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Electronic properties of novel polypyrrole and polyaniline materials: a resistometric approach

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**ELECTRONIC PROPERTIES OF NOVEL
POLYPYRROLE AND POLYANILINE MATERIALS:
A RESISTOMETRIC APPROACH**

A thesis submitted in fulfilment of the requirements for the award of the
degree of

DOCTOR OF PHILOSOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

AFSHAD TALAIE (B.E., M.E., M.Sc.)

CHEMISTRY DEPARTMENT

DECEMBER, 1994

This is to certify that the work described in this thesis has not been submitted for a higher degree at any other university or institution.

Afshad Talaie

In Memoriam

I dedicate this thesis to the memory of my beloved people whose blood and lives saved Iran during the recent 8 year war. If Iran was not as it is I would not be able even to think of Ph.D study. I would like also to dedicate this thesis to the following people:

1. My family including parents, sisters and brothers whose prayers and encouragement have given me a great motivation and impetus to achieve whatever I have tried so far.
2. Tony Zwing a real "great man".
3. Those scientiscts who dedicated their lives for peace and equality.

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II

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Finally, my very very special thanks to my family, my parents, my sisters and my brothers of whom I am very proud. The family who has provided everything for me to achieve my goals. Being part of this family means having great motivation to achieve whatever positive goals one has. Their prayers and support for me have been continuous.

ABSTRACT

In this project two different resistometric strategies, DC and pulse resistometry, have been employed. Both DC and pulse resistometry can be used to monitor changes in resistance of conducting polymers as a function of applied potential. Care should be taken in any quantitative comparison of the measurements obtained, since the technique used for resistance measurements are not identical. However, it can be said that the DC resistometry method is capable of providing data on the rate of change of resistance as a function of applied potential more sensitively than the pulse method. In contrast, the pulse method is more applicable over a wider potential range.

The switching properties of conducting polymers are critical to numerous applications. The resistance/potential (R/E) profiles obtained in this investigation, have been shown to be dependent on various parameters. These includes the nature of the monomer and counterion used, the method of growth and the nature of the electrolyte solution.

In this thesis, a new simultaneous analysis technique was also introduced by a combination of several simple methods. This technique denoted S.M.A.C. enables the relationship between charge transfer, mass changes and resistance changes to be determined simultaneously, in-situ and in 'real time'. Using this method the effect of the chaotropic nature of the cations used in the electrolyte solution on the R/E profile of conducting polymers was examined. It was found that the nature of the cation, while not obvious in cyclic voltammetry, has a marked effect on the changes in resistance and mass that occur within the polymer upon reduction/oxidation.

IV

The effect of pH on the resistance of the polymer has also been studied. The DC technique was mainly used for pH detection studies in both the stationary and the flow system. Different polymeric sensing materials including PPy/Cl, PPy/PVS, PAn/Cl and PPy/PVS-PAn/Cl were employed. Interesting results were observed when PPy/PVS was used. In the flow system a new approach to the configuration and the shape of sensing material was applied using a "moving tape". The moving tape experimental results hold promise further investigation of pH detection.

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19. **A. Talaie**, and G.G. Wallace, "Effect of electrolyte composition on the electrodynamic properties of conducting polymers:The chaotropic effect", Synth. Met., Submitted.

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ABBREVIATIONS

A	Surface area
A ⁻	Anion
Ag/AgCl	Silver/silver chloride reference electrode
BSA	Benzenesulfonic acid
CV	Cyclic voltammetry
CR	Cyclic resistometry
DBSA	Dodecylbenzenesulfonic acid
E	Potential
EQCM	Electrochemical quartz crystal microbalance
F	Oscillation frequency of a quartz crystal electrode
g	Gram
Hz	Hertz
i	Current
mC	Millicoulomb
NDS	Naphtalenedisulfonic acid
PAn/Cl	Polyaniline chloride
PPy/Cl	Polypyrrole chloride
PPy/NDS	Polypyrrole naphtalenedisulfonic acid
PPy/PTS	Polypyrrole P-toluene sulfonate
PPy/PVS	Polypyrrole polyvinylsulfonate
PVS	Polyvinylsulfonate acid, sodium salt

Q	Charge
QCM	Quartz crystal microbalance
R	Resistance
R/E	Resistance/potential
SBSA	4-Sufobenzoic acid
V	Volt
vs	Versus

SYMBOLS

DF	Frequency changes
Dm	Mass changes
σ	Conductivity

TABLE OF CONTENTS

ACKNOWLEDGEMENT	I
ABSTRACT.....	III
LIST OF PUBLICATIONS.....	V
ABBREVIATIONS.....	VIII
CHAPTER 1.....	1
GENERAL INTRODUCTION TO CONDUCTING POLYMER SCIENCE AND TECHNOLOGY.....	1
1.1 Historical background.....	2
1.2 The polymerisation process.....	5
1.2.1 Polypyrrole.....	5
1.2.2 Polyaniline.....	8
1.3 Conduction mechanism.....	11
1.3.1 Polypyrrole.....	11
1.3.2 Polyaniline.....	12
1.4 Parameters affecting the conductivity of conducting polypyrrole and polyanilines.....	14

XI

1.4.1 Dopants.....	14
1.4.2 Effect of polymerisation technique on the conductivity of the resultant polymer.....	15
1.4.3 The effect of temperature on the conductivity of the resultant polymer.....	16
1.4.4 Effect of pH.....	16
1.5 Applications.....	17
1.6 techniques for conductivity determination.....	18
1.6.1 A review.....	18
1.6.2 DC and pulse conductivity measurement used in this project...	26
1.6.2.1 DC method.....	26
1.6.2.2 Pulse resistometry.....	27
1.7 Aims of this project.....	29

CHAPTER 2.....30

RESISTOMETRIC STRATEGIES FOR IN_SITU CONDUCTIVITY INVESTIGATIONS INVOLVING CONDUCTIVE ELECTROACTIVE POLYMERS.....30

2.1 Introduction.....	31
2.2 Aims and approach of this chapter.....	31
2.3 Experimental.....	32
2.3.1 Instrumentation.....	32
2.3.2 Reagents and standard solutions.....	33
2.3.3 Procedure.....	34
2.4 Results and discussion.....	37

2.5 Conclusion.....	55
---------------------	----

CHAPTER 3.....	56
----------------	----

THE EFFECT OF THE SULFONATED AROMATIC COUNTERIONS ON THE ELECTROCHEMICAL PROPERTIES OF POLYPYRROLES-A STUDY USING PULSE RESISTOMETRY.....	56
--	----

3.1 Introduction.....	57
3.2 Aims and approach of this chapter.....	57
3.3 Experimental.....	58
3.3.1 Instrumentation.....	58
3.3.2 Reagents and standard solutions.....	59
3.4 Results and Discussion.....	60
3.5 Conclusion.....	72

CHAPTER 4.....	74
----------------	----

DETAILED STUDIES INTO THE SWITCHING PROCESSES FOR POLYPYRROLE/PTS.....	74
---	----

4.1 Introduction.....	75
4.2 Aims and approach of this chapter.....	76
4.3 Experimental.....	76
4.3.1 Instrumentation.....	76

XIII

4.3.2 Reagents and standard solution.....	77
4.4 Results and discussion.....	77
4.4.1 The effect of parameters involved during polymerisation on the polymer resistivity.....	77
4.4.1.1 The galvanostatic method.....	78
4.4.1.2 The potentiostatic method.....	79
4.4.1.3 The potentiodynamic method.....	82
4.4.2 The effect of the parameters involved on the conductivity measurement after polymerisation.....	86
4.4.2.1 The effect of the concentration of the supporting electrolyte.....	86
4.4.2.2 The effect of the nature of the supporting electrolyte..	87
4.4.3 The effect of scan rate on the R/E response.....	88
4.4.4 Effect of overoxidation on the polymer R/E curves.....	90
4.5 Conclusion.....	91

CHAPTER 5.....92

S.M.A.C.-ANOTHER DIMENSION IN ELECTROCHEMICAL ANALYSIS.....92

5.1 Introduction.....	93
5.2 Aims and approach of this chapter.....	94
5.3 Experimental.....	94
5.3.1 The experimental set-up and instrumentation.....	94
5.3.2 Reagents and standard solutions.....	95
5.4 Results and discussion.....	97

5.4.1 Calibration and reliability of the S.M.A.C.....	97
5.4.2 S.M.A.C. study during polymer growth.....	101
5.4.3 S.M.A.C. study after polymerisation.....	105
5.5 Conclusion.....	135

CHAPTER 6.....	136
-----------------------	------------

THE EFFECT OF PH ON THE R/E RESPONSE OF POLYPYRROLE AND POLYANILINE MATERIALS.....	136
---	------------

6.1 Introduction.....	137
6.2 Aims and approach of this chapter.....	138
6.3 Experimental.....	138
6.3.1 Instrumentation.....	138
6.3.2 Reagents and standard solutions.....	138
6.3.3 Procedure.....	139
6.4 Results and discussion.....	139
6.4.1 The stationary system.....	139
6.4.1 Polypyrrole/Cl.....	139
6.4.2 Polypyrrole/PVS.....	144
6.4.3 Polyaniline/Cl.....	146
6.4.4 Polypyrrole/PVS-Polyaniline/Cl composite.....	150
6.4.2 Thw flow system.....	156
6.4.2.1 The sandwich electrode.....	156
6.4.2.2 Moving tape.....	159
6.5 Conclusion.....	164

CHAPTER 7.....165

GENERAL CONCLUSION.....165

REFERENCES.....170

CHAPTER 1

GENERAL INTRODUCTION TO CONDUCTING POLYMER SCIENCE AND TECHNOLOGY

1.1. Historical Background

Synthetic polymers have been known and used as excellent insulators for many years ¹. According to Billingham and Calvert ² "For most of history of the polymer technology one of the most valued properties of these polymers has been their ability to act as excellent electrical insulators....". Over the past 20 years there has been an enormous effort to introduce new materials denoted "conducting polymers" ³. The conductivity of these materials were discussed and compared with metals ⁴. Walton ⁵ pointed out that conducting polymers such as polypyrrole has already matched the conductivity of copper (Fig. 1.1). Heeger ⁴ even raised a question as to whether a conducting polymer can be designed and manufactured with conductivity higher than that of copper. As a result of these investigations there have been many papers published in the Journal of "Synthetic Metals" because of the "metallic" conductivity of conducting polymers ⁶⁻¹⁰.

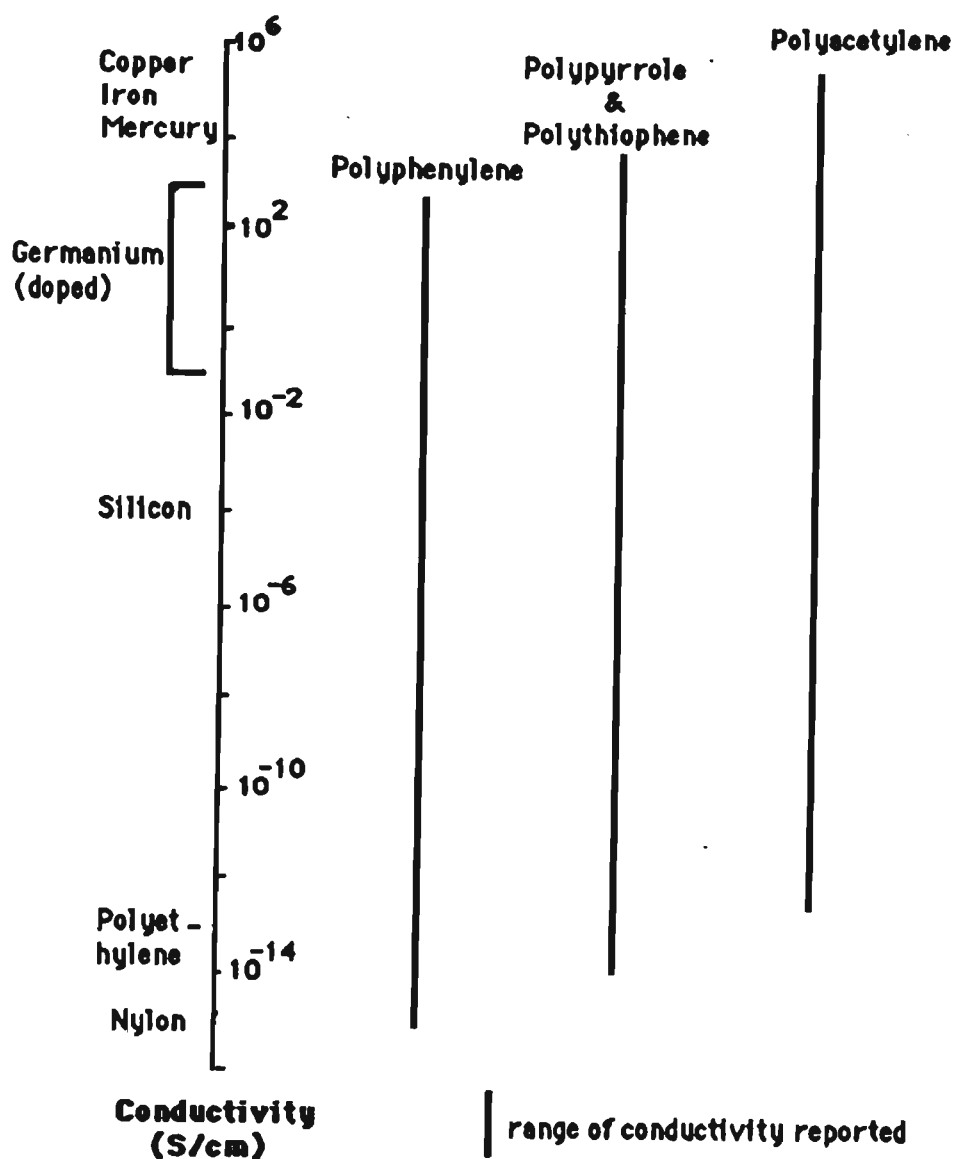


Figure 1.1: Comparison between the conductivity of conducting polymers and metals (see reference 5)

One of the most widely studied conducting polymer, polyacetylene, was first synthesised in 1958 ¹¹. Heeger and MacDiarmid showed that doping polyacetylene with iodine endowed the polymer with metallic properties, including an increase in conductivity of 10 orders of magnitude ^{12,13}.

In 1862, Letheby ¹⁴ reported the anodic oxidation of aniline in a solution of diluted sulphuric acid. However, the current phase of polyaniline research began in 1980, with several group following suit during the following decade ^{15,16}. In 1989, MacDiarmid ¹⁵ argued that the fascination of the conducting polymer community with this challenging and potentially technologically important polymer system can be realised by the fact that there have been almost 500 publications and patents involving this material between only 1986-1989.

In 1968 Dall'Olio ³ reported the formation of pyrrole black on a Pt electrode during the anodic oxidation of pyrrole in dilute sulphuric acid. Conductivity measurements carried out on the isolated solid state materials suggested a conductivity value of 8 S/cm. In 1979, Diaz et.al. ¹⁷ made the first flexible polypyrrole film with a conductivity value of 100 S/cm.

A common feature of all of these three popular conducting polymers (polyacetylene, polyaniline and polypyrrole) is the existence of conjugated double bonds ¹⁸. The chemical structure of these polymers is shown in Fig. 1.2.

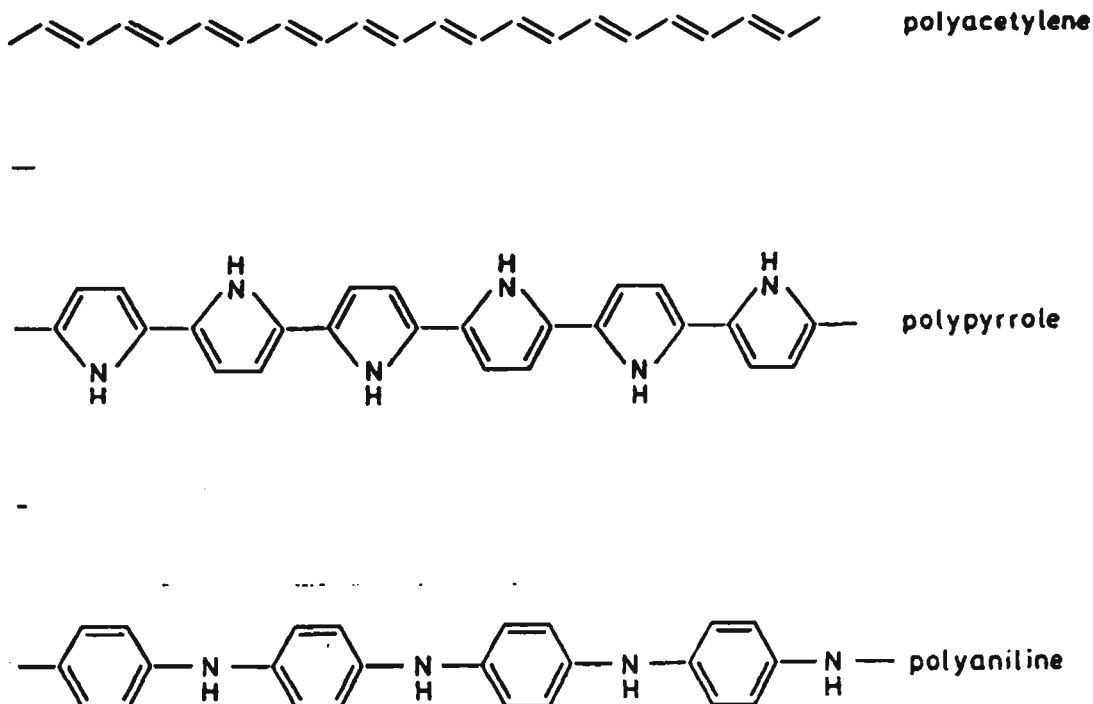


Figure 1.2: Chemical structure of the three most important conducting polymers with conjugated double bond(see reference 18)

1.2. The polymerisation process

1.2.1 Polypyrrole

The most widely used method for producing intrinsically conductive polypyrrole is oxidation of the monomer. This electrosynthesis has two advantages.: (i) the polymers are formed in the doped, i.e. conducting state, and (ii) the films possess favourable mechanical and electrical properties ³.

The mechanism of polymerisation, shown in Fig 1.3, involves the oxidation of the monomer to generate a radical cation ².

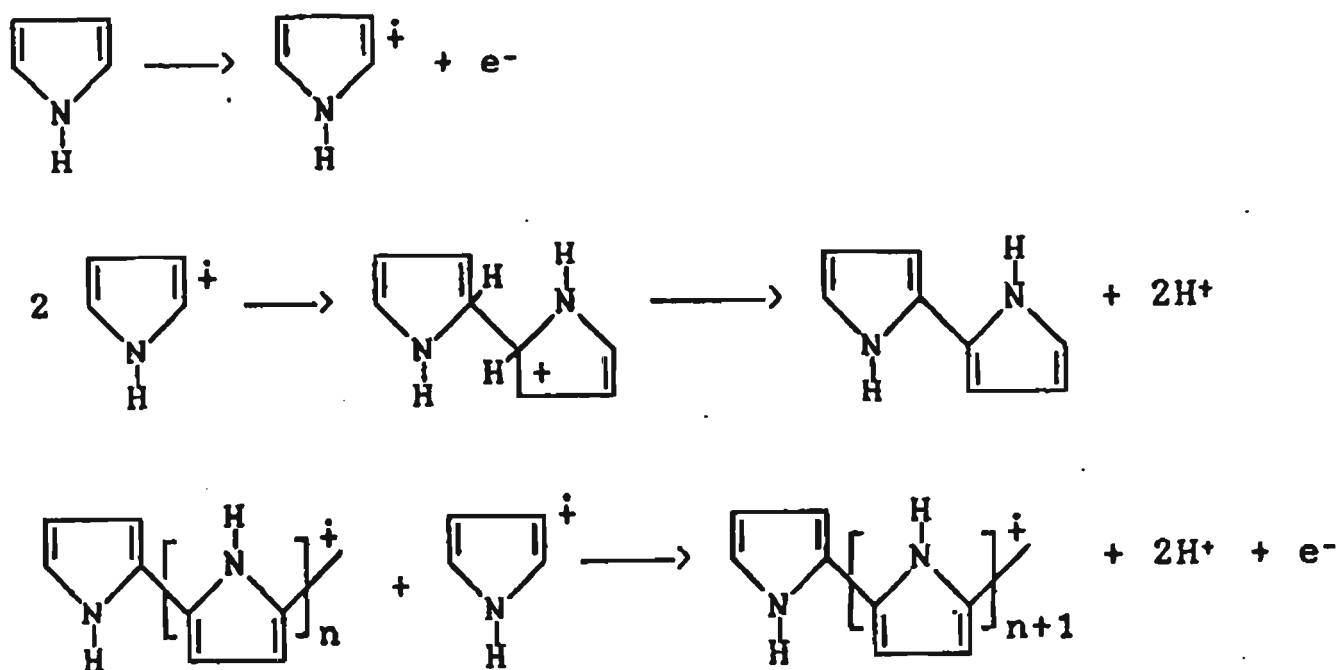


Figure 1.3: *proposed mechanism of electrochemical polymerisation of pyrrole (see references 2 and 3)*

Billingham and Calvert ² said that provided that there are no nucleophiles in the system capable of reacting with the radical cations, they will couple to give a dimeric di-cation, which readily eliminates 2H^+ , re-aromatising to give the polymer dimer. Then the dimer propagation, on the electrode surface, continues to give a high weight polymer at the termination process.

Heinze ³ reviewed the electrodeposition of polypyrrole as well. He believes that there are two possibilities of the electrodeposition mechanism as illustrated in Fig. 1.4.

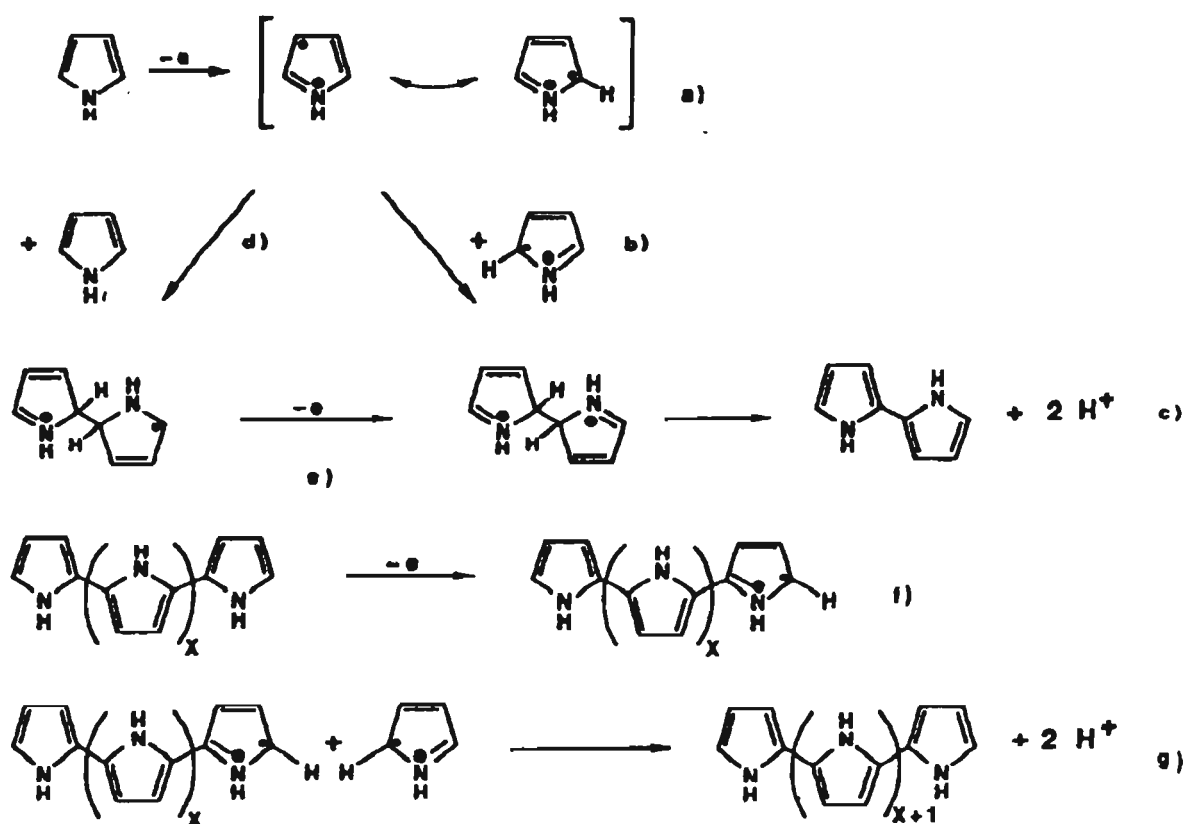


Figure 1.4: Two proposed different mechanism routes of electrodeposition of pyrrole(see reference 3)

Heinze reviewed Diaz et.al. comments ^{19,20} and suggested that "...in the polymerisation of pyrrole the monomers dimerize after oxidation at the electrode and that protons are eliminated from the doubly-charged dihydrodimers, forming the neutral species.". They stated that since the dimer is more easily oxidizable than the monomer, the first possible mechanism is that the dimer is immediately reoxidized to the cation. Chain growth is then accompanied by the addition of new cations of the monomeric pyrrole to the already charged oligomers (dimers). This in turn is followed by another proton elimination and the oxidation of the propagated oligomeric unit to a cation (Fig. 1.4: in the route designated a-b-c-f-g).

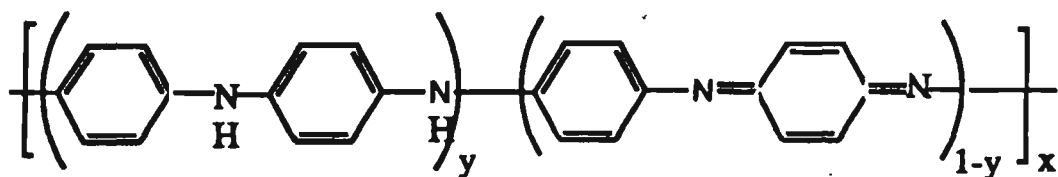
However other researchers ^{3,21-24} who have questioned this mechanism, stated that the strong coulombic repulsion between small cation

radicals renders a direct dimerization of such particles improbable. They believe that electrophilic attack by the radical cation on the neutral monomer produces the single-charged dihydroderivative, which eliminates its proton only after a further charge transfer, becoming the neutral dimer as shown in Fig. 1.4 in the route designated a-d-e-c-f-g.

Heinze ³ believes that this second mechanism does not contain sufficient information to characterise the chain propagation process; as growth is observed experimentally only when the oxidation of the monomer occurs parallel to the oxidation of the film ^{25,26}. Therefore, the best possible mechanism for electrodeposition of pyrrole is what was shown in Figures 1.3 and 1.4: a-b-c-f-g.

1.2.2. Polyaniline

Billingham and Calvert ² have gathered very detailed information on the polymerisation of aniline. They reported part of a review by MacDiarmid et.al.²⁷ who have done many studies of polyaniline. They suggest that polyaniline can exist in the form of a wide range of structures, which can be regarded as copolymers of reduced(amine) and oxidised(imine) units of the following unit:



The fully reduced form($y=1$) is "leucoemeraldine", the fully oxidised form ($y=0$) is " Pernigraniline" and the 50% oxidised structure($y=0.5$) is "

emeraldine". Each of these forms of polyaniline can exist as the base or as its salt, formed by protonation. Thus we can envisage four repeat units in the polymer chain, in amounts which depend on the extent of both oxidation and protonation of the structure as shown in Fig. 1.5.

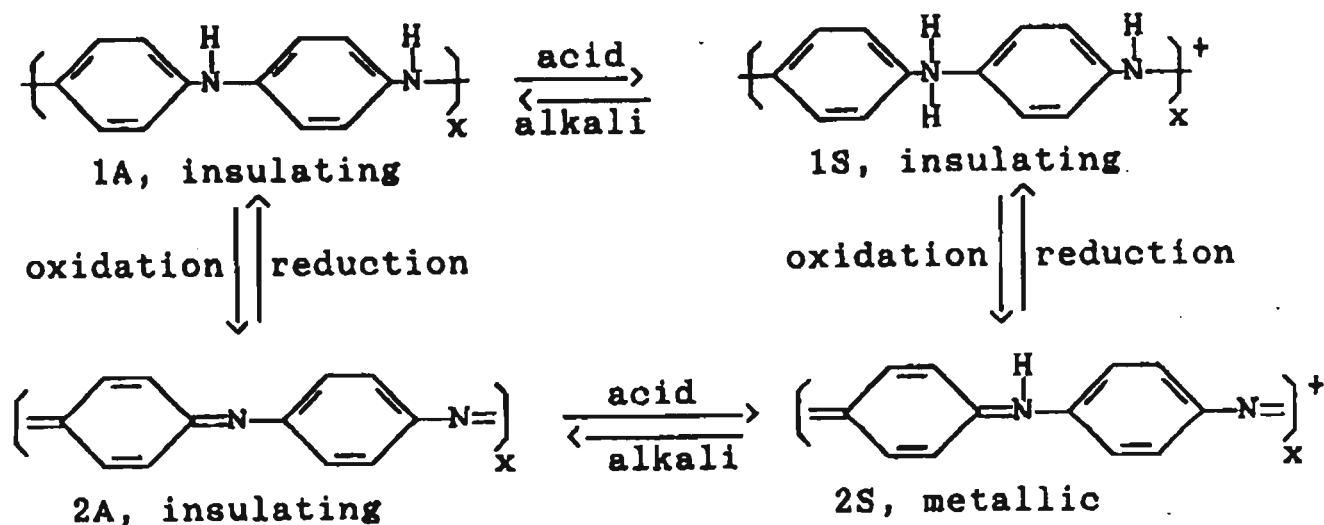


Figure 1.5: *The possible structure of a polyaniline chain*

Several variations of a basic reaction mechanism have been proposed so far which differ in some details but all involve the formation of radical cation intermediates from the aniline 28-32. A general reaction scheme has been provided by Evans ¹¹ and illustrated in Fig. 1.6.

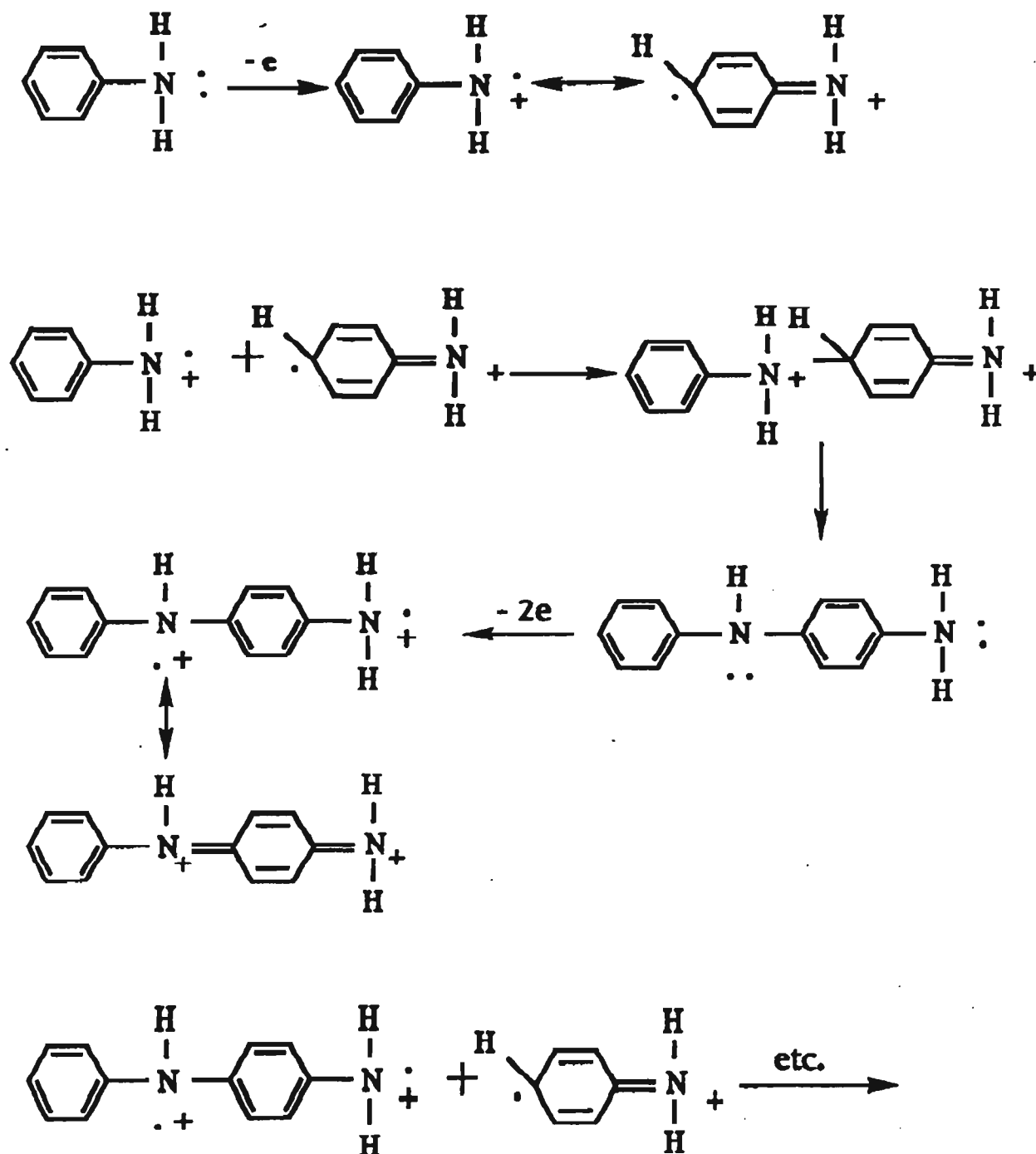


Figure 1.6: General reaction scheme for the polymerisation of aniline (see reference 11).

Wnek ³³ determined that the structure of the oxidised insulating form of polyaniline is approximately a 50% copolymer of diamine and diimine units corresponding to the emeraldine structure. This suggestion has been supported by Hjertberg et.al ³⁴ and Vachan et.al ³⁵. There is another

suggestion which states that the normal electrochemical synthesis leads to partially cross-linked polymers ³⁶.

1.3. Conduction mechanism

Conduction mechanism have been perhaps the most controversial part of the characterization of conducting polymers. Evans ¹¹ stated that "both theoretical and experimental evidence suggest that the precise nature of the charge carriers in conjugated polymer systems vary from material to material, and it is still a subject of debate in many cases.". Therefore, the conduction mechanism of polypyrrole and polyaniline should be reviewed separately.

1.3.1. Polypyrrole

There have been many theoretical models to explain the conduction mechanism of polypyrrole. These vary from a semi-conductor ^{37,38} behaviour to charge transport theory ³⁹ and Hopping model. There is also a large body of data suggesting that the actual mechanism of conduction involves variable range hopping ⁴⁰⁻⁴⁶. There are other theories which indicate that the conduction mechanism that charges in doped polypyrrole appears to be localised on the pyrrole rings ^{47,48} Although Street et.al ⁴⁹ provided data to suggest that initially on doping, polypyrrole contains a large number of highly mobile spins, there are other evidence of a metallic conduction mechanism ⁵⁰. Teasdale ⁵¹ also has a review on the conduction mechanism based on the polaron and bipolaron theory. He said that the polymer is first-oxidised to the polaron state. In this state the polymer does not show good conductivity. As further oxidation takes place the polarons begin to interact and couple to form bipolarons. In this theory, bipolarons are the main charge carriers in conducting polypyrrole which are responsible

for its conductivity. The schematic of polaron and bipolaron is given in Fig 1.7.

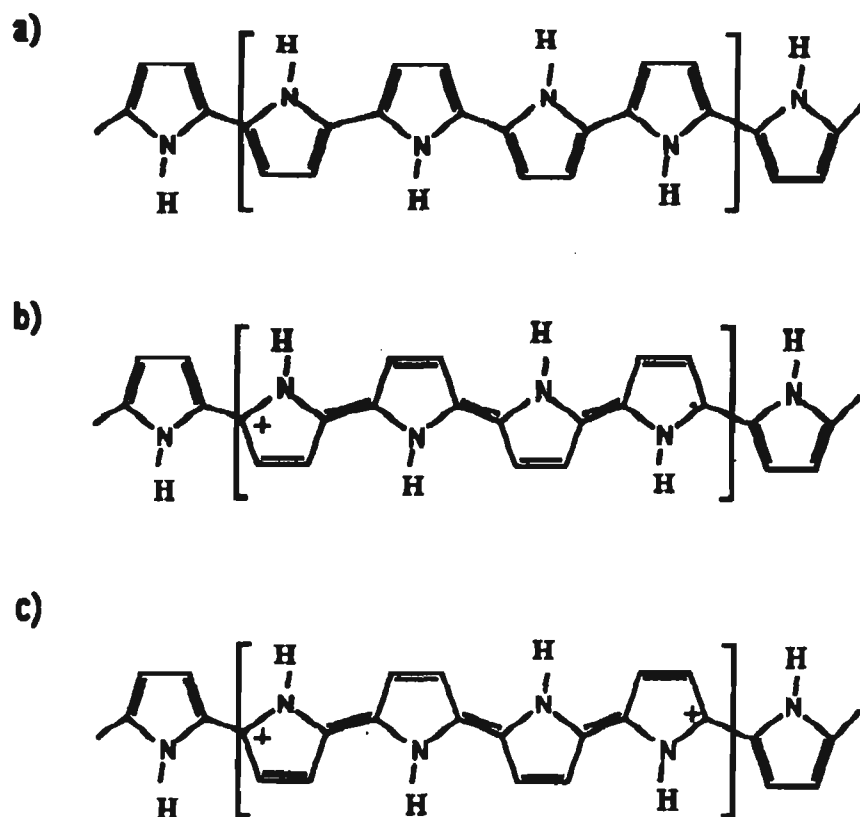


Figure 1.7: Schematic of different forms of polypyrroles (a) undoped polypyrrole (b) polarons (c) bipolarons

1.3.2. Polyaniline

Polyaniline exhibits an unusual form of electronic behaviour, in that it can be switched from conducting to insulating forms by variation in pH, without any change in the electronic oxidation state ^{52,53}. The dependence of conductivity on both oxidation and protonation has already attracted many researchers' attention ⁵⁴⁻⁵⁷. On the grounds of these investigations, Billingham ² argued that the possibility of generating conducting structures by proton abstraction from CH₂ groups in otherwise conjugated chains can be demonstrated by using a very strong base. Perhaps MacDiarmid's model ⁵⁸ is one of the best model to explain the conduction mechanism of

polyaniline. This model describes some of the processes which can take place in the poly(emeraldine) form on changing the pH of the solution with which the material is in contact. MacDiarmid et.al ⁵⁸ argued that there are four idealised forms(Fig. 1.5) when polyaniline synthesis and any subsequent treatment are carried out. As can be seen in the figure, the polymers in the left-hand column are considered as being derived from the amine, 1A (A=amine), and are hence designated (in increasing degree of oxidation) as 1A and 2A. On the other hand the material in the right-hand column are regarded as being derived from the ammonium salt, 1S (S=salt), and are hence designated (in increasing degree of oxidation) as 1S and 2S. All of these four forms may be interconverted at will by chemical and/or electrochemical oxidation/reduction. In addition, MacDiarmid et.al ⁵⁸ believe that form 1A may be converted to form 1S by treatment with an aqueous protonic acid, such as HCl. The acid may also be removed to regenerate the A form by treating the S form with an aqueous solution of base such as KOH.

Wnek ⁵⁹ suggests that upon protonation semiquinone radical cations can be generated that are responsible for dramatic increase in conductivity of the polymer. He believes that the principal mode of conduction involves the intermediacy of a semiquinone radical cation.

Evans ¹¹ argues that in view of the complexity of the material, it is difficult to unequivocally assign a particular mechanism for electronic conduction in the polymer, although some evidence exists to suggest that it involves three-dimensional-range hopping as found for other polymers ⁶⁰. It has been found that the conductivity of polyaniline is a combination of both ionic and electronic conductionl ⁶¹.

1.4. Parameters affecting the conductivity of conducting polypyrrole and polyanilines

It has been found that the conductivity of conducting polymers is dependent on many factors. Amongst them, the dopants, the electrochemical polymerisation technique, temperature and pH have been found to have very significant effect on the conductivity of the polypyrrole and polyaniline materials. Therefore, we have paid particular attention to reviewing the effect of these factors on the conductivity of the produced polymer.

1.4.1 Dopants

Doping is the term applied to the process of changing the state of oxidation or reduction of conjugated polymers with a concomitant change in the electronic properties of the material. There have been many studies which suggest a crucial effect of dopants (counterions) on the conductivity of the resultant polymer ⁶²⁻⁷¹.

Kuwabata et.al ^{67,69} have also pointed out that the conductivity of polypyrrole films is dependent on the type of organic dopants used during electrodeposition. They suggest that the polymer conductivity decreases as the number of sulphonate groups of the organic dopants increases. Cao et.al ⁶⁶ argue that there is a significant effect of the counterion on the conductivity of protonated emeraldine salt when the substitute group varies from C₆H₁₃ to C₈H₁₇. The latter counterion conferred conductivity that was as high as twice that which was observed for the former one. Park et.al.⁷² also stated that the electrical conductivity of polyaniline decreases to a limiting value

after electrochemical dedoping. There are other reports which indicate that the synthesis of polypyrrole in the presence of large amphiphilic surfactant anions results in the formation of films with improved electrical properties 73-77.

1.4.2. Effect of polymerisation technique on the conductivity of the resultant polymer

There have been many reports on the significance of the technique used during electrosynthesis of conducting polymers 78,79. Higawara et.al.⁷⁹ stated the advantage of the potentiostatic method in terms of controlling the anodic potential. Otero and Delarreta ⁸⁰ found that the potential at which polymer was deposited affected the morphology of the polymer resulting in different conductivities. Satoh et.al. ⁷⁴ found that increasing the polymerisation potential in aqueous solutions reduced the conductivity of their products, with maximum conductivity being achieved at a potential of 600 mV. Others however, have found that a higher potential increases the conductivity of the product. They show this is attributed to morphological effects rather than changes in the inherent conductivity of the material at a molecular level ⁸¹.

Many researchers have preferred the galvanostatic method for electrodeposition of their polymers. Therefore, the effect of current density on the conductivity of the resultant polymer has been the centre of their attention 78,82 In these investigations the effect of current density on morphology of the products and hence on the conductivity of the polymers have been discussed. Peres et. al. ⁸³ proved that under electrochemical polymerisation conditions they employed, the conductivity of polypyrrole materials can be increased by increasing the current density. They observed an initial conductivity increase which levelled off as the current density

increased. Werner et.al. ⁸⁴ pointed out that structural changes in the polymer due to different polymerisation kinetics at high current densities have been responsible for these results. They provided different SEMs to show that morphological changes took place at the polymer surface as the current density was increased.

1.4.3. The effect of temperature on the conductivity of the resultant polymer

Samuelson and Druy ⁸⁵ showed the effect of temperature on the conductivity of polypyrroles. They suggested that the conductivity of conducting polypyrroles increases by heating up to a certain point and then decreases after because of polymer degradation. Oka and Okiyoharra ⁸⁶ have also studied the temperature dependency of the conductivity of polyaniline materials in both doped and undoped forms. They found that the conductivity of undoped polyaniline is more sensitive to temperature than the doped one. Truong ⁸⁷ reported on the thermal degradation of polypyrrole. He found that at high ageing temperature (120 and 150⁰ C) the oxygen diffusion into the bulk is predominant. He concluded that as ageing temperature decreases, thermal degradation of polypyrrole films exhibits a transition from a diffusion-controlled mechanism to a reaction-controlled mechanism. Neoh et.al ⁸⁸ and Dervux et.al ⁸⁹ have also shown the conductivity dependence of polyaniline and polypyrrole materials, respectively, with temperature in different environments. Therefore, it is necessary that all experimental work should be carried out at constant temperature while the effect of other factors on the polymer conductivity is investigated.

1.4.4. Effect of pH

It has been reported that both polypyrrole and polyaniline are pH sensitive materials with respect to their conductivities ⁹⁰⁻⁹². However, it has been proven that polyaniline conductivity is inherently dependent on protonation and deprotonation processes by Acid/base and base/Acid treatment ^{88,93}. The effect of pH on the conductivity of polyaniline and polypyrrole materials is discussed in chapter 6.

1.5. Applications

There have been large programs aimed at developing conducting polymers for sensing technologies and other applications since they were discovered. They have been introduced as potentially novel materials in different technologies as diverse as molecular electronics ^{113,114}, leak detection ¹⁰⁴, chemical sensors ¹⁰⁶, electrochemical sensors ^{94,105}, batteries ^{101,102,107}, electrochromic devices ¹⁰⁸, corrosion prevention ^{110,111}, information storage memories ^{105,109} membranes ^{97,98,103}, catalysis ^{95,96,112} and even chromatography ^{99,100}.

It has been argued ³ that polypyrrole is a promising candidate for a polymer battery that does not possess the typical disadvantages of polyacetylene because of its open circuit voltage ¹¹⁵⁻¹¹⁹. Heinze said "PPy has a long lifetime and a relatively slow self-discharging rate. The suitability of polypyrrole ¹²⁰⁻¹²² and polyaniline ^{123,124} as electrochromic displays have been intensively studied.

Although there have been many reports on the technical and commercial potential of conducting polymers in applications, there are other reports

which provide negative perspectives of these materials with respect to their applications 2,125.

There is an extremely surprising comment by Billingham and Calvert ² that "if one asks what are the application of conducting polymers, the short answer is "none"." Wessling ¹²⁵ also reported on the crisis in the conducting polymers field. He argued that the basic research on conducting polymers started much too early with a major concentration on application of the materials' properties. He believes that there is no clear interpretation and no deep understanding of the conducting behaviour of conducting polymers. Although these researchers disclose some disadvantages of conducting polymers in application, there is no doubt that they are still attractive materials to be studied for commercial applications even if we have a long way to achieve this.

1.6. Techniques for conductivity determination

The most popular test for dry and ex-situ conductivity measurement is the four-point probe technique ¹²⁶⁻¹²⁸. This technique allows one to measure the volume resistivity, R_v , of a conducting polymer film. This test method applies to all materials that exhibit volume resistivity in the range of 1 to 10^7 ohm.cm. The apparatus has four electrode (two outer and two inner electrodes). The conductivity value is calculated according to:

$$R_v = [(X.Y)/z].(\Delta E/i)$$

$$\text{Conductivity} = 1/R_v$$

X= Thickness of conducting polymer film (cm)

Y= Width of conducting polymer film (cm)

Z= Distance between potential electrodes (cm)

ΔE = Potential difference over inner electrodes

i = Constant current passed through outer electrodes

The samples to be measured can have any width up to 0.5 cm and must be long enough to cover all four electrodes. The determination of the film thickness, X , and width, Y , is very important as this is the major source of error in the technique. This test method is useful for the comparison of materials as far as their conductivities are concerned. However, this method can not be used in-situ.

Since the realisation of the importance of in-situ conductivity measurement, there have been reported a few methods to investigate the conductivity value of conducting polymers in solution. These methods mainly involve the introduction of a new configuration of the working electrode in an electrochemical cell to enable one to measure the resistance of the polymer during oxidation/reduction.

In 1984, there were two reports by Wrighton et.al ^{129,130} to show the ability to coat different adjacent gold microelectrodes and connect them with polypyrrole(Fig1.8). They introduced a microelectronic device with characteristics of transistor ¹³⁰.

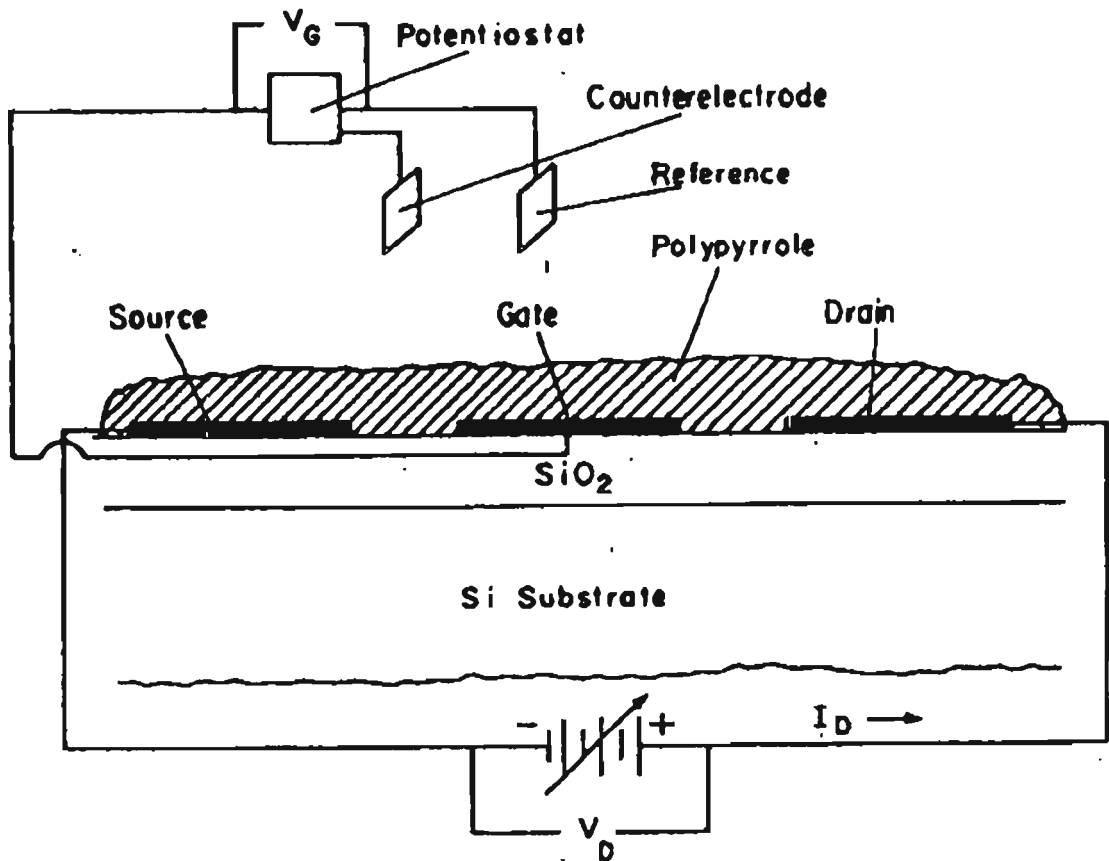


Figure 1.8: Cross-sectional view of a microelectronic device in an electrochemical cell(see reference 129)

One year after, in 1985, Paul et.al ¹³¹ used the same micro electrode in a new electrochemical set up to characterise a polyaniline based microelectrode device(Fig. 1.9)

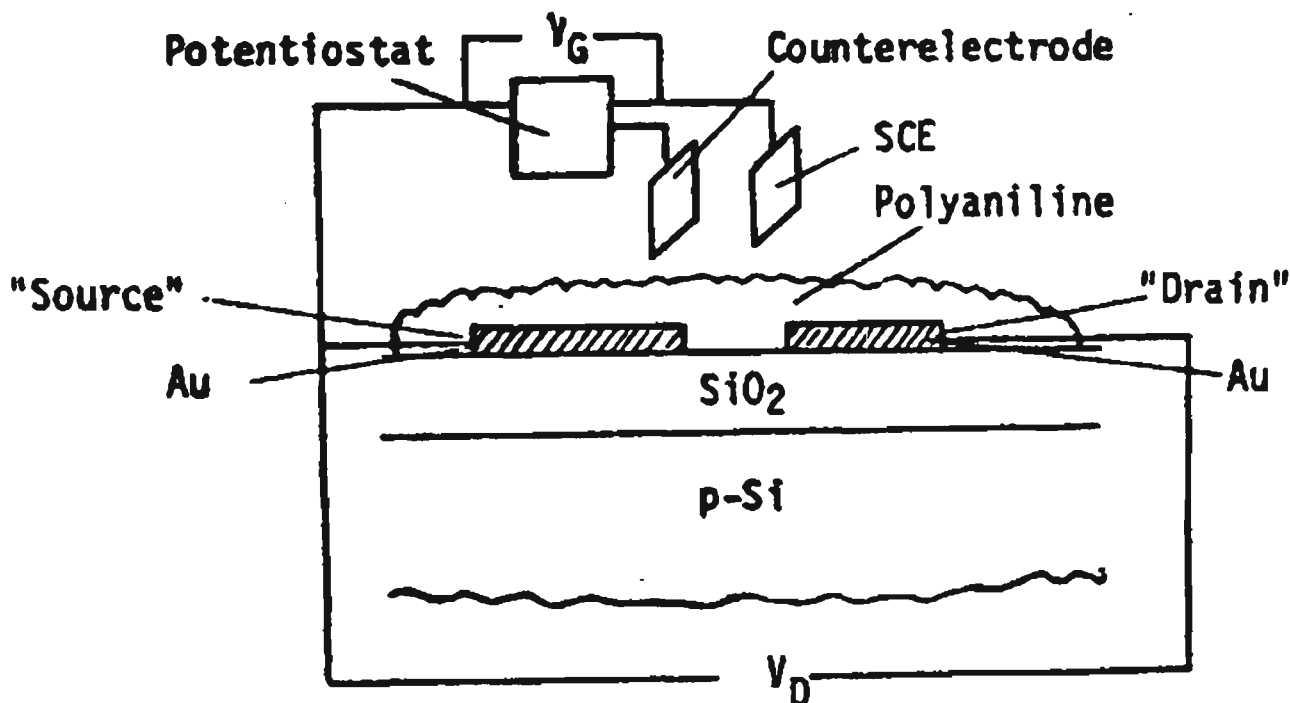


Figure 1.9: Configuration of Polyaniline-based Microelectrode Device in an electrochemical set up(see reference 131).

