SO_4.

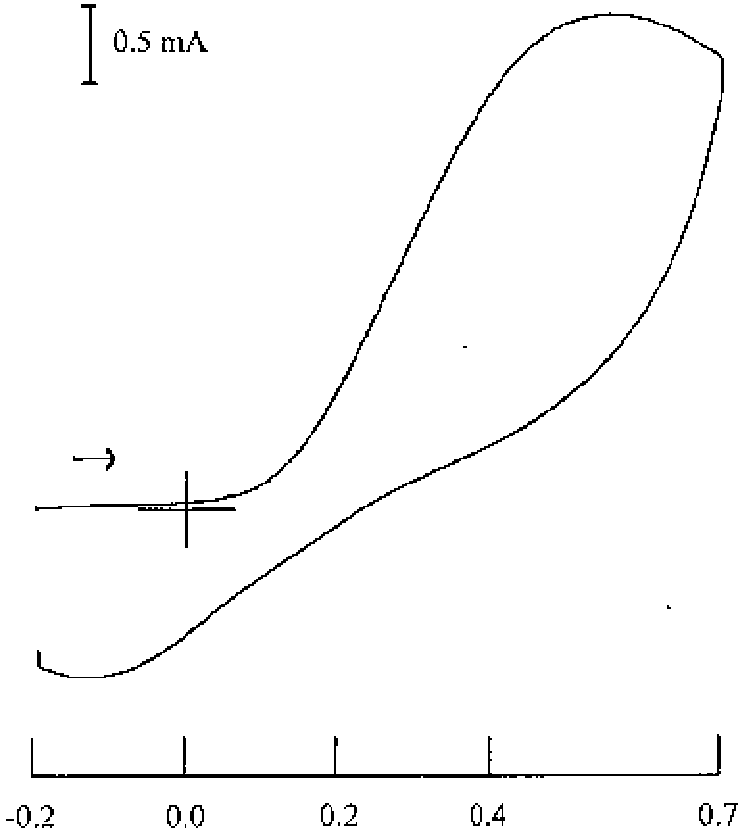


Fig. 3.3.22: CV of a CH_3-PANI electrode (10 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. CH_3-PANI film was prepared from an aqueous solution containing 0.5 M toluidine + 0.8 M H_2SO_4.

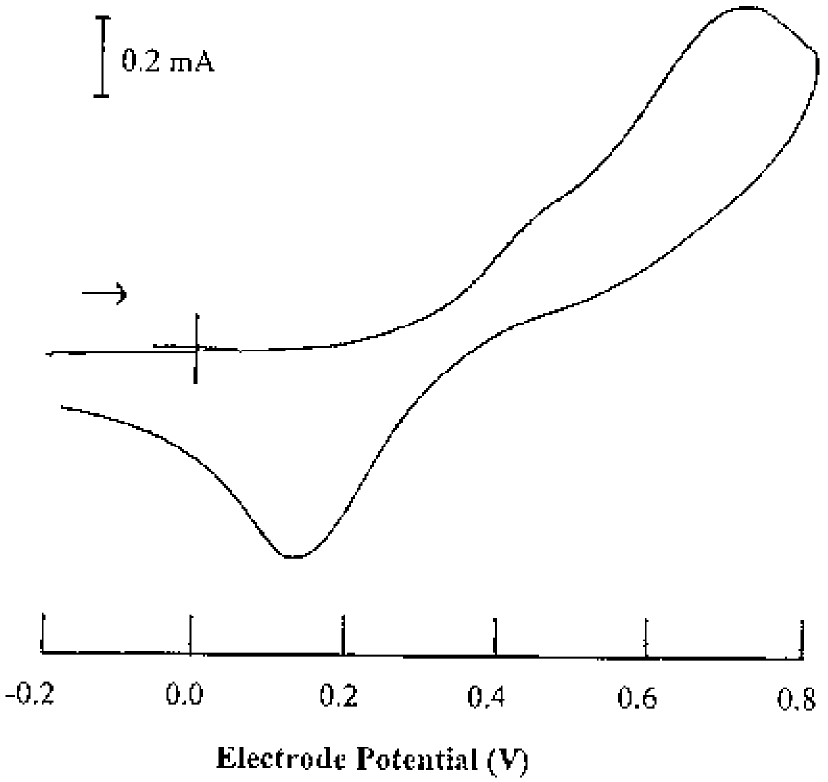


Fig. 3.3.23: CV of a CH_3-PANI electrode (1 cycle) in an aqueous solution containing 0.01 M Hydroquinone + 0.1 M Na_2SO_4. CH_3-PANI film was prepared from an aqueous solution containing 0.5 M toluidine + 0.8 M H_2SO_4.

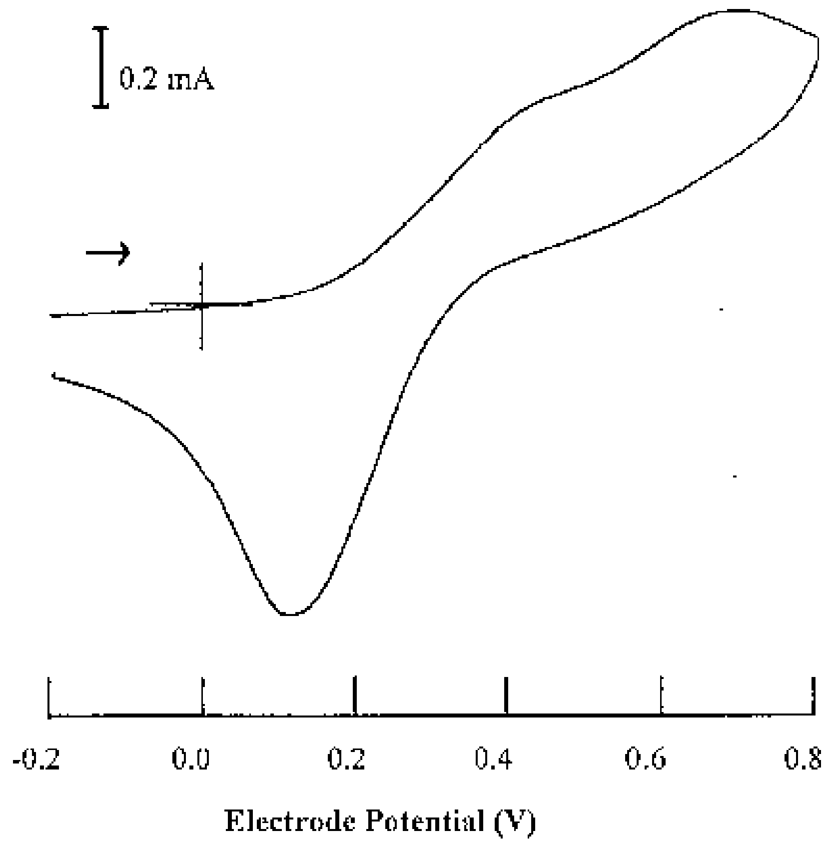


Fig. 3.3.24: CV of a CH$_3$-PANI electrode (5 cycles) in an aqueous solution containing 0.01 M Hydroquinone + 0.1 M Na$_2$SO$_4$. CH$_3$-PANI film was prepared from an aqueous solution containing 0.5 M toluidine + 0.8 M H$_2$SO$_4$.

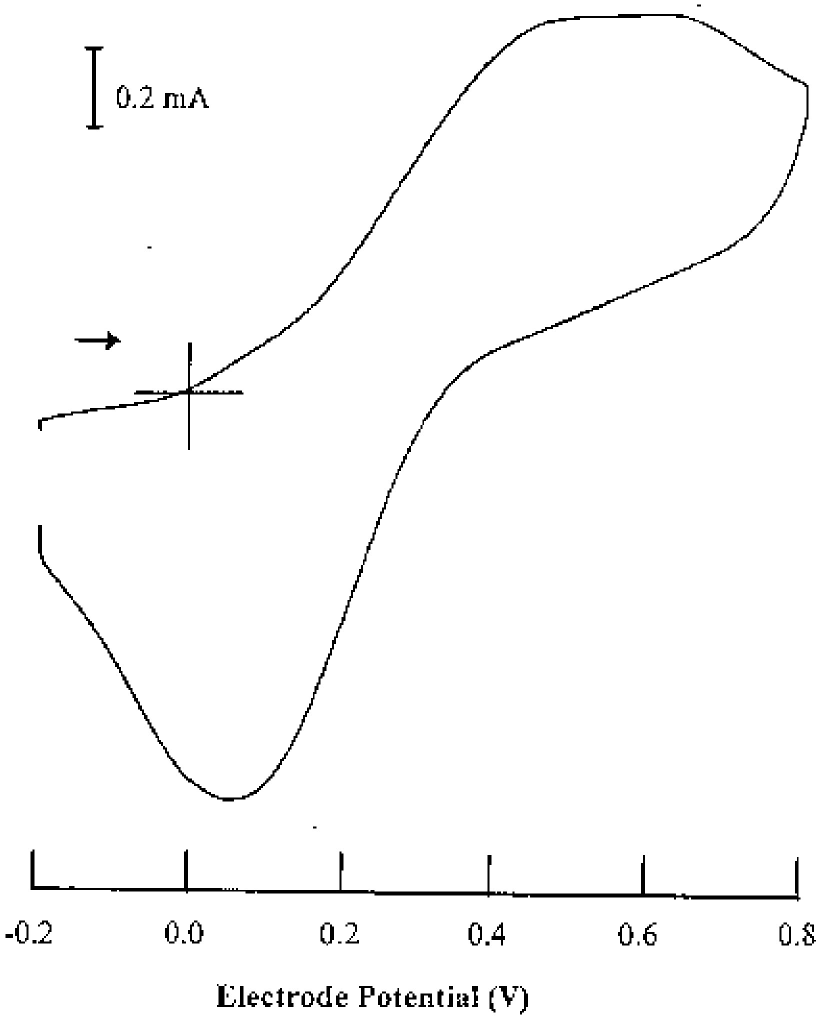


Fig. 3.3.25: CV of a CH_3-PANI electrode (10 cycles) in an aqueous solution containing 0.01 M Hydroquinone + 0.1 M Na_2SO_4. CH_3-PANI film was prepared from an aqueous solution containing 0.5 M toluidine + 0.8 M H_2SO_4.

Table-3.3.4: Redox behavior of CH_3-PANI electrode (CH_3-PANI film was prepared from an aqueous solution containing 0.5 M *o*-toluidine + 0.8 M H_2SO_4)

Electrolyte solution	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.1 M $K_4Fe(CN)_6$	1	+0.44	+0.05
	5	+0.43	+0.05
	10	+0.62	-0.10
0.01M HQ + 0.1 M Na_2SO_4	1	+0.74	+0.14
	5	+0.71	+0.12
	10	+0.72	+0.06

It is seen from the table that the oxidation and reduction potential of the Fe^{2+}/Fe^{3+} system was quite similar for the modified CH_3-PANI electrode compared to that for the bare Pt electrode and PANI electrode. When the thickness of polymer on Pt was increased the redox potential occurred at higher potential showing less spontancity that may be due to the less chance of injection of electrons through the thick polymer. On the other hand, for the Q/QH_2 system, the oxidation potential is much higher for CH_3-PANI electrode than that for the bare Pt electrode or PANI electrode but the reduction potential is slightly lower. These observations suggest that on the modified CH_3-PANI electrode the oxidation of hydroquinone could have been less spontaneous. Reduction of quinone to hydroquinone occurred at slightly lower potential suggesting higher tendency of being reduced in case of CH_3-PANI modified electrode. When the thickness of the polymer on the Pt electrode was increased to 5 cycles or 10 cycles there was no such significant change on redox potential. The difference in the redox potential may arise from the dissimilar chemical functionality of the polymer. Since in the CH_3-PANI matrix, there exist a $-CH_3$ group in the polymer chain, the redox process may be altered due to the functionality of the polymer chain and thus results difference in the redox potential with CH_3-PANI than PANI.

Next, redox behavior of the CH_3-PANI modified Pt electrode as shown in Figs. 3.3.26 - 3.3.27 was examined. CH_3-PANI film was prepared either from a CH_3CN solution containing 0.5 M toluidine + 0.1 M $LiClO_4$, or from a DMF solution containing 0.5 M toluidine + 0.1 M $LiClO_4$. The results are summarized in the following Table-3.3.5:

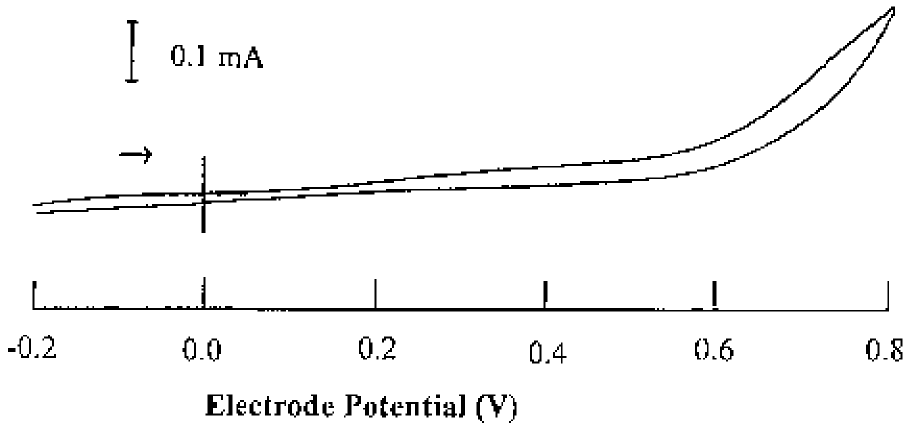


Fig. 3.3.26: CV of a CH_3-PANI electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI film was prepared from a CH_3CN solution containing 0.5 M toluidine + 0.1 M $LiClO_4$.

