Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Gaetan M. A. Girard

July 2016

A thesis submitted to the Faculty of Science, Engineering and Built Environment, Deakin University, for the degree of Doctor of Philosophy.
I am the author of the thesis entitled

“Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries”

submitted for the degree of Doctor of Philosophy

This thesis may be made available for consultation, loan and limited copying in accordance with the Copyright Act 1968.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: GAETAN GIRARD

Signed: [Signature Redacted by Library]

Date: 1/11/2016
I certify the following about the thesis entitled (10 word maximum)

“Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries”

submitted for the degree of Doctor of Philosophy

a. I am the creator of all or part of the whole work(s) (including content and layout) and that where reference is made to the work of others, due acknowledgment is given.

b. The work(s) are not in any way a violation or infringement of any copyright, trademark, patent, or other rights whatsoever of any person.

c. That if the work(s) have been commissioned, sponsored or supported by any organisation, I have fulfilled all of the obligations required by such contract or agreement.

I also certify that any material in the thesis which has been accepted for a degree or diploma by any university or institution is identified in the text.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: GAETAN GIRARD

Signed:

Date: 24/6/2016
Acknowledgments

First of all, I would like to express my best regards to my principal supervisor, Associate Professor Patrick Howlett for giving me the opportunity to complete my PhD at Deakin University. AsProf. Howlett has been very helpful thanks to his unquestionable expertise in lithium battery science and ionic liquids. I have learnt so much from his inputs based on his knowledge and experience on data analysis and interpretation. His enthusiasm and encouragement have inspired me over three years of research. He also demonstrated great support in the decisions I was making related to this project. Thank you for being such a great supervisor!

Secondly, I would like to thank my co-supervisors, Prof. Maria Forsyth at Deakin University and Prof. Douglas R. MacFarlane at Monash University. A great thanks for providing such a positive team environment, their invaluable advices and their support. Prof. Maria Forsyth was very generous to offer me an internship placement within her research group in 2012 from which the decision of doing a PhD in the same research group originated.

Thirdly, I would like to thank our collaborators from Cytec Solvay Group, Dr. Serguei Zavorine, Dr. Donato Nucciarone and Dr. Michael Moser. Thank you for meeting us twice in Australia and for providing us with an excellent range of novel ionic liquids. They have also been very supportive during our monthly videoconferences despite the time difference.

The next person I would like to acknowledge is Dr. Matthias Hilder. He has been a friend, a mentor, a teacher. Whenever I needed help and support, Matthias was always available. Thank you for all our constructive discussions, these café Latté and chocolates. Matthias gave me valuable advice and help throughout my PhD, I learnt a lot from his expertise in chemistry and spectroscopy. On my first day of candidature he advised me “Get a Gmail account and you will get your PhD”. I did sign up for a Gmail account on the same day. Once again, a big thank you to the Australian team in this project!
Thank you to our collaborators from CNRS-IMN Nantes in France in particular Prof. Dominique Guyomard and Prof. Jean Le Bideau who I visited two times during my PhD. I would like to thank Dr. Nicolas Dupré for his expertise and help with the MAS NMR experiments.

I also want to thank the team members of the soft x-ray spectroscopy trial at the Australian Synchrotron: Dr. Anthony Somers, Dr. Robert Kerr, Dr. Xiaoen Wang from Deakin University and Dr. Bruce Cowie from the Australian Synchrotron.

Special thanks to Dr. Haijin Zhu who assisted with the NMR diffusion experiments in Geelong, Vincent Stafrace from ProDigitek Pty Ltd for his help with BioLogic instruments, Dr. Paul Bayley who initiated the NMR experiments in the UK and helped me with his experience and knowledge.

I would also like to thank Dr. Damien Callahan and A / Prof. Kieran Lim at Deakin University. Thank you for giving me the opportunity to become a laboratory demonstrator and a tutor in chemistry.

Thank you to all the members of the Electromaterials group at IFM Deakin University. Especially thank you to Dr. Cristina Pozo-Gonzalo, Dr. Jenny Yan, Dr. Timothy Khoo, Dr. Peipei Huang, Danah Tawfiq Hasan Al-Masri.

I cannot say how much I would like to thank my close friends Asimo and Tania for your motivation and support throughout the PhD.

Of course an immense thank you to my family overseas for the great support and memories! Especially to my parents who have always been present. Thank you to my sisters, Tiphaine and Florine for all the laughs!

Finally and most importantly thank you to my partner, Fabrizio Casauria, for his invaluable support and for believing in me.
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Publications

2016


2015


Abstract

Very few studies report properties of phosphonium alkyl bis(fluorosulfonyl)imide (FSI) ionic liquids that are superior than their ammonium analogues. Thus the focus of this study is to evaluate their properties as a potential electrolyte for lithium (Li) battery applications in terms of physicochemical and electrochemical properties, cycling performance at a lithium metal electrode and solid electrolyte interphase (SEI) formation, lithium metal surface characterisation and full battery device performance. Room Temperature Ionic Liquids (RTILs), salts that are liquid at room temperature, are a new class of materials having very promising properties for electrolyte applications including electrochemical stability, high ionic conductivity and non-flammability. With these characteristics, RTILs were proposed to replace the hazardous and flammable organic solvents used in commercial electrochemical devices. There are a few small phosphonium RTILs available on a large scale. These have recently been reported to have promising transport and electrochemical properties. Herein the focus is on trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide ([P111i4][FSI]). This small alkyl phosphonium FSI IL combines a low viscosity and higher conductivity, which is superior to other well-studied RTILs, e.g. ammonium ILs in particular, which make them very promising candidates for lithium battery applications.

First the physicochemical and electrochemical properties of the P111i4FSI:LiFSI electrolytes were determined for a wide range of compositions with the saturation concentration being 3.8 moles of LiFSI per kg of IL (i.e. molar ratio LiFSI/P111i4FSI = 1.2:1) referred to as the highly concentrated IL electrolyte. Techniques employed included differential scanning calorimetry (DSC), electrochemical impedance spectroscopy (EIS), nuclear magnetic resonance (NMR) and cyclic voltammetry (CV). This phosphonium IL was characterised by its high fluidity, high ionic conductivity (41 ± 10 mPa.s and 7.3 ± 0.1 mS.cm⁻¹ at 25 °C) and wide electrochemical window (6 V vs. Ag/AgOTf). The Li⁺ cation diffusivity was found to exceed that of other ionic species in the electrolyte at ambient temperature.
At concentrations above 2.0 mol.kg\(^{-1}\) the glass transition temperature is very low (\(i.e.\) \(– 81.7 \pm 0.2 \, ^\circ C\) for the solution of 2.0 mol.kg\(^{-1}\) of salt in IL), suggesting that the electrolyte can be used over a wide temperature range, even including low temperatures.

The performance of the IL electrolytes at the Li metal electrode was also studied. Li metal batteries are exceeding Li ion in terms of capacity. Li metal electrodes were also of particular interest because of their high theoretical capacity, 3860 Ah.kg\(^{-1}\). The focus of the project was on the Li surface characteristics since during cycling a SEI layer is formed which dictates cycling performance. The SEI formation at the Li electrode was studied using Li \(|\) Li symmetric cells using galvanostatic cycling, impedance spectroscopy and scanning electron microscopy imaging during various stages of cycling. Unlike commercial organic carbonate-based electrolytes, the highly concentrated IL electrolyte shows outstanding lithium cyclability at 25 and 50 °C suggesting the electrolyte is electrochemically compatible with Li metal and also supports Li\(^+\) ion transport. The cells showed excellent cycling efficiency (> 99.3 %) even at remarkably high current rates (\(i.e.\) 6 mAh.cm\(^{-2}\)) over a large number of cycles (500). Interestingly Li metal is significantly more stable in the IL electrolyte with the highest lithium salt by creation of a uniform nanostructured deposit at the Li electrode. This is rather counterintuitive considering the high viscosity and low conductivity at such concentration and offers a new approach to electrolyte design.

It is known that the SEI chemically formed at the Li metal electrode plays a critical role in the cycling performance of Li. The surface of the SEI after reaction with the electrolytes upon cycling was studied using spectroscopic techniques including magic angle spinning NMR (MAS-NMR), attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and soft x-ray photoelectron spectroscopy (XPS). During cycling, the anion is electrochemically reduced and the resulting breakdown products react with the lithium metal surface forming a SEI layer consisting of the following chemical species: LiF, LiOH, Li\(_2\)S, Li\(_2\)CO\(_3\) with traces of entrapped RTIL being present. Similarities in chemical composition were observed between the SEI formed in both dilute (solution of 0.5 mol.kg\(^{-1}\) of salt in IL) and highly concentrated IL electrolytes during cycling.
However the main differences were found to be the formation of a thicker SEI with larger amounts of reduced species from the anion in the case of the high Li salt concentration supporting the above statement regarding superior performance of these samples.

Finally, a full battery was made and its performance studied. The full cell consisted of a lithium metal anode, a high voltage cathode (NMC: LiNiMnCoO₂) and the P\textsubscript{111}i₄FSI:LiFSI electrolyte. High charge and discharge capacities as well as reasonable rate capability (up to 4 C) are achieved in the highly concentrated IL electrolyte. The cells also show a good capacity retention (> 90 %), maintaining a minimal discharge capacity of 130 mAh.g⁻¹ over 200 cycles which is close to commercial electrolytes using NMC cathodes. This performance was correlated with electrolyte’s transference number (increased with increasing salt concentration) and transport properties.

All these findings suggest that P\textsubscript{111}i₄FSI electrolytes with high LiFSI salt concentration are superior to commercial organic solvent electrolytes in terms of safety and performance.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgOTf</td>
<td>silver trifluoromethanesulfonate</td>
</tr>
<tr>
<td>BEPy</td>
<td>N-n-butyl-N-ethylpyrrolidinium</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;mim</td>
<td>N-ethyl-N-methylimidazolium</td>
</tr>
<tr>
<td>C&lt;sub&gt;4&lt;/sub&gt;mim</td>
<td>N-butyl-N-methylimidazolium</td>
</tr>
<tr>
<td>C&lt;sub&gt;4&lt;/sub&gt;mipp</td>
<td>N-propyl-N-methylpiperidinium</td>
</tr>
<tr>
<td>C&lt;sub&gt;4&lt;/sub&gt;mipp</td>
<td>N-butyl-N-methylpiperidinium</td>
</tr>
<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;mpyr</td>
<td>N, N-dimethylpyrrolidinium</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;mpyr</td>
<td>N-ethyl-N-methylpyrrolidinium</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;mpyr</td>
<td>N-propyl-N-methylpyrrolidinium</td>
</tr>
<tr>
<td>C&lt;sub&gt;4&lt;/sub&gt;mpyr</td>
<td>N-butyl-N-methylpyrrolidinium</td>
</tr>
<tr>
<td>DEC</td>
<td>diethyl carbonate</td>
</tr>
<tr>
<td>DMC</td>
<td>dimethyl carbonate</td>
</tr>
<tr>
<td>DEME</td>
<td>N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium</td>
</tr>
<tr>
<td>EC</td>
<td>ethylene carbonate</td>
</tr>
<tr>
<td>EMC</td>
<td>ethyl methyl carbonate</td>
</tr>
<tr>
<td>EMI</td>
<td>1-ethyl-3-methylimidazolium</td>
</tr>
<tr>
<td>FSI</td>
<td>bis(fluorosulfonfyl)imide</td>
</tr>
<tr>
<td>GC</td>
<td>glassy carbon</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>P&lt;sub&gt;111i4&lt;/sub&gt;</td>
<td>trimethyl(isobutyl)phosphonium</td>
</tr>
<tr>
<td>P&lt;sub&gt;1113&lt;/sub&gt;</td>
<td>trimethyl(propyl)phosphonium</td>
</tr>
<tr>
<td>P&lt;sub&gt;333i&lt;/sub&gt;</td>
<td>tripropyl(methyl)phosphonium</td>
</tr>
</tbody>
</table>
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