Paul and coworkers used this device to measure in-situ conductivity of polyaniline in 0.5 M NaHSO₄ as a function of potential V_G shown in the Figure. They monitored the resistance between two polyaniline connected electrodes by measuring I_D vs. V_D at a given V_G (Figure 1.9). It is important to note that variation in V_G is effectively variation in the electrochemical potential of the polymer.

In 1986, Gholamian et.al.¹³² introduced new configurations of the working electrode adapted from that used by Paul et. al.¹³¹. This new working electrode consisted of two parallel platinum wires(1mm diameter) set up very close to each other (Figure 1.10). The polymerisation was carried out simultaneously on both wires. The polymer was grown on the two wires and finally bridged the gap between them. One of the wires was used for the potentiostatic control of the polymer (W), and voltage drop in the polymer

was monitored using the second wire (P). Then the resistance of the polymer was deduced by taking the ratio of voltage drop to potentiostatic current.

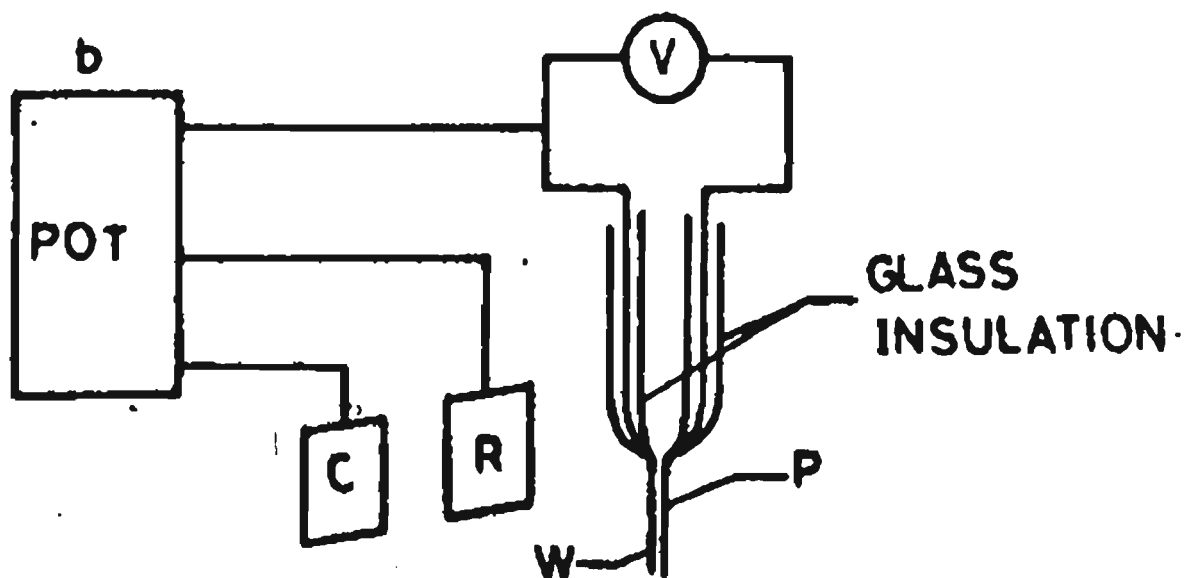


Figure 1.10: *Schematic illustration of the electrode configuration used for measurement of polymer resistance*
(see reference 132)

In 1988, Genies et.al¹³³ determined (Fig.1.11) the in-situ conductivity of polyaniline at different potentials using almost the same configuration of working electrode as that used by Wrighton et.al¹²⁹⁻¹³¹.

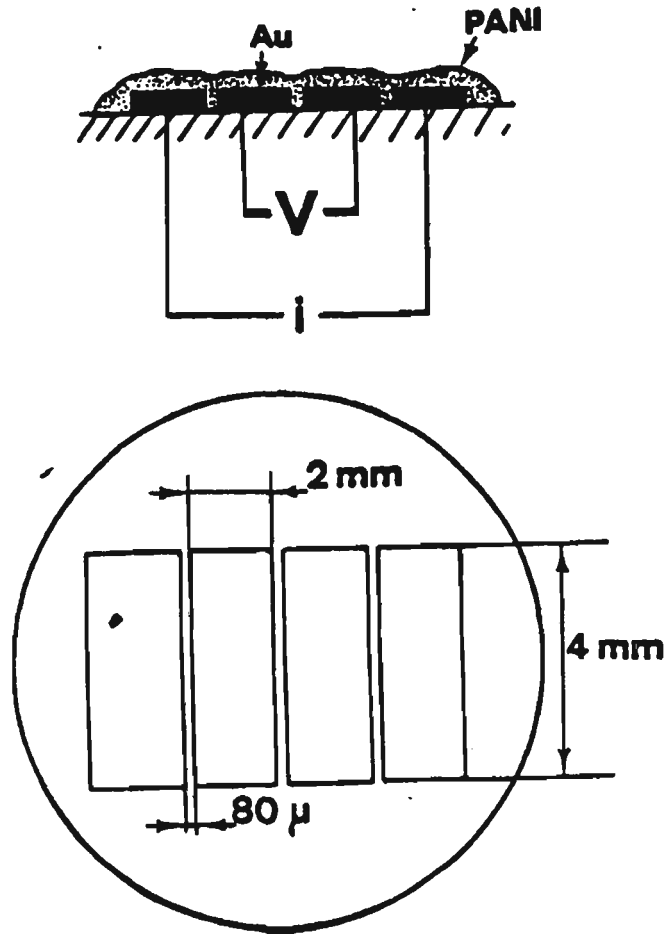


Figure 1.11: *Schematic representation and dimensions of the four gold electrodes sealed in epoxy glue used for in-situ conductivity measurement of polyaniline film.*

(see reference 133)

Schivon et.al ¹³⁴ suggested a new terminology, "two-band electrode", for the new configuration of working electrode. In their investigations conductivity measurement was performed with the apparatus illustrated in Fig. 1.12 following the method used by Wrighton et.al ^{129,130,131,135}.

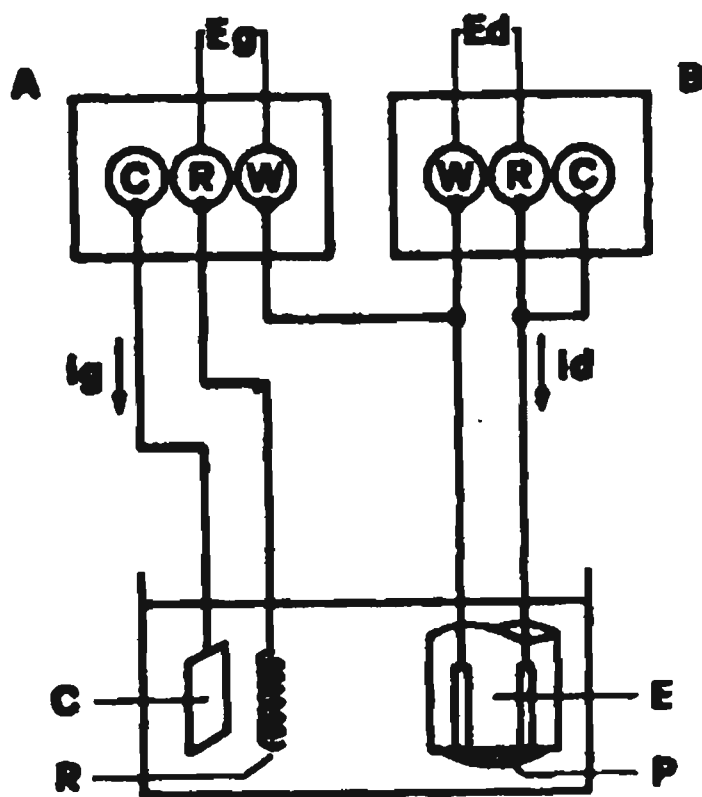


Figure 1.12: Schematic representation of the electrochemical apparatus for in-situ conductivity measurements: A= Potentiostat for changing the oxidation level of polymer P; B= Potentiostat for d.c. conductivity measurements; E= two band electrode; R= reference electrode; C= Counter electrode; E_g and i_g = gate voltage and current; E_d and i_d = drain voltage and current (see reference 134)

The polymer deposit was left at the desired potential (gate potential, E_g) by the first potentiostat A and a small amplitude d.c. voltage (drain voltage, E_d) applied between the two bands with the second potentiostat B. After reaching equilibrium (zero gate current, i_g) the stable drain current i_d was recorded. In order to minimise deviations from equilibrium, E_d was kept low (10 mV) in comparison with the range of E_g for electrochemical switching.

Although Wrighton and coworkers' technique was followed as a popular method by others, Feldman and co workers ^{136,137} had a different approach to in-situ conductivity measurement using a modified twin-electrode thin-layer cell as illustrated in Fig 1.13 to investigate in-situ "static" and "dynamic" conductivity of solvent-wetted polypyrrole films.

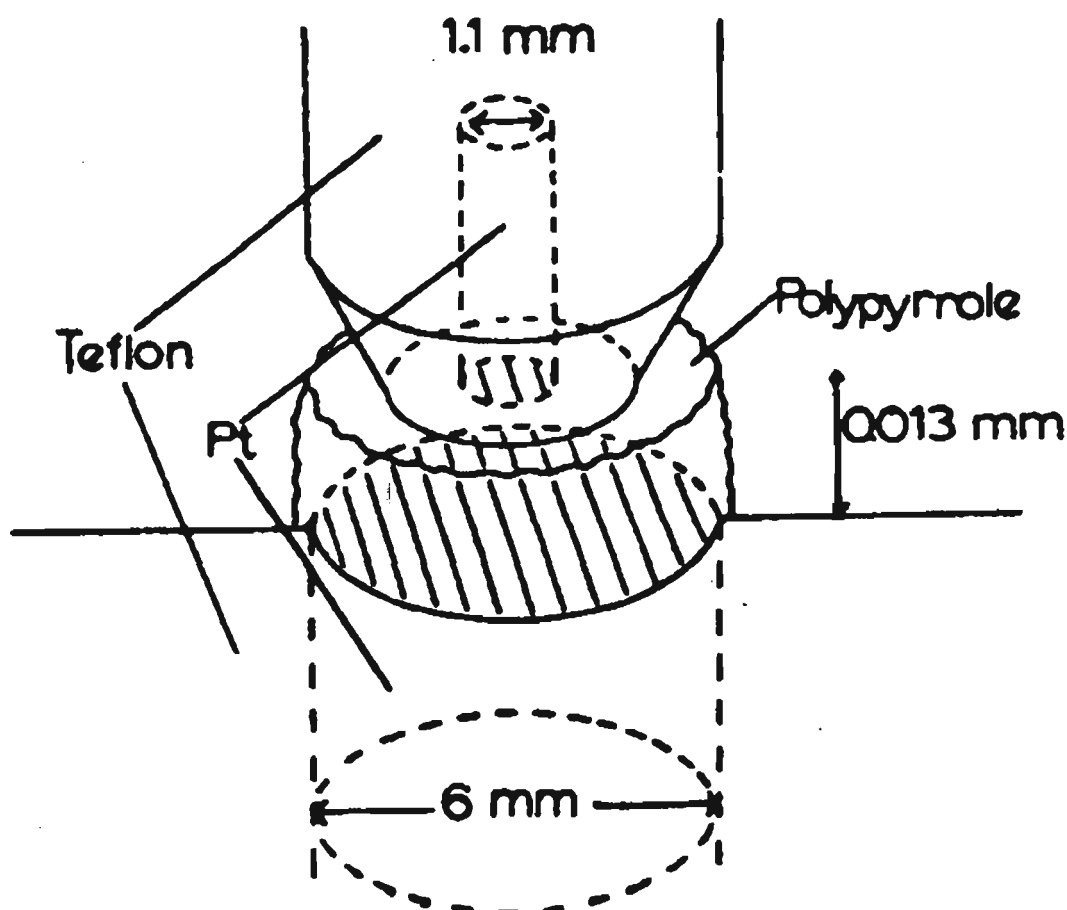


Figure 1.13: Schematic illustration of a twin-electrode thin-layer cell used for conductivity measurements
(see reference 137)

For "static" conductivities, the upper Pt disk electrode was used. It was made by polishing a 18 gauge Pt wire (area = $8 \times 10^{-3} \text{ cm}^2$) and then mounted in a Teflon cylinder. For "dynamic" measurements, a 36 gauge Pt wire (area = $3.14 \times 10^{-4} \text{ cm}^2$) was sealed in a glass capillary, polished and mounted into a similar Teflon holder. Electrical contact was made by silver epoxy.

Feldman. et al.¹³⁷ explained their "static measurements" that "... the polypyrrole film was grown on the lower electrode. Then the monomer solution was replaced with 0.1 M Et₄NClO₄/ acetonitrile, and the gap between the two facing electrodes was slowly closed until the resistance between the two working electrodes dropped; indicating that the upper electrode had connected the polypyrrole film. The electrode separation was then slowly decreased further until the resistance stopped decreasing and the micrometer reading was noted. Next, the micrometer gap was re-opened (1mm) and the film potentiostated at the desired potential until the resulting film's charging current decayed. Maintaining the polypyrrole coated film at the same potential, two electrodes were then re-positioned to the previously noted separation. This procedure was followed for a series of film potentials (oxidation states) and the conductivity was deduced from the current recorded.".

For " dynamic" experiments, the polymer film was deposited on the upper electrode which had a smaller surface area.. Then, the gap between the electrodes was closed to minimum resistance as above. The electrodes were ,in this case, not subsequently separated. The film oxidation state was varied by scanning the potential at a slow rate for both electrodes, relative to a reference electrode.

1.6.2. DC and Pulse conductivity measurement used in this project

1.6.2.1 DC method

This method was introduced by Holze and Lippe ¹³⁸ in 1990. They measured in-situ conductivity with a two-electrode array, called by us "sandwich" electrode illustrated in Fig.1.14.

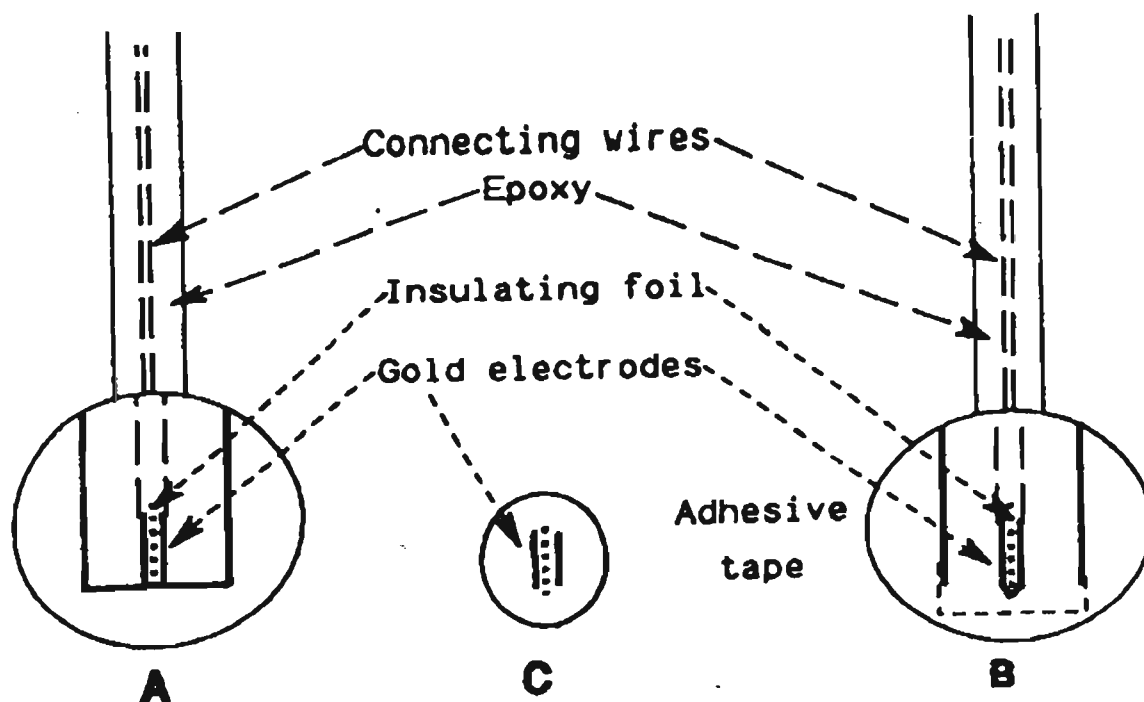


Figure 1.14: Cross section of the electrode (A) before, (B) after grinding/polishing, and (C) top view (see reference 138)

Electrochemically induced changes in the polymer can be obtained by applying appropriate electrode potentials to both electrodes which are connected together as the working electrode. Then the electrodes are disconnected and 10 mV DC. is applied across the electrodes to calculate the resistance of the polymer bridging the electrodes by recording the current and using Ohm's law.

1.6.2.2. Pulse resistometry

This technique was invented by Fletcher and coworkers ¹³⁹ to measure in-situ ohmic cell resistance during conventional electrochemistry in a three-electrode electrochemical cell. This method involves interrupting the potentiostat circuit for 33 times per second. During each interruption a square wave current pulse of 100 mA amplitude, shown in Figure 1.15, is applied across the working and counter electrodes of the electrochemical cell. Then the potential difference between the reference and working electrodes is measured; which is related to the resistance between these two electrodes.

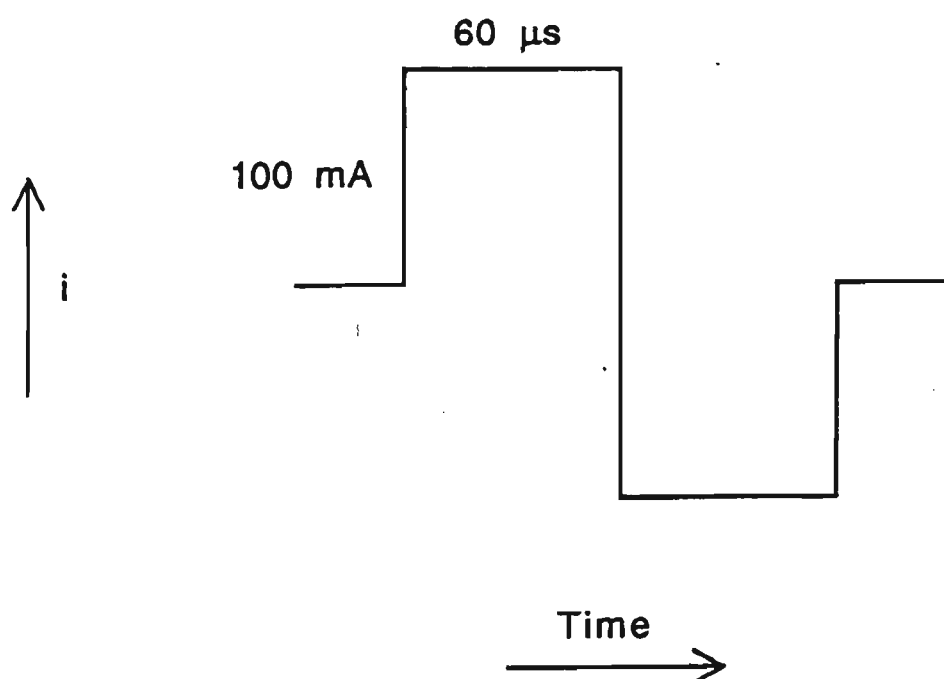


Figure 1.15: *Square wave galvanostatic pulse used in the pulse resistometry technique*

Fletcher and coworkers ¹³⁹ argued that because the galvanic pulse is very fast the double layer charge and faradaic reactions are not involved in this resistance output. Therefore, simply by using Ohm's law the potential difference between the reference and the working electrodes can be converted to an ohmic resistance of the cell. These two DC and Pulse resistometry method are discussed and compared in details in chapter 2.

1.7. Aims of this project

As shown by this review, the importance of the characterisation of conducting polymers in the better understanding of their conductivity behaviour can not be underrated. Wessling[1.126] has highlighted characterisation as a weakness and a gap in the field of conducting polymers. Thus the bulk of this project has been focused on developing new in-situ multidimensional characterisation techniques. To bridge this gap, our approach to characterisation is in applying new resistometric studies to these novel materials. We have also considered the potential application of these novel materials in sensing technology based on the information obtained through our characterisation techniques. Two new in-situ and simultaneous techniques, Cyclic Resistometry (CR) and S.M.A.C. (Simultaneous Multidimensional Analysis of Conductors) are introduced and used for detailed characterisation of both polypyrrole and polyaniline materials. In addition simple sensor devices and instruments are designed and recommended for future work.

CHAPTER 2

RESISTOMETRIC STRATEGIES FOR IN-SITU CONDUCTIVITY INVESTIGATIONS INVOLVING CONDUCTIVE ELECTROACTIVE POLYMERS

2.1. INTRODUCTION

Conductive Electroactive Polymers (CEPs) such as polypyrroles and polyanilines have unique properties as far as their resistive properties are concerned. These materials can be oxidised and reduced using electrical stimuli. This process is accompanied by ion movement into/ out of the polymer and induces changes in the resistance of the polymer.

The "dynamic conductivity", insulator-metal transition, of CEPs is a unique physico-chemical property¹⁴⁰⁻¹⁴². A great deal of research on the intrinsic and dynamic conductivity of these polymers^{143,144,70} has been carried out over the previous decade. These efforts have resulted in various applications involving CEPs in electronic and sensing devices such as biosensors¹⁵⁹ and semi-conductors^{145,146,147,129,130}.

Although the conductivity of CEPs is a thoroughly investigated subject¹⁴⁸, there have only been a few in-situ conductivity measurement studies^{70,149,132}. From the electrochemistry point of view, it is very important to study the conductivity of the electroactive polymers in-situ during the doping-undoping process. This should lead to a better understanding of the physical and chemical changes occurring at the macromolecular level.

2.2. AIMS AND APPROACH OF THIS CHAPTER

In this chapter, DC and pulse resistometry^{150,151} are compared. The advantages/disadvantages of these methods are discussed. The two above mentioned techniques are explained and discussed in two separate sections. To investigate the differences between the techniques two polymeric structures, polypyrrole and polyaniline, have been considered. At the end

of this chapter, the importance of using these two techniques in the characterisation or application of conducting polymers is discussed.

2.3. EXPERIMENTAL

2.3.1. Instrumentation

Cyclic voltammograms were obtained using a CV-27 BAS (BioAnalytical Systems, U.S.A), a Mac Lab (Analog-Digital Instrument, Australia) interface and an Apple Macintosh computer. A resistometer was purchased from CSIRO, Division of Mineral Products, Australia. This was used for the pulse resistometry experiments. A home made (Electronic workshop of the Faculty of Science, Wollongong University) 10 mV DC power supply was also employed based on the published DC technique ¹³⁸. The circuit diagram for this power supply is shown in Figure 2.1. This is a slight modification to that was published ¹³⁸.

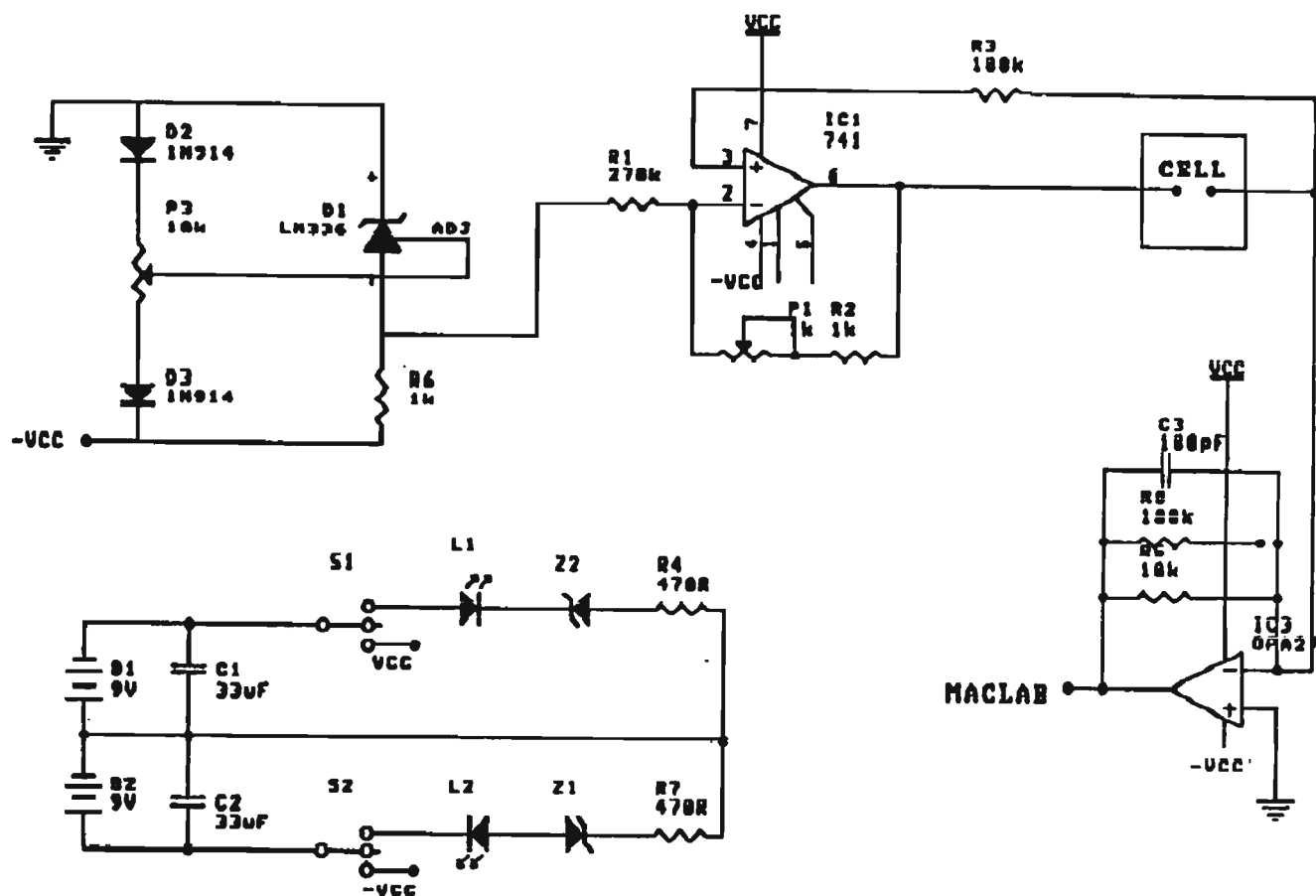


Figure 2.1: *The circuit diagram for the 10 mV DC power supply used for DC resistometry.*

2.3.2. Reagents and standard solutions

Aniline and pyrrole were obtained from Aldrich and were distilled immediately before use. Hydrochloric acid, nitric acid, sulfuric acid, para-toluene sulfonic acid (sodium salt) and sodium chloride were also purchased from Aldrich. All solutions were purged with Nitrogen for 15 minutes before use. All polymers were deposited potentiostatically on to a platinum sandwich electrode as described in Figures 2.2 and 2.3.

2.3.3. Procedure

A DC resistance measurement technique for conductivity studies of CEPs has been described previously ¹³⁸. The electrode configuration used as the working electrode is shown in Figure 2.2.

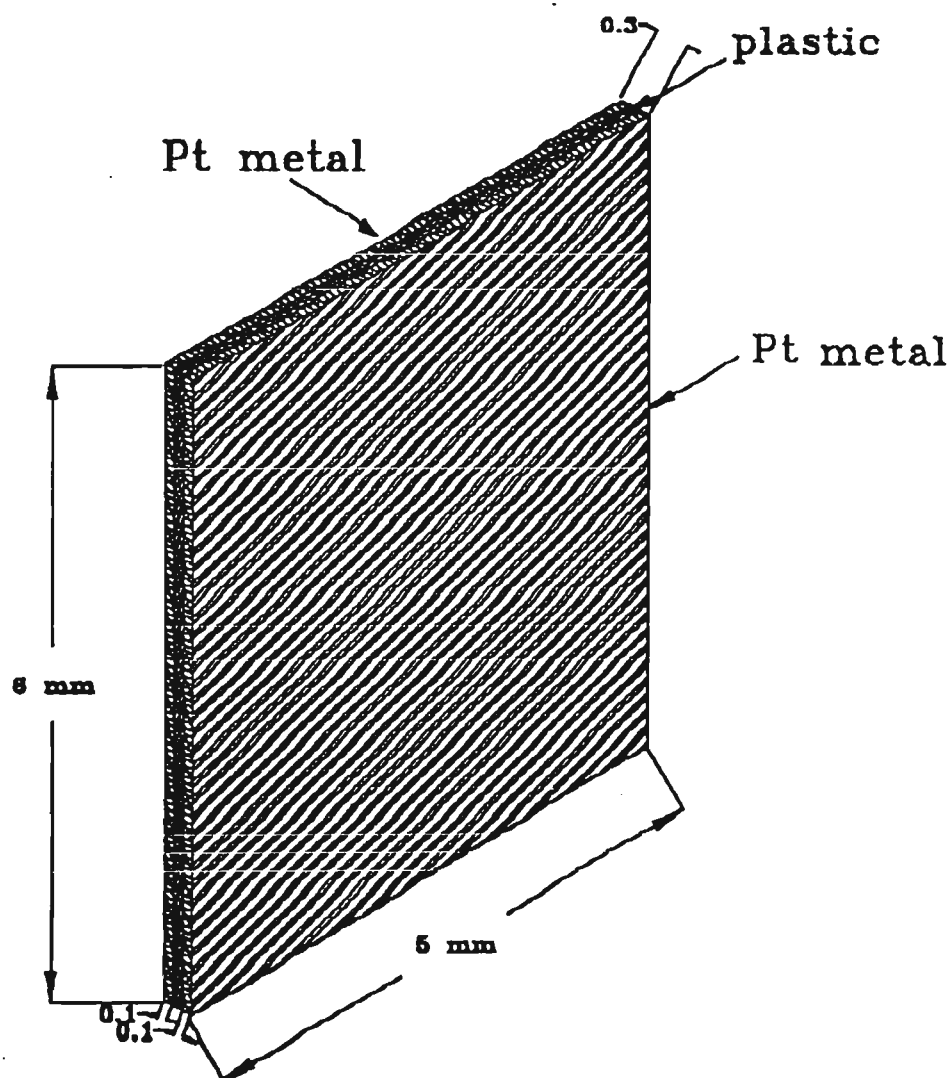


Figure 2.2: *Polymer electrode configuration used for DC resistance measurements.*

A schematic outlining the mechanism of operation of this method is shown in Figure 2.3..

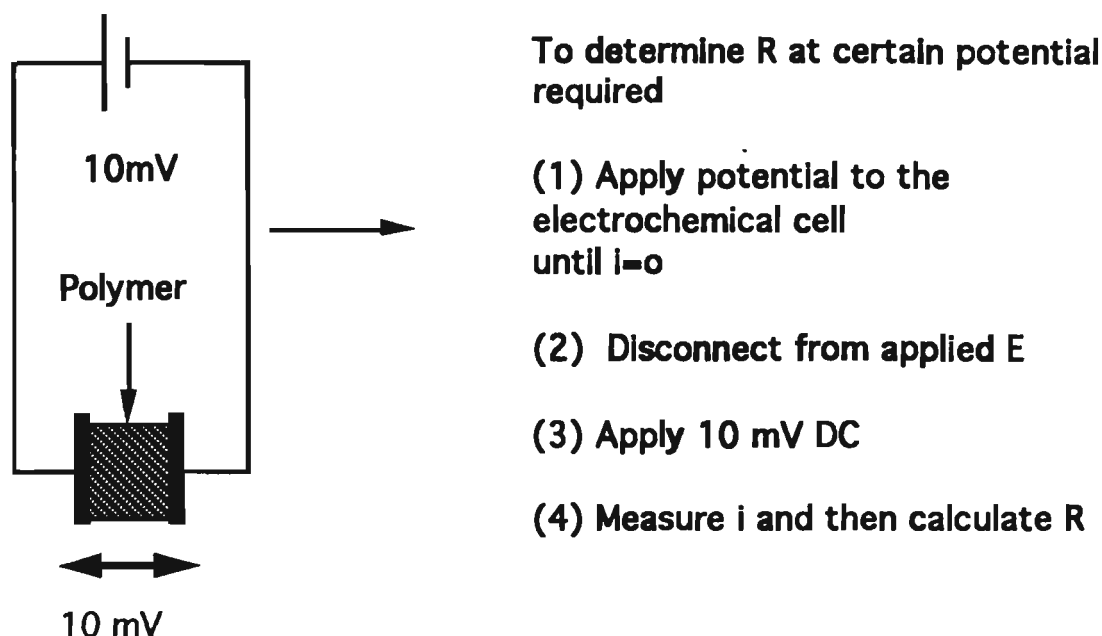


Figure 2.3: *The DC resistometry method*

This technique involved application of a constant potential, in the electrochemical cell, until equilibrium is reached ($i=0$). Then this potential was switched off and a small potential (10 mV DC) was imposed across the polymer. Measurement of the current generated when 10 mV DC is applied allows calculation of the resistance using Ohm's law.

The electrochemically synthesised polymer under investigation should grow on both electrodes and cover the small gap between them. A typical example of this bridge is shown in Figure 2.4 and 2.5. It was found by us that for the electrodeposition of polyaniline and polypyrrole potentiostatically, 20 and 100 mC charge respectively is required to fill the gap between the electrodes

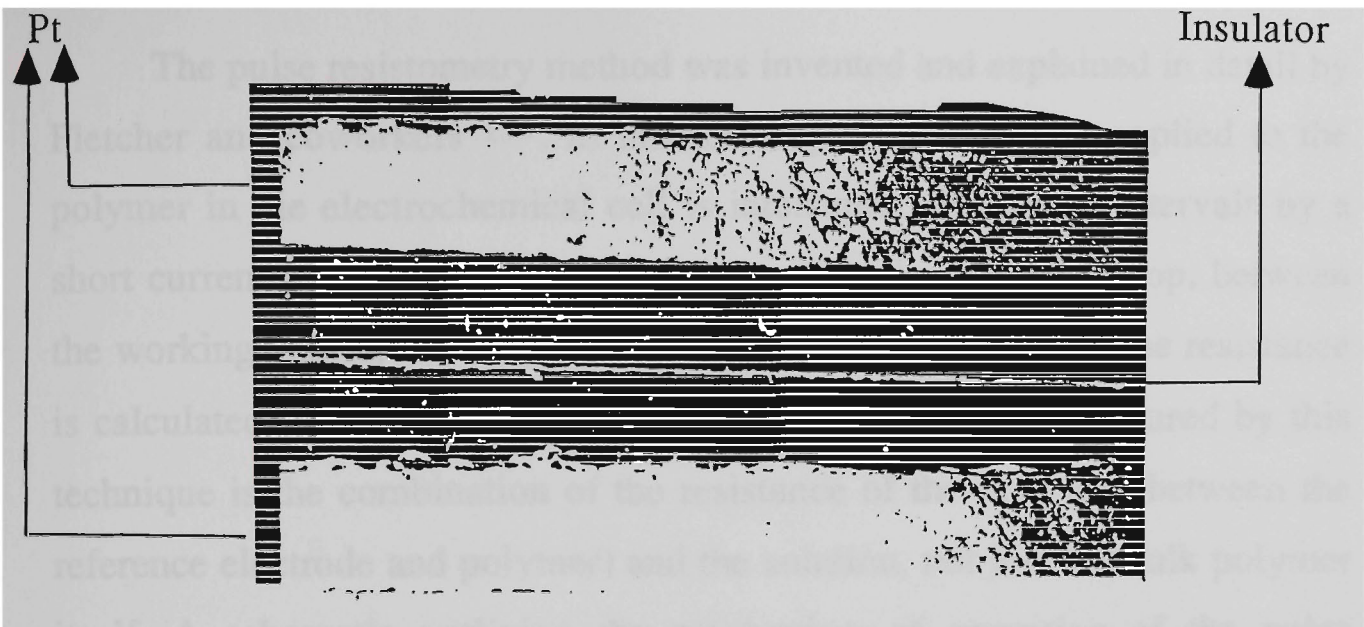


Figure: 2.4. *The SEM (X100) of blank sandwich electrode consisted of two platinum plate separated by a plastic insulator and mounted in a plastic syringe.*

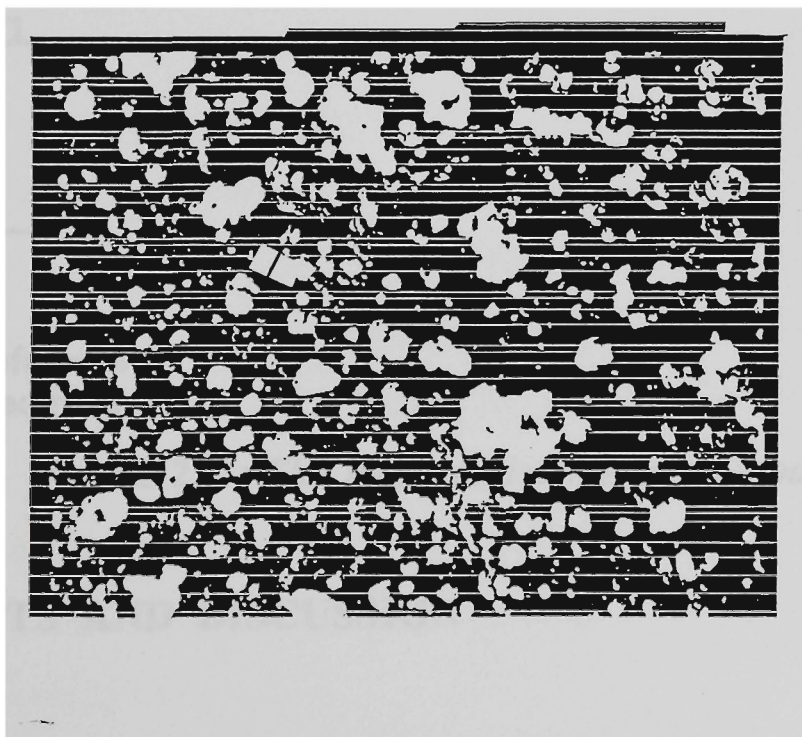


Figure 2.5: *The SEM (X100) of the sandwich electrode coated with PPy/Cl*

The pulse resistometry method was invented and explained in detail by Fletcher and coworkers ¹³⁹. In this technique the potential applied to the polymer in the electrochemical cell is interrupted at regular intervals by a short current pulse. During these current pulses the potential drop, between the working and reference electrodes, is recorded from which the resistance is calculated. It is essential to mention that the resistance measured by this technique is the combination of the resistance of the polymer (between the reference electrode and polymer) and the solution, not just the bulk polymer itself. A schematic outlining the mechanism of operation of the pulse resistometry method is presented in Figure 2.6.

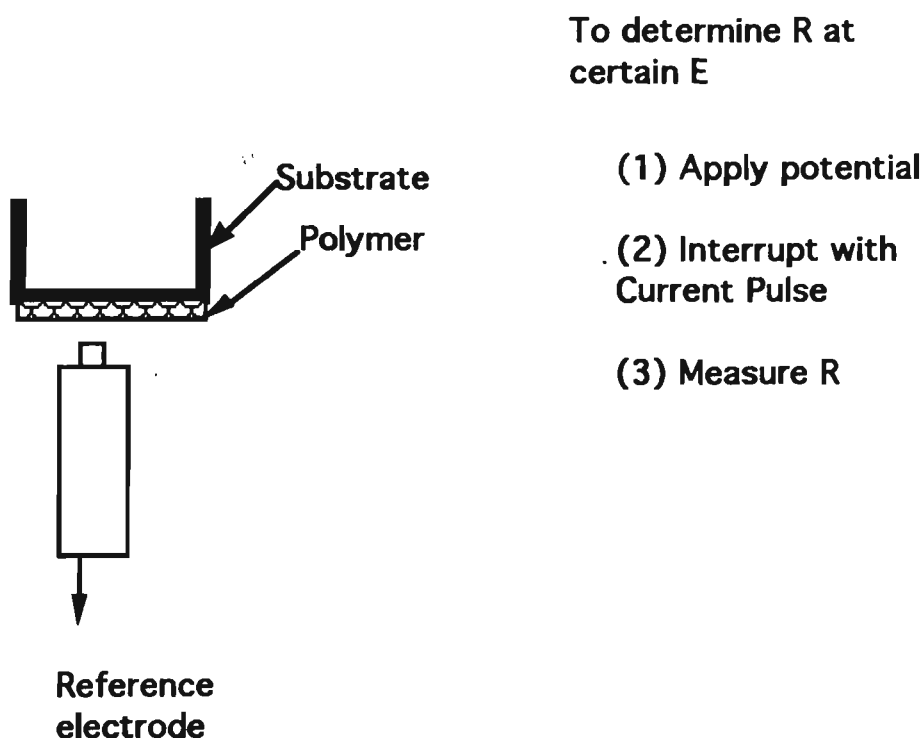


Figure 2.6 : *The pulse resistometry method.*

2.4. RESULTS AND DISCUSSION

Illustrative studies, first, were carried out to demonstrate the nature of the resistance transitions that occur during the oxidation/reduction of polyaniline and polypyrrole. The results are shown in Figures 2.7 and 2.8.

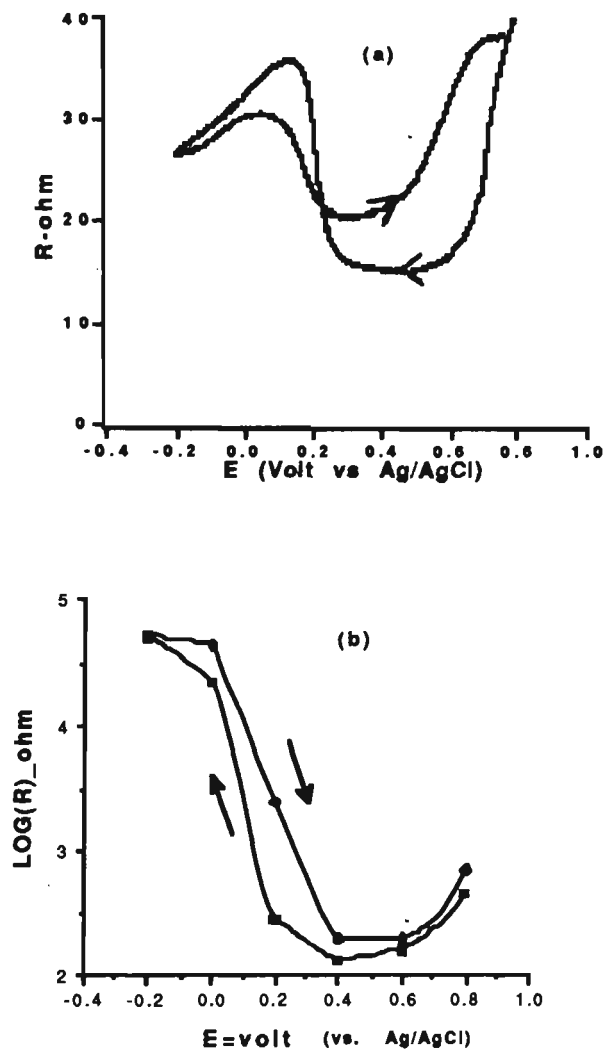
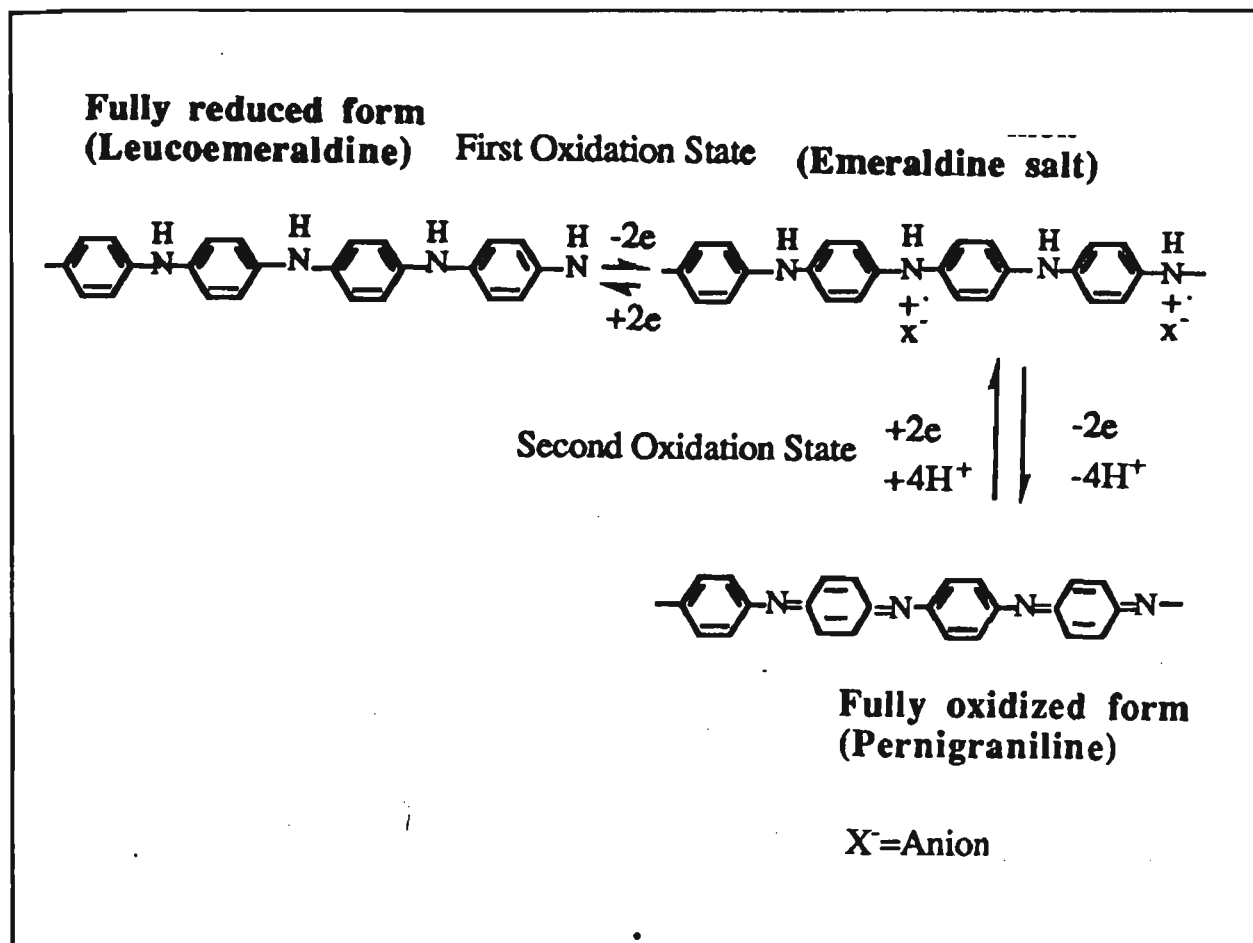


Figure 2.7: Polyaniline chloride oxidised /reduced in 1M HCl. Polymer was grown potentiostatically at $E = 0.8 \text{ V}$ ($Q = 20 \text{ mC.}$)

(a) Pulse resistometry: Initial $E = 0.4 \text{ V}$, scan rate = 10 mV/sec . Reference electrode was Ag/AgCl, Working electrode was the sandwich electrode shown in Fig.:2.3 and the Auxiliary electrode was platinum.