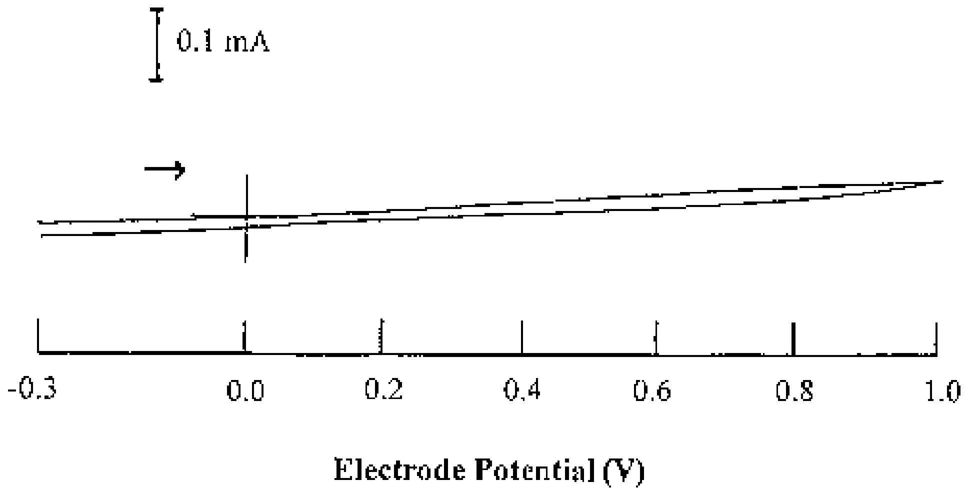


Fig. 3.3.27: CV of a CH_3-PANI electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI film was prepared from a DMF solution containing 0.5 M toluidine + 0.1 M $LiClO_4$.

Table-3.3.5: Redox behavior of CH_3-PANI electrode in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$

Solvent used for the preparation of CH_3-PANI	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.8 M H_2SO_4 solution in H_2O	5	+0.43	+0.05
0.1 M $LiClO_4$ solution in CH_3CN	5	-	-
0.1 M $LiClO_4$ solution in DMF	5	-	-

The results shows that the oxidation and reduction of ferrous-ferric system occurred at +0.43 V and +0.05 V respectively when CH_3-PANI was synthesized from an aqueous solution containing 0.8 M H_2SO_4. But when CH_3-PANI was prepared from other solutions such as 0.1 M $LiClO_4$ in CH_3CN or 0.1 M $LiClO_4$ in DMF there was no such redox peaks. Since CH_3-PANI films were prepared from different solvents, the resulted film may possess dissimilar morphological structures. The morphological structure dominates the redox process involving the transfer of electron among the redox species of the system employed.

D. PANI/CH_3-PANI Electrode

Electrode modification was further attempted involving copolymeric film. A copolymeric film of PANI and CH_3-PANI was prepared electrochemically using the corresponding monomers in the appropriate electrolytic solutions. The Pt electrode thus coated with PANI/CH_3-PANI was employed as the modified electrode to examine the redox activity of the electrode for some selective systems, such as Fe^{2+}/Fe^{3+} and H_2Q/Q couples.

Redox behavior of the PANI/CH_3-PANI modified electrode, when PANI/CH_3-PANI film was prepared from an aqueous solution containing 0.5 M aniline, 0.5 M *o*-toluidine and 0.8 M H_2SO_4, as shown in Figs. 3.3.28-3.3.33 is summarized in the following Table-3.3.6:

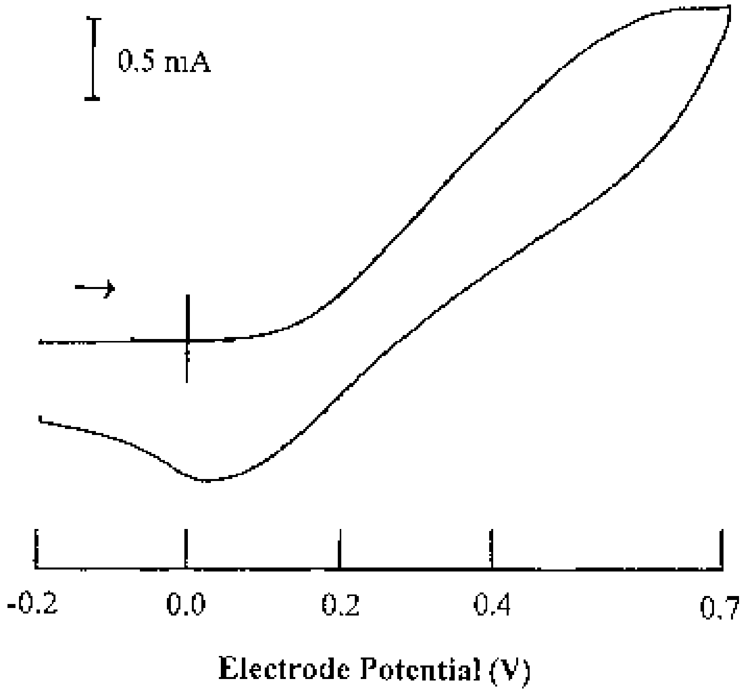


Fig. 3.3.28: CV of a PANI/CH_3-PANI electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI/CH_3-PANI was prepared from an aqueous solution containing 0.8 M H_2SO_4, 0.5 M aniline and 0.5 M *o*-toluidine

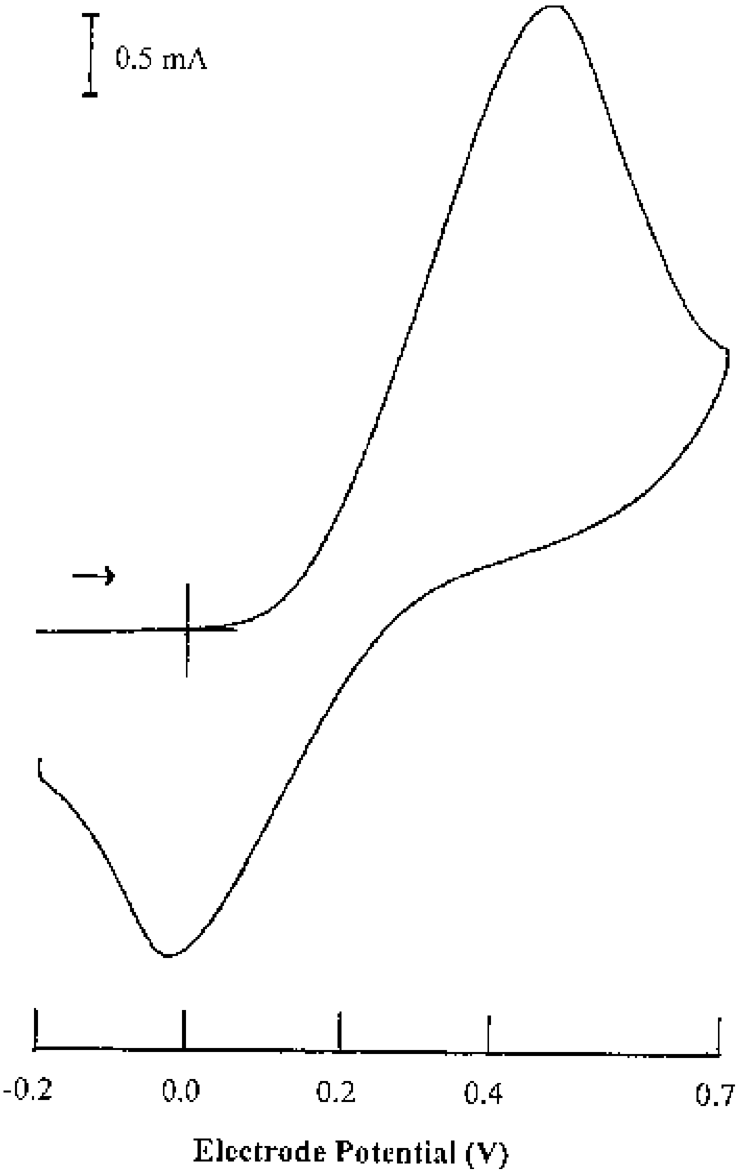


Fig. 3.3.29: CV of a PANI/CH_3-PANI electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI/CH_3-PANI was prepared from an aqueous solution containing 0.8 M H_2SO_4, 0.5 M aniline and 0.5 M *o*-toluidine.

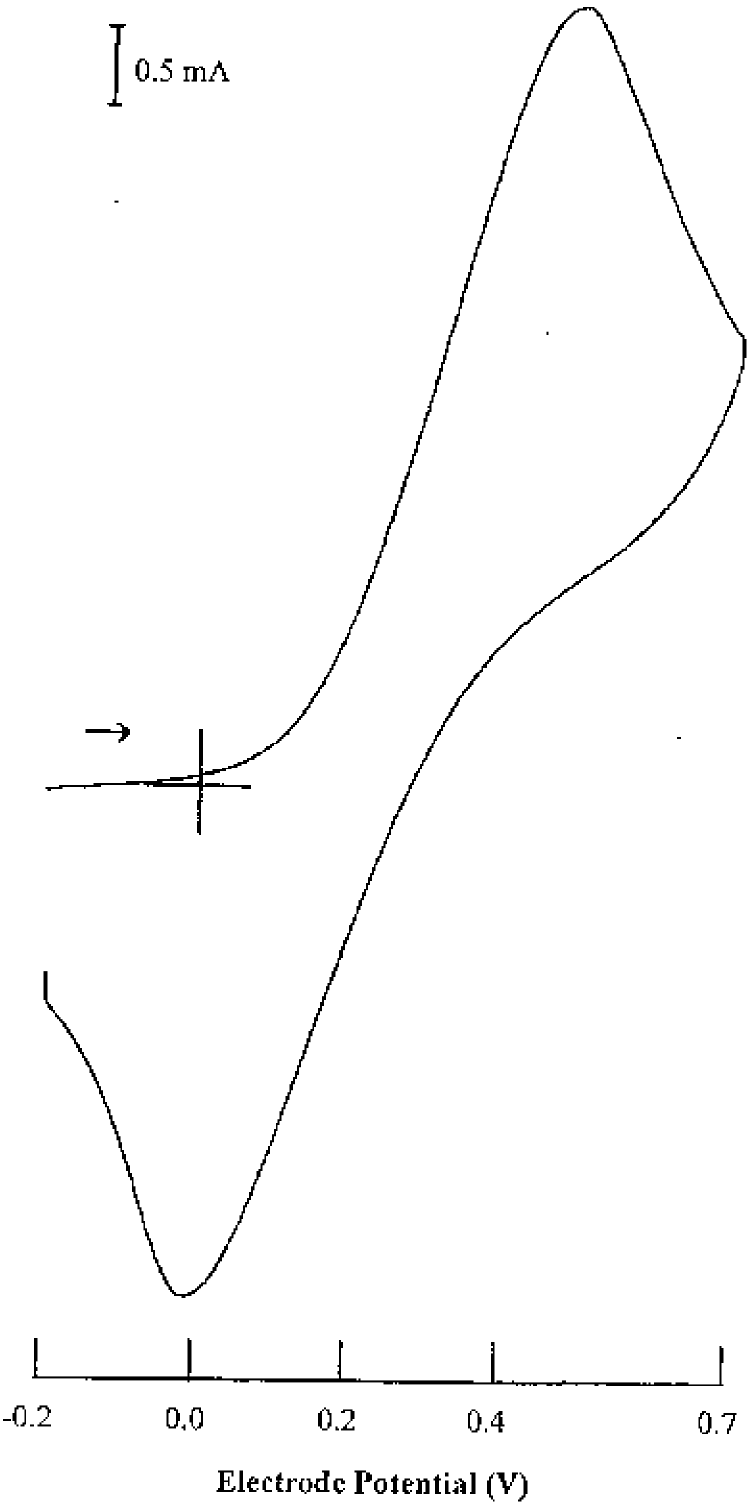


Fig. 3.3.30: CV of a PANI/CH_3-PANI electrode (10 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI/CH_3-PANI was prepared from an aqueous solution containing 0.8 M H_2SO_4, 0.5 M aniline and 0.5 M *o*-toluidine

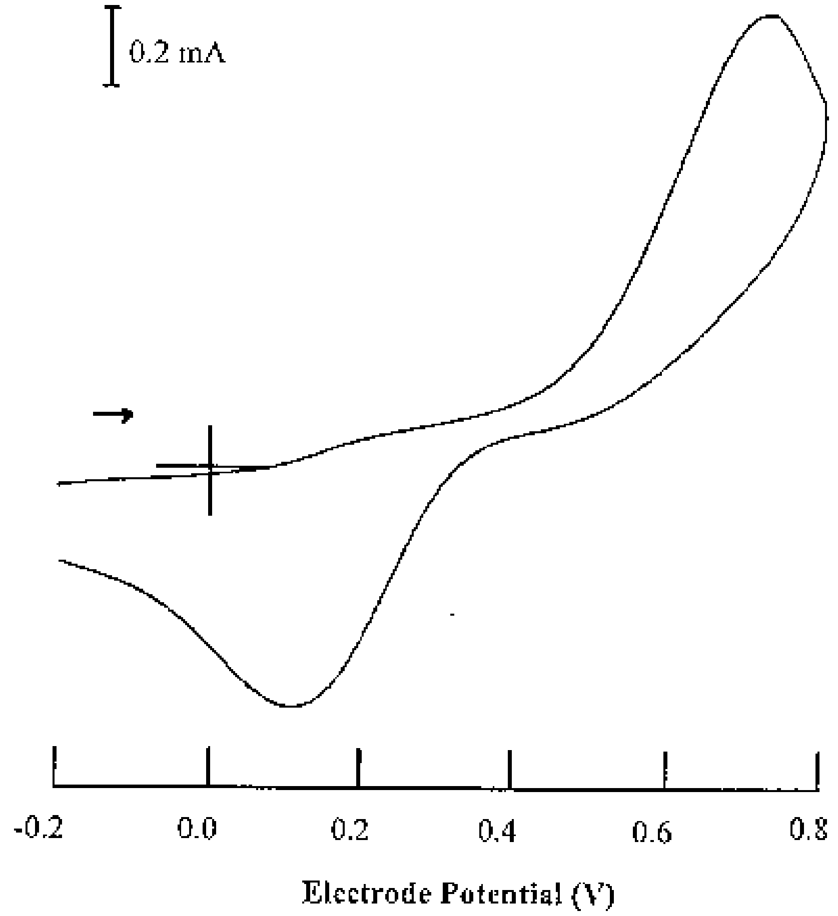


Fig. 3.3.31: CV of a PANI/CH$_3$-PANI electrode (1 cycle) in an aqueous solution containing 0.01 Hydroquinone + 0.1 M Na_2SO_4. PANI/CH$_3$-PANI was prepared from an aqueous solution containing 0.8 M H_2SO_4, 0.5 M aniline and 0.5 M *o*-toluidine

