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Studies of inherently conducting polymers in ionic liquids

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**STUDIES OF INHERENTLY
CONDUCTING POLYMERS IN
IONIC LIQUIDS**

**A thesis submitted to satisfy the requirements for the
award**

DOCTOR OF PHILISOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

JAKUB MAZURKIEWICZ, BSc. (Hons)

**DEPARTMENT OF CHEMISTRY –
INTELLIGENT POLYMER RESEARCH
INSTITUTE**

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“I am enthusiastic over humanity's extraordinary and sometimes very timely ingenuities. If you are in a shipwreck and all the boats are gone, a piano top buoyant enough to keep you afloat may come along and make a fortuitous life preserver. This is not to say, though, that the best way to design a life preserver is in the form of a piano top. I think we are clinging to a great many piano tops in accepting yesterday's fortuitous contrivings as constituting the only means for solving a given problem.”

- Buckminster Fuller

ABSTRACT

In this dissertation, the effect of ionic liquid (IL) or classical electrolyte (CE) employed on the redox behaviour of many inherently conducting polymers (ICPs) was investigated with the ultimate goal of producing flexible batteries.

ICPs can be used in a range of unique applications, and also to replace many metal conductors or inorganic semiconductors. Commercialisation of ICPs has, however, been limited. Ion and solvent transport in ICPs during redox cycling almost universally leads to breakdown of redox activity and desired properties of the material. ILs comprise of neat ions in the form of a room temperature melt. ILs show great promise as novel electrolytes to enhance the stability of ICPs beyond that observed in CEs and paves the way to commercialisation of ICP devices.

Chapter 3 describes fundamental investigations of ICP / IL systems on Pt disk electrodes. The redox cycling stability of polypyrrole was increased over those of CE systems in the IL 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆). The electroactivity in this system showed no degradation over 900 redox cycles. The use of 1-ethyl-3-methylimidazolium (bis) trifluoromethanesulfonimide (EMITFSI) also improved the redox stability of polypyrrole in comparison to the CE systems. The stable potential windows of polypyrrole were significantly improved in both IL systems compared to CEs.

The transitional behaviour between ILs and CEs was investigated by diluting ILs in a common neutral solvent electrolyte, propylenecarbonate (PC). In such IL / CE mixtures,

differences were noted in the electrolyte conductivity profile and ICP electroactivity with respect to concentration of IL. BMIPF₆ exhibited a significantly higher degree of ion pairing than EMITFSI, and the strong ion pairing property of BMIPF₆ is thought to be responsible for unique electrochemical observations absent from the ICP in EMITFSI systems.

N-doping is an attractive feature of some ICPs and has promise in charge storage applications, providing significant driving potential differences of two or more volts against p-doped electrodes. As ILs were found to enhance redox stability of common p-doping processes in ICPs, investigations were conducted in Chapter 4 to see if the same was true for inherently unstable n-doping processes.

Poly-3-*p*-flourophenylthiophene (P3PFTh) was chosen as a model n-doping system, due to its well published n-doping behaviour in classical electrolytes. Surprisingly, n-doping responses of P3PFTh in EMITFSI were very poor. The reasons behind this were explored by testing other n-dopable polymers in EMITFSI to isolate whether EMITFSI was inherently preventing n-doping, and P3PFTh was tested with different ILs to investigate P3PFTh / EMITFSI incompatibility.

EMITFSI used as an electrolyte was found to decrease electroactivity of the n-doping processes in most polythiophenes, with the exception of polybithiophene (PBiTh). The stability of n-doping PBiTh in EMITFSI did not, however, improve to an extent that would allow derivative devices to be practical.

Spectroelectrochemical Raman studies of the n-doping processes of polythiophenes in EMITFSI were conducted *in-situ* to reveal behaviour that may be responsible for poor electrochemical responses. Raman studies showed that both the p-doping and n-doping process in polythiophenes occurred with a ‘reverse’ mechanism of ion expulsion upon doping (whereas doping processes of ICPs in CEs usually occur by ion insertion). The Raman studies also indicated that the physical structure of polythiophene had a large effect on the resulting electrochemistry, to an extent that impeded doping processes.

The structure-activity relationships of P3PFTh were investigated by CV using a range of growth and cycling electrolytes. Observations were analysed chemometrically to identify the effects on electrochemical parameters of electrolyte component (anion or cation), whether the dominating effect was from growth or cycling electrolyte, and which particular doping / dedoping process was affected by these parameters.

