1993

Electrochemically controlled transport across conducting electroactive polypyrrole membranes

Huijun Zhao
University of Wollongong

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DEDICATED TO MY BELOVED FATHER,

SHILIN ZHAO
ELECTROCHEMICALLY CONTROLLED TRANSPORT ACROSS CONDUCTING ELECTROACTIVE POLYPYRROLE MEMBRANES

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

of

DOCTOR OF PHILOSOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

HUIJUN ZHAO, BSc, MSc

CHEMISTRY DEPARTMENT

JULY 1993
DECLARATION

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

Huijun Zhao
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ABSTRACT

A new membrane system, electrochemically controlled transport across conducting electroactive polypyrrole membranes has been demonstrated. This work describes the synthesis and characterisation of free-standing polypyrrole membranes, and their use for electrochemically controlled transport. This new membrane system is novel and exciting as it utilises the unique feature of electroactive polypyrrole resulting in dynamic controllable separations.

A range of free-standing polypyrrole membranes containing a series of sulfonated counterions have been successfully synthesised, by a range of methods including mixed counterions and multi-layer polymerisation.

The properties of the polypyrrole membranes were characterised using numerous techniques. The data indicated that all membranes investigated are adequate for use in the studies of the electrochemical control of transport. The electrochemical properties of the polypyrrole, especially the ion incorporation and expulsion properties were characterised by cyclic voltammetry, chronoamperometry and chronopotentiometry. The results show that changes in the redox state of the polymer accompany the ion movement into and/or out of the polymer.

The hardware for a conducting polymer membrane transport system has been developed and some parameters affecting the performance of the system have been explored. It was found that the size of the membrane and the shape of the connection was important for the cell design, as well as the electrode arrangement which influenced the direction of the mass transport.
Electrochemically controlled transport across free-standing polypyrrole membranes has been investigated. The transport properties and separation capabilities of the membranes were determined using a range of chemicals. Results show that transport across the membrane can be switched on and off by application of an appropriate electrical potential. With this technique, the transport and separation properties of the membrane can be dynamically controlled in-situ.

The mechanisms for the transport of both electroinactive and electroactive species across the polypyrrole membrane have been explored.
PUBLICATIONS:


9. "Conducting Electroactive Polymer Membrane System"
<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>A</td>
<td>Ampere</td>
</tr>
<tr>
<td>A^-</td>
<td>Anion</td>
</tr>
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<td>AA</td>
<td>Atomic Absorption Analysis</td>
</tr>
<tr>
<td>BA</td>
<td>Benzoic Acid</td>
</tr>
<tr>
<td>BS</td>
<td>1, 3-Benzenedisulfonic acid, disodium salt</td>
</tr>
<tr>
<td>BSA</td>
<td>Benzenesulfonic acid, sodium salt</td>
</tr>
<tr>
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<tr>
<td>C</td>
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<td>Counterion</td>
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<tr>
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<td>Chronoamperometry</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
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<tr>
<td>CP</td>
<td>Chronopotentiometry</td>
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</tr>
<tr>
<td>D</td>
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</tr>
<tr>
<td>DCA</td>
<td>Dynamic contact angle analysis</td>
</tr>
<tr>
<td>DS</td>
<td>Dodecylsulfate</td>
</tr>
<tr>
<td>e^-</td>
<td>Electron</td>
</tr>
<tr>
<td>E</td>
<td>Potential</td>
</tr>
<tr>
<td>E_{app}</td>
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</tr>
<tr>
<td>E_f</td>
<td>Final potential</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>------------</td>
</tr>
<tr>
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<td>Initial potential</td>
</tr>
<tr>
<td>E_p</td>
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</tr>
<tr>
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<td>Anodic peak potential</td>
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<tr>
<td>E_p_c</td>
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<td>Faraday constant</td>
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<td>GCE</td>
<td>Glassy carbon disc electrode</td>
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<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>HBA</td>
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<td>i_p_c</td>
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</tr>
<tr>
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</tr>
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<tr>
<td>LSSV</td>
<td>Linear Sweep Stripping Voltammetry</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
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<td>Cation</td>
</tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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<tr>
<td>m_V</td>
<td>Millivolt</td>
</tr>
<tr>
<td>n</td>
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</tr>
<tr>
<td>NPS</td>
<td>1,5-Naphthalenedisulfonic acid</td>
</tr>
<tr>
<td>P</td>
<td>Permeability</td>
</tr>
<tr>
<td>PAR</td>
<td>Princeton Applied Research</td>
</tr>
<tr>
<td>PP</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PTA</td>
<td>p-Toluic acid</td>
</tr>
<tr>
<td>PTS</td>
<td>p-Toluenesulfonic acid</td>
</tr>
<tr>
<td>Q</td>
<td>Charge</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz Crystal Microbalance</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>S</td>
<td>Separation coefficient</td>
</tr>
<tr>
<td>S</td>
<td>Solubility</td>
</tr>
<tr>
<td>SBA</td>
<td>p-sulfobenezoeic acid</td>
</tr>
<tr>
<td>T</td>
<td>Time</td>
</tr>
<tr>
<td>TPA</td>
<td>Terephthalic acid</td>
</tr>
<tr>
<td>V</td>
<td>Volts</td>
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<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometres</td>
</tr>
<tr>
<td>Ω</td>
<td>Ohms</td>
</tr>
<tr>
<td>σ</td>
<td>Conductivity</td>
</tr>
<tr>
<td>σ&lt;sub&gt;v&lt;/sub&gt;</td>
<td>Volume conductivity</td>
</tr>
<tr>
<td>ξ</td>
<td>Asymmetric factor</td>
</tr>
</tbody>
</table>
# CONTENTS

Acknowledgements ............................................................... I
Abstract .............................................................................. II
Publications .......................................................................... IV
Abbreviations ......................................................................... VI

CHAPTER 1
GENERAL INTRODUCTION ......................................................... 1

1.1 Conventional Membranes .................................................... 3
1.1.1 History of membrane technology development ......................... 4
1.1.2 Membrane definition and classification .................................... 6
1.1.3 Membrane separation processes and mechanisms of separation ............. 8
1.1.4 Preparation of synthetic membranes ....................................... 12
1.1.5 Characterisation of the membrane ......................................... 13
1.1.6 Control of transport in membrane processes .............................. 15
1.2 Conducting Electroactive Polymer Membranes ......................... 17
1.2.1 Development of conducting polymers .................................... 18
1.2.1.1 Conducting polypyrrole synthesis .................................. 18
1.2.1.2 Characterisation of polypyrroles .................................... 26
1.2.1.3 Switching properties of polypyrroles ............................... 28
1.2.2 Conducting polymer membranes ......................................... 29
1.3 Aims of the Project ......................................................... 30
CHAPTER 2
STUDIES OF ELECTROCHEMICAL DEPOSITION
OF POLYPYRROLE ........................................32

2.1 Introduction ..................................................................33
2.2 Experimental .................................................................35
2.2.1 Reagents and materials .............................................35
2.2.2 Instrumentation ..........................................................36
2.3 Results and Discussion ..................................................37
2.3.1 Cyclic voltammetry ....................................................37
2.3.2 Chronoamperometry ..................................................42
2.3.3 Chronopotentiometry ..................................................48
2.4 Conclusions .................................................................54

CHAPTER 3
POLYPYRROLE MEMBRANE SYNTHESIS AND
CHARACTERISATION .............................................56

3.1 Introduction ..................................................................57
3.2 Experimental .................................................................58
3.2.1 Reagents and Materials .............................................58
3.2.2 Instrumentation ..........................................................58
3.2.3 Procedures .................................................................58
3.2.3.1 Preparation of polypyrrole membranes ..................58
3.2.3.2 Characterisation methods ......................................61
3.3 Results and Discussion ..................................................62
3.3.1 Preparation of PP/PTS membranes ............................63
3.3.1.1 Choice of the substrate ........................................63
3.3.1.2 Effect of current density and composition of
the polymerisation solution .................................................64
3.3.1.3 Effect of stirring the polymerisation solution ............69
3.3.1.4 Effect of the polymerisation solution pH ..................71
3.3.2 Effect of the counterion employed
during the membrane synthesis ........................................71
3.3.3 Characterisation of polypyrrole membranes using SEM ....74
3.3.3.1 Effect of chemical conditions during polymerisation on
the surface morphology of the membrane .........................74
3.3.3.2 Effect of electrochemical conditions used during
polymerisation on the membrane morphology ....................76
3.3.3.3 Effect of the counterion on the morphology .................77
3.3.4 Membrane composition .............................................89
3.3.5 Membrane permeability .............................................89
3.4 Conclusions ................................................................90

CHAPTER 4
ELECTROCHEMICAL PROPERTIES
OF POLYPYRROLE FILMS ......................................................92

4.1 Introduction ..................................................................93
4.2 Experimental ..............................................................94
4.2.1 Reagents and solutions ..............................................94
4.2.2 Instrumentation .........................................................94
4.2.3 Preparation of the polymer coated electrode .................95
4.3 Results and Discussion ..................................................96
4.3.1 Cyclic voltammetry ....................................................96
4.3.1.1 Effect of the cation in the electrolyte solution ............96
4.3.1.2 Effect of the anion in the electrolyte solution .............99
4.3.1.3 Effect of the counterion employed during polymerisation
4.3.1.4 Effect of the counterion employed during polymerisation on the current responses in the regions 1 and 2 of cyclic voltammograms ...........................................101

4.3.1.5 Ion exchange properties of the polypyrrole films ..........112

4.3.1.6 Cyclic voltammetry under hydrodynamic conditions ......114

4.3.2 Chronoamperometry ..................................................118

4.4 Conclusion ........................................................................123

CHAPTER 5
ELECTROCHEMICALLY CONTROLLED TRANSPORT
OF ELECTROINACTIVE SPECIES ACROSS PP/PTS MEMBRANES ...........................................125

5.1 Introduction ........................................................................126

5.2 Experimental ......................................................................128

5.2.1 Reagents and solutions ..................................................128

5.2.2 Instrumentation ...............................................................128

5.2.3 Procedures .......................................................................130

5.3 Results and Discussion .........................................................132

5.3.1 Electrochemical control of membrane transport ..........132

5.3.1.1 Effect of potential waveforms applied .........................132

5.3.1.2 Effect of different electrode arrangements ..................149

5.3.2 Electrotransport cell design ..............................................154

5.3.2.1 Electrical connection to the membrane .......................155

5.3.2.2 Effect of membrane area (diameter) and thickness ......159

5.3.2.3 Effect of the side of the membrane exposed to the source solution ................................................161

5.3.3 Effect of chemical conditions used on
CHAPTER 6
EFFECT OF THE COUNTERION EMPLOYED DURING SYNTHESIS ON TRANSPORT OF ELECTROINACTIVE SPECIES ACROSS POLYPYRROLE MEMBRANES .......180

6.1 Introduction .................................................................181
6.2 Experimental ...............................................................182
6.2.1 Reagents and solutions ..............................................182
6.2.2 Instrumentation .........................................................182
6.2.3 Procedures ...............................................................182
6.3 Results and Discussion ..................................................184
6.3.1 Cyclic voltammetry ....................................................184
6.3.2 Transport of K+ across polypyrrole membranes
  containing different counterions .................................190
6.3.3 Transport of Ca^{2+} across polypyrrole membrane
  containing different counterions ................................195
6.3.4 Separation experiments ............................................199
6.4 Conclusions ...............................................................201

CHAPTER 7
EFFECT OF DODECYLSULFATE ON THE SYNTHESIS AND TRANSPORT PROPERTIES OF POLYPYRROLE MEMBRANES .................................................................202
7.1 Introduction ..........................................................203
7.2 Experimental ..........................................................204
7.2.1 Reagents and solutions ..........................................204
7.2.2 Instrumentation ....................................................205
7.2.3 Procedures ..........................................................205
7.2.3.1 Mixed counterion membrane preparation ....................205
7.2.3.2 Layered membrane preparation ................................205
7.2.3.3 Transport experiment set up ..................................206
7.3 Results and discussion ..............................................207
7.3.1 Mixed counterion membrane preparation and characterisation ..............................................207
7.3.1.1 Mechanical properties and conductivities of DS containing membranes .......................207
7.3.1.2 Surface morphology of the DS containing membranes .............................................209
7.3.1.3 Dynamic contact angle analyses ................................214
7.3.1.4 Cyclic voltammetry .............................................218
7.3.2 Layered membrane preparation ..................................221
7.3.3 Transport across mixed counterion membranes .............224
7.3.4 Transport across layered membranes ..........................233
7.4 Conclusions ..........................................................236

CHAPTER 8
ELECTROCHEMICALLY CONTROLLED TRANSPORT OF ELECTROACTIVE SPECIES ACROSS PP/PTS MEMBRANES ..............................................238

8.1 Introduction ..........................................................239
8.2 Experimental ..........................................................239
8.2.1 Reagents and solutions ..........................................239
8.2.2 Instrumentation ....................................................240
8.2.3 Procedures .................................................................240
8.3 Results and Discussion ....................................................241
8.3.1 Electrochemical studies ................................................241
8.3.2 Transport of Cu(II) ......................................................247
8.3.2.1 Effect of electrochemical conditions
on Cu (II) transport ............................................................248
8.3.2.2 Effect of chemical conditions on Cu(II) transport .......255
8.3.3 Transport of Zn(II) .......................................................257
8.3.2.1 Effect of electrochemical conditions
on Zn(II) transport ............................................................257
8.3.2.2 Effect of chemical conditions on Zn(II) transport .......263
8.3.4 Separation experiments ................................................265
8.3.5 A possible transport mechanism
for electroactive species ....................................................269
8.4 Conclusions .................................................................271

CHAPTER 9
GENERAL CONCLUSIONS ..................................................273

REFERENCE .................................................................277
CHAPTER 1

GENERAL INTRODUCTION
The idea of polymeric materials that can respond to changing environmental conditions and external stimuli in a predetermined manner (so called intelligent materials) is one that will be increasingly influential in many fields in the future. Conducting electroactive polymers are well known to be intelligent materials since previous studies have indicated that they can perform such tasks very well. For example, they can respond to heat [1], light [2], or electrical stimuli [3] by changing their physical or chemical properties. The unique properties of conducting electroactive polymers have been used in sensors [4,5], chromatographic stationary phases [6], rechargeable batteries [7,8], electronic displays [9] and electronic circuits [10].

One area where intelligent materials could potentially make a significant impact is that of membrane technology. Membranes are utilised to perform separations in a wide range of applications. The proliferation of membrane technology is likely to continue as more sophisticated systems are designed to suit specific applications.

It is well known that the transport properties of biological membrane systems are controlled by specific stimuli in-situ. Such membranes can respond to environmental changes and/or external stimulation to change transport properties. When information is received from environmental changes or external stimuli, the membrane adjusts the permeability and/or selectivity appropriately, according to the information obtained. Now, let us consider synthetic or artificial membranes, if we can synthesise a membrane with such properties, then this membrane begins to accrue some semblance of intelligence—"intelligent membranes". The application of synthetic membranes will not only be for separation and purification, but also for many other new applications. For example, artificial cell membranes could be made by this type of membranes.
Some fundamental research work has attempted to develop intelligent chemical systems[11]. Intelligent membranes are an integral part of intelligent chemical systems. Controlled membrane transport is an integral part of intelligent membrane systems operation.

One of the limitations of conventional membranes is that, however sophisticated they are, their physical and chemical properties are generally fixed at the time of synthesis and are not dynamic. Conducting, electroactive polymers such as polypyrrole (PP) offer the possibility of membranes with dynamic, controllable properties through the manipulation of the different redox states in which they can exist.

This work investigates the physical, chemical and electrochemical properties of conducting polymers for use in membrane transport. Procedures suitable for membrane synthesis have been developed. An electroactive conducting polymer membrane system has been established and electrochemically controlled transport of chemicals across these membranes has been explored.

This chapter reviews development of conventional membrane and conducting polymer membrane technology.

1.1 CONVENTIONAL MEMBRANES

A membrane is used in separation technology wherein it acts as a barrier to prevent mass movement but allows restricted and/or regulated passage of one or several species through it. The advantage of membrane separation lies in the relatively low energy requirements as compared with other separation processes such as distillation, extraction and
crystallisation. The reason for this is that membrane separation processes generally do not involve phase transitions.

1.1.1 History of Membrane Technology Development

The history of membrane technology development can be traced back to the middle of the eighteenth century [12]. Membrane development was carried by chemists, physicists, biologists, biochemists and zoologists. For example, since the studies by Overton [13] in 1902, much work has been done on the lipid layer of the cell wall, in order to understand membrane phenomena in biological systems. This review, therefore, will just concentrate on synthetic membranes.

Until early in this century, the technology of synthetic membranes was at a very low level. Research had stagnated at the level of observation of membrane phenomena. The important development in these early studies was the elucidation of the barrier properties and related phenomena of the membrane [12,14-19]. One of the limitations for membrane development was that artificial membranes were not readily available. A very important early synthetic membrane was discovered by Bechgold [20] in 1907. He used nitrocellulose to produce better quality porous membranes. A similar membrane was synthesised by Zsigmondy and Bachman [21] in 1918, this was later developed into the first commercial synthetic membrane by Sartorius in Germany [22]. However, during this period of time, the type of membranes used were all porous ones and the synthetic materials employed were limited to cellulosenitrate or cellulanitrate-cellulosacetate.
Since the 1930s, membrane science has advanced both theoretically and experimentally, and a number of membrane science topics have been thoroughly investigated, these include:

(i) Different types of membranes have been defined and successfully synthesised [23-32];

(ii) Different membrane preparation methods and formation mechanisms have been explored [33,34];

(iii) Membrane transport mechanisms and models corresponding to different types of membranes and membrane processes have been studied [23,35-45].

(iv) With respect to applications, membrane technologies have been applied to different industrial areas to solve numerous specific separation problems. Some examples which relate to the early use of membranes are listed in Table 1.1.

Even today, the search for new and better membranes still continues not only for membrane processes yet to reach the stage of commercialisation, but to improve existing membrane processes.

Table 1.1 Development of (technical) membrane process

<table>
<thead>
<tr>
<th>Membrane Process</th>
<th>Country</th>
<th>Year</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>microfiltration*</td>
<td>Germany</td>
<td>1920</td>
<td>laboratory use (bacteria filter)</td>
</tr>
<tr>
<td>ultrafiltration*</td>
<td>Germany</td>
<td>1930</td>
<td>laboratory use</td>
</tr>
<tr>
<td>hemodialysis*</td>
<td>Netherlands</td>
<td>1950</td>
<td>artificial kidney</td>
</tr>
<tr>
<td>electrodialysis#</td>
<td>USA</td>
<td>1955</td>
<td>desalination</td>
</tr>
<tr>
<td>hyperfiltration#</td>
<td>USA</td>
<td>1960</td>
<td>sea water desalination</td>
</tr>
<tr>
<td>ultrafiltration#</td>
<td>USA</td>
<td>1960</td>
<td>conc. of macromolecules</td>
</tr>
<tr>
<td>emulsion liquid membrane*</td>
<td>USA</td>
<td>1972</td>
<td>metal ion separation</td>
</tr>
<tr>
<td>gas separation# membrane</td>
<td>USA</td>
<td>1979</td>
<td>hydrogen recovery</td>
</tr>
<tr>
<td>distillation#</td>
<td>Germany</td>
<td>1981</td>
<td>concentration of aqueous solution</td>
</tr>
<tr>
<td>pervaporation#</td>
<td>Germany/Net herlands</td>
<td>1982</td>
<td>dehydration of organic solvents</td>
</tr>
</tbody>
</table>

* laboratory scale, # industrial scale. Adapted from ref. [25]
1.1.2 Membrane Definition and Classification

A membrane is defined as a selective barrier between two phases. This is a macroscopic definition, and provides no information about the membrane structure or function.

Membranes can be classified in numerous ways. The clearest classification of membranes is between those that are synthetic and those that are natural. These two types of membrane differ completely in structure and functionality. Classification of artificial membranes can be also achieved in terms of the application area or separation processes or in terms of their physical or chemical dimensions. Classification of membranes by applications or separation processes provides no information on the membrane preparation, the materials or the physical/chemical dimensions of the membrane. For example, Reverse Osmosis membranes are named based on the separation process employed but they can be prepared using different methods and different materials. Similarly, a classification of membranes by their physical or chemical dimensions provides no information on their intended applications.

Some workers [46] propose that membranes can be divided into Reverse Osmosis, ultrafiltration, and microfiltration membranes. These three major classes are distinguished by application area or separation process. The separation process in which the membranes are employed are pressure driven and separations are based on particle or molecular size.

Classification according to the physical dimensions of the membrane was also proposed [47]. In this case, membranes are divided into heterogeneous and homogenous or symmetric and asymmetric. For example, a bulk liquid membrane is a homogeneous, symmetric membrane, while supported liquid membrane is heterogeneous and
symmetric membrane. Some terms often appear in the literature such as ion-exchange membrane, or cellulose acetate membrane. These describe membrane's chemical properties or the synthetic material used.

Lakshminarayanaiah [11,48] proposed a classification of membranes that combined the membrane physical dimensions and chemical structure (Figure 1.1).

Figure 1.1 Classification of membranes (take from ref. 11)
1.1.3 Membrane Separation Processes and Mechanisms of Separation

Transport across membranes can be divided into active transport or passive transport. It is determined by the type of membrane used and the operational conditions employed. Generally, in active transport a driving force (energy) is provided by a specific chemical reaction taking place within the membrane phase or the opposite bulk phase. In passive transport, the driving force for mass transfer is a difference in chemical or electrochemical potential across the membrane. Most of the membranes that have been developed and successfully applied in industrial areas, use passive transport.

Various models suggest fundamental differences between the separation mechanisms of the membrane processes. Membrane processes can be classified according to the driving force. Such a classification is given in Table 1.2.

**Table 1.2 Classification of membrane processes**

<table>
<thead>
<tr>
<th>Pressure Difference</th>
<th>Concentration Difference</th>
<th>Temperature Difference</th>
<th>Electrical Potential Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>microfiltration</td>
<td>pervaporation</td>
<td>thermo-osmosis</td>
<td>electrodialysis</td>
</tr>
<tr>
<td>ultrafiltration</td>
<td>gas separation</td>
<td></td>
<td>electro-osmosis</td>
</tr>
<tr>
<td>hyperfiltration</td>
<td>dialysis</td>
<td>membrane</td>
<td></td>
</tr>
<tr>
<td>piezodialysis</td>
<td>liquid membranes</td>
<td>distillation</td>
<td></td>
</tr>
</tbody>
</table>
Osmosis

When solutions of two different concentrations are separated by a membrane, an osmotic pressure occurs. Osmosis can also occur when the membrane employed is permeable to the solvent but impermeable to the solute. For a porous membrane such as microfiltration and ultrafiltration membranes, the osmosic pressure obtained is negligible since these membranes are solute permeable. For a non-porous membrane osmotic pressure can be expressed by the Van't Hoff equation (equation 1.1)

\[ \Pi = C_jRT/M \]  

(1.1)

Where, \( \Pi \): osmotic pressure; \( C_j \): solute concentration; \( M \): mole weight; \( T \): temperature and \( R \): gas constant.

Pressure driven membrane process

Pressure driven membrane processes can be divided into three different classes (see Table 1.3). These membrane processes can be used to concentrate or purify a dilute solution. The separation achieved is based on differences between the membrane pore size and the solute particle size or solute solubility and diffusivity in the membrane matrix (Table 1.3).
Table 1.3 Pressure driven membrane processes

<table>
<thead>
<tr>
<th>Microfiltration</th>
<th>Ultrafiltration</th>
<th>Hyperfiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td>separation of particles (&gt;100 nm)</td>
<td>separation of macromolecules (1-100 nm)</td>
<td>separation of small size solutes (0.1-1 nm)</td>
</tr>
<tr>
<td>applied pressure: &lt;2 bar</td>
<td>applied pressure: 1-10 bar</td>
<td>applied pressure: 0.1-1 bar</td>
</tr>
<tr>
<td>separation based on particle size</td>
<td>separation based on particle size</td>
<td>separation based on difference in solubility and diffusivity</td>
</tr>
<tr>
<td>(Darcy's law, Kozeny-Carman equation)</td>
<td>(Darcy's law)</td>
<td>(various models)</td>
</tr>
</tbody>
</table>

Concentration difference as the driving force

Generally, driving forces are only applicable to nonporous membrane. The processes are summarised in Table 1.4.

Table 1.4 summary of concentration difference driven membrane processes

<table>
<thead>
<tr>
<th>Gas separation</th>
<th>Pervaporation</th>
<th>Liquid membrane</th>
<th>dialysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>nonporous membrane</td>
<td>nonporous membrane</td>
<td>nonporous membrane</td>
<td>nonporous membrane</td>
</tr>
<tr>
<td>operation pressure: upstream or downstream to 100 bar.</td>
<td>driving force: vapour pressure or activity difference.</td>
<td>Driving force: concentration difference</td>
<td>Driving force: concentration difference</td>
</tr>
</tbody>
</table>

Thermally driven membrane processes

Therm-osmosis (therm-diffusion) processes often occur when a nonporous membrane separates two phases held at different temperatures. A
temperature gradient induces mass flow across the membrane (Soret effect). No phase transitions occur in these processes. Fourier's law can be used to express these processes [45].

Membrane distillation is a process in which two liquids or solutions at different temperatures are separated by a porous membrane. The liquids or solutions must not wet the membrane otherwise the pores will be filled immediately as a result of capillary forces. Membrane distillation is the only process in which the membrane is not directly involved in separation. Selectivity is completely determined by the vapour-liquid equilibrium involved. These membrane processes have been applied to different industrial areas. For example, purification of water for the semiconductor industry, boiler feed water for power plants and the desalination of seawater [49].

**Electrically driven membrane processes**

In these processes the membrane used is an ion-exchange membrane. The transport of charged species across the membrane is driven by a difference in the electrical potential. The separation principle can be expressed by a Donnan exclusion mechanism. These processes have been used in desalination of water, desalination in food and pharmaceutical industry. It has also been applied for production of sulfuric acid and sodium hydroxide [50].

In addition, the influence of the chemical nature of the membrane materials should be noted. It has been recognised that for porous membranes permeation of liquids is a property determined principally by the membrane's morphology, with only some influence due to the membrane's chemical nature. Unique transport performance does not
result from any particular characteristic of the membrane material. Only when diffusive transport (in the case of non-porous membranes) governs the mass transfer or active transport is induced does the membrane's chemical nature and structure becomes important.

1.1.4 Preparation of Synthetic Membranes

A number of different techniques are available for synthetic membrane preparation. These techniques are based on different formation mechanisms or different operation processes. The choice of the techniques for membrane preparation depends mainly on the material used and on the desired membrane structure. Table 1.5 lists the techniques used for membrane preparation and the type of membrane that results.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Materials</th>
<th>Membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintering</td>
<td>thermal stable materials (powder form)</td>
<td>porous membranes</td>
</tr>
<tr>
<td></td>
<td>i.e. aluminium oxide, zirconium oxide,</td>
<td>pore size: 0.1-10μm maximum porosity: 80%</td>
</tr>
<tr>
<td></td>
<td>graphite carbon, silicates, polyethylene,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>polypropylene</td>
<td></td>
</tr>
<tr>
<td>Stretching</td>
<td>semi-crystalline polymer materials</td>
<td>porous membranes</td>
</tr>
<tr>
<td></td>
<td>i.e. polytetrafluoroethylene, polyethylene</td>
<td>pore size: 0.1-3μm maximum porosity: 90%</td>
</tr>
<tr>
<td>Track-etching</td>
<td>polycarbonate</td>
<td>porous membranes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pore size: 0.02-10μm maximum porosity: 10%</td>
</tr>
<tr>
<td>Template leaching</td>
<td>Na₂O-B₂O₃-SiO₂</td>
<td>porous membranes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pore size: &gt;0.05μm</td>
</tr>
<tr>
<td>Coating</td>
<td>asymmetric membranes, porous and non-porous</td>
<td></td>
</tr>
<tr>
<td></td>
<td>membranes</td>
<td></td>
</tr>
<tr>
<td>Phase inversion</td>
<td>soluble polymer materials</td>
<td>porous membranes and non-porous membranes</td>
</tr>
<tr>
<td>(precipitation by</td>
<td></td>
<td></td>
</tr>
<tr>
<td>solvent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>evaporation, the vapour phase, precipitation by</td>
<td></td>
<td></td>
</tr>
<tr>
<td>controlled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>evaporation, thermal precipitation and immersion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>precipitation)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.5 The techniques for membrane preparation
Synthetic membranes can be made from a large number of different materials. The choice of the synthesis technique is based on the material employed.

### 1.1.5 Characterisation of the Membrane

It is well known that membrane transport properties and their functionality are related to membrane structure and the intrinsic properties of the membrane materials.

Characterisation measurements can be divided into two classes. The first class of characterisation measurements provides information on the intrinsic properties of the membrane, such as structural, morphological properties (pore size, pore size distribution, symmetric and asymmetric), mechanical and chemical properties. These properties are all independent of the actual membrane application. On other hand, membrane performance should be characterised with the actual application area in mind. Permeability, reproducibility, stability and lifetime must be characterised in-situ to obtain appropriate results. These properties are not only related to the intrinsic properties of the membrane, but also related to the actual application area. To characterise these properties, established techniques or methods are not readily available.

A number of techniques are available for characterising the physical dimensions of the membranes. The characterisation technique employed depends on the kind of information required and the type of the membrane used. For example, the pore size of membranes covers a range of five orders of magnitude; various classes of pore size have their
own characterisation methods. Table 1.6 summarises the techniques/methods that have been applied.

**Table 1.6 Techniques for membrane characterisation**

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Information Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scanning electron Microscopy (SEM)</td>
<td>surface morphology, porous structure (pore size, pore distribution, surface porosity and geometry of the pores)</td>
</tr>
<tr>
<td>Bubble-point Method#</td>
<td>maximum pore size</td>
</tr>
<tr>
<td>Mercury Intrusion Method#</td>
<td>pore size and pores distribution</td>
</tr>
<tr>
<td>Permeability Method#*</td>
<td>pore size, pore distribution and permeability</td>
</tr>
<tr>
<td>Gas adsorption-desorption#</td>
<td>pore size and pore distribution</td>
</tr>
<tr>
<td>Theroporometry#</td>
<td>pore size and pore distribution</td>
</tr>
<tr>
<td>Permporometry#</td>
<td>pore size and pore distribution for active pores</td>
</tr>
<tr>
<td>Solution Rejection Measurement#*</td>
<td>real pore size</td>
</tr>
<tr>
<td>Differential Scanning Calorimetry*</td>
<td>chemical reaction, phase transition and degree of crystallisation</td>
</tr>
<tr>
<td>Differential Thermal Analysis*</td>
<td>density</td>
</tr>
<tr>
<td>Density Gradient Columns* (pycnometer or dilatometry)</td>
<td>size and shape of the crystalline</td>
</tr>
<tr>
<td>Wide-angle X-ray diffraction* (WAXS)</td>
<td></td>
</tr>
<tr>
<td>Electron Spectroscopy for Chemical Analysis#* (ESCA)</td>
<td>surface properties</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy#* (XPS)</td>
<td></td>
</tr>
<tr>
<td>Secondary Ion Mass Spectroscopy#* (SIMS)</td>
<td></td>
</tr>
<tr>
<td>Auger Electron Spectroscopy#* (AES)</td>
<td></td>
</tr>
</tbody>
</table>

# applicable to porous membrane; * applicable to non-porous membrane.
1.1.6. Control of Transport in Membrane Processes

After membrane synthesis, controlled transport in membrane processes can be achieved by:

(i) adding a driving force (energy) into the system or

(ii) varying the membrane structure to switch transport on/off.

Usually controlled transport is achieved by adding a driving force (energy) into the system. For instance, in the membrane processes of microfiltration, ultrafiltration and reverse osmosis, the application of an external pressure as the driving force is required, and in electrodialysis process, an external electrical field is required. The advantages of the methods are

(i) simple operation; and

(ii) suitable for large scale applications.

The disadvantages are that:

(i) the amount of transport is related to the amount of energy expended;

(ii) selective transport is difficult to achieve; and

(iii) these systems are difficult to apply to natural or biological systems.

In addition, the driving force cannot do anything to vary the membrane structure or chemical properties, Therefore it would be difficult to develop this type of system into a intelligent one

Another route to control the transport is varying the structure, morphology and/or physical, chemical properties of the membrane by application of an external stimulus. In this case, transport is active and
the external stimulus induces a chemical reaction in the membrane. For example, facilitated membrane transport across liquid membranes can be turned on/off by switching the carrier between active and inactive forms. Shinkai and co-workers [51] carried out extraction experiments on a crown ether with a redox-functional thiol group and were able to exploit oxidised and reduced forms (see Figure 1.2).

![Redox switching of crown ether thiol group.](image)

**Figure 1.2 Redox switching of crown ether thiol group.**

A similar system has also been reported by Shinkai and co-workers [52] where they presented a photo-responsive crown ether of liquid membrane carrier molecules. Other than these, control of transport by controlling solution pH [53,54] and temperature [55] have been reported.

The advantages of using this method to control transport are that:

(i) the amount of transport is not just related to the amount of energy expended, it is related to the state of the membrane;

(ii) selective transport can be achieved and

(iii) can be applied to biological systems.

The disadvantages of the methods are:

(i) Generally the operation is difficult and

(ii) specific membranes (which may be difficult to synthesise) are required.
Since the controlled transport to be carried out in these systems is similar to the case of natural or biological membrane systems, therefore, it may be possible to develop it into an intelligent membrane system.

As mentioned at the beginning of this chapter, because of the limitations of a conventional membrane it is difficult to find a membrane system where the transport properties can be dynamically controlled in-situ.

1.2 CONDUCTING ELECTROACTIVE POLYMER MEMBRANES

Conducting electroactive polymers have been investigated extensively since the 1970s. However, only a few workers have reported the feasibility of using conducting polymers as membrane materials and until now, electrochemically controlled transport across a free-standing conducting polymer membrane has not been reported in the literature. The development of intelligent polymer membranes based on such materials was first investigated in our laboratory.

This section reviews the research on conducting polypyrroles and conducting polypyrrole membranes. Polypyrrole was chosen since:

(1) Free-standing polypyrrole films with good mechanical properties, conductivity, uniformity and electroactivity have been prepared using electrochemical polymerisation methods [56];

(2) It is physically and chemically stable in air and solution [57];

(3) It has been extensively investigated and a large amount of background information is available [58].
1.2.1 Development of Conducting Polymers

Polypyrrole blacks have been known since 1916 [60], when they were first obtained as powders by chemical oxidation of the pyrrole monomer. The first electrochemical preparation of polypyrrole was reported by Dall'olio and co-workers in 1968. However, these polymer materials did not arouse further interest until 1977 when Shirakawa and co-workers [61] demonstrated that polyacetylene possesses metallic conductivity. This excited a surge of development in this new class of conducting polymer materials [62]. In 1979, an improved electrochemical technique was reported by Diaz and co-workers [56]. They showed that electrochemical oxidation of pyrrole resulted in the deposition of a conducting polypyrrole on the anodic surface and that the polymer can be peeled from the electrode. This was the first time free-standing conducting polypyrrole films have been obtained. Since then, other kinds of conducting polymers have been synthesised in the same way [63,64].

1.2.1.1 Conducting Polypyrrole Synthesis

Conducting polymers such as polypyrrole can be synthesised using chemical or electrochemical polymerisation methods [56,62]. In both cases, the important step is to incorporate certain chemicals into the polymer by a process called "doping". The polymerisation reaction can be expressed by the following equation:
Where \( n \) is usually 2 to 4 and \( C^- \) is a negatively charged ion, called the dopant or counterion.

Chemical polymerisation is carried out using a specific oxidant, and electrochemical polymerisation is carried out by application of an anodic current or potential in a polymerisation solution containing the monomer and dopant (counterion).

The chemical polymerisation process involves mixing the pyrrole monomer with a polymerisation agent. Usually a polymerisation agent contains an oxidant, a doping anion and solvent. The oxidant is known to be very important in the chemical preparation of pyrrole [65]. Recently only a few oxidants have been reported to be suitable for oxidation of pyrrole. \( Fe^{3+} \) (as the \( FeCl_3 \)) has received much attention as an oxidant [65-78]. Other transition metal ions such as \( Cu^{2+} \) [68,69,79-81] and \( Ag^+ \) [82] have also been used. Halogen [72,83,84], p-chloranil [72,85], \( H_2O_2 \) [86] and \( K_2S_2O_4 \) [77] have also been reported. Various forms of polypyrrole can be obtained by application of different operation methods. The three major procedures used for chemical polymerisation of pyrrole are summarised in Figure 1.3.

In brief, using chemical polymerisation methods, polypyrrole particles, colloids, latexes and composite films, supported films or free-standing films can be produced [72,73,75,77,78,83,87-89]. Nevertheless, it has not been easy to prepare homogeneous and free-standing polypyrrole films with good mechanical properties and uniformity [77,90].
Furthermore, the appropriate polymerisation conditions for obtaining high quality polypyrrole and the effect of the polymerisation conditions on the resultant polymers has not been widely investigated and so no general guidelines have been established for chemical polymerisation methods [91].

(I) Mixing

PARAMETERS:
The nature of the monomer and concentration;
The nature of the oxidant and concentration;
The nature of the solvent and the ratio between the monomer and oxidant.

PRODUCTS:
particles, colloids and latexes (72, 78, 87, 88).

(ii) Dipping

PARAMETERS:
The nature of the monomer and concentration;
The nature of the oxidant and concentration;
The nature of the solvent;
The ratio between the monomer and oxidant;
The type of the polymer and substrate materials.

PRODUCTS:
conducting polymer coated films and composite films (73, 83).

(iii) Interfacial Polymerisation

PARAMETERS:
The nature of the monomer and concentration;
The nature of the oxidant and concentration;
The nature of the solvent;
The ratio between the monomer and oxidant;
The type of the substrate membrane materials.

PRODUCTS:
conducting polymer coated films or free-standing films (75, 77, 89).

Notes: M: monomer; O: oxidant; S: solvent.

Figure 1.3 Synthesis of polypyrrole using chemical polymerisation methods
Since the new route for synthesis of polypyrrole was reported by Diaz and co-workers [56], electrochemical synthesis of polypyrrole have been widely investigated. Electropolymerisation can be carried out using three techniques:

(i) Potentiodynamic (sweep potential or pulsed potential),

(ii) Potentiostatic and

(iii) Galvanostatic.

The system involves a polymerisation cell, an electrochemical system and a polymerisation solution. Figure 1.4 shows the most important parameters that influence the polymer synthesis.

The potentiodynamic method is usually employed for investigating the mechanism of polymerisation or polymer formation. In this case, the electrodes are set up in a polymerisation solution. The polymer is formed through the application of a dynamic positive potential (e.g. potential sweep or pulsed potential). The current measured as a function of applied potentials also serves to monitor the polymerisation process. Information such as the initial polymerisation potential, the initial polymer formation potential and over-oxidation potential can be obtained. Some kinetic properties of the electrochemical process during polymerisation can also be observed. When a rotating working electrode is employed, more information can be obtained [92,93]. However, because of the low current efficiency and reproducibility, generally this method is not used for production of polymer films [94].