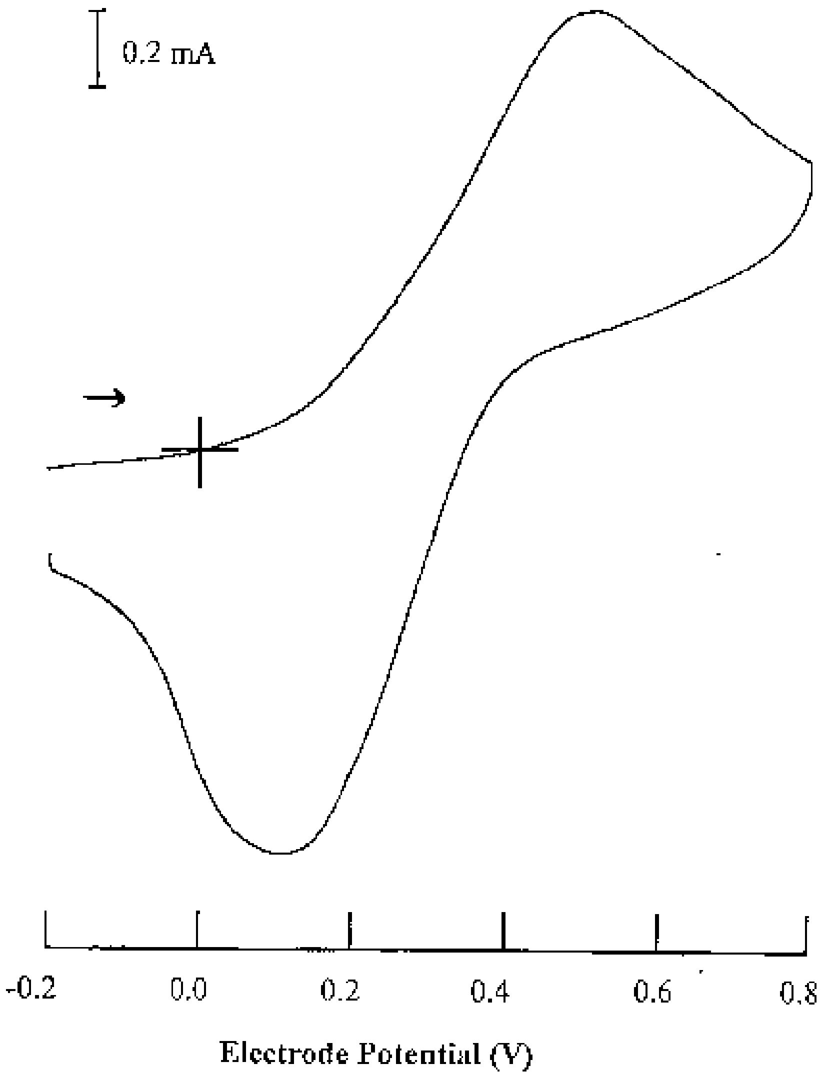


Fig. 3.3.32: CV of a PANI/CH_3-PANI electrode (5 cycles) in an aqueous solution containing 0.01 Hydroquinone + 0.1 M Na_2SO_4. PANI/CH_3-PANI was prepared from an aqueous solution containing 0.8 M H_2SO_4, 0.5 M aniline and 0.5 M *o*-toluidine.

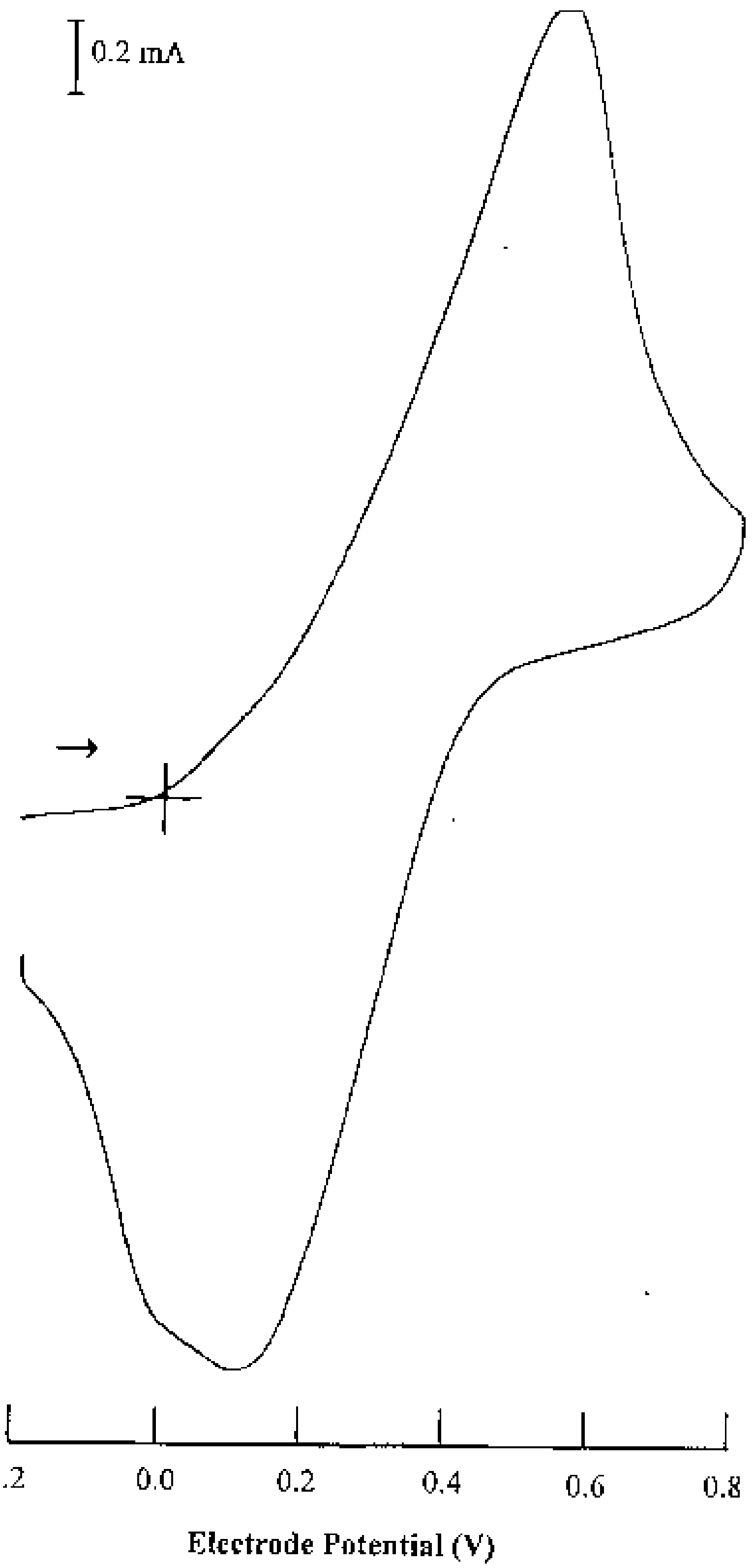


Fig. 3.3.33: CV of a PANI/CH_3-PANI electrode (10 cycles) in an aqueous solution containing 0.01 Hydroquinone + 0.1 M Na_2SO_4. PANI/CH_3-PANI was prepared from an aqueous solution containing 0.8 M H_2SO_4, 0.5 M aniline and 0.5 M *o*-toluidine.

Table-3.3.6: Redox behavior of PANI/CH_3-PANI electrode (PANI film was prepared from an aqueous solution containing 0.5 M aniline + 0.5 M *o*-toluidine + 0.8 M H_2SO_4)

Electrolyte solution	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.1 M $K_4Fe(CN)_6$	1	+0.56	+0.04
	5	+0.50	-0.07
	10	+0.52	-0.09
0.01M HQ + 0.1 M Na_2SO_4	1	+0.75	+0.12
	5	+0.50	+0.10
	10	+0.55	+0.10

It can be seen from the result that the oxidation potential of the Fe^{2+}/Fe^{3+} system was slightly higher for the modified PANI/CH_3-PANI electrode compared to that for the PANI and CH_3-PANI electrode. It indicates that the oxidation of ferrous to ferric on the PANI/CH_3-PANI coated Pt electrode will be slightly less spontaneous. When the same redox reaction was carried out with more thicker films, e.g., five, ten cycle films, no change in the redox potential was observed. Again, for the Q/QH_2 system, the oxidation potential is seen to be much higher for PANI/CH_3-PANI electrode compared to that for the thicker films (5 cycle, 10 cycle films). However, the observed result clearly indicates that copolymer modified electrode, both the thin and thick, can be used for performing the redox processes studied. So PANI/CH_3-PANI coated Pt electrode can easily be used as a new modified electrode for such two electron oxidation system. Reduction of quinone to hydroquinone occurred at slightly lower potential suggesting better electrode activity for the PANI/CH_3-PANI modified electrode compared to bare Pt electrode. When the thickness of the polymer on the Pt electrode was increased to 5 cycles or 10 cycles no significant change on redox potential was observed.

E. PANI/CH_3-PANI/SiO_2 Electrode

Electrode modification was also performed with copolymer-inorganic oxide composite film. A polymeric composite film of PANI/CH_3-PANI/SiO_2 was prepared by an electrochemical means. The composite film was then coated on the Pt electrode as before and the film was used as the electrode modifier to study the redox behavior of some systems discussed bellow:

To examine the electrochemical redox behavior of the PANI/CH_3-PANI/SiO_2 modified composite electrode both in Fe^{2+}/Fe^{3+} and H_2Q/Q system voltametry technique was adopted as before. The typical CV's are presented in Figs. 3.3.34 - 3.3.39 and results are summarized in the following Table - 3.3.7:

Table-3.3.7: Redox behavior of PANI/CH_3-PANI/SiO_2 electrode

Electrolyte solution	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.1 M $K_4Fe(CN)_6$	1	+0.40	+0.04
	5	+0.46	+0.02
	10	+0.50	-0.06
0.01M HQ + 0.1 M Na_2SO_4	1	+0.68	+0.10
	5	+0.51	+0.12
	10	+0.54	+0.10

The result shows that the oxidation potential of the Fe^{2+}/Fe^{3+} system is slightly lower for the modified PANI/CH_3-PANI/SiO_2 electrode compared to that for the PANI/CH_3-PANI coated Pt electrode. It indicates that the oxidation of ferrous to ferric on the PANI/CH_3-PANI coated Pt electrode would be slightly easier in this case. When the thicker film electrodes were employed, there was no such change in their redox potential. For the Q/QH_2 system, the oxidation potential is also slightly lower when PANI/CH_3-PANI/SiO_2 films coated on the Pt electrode compared to that for the PANI/CH_3-PANI electrode. The CV's showed slightly higher oxidation potential for the thin film (1 cycle) compared to that for thicker one (5, 10 cycle films). It indicates that when the thickness of the composite on the Pt electrode was increased oxidation occurred more easily. Reduction of quinone to hydroquinone occurred in this case almost at the same potential for the PANI/CH_3-PANI modified electrode. When the thickness of the polymer on the Pt electrode was increased to 5 cycles or 10 cycles there was no significant change on redox potential.

F. PP electrode

Polypyrrole is known to be an excellent conductive polymer having heteroatoms in the monomer unit. Its use as an electrode material is well addressed by many previous workers. In this work, attempt was also made to modify Pt electrode by coating with a PP film onto its surface. PP film was deposited electrochemically onto the Pt substrate from an appropriate electrolytic solution. The Pt electrode thus modified with the PP film was then utilized to access the redox behavior of the coupls Fe^{2+}/Fe^{3+} and H_2Q/Q.

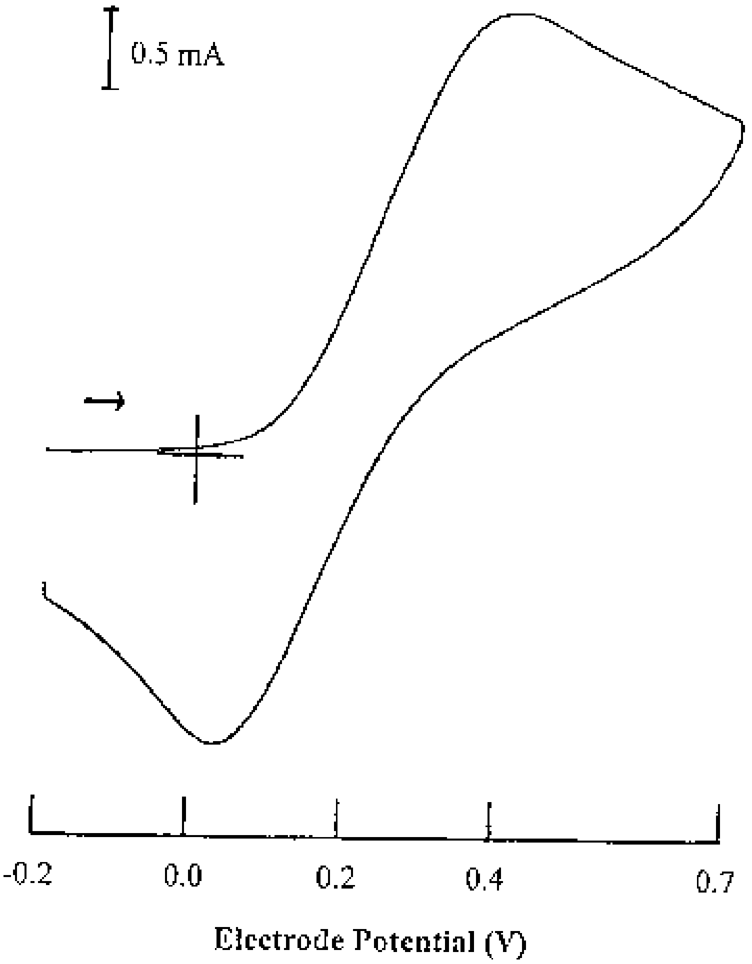


Fig. 3.3.34: CV of a PANI/CH_3-PANI/SiO_2 electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$.