- $P_{3321}$ ethyl methyl dipropyl phosphonium
- $P_{3221}$ diethyl methyl propyl phosphonium
- $P_{2221}$ triethyl(methyl)phosphonium
- $P_{2225}$ triethyl(pentyl)phosphonium
- $P_{111(1O1)}$ trimethyl(1-methoxymethyl)phosphonium
- $P_{222(2O1)}$ triethyl(2-methoxyethyl)phosphonium
- $P_{222(CH2)3CN}$ triethyl cyanopropyl phosphonium
- $P_{4441}$ tributyl(methyl)phosphonium
- $P_{4444}$ tetrabutylphosphonium
- $P_{cytop17026}$ 3,7-dimethyloctane, ethyl, hexyl phosphonium

TFSI or NTf$_2$ bis(trifluoromethanesulfonyl)imide

TMS tetramethylsulfone

VC vinylene carbonate
Table of contents

Acknowledgments ........................................................................................................I
Publications ................................................................................................................III
Abstract .....................................................................................................................IV
Abbreviations ........................................................................................................... VII
Table of contents ........................................................................................................IX

Chapter 1 Introduction .......................................................................................... 1
  1.1 Setting the scene ............................................................................................ 2
  1.2 Batteries ........................................................................................................ 3
    1.2.1 General principle .................................................................................... 3
    1.2.2 Performance indicators ......................................................................... 6
    1.2.3 Lithium batteries .................................................................................... 8
  1.3 Electrolytes .................................................................................................... 9
    1.3.1 Ionic liquids: general properties ........................................................... 11
    1.3.2 Ionic liquids as electrolytes for lithium batteries ................................. 15
  1.4 Literature review ........................................................................................... 17
    1.4.1 Initial research on the use of RTILs in lithium metal batteries ............ 17
    1.4.2 Quaternary ammonium cations ............................................................ 20
    1.4.3 Phosphonium ILs and Li batteries ........................................................ 25
    1.4.4 FSI versus TFSI based ILs ................................................................. 28
    1.4.5 Battery performance of ILs ................................................................. 29
    1.4.6 SEI formation in ILs ............................................................................. 32
      1.4.6.1 SEI formation and stability in ILs .................................................... 33
      1.4.6.2 Surface characterisation of the anode in an IL electrolyte .......... 34
    1.4.7 Lithium metal cycling and surface morphology .................................. 38
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Chapter 1
1.4.8 Lithium transport ................................................................. 43
1.4.9 Literature review conclusion .................................................. 44
1.5 Aim of this research .................................................................. 45
1.6 References .................................................................................. 47

Chapter 2
2.1 Materials and preparation procedures ......................................... 59
  2.1.1 Electrolytes ............................................................................. 59
    2.1.1.1 Room Temperature Ionic Liquids (RTILs) ............................. 59
    2.1.1.2 Other electrolyte materials ................................................. 61
    2.1.1.3 Preparation of IL-based electrolytes ................................... 61
    2.1.1.4 Standard organic carbonate electrolyte ............................... 63
  2.1.2 Inert atmosphere glovebox (Argon) ....................................... 63
  2.1.3 Fabrication of high voltage cathodes for Li batteries .............. 64
  2.1.4 Li symmetrical coin cells (CR2032 type) ................................. 65
2.2 Electrolyte characterisation .......................................................... 68
  2.2.1 Water content ....................................................................... 68
  2.2.2 Differential Scanning Calorimetry (DSC) ................................. 68
  2.2.3 Density/Dynamic viscosity ..................................................... 68
  2.2.4 Ionic conductivity (Electrochemical Impedance Spectroscopy)...... 69
  2.2.5 Nuclear Magnetic Resonance (NMR) – Diffusion measurements...... 70
  2.2.6 Cyclic voltammetry ............................................................... 72
  2.2.7 Chronoamperometry (CA) ....................................................... 75
2.3 Surface characterisation: spectroscopic techniques ...................... 76
  2.3.1 Electrochemical impedance spectroscopy (EIS) ....................... 76
  2.3.2 Scanning electron microscopy (SEM) ....................................... 82
  2.3.3 Attenuated total reflection – Fourier transform infrared spectroscopy (ATR-FTIR) ............................................................... 84
2.3.4 Synchrotron X-ray photoelectron spectroscopy (SXR XPS) ..............85
2.3.5 Magic angle spinning NMR (MAS NMR) ...........................................89
2.4 References ................................................................................................91

Chapter 3 Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content ...........................................93
3.1 Introduction .............................................................................................94
3.2 Results .......................................................................................................95
3.2.1 Selection of a promising ionic liquid ...................................................95
3.2.2 Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content .........................97
3.2.3 FTIR studies of P_{1114}FSI electrolytes .............................................114
3.3 Conclusions ..............................................................................................117
3.4 References ................................................................................................118

Chapter 4 Rate and cycling performance of lithium metal electrodes in trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide ionic liquid ..................124
4.1 Introduction ..............................................................................................125
4.2 Experimental methods .............................................................................126
4.3 Results ........................................................................................................126
4.3.1 Li metal plating / stripping cycling stability and rate capability of P_{1114}FSI IL electrolytes .....................................................................................126
4.3.1.1 Lithium salt concentration dependence of the cycling performance 126
4.3.1.2 Conventional amount of charge applied (4.0 \times 10^{-2} \text{ mg.cm}^{-2}, \text{ e.g. } 0.16 \text{ mAh.cm}^{-2}) – rate capability study .........................................................130
4.3.2 Cycling performance of Li symmetric cells at 25 °C: ‘0.5C’ 3 mAh.cm^{-2} 133
4.3.3 In-situ EIS characterisation of Li metal electrodes ............................136
4.3.4 Cycling performance of Li symmetric cells at 50 °C: ‘0.5C’ - 3 mAh.cm^{-2} 139

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries XI
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
5.4.2 A proposed mechanism of SEI formation at the lithium metal electrode

5.3 Conclusions

5.4 References

Chapter 6 Lithium cell studies using high voltage NMC cathodes

6.1 Introduction

6.2 Experimental methods

6.2.1 Lithium transference numbers

6.2.2 Lithium battery tests

6.2.3 Immersion tests

6.2.4 SEM

6.2.5 ATR-FTIR

6.3 Results and Discussion

6.3.1 Lithium transference numbers

6.3.2 Rate capability of Li battery cells

6.3.3 Longer term cycling behaviour of Li battery cells at 25 °C

6.3.4 Li battery cells performance at elevated temperature (50 °C)

6.4 Conclusions

6.5 References

Chapter 7 Summary and Future Work

7.1 Summary

7.2 What are the main challenges for the use of ionic liquid electrolytes in lithium batteries

7.3 Suggestions for future work

7.4 References
Chapter 1

Introduction
1.1 Setting the scene

For centuries our society has relied on fossil fuels as a source of energy, the combustion reaction being a technological revolution but also resulting in emissions of carbon dioxide which have been shown to drive global climate change.\(^1\)\(^-\)\(^2\) In addition to these negative aspects, the limited availability of fossil fuels will be an increasing challenge in the near future. Batteries are electrochemical devices that can store energy.\(^1\) They convert chemical energy into electrical energy. There are many different battery technologies available\(^1\)\(^-\)\(^2\). Some have drawbacks regarding their performance\(^2\) (e.g. low potential), safety\(^2\) (e.g. flammability) or toxicity\(^2\) (e.g. cadmium). On the other hand, batteries can be environmentally friendly\(^2\) and also act as an energy storage device for other sustainable energy systems (e.g. some alternative energies such as wind or solar require an energy storage unit to overcome challenges with non-continuous energy production).

Lithium batteries\(^2\)\(^-\)\(^5\) are very promising systems due to their light weight, high energy density and power density. Those features make them very attractive for large-scale applications such as electric vehicles (EV).\(^6\)\(^-\)\(^7\) Some main challenges include \(i\) the replacement of flammable solvent-based electrolyte\(^5\) (the highly reactive lithium is not compatible with aqueous electrolytes and thus requires organic solvents that are flammable and can contribute to explosions; Figure 1), \(ii\) the enhancement of energy density\(^4\) (the amount of energy stored e.g. the distance a EV can run), \(iii\) the enhancement of power density\(^4\) (e.g. the delivery rate e.g. how fast the EV can go) and \(iv\) the cost.\(^2\)

![Figure 1 Damaged Li battery from a Boeing 787 Dreamliner in January 2013 (right, http://www.nytimes.com/2014/12/02 retrieved in May 2015)](image)

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
An appealing and very promising research approach that is attracting substantial interest, judging by the increasing number of publications, involves the replacement of hazardous organic solvent electrolytes with non-volatile, non-flammable, conductive, electrochemically and thermally stable fluids, known as “ionic liquids” (ILs). However, one principal issue concerning the use of ILs in such systems is their compatibility with the cell electrodes and their ion transport properties. This project investigates the properties of a range of new phosphonium-based ILs which have received significantly less attention as potential electrolytes for lithium-ion batteries. The project aims for better understanding of the mechanism of lithium ion transport and charge transfer at the negative electrode in these batteries.

1.2 Batteries

1.2.1 General principle

Batteries and capacitors are two leading energy storage technologies nowadays. They are both based on electrochemistry. The fundamental difference is that in batteries the charge is stored in the bulk of the electrode material (slower delivery but large amount of energy stored) while in capacitors the charge is stored on the electrode surface (fast delivery but small amount of energy stored). Batteries can be classified into two distinct types: primary (disposable) or secondary (rechargeable) batteries. In this project the focus is on secondary lithium batteries, with their unique chemistry (as shown in Figure 2) allowing them to be electrically reversible.

A battery is a device that converts chemical energy, stored within the electrode materials, into useable electrical energy. This energy conversion is achieved by an electrochemical reduction-oxidation (redox) reaction between the active electrode materials. There are three main components: two electrochemically active electrodes (electrically connected) and an ion conductive electrolyte.
The anode is the negative electrode which is being oxidised during discharge, e.g. release of electrons providing flow of electric current. Lithium batteries are particularly attractive since lithium has one of the most negative electrode potentials (-3.05 V vs. SHE) plus it is very light thus combining a high energy and power density, all important for the device performance. Here the anode is based on lithium either in neat metallic form (lithium metal batteries) or being intercalated into graphite (Figure 3) as LiC₆ (lithium ion batteries). The reaction of lithium being oxidised to lithium cations is the following:

- in a lithium metal battery: \( \text{Li}(s) \leftrightarrow \text{Li}^+(\text{so}) + e^- \) (1)
- in a lithium-ion battery: \( \text{LiC}_6(s) \leftrightarrow \text{graphite} \,(6\text{C})_s + \text{Li}^+(\text{so}) + e^- \) (2)

The cathode is the positive electrode that is being reduced during discharge, e.g. uptake of electrons, previously released by the anode. In lithium batteries it usually consists of crystalline transition metal oxides with layered structures (e.g. LiₓMₓOₓ with M = transition metal) including layered oxides with α-NaFeO₂ structures (e.g. LiCoO₂, Figure 3), spinel structures (e.g. LiMn₂O₄) and polyanionic compounds with olivine structures (e.g. LiFePO₄). The insertion of lithium cations into the cathode materials lowers the oxidation state of the transition metal thus reducing it.

\[
\text{Li}_{1-x}M_xO_{0.5}(s) + x\text{Li}^+(\text{so}) + xe^- \leftrightarrow \text{Li}_xM_xO_{0.5}(s) + e^- (3)
\]

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
The electrolyte contains mobile ions and is an ion-conductive medium that allows the internal transfer of ionic charge between the anode and cathode. Its primary role is to balance and separate the charge between the anode and the cathode. During the discharge, the anode is oxidised (positive charge around the anode) and the cathode is reduced (negative charge). The redox potentials of low-potential anodes such as Li or Na exceed the electrochemical stability limit of water, thus making these anodes incompatible with aqueous electrolytes.