Potentiostatic methods can be used for free-standing film synthesis. The major problems are that during polymerisation, the current density varies and polymerisation efficiency is sensitive to the changes of the
chemical conditions such as the concentration and the solvent. Therefore, for the purpose of production of reproducible films, potentiostatic methods are not convenient.
With galvanostatic methods, the polymerisation is carried out by application of a constant anodic current [95]. This is much simpler and easier to work with. It is therefore much more commonly used for production of polypyrrole films than potentiostatic methods [96-98].

Many factors have been found to influence the properties of the polymers. These include the solvent system [99-101], substrate [102], counterion [103,104] and synthesis conditions (see Figure 1.4). The solvent system used in the electrochemical polymerisation of pyrrole has been widely investigated [105]. Most work is performed in aprotic solvents because the polymerisation reaction is sensitive to the nucleophilicity of the electrolyte. Solvent systems previously employed for electrosynthesis were organic solvent such as acetonitrile, aqueous or mixed organic solvents with a small amount of water. Until recently, most synthesis work was carried out using an organic solvent system [106-109]. Acetonitrile was reported to be the best organic solvent for polypyrrole synthesis [105]. Mixing an organic solvent with a small amount of water produced a positive effect on both the rate of polymerisation reaction and the properties of the polymer films [56,106,110-112]. For instance, Downard and co-workers [110] showed that acetonitrile with a 0.1M H₂O content, enhanced the rate of the pyrrole polymerisation reaction by a factor of 100, while the mechanical properties, and conductivity of the films was similar as prepared from pure acetonitrile.

In the past few years, there has been increasing interest in the use of aqueous solution for electrosynthesis of polypyrrole [107,113-119]. Advantages of the aqueous solvent system include:

(i) the rate of the polymerisation reaction is much faster;
(ii) current efficiency is higher;

(iii) a much larger amount of counterion can be used;

(iv) a wider range of electrochemical synthesis conditions can be employed.

Also, with respect to potential commercial application, the use of aqueous solutions is advantageous since these solutions are cheap, non-toxic and easier to work with than organic synthesis solutions. Many high quality polypyrrole films have been prepared using aqueous solutions [120-123].

It is known that the counterion plays an important role in electrosynthesis of polypyrrole since the counterion is incorporated into the polymer during the polymerisation process. Physical properties of the polypyrrole such as conductivity, mechanical strength, structure, morphology, uniformity, porosity and adhesion are known to be influenced by the counterion incorporated [110]. Some workers have reported that counterions can introduce their special chemical properties into the resultant polymers. For example, chemically active polymers have been prepared by incorporation of chemical active counterions [124-126]. Not only physical and chemical properties of the polymer are influenced by the counterion incorporated, but also electrochemical properties are more likely to be influenced by counterion incorporated [127]. The choice of the counterion is based on the application intended. Generally, the counterion should be soluble in the solvent and ideally electroinactive. They can be small inorganic anions [128], medium size organic anions [128] or large size organic anions or polyelectrolytes [128]. In all cases, the properties of the polymer are determined by the nature of the counterions [129-132].
The polymerisation solution may contain more than one type of the monomer in order to produce copolymers.

The choice of the substrate is known to be important in processing (because adhesion between the polymer film and different substrates is different) and also influences the polymer formation and morphology. The substrate roughness and geometry have reported to influence the resultant polymer morphology and uniformity [95]. A summary of the different substrate materials used for polypyrrole synthesis is shown in Table 1.7.

Chemical synthesis conditions such as the concentration of monomer and counterion, the ratio between the monomer and the counterion, and solution pH have also been reported to influence the physical properties of the polymers [107].

Physical properties of the polymer are also affected by the electrochemical synthesis conditions [4,5]. For instance, Maddison and co-workers [107] optimised the electrosynthesis conditions for polypyrrole doped with p-toluenesulfonate, the results showed that the polymer morphology, conductivity and mechanical properties were strongly influenced by the electrosynthesis conditions such as applied potential or current density employed.
Table 1.7 Substrates for Electrosynthesis of Polypyrrole

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Material</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td></td>
<td>aqueous; acetonitrile</td>
<td>118, 119</td>
</tr>
<tr>
<td>Gold</td>
<td></td>
<td>aqueous</td>
<td>105</td>
</tr>
<tr>
<td>Gold Plated Stainless Steel</td>
<td></td>
<td>aqueous</td>
<td>107</td>
</tr>
<tr>
<td>Aluminium</td>
<td></td>
<td>aqueous; acetonitrile; methanol</td>
<td>133, 134</td>
</tr>
<tr>
<td>Copper</td>
<td></td>
<td>propylene carbonate</td>
<td>95</td>
</tr>
<tr>
<td>Iron</td>
<td></td>
<td>acetonitrile</td>
<td>135</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td></td>
<td>acetonitrile</td>
<td>135</td>
</tr>
<tr>
<td>Titanium</td>
<td></td>
<td>acetonitrile; propylene carbonate</td>
<td>135</td>
</tr>
<tr>
<td>Mercury</td>
<td></td>
<td>aqueous</td>
<td>115, 136</td>
</tr>
<tr>
<td>Glassy Carbon</td>
<td></td>
<td>aqueous; acetonitrile; propylene carbonate</td>
<td>111, 137</td>
</tr>
<tr>
<td>Carbon Felt</td>
<td></td>
<td>propylene carbonate</td>
<td>95</td>
</tr>
<tr>
<td>Vitreous Carbon</td>
<td></td>
<td>acetonitrile</td>
<td>120</td>
</tr>
<tr>
<td>Tin Oxide</td>
<td></td>
<td>aqueous</td>
<td>90</td>
</tr>
<tr>
<td>Pyrolytic Graphite</td>
<td></td>
<td>acetonitrile</td>
<td>137</td>
</tr>
<tr>
<td>Indium Tin Oxide</td>
<td></td>
<td>aqueous; acetonitrile; propylene carbonate</td>
<td>121, 138,</td>
</tr>
<tr>
<td>Conducting Glass</td>
<td></td>
<td>nitrobenzene</td>
<td>139</td>
</tr>
</tbody>
</table>

1.2.1.2 Characterisation of Polypyrroles

In order to determine the physical, chemical and electrochemical properties of polypyrrole, many techniques have been employed (Table 1.8).
<table>
<thead>
<tr>
<th>Techniques</th>
<th>References</th>
<th>Information Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Analysis</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>FAB/MS</td>
<td>141, 142</td>
<td>Polymer composition</td>
</tr>
<tr>
<td>EDS</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>XPs</td>
<td>144-146</td>
<td>Counterion identification</td>
</tr>
<tr>
<td>EPMA</td>
<td>147</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>140, 148</td>
<td>Polymer morphology</td>
</tr>
<tr>
<td>FTIR</td>
<td>149</td>
<td></td>
</tr>
<tr>
<td>NMR</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>ESR</td>
<td>151</td>
<td></td>
</tr>
<tr>
<td>IR</td>
<td>148, 152, 153</td>
<td>Polymer structure</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>140, 148, 154</td>
<td></td>
</tr>
<tr>
<td>Mossbauer Spectroscopy</td>
<td>155</td>
<td></td>
</tr>
<tr>
<td>Spectroscopic Ellipsometry</td>
<td>156</td>
<td></td>
</tr>
<tr>
<td>TG/DTA</td>
<td>152, 157, 158</td>
<td>Thermal properties</td>
</tr>
<tr>
<td>High Resolution Electron</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>Energy-loss Spectroscopy</td>
<td>151</td>
<td>Conduction mechanism</td>
</tr>
<tr>
<td>ESR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Four Point Probe Technique</td>
<td>140, 148, 160</td>
<td>Polymer conductivity</td>
</tr>
<tr>
<td>Dynamic Mechanical Analysis</td>
<td>161</td>
<td>Polymer mechanical properties</td>
</tr>
<tr>
<td>Chronopotentiometry</td>
<td>162</td>
<td>Polymerisation mechanism, formation mechanism and polymer electrochemical properties</td>
</tr>
<tr>
<td>Chronoamperometry</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>Impedance Measurement</td>
<td>164</td>
<td></td>
</tr>
<tr>
<td>Cyclic Voltammetry</td>
<td>165, 166</td>
<td></td>
</tr>
</tbody>
</table>

In recent years, some new techniques such as Quartz crystal microbalance (QCM) [167, 168], cyclic resistometry [169] and Dynamic contact angle [169] techniques have been developed as useful tools for studying...
dynamic interactions on conducting polymers. All these techniques provide in-situ or dynamic information. For example, by combining the QCM method with electrochemical methods (EQCM), mass changes during the polymerisation or after polymerisation, under potential control, can be measured. Cyclic resistometry can provide information about resistance changes under potential control. Dynamic contact angle measurement gives information on the polymer surface properties, in particular the wettability of the surface.

1.2.1.3 Switching Properties of Polypyrroles

The pyrrole polymerisation reaction is an irreversible reaction (see equation 1.2). After polymerisation, application of a potential to the polymer electrode repeatedly cycled between a cathodic and anodic potential results in a reversible redox reaction taking place as shown in equation 1.3.

\[
\text{H}_n \text{N} \quad \text{O}^\text{-} \quad \text{O} \quad \text{H}_n \text{N} \\
^\text{+} \quad \text{C}^- \\
\text{Reduction} \quad \text{Oxidation}
\]

Variation of the redox states leads to a change in the physical and chemical properties of the polymer. By controlling the applied potential, polypyrrole can be switched between a conducting state (oxidised) and less conducting state (reduced). The ion exchange properties can be switched from anion to cation exchangers [127]. Ion movement into and out of the polymer accompany changes in the polymer redox states. This unique property is a process of fundamental importance, but it is of
practical interest as well. Some of the potential application areas of conducting polymers such as electrochromic displays and charge-storage devices are based on these reactions.

### 1.2.2 Conducting Polymer Membranes

With conducting polymer membranes, the unique properties of the conducting polymer can be utilised to control transport properties. This control is enabled by manipulation of the redox states of the polymer in-situ. Some researchers have reported on the feasibility of conducting polymer membrane synthesis and on electrochemically controlled transport across conducting polymer membranes [170-176]. Most of the membranes reported were supported membranes [172-176], only Wang and co-workers [170,171] used a free-standing polypyrrole film as a membrane but the area of the membrane they used was only 0.03cm² due to the limited mechanical strength of the polymer.

Transport of electrolyte across a conducting polymer membrane has been reported previously, using an applied electrical potential across the membrane. Wang and co-workers [170,171] discussed the effect of the direction of the electrical field on anion transport. By using polypyrrole coated gold minigrid membranes, Burgmayer and co-workers [176] proposed that the ionic resistance or ion permeability of the membrane can be varied by changes in the redox states of the membrane. They reported that ion permeation of a polypyrrole membrane in the oxidised state was much larger than that the reduced polypyrrole membrane. However, no quantitative transport studies were carried out in these papers.
Synthesis of the conducting polymer membrane is based on the same principles as synthesis of conducting polymers in general (see above). However, due to the special application purpose, some additional requirements such as mechanical properties, uniformity, pore size, porosity, conductivity, electroactivity and reversibility must be considered. In the current literature, no data on synthesis of free standing polypyrrole membranes was available.

1.3 AIMS OF THE PROJECT

The main aim of this project is to demonstrate the feasibility of electrochemically controlled transport across polypyrrole membranes.

Two major aspects have been addressed in this project:

(1) Polypyrrole membrane synthesis and characterisation;

(2) Electrochemically controlled transport across polypyrrole membranes.

Part 1 (Chapter 2 and Chapter 3) involves the fundamental aspects of electrochemical synthesis and characterisation of polypyrrole membranes. The initial research was aimed at investigation of the important parameters that could influence polypyrrole synthesis. Subsequent investigation was focussed on electrochemically synthesising free-standing polypyrrole membranes. In this approach, a range of counterions and substrates were employed; Chemical and electrochemical synthesis conditions have been optimised; Mixed counterion and multilayer-deposition techniques were developed. In order to determine whether the membranes obtained were appropriate
for the purpose of electrochemical control of transport, numerous techniques were used for membrane characterisation.

The electrochemical control of transport was carried out in part 2 of this thesis (Chapter 4 to 8). In order to understand the mechanism of the transport, investigation of electrochemical properties, especially ion incorporation and expulsion properties of the polypyrrole films were then considered. In this phase of study, factors influencing ion incorporation/expulsion properties have been outlined.

Electrochemically controlled transport across conducting electroactive polypyrrole membranes was next considered. In this approach, the first aim was to switch on/off transport across the membrane by means of application of an electrical stimulus. By the same means, controlled rate of transport across the membrane and modified separation capability of the membrane were investigated. As the test case, transport of both electroinactive and electroactive ions across the membrane was investigated. Other factors such as the chemical conditions used and the membrane synthesis conditions employed on the transport across the membrane were involved. The relative studies such as the electrotransport cell design was also explored.

The ion incorporation/expulsion mechanism and the deposition/stripping mechanism for electroinactive and electroactive species transport across the polypyrrole membrane was evaluated.

Further investigation was carried out to determine the transport properties of the polypyrrole membranes synthesised using different counterions and different techniques.
CHAPTER 2

STUDIES OF ELECTROCHEMICAL DEPOSITION OF POLYPYRROLE
2.1 INTRODUCTION

Since the discovery that polypyrrole could be deposited onto an electrode surface by electropolymerisation [56], the mechanism of polymerisation and deposition have been studied extensively [177,178]. However, there are still gaps in our understanding. In order to optimise conducting polymer synthesis, an investigation of the important parameters influencing the process is necessary. This is especially important for synthesis of conducting polymer membranes.

It is generally agreed that the electropolymerisation of pyrrole is by an E(CE)n mechanism [178-183]. More detailed studies have been concerned with where and when these chemical/electrochemical reactions take place. However, a nucleation/growth mechanism has now been accepted by most researchers for heterocyclic conducting polymers [184-191]. It may be described as follows:

1. Monomer oxidation

\[
\text{Oxidised} \quad \text{+ e} \]

2. Radical - Radical coupling

\[
+2H^+ \]
3. Chain propagation

\[
\begin{array}{c}
\text{Oxidised} \\
\text{Dimers and} \\
tetramers are shown, but oligomers of all sizes are expected. The 
mechanism described above involves a nucleation process, where neutral 
monomer is adsorbed onto the electrode surface prior to oxidation and 
then subsequent polymerisation/deposition occurs. This contrasts with 
the view [189,190 that nucleation and growth equates to the formation of 
oligomer chains of sufficient length such that the oligomer is insoluble 
and precipitates on the electrode surface. Growth then involves the 
addition of neutral monomer to the end of this chain. The problem with 
this latter model is that the addition of monomer to the chain does not 
increase the electroactive surface area available for electron transfer, and 
it would result in one dimensional growth. This is contrary to most 
results observed during polymer growth. For example, current increases 
with time during polymerisation have been reported and this suggests that}
\end{array}
\]
the electroactive surface area of the electrode increases with time [178,181,182,185,192]. SEM studies [193,194] show that the polymer surface appears to be made up of overlapping three dimensional nuclei.

In this work, a study of polypyrrole deposition during the electrochemical polymerisation process has been carried out. Cyclic voltammetric (potentiodynamic), chronoamperometric (potentiostatic) and chronopotentiometric (galvanostatic) methods were employed to investigate the effect of different polymerisation methods on the resulting polymer. The effect of the electrochemical conditions on the polymerisation have been taken into account. The effect of the counterion employed during polymerisation on the polypyrrole synthesis has also been investigated. In addition, investigation of the effect of stirring on the synthesis have been carried out using a rotating disc electrode.

2.2 EXPERIMENTAL

2.2.1 Reagents and Materials

All inorganic reagents were of analytical reagent (AR) grade purity. All reagents used as counterions were supplied commercially and used as received (Table 2.1). Pyrrole (SIGMA) was distilled before use.

All solution were prepared in deionised Milli-Q water (18 MΩ cm). A glassy carbon disc working electrode (4.0 mm diameter), Ag/AgCl (3M NaCl) reference electrode and a platinum gauze auxiliary electrode was used throughout this work.
### Table 2.1 The Counterions used for polypyrrole synthesis

<table>
<thead>
<tr>
<th>COUNTERIONS</th>
<th>SUPPLIERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzenesulfonic acid, sodium salt (BSA)</td>
<td>Aldrich Chemical Company, Inc.</td>
</tr>
<tr>
<td>p-Toluenesulfonic acid, sodium salt (PTS)</td>
<td>MERCK Schuchardt</td>
</tr>
<tr>
<td>4-Ethylbenzenesulfonic acid (EBS)</td>
<td>Aldrich Chemical Company, Inc.</td>
</tr>
<tr>
<td>2-Mesitylenesulfonic acid (MS)</td>
<td>Aldrich Chemical Company, Inc.</td>
</tr>
<tr>
<td>1,3-Benzenedisulfonic acid, disodium salt (BS)</td>
<td>SIGMA</td>
</tr>
<tr>
<td>1,5-Naphthalenedisulfonic acid (NPS)</td>
<td>Aldrich Chemical Company, Inc.</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate (DS)</td>
<td>SIGMA</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>BDH</td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>BDH</td>
</tr>
</tbody>
</table>

### 2.2.2 Instrumentation

All experiments were carried out using a normal three electrode electrochemical cell. The cyclic voltammetry experiments were carried out using a Bioanalytical System (BAS) Model 100A Electrochemical analyser. A BAS CV-27 voltammograph and a home made galvanostat were employed for chronopotentiometry studies.

A rotating disc electrode (made in 7th Shandong Dian Xun Chang, China) fitted with a 4.0 mm glassy carbon disk, was used for studies of the effect of stirring on polymer formation.

An X-Y recorder (Houston Instrument) was used to record the chronopotentiograms or chronoamperograms.
2.3 RESULTS AND DISCUSSION

Cyclic voltammetry (CV), chronoamperometry (CA) and chronopotentiometry (CP) were employed for the growth studies. For each method, the effect of the electrochemical conditions used and the different counterions employed was investigated.

2.3.1 Cyclic Voltammetry

Cyclic voltammetry was carried out in solutions that were 0.20M in pyrrole and 0.05M in supporting electrolyte. In each case, the voltammograms were recorded using both static and hydrodynamic conditions (electrode rotation).

Figure 2.1(a) shows cyclic voltammograms recorded in PTS containing solution under static conditions. The current on the first positive sweep remained around zero until about 0.56V (point A), then increased sharply at a potential of about 0.73V (point B). This observation indicated that initial monomer oxidation started at 0.56V (point A), and deposition of polypyrrole occurred when the potential was more positive than 0.73V (point B). The current observed in the reverse sweep had the same trend but was slightly higher in value at potentials between 0.56V and 1.0V. This is often referred to as a "nucleation loop" and is a common observation where a conducting polymer phase is formed by a nucleation/growth mechanism [185,192]. The current-potential plot for subsequent cycles had a similar shape, but an increase in the current values with additional potential sweeps was observed. This was due to an increasing electroactive surface area of the electrode. Further more, this indicates continuous polymer deposition was occurring. Also, a greater current increase was observed at slightly less positive potentials for later cycles. This suggests that pyrrole oxidation and polypyrrole deposition
occur more readily on the polypyrrole surface than on a glassy carbon surface.

Figure 2.1(b) illustrates the cyclic voltammogram recorded under hydrodynamic conditions. The nucleation loop was still present, indicating a nucleation/growth mechanism. Compared to Figure 2.1(a), in the first cycle the current rose at a more positive potential (point A, about 0.6V) and increased sharply at a more positive potential (point B, about 0.90V). The current observed was also smaller in magnitude than that measured under static conditions. These observations suggest that the monomer oxidation and/or the polymer formation process was a slow reaction. Furthermore, the processes were limited by an electrochemical step since the electrode rotation did not result in an increased current as would be effected is the rate was controlled by physical variable, eg diffusion. It has been suggested [189,190] that polymer growth involves addition of neutral monomer to the end of the polymer chain. If this were the case, rotation of the electrode would increase the amount of monomer transported to the electrode surface and hence increase the current observed. However, the slow current rise observed in this experiment between 0.65V and 0.90V suggests that polymerisation in this potential range involves a slow step which could be a radical-radical coupling [185,192].

Experiments were then carried out using different counterions to examine the effect of the counterion on the polypyrrole synthesis. Some typical examples are shown in Figures 2.2 and 2.3. The monomer oxidation potential (point A) and polymer deposition potential (point B) observed are summarised in Table 2.2. All voltammograms obtained revealed a nucleation loop, indicating a nucleation/growth mechanism. Voltammograms recorded under static conditions showed that pyrrole
oxidation started at very similar potentials (point A, around 0.53V to 0.59V), independent of the counterion employed. This observation suggests that oxidation of pyrrole was mainly dependent on the nature of the monomer (Table 2.2). The deposition potential (point B) differed greatly for different counterions indicating the polymer deposition was affected by the counterion employed (Table 2.2). The current measured at 0.75V for the first cycle increased in the order:

\[ \text{NPS} > \text{EBS} > \text{BS} > \text{MS} > \text{PTS} > \text{BSA} > \text{NO}_3^- > \text{Cl}^- . \]

This suggests that the counterion employed strongly affects the rate of polymerisation and/or polymer deposition. For instance, using NPS as the supporting electrolyte, at a potential of 0.75V, the current obtained was about 8 times larger than when PTS was used (Table 2.2).

![Cyclic voltammogram of 0.2 mol/L pyrrole solution in 0.05 mol/L PTS at a glassy carbon disc electrode. Scan rate=50 mV/sec. (a) static and (b) Rotation rate=2000 rpm. Dense line: first cycle; Dotted line: 5th cycle.](image)

**Figure 2.1** Cyclic voltammogram of 0.2 mol/L pyrrole solution in 0.05 mol/L PTS at a glassy carbon disc electrode. Scan rate=50 mV/sec. (a) static and (b) Rotation rate=2000 rpm. Dense line: first cycle; Dotted line: 5th cycle.
<table>
<thead>
<tr>
<th>COUNTERION</th>
<th>Oxidation Potential (point A) V</th>
<th>Polymer Deposition Potential (point B) V</th>
<th>Current Observed at 0.75V for first cycle (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻</td>
<td>0.58</td>
<td>0.77</td>
<td>&lt;15</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.59</td>
<td>0.80</td>
<td>71</td>
</tr>
<tr>
<td>BSA</td>
<td>0.58</td>
<td>0.75</td>
<td>100</td>
</tr>
<tr>
<td>PTS</td>
<td>0.56</td>
<td>0.73</td>
<td>170</td>
</tr>
<tr>
<td>EBS</td>
<td>0.55</td>
<td>0.65</td>
<td>860</td>
</tr>
<tr>
<td>MS</td>
<td>0.55</td>
<td>0.70</td>
<td>350</td>
</tr>
<tr>
<td>BS</td>
<td>0.53</td>
<td>0.68</td>
<td>420</td>
</tr>
<tr>
<td>NPS</td>
<td>0.53</td>
<td>0.62</td>
<td>1400</td>
</tr>
</tbody>
</table>

Experiments were carried out in a solution containing 0.2 M pyrrole and 0.05 M counterion under static conditions. Scan rate: 50mV/sec.

**Figure 2.2** Cyclic voltammogram of 0.2 mol/L pyrrole solution in 0.05 mol/L NPS at a glassy carbon disc electrode. Scan rate=50 mV/sec. (a) the voltammogram recorded under static conditions and (b) rotation rate=2000 rpm. Dense line: first cycle; Dotted line: 5th cycle.
Figure 2.3 Cyclic voltammogram of 0.2 mol/L pyrrole solution in 0.05 mol/L NaCl at a glassy carbon disc electrode. Scan rate=50 mV/sec. (a) the voltammogram recorded under static conditions and (b) rotation rate=2000 rpm. Dense line: first cycle; Dotted line: 5th cycle.

The voltammograms recorded with a rotating electrode show a large difference for different counterions (see Figure 2.1 to 2.3). In the cases of NPS, EBS and BS, there was no applicable difference in the current observed when the electrode was rotating or stationary. For PTS, BSA, Cl\(^{-}\) and NO\(_3\)\(^{-}\), there was a marked decrease in current for the rotating disk compared with a stationary electrode. These suggest that the kinetic behaviour of the polymerisation process is largely dependent on the counterion employed.

However, all of the above experiments suggest that for pyrrole polymerisation in aqueous medium, the initial oxidation potential is mainly governed by the nature of the monomer itself. The counterion employed influences the polymer deposition potentials and the rate of monomer oxidation and/or polymer deposition. Also, the results suggest
that potentiodynamic polymerisation, may be useful for the mechanistic studies but not suitable for membrane synthesis since:

(i) the rate of the polymerisation is slow and varies with time.

(ii) the reproducibility of the product is poor and non-controllable.

Generally, if the current efficiency of the polymerisation reaction is known, the amount of polymer per unit area can be controlled by monitoring the charge passed during the polymerisation processes. However, with potentiodynamic polymerisation the current observed for later cycles are due to numerous reactions, not just the polymerisation process. Therefore, the percentage of charge passed due to the polymerisation reaction was indeterminable and hence the amount of polymer per unit area is very difficult to control.

2.3.2 Chronoamperometry

Throughout this part of the work, the investigation of pyrrole polymerisation and polypyrrole deposition was considered using a single potential step. The experiments were carried out using a procedure of 2.0 minutes with no stirring followed by 2.0 minutes of electrode rotation to determine whether or not the polymerisation process is mass transfer controlled. The solutions used were the same as used for the cyclic voltammetry experiments. The influence of experimental parameters was investigated. In general, the rate of electrode rotation was fixed at 1000 rpm.

The chronoamperometric responses to a single potential step in 0.2M pyrrole and 0.05M PTS solution are shown in Figure 2.4. When the
potential was stepped from 0V to 0.5V (Figure 2.4(1)), a sharp current spike was observed which then decayed to a constant, small value (about 1μA, 0 to point A) indicating that no polymer deposition had occurred. When the electrode was rotated (after point A), the current eventually levelled off to the same value as that under the former static conditions.

When the applied potential was stepped from 0V to 0.60V (Figure 2.4(2)), the initial current spike was followed by a rising transient indicating the deposition and subsequent growth of the polymer film (0 to point A). The sharp drop in current was caused by the decay of the charging current, which was much faster than the increasing faradic current during the initial stage of polymerisation/deposition. The rising transient part of the curve is due to an increase in the electroactive surface area caused by the polymer deposition and expansion of polymeric nuclei. These observations suggest that the polymerisation processes were facilitated by a nucleation/growth mechanism [185,192] under static conditions. When the electrode was rotating (curve 2, after point A), the current increased sharply as a result of a changing double layer thickness, then a sharp drop in the current was observed. This was not a surprising result since cyclic voltammetry experiments with a rotated electrode already indicated that the electron transfer in the oxidation of pyrrole was slow. The same conclusions were reached by John and Wallace when they studied the electropolymerisation mechanism of pyrrole using a macro-electrode with stirred solution or a micro-electrode under static conditions [192].

A similar behaviour was also observed when the potential was stepped from 0 to 1.0V (Curve 3). But the current values obtained under both static or rotating electrode were much larger than that obtained in the case of 0.6V applied (curve 2). This indicates that the rate of pyrrole
polymerisation and/or polypyrrole deposition is dependent on the applied potential.

When the potential was stepped from 0 to 1.7V (curve 4), under static conditions (0 to point A) the current observed decreased with time. A rising transient current did not appear. This may be due to the polypyrrole over oxidation and/or mass transfer limiting the process. When the electrode was rotated (after point A) a rising current was observed. Under this condition, mass transfer is greatly improved indicating that under this high applied potential polymerisation/deposition processes are limited by mass transfer.

Experiments were then considered using different counterions as the supporting electrolyte. A typical example is given in Figure 2.5. Compared to PTS, it was found that by using NPS as the counterion, the current values for both static and rotating electrode were much greater. It was also observed the potential at which the current increases caused by rotating the electrode was much lower for NPS than PTS (0.7V and 1.7V respectively, see Curve 3). These observations suggest that the rate of the pyrrole polymerisation using NPS as counterion was faster than using PTS as the counterion. This is in agreement with the data obtained from CV experiments. The effect of the counterion used on the rate of polymerisation are summarised in Table 2.3. It is in the order of:

NPS>EBS>PTS>BSA.
Figure 2.4 Chronoamperometric responses at different potentials for oxidation of 0.2 mol/L pyrrole in 0.05 mol/L PTS at a glassy carbon disc electrode. 0 to A: static, after A: Rotation rate=1000 rpm., $E_f=0.00V$, (1) $E_f=0.50V$, (2) $E_f=0.60V$, (3) $E_f=1.0V$, (4)1.7V, (vs Ag/AgCl).
Figure 2.5 Chronoamperometric responses at different potentials for oxidation of 0.2 mol/L pyrrole in 0.05 mol/L NPS at a glassy carbon disc electrode. 0 to A: static; after A: Rotation rate=1000 rpm,. $E_f=0.00V$, (1) $E_f=0.55V$, (2) $E_f=0.60V$, (3) $E_f=0.7V$, (4)$0.75V$, (vs Ag/AgCl).
Table 2.3 Effect of the counterion employed on the rate of polymerisation/deposition

<table>
<thead>
<tr>
<th>Counterions</th>
<th>Applied Potential (V) vs Ag/AgCl</th>
<th>Current obtained (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSA</td>
<td>0.70</td>
<td>0.95</td>
</tr>
<tr>
<td>PTS</td>
<td>0.70</td>
<td>1.27</td>
</tr>
<tr>
<td>EBS</td>
<td>0.70</td>
<td>2.51</td>
</tr>
<tr>
<td>NPS</td>
<td>0.70</td>
<td>4.86</td>
</tr>
</tbody>
</table>

Notes: Polymerisation was carried out in 0.20M pyrrole and 0.05M counterion solutions under static conditions. The current density was measured after the polymerisation had continued for 60 seconds.

Further experiments were carried out to determine the effect of the counterion on the initial monomer oxidation potential, polymer deposition potential and mass transport limiting potential. The results in Table 2.4 show that initial oxidation potentials and initial polymer deposition potentials for different counterions were very similar. This is different from the data obtained by a potentiodynamic method (CV) where the polymer deposition potential was influenced by the counterion employed.

Table 2.4 Effect of the counterion employed on the rate of polymerisation/deposition

<table>
<thead>
<tr>
<th>Counterions</th>
<th>Oxidation Potential (V) vs Ag/AgCl</th>
<th>Polymerisation Potential (V) vs Ag/AgCl</th>
<th>Mass transport limited potential (V) vs Ag/AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSA</td>
<td>0.52</td>
<td>0.58</td>
<td>&lt;1.3</td>
</tr>
<tr>
<td>PTS</td>
<td>0.54</td>
<td>0.58</td>
<td>&lt;1.3</td>
</tr>
<tr>
<td>EBS</td>
<td>0.52</td>
<td>0.56</td>
<td>&lt;1.1</td>
</tr>
<tr>
<td>NPS</td>
<td>0.53</td>
<td>0.56</td>
<td>&lt;0.8</td>
</tr>
<tr>
<td>DS</td>
<td>0.52</td>
<td>0.54</td>
<td>&lt;0.8</td>
</tr>
</tbody>
</table>

Note: the polymerisation was carried out in static state using the same polymerisation solutions as described in table 2.3.

The potential at which the polymerisation rate became limited by mass transfer was estimated by rotating the electrode and seeing whether the current increased or decreased. A current increase indicates mass transfer control.
However, the above data suggests that the counterion indeed plays an active role in the electropolymerisation of pyrrole. The results confirmed that the rate of polymerisation and/or polymer deposition is strongly influenced by the counterions employed. The hydrodynamic behaviour is also influenced by the counterion employed.

With respect to the membrane synthesis, the following points should be made about potentiostatic (controlled potential) methods:

(i) the rate of polymerisation was not constant during the polymerisation process;

(ii) with the same applied potential, the rate of polymerisation was sensitive to the counterion employed;

(iii) the method was sensitive to experimental conditions such as the monomer and counterion concentration and the hydrodynamic conditions of the solution.

In order to obtain reproducible products, (i) and (ii) can be solved by monitoring the charge passed using a coulometer. Problem (iii) is a practical one and can be best solved by careful control of the environmental conditions. It may be concluded that the potentiostatic synthesis of polypyrrole is applicable to membrane synthesis but not easy in practical terms.

2.3.3 Chronopotentiometry

In this section of the work, the pyrrole polymerisation process was investigated using a single current step (controlled current) technique. The experiments were carried out using the same polymerisation solution
and the same electrodes as used in Section 2.3.2. With each experiment the chronopotentiogram recorded involved three different parts: static condition (0 to point A) followed by rotation of the electrode (after point A). The rate of rotation was fixed at 1000 rpm unless otherwise stated.

Figure 2.6 shows the chronopotentiograms recorded at different current densities in a 0.2M pyrrole and 0.05M PTS solution (the corresponding experiments of chronoamperograms are shown in Figure 2.4). In the first static part of the chronopotentiogram (0 to point A), the potential rose sharply to the highest value when the current was applied (except for 0.25mA/cm² Curve 1). Subsequently, a decrease in the potential was observed (except Curve 4, 20mA/cm²). The higher potential observed with the initial applied current may be due to the fact that polymer formation on the bare glassy carbon electrode was difficult (as already proposed in section 2.3.1). The subsequent decrease in current suggests that polymer formation on the polypyrrole surface was easier. The reason for the potential rise in the case of Curve 4 is presumably due to the fact that the polymerisation is controlled by mass transport or that the polymer is being overoxidised at these potentials. It was also found that an increase in the applied current density resulted in an increase in the electrode potential (see Curves 1 to 4).

Under electrode rotation (after point A), the potential initially increased sharply, then levelled out to an almost constant value (Curves 1 to 3). This indicates that polymerisation of pyrrole with a rotating electrode was more difficult than that under static conditions since a higher energy was required. In the case of Curve 4, the potential decreased under stirred conditions because the mass transfer was slower than the electron transfer.
Figure 2.6 Chronopotentiometric responses at different current densities for oxidation of 0.2 mol/L pyrrole in 0.05 mol/L PTS at a glassy carbon disc electrode. 0 to A: static; After A: Rotation rate=1000rpm. (1) 0.25mA/cm²; (2) 2.0mA/cm²; (3) 10.0mA/cm²; (4) 20.0mA/cm².
The next phase in this sequence of experiments was carried out to investigate the effect of the counterion. A typical example (using NPS) is shown in figure 2.7. Compared to polymerisation using PTS (Figure 2.6), under the static conditions (0 to point A), the results show that much lower energy (less positive potential) was required to generate the same electron flux (current density). This indicates that the pyrrole oxidation and/or polymerisation with NPS as the counterion was easier, and rate of electron transfer in the polymerisation process was faster than for PTS.

Compared to PTS, when NPS was employed within a current density range of 0.25 to 8.0mA/cm² (Curves (1) to (3)), electrode rotation had little affect on the electrode potential. This suggests that the reaction with NPS was not sensitive to electrode rotation.
Figure 2.7. Chronopotentiometric responses at different current densities for oxidation of 0.2 mol/L pyrrole in 0.05 mol/L NPS at a glassy carbon disc electrode. 0 to A: static; After A: Rotation rate=1000rpm. (1) 0.25mA/cm²; (2) 2.0mA/cm²; (3) 8.0mA/cm²; (4) 20.0mA/cm².

Results of studies of applied current densities and mass transfer limiting current for various counterions are given in Table 2.5. For all counterions studies current densities of less than about 10mA/cm² result in polymerisation being controlled by the electron transfer process.

Table 2.5 Effect of the counterion employed on the mass transfer limited current density

<table>
<thead>
<tr>
<th>Counterions</th>
<th>Applicable current range (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSA</td>
<td>&lt;13</td>
</tr>
<tr>
<td>PTS</td>
<td>&lt;15</td>
</tr>
<tr>
<td>BS</td>
<td>&lt;19</td>
</tr>
<tr>
<td>EBS</td>
<td>&lt;25</td>
</tr>
<tr>
<td>NPS</td>
<td>&lt;30</td>
</tr>
<tr>
<td>DS</td>
<td>&lt;30</td>
</tr>
</tbody>
</table>

Note: The data were obtained under static conditions using the same polymerisation solution as described in Table 2.3. The mass transfer limiting current is measured at the commencement of the potential decrease by rotating the electrode after stationary polymerisation for 2 minutes.

It is important to note the differences between the controlled potential controlled current techniques. For a given system, when the
polymerisation is carried out using controlled potential techniques, the working electrode energy level is fixed. The rate of the oxidation reaction is mainly dependent on the rate of mass transfer and the electroactive surface area of the electrode. When the polymerisation is carried out using controlled current techniques, the situation is totally different. With application of a constant current, the rate of the reaction was constant, irrespective of changes in the electroactive surface area or rate of mass transfer. Therefore, the working electrode energy level (potential) and the rate of electron transfer may vary. Understanding the different behaviour obtained from chronoamperometry and chronopotentiometry experiments is important in choosing the appropriate technique for a given polymerisation.

Comparing the three polymerisation methods presented in this chapter, galvanostatic (controlled current) polymerisation is the most suitable technique for polypyrrole membrane synthesis. The advantages of a controlled current technique are:

(i) if the reaction is not governed by mass transport, then the rate of the polymerisation is constant throughout the polymerisation process;

(ii) within a wide applied current density range, the rate of pyrrole polymerisation is independent of the counterions employed;

(iii) the method is not very sensitive to changes in hydrodynamic conditions;

(iv) the amount of polymer per unit area can be simply controlled by controlling the time of polymerisation.

Therefore, galvanostatic methods will be considered for membrane synthesis throughout the subsequent work.
2.4 CONCLUSIONS

In the course of this work, investigation of polypyrrole deposition during electrochemical polymerisation has been carried out using a range of electrochemical techniques. The effects of the counterion and synthesis conditions have been studied. The following conclusions may be made:

(1) The initial monomer oxidation potential is mainly governed by the nature of the pyrrole monomer. The counterion employed has little effect on this parameter.

(2) The rate of polypyrrole deposition is strongly influenced by the counterion employed during polymerisation. The rate of polymerisation using different counterions is in order of:

\[ \text{NPS} > \text{EBS} > \text{BS} > \text{PTS} > \text{BSA} > \text{Cl}^- \].

(3) Stirring has a dramatic effect on the polymerisation process. The rate of polymerisation decreases when the electrode is rotated. These effects are dependent on the counterion uses. It may be concluded that non-stirred conditions are better for reproducibly preparing films. This condition will be applied for subsequent membrane synthesis.

(4) All the results in this work show that the counterion is not passively incorporated into the polymer to neutralise the positive charge. Instead it plays an active role to influence the polymerisation process.

(5) Galvanostatic polymerisation is most suitable for membrane as the current density is therefore controlled. A constant rate of polymerisation is achievable only when the reaction is
electrochemically controlled and not determined by diffusion processes. For all counterions studied current densities of less than 10mA/cm² resulted in electrochemically limited controlled polymerisation process. A mass transfer limited rate is likely to be disadvantageous for membrane synthesis because it results in non-uniform rates of deposition on the electrode and hence membranes with irreproducible thickness.