Chapter 5 describes electrochemical charge storage devices based on IL electrolytes using various substrates, polymers and configurations. The highest capacity device was based on polyaniline doped with ferrocene sulphonic acid on carbon fibre textile for both anode and cathode, with a polyvinylidene fluoride (PVDF) separator and EMITFSI electrolyte. The flexible charge storage device produced in this way had a maximum charge capacity of 58 mAh/g, but degraded quickly on cycling. The most stable device was constructed similarly to the highest capacity device, but used polypyrrole and poly-3-methylthiophene electrodes, with maximum charge capacity of 17 mAh/g, remaining unchanged for 60 cycles.

DECLARATION

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

Jakub Mazurkiewicz

PUBLICATIONS

Journal Papers

1. Lu, Wen, G. Fadeev Andrei, Baohua Qi, Elisabeth Smela, R. Mattes Benjamin, Jie Ding, M. Spinks Geoffrey, **Jakub Mazurkiewicz**, Dezhi Zhou, G. Wallace Gordon, R. Macfarlane Douglas, A. Forsyth Stewart and Maria Forsyth. "*Use of ionic liquids for pi-conjugated polymer electrochemical devices.*" *Science*, 2002 297: 983-7.
2. **Jakub Mazurkiewicz**, Peter Innis, Gordon Wallace, D. R. Macfarlane, M Forsyth "*Conducting polymer electrochemistry in ionic liquids.*" *Synthetic Metals*, 2003 135-136: 31-32.
3. Peter Innis, **Jakub Mazurkiewicz**, T Nguyen, Gordon Wallace, D Macfarlane. "*Enhanced electrochemical stability of polyaniline in ionic liquids.*" *Current Applied Physics*, 2004 4: 389-393.

Conference Proceedings

- 1. Jakub Mazurkiewicz, Gordon Wallace, Peter Innis, .** *"Flexible fabric batteries from conductive polymers and ionic liquids."* ICSM 04: The role and impact of Nanoscience & Nanotechnologies, IPRI - University of Wollongong, 2004: 112.
- 2. Jakub Mazurkiewicz, Gordon Wallace, Peter Innis.** *"p- and n-doping in poly (bithiophene) using ionic liquid electrolyte."* ICSM 04: The role and impact of Nanoscience & Nanotechnologies, IPRI - University of Wollongong, 2004: 112.
- 3. Wallace, G. G., D. Zhou, J. Ding, B. Xi, P. Innis, J. Mazurkiewicz, G. M. Spinks, J. Gillespie, D. R. Macfarlane and S. Forsyth.** *"Ionic liquids and helical interconnects: Bringing the electronic Braille screen closer to reality."* EAP Actuators and Devices. SPIE. ,2003. 5051

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TABLE OF CONTENTS

CHAPTER 1

| | |
|--|-----------|
| GENERAL INTRODUCTION..... | 1 |
| 1.1 Overview..... | 1 |
| 1.2 Conducting Polymers..... | 1 |
| 1.3 Limitations of Conducting Polymers..... | 3 |
| 1.4 Conductivity and Charge Transport in Conductive Polymers..... | 3 |
| 1.4.1 Electronic Bands and Electrical Conductivity | 4 |
| 1.4.2 Doping and Charge Conduction in ICPs..... | 7 |
| 1.5 Ionic Liquids | 8 |
| 1.5.1 What are Ionic Liquids?..... | 8 |
| 1.5.2 Why are Ionic Liquids, liquid?..... | 9 |
| 1.6 Contrasts of Ionic Liquids and Classic Electrolytes | 10 |
| 1.6.1 Introduction..... | 10 |
| 1.6.2 Charge Conduction in a Classical Electrolyte (CE)..... | 10 |
| 1.6.3 Charge Conduction in Ionic Liquids..... | 11 |
| 1.7 Interaction of Conducting Polymers with Electrolytes | 13 |
| 1.8 Outline of Objectives..... | 17 |
| 1.9 References | 17 |

CHAPTER 2

ELECTROCHEMICAL METHODS AND

INTERPRETATION 23

| | | |
|------------|---|-----------|
| 2.1 | Introduction | 23 |
| 2.2 | Measuring and Controlling Electrochemistry..... | 23 |
| 2.3 | Cyclic Voltammetry | 27 |
| 2.4 | Factors Influencing CV..... | 29 |
| 2.5 | Deconvoluting Cyclic Voltammetry of ICPs..... | 30 |
| 2.6 | Deconvolution of ICP CV's with Statistical Distribution | |
| | Functions | 32 |
| | 2.6.1 The Statistical Gaussian Energy Dispersion Function for ICPs..... | 33 |
| 2.7 | Theoretical experiments with the Gaussian Model..... | 36 |
| 2.8 | Capacitive Effects of Oxidised ICPs..... | 41 |
| 2.9 | References | 44 |