Alternatives are non-aqueous organic molecular solvent electrolytes. These are solutions of organic carbonate based solvents with lithium conducting salts (lithium hexafluorophosphate, LiPF₆) to enable ionic transport in a high permittivity, low viscosity organic carbonate mixture (e.g. ethylene carbonate EC and diethylene carbonate DEC). Another class is solid state electrolytes based on ion conductive ceramics and gel polymer electrolytes.

As mentioned above, ionic liquids are a promising new class of electrolytes currently under investigation. Table 1 summarises the different classes of electrolytes.
Table 1 Advantages and disadvantages of conventional and new generation electrolytes in lithium-ion batteries

<table>
<thead>
<tr>
<th></th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid electrolyte</td>
<td>High conductivity</td>
<td>High vapor pressure</td>
</tr>
<tr>
<td>(organic solvent)</td>
<td>Low viscosity</td>
<td>Low flash point</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Limitation at low temperatures (&lt; -10 °C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Flammable</td>
</tr>
<tr>
<td>Solid state</td>
<td>Non flammable</td>
<td>Slow kinetics</td>
</tr>
<tr>
<td>electrolyte</td>
<td>No thermal runaway</td>
<td>Low ionic conductivity</td>
</tr>
<tr>
<td></td>
<td>High energy density</td>
<td>High interfacial resistance</td>
</tr>
<tr>
<td>Ionic liquids</td>
<td>Non-volatile</td>
<td>Still relatively low conductivity and high viscosity</td>
</tr>
<tr>
<td></td>
<td>Non-flammable (high temperature applications)</td>
<td>High cost (anion)</td>
</tr>
<tr>
<td></td>
<td>Low melting point</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wide electrochemical window</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(high voltage application)</td>
<td></td>
</tr>
</tbody>
</table>

1.2.2 Performance indicators

What is the ideal battery? A battery is characterised by:

- high safety: non-toxic electrode materials, non-flammable electrolytes
- high energy density: the amount of energy stored per unit weight or volume, (depends on the density of the material and its electrochemistry, described by watt-hour per unit weight or volume); specific energy density is calculated as the product of specific capacity and averaged output voltage
- high power density: rate of delivery (described by watt per unit weight or volume)
- long cycle life with high faradaic efficiency (ratio of charge introduced vs charge delivered)
- high cell potential (energy difference between the two electrode materials)
- high charging/discharging delivery rates (determined by conductivity and electrode reaction kinetics)
- wide operating temperature range: mainly limited by the reactivity of the electrolytes at charged electrode surfaces
- low cost
- environmentally friendly / recyclable

Figure 4, recently published by Nexergy (http://www.iccnexergy.com/battery-systems/battery-energy-density-comparison retrieved in November 2013), illustrates the energy density and specific energy of lead acid, nickel-cadmium (NiCd), nickel-metal-hydride (NiMH) and Li batteries. Because of highest energy density and specific energy it is of great importance that research focuses on improving lithium batteries.

Figure 4 Energy density and specific energy of rechargeable batteries, sourced from Nexergy 2013 (http://www.iccnexergy.com/battery-systems/battery-energy-density-comparison retrieved in November 2013)
1.2.3 Lithium batteries

Lithium rechargeable batteries are the most popular electrochemical storage devices due to their excellent properties: they have high energy densities, can sustain high discharge rates and have long cycle life.\textsuperscript{17-18} For many years now they have been used in smartphones and laptops. More recently they are being considered by the automotive industry for electric vehicle (EV) and hybrid electric vehicle (HEV) applications.\textsuperscript{7} Their technology still has to be optimised for a widespread use in electric vehicles, and the research in this field is still growing.\textsuperscript{1, 18-19}

The conventional technology established in most commercial lithium ion batteries consists of a graphite anode (theoretical capacity 372 mAh.g\textsuperscript{-1}), a liquid electrolyte (lithium salt dissolved into organic carbonate solvents) and a lithium cobalt oxide (LiCoO\textsubscript{2}) cathode.\textsuperscript{18} This technology usually offers a coulombic capacity of 400 Wh.L\textsuperscript{-1} minimum, an operating voltage window from 4.2 V to 3.0 V, a discharge capacity maintained above 90 % available at a 1 hour discharge current rate (1 C).\textsuperscript{18, 20}

For electric vehicle applications, the need for safe batteries delivering a higher capacity with higher C-rate and cycle-ability is critical. Lithium metal (highest theoretical capacity 3860 mAh.g\textsuperscript{-1}) is therefore an ideal candidate anode material. The capacity of a conventional battery used in smartphones or laptops ranges from 1 to 4 Ah, whereas the capacity of a single cell for an EV or HEV has to be in the range of 7 – 10 Ah.\textsuperscript{7} There have been serious safety concerns raised with such high capacities: a large amount of charge being discharged in a very short time can possibly result in internal short circuit, fire or explosion.\textsuperscript{21} These factors are driving researchers to investigate novel battery systems based on the lithium technology for high energy density: lithium-air and lithium-sulphur batteries are two examples.\textsuperscript{18}

Table 2 illustrates a summary of advantages and challenges for these two systems.
Table 2 A comparison between lithium-air and lithium-sulfur batteries

<table>
<thead>
<tr>
<th></th>
<th>Lithium-air\textsuperscript{18, 22}</th>
<th>Lithium-sulfur\textsuperscript{23-25}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Redox reaction</strong></td>
<td>$2\text{Li}_3 + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$</td>
<td>$2\text{Li}_3 + \text{S} \leftrightarrow \text{Li}_2\text{S}$</td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td>Li metal</td>
<td>Li metal</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td>Porous carbon material</td>
<td>Sulfur-carbon composite</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>Non-aqueous / aqueous</td>
<td>Non-aqueous liquid electrolyte</td>
</tr>
<tr>
<td><strong>Advantages</strong></td>
<td>High capacity energy storage: high theoretical energy density (11 250 Wh.kg\textsuperscript{-1} Li)</td>
<td>Large scale energy storage applications: Low cost, natural abundance of elemental sulfur High theoretical energy density (2500 Wh.kg\textsuperscript{-1}) Beneficial use of RTILs</td>
</tr>
<tr>
<td><strong>Challenges</strong></td>
<td>Challenges of using lithium metal previously mentioned (formation of Li dendrites, low plating / stripping efficiency) Stability of components to both O\textsubscript{2} and its reduction products (LiOH, H\textsubscript{2}O\textsubscript{2}) Fast diffusion of O\textsubscript{2}</td>
<td>Challenges of using lithium metal previously mentioned: limited cycling performance (poor capacity retention) High self-discharge rate Dissolution of long-chain lithium polysulfides into electrolyte</td>
</tr>
</tbody>
</table>

1.3 Electrolytes

In the research community a common approach to improve the safety of lithium battery technologies has been to develop safer electrolytes.\textsuperscript{4, 11, 18} A battery with high voltage and high performance electrode materials cannot operate if the electrode materials are not compatible with the electrolyte. The most important properties for an electrolyte are: a wide electrochemical window, high ionic conductivity and thermal and electrochemical stability. In most cases of lithium rechargeable battery failure, a thermal runaway is associated with an electrode process. With transition metal oxides it is usually a structural decomposition which goes into thermal runaway and the electrolyte becomes a “fuel reservoir” to this process.\textsuperscript{1, 6, 18}
In 2010 Goodenough et al. reported the electrolyte properties considered as the most critical for battery operation: large voltage window, low volatility and non-flammability. In the case of all lithium battery technologies with liquid electrolytes, non-aqueous organic carbonate solvents have been mainly used as the electrolyte component due to their good electrochemical and transport properties (high ionic conductivity, large operating voltage window). Table 3 presents the chemical structures and relevant physical properties of the most commonly used organic carbonate solvents. The main issues when using these organic carbonate solvents are their volatility and flammability (low flash points). In summary, there are main three causes of battery failure:

- An internal short between the two electrodes: this can be caused by lithium dendrite growth penetrating through the separator, presence of impurities, electrical short circuit (leading to ignition) or mechanical damage.
- A significant heating of the battery.
- A decomposition of the battery components: the electrode (in general the cathode) at high voltages (> 4.6 V vs. Li | Li⁺) due to structural changes during delithiation; the electrolyte with a narrow electrochemical window

Table 3 Physical properties of alkyl carbonates traditionally used as electrolytes including their melting point (M.P), boiling point (B.P) and flashing point (F.P). The data were collected from Merck™ and Sigma Aldrich™ websites.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>M.P (°C)</th>
<th>B.P (°C)</th>
<th>F.P (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Carbonate</td>
<td><img src="image" alt="EC Structure" /></td>
<td>36</td>
<td>348</td>
<td>150</td>
</tr>
<tr>
<td>(EC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene Carbonate</td>
<td><img src="image" alt="PC Structure" /></td>
<td>-49</td>
<td>243</td>
<td>123</td>
</tr>
<tr>
<td>(PC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>M.P (°C)</th>
<th>B.P (°C)</th>
<th>F.P (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl Carbonate (DMC)</td>
<td><img src="#" alt="Structure" /></td>
<td>0.4 - 5</td>
<td>90</td>
<td>14</td>
</tr>
<tr>
<td>Diethyl Carbonate (DEC)</td>
<td><img src="#" alt="Structure" /></td>
<td>- 43</td>
<td>126</td>
<td>31</td>
</tr>
<tr>
<td>Vinylene Carbonate (VC)</td>
<td><img src="#" alt="Structure" /></td>
<td>19 - 22</td>
<td>162</td>
<td>73</td>
</tr>
</tbody>
</table>

These phenomena lead to a decomposition of the organic carbonate solvents and result in thermal runaway. Due to these issues, the investigation of alternatives and safer electrolytes has become critical for the development of advanced energy storage devices based on the lithium chemistry. Therefore the aim of this research is to investigate a new class of materials, ionic liquids, as electrolytes for lithium rechargeable batteries. The interest in these materials is related to their wide safety operating range and similar, if not improved, performance when compared to the conventional organic carbonate electrolytes.

1.3.1 Ionic liquids: general properties

Ionic liquid (IL) is the accepted term for low-melting salts, typically melting below 100 °C and ideally below room temperature, resulting from weak electrostatic interactions of the mainly organic ions (in contrast to high melting inorganic salts with strong electrostatic interactions). If molten at room temperature, they are typically referred to as room temperature ionic liquids (RTILs). They are also called “Molten Salts” or “Liquid salts”. The first RTIL was discovered by Walden in 1914 and chloroaluminate-based salts were synthesised by Hurley and Wier in 1951. The research on ILs only took off in 1992 when Wilkes and Zaworotko reported air and water stable imidazolium-based ILs.
ILs, usually composed of an organic cation (large, asymmetric) and an inorganic/organic anion (flexible, small, with a delocalised charge) represent a new class of room temperature fluids with very interesting properties for electrolyte applications as shown in Figure 5. An important property of RTILs is that the charge on both cation and anion is spread across the molecule. Another significant property is that when the cation is small and asymmetric the lattice energy of the salt is smaller, explaining weak intermolecular forces within the salt and lowering melting points.