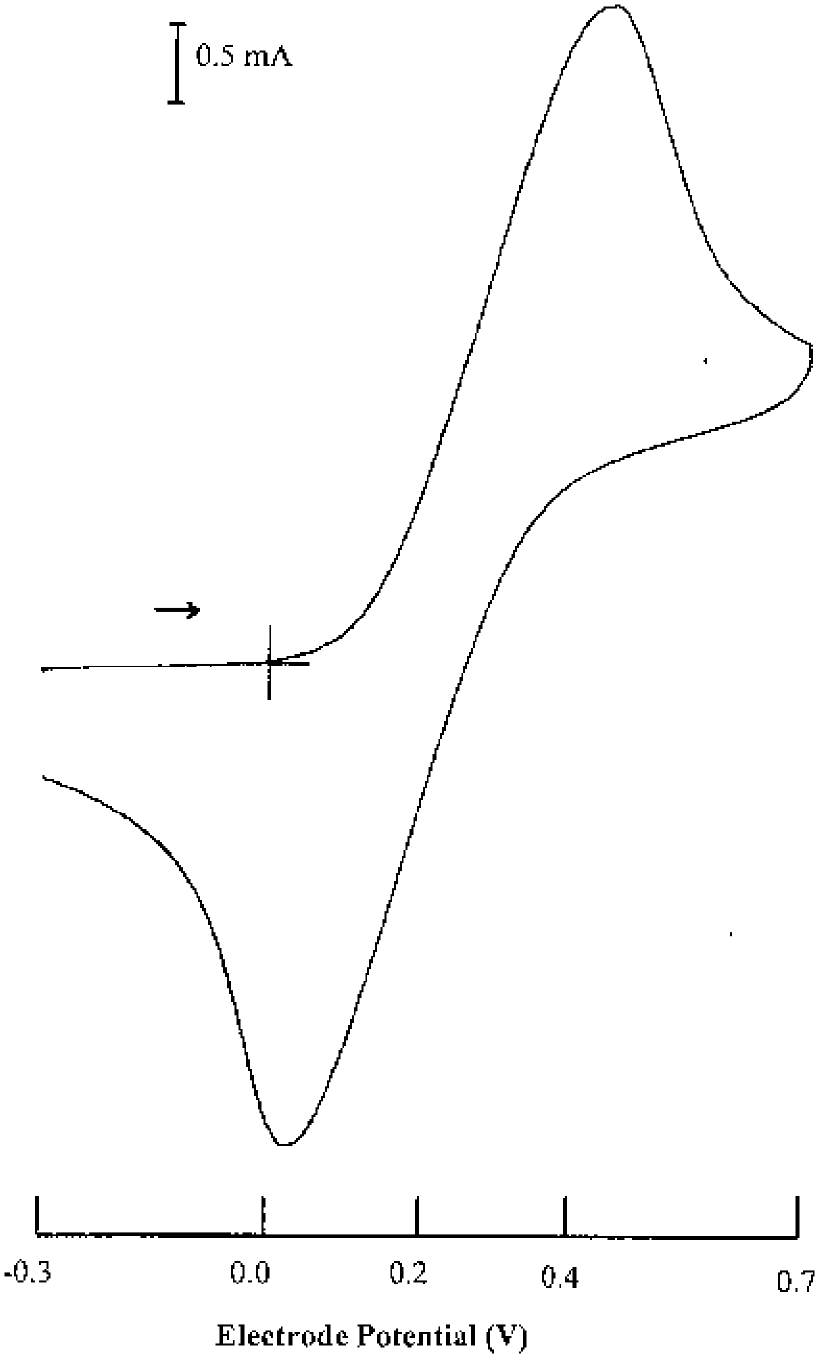


Fig. 3.3.35: CV of a PANI/CH_3-PANI/SiO_2 electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$.

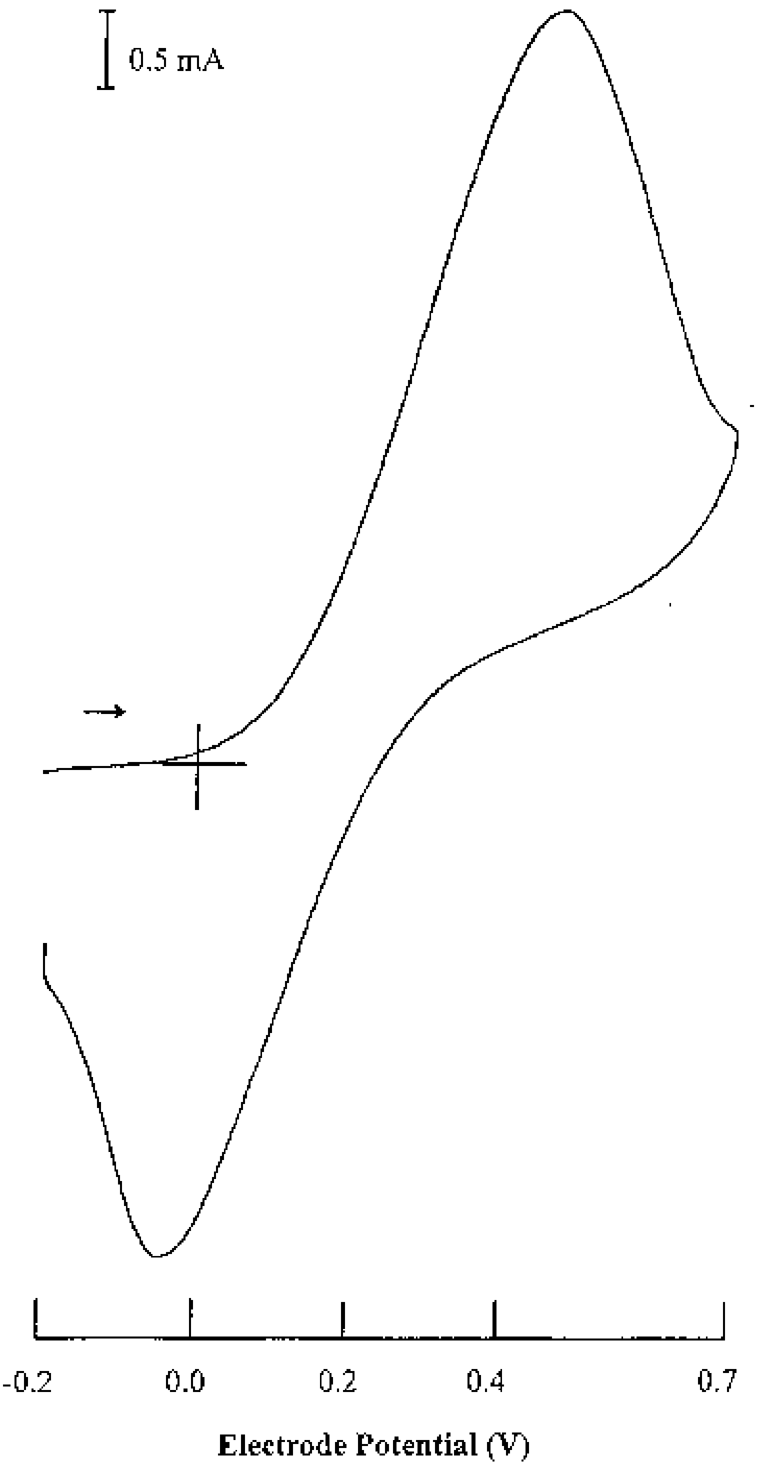


Fig. 3.3.36: CV of a PANI/CH_3-PANI/SiO_2 electrode (10 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$.

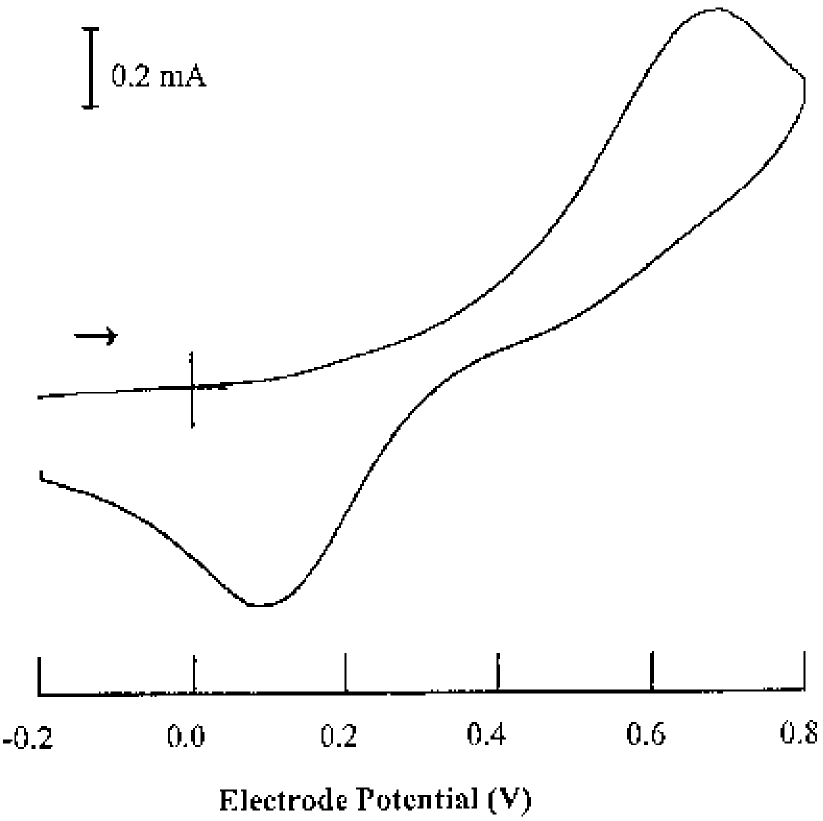


Fig. 3.3.37: CV of a PANI/CH_3-PANI/SiO_2 electrode (1 cycle) in an aqueous solution containing 0.01 Hydroquinone + 0.1 M Na_2SO_4.

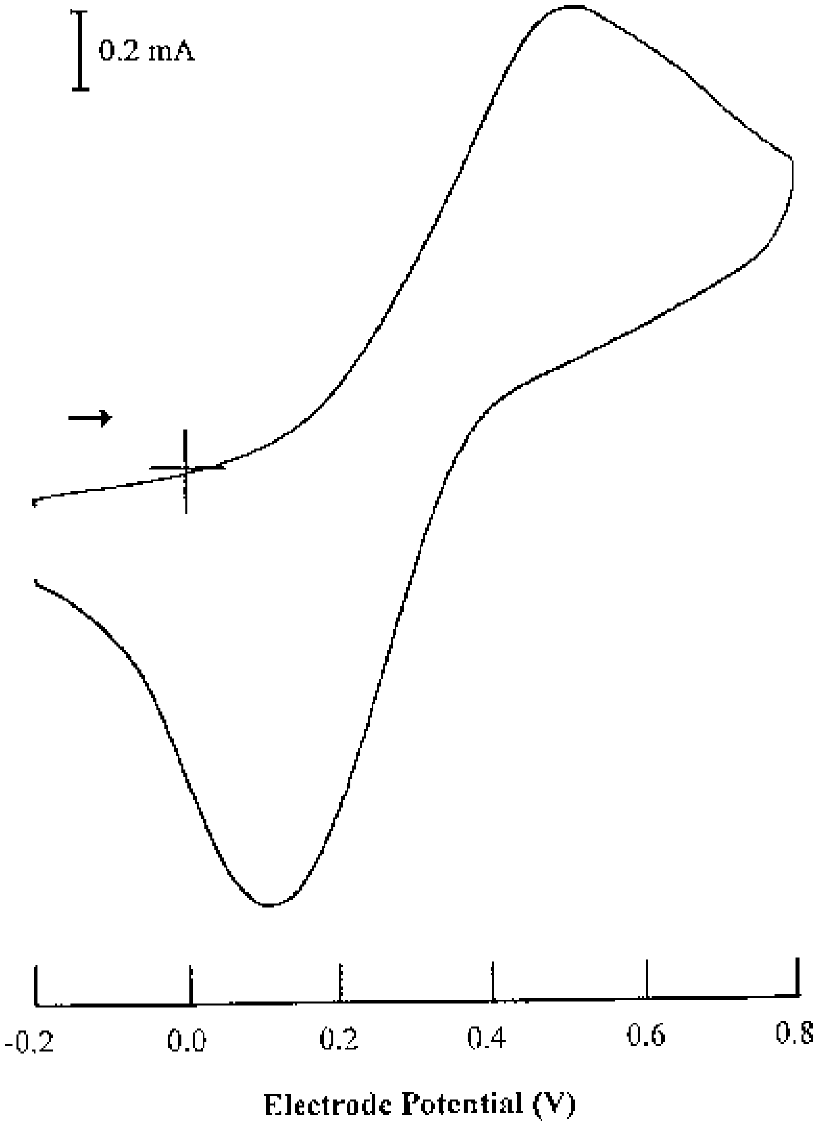


Fig. 3.3.38: CV of a PANI/CH_3-PANI/SiO_2 electrode (5 cycles) in an aqueous solution containing 0.01 Hydroquinone + 0.1 M Na_2SO_4.