CHAPTER 3

EFFECTS OF IONIC LIQUID AS AN

ELECTROLYTE IN CONDUCTING POLYMER

SYSTEMS..... 46

| | | |
|------------|------------------------------------|-----------|
| 3.1 | Introduction | 46 |
| 3.2 | Experimental Procedure..... | 48 |

| | |
|---|-----------|
| 3.2.1 General Electrochemistry..... | 48 |
| 3.2.2 Materials..... | 49 |
| 3.2.3 Conductivity Measurements..... | 49 |
| 3.3 Results and Discussion..... | 50 |
| 3.3.1 Cyclic Voltammetry of Various Electrolyte Systems | 50 |
| 3.3.2 Cyclic Voltammetry of Polypyrrole / PF ₆ Film in BMIPF ₆ and EMITFSI..... | 52 |
| 3.3.3 Potential Window of Polypyrrole / PF ₆ Film in BMIPF ₆ and EMITFSI..... | 61 |
| 3.3.4 Redox Cycling Stability of Polypyrrole / PF ₆ Film in BMIPF ₆ and EMITFSI | 65 |
| 3.3.5 Kinetic Studies of Polypyrrole / PF ₆ Film in BMIPF ₆ and EMITFSI..... | 69 |
| 3.3.6 Electrochemistry of Conducting Polymers with Respect to BMIPF ₆ and EMITFSI Quantity in PC..... | 72 |
| 3.3.7 Ionic Conductivity as a Function of BMIPF ₆ and EMITFSI Quantity in PC..... | 73 |
| 3.3.8 Conducting Polymer CVs as a Function of BMIPF ₆ and EMITFSI Quantity in PC | 78 |
| 3.3.9 Polypyrrole / PF ₆ CVs as a Function of BMIPF ₆ and EMITFSI Quantity in PC..... | 79 |
| 3.3.10 Poly-3-methylthiophene (P3MeTh) / PF ₆ CVs as a Function of BMIPF ₆ and EMITFSI Quantity in PC..... | 82 |
| 3.3.11 Polybithiophene (PBiTh) / PF ₆ CVs as a Function of BMIPF ₆ and EMITFSI Quantity in PC..... | 85 |

| | | |
|------------|---|-----------|
| 3.3.12 | Polyaniline (PAn) / PF ₆ CVs as a Function of BMIPF ₆ and EMITFSI Quantity in PC | 88 |
| 3.4 | General Conclusions | 91 |
| 3.5 | References | 92 |

CHAPTER 4

STUDIES OF N-DOPING POLYTHIOPHENES 95

| | | |
|------------|---|------------|
| 4.1 | General Introduction | 95 |
| 4.2 | Experimental..... | 96 |
| 4.2.1 | General Electrochemistry | 96 |
| 4.2.2 | In-Situ Raman | 97 |
| 4.2.3 | Theoretical Calculations of Raman Spectral Features | 97 |
| 4.2.4 | Structure-Electroactivity Relationships for Poly-3- Paraflourophenylthiophene (P3PFTh) | 98 |
| 4.3 | Results and Discussion | 100 |
| 4.3.1 | CV and In-Situ Raman Spectral Studies of Polythiophenes in EMITFSI | 100 |
| 4.3.1.1 | Poly-3-paraflourophenylthiophene (P3PFTh) in EMITFSI..... | 100 |
| 4.3.1.2 | CV and Raman Studies of P3MeTh in EMITFSI | 104 |
| 4.3.1.3 | Polyterthiophene in EMITFSI..... | 108 |
| 4.3.1.4 | Polybithiophene (PBiTh) in EMITFSI..... | 110 |
| 4.3.1.5 | Summary of Results from Section 4.3.1 | 113 |
| 4.3.2 | Studies of P3PFTh in Various Ionic Liquids | 113 |
| 4.3.3 | Structure-Electroactivity Relationships of P3PFTh..... | 118 |

| | |
|---|------------|
| 4.4 Electrochemometrics – Use of Multidimensional | |
| Scaling..... | 120 |
| 4.4.1 MDS Analysis of Peak Potentials in P3PFTh Systems..... | 122 |
| 4.4.2 MDS Analysis of Faradaic Charge in P3PFTh Systems..... | 125 |
| 4.4.3 MDS Analysis of Surface Concentration in P3PFTh Systems | 127 |
| 4.4.4 MDS Analysis of Peak Heights in P3PFTh Systems..... | 128 |
| 4.4.5 MDS Analysis of Half-Peak Widths in P3PFTh Systems | 130 |
| 4.5 General Conclusions | 131 |
| 4.6 References | 135 |