Consequently galvanostatic polymerisation with low current densities (less than 10 mA/cm²) will be used throughout the subsequent work on membrane preparation.
CHAPTER 3

POLYPYRROLE MEMBRANE SYNTHESIS AND CHARACTERISATION
3.1 INTRODUCTION

As mentioned in Chapter 1, the synthesis of conducting polymers has been extensively investigated previously. Nevertheless, only a few reports dealing with conducting polymer membranes are available (77,170-176). Consequently, little is known about the specific synthesis requirements for producing robust, practical membranes from these materials. It was, therefore, necessary in the course of this work to establish routine synthesis and characterisation techniques for conducting polymer membranes.

High quality free-standing polypyrrole films can only be produced using electrochemical polymerisation methods [56]. Therefore, only electrochemical methods were considered here. In this chapter, using PP/PTS membrane synthesis as a typical example, the influence of experimental factors has been investigated. Subsequently, synthesis of polypyrrole membranes using a series of different counterions was carried out.

Characterisation of the membranes was carried out using many different techniques yielding complementary information about the synthesis and the resultant membranes and its properties (Table 3.1). The electrochemical properties of the membranes are discussed in Chapter 4.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Information Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Analysis</td>
<td>Membrane composition</td>
</tr>
<tr>
<td></td>
<td>Counterion identification</td>
</tr>
<tr>
<td>Scanning Electron Microscopy (SEM)</td>
<td>Membrane surface morphology</td>
</tr>
<tr>
<td>Four Point Probe</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Dynamic Mechanical Analysis</td>
<td>Membrane mechanical properties</td>
</tr>
<tr>
<td>Chronopotentiometry</td>
<td>Polymerisation mechanism, formation mechanism and</td>
</tr>
<tr>
<td>Chronoamperometry</td>
<td>polymer electrochemical properties</td>
</tr>
<tr>
<td>Cyclic Voltammetry</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1 Membrane characterisation techniques used in this work
3.2 EXPERIMENTAL

3.2.1 Reagents and Materials

All reagents used were as described in Chapter 2 unless otherwise stated.

For membrane synthesis a three electrode system was employed. The auxiliary electrode was a large surface-area Reticulated Vitreous Carbon plate (RVC, obtained from Energy Research Generation, Inc.) and the reference electrode was Ag/AgCl (3M NaCl, BAS). Various materials were employed as the working electrode. (Table 3.2) The working electrode surface was polished to a mirror finish and the back of the working electrode was then covered with a thin layer of silicone.

All solutions were prepared using deionised Milli-Q water (18Ω cm).

3.2.2 Instrumentation

The polymerisation was carried out using a Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat in conjunction with a PAR Model 179 Digital Coulometer. DC-conductivity of the membranes was obtained using a standard four-point probe (made at the University of Technology, Sydney, Australia). The tensile strength of the membrane was measured using a Instron 4303 Dynamic Mechanical Analyser. The cross flow filtration system (made at Memtec, Australia) was used to measure the permeability of the membranes.

3.2.3 Procedures

3.2.3.1 Preparation of Polypyrrole Membranes

The electrosynthesis cell was set up as shown in Figure 3.1. The cell was glass chamber incorporating a three electrode system. An RVC plate
(1x8x1cm) was used as the auxiliary electrode and a Ag/AgCl (3M NaCl) reference electrode contacted the solution via a salt bridge. Except for investigations involving the effect of the substrate materials on the synthesis, all membranes were prepared using a stainless steel plate (No 316, Goodfellow) as a working electrode. The valid surface area of this electrode was 4.3 x 6.3 cm. The distance between the working electrode and auxiliary electrode was fixed at 3.5 cm. The volume of the polymerisation solution used was 150 ml.

In all cases, the working electrode was pretreated before use. The pretreatment of the electrode involved polishing the surface with 1.0 μm aluminium oxide powder followed by rinsing with distilled water until water adhered to all of the surface of the electrode.

Polymerisation was carried out using galvanostatic methods. A variety of experimental conditions were employed, and a range of polymerisation solutions were used as detailed later.

**Figure 3.1 Electropolymerisation cell**
The general membrane preparation procedures employed in this work can be outlined as follows:

1. set up instruments and select the electrochemical polymerisation conditions;

2. pretreat the working electrode;

3. add 150 ml of polymerisation solution into the electrosynthesis cell and deoxygenate the solution for 4 minutes using a nitrogen stream. Stop the nitrogen stream and allow 2 minutes before starting the polymerisation. (This enabled bubbles to disperse from the solution. If this was not done, the membrane obtained always had pin holes as small bubbles adsorbed on the working electrode surface, inhibiting polymer deposition.);

4. initiate the polymerisation reaction;

5. after polymerisation is complete, remove the working electrode from the cell, rinse with distilled water, then soak the electrode in deionised water for 30 minutes, changing the water every 10 minutes to remove all the polymerisation reagent from the membrane completely;

6. finally, carefully peel off the membrane from the electrode and dry in air.

With experiments for the investigation of the effect of the substrate, the experimental procedure used was as described above. The polymerisation solution contained 0.2M pyrrole and 0.05M PTS. The
current density used was 2.0mA/cm² and polymerisation time was 10 to 20 minutes.

3.2.3.2 Characterisation Methods

Scanning Electron Microscopy (SEM) was used to characterise the surface morphology of the membrane. The samples were prepared by cutting the membrane into small pieces and securing on an aluminium sample tray by means of conductive carbon paint. SEM photographs of both sides of the membrane were taken. In addition, in order to obtain high quality photographs, the sample was covered with a very thin layer of gold metal by vacume deposition prior to exposure. SEM was also used to measure the thickness of the membrane by taking photographs of the cross section.

The samples for conductivity measurements were prepared by cutting the membrane into pieces of about 0.3 x 6 cm. The accurate width was measured using a micrometer and the thickness measured using SEM techniques. The conductivity measured in this work was volume conductivity calculated according to the following equation:

\[ R_v = \frac{X \cdot Y \cdot \Delta E}{Z \cdot i} \quad (\Omega \cdot \text{cm}) \]  
\[ \sigma_v = \frac{1}{R_v} \quad (\text{S/cm}) \]  

Where \( R_v \) is the volume resistivity and \( \sigma_v \) is the volume conductivity, \( X \) and \( Y \) are the sample thickness and width respectively; \( Z \) is the distance between the two potential electrodes; \( \Delta E \) is the potential difference
between the potential electrodes and i is the current passed through the outer electrodes.

Samples for mechanical tensile strength measurements were prepared by cutting the membrane into pieces of about 1.0 x 4.0 cm.

Permeability measurements were carried out using a cross section filtration apparatus. The experimental set up is shown in Figure 3.2. The feed solution used was 2.0% NaCl at an applied pressure of 100 atm. During the experiment, the sample volume was measured as a function of time. After the experiment, the concentration of the Na⁺ in the sample solution was analysed using Atomic Absorption Spectrometry, enabling the percentage of NaCl rejected from the membrane to be calculated.

![Figure 3.2 Experimental set up for cross flow filtration](image)

3.3 RESULTS AND DISCUSSION

As discussed in Chapter 2, three electrochemical polymerisation methods can be used for polypyrrole synthesis: potentiodynamic methods,
potentiostatic methods and galvanostatic methods. For the purpose of membrane synthesis, a method that can produce a membrane reproducible with controlled thickness and density is required. Based on these requirements, galvanostatic polymerisation was chosen.

3.3.1 Preparation of PP/PTS Membranes

3.3.1.1 Choice of the Substrate

A large number of substrate materials have been used for polypyrrole synthesis (Chapter 1, Table 1.7). A primary criterion in membrane synthesis is that after the polymerisation, the polymer film must be able to be peeled off the substrate. Therefore, the adhesion between the polymer film and the substrate is very important. To investigate the suitability of different substrate materials, polymerisations were performed using different materials as the working electrode. The results (Table 3.2) show that with electroactive substrate materials such as lead, copper and iron, the polypyrrole was not formed on the substrate surface under the experimental conditions used since these materials can be oxidised at the potentials lower than that of the polymer formation. Using glassy carbon plate and carbon foil, polymer formation was good, but the film produced could not be peeled off these substrates. Gold foil produced polymer films that can be peeled off easily, but usually with a large amount of gold adhering to it. The polymer film could be peeled off both stainless steel and platinum without any damage but the operation was much easier in the case of stainless steel. Therefore, stainless steel was the preferred working electrode for polypyrrole membrane synthesis.
Table 3.2 Effect of substrate materials on electrosynthesis of polypyrrole membranes

<table>
<thead>
<tr>
<th>Substrate Materials</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>No Polymer was formed</td>
</tr>
<tr>
<td>copper</td>
<td>No Polymer was formed</td>
</tr>
<tr>
<td>iron</td>
<td>No Polymer was formed</td>
</tr>
<tr>
<td>Glassy Carbon plate</td>
<td>polymer cannot be peeled off</td>
</tr>
<tr>
<td>Carbon foil</td>
<td>polymer cannot be peeled off</td>
</tr>
<tr>
<td>Gold foil</td>
<td>polymer can be peeled off, but film always with gold adhering</td>
</tr>
<tr>
<td>Platinum</td>
<td>polymer can be peeled off</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>polymer can be peeled off</td>
</tr>
</tbody>
</table>

Notes: (1) All substrate materials were polished to a mirror finish; (2) The polymerisation solution was 0.2 M pyrrole and 0.03 M PTS; (3) Galvanostatic growth was employed. Current density 2.0mA/cm² and charge passed during polymerisation was 1.20C/cm².

3.3.1.2 Effect of Current Density and Composition of the Polymerisation Solution

In order to investigate the influence of these factors on membrane synthesis, experiments were carried out using various polymerisation solutions and applied current densities. The effect on the conductivity, tensile strength and the weight of the resultant membrane was investigated (Tables 3.3 to 3.5). These properties are the basic requirements for subsequent use of a membrane in electrochemical controlled transport. The polymer weight is directly related to the current efficiency since the same charge was passed during polymerisation.
Table 3.3 Effect of the applied current density and the composition of the polymerisation solution on polymer mass, conductivity and tensile strength

<table>
<thead>
<tr>
<th>Composition of polymerisation solution</th>
<th>Current Density (mA/cm²)</th>
<th>Tensile strength (MPa)</th>
<th>Conductivity (S/cm)</th>
<th>Polymer weight (x10⁴g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25</td>
<td>65-85</td>
<td>45-65</td>
<td>4.60 ± 0.10</td>
</tr>
<tr>
<td>0.1M Pyrrole and 0.05M PTS</td>
<td>0.50</td>
<td>65-80</td>
<td>45-75</td>
<td>5.00 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>60-95</td>
<td>40-80</td>
<td>5.19 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>70-90</td>
<td>45-75</td>
<td>4.75 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>65-95</td>
<td>50-80</td>
<td>4.35 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>65-90</td>
<td>40-60</td>
<td>4.88 ± 0.10</td>
</tr>
<tr>
<td>0.1M Pyrrole and 0.2M PTS</td>
<td>0.50</td>
<td>60-90</td>
<td>50-75</td>
<td>5.14 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>70-85</td>
<td>55-80</td>
<td>5.19 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>70-95</td>
<td>50-80</td>
<td>5.34 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>75-95</td>
<td>55-75</td>
<td>4.42 ± 0.10</td>
</tr>
</tbody>
</table>

Notes: (1) All membranes were prepared using the procedure described in Section 3.2; (2) The working electrode was a stainless steel plate; (3) The charge passed during polymerisation was controlled at 1.2C/cm².
**Table 3.4** Effect of the applied current density and the composition of the polymerisation solution on polymer mass, conductivity and tensile strength

<table>
<thead>
<tr>
<th>Composition of polymerisation solution</th>
<th>Current density (mA/cm²)</th>
<th>Tensile strength (MPa)</th>
<th>Conductivity (S/cm)</th>
<th>Polymer weight (x10⁴g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2M Pyrrole and 0.05M PTS</td>
<td>0.25</td>
<td>55-70</td>
<td>65-90</td>
<td>5.44 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>55-70</td>
<td>70-90</td>
<td>5.50 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>70-80</td>
<td>90-110</td>
<td>5.88 ± 0.05</td>
</tr>
<tr>
<td>0.05M PTS</td>
<td>4.00</td>
<td>65-80</td>
<td>95-120</td>
<td>5.83 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>65-85</td>
<td>90-115</td>
<td>5.66 ± 0.05</td>
</tr>
<tr>
<td>0.2M Pyrrole and 0.1M PTS</td>
<td>0.25</td>
<td>45-65</td>
<td>65-85</td>
<td>5.48 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>45-60</td>
<td>60-90</td>
<td>5.50 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>50-70</td>
<td>80-95</td>
<td>5.85 ± 0.06</td>
</tr>
<tr>
<td>0.1M PTS</td>
<td>4.00</td>
<td>55-70</td>
<td>90-95</td>
<td>5.88 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>55-70</td>
<td>80-100</td>
<td>5.72 ± 0.04</td>
</tr>
<tr>
<td>0.2M Pyrrole and 0.2M PTS</td>
<td>0.25</td>
<td>50-65</td>
<td>60-90</td>
<td>5.40 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>45-65</td>
<td>60-95</td>
<td>5.61 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>55-70</td>
<td>80-100</td>
<td>5.84 ± 0.10</td>
</tr>
<tr>
<td>0.2M PTS</td>
<td>4.00</td>
<td>50-70</td>
<td>80-105</td>
<td>5.98 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>55-75</td>
<td>85-105</td>
<td>5.69 ± 0.08</td>
</tr>
</tbody>
</table>

* Experimental conditions: see Notes, Table 3.3
<table>
<thead>
<tr>
<th>Composition of polymerisation solution</th>
<th>Current Density (mA/cm²)</th>
<th>Tensile Strength (MPa)</th>
<th>Conductivity (S/cm)</th>
<th>Polymer weight (x10⁴/g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4M Pyrrole and 0.05M PTS</td>
<td>0.25</td>
<td>40-55</td>
<td>65-95</td>
<td>5.45 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>40-50</td>
<td>70-95</td>
<td>5.46 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>45-60</td>
<td>85-125</td>
<td>5.89 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>4.00</td>
<td>50-60</td>
<td>85-120</td>
<td>6.02 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>55-65</td>
<td>85-120</td>
<td>6.16 ± 0.05</td>
</tr>
<tr>
<td>0.4M Pyrrole and 0.2M PTS</td>
<td>0.25</td>
<td>40-50</td>
<td>75-95</td>
<td>5.35 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>35-50</td>
<td>80-95</td>
<td>5.41 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>45-55</td>
<td>85-120</td>
<td>5.85 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>4.00</td>
<td>45-60</td>
<td>90-110</td>
<td>6.10 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>45-60</td>
<td>90-120</td>
<td>6.18 ± 0.10</td>
</tr>
<tr>
<td>0.4M Pyrrole and 0.4M PTS</td>
<td>0.25</td>
<td>35-45</td>
<td>80-90</td>
<td>5.39 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>40-50</td>
<td>85-100</td>
<td>5.45 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>40-55</td>
<td>95-120</td>
<td>6.00 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>4.00</td>
<td>40-55</td>
<td>95-125</td>
<td>6.05 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>45-65</td>
<td>90-110</td>
<td>6.10 ± 0.10</td>
</tr>
</tbody>
</table>

* Experimental conditions: see Notes, Table 3.3

**Effect of the Composition of the Polymerisation Solution**

The results shown in Table 3.3 to 3.5 indicate that for a given current density and constant pyrrole monomer concentration, counterion concentration had little effect on the membrane properties (conductivity and tensile strength) or the polymerisation efficiency. Under the same electrochemical conditions, an increase in the pyrrole monomer
concentration resulted in a decrease in the tensile strength of the membrane, an increase in the conductivity and in the polymer weight. The increase of the polymer weight indicates an increase in polymerisation efficiency.

**Effect of Applied Current Density**

For a given polymerisation solution, in most cases, an increase in applied current density resulted in a slight increase in the tensile strength and conductivity. When the pyrrole concentration was less than 0.2M, as the applied current density increased, the polymer weight initially increased and then decreased (Table 3.3 and 3.4). When a pyrrole concentration of 0.4M was used (Table 3.5), an increase in both the applied current density and the polymer weight occurred. These observations indicate that both applied current density and concentration of pyrrole monomer can influence the polymerisation efficiency.

**The Problems of Low Reactant Concentration**

The above results were obtained using high concentrations of reactants. Low concentrations of reactants were found to be unsuitable for use in membrane synthesis. In these experiments a batch of polymerisation solution was repeatedly used to form polypyrrole membranes. Firstly, using a solution of 0.05M or 0.001M pyrrole, the polymerisation efficiency decreased with number of times used, one batch of polymerisation solution (150ml) could produce only two or three membranes (Table 3.6). Secondly, the membranes produced under these conditions were always non-uniform and exhibited pin-holes.
Furthermore, these membranes were difficult to peel off the stainless steel substrate.

Table 3.6 Membrane synthesis using low concentration of reactants

<table>
<thead>
<tr>
<th>Number of membranes produced</th>
<th>Polymer weight ($10^4$g/cm²)</th>
<th>Polymer weight ($10^4$g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0.05 M pyrrole + 0.05M PTS)</td>
<td>(0.001M py + 0.05 M PTS)</td>
</tr>
<tr>
<td>1</td>
<td>4.13 ± 0.10</td>
<td>2.11 ± 0.23</td>
</tr>
<tr>
<td>2</td>
<td>4.09 ± 0.10</td>
<td>1.91 ± 0.21</td>
</tr>
<tr>
<td>3</td>
<td>3.93 ± 0.13</td>
<td>1.80 ± 0.20</td>
</tr>
<tr>
<td>4</td>
<td>3.65 ± 0.24</td>
<td>1.64 ± 0.25</td>
</tr>
<tr>
<td>5</td>
<td>3.51 ± 0.28</td>
<td>1.49 ± 0.28</td>
</tr>
</tbody>
</table>

All membranes were prepared using current density of 2.0mA/cm², and charge passed was controlled at 1.2C/cm².

3.3.1.3 Effect of Stirring the Polymerisation Solution

As described in Chapter 2, stirring the polymerisation solution influences the rate of polymerisation and the current efficiency.

The results in Table 3.7 were obtained under different hydrodynamic conditions. The solution was stirred by a home made-stirrer (see Figure 3.3). It was found that the polymer deposition efficiency decreased as the rotation rates increased at low current densities.

It was also found that formation of reproducible membranes was not possible using stirred solution conditions as the thickness of the membrane was not uniform. Also, during the polymerisation, the reaction of the auxiliary electrode generally produced H₂(g) and stirring the solution caused some small gas bubbles to be adsorbed onto the
working electrode surface, resulting in poor quality membranes as evidenced by the formation of pinholes and poor mechanical strength.

From this it was obvious that stirring the polymerisation solution was not suitable for membrane synthesis.

**Table 3.7 Effect of stirring the polymerisation solution**

<table>
<thead>
<tr>
<th>Rotation rate (rpm)</th>
<th>Current Density (mA/cm²)</th>
<th>Polymer weight (10⁴ g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.0</td>
<td>5.2 - 5.4</td>
</tr>
<tr>
<td>200</td>
<td>8.0</td>
<td>5.4 - 5.6</td>
</tr>
<tr>
<td>500</td>
<td>2.0</td>
<td>4.8 - 5.3</td>
</tr>
<tr>
<td>500</td>
<td>8.0</td>
<td>5.0 - 5.5</td>
</tr>
<tr>
<td>1000</td>
<td>2.0</td>
<td>3.1 - 4.9</td>
</tr>
<tr>
<td>1000</td>
<td>8.0</td>
<td>5.0 - 5.3</td>
</tr>
<tr>
<td>2000</td>
<td>2.0</td>
<td>2.1 - 3.2</td>
</tr>
<tr>
<td>2000</td>
<td>8.0</td>
<td>4.5 - 5.1</td>
</tr>
</tbody>
</table>

Note: Composition of polymerisation solution: 0.20M Pyrrole and 0.05M PTS. Current density: 2.0mA/cm², Charge passed: 0.12C/cm². Substrate: stainless steel

**Figure 3.3 Scheme of the stirrer**
3.3.1.4 Effect of the Polymerisation Solution pH

The results in Table 3.8 were obtained using different pH values for the polymerisation solution.

**Table 3.8 Effect of the initial solution pH**

<table>
<thead>
<tr>
<th>Initial Solution pH</th>
<th>0</th>
<th>5.6</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer weight</td>
<td>5.76 - 5.98</td>
<td>5.83-5.93</td>
<td>little polymer deposited</td>
</tr>
<tr>
<td>(10^4g/cm²)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength</td>
<td>60 - 85</td>
<td>70 - 80</td>
<td>-</td>
</tr>
<tr>
<td>(MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductivity (S/cm)</td>
<td>85-110</td>
<td>90-110</td>
<td>-</td>
</tr>
</tbody>
</table>

Notes: (1) The pyrrole concentration was fixed at 0.2M Current density was 2.9mA/cm² and charge passed during polymerisation was 1.2C/cm². Working electrode used was 4.5x6.0cm² stainless steel plate. (2) The solution was prepared using 0.05M PTS acid gives pH=0; and 0.05M PTS sodium salt gives pH = 5.6. pH = 12 was obtained by adding 0.01M NaOH to 0.05M PTS sodium salt solution.

The results show that for pH values of 0 and 5.6, the resulting membranes had very similar conductivities and tensile strengths. However, when the solution pH was 12, polymerisation was severely inhibited. Only a small amount of polymer deposited on the electrode and this was difficult to remove from the substrate.

3.3.2 Effect of the Counterion Employed during Membrane Synthesis

As described in Chapter 1, (Section 1.2.1.1), the properties of the conducting polymers are influenced by the nature of the counterion incorporated. A large range of anions have been successfully incorporated into polypyrrole (PP) during electrochemical polymerisation, but due to the special requirements of membrane synthesis, only a small range of anions can be used for this application.
An important factor in polypyrrole membrane synthesis is that after polymerisation, the resultant film must be able to be peeled off the substrate. Also, the PP film must be sufficiently robust to partition two solutions and to be used practically as a membrane.

In this section, a range of counterions with different functional groups were investigated with respect to the ability to produce polypyrrole membranes. All experiments were carried out galvanostatically using a current density of 2.0mA/cm$^2$ and charge passed was controlled at 1.2C/cm$^2$. All the polymerisation solutions contained 0.2M pyrrole and 0.05M counterion. The experimental conditions were chosen using the results in Chapter 2 and were deemed to be suitable, if not optimum, in all cases.

Initially, a range of small inorganic anions was considered (Table 3.9). It was found that under the experimental conditions employed, the polymer formed could not be peeled off the stainless steel electrode because these polymers were too soft.

<table>
<thead>
<tr>
<th>Counterion</th>
<th>Films</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$^-$</td>
<td>PP/F$^-$</td>
<td>Too soft, could not be peeled off the substrate</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>PP/Cl$^-$</td>
<td></td>
</tr>
<tr>
<td>Br$^-$</td>
<td>PP/Br$^-$</td>
<td></td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>PP/NO$_3^-$</td>
<td>without damage</td>
</tr>
<tr>
<td>HPO$_4^{2-}$</td>
<td>PP/HPO$_4^{2-}$</td>
<td></td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>PP/SO$_4^{2-}$</td>
<td></td>
</tr>
</tbody>
</table>
Some counterions based on benzoic acid were then investigated (Table 3.10). Except for p-Sulfobenzoic acid, the films were difficult to peel off the substrate since the polymers formed were brittle and adhered to the electrode.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Counterions</th>
<th>Comments on Mechanical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/BA</td>
<td><img src="image" alt="Benzoic acid" /></td>
<td>Brittle</td>
</tr>
<tr>
<td>PP/PTA</td>
<td><img src="image" alt="p-Toluic acid" /></td>
<td>Brittle</td>
</tr>
<tr>
<td>PP/BHA</td>
<td><img src="image" alt="p-Hydroxybenzoic acid" /></td>
<td>Brittle</td>
</tr>
<tr>
<td>PP/TPA</td>
<td><img src="image" alt="Terephthalic acid" /></td>
<td>Brittle</td>
</tr>
<tr>
<td>PP/SBA</td>
<td><img src="image" alt="p-Sulfobenzoic acid" /></td>
<td>good</td>
</tr>
</tbody>
</table>

Table 3.10 Effect of organic counterion

A series of sulfonated aromatic counterions were then tested. The results (Table 3.11) show that all polymers formed could be peeled off the substrate very easily and that all had adequate mechanical properties and conductivity. Also, these films were flexible. The later transport studies show that all these films could be used as a membrane.

It is difficult to relate differences in conductivity, tensile strength and adhesive properties of the membrane to the counterion employed, but in
most cases, free-standing polypyrrole membranes can be prepared using sulfonated aromatic counterions.

**Table 3.11. Preparation of Polypyrrole membranes using different counterions**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PP/BSA</th>
<th>PP/PTS</th>
<th>PP/EBS</th>
<th>PP/MS</th>
<th>PP/BS</th>
<th>PP/NPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counterions</td>
<td>SO$_3^-$</td>
<td>SO$_3^-$</td>
<td>SO$_3^-$</td>
<td>SO$_3^-$</td>
<td>SO$_3^-$</td>
<td>SO$_3^-$</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>17-23</td>
<td>70-80</td>
<td>60-70</td>
<td>36-47</td>
<td>40-55</td>
<td>40-50</td>
</tr>
<tr>
<td>Conductivity (S/cm)</td>
<td>19-20</td>
<td>90-110</td>
<td>90-110</td>
<td>50-70</td>
<td>47-70</td>
<td>50-70</td>
</tr>
</tbody>
</table>

BSA: Benzenesulfonic acid, sodium salt
PTS: p-Toluenesulfonic acid, sodium salt
EBS: 4-Ethylbenzenesulfonic acid
MS: 2-Mesitylenesulfonic acid
BS: 1,3-Benzenedisulfonic acid, disodium salt
NPS: 1,5-Naphthalenedisulfonic acid

3.3.3 Characterisation of Polypyrrole Membranes Using SEM

In this section, the membranes investigated were those described in Table 3.11 and those for use in subsequent transport studies.

3.3.3.1 Effect of Chemical Conditions during Polymerisation on the Surface Morphology of the Membrane

Many workers [90,95,107] have reported that the surface morphology of the polypyrrole film can be influenced by the growth conditions such as the monomer concentration, the counterion concentration and the ratio of two. Under the same electrochemical conditions and using PTS as the
counterion in all cases, changes in pyrrole concentration made significant differences to the resulting membrane surface morphology (Figure 3.4, 3.5 and 3.6). In all cases, the micrographs for the solution side of the membranes (the side exposed to solution during growth) revealed a "nodular morphology" and for the plate side (face to the electrode) a flat, smooth surface was observed. The nodular morphology may have been caused by polymer surface irregularities producing localised over-potentials so that the local current density might vary substantially from the electrode bulk current density. This would lead to more polymer being produced at sites of high current density giving rise to a rough, nodular surface morphology [107].

Another explanation of this may be three dimensional growth. After an initial stage of polymerisation, some polymer nuclei are formed on the electrode surface. The polymer growth at these active points is more efficient than others, and three dimensional growth results in the volume of these polymer nuclei becoming larger. This would result in the nodular morphology observed.

The solution side micrograph of the membrane prepared in low pyrrole concentration is presented in Figure 3.4(I). The morphology is smoother than others (Figure 3.5 (I) and 3.6(I)) over most of the surface area, but some spherical nodules are randomly situated across the surface. The plate side of the membrane morphology was smooth when 0.1M and 0.2M of pyrrole was employed (Figure 3.4(II) and 3.5(II)), but when 0.4M pyrrole was used, a pock-marked surface morphology was observed (Figure 3.6(II)). The pock-marked morphology suggest the film was less dense. This agrees with the results obtained from the mechanical tensile strength measurements (Table 3.3, 3.5).
Not all of the micrographs are shown here since there are some similarities between them. For instance, varying the PTS concentration in the range of 0.05M to 0.4M, produced membranes with similar surface morphology to that produced using 0.2M pyrrole and 0.05M PTS (Figure 3.5).

### 3.3.3.2 Effect of the Electrochemical Conditions Used during Polymerisation on the Membrane Morphology

The current density used during polymerisation has been reported to influence the polymer morphology [107]. Membranes were prepared using the same polymerisation solution (0.2M pyrrole + 0.05M PTS) but different applied current densities. The micrographs of these membranes are shown in Figure 3.5 to 3.9. With low current density (0.5mA/cm²) the micrograph of the solution side of the membrane reveals that small "hills" are present on the surface, while the plate side reveals a pockmarked morphology (Figure 3.7(I), (II)). When the current densities used were greater than 2.0mA/cm², the micrographs of the solution side membrane show a reduction in the size of the background nodules. However, the number and size of irregular shaped nodules present on the top of the background nodules appears to be increased (Figure 3.5(I) and 3.5(II), 3.9(I)).

The influence of the current density on the morphology of the plate side membrane was small. With high current densities (4.0mA/cm², 8.0mA/cm²), the micrograph (not shown) of the plate side of the membrane was similar as shown in Figure 3.5(II). With high pyrrole concentration, the effect of the current density on the morphology was the same as described above. A typical example is shown in Figure 3.10.
3.3.3.3 Effect of the Counterion on the Morphology

The literature states that the counterion employed during polymerisation has a strong influence on the polymer surface morphology [5,114,123].

In this work, all membranes were prepared in a solution containing 0.2M pyrrole and 0.05M counterion and a current density of 2.0mA/cm² was applied during synthesis. These conditions were chosen since they produced optimal results in studies done in Chapter 2. The micrographs of the membranes prepared in this work (Figure 3.5, 3.11 to 3.15) show that the counterions employed had a dramatic effect on the membrane surface morphology. Large differences between micrographs of PP/PTS and PP/BSA membranes were observed (Figure 3.5, 3.11). The solution side of the PP/BSA membrane revealed nodular morphology similar to the PP/PTS membrane but there were also some small undulations on the surface. The plate side of the PP/BSA membrane was by contrast, rough and porous. This is a surprising result as PTS and BSA are almost identical, with PTS having only an CH₃ group on the para position (Table 3.12). With the EBS molecule the methyl group (-CH₃) of a PTS molecule is replaced by an ethyl group (-CH₂CH₃). Even so, the micrographs of PP/EBS membrane (Figure 3.12) revealed qualitatively the same surface morphology as a PP/PTS membrane. The MS molecule has two more methyl groups than PTS, but the surface morphology of the membrane produced was similar (Figure.3.13(I) and (II)). The micrographs of PP/MS show that the plate side of the membrane (Figure 3.13(II)) had a very similar surface morphology to that observed with the PP/PTS membrane. The solution side (Figure 3.13(I)) revealed a nodular morphology, with some spherical growths randomly distributed on the top of the background nodule surface.
BS is a doubly charged anion and the solution side of the resultant PP/BS membrane is smoother than all others (Figure 3.14(I)), but again spherical growth exist on the surface. The plate side (Figure 3.14(II)) is smooth, and porous, but with a pore size much smaller than in the case of PP/BSA. NPS is also a doubly charged anion, but the solution side of the PP/NPS membrane was different from PP/BS. A much rougher surface with a large spherical nodules was observed (Figure 3.15(I)). However, the plate side of the membrane (Figure 3.14(II)) was qualitatively the same as PP/BS.

From these observations, it can be concluded that if the counterion used was more hydrophobic than PTS, the plate side of the membrane prepared using these counterions was always smooth and non-porous. The effect on the solution side morphology was more complicated, and it was difficult to relate these to the chemical structure of the counterion employed.

Figure 3.4 Scanning Electron micrographs of a PP/PTS membrane. Current density: 2.0mA/cm² Polymerisation solution: 0.1 M pyrrole +0.05M PTS. (I) solution side; (II) plate side.
Figure 3.5 Scanning Electron micrographs of a PP/PTS membrane. Current density: 2.0 mA/cm² Polymerisation solution: 0.2 M pyrrole + 0.05M PTS. (I) solution side; (II) plate side.
Figure 3.6 Scanning Electron micrographs of a PP/PTS membrane. Current density: 2.0mA/cm² Polymerisation solution: 0.4 M pyrrole +0.05M PTS. (I) solution side; (II) plate side.
Figure 3.7 Scanning Electron micrographs of a PP/PTS membrane. Current density: 0.5mA/cm² Polymerisation solution: 0.2 M pyrrole +0.05M PTS. (I) solution side; (II) plate side.
Figure 3.8 Scanning Electron micrographs of a PP/PTS membrane (solution side). Current density: 4.0 mA/cm$^2$ Polymerisation solution: 0.2 M pyrrole +0.05M PTS.

Figure 3.9 Scanning Electron micrographs of a PP/PTS membrane (solution side). Current density: 8.0 mA/cm$^2$ Polymerisation solution: 0.2 M pyrrole +0.05M PTS.
Figure 3.10 Scanning Electron micrographs of a PP/PTS membrane. Current density: 8.0mA/cm² Polymerisation solution: 0.4 M pyrrole +0.4M PTS. (I) solution side; (II) plate side.
Figure 3.11 Scanning Electron micrographs of a PP/BSA membrane. Current density: 2.0mA/cm² Polymerisation solution: 0.2 M pyrrole +0.05M BSA. (I) solution side; (II) plate side.
Figure 3.12 Scanning Electron micrographs of a PP/EBS membrane. Current density: 2.0mA/cm$^2$ Polymerisation solution: 0.2 M pyrrole +0.05M EBS. (I) solution side; (II) plate side.
Figure 3.13 Scanning Electron micrographs of a PP/MS membrane. Current density: 2.0 mA/cm$^2$ Polymerisation solution: 0.2 M pyrrole +0.05M MS. (I) solution side; (II) plate side.
Figure 3.14 Scanning Electron micrographs of a PP/BS membrane. Current density: 2.0mA/cm$^2$ Polymerisation solution: 0.2 M pyrrole +0.05M BS. (I) solution side; (II) plate side.
Figure 3.15 Scanning Electron micrographs of a PP/NPS membrane. Current density: 2.0mA/cm² Polymerisation solution: 0.2 M pyrrole +0.05M NPS. (I) solution side; (II) plate side.
3.3.4 Membrane Composition

Elemental analysis (carried out at Australian National University) was used to determine the membrane composition (Table 3.12). It was found that for all singly charged counterions, the ratio of the pyrrole unit to the counterion was about 3 to 1 and for doubly charged counterions, the ratio was about 6 to 1.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>Py/C- (mole ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PTS</td>
<td>58.50</td>
<td>4.43</td>
<td>10.97</td>
<td>6.90</td>
<td>3.64</td>
</tr>
<tr>
<td>PP/BSA</td>
<td>57.10</td>
<td>3.88</td>
<td>11.04</td>
<td>7.77</td>
<td>3.31</td>
</tr>
<tr>
<td>PP/EBS</td>
<td>59.21</td>
<td>4.58</td>
<td>10.25</td>
<td>7.73</td>
<td>3.03</td>
</tr>
<tr>
<td>PP/MS</td>
<td>58.79</td>
<td>4.94</td>
<td>9.62</td>
<td>7.08</td>
<td>3.11</td>
</tr>
<tr>
<td>PP/BS</td>
<td>50.79</td>
<td>3.65</td>
<td>9.75</td>
<td>7.42</td>
<td>5.9</td>
</tr>
<tr>
<td>PP/NPS</td>
<td>51.78</td>
<td>3.62</td>
<td>10.73</td>
<td>8.01</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Note: (1) The ratio of pyrrole units to counterion was calculated as in reference [194].
(2) The experimental conditions used for these membranes preparation was the same as used in Table 3.11.

3.3.5 Membrane Permeability

The permeability of both PP/PTS and PP/NPS membranes was measured by cross-section filtration experiments. The results (Table 3.13) indicate that both membranes were nonporous since the volume flux observed was extremely small (indeed much smaller than the normal commercial nonporous membrane, which has a volume flux of about 50L/m² day) with a very high salt rejection.

The PP/PTS membrane had a lower volume flux and a higher solute rejection than that observed for a PP/NPS membrane indicating that the
pore size of the PP/PTS membrane was smaller than that of PP/NPS membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Volume Flux (L m⁻² day⁻¹)</th>
<th>Solute Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PTS</td>
<td>3.6 ± 1.0</td>
<td>95 - 98</td>
</tr>
<tr>
<td>PP/NPS</td>
<td>6.0 ± 1.0</td>
<td>87 - 91</td>
</tr>
</tbody>
</table>

3.4 CONCLUSION

A range of polypyrrole free-standing membranes has been successfully synthesised galvanostatically by incorporation of a series of sulphonated aromatic counterions (Table 3.11). Some parameters that effect the membrane synthesis have been investigated. The following conclusions can be made:

1) The substrate material employed plays a critical role in the formation of polypyrrole free-standing membranes. Stainless steel is suitable as the working electrode for the preparation of the free-standing membranes containing sulfonated aromatic counterions.

2) The composition of the polymerisation solution for membrane synthesis should contain a relatively high concentration of the reactants (monomer and counterions). A solution containing 0.2M pyrrole and 0.05M counterion can be used for the free-standing membrane synthesis by incorporating sulfonated aromatic counterions. Also, a large ratio between the
polymerisation solution volume \( (V) \) and working electrode area \( (A) \) is required.

(3) The polymer deposition efficiency is slightly dependent on the current density employed, in the range of 2.5-8.0 mA/cm\(^2\).

(4) In the case of electrochemical synthesis, reproducible membranes can be obtained when the polymerisation is carried out under non-stirred conditions.

(5) It was found that membranes can be prepared when the polymerisation solution pH is lower than pH = 5.6.

(6) The counterion employed has a strong influence on the membrane properties. The small inorganic counterions or ones based on benzoic acid investigated in this work were not suitable for making free-standing polypyrrole films.

(7) Membrane composition has been determined using elemental analysis. The pyrrole unit to counterion ratio can be calculated from elemental analysis data. For all membranes containing a singly charged sulfonated aromatic counterion, this ratio is about 3 to 1 and for double charged counterions is about 6 to 1.

(8) The polypyrrole membranes prepared using sulfonated aromatic counterions employed in the work are non-porous. Their permeability is less than 10 L/m\(^2\) day and about 90\% of the solute is rejected.
CHAPTER 4

ELECTROCHEMICAL PROPERTIES OF POLYPYRROLE FILMS
4.1 INTRODUCTION

It has been shown in Chapter 3 that the nature of the incorporated counterion usually has a strong influence on the physical characteristics of the polymer [114,129,131,132]. However, it also affects the chemical and electrochemical properties of the polymer. For example, ion exchange (ion incorporation and expulsion) properties of the polymer vary greatly depending on the nature of the incorporated counterion [111,127,195-197].

By incorporation of immobile anions, polypyrrole films with fixed negative charged sites have been successfully prepared [127]. These polymers possess cation exchange properties. By incorporation of dodecylsulphate, the ion exchange properties of the polymer can be switched from an anion exchanger to a cation exchanger by application of a potential [127].

