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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**

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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 (BMIPF<sub>6</sub>). 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. BMIPF<sub>6</sub> exhibited a significantly higher degree of ion pairing than EMITFSI, and the strong ion pairing property of BMIPF<sub>6</sub> 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*-fluorophenylthiophene (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.

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- 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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## LIST OF ABBREVIATIONS

|                  |  |
|------------------|--|
| 3MeTh            | 3-Methylthiophene                            |
| 3PFTh            | 3-Parafluorophenylthiophene                  |
| A                | Electrode area (cm <sup>2</sup> )            |
| ACN              | Acetonitrile                                 |
| $A_{ox}$         | activity (concentration) of oxidised species |
| $A_{red}$        | activity (concentration) of reduced species  |
| AUX              | auxillary electrode                          |
| B                | Bipolaronic                                  |
| BF <sub>4</sub>  | tetrafluoroborate                            |
| BiTh             | 2,2'-Bithiophene                             |
| BMI              | 1-Butyl-3-methylimidazolium                  |
| C                | analyte's concentration (mol/L)              |
| cet              | Cetrimide                                    |
| ClO <sub>4</sub> | 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-  |
| <b>P</b>         | Polaronic                                    |
| PC               | Propylenecarbonate                           |
| PCA              | Principal component analysis                 |
| PF <sub>6</sub>  | 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.     |
| $\sigma$  | peak width at half height                |