CHAPTER 5

CHARGE STORAGE IN CONDUCTING

POLYMERS..... 137

| | |
|--|------------|
| 5.1 Introduction | 137 |
| 5.1.1 Environmental Considerations of Conducting Polymers..... | 138 |
| 5.1.2 Material Considerations of Conducting Polymers..... | 138 |
| 5.1.3 Ionic Liquids for Battery Use..... | 139 |
| 5.2 Experimental..... | 139 |
| 5.2.1 Substrates | 140 |
| 5.2.2 Materials..... | 141 |
| 5.2.3 Chemical Synthesis of ICP Dispersions..... | 141 |
| 5.2.4 General Electrochemistry..... | 142 |
| 5.2.5 Device Construction and Testing..... | 142 |

| | |
|--|------------|
| 5.2.6 Device Testing Procedure | 143 |
| 5.2.7 Polypyrrole Unsealed Membrane in Laminate Devices..... | 144 |
| 5.2.8 Polypyrrole / Poly-3-methylthiophene in Sealed Laminate Devices..... | 145 |
| 5.2.9 Polyaniline Doped with Ferrocene Sulphonic Acid in Sealed Laminate Devices..... | 146 |
| 5.2.10 Polypyrrole / PEDOT from Pre-formed Dispersion in Sealed Laminate Devices..... | 146 |
| 5.3 Results and Discussion..... | 147 |
| 5.3.1 General Construction and Form of Flexible Conducting Polymer Batteries | 147 |
| 5.3.2 Electrode Substrates for Flexible Battery Devices..... | 149 |
| 5.3.2.1 Electrochemical Studies of Substrates | 149 |
| 5.3.3 Polypyrrole Unsealed Membrane Laminate Device | 154 |
| 5.3.4 Polypyrrole / Poly-3-methylthiophene in a Sealed Laminate Device | 157 |
| 5.3.5 Polyaniline Doped with Ferrocene Sulphonic Acid in Sealed Laminate Devices..... | 163 |
| 5.3.5.1 Polyaniline Doped with Ferrocene Sulphonic Acid on (Pt)-Ni-Cu-Coated Polyester in a Sealed Laminate Device..... | 165 |
| 5.3.5.2 Polyaniline Doped with Ferrocene Sulphonic Acid on Carbon Felt in a Sealed Laminate Device..... | 169 |
| 5.3.5.3 Polyaniline Doped with Ferrocene Sulphonic Acid on Zorflex Carbon Fabric in a Sealed Laminate Device..... | 172 |

| | |
|---|------------|
| 5.3.6 Polypyrrole / PEDOT from Pre-formed Dispersion in a Sealed Laminate Device | 176 |
| 5.4 General Conclusions | 179 |
| 5.5 References | 181 |
| CHAPTER 6 | |
| CONCLUDING REMARKS | 186 |
| 6.1 General Conclusions | 186 |
| 6.2 Suggested Future Work | 191 |
| APPENDIX..... | 192 |

LIST OF FIGURES

| | |
|---|----|
| Figure 1.1- Structures and names of some common inherently conducting polymers (ICPs). | 2 |
| Figure 1.2- The electronic band structures of various classes of materials. | 4 |
| Figure 1.3- Ion migration in a classical electrolyte..... | 11 |
| Figure 1.4- Charge conduction via hopping in ionic liquids..... | 11 |
| Figure 1.5- Possible phases of ionic liquid in a neutral solvent..... | 12 |
| Figure 1.6- Proposed mechanism of ion and solvent movement into an ICP..... | 14 |
| Figure 1.7- Proposed ion movement of an ionic liquid in a conducting polymer..... | 16 |
| Figure 2.1- I / E / t surface for an arbitrary chemical reaction ⁶⁷ | 25 |