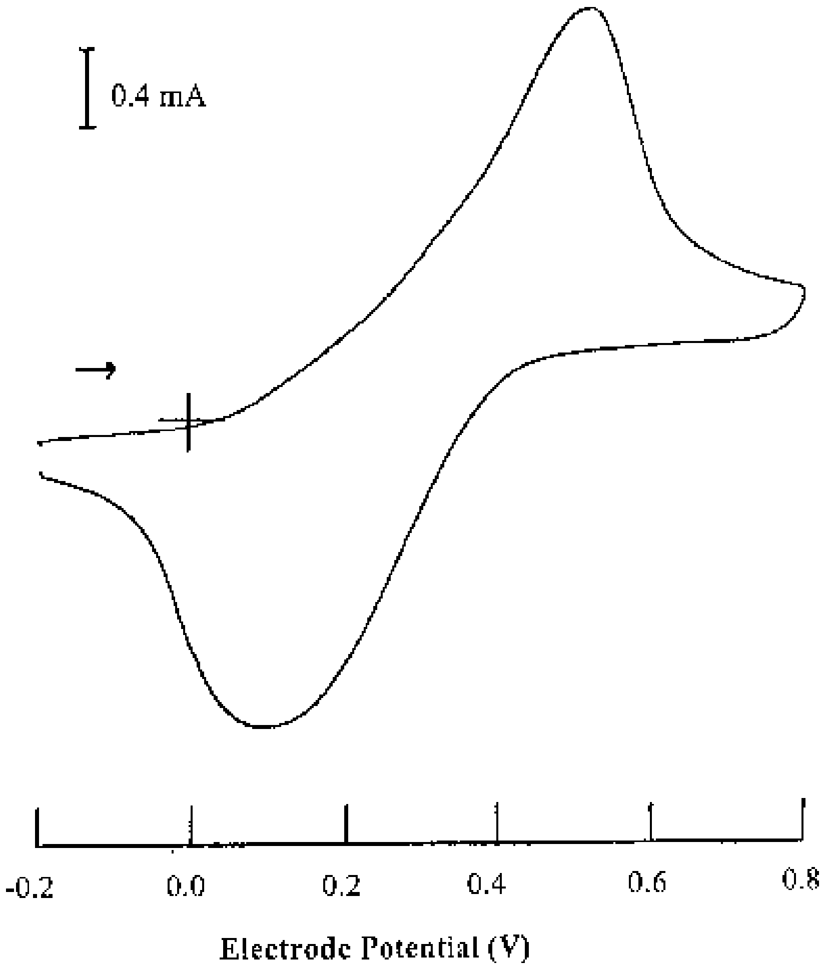


Fig. 3.3.39: CV of a PANI/CH_3-PANI/SiO_2 electrode (10 cycles) in an aqueous solution containing 0.01 M Hydroquinone + 0.1 M Na_2SO_4.

Redox behavior of the modified PP coated Pt electrode, when PP film was prepared from an aqueous solution containing 0.5 M pyrrole and 0.1 M $LiClO_4$, are shown in Figs. 3.3.40 - 3.3.41 and the results are summarized in the following Table-3.3.8:

Table-3.3.8: Redox behavior of PP electrode

Electrolyte solution	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.1 M $K_4Fe(CN)_6$	1	+0.42	+0.07
0.01M HQ + 0.1 M Na_2SO_4	1	+0.51	+0.13

It can be seen from the results that the oxidation potential for the oxidation of ferrous to ferric was slightly lower (+0.42 V) for the modified PP coated Pt electrode than that (+0.44 V) for the bare Pt electrode but the reduction potential was slightly higher in the case of PP electrode. And for the Q/QH_2 system, the oxidation potential is much smaller (+0.51 V) for PP electrode than that (+0.60 V) for the bare Pt electrode but the reduction potential is slightly higher. These observations suggest that with the modified PP electrode, the oxidation of ferrous and hydroquinone could have been easier compared to that on the bare Pt electrode.

G. PANI/PP Electrode

Then a film of copolymer comprising PANI and PP was synthesized electrochemically and coated as before onto the bare Pt electrode to use the coated electrode as a modifier in analyzing the redox behaviors of the couples Fe^{2+}/Fe^{3+} and H_2Q/Q in aqueous medium. Redox behavior of the PANI/PP coated Pt electrode, when PANI/PP film was prepared from an aqueous solution containing 0.5 M aniline, 0.5 M pyrrole, 0.1 M $LiClO_4$ and 0.8 M H_2SO_4, are shown in Figs. 3.3.42 - 3.3.43. The results are summarized in the following Table - 3.3.9:

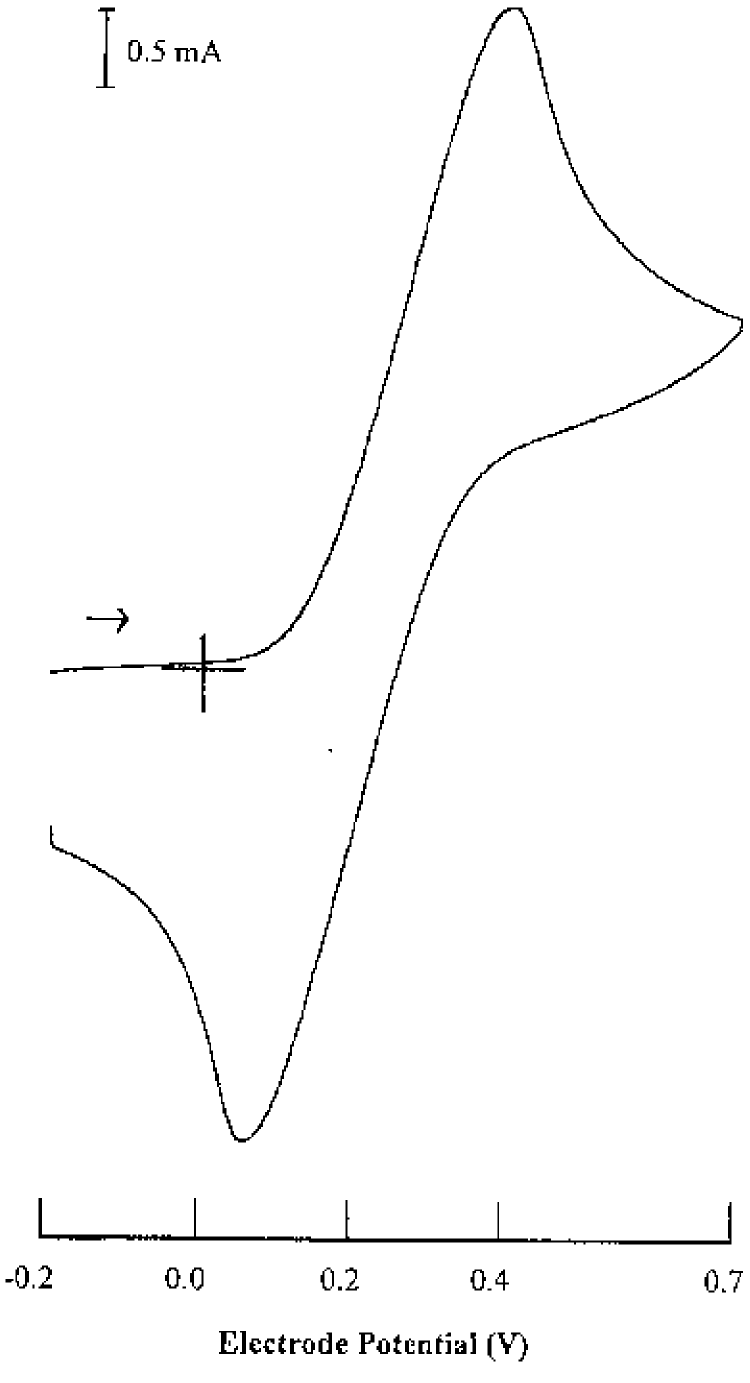


Fig. 3.3.40: CV of a PP electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PP film was prepared from an aqueous solution containing 0.5 M pyrrole and 0.1 M $LiClO_4$.

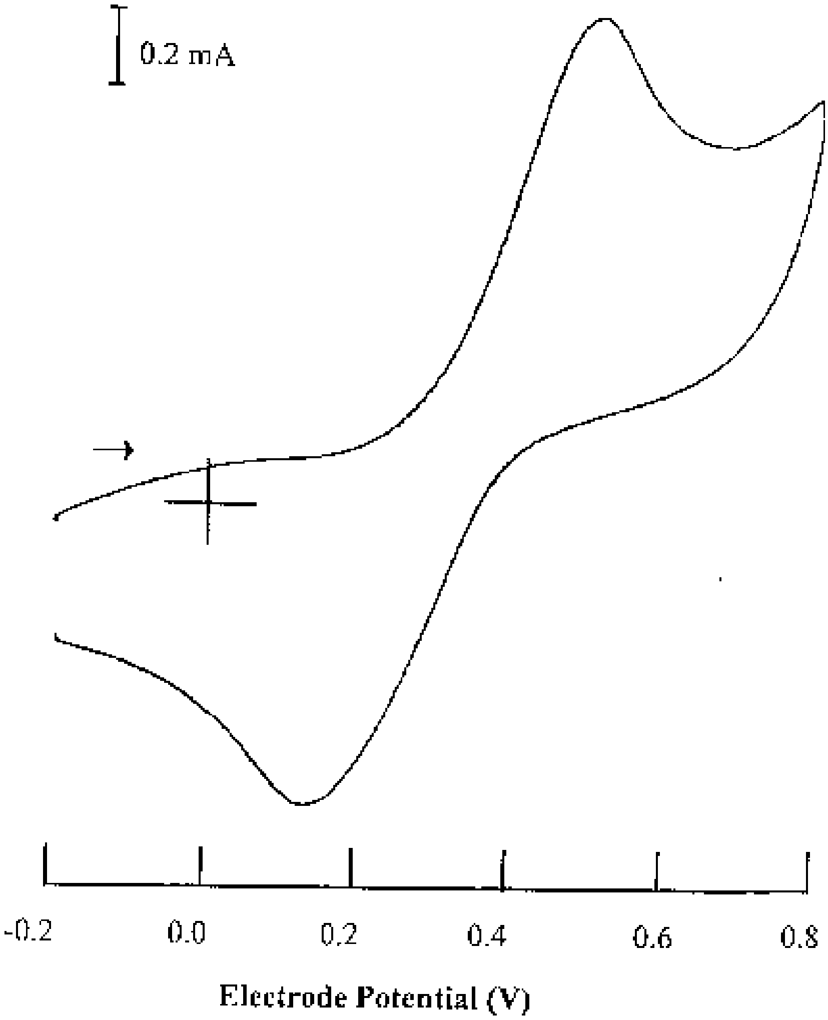


Fig. 3.3.41: CV of a PP electrode (1 cycle) in an aqueous solution containing 0.01 M Hydroquinone + 0.1 M Na_2SO_4. PP film was prepared from an aqueous solution containing 0.5 M pyrrole and 0.1 M $LiClO_4$.

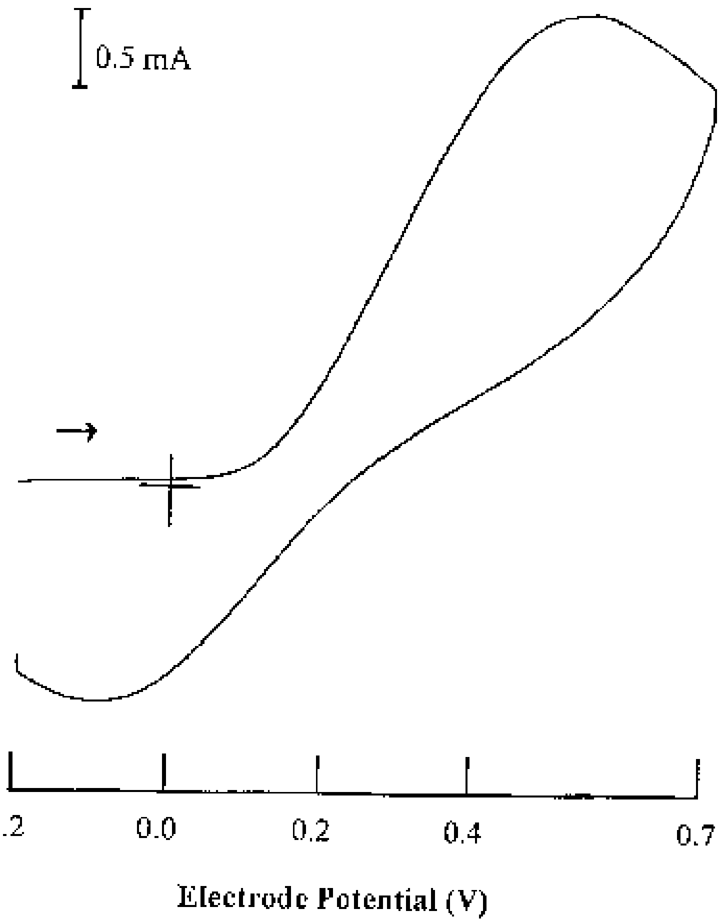


Fig. 3.3.42: CV of a PANI/PP electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI/PP film was prepared from an aqueous solution containing 0.5 M aniline, 0.5 M pyrrole, 0.1 M $LiClO_4$ and 0.8 M H_2SO_4.