To investigate the ion incorporation and expulsion properties of conducting polymers, electron probe microanalysis [111], quartz crystal microbalance [196] and electrochemical methods [127] have been reported to be useful. All these investigations suggest that changes in the redox states of the polymer are always accompanied by ion movement in and out of the polymer (ion exchange).

In the case of electrochemically controlled transport, the conducting polymer membrane is used as a working electrode. When the redox state of the membrane is varied, ion movement in and out of the membrane may be used to induce transport across the membrane. The same electrochemical reactions are applicable in conducting polymer membrane systems as for a normal electrochemical cell.
The major purpose of this chapter is to investigate the ion incorporation and expulsion properties of polypyrrole films. The techniques used in this chapter are cyclic voltammetry and chronoamperometry. In order to investigate the kinetic properties of the system, experiments were carried out under both static and stirred conditions. Various counterions were employed for polymer synthesis and a range of supporting electrolytes were considered.

4.2 EXPERIMENTAL

4.2.1 Reagents and Solutions

All chemicals used as the supporting electrolytes were AR grade. All counterions used for the preparation of polypyrrole were commercial supplied and used as received. Pyrrole (SIGMA) was freshly distilled before use. All solutions were made up with type 1 Milli-Q deionised water (18MΩ cm). The polymerisation solutions were prepared by dissolving 0.20M pyrrole and 0.05M counterion in Milli-Q water.

All electrolyte solutions were prepared by dissolving 0.20M electrolyte in Milli-Q water.

4.2.2 Instrumentation

Cyclic voltammetry and chronoamperometric experiments were carried out using a BAS-100A Electrochemical Analyser. A galvanostat (Faculty Science workshop, University of Wollongong) was used for the electropolymerisation of pyrrole. A single compartment, three electrode electrochemical cell was used throughout this work. The auxiliary
electrode was a piece of platinum mesh (1.2 x 7.0 cm, 100 lines/inch), and a BAS Ag/AgCl (3M NaCl) reference electrode together with a double junction salt bridge was employed.

The working electrode used for both electropolymerisation and electrochemical studies was a rotating disc electrode (manufactured in 7th Shan dong Dian Xun Chang, China) with a glassy carbon disc (d=4.0mm). The electrode used for electrochemical polymerisation was pretreated as described in chapter 3.

4.2.3 Preparation of the Polymer Coated Electrode

For electrochemical studies, the working electrode was prepared by electrochemically deposition of polypyrrole onto a glassy carbon disc electrode.

In all cases, the polymerisation was carried out galvanostatically using a current density of 2.0mA/cm². The amount of the polymer deposited was controlled by monitoring the amount of charge passed during the polymerisation. It was controlled at 0.12 C/cm² unless otherwise stated. After the polymerisation, the electrode was carefully rinsed with Milli-Q water to remove all surface liquids.
4.3 RESULTS AND DISCUSSION

4.3.1 Cyclic Voltammetry

4.3.1.1 Effect of the Cation in the Electrolyte Solution

In this section of work, a PP/PTS coated glassy carbon working electrode was employed. In order to determine the effect of the cation in the electrolyte solution on the cyclic voltammetry (CV) responses, the anion in the electrolyte solution was fixed (Cl⁻) and the cation was varied.

Figure 4.1 shows CVs recorded in 0.2M of KCl, NaCl, and CaCl₂. It was found that the shape of the voltammograms in regions 3 and 4 did not change much when the cation was varied, but the responses in region 1 and 2 were markedly affected by the nature of the cations employed. The current observed in regions 1 and 2 for K⁺ was larger than for Na⁺ or Ca²⁺. In fact when Ca²⁺ was used, the current peaks in region 1 and 2 did not appear. Also, the responses in region 1 and 2 were found to be related to each other: if one was large, the other was also large. The behaviour observed was indicative of a reversible redox couple.

These observations indicate that the responses in region 1 and 2 are sensitive to changes of the cation in the supporting electrolyte solution. Since all cations used were electroinactive species, it is reasonable to suppose that the cation was involved in the redox reaction of the polymer by moving into (incorporation) and out of the polymer (expulsion) due to:

Reduction Reaction

\[
PP^+C^-_{(film)} + M^+_{(solution)} + e \rightarrow PP^0C^-M^+_{(film)} \quad (4.1)
\]

Oxidation Reaction
where \( \text{PP}^+ \) and \( \text{PP}^0 \) are the oxidised and reduced forms of polypyrrole respectively; \( \text{C}^- \) is the counterion incorporated during electropolymerisation and \( \text{M}^+ \) is the cation present in the electrolyte solution.

The above reactions take place because the mobility of the counterion (PTS) is much lower than the cation so when the polymer is reduced or oxidised charge balance is achieved predominantly via cation movement into and out of the polymer.

In a cyclic voltammogram, the current integral is a measure of the extent of a particular electrochemical reaction. The corresponding potential indicates the energy required for the reaction to take place and the potential difference (\( \Delta \text{Ep} = \text{Ep}_a - \text{Ep}_c \)) indicates the reversibility or otherwise of the reaction.

In Figure 4.1, the current integrals observed in regions 1 and 2 were in the order of \( \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} \) indicating that the amount of \( \text{K}^+ \) being incorporated and expelled was larger than for \( \text{Na}^+ \) or \( \text{Ca}^{2+} \). Also, the cation incorporation peak potentials (region 1) were shifted slightly to more negative potentials when the cations employed was varied from \( \text{K}^+ \) to \( \text{Na}^+ \) and \( \text{Ca}^{2+} \). This indicates that the \( \text{K}^+ \) ion is more readily incorporated. The reversibility of the \( \text{K}^+ \) ion's incorporation and expulsion reactions was similar to that observed for the \( \text{Na}^+ \) ion since the \( \Delta \text{Ep} \) observed was similar. In addition to the above, the mobility of the cations is in the order: \( \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} \) [198]. The current responses in regions 1 and 2 observed was in the same order. This therefore suggests that the reactions (4 - 1) and (4 - 2) are dependent on the cation mobility.
Figure 4.1 Cyclic voltammograms of a PP/PTS coated glassy carbon electrode in (a) 0.2M KCl, (b) 0.2M NaCl and (c) 0.2M CaCl₂. Scan rate=20mV/s. The polymer was grown for 1.0 minute at 2.0 mA/cm² from 0.2M pyrrole in 0.05M PTS. Dot line: 1st cycle; Dense line: 5th cycle.
4.3.1.2 Effect of the Anion in the Electrolyte Solution

In order to determine the effect of the anion in the electrolyte solution on the cyclic voltammetric responses, the cation was fixed using Na\(^+\) and the anion was varied. All anions were soluble in water and electroinactive in the potential range investigated. The cyclic voltammograms in Figure 4.2 were recorded from 0.2M of various electrolyte solutions, the working electrode used was the same as used in Figure 4.1.

![Cyclic voltammograms](image)

**Figure 4.2** Cyclic voltammograms of a PP/PTS coated glassy carbon electrode in 0.2M of (a) NaNO\(_3\), (b) Na\(_2\)CO\(_3\), (c) Na\(_2\)SO\(_4\), (d) BSA, (e) PTS and (f) DS. Scan rate=20mV/s. The polymer was grown for 1.0 minutes at 2.0mA/cm\(^2\) from 0.2M pyrrole in 0.05M PTS. Dot line: 1st cycle; Dense line: 5th cycle.
These CVs reveal that the shape of the curves in regions 1 and 2 did not change much when using a singly charged anion solution (Figure 4.1(b) and Figure 4.2(a),(d),(e),(f)). In all cases however, the responses observed in regions 3 and 4 were dramatically influenced by the anions employed, with an increase in the size of the anions (decrease in the mobility) resulting in decreased current responses. These observations indicated that the responses in regions 3 and 4 are sensitive to the anion employed. The reactions occurring may be described as:

**Reduction Reactions:**

\[ PP^+C^-_{(film)} + e \rightarrow PP^0_{(film)} + C^-_{(solution)} \]  \hspace{1cm} (4.3)

\[ PP^+A^-_{(film)} + e \rightarrow PP^0_{(film)} + A^-_{(solution)} \]  \hspace{1cm} (4.4)

**Oxidation Reactions:**

\[ PP^0_{(film)} C^-_{(solution)} - e \rightarrow PP^+C^-_{(film)} \]  \hspace{1cm} (4.5)

\[ PP^0_{(film)} + A^-_{(solution)} - e \rightarrow PP^+A^-_{(film)} \]  \hspace{1cm} (4.6)

Where \( A^- \) is the anion present in the solution.

Which of these reactions occurs is dependent on the anion and counterion mobility (or size) and concentrations. When larger organic anions in solution were employed (curve (d),(e), and (f)), a very small current response in regions 3 and 4 was observed indicating anion incorporation and expulsion reactions were inhibited. This is because both counterion and anion have a small mobility. In these cases, as described above, the charge balance achieved was due to cation incorporation and expulsion (equations (4-1) and (4-2)).
In the cases of small inorganic anions present in the solution (Figure 4.1(b) and Figure 4.2(a)), large current responses in regions 3 and 4 were observed. Two major suggestions can be made from these observations: either the current responses were mainly due to anion incorporation and expulsion (equation (4-4) and (4-6)), or that the amount of anion (A\textsuperscript{-}) incorporated was much more than that counterion (C\textsuperscript{-}) being expelled. When a positive enough potential is applied, it causes the density of the positive charge on the polymer backbone to increase such that additional anions are required. Even if the counterion is fixed in the polymer matrix (such as DS) the reactions (4-4) and (4-6) can still be observed when a small inorganic anion is employed. Also, there is very little opportunity for the reaction (4-5) to take place since normally the concentration of A\textsuperscript{-} is much higher than C\textsuperscript{-} in the solution.

In the presence of doubly charged anions (Figure 4.2,(b),(c)), the sharp cation incorporation peak was not present indicating that cation responses can be influenced by the anions employed (and vice versa). These anions can be incorporated into the polymer matrix (equation 4.6), and the mobility of these anions is not as high as the small inorganic anions (such as Cl\textsuperscript{-}), so they will remain in the polymer matrix resulting in the cation incorporation process becoming more complicated (because the mobility of C\textsuperscript{-} and A\textsuperscript{-} was different).

4.3.1.3 Effect of the Counterion Employed during Polymerisation on the Current Responses in the Regions 1 and 2 of Cyclic Voltammograms

In this section, various counterions were employed for polypyrrole synthesis. For each polymer electrode, the cyclic voltammetric
experiments were performed using solutions containing various cations, the anion being fixed (using Cl\textsuperscript{-}). The results (Figure 4.1, Figure 4.3 to 4.6) reveal that the voltammetric responses were strongly influenced by the counterion employed. It was found that for a given polymer electrode, the variation of the counterions had the same effect on the cyclic voltammetric responses as was discussed in section 4.3.1.1. This confirmed the idea that the responses in regions 1 and 2 were mainly due to cation incorporation and expulsion (equation (4-1), (4-2)). For a given electrolyte solution, an increase in the mobility of the counterion resulted in a decrease in the current responses in regions 1 and 2, and an increase for those in regions 3 and 4.

If the size of the counterion was larger that PTS, the current integral (peak area) in regions 1 and 2 observed was larger than that observed using a PP/PTS electrode. Conversely, the current integral in regions 3 and 4 was smaller than that observed using a PP/PTS electrode.

For Ca\textsuperscript{2+} containing solutions, (an increase in the size of the counterion), the current integral in regions 1 and 2 observed increased dramatically (Figure 4.3(c), 4.4(c)). This effect could be because a larger counterion produced a polypyrrole film with a large pore size, allowing Ca\textsuperscript{2+} to easily diffuse into the polymer. Also, large counterions generally have low mobility, and therefore the counterion diffuses slowly away when the polymer was reduced. Consequently, the charge balance is more readily achieved by the cation moving into the polymer. This results in increased cation incorporation responses. With small inorganic counterions (such as Cl\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-}-Figure 4.5, 4.6), very small current responses in regions 1 and 2 were observed. This was because these small counterions have a high mobility. In these cases, charge balance was achieved predominantly by the counterions moving into and out of
the polymer (equation (4-3) to (4-6)). The large current responses observed in regions 3 and 4 support this conclusion.

Figure 4.3 Cyclic voltammograms of a PP/NPS coated glassy carbon electrode in (a) 0.2M KCl, (b) 0.2M NaCl and (c) 0.2M CaCl$_2$. Scan rate=20mV/s. The polymer was grown for 1.0 minute at 2.0mA/cm$^2$ from 0.2M pyrrole in 0.05M NPS. Dot line: 1st cycle; Dense line: 5th cycle.
Figure 4.4 Cyclic voltammograms of a PP/DS coated glassy carbon electrode in (a) 0.2M KCl, (b) 0.2M NaCl and (c) 0.2M CaCl₂. Scan rate=20mV/s. The polymer was grown for 1.0 minute at 2.0mA/cm² from 0.2M pyrrole in 0.05M DS. Dot line: 1st cycle; Dense line: 5th cycle.
Figure 4.5 Cyclic voltammograms of a PP/Cl-coated glassy carbon electrode in (a) 0.2M KCl, (b) 0.2M NaCl and (c) 0.2M CaCl₂. Scan rate=20mV/s. The polymer was grown for 1.0 minute at 2.0mA/cm² from 0.2M pyrrole in 0.05M Cl⁻. Dot line: 1st cycle; Dense line: 5th cycle.
Figure 4.6 Cyclic voltammograms of a PP/NO$_3^-$-coated glassy carbon electrode in (a) 0.2M KCl, (b) 0.2M NaCl and (c) 0.2M CaCl$_2$. Scan rate=20mV/s. The polymer was grown for 1.0 minute at 2.0mA/cm$^2$ from 0.2M pyrrole in 0.05M NO$_3^-$· Dot line: 1st cycle; Dense line: 5th cycle.
4.3.1.4 Effect of the Counterion Employed during Polymerisation on the Current Responses in the Regions 3 and 4 of Cyclic Voltammograms

In this section, the preparation of polypyrrole coated electrodes was as described in section 4.3.1.3. In order to investigate the influence of the counterion on the anion responses, the cation was fixed using Na\(^+\) and various anions were employed.

For a given polymer electrode, the voltammograms in Figure 4.7 to 4.10 suggest that an increase in the size of the anion in the solution resulted in a decrease in the current responses in ranges 3 and 4. This is in agreement with the observation using the PP/PTS electrode.

For a given electrolyte solution, changes in the counterion had a dramatic effect on the cyclic voltammetric responses. For example, the voltammograms recorded in a PTS sodium salt solution (Figure 4.2(e), 4.7(b), 4.8(a), 4.9(f) and 4.10(d)) an increased current response in regions 3 and 4 was observed with increasing size of the counterion. This may be due to the fact that the larger counterions formed polypyrrole films with a larger pore size allowing anion incorporation and expulsion to take place more easily.

For polymer films prepared using organic counterions, the large current responses in regions 3 and 4 were observed only when small inorganic anions were used (Figure 4.1(b), 4.3(b), 4.4(b)). If the anion size was similar to the counterion size then smaller current responses were found (Figure 4.2, 4.7, 4.8). This suggests that the mobility of these counterions in the polymer matrix was small, and that the anion responses in regions 3 and 4 were mainly due to anion (in the solution) incorporation and expulsion (equation (4-4), (4-6)).
With small inorganic counterions, (Figure 4.9, 4.10) when the size of the anion in the solution was similar, or even large than the counterion in the polymer (Figure 4.9(b), (c)), large current responses in regions 3 and 4 can still be observed. This may be explained by the high mobility of these small inorganic counterions in the polymer matrix.

Figure 4.7 Cyclic voltammograms of a PP/NPS coated glassy carbon electrode in 0.2M of: (a) BA, (b) PTS and (c) DS. Scan rate=20mV/s. The polymer was grown for 1.0 minute at 2.0mA/cm² from 0.2M pyrrole in 0.05M NPS. Dot line: 1st cycle; Dense line: 5th cycle.
Figure 4.8 Cyclic voltammograms of a PP/DS coated glassy carbon electrode in 0.2M of: (a) PTS, (b) NPS and (c) DS. Scan rate=20mV/s. The polymer was grown for 1.0 minute at 2.0mA/cm² from 0.2M pyrrole in 0.05M DS. Dot line: 1st cycle; Dense line: 5th cycle.
Figure 4.9 Cyclic voltammograms of a PP/Cl-coated glassy carbon electrode in 0.2M of: (a) NaCl, (b) NaBr (c) NaNO₃, (d) Na₂SO₄, (e) BA, (f) PTS and (g) DS. Scan rate=20mV/s. The polymer was grown for 1.0 minute at 2.0mA/cm² from 0.2M pyrrole in 0.05M Cl⁻. Dot line: 1st cycle; Dense line: 5th cycle.
Figure 4.10 Cyclic voltammograms of a PP/NO$_3^-$-coated glassy carbon electrode in 0.2M of: (a) NaCl, (b) NaNO$_3$, (c) BA, (d) PTS and (e) DS. Scan rate=20mV/s. The polymer was grown for 1.0 minute at 2.0mA/cm$^2$ from 0.2M pyrrole in 0.05M NO$_3^-$. Dot line: 1st cycle; Dense line: 5th cycle.
4.3.1.5 Ion Exchange Properties of the Polypyrrole Films

As described above, during the redox cycling some anion in the solution can be incorporated into the polymer (equations (4-3) to (4-4)). This resulted in the composition of the polymer being changed with some new counterions being included. In this section, the effect of the new counterion on the electrochemical behaviour is discussed. An interesting trend can be observed from Figures 4.1 to 4.10. It was found that the current responses for the first cycle of the voltammogram were related to the size difference between the counterion (C\textsuperscript{-}) in the polymer matrix and the anion (A\textsuperscript{-}) in the electrolyte solution. When the size of the counterion was larger than the size of the anion present in the solution, (For example in Figure 4.1, 4.3, 4.4 and 4.2 (a) to 4.2(d)), the current observed for the first cycle of the voltammograms in region 4 was always smaller than that observed in later cycles. When the anion was larger than the counterion, (for examples, Figure 4.2(f), 4.77(c), 4.9(d) to 4.9(g) and 4.10(c) to 4.10(e)), the current observed during the first cycle in region 4 was always larger than that seen in later cycles. This is evidence that anions can be introduced into the polymer. As described above, the responses in region 4 corresponds to anion expulsion (equation (4-3),(4-4)). During the first redox cycle, only C\textsuperscript{-} is present in the polymer and A\textsuperscript{-} exists only in the solution. When C\textsuperscript{-} is larger and hence less mobile than A\textsuperscript{-}, then during this first cycle, the anion expulsion reaction can only be due to the expulsion of C\textsuperscript{-} into the solution (equation 4-3). After this, A\textsuperscript{-} is present in the polymer (due to anion exchange) and is the dominant anion (because of the large concentration of A\textsuperscript{-} in the solution). Therefore, during second and subsequent cycles the anion expulsion reactions occurring will be mainly due to A\textsuperscript{-} movement back into the solution (equation 4-4). Because A\textsuperscript{-} is more mobile than C\textsuperscript{-} then
one would expect a greater anion movement (region 4) to be seen for later cycles compared with the first cycle. This is what is observed in the voltammogram in Figure 4.1, 4.2 (a) to (d), 4.3 and 4.4.

Similarly, when C\textsuperscript{−} was smaller than A\textsuperscript{−} and hence more mobile, reaction (4-3) occurring during the first redox cycling resulted in a larger current in region 4 for the first cycle of the voltammogram. In later cycles, most of the C\textsuperscript{−} is replaced by A\textsuperscript{−} which has a low mobility and hence is very difficult to expel. This would result in smaller currents in region 4 being observed in later cycles. This also indicates that reaction (4-5) was not favoured. If reaction (4-5) had occurred, the current in region 4 for later cycles would have remained at the same value as the first cycle.

When small inorganic counterions (C\textsuperscript{−}) and organic anions (A\textsuperscript{−}) were employed (Figure 4.9(d) to (g) and 4.10(c) to (e)), it was found that the cation incorporation and expulsion peaks clearly existed in regions 1 and 2; however, when a small inorganic anion (A\textsuperscript{−}) was employed, the peaks observed in regions 1 and 2 were much less significant (Figure 4.9(a) to (c), 4.10(a) and (b)). This was because C\textsuperscript{−} had been replaced by A\textsuperscript{−}, and A\textsuperscript{−} was difficult to expel since A\textsuperscript{−} has low mobility, and the charge balance achieved was then due to cation incorporation and expulsion.

These reactions could be described as in equations 4.3, 4.6 as follows:

\textbf{Reduction Reaction:}

\[
PP + A^{-}_{(film)} + M^+ + e \rightarrow PP^0 A^- M^+_{(film)}
\]  

\textbf{Oxidation Reaction:}
In this part of the work, a rotating disc electrode was employed. Cyclic voltammograms (Figure 4.11) were recorded in 0.2M KCl solution using a rotation rate of 2000 rpm. It was found that the characteristics of the responses in regions 3 and 4 were very similar to those observed under static conditions, but a marked change in regions 1 and 2 was observed. When the electrode was rotated, the peak width in region 1 increased and the cathodic current at the switching potential (-1.0V) remained at a high value. These observations could be due to mass transport being improved when the electrode was rotated. Also, the cation expulsion peak height and peak area observed in region 2 increased. These same effects were observed when the voltammograms were recorded in NaCl solution. Experiments in CaCl$_2$ solution (Figure 4.12) showed that the cation incorporation peak height and peak area observed in region 1 were dramatically increased as the rotation of the electrode was increased. However, the increase in the rotation rate did not cause an increase in the peak height; it only caused the increase in the peak width and the current value at the switching potential (-1.0V). Also, the peak potentials ($E_{pc}$) observed were about -0.45V, and this value was much more positive than that observed for K$^+$($E_{pc} = -0.71$V).

This suggests that the energy required for the Ca$^{2+}$ incorporation was much less than the K$^+$ incorporation as suggested previously [199]. All these observations indicate that as the mobility of the Ca$^{2+}$ ion both in the solution and in the polymer matrix was lower, with the incorporation process being limited by mass transfer. Mass transfer can be divided into

$$PP^0A^-M^+_{(film)} - e \rightarrow PP^+A^-_{(film)} + M^+_{(solution)} \quad (4.8)$$
two different parts: mass transport across the double layer from the bulk solution and mass transfer through the polymer matrix. If one of these steps is slow, this will result in the system being limited by mass transfer. Figure 4.12 illustrates this point. Under static conditions (4.12(a)), there is no Ca\(^{2+}\) incorporation peak as mass transfer is the limiting step in the process. By rotating the electrode, however, the Nernst layer thickness is reduced and mass transfer no longer is the limiting step. This is reflected in the increasing cation incorporation responses with increased rotation rate.

\textit{Figure 4.11} Cyclic voltammograms of a PP/PTS coated glassy carbon electrode in a 0.2M KCl solution. Scan rate=20mV/s.; Rotation rate=2000rpm; The polymer was grown for 1.0 minute at 2.0mA/cm\(^2\) from 0.2M pyrrole in 0.05M PTS.
Voltammograms recorded in a larger anion containing solution show that the electrode rotation caused an increase in both cation and anion responses. Results using NaPTS as electrolyte are shown in Fig. 4.13.

Rotating electrode studies show that with organic counterions such as BSA, EBS, MS and NPS in the polymer, the effect of stirring was similar to that observed with PTS. In the case of small inorganic counterions such as $F^-$, $Cl^-$, $Br^-$, $NO_3^-$, however, rotation causes an increase in the cation incorporation response. A typical example is given in Figure 4.14. If we consider that the rotation of the electrode has only a small effect on the mass transfer inside of the polymer matrix but a large effect on the mass transfer across the Nernst layer, then these results can be explained.

**Figure 4.12** Cyclic voltammograms of a PP/PTS coated glassy carbon electrode in a CaCl$_2$ solution. Scan rate=20mV/s; Rotation rate: (a) 0 rpm, (b) 100rpm, (c) 1000rpm and (d) 5000rpm. The polymer was grown for 1.0 minute at 2.0mA/cm$^2$ from 0.2M pyrrole in 0.05M PTS.
Figure 4.13 Cyclic voltammogram of a PP/PTS coated glassy carbon electrode in 0.2M PTS solution. Scan rate=20mV/s, Rotation rate=2000rpm. The polymer was grown for 1.0 minute at 2.0mA/cm² from 0.2M pyrrole in 0.05M PTS.

Figure 4.14 Cyclic voltammograms of a PP/Cl-coated glassy carbon electrode in a 0.2M NaCl. Scan rate=20mV/s; (a) static and (b) Rotation rate=2000rpm. The polymer was grown for 1.0 minutes at 2.0mA/cm² from 0.2M pyrrole in 0.05M Cl⁻.
4.3.2 Chronoamperometry

Figure 4.15 shows the chronoamperometric responses for a PP/PTS coated glassy carbon electrode in a 0.2M KCl solution. A pulsed potential with pulse width of 500ms and pulse range between +0.7V to -1.0V was employed. It was found that with a positive potential step (-1.0V → 0.70V), the anodic responses observed were not influenced by the electrode rotation. However, for the negative potential step (0.7V → -1.0V), when the electrode was rotated a noticeable difference in the cathodic responses (curve (a)) was observed. Compared with the static case (curve (b)), the current decay is much slower and forms a "shoulder" on the current-time curve. The width of the shoulder can be denoted as the "transition time" T. T must correspond to a physical or chemical process.

![chronoamperometric responses](image)

**Figure 4.15** Chronoamperometric responses of a PP/PTS coated glassy carbon electrode in a 0.2M KCl solution. The potential stepped from -1.00V → +0.70V → -1.00V (vs Ag/AgCl). (a) Rotation rate=2000rpm; (b) static. The polymer was grown for 1.0 minute at 2.0mA/cm² from 0.2M pyrrole in 0.05M PTS.
The chronoamperometric responses in Figure 4.16 show that the transition time $T$ was observed only when the negative potential step was applied (Figure 4.16(b)). It is likely that $T$ is related to the cation incorporation response (equation (4-1)). In order to confirm this, the chronoamperometric experiments were performed using various cations and anions in solution. Typical results are shown in Figure 4.17. The results show that with the NaCl solution, $T$ was observed when the negative pulse was applied. Compared with the value of $T$ obtained using KCl for the cathodic process, the transition time $T$ was almost the same. During this period, however, the current observed was smaller. Also, the commencement of the "shoulder" occurred 50ms later than that with the KCl. When the CaCl$_2$ solution was employed, a normal current decay profile was observed (curve (b)), and the transition time $T$ was much less defined. These observations indicate that the transition time $T$ is sensitive to the nature of the cation. When an experiment was performed in a PTS sodium salt solution, the transition time was observed on the cathodic response (curve (c)), indicating that $T$ is not sensitive to changes in the anion.

If these observations are combined with the results obtained using cyclic voltammetry (section 4.3.1), it is clear that the transition time $T$ is related to the cation incorporation reaction (equation 4-1)).
Figure 4.16 Chronoamperometric responses of a PP/PTS coated glassy carbon electrode in a 0.2M KCl solution. The potential stepped for (a) was from 0.00V→+0.70V→0.00V, (b) was from 0.00V→-1.00V→0.00V (vs Ag/AgCl). Rotation rate=2000rpm. The polymer was grown for 1.0 minutes at 2.0mA/cm² from 0.2M pyrrole in 0.05M PTS.

Figure 4.17 Chronoamperometric responses of a PP/PTS coated glassy carbon electrode in 0.2M of: (a) NaCl, (b) CaCl₂, and (c) PTS. The potential was stepped from -1.00V→0.70V→-1.00V (vs Ag/AgCl). Rotation rate=2000rpm. The polymer was grown for 1.0 minute at 2.0mA/cm² from 0.2M pyrrole in 0.05M PTS.
The effect of the counterion employed during polymerisation on the chronoamperometric responses was also considered. It was found that with larger counterions such as NPS, the transition time $T$ was much smaller than that observed using PP/PTS in a KCl solution. With small counterions such as Cl$^-$, F$^-$, NO$_3^-$, the transition time $T$ was not observed but an anion expulsion peak was observed with the positive potential step (-1.0 → 0.7V). A typical result is given in Figure 4.18. This agrees with the results obtained during cyclic voltammetry and further confirms that $T$ is a parameter related to cation incorporation. $T$ is only observed when the anion is large and less mobile, enabling the cation to compete for sites within the polymer.

![Figure 4.18](image)

*Figure 4.18* Chronoamperometric responses of a PP/Cl$^-$ coated glassy carbon electrode in a 0.2M CaCl$_2$ solution. The potential was stepped from -1.00V → 0.70V → -1.00V (vs Ag/AgCl). Rotation rate=2000rpm. The polymer was grown for 1.0 minute at 2.0mA/cm$^2$ from 0.2M pyrrole in 0.05M NaCl.
Figure 4.19 Chronoaperometric responses of a PP/PTS coated glassy carbon electrode in 0.2M of: (a) KCl solution. The potential was stepped from -1.00V→0.70V→1.00V (vs Ag/AgCl). Rotation rate=2000rpm. The polymer was grown for (a) 10.0sec., (b) 20.0sec., (c) 120.0 sec. and (d) 300.0sec. at 2.0mA/cm² from 0.2M pyrrole in 0.05M PTS.

From a qualitative point of view, the above observations suggest that the transition time T is related to the time needed for a cation moving into and out of the polymer. If this is the case, then T should increase as the thickness of the polymer is increased. Figure 4.19 and Table 4.1 give the relationship between T and the polymer thickness.

<table>
<thead>
<tr>
<th>Thickness *(μm)</th>
<th>0.075</th>
<th>0.15</th>
<th>0.30</th>
<th>0.45</th>
<th>0.90</th>
<th>2.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (ms)</td>
<td>16</td>
<td>35</td>
<td>93</td>
<td>133</td>
<td>493</td>
<td>1253</td>
</tr>
</tbody>
</table>

* The value of 2.25μm was measured using SEM techniques, all other were calculated based on this value since QCM studies have indicated that the polymerisation at these conditions was linear [167,169].
These results show that $T$ increases non-linearly with polymer thickness. This indicates that the cation incorporation is largely governed by mass transfer. It is known, however, that under these conditions the limiting step is unlikely to be mass transport across the double layer from the solution. It is more likely that it is limited by the mass transport through the polymer.

4.4 CONCLUSIONS

To determine the mechanism of control of transport across conducting polypyrrole membranes, the electrochemical properties of polypyrrole have been investigated.

The following conclusions can be drawn:

(1) A change in the redox state of the conducting polymer is accompanied by ion movement into and out of the polymer. The possible reactions occurring are given by equations (4.1) to (4.8).

(2) The cyclic voltammetric responses in regions 1 and 2 have been shown to be associated with cation incorporation and expulsion reactions. In regions 3 and 4 the responses result from anion incorporation and expulsion reactions.

(3) Cation incorporation and expulsion responses can be observed only when large organic counterions were employed for polymer synthesis. With small inorganic counterions such as Cl$^-$ or NO$_3^-$ the cation incorporation and expulsion responses were less well defined. For a given counterion, the K$^+$ and Na$^+$ ions were found to be much easier to incorporate into the polymer than were Ca$^{2+}$
and Mg\(^{2+}\) under static conditions. Therefore, the cation incorporation responses are dependent on the mobility difference between the cation in the solution and the counterion in the polymer. A large difference in the mobility produces a large cation incorporation response when an appropriate negative potential was applied.

(4) Anion incorporation and expulsion responses are dependent on the mobility of the anion in the solution. The presence of inorganic (small) anions in the solution gives large responses. The size or mobility of the counterion has only a slight influence on the anion responses. When an organic counterion is employed, the anion responses in subsequent redox cycles are mainly due to the reactions shown in equations (4.4) and (4.6).

(5) When a small inorganic counterion is employed for polymer synthesis and an organic anion was present in the solution, the reactions in equations (4.7) and (4.8) can take place to induce additional cation incorporation and expulsion responses.

(6) When a polymer containing small counterion is employed, the electrode rotation leads to an increase in the cation incorporation responses and when an organic counterion containing a polymer is used, the rotation of the electrode results in an increase in both cation and anion responses.

(7) A transition time \(T\) has been defined from chronoamperometric data and the physical significance of this has been discussed. It has been shown that \(T\) is related to cation incorporation processes.
CHAPTER 5

ELECTROCHEMICALLY CONTROLLED
TRANSPORT OF ELECTROINACTIVE SPECIES
ACROSS PP/PTS MEMBRANES
5.1 INTRODUCTION

Oxidation and reduction of a polypyrrole film can be achieved by application of an appropriate electrical potential, and these processes involve ion movement into and out of the polymer (see Chapter 4). Therefore, this unique property of the conducting polymer may be utilised for control of transport.

The main aim of this study is to investigate the electrochemically controlled transport across a conducting polypyrrole membrane. In this work, polypyrrole/p-toluenesulfonate membranes (PP/PTS) were used as the test case because numerous PP/PTS membranes with adequate mechanical properties and conductivity have been synthesised (see Chapter 3). Some electroinactive salts such as KCl, NaCl, CaCl₂ and MgCl₂ were employed for the investigation. The external electrical stimulation for studies of electrochemical control of transport was achieved using different potential waveforms such as constant potential, sweep potential and pulsed potential (Figure 5.1). The effect of applied potential waveform on the membrane transport performance was investigated. This involved studies of the switching properties of the membrane and of the rate of transport across the membrane. For each potential waveform, several parameters were varied (Figure 5.1). Different electrotransport cell set-ups were employed to investigate the effect of the electrode arrangement on the membrane transport. The effect of the cell design and the chemical conditions used were explored. The separation capability of the membrane was determined using different mixed-ions source solutions and the effect of the applied potential waveform on the membrane separation properties was studied. The membrane reproducibility and stability were also examined.
**Figure 5.1** Electrochemical factors in conducting polymer membrane systems.
5.2 EXPERIMENTAL

5.2.1 Reagents and Solutions

All chemicals for membrane preparation were as described in previous chapters. All chemicals for transport studies were AR grade and used as received. All solutions were prepared by dissolving the chemicals in Milli-Q deionised water (18MΩ.cm).

The polymerisation solution for membrane preparation contained 0.20M pyrrole (freshly distilled) and 0.05M p-toluenesulfonate (PTS) sodium salt unless otherwise stated.

5.2.2 Instrumentation

Cyclic voltammetry was carried out using a BAS-100A Electrochemical Analyser in a three electrode electrochemical cell. The electrodes used were as described in Chapter 4. Instruments for membrane preparation were as in Chapter 3. A stainless steel plate was used as a working electrode throughout this work. The synthesis cell used was as in Chapter 3. Application of different electrical potential waveforms to the membrane was achieved by use of a potentiostat (PAR, model 173) coupled to a signal generator (built in-house). For application of sweep potential waveforms, the potentiostat was combined with a PAR-175. In order to investigate the influence of the electrical force, an automatic switch was employed and controlled by the signal generator.
Figure 5.2 Electrotransport cell setups
All transport experiments were conducted in an electrochemical transport cell (Figure 5.2) where the membrane (area=8.0 cm²) acted as the working electrode. This separated the source solution compartment from the receiving solution compartment. Two platinum meshes (2.5 x 2.5 cm², 100 lines/inch) were used as auxiliary electrodes, one on each side of the cell (see Figure 5.2 (I), (II)), but for some experiments, the auxiliary electrode was placed only in the source side solution (see Figure 5.2(III)). A Ag/AgCl (3M NaCl) reference electrode was connected to one or both compartments of the cell via a single or two-pronged salt bridge (Figure 5.2). The source and receiving solutions were stirred by small electric stirrers.

Analysis of cations was carried out using Atomic Absorption Analysis (VARIAN Spectr AA 20 AAS) and analysis of the anions by ion-exchange HPLC (Waters 501 HPLC pump, and Waters IC-Pak™ Anion Column). For the latter a conductivity detector was employed for all anions with the exception of Cl⁻. In this case Cl⁻ analysis was carried out using an electrochemical method and a silver working electrode.

5.2.3 Procedures

Membrane Preparation

All membranes used for this work were prepared galvanostatically according to procedures described in chapter 3.

Except for the membranes used for the experiments in section 5.3.3.1 and 5.3.6, all membranes were prepared using a current density of 2.0 mA/cm². The charge passed during the polymerisation was 1.20 C/cm². The polymerisation solution was 0.20M pyrrole with 0.05M PTS.
Transport Experiments

(i) set up the appropriate electrochemical transport cell (Figure 5.2);

(ii) check electrode connections;

(iii) fill each compartment of the cell with an equal volume (60ml) of the appropriate solutions;

(iv) start the transport experiments.

Generally, the electrical stimulus was applied after 40.0 minutes and was continued for 60.0 minutes. This was followed by a period of time without applied potential (generally 40.0 minutes). During the experiments, samples were withdrawn every 20.0 minutes. The volume of the samples withdrawn were dependent on the sensitivity of the analytical methods employed, and if necessary, the sample was diluted.

Notes:

(i) Except for the experiments in section 5.3.2.3, in all experiments, the membrane was set up using the solution side of the membrane exposed to the source solution.

(iii) All fluxes shown in this work are average fluxes and measured during the applied electrical potential, since in most cases the transport behaviour was linear during this period.
5.3 RESULTS AND DISCUSSION

5.3.1 Electrochemical Control of Membrane Transport

In this section, the effect of the electrochemical conditions used on the transport across the membrane was investigated. (Figure 5.1).

5.3.1.1 Effect of Potential Waveforms Applied

Initially the transport of K⁺ across the PP/PTS membrane was investigated when a constant positive or negative potential was applied to the membrane (Figure 5.3). It was found that no significant transport occurred when no potential was applied. The rate of K⁺ transport across the membrane with a negative applied potential (-1.0V, curve A) was faster than that with a positive applied potential (+0.70V, Curve B). The transport in both cases was non-linear. The transport of the corresponding anions followed the same trend. The individual quantities of the cation and anion are listed in Table 5.1.

![Graph showing transport of K⁺ across PP/PTS membrane. Source solution: 0.2M KCl, Receiving solution: deionised water. Constant potential was applied between 40.0 to 100.0 minutes, (A) -1.00V and (B) +0.70V (vs Ag/AgCl).](image)

Figure 5.3 Transport of K⁺ across PP/PTS membrane. Source solution: 0.2M KCl, Receiving solution: deionised water. Constant potential was applied between 40.0 to 100.0 minutes, (A) -1.00V and (B) +0.70V (vs Ag/AgCl).
Table 5.1 Total quantity of cation and anions transported

<table>
<thead>
<tr>
<th>Applied Potential (V) vs Ag/AgCl</th>
<th>+0.70</th>
<th>-1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity of K⁺ (mole)</td>
<td>1.73 x 10⁻⁷</td>
<td>7.7 x 10⁻⁶</td>
</tr>
<tr>
<td>Quantity of Cl⁻ (mole)</td>
<td>Undefined</td>
<td>4.1 x 10⁻⁶</td>
</tr>
<tr>
<td>Quantity of PTS (mole)</td>
<td>Undefined</td>
<td>3.9 x 10⁻⁶</td>
</tr>
<tr>
<td>Total quantity of anions (mole)</td>
<td>-</td>
<td>8.0 x 10⁻⁶</td>
</tr>
</tbody>
</table>

Experimental conditions used were as in Figure 5.3. Detection limit was 1 x 10⁻⁷ mol.