RTILs are attractive for a wide range of applications including electrochemical devices due to their unique physicochemical properties. In particular, ILs were proposed as electrolyte components for lithium batteries, super or ultra capacitors, fuel cells, photoelectrochemical cells, ionogels and also as lubricants and corrosion inhibitors.

The following Table 4 lists various types of anion and cation that comprise the most commonly studied RTILs (data were collected from Cytec Canada Inc. and from the Merck™ website), including their chemical structure and melting points (M.P.).
Table 4 Anions and cations in RTILs, data collected from Cytec Canada Inc. and from the Merck™ website.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Example of IL</th>
<th>Example of anion structure</th>
<th>M.P (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyanoborate</td>
<td>$I$-ethyl-3-methylimidazolium tetracyanoborate</td>
<td><img src="image" alt="CN_B_CN_NC_B_CN" /></td>
<td>13</td>
</tr>
<tr>
<td>Fluoroborate</td>
<td>triethyl(2-(2-methoxyethoxy)ethylphosphonium tetrafluoroborate</td>
<td><img src="image" alt="F_B_F_F" /></td>
<td>-50</td>
</tr>
<tr>
<td>Halides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>trihexyl(tetradecyl)phosphonium chloride</td>
<td><img src="image" alt="Cl^-" /></td>
<td>-5</td>
</tr>
<tr>
<td>Dicyanamides</td>
<td>triethyl(butyl)phosphonium dicyanamide</td>
<td><img src="image" alt="N==N==N" /></td>
<td>5</td>
</tr>
<tr>
<td>Imides (or Amides)</td>
<td>bis(fluorosulfonyl)imide</td>
<td><img src="image" alt="S_N_(O_F_F)" /></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide</td>
<td><img src="image" alt="S_N_(O_F_F)" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>bis(trifluoromethanesulfonyl)imide</td>
<td><img src="image" alt="S_N_(O_F_F)" /></td>
<td>21</td>
</tr>
<tr>
<td>Phosphates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorophosphates</td>
<td>$I$-butyl-3-methylimidazolium hexafluorophosphate</td>
<td><img src="image" alt="F_F_F" /></td>
<td>12</td>
</tr>
<tr>
<td>Alkylphosphates (DMP)</td>
<td>dimethyldiisobutyl phosphonium dimethylphosphate</td>
<td><img src="image" alt="O-P-O" /></td>
<td>&lt;25</td>
</tr>
<tr>
<td>Fluorohydrogenate</td>
<td>tri-$n$-butylmethylphosphonium fluorohydrogenate</td>
<td><img src="image" alt="F-H-F-H-F" /></td>
<td>-24</td>
</tr>
</tbody>
</table>
# Chapter 1

## Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

<table>
<thead>
<tr>
<th>Anion</th>
<th>Example of IL</th>
<th>Example of anion structure</th>
<th>M.P (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfates</td>
<td>Methylsulfate</td>
<td>tributyl(methyl) phosphonium methylsulfate</td>
<td>liquid</td>
</tr>
<tr>
<td></td>
<td>Triflate (trifluoromethanesulfonate)</td>
<td>triethyl(2-((2methoxyethoxy)ethyl) phosphonium triflate</td>
<td>-16</td>
</tr>
<tr>
<td>Tosylates</td>
<td>triisobutyl(methyl) phosphonium tosylate</td>
<td>low melting solid</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cation</th>
<th>Example of IL</th>
<th>Example of cation structure</th>
<th>M.P (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary phosphonium</td>
<td>trimethyl(isobutyl) phosphonium bis(fluorosulfonyl)imide</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>triethyl(methoxyethyl) phosphonium bis(fluorosulfonyl)imide</td>
<td>-18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>triethyl(cyanopropyl) phosphonium bis(fluorosulfonyl)imide</td>
<td>-8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>triethyl((1,3-dioxolane)ethyl) phosphonium bis(trifluoromethanesulfonfyl)imide</td>
<td>&lt;-15</td>
<td></td>
</tr>
</tbody>
</table>

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
1.3.2 Ionic liquids as electrolytes for lithium batteries

Before any further discussion it is important to mention that only a few ILS are suitable as electrolytes for lithium batteries. Figure 6 presents the chemical structure of the most common IL cations and anions studied: the pyrrolidinium cation and the bis(fluorosulfonyl)imide and bis(trifluoromethanesulfonyl)imide anions. The imidazolium cation has also been the object of numerous publications, in particular the 1-ethyl-3-methylimidazolium cation due to its low viscosity and low melting points with a wide range of anions. However this cation has a low cathodic stability for its practical use in lithium batteries: its cathodic limiting potential is more positive than the redox potential of lithium (ca. + 1.0 V vs. Li/Li⁺).
Quaternary ammonium RTILs tend to show high cathodic stability\textsuperscript{47-50} but can also show higher viscosity and lower conductivity than ILs based on the imidazolium cation.

As a general rule liquid electrolytes need to be ionically conductive. RTILs meet this requirement since they are made of mobile ions. They also have low melting points essential for efficient device operation (e.g. the conductivity/mobility/transport is much better in the liquid phase). Also ionic liquids are electrochemically stable. The anodic and cathodic stability is important since this is the region where Li electrochemistry takes place (e.g. cycling). During the discharge/charge processes of a Li-ion battery, Li\textsuperscript{+} ions migrate between the two electrodes through the electrolyte. In a new class of electrolyte, it is therefore important to study the migration of Li\textsuperscript{+} ions (charge carriers) into the electrolyte and the reactivity of Li\textsuperscript{+} ions with the electrodes to see whether they both are compatible. An IL-lithium salt mixture needs to meet the following requirements\textsuperscript{4,6} to find application as an electrolyte component in lithium batteries:

- high ionic conductivity ($\geq 10^{-3}$ S.cm\textsuperscript{-1}) even at sub-ambient temperature in order to assure sufficiently high Li\textsuperscript{+} transport properties through the electrolyte

- low viscosity for the same reasons when the lithium salt is added to the IL
Chapter 1

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

- wide electrochemical stability (4 – 5 V) in particular high reductive stability of the IL cation to allow reversible Li\(^+\) intercalation, even at high voltages, without any relevant decomposition/degradation
- hydrophobicity to minimise water incorporation into the battery
- compatibility with commercially available high voltage electrodes

1.4 Literature review

In this section, a review of relevant research conducted on RTIL-based electrolytes in lithium batteries is reported.

1.4.1 Initial research on the use of RTILs in lithium metal batteries

With a high theoretical capacity (3860 mAh.g\(^{-1}\)) lithium metal has by default been the anode for lithium metal batteries.\(^{18}\) This material possesses the highest volumetric and gravimetric theoretical capacities amongst all other anodes. However, major safety concerns related to the formation of lithium dendrites during battery operation inhibit the use of lithium metal with standard liquid electrolytes. Therefore, the use of room temperature ionic liquids (RTILs) as electrolyte components to establish safer lithium batteries could be an alternative approach for EV and large-scale applications. Table 5 presents a selection of initial research results on the use of RTILs in lithium metal batteries.

In 2001 Tatsuma et al.\(^{51}\) reported the suppression of lithium dendrite formation in an ethylene glycol dimethacrylate (EGD) based polymer gel electrolyte. In 2003 Howlett et al.\(^{58}\) reported lithium dendrite growth rate in a RTIL solution for the first time. The dendrite growth rate was revealed to be slower in the case of the RTIL solution than in that of an organic carbonate solution. The morphological changes of the Li surface cycled in each solution were acquired with an optical cell and the images revealed less dendrite formation in the case of the RTIL solution, as illustrated in Figure 7 and Figure 8.
More recently Bhatt et al.\textsuperscript{52} reported lithium dendrite formation in the mixture \( \text{C}_3\text{mpyrFSI} / \text{LiFSI} \), showing a pre-deposition effect on the lithium metal electrode. Several possible mechanisms of lithium dendrite formation have been proposed in the literature. Most of them proposed a crystal growth mechanism occurring during electrodeposition due to the function of current or gradient of driving forces and lithium salt concentration.\textsuperscript{53-54} Nevertheless the mechanism of dendrite growth suppression in ILs still remains unclear.

### Table 5 Initial results on the use of RTILs in lithium metal batteries

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Electrolyte</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992</td>
<td>Wilkes\textsuperscript{31}</td>
<td>\text{C}_2\text{mimCH}_3\text{CO}_2</td>
<td>First RTIL stable against moisture</td>
</tr>
<tr>
<td>1995</td>
<td>Koch\textsuperscript{55}</td>
<td>\text{C}_2\text{mimTFSI}, \text{C}_3\text{dmimTFSI}</td>
<td>Investigation of the SEI layer</td>
</tr>
<tr>
<td>1997</td>
<td>Fuller\textsuperscript{56}</td>
<td>\text{C}_2\text{mimBF}_4</td>
<td>Physicochemical properties of imidazolium cations</td>
</tr>
<tr>
<td>1999</td>
<td>MacFarlane\textsuperscript{57}</td>
<td>\text{C}_3\text{mpyrTFSI}</td>
<td>Ionic liquid plastic crystal mixed with lithium revealed high ionic conductivity (2 \times 10^{-4} \text{S.cm}^{-1} at 60 °C)</td>
</tr>
<tr>
<td>2003</td>
<td>Howlett\textsuperscript{58}</td>
<td>\text{C}_2\text{mimTFSI} with \text{LiTFSI} (\text{C}_2\text{mim} = \text{EMIM})</td>
<td>Characterisation of lithium metal surface: optical imaging of lithium dendrite growth; growth rate of dendrites slower in RTIL solution than in standard organic carbonate solution (1 M LiPF\textsubscript{6} in PC)</td>
</tr>
</tbody>
</table>
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Figure 7 Morphological changes (optical cell setup) during cycling of a Li | Li cell with 1 M LiPF₆ in PC electrolyte at 1 mA.cm⁻², from Howlett et al.⁵⁸

Figure 8 Morphological changes (optical cell setup) during cycling of a Li | Li cell with 20 mol% LiTFSI in EMIMTFSI electrolyte at 1 mA.cm⁻², from Howlett et al.⁵⁸
1.4.2 Quaternary ammonium cations

ILs formed by quaternary ammonium cations (N-alkyl-N-methyl-pyrrolidinium) with hydrophobic perfluoralkylsulfonylimide anions, e.g., bis(fluorosulfonyl)imide (FSI) and bis(trifluoromethanesulfonyl)imide (TFSI) have been widely investigated because of their attractive properties: sub-ambient melting temperature, high conductivity at room temperature, and good electrochemical stability. Since the literature is voluminous, Table 6 summarises selected results of quaternary ammonium RTILs used in lithium batteries, representing some of the key papers published in the last decade relevant to this research.

In 2004, Howlett et al. reported efficient Li deposition/dissolution on platinum (Pt) and nickel (Ni) electrodes at 50 °C in the IL formed of N-methyl-N-butylpyrrolidinium (C4mpyr+) and the TFSI anion. In 2008, Saint et al. observed improved Li mobility (e.g. fast charge discharge kinetics and rate capabilities) in N-methyl-N-propylpyrrolidinium (C3mpyr+) combined with the smaller FSI anion, suggesting that a smaller cation and anion can lead to improved Li transport.