(b) DC resistometry: electrodes as in (a) Initial $E = 0.4 \text{ V}$

As can be observed (Figure 2.7), polyaniline/chloride undergoes two resistance transitions which correspond to the oxidation/reduction processes that occur according to:



The polymer is most conductive while it is half reduced and half oxidised (emeraldine salt). These results are consistent with the theory and practical results published by Focke and Wnek ¹⁵⁷. They studied the effect of redox potential on the conductivity of a polyaniline film in an acidic electrolyte. They suggested that at very low potential (cathodic) the polyaniline material is fully reduced and the conductivity is low. As the redox potential is increased anodically the polymer is oxidised and radical cation (polarons) are formed on the polymer chain. On further doping they also experience an increase in the conductivity. The insulator-conductor transition is driven by the unpinning of the polarons. They believe that in the conductive state the charge defects is high and the polarons are not associated with specific counterions any more; rather, they are subjected to the mean field of a number of surrounding counterions. Consequently, the polarons are able to diffuse freely and the conductivity is high. They continued their

justifications from the physicist point of view that as the potential increases further the polarons become thermodynamically unstable with respect to bipolaron formation and a gap appears in the conduction band. The bipolarons deprotonate to form neutral quinone-dimine units. These act as barriers to charge transport and, with the concomitant decrease in the number of charge carriers, the conductivity decreases. They also stressed that this aspect is complicated further by the fact that polyaniline is hydrolytically unstable at higher potentials.

On the other hand, PPy/PTS undergoes just one resistance transition (Figure 2.8). The polymer is conductive at positive potentials (> 0 V) and is resistive at negative potentials (< -0.2 V). Both polymers are most conductive when the potential applied is around $E = +0.4$ V no matter which resistometric technique is used. This is in agreement with previous conductivity investigations ^{140,70,132,139,152,137}.

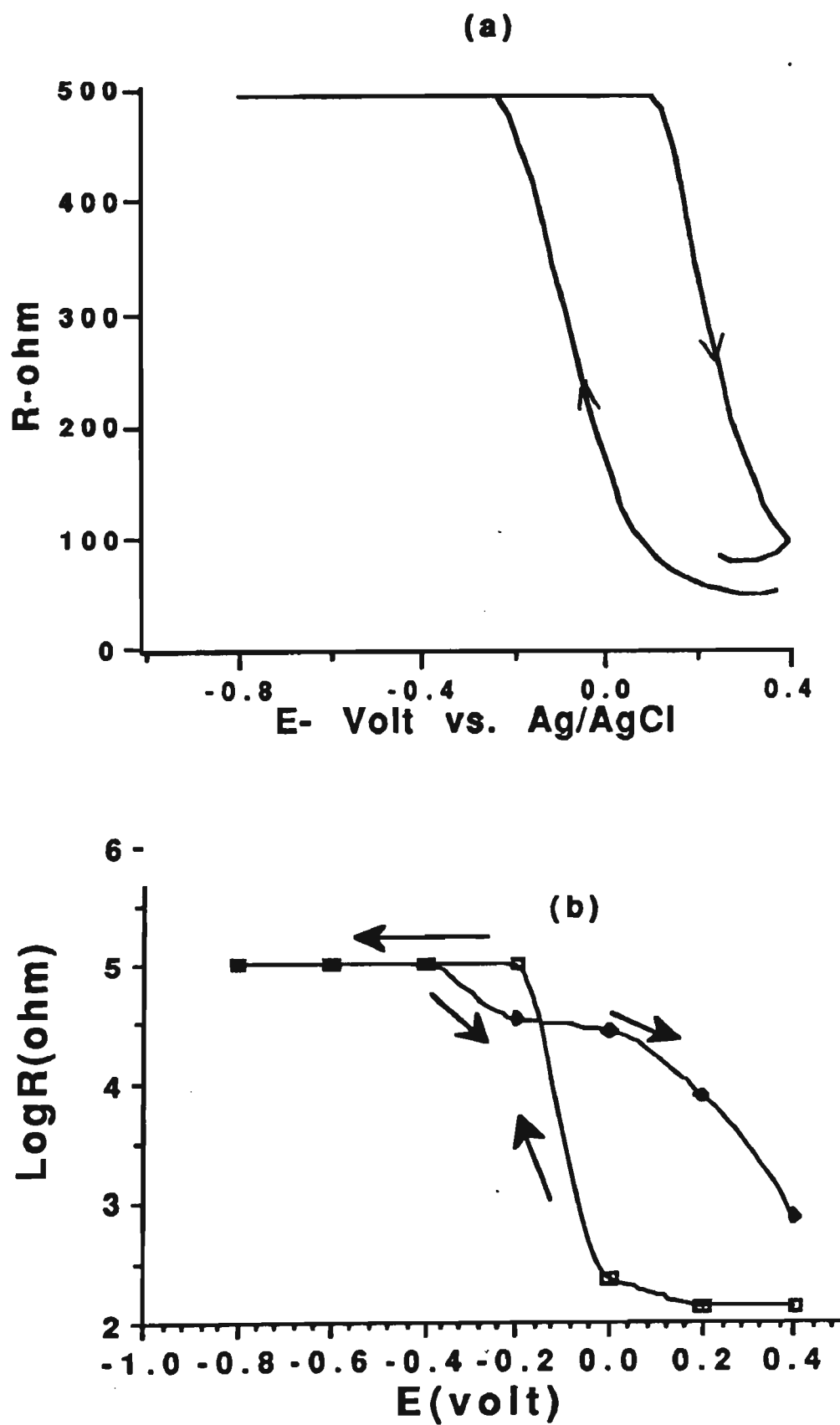
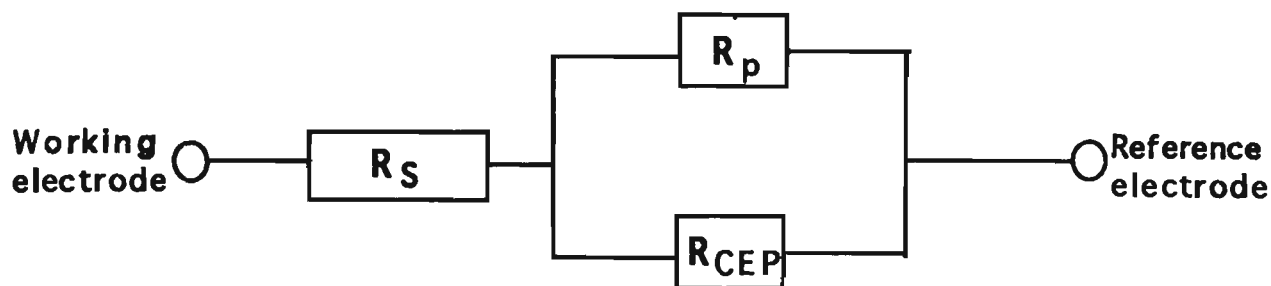


Figure 2.8: Polypyrrole/PTS oxidised/reduced in 1M HCl.

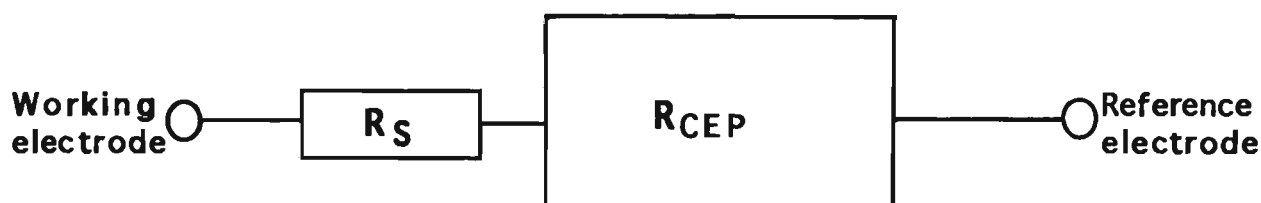
(a) Pulse resistometry: Scan rate = 10 mV/sec. Electrodes as in Figure 2.7.

(b) DC resistometry. The conditions as in Figure 2.7 (b)

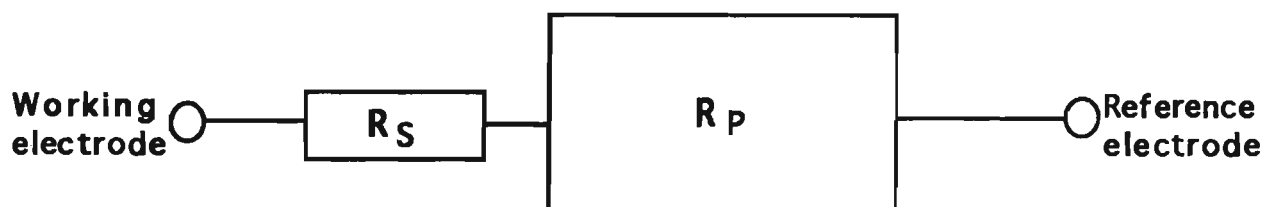
Closer examination of Figures 2.7 and 2.8, however, shows that the two techniques considered reveal different information about the electrodynamic properties of conducting polymers. The magnitude of the resistance changes do differ markedly from one technique to the other. This may be due to the fact that polymer thickness is different. However it is possible that differences in morphology, or even molecular structure of the polymers due to differences in polymer synthesis conditions can not be ignored. This difference can be also justified by Fletcher's models ^{153,154}. As the resistance of the solution is involved in the resistance recorded by the pulse resistometry procedure, then the resistance of the reduced form of the polymer measured with this technique is the resistance of the solution in the pores of the polymer structure. Therefore, the resistance in the reduced form is not very high. In the oxidised form, if the polymer is very conductive then the current flows through the most conductive path within the polymer which is the bulk polymer and not the pores. The electronic model for such an analysis is presented in Fig.2.9.



OXIDISED REGION: $R_{CEP} \ll \ll R_p$



REDUCED REGION: $R_{CEP} \gg \gg R_p$



R_S = Resistance of the Solution

R_{CEP} = Resistance of the Conductive Electroactive Polymer

R_p = Resistance of the Pores

Figure 2.9: *The electronic model for pulse resistometry.*

Unlike the pulse resistometry strategy, the bulk polymer resistance can be monitored by using the DC method. When the polymer is reduced it behaves as an insulator because it is in the undoped or less doped form. The

undoping process in this method generates very resistive values due to the nature of the measurement being independent of the pores in the polymer. The resistance results in the reduced form is independent of the pores because the polymer between the plates is so much thicker than the polymer on the plates. For very thick polymer, the possibility of the pores in connecting two plates is very slim. As shown in Figures 2.3 and 2.6 with the DC measurement technique, the resistance is measured across the plates whereas with the pulse resistometric method the resistance is measured through the polymer. Therefore, the amount of polymer involved in the resistance measurement using the pulse and DC methods are different.

Another major difference between these two techniques is related to the monitoring of the kinetics of the resistance changes. With the DC method we allowed the oxidation/reduction to go to completion and then the resistance was measured. This was not the case with pulse resistometry. To illustrate this difference a series of PPy/PTS and PAn/Cl polymers were investigated in different acid solutions.

Careful studies of Figures 2.7, 2.9 and 2.11 reveal the differences in the conductivity of PAn/Cl in different acidic media of the same pH. According to the pulse resistometry result PAn/Cl is more resistive in sulfuric acid than in nitric and hydrochloric acids in its half oxidised and half reduced form. However, it can be easily seen that when the polymer is in sulfuric acid the resistance of the fully reduced form decreases by a greater extent than that observed in the case of nitric and hydrochloric acids. This can perhaps be due to the effect of pH as 1M sulfuric acid does not have a pH value of 0, and in the case of polyaniline which is a pH sensitive material (as discussed in chapter 6) small changes in pH can affect the resistance of the polymer. Therefore it was perhaps better to prepare

different acid solutions with the same normality ($N=1$) We found that even 1N of HCl and H_2SO_4 do not have the same pH²⁰⁰. Therefore, to investigate the effect of anions in different acids one of the possible way was to prepare 1M of solutions to keep the concentration of the anions the same since making exactly the same pH was very difficult practically. Although titration is an alternative method to prepare the same pH of different solutions, the activity of the solution can affect the pH; for example 1N sulfuric acid has $pH=0.3$ and 1N HCl has $pH=0.1$ ²⁰⁰. As it was found (chapter 6) that polypyrrole/PTS is not pH sensitive in very low pHs, and that for this polymer we have also experienced greater changes in resistance in sulfuric acid, then perhaps the anions in the acidic media play the dominant role. Owing to the presence of the doubly charged sulfate (SO_4^{--}) the polymer perhaps behaves in a different way as compared with being in the presence of the singly charged chloride(Cl^-) or nitrate(NO_3^-).

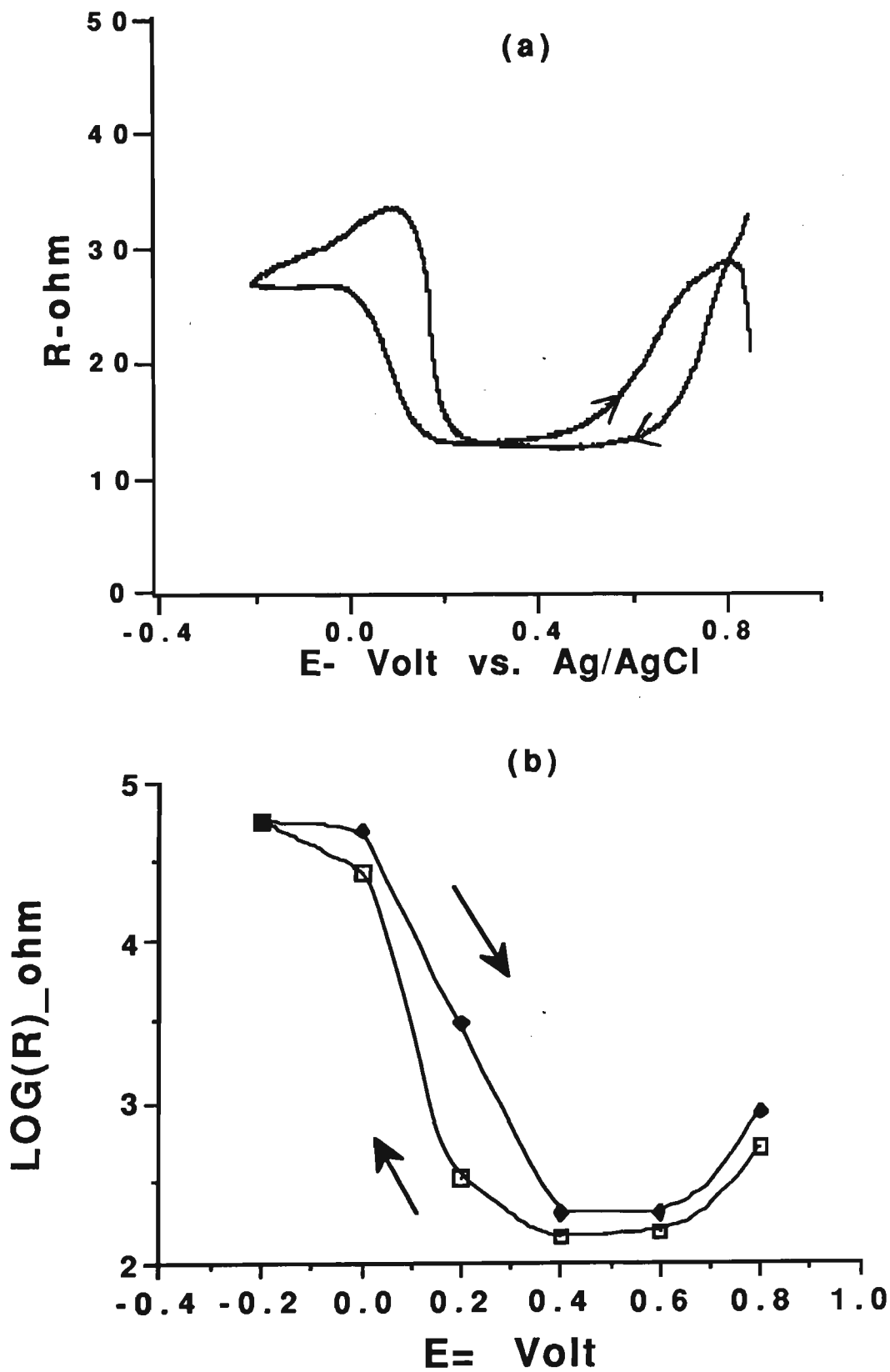


Figure 2.10: Polyaniline Chloride oxidised /reduced in 1M HNO₃ (a)

Pulse resistometry: Conditions the same as in Figure 2.7

(b) DC resistometry

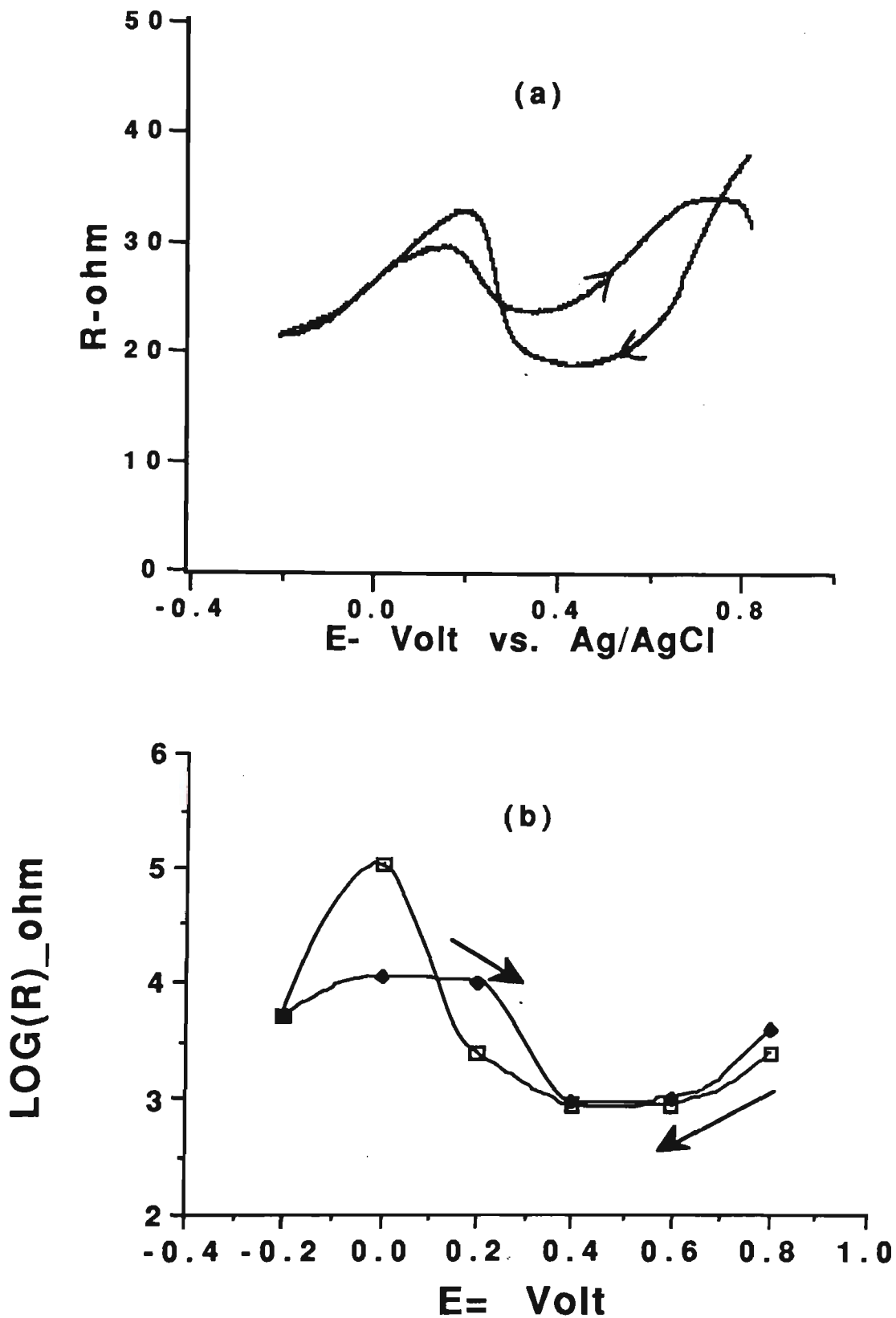


Figure 2.11: *Polyaniline chloride oxidised/reduced in 1M H₂SO₄.*

(a) *Pulse resistometry: Conditions as in Figure 2.7.*

(b) *DC resistometry.*

The DC resistommograms also indicate the same fact. PAn/Cl in HCl and HNO₃ has a similar resistance behaviour. However, the behaviour of the

polymer in H_2SO_4 is clearly different. The polymer is more resistive in its oxidised form and is less resistive in its fully reduced form than in HCl and HNO_3 . This is an obvious effect of the electrolyte in the resistance of the bulk polymer.

PPy/PTS was also studied in these acids. Figures 2.7, 2.12 and 2.13 were recorded while the conductivity of the polymer was investigated in HCl , HNO_3 and H_2SO_4 . It seems that the differences between the techniques are more obvious through the study of this polymer. This polymeric structure is more resistive in HCl when reduced(Fig. 2.8.a).

A very interesting result in this series of experimental work is a clear change which can be noticed with the DC method when these two polymers were studied in sulfuric acid (Figures 2.11.b and 2.13.b) , as compared with when HCl and HNO_3 were used. This suggests that the DC technique, being a longer time scale method, obviously allows changes and rearrangement to occur in the polymer that are not obvious with the dynamic pulse resistometry method.

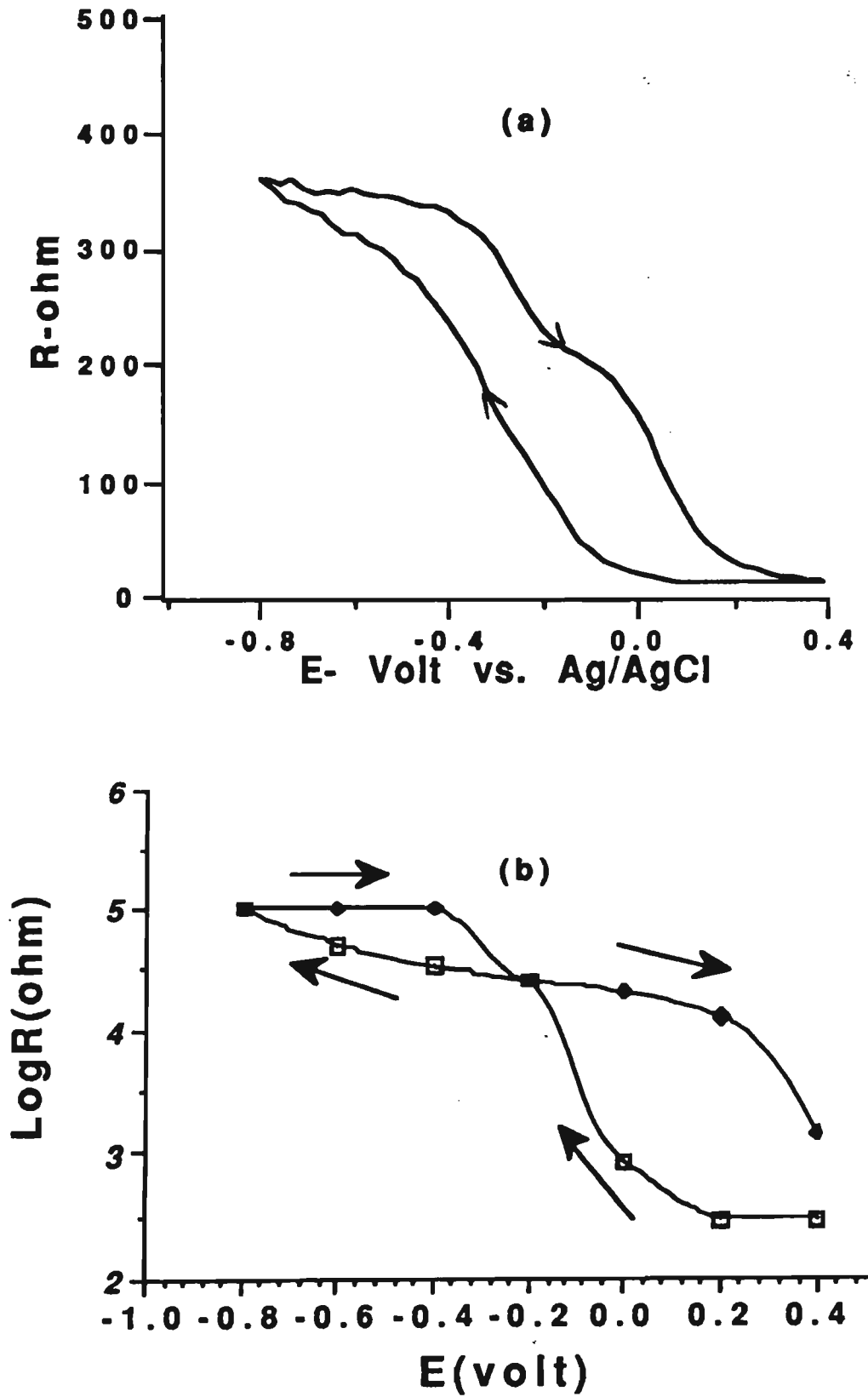


Figure 2.12: Polypyrrole/PTS oxidised/reduced in 1M HNO₃. (a) Pulse resistometry: Conditions are the same as in Figure 2.6. (b) DC resistometry.

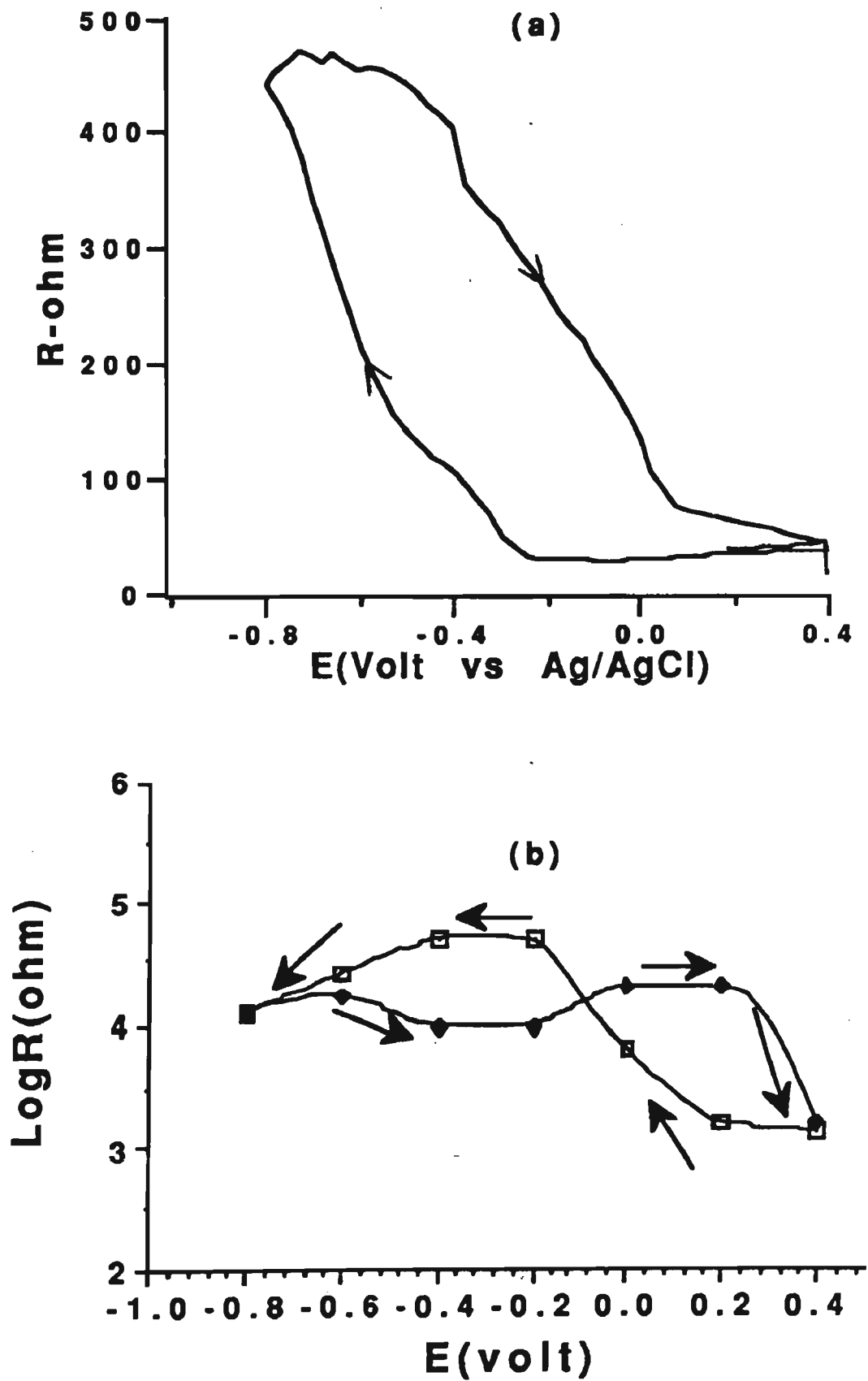


Figure 2.13: Polypyrrole/PTS in 1M H₂SO₄ . (a) Pulse resistometry
(b) DC resistometry

Further differences in the two resistometric procedures can be highlighted through consideration of Figures 2.14 and 2.15. The sensitivity of the techniques with respect to the pH of the electrolyte and the potential applied was studied separately. Our main objective was to find out the minimum resistance changes which can be monitored by each technique with changes in potential or pH.

To investigate the potential dependency of the techniques, PPy/PTS was studied in 1M NaCl. The kinetic information obtainable using the pulsed resistometry method is perhaps more closely demonstrated with an example using a potential step waveform (Figure 2.14). The potential was changed from 0.0V to -0.4V (increments of 0.1V) in the electrochemical cell. Then the resistance was measured using both resistometric methods. The pulse resistometry technique (2.14. a) is capable of detecting smaller changes in resistance of the polymer than the DC method (2.14. b). This is because of the dynamic nature of the technique to collect kinetic information at the polymer solution interfaces. This is a fast and dynamic technique by which information on changes in resistance, as a function of potential and time, are easily obtained. Therefore, the pulse method is strongly recommended for characterisation studies ^{150,151}. This technique enables us to find the potential at which the polymer is very conductive and stable.

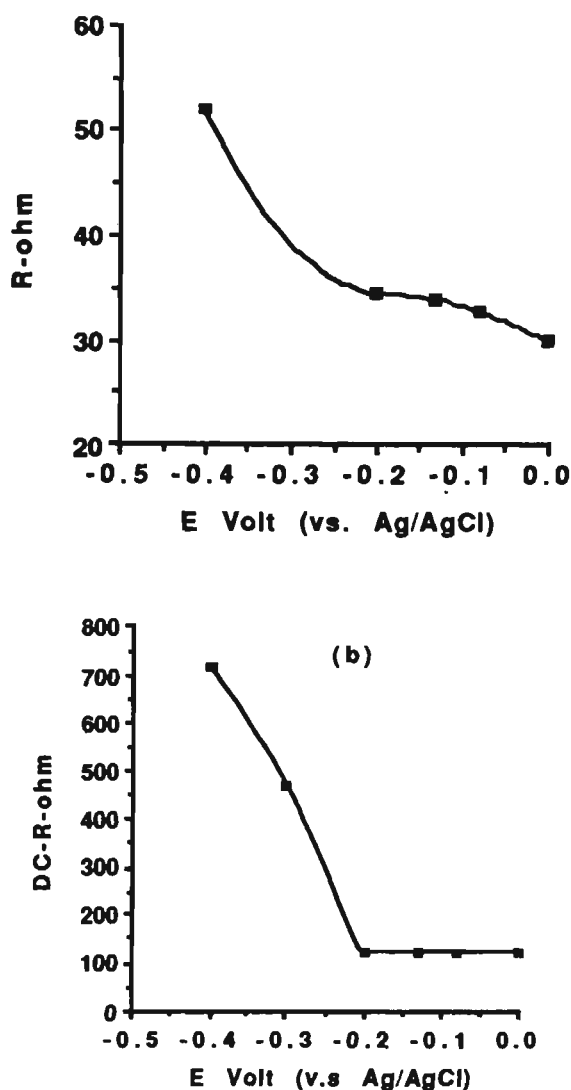


Figure 2.14: Limit of detection of resistance using Polypyrrole/PTS in 1M NaCl.

(a) Pulse resistometry: Conditions as in Figure 2.8.

(b) DC resistometry

As can be observed, the changes in the resistance of the system as a function of potential is more sensitive using the DC technique than pulse resistometry. However, the range of resistance detection as a function of potential is narrower using the DC method as there were no resistance changes recorded over the range of potential between 0.0V to -0.2V.

Another practical consideration in terms of monitoring changes in resistance is the limit of detection. This is particularly important with respect to the use of conducting polymers in sensing applications. As part of my work I have been interested in the development of polymer sensors that are sensitive to changes in pH. PAn/Cl is a pH sensitive material 155-158. Therefore, it was selected for the pH sensitivity study. Different pHs were made from aqueous HCl ³² and the resistance of the polymer was investigated in these solutions.

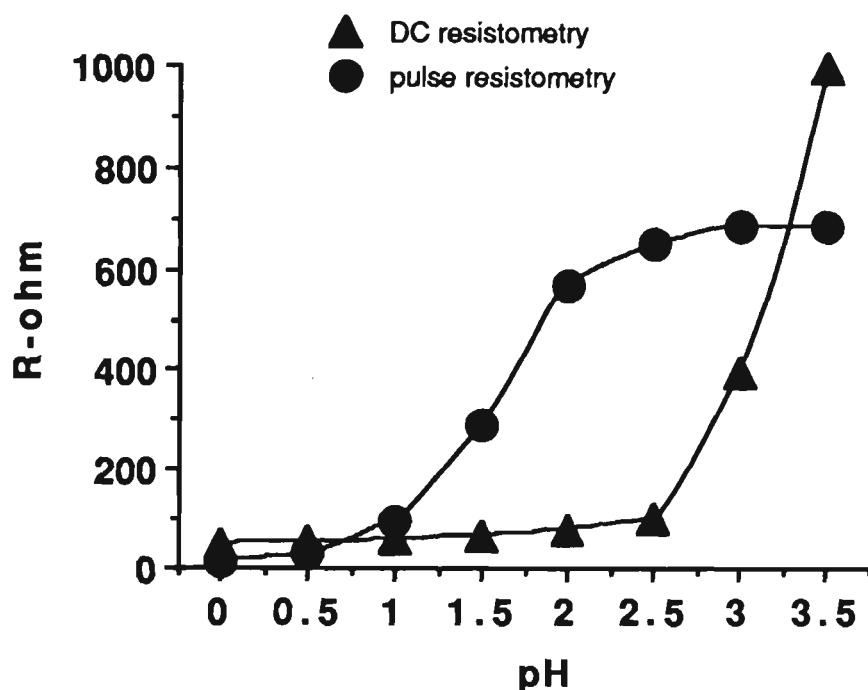


Figure 2.15: *R vs. pH plot for Polyaniline Chloride was used as in Figure 2.5. Then the polymer was studied in different HCl solutions with different pH. The polymer was left at $E=0.4$ V during resistance measurements vs. pH. The resistance was recorded when no further changes in its value was observed.*

It was found that the minimum changes of resistance that could be measured in this work was 50 ohm for DC and 50 ohm for pulse methods. This corresponds to a minimum change of pH measurement of 2 and 1 respectively.

With respect to applications, pulse resistometry is not a useful method for pH detection. This method should be used in an electrochemical cell. The major disadvantage of this method is that it is too sensitive to changes in solution resistance. The use of auxiliary and reference electrodes is required and this complicates the experimental set up. Moreover, the reference electrode itself needs careful maintenance.

On the other hand, the DC method is strongly recommended for sensing technology. This is a simple technique by which the resistance of bulk polymers is measured.

2.5 CONCLUSION

Both DC and pulse resistometry can be used to monitor changes in resistance of conducting polymers as a function of applied potential (oxidation state) or the chemical composition of the solution. Care should be taken in any quantitative comparison of the measurements obtained, since conditions used for polymer growth are not identical. However, it can be said that the DC resistometry method is capable of providing data on the rate of change of resistance as a function of applied potential more sensitively than the pulse method. In contrast, the pulse method is more applicable over a wider potential range. In addition the pulse technique is also more sensitive in detecting resistance changes in solutions with respect to different pHs. The data obtained to date indicates that resistance measuring techniques provide a fundamental adjunct to conventional techniques, such as Cyclic Voltammetry, in the study of the fundamental electronic properties of conducting polymers. Moreover, measuring changes in properties such as resistance provides an alternative signal generation mechanism for utilization in the development of sensors. Studies of these properties, and the effect of sensor environment on them, will provide necessary information for the development and expansion of new sensing technologies involving polymeric materials.

Chapter 3

THE EFFECT OF THE SULFONATED AROMATIC COUNTERIONS ON THE ELECTROCHEMICAL PROPERTIES OF POLYPYRROLES- A STUDY USING PULSE RESISTOMETRY

3.1. INTRODUCTION

As has been concluded in the previous chapter, the pulse resistometry technique is capable of providing invaluable kinetic information as related to changes in polymer resistance upon oxidation/reduction. Therefore, this technique has been employed in the following characterization study to investigate the effect of the sulfonated aromatic counterions, employed during the polymerisation process, on the electrochemical properties of polypyrroles.

The counterions chosen in this work were a range of sulfonated aromatics since these are known to provide conducting polymers with optimal mechanical and electrical properties ¹⁶⁰⁻¹⁶². These properties are essential if practical applications are to be realised ⁷⁰. While other workers ^{70,163} have considered the effect of simple non aromatic and very few aromatic counterions ¹⁶⁰ on resistance - potential behaviour, the influence of the structure of the important sulfonated aromatic counterions is yet to be reported.

3.2. AIMS AND APPROACH OF THIS CHAPTER

This chapter introduces and evaluates the pulse resistometry technique for characterisation of polypyrroles, with aromatic counterions incorporated. Comparison between characteristic parameters of the cyclic voltammetry (CV) and cyclic resistometry (CR) experiments has been considered as well. In order to gain "real-time" information changes in the resistance of the polymer as a function of the charge consumed have been examined. It has already been noted ¹⁶⁴ that the use of conducting polymer materials often involves the use of repetitive potential pulses. Therefore, to

complete this characterisation examination, the effect of pulse waveform on the resistance of polypyrroles, using different sulfonated aromatic counterions, was also considered.

3.3. EXPERIMENTAL

3.3.1 INSTRUMENTATION

The experimental set up used in this study is illustrated in Figure 3.1. The potentiostat and the electrochemical cell are connected together via the resistometer. This set up is capable of simultaneously measuring in-situ changes in resistance (R), current (i) and charge (Q) during the electrochemical reaction in "real-time". All results reported in this chapter were carried out when R , i and Q were measured simultaneously.

The potentiostat used in this study was a BAS CV27 Voltammograph (Bio Analytical Systems, Lafayette, P.A. U.S.A.). Data were collected using a MacLab (Analog Digital Instruments, Sydney, Australia) interface and a Macintosh computer. A resistometer, supplied by CSIRO, (Division of Mineral Products), Melbourne, Australia, was employed.

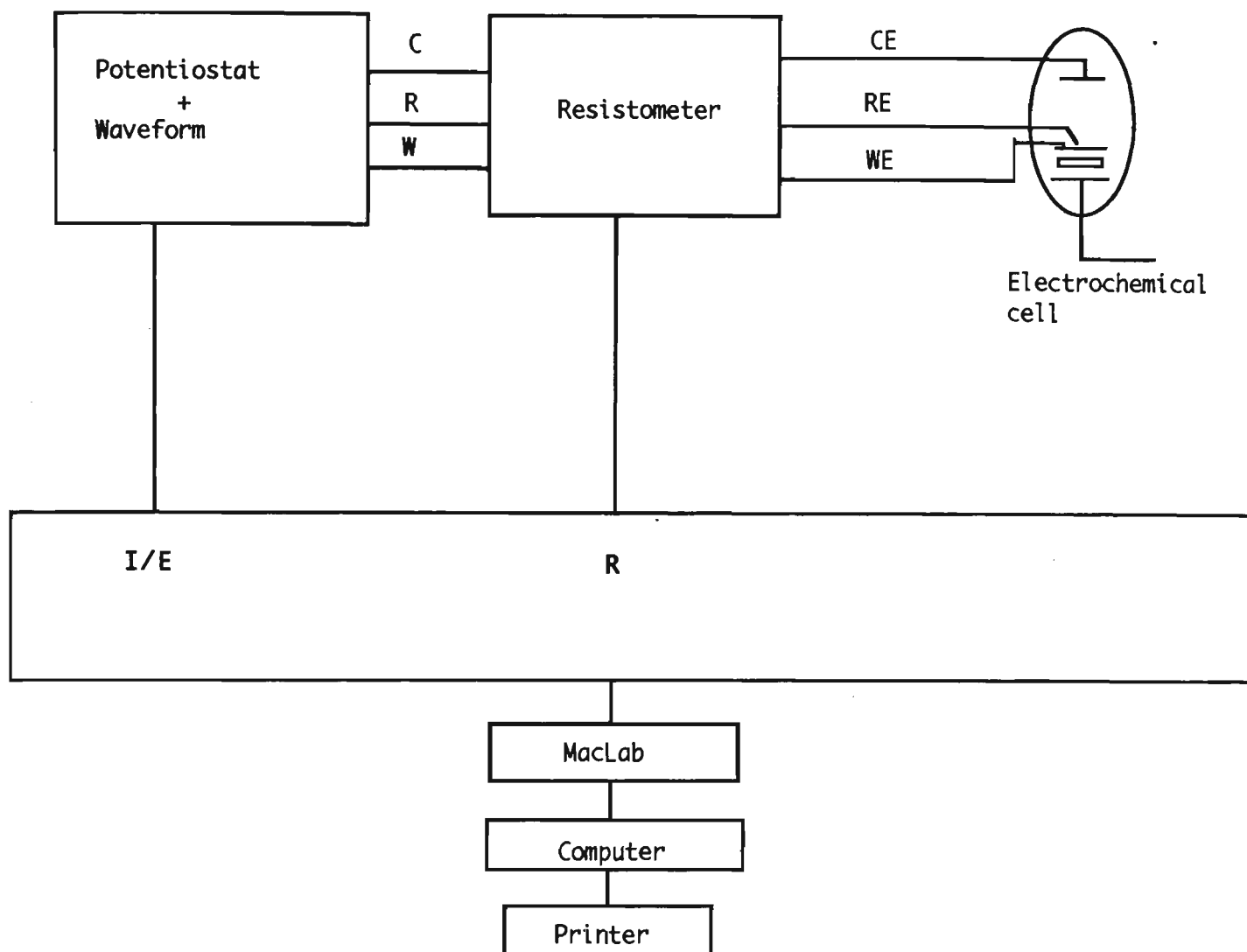
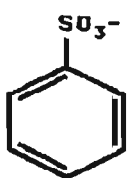


Figure 3.1: The schematic of the in-situ resistance measurement set up.

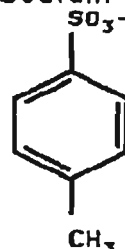
3.3.2. REAGENTS AND STANDARD SOLUTIONS

The polymer synthesis solution consisted of 0.1 M pyrrole (Sigma), freshly redistilled prior to use, and 0.025 M of the sulfonated counterions (Aldrich) shown in table 3.1. These components were dissolved in deionised (milli-Q) water. Nitrogen was used for deoxygenation of the solutions before the polymerisation process. The supporting electrolyte used in this study was 1M NaCl. This was deoxygenated whenever the experiment was carried out.

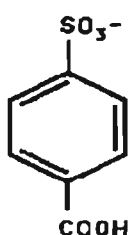
a. Benzenesulfonic acid,
Sodium salt (BSA)



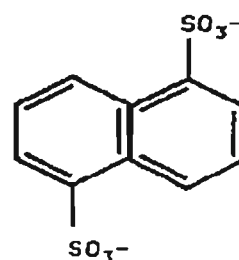
b. P-Toluenesulfonic acid,
Sodium salt (PTS)



c. 4-Sulfobenzolic acid,
Sodium salt (SBSA)



d. Naphthalene disulfonic acid,
Sodium salt (NDS)



e. Dodecylbenzenesulfonic acid,
Sodium salt (DBSA)

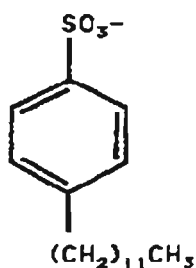


Table 1

Table 3.1: Sulfonated aromatic compounds.

3.4. RESULT AND DISCUSSION

All polymers were potentiostatically deposited onto a platinum disc substrate with (diameter = 1.62 mm) and the total charge consumed was 5 mC (ca. 1 μm thickness). A Ag/AgCl reference electrode and a platinum counter electrode were employed. Electrochemical characterisation was carried out in the three electrode electrochemical cell, including counter

electrode (CE), reference electrode (RE) and working electrode (WE), using cyclic voltammetry (i vs E), cyclic resistometry (R vs E) and coulometry (Q vs R).

As was noted in chapter 2 the pulse resistometric measurement includes a component due to solution resistance. However with the solution employed in this work (1M NaCl) the solution resistance was found to be essentially constant over the potential range considered (Figure 3.2).

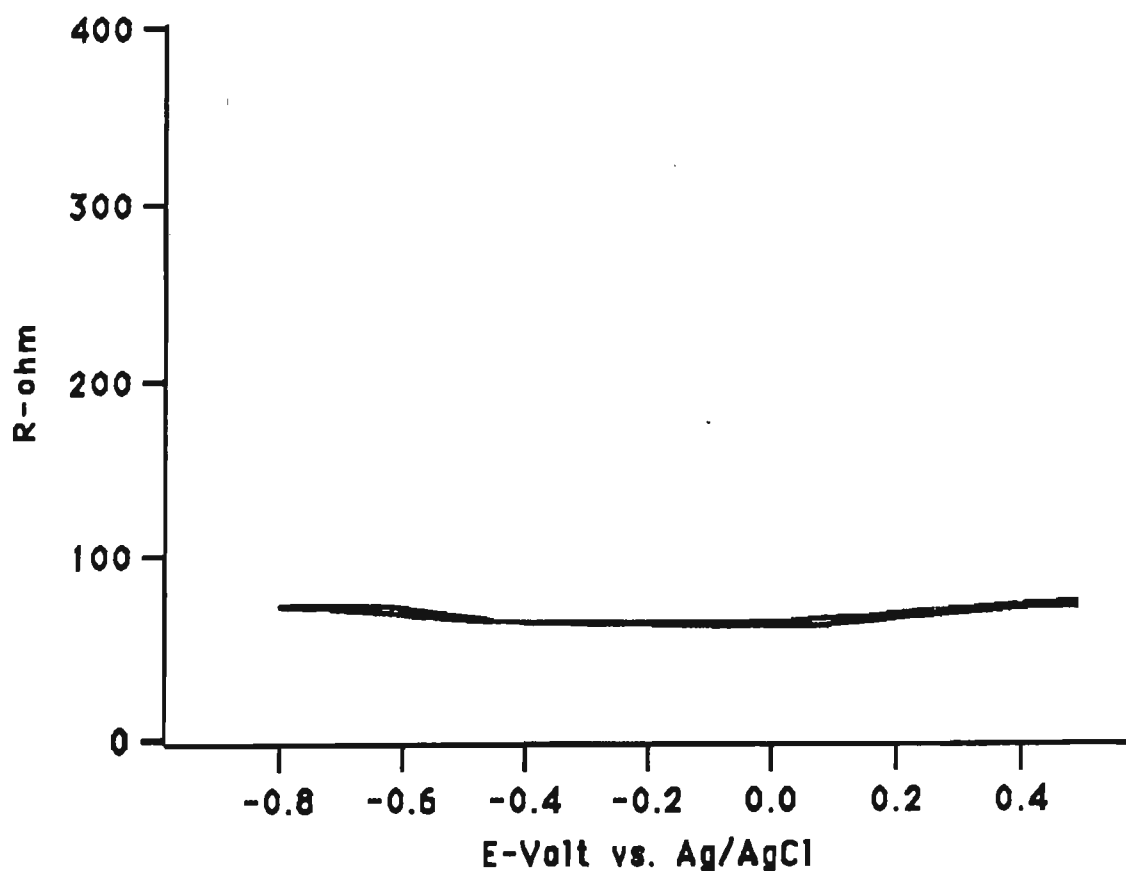


Figure 3.2: Cyclic resistogram obtained using a platinum disc electrode in 1M NaCl; scan rate=100 mV/sec.

The sulfonated aromatic compounds shown in Table 3.1 were then considered as counterions. All polymers were grown under potentiostatic conditions and in all cases a stable, conductive electroactive polymer was formed. The normal oxidation/reduction process (equations 3.1 and 3.2) was observed using cyclic voltammetry (Figure 3.3.).

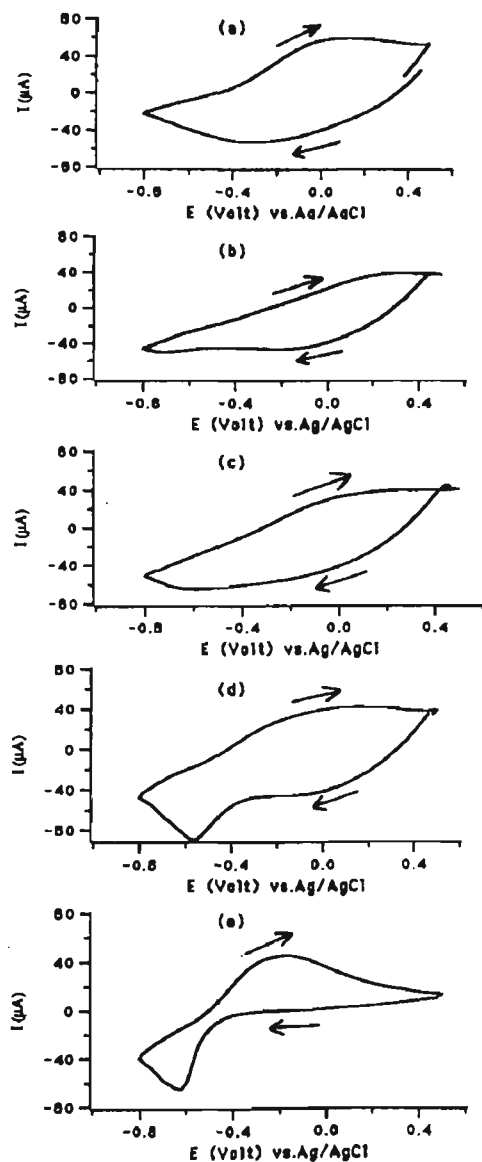
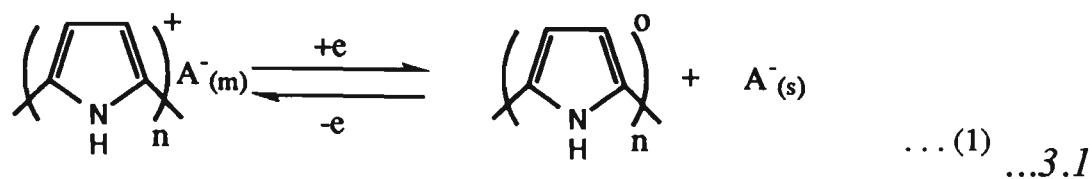


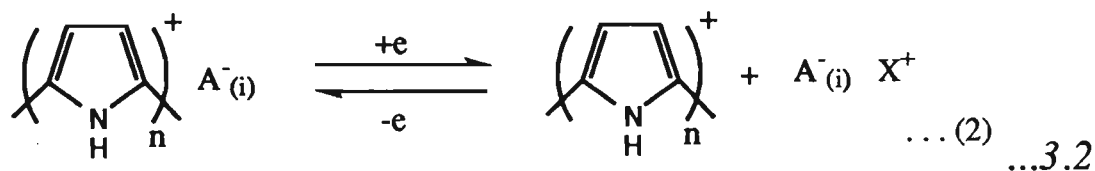
Figure 3.3: Cyclic voltammograms obtained after growth for polymer containing (a) BSA, (b) PTS, (c) SBA, (d) NDS, and (e) DBSA (supporting electrolyte, 1M NaCl; scan rate, 100 mV/sec).