It was found that within experimental error (±2 x 10⁻⁷ mol) an equal amount of cation and anions were transported across the membrane. The anion content of the receiving solution observed was not only that transported from source solution (Cl⁻) but also expelled from the membrane (PTS).

In order to determine the membrane transport properties as a function of the membrane oxidation state, a range of potentials was applied (Table 5.2). The results show that the flux obtained at positive potentials was lower than the flux obtained at negative potentials. Moreover, the flux increased when a more negative potential was applied.

Although the transport across the membrane can be switched on/off and the rate of transport can be controlled by application of a constant potential waveform, the transport cannot be sustained.

Table 5.2 Effect of applied potential on the flux of K⁺

<table>
<thead>
<tr>
<th>Applied potential (V) vs Ag/AgCl</th>
<th>-1.00</th>
<th>-0.80</th>
<th>-0.50</th>
<th>-0.20</th>
<th>0.0</th>
<th>+0.70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux of K⁺ (10¹⁰ mol cm⁻² s⁻¹)</td>
<td>2.66</td>
<td>1.75</td>
<td>0.66</td>
<td>0.16</td>
<td>0.05</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Note: Except for the applied potential, all experiment conditions were as in Figure 5.3.

The above transport results can be explained using equations (4.1 to 4.8). It is known [56] that after electrochemical synthesis, the natural state of
the polypyrrole membrane is the oxidised form and the positive charge has been neutralised by the counterion incorporated during polymerisation (Figure 5.4, (a)). It is also known [111] that when a polypyrrole film is immersed in an anion containing solution, an ion exchange reaction could take place between the counterion in the polymer and the anion in the solution (Figure 5.4, (b)). During transport experiments, the membrane is set up in the electrochemical transport cell. When KCl and deionised water are used as the source and the receiving solutions respectively, an ion-exchange reaction takes place between the Cl\(^-\) in the source solution and the counterion in the membrane. Under these conditions we can ignore OH\(^-\), the other anion present, because the concentration of OH\(^-\) in both solutions is very low, about 10\(^{-7}\)M. When the ion-exchange reactions come to equilibrium, some cations may also form a double layer on the surface of the membrane pores.

The possible situation at one pore of the membrane is given in Figure 5.4. Under these circumstances the transport of ions across the membrane is very difficult since the electroneutrality has to be maintained. This may explain why no significant transport is observed when no potential is applied.
(a): Polypyrrole membrane in natural oxidised state; anion exchange could occur between the anion in the solution and the counterion in the membrane.

(b): Before potential applied, ion exchange reaches equilibrium; some cations could exist inside of the membrane pores to establish a double layer.

(c): Membrane is reduced causing either/both incorporation of cation or/and expulsion of anion.

(d): Membrane is oxidised causing either/both incorporation anion or/and expulsion of cation.

Auxiliary electrode is placed in the source side of the solution.

Arrow shows the direction of electron or ion movement.

Figure 5.4 Electrochemically controlled transport of electroinactive species across a conducting polymer membrane.
Figure 5.5 The direction of the driving force, (i) application of a positive potential and (ii) negative potential.

Application of a positive potential, for example +0.70V, to the membrane does not alter the redox state of the membrane since the membrane is still at the oxidation state. However, a +0.70V applied potential causes more anion to be incorporated from the solution since the applied potential is more positive than that of the "natural" potential of the membrane, and the additional positive charge needs to be neutralised [196]. Therefore, no ions would be expelled under these conditions. Figure 5.5 (i) shows the electrical field imposed when a positive potential is applied to the membrane. There is no driving force to allow ions to be released into the receiving solution.

When a constant negative potential, for example -1.0V, is applied to the membrane, the membrane will be reduced to its neutral state. The accompanying ion incorporation and expulsion reactions are shown in equations (4.1, 4.3, 4.4 and 4.7). This process is shown in Figure 5.4 (c), whereas the membrane is reduced, the positive charge on the polymer backbone is removed and the counterions are no longer maintained within the membrane pores. Consequently, they may diffuse into both sides of the solution causing anion transport across the membrane. However, under these conditions, the electrical driving force
can drive the cation from the source solution into the membrane pores (Figure 5.5 (ii)), and the remaining counterion (free counterion) in the pores allows the cation to diffuse into the pores. Therefore, the cation could diffuse through the membrane separately or as ion-pairs. This results in cation transport across the membrane.

Based on the above model, the maximum amount of ions that can be transported across the membrane is dependent on the degree of polymer reduction and the quantity of the polymer. These factors control the number of mobile counterions in the polymer.

It is possible to use the above to explain why the transport across the membrane with a constant negative applied potential cannot be sustained. In this case, the electrical field acts as a driving force and obstructs the anions moving into the membrane pores (see Figure 5.5(ii) and the arrow in Figure 5.4). In other words, because electroneutrality must be maintained, the maximum amount of ions that can be transported across the membrane must be less than or equal to the amount of mobile counterions in the membrane before the potential is applied. Substantiation of this hypothesis is given by the results of transport experiments conducted with different masses of polymer (Table 5.3). The mass of the membrane was controlled by controlling the charge passed (C/cm²) during electrosynthesis. These results show that the total quantity of K⁺ transported increases with the mass of the polymer.

The non-linear transport behaviour is also explained by the above factors. The concentration of mobile counterions in the membrane decreases with time resulting in a decreasing rate of transport for the anion.
Table 5.3 Effect of mass of the polymer on the total quantity of K⁺ transported

<table>
<thead>
<tr>
<th>Mass of the Polymer in terms of charge passed during electrosynthesis (C/cm²)</th>
<th>1.20</th>
<th>2.40</th>
<th>3.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity of K⁺ transported (mole)</td>
<td>7.7 x 10⁻⁶</td>
<td>11.9 x 10⁻⁶</td>
<td>14.6 x 10⁻⁶</td>
</tr>
</tbody>
</table>

Experimental conditions used were as in Figure 5.(A) except for the thickness of the membrane (mass).

With a constant negative potential applied, only a certain amount of anion can be released from the membrane, and the electrical field does not allow anion in the solution to diffuse into the membrane pores, resulting in non-linear transport, which is limited by the total mass of the polymer. To overcome this problem, cyclic sweep potential waveforms were considered since under these conditions, the redox states of the membrane can be reversibly altered and the anion can be re-incorporated during the anodic cycle (equations 4.2, 4.5, 4.6, and 4.8). The results in Figure 5.6 show the transport of K⁺ across the PP/PTS membrane using applied cyclic sweep potential waveforms. It was found that with no application of potential, no significant transport occurred, while with cyclic sweep potentials, almost linear transport was observed. The fluxes obtained using different scan rates are given in Table 5.4. It shows that a decrease in the scan rate resulted in an increase in the rate of K⁺ transport. Also, the fluxes obtained were higher than that obtained using constant potential waveforms.
Figure 5.6 Transport of K⁺ across a PP/PTS membrane. Source solution: 0.2M KCl, Receiving solution: deionised water. Cyclic sweep potential waveforms were applied between 40.0 to 100.0 minutes, Potential Range: +0.700V to -1.00V (vs Ag/AgCl). Scan rate: (1) 5.0mV/sec., (2) 50mV/sec., (3) 200mV/sec., (4) 500mV/sec. and (5) 1000mV/sec..

Table 5.4* Effect of scan rate on the flux of K⁺

<table>
<thead>
<tr>
<th>Scan rate (mv/sec)</th>
<th>5.0</th>
<th>50.0</th>
<th>200</th>
<th>500</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux of K⁺ (10⁻¹⁰ mol cm⁻²s⁻¹)</td>
<td>9.7</td>
<td>8.5</td>
<td>6.4</td>
<td>5.0</td>
<td>3.6</td>
</tr>
</tbody>
</table>

*Fluxes were calculated from Figure 5.6.

Using cyclic sweep potential waveforms, the transport mechanism could be described using Figure 5.4 (c) and (d), namely the "ion incorporation/expulsion mechanism" since these processes (equations 4.1 to 4.8) accompany redox cycling. Based on this mechanism, the situation for ion transport across the membrane is as described in constant applied potential cases. The major difference is that when the membrane is re-oxidised, cation can be expelled and anion can be re-incorporated from
the source solution. Repeated cycles of oxidation and reduction of the membrane results in a constant rate of ion transport across the membrane being linear and can be sustained for a longer period of time.

The reason for the decreased flux observed at increased scan rates may be because the oxidation/reduction processes are limited by ion diffusion to the membrane surface. Also, at fast scan rates, the ions released into the receiver solution by one phase of the redox reaction are unable to diffuse away from the membrane before the next phase of the redox reaction causes them to be re-incorporated.

With application of a cyclic potential waveform to the membrane, ion transport across the membrane was sustained. However, during one cycle of potential sweep, a high degree of polymer reduction or oxidation can be achieved only at extreme potentials and therefore during much of the scan little transport results because efficient incorporation and expulsion reactions take place only above a certain threshold potential. Also, since the distance between the auxiliary electrode and working electrode in the electrotransport cell was fixed, larger electrical field strength can only be achieved by application of more extreme potentials. However, the use of a pulsed potential waveform enables the potential and hence the redox state to be changed quickly and held at that potential for a given time to allow ion movement to occur. This should result in much greater efficiency and higher fluxes.

In this part of the work, pulsed potential waveforms were employed. Both symmetric and asymmetric pulsed potentials with different potential ranges and frequencies were considered. All experiments were carried out using 0.2M KCl or 0.2M NaCl as the source solutions and deionised water as the receiving solution. The electrotransport cell set up was as
shown in Figure 5.2 (III). The results in Figure 5.7 show the effect of
potential range on the K+ transport across the membrane. A symmetric
pulsed potential with pulse width of 50 seconds was employed.
According to the data obtained from cyclic voltammetry experiments
(Figure 5.8), a set of potential ranges was selected in accordance with the
prior knowledge of the potential required to change the redox states of a
PP/PTS membrane. It was found that the membrane transport can be
switched on when the pulsed potential was applied and switched off when
the potential was removed. Furthermore, linear transport behaviour was
observed. The fluxes listed in Table 5.5 were calculated based on the
results in Figure 5.7. They indicate that for the same potential range
(For example +0.70V to -1.0V), the flux of K+ observed using the pulsed
potential waveform (Table 5.5) was much larger than that using the
cyclic potential one (Table 5.4).

The results also show that changes in the pulsed potential range have a
marked effect on the rate of K+ transport. Significant transport can
occur only when the redox states of the membrane were altered and when
this change was more efficient, the fluxes obtained were larger. For
example, the smallest flux was obtained when the potential applied did
not change the redox state of the membrane(see experiment #6, and
Figure 5.8(6)) and the largest flux was obtained when the applied
potential was able to completely change the redox state of the membrane
(see experiment #1 and Figure 5.8 (1)).
Figure 5.7 Transport of K⁺ across a PP/PTS membrane. Source solution: 0.2M KCl, Receiving solution: deionised water. The symmetric pulsed potential waveforms were applied between 40.0 to 100.0 minutes, Pulse Width: 50sec. Potential Range: (1) +0.700V to -1.00V, (2) 0V to -1.00V, (3) -0.20V to -0.80V, (4) -0.75V to -1.0V, (5) +0.70V to -0.50V and (6) +0.70V to 0V (vs Ag/AgCl).

Table 5.5 Effect of the potential range on K⁺ transport

<table>
<thead>
<tr>
<th>Experiment</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential Range (V) vs Ag/AgCl</td>
<td>0.70/-1.0</td>
<td>0.0/-1.0</td>
<td>-0.75/-1.0</td>
<td>-0.2/-0.8</td>
<td>0.70/-0.50</td>
<td>0.70/0.0</td>
</tr>
<tr>
<td>Flux of K⁺ (10⁹mol.cm⁻²s⁻¹)</td>
<td>2.0</td>
<td>0.96</td>
<td>0.33</td>
<td>0.47</td>
<td>0.21</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Redox States</td>
<td>FO/FR</td>
<td>NFO/FR</td>
<td>NO/FR</td>
<td>NFO/NFR</td>
<td>FO/NFR</td>
<td>FO/NFR</td>
</tr>
</tbody>
</table>

Notes: FO or FR: fully oxidised or reduced, NO: not oxidised, and NFO or NFR: not fully oxidised or reduced.
Figure 5.8 Cyclic voltammograms of PP/PTS coated glassy carbon electrode at different potential range in 0.2M KCl solution. Scan rate: 20mV/sec. Potential Range: (1) +0.700V to -1.00V, (2) 0V to -1.00V, (3) -0.75V to -1.0V, (4) -0.20V to -0.80V, (5) +0.70V to -0.50V and (6) +0.70V to 0V (vs Ag/AgCl).
The same experiments were carried out using a NaCl source solution (Table 5.6). The effect of the applied potential range on the transport of Na⁺ across the membrane followed the same trend. However, for the same potential ranges, fluxes for Na⁺ transport were lower than the fluxes obtained for K⁺ transport.

<table>
<thead>
<tr>
<th>Potential Range (V) vs Ag/AgCl</th>
<th>Flux of Na⁺ (10⁹ mol cm⁻²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7/-1.0</td>
<td>1.41</td>
</tr>
<tr>
<td>0.0/-1.0</td>
<td>0.87</td>
</tr>
<tr>
<td>0.7/-0.5</td>
<td>0.09</td>
</tr>
<tr>
<td>0.7/0.0</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Experiments were carried out using a PP/PTS membrane. Source solution: 0.2M NaCl; Receiving solution: deionised water. Symmetric pulsed potential waveforms with different potential range were applied between 40.0 to 100.0 minutes; Pulse Width: 50sec.

The mechanism of transport using a pulsed potential waveform was the same as described for the cyclic sweep potential waveforms and involves ion incorporation/expulsion (Figure 5.4).

Figure 5.9 shows the influence of the pulse width on the transport of K⁺ across the membrane. The pulse range was fixed using 0.7V to -1.0V and the pulse width was varied from 1.0 second to 100 seconds. The fluxes in Figure 5.10 were calculated based on the data in Figure 5.9. Linear, sustainable transport behaviour occurred during application of the pulsed potentials (Figure 5.9). Also, the flux for K⁺ transport initially increased with pulse width to reach a maximum at a pulse width of 20 seconds, then the flux slowly decreased (Figure 5.10).
Figure 5.9 Transport of $K^+$ across PP/PTS membrane. Source solution: 0.2M KCl, Receiving solution: deionised water. The symmetric pulsed potential waveforms with different pulse width were applied between 40.0 to 100.0 minutes. Potential Range: +0.700V to -1.00V (vs Ag/AgCl).

Figure 5.10 Effect of pulse width on the flux of $K^+$ transported across PP/PTS membrane during application of pulsed potential.
This phenomenon can be explained in terms of a membrane time constant which is the time required for the membrane to be fully oxidised or reduced. This time constant arises because of the resistance and capacitive effects of the conducting polymer membrane. Therefore, according to the ion incorporation/expulsion mechanism (Figure 5.4), a pulse width that is too short could cause two unfavourable affects on transport across the membrane: (i) the incorporation step will not have time to incorporate large quantities of ions into the membrane; (ii) the released ions might not be able to diffuse into the solution before the reincorporation step is activated by the anodic or cathodic potentials. Conversely, when the pulse width is just long enough to allow the membrane to be fully oxidised and reduced then the ion incorporation and expulsion will be completed. This leads to maximum transport efficiency.

The use of longer pulse widths leads to a loss in electrochemical reversibility. The current-time profile in Figure 5.11 shows that with a 50 second pulse width, the maximum current decreased over the first 10 cycles and then became constant. This suggests that after 10 cycles of the pulsed potential, the electrochemical reversibility of the membrane became constant. If we look at one cycle of the pulse (between A and B), it shows that oxidation and reduction occurred within 5 to 20 seconds. After 40 seconds, the oxidation/reduction current was low. When the pulse width was larger than 50 seconds, a decreasing trend of the maximum current was observed. This indicates a decrease in the electrochemical reversibility of the membrane and results in a decrease in the electroactive surface area of the membrane. The charge capacity of the membrane is small and with wider pulses the concentration of the ion in the membrane will decrease and cause a decrease in the flux. This
factor can also be considered in terms of efficiency, since for a given period of time a smaller number of wider pulses can be applied, compared to smaller widths, resulting in a flux drop.

Figure 5.11 Current-time profile recorded during transport experiment. Source solution: 0.2M KCl, Receiving solution: deionised water. Symmetric pulsed potential waveforms were applied between 40.0 to 100.0 minutes. Pulse width: 50sec. Potential Range: +0.700V to -1.00V (vs Ag/AgCl).

The effect of asymmetric pulse widths on ion transport was then considered. When the anodic potential pulse width was fixed at 50
seconds whilst changing the duration of the cathodic potential pulse, it was found that the largest flux was obtained when the pulse widths became symmetric. This was true for the opposite situation when the cathodic part was fixed and the anodic potential frequency varied (Figure 5.12). This membrane transport behaviour can be simply explained in terms of the membrane's electrochemical reversibility. An asymmetric pulse width applied to the membrane, for example, with the pulse width of the anodic component being larger than the cathodic pulse width, will result in the membrane being oxidised more completely than it is reduced and these effects can be accumulated. This results in the anion expulsion or cation incorporation reactions (equations 4.1, 4.3, 4.4 and 4.7) being the limiting step, causing the fluxes obtained to decrease.

**Figure 5.12** Effect of asymmetric pulse width on transport of K⁺ across PP/PTS membrane. Source solution: 0.2M KCl; Receiving solution: deionised water; Potential Range: +0.700V to -1.00V (vs Ag/AgCl). (1) Positive potential pulse width was fixed at 50 seconds, Negative potential pulse width was varied from 2.5sec. to 100sec, and (2) negative potential pulse width was fixed at 50 seconds, positive potential pulse width were varied from 2.5sec. to 100sec.
5.3.1.2 Effect of Different Electrode Arrangements

In this part of the work, the effect of the electrode arrangement in the electrotransport cell was investigated.

Experiments were conducted with 0.20M KCl in one compartment and 0.20M NaCl in another whilst the electrochemical cell setup was as in Figure 5.2. A symmetric pulsed potential waveform with 50 seconds pulse width and area +0.70V to -1.00V pulse range was employed. The samples were taken from both compartments and analysed.

With no applied potential, when one cell compartment contained NaCl and the other contained an equal concentration of KCl then transport of both K⁺ and Na⁺ across the membrane was observed (Figure 5.13). A possible transport mechanism is proposed in Figure 5.14. Transport occurred because of ion-exchange reactions taking place [111]. If the NaCl solution is replaced with deionised water, no measurable transport of K⁺ could be observed even after 20 hours.

Figure 5.13 Transport of K⁺ and Na⁺ across PP/PTS membrane with no application of potential. Left side solution: 0.2M KCl Right side solution: 0.2M NaCl. (1) K⁺ transported to right side solution and (2) Na⁺ transported to left side solution.
When the electrotransport cell setup shown in Figure 5.2(III) was employed, a faster rate of transport was observed for the ion in the compartment containing the auxiliary electrode (Figure 5.15, 5.16). Since the same pulsed potential was applied, the membrane must undergo the same redox reactions regardless of where the auxiliary electrode was placed. Therefore, this difference must be due to the electrical field set up by the potential gradient between the membrane and auxiliary electrode (See Figure 5.5). This electrical field would mainly exist in the compartment which had the auxiliary electrode setup in it. This is because as the conducting polymer is a conductor it can shield the electrical field. In fact, under these conditions, the transport across the membrane was performed by two different processes; one was an ion incorporation/expulsion process and another was an ion-exchange process. For ions in the compartment with the auxiliary electrode, transport was mainly governed by the ion incorporation/expulsion mechanism, and in another compartment, ion transport was induced by the ion-exchange mechanism.
When the auxiliary electrodes was set up in both compartments (Figure 5.5(I)), the same rate of transport for both K\(^+\) and Na\(^+\) was obtained (Figure 5.17).

![Figure 5.15](image1.png)  
**Figure 5.15** Transport of K\(^+\) and Na\(^+\) across a PP/PTS membrane with application of a pulsed potential. Left side solution: 0.2M KCl, Right side solution: 0.2M NaCl. The auxiliary electrode was placed in left side of the cell (see Figure 5.2, (II)). (1) K\(^+\) transported to right side solution and (2) Na\(^+\) transported to left side solution.

![Figure 5.16](image2.png)  
**Figure 5.16** Transport of K\(^+\) and Na\(^+\) across PP/PTS membrane with application of a pulsed potential. Left side solution: 0.2M KCl, Right side solution: 0.2M NaCl. The auxiliary electrode was placed in right side of the cell (see Figure 5.2, (III)). (1) Na\(^+\) transported to left side solution and (2) K\(^+\) transported to right side solution.
Figure 5.17 Transport of $K^+$ and $Na^+$ across PP/PTS membrane with application of a pulsed potential. Left side solution: 0.2M KCl, Right side solution: 0.2M NaCl. The auxiliary electrodes were placed in both sides of the cell. (see Figure 5.2, (I)) (1) $Na^+$ transported to left side solution and (2) $K^+$ transported to right side solution.

Figure 5.18 Transport of $K^+$ and $Na^+$ across PP/PTS membrane with application of a pulsed potential. Left side solution: 0.2M KCl, Right side solution: 0.2M NaCl. The auxiliary electrodes were located in both sides of the cell. When the positive component of the pulse was applied to the membrane, the auxiliary electrode in right side of the cell was switched on. When the negative component was applied to the membrane, the auxiliary electrode in left side of the cell was switched on (see Figure 5.2, (II)). (1) $K^+$ transported to right side solution and (2) $Na^+$ transported to left side solution.
Further experiments were performed to investigate the influence of the electric field direction. As shown in Figure 5.5, an electric field can be established between the auxiliary electrode and the membrane (working electrode) and the direction of this field can be varied by application of different potentials. In this series of experiments, the electrotransport cell was set up as shown in Figure 5.5(II). and an automatic switch was employed. This switch was controlled by a pulse generator and could switch between the two auxiliary electrodes, one located in each compartment of the cell. Using this hardware, the one compartment will always have a positive potential gradient and the other a negative
potential gradient. Therefore, the direction of the electrical field for a given compartment was fixed. The results (Figure 5.18, 5.19) show that K\(^+\) and Na\(^+\) transport across the membrane only occurred when the direction of the electrical field in that compartment was as shown in Figure 5.5(ii). It was clearly shown that the electrical field drives in K\(^+\) transport across the membrane and obstructs the Na\(^+\) transport. Conversely, in Figure 5.19, with the electrical field in the KCl side as shown in Figure 5.5(i) and in the NaCl side as shown in Figure 5.5(ii), transport of Na\(^+\) across the membrane occurred and transport of K\(^+\) across the membrane did not occur. It may be concluded that the direction of the potential gradient plays an important role in transport across conducting polymer membranes.

5.3.2 Electrotransport Cell Design

In this part of the work, changes in the electrotransport cell design were considered. Important parameters such as the membrane area and thickness; the connection between the membrane and the instrument and the side of the membrane exposed to the source solution were examined.

The electrochemical cell setup was as shown in Figure 5.2(III). A symmetric pulsed potential with a 50 second pulse width and +0.7V to -1.0V pulse range was employed. All experiments were carried out using 0.20M KCl as the source solution and deionised water as the receiving solution.
5.3.2.1 Electrical Connection to the Membrane

A previous report [200] pointed out that the polypyrrole reduction and oxidation reaction is not fast. For example as shown in the schematic drawing below when a negative potential is applied, the colour of the polymer is changed beginning from where the membrane is connected to the outside circuit, and as time passes, the area of the polymer that changes colour becomes larger. This behaviour indicates that the polymer reduction reaction is slow and time dependent since the colour of the polymer relates to the redox states of the polymer. The polymer oxidation process behaves in a similar manner.

The polymer reduction process may be described as follows:

\[
\begin{align*}
\text{CHANGE IN POLYMER CONFORMATION} \\
\text{CHARGE (+)} \\ \\
\text{CHARGE (-)} \\
\text{CHARGE (O)} \\
\end{align*}
\]

(5.1)

where \(k_1\) is the rate constant of the polymer reduction reaction, and \(k_2\) is the rate constant of the polymer reconstruction reaction.

The polymer reduction reaction is much faster than the chemical processes that accompany it, in other words, \(k_1 \gg k_2\).

Also, the resistance of the polypyrrole films varies with the redox state, when the polymer is reduced, the resistance is increased [169].
Therefore, the conducting polymer is not an ideal conductor. Given these points then the electrical connection between the membrane and the outside circuit becomes critical if efficient electrochemically controlled transport across the membrane is to be reached. A simple illustration can be given here. When polymer reduction causes an increase in the resistance of the polymer, it results in a potential drop across the distance between the connector to the point where the resistance is measured. (Figure 5.20).

**Figure 20 Electrical connections to the membrane.**

At that point (A or B), the real potential must be much lower than the potential provided from the instrument. For instance, when we apply -1.0V from the potentiostat, if the minimum current is 0.8 mA and the resistance between connection and point A is 1KΩ (this is possible) then the potential drop between the connector and point A is 0.8V (ΔE = IR). Thus the real potential at point A will be just -0.2V. At this potential the cation incorporation is not possible. This will result in the valid transport area of the membrane being decreased.
The effect of the connection point on the K⁺ flux is shown in Table 5.7. With these experiments, the electrotransport cell setup was as shown in Figure 5.2(III) and the auxiliary electrode was placed in the source solution.

**Table 5.7 Effect of the electrical connection point on K⁺ transport**

<table>
<thead>
<tr>
<th></th>
<th>One Side Connection</th>
<th>Two Side Connection</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLUX (mol cm⁻²sec)</td>
<td>1.78x10⁻⁹, 1.83x10⁻⁹, 1.85x10⁻⁹</td>
<td>1.71x10⁻⁹, 1.83x10⁻⁹, 1.88x10⁻⁹</td>
</tr>
</tbody>
</table>

Results were obtained using a symmetric pulsed potential with a 50 seconds pulse width and a -1.0V to +0.7V pulse range. Source solution: 0.2M KCl; Receiving solution: deionised water. Each experiment with results being given in the table was repeated three times.

One side connection means that the outside circuit was contacted on just one side of the membrane (Figure 5.21(a), while a two side connection involved contacting both sides (Figure 5.21(b)). These results show that in both cases, the fluxes obtained were similar. In this experiment, the membrane used was thin (4-5μm) and so potential drop along the cross section was very low.

*Figure 5.21 Schematics of electrical connection to membrane*
The effect of the connection geometry on the rate of K⁺ transport is given in Table 5.8. All experiments were performed under the same electrochemical conditions as used in Table 5.7.

**Table 5.8 Effect of the electrical connection geometry on K⁺ transport**

<table>
<thead>
<tr>
<th>Point Connection</th>
<th>Circular Connection</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLUX (mol cm⁻² sec⁻¹)</td>
<td>FLUX (mol cm⁻² sec⁻¹)</td>
</tr>
<tr>
<td>1.78x10⁻⁹, 1.85x10⁻⁹, 1.83x10⁻⁹</td>
<td>2.31x10⁻⁹, 2.10x10⁻⁹, 2.45x10⁻⁹</td>
</tr>
</tbody>
</table>

Experimental conditions were as in Table 5.7, except the connection geometry used was different. Each experiment was repeated three times.

These results were obtained using a one side connection (source side, Figure 5.21(a)). The connections used were a point or circular in geometry (Figure 5.22). The possible potential distribution (isopotential) are also given in Figure 5.22. With a circular connection, the K⁺ flux obtained was more than 20% higher than the flux obtained using a point connection (Table 5.8). This may be due to an even distribution of potential over the area of the membrane in the case of a circular connection (Figure 5.22(b)). This in turn increases the electroactive area. With a point connection, the membrane was checked after the experiment. It was found that two different colours existed in parts of the membrane. A green colour was observed in region A (Figure 5.21(a)) and the rest of the membrane was dark-red. The different coloured regions are due to the different redox states of the polymer [200].
5.3.2.2 Effect of Membrane Area (diameter) and Thickness

Experiments investigating the effect of the membrane area (diameter) and membrane thickness on the K⁺ transport were performed using a one side point connection cell (Figure 5.21(a) and 5.22(a)).

It was found that the use of membranes with smaller area (diameter) gives larger fluxes for K⁺ transport (Table 5.9).

<table>
<thead>
<tr>
<th>Membrane diameter (cm)</th>
<th>Membrane area (cm²)</th>
<th>Flux of K⁺ ($10^9$mol cm⁻²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>3.8</td>
<td>2.81</td>
</tr>
<tr>
<td>3.2</td>
<td>8.0</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Experimental conditions used were the same as in Table 5.7.

These results indicate that for membranes with large areas(diameters) some of the membrane is not involved in transport (see section 5.3.2.1). Again, the membrane was checked after use in the above transport experiments. With the larger area membrane it was found that two
different colours existed on parts of the membrane indicating two
different redox states of the polymer [200]. Only one colour was
observed when a smaller area membrane was employed indicating one
redox state existed.

Membranes used to investigate the effect of membrane thickness were
prepared using a galvanostatic method at a current density of 2.0mA/cm²
with different quantities of charge passed (See Table 5.10).

<table>
<thead>
<tr>
<th>Charge passed (C/cm²)</th>
<th>1.2</th>
<th>1.8</th>
<th>2.4</th>
<th>3.0</th>
<th>3.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 5.10 The quantity of charge passed and the resultant membrane thickness

Experimental conditions were as in Table 5.7.

Transport results using these different membranes show that the flux
increased as the membrane thickness increased up to 10µm (Figure 5.23).
Beyond this thickness, the flux decreased. With thinner membranes the
rate is obviously dependent on the number of accessible charge sites
(incorporation capacity) present during potential pulsing. In addition,
thickness of the membrane may directly influence the flux. When the
thickness of the membrane is increased the total resistance of the
membrane decreases resulting in an increased electroactive transport
area. However, as the membrane thickness increased further the flux is
like to decrease due to hindered transport through the thicker membrane.
The rate is then diffusion controlled through the polymer matrix. Also
as described previously, it is difficult to make thick polypyrrole
membranes with good uniformity and uniform electronic properties.
Consequently, there may be "dead spots" in these membranes as far as
potential/redox switching is concerned. After the above experiments, it
was found that when the thickness of the membrane was over 8μm, after two hours of applied pulsed potential, some area of the membrane resembled a "plastic foam" indicating large structural changes.

![Graph showing the effect of membrane thickness on transport of K+]  

Figure 5.23 Effect of membrane thickness on transport of K+ across PP/PTS membrane. Source solution: 0.2M KCl, Receiving solution: deionised water. A symmetric pulsed potential waveform with 50 seconds pulse Width and +0.700V to -1.00V pulse Range was applied.

5.3.2.3 Effect of the Side of the Membrane Exposed to the Source Solution

The membrane growth surface (solution side, exposed to polymerisation solution during synthesis) and electrode side (plate side, connected to the electrode during syntheses) might have different surface properties since the first layer of polymer formation was on the electrode material surface and later polymer deposition was on the polymer which had formed. The SEM studies in Chapter 3 have shown that the different sides of the membrane have different surface morphology. The effect of this on the membrane transport properties was investigated. This can be
determined by setting up the membrane using the different sides exposed to the source solution. The results show that for a PP/PTS membrane, it was immaterial which side of the membrane was exposed to the source solution (Figure 5.24).

![Graph](image)

**Figure 5.24** Effect of the side of the membrane exposed to the source solution on the transport of K⁺ across PP/PTS membrane. Source solution: 0.2M KCl, Receiving solution: deionised water. A symmetric pulsed potential waveform with 50 seconds pulse Width and +0.700V to -1.00V pulse Range was applied between 40.0 to 100 minutes. (1) Plate side and (2) solution side of the membrane were exposed to the source solution.

5.3.3 Effect of Chemical Conditions used on the Membrane Transport

In the previous sections, investigations concentrated on the effect of electrochemical conditions on the membrane transport. In this section the effect of chemical conditions such as source solution concentration and pH were considered.
The electrochemical conditions were fixed. A symmetric pulsed potential with 50 seconds pulse width and +0.7V to -1.0V pulse range was employed. The cell set up was the same as described in Figure 5.2 (III).

Other workers [201] have reported that protons can effectively compete with other cations for the anionic sites induced by the reduction of conducting electroactive polymers. In this work we also found this to be the case. When the pH of the source solution was decreased below 3 the rate of transport of K+ ions also decreased (Figure 5.25). The same behaviour was found when source solutions containing different ions were employed (Table 5.11).

![Graph](image_url)

**Figure 5.25** Effect of the source solution pH on the transport of K+ across PP/PTS membrane. Source solution: 0.2M KCl with various pH. Receiving solution: deionised water. A symmetric pulsed potential waveform with 50 seconds pulse Width and +0.700V to -1.00V pulse Range. Waveform is applied between point A to B.
Electrochemical conditions were as in Table 5.7. Source solution: 0.2 M salt; Receiving solution: deionised water. pH was adjusted using KOH (for K⁺ transport), NaOH (for Na⁺ transport) and HCl.

A typical example given here was that of transport of KCl across the membrane. Keeping all other conditions constant and varying the KCl concentration in the source solution, the flux was found to increase as the concentration of potassium ions in the source solution increased, at least up to 0.10M (Figure 5.26). At higher concentration, the transport was no longer diffusion controlled but limited by the incorporation/expulsion processes induced by the electrical stimulus.

### Table 5.11 Effect of the source solution pH

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>2.0</th>
<th>3.0</th>
<th>4.3</th>
<th>6.0</th>
<th>6.4</th>
<th>7.3</th>
<th>9.0</th>
<th>10.0</th>
<th>10.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux of K⁺</td>
<td>0.26</td>
<td>1.83</td>
<td>1.91</td>
<td>1.95</td>
<td></td>
<td></td>
<td>2.10</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>(10⁹mol cm⁻²s⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flux of Na⁺</td>
<td>0.09</td>
<td>1.18</td>
<td>1.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>(10⁹mol cm⁻²s⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5.26** Effect of the source solution concentration on the transport of K⁺ across PP/PTS membrane. Source solution: various concentration of KCl, Receiving solution: deionised water. A symmetric pulsed potential waveform with 50 seconds pulse Width and +0.700V to -1.00V pulse Range was applied.
5.3.4 Transport of Other Species

Keeping Cl⁻ as the anion, the effect of the cation (Na⁺, Ca²⁺, Mg²⁺) in the source solution was investigated using various electrochemical conditions. It was found that manipulating the electrochemical conditions such as the potential range, pulse frequency and the electrotransport cell setup influences the transport of these ions across the membrane in a similar way to that observed for K⁺. This suggests that the transport of these electroinactive species across the membrane was controlled by the same transport mechanism. Typical results comparing transport of these cations are shown in Table 5.12.

**Table 5.12** The fluxes of Na⁺, Ca²⁺ and Mg²⁺

<table>
<thead>
<tr>
<th>Cation employed</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux obtained</td>
<td>1.4x10⁻⁹</td>
<td>2.0x10⁻¹⁰</td>
<td>4.4x10⁻¹¹</td>
</tr>
</tbody>
</table>

* A symmetric pulsed potential with 50 second pulse width and +0.70V to -1.0V pulsed range was employed. The electrotransport cell set up was as shown in figure 5.2(III). Source solution was 0.2M cation and receiving solution was the deionised water.

As outlined in Chapter 4, incorporation of Ca²⁺ or Mg²⁺ into PP/PTS films was much more difficult than incorporation of K⁺ and Na⁺ since the mobility of the Ca²⁺ and Mg²⁺ ions is small since they are divalent cations. If we consider that the transport of Ca²⁺ and Mg²⁺ across PP/PTS membrane was due to the same mechanism as for transport of K⁺ and Na⁺, then, according to the studies in Chapter 4 (equation 4.1 to 4.8), a low rate of transport was to be expected.

In order to investigate the effect of the anion in the source solution on the cation transport across the membrane, the cation was fixed using 0.2M Na⁺. Table 5.13 lists the various anions in the source solution and their influence on the Na⁺ transport.
Table 5.13* Effect of the anion in the source solution on the cation transport

<table>
<thead>
<tr>
<th>Anion Employed</th>
<th>Flux of Na⁺ (mol cm⁻²s⁻¹)</th>
<th>Flux of anion (mol cm⁻²s⁻¹)</th>
<th>Flux of PTS (mol cm⁻²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>1.4x10⁻⁹</td>
<td>1.3x10⁻⁹</td>
<td>1.4x10⁻¹⁰</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1.6x10⁻⁹</td>
<td>8.1x10⁻¹⁰</td>
<td>9x10⁻¹¹</td>
</tr>
<tr>
<td>CH₃COO⁻</td>
<td>6.4x10⁻¹⁰</td>
<td></td>
<td>1.9x10⁻¹⁰</td>
</tr>
<tr>
<td>C₆H₅COO⁻</td>
<td>4.8x10⁻¹⁰</td>
<td>3.1x10⁻¹⁰</td>
<td>1.2x10⁻¹⁰</td>
</tr>
<tr>
<td>PTS⁻</td>
<td>3.9x10⁻¹⁰</td>
<td></td>
<td>4.2x10⁻¹⁰</td>
</tr>
<tr>
<td>NPS²⁻</td>
<td>2.4x10⁻¹⁰</td>
<td>2.1x10⁻¹¹</td>
<td>1.9x10⁻¹⁰</td>
</tr>
</tbody>
</table>

* The experimental conditions were the same as described in Table 5.12.

It was found that an increase in the size of the anion resulted in a decrease in the rate of Na⁺ transport across the membrane. This may be due to the transport being limited by the anion transport across the membrane since the results in chapter 4 have shown that a large anion is difficult to incorporate.

5.3.5 Effect of Membrane Synthesis Conditions

Membranes used for all the previous transport studies were prepared using the same conditions. Investigation of the membrane synthesis conditions effect on the resultant membrane transport properties were next carried out.

The membranes used were prepared galvanostatically according to the procedure described in Chapter 3. In all membrane preparations the charge passed during polymerisation was controlled at 1.2 C/cm². The transport experiments was set up as described in section 5.3.3. As outlined in Chapter 3, the physical properties of the membrane such as conductivity and mechanical properties can be influenced by the current
density employed during synthesis. However, this has only a small influence on the resultant membrane transport properties (Table 5.14).

**Table 5.14** Effect of current densities on the fluxes of K+ transported

<table>
<thead>
<tr>
<th>Current Density (mA/cm²)</th>
<th>0.25</th>
<th>0.50</th>
<th>2.0</th>
<th>4.0</th>
<th>8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_s$ $(10^9 \text{mol cm}^{-2}\text{s}^{-1})$</td>
<td>1.7</td>
<td>1.6</td>
<td>2.1</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>$F_p$ $(10^9 \text{mol cm}^{-2}\text{s}^{-1})$</td>
<td>1.4</td>
<td>1.5</td>
<td>1.9</td>
<td>1.9</td>
<td>1.6</td>
</tr>
<tr>
<td>$F_s/F_p$</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Notes: (i) The polymerisation solution contained 0.20M pyrrole and 0.05M PTS; (ii) The current densities varied from 0.25mA/cm² to 8.0mA/cm², but the charge passed during polymerisation was controlled at 1.2C/cm² and (iii) $F_s$ and $F_p$ was the flux obtained using solution side of the membrane and plate side of the membrane exposed to the source solution.