Yoon et al. studied the stability of lithium in the IL C3mpyrFSI but for the first time at high Li salt concentration (up to a 1:1 molar ratio C3mpyr+: Li+) by using the same FSI anion for both IL and Li salt. The lithium bis(fluorosulfonyl)imide (LiFSI) salt was shown to readily dissolve at relatively high concentration in FSI-based ILs.
<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Electrolyte</th>
<th>Electrodes</th>
<th>Results</th>
</tr>
</thead>
</table>
| 2004 | Howlett      | C4mpyr TFSI with 0.5 mol.kg⁻¹ LiTFSI  | Li | Li | - Li⁺ reversible deposition/dissolution on a Pt electrode at 50 °C  
- Coulombic efficiency (CE) reaches almost 100 % for 350 cycles on Pt electrode and > 99.1 % for 464 cycles on Cu electrode (0.1 mA.cm⁻²) |
| 2006 | Matsumoto    | C3mpyr FSI (= PYR₁₃FSI)  
C3mpip FSI (= PP₁₃FSI)  
EMIFSI | Li | LiCo₂ | - Stable cycling over 50 cycles of C₃mpyr FSI/ LiTFSI in a Li | LiCo₂ cell at the 0.1 C rate.  
- Initial capacity: 140 mAh.g⁻¹  
- Introduction of smaller anion as a fast charging / discharging ionic liquid electrolyte. |
| 2007 | Fernicola    | C₂₄pyr TFSI = BEPy TFSI              | Li | LiFePO₄ | Good charge-discharge efficiency and capacity retention |
| 2008 | Saint        | C₃mpyr FSI / TFSI with 0.5 mol.kg⁻¹ LiTFSI | Li | LiMnO₂ | - Improved Li behaviour: smaller ammonium cation  
- 80 mAh.g⁻¹ for C₃mpyr TFSI  
- 120 mAh.g⁻¹ for C₃mpyr FSI at 5th cycle |
<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Electrolyte</th>
<th>Electrodes</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>Zhou</td>
<td>C₃mpyr FSI</td>
<td>-</td>
<td>Lower melting point for FSI based ILs than TFSI based ILs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₄mpyr FSI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td>Bhatt</td>
<td>C₃mpyr FSI with 0.2, 0.45 mol.kg⁻¹ LiFSI</td>
<td>Li</td>
<td>Li</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td>Best</td>
<td>C₃mpip FSI</td>
<td>Li</td>
<td>Li</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₃mpyr FSI</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂mim FSI</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₄mim FSI</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>P₆₆₆₁₄ FSI</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>with 0.2, 0.5 and 1.0 mol.kg⁻¹ of LiTFSI, LiBF₄ or LiPF₆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>Balducci</td>
<td>C₄mpyr TFSI 50% + (EC:DEC:DMC, 1:1.1, w/w) 50% with 0.3M LiTFSI</td>
<td>Li</td>
<td>silicon + graphite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>Kim</td>
<td>C₃mpyr TFSI</td>
<td>Li</td>
<td>LiFePO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Year</td>
<td>Author</td>
<td>Electrolyte</td>
<td>Electrodes</td>
<td>Results</td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
<td>-------------</td>
<td>------------</td>
<td>---------</td>
</tr>
<tr>
<td>2012</td>
<td>Matsui\textsuperscript{68}</td>
<td>EMIM FSI + LiTFSI</td>
<td>Li</td>
<td>NMC</td>
</tr>
<tr>
<td>2013</td>
<td>Wong\textsuperscript{69}</td>
<td>C\textsubscript{4}mpyr TFSI 0.5 mol.L(^{-1}) LiTFSI</td>
<td>Li</td>
<td>LiFePO(_4)</td>
</tr>
<tr>
<td>2013</td>
<td>Xiang\textsuperscript{70}</td>
<td>C\textsubscript{4}mpip (= PP(_{14})) TFSI (60 wt%) + TMS (40 wt%) + 0.5 mol.L(^{-1}) LiTFSI</td>
<td>Li</td>
<td>LiFePO(_4)</td>
</tr>
<tr>
<td>2013</td>
<td>Yoon\textsuperscript{62}</td>
<td>C\textsubscript{3}mpyr FSI</td>
<td>Li</td>
<td>LiCoO(_2)</td>
</tr>
<tr>
<td>2014</td>
<td>Evans\textsuperscript{71}</td>
<td>C\textsubscript{3}mpyr FSI + 1.2 mol.L(^{-1}) LiFSI C\textsubscript{3}mpyr FSI + 10 vol% (or 50 vol%) EC:EMC (1:2 wt.) + 1.2 mol.L(^{-1}) LiFSI</td>
<td>Li</td>
<td>NMC half cell</td>
</tr>
<tr>
<td>2015</td>
<td>Yoon\textsuperscript{72}</td>
<td>C\textsubscript{3}mpyr FSI</td>
<td>-</td>
<td>- Highly concentrated IL electrolyte shows promising transport properties (greater ionic dissociation, high relative Li(^+) ion mobility)</td>
</tr>
<tr>
<td>Year</td>
<td>Author</td>
<td>Electrolyte</td>
<td>Electrodes</td>
<td>Results</td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
<td>-------------</td>
<td>------------</td>
<td>---------</td>
</tr>
</tbody>
</table>
| 2015 | Chancelier | $\text{C}_4\text{mim} (= \text{C}_1\text{C}_4\text{Im}) \text{ TFSI}$  
$\text{C}_4\text{mpyr} \text{ TFSI}$  
$1 \text{ mol.L}^{-1} \text{ LiTFSI}$ | LTO | NMC | Initial capacity (0.05 C for 1st 5 cycles): 165 mAh.g$^{-1}$ for $\text{C}_1\text{C}_4\text{Im} \text{ TFSI}$, 83 mAh.g$^{-1}$ for $\text{C}_4\text{mpyr} \text{ TFSI}$  
Stable cycling over 100 cycles at 25 °C at the 0.1 C rate:  
discharge capacity < 120 mAh.g$^{-1}$ for $\text{C}_1\text{C}_4\text{Im} \text{ TFSI}$,  
discharge capacity < 50 mAh.g$^{-1}$ for $\text{C}_4\text{mpyr} \text{ TFSI}$  
Capacity fading for all electrolytes at 60 °C (sharp drop < 120 mAh.g$^{-1}$ for $\text{C}_1\text{C}_4\text{Im} \text{ TFSI}$ after 40 cycles)  
Superior performance with $[\text{EC}:\text{DEC}][\text{LiPF}_6]$ electrolyte |
| 2015 | Chaudoy | $\text{C}_3\text{mpyr FSI}$  
$\text{C}_4\text{mpyr FSI}$  
$0.6$ and $1 \text{ mol.L}^{-1} \text{ LiTFSI}$ | Li | NMC | Discharge capacity of the NMC cathode of 161 mAh.g$^{-1}$ at 25 °C at 0.1 C rate with $\text{C}_3\text{mpyr FSI} + 0.6 \text{ mol.L}^{-1} \text{ LiTFSI}$ (91 mAh.g$^{-1}$ at 1 C rate)  
Discharge capacity decreases when the discharge rate increases. Interestingly, an increase of lithium salt concentration (from 0.6 to 1 mol.L$^{-1}$) improves the discharge capacity at high discharge rate (1 C rate) while a slight decrease is observed at lower rate (C / 10 rate) |
As a first conclusion, it seems that the common RTILs are often based on nitrogen-based cations\textsuperscript{11, 60}. On the other hand, phosphonium-based ILs have only recently started to receive attention as potential substitutes for their ammonium counterparts\textsuperscript{8}.

1.4.3 Phosphonium ILs and Li batteries

Recent applications of phosphonium based ILs include the use as extraction solvents\textsuperscript{75-76}, chemical synthesis solvents\textsuperscript{77}, lubricants\textsuperscript{42}, electrolytes in lithium batteries\textsuperscript{32, 78-83} and super-capacitors\textsuperscript{37}, and also in corrosion inhibition\textsuperscript{43}.

As shown in Table 7 the interest in phosphonium ILs for electrolytes in batteries is much more recent. While ILs containing nitrogen-based cations have undergone extensive investigation in recent times\textsuperscript{4, 9, 11, 60-63, 65-66, 84-85}, studies involving quaternary phosphonium systems are much rarer\textsuperscript{8}. Initial studies were based on relatively large phosphonium cations such as tri-\textit{n}-hexyl(tetradecyl)phosphonium (P\textsubscript{666(14)})\textsuperscript{8}. These bulky cations tend to have high viscosity and low conductivity and their electrochemical application has been restricted. However recent studies reporting the synthesis of smaller and asymmetrical phosphonium cations showed that many properties of novel phosphonium ILs are superior to the isoelectronic ammonium derivatives including\textsuperscript{8}:

- improved transport properties, for example improved ionic conductivity\textsuperscript{32, 82}
- more thermally stable with respect to degradation under various conditions\textsuperscript{32}
- their electrochemical windows are quite similar\textsuperscript{32}
- low melting points can be achieved\textsuperscript{83}
- they are available on a large scale (cost)\textsuperscript{76}
An IL based on the trimethyl(hexyl)phosphonium cation with a low melting point (7 °C) was first reported by Matsumoto et al. Armel et al. recently reported a series of low viscosity RTILs based on asymmetric diethylmethyl(isobutyl)phosphonium cations for dye-sensitised solar cells. Lowering the viscosity of RTILs is one major requirement as it influences the rate of mass transport in the electrolyte. Due to the large cations used, the traditional phosphonium RTILs generally have high viscosity, so efforts to obtain low viscosity phosphonium RTILs continue. Tsunashima et al. have designed phosphonium RTILs derived from triethylphosphine, introducing smaller cations that led to improved transport properties. By reducing the packing of ions, an asymmetry in the cation structure combined with the TFSI- anion allowed the formation of low-melting salts. The introduction of a methoxy group in one chain of the cation did not significantly alter the IL properties other than a reduction in viscosity, but the electrochemical stability was not changed.

In 2011 Tsunashima showed that cycling of Li | LiCoO₂ cells was possible in a TFSI-based phosphonium electrolyte. The same article confirmed that asymmetrical cations seem to give better charge/discharge cycleabilities than organic electrolytes. However, according to the authors, the transport properties do not always reflect capacity retention. Indeed, electrolyte made with P₄₄₄₁TFSI showed a higher Faradaic efficiency than the one with P₂₂₂₅TFSI, even though the transport properties were superior for the P₂₂₂₅TFSI IL. Only recently the properties of more promising ILs have been reported by Tsunashima et al. They designed smaller cations such as P₁₁₁₃⁺ (low melting point of P₁₁₁₃F₅I: 0 °C) or P₁₁₁₁(101)⁺.
However their interaction with Li cell electrodes has not been reported and it is important to find out whether they can sustain repeated cycling over a long period of time. The following section discusses the FSI anion in more detail.