In the case of the mobile counterion, (BSA), just a single oxidation/reduction process was observed (Figure 3.3) This is attributed to anion expulsion upon reduction and re-incorporation upon oxidation according to:



where $A^-_{(m)}$ is mobile counterion incorporated into the polymer during synthesis and $A^-_{(s)}$ is that counterion expelled into solution.

With other large counterions (eg. NDS) two distinct couples were observed on the cyclic voltammograms (Fig. 3.2(d)). The more negative of these two couples has been associated with cation incorporation/expulsion¹⁶⁵. Such responses are more apparent when the counterion A^- is less mobile and the cation is incorporated to ensure charge compensation. Naoi et al.¹⁶⁶ have also proven such phenomenon by examining mass increases due to cations being incorporated into the polymer film to maintain charge neutrality. This cation incorporation process can be described as:



where $A^-_{(i)}$ is the immobile counterion incorporated into the polymer and X^+ is the cation from the electrolyte solution.

As the size of the counterion is increased further (eg. DBSA) only the more negative, cation response, is observed (Fig. 3.3(e)). As can be seen from the Figure 3.3 some polymers do not show well defined oxidation peaks. Zhang and Dong⁷⁰ also did not observe well defined anodic peaks for some non aromatic counterions they incorporated into the polypyrrole films.

It was found that, as the size of the counterion becomes bigger, the potential at which the cation incorporation response appears, shifts to more negative potentials. Another important observation is that the same effect is seen for the anodic peak. Zhang and Dong argue that the anodic peak is related to the anion movement and dopant nature. Although the oxidation and reduction peaks reported in Fig. 3.3 are poorly defined, the resistograms in Fig. 3.4 suggest better defined transitions between the oxidised and reduced forms of the polymers.

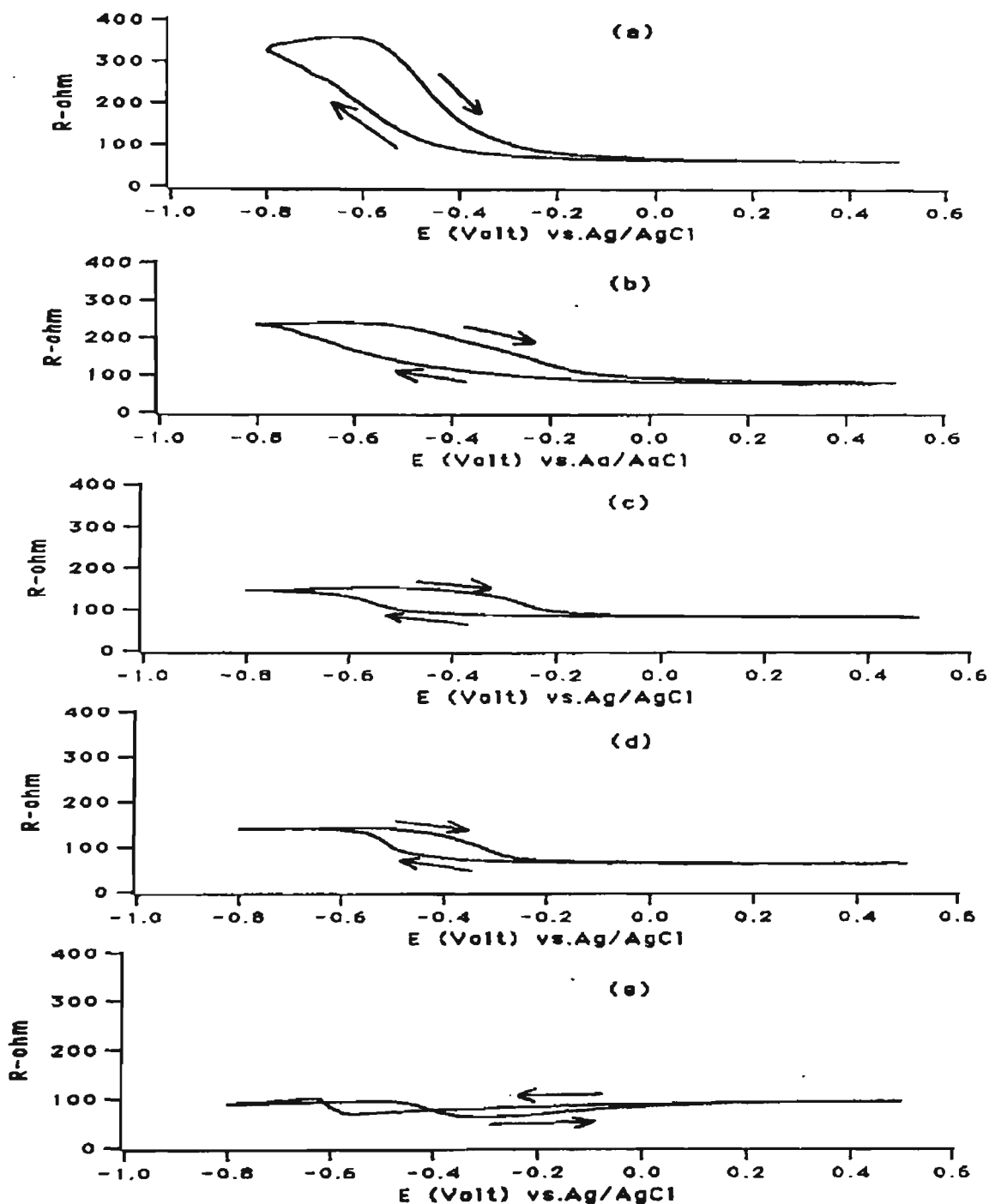


Figure 3.4: Cyclic resistograms obtained after growth (for polymer containing (a) BSA, (b) PTS, (c) SBA, (d) NDS and (e) DBS. Supporting electrolyte was 1M NaCl ; scan rate, 100 mV/s) .

It was found that the maximum changes in resistance were observed using the BSA counterion (Fig. 3.4(a)). As explained above, anion

movement is most easily achieved with this counterion. Consequently the reduction process equation 3.1 is most efficient and the material is transformed to the less conducting form. Addition of any further functional groups to BSA inhibits the rate and magnitude of the resistance transition as the potential is scanned in a negative direction. Even the addition of a single methyl group to produce the PTS counterion has a marked effect on the potential vs. resistance curve obtained.

Zhang and Dong (4) have argued that more hydrophilic polymers are reduced less efficiently in organic solvents. Presumably the reverse holds and addition of the methyl group in this case causes production of a more hydrophobic polymer and consequently less efficient reduction in water. However, hydrophobic/hydrophilic character is not the only property that should be considered. For example the addition of a carboxyl group to the counterion to form SBSA also results in less efficient oxidation/reduction (Fig.3.3) and concomitantly less marked increase in resistance (Fig.3.4). Obviously then it is not just the anion-solvent interactions that are important but also the affinity of the anion for the polymer, and the mobility within the polymer. This is particularly noticeable when larger anions, eg. DBSA, are employed (Fig. 3.4(e)). As shown above (using cyclic voltammetry) significant current flow is observed with these counterions, however it is associated with cation movement. The influx of cations will be accompanied by an influx of water since the cations are solvated ¹⁶⁶. The inclusion of water in the polymer structure may explain why the resistance change is not so large. And so, it is not just the extent of the oxidation/reduction occurring that determines the resistance changes observed; it is also the nature of these processes i.e. whether anion or cation movement is involved.

Moreover, the physical properties (resistivity-conductivity) can be affected by the morphological structure of the resultant polymer. Mitchell and coworkers ¹⁶³ pointed out that the type of molecular organisation, isotropic or anisotropic, changed the DC conductivity of polypyrrole with aromatic and non-aromatic counterions. They showed that simply by using toluene sulfonate counterion and creating an anisotropic polypyrrole, the DC conductivity of the polymer increased more than 10 times compared with what was observed for polypyrrole/sulfate. The latter polymer has been found to be anisotropic material ¹⁶³.

It should be noted that in all cases a hysteresis is observed; ie. the potential must be scanned more positive in order to re-oxidise the polymer to the conducting state. This is presumably due to the fact that it is more difficult to inject charge into the reduced (more resistive) materials. Interestingly for DBSA, upon re-oxidation the resistance actually drops below the original value for some period of the potential range indicating as if a more conducting pathway has been formed during the reduction process. This is because, with the larger counterions, significant amounts of cation are incorporated ¹⁶⁷.

Plots of Q vs R for each polymer system are readily extracted from the above data (Figure 3.5). In all cases a threshold level of charge removal is required to trigger the increase in resistance.

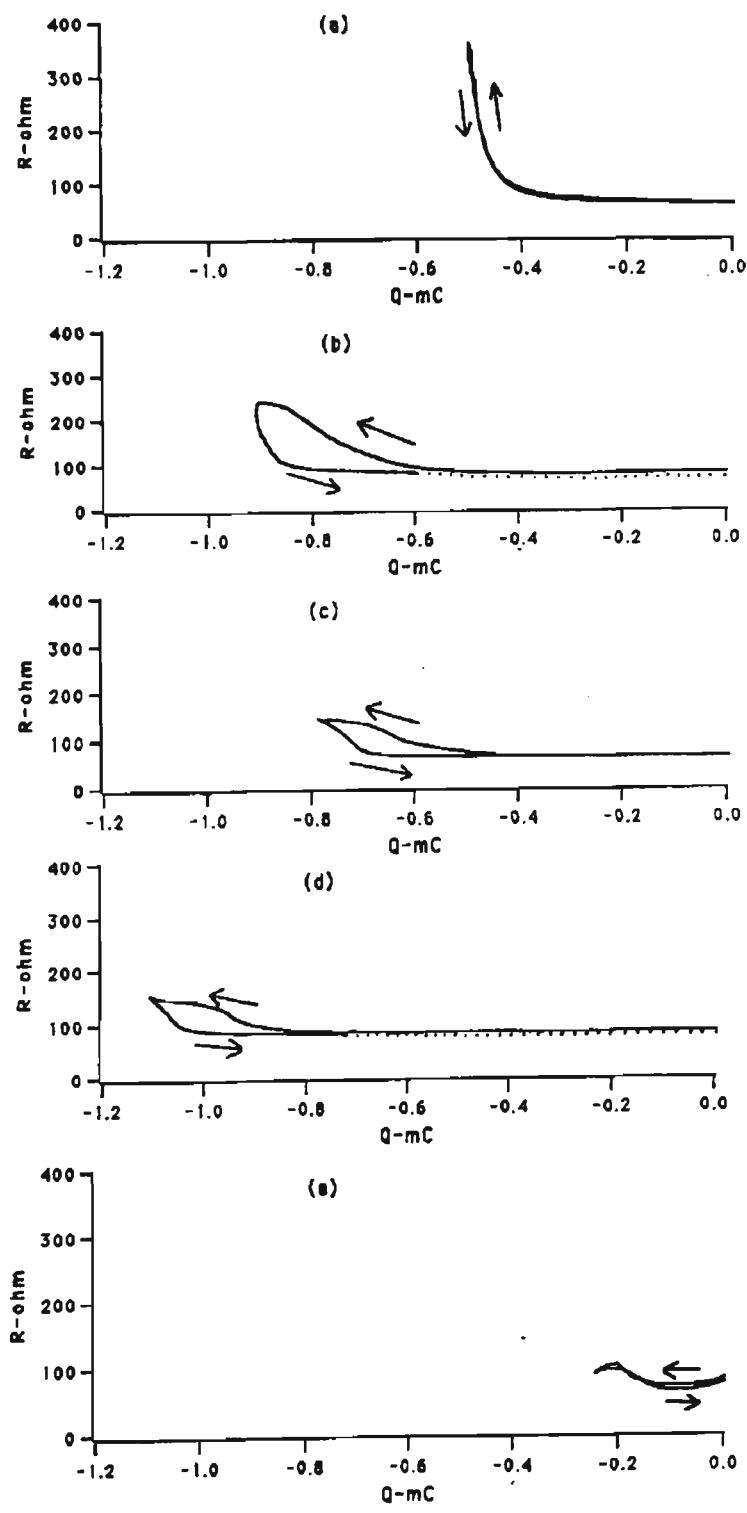


Figure 3.5: Plots of Q vs. R for polymer containing (a) BSA, (b) PTS, (c) SBA, (d) NDS and (e) DBSA. Other conditions are the same as in Figure 3.4.

The amount of charge required to induce this trigger is important for numerous technological applications since it determines the current flow that can be sustained before resistance increases are encountered. In applications that require imposition of negative potentials such as batteries, sensors and membrane separations this will be important. The threshold trigger is most clearly defined with BSA (Fig. 3.5(a)). Also, the polymer containing BSA shows reversible behaviour ie. the same amount of charge must be inserted as was extracted in order to restore the conductivity of the polymer (Fig. 3.5(a)). For PTS, SBSA and NDSA increasing amounts of charge must be removed to trigger the increase in resistance. As expected the more hydrophobic or less mobile the counterion the more charge must be injected; ie. the more positively charged sites must be created to expel it and cause a change in resistance. An interesting result is again evident with NDS, where significant amounts of charge can be inserted and extracted but only minor changes in resistance are observed; again emphasising the importance of the nature of the processes occurring.

In all cases, less charge insertion was required to restore the conductivity. This is presumably due to the fact that in order to reach maximum resistance all of the conducting pathways have to be shut off. However, upon reoxidation re-establishment of just some pathways will be sufficient to restore conductivity. A further contributing factor may be that a "new" material is formed during reduction of these polymers. The use of DBSA as a counterion has some dramatic effects on the potential/resistance behaviour. Only a small amount of charge is required to trigger the small change in resistance. It is well known that the movement of larger chain hydrophobic counterions is extremely restricted ¹⁶⁶. Consequently the electrochemical reduction is inefficient due to perturbed anion movement and the reduction process is accompanied by cation insertion. As stated

above such electrochemical processes do not result in rapid changes in resistance.

The resistance/time behaviour upon application of potential pulses (Chronoresistograms) for each polymer system was also recorded (Figure 3.6).

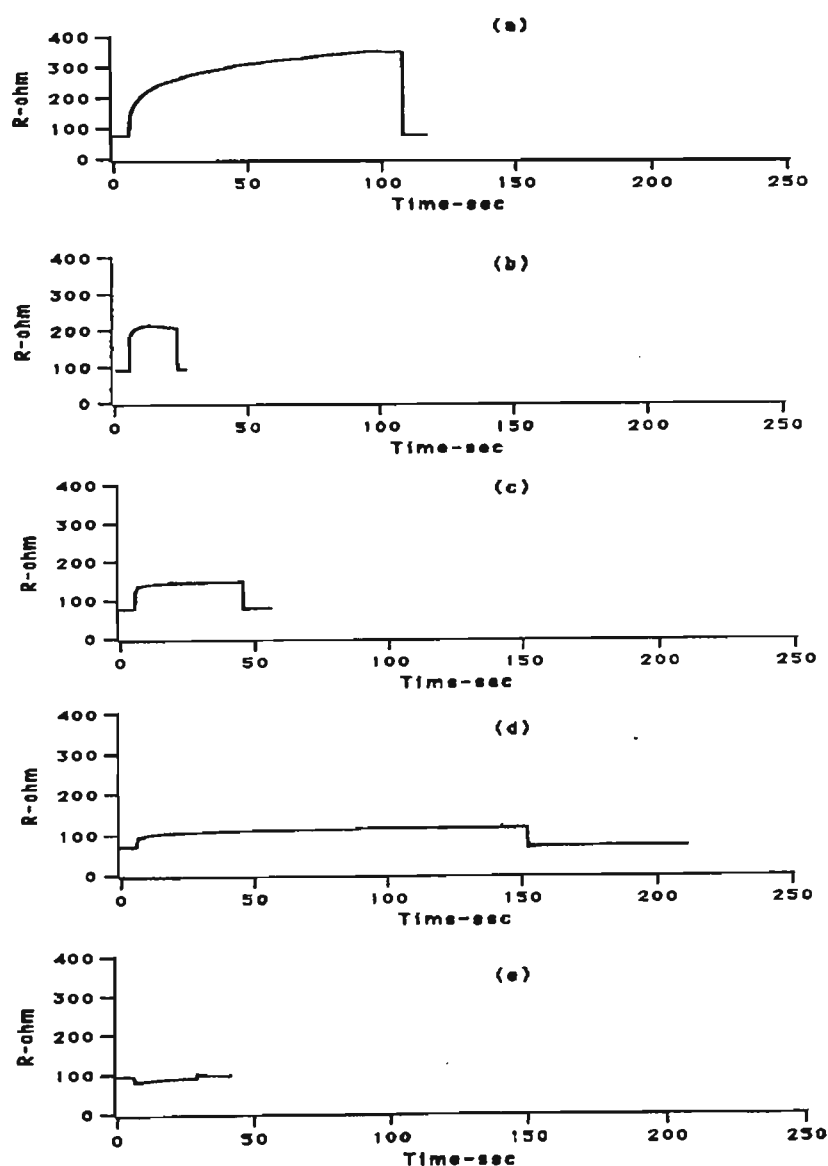


Figure 3.6: Chronoresistograms obtained at each of the electrodes. (a) BSA. Potentials applied: $E = 0$ V for 0-6 s; $E = -0.8$ V for 6-108 s; $E = 0$ V for 108-117 s. (b) PTS. Potentials applied: $E = 0$ V for 0-6 s; $E = -0.8$ V for 6-24 s; $E = 0$ V for 24-27 s. (c) SBA. Potentials applied: $E = 0$ V for 0-6 s; $E = -0.8$ V for 6-46 s; $E = 0$ V for 46-56 s. (d) NDS. Potentials applied: $E = 0$ V for 0-6 s; $E = -0.8$ V for 6-152 s; $E = 0$ V for 152-212 s. (e) DBSA. Potentials applied: $E = 0$ V for 0-6 s; $E = -0.8$ V for 6-29 s; $E = 0$ V for 29-41 s.

The chrono-resistograms show that in all cases the resistance transition with the positive going pulse was rapid. That is the resistance rapidly decreased upon oxidation with all counterions. With the negative going pulse the transition was slower. This is, as stated above, due to the increased number of paths that must be shut down to complete the increase in resistance transition.

The increase in resistance transition with BSA appears to be slower than with the other counterions investigated. This is due to the fact that the resistance of the reduced BSA material is greater in magnitude. Close examination of the data reveals that the initial part of the resistance transition up to 200 ohm is similar in rate to the other counterions, but further reduction and further increases in resistance then become difficult. Zhao et. al ¹⁶⁰ have also pointed out that the structure of the sulfonated counterion affects the polymer dry conductivity. They pointed out that for polypyrrole, PTS is the best counterion, amongst those employed, to obtain a good dry conductivity.

3.5. CONCLUSION

In this chapter the capability of pulse resistometry to gain valuable real time information in the characterisation of conducting polymers has been shown useful. It has been pointed out that while cyclic voltammograms lack well defined oxidation/ reduction peaks, the cyclic resistograms highlight the important differences in resistance- potential properties that are induced even by the most subtle changes in molecular structure of the sulfonated counterions. This can be more appreciated by considering a very small

amount of counterion used during polymer synthesis and the fast scan rate used during the experiments.

The changes can greatly influence the nature of the electrochemical processes occurring and, hence, determine the composition and bulk (resistance) properties of the conducting polymers. The pulse resistometry results are not only in agreement with the other results reported, but also provides more in-situ and 'real time' information.

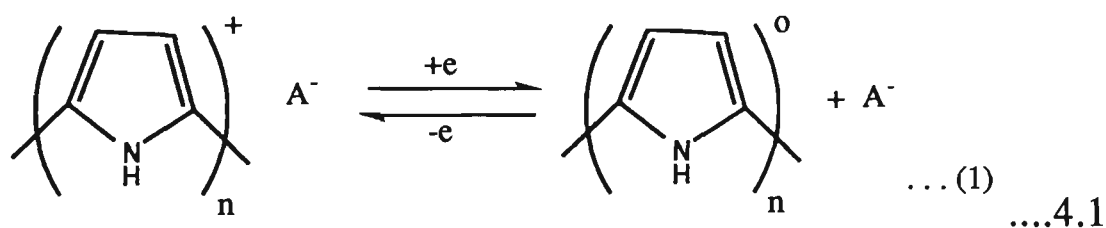
CHAPTER 4

**DETAILED STUDIES INTO THE SWITCHING
PROCESSES FOR POLYPYRROLE/PTS**

4.1. INTRODUCTION

To utilise the potential of conductive, electroactive polymers (CEPs) in sensor applications, it is necessary for processes occurring at the polymer solution interface to be well characterised. It has already been shown in the previous chapter that the counterion incorporated during polymerisation has a marked effect on the electronic and electrochemical properties of the resultant polymers ^{168,169,62}.

The switching ability of conducting polymers, such as polypyrroles, between the reduced and oxidised states has attracted the immediate attention of energy technologists who realised the potential to be gained from lighter weight batteries. Furthermore, those involved in electronics also realised that bistable polymer devices could be made in any shape or size. This process for polypyrroles can be described as:



Where A^- is PTS in our case. The importance of this electrochemical process has resulted in many studies on the subject. However to date the tools available to study the process have been limited. Only electrochemical techniques such as cyclic voltammetry, chronopotentiometry and chronoamperometry provide direct, in-situ, information on the process. However these techniques are only capable of monitoring the electrochemical processes (changes in potential or current flow) occurring. Therefore, the main focus in this chapter is on the resistance trend during the oxidation and reduction process. The comparison between the CV and the CR method has been done in the previous chapter.

4.2. AIMS AND APPROACH OF THIS CHAPTER

In this chapter the effect of polymer synthesis conditions as well as post-polymerisation treatment on the resistance/potential (R/E) profile have been investigated by using the pulse resistometry method.

4.3. EXPERIMENTAL

4.3.1. INSTRUMENTATION

A home made galvanostat was used for galvanostatic polymerisation. A BioAnalytical System (BAS) model CV-27 was used for potentiostatic and potentiodynamic electrodeposition. The resistometer was purchased from CSIRO (Division of Mineral Products), Melbourne, Australia. Data collection was carried out using a Macintosh computer.

All reagents were of analytical reagent (AR) grade unless otherwise stated.

Electrodeposition was carried out in a three-electrode system electrochemical cell using a platinum disc substrate (diameter = 1.62 mm) as the working electrode and a Ag/AgCl as the reference electrode. A Pt electrode was also used as the counter electrode. Different techniques (galvanostatic, potentiostatic and potentiodynamic) were employed in this investigation for electrodeposition from a monomer solution containing 0.1 M pyrrole and 0.025 M PTS salt in Milli-Q deionised water. Resistance changes were simultaneously monitored during polymer growth by using the resistometer coupled to a CV 27 voltammograph. Resistometry after polymer growth was conducted in 1 M NaCl supporting electrolyte unless otherwise stated.

4.3.2. REAGENTS AND STANDARD SOLUTION

Pyrrole was provided by Sima. Sodium chloride, calcium chloride and lithium chloride were obtained from BDH. Sodium paratoluene sulfonate was obtained from Aldrich.

4.4. RESULTS AND DISCUSSION

As has been already pointed out in Chapter 3 the molecular structure of conducting polymers affects their intrinsic electronic properties. In this section the effect of different parameters varied during and after electrodeposition on the in-situ conductivity of the resultant polymers is discussed.

4.4.1. The effect of parameters involved during polymerisation on the polymer resistivity

There are different methods for the electrodeposition of conducting polymers on substrates. The most commonly employed are: galvanostatic(GSM), potentiostatic(PSM) and potentiodynamic(PDM). In the following discussion, different conditions were considered for each method and then comparison between the results was carried out for each method separately.

4.4.1.1. The galvanostatic method

Figure 4.1 demonstrates that if less charge is consumed (a shorter duration of time used at constant current density) during the galvanostatic polymerisation, the resultant polymer shows less changes in the resistance during the doping-dedoping process in the electrolyte. Nevertheless, if the polymer is very thick (current density=1mA and t=8 min) the magnitude of the changes in the resistance decreases. This suggests that with "thicker" polymers the efficiency of reduction decreases. The counterion (PTS here) can not move easily from the bulk polymer to the solution as it may be trapped in the bulk polymer. This results in less changes in the resistance value of the polymer.

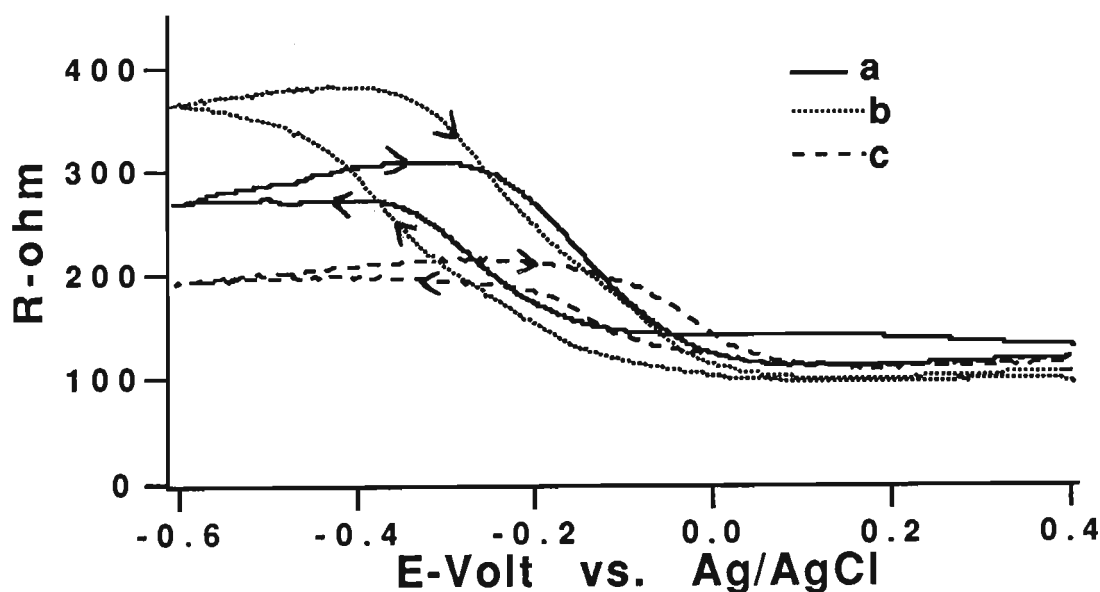


Figure 4.1: *The effect of charge consumed during galvanostatic polymerisation. on the R/E response. Polymers prepared as in the Experimental section and studied in 1M NaCl using a scan rate = 10 mV/sec. (a) $j = 1 \text{ mA/cm}^2$ and $t = 1 \text{ min}$ (b) $j = 1 \text{ mA/cm}^2$ and $t = 4 \text{ min}$ (c) $j = 1 \text{ mA/cm}^2$ and $t = 8 \text{ min}$*

The effect of the current density employed during galvanostatic growth on the electronic properties of the resultant polymer was considered (Figure 4.2). It was found that when a high current density ($j = 4 \text{ mA/cm}^2$) was used the R/E response did not exhibit the resistance transition expected. This is due to the scientific fact reported in the literature ⁸² that the morphology plays an important role in the polymer conductivity. Using different current densities results in various polymer of different morphologies.

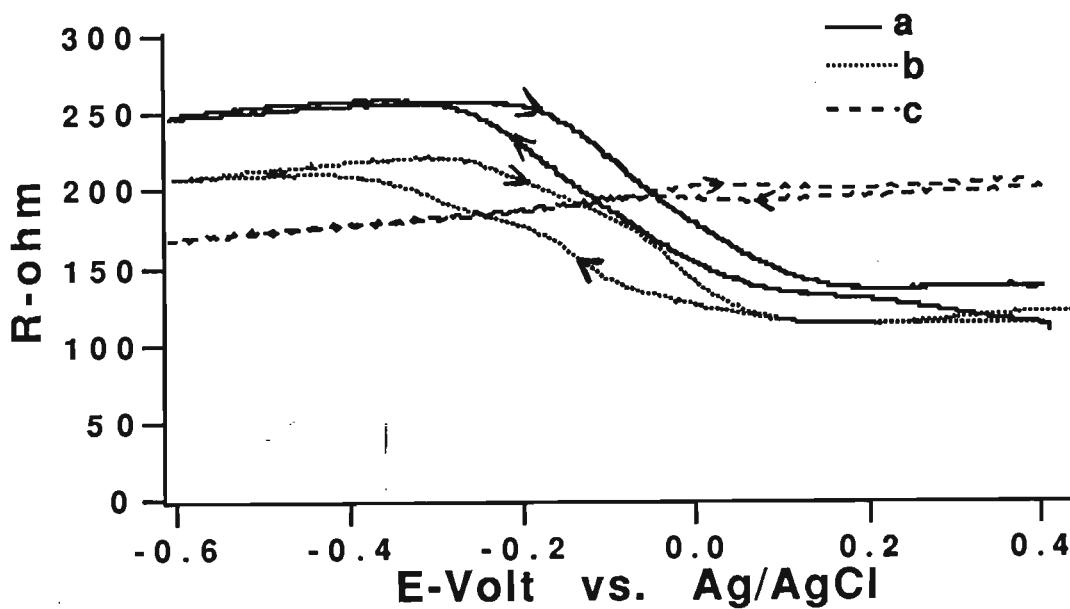


Figure 4.2: The effect of current density on the R/E response. Polymers prepared as in Experimental section and studied in 1M NaCl using scan rate = 10 mV/sec. (a) $j = 0.5 \text{ mA/cm}^2$ and $t = 16 \text{ min}$ (b) $j = 2 \text{ mA/cm}^2$ and $t = 4 \text{ min}$ (c) $j = 4 \text{ mA/cm}^2$ and $t = 2 \text{ min}$

4.4.1.2. The Potentiostatic method

Hagiwara et al. ⁷⁹ pointed out that the galvanostatic method has a disadvantage over the potentiostatic method (PSM) in terms of control of the anodic potential. They proved that using the PSM highly-ordered polypyrroles can be prepared.

In this section the comparison between the electronic properties of the resultant polymers grown at different potentials for the same time is considered. Figure 4.3 shows that the greater the potential used during growth with PSM, then the bigger the changes in the conductivity of the polymer upon oxidation/reduction. As Otero and Larreta pointed out before⁸⁰, the electrochemical conditions employed during PSM influence morphology, appearance and adherence of the polymer. These changes in morphology presumably also influence the R/E behaviour.

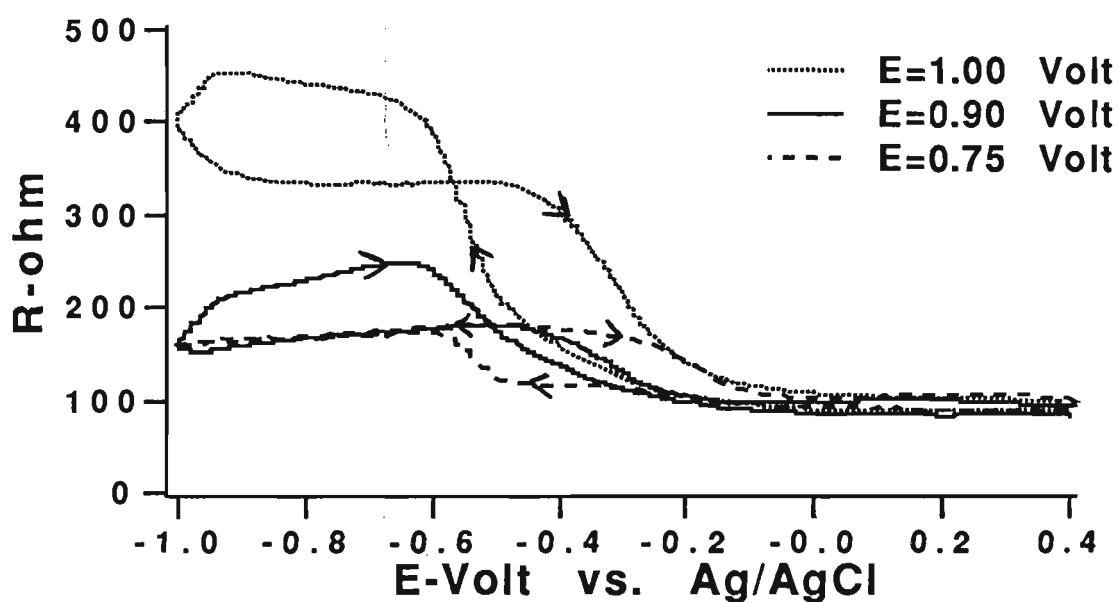


Figure 4.3: The effect of potential at which the polymers are grown on the R/E response curve. Charge consumed during polymerisation = 8 mC for all polymers. Other conditions are as in Figure 4.2.

Polymer grown at $E = 0.75$ V shows the typical resistance changes expected for polypyrroles. The resistance of the polymer is almost unchanging while the potential applied decreases from 0.4 V to -0.2 V. It is around -0.2 V that the resistance transition starts. This is the same for all the polymers shown in Fig. 4.3. The polymers have different resistivities in the reduced state. The polymers grown at potentials greater than 0.75 V have a

cross over in the trend of changes in the polymer resistance during the oxidation/reduction. This occurs while the potential applied is between $E = -0.6$ V and $E = -0.9$ V.

The effect of charge consumed during polymerisation on the electrical properties of the polymer was studied using the potentiostatic method. As can be observed in Figure 4.4 the greater the amount of polymer deposited the less resistive it is at positive potentials (oxidised form). This is expected as the greater amount of polymer deposited creates a bigger surface area.

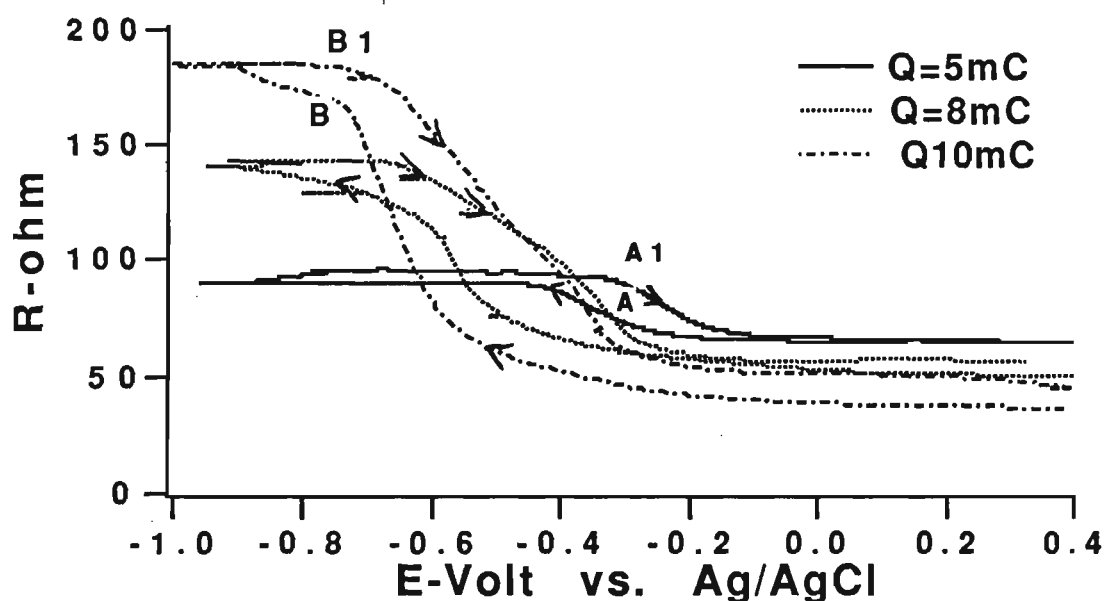


Figure 4.4: *The effect of charge consumed during polymerisation on the R/E response .*

Supporting electrolyte: 1M NaCl and scan rate= 10 mV/sec. Polymers were grown at $E=0.75$ V.

On the other hand at negative potentials more cathodic than -0.70V , the thicker the polymer then the less conductive it becomes. This can be explained by Fletcher's theory¹⁵⁴. According to his model the conducting polymers can be simulated as an equivalent circuit which includes different impedance components in parallel and series forms. Two main components of

this model are resistance of solution in pores and the resistance of the polymer itself. At the negative potential where the polymer is almost fully reduced the bulk polymer itself acts as an insulator and does not play any important role in the conductivity of the system. This is when the pores become the dominant feature in determining the conductivity.

4.4.1.3. The Potentiodynamic method

Employing the potentiodynamic method, the effect of charge consumed during the polymerisation on the polymer conductivity was examined. This was done through two different sets of experiments. First, the charge consumed using this method was varied by changing the number of sweeps when the scan rate was constant (scan rate= 100 mV/sec) during electrodeposition. The effect on the resultant R/E curves is shown in Figure. 4.5. The greater the number of sweeps during polymerisation, the greater the magnitude of resistance when the polymer was oxidised/reduced. This is in agreement with the studies where the effect of the charge consumed during polymerisation was investigated using the GSM.

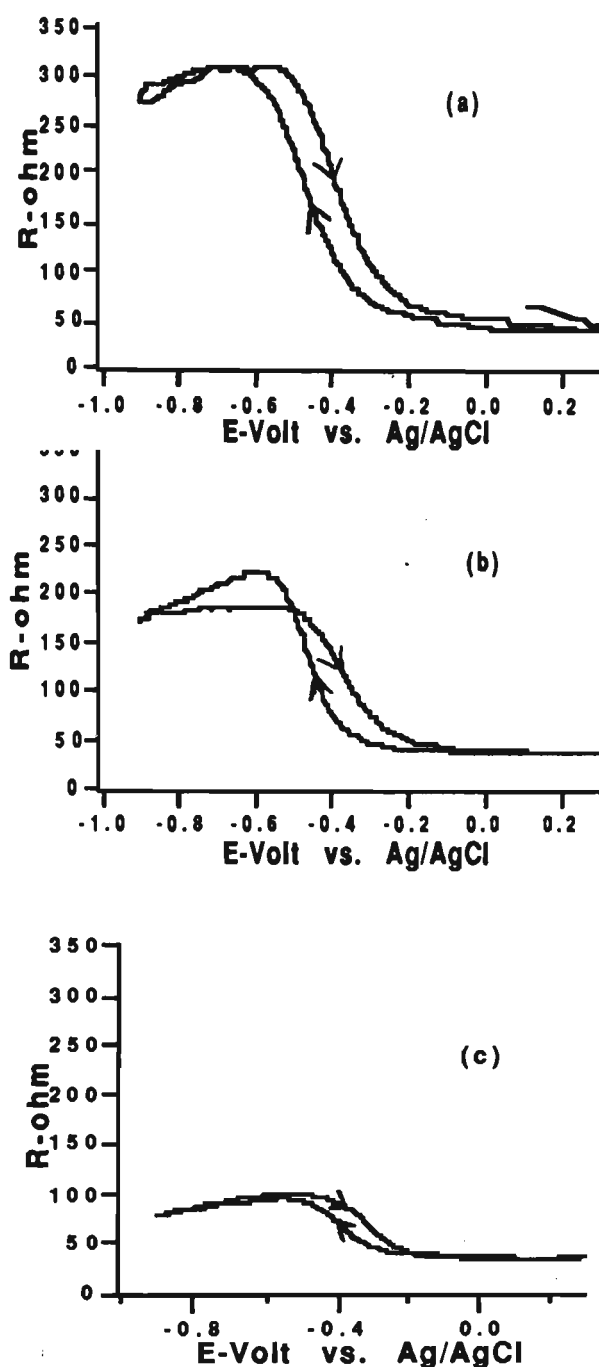


Figure 4.5: *The effect of charge consumed during polymerisation on the R/E response curves.*

1M NaCl as supporting electrolyte with scan rate = 10 mV/sec. All polymers were scanned until steady state cyclic voltammograms were obtained. Polymers were grown potentiodynamically between $E_1 = 0.8$ V and $E_2 = -1.0$ V with scan rate = 100 mV/sec. Number of sweeps = a. 50 b. 20 c. 10

Increasing the sweep number causes more deposition seeing as during each sweep to positive potentials more monomer is oxidised. By consuming more charge during polymerisation using the PDM, changes similar to the

potentiostatic method can be observed. This means that in both cases the polymer becomes more resistive in its reduced form and more conductive in its oxidised form. However the rates of changes are different due to using two different techniques and different conditions during growth. As can be seen for all results the resistance of the system starts to decrease as we go to more negative potentials in the case of the polymers produced potentiodynamically. This is because with the potentiodynamic technique it is possible that some parts of the electrode are not covered by polymer.

Figure. 4.6 reveals the same fact. In this experiment the number of sweeps during polymerisation was 10 and the scan rate was varied in different experiments. By decreasing the scan rate a greater amount of polymer was deposited at positive potentials on the surface of the electrode.

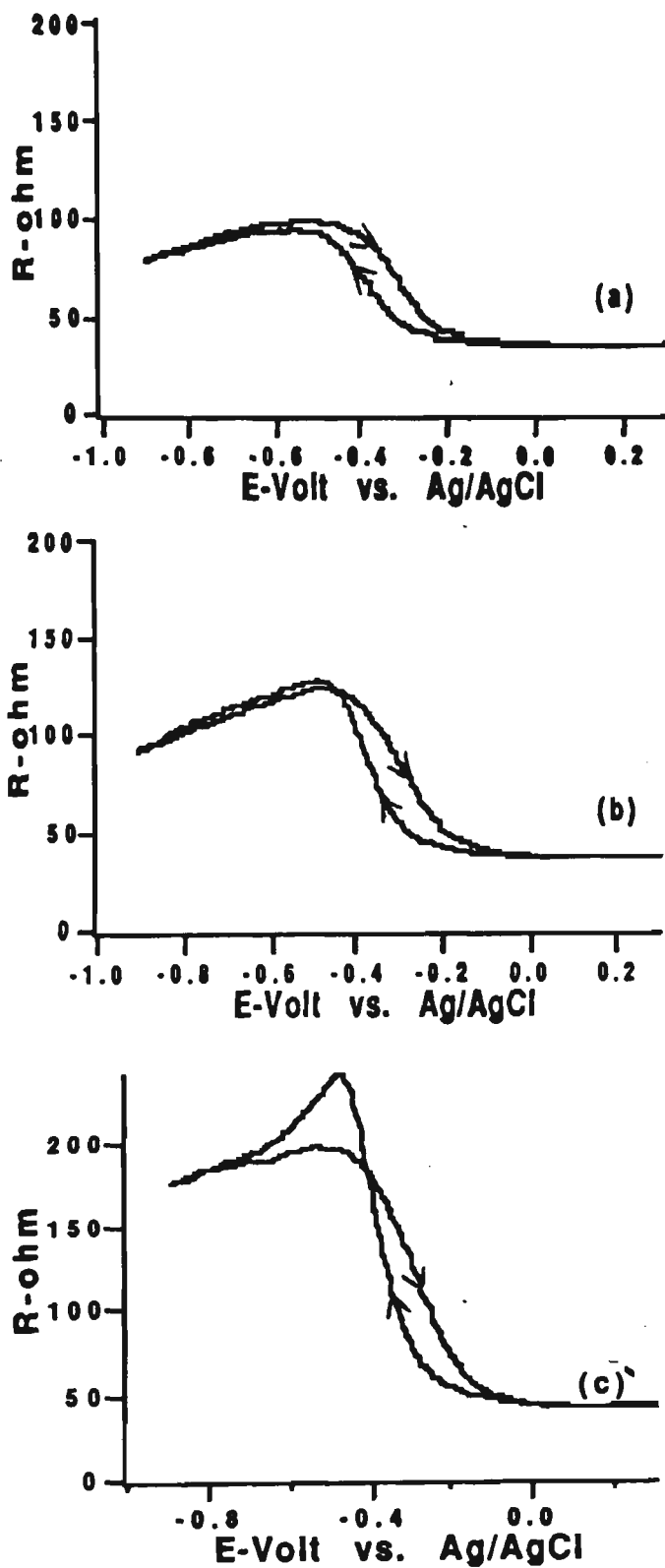


Figure 4.6: *The effect of charge consumed during polymerisation on R/E response.*

Scan rate during growth= a. 100 mV/sec b. 50 mV/sec and c. 10 mV/sec. No of sweeps= 10. Other conditions are the same as in Figure 4.5.

4.4.2. The effect of the parameters involved on the conductivity measurement after polymerisation

In this part the importance of the role of the supporting electrolyte and some other characterisation conditions on the relationship between the redox reaction and polymer conductivity is shown. Both concentration and type of the supporting electrolyte affect the changes in the conductivity during the redox reaction.

4.4.2.1. The effect of the concentration of the supporting electrolyte

As the concentration of the supporting electrolyte decreases the solution conductivity and the driving force for ion exchange decreases for the reduction/oxidation process. Therefore smaller changes in the conductivity are expected (Figure 4.7). A smaller concentration results in a less conductive background. As discussed already ¹⁵¹ the resistance measured is the combination of polymer resistance and that of the supporting electrolyte. Thus the higher the concentration of the salt solution the higher the value of the conductivity observed.

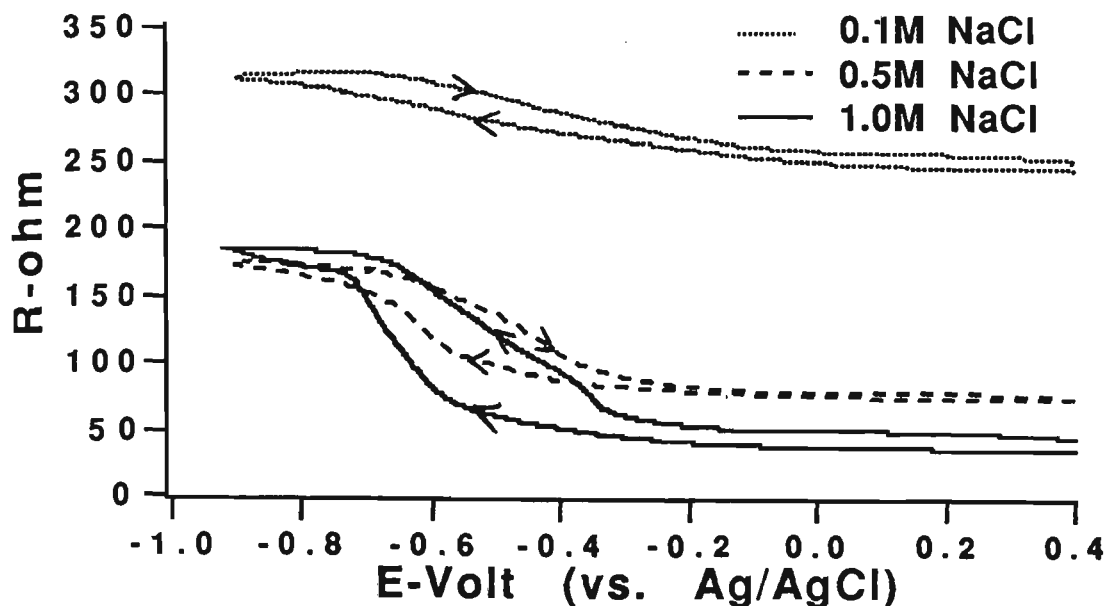


Figure 4.7: The effect of the supporting electrolyte concentration on the R/E response.

Scan rate = 10 mV/sec

Polymers were grown at $E = 0.75$ V and $Q = 8$ mC. Monomer solution was 0.1M Pyrrole and 0.025 M NaPTS.

4.4.2.2. The effect of the nature of the supporting electrolyte

Changing the cation in the supporting electrolyte gives very interesting results as far as the electronic properties of PPy/PTS are concerned. Employing di-cations such as calcium a more marked change in resistance was observed upon reduction (Figure 4.8). This cation could balance the charge of the anions in the polymer and result in more resistive pores. Moreover, the cation mobility should be considered as a factor to affect the R/E profile. The figure reveals that the cation incorporation process induces a mechanism of resistance change different from that observed for anion expulsion.

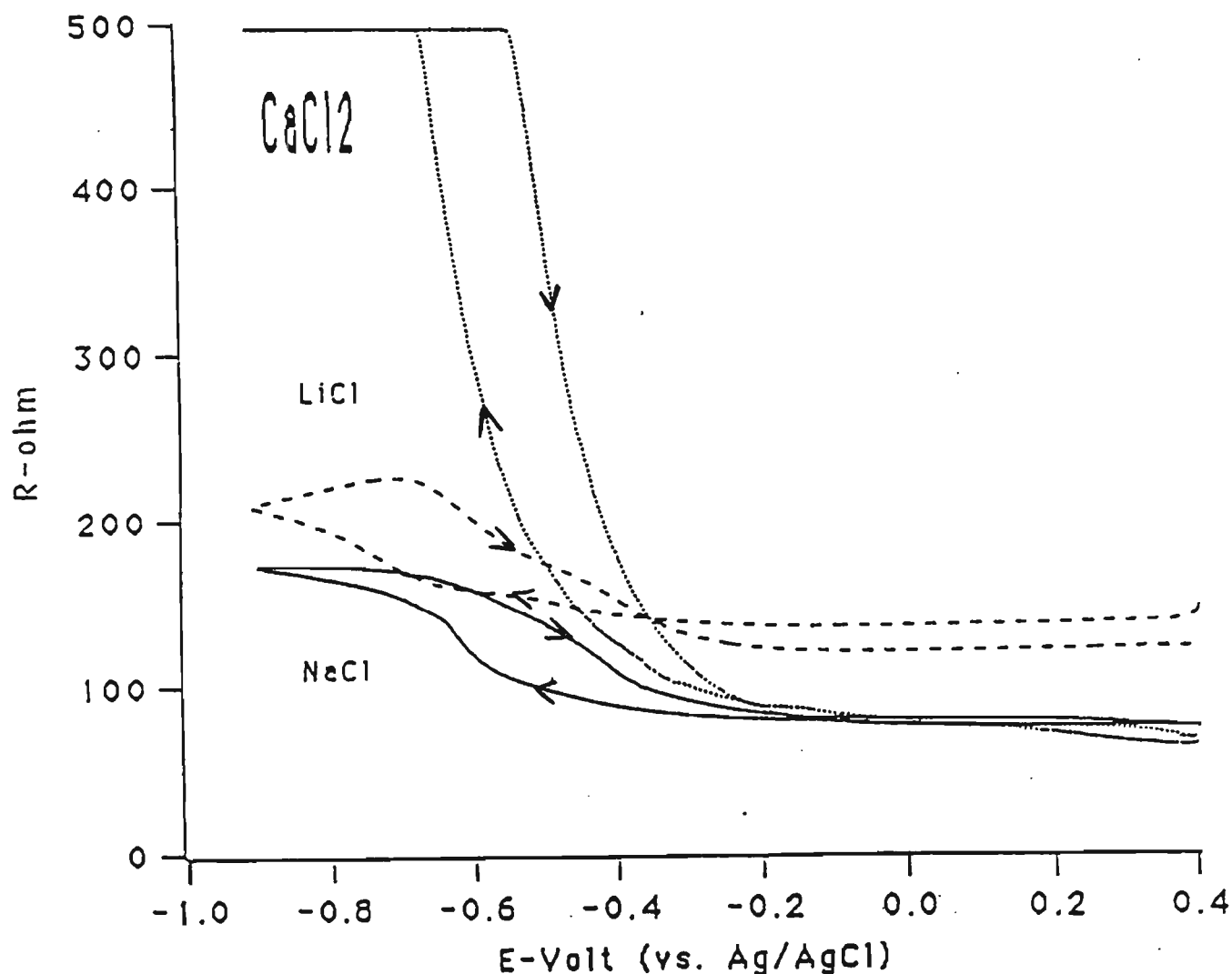


Figure 4.8: *The effect of type of supporting electrolyte on R/E response. Scan rate = 10 mV/sec. Polymer was grown at $E = 750$ mV with $Q = 10$ mC.*

4.4.3. The effect of scan rate on the R/E response

The effect of scan rate used for characterisation studies was the next factor to be investigated. In Figure 4.9 and Figure 4.4 we see that with increased scan rates the magnitude of resistance observed decreased as the polymer is switched from the oxidised form to the reduced form. This is expected because as the scan rate decreases there is more time for the anion to move from the polymer to the solution and consequently greater changes

in conductivity can be observed. However, the difference in the magnitude of the changes decreases as scan rate increased.