The results also show that using different sides of the membrane exposed to the source solution the fluxes observed were similar and decreased slightly as the current density decreased (less than 2.0mA/cm²).

The effect of the composition of the polymerisation solution on the resultant membrane's transport properties was then investigated (Table 5.15). It was found that for a given monomer concentration, varying the concentration of counterion had little effect on the transport of K+ across the membrane. Contrastingly, increasing the concentration of the monomer (from 0.1M to 0.2M pyrrole), resulted in increased flux. Again, approximately the same fluxes were observed when different sides of the membrane were exposed to the source solution.
Table 5.15 Effect of composition of the polymerisation solution on K⁺ transport

<table>
<thead>
<tr>
<th>Solution Composition (Pyrrole/PTS)</th>
<th>$F_s$ ($10^9 \text{mol cm}^{-2} \text{s}^{-1}$)</th>
<th>$F_p$ ($10^9 \text{mol cm}^{-2} \text{s}^{-1}$)</th>
<th>$F_s/F_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 M/0.05M</td>
<td>1.3</td>
<td>1.4</td>
<td>0.93</td>
</tr>
<tr>
<td>0.10M/0.1M</td>
<td>1.7</td>
<td>1.7</td>
<td>1.0</td>
</tr>
<tr>
<td>0.20M/0.05M</td>
<td>2.1</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>0.20M/0.10M</td>
<td>2.0</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>0.20M/0.20M</td>
<td>2.1</td>
<td>2.0</td>
<td>1.1</td>
</tr>
<tr>
<td>0.20M/0.40M</td>
<td>2.3</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>0.40M/0.05M</td>
<td>2.2</td>
<td>2.3</td>
<td>1.0</td>
</tr>
<tr>
<td>0.40M/0.10M</td>
<td>2.1</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>0.40M/0.20M</td>
<td>2.4</td>
<td>2.4</td>
<td>1.0</td>
</tr>
<tr>
<td>0.40M/0.40M</td>
<td>1.9</td>
<td>2.0</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Note: Current density = 2.0mA/cm²; Charge Passed = 1.20C/cm²

5.3.6 Separation Experiments

The results in the previous sections have shown that many parameters can influence the transport of electroinactive species across conducting polymer membranes. They also show that when the experimental conditions were fixed, the rate of transport was governed by the nature of the transport species. For example, under the same experimental conditions the rate of transport was always in order of K⁺>Na⁺>Ca²⁺>Mg²⁺. All these observations lead to the expectation that separation of ions using conducting polymer membrane systems should be possible.

Consequently, the separation of electroinactive species was considered. The transport cell was set up as shown in Figure 5.2(III). Generally, the source solution used was equal concentrations (0.10M) of a mixture of two cations and the receiving solution was deionised water. Figure 5.27 shows some typical examples for separation of electroinactive species and separation coefficients of these species are listed in Table 5.16.
**Figure 5.27** Some typical examples for separation of electroinactive species using PP/PTS membranes. A symmetric pulsed potential with 50 seconds pulse width and +0.70V to -1.00V pulse range was applied between point A and B.
Table 5.16 Separation coefficients for separation of electroinactive species using PP/PTS membranes

<table>
<thead>
<tr>
<th>SK+/Na⁺</th>
<th>SK+/Ca²⁺</th>
<th>SK+/Mg²⁺</th>
<th>SN⁺/Ca²⁺</th>
<th>SN⁺/Mg²⁺</th>
<th>SCa²⁺/Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>122</td>
<td>195</td>
<td>33</td>
<td>32</td>
<td>3.6</td>
</tr>
</tbody>
</table>

S is separation coefficient.

Except for the source solution, other conditions were as in Table 5.7. The source solutions used were 0.1 M of mixture.

Results show that a high separation coefficient can be achieved when mixture of K⁺/Ca²⁺, K⁺/Mg²⁺, Na⁺/Ca²⁺ or Na⁺/Mg²⁺ were used in the source solution, and even for pairs of species similar in nature such as K⁺/Na⁺ or Ca²⁺/Mg²⁺, a separation can be achieved.

The effect of electrochemical conditions on the membrane separation properties was then considered. Experiments were set up using a source solution containing 0.10M KCl +0.10M NaCl. The effect of the pulse range on the separation coefficient was examined. The pulse range chosen has a large effect on the different redox states obtained and not surprisingly the results show that the membrane separation coefficient can be strongly influenced by the pulse range employed (Table 5.17).

Table 5.17 Effect of pulse range on the selectivity

<table>
<thead>
<tr>
<th>Experiment</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Range (V) vs Ag/AgCl</td>
<td>0.70/-1.0</td>
<td>0.0/-1.0</td>
<td>-0.75/-1.0</td>
<td>-2.0/0.80</td>
<td>0.7/-0.50</td>
<td>0.70/0.0</td>
</tr>
<tr>
<td>Flux of K⁺(F⁺) (10⁹ mol cm⁻² s⁻¹)</td>
<td>1.8</td>
<td>0.92</td>
<td>0.31</td>
<td>0.43</td>
<td>0.17</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Flux of Na⁺(F⁺) (10⁹ mol cm⁻² s⁻¹)</td>
<td>0.51</td>
<td>0.12</td>
<td>0.07</td>
<td>0.061</td>
<td>0.059</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Separation Coefficient ( S = F_K⁺/F_{Na⁺} )</td>
<td>3.5</td>
<td>7.7</td>
<td>4.4</td>
<td>7.2</td>
<td>2.9</td>
<td>-</td>
</tr>
</tbody>
</table>

Electrochemical conditions used were as in Table 5.5. Source solution: 0.1M K⁺+0.1M Na⁺; Receiving solution: deionised water.
In most cases higher selectivity was achieved at some sacrifice of the flux. Factors influencing the selectivity of, for example Na⁺ and K⁺, are the difference in mobility and the fact that different ions are incorporated and/or expelled at slightly different potentials (as observed in cyclic voltametric experiments in Chapter 4). These can be used to fine-tune a separation.

The effect of pulse width on selectivity is shown in Table 5.18. Obviously, the length of the pulse dictates the time in which incorporation/expulsion of each cation can proceed, and this has an effect on the selectivities attainable.

<table>
<thead>
<tr>
<th>Pulse Width (sec)</th>
<th>5.0</th>
<th>10.0</th>
<th>20.0</th>
<th>50.0</th>
<th>100.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux of K⁺ (F⁺)</td>
<td>0.68</td>
<td>1.4</td>
<td>1.8</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>(10⁹ mol cm⁻² s⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flux of Na⁺ (F⁺)</td>
<td>0.14</td>
<td>0.41</td>
<td>0.33</td>
<td>0.52</td>
<td>0.48</td>
</tr>
<tr>
<td>(10⁹ mol cm⁻² s⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separation Coefficient S = F⁺</td>
<td>4.9</td>
<td>3.4</td>
<td>5.5</td>
<td>3.3</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Except for the source solution, other experimental conditions were as in Figure 5.10. The solutions used were as in Table 5.17.

Furthermore, the influence of the use of asymmetric pulse widths on selectivity was found to be very interesting (Figure 5.28). Fixing the cathodic potential pulse width at 50 seconds, the separation coefficient decreased almost linearly as the anodic potential pulse width increased (curve A). Conversely, when the anodic potential pulse width was fixed at 50 seconds, the separation coefficient increased almost linearly with an increase in the cathodic potential pulse width (curve B). These results suggest that sodium cations were more difficult to incorporate into the
membrane since a longer cathodic potential pulse was required for its insertion.

![Diagram showing the effect of asymmetric pulse width on the separation coefficient.](image)

**Figure 5.28** Effect of asymmetric pulse width on the separation coefficient. Membrane: PP/PTS, Source solution: 0.1M KCl and NaCl, A asymmetric pulsed potential with +0.70V to -1.00V pulse range was applied. (A) Fixing the cathodic pulse width at 50.0 seconds and varying the anodic pulse width from 2.5 to 100.0 seconds, (B) Fixing the anodic pulse width at 50.0 seconds and varying the cathodic pulse width from 2.5 to 100.0 seconds.

The selectivity was also found to be influenced by the molar ratio between K⁺ and Na⁺ present in the source solution (Table 5.19 and 5.20).

**Table 5.19** Effect of molarity ratio on the separation coefficient (KCl=0.1M)

<table>
<thead>
<tr>
<th>Concentration of NaCl (M)</th>
<th>0.025</th>
<th>0.05</th>
<th>0.10</th>
<th>0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molarity Ratio K⁺/Na⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Separation Coefficient (S=F_{K⁺}/F_{Na⁺})</td>
<td>11.0</td>
<td>7.4</td>
<td>3.4</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Except for the source solution, conditions were as in Table 5.16. The source solution contained 0.1 M KCl and various concentration of NaCl.
Table 5.20 Effect of molarity ratio on separation coefficient
(NaCl=0.1M)

<table>
<thead>
<tr>
<th>Concentration of KCl (M)</th>
<th>0.025</th>
<th>0.05</th>
<th>0.10</th>
<th>0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molarity Ratio K⁺/Na⁺</td>
<td>0.25</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Separation Coefficient S=F∞⁺/FNa⁺</td>
<td>1.1</td>
<td>2.1</td>
<td>3.4</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Except for the source solution, conditions were as in Table 5.19. The source solution contained 0.1 M NaCl and various concentrations of KCl.

The results suggest that the rate of transport for K⁺ with the applied electrical stimulus was much higher than for sodium ions. For instance, when the ratio of K/Na was 1:4, the separation coefficient obtained was about 1, and when the ratio of K/Na was 4:1, the separation coefficient obtained was 11.

5.3.7 Reproducibility and Stability of the Membrane

The reproducibility of the membrane in terms of transport flux or permeability is very important for membrane research and potential applications. For example, without good reproducibility, systematic studies of membrane transport properties and/or determination of the effect of parameters on the membrane transport properties is not possible. The investigation of the membrane reproducibility was considered in this part of the work. The membranes were prepared according to the procedures described in Chapter 3, the polymerisation solution was 0.20M pyrrole and 0.05M PTS; the current density for polymerisation was 2.0mA/cm² and charge passed during polymerisation was 1.20C/cm². The experiments considered both membranes that were produced from one batch (Figure 5.29) and from different batches (Figure 5.30). The fluxes, standard derivation and variation coefficient are summarised in Table 5.21 and 5.22. The transport behaviour of the
membrane produced even from different batches, the variation coefficient being still less than 5%.

**Figure 5.29** Reproducibility of transport of $K^+$ across PP/PTS membranes produced from the same batch of the polymerisation solution. Source solution: 0.2M KCl. Receiving solution: deionised water. A symmetric pulsed potential with +0.70V to -1.00V pulse range and 50.0 seconds potential range was applied between 40.0 to 100 minutes.

**Figure 5.30** Reproducibility of transport of $K^+$ across PP/PTS membranes produced from different batches of the polymerisation solution. Source solution: 0.2M KCl. Receiving solution: deionised water. A symmetric pulsed potential with +0.70V to -1.00V pulse range and 50.0 seconds potential range was applied between 40.0 to 100 minutes.
Table 5.21 Determination of membrane reproducibility using membranes produced from the same batch of polymerisation solution

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux of K⁺ (10⁹mol cm⁻²s⁻¹)</td>
<td>1.85</td>
<td>1.93</td>
<td>1.77</td>
<td>1.83</td>
<td>1.85</td>
</tr>
<tr>
<td>X (mol cm⁻²s⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S/X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental conditions were as in Figure 5.29. X = \( \frac{\sum X_i}{n} \), is the average flux; n is the numbers of experiments; \( S = (\frac{\sum (X_i-X)^2}{n-1})^{1/2} \) is the standard derivation and \( \frac{S}{X} \) is the variation coefficient.

Table 5.22 Determination of the membrane reproducibility (the membrane produced from different batches of polymerisation solutions)

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux of K⁺ (10⁹mol cm⁻²s⁻¹)</td>
<td>1.85</td>
<td>1.94</td>
<td>1.75</td>
<td>1.85</td>
<td>1.69</td>
<td>1.88</td>
<td>1.83</td>
</tr>
<tr>
<td>X (mol cm⁻²s⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S/X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental conditions were as in Figure 5.29. X = \( \frac{\sum X_i}{n} \), is the average flux; n is the numbers of the experiments; \( S = (\frac{\sum (X_i-X)^2}{n-1})^{1/2} \) is the standard derivation and \( \frac{S}{X} \) is the variation coefficient.

The determination of the stability of PP/PTS membrane in terms of flux changes with time was then considered. The membranes were produced on one day but from different batches of the polymerisation solution.
The membranes were then stored by placing each between sheets of tissue paper in the laboratory environment. The fluxes reported are the average flux obtained from three experimental results.

Figure 5.31 gives the relationship between the average flux and the membrane storage time. It was found that the fluxes only decreased slightly even after one year indicating that the transport properties of the membrane were very stable with storage.

![Graph showing the relationship between flux and time](image)

**Figure 5.31** The stability of PP/PTS membranes.

### 5.4 CONCLUSIONS

The electrochemically controlled transport of electroinactive species across PP/PTS membranes has been systematically investigated. The hardware for transport studies has been established and a transport mechanism elucidated. The following conclusions can be drawn:

1. Transport across the membranes can be switched on and off by application of an external electrical potential
(2) The transport properties of the membrane can be varied by application of different potential waveforms. Pulsed potential waveforms were found to be more efficient than constant potential waveforms or sweep potential waveforms.

(3) For a given potential waveform, changes in the electrochemical conditions resulted in changes in the rate of transport. In the case of a constant potential waveform, significant transport was observed only when a negative potential was applied. When a more negative potential was used, faster transport was observed. The total mass that could be transported was related to the total quantity of polymer. With sweep potential waveforms, linear transport is observed, with slow scan rates giving larger fluxes. In the case of pulsed potential waveforms, the transport is also linear and efficient transport was observed when the potential applied was able to fully oxidise and reduce the membrane. Varying the pulse width strongly influences the rate of transport. With a symmetric applied pulse potential, a 20.0 seconds pulse width gave the highest flux and with an asymmetric applied pulse potential, the fluxes obtained were always smaller than those obtained using a symmetric pulse.

(4) Investigation of the electrotransport cell design showed that the side of the membrane that was contacted to the outside electronic circuit did not effect the rate of transport. However, the shape of the connector used markedly affected the rate of transport, a larger flux was observed when a circular connection was employed. The size of the membrane also influenced the rate of transport, a smaller diameter membrane giving a larger flux (per cm$^2$ of membrane surface).
(5) The largest fluxes were obtained using a membrane thickness between 8 to 10 μm, but better reproducibility was observed using 4μm.

(6) There was no significant difference in the observed rate of transport when different sides of the PP/PTS membrane was exposed to the source solution.

(7) Under the same electrochemical conditions, the rate of transport for different cations was in the following order:

$$K^+ > Na^+ > Ca^{2+} > Mg^{2+}$$

The rate of transport can be influenced by the anion employed. Large fluxes were observed when small anions were employed.

(8) Chemical conditions such as source solution pH and concentration also influence transport. When the source solution pH was lower that 2, the flux obtained was about ten times smaller than that obtained at higher pH. Increasing the concentration of the transport species above 0.1M, had only a small effect on the rate of transport.

(9) The membrane synthesis conditions such as current densities and the composition of the polymerisation solution have a slight influence on the rate of transport.

(10) The membrane separation capability for different cation mixtures in solution is in the order

$$S_{K^+/Mg^{2+}} > S_{K^+/Ca^{2+}} > S_{Na^+/Ca^{2+}} > S_{Na^+/Mg^{2+}} > S_{Ca^{2+/Mg^{2+}}} > S_{K^+/Na^+}$$
(11) Separation properties of the membrane can be modified by application of various electrical stimuli. In most cases a higher selectivity was achieved at some sacrifice of the flux.

(12) The membrane reproducibility and stability was good, the variation coefficient in the measured flux was less than 5% with the fluxes only slightly decreasing over the period of one year.

(13) Transport of an electroinactive species across a conducting polypyrrole membrane can undergo two different mechanisms. An ion incorporation/expulsion mechanism can be used for an electrically stimulated transport across the membrane. In addition, ion exchange mechanisms can occur.
CHAPTER 6

EFFECT OF THE COUNTERION EMPLOYED DURING SYNTHESIS ON TRANSPORT OF ELECTROINACTIVE SPECIES ACROSS POLYPYRROLE MEMBRANES
6.1 INTRODUCTION

It is well known that the properties of conducting polymer materials are strongly influenced by the counterion employed during synthesis. Some previous reports have pointed out that the conductivity, mechanical properties, surface morphology and chemical or electrochemical characteristics of the conducting polymer are greatly affected by the counterion employed during synthesis [202]. The results presented in the previous chapters have shown that the transport properties of the membrane are governed by the chemical or electrochemical properties of the membrane such as the ion incorporation/expulsion and ion exchange. The effect of the counterion on polymer synthesis was outlined in Chapter 2 and the effect of the counterion on the membrane synthesis was investigated in Chapter 3 where it was concluded that the membrane physical properties such as conductivity, mechanical properties and surface morphology are dramatically influenced by the counterion employed. In Chapter 4, it was shown that the ion incorporation/expulsion properties of the polypyrrole film in certain instances is governed by the counterion employed. In this chapter, the effect of the counterion employed during synthesis on the resultant membrane transport properties is described.

A large range of synthesis counterions were originally considered (see Table 3.11). Sulfonated aromatic counterions were considered since mechanically stable conducting polymer materials may be produced using them. K\(^+\) and Ca\(^{2+}\) ions were used as test cases to determine the membrane transport properties and separation capabilities.
6.2 EXPERIMENTAL

6.2.1 Reagents and Solutions

All chemicals and solutions were the same as those used in previous chapters.

6.2.2 Instrumentation

All instruments used for this work including the membrane synthesis cell and electrode materials have been described in previous chapters.

6.2.3 Procedures

Membrane Preparation

All membranes were prepared by electrochemical polymerisation methods according to the procedure described in chapter 3. Polymerisation was carried out galvanostatically using a current density of 2.0mA/cm² and 1.20C/cm² charge passed. In all experiments, the polymerisation solution consisted of 0.20M pyrrole and 0.05M counterion as the supporting electrolyte.

Transport Experiments

The electrotransport cell setup was as shown in Figure 5.2(III). The auxiliary and reference electrodes were placed in the source solution compartment. Electrochemical control of transport was achieved by application of a symmetric pulsed potential waveform to the membrane.
with a pulse width of 50 seconds and a potential range of +0.70V to -1.0V (vs Ag/AgCl).

Experiments were conducted using the different sides of the membrane exposed to the source solution.

The source solution used for transport studies was 0.2M KCl or CaCl₂ and for separation experiments it was a 0.1M KCl/CaCl₂ mixture. The receiving solution was deionised water. The capacities of each compartment in the transport cell was 60 ml. The solutions in both compartments were well stirred. The electrical stimulus was applied according to the following program:

During experiments samples were taken every 20 minutes from the receiving solution. The sample analysis was carried out using Atomic Absorption Spectrometry (AA). The transport results were recorded by measuring the changes in the concentration of the species transported as a function of time. Generally, the fluxes were the average fluxes measured during the period of applied electrical stimulus.
6.3 RESULTS AND DISCUSSION

In this section, in order to explain the effect of the counterion employed on the resultant membrane transport properties, the cyclic voltammetry of the polypyrrole polymer has been examined. Transport of $\text{K}^+$ and $\text{Ca}^{2+}$ across different membranes was also investigated. The membrane separation properties were determined using a source solution containing 0.10M KCl and 0.10M CaCl$_2$.

6.3.1 Cyclic Voltammetry

Initial experiments involved a study using cyclic voltammetry to determine the effect of the counterion incorporated during synthesis on the electrochemical properties of the polymers.

Polymers containing each of the sulfonated counterions were deposited onto glassy carbon electrodes. Cyclic voltammograms were recorded in 0.20M KCl or 0.20M CaCl$_2$. The cyclic voltammograms for PP/PTS and PP/NPS films were described in Chapter 4 (Figure 4.1 and 4.3 respectively). Voltammograms for membranes other than these are shown in Figures 6.1 to 6.4.

The cyclic voltammograms obtained for all polypyrrole films revealed very similar characteristics to those observed in Chapter 4. For example, the cyclic voltammogram for PP/EBS recorded in KCl solution (Figure 6.2(a)) reveals two distinct redox processes. These correspond to incorporation (region 1) and expulsion (region 2) of the cation and incorporation (region 3) and expulsion (region 4) of the anion. In all cases cation responses in CaCl$_2$ solution were less well defined confirming that the cation plays a part in the redox process and that Ca$^{2+}$
is more difficult to incorporate than K+. In the case of PP/BSA (Figure 6.1(b),) and PP/PTS (Figure 4.1(c)), the Ca\(^{2+}\) incorporation peak did not appear while for all others a Ca\(^{2+}\) incorporation peak was observed. However, as the size of the sulfonated counterion incorporated during synthesis was increased, the Ca\(^{2+}\) incorporation response was more evident (compare Figure 4.1(c), 6.1(b), 6.2(b) and 6.3(b) with 4.3(c) and 6.4(b)).

The cation responses in KCl media were also influenced by the counterion employed. It was found that with singly charged counterions, the cation incorporation peak in region A were always sharp and with doubly charged counterions, the peaks in region A was broader and may indeed represent two responses. This may be due to the two different negatively charged sites for each counterion existing in the polymer matrix. During redox cycling the ion incorporation and expulsion ability of the two sites may occur at slightly different potentials.
Figure 6.1 Cyclic voltammograms of PP/BSA recorded in (a) 0.2M KCl and (b) 0.2M CaCl\textsubscript{2}. Scan rate: 50 mV/s.
Figure 6.2 Cyclic voltammograms of PP/EBs recorded in (a) 0.2M KCl and (b) 0.2M CaCl₂. Scan rate: 50 mV/s.
Figure 6.3 Cyclic voltammograms of PP/MS recorded in (a) 0.2M KCl and (b) 0.2M CaCl₂. Scan rate: 50 mV/s.
Figure 6.4 Cyclic voltammograms of PP/BS recorded in (a) 0.2M KCl and (b) 0.2M CaCl₂. Scan rate: 50 mV/s.
6.3.2 Transport of K⁺ across Polypyrrole Membranes Containing Different Counterions

Electrochemically controlled transport of K⁺ across a number of polypyrrole membranes was considered. Some typical results are shown in Figures 6.5 to 6.7. It was found that no significant transport occurred before an electrical potential was applied. Application of a pulsed potential was necessary to initiate and sustain transport. When the applied potential was removed, the rate of transport decreased to almost zero. This behaviour is the same as observed in chapter 5 for transport of K⁺ across PP/PTS membranes. In chapter 5, an ion-incorporation/expulsion mechanism was proposed for electrochemically controlled transport of electroinactive species across a PP/PTS membrane. Based on the cyclic voltammetric results obtained in Chapter 4 and in this chapter, it is reasonable to believe that this mechanism can also be applied to the transport of electroinactive ions across polypyrrole membranes containing different counterions.

Comparing all membranes, the PP/PTS membrane (Figure 5.24) was the only one where the rate of K⁺ transported across the membrane was similar irrespective of which side of the membrane was exposed to the source solution. Membranes grown using other sulfonated counterions exhibited some asymmetric character (see Figure 6.5 to 6.7).
Figure 6.5 Electrochemically controlled transport of K⁺ across PP/EBS membranes. Source solution: 0.2M KCl, Receiving solution: deionised water. Time A: potential routine applied, Time B: potential routine removed. (1) Solution side, (2) Plate side of the membrane exposed to the source solution.

Figure 6.6 Electrochemically controlled transport of K⁺ across PP/MS membranes. Source solution: 0.2M KCl, Receiving solution: deionised water. Time A: potential routine applied, Time B: potential routine removed. (1) Solution side, (2) Plate side of the membrane exposed to the source solution.
Figure 6.7 Electrochemically controlled transport of K⁺ across PP/NPS membranes. Source solution: 0.2M KCl, Receiving solution: deionised water. Time A: potential routine applied, Time B: potential routine removed. (1) Solution side, (2) Plate side of the membrane exposed to the source solution.

The extent of the asymmetric transport behaviour can be estimated using the ratio of the fluxes obtained when different sides of the membrane were exposed to the source solution. It may be expressed as in equation 6.1.

\[ \xi = \frac{F_S}{F_P} \]  

(6.1)

where \( \xi \) is defined as the asymmetric factor for the membrane, \( F_S \) and \( F_P \) are the fluxes obtained using the solution side or the plate side of the membrane respectively.

Fluxes obtained for transport of K⁺ across each of these membranes are shown in Table 6.1. In all cases, \( \xi \) is larger than 1. This means that the rate of transport was faster when the solution side of the membrane was exposed to the source solution. Except for the PP/BS membrane, the
fluxes obtained with the solution side of the membrane increased as the molecular weight of the counterion increased. A similar trend was observed for the plate side fluxes, although the plate side flux for the PP/PTS membrane was unusually high. The asymmetric transport coefficient $\xi$ appears to be related to the counterion employed, but it is difficult to see a regular relationship between $\xi$ and the counterion size or charge. However, the flux across the membrane and the extent of any asymmetric behaviour depends on the counterion size.

Many factors such as the surface characteristic and the chemical structure of the membrane could lead to asymmetric transport. The results in chapter 2 have shown that during electrosynthesis, the counterion is not just passively incorporated into the polymer matrix to maintain electroneutrality but it also plays an active role in determining the rate of the polymerisation. This in turn will affect the polymer structure. In addition, it is known that membranes prepared with different counterions have different surface characteristics (Chapter 3). This again might lead to asymmetric transport behaviour.

As mentioned in chapter 3, polypyrrole membranes prepared using electrochemical methods are non-porous.

Generally, the transport across a non-porous membrane can be described in terms of a solution-diffusion mechanism, i.e.

$$ P = S \times D $$

(6.2)

where $P$ is the permeability, $S$ is the solubility and $D$ is the diffusivity.

Since the permeability ($P$) is proportional to the flux, then the rate of transport can be described using the permeability. In the case of
electrochemically controlled transport across conducting polymer membranes, the significance of the solubility \( S \) can be considered as the ion incorporation ability of the membrane.

The cyclic voltammetric results in Chapter 4 and in this chapter have shown that an increase in the molecular weight of the counterions lead to an increase in the ion incorporation ability of the polymer. In other words, this leads to an increase in the solubility \( S \). Chronoamperometric results in chapter 4 suggest that the diffusivity of the incorporating ion increases when the higher molecular weight counterions are employed during the membrane synthesis. Therefore according to equation (6.2), for a given source solution, the permeability of a ion increases as the molecular weight of the counterion increases.

The concentration-time profile for transport of KCl across a PP/PTS membrane (Figure 5.24) shows linear transport behaviour during the application of a pulsed potential no matter which side of the membrane was exposed to the source solution. In other words, the rate of transport was independent of time. In all other cases, when the solution side of the membrane was exposed to the source solution, the rate of transport observed during application of an electrical stimulus was almost linear but when the plate side of the membrane was exposed, the rate of transport decreased with time (see Figure 6.5 to 6.7, curve 2).

Furthermore, in the case of PP/NPS, when the potential was removed, the transport still continued (Figure 6.7). Similar behaviour was observed when a PP/BS membrane was employed. For all membranes with singly charged counterions this behaviour was not observed (Figure 6.5 and 6.6). This may be because the doubly charged counterions can act to balance two types of positive charges during the redox cycling
process. Here the counterion may "use" only one negative charge to neutralise the positive charges on the polymer backbone and the other one may combine with a cation (M⁺) incorporated from the solution. The solution anion (A⁻) may also be incorporated into the polymer matrix to neutralise positive charge on the polymer backbone. When the applied potential is removed, both cations and mobile anions are present in the polymer and may diffuse through the membrane resulting in the continued transport observed.

**Table 6.1 Effect of the counterion employed during synthesis on the transport properties of the membrane**

<table>
<thead>
<tr>
<th>Membranes</th>
<th>PP/BSA (mol cm⁻² s⁻¹)</th>
<th>PP/PTS (mol cm⁻² s⁻¹)</th>
<th>PP/EBS (mol cm⁻² s⁻¹)</th>
<th>PP/MS (mol cm⁻² s⁻¹)</th>
<th>PP/BS (mol cm⁻² s⁻¹)</th>
<th>PP/NPS (mol cm⁻² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fp</td>
<td>2.8x10⁻¹⁰</td>
<td>1.9x10⁻⁹</td>
<td>1.3x10⁻⁹</td>
<td>1.6x10⁻⁹</td>
<td>1.4x10⁻⁹</td>
<td>2.2x10⁻⁹</td>
</tr>
<tr>
<td>Fs</td>
<td>6.4x10⁻¹⁰</td>
<td>2.1x10⁻⁹</td>
<td>3.4x10⁻⁹</td>
<td>3.6x10⁻⁹</td>
<td>2.9x10⁻⁹</td>
<td>3.5x10⁻⁹</td>
</tr>
<tr>
<td>ξ=Fₛ/Fₚ</td>
<td>2.3</td>
<td>1.1</td>
<td>2.6</td>
<td>2.3</td>
<td>2.1</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Notes: Fₛ and Fₚ are average fluxes of K⁺, they were measured when the electrical stimuli was applied; The subscript S and P correspond to the experimental set up using solution side (Fₛ) and plate side (Fₚ) of the membrane exposed to the source solution.

### 6.3.3 Transport of Ca²⁺ across Polypyrrole Membrane Containing Different Counterions

Some typical results for transport of Ca²⁺ across polypyrrole membranes are shown in Figure 6.8 to 6.10. Once again with no electrical stimulus no significant transport was observed. However, transport could be initiated by application of a pulsed potential and when this potential was removed the transport ceased. With transport of Ca²⁺, the PP/PTS membrane was unusual in that it was the only membrane which had almost symmetric transport behaviour. For the other membranes some
asymmetric transport behaviour was observed. Fluxes for the transport of Ca\textsuperscript{2+} across all the membranes are summarised in Table 6.2.

In all cases, fluxes were lower compared with those for K\textsuperscript{+}. Again, as the size of the counterion increased, the Ca\textsuperscript{2+} fluxes increased and no regular relationship was found between the asymmetric coefficient \( u \) and the counterion size or charge number. One purpose of these experiments was to determine the effect of the charge of the solution cation and the membrane counterion upon the transport across the membrane. Does a doubly charged counterion in the membrane enable a doubly charged cation to be more readily transported across the membrane than a membrane containing a singly charged counterion? The results indicate that for K\textsuperscript{+}, both the solution side and plate side fluxes are related to the molecular size of the counterions rather than to the charge number. When the potential was removed, the transport was observed to continue when the PP/NPS and PP/BS membrane were employed. Also, in most cases, the transport of Ca\textsuperscript{2+} across PP membranes was not linear.

For a given membrane, the rate of transport for different species is dependent on the ability of the polymer to incorporate these species. For K\textsuperscript{+} and Ca\textsuperscript{2+}, the cyclic voltammetric results show that K\textsuperscript{+} is much more readily incorporated than Ca\textsuperscript{2+}. Thus according to equation (6.2), the solubility of Ca\textsuperscript{2+} ions in the polymer was lower than that of K\textsuperscript{+} ions resulting in a lower flux across the membrane.
Figure 6.8 Electrochemically controlled transport of Ca\(^{2+}\) across a PP/EBS membrane. Source solution: 0.2M CaCl\(_2\), Receiving solution: deionised water. Time A: potential routine applied, Time B: potential routine removed. (1) Solution side; (2) plate side of the membrane exposed to the source solution.

Figure 6.9 Electrochemically controlled transport of Ca\(^{2+}\) across a PP/MS membrane. Source solution: 0.2M CaCl\(_2\), Receiving solution: deionised water. Time A: potential routine applied, Time B: potential routine removed. (1) Solution side; (2) plate side of the membrane exposed to the source solution.
Figure 6.10 Electrochemically controlled transport of Ca$^{2+}$ across a PP/NPS membrane. Source solution: 0.2M CaCl$_2$, Receiving solution: deionised water. Time A: potential routine applied, Time B: potential routine removed. (1) Solution side; (2) plate side of the membrane exposed to the source solution.

Table 6.2 Effect of the counterion incorporated during synthesis on the transport of Ca$^{2+}$ across selected polypyrrole membranes

<table>
<thead>
<tr>
<th>Membranes</th>
<th>PP/BSA</th>
<th>PP/PTS</th>
<th>PP/EBS</th>
<th>PP/MS</th>
<th>PP/BS</th>
<th>PP/NPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_p$</td>
<td>0.2</td>
<td>1.7</td>
<td>4.0</td>
<td>3.9</td>
<td>0.8</td>
<td>6.6</td>
</tr>
<tr>
<td>($10^{10}$mol cm$^{-2}$s$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_s$</td>
<td>0.6</td>
<td>2.0</td>
<td>8.2</td>
<td>12.0</td>
<td>3.8</td>
<td>15.0</td>
</tr>
<tr>
<td>($10^{10}$mol cm$^{-2}$s$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\xi=F_s/F_p$</td>
<td>2.7</td>
<td>1.2</td>
<td>2.1</td>
<td>3.1</td>
<td>4.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>
6.3.4 Separation Experiments

To examine the separation capabilities of the membranes described above, a mixed source solution containing 0.10M KCl and 0.10M CaCl₂ was employed. The solution side of the membrane was exposed to the source solution since this configuration results in the highest flux. All other experimental conditions were the same as in section 6.3.3. A typical result (of PP/NPS membrane) is shown in Figure 6.11. The concentration-time profiles for the PP/BS membrane were very similar to those of the PP/NPS membrane. Results for other membranes are not shown since transport behaviour was similar to that observed for the PP/PTS membrane (Figure 5.27, (b)). The separation coefficients of all membranes for K⁺ and Ca²⁺ are summarised in Table 6.3. The results show that an increase in the size of the counterion results in a decrease in the membrane separation coefficient (Flux K⁺/Flux Ca²⁺). In the mixed solution the flux of K⁺ was found to remain relatively constant (see Table 6.1), while the flux for Ca²⁺ transport decreased markedly with a decreased size in the counterion (Table 6.2). These factors combined to influence the selectivity of the membranes. Clearly, K⁺ ions compete more efficiently for available ion exchange sites than the Ca²⁺ ions, leading to the separation of K⁺ from Ca²⁺.
Figure 6.11 Electrochemically controlled transport of K⁺ and Ca²⁺ across a PP/NPS membrane. Source solution: 0.1M KCl + 0.1M CaCl₂, Receiving solution: deionised water. Time A: potential routine applied, Time B: potential routine removed. (1) K⁺ transport; (2) Ca²⁺ transport.

Table 6.3 Effect of the counterion incorporated during synthesis on separation properties of the membranes

<table>
<thead>
<tr>
<th>Membranes</th>
<th>PP/BSA (10^9 mol cm⁻²s⁻¹)</th>
<th>PP/PTS</th>
<th>PP/EBS</th>
<th>PP/MS</th>
<th>PP/BS</th>
<th>PP/NPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux K⁺</td>
<td>0.24</td>
<td>1.9</td>
<td>2.9</td>
<td>3.1</td>
<td>2.6</td>
<td>3.5</td>
</tr>
<tr>
<td>Flux Ca²⁺</td>
<td>&lt;0.1</td>
<td>2.0</td>
<td>4.9</td>
<td>5.4</td>
<td>6.0</td>
<td>9.4</td>
</tr>
<tr>
<td>FK⁺/FCa²⁺</td>
<td>&gt;240</td>
<td>95</td>
<td>59</td>
<td>57</td>
<td>43</td>
<td>37</td>
</tr>
</tbody>
</table>
6.4 CONCLUSIONS

The effect of the counterion employed during synthesis on the resultant membrane transport properties has been investigated.

Except for the PP/PTS membrane, asymmetric transport behaviour was observed for all membranes. The solution side fluxes obtained were larger than the plate side fluxes. The extent of the asymmetric transport, as determined by $u$, are in the order

(1) For $K^+$:

$$PP/EBS > PP/BSA = PP/MS > PP/BS > PP/NPS > PP/PTS$$

(2) For $Ca^{2+}$:

$$PP/BS > PP/MS > PP/BSA > PP/NPS > PP/EBS > PP/PTS$$

The rate of transport increased as the size of the counterion increased.

The separation capabilities of the membrane decreased as the size of the counterion increased. The separation coefficient $S=F_{K^+}/F_{Ca^{2+}}$ varied in the order of:

$$PP/BSA > PP/PTS > PP/EBS > PP/MS > PP/BS > PP/NPS.$$
CHAPTER 7

EFFECT OF DODECYLSULFATE ON THE SYNTHESIS AND TRANSPORT PROPERTIES OF POLYPYRROLE MEMBRANES
7.1 INTRODUCTION

Methods for conducting polypyrrole membrane synthesis have been outlined in chapter 1. The effect of sulfonated counterions on the synthesis and transport properties of the membrane has been investigated in previous chapters. The membrane preparation method considered in the previous chapters used a polymerisation solution containing a single counterion. The results have shown that the counterion employed during synthesis determines the physical, chemical and transport properties of the conducting polymer membranes produced [202].

A large number of counterions have been used for polypyrrole synthesis [202]. In fact, due to special requirements, such as mechanical properties, uniformity and adhesive properties only a small number of them are suitable for the synthesis of free standing membranes using normal polymerisation methods. Some counterions have very attractive chemical or electrochemical properties but due to practical problems cannot be used for free standing polypyrrole membrane synthesis. For instance polymers containing dodecylsulfate (DS) have been reported to possess unique electrodynamic behaviour [127]. Although the polymer can be oxidised and reduced, the mobility of the DS is low and charge balance is achieved predominantly via the movement of cations into and out of the polymer. Since DS is a surfactant molecule the surface hydrophobicity and some other surface characteristics of the membrane may also be changed. These could lead to changes in membrane transport properties but such a counterion cannot be used to produce free standing membranes because the tensile strength of the polymer is low, and the surface morphology is rough and porous [203].
However, in order to increase the number of counterions suitable for use in free standing membranes and to modify the transport properties of the membrane, the development of new membrane synthetic methods is necessary.

In this chapter, as part of our ongoing studies on the effect of counterions and membrane preparation methods on membrane synthesis and the resultant membrane transport properties, the effect of the presence of a surfactant molecule during membrane synthesis has been considered. The surfactant molecule used was dodecylsulfate (DS). Two new synthesis methods: "mixed counterion" and "multilayer polymerisation" methods have been investigated using PTS and DS as the counterions. By using the mixed counterion polymerisation and multilayer polymerisation methods, stand alone mixed counterion membranes(PP/PTS-DS) and layer membranes(PP/PTS/PP/DS and PP/DS/PP/PTS) have been successfully prepared. The electrochemically controlled transport of electroinactive species across these membranes was investigated.