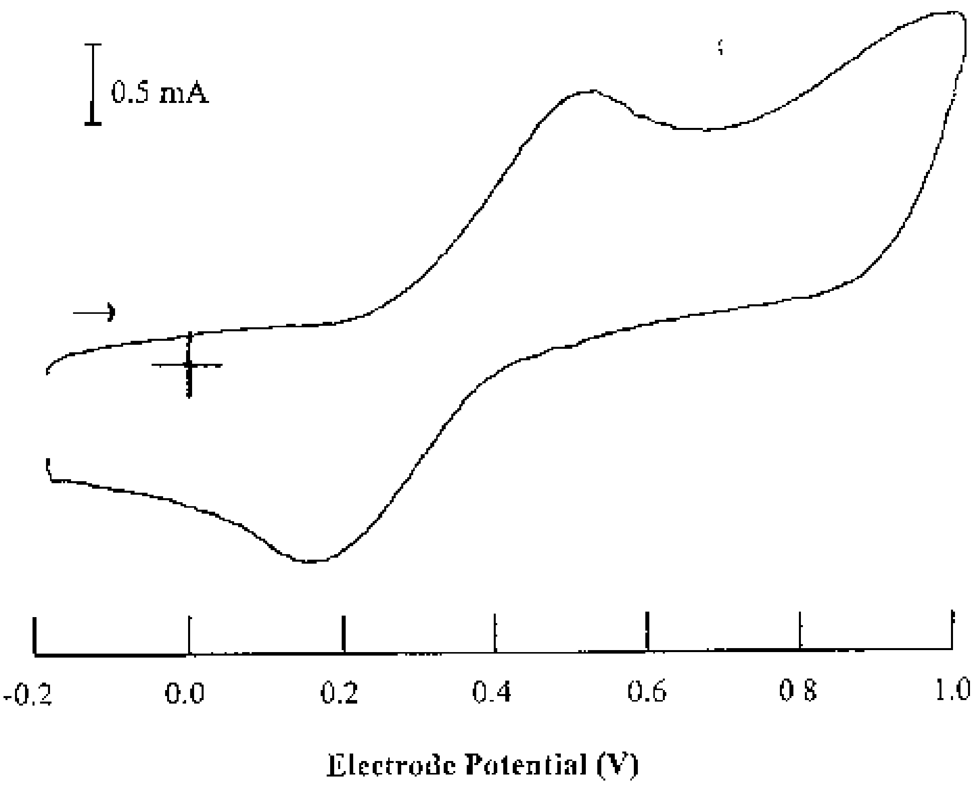


Fig. 3.3.43: CV of a PANI/PP electrode (1 cycle) in an aqueous solution containing 0.01 M Hydroquinone + 0.1 M Na_2SO_4. PANI/PP film was prepared from an aqueous solution containing 0.5 M aniline, 0.5 M pyrrole, 0.1 M $LiClO_4$ and 0.8 M H_2SO_4.

Table-3.3.9: Redox behavior of PANI/PP electrode

Electrolyte solution	Oxidation Potential (V)				Reduction Potential (V)			
	Bare Pt electrode	PANI electrode	PP electrode	PANI/PP electrode	Bare Pt electrode	PANI electrode	PP electrode	PANI/PP electrode
0.1M $K_4Fe(CN)_6$	+0.44	+0.42	+0.42	+0.57	+0.05	+0.05	+0.07	-0.01
0.01M HQ +0.1M Na_2SO_4	+0.60	+0.49	+0.51	+0.51	+0.09	+0.16	+0.13	+0.17

It can be observed from the result that the oxidation potential of the Fe^{2+}/Fe^{3+} couple was much higher for the modified PANI/PP electrode compared to that for the modified PANI and PP coated Pt electrode It indicates that the oxidation of ferrous to ferric on the PANI/CH_3-PANI coated Pt electrode will be harder. But for the Q/QH_2 system, the oxidation potential is much lower for the modified PANI/PP electrode compared to others. The reduction potential of the copolymer electrode is lower in the case of Fe^{2+}/Fe^{3+} system but higher in case of the Q/QH_2 system. So it can be stated that PANI/PP coated Pt electrode can easily be used as a new modified electrode for such two electron oxidation system because both oxidation and reduction can happen within a small range of potential.

II. PANI/PP/SiO_2 Electrode

The matrix PANI/PP was further modified by dispersing SiO_2 in it. The resulted composite matrix PANI/PP/SiO_2 was then coated onto the Pt surface to use the composite film as an electrode modifier. The details of the preparation PANI/PP/SiO_2 composite has been discussed elsewhere in the experimental section. Redox behavior of the PANI/PP/SiO_2 coated Pt electrode is shown in Figs 3.3.44 - 3.3.45. The observed results are summarized in the following Table-3.3.10:

Table-3.3.10: Redox behavior of PANI/PP/SiO_2 electrode

Electrolyte solution	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.1 M $K_4Fe(CN)_6$	1	+0.44	+0.04
0.01M HQ + 0.1 M Na_2SO_4	1	+0.55	+0.16

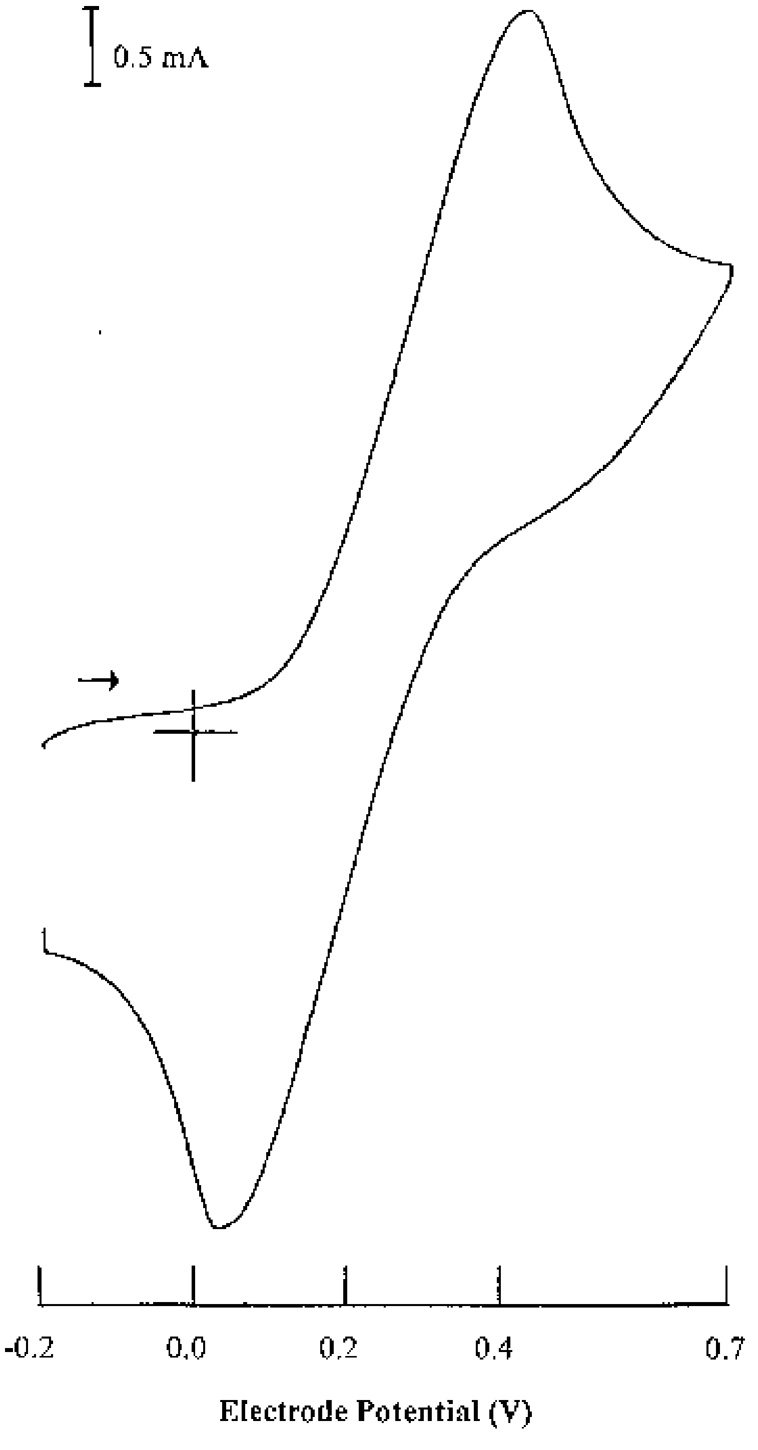


Fig. 3.3.44: CV of a PANI/PP/SiO_2 electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$.

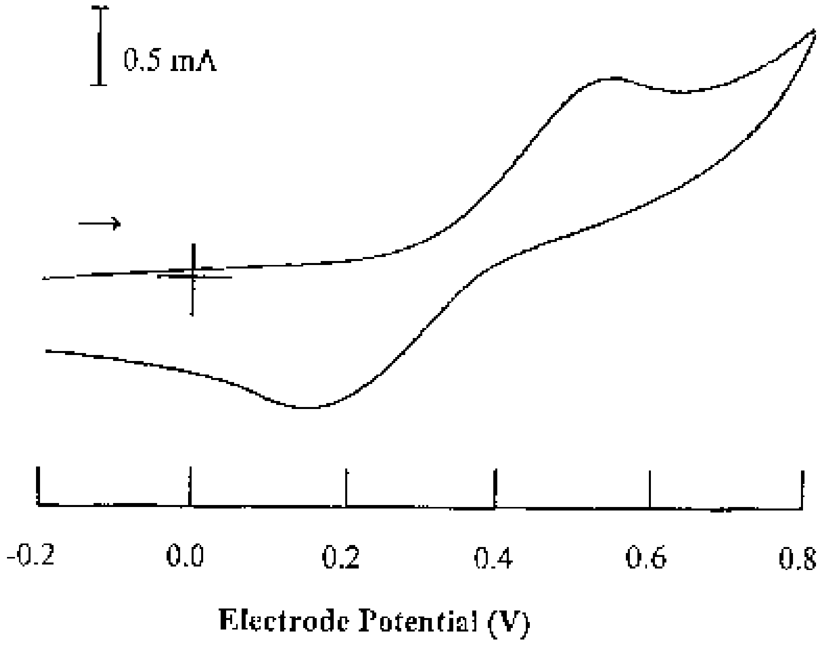


Fig. 3.3.45: CV of a PANI/PP/SiO_2 electrode (1 cycle) in an aqueous solution containing 0.01 M Hydroquinone + 0.1 M Na_2SO_4.

Using PANI/PP/SiO$_2$ modified electrode, the results show a lower oxidation potential for the ferrous/ferric system but slightly higher for the two electron transfer oxidation quinone/hydroquinone system. The reduction potential was found at slightly higher value for Fe^{2+}/Fe^{3+} system for the modified PANI/PP/SiO$_2$ coated Pt electrode than that for the PANI/PP electrodes.

I. PABA Electrode

PABA is one of the less studied conducting polymers. However, PABA was utilized in this work to modify the Pt electrode and the electrode thus modified was then used to control the redox processes for the Fe^{2+}/Fe^{3+} and H$_2$Q/Q couples. Redox behavior of the modified PABA coated Pt electrode, when PABA film was prepared from an aqueous solution containing 0.5 M 2-amino benzoic acid and conc. H$_2$SO$_4$, as shown in Figs. 3.3.46 - 3.3.48. The results are summarized in the following Table - 3.3.11:

Table-3.3.11: Redox behavior of PABA electrode

Electrolyte solution	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.1 M K$_4$Fe(CN)$_6$	1	+0.50	-0.09
	5	+0.47	+0.05
	10	+0.45	-0.06

The result shows that the oxidation potential for the oxidation of ferrous to ferric was slightly higher (+0.50 V) for the modified PABA coated Pt electrode than that (+0.44 V) for the bare Pt electrode but the reduction potential was slightly lower in the case of PABA electrode. So the range of potential that have to apply for this redox reaction somehow increased. When the thickness of the PABA was increased oxidation occurred at more or less in the similar potential range. These observations suggest that the PABA can be used as a modified electrode to study the redox couple Fe^{2+}/Fe^{3+} in aqueous solution. The present study also demonstrate that the less studied PABA could be an efficient modifier and able to act as high as those of well studied conductive polymers like PANI, PP etc.

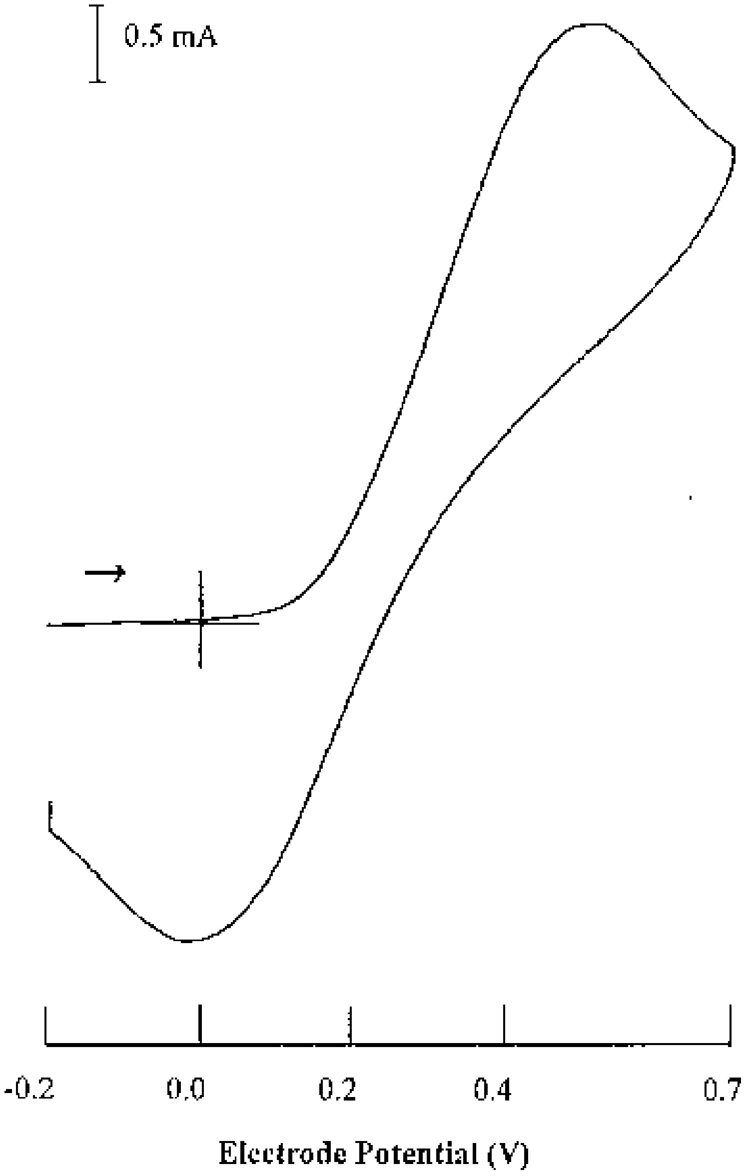


Fig. 3.3.46: CV of a PABA electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PABA film was prepared from an aqueous solution containing 0.5 M 2-amino benzoic acid and conc. H_2SO_4.