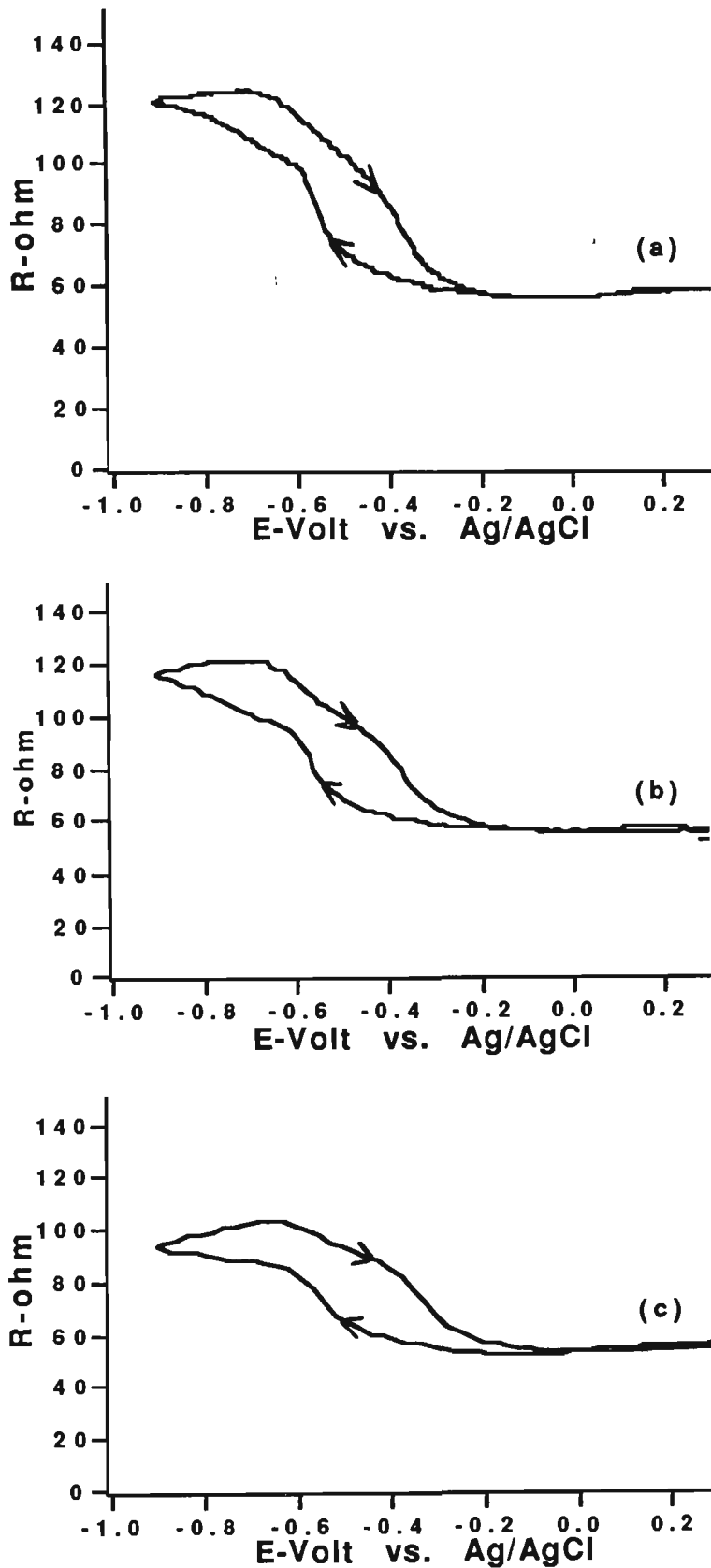


Figure 4.9: Effect of scan rate on the polymer R/E response. Supporting electrolyte: 1M NaCl, scan rate = a. 20 mV/sec b. 50 mV/sec c. 100 mV/sec. Polymer was the same as described in Figure 4.8.

4.4.4. Effect of overoxidation on the polymer R/E curves

Another experiment was performed to investigate the effect of overoxidation on the in-situ conductivity of PPY/PTS. In the previous section it was found that if the polymer is grown at $E=0.75$ V using PSM a typical R/E for this polymer can be obtained. This polymer, after growth, was studied over different potential ranges to investigate the effect of exposure to more positive potentials on the R/E response.

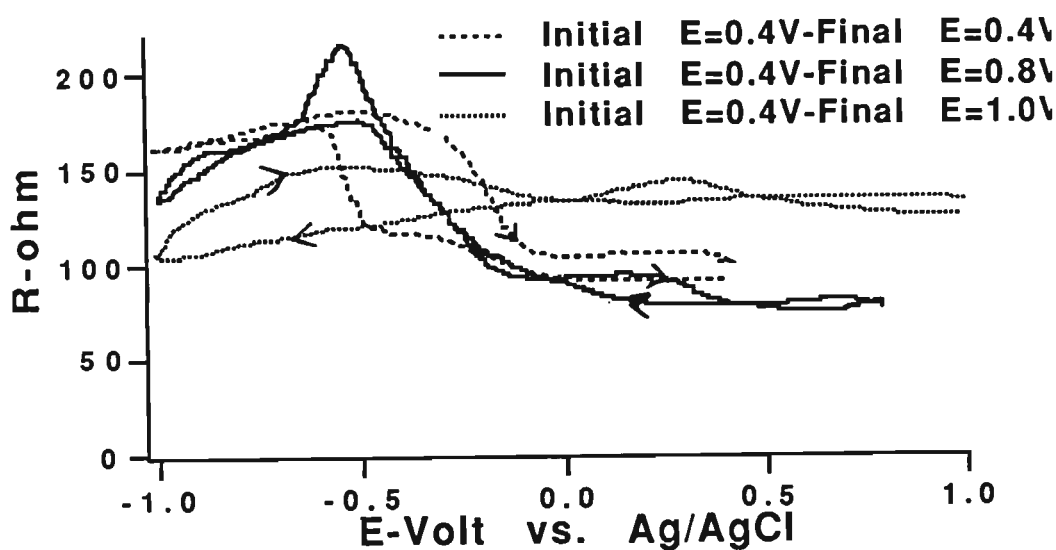


Figure 4.10: Effect of potential range on R/E response. Supporting electrolyte = 1M NaCl, scan rate = 10 mV/sec. All polymers were scanned until steady state cyclic voltammograms were observed. The polymer was grown as in Figure 4.8

Figure 4.10 suggests that scanning up to 0.80 V increased the magnitude of the resistance transition observed. However, eventually upon scanning to 1.00 V irreversible overoxidation of the polymer occurred resulting in irreversible breakdown and loss of conductivity.

4.5. CONCLUSION

The switching properties of conducting electroactive polymers are critical to numerous applications. The resistance/potential profiles obtained, have been shown to be dependent on various parameters. These include the amount of charge consumed and the nature of the polymerisation technique used during the polymerisation. The nature of the electrolyte and post-polymerisation conditions have also shown to have marked effects on the R/E profiles for polypyrrole/PTS.

Chapter 5

**S.M.A.C. - ANOTHER DIMENSION IN
ELECTROCHEMICAL ANALYSIS.**

5.1. INTRODUCTION

In chapter 3 the usefulness and capability of the pulse resistometry technique for characterisation of CEPs have been demonstrated. It was suggested that the nature of the supporting electrolyte can affect the electronic properties of the polymers. Using Electrochemical Quartz Crystal Microbalance (EQCM),^{166,170} the anion and cation movements out of and into the polymer, which results in changes in mass of the polymer electrode, can be monitored in-situ as different potentials are applied. EQCM is an extremely sensitive technique capable of monitoring mass changes in the nanogram range^{171,172}. Its high sensitivity permits resolution of mass changes less than 100 ng/cm²¹⁷³. Electrogravimetry is of great interest for the study of CEPs. It allows the determination not only of the mass variation due to ionic migration during an electrochemical doping-dedoping process but also of the mass variation caused by polymer deposition during electrodeposition^{173,174}.

As discussed in chapter 3, the counterion incorporated during polymerisation influences the electrochemical characteristics of the resultant polymer. In this chapter such effects are reported by using another dimension to the pulse resistometry. A new set up that allows voltammetry, resistometry and EQCM experiments to be carried out in-situ and simultaneously on a polymer coated electrode has been constructed and implemented. The technique has been denoted S.M.A.C. (Simultaneous, Multidimensional Analysis of Conductors).

5.2. AIMS AND APPROACH OF THIS CHAPTER

Using the silver deposition and anodic stripping of silver the compatibility of EQCM and the pulse resistometry method has been investigated. Then polypyrrole materials containing three different counterions (mobile (Cl^-), less mobile (PTS^-) and immobile (DBS^-)) have been studied using this multidimensional technique.

The main objective of this chapter is, first, to demonstrate the capability of the new S.M.A.C. set up to gain mass and resistance data as a function of applied potential for different polypyrrole materials. Then, the effect of electrolyte composition on the electrodynamic properties of polypyrroles has been discussed using S.M.A.C.

5.3. EXPERIMENTAL

5.3.1 The experimental set-up and instrumentation

The experimental set up (Figure 5.1) is a new multidimensional technique employed for this investigation. To construct this set up, the EQCM instruments have been simply combined to the set up already reported in chapter 3. However, the working electrode for this study is a gold quartz crystal as it is required for the EQCM experiment.

A home made galvanostat was used for electrodepositions of polypyrroles. A Bio Analytical Systems (BAS) model CV-27 Voltammograph was used throughout this work. The same resistometer used in chapter 2 was employed for collecting the resistance data. The electrochemical quartz crystal microbalance was built in house based on a

design previously published ¹⁷¹ and slightly modified by our electronics workshop of the Faculty of Science at Wollongong University. The 10 MHz crystals (surface area= 0.25 cm²) were purchased from International Crystal MFG. Co. Inc. U.S.A. According to the supplier the density and shear modulus of the crystals were 2.65 g cm⁻³ and 2.98 x 10¹¹ dynes cm⁻² respectively. All experiments were carried out in a Faraday cage.

5.3.2. Reagents and standard solutions

All reagents were of analytical reagent (AR) grade purity unless otherwise stated. Pyrrole was provided by Sigma. Sodium chloride, sodium dodecylbenzene sulfonate (DBS), Sodium paratoluene sulfonate (PTS) were obtained from Aldrich calcium chloride, magnesium chloride, potassium chloride, lithium chloride, silver nitrate and perchloric acid were purchased from BDH. Nitrogen was used for de-oxygenation prior to (15 minutes) polymerisation processes. The gold crystal was first pretreated in 0.2 M perchloric acid by cycling the potential between 1.4 V and 0 V for 15 minutes as recommended by Bruckenstein and Shay ¹⁷¹.

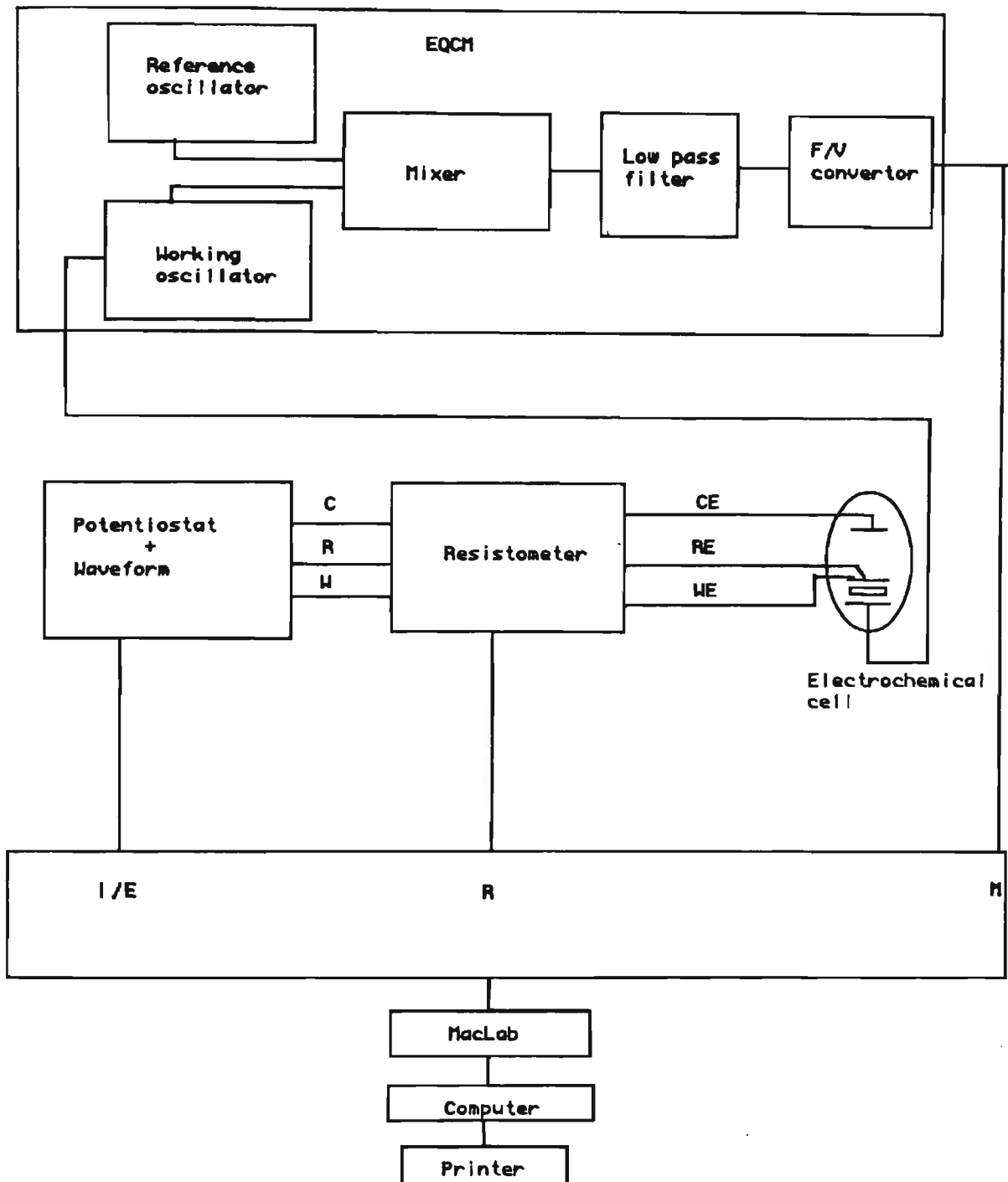


Figure 5.1: The block diagram of the S.M.A.C.

5.4. RESULTS AND DISCUSSION

5.4.1. Calibration and reliability of the S.M.A.C.

The simultaneous analysis technique, using the apparatus described in the experimental section and depicted in figure 5.1 involves:

- Application of a potential waveform with normal current sampling routines such as carried out by the BAS CV27 Voltammograph. This was used to obtain a voltammogram or chronoamperogram.
- Continuous monitoring of the oscillation frequency of the quartz crystal during this period to obtain a massogram.
- Interruption of the potential waveform with short current pulses to obtain the resistogram, as described previously ¹⁷¹.

The calibration of the EQCM set up was done according to the method described by Bruckenstein and Shay ¹⁷¹. Silver was deposited at the surface of the gold electrode potentiostatically and the frequency changes were recorded as a function of the charge consumed during the deposition (Fig. 5.2). According to Faraday's law (Eq. 5.1) the mass of different materials deposited at the electrode by a given quantity of electricity is proportional to the respective equivalent mass. From the charge passed in the electrodeposition of silver ions at constant potential (Fig. 5.2), the mass sensitivity of 0.965 Hz ng⁻¹ was obtained. This coefficient factor was used throughout this chapter to convert frequency measurements to mass data.

$$\Delta m = (A_{Ag} \Delta Q) / ZF \quad \dots \text{Eq. 5.1}$$

where A_{Ag} is the atomic weight of silver (107.87 g/mol), Z is electrovalency (=1) and F the Faraday constant ($F=96485 \text{ C mol}^{-1}$).

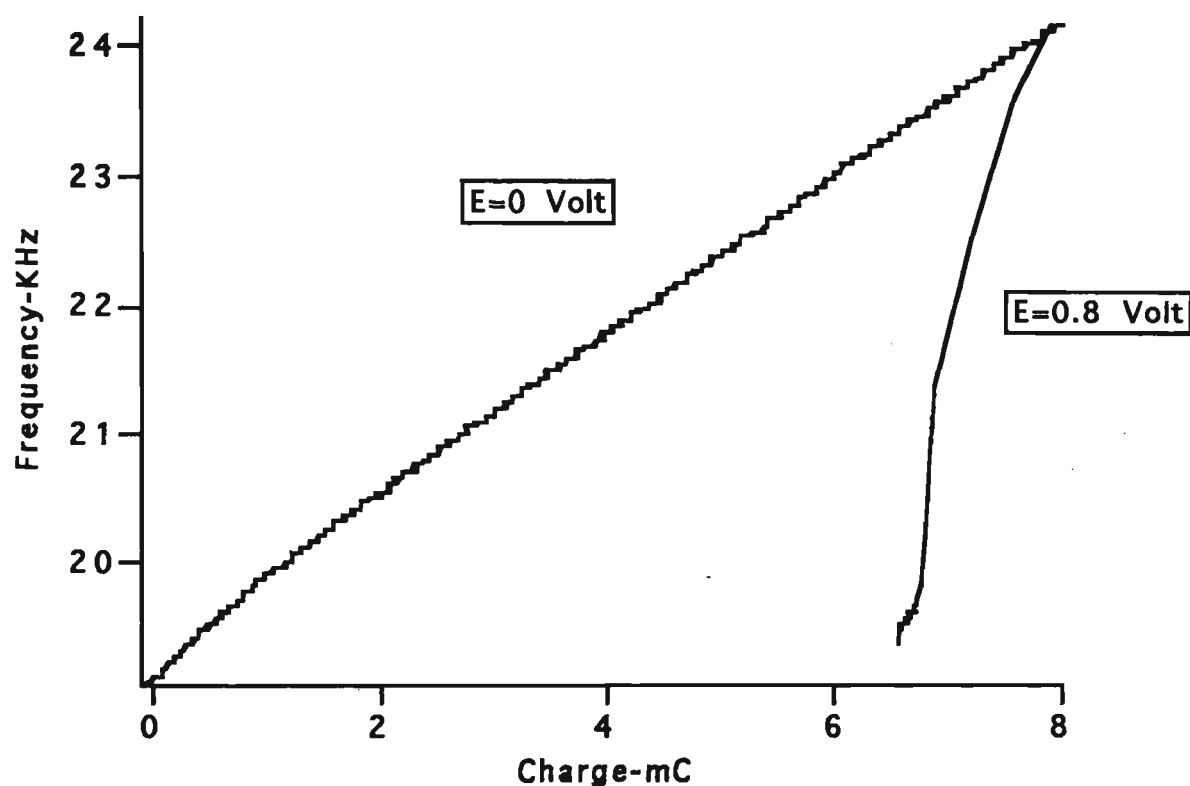


Figure 5.2: *Potentiostatic deposition and anodic stripping of silver*

To prove that there was no interference between the EQCM and the pulse resistometry, silver deposition was again considered. However, silver deposition and the anodic stripping experiment was carried out with the potentiodynamic method. As shown in Figures 5.3 and 5.4, acceptable reproducibility in the resistance, mass and current changes can be observed during the potentiodynamic deposition and stripping of the silver on the gold crystal electrode while the EQCM and the pulse resistometry were used together and separately.

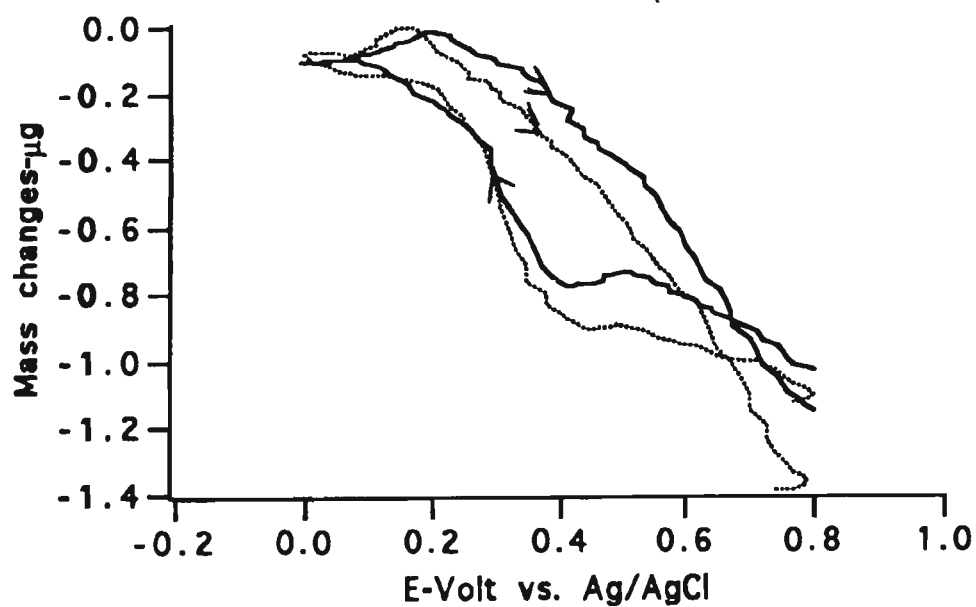
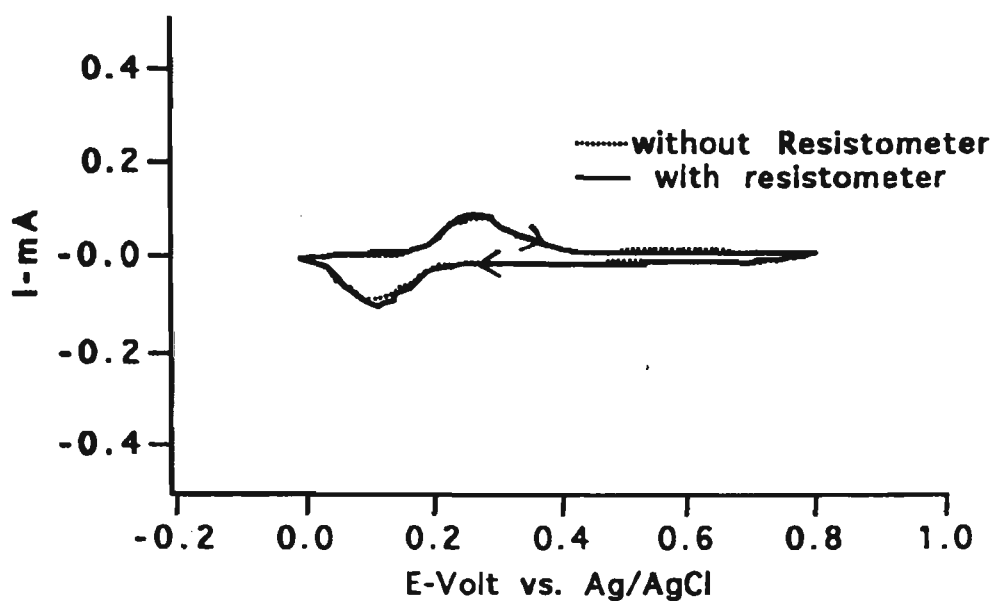


Figure 5.3: Potentiodynamic deposition and stripping of silver. Scan rate = 100 mV/sec . (a) Cyclic voltammetry
(b) Mass vs. Potential

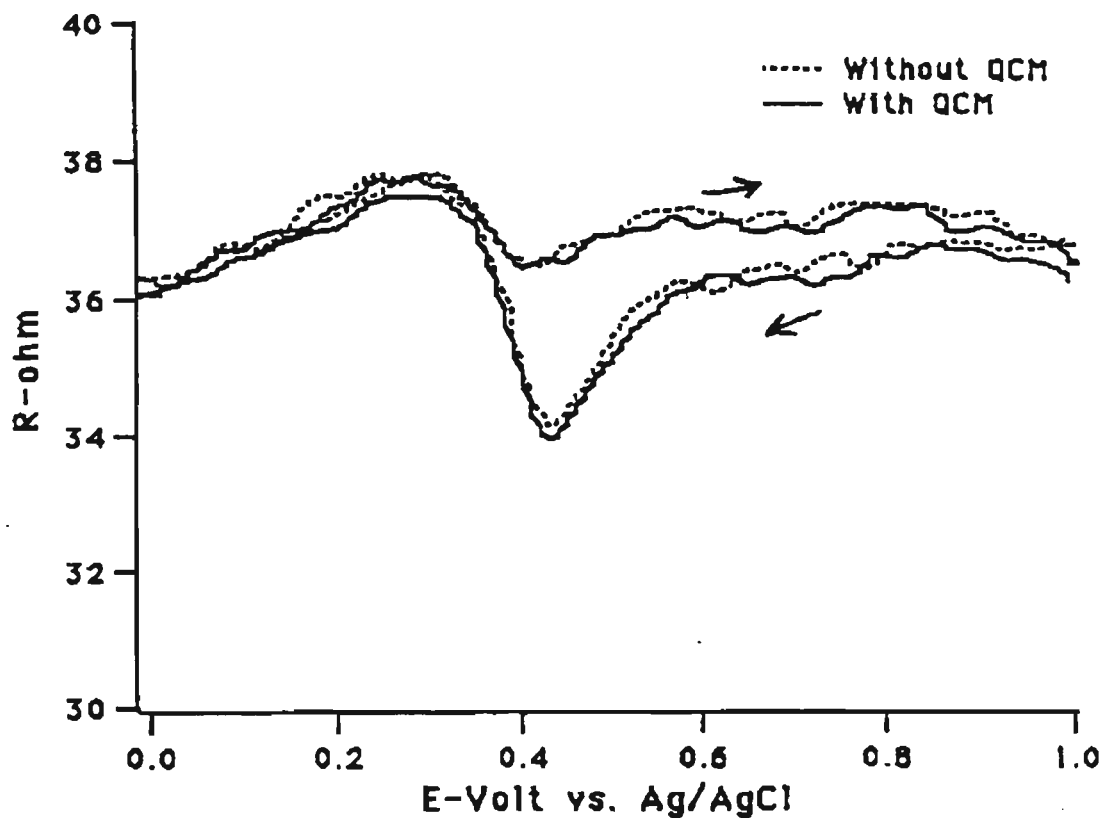
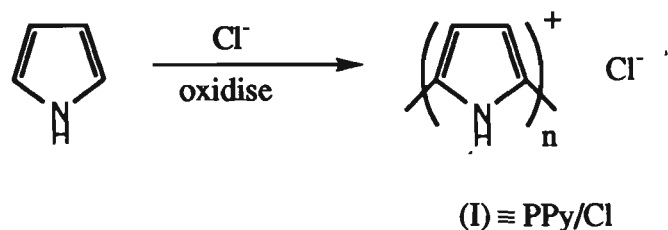


Figure 5.4: *Potentiodynamic deposition and stripping of silver. Scan rate = 100 mV/sec : Cyclic resistometry plot*

These Figures are the result of three different experiments: 1. The EQCM experiment. 2. The pulse resistometry experiment. 3. The combination of the EQCM and the pulse resistometry simultaneously. As can be seen from the Figures, a little difference between the mass and resistance can be observed when the EQCM and the pulse resistometry are used together. This difference is small enough to prove the reliability of the new simultaneous multidimensional technique if the EQCM and pulse resistometry are combined.

5.4.2 S.M.A.C study during polymer Growth

Polymerisation of pyrrole monomer to form a conducting polymer (I = polypyrrole - shown below) may be described, according to:



The product is an insoluble conducting polymer that deposits on the electrode and subsequently continues to grow on top of itself. The mass deposited during polymerisation (current density = 2mA/cm² and time = 2 min) can be monitored using the quartz crystal microbalance technique (Figure 5.5.a). The almost linear increase of mass with time can be correlated with the charge that flows during polymerisation. It was found that 60 mC produced 17 µg of polymer. As a result of polymerisation, the surface area of the electrode also increases and this results in decreased resistance (60 ohm) of the electrode assembly (Figure 5.5.b).

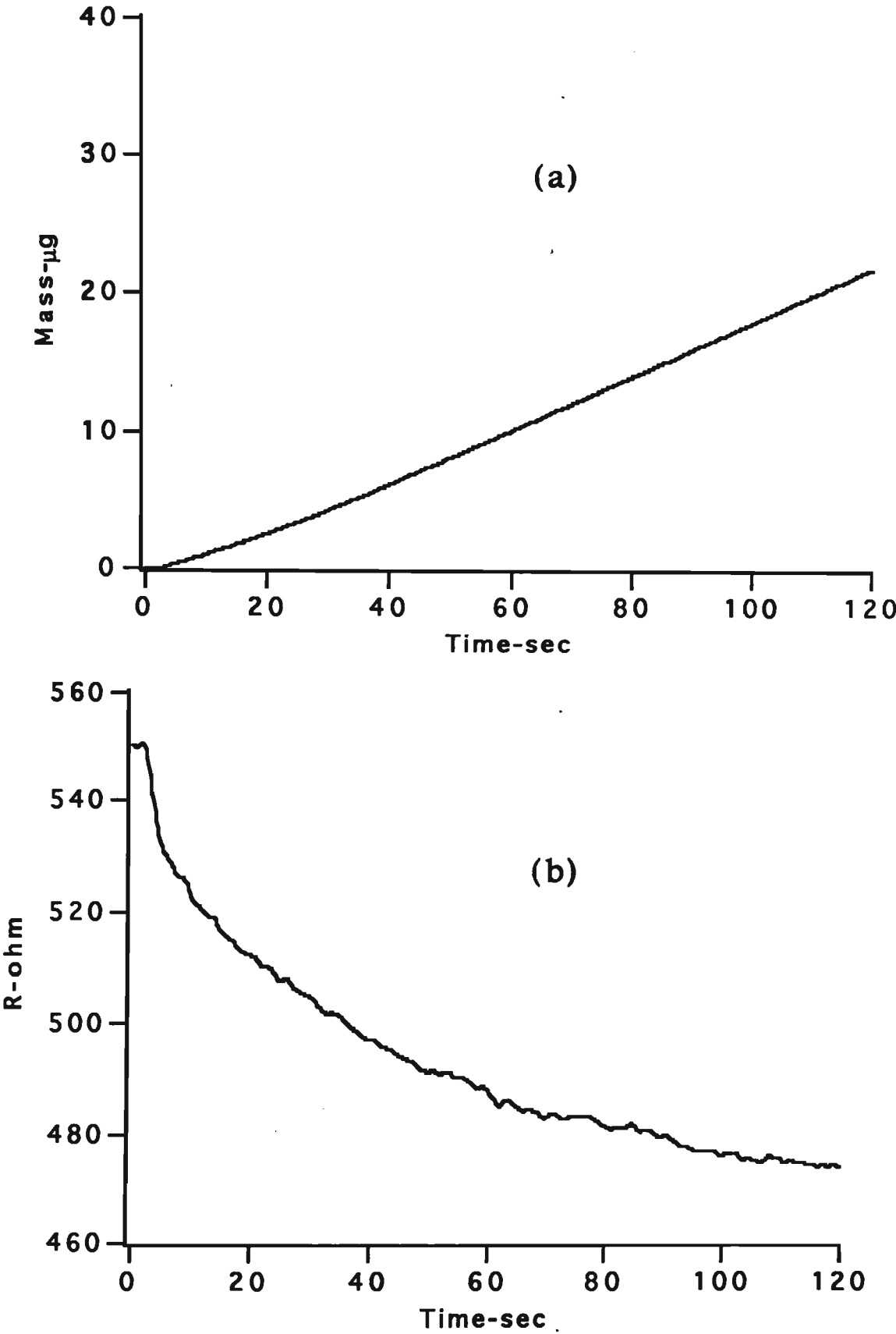


Figure 5.5: Mass and resistance changes for PPy/Cl during growth

According to Figure 5.6 when using PTS as the counterion, 24 μg mass deposition and 70 ohm resistance reduction was recorded for the same charge consumption as that for PPy/Cl when PTS was used as a counterion.

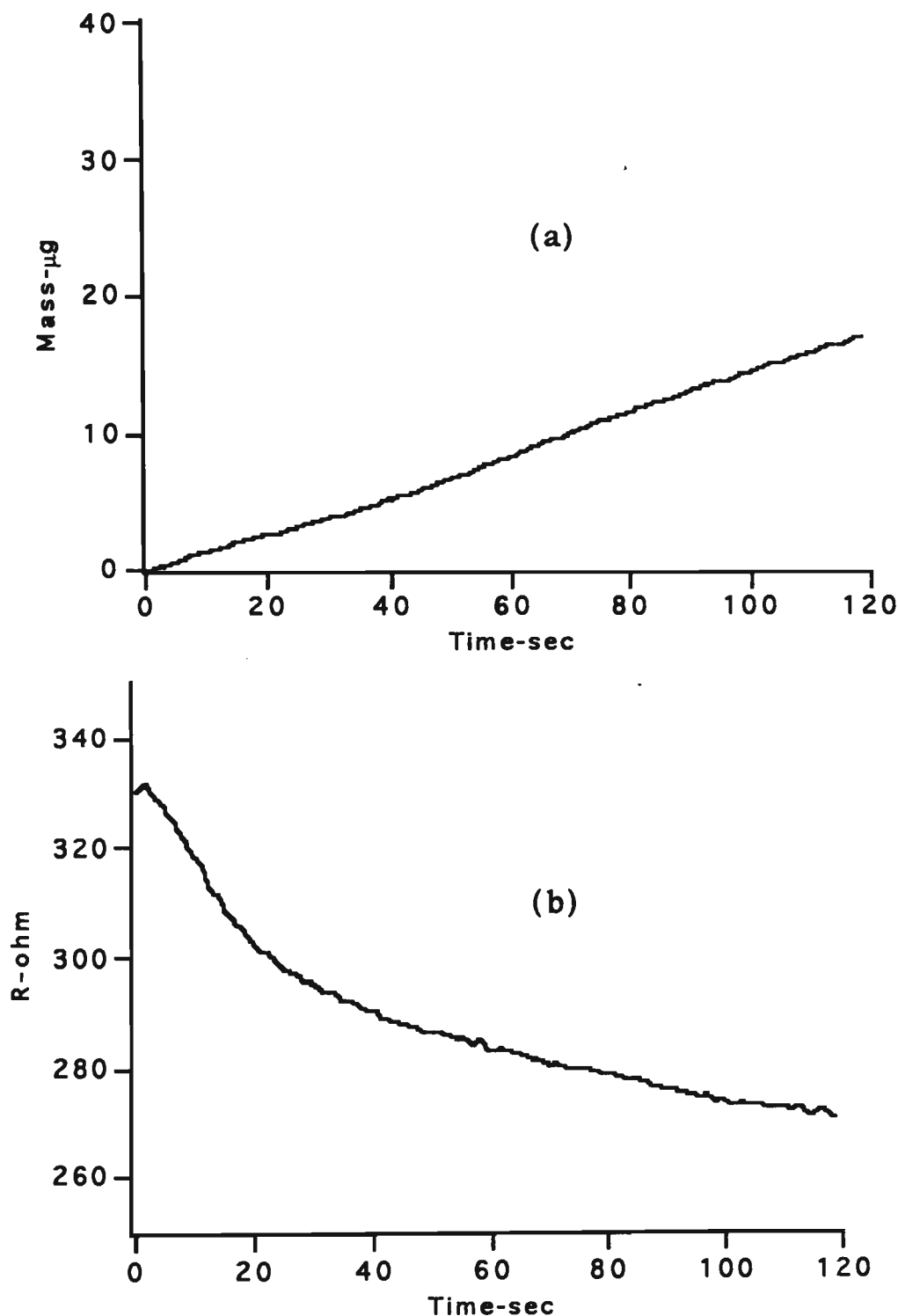


Figure 5.6: Mass and resistance changes for PPy/PTS during growth

In contrast when DBS was used as the counterion, under the same conditions used for polymerisation of PPy/Cl and PPy/PTS, 50 ohm

decrease in resistance and 40 μg increase in mass was observed (Figure 5.7).

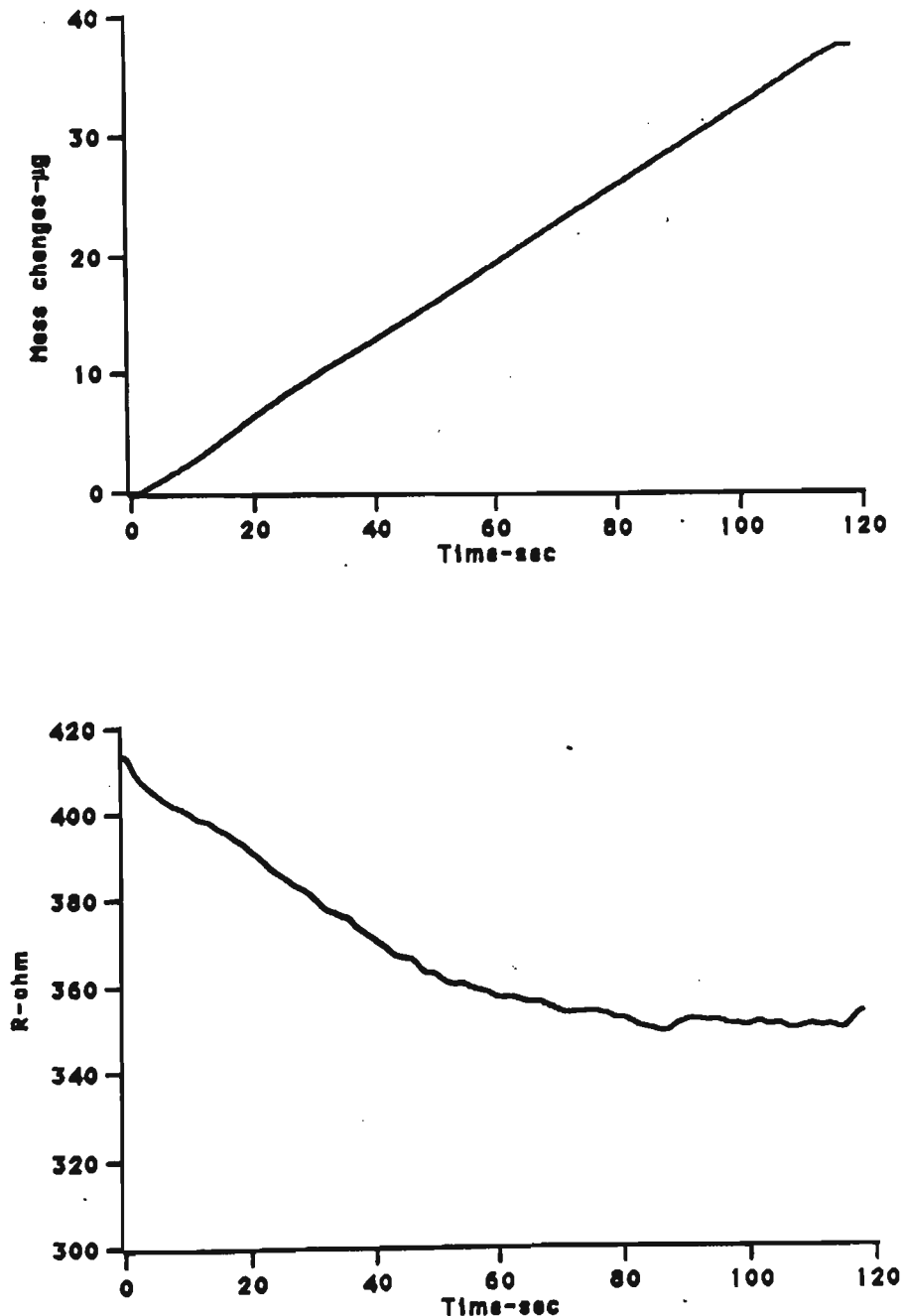


Figure 5.7: Mass and resistance changes for PPy/DBS during growth

These results indicate that simply by changing the counterion different polymer materials can be created. Based on these resistance changes it can be said that PPy/PTS is a more conductive system during polymerisation. Zhao et. al (5.2) also found that PPy/PTS had the best conductivity amongst those sulfonated aromatic counterions incorporated in polypyrrole. As far

as the mass changes are concerned PPy/DBS has shown the biggest change in mass. This is perhaps due to the size of the counterion. However, there are other effects such as swelling as a result of water in the polymer. Bacskai et. al¹⁷⁵ investigated such an effect and found that the mass can increase as a result of swelling of the film.

Viscosity and the height of the solutions are two other important factors which should be considered whenever the EQCM technique is used. It was found that increasing the height of the solution could result in decreasing the frequency recorded¹⁷¹. This was considered whenever S.M.A.C was used and all solutions were at the same heights. The same authors reported the effect of viscosity in their papers and proved that viscosity changes can vary the frequency changes. Considering the fact that all solutions in the S.M.A.C. investigations were aqueous, the viscosity factor is negligible. Thus, the main parameter in the changes of the mass and resistance observed during the polymer synthesis is the type of the counterion used.

5.4.3 S.M.A.C study after polymerisation :

The three polymers discussed above were then studied in 1 M NaCl after polymerisation. As there is a possibility of changes in the mass and resistance of blank crystal in 1M NaCl itself during our study, the first experimental work in this section was carried out with the blank crystal in this electrolyte. According to Figure 5.8 changes in the mass and resistance of the blank crystal is negligible compared with that observed for the crystals coated with the polymers.

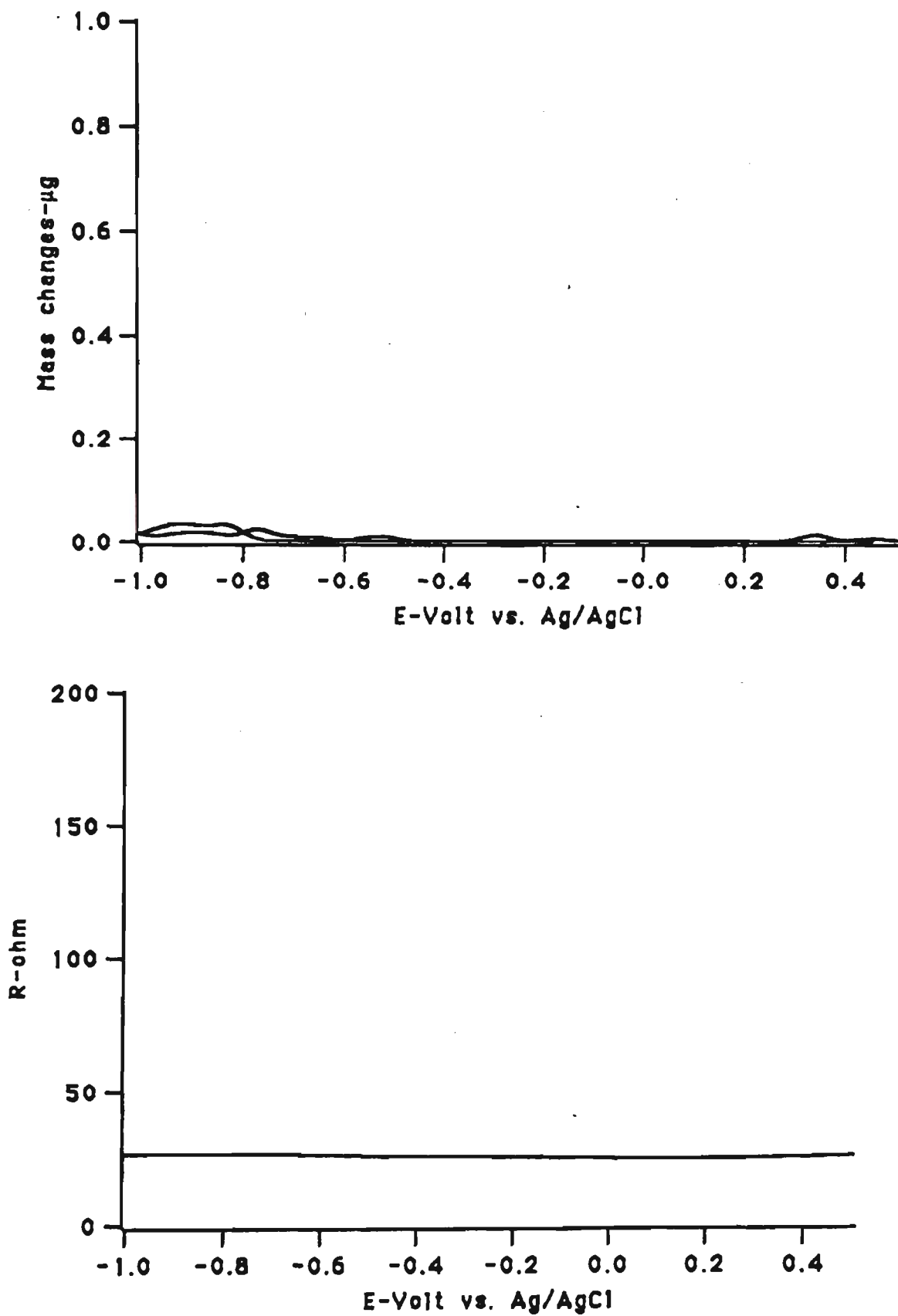
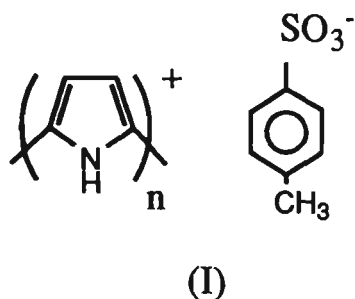


Figure 5.8: Mass and resistance changes of the blank crystal in 1M NaCl.

Scan rate = 100 mV/sec

Using PPy/PTS (I) (shown below) as a test case, in-situ mass, resistance and current data were collected as the potential was cycled between -0.8V and +0.4V in 1M NaCl. Simultaneous data is plotted in Figure 5.9.



Simultaneous in-situ analysis here reveals that the mass decrease varies almost linearly as a function of potential from +0.40 to -0.20 V and then levels off. This confirms a continuous reduction model as suggested by Tanguy 176-178 and others 150 previously. Note also that despite this constant drain of ions from the polymer the resistance remains low and constant in this potential region. It is not until approximately -0.50 V, when the mass of the polymer stabilises, that the resistance switch is triggered.

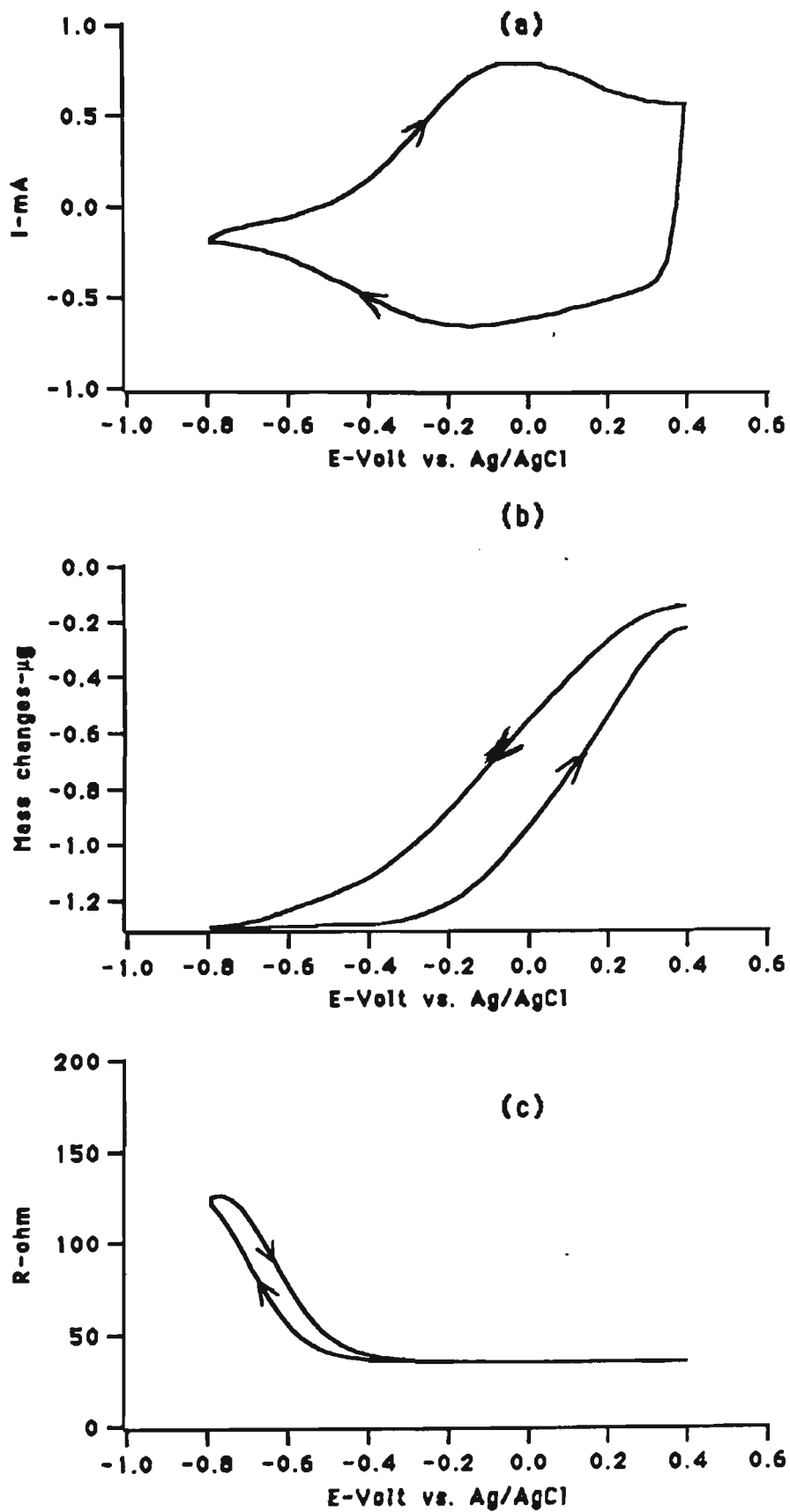


Figure 5.9: *In-situ characterisation of PPy/PTS in 1M NaCl. Scan rate= 100 mV/sec. (a) Changes in current. (b) Changes in mass. (c) Changes in resistance*

This non-linear relationship between current, mass flow and changes in the resistance properties are perhaps more obvious when pulsed potential waveforms are employed (Figure 5.10. and 5.11). Two potential pulse regimes that emphasise this non-linearity have been chosen. As shown in Figure 5.10, a potential pulse over the range 0.00 V to +0.40 V reveals a significant current and hence mass flow but only a minimal change in resistance.