### Table 7 Selected results on phosphonium RTILs for Li batteries

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Electrolyte</th>
<th>Electrodes</th>
<th>Results</th>
</tr>
</thead>
</table>
| 2008 | Tsunashima     | P$_{222(201)}$ TFSI | Li | LiCoO$_2$ | - Initial discharge capacity (P$_{222(201)}$ TFSI): 140 mAh.g$^{-1}$, 90% capacity retention after 30 cycles  
- Initial (DEME TFSI): 149 mAh.g$^{-1}$ |
|      |                | P$_{2225}$ TFSI | Li | LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ | - P$_{222(201)}$ TFSI with 1M LiTFSI: initial 147 mAh.g$^{-1}$, no significant capacity reduction over 30 cycles (96% capacity retention after 30 cycles)  
- P$_{2225}$ TFSI with 1M LiTFSI: initial 126 mAh.g$^{-1}$, low capacity retention after 30 cycles (63%) |
| 2011 | Tsunashima     | P$_{2225}$ TFSI | Li | LiCoO$_2$ | - High cycling efficiency of P$_{4441}$ TFSI  
- Initial (P$_{4441}$ TFSI): 160 mAh.g$^{-1}$, 97% capacity retention after 20 cycles |
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Electrolyte</th>
<th>Electrodes</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>2015</td>
<td>Tsunashima\cite{83}</td>
<td>P$_{1113}$ FSI</td>
<td>-</td>
<td>- Higher electrochemical stability than TFSI counterparts (only physical properties reported)\newline P$_{1113}$: small and asymmetric cation\newline - Smaller and asymmetric cation seems to be lead to lower melting points and improved transport properties</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P$_{111(101)}$ FSI</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 2016 | Hilder\cite{86} | P$_{222(CH2)3CN}$ FSI with 1 M LiFSI | Li | NMC | High discharge capacity (140 mAh.g$^{-1}$) and efficiencies $>$ 98 % at 0.1 C and 0.2 C rates (over 20 cycles)\newline Performance of phosphonium IL electrolyte matches that of a commercial standard electrolyte |
|      |          |                                      |            |                                                                                                                                                    |

1.4.4 FSI versus TFSI based ILs

Perfluoroalkylanions were successfully proposed as anions for lithium battery electrolytes\cite{11}, showing excellent electrochemical performance. Among them, TFSI\cite{33} was found to be among the best because of its high anodic potential stability, good conductivity, thermal stability and hydrophobicity\cite{4}. In particular, MacFarlane et al.\cite{60}, Passerini et al.\cite{92} and Tatsumi et al.\cite{49} have demonstrated the feasibility of pyrrolidinium-TFSI ILs as lithium battery electrolyte components, improving the performance, cyclability and long-term stability of electrochemical storage devices.

![Figure 10 Chemical structure of the FSI anion](image)

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Interest has progressively grown for the FSI anion (Figure 10)\textsuperscript{11, 83, 93}. FSI-based ILs exhibit better physical and transport properties than their corresponding TFSI-based materials\textsuperscript{32, 52, 63, 82-83, 86} including lower melting point\textsuperscript{82-83} (e.g., 0 °C for \(\text{P}_{1113}\text{FSI}\) and 40 for \(\text{P}_{1113}\text{TFSI}\)), lower viscosity\textsuperscript{82, 86} resulting in higher ionic conductivities\textsuperscript{86} (e.g., 8.9 mS cm\textsuperscript{-1} for \(\text{P}_{111(S101)}\text{FSI}\) and 4.1 mS cm\textsuperscript{-1} for \(\text{P}_{111(S101)}\text{TFSI}\) at 25 °C).\textsuperscript{83} On the other hand, the FSI ILs seem to have a lower electrochemical and thermal stability compared to their TFSI counterparts\textsuperscript{94} due to the reactivity of the fluorine atoms directly bonded to the sulfonyl groups. Also, FSI-based ILs seem to be more prone to corrosion of aluminium (current collector used in Li batteries) than TFSI-based ILs which were shown to have beneficial properties regarding aluminium passivation.\textsuperscript{95} Aluminium corrosion in FSI systems at high oxidation potentials (\(> 4.0 \text{ V vs. Li / Li}^+\)) has been reported.\textsuperscript{96}

1.4.5 Battery performance of ILs

MacFarlane et al.\textsuperscript{12} recently published a perspective which highlighted recent key papers in the IL battery performance field. Battery performance of FSI electrolytes (EMI FSI, C\textsubscript{3}mpyr FSI and C\textsubscript{3}mpip FSI) were first reported by Matsumoto et al.:\textsuperscript{63} a Li \mid \text{LiCoO}_2 cell containing EMI FSI showed a high charge rate cycling when compared to previously reported IL electrolytes. The cell containing C\textsubscript{3}mpyr FSI also gave good cyclability. Yoon et al.\textsuperscript{62} recently studied Li \mid \text{LiCoO}_2 cells containing C\textsubscript{3}mpyr FSI with high Li concentration and found that the rate capability was higher than that of cells with lower Li concentration. High concentration of lithium was shown to give remarkable rate capability in comparison to a standard organic carbonate electrolyte, as illustrated in Figure 11.
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Figure 11 Charging profiles of Li | LiCoO₂ cells (from 1 C to 5 C); solid bold line: organic liquid electrolyte (1 M LiPF₆, EC:DMC = 50:50 vol.%), dashed line: 3.2 mol.kg⁻¹ LiFSI in C₃mpyrFSI, from Yoon et al.⁶²

For the phosphonium cation Tsunashima et al. first reported the use of small phosphonium cations⁷⁸ such as P₂₂₂(2O₁) TFSI and P₂₂₂₅ TFSI in Li | LiCoO₂ cells. The charge-discharge profiles revealed high recharge ability and cycle ability of P₂₂₂(2O₁) TFSI-based cells, as illustrated in Figure 11. Sufficient capacities were obtained at the first cycle (charge capacity: 152 mAh.g⁻¹ and discharge capacity: 141 mAh.g⁻¹). Similar results were observed in the cycling performance of high voltage cathodes (e.g. lithium nickelate cathode, LiNi₀.₈ Co₀.₁Mn₀.₁O₂) in the same ILs.⁸⁰ Recently, they also showed that asymmetric cations gave better cycling efficiency and capacity retention than symmetric cations⁹¹.

In the case of highly viscous phosphonium RTILs, electrolytic properties of mixtures consisting of the RTIL and a conventional organic electrolyte (1 M LiPF₆ in EC:EMC 1:2 vol/vol) were reported.⁹⁷ The cycling performance of LiCoO₂ cathode in mixed electrolytes was described. The results suggested P₂₂₂₅ TFSI and P₄₄₄₁ TFSI to be effective additives by improving cycling efficiency.
The majority of reports have used quaternary ammonium and phosphonium TFSI based electrolytes due to their high anodic electrochemical stability. Cyclic pyrrolidinium and piperidinium TFSI ILs also showed efficient lithium cycling due to their low viscosity and high anodic stability. One main areas of focus nowadays is high voltage applications to maximise energy density (i.e., the ability of charging above 4.5 V). Typical initial capacities reported using the LiCoO₂ cathode vary between 140 and 150 mAh.g⁻¹ corresponding to the theoretical capacity of LiCoO₂ for a conventional range of 3.0 - 4.2 V. Most reports on high voltage Li metal batteries utilise TFSI based IL electrolytes. The first study using FSI based IL electrolytes was reported by Matsumoto et al. showing significantly high rate charging capability in comparison to other electrolyte materials. Further reports showed the formation of an effective SEI by the FSI⁻ anion to prevent irreversible intercalation of IL cations in graphite electrodes. Nevertheless because of a poorer anodic electrochemical stability compared to the TFSI⁻ anion, FSI based IL electrolytes have rarely been reported for any high voltage cell applications.
Reliable cell cycling with IL electrolytes has also been reported with other high capacity / high voltage electrodes, such as silicon composite anodes \(^{101}\) and LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\); \(^{80}\) LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\); \(^{102}\) and LiVPO\(_4\)F\(^{103}\) as cathodes. No significantly promising candidate for replacing TFSI based IL electrolytes or conventional organic liquid electrolytes has yet been found. Therefore, one of the main areas of focus in research on ILs for lithium battery applications is the design of both cation and anion functionality. \(^{48, 50, 83, 104}\) The contribution of the IL structure to the effective formation of the SEI has also became an important area of focus.

1.4.6 SEI formation in ILs

Passerini et al. \(^4\) recently published a review of SEI formation and thermal stability in ILs while Zhang et al. published a review of SEI formation at the Li metal anode. \(^{105}\) The SEI is an interlayer film with beneficial properties regarding the battery performance which \(^4, 11-12, 19:\)

- stabilises the electrode by forming an electrode/electrolyte interphase (e.g. prevents electrode corrosion; passivation)
- is formed on the electrode surface during the initial charge/discharge cycle
- results from the reaction of the electrode material with decomposition products of the electrolyte
- is a Li\(^+\) ion conductor (e.g. the electrode is passivated while still being electrochemically active)
- is insoluble in the electrolyte
1.4.6.1 SEI formation and stability in ILs

In this section the outcomes of recent research pertaining to SEI formation in an IL electrolyte is summarised2, 4, 6, 52, 66, 106-109:

- SEI formation results from a chemical interaction of the IL electrolyte on the electrode107
  - the Li surface morphology changes due to the build-up of passivation products
  - the Li electrode resistance increases with the SEI formation (this is where electrochemical techniques can be correlated with spectroscopic techniques)

- the chemical interaction of the IL electrolyte on the electrode is rate dependent52

- the possible mode of film formation results from the decomposition of the anion of the IL (e.g. TFSI and FSI) in the presence of Li66, 106, 109

- the role of the cation in the formation of the film is still not clear at this date6

- organic additives (e.g. phosphides, sulfonate esters) assist in forming stable interfacial films on high-voltage cathodes thus preventing the decomposition of the electrolyte108.

To ensure stable device operation, the SEI must4, 105:

- support lithium ion transport: it must allow insertion/extraction of Li\(^+\) ions to the electrode. If there is no lithium transport between the electrode and the electrolyte the basic operating principle of the electrode is suppressed and the electrode thus becomes electrochemically inactive.

- protect the electrode material from competitive side reactions (e.g. corrosion): if not passivated the electrode material is decomposed rather than being electrochemically converted into energy.

- be insoluble in the electrolyte, otherwise a solid SEI cannot be formed and would dissolve into the electrolyte.
1.4.6.2 Surface characterisation of the anode in an IL electrolyte

To understand the composition and structure of the SEI layer in IL electrolytes the following spectroscopic techniques have mainly been used:

- Electrochemical impedance spectroscopy (EIS)\(^{62, 66, 85, 110-111}\)
- Scanning electron microscopy (SEM)\(^{58, 106, 112}\)
- Optical microscopy \(^{58, 60}\)
- Fourier transform Infrared (FTIR)\(^{107}\)
- X-ray diffraction (XRD)\(^{106, 113}\) (qualitative bulk technique)
- X-ray photoelectron spectroscopy (XPS)\(^{106, 109, 114}\)
- Raman spectroscopy\(^{106, 115-117}\)
- Focussed ion beam SEM (FIB-SEM) and/or Transmission electron microscopy (TEM)\(^{118}\)

Table 8 presents selected relevant RTIL research results for SEI study in lithium batteries.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Electrolyte</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>Howlett(^{58})</td>
<td>C(_2)mim NTf(_2) with LiTFSI with Li</td>
<td>Using an optical cell, the lithium surface was investigated with Raman spectroscopy and lithium dendrite was imaged on a Cu substrate. In the RTIL the growth of lithium dendrites were distinctively reduced, while the conventional organic solution exhibited (1M LiPF(_6) in PC). The cycled Li metal electrode was shown to be compact and dendrite free.</td>
</tr>
<tr>
<td>2004</td>
<td>Howlett(^{60})</td>
<td>C(_4)mpyr TFSI C(_3)mpyr TFSI</td>
<td>Stable SEI formed on Cu substrate and characterised by XPS. XPS analysis showed that SEI composition consisted of reduction products of the TFSI anion and significant quantities of native Li surface species (Li(_2)O, LiOH, Li(_2)CO(_3))</td>
</tr>
</tbody>
</table>