| | |
|--|----|
| Figure 2.2- A general schematic of a potentiostat..... | 27 |
| Figure 2.3- Example of cyclic voltammetry – PPy / PF ₆ film in BMIPF ₆ ionic liquid. | 28 |
| Figure 2.4- Structural diagrams of polythiophene in its polaronic and bipolaronic representations, for both p-doped and n-doped states..... | 34 |
| Figure 2.5- Current vs. potential plot of different E _{ox} B values..... | 37 |
| Figure 2.6- Current vs. potential plot of different σ _B values..... | 38 |
| Figure 2.7- (a) current vs. potential plot of different N _s values, (b) the same plot as (a) showing how half peak width remains constant when kinetic parameters are not altered. | 39 |
| Figure 2.8- A CV of polypyrrole film (black) in propylenecarbonate solvent with tetrabutylammonium hexafluorophosphate as a dissolved electrolyte..... | 41 |
| Figure 2.9- A CV of polypyrrole film (black) in propylene carbonate solvent with tetrabutylammonium hexafluorophosphate as a dissolved electrolyte..... | 43 |
| Figure 3.1- Cyclic voltammetry of various electrolytes. Scan rate = 200 mV/s..... | 51 |
| Figure 3.2- CVs of PPy / PF ₆ film in a classical electrolyte, 0.25 M TBAPF ₆ in PC..... | 53 |
| Figure 3.3- CVs of PPy / PF ₆ film in BMIPF ₆ under non-purged conditions..... | 54 |
| Figure 3.4- CVs of PPy / PF ₆ film in BMIPF ₆ under constant N ₂ purging. E _{ox} = oxidation peak, E _{red} = reduction peak..... | 55 |
| Figure 3.5- CVs of PPy / PF ₆ film in BMIPF ₆ with constant wet N ₂ purging..... | 56 |
| Figure 3.6- CVs of PPy / PF ₆ film in BMIPF ₆ with constant dry air purging..... | 57 |
| Figure 3.7- CVs of PPy / PF ₆ film in EMITFSI under non-purged conditions..... | 58 |

| | |
|---|----|
| Figure 3.8- CVs of PPy / PF ₆ film in EMITFSI under constant N ₂ purging..... | 58 |
| Figure 3.9- CVs of PPy / PF ₆ film in EMITFSI with constant wet N ₂ purging..... | 58 |
| Figure 3.10- CVs of PPy / PF ₆ film in EMITFSI with constant dry air purging. | 59 |
| Figure 3.11- CVs obtained for potential window of PPy / PF ₆ film in 0.25 M TBAPF ₆ / PC. | 62 |
| Figure 3.12- CVs obtained for potential window of PPy / PF ₆ film in non- purged BMIPF ₆ | 62 |
| Figure 3.13- CVs obtained for potential window of PPy / PF ₆ film in non- purged EMITFSI. | 63 |
| Figure 3.14- CVs obtained for potential window of PPy / PF ₆ film in BMIPF ₆ with N ₂ purging. | 64 |
| Figure 3.15- CVs obtained for potential window of PPy / PF ₆ film in EMITFSI with N ₂ purging. | 64 |
| Figure 3.16- CVs of PPy / PF ₆ film in 0.25 M TBAPF ₆ / PC. | 65 |
| Figure 3.17- CVs of PPy / PF ₆ film in non-purged BMIPF ₆ | 66 |
| Figure 3.18- CVs of PPy / PF ₆ film in EMITFSI, non-purged. | 67 |
| Figure 3.19- CVs of PPy / PF ₆ film in N ₂ purged BMIPF ₆ | 67 |
| Figure 3.20- CVs of PPy / PF ₆ film in EMITFSI, N ₂ purged. | 68 |
| Figure 3.21- Square root of scan rate vs. peak current for PPy / PF ₆ films in various electrolytes..... | 71 |
| Figure 3.22- Conductivity of BMIPF ₆ in PC and EMITFSI in PC at different concentrations of IL, % mol/mol. | 74 |
| Figure 3.23- Conductivity of BMIPF ₆ in PC and EMITFSI in PC at different concentrations of IL, % w/w. | 74 |