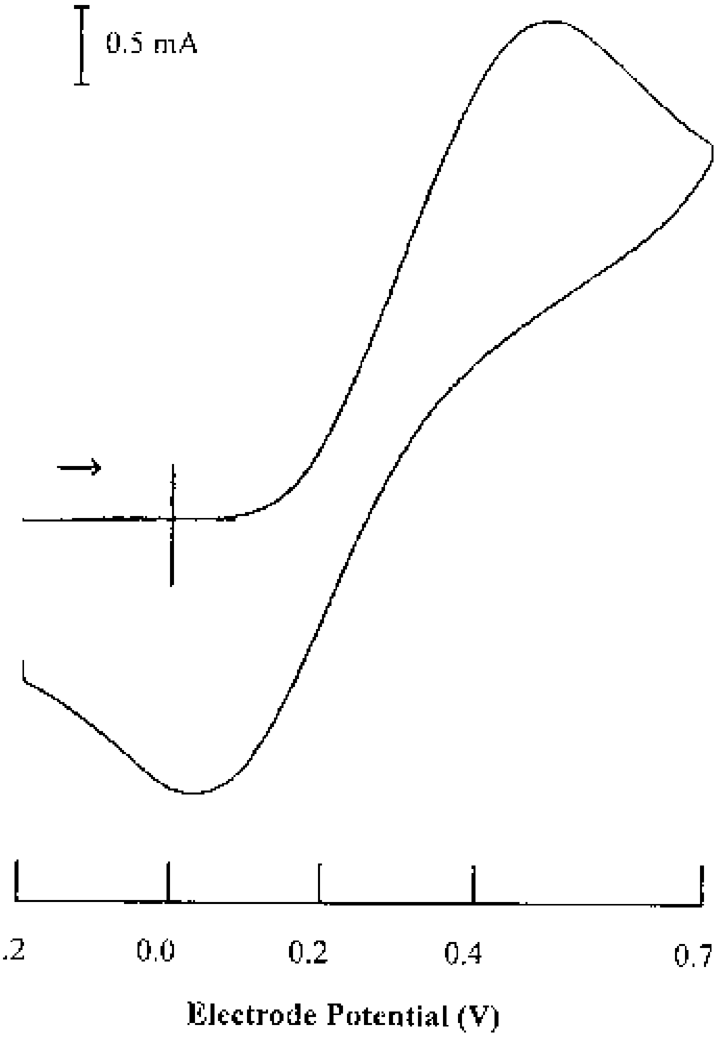


Fig. 3.3.47: CV of a PABA electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PABA film was prepared from an aqueous solution containing 0.5 M 2-amino benzoic acid and conc. H_2SO_4.

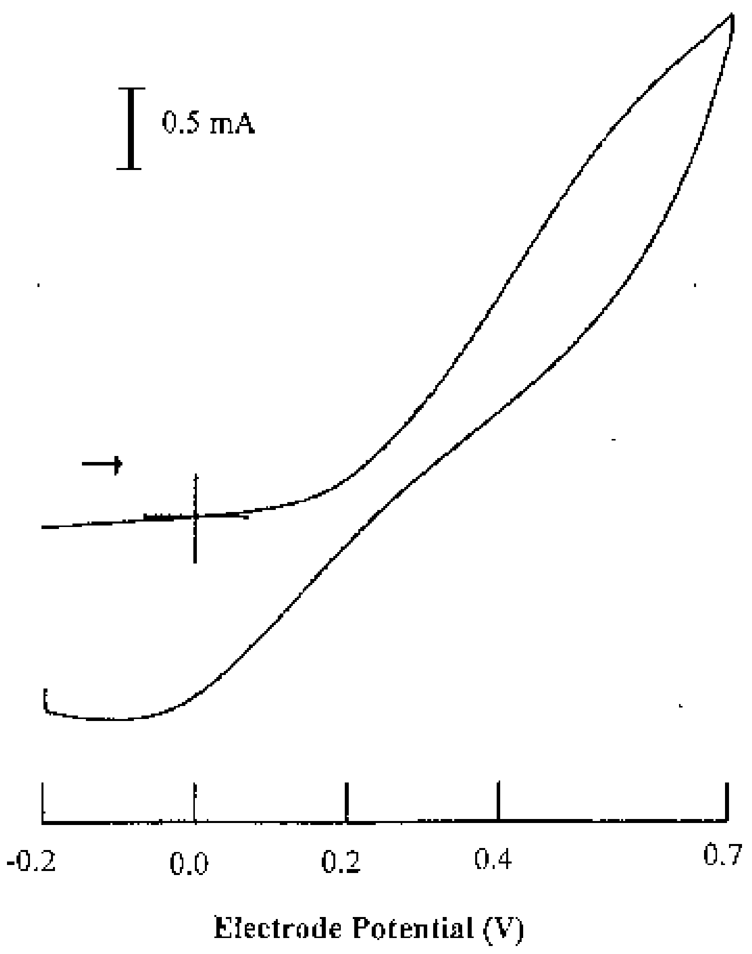


Fig. 3.3.48: CV of a PABA electrode (10 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PABA film was prepared from an aqueous solution containing 0.5 M 2-amino benzoic acid and conc. H_2SO_4.

J. PANI/PABA Electrode

Study with PABA was further extended by preparing a copolymer with PANI. The copolymer PANI/PABA film was synthesized electrochemically and deposited onto a Pt substrate following the same procedure mentioned earlier. The resulting PANI/PABA film was then used as modified electrode and analyzed the redox behavior for the Fe^{2+}/Fe^{3+} and H_2Q/Q couples. Redox behavior of the modified PANI/PABA coated Pt electrode, when PANI/PABA film was prepared from an aqueous solution containing 0.5 M aniline, 0.5 M 2-amino benzoic acid and concentrated H_2SO_4, are shown in Figs. 3.3.49 - 3.3.51. The observed features are summarized in the following Table-3.3.12:

Table-3.3.12: Redox behavior of PANI/PABA electrode

Electrolyte solution	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.1 M $K_4Fe(CN)_6$	1	+0.45	+0.06
	5	-	-
	10	-	-

It is observed from the result that the oxidation potential of the Fe^{2+}/Fe^{3+} system was slightly lower for the modified PANI/PABA electrode (1 cycle) compared to that for the modified PABA coated Pt electrode. It indicates that the oxidation of ferrous to ferric on the PANI/PABA coated Pt electrode will be easier than this oxidation on PABA electrode. The reduction of ferric ion to ferrous ion happened at comparatively less negative potential. So it can be stated that PANI/PABA coated Pt electrode can easily be used as a new modified electrode for such one electron oxidation systems because both oxidation and reduction can happen at the lower potential. However, on thickening the copolymer film the redox response could hardly be observed on the PANI/PABA films (5, 10 cycle thick).

K. CH_3-PANI/PABA Electrode

Attempt was also made to synthesis a copolymer of CH_3-PANI/PABA by adopting the same electrochemical means and to coat a Pt surface with the film of the copolymer for its use as modified electrode to detect redox responses of the Fe^{2+}/Fe^{3+} and H_2Q/Q couples. Redox behavior of the modified CH_3-PANI/PABA coated Pt electrode, when CH_3-PANI/PABA film was prepared from an

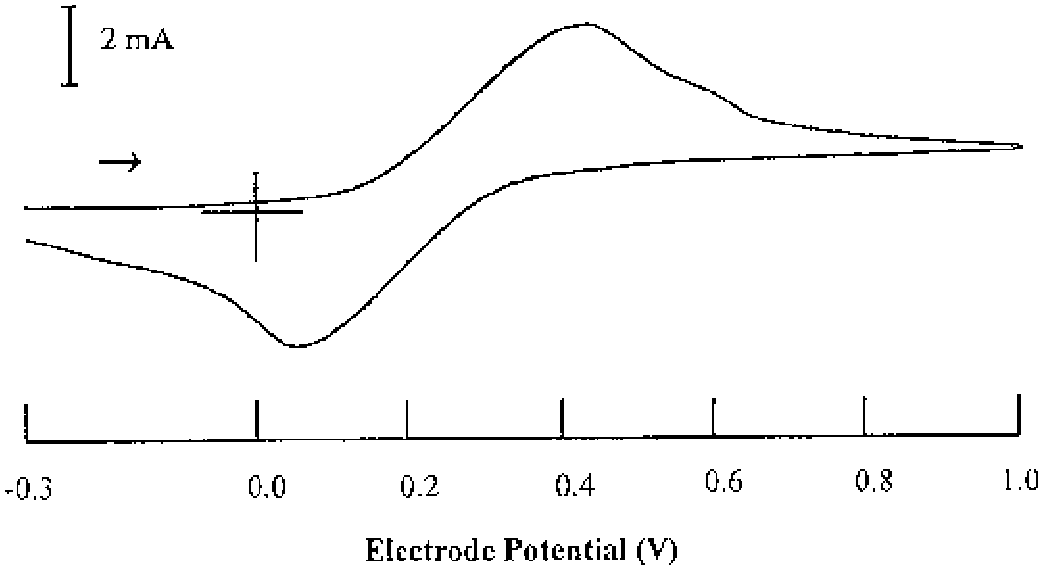


Fig. 3.3.49: CV of a PANI/PABA electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI/PABA film was prepared from an aqueous solution containing 0.5 M aniline, 0.5 M 2-amino benzoic acid and 0.8M H_2SO_4.

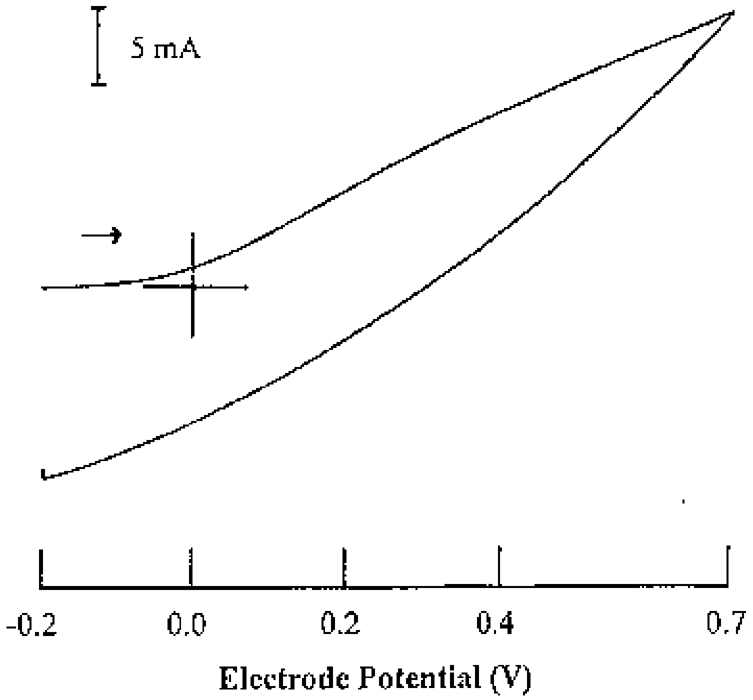


Fig. 3.3.50: CV of a PANI/PABA electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI/PABA film was prepared from an aqueous solution containing 0.5 M aniline, 0.5 M 2-amino benzoic acid and 0.8M H_2SO_4.

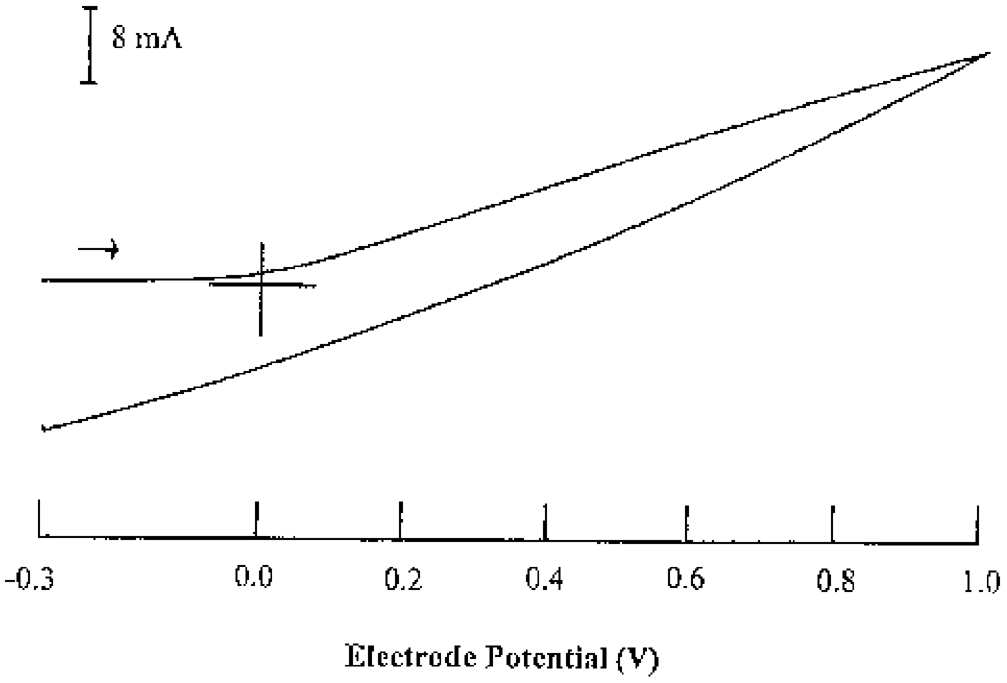


Fig. 3.4.51: CV of a PANI/PABA electrode (10 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. PANI/PABA film was prepared from an aqueous solution containing 0.5 M aniline, 0.5 M 2-amino benzoic acid and 0.8M H_2SO_4.

aqueous 0.8M H_2SO_4 solution containing 0.5M *o*-toluidine and 0.5M 2-amino benzoic acid, are shown in Figs. 3.3.52 - 3.3.54. The results are summarized in the following Table - 3.3.13:

Table-3.3.13: Redox behavior of CH_3-PANI/PABA electrode

Electrolyte solution	Thickness (No. of cycles)	Oxidation Potential (V)	Reduction Potential (V)
0.1 M $K_4Fe(CN)_6$	1	+0.41	+0.06
	5	+0.41	+0.06
	10	+0.45	+0.02

It can be seen from the table that the oxidation of the Fe^{2+} occurred at slightly lower potential when the modified CH_3-PANI/PABA electrode was used instead of PANI, PABA or PANI/PABA electrode. So among the modified electrodes studied, CH_3-PANI/PABA coated Pt electrode seems to be suitable for the oxidation reaction of ferrous ion. The reduction potential of Fe^{3+} for CH_3-PANI/PABA is identified with that of the PANI/PABA and less negative than PABA electrode. So it can be stated that CH_3-PANI/PABA coated Pt electrode can easily be used as a useful electrode modifier for one electron oxidation systems because both oxidation and reduction can happen within a small potential window. Furthermore, the CH_3-PANI/PABA film seems to be redox responding even its thickness got increased to 5 or 10 cycle thick. This might open an opportunity to fabricate organic modified electrodes having 3-D orientations and should have application in electronics and opto-electronic sensing devices.