Table 8 Initial RTIL research results for SEI study in lithium metal batteries
<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Electrolyte</th>
<th>Results</th>
</tr>
</thead>
</table>
| 2006 | Howlett\textsuperscript{106} | C\textsubscript{4}mpyr TFSI  
C\textsubscript{3}mpyr TFSI | XRD / XPS / Raman / EIS techniques were used:  
- RTIL present on the surface SEI composed of reduction products of the anion (Li\textsubscript{2}O, Li\textsubscript{2}CO\textsubscript{3}, Li\textsubscript{2}S, LiF)  
- Use of an optical cell allowed the acquisition of in-situ Raman spectra: this enabled the electrolyte composition to be monitored as a function of cycling and allowed spectra to be obtained from the lithium surface.  
- EIS: Equivalent Electric Circuits (EECs) were used to fit the EIS data on order to predict a layered structure. |
| 2009 | Sutto\textsuperscript{113} | C\textsubscript{2}mim  
C\textsubscript{4}mim  
C\textsubscript{3}dmim with \textit{LiPF\textsubscript{6} / LiBF\textsubscript{4}} | The authors demonstrated the intercalation of imidazolium cations and lithium ion into a graphite electrode using XRD. C\textsubscript{2}mim cation does not intercalate into graphite layers while the C\textsubscript{4}mim and C\textsubscript{3}dmim cations do intercalate. |
| 2012 | Basile\textsuperscript{119} | C\textsubscript{3}mpyr FSI  
with \textit{LiBF\textsubscript{4}} | Formation of a smooth and stable SEI on Li metal after extensive cycling attributed to the LiFSI salt  
- SEM: images acquired as a function of reaction time: morphological changes at the Li surface  
  - surface cracking after 7 days interaction  
  - Smoothing after 12 days  
- FT-IR: reaction products + electrolyte species on the Li surface  
- XRD: amorphous nature of the SEI film |
### Table 1. Recent literature on phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Electrolyte</th>
<th>Results</th>
</tr>
</thead>
</table>
| 2012 | Basile   | C₃mpyr FSI with LiBF₄       | - XPS: evidence of decomposition products (anion) on the Li surface (Li₂O, Li₂CO₃, Li₂S, LiF)  
     |          |                              | - EIS: electrode resistance decreased after cycling                     |
| 2013 | Basile   | C₃mpyr FSI + 0.5 mol.kg⁻¹ LiFSI | SEM imaging showed morphological changes of the lithium surface had occurred but no evidence of needle-like dendrite based growth was found after 5000 cycles (Li | Li) |
| 2015 | Grande   | C₄mpyr TFSI and C₄mpyr TFSI / FSI | Beneficial influence of the FSI anion over the SEI layer on Li metal by suppressing dendrite growth and resulting in fast cathodic reactivity. Hypothesis of a pore clogging mechanism |
|      |          |                              | Techniques used: SEM, XPS                                              |

Howlett et al. reported a thorough surface characterisation of the SEI layer formed on the Li surface in a solution of 0.5 mol.kg⁻¹ of LiTFSI in the IL N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (C₃mpyrTFSI). Recently Basile et al. reported the cycle-ability of Li in the bis(fluorosulfonyl)imide (FSI) based ammonium counterpart (same cation with a smaller anion). The authors noticed the formation of a smooth and stable SEI on Li metal after extensive cycling accredited to the lithium bis(fluorosulfonyl)imide (LiFSI) salt. In their work the unstable behaviour of the cycling of Li | Li cells over 5000 cycles at 0.1 mA cm⁻² was attributed to surface reorganisation. However no evidence for lithium dendrite formation was observed; SEM imaging showed morphology changes that occurred during cycling but no evidence of needle-like dendrite features was observed.

More recently Grande et al. reported the beneficial influence of the FSI anion on the Li metal SEI layer, resulting in suppression of dendrite growth and fast cathodic reactivity.
The study showed that the induced inhomogeneous deposition on the Li surface was related to SEI cracking and revealed the presence of bundled Li fibers located underneath the pre-existing SEI and nanorod-shaped features resulting from Li extrusion.

In the case of the IL C₃mpyr FSI, the SEI formed on the Li substrate was characterised as having a dynamic behaviour with a relatively complex chemistry during cycling. The rapid chemical decomposition of the IL was shown to form a SEI composed of the breakdown products of the IL components in the absence of an applied voltage. Several reduction pathways were also suggested to describe the breakdown mechanism of Li salt / IL mixture forming a passivation film on the Li electrode.

The dynamic behaviour of the SEI was interpreted as a result of successive reactions that involved both IL cation and anion: (i) reactions of IL cations and anion with Li metal, (ii) reaction of the salt anion and (iii) breakdown of the salt anion. The main breakdown products identified by several spectroscopic techniques (FTIR, XPS) were found to be LiF, LiOH and cation breakdown products (such as methylpyrrolidine). Morphological changes of the Li surface were also observed at different intervals of surface conditioning time. Recent papers focusing mainly on lithium-sulfur batteries, also studied the Li electrode surface with IL electrolytes using the same techniques. There has not yet been any thorough characterisation of the anode surface with a phosphonium-based IL electrolyte.

To summarise, literature reports indicate the importance of the SEI film in IL based cell operation and performance. It is indicated that the IL anion plays an important role in SEI formation, as do impurities. The role of the cation is less clear. The surface handling required to reliably characterise the SEI layer is also important, hermetic transfer of electrode surfaces is needed to avoid atmosphere exposure and contamination of the surface.
1.4.7 Lithium metal cycling and surface morphology

This section presents the ‘state of the art’ on Li metal cycling available in the literature. In the last two years there has been a considerable increase in the number of publications on the use of Li metal electrodes. Particular interest has been addressed to high Li salt concentrations, fast-charging applications, alternate solvents and solid electrolytes.\textsuperscript{18, 36}

It is well established that Li metal cycling efficiency in organic carbonate electrolytes is very poor and results in dendritic or mossy Li metal deposits and low coulombic efficiency (CE), less than 80%.\textsuperscript{125}

Therefore in the context of rechargeable batteries, the use of Li metal requires alternative solvents. Electrolytes based on RTILs have recently been the subject of great interest due to their low reactivity with Li metal resulting in a lower propensity for dendritic Li morphology and improved coulombic efficiency for Li plating/stripping\textsuperscript{60, 62, 106, 111, 121}, however, these features are not retained for long-term cycling or when high current densities are applied.\textsuperscript{50, 126} Nevertheless, some RTILs have been targeted as potential alternative electrolytes for lithium batteries.\textsuperscript{9, 11, 124} They have numerous features that should lend themselves for use in high-energy lithium batteries such as negligible volatility and flammability, high ionic conductivity and wide electrochemical windows.\textsuperscript{12}

Interfacial studies of ILs on Li metal originally started with ammonium-based ILs. For example, Howlett et al. demonstrated that 0.5 mol.kg\textsuperscript{-1} of LiTFSI in the ionic liquid N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (C\textsubscript{3}mpyrTFSI) supported high cycling efficiency (> 99 %) on copper at low current densities.\textsuperscript{60, 106} Recently Basile et al. reported the cycle-ability of Li in the bis(fluorosulfonyl)imide (FSI) based ammonium counterpart (same cation with a smaller anion).\textsuperscript{120} They noticed the formation of a smooth and stable SEI on Li metal after extensive cycling accredited to the lithium bis(fluorosulfonyl)imide (LiFSI) salt. In their work the unstable behaviour of the cycling of Li | Li cells over 5000 cycles at 0.1 mA cm\textsuperscript{-2} was attributed to surface reorganisation. However no evidence for lithium dendrite formation was observed; SEM imaging showed morphology changes that occurred during cycling but no evidence of needle-like dendrite features was observed.
More recently Grande et al.\textsuperscript{121} reported the beneficial influence of the FSI anion on the Li metal SEI layer, resulting in suppression of dendrite growth. In most previous reported literature, the Li salt concentration used was typically around 0.5 to 1.0 mol.kg\(^{-1}\) \textit{(i.e. a Li\(^+\) molar ratio of 0.05 with respect to the ionic liquid cation)}. On the other hand, Yoon et al. recently reported that high rate cycling performance (at higher than 3C charge and discharge rates) could be retained in Li | C\textsubscript{3}mpyrFSI | LiCoO\(_2\) cells with surprisingly high LiFSI salt concentration (3.2 mol.kg\(^{-1}\) Li salt \textit{i.e.}, a 1:1 molar ratio of salt and IL) in spite of the high viscosity reduced ionic conductivity that occurs with increasing Li salt concentration.\textsuperscript{127} This study revealed that a highly concentrated IL electrolyte can in principle outperform an organic liquid electrolyte (1M LiPF\(_6\) in EC:DMC). More recently, novel phosphonium-based ILs have demonstrated superior transport properties compared to their ammonium-based counterparts.\textsuperscript{8, 83, 88, 120, 128}

Lin et. al have shown that a hydrophobic phosphonium-based IL electrolyte could operate a Li | LiCoO\(_2\) metal battery at elevated temperature (100 °C).\textsuperscript{128} The authors also found that an increase in the Li salt concentration (up to 1.6 M Li salt into IL) led to a higher capacity retention (90%) than that obtained with lower salt concentrations. As shown in chapter 3 and recently published, trimethyl(isobutyl)phosphonium FSI IL (P\textsubscript{111i4}FSI) readily dissolves high amounts of LiFSI salt and the highly concentrated electrolyte (3.8 mol.kg\(^{-1}\) \textit{i.e.}, a 1:1.2 molar ratio of salt and IL) supported reversible and efficient Li cycling even at switching potentials as negative as - 1.1 V \textit{vs. Li / Li\(^+\)}, indicating high electrolyte stability for Li batteries\textsuperscript{127}.

A growing number of studies have been focusing on high Li salt concentration in electrolytes. Advantages of high Li salt content in the electrolyte have been reported. These include an improvement of Li cycling performance in inorganic-organic salt mixtures in C\textsubscript{3}mpyrFSI (from 1 C to 5 C charging rates in Li | LiCoO\(_2\) cells).\textsuperscript{62} These reports support the hypothesis that high Li salt concentrations can be used to tailor Li-ion transport properties for high-rate charging applications.\textsuperscript{72} At this date the FSI anion is known to be unique in allowing the formation of room temperature highly concentrated inorganic-organic mixtures.
The emerging need for fast-charging applications has also driven research groups to enhance the cycling performance in ILs compared with conventional organic carbonate electrolytes.\textsuperscript{129} The study of Li-metal cycling performance in the IL C\textsubscript{4}mpyrTFSI published by Grande et al.\textsuperscript{129} revealed the critical role of SEI formation in an IL on the long-term cycling performance by establishing a stable multi-layered film in which high coulombic efficiency was maintained but ultimately a ‘pore clogging’ mechanism was postulated to limit the cycle-life of the Li metal electrode. Piper et al.\textsuperscript{130} demonstrated a stable cycling of high-capacity Si nanocomposite anodes in a C\textsubscript{3}mpyrFSI electrolyte with a capacity retention of 77\% after 100 cycles. Li surface analysis and computational simulations were also found to be very helpful in demonstrating the promotion of structural integrity of the Si anode due to the formation of a stable SEI with the FSI\textsuperscript{−} anion.

The use of other solvents such as ether-based electrolytes mainly for Li-air technologies was also reported and highlighted the interest in enhancing Li metal cycling performance.\textsuperscript{131} The investigation showed an inadequate Li-metal cycling performance.