| | |
|---|----|
| Figure 3.24- Predicted viscosities of BMIPF ₆ and EMITFSI at different concentrations in PC. | 76 |
| Figure 3.25- Relative conductivity changes predicted due to viscosity only..... | 76 |
| Figure 3.26- Diagram of the procedure used to develop CV contour plots obtained for ICP films in BMIPF ₆ / PC and EMITFSI / PC of varying composition..... | 78 |
| Figure 3.27- CV of PPy / PF ₆ film in (a) BMIPF ₆ / PC and (b) EMITFSI / PC electrolyte at 50 % w/w composition..... | 79 |
| Figure 3.28 - Three-dimensional (top) and contour plots (bottom) of PPy / PF ₆ CVs at varying concentrations of BMIPF ₆ in PC..... | 80 |
| Figure 3.29- Three-dimensional (top) and contour plots (bottom) of PPy / PF ₆ CVs at varying concentrations of EMITFSI in PC. | 81 |
| Figure 3.30- CV of P3MeTh / PF ₆ film in (a) BMIPF ₆ / PC and (b) EMITFSI / PC electrolyte at 50 % w/w composition. | 82 |
| Figure 3.31- Three-dimensional (top) and contour plots (bottom) of P3MeTh / PF ₆ CVs at varying concentrations of BMIPF ₆ in PC..... | 83 |
| Figure 3.32- Three-dimensional (top) and contour plots (bottom) of P3MeTh / PF ₆ CVs at varying concentrations of EMITFSI in PC..... | 84 |
| Figure 3.33- CV of PBiTh / PF ₆ film in (a) BMIPF ₆ / PC and (b) EMITFSI / PC electrolyte at 50 % w/w composition. | 85 |
| Figure 3.34- Three-dimensional (top) and contour plots (bottom) of PBiTh / PF ₆ CVs at varying concentrations of BMIPF ₆ in PC..... | 86 |
| Figure 3.35- Three-dimensional (top) and contour plots (bottom) of PBiTh / PF ₆ CVs at varying concentrations of EMITFSI in PC. | 87 |

| | |
|---|-----|
| Figure 3.36- CV of PAn / PF ₆ film in (a) BMIPF ₆ / PC and (b) EMITFSI / PC electrolyte at 50% w/w composition..... | 88 |
| Figure 3.37- Three-dimensional (top) and contour plots (bottom) of PAn / PF ₆ CVs at varying concentrations of BMIPF ₆ in PC..... | 89 |
| Figure 3.38- Three-dimensional (top) and contour plots (bottom) of PAn / PF ₆ CVs at varying concentrations of EMITFSI in PC. | 90 |
| Figure 4.1- Spectroelectrochemical cell for the in-situ study of polythiophenes. | 97 |
| Figure 4.2- CV of a P3PFTh / TFSI film grown from and cycled in 0.1 M EMITFSI / acetonitrile..... | 100 |
| Figure 4.3- P3PFTh / TFSI grown from 0.1 M EMITFSI / acetonitrile, and cycled in pure EMITFSI..... | 102 |
| Figure 4.4- Raman spectra of P3PFTh / TFSI in EMITFSI at various potentials..... | 103 |
| Figure 4.5- CV of P3MeTh film grown from 0.1 M EMITFSI / acetonitrile, and cycled in pure EMITFSI..... | 105 |
| Figure 4.6- Raman spectra of P3MeTh in EMITFSI at various potentials. | 106 |
| Figure 4.7- Eigenvector diagram of decathiophene in a C-S-C deformation found in Raman spectra at circa 730 cm ⁻¹ | 107 |
| Figure 4.8- CV of PTerTh / TFSI film grown from 0.1 M EMITFSI / acetonitrile, and cycled in pure EMITFSI..... | 108 |
| Figure 4.9- Raman spectra of PTerTh / TFSI film in EMITFSI at various potentials. | 109 |
| Figure 4.10- Eigenvector diagram of in plane C-H bends of decathiophene found in Raman spectra circa 1040 cm ⁻¹ | 110 |
| Figure 4.11- PBiTh / TFSI film grown from 0.1 M EMITFSI / acetonitrile, and cycled in pure EMITFSI..... | 111 |

| | |
|---|-----|
| Figure 4.12- Raman spectra of PBiTh / TFSI in EMITFSI at various potentials. | 112 |
| Figure 4.13- CV of P3PFTh / BF ₄ film grown from 0.1 M BMIBF ₄ / acetoneitrile, and cycled in pure BMIBF ₄ | 114 |
| Figure 4.14- CV of P3PFTh / PF ₆ film grown from 0.1 M BMIPF ₆ / acetoneitrile, and cycled in pure BMIPF ₆ | 114 |
| Figure 4.15- CV of P3PFTh / ClO ₄ film grown from 0.1 M TMAClO ₄ / acetoneitrile, and cycled in pure BMIBF ₄ | 115 |
| Figure 4.16- CV of P3PFTh / ClO ₄ film grown from 0.1 M TMAClO ₄ / acetoneitrile, and cycled in pure BMIPF ₆ | 116 |
| Figure 4.17- CV of P3PFTh / ClO ₄ film grown from 0.1 M TMAClO ₄ / acetoneitrile, and cycled in pure EMITFSI..... | 116 |
| Figure 4.18- Diagrammatic of protocols used for decomposition and analysis of P3PFTh in various electrolytes. | 120 |
| Figure 4.20- Multidimensional scaling analysis of peak potentials for each sector of P3PFTh in various growth and cycling electrolytes..... | 123 |
| Figure 4.21- Plot of D2 (cycling cation size) from n _{ox} against VDW volume of respective cations. | 124 |
| Figure 4.22- Multidimensional scaling analysis of Faradaic charge for each sector of P3PFTh in various growth and cycling electrolyte conditions. | 126 |
| Figure 4.23- Multidimensional scaling analysis of Surface Concentration (N _s) for each sector of P3PFTh in various growth and electrolyte conditions..... | 128 |
| Figure 4.24- Multidimensional scaling analysis of Peak Heights for each sector of P3PFTh in various growth and electrolyte conditions..... | 129 |