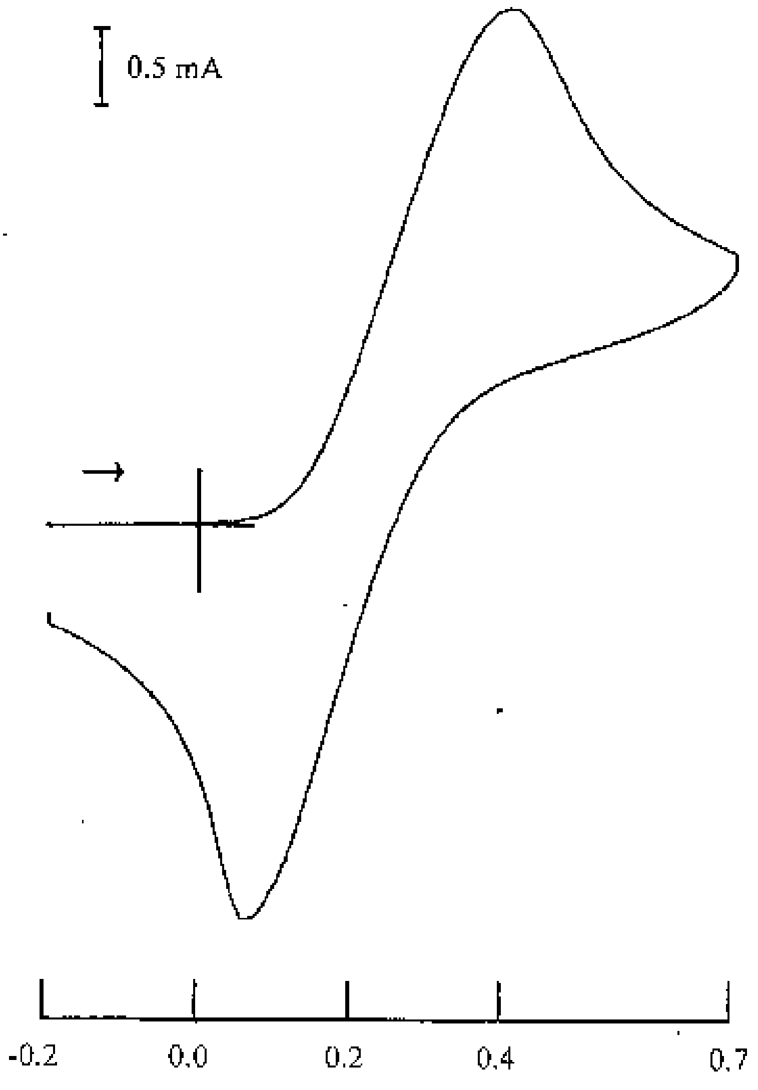


Fig. 3.3.52: CV of a CH_3-PANI/PABA electrode (1 cycle) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. CH_3-PANI/PABA film was prepared from an aqueous 0.8M H_2SO_4 solution containing 0.5 M *o*-toluidine and 0.5M 2-amino benzoic acid.

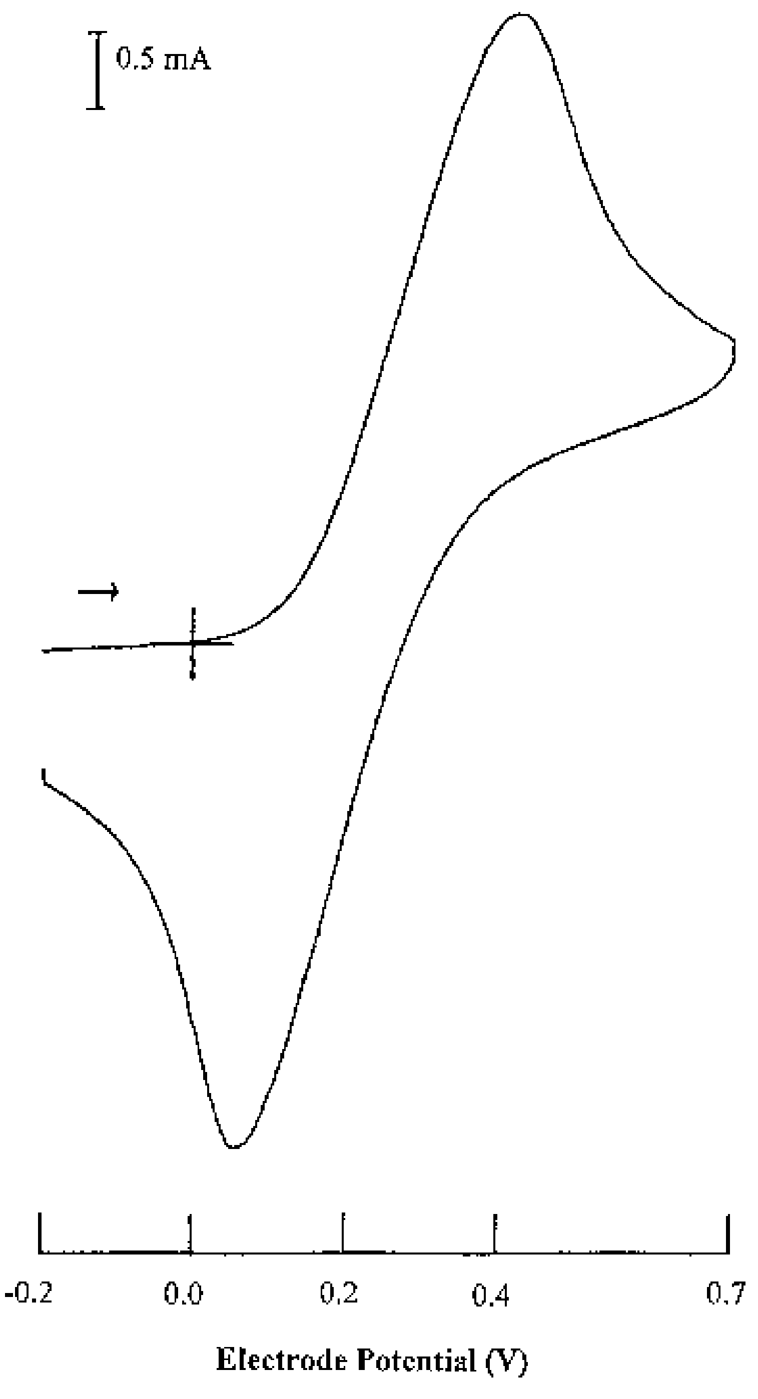


Fig. 3.3.53: CV of a CH_3-PANI/PABA electrode (5 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. CH_3-PANI/PABA film was prepared from an aqueous 0.8M H_2SO_4 solution containing 0.5 M *o*-toluidine and 0.5M 2-amino benzoic acid.

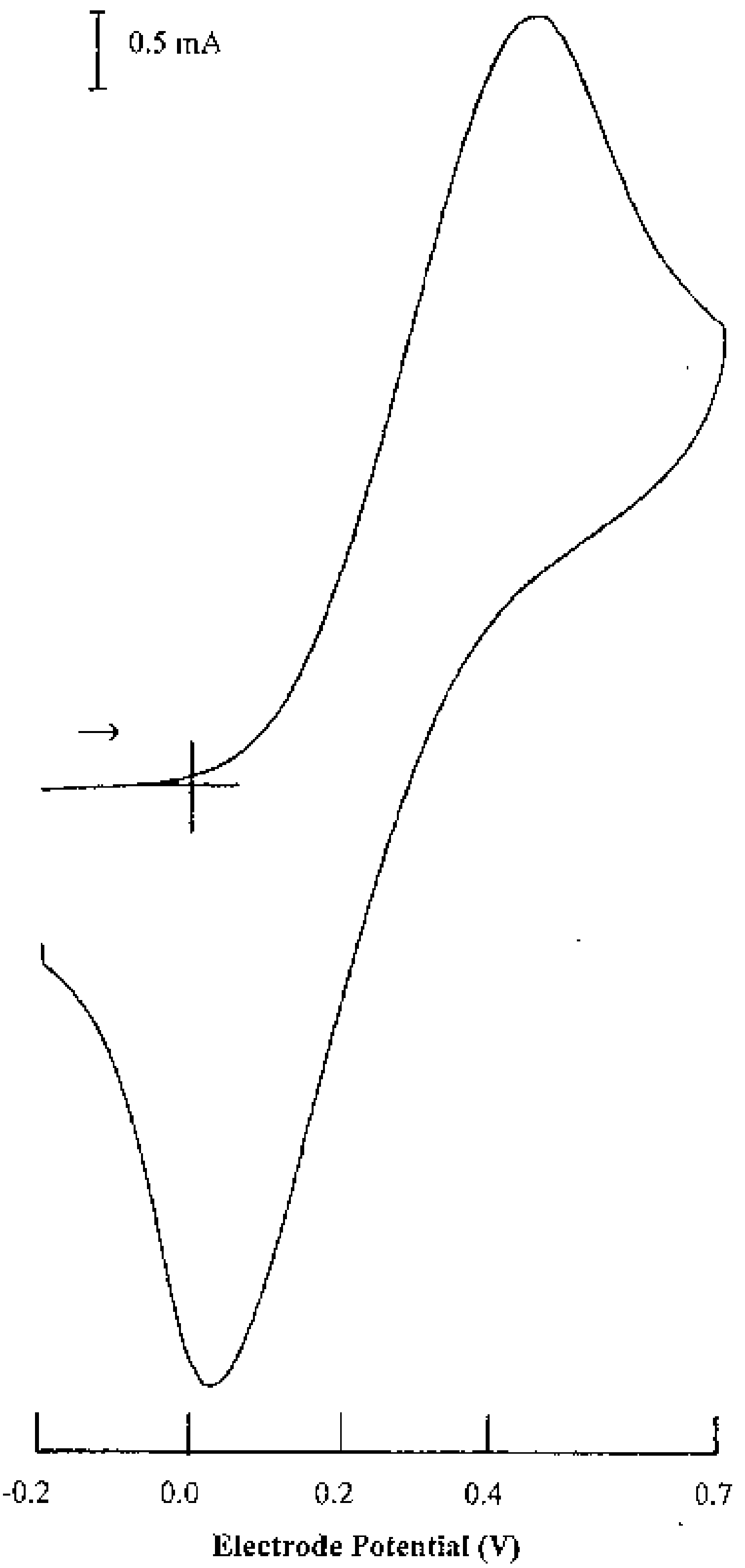


Fig. 3.4.54: CV of a CH_3-PANI/PABA electrode (10 cycles) in an aqueous solution containing 0.1 M $K_4Fe(CN)_6$. CH_3-PANI/PABA film was prepared from an aqueous 0.8M H_2SO_4 solution containing 0.5 M *o*-toluidine and 0.5M 2-amino benzoic acid.

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3.4 Conclusion

Simple electrochemical method provides a facile route for the preparation of conductive polymeric film on a working Pt electrode. The films of co-polymer and its composites with SiO_2 were also found to be prepared with the electrochemical technique. The polymeric films thus prepared were sufficiently free-standing and adhere to the Pt electrode. The free-standing Pt coated polymeric electrodes were found to be good to use as modified electrode to carry out some standard redox processes.

UV-Vis and IR spectra of electrode matrices confirmed the presence of conducting polymeric component and SiO_2 in the matrices studied. The conductivity of the matrices were measured by a two point-probe technique. The conductivity of the studied samples were found to be comparable with that of the conventional inorganic semiconductors suggesting that these material can be used as electrode like the conventional semiconductor. The morphology of the electrode surface were investigated. Formation of polymer, co-polymer and composite matrices results dissimilar surface morphologies for each. The dissimilar surface is very significant in performing any surface processes on it. Indeed, these polymeric matrices were employed as electrode surface in the present work.

The polymeric electrode matrices showed good electro activity both in aqueous and non aqueous solvent. The voltametric features confirmed that these polymeric electrodes can be switched between doped (conductive) to dedoped (insulating) states with concomitant color change. This result suggests their potential use as the new electrode materials.

The electroactivity of the polymeric matrice were found to be suitable in performing some redox reaction on their surfaces. The redox reactions for the couple Fe^{+2} / Fe^{+3} and H_2Q /Q were successfully performed on the polymeric electrode surface. The anodic and cathodic processes involved in these redox reactions were comparable to that performed on the noble Pt metal surface. Thus, it may be concluded that modification of metal electrode with the conducting polymeric components results in a new class of electroactive electrode system which is work friendly both in aqueous and non-aqueous media of an electrochemical system. The critical electrochemical conditions hardly affect the surface of the polymeric electrodes to result any deactivation.