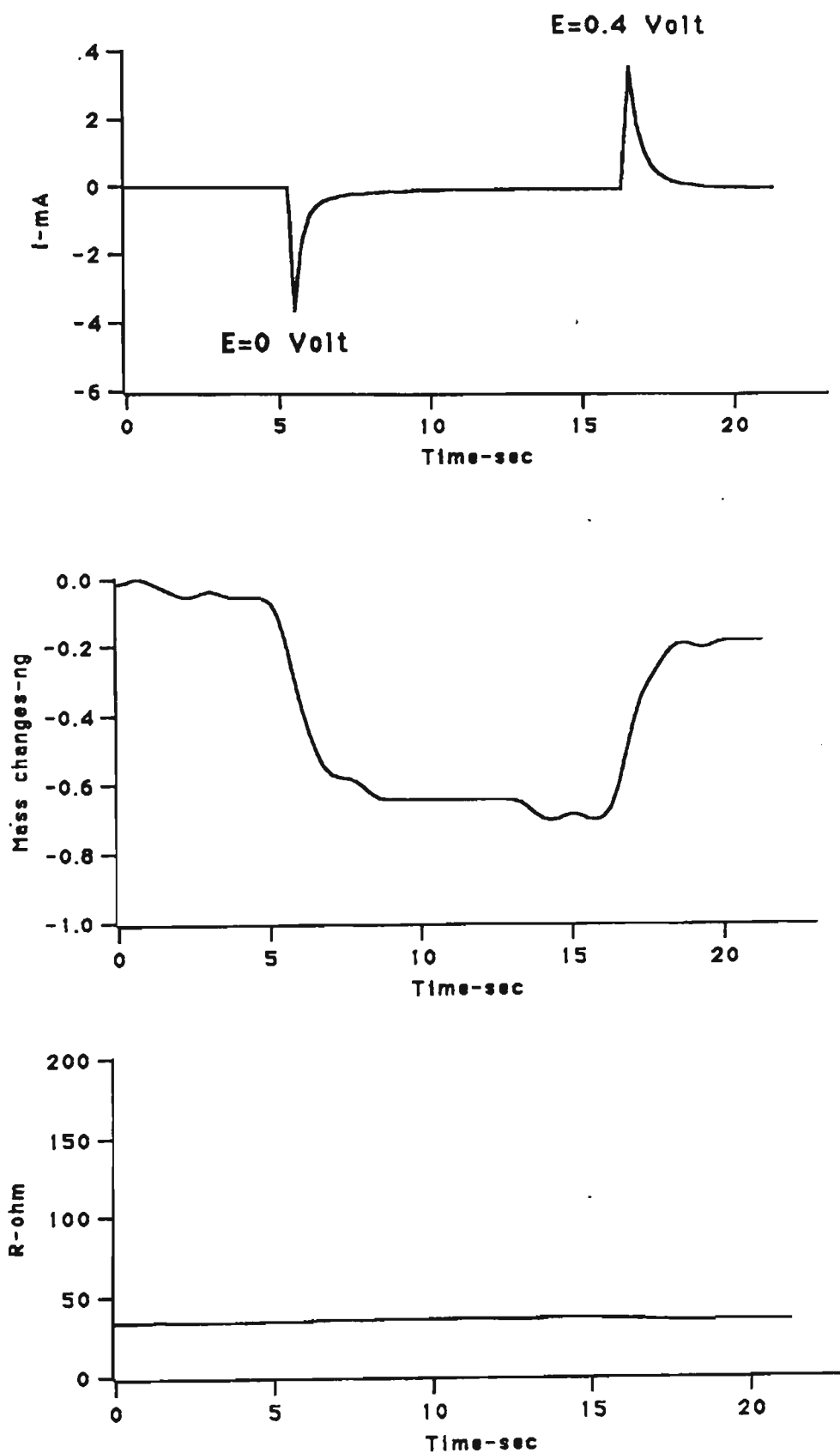


Figure 5.10.: *In-situ monitoring of current, mass and resistance by switching between two different potentials (0 Volt and -0.4 Volt). Supporting electrolyte: 1M NaCl*

However pulses over the range -0.40 V to -0.80 V result in only a small current/mass flow with marked changes in resistance (Figure 5.11.b).

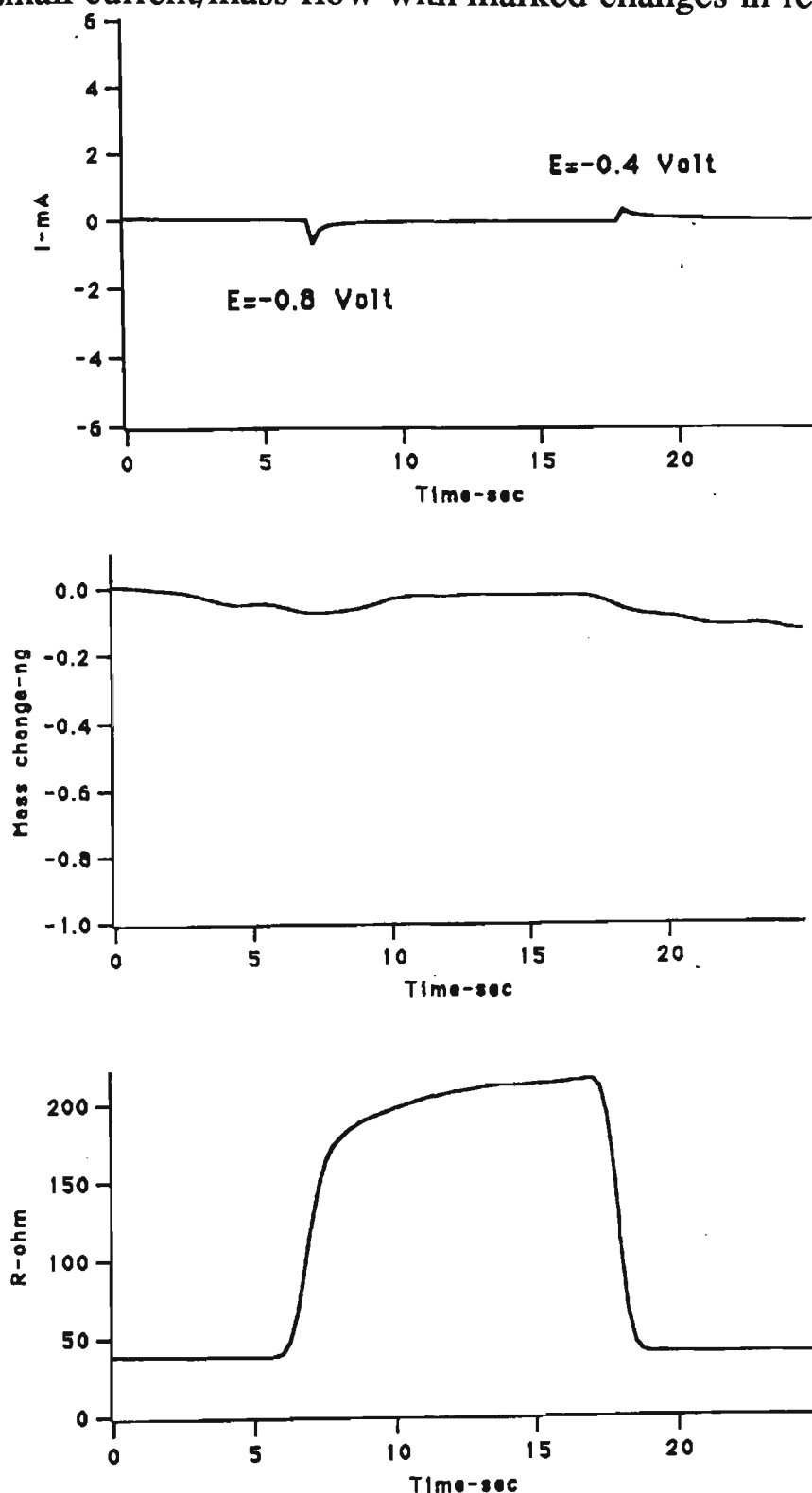


Figure 5.11: *In-situ monitoring of current, mass and resistance by switching between two different potentials.(-0.4 Volt and -0.8 Volt) in $1M\text{ NaCl}$*

These figures (Figures 5.10 and 5.11) reveal that the use of pulsed potential techniques give recordings of current, mass and resistance which

are useful in determining the kinetics of these transient processes. An experiment involving the application of pulses at different durations was carried out. Figure 5.12 shows that the potential pulse width determines the mass flow and consequently changes in resistance that occur. Using short pulse widths (5 sec) it is even possible to minimise the resistance changes.

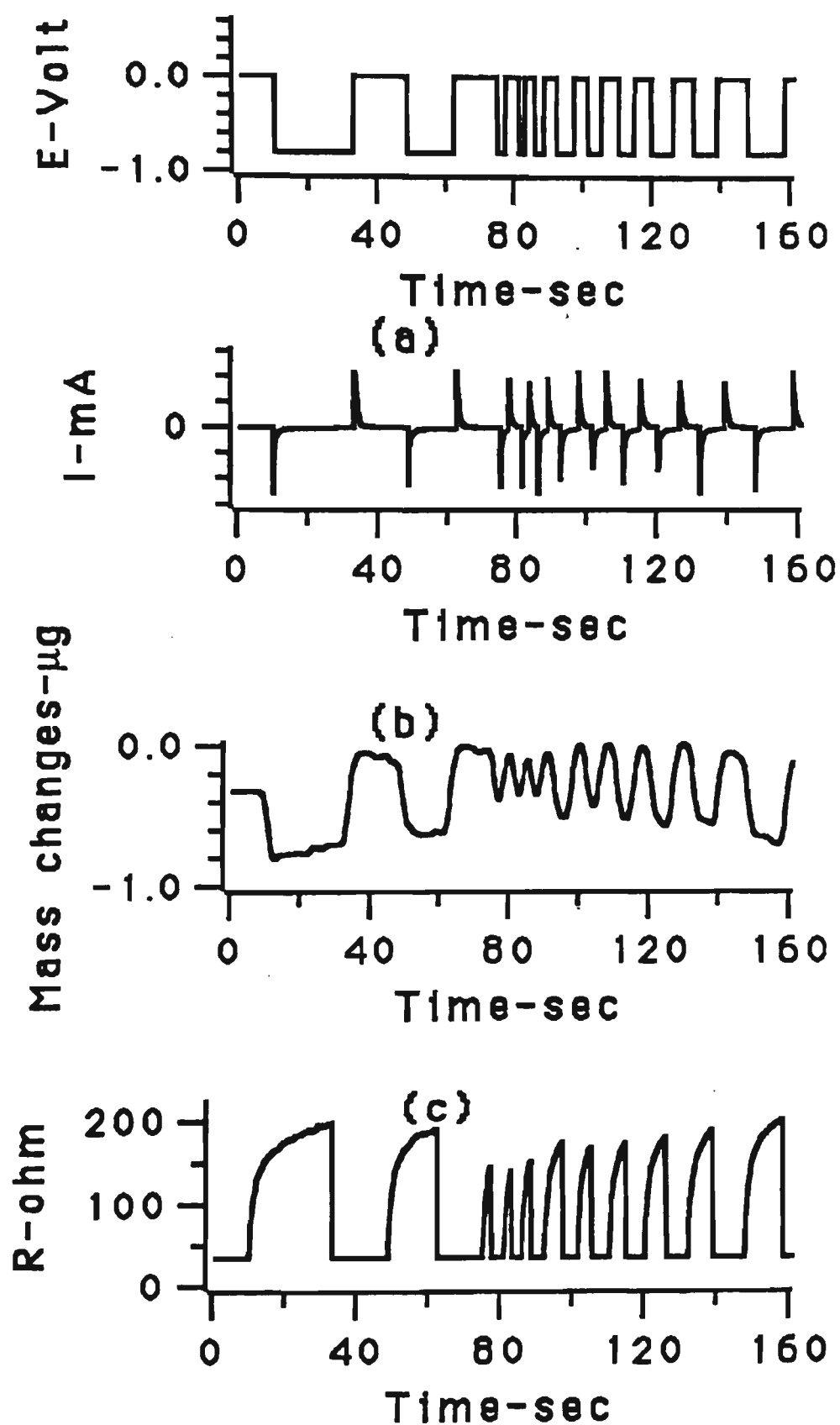


Figure 5.12: Simultaneous current (a), mass (b), resistance (c) changes for PPy/PTS in 1M NaCl. Potential pulse between 0 Volt and -0.8 Volts. Varying pulse widths as shown.

Two other polymer systems PPy/Cl and PPy/DBS were then considered. With PPy/Cl similar behaviour to that observed with PPy/PTS was observed (Figure 5.13).

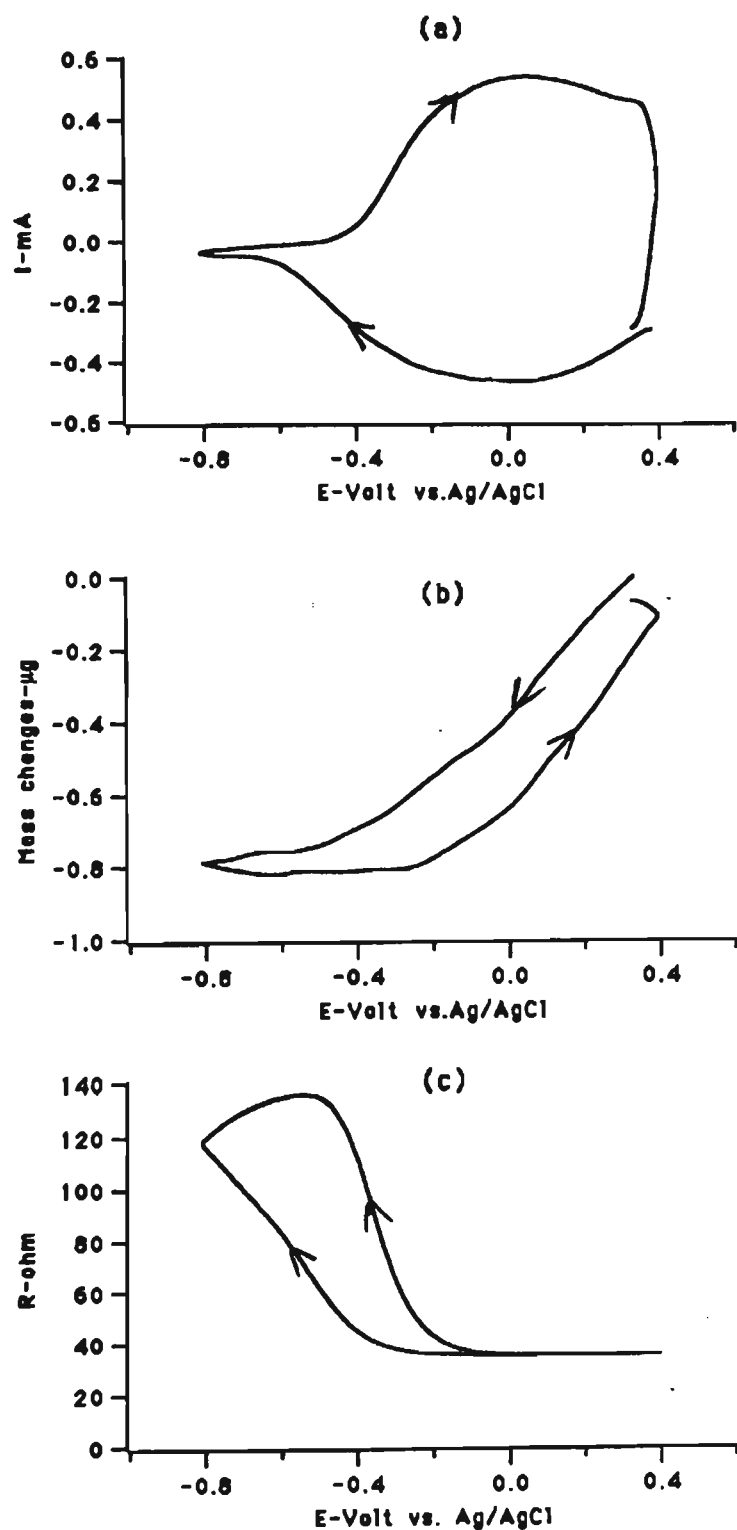


Figure 5.13: *In-situ characterisation of PPy/Cl in 1M NaCl.*

Scan rate = 100 mV/sec. (a), Changes in current, (b) changes in mass, (c) changes in resistance.

With PPy DBS no anion movement was observed (Figure 5.14) instead cation incorporation resulting in an increase in mass was monitored.

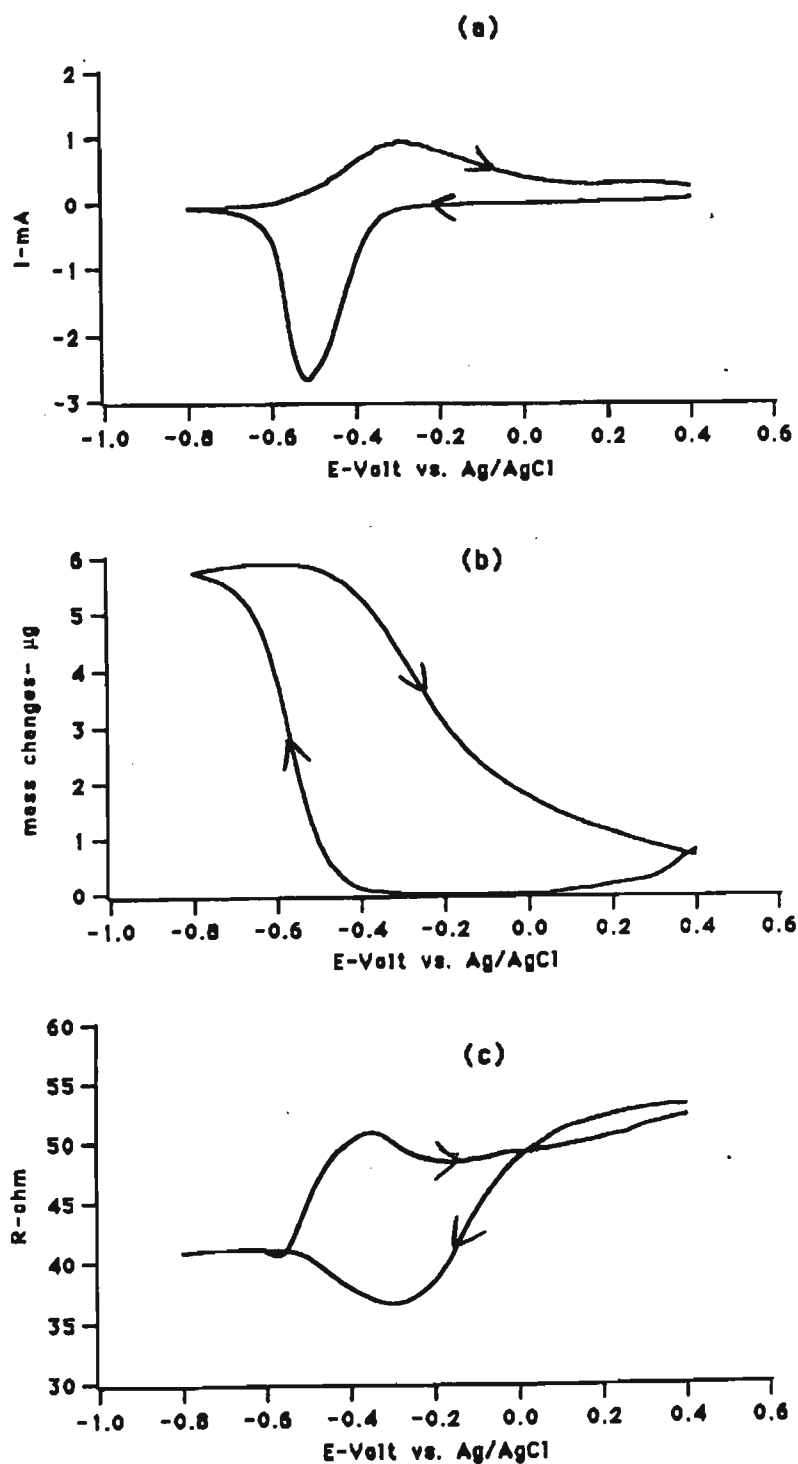


Figure 5.14: *In-situ characterisation of PPy/DBS in 1M NaCl. Scan rate = 100 mV/sec. (a) changes in current, (b) changes in mass, (c) changes in resistance*

A plot of mass change versus resistance for each polymer was obtained (Figure 5.15). A dramatic threshold effect is obvious, confirming that all

conductive pathways must be closed down before a resistance change is observed. An important difference between PPy/Cl and PPy/PTS was observed in the mass/resistance plot indicating that each polymer has a specific transition point. With PPy/Cl the loss of only 0.8 μg resulted in the resistance transition. The mass/resistance plot for PPy/DBS (Fig. 5.15.b) was extremely interesting in that even though relatively large changes in mass were observed (5 μg) only small changes in resistance were observed. This confirms that the relationship between polymer reduction/oxidation and mass change as well as change in polymer resistance is not a linear one and depends on the nature of the mass change occurring.

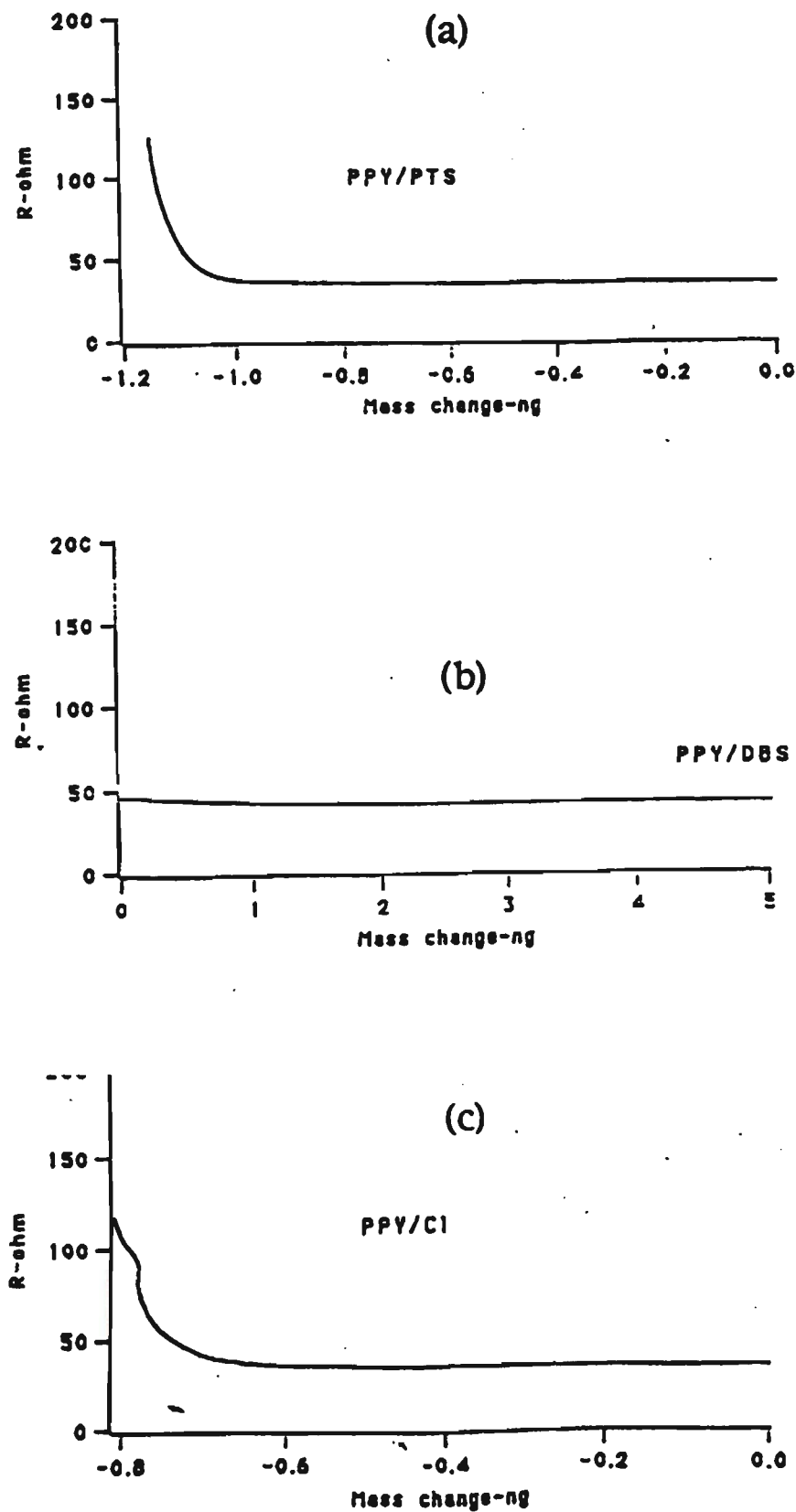


Figure 5.15: Plots of Resistance vs Mass for:

(a) PPy/PTS [Original Polymer Mass= 22 μg]

(b) PPy/DBS [Original Polymer Mass= 33 μg]

(c) PPy/Cl [Original Polymer Mass= 16 μg]

Another series of experiments were carried out to investigate the effect of electrolyte composition on the electrodynamic properties of polypyrroles. Two different polymeric systems, PPy/Cl and PPy/DBS, were studied the effect of varying the nature of the electrolyte cation on the switching process was considered.

Polypyrrole chloride has been already studied in 1M NaCl in this chapter (Fig. 5.13). It was found that in this simple case the anion easily moves from the polymer to the solution over the range of the redox potential for the polymer. Now, we compare this result with other electrolytes such as LiCl, CaCl₂ and MgCl₂. As shown in Figures 5.16 and 5.17, as PPy/Cl is reduced in 1M NaCl or 1M LiCl respectively, anions are expelled continuously from 0.60 to -0.20V. This is indicative of the model originally proposed by Tanguy ¹⁷⁹. This model suggests that the reduction/oxidation process is not discrete but that it occurs over a wide potential range.

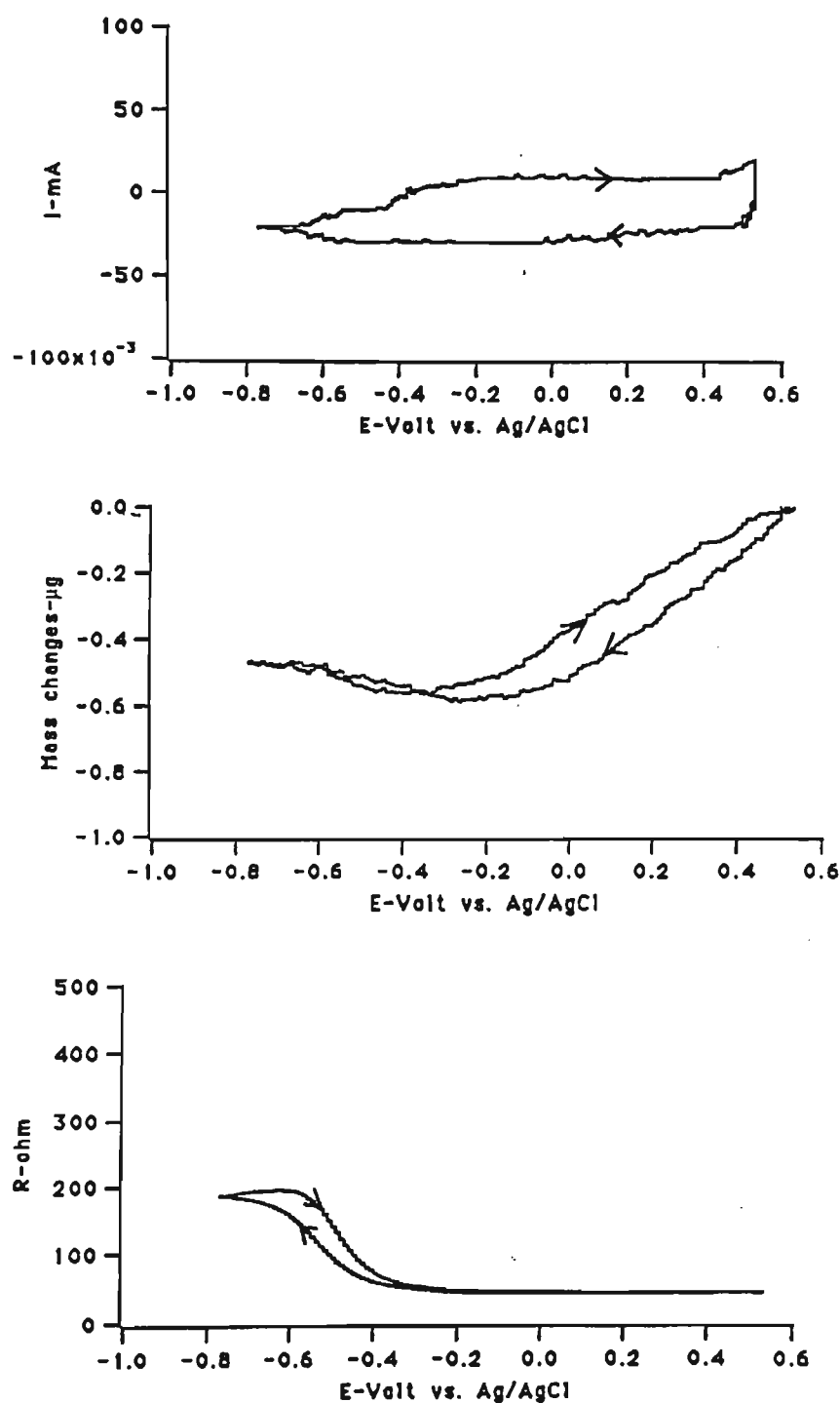


Figure 5.16: Reduction/oxidation of PPy/Cl in 1M NaCl.

Scan rate= 5mV/sec

Monomer solution for growth: 0.1M pyrrole and 0.05 M NaCl. The electrodes are as described in the Experimental section. Polymer was grown galvanostatically at $j=2\text{mA}/\text{cm}^2$ for 2 min.

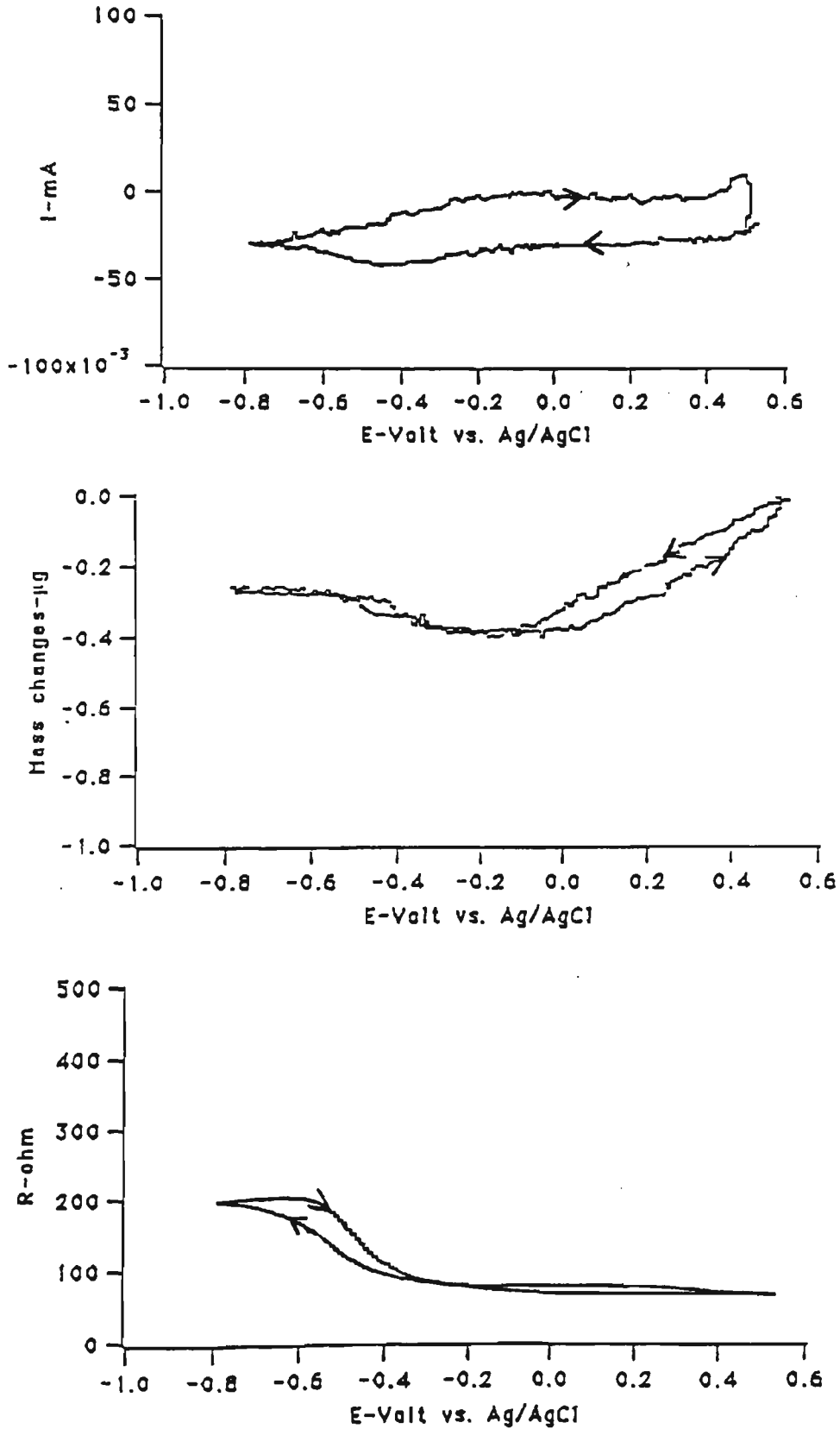


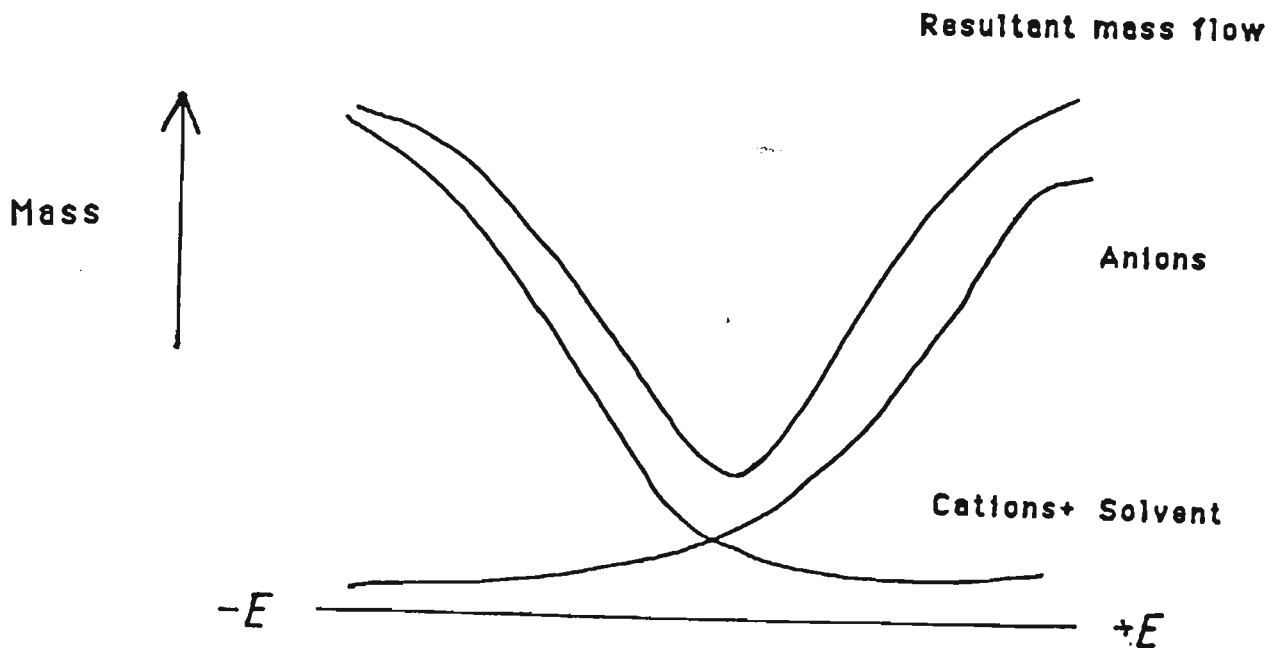
Figure 5.17: *PPy/Cl* in 1M LiCl.

Other conditions are the same as in Figure 5.16.

The mass changes are essentially reversible with the ingress of ions lagging behind the expulsion due to the decreased diffusion coefficient of the ions in the polymer compared to that in solution[6.10].

The resistance change as expected was encountered at a threshold level occurring at -0.40V when the reduction of the polymer was essentially complete. Of course since the reduction process results in increased electronic resistance, further reduction will be more difficult. The increased resistance observed has been associated with the removal of charge from the polymer backbone.

In the case of lithium containing electrolytes, it appears that the mass loss due to ion incorporation is less. However, as shown by others ¹⁸⁰⁻¹⁸² cation/solvent ingress can occur simultaneously with anion egress and the resultant QCM plot is the sum of the mass changes occurring as shown in Figure 5.18. The same amount of charge flow was observed for both Li^+ and Na^+ containing electrolytes so the apparent difference in mass change was not due to electrochemical effects. Inzelt and coworkers ¹⁸³ showed that the difference in mass change in NaCl and LiCl is due to the nature of the cation used in these salts. They found in their investigations that the amount of water carried by individual cations is greater for Li^+ than Na^+ . Therefore, the difference in the mass change, particularly in negative potentials, is due to the difference in the degree of hydration of Li^+ and Na^+ . They suggested that it was in fact $11 \text{ H}_2\text{O}/\text{Li}^+$ and $9 \text{ H}_2\text{O}/\text{Na}^+$ that entered the polymer during reduction.



Schematic 5.18: *Combination of cation/solvent ingress and anion egress*

An interesting result is observed when the cation is Ca^{2+} (Figure 5.19). A 0.5M CaCl_2 electrolyte was used to maintain a constant concentration for the chloride anion. Now the decrease in mass continues until -0.4V and a mass increase that would reflect cation/solvent insertion is obvious. The mass decrease was similar to that observed in NaCl solution. A marked difference is observed in that the change in resistance of the polymer is much larger.

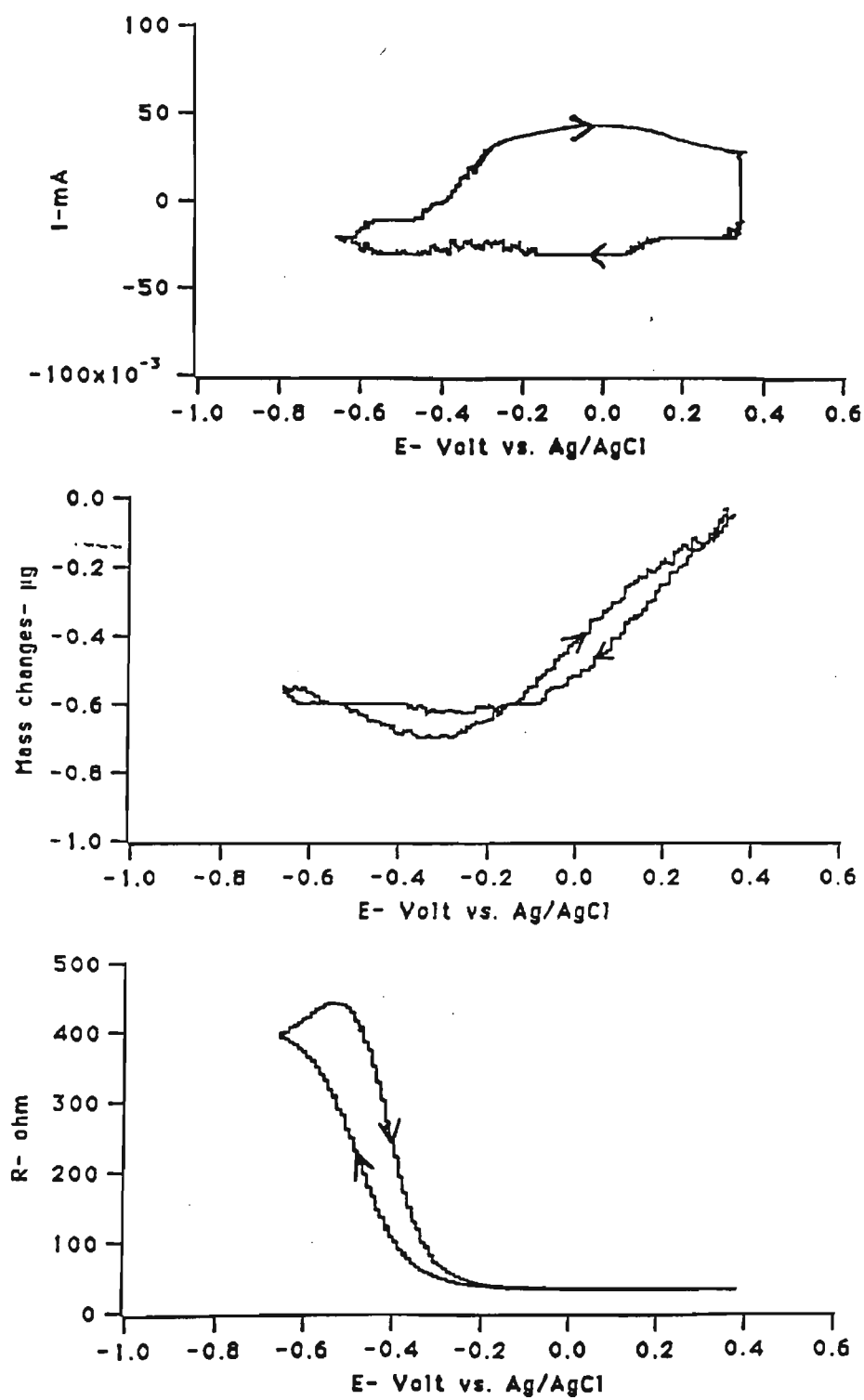


Figure 5.19: *PPy/Cl* in 0.5M CaCl_2 .

Other conditions are the same as in Figure 5.16.

A greater marked change in resistance was observed in MgCl_2 (Fig 5.20). In addition, the switch occurs at -0.5 V in this electrolyte compared with the switch potential = -0.4 in CaCl_2 .

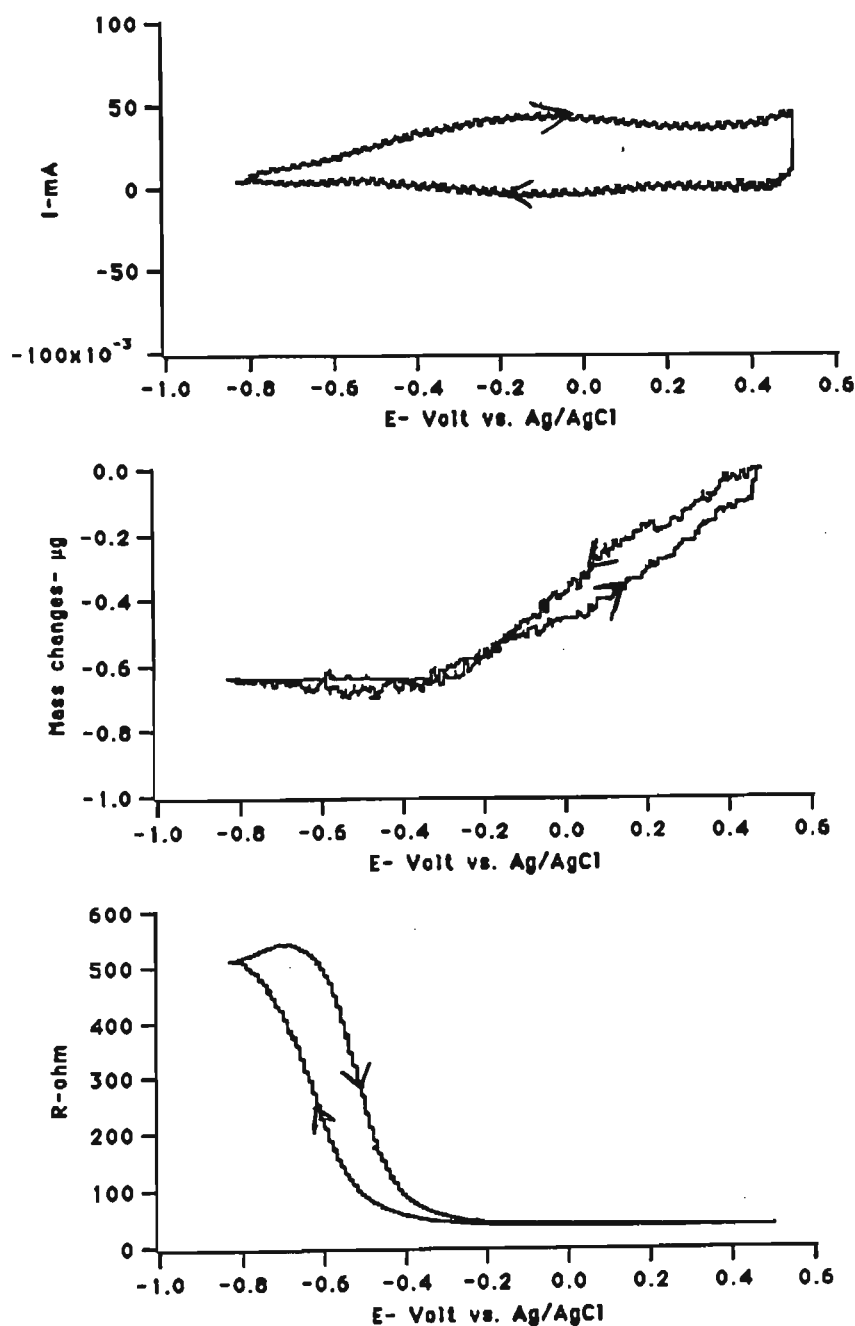


Figure 5.20: *PPy/Cl* in 0.5 M MgCl_2 .

Other conditions are the same as in Figure 5.16.

We believe this may be due to a phenomenon well known to biopolymer researchers where the nature of the electrolyte can have a marked effect on the

water structure ¹⁷⁹ and subsequently on the properties of the polymer. In biochemical studies it has been shown [26] that certain salts can cause salting out; dehydration of protein at biopolymers causing them to precipitate. Ions that do so are known to be chaotropic. Strong chaotropic salts eg. Mg^{2+} and Ca^{2+} disrupt the structure of water and thus decrease hydrophobic interactions, while the more anti-chaotropic salts (Li^+ , Na^+) do not strongly interfere with water structure and hence do not interfere with hydrophobic interactions. The strong chaotropic agents, since they disrupt the water structure, may also dehydrate the polymer chain causing changes in polymer chain conformation. These workers have recognised that salt affect not only electrostatic interactions but also hydrophobic interactions with polyelectrolytes. Perhaps a similar way to "visualise" this is that ions with a high hydration number will compete with the polymer for waters of hydration. Water is removed from the polymer thus causing salting out. This effect can be predicted by considering a lyotropic series of simple ions.

As pointed out recently by Iseki and coworkers ¹⁸⁵ cations can deactivate the electrochemical properties of PPy-tosylate coatings. They suggest that both the size and hydrophobicity of the cation are important in this regard. We suggest that in addition, the chaotropic effect can not be ignored. Such an effect is perhaps more obvious if pulse potential stimuli had been considered.

As illustrated in Figures 5.21 , 5.22 and 5.23, PPy/Cl has shown different electrochemical switching behaviour in different salts. It is important to note that the results are not totally reproducible because the ion exchange between the polymer and the electrolyte solution is not reproducible. For the same duration of pulse stimuli applied, the polymer has reached the most resistive structure in the salt containing the strongest chaotropic agent, Mg^{2+} , and the less resistive structure in NaCl.