| | |
|--|-----|
| Figure 4.25- Multidimensional scaling analysis of Half-peak Width for each sector of P3PFTh in various growth and electrolyte conditions. | 131 |
| Figure 5.1- The interface built to automate the introduction of a load resistor into circuit during a battery discharge cycle. | 143 |
| Figure 5.2- The general form of an electrical battery. | 147 |
| Figure 5.3- The general layout of a flexible battery..... | 148 |
| Figure 5.4- CVs obtained using a carbon felt working electrode in EMITFSI..... | 150 |
| Figure 5.5- CV obtained using Laird technologies Ni-Cu-coated polyester as a working electrode in EMITFSI. | 151 |
| Figure 5.6- Laird Technologies material as in Figure 5.4, but 200 cycles later..... | 152 |
| Figure 5.7- CVs obtained using fine stainless steel mesh working electrode in EMITFSI. | 152 |
| Figure 5.8- CV obtained using a Zorflex® carbon fabric working electrode in EMITFSI. | 153 |
| Figure 5.9- The open-air membrane battery. | 154 |
| Figure 5.10- CVs of: (A) - PPy / ClO ₄ , and (B) - PPy / PSS in EMITFSI on Pt sputter coated PVDF electrodes. | 155 |
| Figure 5.11- Typical charge / discharge curve of PPy / PSS : PPy / LiClO ₄ in EMITFSI in a Pt coated PVDF membrane battery. | 156 |
| Figure 5.12- Charge capacity as a function of cycle number of PPy / PSS : PPy / ClO ₄ in EMITFSI in a Pt coated PVDF membrane battery. | 157 |
| Figure 5.13- The rig required to deposit conducting polymer onto fine stainless steel mesh, side view..... | 159 |
| Figure 5.14- CVs of A – PPy / TFSI and C - P3MeTh / TFSI in EMITFSI on fine stainless steel mesh electrodes. | 160 |

| | |
|---|-----|
| Figure 5.15- A picture of the PPy / TFSI : P3MeTh / TFSI assembled battery..... | 160 |
| Figure 5.16- Typical charge / discharge curve of a PPy / TFSI : P3MeTh / TFSI in EMITFSI in a fine stainless steel mesh battery..... | 161 |
| Figure 5.17- Charge capacity as a function of cycle number of PPy / TFSI : P3MeTh / TFSI in EMITFSI on fine stainless steel mesh battery..... | 162 |
| Figure 5.18- Example of CV growth of PAn / FcHSO ₃ on Pt disk electrode..... | 163 |
| Figure 5.19- CV of PAn / FcHSO ₃ on Pt disk electrode in EMITFSI..... | 164 |
| Figure 5.20- Galvanostatic deposition of polyaniline doped with ferrocene sulphonic acid onto Laird Industries Ni-Cu-coated polyester at 3 $\mu\text{A}/\text{cm}^2$ over 16 hours..... | 165 |
| Figure 5.21- Galvanostatic deposition of polyaniline doped with ferrocene sulphonic acid onto Laird Industries Ni-Cu-coated polyester at 3 $\mu\text{A}/\text{cm}^2$ over 2 hours..... | 166 |
| Figure 5.22- Potentiostatic deposition of polyaniline doped with ferrocene sulphonic acid onto Laird Industries Ni-Cu-coated polyester at 750 mV over 1 hour..... | 166 |
| Figure 5.23- Potentiostatic deposition of polyaniline doped with ferrocene sulphonic acid onto Laird Industries Pt-Ni-Cu-coated polyester at 750 mV over 1 hour..... | 167 |
| Figure 5.24- CV of PAn / FcHSO ₃ on Liard Industries Pt-Ni-Cu-coated polyester in EMITFSI..... | 167 |
| Figure 5.25- Typical charge / discharge curve of PAn / FcHSO ₃ : PAn / FcHSO ₃ on Pt-Ni-Cu-coated polyester in EMITFSI battery..... | 168 |
| Figure 5.26- Charge capacity as a function of cycle number of PAn / FcHSO ₃ : PAn / FcHSO ₃ on Pt-Ni-Cu-coated polyester in EMITFSI battery..... | 169 |