7.2 EXPERIMENTAL

7.2.1 Reagents and Solutions

The surfactant used was dodecylsulfate (DS) sodium salt, supplied by SIGMA and used as received. All other reagents used were described in previous chapters. All solutions used for transport or electrochemical studies were prepared as described in previous chapters.
7.2.2 Instrumentation

All instruments used were as described in previous chapters.

7.2.3 Procedures

7.2.3.1 Mixed Counterion Membrane Preparation

The membranes were prepared using the same procedure described in chapter 3. The polymerisation solutions contained 0.20M pyrrole, 0.05M PTS and various concentrations of DS, the ratio of PTS/DS was varied from 5:1 to 10:1 to 20:1 to 50:1. The polymerisation was carried out galvanostatically using a current density of 2.0mA/cm². The charge density passed during polymerisation was 1.20C/cm². The synthesis cell used was as described in chapter 3.

7.2.3.2 Layered Membrane Preparation

The synthesis cell set up was as described in chapter 3 and the same stainless steel working electrode was employed. Polymerisation for each layer was carried out galvanostatically with a current density of 2.0mA/cm² and a charge density of 0.6C/cm². The polymerisation solution for each polymerisation step was 0.20M pyrrole and 0.05M counterion(PTS or DS) in aqueous solution. When the polymerisation of the first layer of the membrane was completed, the electrode coated with the first layer was removed from the solution used, rinsed with distilled water and then placed in another polymerisation solution to form the second layer of the polymer. The preparation of each polymer layer was as outlined in chapter 3, but the membrane was only peeled off the substrate when the final polymer layer formation was completed.
7.2.3.3 Transport Experiment Set up

The transport cell set up was as described in chapter 5, Figure 5.2(III). The auxiliary and reference electrodes were set up in the source solution compartment. The applied electrical stimulus was a symmetric pulsed potential waveform with pulse width of 50 seconds and pulse range of +0.70V to -1.0V (vs Ag/AgCl, 3M NaCl).

The source solutions used were: (i) 0.2M KCl; (ii) 0.2M NaCl; (iii) 0.2M CaCl\textsubscript{2} or (iv) 0.10M KCl +0.10M NaCl or (v) 0.10M KCl +0.10M CaCl\textsubscript{2}. In all experiments, the receiving solution used was deionised water. The volume of the solution in each compartment of the transport cell was 60 ml.

For each given source solution, the membrane was set up using different sides exposed to the source solution. During transport experiments, samples were taken every 20 minutes from the receiving solution and analysed for metal ions using atomic absorption spectrometry.

The electrical stimulus was applied according to the same procedure as shown in Chapter 6.

The fluxes reported in this chapter were the average fluxes measured when the electrical potential was applied to the membrane.
7.3 RESULTS AND DISCUSSION

7.3.1 Mixed Counterion Membrane Preparation and Characterisation

Initial work was concerned with the preparation of materials with adequate mechanical properties to be used as stand alone membranes.

Attempts to produce conducting polypyrrole membranes with DS as the sole counterion were unsuccessful. Membranes prepared had inadequate mechanical properties and could not be prepared uniformly nor pinhole free. Consequently synthesis of membranes using a mixed counterion method was considered. This uses a polymerisation solution containing two or more counterions. Since polypyrrole membranes with good mechanical properties and uniformity have been prepared using PTS as the sole counterion (see chapter 3 and 5), in this work a polymerisation solution containing PTS and DS was employed. The effect of DS on the membrane produced was considered using conductivity measurements, tensile strength tests, scanning electron microscopy (SEM), dynamic contact angle (DCA) analysis and cyclic voltammetry (CV).

7.3.1.1 Mechanical Properties and Conductivities of DS Containing Membranes

The effect of the presence of DS in the polymerisation solution on the conductivity and tensile strength of the resultant membranes is shown in Table 7.1. The presence of DS decreased both the conductivity and
tensile strength, but at concentrations of DS < 0.005M the mechanical properties of the membrane were adequate for the required purpose.

### Table 7.1 Conductivity and tensile strength data for polypyrrole membranes

<table>
<thead>
<tr>
<th>Composition of Polymerisation Solution</th>
<th>Resultant Membranes</th>
<th>Conductivity $\sigma_v$ (S/cm)</th>
<th>Tensile strength (MPa)</th>
<th>Thickness $\mu$m</th>
<th>Conductance $\sigma$ (S)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2M Py 0.05M PTS No DS</td>
<td>PP/PTS (PTS)</td>
<td>105±10</td>
<td>70±6</td>
<td>4.0±0.3</td>
<td>0.042</td>
</tr>
<tr>
<td>0.2M Py 0.05M PTS 0.001M DS</td>
<td>PP/PTS/DS (DS 1#)</td>
<td>94±6</td>
<td>63±6</td>
<td>4.5±0.3</td>
<td>0.041</td>
</tr>
<tr>
<td>0.2M Py 0.05M PTS 0.0025M DS</td>
<td>PP/PTS/DS (DS 2#)</td>
<td>82±5</td>
<td>55±6</td>
<td>5.0±0.3</td>
<td>0.041</td>
</tr>
<tr>
<td>0.2M Py 0.05M PTS 0.005M DS</td>
<td>PP/PTS/DS (DS 3#)</td>
<td>73±7</td>
<td>24±5</td>
<td>5.5±0.3</td>
<td>0.040</td>
</tr>
<tr>
<td>0.2M Py 0.05M PTS 0.01M DS</td>
<td>PP/PTS/DS (DS 4#)</td>
<td>70±7</td>
<td>12±3</td>
<td>6.0±0.3</td>
<td>0.042</td>
</tr>
<tr>
<td>0.2M Py 0.05M PTS 0.02M DS</td>
<td>PP/PTS/DS (DS 5#)</td>
<td>65±7</td>
<td>5±2</td>
<td>6.3±0.3</td>
<td>0.042</td>
</tr>
<tr>
<td>0.2M Py 0.05M DS No PTS</td>
<td>PP/DS (DS 0#)</td>
<td>40±9</td>
<td>3±2</td>
<td>9.0±0.3</td>
<td>0.036</td>
</tr>
</tbody>
</table>

Notes: All membranes were prepared under the same electrochemical conditions. Current density: 2.0mA/cm², Polymerisation time: 10.0min. Amount of charge density passed during polymerisation: 1.20C/cm².

*See text.

The thickness of the membrane was measured using SEM (Table 7.1). As the DS concentration employed during polymerisation increased, the thickness of the membrane also increased. Since the same amount of charge was consumed in the preparation of all membranes, if we assume
that the polymerisation/deposition efficiency are the same, then this observation suggests that the DS containing membrane is less dense.

It should be mentioned that in Table 7.1 the conductivities were measured in terms of volume conductivity calculated according to equations 3.1 and 3.2. These results shown that the membrane conductivity changes may be due to differences in the density of the materials produced. Based on the assumption made above, that is that the current efficiency was the same for different concentrations of DS present in the polymerisation solution, then the amount of the polymer per unit area should be the same for all of the above membranes. Thus, eliminating the membrane thickness ($X$) from the equation 3.1 yields:

$$R = \frac{Y \Delta E}{Zi} \left(\Omega\right)$$  \hspace{1cm} (7.1)

and $\sigma = \frac{1}{R} \left(S\right)$  \hspace{1cm} (7.2)

Where $s$ is the conductance of the material; it is the value of the electrical conductivity for the same amount (by mass) of polymer material per unit area and is independent of the density of the polymer materials. According to equation (7.1) and (7.2), the conductances of the membranes are calculated and listed in Table 1. It was found that except for the membrane prepared using DS as the sole counterion, all other membranes had very similar conductance values.

### 7.3.1.2 Surface Morphology of DS Containing Membranes

SEM revealed that an increase in the concentration of DS present in the polymerisation solution resulted in greater surface roughening on both
sides of the membrane (Figure 7.1 to 7.3); in particular for the plate side. This suggests that the DS containing membrane is more porous and therefore less dense, in agreement with the fact that the thickness of the membranes increased as the DS concentration increased, using the same charge passed.

Also, the solution side of the DS containing membrane revealed a "cauliflower" surface morphology. When the ratio of PTS/DS presence was 50:1 (DS1#, Figure 7.1 (a)), only a small number of "cauliflowers" were formed on the surface. The background surface was similar to the PTS membrane surface (see Figure 3.5(I)), indicating that under these conditions the polymer contained mainly incorporated PTS. As the concentration of DS in the polymerisation solution increased, the "cauliflowers" completely covered the surface (see Figure 7.2 and 7.3); indicating the increasing incorporation of DS.
Figure 7.1 Scanning Electron micrographs of a PP/PTS/DS membrane (DS1#). (a) solution side and (b) plate side.
Figure 7.2 Scanning Electron micrographs of a PP/PTS/DS membrane (DS3#). (a) solution side and (b) plate side.
Figure 7.3 Scanning Electron micrographs of a PP/PTS/DS membrane (DS4#). (a) solution side and (b) plate side.
7.3.1.3 Dynamic Contact Angle Analyses

Dynamic contact angle analyses was carried out using distilled water as the test liquid. With this technique an advancing and a receding contact angle are obtained by immersing and withdrawing the sample. The advancing contact angle indicates the wettability of the surface. In water this is the equivalent to a measure of the hydrophillicity (low contact angles) or hydrophobicity (high contact angles). The receding contact angle provides a measure of the adhesion of the liquid to the surface [204]. Two consecutive cycles are performed so that the properties of the dry and wet polymer surface can be compared (This is only useful for the advancing contact angle as the receding one always measures a wet surface. The data are summarised in Table 7.2. It was found that the surfactant had an effect on each surface of the membrane. However, the actual concentration of surfactant, over the range investigated here, was not critical as judged by the contact angles obtained with the first cycle. The results for the second cycle do indicate a difference but not in a manner that offers an explanation.

The presence of the surfactant, at each of the concentrations used here, had the effect of increasing the hydrophobic nature of the plate side of the membrane. This is determined by comparing the $\theta_a$ of the PP/PTS (30°) with those of the membranes grown in the presence of DS (ca 86°) for the plate side. Water was also found to adhere much less strongly to the polymers containing DS. This is confirmed by the change in $\theta_r$ values. This also implies a greater degree of hydrophobicity.

The effect on the solution side of the membrane was different. In this instance there was a slight increase in the wettability of the polymer with the presence of surfactants, although the surface remained very
hydrophobic ($\theta_a = 105^\circ$ for PP/PTS compared with $\theta_a = 91^\circ, 91^\circ$ and $86^\circ$ for the three samples containing DS).

Table 7.2 The results of the dynamic contact angle analysis on PP/PTS/DS membranes

<table>
<thead>
<tr>
<th>MEMBRANES</th>
<th>DYNAMIC CONTACT ANGLE</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1</td>
<td>Cycle 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\theta_a$</td>
<td>$\theta_r$</td>
<td>$\theta_a$</td>
</tr>
<tr>
<td>PP/PTS (Plate side)</td>
<td>39°</td>
<td>Undefined</td>
<td>28°</td>
</tr>
<tr>
<td>PP/PTS (Solution side)</td>
<td>105°</td>
<td>47°</td>
<td>101°</td>
</tr>
<tr>
<td>DS 1# (Plate side)</td>
<td>89°</td>
<td>79°</td>
<td>49°</td>
</tr>
<tr>
<td>DS 1# (Solution side)</td>
<td>91°</td>
<td>79°</td>
<td>79°</td>
</tr>
<tr>
<td>DS 2# (Plate side)</td>
<td>87°</td>
<td>79°</td>
<td>91°</td>
</tr>
<tr>
<td>DS 2# (Solution side)</td>
<td>91°</td>
<td>79°</td>
<td>Undefined</td>
</tr>
<tr>
<td>DS 3# (Plate side)</td>
<td>83°</td>
<td>79°</td>
<td>92°</td>
</tr>
<tr>
<td>DS 3# (Solution side)</td>
<td>86°</td>
<td>78°</td>
<td>Undefined</td>
</tr>
</tbody>
</table>

Notes: $\theta_a$ and $\theta_r$ are the advancing contact angle and receding contact angle; DS 1#, DS 2# and DS 3# are the surfactant containing membranes prepared using different concentration of DS (See table 7.1).

The force-stage position curves obtained for the PP/PTS membrane and surfactant containing membrane (DS3#) are shown in Figure 7.4 and 7.5 respectively. The presence of the DS obviously has a marked effect on the polymer - solvent interactions.

However, an unusual force-distance curve was obtained when the solution side of the surfactant containing membrane was exposed to the test liquid (Figure 7.5 (b)). This observation indicates that the different sides of the DS containing membrane had quite different surface characteristics. The solution side of the membrane was shown to be immediately wettable.
whereas the plate side of the membrane was not (Figure 7.5 (a) and (b) scan 1). The second scan confirms the irreversible wetting of PP-DS (solution side) with the second advancing curve retracing the initial receding curve.

**Figure 7.4** Dynamic contact angle analysis force-stage position curves of PP/PTS membrane, (a) Plate side of membrane exposed to test liquid, and (b) Solution side of membrane exposed to test liquid. ——— First cycle and ........ Second cycle.
Figure 7.5 Dynamic contact angle analysis force-stage position curves of DS3# membrane, (a) Plate side of membrane exposed to test liquid, and (b) Solution side of membrane exposed to the test liquid. First cycle and Second cycle.
7.3.1.4 Cyclic Voltammetry

Figure 7.6 shows cyclic voltammograms recorded in a 0.20M KCl solution. As indicated in Chapter 4, the CV responses in Regions 1 and 2 correspond to the cation incorporation/expulsion reactions (equations (4-5) and (4-8)) and the responses in Regions 3 and 4 correspond to the anion incorporation/expulsion reactions (equations 4-6 and 4-7). As the concentration of DS present in the polymerisation solution was increased because DS is large and immobile, the incorporation/expulsion of anions (Regions 3/4) became more difficult and the incorporation/expulsion of cations were favoured.

Similar behaviour was observed when voltammograms were recorded in NaCl (Figure 7.7) and CaCl₂ (Figure 7.8). However, it was found that the presence of DS increased markedly the Ca^{2+} incorporation responses. This may be due to the larger pore size of the polymer when the DS was introduced into the polymer.

The voltammograms in Figure 7.9(a), recorded in a solution containing both 0.10M KCl and 0.10M CaCl₂, were characteristic of that observed when only KCl was used as the supporting electrolyte (Figure 7.9(b)). This behaviour can be explained since K⁺ ions are much more readily incorporated.
Figure 7.6 Cyclic Voltammetry of the surfactant containing Films in 0.2M KCl solution, (a). PP/PTS, (b). DS2#, (c). DS3# and (d). DS0#. Scan rate=20 mV/s.
Figure 7.7 Cyclic Voltammetry of the surfactant containing Films in 0.2M NaCl solution, (a). PP/PTS, (b). DS1#, and (c). DS3# Scan rate=20 mV/s.

Figure 7.8 Cyclic Voltammetry of the surfactant containing Films in 0.2M CaCl$_2$ solution, (a). PP/PTS, (b). DS2#, and (c). DS3# Scan rate=20 mV/s.
Figure 7.9 Cyclic Voltammetry of the DS3# in a solution containing (a) 0.1M CaCl₂, (b) 0.1M KCl and 0.1M CaCl₂ and (c) 0.2M KCl. Scan rate=20 mV/s.

7.3.2 Layered Membrane Preparation

The success of layer membrane preparation was dependent upon the nature of the counterions employed and the order of polymerisation of the layers. It was found that when two similar counterions such as PTS, NPS, BSA, and BS were employed, a membrane with good uniformity and adhesion between each layers was obtained, no matter which polymer layer was formed first on the substrate. When counterions which exhibits large differences in chemical or physical properties (such as PTS and DS), the structure and morphology of the layered membrane was found to be dependent on the order of the polymerisation. For instance, when PTS was used for the first polymer layer and a DS containing layer was grown subsequently on this polymer surface, then the layer
membrane obtained (PP/PTS/PP/DS) was always uniform as shown in Figure 7.10.

However, using DS as the counterion to form the first layer of the membrane and then polymerising a PP/PTS layer on top, resulted in a membrane that was wrinkled, rough and porous (see Figure 7.11).

Also, on comparing the solution side morphology of the layer membranes with single layer membranes prepared using the same counterions (Chapter 3), it is found that the surface morphology is markedly different. This suggests that the structure and morphology of the top polymer layer is influenced by the first polymer layer (substrate layer). The major problem for layer membrane synthesis lies in the compatibility of the two layers.

![Figure 7.10 Scanning Electron micrographs of a PP/PTS/PP/DS membrane. (a) solution side (DS side) and (b) plate side (PTS side).](image-url)
Figure 7.11 Scanning Electron micrographs of a PP/DS/PP/PTS membrane. (a), (b) plate side (DS side) and (c), (d) solution side (PTS side).
7.3.3 Transport across Mixed Counterion Membranes

As outlined in chapter 5, electrochemically controlled transport of electroinactive species across a PP/PTS membrane was observed to be independent of the membrane side exposed to the source solution. For a number of other counterions (e.g. NPS) the resultant membranes showed anisotropic, asymmetric transport behaviour.

With surfactant containing membranes, this was also the case. However, the extent of the anisotropy was generally larger. In addition, in contrast to the single counterion case, the surfactant membrane exhibited preferential transport in the opposite direction (i.e. transport from the plate side to the solution side is favoured).

The results obtained for typical transport experiments are shown in Figure 7.12. The membranes used were PP/PTS membrane (PTS) and PP/PTS/DS membrane (DS3#). This shows that the PTS containing membrane has similar flux valves for K+ transport when different sides of the membrane are exposed to the source solution. However, asymmetric transport was observed when the DS3# membrane was employed (Figure 7.12, curve 2p,2s), a large flux was obtained when the plate side of the membrane was exposed to the source solution, $\xi = F_p/F_s = 2.85$. 
**Figure 7.12** Transport of KCl across PP/PTS and surfactant containing membranes (DS3#). Source solution: 0.2M KCl; Receiving solution: deionised water. (1s), (1p): solution side or plate side of PP/PTS membrane exposed to the source solution, (2s), (2p): solution side or plate side of DS3# membrane exposed to the source solution. Time A: potential pulse routine applied and Time B: potential pulse routine removed.

The permeability of the membrane has been determined by use of the membrane in a filtration experiment (see section 3.2.3.2 and Figure 3.2). It was found that about 80% of NaCl was rejected when 100atm pressure was applied. This indicates that the membrane is nonporous membrane with pore size in the range of a reverse osmosis membrane, i.e. <1nm. The SEM studies (Figure 7.1 to 7.3) suggest that the DS membrane cross sectional structure may be described as shown in Figure 7.13. Since the initial polymer formation on the substrate surface was not well-distributed, the substrate side (plate side) of the membrane was porous and non uniform. As the polymer grew, three dimensional growth resulted in the pores becoming smaller and smaller, until a dense skin layer was formed on the solution side of the membrane. This is an
asymmetric structure, and asymmetric transport behaviour might be expected due to this unique structure.

**SOLUTION SIDE OF THE MEMBRANE**

![Image of the membrane cross sectional structure]

**PLATE SIDE OF THE MEMBRANE**

*Figure 7.13 The DS membrane cross sectional structure.*

When the plate side of the membrane was exposed to the source solution, the high active surface area and open porous structure allows ions to easily diffuse into the pores from the source solution. When the redox state of the membrane is repetitively changed, the ions in the pores are readily incorporated into the polymer matrix. This results in the concentration of the ions in the porous layer rapidly attaining a high value. In addition, there is only a small concentration gradient in this region. The incorporated ions may be expelled into either the source or receiving solution through the redox changes occurring in the membrane. However, the high concentration gradient across the thin dense layer ensures that there is some net transport into the receiving solution. In this case the ion concentration distribution may be depicted as in Figure 7.14(A).
As described above, this membrane is non-porous membrane. Generally, the transport across a non-porous membrane can be described by a diffusion model, thus

\[ J = -\frac{D K}{A} \Delta C \]  

(7.3)

Where, \( J \) is the flux of a component through a plane (of surface area \( A \)) perpendicular to the direction of diffusion and is proportional to the concentration gradient \( \Delta C \) and \( D \) is the diffusion coefficient. Accordingly, when the plate side of the membrane was exposed to the source solution (see Figure 7.14(A)) a large concentration difference \( (\Delta C = C_2 - C_1) \) results in a large flux.

In contrast, when the solution side of the thin dense layer acts as a effective barrier to incorporation, the dense side of the membrane has only a small active surface area, making ion incorporation difficult. In addition, any ions which do penetrate through into the porous region are hindered in their passage to the receiving solution because of the long path-length of this layer. The ions will be repeatedly incorporated and
expelled slowing down the net transport into the receiving solution. Figure 7.14(B) shows a suggested concentration distribution of the ion in the membrane.

Similar behaviour was also observed for \( \text{Na}^+ \) and \( \text{Ca}^{2+} \) transport across the DS containing membrane as shown in Table 7.4 and 7.5. The effect of the surfactant concentration in the polymerisation solution on the resultant membranes' asymmetric transport properties are summarised in Table 7.3 to 7.5. It is seen that \( F_s \) decreased and \( F_p \) increased as the DS concentration increased. Hence, asymmetric transport \((\xi = F_p/F_s)\) increased as the DS concentration increased. This might be explained by the proposed asymmetric membrane structure. As shown in Figure 7.1 to 7.3, the porosity of the plate side of the surfactant membranes increased as the surfactant concentration increased. This resulted in increasing asymmetric structure of the membrane which leads to the asymmetric transport behaviour observed.

**Table 7.3 Effect of DS concentration on the transport of \( \text{K}^+ \) across the membrane**

<table>
<thead>
<tr>
<th>MEMBRANES</th>
<th>PP/PTS</th>
<th>PP/PTS/DS (DS 1#)</th>
<th>PP/PTS/DS (DS 2#)</th>
<th>PP/PTS/DS (DS 3#)</th>
<th>PP/PTS/DS (DS 4#)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_s \times 10^9 ) (mol/cm(^2) sec)</td>
<td>1.90</td>
<td>1.24</td>
<td>1.22</td>
<td>0.95</td>
<td>0.84</td>
</tr>
<tr>
<td>( F_p \times 10^9 ) (mol/cm(^2) sec)</td>
<td>1.81</td>
<td>2.25</td>
<td>2.52</td>
<td>2.71</td>
<td>3.72</td>
</tr>
<tr>
<td>Asymmetric Factor ( \xi = F_p/F_s )</td>
<td>0.95</td>
<td>1.81</td>
<td>2.07</td>
<td>2.85</td>
<td>4.43</td>
</tr>
</tbody>
</table>

Notes: All experiments were carried out using a source solution of 0.2M KCl. \( F_s \) and \( F_p \) are the average fluxes of \( \text{K}^+ \), when the electrical stimuli was applied, and were measured using "solution side"\( (F_s) \) and "plate side"\( (F_p) \) of the membrane exposed to the source solution. The ratio of \( F_p/F_s \) is called "Asymmetric factor" which indicates the difference in the rate of transport between different sides of the membranes exposed to the source solution.
### Table 7.4 Effect of DS concentration on the transport of Na$^+$ across the membrane

<table>
<thead>
<tr>
<th>MEMBRANES</th>
<th>PP/PTS</th>
<th>PP/PTS/DS (DS1#)</th>
<th>PP/PTS/DS (DS2#)</th>
<th>PP/PTS/DS (DS3#)</th>
<th>PP/PTS/DS (DS4#)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_S \times 10^9$# (mol/cm$^2$ sec)</td>
<td>1.34</td>
<td>1.19</td>
<td>0.66</td>
<td>0.68</td>
<td>0.94</td>
</tr>
<tr>
<td>$F_P \times 10^9$# (mol/cm$^2$ sec)</td>
<td>1.40</td>
<td>1.71</td>
<td>2.09</td>
<td>2.36</td>
<td>3.38</td>
</tr>
<tr>
<td>Asymmetric Factor $\xi = (F_P/F_S)$#</td>
<td>1.04</td>
<td>1.44</td>
<td>3.17</td>
<td>3.47</td>
<td>3.60</td>
</tr>
</tbody>
</table>

Notes: All experiments were carried out using a source solution of 0.2M NaCl. # see Table 7.3.

### Table 7.5 Effect of DS in the polymerisation solution on the transport of Ca$^{2+}$ across the membrane

<table>
<thead>
<tr>
<th></th>
<th>PP/PTS (PTS)</th>
<th>PP/PTS/DS (DS 3#)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_S \times 10^9$ # (mol/cm$^2$ sec)</td>
<td>0.24</td>
<td>1.01</td>
</tr>
<tr>
<td>$F_P \times 10^9$# (mol/cm$^2$ sec)</td>
<td>0.17</td>
<td>1.55</td>
</tr>
<tr>
<td>Asymmetric Factor $\xi = (F_P/F_S)$#</td>
<td>0.84</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Notes: The results obtained using 0.2M CaCl$_2$ as a source solution. # See Table 2.

To examine the separation properties of the DS containing membranes, a source solution containing 0.10M KCl + 0.10M NaCl, or 0.10M KCl + 0.10M CaCl$_2$ was undertaken.

A typical experiment for separation of K$^+$ and Na$^+$ is shown in Figure 7.15 and the effect of the presence of DS on the membrane separation...
properties is summarised in Table 7.6. It reveals that the presence of DS resulted in the membrane separation coefficient (Flux K+/Flux Na+) becoming smaller and asymmetric separation (δp/δs) slightly increasing. Similar behaviour was observed for separation of K+ and Ca2+ (Table 7.7). It may be concluded that the separation ability of a DS containing membrane is less than that of a PP/PTS membrane. This can be explained due to enhanced ability of ion incorporation for the DS containing membranes. As outlined in Chapter 6 equation (6-2), the transport through a non porous membrane can be described in terms of a solution-diffusion mechanism,

\[ P = S \times D \] (6-2)

For a given mixture, permeability of a component can be written as:

\[ P_i = S_i \times D_i \] (7-4)

Generally, for the separation of two components, the selectivity is given by the ratio of the components permeability, thus:

\[ \delta_{i/j} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \times \frac{D_i}{D_j} \] (7.5)

where \( \delta \) is the selectivity factor and i, j refer to the different species in the mixture.

If we assume that the diffusion of component i and j is independent of the concentrations, equation (7.5) can be written as:

\[ \delta_{i/j} = K_{i/j} \times \frac{S_i}{S_j} \] (7.6)

where \( K_{i/j} = \frac{D_i}{D_j} \) is a constant.
Equation 7.6 indicates that the selectivity of the membrane is determined by the ratio of the solubility of the components. In other words, it is dependent on the ratio of the concentration of the transported species in the membrane.

In this instance, the solubility ($S$) is directly dependent on the ion incorporation ability of the membrane. The experiments involving $K^+$ and $Ca^{2+}$ separation may be used to explain why the DS containing membrane has lower separation ability. As mentioned previously, the ion incorporation and expulsion ability can be examined using cyclic voltammetry. In Figures 7.6 and 7.9, cyclic voltammograms were recorded in KCl and CaCl$_2$ solution. An increase in the concentration of DS in the polymerisation solution resulted in an increased ability of the polymer to incorporate $K^+$ and $Ca^{2+}$ ions. Furthermore, the increase for $Ca^{2+}$ is dramatically larger than the increase for $K^+$. In other words, the presence of DS increases both $S_{K^+}$ and $S_{Ca^{2+}}$, particularly the latter. This results in a decrease in the ratio of $S_{K^+}/S_{Ca^{2+}}$. According to the equation 7.6, the selectivity of the membrane is therefore decreased. The higher selectivity obtained with the PP/PTS membrane is due to the difficulty in incorporating $Ca^{2+}$ (see Figure 7.8, curve 1). It should be noted that in all cases, $F_s$ values obtained using PP/PTS membranes were larger than those obtained using DS containing membranes, and $F_p$ obtained using PP/PTS membranes were smaller than that for DS containing membranes.
Figure 7.15 Transport of $K^+$ and $Na^+$ across DS3# membranes. Source solution: 0.1M KCl+0.1M NaCl, Receiving solution: deionised water. (1) $K^+$ and (3) $Na^+$ transport, plate side of membrane exposed to source solution. (2) $K^+$ and (4) $Na^+$ transport, solution side of membrane exposed to source solution. Time A: potential pulse routine applied and Time B: potential pulse routine removed.

Table 7.6 Effect of DS concentration on membrane separation properties.

<table>
<thead>
<tr>
<th>MEMBRANES</th>
<th>PP/PTS (FS)</th>
<th>PP/PTS (FP)</th>
<th>PP/PTS/DS (DS 2# FS)</th>
<th>PP/PTS/DS (DS 2# FP)</th>
<th>PP/PTS/DS (DS 3# FS)</th>
<th>PP/PTS/DS (DS 3# FP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{K^+} \times 10^9$ (mol/cm$^2$ sec)</td>
<td>1.65</td>
<td>1.54</td>
<td>0.96</td>
<td>1.78</td>
<td>0.70</td>
<td>1.88</td>
</tr>
<tr>
<td>$F_{Na^+} \times 10^9$ (mol/cm$^2$ sec)</td>
<td>0.57</td>
<td>0.53</td>
<td>0.47</td>
<td>0.79</td>
<td>0.45</td>
<td>0.97</td>
</tr>
<tr>
<td>Separation Coefficient</td>
<td>2.89</td>
<td>2.91</td>
<td>2.04</td>
<td>2.25</td>
<td>1.56</td>
<td>1.94</td>
</tr>
<tr>
<td>S ($F_{K^+}/F_{Na^+}$)</td>
<td>1.01</td>
<td>1.10</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: The experiments were carried out in a source solution containing 0.10 M KCl and 0.1 M NaCl. # $S_p/S_s$ is the asymmetric factor of the membrane separation properties, it indicates the membrane separation coefficient difference using different sides of the membrane exposed to the source solutions.
Table 7.7 Comparision of separation properties of PP/PTS and PP/PTS/DS membranes

<table>
<thead>
<tr>
<th></th>
<th>PP/PTS (Fs)</th>
<th>PP/PTS (Fp)</th>
<th>PP/PTS/DS (DS 3# Fs)</th>
<th>PP/PTS/DS (DS 3# Fp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FK⁺Fs×10⁹ (mol/cm² sec)</td>
<td>1.91</td>
<td>1.84</td>
<td>0.863</td>
<td>2.44</td>
</tr>
<tr>
<td>FCa²⁺Fs×10⁹ (mol/cm² sec)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.153</td>
<td>0.27</td>
</tr>
<tr>
<td>Separation Coefficient S(FK⁺/FCa²⁺)</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>5.64</td>
<td>9.07</td>
</tr>
</tbody>
</table>

Notes: The experiments were carried out using a 0.10 M KCl and 0.10 M CaCl₂ containing solution as the source solution. # see Table 7.6

7.3.4 Transport across Layered Membranes

Asymmetric transport behaviour was also observed when layered membranes were employed (Figure 7.16 and 7.17). It was found that a higher rate of transport was obtained when the PP/PTS side of the membrane was exposed to the source solution irrespective of the order of the polymerisation process. The fluxes obtained and the asymmetric transport ratios are summarised in Table 7.8.
Figure 7.16 Transport of K⁺ across PP/PTS/PP/DS layered membrane. Source solution: 0.2M KCl; Receiving solution: deionised water. (1) PP/PTS side exposed to source solution; (2) PP/DS side exposed to source solution. Time A: potential pulse routine applied and Time B: potential pulse routine removed.

Figure 7.17 Transport of K⁺ across PP/DS/PP/PTS layered membrane. Source solution: 0.2M KCl; Receiving solution: deionised water. (1) PP/PTS side exposed to source solution; (2) PP/DS side exposed to source solution. Time A: potential pulse routine applied and Time B: potential pulse routine removed.
Table 7.8 Effect of the sides of the membrane exposed to the source solution on the fluxes transported

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PP/PTS/PP/DS</th>
<th>PP/DS/PP/PTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPTS</td>
<td>$1.7 \times 10^{-9}$</td>
<td>$1.6 \times 10^{-9}$</td>
</tr>
<tr>
<td>(mol cm$^{-2}$ sec$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FDS</td>
<td>$1.3 \times 10^{-10}$</td>
<td>$1.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>(mol cm$^{-2}$ sec$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FPTS/FDS</td>
<td>13.1</td>
<td>11.4</td>
</tr>
</tbody>
</table>

Note: Fluxes were calculated from Figure 7.16 and 7.17.

This asymmetric transport might be due to one or more of the following factors:

(i) Asymmetric structure in terms of surface morphology and porosity;

(ii) Asymmetric composition in terms of different polymer layers containing different counterions;

(iii) Asymmetric surface chemical properties in terms of different surface force, wettability or polarity; and

(iv) the nature of the junction between the two layers which form another interface.

However, because in the case of the layer membrane, two independent polymers are present, the anisotropy observed may be due to some other contributing factors.
7.4 CONCLUSIONS

Surfactant containing polypyrrole membranes including layer membranes have been synthesised. The transport properties of these membranes have been investigated.

Mixed counterion membrane:

(1) Surfactant-containing free-standing membranes can be prepared electrochemically using a mixed counterions polymerisation solution. The results indicate that the tensile strength of the membrane decreases with increasing surfactant concentration. Surfactant containing membranes with adequate mechanical properties can be obtained using a mixed counterions polymerisation solution containing 0.005M DS or less. The presence of the surfactant in the polymerisation solution has a marked influence on the surface morphology of the membrane. Membranes prepared using a high concentration of surfactant have a more porous structure. The different sides of the surfactant containing membranes have different surface properties; irreversible wetting behaviour was observed on the solution side of the membrane.

(2) Asymmetric transport behaviour was observed when a surfactant was employed in the mixed counterion case. Using the plate side of the membrane exposed to the source solution gives a larger flux than that using the solution side. This is in contrast to that observed for membranes using PTS counterion alone. An increase in the DS concentration in the polymerisation solution leads to an increase in the asymmetric transport properties of the resultant membrane.
(3) The separation coefficient of a surfactant containing membrane decreases as the concentration of DS in the polymerisation solution increases. Different sides of the membrane have similar separation capabilities.

**Layered membrane:**

(1) Layered membranes have been prepared using a two step polymerisation technique. The morphology of the top layer membrane is influenced by the substrate layer below.

(2) Greater asymmetric transport properties were observed when a layered membrane was employed. A larger flux for $K^+$ was always obtained when the PP/PTS side of the membrane was exposed to the source solution, irrespective of the sequence of the electrosynthesis of the layers.
CHAPTER 8

ELECTROCHEMICALLY CONTROLLED TRANSPORT OF ELECTROACTIVE SPECIES ACROSS PP/PTS MEMBRANES
8.1 INTRODUCTION

Electrochemically controlled transport of electroinactive species across conducting polymer membranes has been discussed in Chapter 5. The transport mechanism is different for electroactive species since such species may undergo electrochemical reactions when the electrical stimulus is applied. Therefore, simple ion incorporation/expulsion mechanisms are not applicable in this case.

In this chapter, the electrochemically controlled transport of metal ions such as Cu(II) and Zn(II) across conducting polymer membranes was investigated. In order to compare the results obtained in this chapter with those in Chapter 5 for transport of electroinactive species, the PP/PTS membrane was chosen. Cu(II) and Zn(II) were chosen as the transport species because of the difference in their redox potentials.

Separation of the two electroactive species from each other and separation of a mixture of electroactive and electroinactive species was also studied in the course of this work.

8.2 EXPERIMENTAL

8.2.1 Reagents and Solutions

The reagents used are the same as described in chapter 5. All inorganic reagents were of analytical reagent grade.

The solutions used for membrane preparation contained 0.20M pyrrole and 0.05M PTS.
All solutions were prepared using deionised water dispensed from a Milli-Q water purification system (18MΩcm).

The source solution used for Zn(II) transport experiments was 0.20M Zn(NO₃)₂, and for Cu(II) transport experiments was 0.10M CuSO₄ or 0.10M Cu(NO₃)₂. For the separation experiments, the source solution was 0.10M Zn(NO₃)₂ mixed with 0.10M Cu(NO₃)₂, or 0.10M Cu(NO₃)₂ +0.10M KNO₃, or 0.10M Zn(NO₃)₂ + 0.10M KNO₃. The receiving solution used was deionised water or 1M H₂SO₄ unless otherwise stated.

### 8.2.2 Instrumentation

All instrumentation used for this work was the same as in Chapter 5.

### 8.2.3 Procedures

**Membrane Preparation**

The preparation of the PP/PTS membrane is described in Chapter 5. The charge density was maintained at 1.20 C/cm².

**Electrotransport Cell Set up**

Most of the experiments were carried out using the cell set up as shown in Figure 5.2 (III). For some experiments the cells in Figure 5.2 (I) and (II) were also employed.
Experimental Procedure

In the majority of the transport experiments, the electrical stimuli were applied in the following way: no applied potential (30 minutes) followed by applied potential for 120 minutes after which the potential was discontinued. During the experiments, generally, samples were taken every 30 minutes from the receiving solution.

8.3 RESULTS AND DISCUSSION

8.3.1 Electrochemical Studies

In order to investigate the electrochemical behaviour of electroactive species (such as Cu(II) and Zn(II)) on the conducting polymer electrode, a PP/PTS coated glassy carbon working electrode was employed. The electrodes were prepared using the methods described in Chapter 4.

A cyclic voltammogram of a PP/PTS coated electrode was recorded in 0.2M KNO₃ under static conditions (Figure 8.1). The responses of the polymer in an electroinactive supporting electrolyte are due to ion incorporation and expulsion reactions (see Chapter 4).

A cyclic voltammogram of a PP/PTS was then recorded using a solution containing 0.2M KNO₃ and 25ppm Cu(II) ions (in NO₃⁻ salt form) at pH=4 (Figure 8.2). On comparing with Figure 8.1, the voltammogram in Figure 8.2 clearly shows the responses due to the polymer oxidation and reduction but also shows two other sharp peaks (Peak A and B). Peaks A and B increased as the concentration of Cu(II) ions increased. The cathodic copper reduction peak potential (Epc) was at about -0.50V
This difference is much larger than would be expected for a reversible system which is:

$$\Delta E = E_{pa} - E_{pc} = \frac{0.058}{n} \text{V} \quad \text{for copper n=2, so } \Delta E \text{ is 0.029V}$$

When the experiment was repeated using a bare glassy carbon electrode in the same solution as used in Figure 8.2, $E_{pa}$ and $E_{pc}$ were 0V and -0.31V respectively ($\Delta E = 0.31V$). This value is smaller than that obtained for the polymer coated electrode indicating the reversibility of the copper reactions on the glassy carbon electrode (GCE) is better, compared to those on the polymer coated electrode. Furthermore, this change resulted mainly from $E_{pc}$ shifting to a more positive potential when the glassy carbon electrode was employed. Cyclic resistometry studies [169] have shown that the resistance of polypyrrole increases sharply in the potential range -0.3 to -0.6V (vs Ag/AgCl, 3M NaCl). The reduction of copper ions on a polymer electrode occurs at a more negative potential and the oxidation at a more positive potential than for

*Figure 8.1 Cyclic voltammogram of PP/PTS recorded in 0.2M KNO₃ solution. Scan rate=100mV/s.*
reduction at a bare GCE. This may be due to changes in the resistance of the polymer and would indicate that the redox reactions of the polymer can have an influence on the metal ion redox reactions.