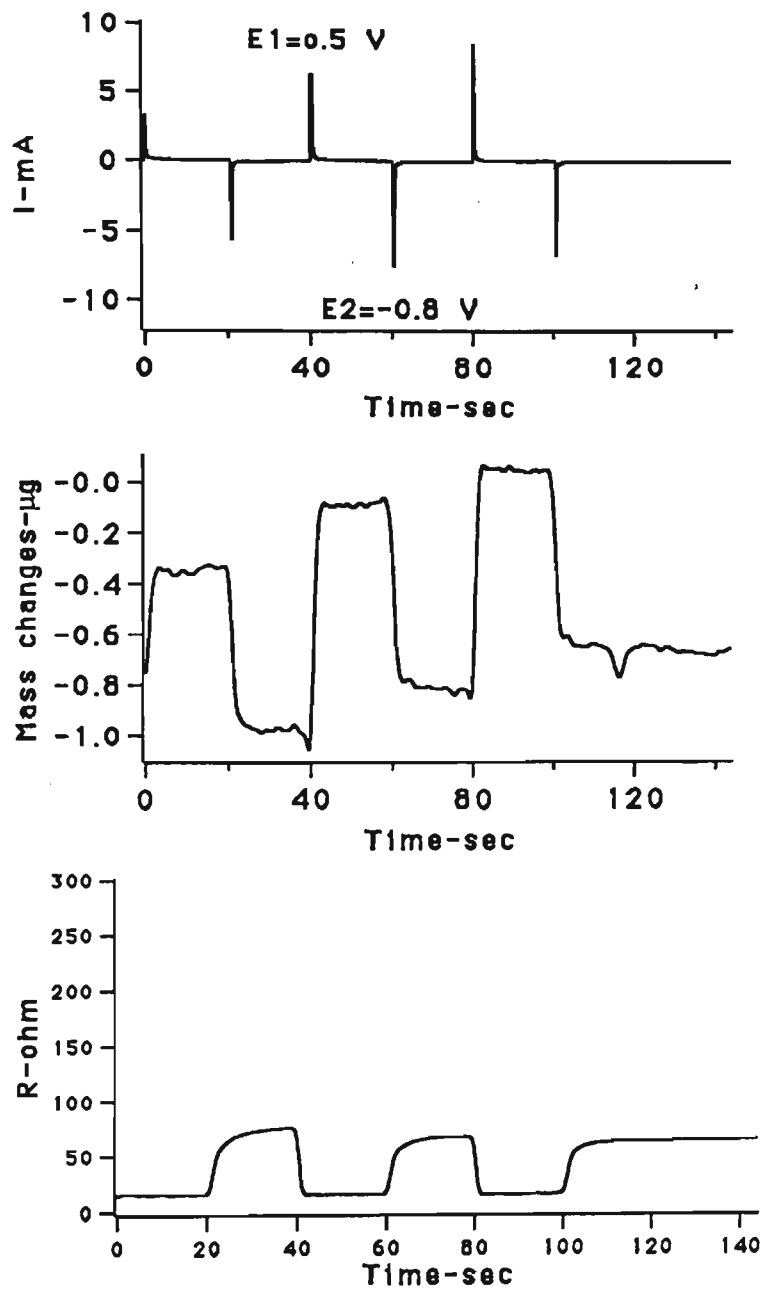


Figure 5.21: *PPy/Cl* in 1M NaCl.

polymer was grown the same as in Figure 5.16.

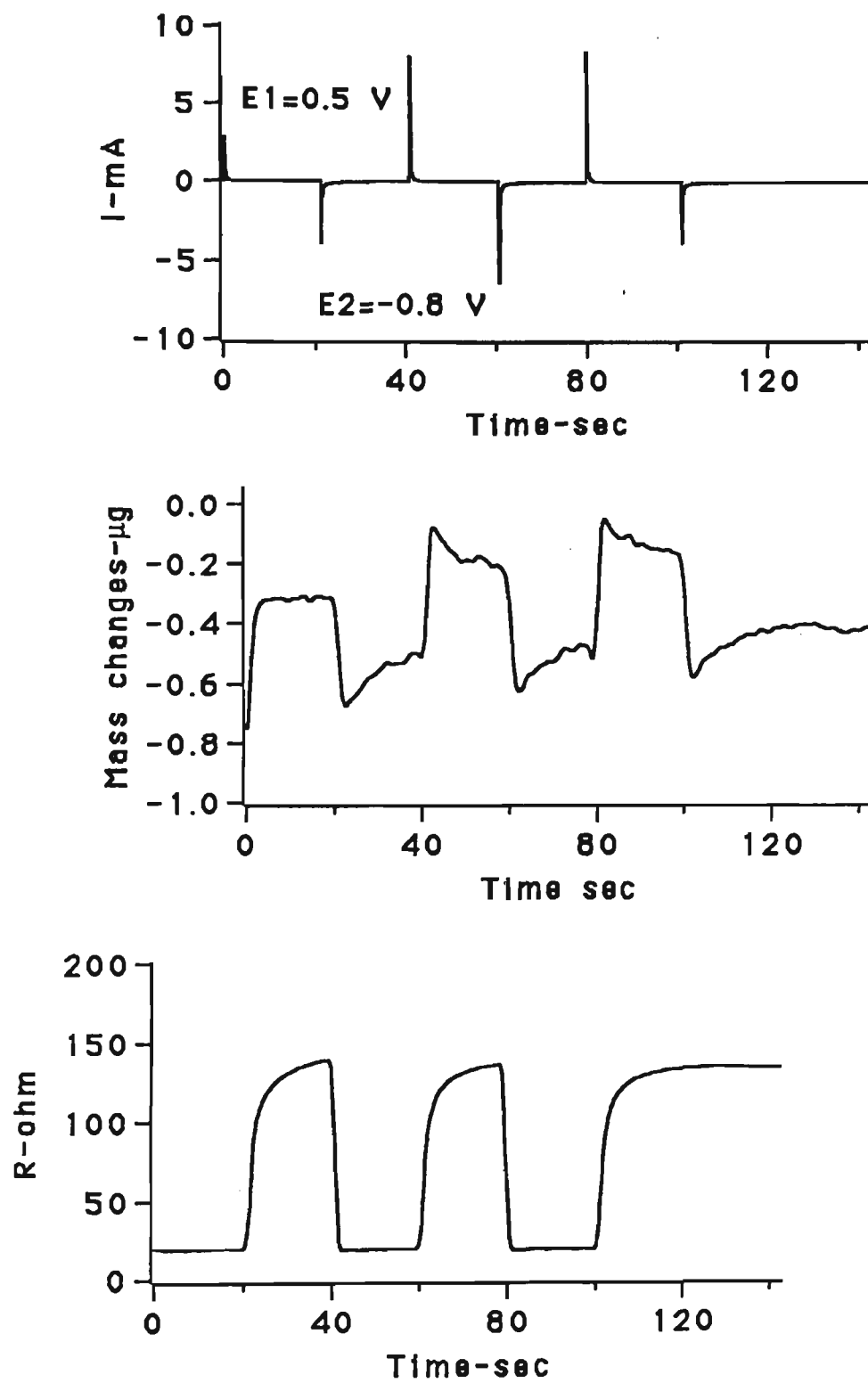


Figure 5.22: *PPy/Cl* in 0.5M CaCl_2 .

Polymer was grown the same as in Figure 5.16.

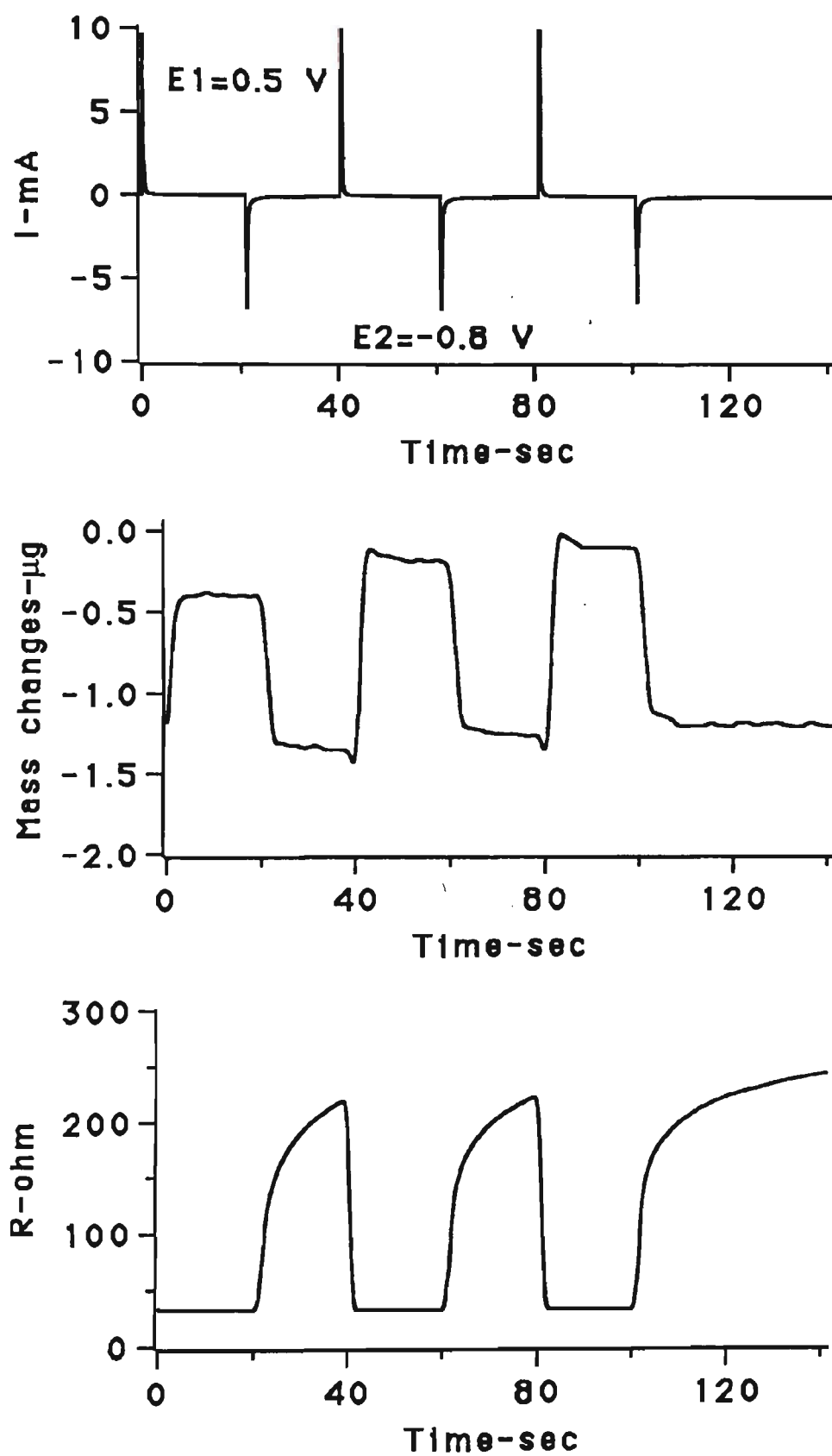


Figure 5.23: *PPy/Cl* in 0.5M MgCl_2 .

Polymer was grown the same as in Figure 5.16.

Upon reduction of PPy/DBS, cation insertion from the electrolyte solution into the polymer, rather than anion movement from the polymer to the solution occurs. Previous workers have shown ^{186,187,167} that the contribution of anions and cations to the molar transport is strongly dependent on the dopant ions. Heinze ¹⁸¹ and Qiu ¹⁸⁷ have also shown that when the counterion incorporated to the polymer is immobile, in contrast to anion specific transport in the case of a simple mobile counterion like chloride, cation specific transport takes place. In the following investigation the chaotropic effect on PPy/DBS is discussed.

Figures 5.24 and 5.25 show a very obvious effect between a salt which is and a salt which is not a strong chaotropic agent. The most obvious effect is on the potential at which current, mass and resistance changes happen. The mass and resistance transition begins at more positive potential for the polymer in 0.5M CaCl₂ compared with in 1M NaCl. This is a significant effect of chaotropic ions used as a cation in the salt electrolyte.

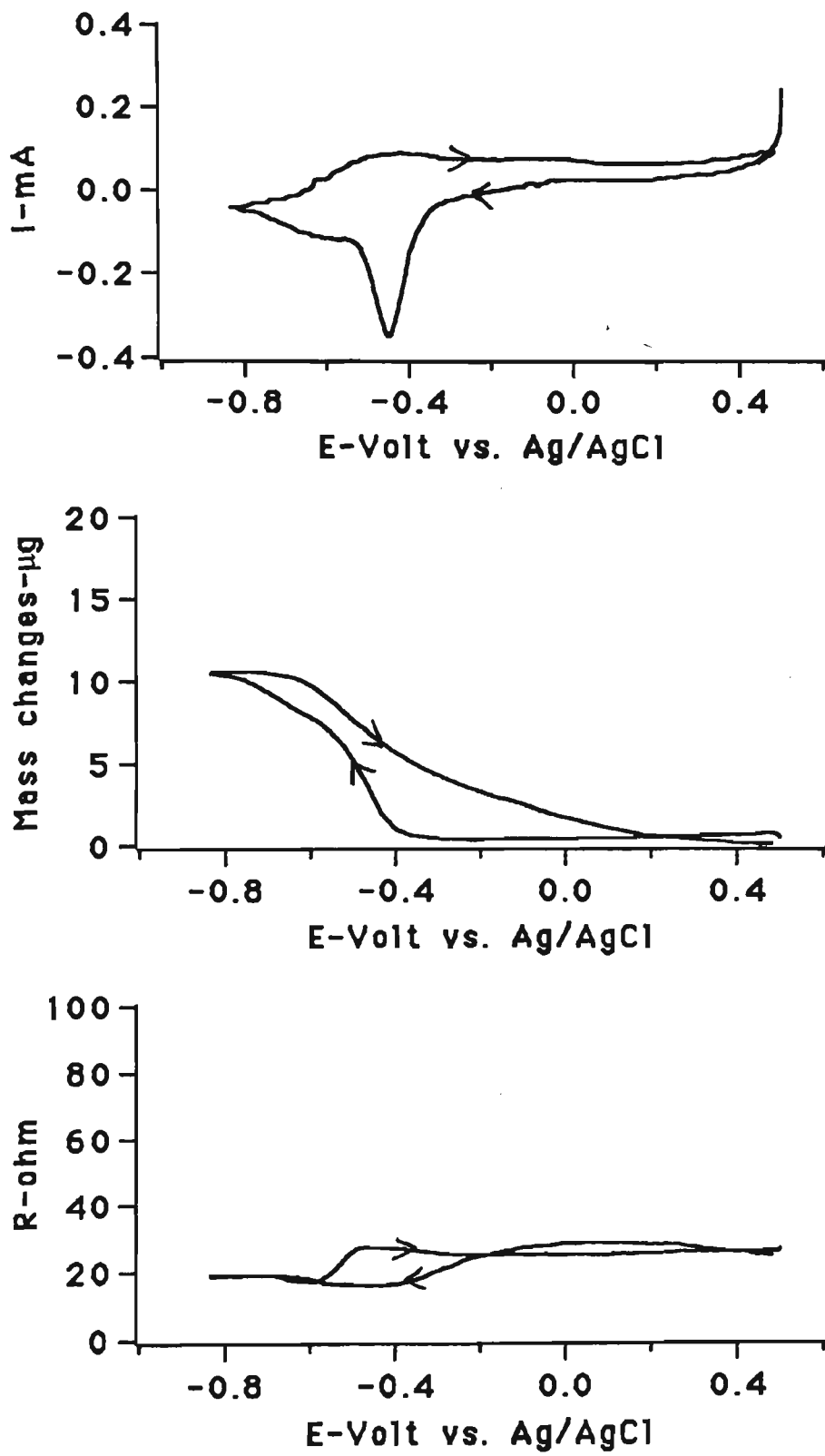


Figure 5.24: *PPy/DBS in 1M NaCl. Scan rate =10 mV/sec.*

Monomer solution: 0.1M pyrrole and 0.05 M DBSNa. Other conditions are the same as in Figure 5.16.

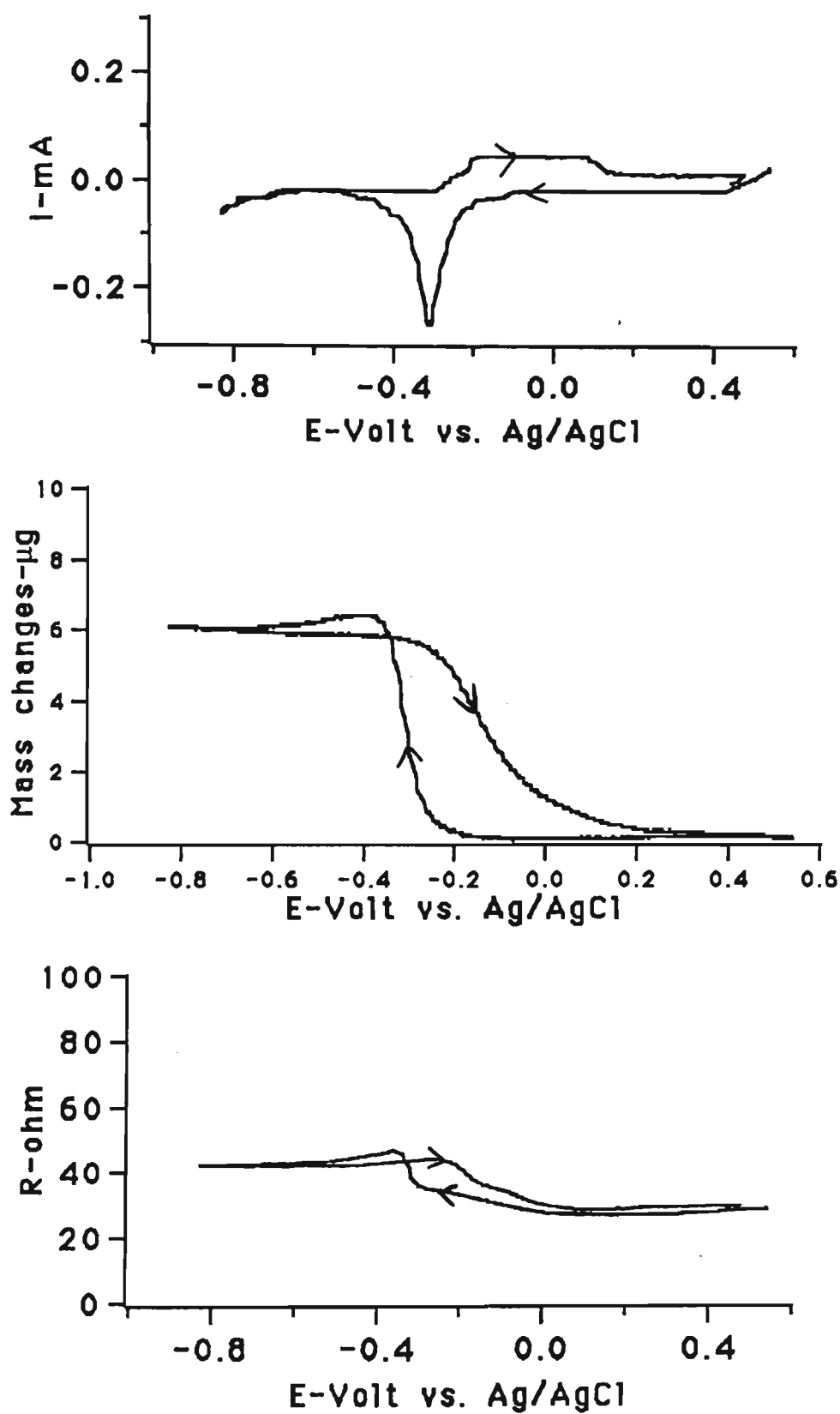


Figure 5.25: *PPy/DBS in 0.5M CaCl₂. Scan rate = 10 mV/sec.*

Monomer solution: 0.1M pyrrole and 0.05 M DBSNa. Other conditions are the same as in Figure 5.16.

Changes are more obvious in mass and resistance in the potentials more negative than -0.2V . In fact, this is the region that solvated and hydrated cations play decisive roles. Naoi and coworkers [6.14] discussed that the cation movements can affect the polymer morphology resulting in different mass and resistance behaviour. Heinze and Bilger [6.2] supported this theory through an investigation on the relationship between the morphology and ion migration.

The pulse investigation of PPy/DBS in the same salts shows that even in the case of immobile DBS, used as counterion incorporated into polypyrrole, more mass and resistance changes can be observed (Figures 5.26 and 5.27) if the salt electrolyte contains a strong chaotropic agent. It has been found that the chaotropic effect is much more obvious when the resistance behaviour of the polymer is studied. This is expected as the morphological changes, due to the presence of different cations, create more electronic changes. The charge carriers and electrons move through the polymer. Therefore, any changes in the morphology or surface roughness due to the cation movement results in conductivity changes. This is what Smyrl¹⁶⁷ and Heinze¹⁸¹ pointed out.

A $4\text{ }\mu\text{g}$ mass change was observed for PPy/DBS in 1M NaCl compared with a $5\text{ }\mu\text{g}$ change in 0.5M CaCl_2 . As far as resistance changes are concerned, the polymer shows an almost doubling of the resistance change during the oxidation/reduction in calcium chloride as compared with sodium chloride. This is expected as the chaotropic effect changes the polymer conformation and configuration; which is related to the electronic properties of the macromolecule.

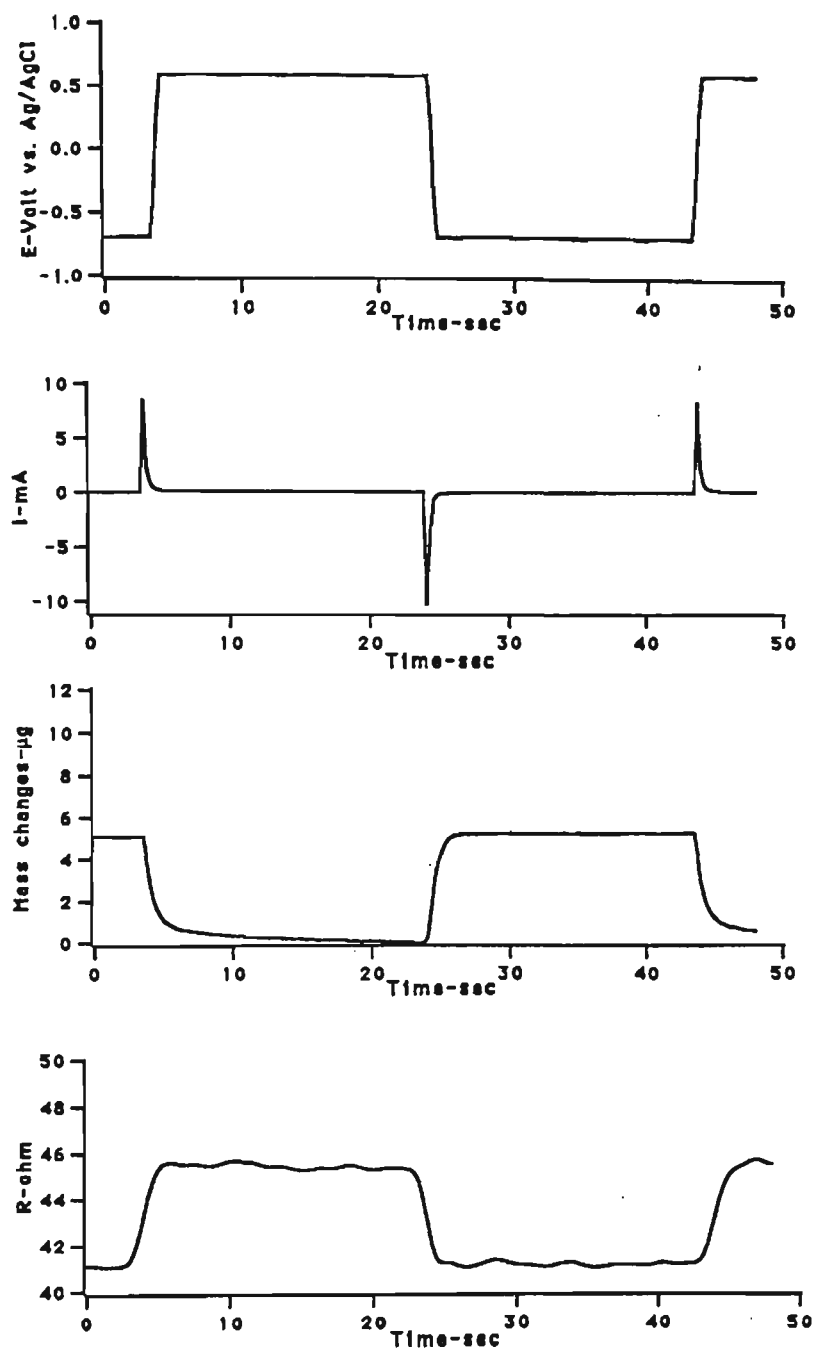


Figure 5.26: *PPy/DBS in 1M NaCl.*
Other conditions are the same as in Figure 5.24.

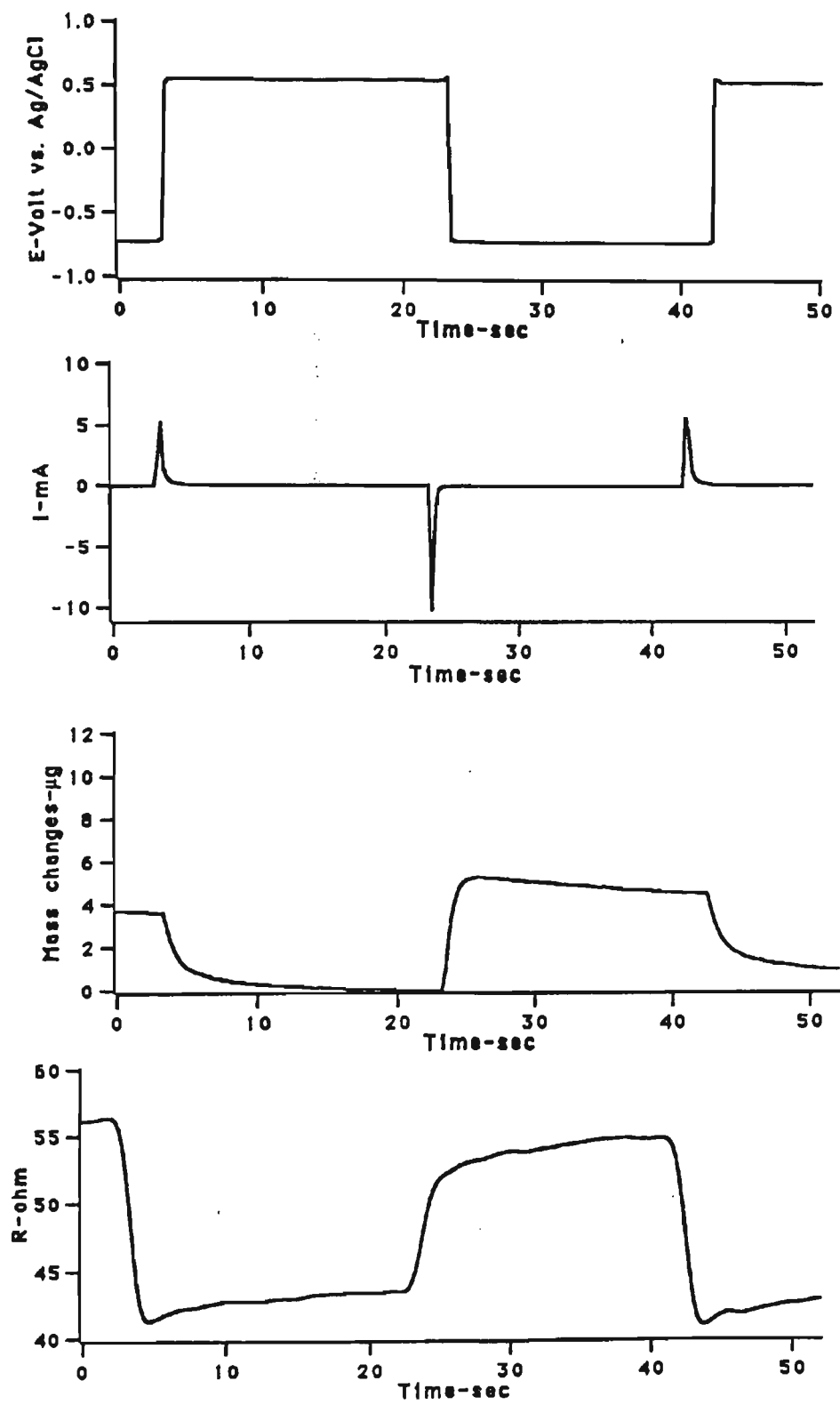


Figure 5.27: *PPy/DBS in 0.5M CaCl_2 .*
Other conditions are the same as in Figure 5.24.

5.5 CONCLUSION

A new simultaneous analysis technique is achieved by a combination of several simple methods. This technique enables the relationship between charge transfer, mass changes and resistance changes to be determined simultaneously and in-situ. It has also been shown that simply by using a strong chaotropic agent in the supporting electrolyte, significant changes can be observed in the electronic properties of the conductive, electroactive polymers. The electrolyte composition not only influences the electrodynamic properties of the polymer during the redox process but also affects the polymer structure; and so creates different morphologies which result in different mass, and particularly resistance changes upon switching.

CHAPTER 6

THE EFFECT OF pH ON THE R/E RESPONSE OF POLYPYRROLE AND POLYANILINE MATERIALS

6.1. INTRODUCTION

As explained in chapter 1 polyaniline and polypyrrole are pH sensitive materials. The effect of pH on R/E response curves for polypyrroles and polyanilines has been investigated. The use of these materials as pH sensors has also been discussed in the application sections.

The monitoring of pH of solutions is widely required in laboratories, clinics and industries as many chemical processes are pH dependent. Although the glass bulb pH electrode is a well established tool in the measurement of pH, there are some disadvantages with this type of electrode. Glass pH electrodes do not provide accurate data at very high and very low pH values because of alkaline error and dehydration respectively 188,189. The electrode also needs special care and treatment before and after use 189. Improvement of pH measuring techniques to overcome existing problems may be achieved by exploration of new sensing materials. Natan et.al have recently introduced pH sensitive microelectrochemical transistors based on WO_3 190 and $\text{Ni}(\text{OH})_2$ 191. In this work the use of conducting polymers to form the basis of new pH sensors has been considered. In acidic media polyaniline can be oxidised and reduced from a more conductive (oxidised) to less conductive (reduced) form; deprotonation of the polymer at high pHs results in decreased conductivity 192,143. The conductivity of polypyrroles in the oxidised form is also known to be pH dependent with resistance increasing dramatically above pH 12 193,194.

6.2. AIMS AND APPROACH OF THIS CHAPTER

In this work the sandwich electrode described in chapter 2 has been employed. In this chapter we first demonstrate the effect of pH on PPy/Cl, PPy/PVS, PAn/Cl and PPy/PVS-PAn/Cl composite in a stationary cell. Then we point out the practical utility of the conductive polymer electrodes in monitoring solution pH in a continuous flow system.

6.3. EXPERIMENTAL

6.3.1. Instrumentation

Voltammetric data were obtained using a BAS CV 27 Voltammograph. Data were collected using a Maclab (Analog-Digital Instruments, Sydney, Australia) interface or Electrolab and an Apple computer. Pulse resistometry measurements were facilitated by the use of a resistometer developed at CSIRO Division of Mineral Products, Melbourne, Australia. A 10 mV DC, home made, power supply was employed for applying voltage, and a multimeter model HP 3465B was used for recording currents. The injector used in the flow injection experiments was model Rheodyne 7125 with sample loop of 20 μ g.

6.3.2. Reagents and standard solutions

All reagents were of analytical grade purity unless otherwise stated. Pyrrole was obtained from Aldrich and aniline was obtained from BDH. All salts were also obtained from Aldrich and all acids were supplied by BDH. All aqueous solutions were prepared in deionised (Milli-Q) water.

6.3.3. Procedure

Polymerisations were carried out potentiostatically in the three electrode electrochemical cell. All polymers were grown at constant charge and constant potential (for polypyrroles $E=0.75$ V and $Q=100$ mC, for polyanilines $E=0.80$ V and $Q=20$ mC). The working electrode was the sandwich electrode described in chapter 2, the reference and auxiliary electrodes were Ag/AgCl and platinum plate respectively. Solutions of different pHs were made from HCl and NaOH by dilution with 1M NaCl to keep the ionic strength almost constant. The polymer resistance was recorded in different solutions when the values had stabilised. This varied from durations of 1 min to 3 min. The time response of each polymer during its metallic/insulator transition was measured by immersing the polymer in solution of higher pH and then to a lower pH. Then the current was recorded at each time the changes were observed. The resistance was then calculated and the curves of R vs time were plotted.

6.4. RESULTS AND DISCUSSION

In chapter 2 it was concluded that pulse resistometry is a useful technique for characterisation of conducting polymers, and DC resistometry is a simple and helpful technique for applying conducting polymers in sensing technology. Initially the pulse resistometry was used to investigate the effect of solution pH on the polymers used in this work.

6.4.1 The stationary system

6.4.1.1 Polypyrrole/Cl

PPy/Cl was deposited on/in the sandwich electrode potentiostatically at $E = 750$ mV until the charge consumption was 100 mC. The pulse resistometry result (Fig.6.1) suggests that the polymer is very conductive at $E = 400$ mV. As other researchers^{194,195} pointed out, the conductivity of polymers decreased with increased pH of the solution in contact with the polymers. Therefore, it is better to use the polymer with the best possible conductivity in the study of the effect of solution pH on the resistance of the polymers.

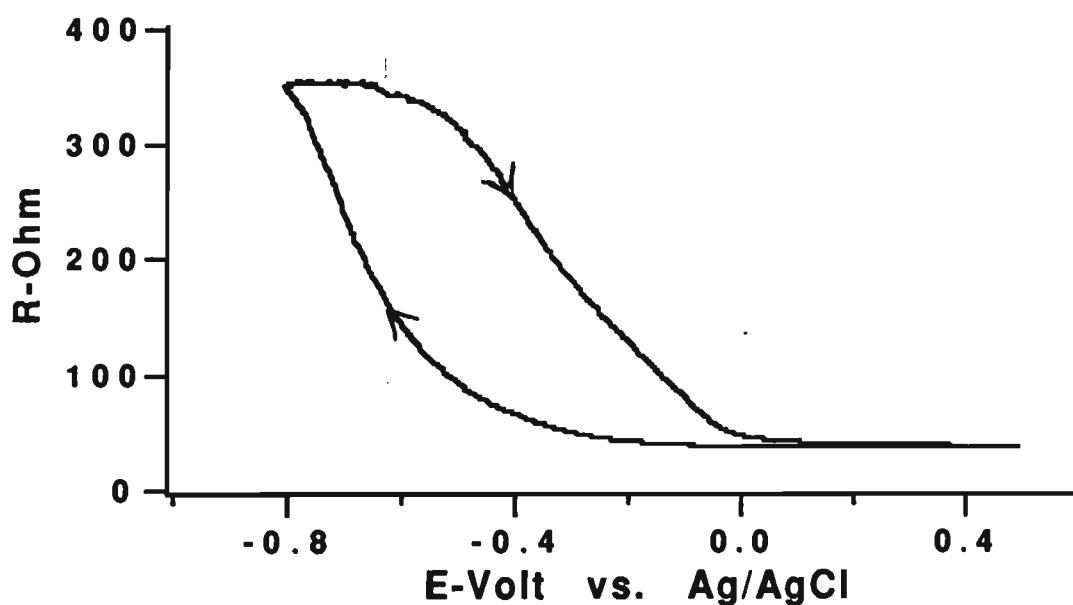


Figure 6.1. *R/E response during oxidation/reduction of Polypyrrole Chloride in 1M NaCl using the pulse resistometry method.*

Scan rate = 10 mV/sec.

The polymer resistance was determined, using the DC method, after application of $E = 400$ mV to the electrochemical cell for a sufficient time to allow the polymer to reach equilibrium at this potential. Then pH vs resistance plot for PPy/Cl was obtained (Figure 6.2). In this experiment the polymer was left in solutions of different pHs till no further resistance changes were observed.

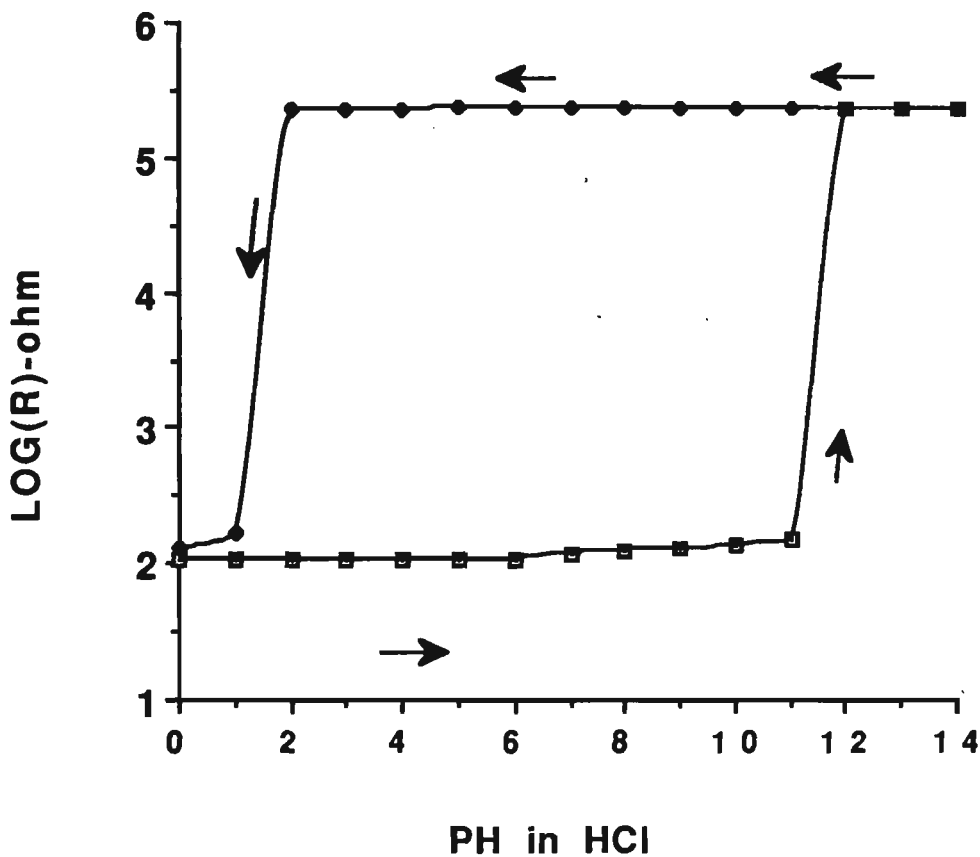


Figure 6.2: *The resistance behaviour of PPy/Cl in solutions with different pH s .*

The polymer remains very conductive ($R=100$ ohm) from pH 0 to pH=11. It is at pH 11 that a sudden increase in the resistance of the polymer occurred. The surprising feature of this polymer is that when the solution pH was decreased the polymer remains resistive until pH=2. This suggests that a marked change in polymer properties occurs as a result of exposure to high pH. Pei and Qian ¹⁹⁵ suggested that protonation and deprotonation of polypyrrole occurred in different pH solutions. They used in-situ optical absorption spectra to study this process. They found that in a basic solution at pH=11, the absorption band which was around 460 nm for pristine PPy

shifted to 390 nm, close to the value for the bandgap transition in neutral PPy⁰. In acidic solutions this absorption band was shifted to 470 nm. They believe that this is probably due to the protonation of PPy chains.

In their studies they published a very interesting plot which shows the dependency of Cl⁻ content in PPy/Cl films on the pH. The plot showed that with increasing pH from 0 to 13 two stages of Cl⁻ expulsion from the PPy film exist: one in the pH range of 2-4, the other in the pH range of 9-11. They argue that the process involved in the latter pH range may be associated with the deprotonation of PPy. They supported their ideas by looking at the amount of H⁺ in the polymer film. They have shown that the amount of hydrogen ion increases with decreasing solution pH. This is in agreement with their protonation theory.

There might also be a hydroxy attack on the polymer chain in addition to the deprotonation process at high pHs. That is why it is very hard for the polymer to reach its initial conductivity at pH between 10 to 3 while the acid/base treatment test was followed by base/acid treatment. In fact even by immersing the polymer in pH 2 solution, after being in pH 12 solution (Fig.6.3), the polymer requires a minimum of 200 sec to attain its initial conductivity. In Figure 6.3 the polymer was removed after 60 sec from the solution of pH 12 and was immersed in a solution of pH 1. Then the changes in the resistance of the polymer was recorded as a function of time until no further changes occurred. This means that there is ion hydroxy attack of the polymer chain but the effect is not that enough to render the deprotonation process irreversible. This means that the attack does not change the structure of the polymer very effectively. However, there is likely to be hydroxyl ion attack because ion exchange and protonation processes are not slow processes and the polymer has been left in the solutions with different pHs

for at least for min for each solution in the experiments shown in Figure 6.2.. Therefore, it is better to suggest that there is a combination of ion exchange, protonation/deprotonation and hydroxyl ion attack in the interpretation of the results. Wegner and coworkers ¹⁹⁶ suggest that the nucleophilic attack of OH^- of oxidised pyrrole units leads to the structure in which the π -system of the polymer chain is partially interrupted.

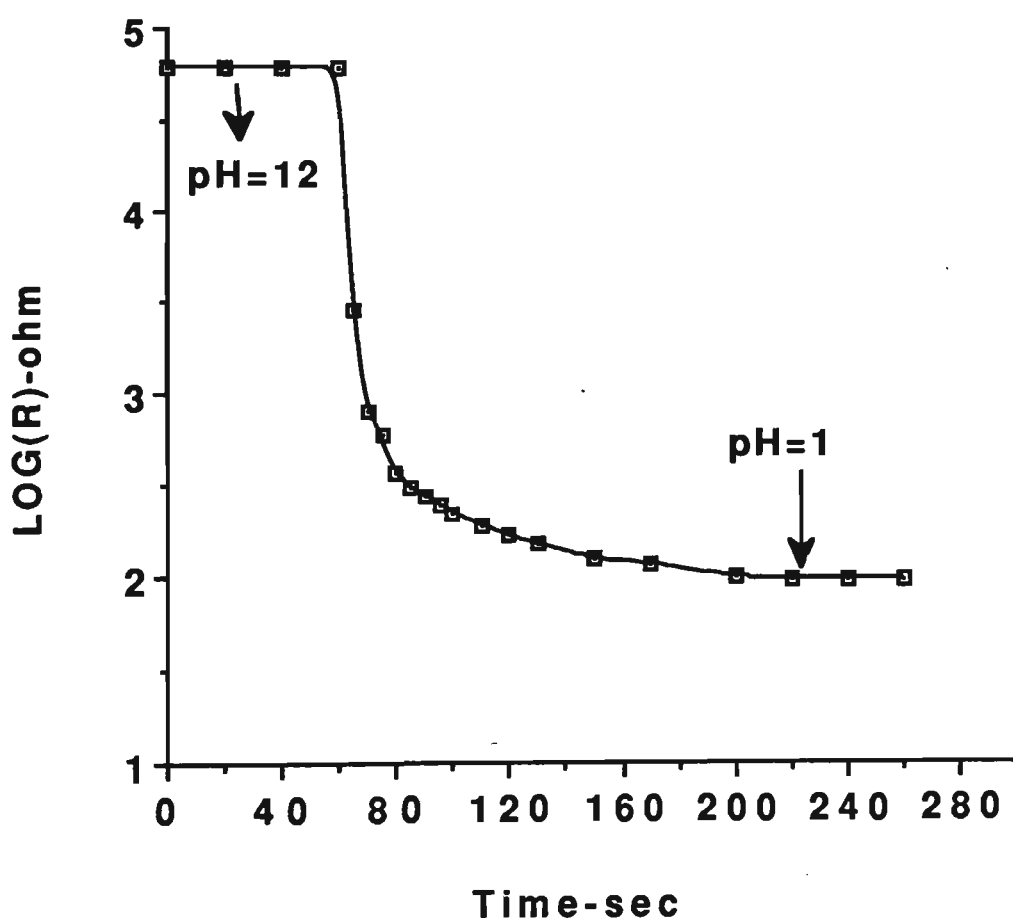


Figure 6.3: Resistance behaviour as a function of time for base/acid treatment of PPy/Cl. The same polymer was used in Fig.6.2.

Munstedt ¹⁹⁴ supports the idea that there is hydroxyl ion involvement in the sudden decrease in conductivity of polypyrroles in solutions of pH around 12. He rejects the assumption of the insertion of OH^- as the process

of retaining the electroneutrality of the polymer. However, he argues that there is another way of hydroxyl ion attack of the polymer. His hypothesis is that OH^- forms covalent bonds with polypyrrole. In his view, this reaction decreases the conjugation length and following from that the conductivity becomes lower. Comparing this assumption with Pei and Pei and Qian's hypothesis¹⁹⁵ that the deprotonation process is a dominant process in changing the conductivity of polypyrroles, we suggest that it is a combination of these processes that occur as a result of the effect of pH of the solution.

6.4.1.2 Polypyrrole/PVS

A very interesting and surprising feature has been found for electroactive and conductive PPy/PVS (Fig. 6.4) in solutions with different pHs (Fig. 7.5).

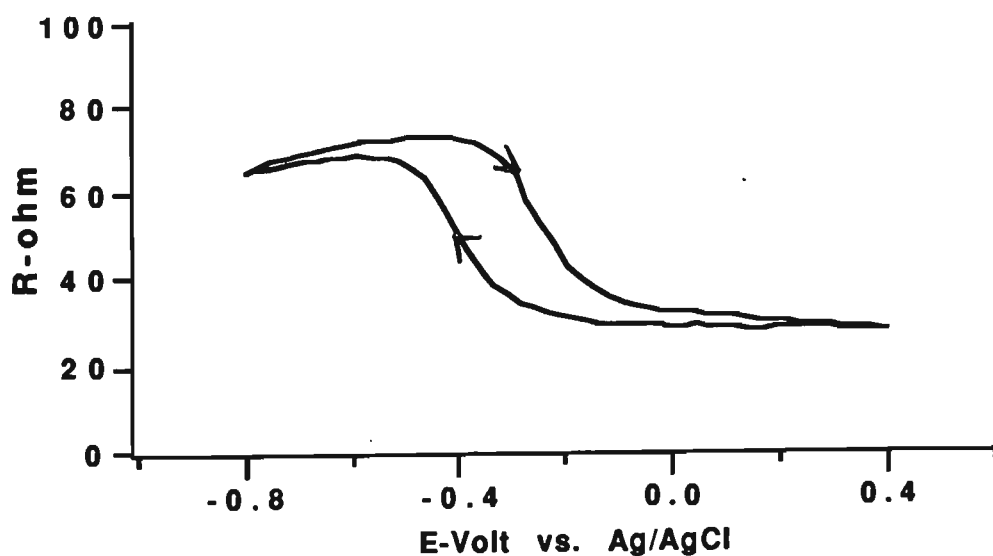


Figure 6.4: The R/E response for PPy/PVS in 1M NaCl with scan rate = 100 mV/sec using the pulse resistometry method.

According to Figure 6.4 the resistance transition for this polymer begins at -0.2 V, and a 50 ohm difference in the resistance value between its oxidised form and reduced form was observed.

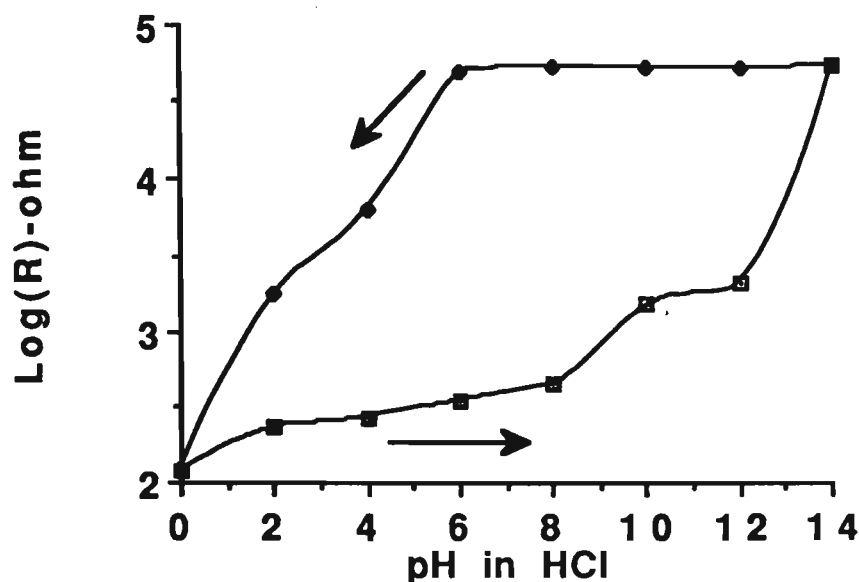


Figure 6.5: *The resistance behaviour of PPy/PVS in solutions with different pHs using the DC resistometry method.*

As Figure 6.5 illustrates, the polymer conductivity varies as a function of solution pH over the range of pH between 1 and 14. However, Munstedt's theory about hydroxyl ion incorporation into the polypyrrole is not very clearly observed in this figure as the polymer remains very resistive from pH 14 to pH 6 during base/acid treatment whereas in acidic media with pH less than 4 the polymer resistance becomes closer to its initial conductivity. This is perhaps an effect of a large size counterion (at the same polymerisation conditions) which prevents the insertion of OH^- to the bulk of the polymer. Therefore, it is easier for this polymer, compared with PPy/Cl to regain its initial conformation during the protonation process as the hydroxyl ion can be easily removed by H^+ from the surface of the polymer film.

The time response curve obtained for this polymer upon exposure to low pH solutions (Fig.6.6) suggests that the lag time is smaller compared to PPy/Cl.

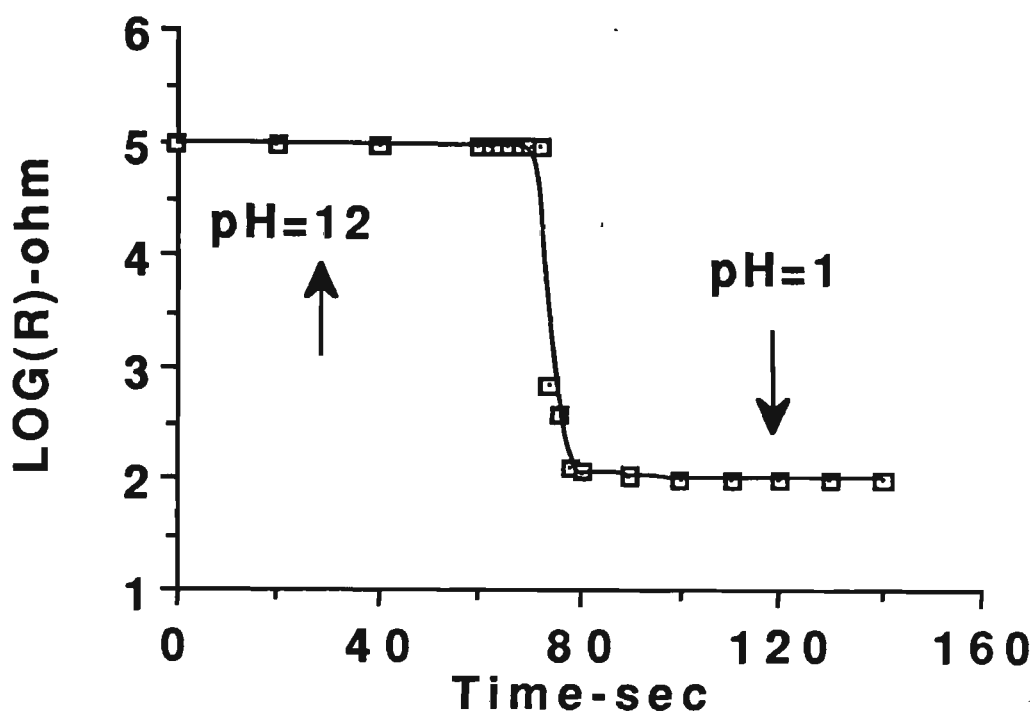


Figure 6.6: *The resistance behaviour of PPy/PVS as a function of time, base/acid treatment. The same polymer was used in Fig.6.5.*

6.4.1.3. Polyaniline/Chloride (PAn/Cl)

Polymer was deposited on/in the sandwich electrode using controlled potential ($E=800$ mV) till 20 mC of charge was consumed. Therefore, this polymer is thinner than polypyrroles. In fact our interest was in making the film on the electrode as thin as possible whilst filling the gap between the plates on the sandwich electrode. This makes the polymer more sensitive to pH. However, this makes the comparison between the polypyrroles and polyaniline more difficult. Thus whenever the comparison is carried out it is based on the minimum thickness by which the plates are connected by the polymers. The post-polymerisation resistogram result for this polymer in HCl is plotted in Figure 6.7. Polyaniline chloride was also made chemically using the method described previously ¹⁷¹.