| | |
|--|-----|
| Figure 5.27- CV of PAn / FcHSO ₃ on carbon felt in EMITFSI..... | 170 |
| Figure 5.28- Typical charge / discharge curve of a PAn / FcHSO ₃ : PAn / FcHSO ₃ on carbon felt in EMITFSI battery. | 171 |
| Figure 5.29- Charge capacity as a function of cycle number of a PAn / FcHSO ₃ : PAn / FcHSO ₃ on carbon felt in EMITFSI battery. | 172 |
| Figure 5.30- CV of PAn / FcHSO ₃ on Zorflex woven carbon fabric..... | 173 |
| Figure 5.31- Typical charge / discharge curve of a PAn / FcHSO ₃ : PAn / FcHSO ₃ on Zorflex carbon fabric in EMITFSI battery. | 174 |
| Figure 5.32- Charge capacity as a function of cycle number of PAn / FcHSO ₃ : PAn / FcHSO ₃ on Zorflex carbon fabric in EMITFSI battery. | 175 |
| Figure 5.33- CV of A – PEDOT / PSS and B – PPy / PSS in EMITFSI on fine stainless steel mesh. | 177 |
| Figure 5.34- Typical charge / discharge curve of a PPy / PSS : PEDOT / PSS on fine stainless steel mesh in EMITFSI battery. | 177 |
| Figure 5.35- Charge capacity Vs cycle number of a PEDOT / PSS : PPy / PSS battery, at different charge rates..... | 178 |

LIST OF ABBREVIATIONS

| | |
|------------------|--|
| 3MeTh | 3-Methylthiophene |
| 3PFTh | 3-Parafluorophenylthiophene |
| A | Electrode area (cm ²) |
| ACN | Acetonitrile |
| A_{ox} | activity (concentration) of oxidised species |
| A_{red} | activity (concentration) of reduced species |
| AUX | auxillary electrode |
| B | Bipolaronic |
| BF ₄ | tetrafluoroborate |
| BiTh | 2,2'-Bithiophene |
| BMI | 1-Butyl-3-methylimidazolium |
| C | analyte's concentration (mol/L) |
| cet | Cetrimide |
| ClO ₄ | Perchlorate |
| c^o | Initial concentration |
| CV | Cyclic Voltammetry |
| D1 | Dimension 1 |
| D2 | Dimension 2 |
| D^o | Diffusion constant |
| E | Overpotential |
| E^o | Standard potential of reaction |
| EDOT | 3,4-Ethylenedioxythiophene |
| EMI | 1-Ethyl-3-methylimidazolium |
| F | Faraday's constant |
| FEM | Finite element method |
| GC | Glassy carbon |
| I | Current |
| ICP | Inherently conducting polymer |
| IL | Ionic liquid |
| IR | Internal resistance |
| Li | Lithium |
| MDS | Multidimensional scaling |
| n | Number of electrons involved in process |
| Ns | Density of conjugated chain segments. |
| P | Poly- |
| P | Polaronic |
| PC | Propylenecarbonate |
| PCA | Principal component analysis |
| PF ₆ | Hexafluorophosphate |
| Pt | Platinum |
| PVDF | Polyvinylidene fluoride |

| | |
|-----------|--|
| Py | Pyrrole |
| R | Gas constant |
| R | Universal gas constant (8.314 J / mol K) |
| RE | Reference electrode |
| RSQ | Proportion of variance |
| SEM | Scanning electron microscopy |
| t | time (seconds) |
| T | Temperature in Kelvin |
| TBA | Tetrabutylammonium |
| TEA | Tetraethylammonium |
| TerTh | 2,2':5',2"-Terthiophene |
| TFSI | (bis)trifluoromethanesulfonimide |
| TMA | tetramethylammonium |
| V | Voltage / Volts |
| WE | Working Electrode |
| x | distance from electrode |
| E | applied potential. |
| E_{oxP} | mean potential of polaron formation. |
| σ | peak width at half height |