Figure 8.2 Cyclic voltammogram of PP/PTS recorded in a solution containing 0.2M KNO₃ and 25ppm Cu(II); pH=4.0. Scan rate=100mV/s.

Figure 8.3 shows another CV using the polymer coated electrode with the solution pH adjusted to pH=2, and reveals that the copper redox responses were dramatically enhanced compared to those observed in a solution with pH=4. This suggests that the copper redox reactions taking place in a more acidic solution are more efficient.

Similarly, the electrochemical behaviour of zinc ions on the polymer electrode was investigated. Cyclic voltammograms were recorded using a 0.2M KNO₃ solution containing 100ppm Zn(II) (in NO₃⁻ salt form) at
pH=4.9 (Curve 1) and pH=2 (Curve 2) (Figure 8.4). No zinc reduction or oxidation peak was observed in either solution. The current increased sharply around -1.1V to -1.2V and this may be due to water reduction, i.e., production and adsorption of H₂ on the electrode surface. The reason for the zinc reduction and oxidation peaks not being observed (at approximately -1.0 and -0.9V vs Ag/AgCl respectively) may be due to the fact that they were masked by the above water reaction.

Figure 8.3 Cyclic voltammogram of PP/PTS recorded in a solution containing 0.2M KNO₃ and 25ppm Cu(II); pH=2.0. Scan rate=100mV/s.
Figure 8.4 Cyclic voltammogram of PP/PTS recorded in a solution containing 0.2M KNO₃ and 100ppm Zn(II). (1) pH=4.9, (2) pH=2.0. Scan rate=100mV/s.

Figure 8.5 Linear sweep stripping voltammogram of PP/PTS recorded in a solution containing 0.2M KNO₃ (1) or 0.2M KNO₃ and 100ppm Zn(II) (2,3). pH=2.0. Scan rate=100mV/s. Deposition potential=-1.30V. Deposition time: (1), (2) 30s, and (3) 60s.
Figure 8.6 Chronoamperometric responses of PP/PTS recorded in: (1) 0.2M KNO₃ or (2 to 4) 0.2M KNO₃ and 100ppm Zn(II). pH=2.0. 
**E_i:** 0.0V, **E_f:** (1) -1.00V, (2) -1.00V, (3) -1.20V and (4) -1.28V.

In order to prove this, attempts were then made to deposit the zinc on the electrode and electrochemically strip it off. Figure 8.5 shows linear sweep stripping voltammograms obtained using PP/PTS coated glassy carbon electrodes. The results show the zinc oxidation peak current increased when deposition time was increased. This indicates that the Zn(II) can be reduced to Zn(0) if the applied potential is more negative than about -1.30V. To confirm this, chronoamperometry was then considered. The results in Figure 8.6 show that Zn(II) was reduced and deposited when -1.28V was applied. Therefore, summarising the above investigations, the redox reactions occurring on the conducting polypyrrole electrode are both ion incorporation and expulsion to maintain charge balance in the polymer and metal ion reduction and oxidation, as shown below.
**Reduction Reactions:**

\[ \text{PP}^+\text{C}^- (\text{film}) + \text{M}^{n+} + (n+1)e \rightarrow \text{PP}^0\text{M}^0 (\text{film}) + \text{C}^- (\text{solution}) \]  \hspace{1cm} (8-1)

\[ \text{PP}^+\text{A}^- (\text{film}) + \text{M}^{n+} + (n+1)e \rightarrow \text{PP}^0\text{M}^0 (\text{film}) + \text{A}^- (\text{solution}) \]  \hspace{1cm} (8-2)

\[ \text{PP}^+\text{C}^- (\text{film}) + \text{Y}^+ + e \rightarrow \text{PP}^0\text{C}^-\text{Y}^+ (\text{film}) \]  \hspace{1cm} (8-3)

**Oxidation Reactions:**

\[ \text{PP}^0\text{M}^0 (\text{film}) + \text{A}^- (\text{solution}) - (n+1)e \rightarrow \text{PP}^+\text{A}^- (\text{film}) + \text{M}^{n+} (\text{solution}) \]  \hspace{1cm} (8-4)

\[ \text{PP}^0\text{C}^-\text{Y}^+ (\text{film})^- e \rightarrow \text{PP}^+\text{C}^- (\text{film}) + \text{Y}^+ (\text{solution}) \]  \hspace{1cm} (8-5)

where \( \text{PP}^+ \) and \( \text{PP}^0 \) are the oxidised and reduced forms of polypyrrole; \( \text{M}^{n+} \) and \( \text{M}^0 \) is the metal ion and metal respectively; \( \text{C}^- \) is the counterion incorporated during synthesis; \( \text{A}^- \) is the anion present in the solution, that could be incorporated into the polymer when an electrical potential is applied or due to the ion-exchange reaction; \( \text{Y}^+ \) are an electroinactive cation present in the solution and the subscripts indicate the phase in which the species occurs. Which reactions are dominating depends on the experimental conditions employed.

**8.3.2 Transport of Cu(II)**

In this part of the work, transport studies of Cu(II) across PP/PTS membranes were carried out. Specifically, the effect of the electrochemical and chemical conditions on the Cu(II) transport across the membrane were investigated.
8.3.2.1 Effect of Electrochemical Conditions on Cu(II) Transport

Initial experiments measured the transport of copper(II) in the absence of an applied potential. Transport experiments were carried out using 0.1M CuSO$_4$ + 1M H$_2$SO$_4$ (Curve 1) or 0.1M CuSO$_4$ (Curve 2) as the source solution, and 1M H$_2$SO$_4$ (Curve 1) or deionised water (Curve 2) as the receiving solution as shown in Figure 8.7. It was found that the rate of Cu(II) transport when 1M H$_2$SO$_4$ was used as the receiving solution was much faster than that obtained using deionised water. The fluxes calculated were 4.1 x 10$^{-12}$ mol cm$^{-2}$s$^{-1}$ with H$_2$SO$_4$ as compared with 5.0 x 10$^{-13}$ mol cm$^{-2}$s$^{-1}$ with deionised water.

![Figure 8.7](image)

*Figure 8.7* Transport of CuSO$_4$ across PP/PTS membrane with no application of potential. 1#, Source solution: 0.1M CuSO$_4$ + 1M H$_2$SO$_4$, Receiving solution: 1M H$_2$SO$_4$, and 2#, Source solution: 0.1M CuSO$_4$, Receiving solution: deionised water.

Under this conditions, Cu(II) transport across the membrane must be due to ion-exchange reactions taking place as described in Chapter 5. Compared with K$^+$ (Flux = 9.4 x 10$^{-11}$ mol cm$^{-2}$s$^{-1}$), the rate of ion-
exchange for Cu(II) was low. This suggests that the mobility of Cu(II) ions in the polymer matrix is small.

Electrochemically controlled transport of Cu(II) across a PP/PTS membrane by application of a constant potential waveform was then investigated (Figure 8.8). This reveals that when a constant positive or negative potential was applied only a small amount of Cu(II) transport took place. When the applied potential was removed, in the case of a small applied negative potential (-0.30V, Curve 2), a small rate of transport persisted. However, with a larger negative applied potential (-0.90V, Curve 3), the rate of transport increased sharply. This is presumably due to chemical oxidation of the copper by oxygen (of standard electrode reductions, equations 8.7 and 8.8). The receiving solution was acidic containing dissolved oxygen (O2). Chemical oxidation of Cu(0) in the membrane pores may therefore occur due to the following reactions:

\[ 2\text{Cu}^0 + \text{O}_2(\text{solution}) + 4\text{H}^+ \rightarrow 2\text{Cu}^{2+} + 2\text{H}_2\text{O} \]  
\[ \text{Cu}^{2+} + 2e \rightarrow \text{Cu}^0 \quad \text{ECu}^{2+/\text{Cu}^0} = 0.158\text{V (vs NHE)} \]  
\[ \text{O}_2 + 4\text{H} + 4e \rightarrow 2\text{H}_2\text{O} \quad \text{E}_{\text{O}_2/\text{H}_2\text{O}} = 1.229\text{V (vs NHE)} \]  

The product Cu(II) then diffuses into the receiving solution resulting in the observed Cu(II) transport after removal of an applied potential.

According to the cyclic voltammetry results (Figure 8.3), Cu(II) reduction starts at about -0.3V. However, at this potential the amount of deposited Cu(0) was small, and its subsequent chemical oxidation did not cause a significant flux for Cu(II) transport. At the potential of -0.90V, the Cu(II) is reduced more readily resulting in a larger amount of deposited Cu(0). This was confirmed by visual examination: a thick
copper metal film was formed on the source side of the membrane surface. In this case, chemical oxidation of Cu(0) will produce a high concentration of Cu(II) in the membrane pores leading to higher Cu(II) transport rate across the membrane. Once the potential is removed, it should be noted that this transport process requires no additional anion transport to maintain the charge balance since to produce one Cu(II) ion, two H⁺ are reduced (see equation 8.6).

![Graph showing transport of Cu(II) across a PP/PTS membrane with application of constant potential waveforms.](image)

**Figure 8.8** Transport of Cu(II) across a PP/PTS membrane with application of constant potential waveforms. (between 0 to point A) Source solution: 0.1M CuSO₄ + 1M H₂SO₄, Receiving solution: 1M H₂SO₄.; 1#, +0.70V, 2#, -0.30V and 3#, -0.90V.

The transport behaviour observed with the application of different pulsed potential waveforms is shown in Figure 8.9. The results show that with no applied potential there was no measurable flux of Cu(II) across the membrane but when a pulsed potential was applied, the rate of transport increased dramatically. When the stimulus was removed, transport was generally still observed. This behaviour was not observed in the experiments with electroinactive species. Table 8.1 shows the fluxes obtained for Cu(II) transport when the electrical stimulus was applied
and after the potential was removed. These fluxes were calculated from the data in Figure 8.9.

Figure 8.9 Transport of Cu(II) across a PP/PTS membrane with application of a pulsed potential waveform (between A and B). Source solution: 0.1M CuSO₄ + 1M H₂SO₄, Receiving solution: 1M H₂SO₄. Pulse Width: 25sec./25sec; Potential Range: 1#, 0.7V/-0.3V, 2#, 0.7V/-0.5V, 3#, 0.7V/-0.7V and 4#, 0.7V/-0.9V.

Table 8.1: Effect of pulsed potential range on the fluxes of Cu(II) transport across a PP/PTS membrane

<table>
<thead>
<tr>
<th>Potential Range (V) vs Ag/AgCl</th>
<th>Flux (mol cm⁻²s⁻¹) During potential applied</th>
<th>Flux (mol cm⁻²s⁻¹) After potential applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.70/-0.30</td>
<td>2.4x10⁻¹¹</td>
<td>4.0x10⁻¹²</td>
</tr>
<tr>
<td>+0.70/-0.50</td>
<td>1.1x10⁻¹⁰</td>
<td>7.8x10⁻¹¹</td>
</tr>
<tr>
<td>+0.70/-0.70</td>
<td>1.5x10⁻¹⁰</td>
<td>6.3x10⁻¹¹</td>
</tr>
<tr>
<td>+0.70/-0.90</td>
<td>9.3x10⁻¹¹</td>
<td>1.2x10⁻¹¹</td>
</tr>
</tbody>
</table>

These results show that when a pulsed potential with the range 0.7V to -0.3V was applied the smallest fluxes (both during and after applied potential) were obtained. This may be explained by the cyclic
voltammetry results shown in Figure 8.3. As mentioned above, at -0.30V the Cu(II) reduction reaction is just promoted. Under this condition, Cu(II) can be transported across the membrane as an electroinactive species, but the results in Figure 8.7 suggest that the mobility of the Cu(II) in the polymer matrix is small. Thus, incorporation of Cu(II) into the polymer matrix (equation 8.3) is difficult. Also, the cation incorporation reaction generally occurs at a more negative potential when the polymer is reduced (see Chapter 4). It might, therefore, be expected that the flux due to Cu(II) transported as an electroinactive species is very small. Experiments 2 and 3 show that as the magnitude of the negative potential increased the fluxes also became larger. According to cyclic voltammetry (Figure 8.3) at these negative potentials, the reactions shown in equations (8-1), (8-2) and (8-4) could take place whereas the results from Figure 8.1 indicate that the reactions (8-3) and (8-5) will not readily occur. In other words, Cu(II) is not incorporated as an electroinactive ion since the Cu(II) reduction reaction has already occurred before the cation incorporation peak potential is reached (see Figure 8.1). The copper metal deposited on the membrane surface causes a change in the membrane surface characteristics preventing cation incorporation taking place. The results suggest that Cu(II) transport across the membrane is not primarily due to a simple ion incorporation/expulsion mechanism as described in Chapter 5.

When a pulse range of +0.70V to -0.90V was applied to the membrane, transport behaviour was quite different to the other experiments. During the period of applied potential the Cu(II) flux was non-linear, decreasing to almost zero toward the end, but after the stimulus was removed the flux was greater than with the other experiments. After this experiment,
visual examination of the membrane revealed that a thick and dense copper metal film had formed on the source side of the membrane surface. With the other potential pulse ranges only a small amount of less dense copper metal was observed, which could be washed off the membrane very easily by water. The non-linear decreasing flux when a high negative potential (-0.9V) was applied, is presumably because the copper metal "plate" formed on the membrane surface obstructs transport. As mentioned above, in most cases, transport was still observed when the stimulus was removed. Some times this transport was even faster than the transport observed during the potential applied regime (see experiment 4).

The results in Figure 8.10 show that the rate of Cu(II) transport increased only slightly by increases in pulse width (Table 8.2).

<table>
<thead>
<tr>
<th>Pulse width (second)</th>
<th>2.0</th>
<th>6.5</th>
<th>12.5</th>
<th>25</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux (10^{10}\text{mol cm}^{-2}\text{s}^{-1})</td>
<td>1.0</td>
<td>1.3</td>
<td>1.3</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>During Potential Applied</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This behaviour contrasts with that for electroinactive metal transport where the rate was very sensitive to changes in the pulsed potential frequency (see Chapter 5). This again suggests that the transport of Cu(II) ions across a PP/PTS membrane is not due to the same mechanism.

Electrochemically controlled transport of Cu(II) by application of an asymmetric pulsed potential was then considered. The pulse range was fixed at ± 0.70V. The ratio of the pulse width between the cathodic component and anodic component used was 1:1, 1:2 or 2:1. Figure 8.11 shows that during the period of applied electrical stimulus the highest
rate of transport was obtained when a symmetric pulse was employed
(curve 1). Comparing the two asymmetric pulse experiments, a higher
rate of transport was observed when the anodic component pulse width
was greater than the cathodic component (curve 2). A non-linear flux
was observed when the asymmetric pulsed potential with a cathodic
component of 50 seconds and anodic component of 25 seconds was
employed (curve 3). It was found that after 30 minutes of the potential
being applied, the rate of transport decreased to a constant small value.
This is probably due to the formation of an impermeable layer of copper
on the membrane surface brought about by the longer period of reducing
potentials applied. This situation is similar to the case of a constant
cathodic applied potential. Unlike the transport of electroinactive species
different asymmetric waveforms gave similar rates of transport.

Figure 8.10 Transport of CuSO₄ across a PP/PTS membrane with
application of a symmetric pulsed potential waveform (between A
and B). Source solutions: 0.1M CuSO₄ + 1M H₂SO₄; Receiving
solution: 1M H₂SO₄. Potential Range: 0.7V/-0.7V; Pulse Widths: (1),
2.0sec.; (2), 6.5sec.; (3), 12.5sec.; (4), 25sec.; and (5), 50sec.
8.3.2.2. Effect of Chemical Conditions on Cu (II) Transport

The effect of the Cu(II) concentration in the source solution was then considered (Figure 8.12). The same electrochemical conditions were used as in Figure 8.9 (curve (3)), but the concentration of Cu(II) in the source solution was varied from 0.05 M to 0.2 M. The results show that in the concentration range investigated, changes in the Cu(II) concentration had little effect on the rate of transport. This suggests that the transport under these conditions was not limited by the mass transport. The reason for this may be attributed to the deposition of copper onto the membrane. When the anodic component of the pulse was applied, the copper metal would be oxidised producing a higher
concentration of Cu(II) ions close to the membrane than in the bulk of the source solution making mass-transport considerations less important.

![Graph showing transport of CuSO₄ across a PP/PTS membrane by application of a symmetric pulsed potential waveforms. Source solution: (1) 0.05M CuSO₄; (2) 0.1M CuSO₄; and (3) 0.2M CuSO₄ in 1M H₂SO₄. Receiving solution: 1M H₂SO₄. Potential Range: 0.7V/-0.7V; Pulse Width: 25/25sec.]

**Figure 8.12** Transport of CuSO₄ across a PP/PTS membrane by application of a symmetric pulsed potential waveforms (between A and B). Source solution: (1) 0.05M CuSO₄; (2) 0.1M CuSO₄; and (3) 0.2M CuSO₄ in 1M H₂SO₄. Receiving solution: 1M H₂SO₄. Potential Range: 0.7V/-0.7V; Pulse Width: 25/25sec.

Changes in the source solution pH have a dramatic effect upon Cu(II) transport (Figure 8.13). It was found that an increase in the pH resulted in a decrease in the flux of Cu(II) transported (see Table 8.3). According to the cyclic voltammetric results in Figure 8.2 and 8.3, the use of lower solution pH enables more efficient electrodeposition and stripping. An increase of the source solution pH causes a decrease in the efficiency of the Cu(II) preconcentration (deposition) and stripping and low copper fluxes.

**Table 8.3 Effect of the Source Solution pH on Cu(II) Flux**

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>0</th>
<th>1.0</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux (mol cm⁻² s⁻¹) During potential applied</td>
<td>1.5 x 10⁻¹⁰</td>
<td>8.2 x 10⁻¹¹</td>
<td>1.5 x 10⁻¹²</td>
</tr>
</tbody>
</table>
Figure 8.13 Transport of CuSO$_4$ across a PP/PTS membrane by application of a symmetric pulsed potential waveform (between A and B). Source solution: 0.1M CuSO$_4$ and (1), pH 0;(2) pH 1.0 and (3) pH 4.0. Receiving solution: 1M H$_2$SO$_4$; Potential Range: 0.7V/-0.7V; Pulse Width: 25/25sec..

8.3.3 Transport of Zinc (II)

8.3.3.1 Effect of Electrochemical Conditions on Zinc (II) Transport.

All work was carried out using 0.20M Zn(NO$_3$)$_2$ as the source solution and deionised water as the receiving solution except for experiments with no applied potential.

Figure 8.14 shows the Zn(II) transport across the membrane with no applied potential. The results show that when an acidic receiving solution was used, a Zn(II) flux of 1.5 x 10$^{-12}$ mol cm$^{-2}$ s$^{-1}$ through the film was obtained. This flux is much higher than that obtained by using deionised water (flux=6.3 x 10$^{-14}$ mol cm$^{-2}$ s$^{-1}$). This behaviour was similar to that
observed in the Cu(II) transport experiments (Figure 8.8). However, the fluxes obtained for Zn(II) were smaller. This suggests that the mobility of Zn(II) ions in the polymer matrix is smaller than that of the Cu(II) ions.

The transport of Zn(II) with a constant applied potential was then investigated (Figure 8.15). Application of increasingly negative potentials resulted in increased transport of Zn(II) through the membrane.

This effect was not observed with Cu(II) under the same conditions. This behaviour might be explained by an ion incorporation/expulsion mechanism. As described in section 8.3.1, Zn(II) may be reduced on the PP/PTS electrode surface at potentials exceeding -1.28 V vs Ag/AgCl. At -1.5 V, Zn(II) may be reduced but the reaction is not very efficient on the polymer surface. Both the incorporation/expulsion reactions of

Figure 8.14 Transport of Zn(NO₃)₂ across a PP/PTS membrane with no application of potential. (1) Source solution: 0.1M Zn(NO₃)₂ +1% HNO₃ (w/w); Receiving solution: 1% HNO₃; (2), Source solution: 0.1M Zn(NO₃)₂; Receiving solution: deionised water.
Zn(II) ions and the redox reactions may occur under these conditions and compete with each other.

![Graph](image)

**Figure 8.15** Transport of Zn(NO₃)₂ across a PP/PTS membrane by application of a constant potential waveform. Source solution: 0.1M Zn(NO₃)₂; Receiving solution: deionised water. (1), no applied potential, (2), +0.7V, (3), -0.9V and (4), -1.5V. The potential was applied between 0 to A.

Experiments were then carried out using a pulsed potential waveform (symmetric) with pulse width of 50 seconds and a potential range varying from 0.7V/-0.9V to 0.7V/-1.7V.

The transport results are shown in Figure 8.16 and the corresponding fluxes are listed in Table 8.4. It was found that as the negative component of the pulse increased in magnitude, the flux of Zn(II) also increased.
Figure 8.16 Transport of Zn(NO₃)₂ across a PP/PTS membrane by application of a symmetric pulsed potential waveform. Source solutions: 0.1M Zn(NO₃)₂; Receiving solution: deionised water; Pulse Width: 50 sec. The Potential was applied between A and B.

Table 8.4 Effect of Pulsed Potential Range on the Fluxes of Zinc(II) Transported.

<table>
<thead>
<tr>
<th>Pulsed Potential Range (V) vs Ag/AgCl</th>
<th>Flux (mol. cm⁻² s⁻¹) (during potential applied)</th>
<th>Flux (mol. cm⁻² s⁻¹) (after potential applied)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70/-0.9</td>
<td>1.9 x 10⁻¹¹</td>
<td>2.2 x 10⁻¹²</td>
</tr>
<tr>
<td>0.7/-1.0</td>
<td>2.0 x 10⁻¹¹</td>
<td>2.9 x 10⁻¹²</td>
</tr>
<tr>
<td>0.7/-1.3</td>
<td>2.9 x 10⁻¹¹</td>
<td>2.4 x 10⁻¹²</td>
</tr>
<tr>
<td>0.7/-1.5</td>
<td>3.2 x 10⁻¹¹</td>
<td>8.0 x 10⁻¹²</td>
</tr>
<tr>
<td>0.7/-1.7</td>
<td>1.1 x 10⁻¹⁰</td>
<td>3.1 x 10⁻¹¹</td>
</tr>
</tbody>
</table>

A substantial rate increase was observed between -1.5V and -1.7V. This is presumably due to enhanced deposition of zinc at more negative potentials. When the negative component of the pulse was more positive than -1.5V, zinc metal deposition is very inefficient and the Zn(II) transport across the membrane presumably occurs by both ion...
incorporation/expulsion processes and deposition/stripping reactions. However, at more negative potentials, since the efficiency of zinc deposition is higher, the Zn(II) transport across the membrane occurs mainly by the same mechanism as proposed for Cu(II); i.e. Zn(II) is reduced and preconcentrated on the membrane when the negative component of the pulse is applied. A high concentration of Zn(II) in the membrane pores is then produced when the positive component of the pulse is applied, resulting in an increase in the rate of Zn(II) transport across the membrane.

Also, after the applied potential was removed, significant transport was only observed when a 0.7V/-1.7V potential was applied to the membrane. This is due to oxidation of zinc metal by oxygen on the membrane surface.

The most efficient transport was obtained with a pulsed potential range of 0.7V/-1.5V (vs Ag/AgCl). A symmetric pulsed potential was used, and pulse widths in the range 2 seconds to 50 seconds were investigated. The results (Figure 8.17) show that the use of increased pulse widths results in increased rate of Zn(II) transport across the membrane. This result is different to that observed for Cu(II) transport, but it is a similar to that for the transport of electroinactive species. This suggests again that the transport of Zn(II) via an ion incorporation/expulsion mechanism is a significant contribution to the total Zn(II) flux.
The experiments in Figure 8.18 were performed using both symmetric and asymmetric pulsed potentials. The pulse range was fixed at +0.70V/-1.5V, but curve 1 was obtained using a symmetric pulse and the ratio of pulse width between the cathodic component and anodic component in curves 2 and 3 was 2:1 and 1:2 respectively. It was found that the fastest rate of transport was obtained when the symmetric pulsed was applied. The smallest flux occurred when the pulse potential was biased towards the anodic component.

This behaviour is different to that observed for Cu\(^{2+}\) transport with asymmetric pulses, and that observed in the transport of electroinactive species. This difference is due to the efficiency of the Zn(II) reduction/deposition reaction over that for the oxidation of Zn(0). With more time spent at negative potentials, more Zn(0) may be preconcentrated on the membrane so that upon oxidation a higher
concentration of Zn(II) ions is produced in the membrane pores. These results show that for zinc two independent transport mechanisms occur simultaneously.

![Figure 8.18 Transport of Zn(NO₃)₂ across a PP/PTS membrane by application of an asymmetric pulsed potential waveform. Source solutions: 0.1M Zn(NO₃)₂; Receiving solutions: deionised water; Potential Range: +0.7V/-1.5V; Pulse Width (Cathodic/Anodic) (1) 50/50 sec.; (2) 100/50 sec.; and (3) 50/100 sec.. The Potential was applied between A and B.](image)

8.3.3.2. Effect of Chemical Conditions on Zn(II) Transport

The effect of the Zn(II) concentration in the source solution was then considered (Figure 8.19) using a symmetric pulsed potential with a pulse width of 50 seconds and a potential range of 0.7V/-1.5V. The fluxes of Zn(II) obtained are listed in Table 8.5. It was found that within the concentration range investigated, changes in the Zn(II) concentration from 0.02 M to 0.20M have little effect on the Zn(II) transport. This behaviour is the same as that observed in the Cu(II) transport experiments. This suggests that the limiting step for Zn(II) transport in
these experiments is not the mass transport to the membrane surface, but Zn(II) diffusion into the polymer matrix.

**Table 8.5** Effect of Zinc (II) Concentration on the Flux of Zinc(II) Transported across a PP/PTS membrane.

<table>
<thead>
<tr>
<th>Concentration employed (M)</th>
<th>0.02</th>
<th>0.04</th>
<th>0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux (mol. cm⁻² s⁻¹)</td>
<td>3.0x10⁻¹¹</td>
<td>2.7x10⁻¹¹</td>
<td>3.3x10⁻¹¹</td>
</tr>
</tbody>
</table>

Experimental conditions used were the same as in Figure 8.19.

Variation in source solution pH was then considered using the same electrochemical conditions as described above. It was found that as the source solution pH decreased, the rate of Zn(II) transport increased. This behaviour contrasts with that for both copper(II) and electroinactive metal ion transport.

![Figure 8.19](image)

**Figure 8.19** Transport of Zn(II) across a PP/PTS membrane by application of a symmetric pulsed potential waveform. Source solution: (1) 0.02M; (2) 0.04M and (3) 0.2M Zn(NO₃)₂. Receiving solution: deionised water. Potential Range: +0.7V/-1.5V, Pulse Width: 50 sec. The Potential was applied between A and B.
Figure 8.20 Transport of Zn(II) across a PP/PTS membrane by application of a symmetric pulsed potential waveform. Source solution: 0.2M Zn(NO₃)₂ with (1) pH=4.96 and (2) pH=1.78. Receiving solution: deionised water. Potential Range: +0.7V/-1.5V, Pulse Width: 50 sec. The Potential was applied between A and B.

8.3.4 Separation Experiments

In this section, the separation of electroinactive species from electroactive species and the separation of a mixture of electroactive species is investigated. The results shown are simple examples to demonstrate separation capabilities.

Figure 8.21 shows the results for the separation of a mixture of K⁺ and Cu(II) ions. These experiments were carried out using a symmetric pulsed potential. The source solution contained 0.1 M Cu(II) and 0.1 M K⁺, the receiving solution was deionised water or 1% HNO₃ solution. When the experimental conditions were based on that used for the K⁺ transport studies (see Chapter 5), it was found that when an electrical stimulus was applied, a large flux of K⁺ was obtained. The separation
coefficient was calculated to be: \( S = \frac{\text{Flux } K^+}{\text{Flux } \text{Cu(II)}} = 226 \). In Chapter 5 experiments on K+ transport revealed that a decrease of the cathodic component of the pulse, resulted in a decrease in the flux of K+ transported.

In this chapter using ±0.7V pulsed potential conditions, Cu(II) is transported across the membrane. Thus, in Figure 8.21 (b), where the same source and receiving solutions as used in Figure 8.21 (a) was employed, but the pulse width was varied, the separation coefficient was sharply decreased to \( S = 42.4 \). Furthermore, when the experiment was performed using the same experimental conditions as used in Figure 8.21 (b), except with 1% of HNO3 added into both source and receiving solutions, (conditions are known to be suitable for Cu(II) transport and to be unsuitable for K+ transport), the separation coefficient again decreased to \( S = 10.9 \) (Figure 8.21 (c)). These results show that careful choice of experimental conditions can significantly change the separation efficiency of electroinactive species from electroactive species.

Table 8.6 summarises the average fluxes of each species transported during application of potential and the separation coefficient (calculated based on the results obtained in Figure 8.21).

These results indicate that the separation coefficient decreased in experiment (b) mainly due to a decrease in the K+ flux, while in experiment (c) the decrease in the separation coefficient resulted from both a decrease in K+ flux and an increase in the copper(II) flux. It may be concluded that because the transport of an electroinactive and electroactive species occurs via different mechanisms, their separation may be manipulated by altering the experimental conditions.
Figure 8.21 Separation of Cu(II) and K⁺ using a PP/PTS membrane. A symmetric pulsed potential was applied between A and B. (a) Pulse Width: 50 sec., Potential Range: +0.7V/-1.0V, Source Solution: 0.1M Cu(NO₃)₂ and 0.1M KNO₃, pH=4.9, Receiving Solution: deionised water. (b) Pulse Width: 25 sec., Potential Range: ±0.7V Source Solution: 0.1M Cu(NO₃)₂ and 0.1M KNO₃, pH=4.9, Receiving Solution: deionised water. (c) Pulse Width: 25 sec., Potential Range: ±0.7V Source Solution: 0.1M Cu(NO₃)₂ and 0.1M KNO₃ in 1% HNO₃ pH=0, Receiving Solution: 1% HNO₃.

Table 8.6 Effect of Experimental Conditions on the Separation Coefficient

<table>
<thead>
<tr>
<th>Experiments</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux of K⁺ (mol cm⁻² s⁻¹)</td>
<td>8.5 x 10⁻¹⁰</td>
<td>1.4 x 10⁻¹⁰</td>
<td>6.1 x 10⁻¹¹</td>
</tr>
<tr>
<td>Flux of copper(II) (mol cm⁻² s⁻¹)</td>
<td>3.2 x 10⁻¹²</td>
<td>3.3 x 10⁻¹²</td>
<td>5.6 x 10⁻¹²</td>
</tr>
<tr>
<td>Separation coefficient S = ( \frac{F_{K⁺}}{F_{Cu⁺}} )</td>
<td>266</td>
<td>42.4</td>
<td>10.9</td>
</tr>
</tbody>
</table>
It is interesting also to consider the separation of Cu(II) from Zn(II); two electroactive species.

In Figure 8.22, the experimental conditions used were suitable for Cu(II) transport. The separation coefficient obtained was:

\[ S = \frac{\text{Flux Cu(II)}}{\text{Flux Zn(II)}} = 117. \]

This is not a surprising result since under these conditions the Zn(II) could not be reduced and deposited on the membrane. However, it demonstrates the utility of the conducting polymer membrane system for effecting separation species. The experimental conditions can be altered to suit the particular separation required.

![Figure 8.22 Separation of Cu(II) and Zn(II) using PP/PTS membrane. A symmetric pulsed potential was applied between A and B. Pulse Width: 50 sec., Potential Range: +0.7V/-1.5V. Source Solution: 0.1M 0.1M Cu(NO₃) and Zn(NO₃)₂+1% HNO₃. Receiving Solution: deionised water.](image)
8.3.5 A Possible Transport Mechanism for Electroactive Species

The results observed for transport of Cu(II) or Zn(II) across PP/PTS membranes suggest that these electroactive species undergo a different transport mechanism to that proposed in Chapter 5 for electroinactive species.

In this section, using the experimental results obtained for Cu(II) and Zn(II) transport, a "Deposition/Stripping" model is proposed to explain the electrochemical control of transport of electroactive species across conducting polymer membranes.

When a reversible continuously pulsed potential is applied to the membrane, the negative component of the pulse performs a deposition process. In this step, the metal ions are preconcentrated onto the membrane (see equation 8.1 to 8.2). The positive component of the pulse performs a stripping process, where the metal is then oxidised (see equation (8-4)) producing a large concentration of metal ions in the membrane pores. These ions diffuse into the receiving solution resulting in net transport.

When a negative potential is applied to the membrane, the conducting polymer will be reduced and consequently, the metal ions will be reduced and deposited at the polymer membrane surface (see equation (8-1) and (8-2)). The surface includes the inside of the membrane pore surface. If the mobility of the counterion in the polymer matrix is small, the H⁺ or some other small electroinactive cations will be incorporated into the polymer matrix to keep electroneutrality (equation (8-3)). Which one of
these reactions occur is dependent on the nature of the counterion (C⁻), the composition of the solution and the electrical stimuli applied. During this phase of the reaction, the PP membrane is reduced and some anions in the membrane are expelled into the solution inducing anion transport. When the positive potential is applied after the negative potential, the PP membrane is re-oxidised. This causes some anions in the solution to be incorporated into the membrane (equation (8-4)). This is important for continuous anion transport. In addition, the metal which was deposited during the negative potential pulse is oxidised to the ion form and diffuses out of the membrane (equation (8-4)). Since the concentration gradient between the membrane and receiving solution is larger than that between the membrane and source solutions, the rate of the diffusion to the receiving solution will be faster. This results in metal ion transport.

As noted in Chapter 3, the PP/PTS membrane is a non-porous membrane. Generally, the transport across a non-porous membrane, can be described using Fickian diffusion:

\[
\text{Flux } J_i = - \frac{DK}{X} WC \quad (8-9)
\]

Where D is the diffusion coefficient of the transporting species; X is the membrane thickness; K is the partition coefficient for transporting species between two phases. The product DK is an often reported quantity for membranes and is called permeability.

The important factor here is that the deposited metals when reoxidised will produce a large concentration of metal ions at the membrane/solution interface and within the pores of the membrane. This represents an enhanced concentration gradient for the metal ions in the membrane pores. According to equation (6-6), the flux will increase and the rate of diffusion of metal ions to both source solution and receiving
solution will increase. This is unlikely for transport of electroinactive species but more likely the situation for Cu (II) transport.

8.4 CONCLUSIONS

Electrochemically controlled transport of electroactive species across PP/PTS membranes has been demonstrated in the course of this work. The following conclusions can be made:

(1) As with electroinactive species, the transport of electroactive species such as Cu(II) and Zn(II) across PP/PTS membranes can be controlled electrochemically by direct application of an electrical stimulus to the membrane.

(2) The rate of transport can be adjusted by application of different potential waveforms and electrochemical conditions. With Cu(II), significant fluxes can be obtained by oxidation of Cu subsequent to the application of a negative potential to reduce it. For Zn(II) transport, a significant flux was observed when a negative potential was applied. This was found to be related to the redox potential of the polymer membrane and the transport species. More efficient transport was observed when pulsed potential waveforms were employed. The rate of transport could be varied by application of various electrochemical conditions such as the pulse range and pulse width. These changes may also be related to the redox potentials. A high flux for an electroactive species was obtained only when the potential applied completely changed the redox states of both the polymer and transport species.
(3) Solution pH has a strong influence on the rate of Cu(II) transport. Use of an acidic solution results in larger fluxes. The rate of Zn(II) transport was less sensitive to changes in pH.

(4) The rate of transport was limited by the electrochemical step when the concentration of Cu(II) is greater than 0.05M and for Zn(II) is greater than 0.02M.

(5) The membrane's separation ability was investigated. The PP/PTS membrane is able to adequately separate K+ from a Cu(II) containing solution and to separate Cu(II) from a Zn(II) containing solution, by manipulation of the electrochemical conditions.

(6) A deposition/stripping model has been proposed to explain the transport of electroactive species across a conducting polymer membrane.
CHAPTER 9
GENERAL CONCLUSIONS
Membrane science and technology has been developing for over a hundred years. Only little attention has been paid to developing a membrane system with dynamic controllable transport/separation properties. Generally, the physical and chemical properties of conventional membranes are fixed after synthesis. This has been mainly limited by the membrane materials. One type of intelligent material—conducting polymers has been applied to membrane technology to make a new class of membranes. Since the physical, chemical and electrochemical properties of such materials can respond to an external stimulus, the transport and separation properties of conducting polymer membranes can be dynamically controlled in-situ. Although conducting polymers have been used for many different application areas, electrochemically controlled transport in a conducting polymer membrane system has not been previously reported.

In this work, we have demonstrated the feasibility of electrochemically controlled transport across polypyrrole free-standing membranes.

By means of application of an electrical stimulus, transport across the membrane can be dynamic switched on and off in-situ. Rate of transport across the membrane can be tuned and the separation capability of the membrane can be modified by application of an appropriate electrical stimulus.

Various potential waveforms were employed as the external stimulus. Continuous sustainable transport has been achieved by application of a cyclic sweep potential or a pulsed potential. The highest flux were obtained using a pulsed potential.

This technique has been applied to both electoinactive and electroactive ions. The transport mechanism for these two types of ions is different.
Electroinactive ions transport across the membrane undergo ion incorporation and expulsion processes, while deposition and stripping processes are dominant for electroactive ions.

In this project, a number of free-standing polypyrrole membranes with adequate conductivity and mechanical properties have been electrochemically synthesised by incorporating sulfonated counterions such as BSA, PTS, EBS, MS, BS and NPS. Mixed counterion and multilayer polymerisation techniques have also been developed. The significance of these latter techniques is that through increasing the range of the possible counterions incorporated into a membrane substantial modification of the membrane transport/separation properties is achievable.

The hardware for a conducting polymer membrane transport system has been developed. With the design of the electrotransport cell, it was found that the size of the cell and the shape of the connection to the membrane was important factors. Larger fluxes can be obtained when a smaller size cell (using smaller membrane) was employed. A circular electrical connection was better than a point one. The direction of the electrical field (act as a driving force) can be varied by different electrode arrangement.

Although extensive investigations on the electrochemical control of transport across these conducting polymer membrane were carried out, some problems remain and further research is required to solve them.

(1) In order to increase the flux, and without loss of selectivity, synthesis and development of a conducting polymer membrane with a suitable pore size and large porosity is necessary.
(2) In order to broaden the scope for new application areas, different transport species for this novel system should be investigated, such as bio-molecules.

(3) Further fundamental work is still required. In particular:

(i) The transport mechanism should be studied in more detail using other techniques such as Quartz Crystal Microbalance and possibly following the transport process using radio-tracer species. These studies will help increase our understanding of the system and hence enhance the potential for further applications.

(ii) The effect of the counterion on polypyrrole formation and the properties of the resultant membrane is worthy of further study. Properties such as mechanical strength and surface character, both important in membrane use, are very dependent on the incorporated counterion which obviously modifies the polymer structure.
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