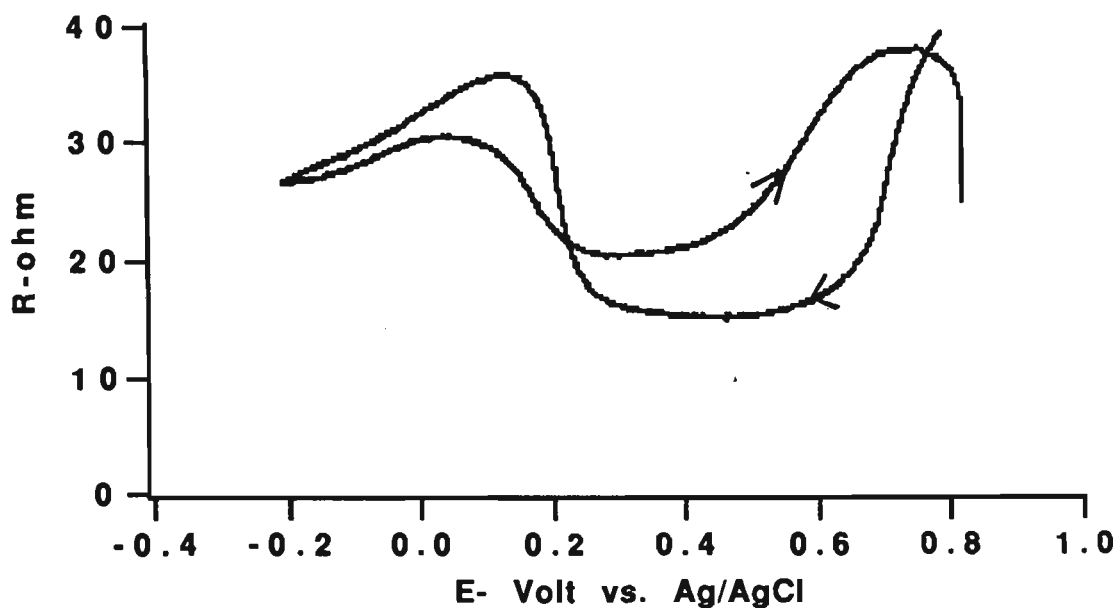


Figure 6.7: The R/E response for PAn/Cl in 1M HCl using pulse resistometry. Scan rate = 100 mV/sec. Polymer was grown as explained in the text.

The polymer behaves as expected and according to published literature 152,197. This polymer was left at $E=400$ mV for pH detection test because the polymer is very conductive at this potential. The electrode was then immersed in solutions with different pHs made immediately before use. The result is shown in Figure 6.8.

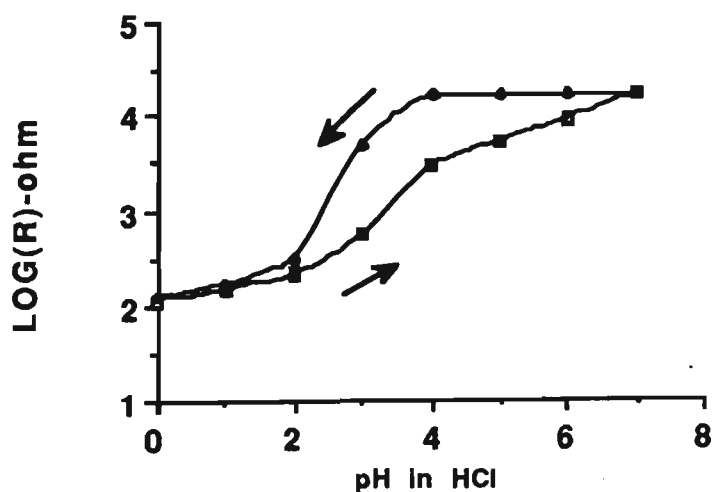


Figure 6.8: The resistance behaviour of PAn/Cl in different pHs using the DC method. The Polymer is the same as in Figure 6.7

The polymer shows better sensitivity and reversibility in both acid/base and base/acid treatment compared with that observed for polypyrroles. The trend of conductivity changes illustrated in Fig. 6.8 is the same as that reported by MacDiarmid et.al ¹⁹⁷ in their investigations. They studied polyaniline conductivity in aqueous HCl at different pHs. They also found that the polymer is very resistive at pHs higher than 4. They believe that protonation and deprotonation of polyaniline results in increasing and decreasing of the polymer conductivity respectively. They argue that by adding a proton, which interacts with the p system the conductivity increases. They suggest the following equation for a simple acid/base interaction, in which no formal oxidation or reduction occurs. They showed that this process is easily reversed by treatment with aqueous base. This is exactly what is suggested in Fig.6.7. In addition to MacDiarmid et.al's studies, there have been other investigations using different analytical techniques to explain the transition occurring at pH 3. Bartonek et.al ¹⁹⁸ have also been interested in investigating the transition from the insulating to the metallic state for polyaniline. They suggested that a critical protonation level is reached by equilibration of polyemeraldine in a medium of pH=3. They argue that this protonation level leads to a rather abrupt phase transition to a state which exhibits vibrational and optical features of a polaron lattice. Pingsheng et.al ¹⁴⁴ have also demonstrated that the apparent activation energy of conductivity of PAN is dependent on pH and shows a transition at pH 3-4.

It has been found that the polymer conductivity is more sensitive to pH while it is studied in a dry form ¹⁹⁹. In another study MacDiarmid et.al ¹⁹⁹ showed that the degree of protonation decreases from nearly 50% at pH 0 to less than 10% at pH 3. This study was carried out while the dry PAN

was used. In this investigation, it has been discussed that the sharp decrease in protonation between pH 2 and 3 suggests that a high degree of protonation are a prerequisite for low resistivity in the dry state. Later Focke et.al ¹⁵² point out that the resistivity in the wet polymer is not as sensitive to the degree of protonation as the resistivity in the completely dry state. It would therefore appear that, for PAn in contact with electrolyte, a marginal degree of protonation is sufficient to induce the conductor-insulator transition. We also studied the effect of pH on the conductivity of dry PAn film using the four point probe method (Fig.6.9). The polymer tape was made chemically ¹⁷¹ and then it was prepared in standard sizes for dry conductivity measurements. The samples were immersed in different solutions made from HCl with different pHs for 2 hours. Then they were tested with the four-point probe in the dry form.

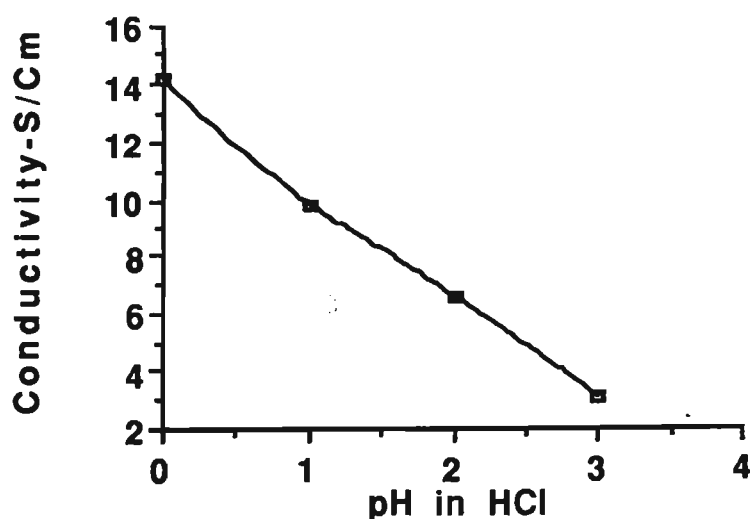


Figure 6.9: Plot of conductivity vs pH for PAn/Cl tape. The tape was made chemically as referred to in the text.

According to this Figure the conductivity (conductivity= 1/resistivity) of the polymer decreases with increasing pH very sensitively. It is very difficult to compare the result obtained in Figure 6.8 with that of Figure 6.9 because

two different methods were employed. However, it can be said that the tape configuration has shown better sensitivity in the way it was tested.

Our switching investigations between pH=5 and pH=0 (insulator-metallic transition) for PAn/Cl (Fig.6.10) also reveals the speed of the insulator-metallic transition for wet polyaniline film. This is so much quicker than that observed for polypyrrole considering the pH range at which polypyrrole shows insulator-metallic transition (pH=12 and pH=1). The polymer was in the solution with pH=5 for 60 sec and then it was immersed in the solution with pH=1.

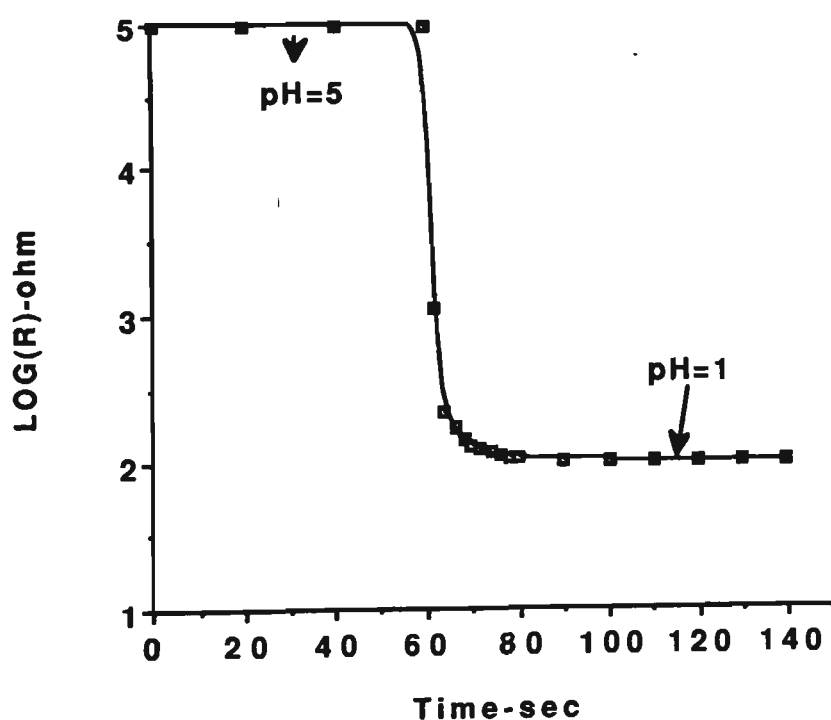
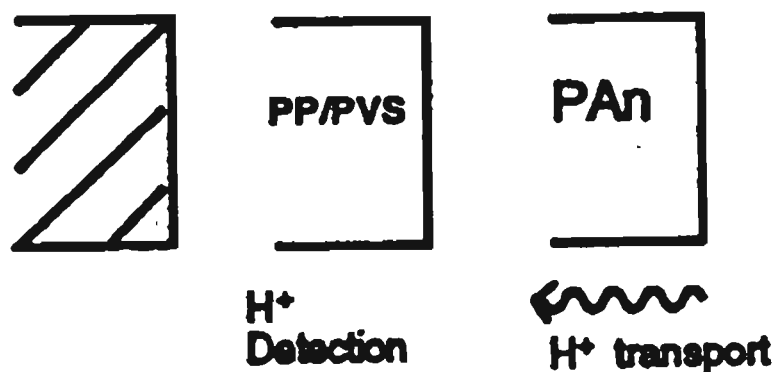


Figure 6.10: *The resistance behaviour of PAn/Cl deposited onto the sandwich electrode as a function of time using the DC resistometry.*

6.4.1.3. Polypyrrole/PVS-Polyaniline/Cl composite.

In the two previous sections we have shown that PPy/PVs and PAn/Cl are pH sensitive. Although PAn/Cl reveals better pH sensitivity over the range of 0-5, it is not suitable for pH greater than 5. In this section a novel layered structure electrode has been considered and the effect of solution pH on resistive properties investigated. The composite is made of PPy/PVS and PAn/Cl. First PPy/PVS was deposited on the electrode with the same conditions explained previously. Then PAn/Cl was deposited on the top of the PPy/PVS, as shown below, using the same monomer solution and conditions described in section 6.4.1.2. for electrodeposition of polyaniline.



As described PPy/PVS was first deposited on the electrode and later was coated with PAn/Cl. Therefore, PAn/Cl is the first to contact with the solution. H⁺ transport takes place through PAn/Cl and travels through PPy/PVS to reach the substrate electrode. Therefore, it can be illustrated as above that H⁺ transport begins at the PAn/Cl layer and H⁺ detection is carried out at the interface between PPy/PVS and the substrate electrode as a result of physical and chemical changes of the composite. In fact the H⁺ is not detected directly but rather as a function of resistance changes in the electrode due to H⁺ effects on the polymer. It is important to note that there is a possibility of direct connection between polyaniline and the platinum

plates on the sandwich electrode as there might be some pores left on the PPy/PVS which can subsequently be filled by polyaniline during its polymerisation on top of the PPy/PVS. This study needs more investigation by SEM. However, as our approach has been the resistometric examination of conducting polymers, it can be expected that the composite electrode shows a combination of polypyrrole/PVS and polyaniline/Cl behaviour in solutions with different pHs.

Characterisation studies were carried out in 1M HCl to investigate the composite electroactivity and conductivity (Figure 6.11). The composite shows the best conductivity at $E=400$ mV. Therefore, the electrode was equilibrated at this potential before resistance vs pH measurements were carried out.

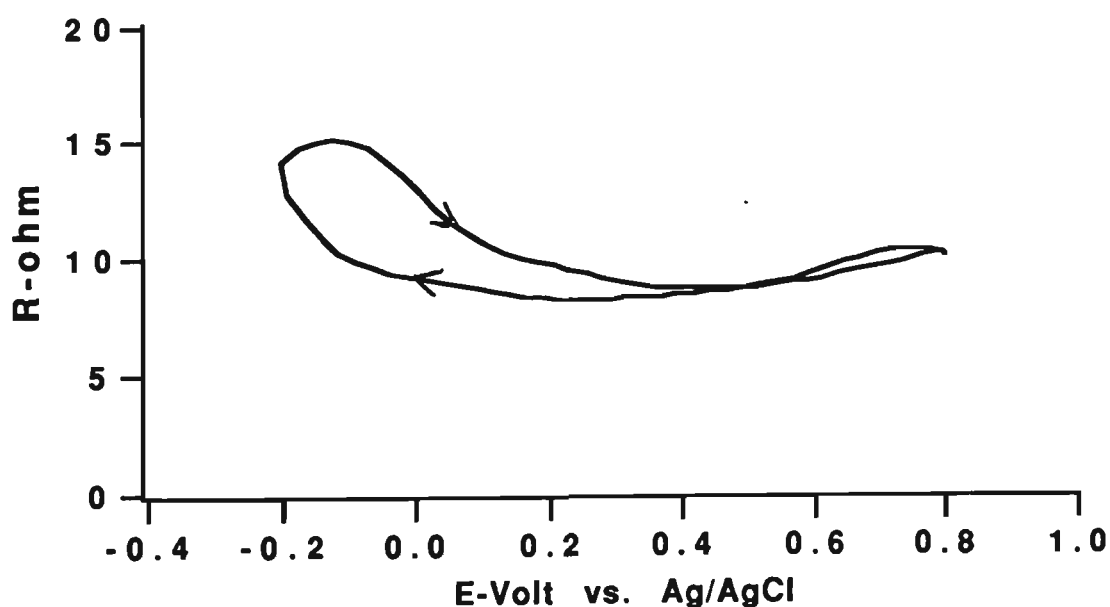


Figure 6.11: The R/E response for PPy/PVS-PAn/Cl composite in 1M HCl using the pulse resistometry method. Scan rate = 100 mV/sec. Polymer was grown as explained in the text.

The pH study for this composite material was carried out over the range of pH=0-14 (Figure 6.12). It was found that the pH- conductivity of

both polymers could be induced using this layered structure. This figure demonstrates a PAn/Cl conductivity behaviour over the range of pH=0-3 and a PPy/PVS conductivity behaviour over the range of pH=4-14. According to the Figure, almost the same order of magnitude of resistance was observed for this novel composite as in Figure 6.8 over pH 0 to 3. As discussed before, this suggests that the polyaniline connected directly to the plate and acts as conducting pathways in lower pHs where PPy/PVS is resistive. Another very important point in this investigation is that the hysteresis is very small. This could also be due to the morphology of the composite. Therefore any certain assumptions can only be made when detailed SEM studies are carried out. These experiments give us an idea about how different sensing materials can be easily made by using different conducting polymers and their composites.

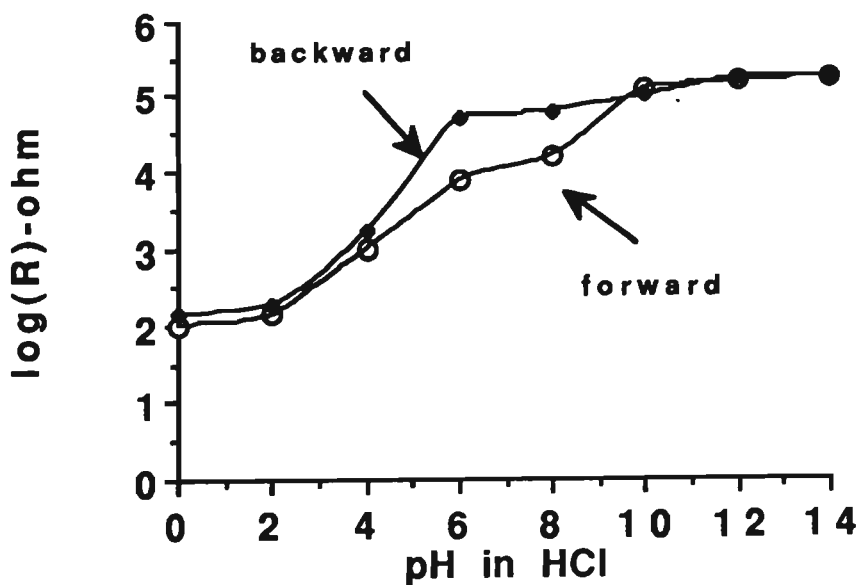


Figure 6.12: The resistance behaviour of *PPy/PVS-PAn/Cl* composite in solutions with different pHs using the DC resistometry method.

Since this novel composite demonstrates interesting pH/R behaviour, it was employed for our investigations on the effect of ions in the acidic

solution on the pH/R response. Two different acids, nitric and sulfuric acids, were used to examine pH/R responses for the composite. The results are shown in Figures 6.13 and 6.14. It was found that the presence of SO_4^{2-} in acidic media creates more changes in the pH/R plot than in the presence of NO_3^- . Interesting differences were observed in the trend of base to acid treatment. The decrease in resistance of the composite begins around pH 8 in HCl and around pH 9 and 6 for the composite in HNO_3 and H_2SO_4 respectively. The hysteresis in H_2SO_4 is also bigger than in the two other acids.

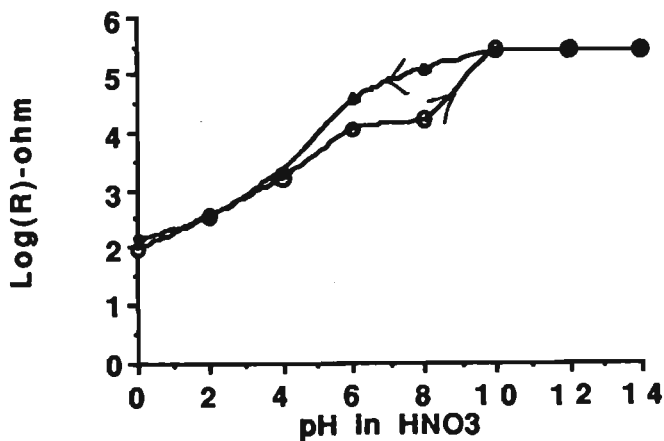


Figure 6.13: *The resistance behaviour of PPy/PVS-PAn/Cl composite in solutions with different pHs using the DC resistometry method.*

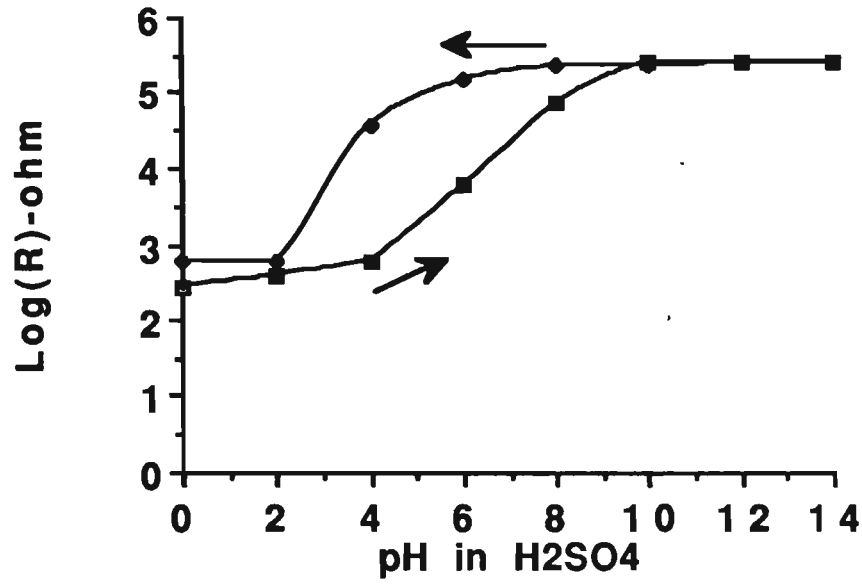


Figure 6.14: *The resistance behaviour of PPy/PVS-PAn/Cl composite in solutions with different pHs using the DC resistometry method.*

The time response of the composite in base/acid treatment was investigated (Fig.6.15) and it was found that the composite has a slower response compared with PAn/Cl.

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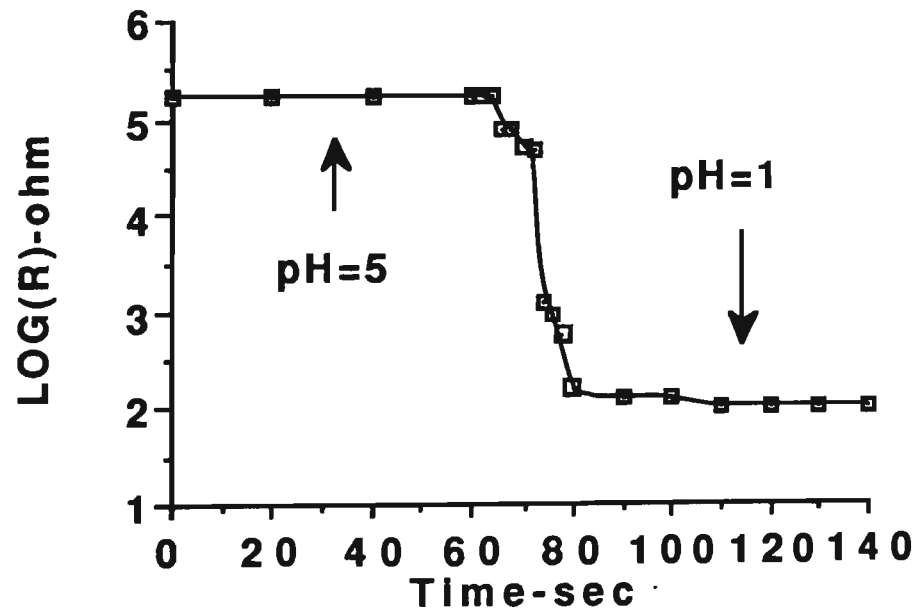


Figure 6.15: *The resistance behaviour of the composite as a function of time,base/acid treatment.*

6.4.2. The flow system

In this section we address the possibility of producing a polymer based pH sensor for applications in the flow system where the polymer sensor functions over the pH range of 0-14. Polyaniline was considered as we might get different results in the flow system compared with the stationary one. The use of both polyaniline and polypyrrole/polyaniline composite has been considered in the application of the resistance measuring technique. Two different pH electrodes in the form of the sandwich or a polymer tape have been used.

6.4.2.1. The sandwich electrode

The electrode used in the previous section was also employed in the flow system investigations. PAn/Cl and the polymer "composite" were deposited in/on the sandwich electrode. A potential of $E=0.4$ V was applied in the electrochemical cell until $i=0$. A very simple set up was designed (Fig.6.16) and used to study the effect of pH on the polymer conductivity in the flow system.

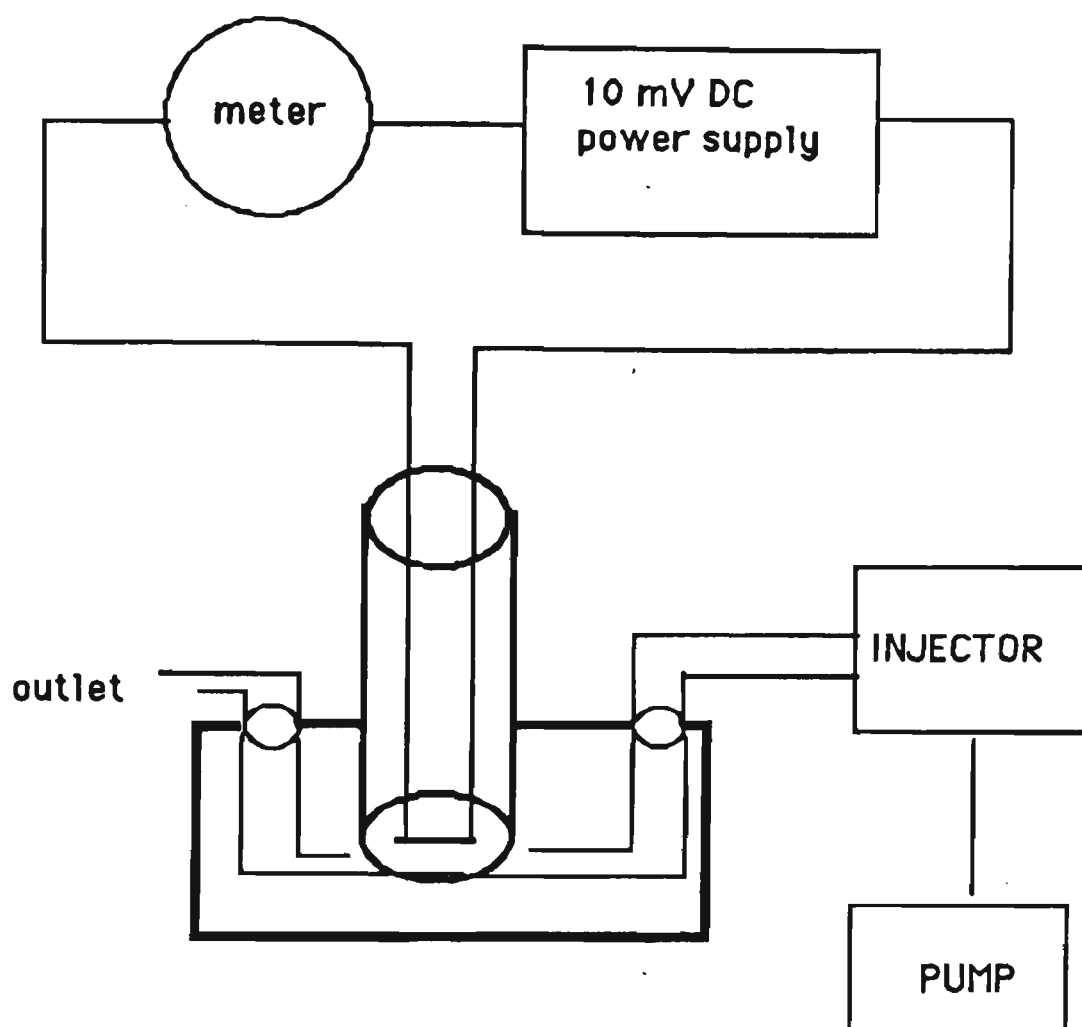


Figure 6.16: *Schematic of the cell used in the Flow system incorporating the sandwich electrode.*

Distilled water was continuously run over the surface of the electrode at the rate of 0.5 ml/min. Then solutions of different pHs were injected at different times and the resistance of the polymer was calculated after recording the maximum current.

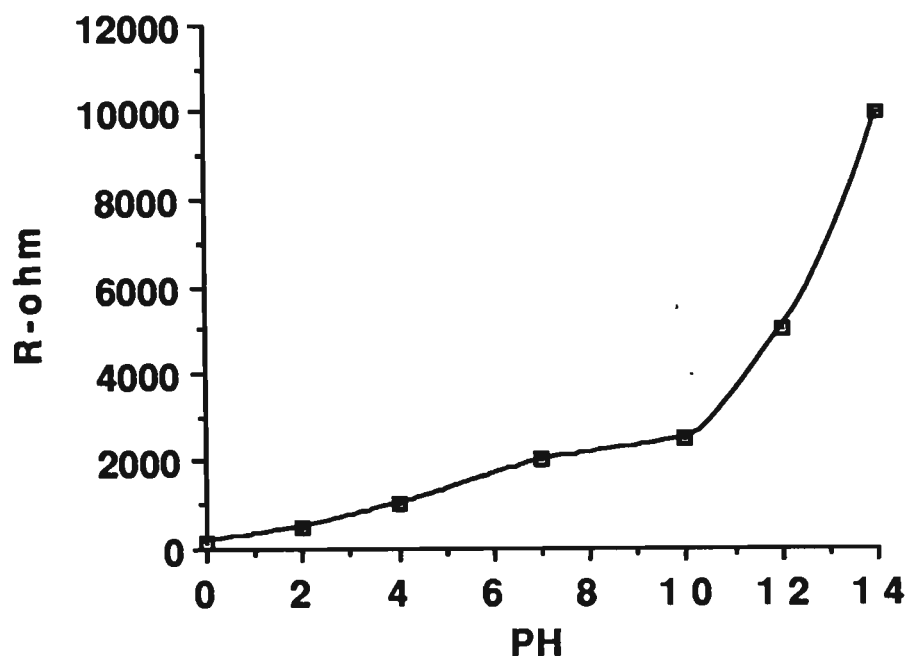


Figure 6.17: Plot of R vs pH for PAn/Cl coated on sandwich electrode in the flow system. The conditions are described in the text.

According to Figure 6.17, in the flow system we are able to monitor changes in conductivity of PAn/Cl over the range of pH 0-14. This means that using the flow system the conductivity of PAn/Cl appears to vary over a larger pH range compared with that observed in the stationary cell. This is perhaps because the polymer is not in contact with the solutions of different pHs for a much shorter time (seconds) compared with minutes in the stationary test. Moreover the surface of the polymer is rinsed continuously with distilled water during the flow through cell experiments.

The same set-up and conditions were used to investigate the pH-conductivity behaviour of the composite. Figure 6.18 reveals that the composite shows almost good sensitivity over the range of pH 0-12. However, there is a sudden increase in resistivity of the polymer between pH=12 and pH=14.

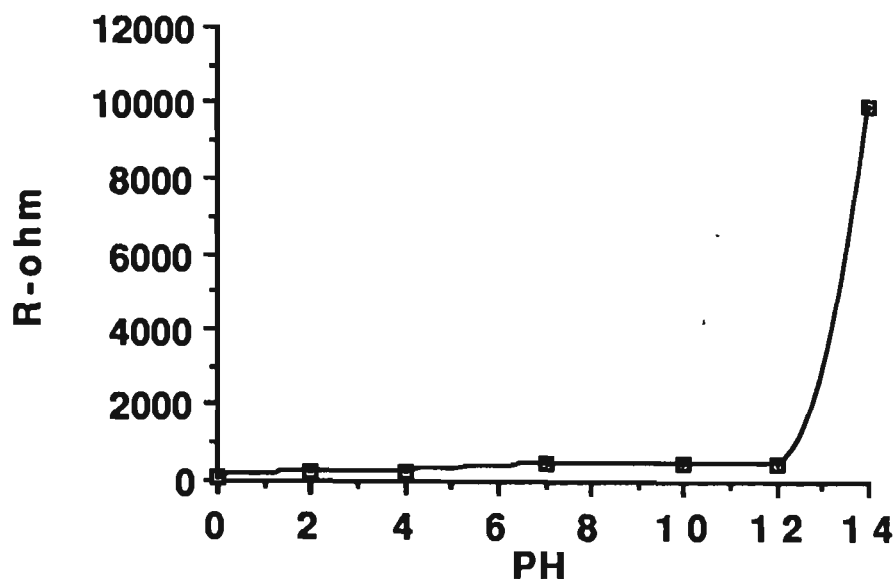
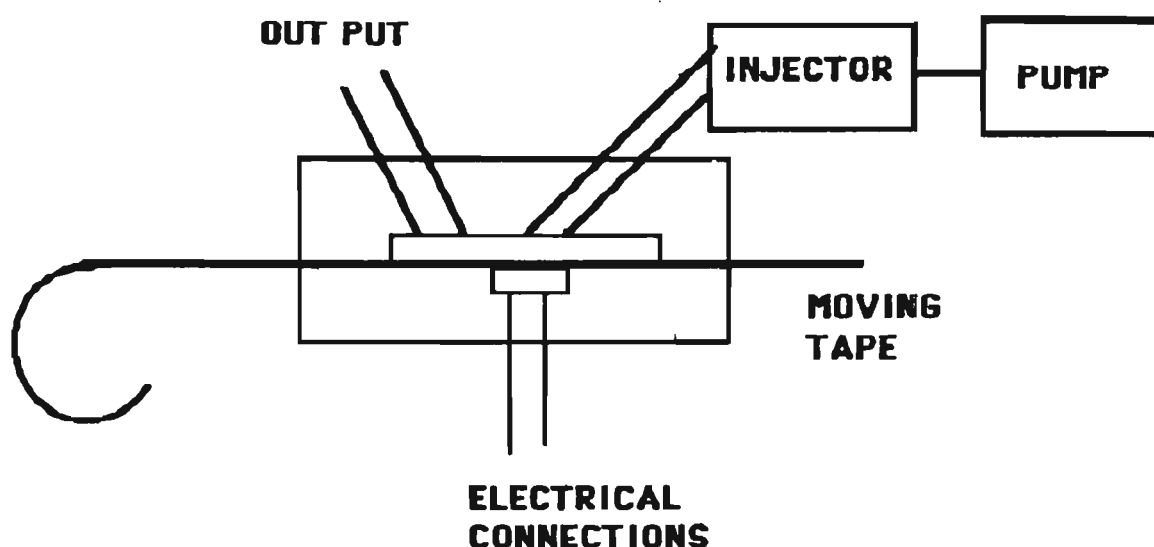


Figure 6.18: *Plot of R vs pH for the composite coated onto sandwich electrode in the flow system.*

6.4.2.2. Moving Tape

In order to obtain a renewable and fresh sensing surface, PAn/Cl was used in the form of a tape. The idea is that the tape moves in the interval at which injection occurs. Therefore, for each injection there is a new sensing surface. The polymer was used in a set up shown in Fig 6.19. In this experiment the current which flows between two different parts of the tape (at electrical connections) was measured while 10 mV DC was applied between these two parts. In other words the electrical connections were connected together by the polymeric tape. Then the same procedure was performed as for the sandwich electrode (Fig.6.16) to calculate the resistance of the polymeric tape at each pH.



6.19: Schematic of the cell designed for moving tape investigation.

A simple experiment to investigate the pH-conductivity behaviour of PAn/Cl film was carried out and the results are plotted in Figure 6.20

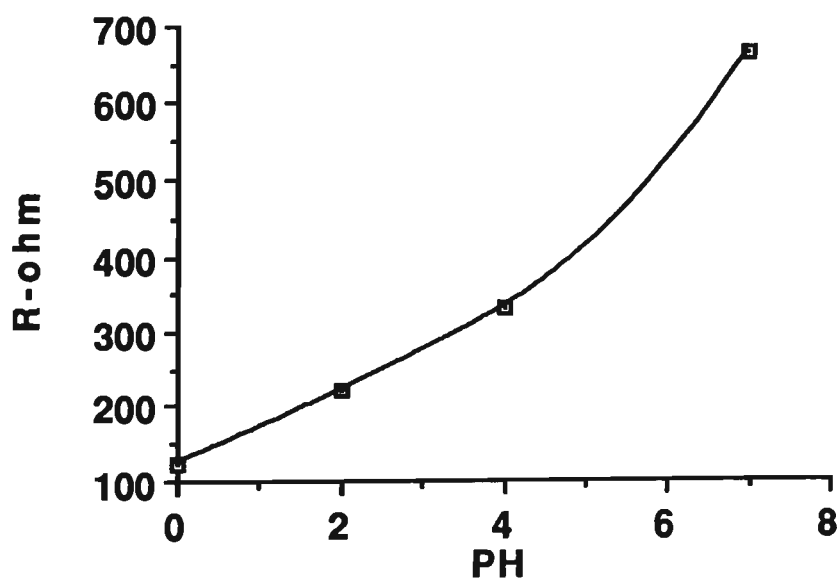


Figure 6.20: Plot of R vs pH for PAn/Cl tape in the flow system..

Problems are in the measurement of the resistance of the tape because the metal electrode contact was not good. During measurement the current flow was found to increase as more pressure was applied to improve the

contact. Since this pressure could not be maintained, the conductivity measured was not accurate and a better design is required for future work. We have since designed a new electrochemical set up (Fig 6.21) and a new pulse generator instrument which also includes a 10mV DC power supply shown in Figure 6.22. This system is based on the wall jet electrode principle where the sample is injected into the eluent which constantly flows to the moving tape. This has dramatically improved the contact situation. This instrument was initially made in Australian Defence Industries (Canberra) based on our design and then was modified in-house by the electronic workshop of the Faculty of Science. With this new set-up we are able to use not only the sandwich electrode but also the tape. A blank sandwich electrode can be used as the metallic contact on the tape for resistance measurement while the polymer is used in a tape form.

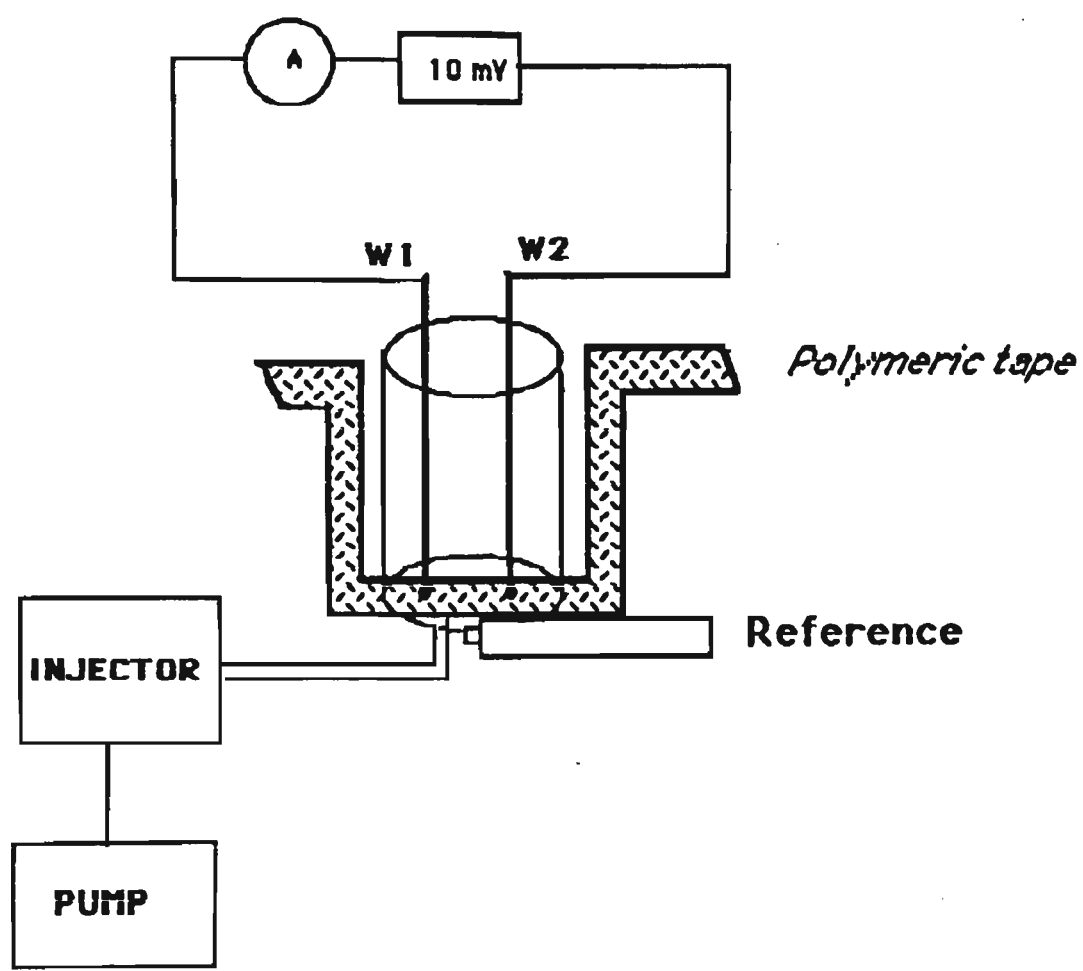


Figure 6.21: *Schematic of cell designed for future work on the effect of pH on polymer conductivity using either the sandwich electrode or the tape.*

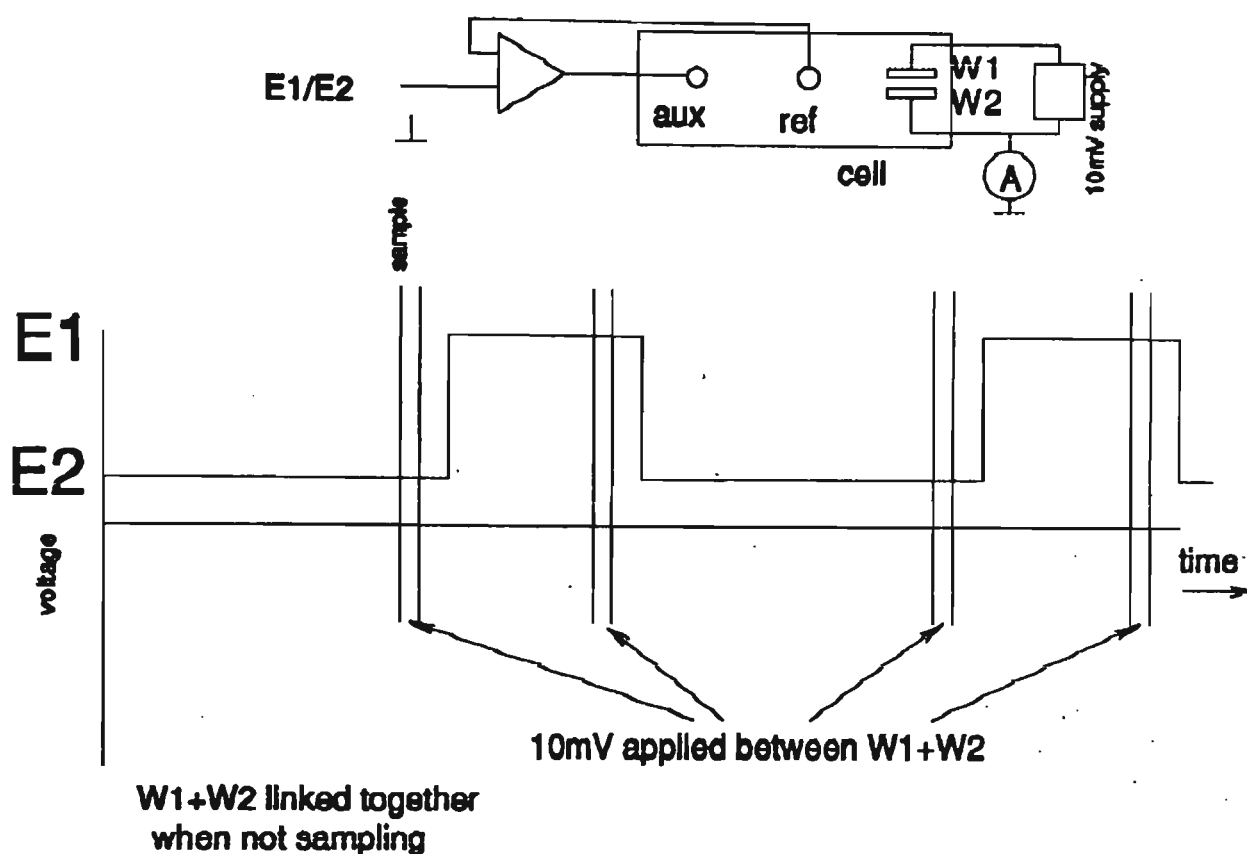


Figure 6.22: Schematic of the new pulse generator for measuring the resistance of the polymer in Flow Injection analysis experiment while the oxidation and reduction states of the polymer can be changed by applying pulses.

In this new set up the oxidation and reduction state of the polymer can be changed by applying pulses between two optional potentials in the range of -2 to +2 volts across the reference and working electrodes. The auxiliary electrode can be one of the stainless steel connections used in the cell to complete the three-electrode configured electrochemical cell. The resistance measurement can be carried out at the sampling points when $W1$ and $W2$ are disconnected automatically by the instrument. This design is a useful tool not only for pH detection but also for anion detection as we are able to apply pulses that will reduce/oxidise the polymer and induce ion exchange processes. As discussed in chapter 3 and 4 this gives different resistance

signal. This new electrode set up and resistance measurement technique are yet to be fully tested and will be the subject of future investigations.

6.5. CONCLUSION

An investigation into the effect of acid/base treatment on the resistivity of conducting polymers has been carried out. These materials perhaps may prove useful as new pH sensors. PAn/Cl and the PPy/PVS-PAn/Cl composite appear to be particularly useful in this regard.

CHAPTER 7

GENERAL CONCLUSION

The initial promise of conducting polymers was a conductivity like copper combined with a processibility like polyethylene. Work over the last 20 years has gone a long way towards this goal, but there is still a long way to go. We can not ignore the fact that the properties of polymer modified electrodes will change with time. Instability of conducting polymers in their electrical properties are responsible for lack of long term successful performance in variety commercialised sensors involving these unusual materials. However, if we can understand and control the dynamic electrical behaviour of these novel polymers, then they may be used to advantage in the development of new sensing technologies. Coming to grips with new dynamic polymer sensing technologies will require us to rethink our use of conventional electrochemical theory and instrumentation. More than ever, versatile instrumentation which enables us to recognise physical properties , including conductivity, of conducting polymer in detail will be required. With such objective this thesis was planned and carried out.

In chapter 2 two different resistance measurement techniques have been introduced and discussed. It was found that with the pulse resistometry technique new in-situ information of conductivity of the polymers can be obtained at "real time" and in the operational environment. The resistance-potential behaviour plots obtained with this method suggest a clear picture of changes in the conductivity of polypyrrole and polyaniline materials during their oxidation/reduction processes. With simple DC resistometry method, we have demonstrated the potential of using the technique in pH detection technology. In this chapter, it has been concluded that the pulse resistometry technique is a useful tool for characterisation of conducting polymers; the DC method was also recommended to be used in applications, such as pH sensors, involving conducting polymers.

In chapter 3 we reported on the importance of the effect of dopants on the conductivity of the polymers. It has been pointed out that important differences in resistance/potential properties can be observed by even the most subtle changes in molecular structure of sulfonated counterions. The changes can greatly influence the nature of electrochemical processes occurring and hence determine the composition and bulk (resistance) properties of the polymer.

In chapter 4, Our attentions were paid to other factors affecting the polymers' conductivity by employing PPy/PTS as a case study. It was deduced that any simple changes in the polymerisation conditions can affect and change the conductivity of the resultant polymer. Different polymerisation methods such PSM,GSM and PDM were used and the difference between the conductivity of the resultant polymer grown with these techniques were highlighted. It was recommended that the optimisation experiments on each techniques should be carried out to gain better conductivity. Supporting electrolyte and its concentration are other parameters which should be considered.It has been illustrated that by simply changing the cation in the supporting electrolyte from sodium to calcium a significant difference in the conductivity of polypyrrole materials can be experienced.

In chapter 5, we add another dimension into electrochemical analysis of conducting polymers by introducing a new technique called "S.M.A.C". It has been demonstrated that mass, charge and resistance changes occurring at the polymer-solution interface can be monitored in-situ and simultaneously while different potential waveforms are applied. The use of S.M.A.C. enables information on the oxidative/reductive transition of conducting polymers to be obtained directly. The electronic properties of the polymers can be

monitored in their operational environment providing much more useful information than previously used ex-situ technique. It was shown how by using this multidimensional technique a better and clearer picture of electronic properties of the polymers can be gained compared with what was obtained in chapter 3 by only using the pulse resistometry. In another section of this chapter the effect of cation was investigated using S.M.A.C. with particular attention on the chaotropic effect by readily changing the cation of the supporting electrolytes. It was argued that a better interpretation of the effect of cation in supporting electrolyte on the conductivity of the polymer can be deduced by this study because of access to in-situ and simultaneous mass, charge and resistance data. Magnesium and calcium have shown very interesting resistance and mass/ potential behaviour due to their chaotropic nature.

Finally, in chapter 6, the potential of using polypyrrole and polyaniline materials as pH sensors have been illustrated. It was found that polyaniline is better material for pH detection technology as its novel conductivity is inherently dependent on protonation. Although the problems for using this material as pH sensor was highlighted, including the effect of ions in the out put signal, it was shown that new sensing materials can be introduced by using a composited made of polyaniline/polypyrrole materials. New material and instrument were made and designed and introduced for more detailed investigations on using conducting polymers in sensing technology in future work. The idea of moving tape still remains a unique approach to overcome some of the problems as a fresh sensor material is always available. Nevertheless, this is the main part of our future work on which there will be more investigations.

Overall, the data obtained to date in this thesis, indicates that we are now perhaps closer to realise the mystery of conduction mechanism at polymer-solution interfaces. Our new in-situ and simultaneous techniques, (CR) and S.M.A.C., perhaps help to improve not well-defined part of polymer science in terms of descriptions of the structure and properties of the polymers. The conducting polymers fall mostly within this blind spot. We recommend the continue of our investigation believing that with respect to chemical and electrical versatility, no other material system approaches the capability of inherently conducting polymers. The ability to design recognition sites at a molecular level (using different counterions), coupled with unique signal generation processes have been shown in this thesis, has enabled the development of a powerful chemical sensing system. Our investigation will be more fruitful if a closer collaboration between chemists, physicists and Engineers will be achieved.

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