Recently, a novel type of IL-based solvent, called ‘solvate ILs’, have received particular interest. These safe and inexpensive mixtures based on a glyme and a Li salt were shown to support the reversibility of the cathodic reaction in Li-air batteries.\textsuperscript{132} The use of ‘solvent-in-salt’ systems with high Li salt concentration has also demonstrated the formation of insoluble polysulfide in Li-S batteries and excellent cycling performance.\textsuperscript{116} As an example, an electrolyte of 4 M LiFSI in dimethoxyethane (DME) exhibited high coulombic efficiencies and excellent rate capability over thousands of cycles.\textsuperscript{133} Another type of IL electrolyte includes nanoparticle hybrids in the form of cations tethered to SiO\textsubscript{2} nanoparticles. In this context enhancement of Li cycling was achieved by the addition of 11 wt \% C\textsubscript{3}mpipTFSI – nanoparticle hybrid to a standard electrolyte.\textsuperscript{134}
Interest in solid electrolytes with Li metal has also been driven by emerging energy storage applications and significant manufacturing advantages compared with liquid electrolytes. Ionogels consisting of a confined C\textsubscript{3}mpyrTFSI inside a SiO\textsubscript{2} polymer matrix exhibited comparable performance to that of the pure IL in a Li | LiFePO\textsubscript{4} cell. Solid-state materials (e.g. organic ionic plastic crystals - OIPC) based on specific ILs and characterised by remarkable ionic conductivity (crystal defects) were shown to support cycling in Li | LiFePO\textsubscript{4} cells, in the case of a phosphonium FSI based OIPC (i.e., chemically similar to the ILs studied in this project) C-rate capability at ambient temperature was demonstrated for the first time.

As discussed earlier, dendrite formation during Li deposition is a critical problem for battery safety. The next paragraph relates to Li surface morphology characterisation by SEM. Microscopic studies have mainly focused on Li surface morphological changes and Li dendrite growth. SEM has been the most useful technique to directly reveal high resolution images of Li dendrite growth since the 1990s. Initial microscopic studies revealed highly dendritic Li deposition in organic carbonate electrolytes, as shown in Figure 13, and confirmed the incompatibility of these electrolytes with Li metal. SEM allowed the establishment of a correlation between surface chemistry Li electrode morphology.

![Figure 13 SEM micrograph obtained from Li electrodes cycled in EC:DEC (1:1 vol/vol) with LiPF\textsubscript{6} (left) and LiBF\textsubscript{4} (right) salts, from Aurbach et al.](image)

Investigation of phosphonium bis(fluorosulfonylimide)-based ionic liquid electrolytes for lithium batteries
Several groups have reported the corrosion of Li metal as well as dendrite growth as a failure mechanism.\textsuperscript{111, 120, 126, 139} Most studies were conducted ex situ (i.e. deposited surfaces transferred to SEM instrument with minimum exposure to air) as described by Kohl et al.\textsuperscript{145} This method has recently been improved with the design of removable load lock chambers from glove boxes to SEM instruments without exposure to air.\textsuperscript{146-147} Studies from Orsini et al.\textsuperscript{146-147} identified accumulation of mossy Li and growth of Li dendrites at a Li / polyethylene interface, as illustrated in Figure 14, resulting in capacity fading and interface collapse.

![Figure 14](image1.png)

Figure 14 (a) Cross section of a Li battery after one charge at 1 C (2.2 mA.cm\(^{-2}\)); (b) surface of the Li anode of a Li battery after one charge at 1 C; (c) Li deposit on the Li surface after one charge at 1 C, from Orsini et al.\textsuperscript{146}

Recent microscopic studies of ILs and concentrated solvate ILs in particular revealed the formation of compact SEI layer at a Li metal electrode, as reported by Qian et al.\textsuperscript{133} in the case of 4 M LiFSI-DME electrolyte with a \(\sim 10 \mu\text{m}\) thick SEI (after 100 cycles, 0.5 mAh.cm\(^{-2}\)) growing slowly during cycling. Grande et al.\textsuperscript{121} also reported the suppression of dendrite growth on the Li metal electrode in a less concentrated electrolyte.

The majority of studies reported to date mainly utilise relatively low current densities (usually between 0.1 and 1.0 mA.cm\(^{-2}\))\textsuperscript{62, 107, 120, 126} which are insufficient to meet the requirements for many applications (> 3 mA.cm\(^{-2}\)).\textsuperscript{88, 137} More importantly, very few studies report the deposition and dissolution of substantial quantities of Li metal, rarely exceeding 0.1 mAh.cm\(^{-2}\).\textsuperscript{62, 129}
However, for practical batteries the transfer of much larger amounts of charge is required (i.e., commercial Li-ion cells typically incorporate cathode loadings which cycle between 3 and 6 mAh.cm\(^{-2}\))^\cite{148}. Advanced Li-S or Li-O\(_2\) cells could be expected to require even larger amounts of Li for practical operation.\cite{36} Recently, several studies have reported significant differences between the SEI properties and cell performance for dilute and highly concentrated IL electrolytes.\cite{62, 72, 121, 149} Thus novel electrolytes that can support high rate and stable cycling of Li metal anodes, for example recently highlighted ‘solvent-in-salt’ electrolytes,\cite{116} are needed to further develop practical rechargeable Li metal batteries.

1.4.8 Lithium transport

As mentioned earlier in the introduction, IL electrolytes have a lower ionic conductivity than the organic carbonates. Thus, there is a need to understand the conduction mechanism in IL electrolytes.

Passerini et al.\cite{150} used NMR spectroscopy (self-diffusion coefficient measurements) to understand the behaviour of C\(_3\)mpyrFSI and C\(_4\)mpyrTFSI and their binary mixtures as electrolytes for lithium batteries. This technique was used to determine diffusivities of each ion in the electrolyte and can be used to better understand the mechanism of ion transport in the IL system.\cite{151, 152} The Li transport mechanism in IL electrolytes at high lithium salt concentration (corresponding to 0.5 molar fraction) has been studied by Yoon et al.\cite{115} for the C\(_3\)mpyr FSI IL system.

It was observed that the diffusivities of all ions decreased as the Li\(^+\) concentration in solution increased. The order of diffusivities of the ions at 25 °C was FSI\(^-\) > C\(_3\)mpyr\(^+\) > Li\(^+\). The rate at which the diffusion coefficient decreased with increasing LiFSI concentration was greatest for the FSI anion, followed by the C\(_3\)mpyr cation. Importantly, the Li\(^+\) diffusivity was less sensitive to concentration, ultimately becoming the most diffusive species at high concentrations.

When one refers to lithium transport in a battery, one critical parameter for lithium batteries\cite{153-154} is the lithium transference number. The Li\(^+\) transference number is defined by the fraction of current transported by the Li\(^+\) cation within the electrolyte in a Li cell.
The same trend was previously reported by Yoon et al. who reported Li\(^+\) transference numbers in their \(N\)-methyl-\(N\)-propylpyrrolidinium FSI and LiFSI systems, with high Li salt content.\(^{62}\) The authors found that an increase in salt concentration increases the Li\(^+\) transference number (up to 0.18 for 3.2 mol.kg\(^{-1}\) LiFSI in \(C_3\)mpyrFSI), however these values are still lower than the 0.65 value reported by Han et al. for an ammonium FSI IL (equimolar mixture of LiFSI and \(N_{23(102)}\)FSI).\(^{155}\) Fernicola et al. also reported a value of 0.4 for a TFSI-based system.\(^{64}\) It should be noted that only Yoon et al. reported transference numbers in the case of high Li salt concentration whereas only Martins et al.\(^{156}\) recently reported a high transference number (0.54) in a phosphonium IL electrolyte (\(P_{222(201)}\)TFSI + 1 M LiTFSI) at a lower Li salt content.

1.4.9 Literature review conclusion

To summarise the findings of the literature review:

- Li-ion batteries are safer than Li metal batteries.
- FSI-based ILs generally have superior transport properties than their TFSI counterparts, e.g. having very good ionic conductivity even at sub-ambient temperature.
- Phosphonium cations were shown to give better transport properties than their ammonium cation counterparts.
- The role of the IL and its impact on the structure and formation mechanism of the SEI layer is important for battery performance.
- Characterisation of the IL interactions with the electrode surface including surface analysis requires different techniques such as SEM, XRD, XPS or FTIR / Raman.

In the context of the present project, it is important to note that none of the publications have investigated high Li salt concentrations (> 0.5 mol.kg\(^{-1}\)) dissolved into phosphonium-based ILs nor characterised the SEI in phosphonium-based ILs.
There is still a need to better understand the transport properties in IL electrolytes and the effect on battery performance. The conductivity of ILs is still relatively low and is associated with their high viscosity.

As yet there is no commercially available Li-ion battery using an IL electrolyte. One of the main reasons is the relatively high cost of ILs and their lower rate capability compared to conventional electrolytes, especially at low temperatures, mainly due to their high viscosity. Phosphonium FSI-based ILs are promising candidates to tackle the issue related to high viscosity. However, they still require further investigation as new materials.

1.5 Aim of this research

This project aims to investigate safe electrolytes for lithium batteries based on novel room temperature phosphonium ionic liquids (RTILs), seeking desirable electrolyte properties as detailed earlier (section 3.2) and also meeting the challenges presented by emerging battery technologies, the main focus being on safety and stability.

Table 9 presents the initial specifications identified as key attributes of the formulated electrolyte.

The project was carried out in collaboration with Cytec Canada Inc., the world leading manufacturer of phosphonium ionic liquids. With their involvement, the project had excellent access to a large range of novel phosphonium ILs, with detailed information pertaining to synthesis and purity. Cytec is interested in pursuing large-scale applications of phosphonium ILs, particularly in electrolyte applications.

In this work the physical properties of a number of novel phosphonium IL electrolytes were determined. Variation of the lithium salt concentration was conducted to better understand the electrochemical and ion transport properties of the formulated IL electrolytes. Their compatibility and electrochemical performance with the lithium metal anode was also investigated. Thirdly, a thorough spectroscopic characterisation of lithium metal surfaces cycled in these electrolytes was conducted to obtain a better understanding of the nature of the SEI formed. The final study reports on the use of phosphonium IL electrolytes in lithium cells incorporating a high voltage cathode material.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Good</th>
<th>Better</th>
<th>Best</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>°C</td>
<td>&lt; 25</td>
<td>&lt; -10</td>
<td>&lt; -30</td>
</tr>
<tr>
<td>Viscosity (@ 25°C)</td>
<td>mPa.s</td>
<td>&lt; 100</td>
<td>&lt; 50</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Conductivity (@ 25°C)</td>
<td>mS.cm⁻¹</td>
<td>&gt;1</td>
<td>-</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Interfacial resistance (EIS)</td>
<td>Ω.cm²</td>
<td>1000</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Electrochemical window vs. Li</td>
<td>V</td>
<td>4.2-4.3</td>
<td>4.6-4.7</td>
<td>&gt; 5</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>m²/s</td>
<td>5.10⁻¹¹</td>
<td>-</td>
<td>5.10⁻⁹</td>
</tr>
<tr>
<td>Flammability</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Nonflammable</td>
</tr>
<tr>
<td>Water content</td>
<td>ppm</td>
<td>&lt; 150</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solvation properties</td>
<td>mol.L⁻¹</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Stability</td>
<td>Years, cycles</td>
<td>-</td>
<td>-</td>
<td>10, 5000</td>
</tr>
</tbody>
</table>

The specific aims of this Ph.D. project are:

- a correlation between the lithium salt concentration and the electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes
- a study of the cycling performance and rate capability of lithium metal electrodes in phosphonium IL electrolytes
- an understanding of lithium transport mechanisms in highly concentrated IL electrolytes
- a demonstration of a lithium metal battery prototype using a promising IL electrolyte and high voltage cathode material

This research relates to the determination of key physical properties of phosphonium FSI electrolyte formulations, which allow adequate ion transport and sufficient electrochemical stability. Electrolytes that support Li electrochemistry are identified. Within these formulations, the determining factors that contribute to SEI formation and their correlation to good performance in a lithium cell are investigated.
1.6 References


Investigation of phosphonium bis((fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Chapter 1

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

22. Adams, J.; Karulkar, M., Bipolar plate cell design for a lithium air battery. *J Power Sources* 2012, 199, 247-255.
39. Di Noto, V.; Negro, E.; Sanchez, J. Y.; Iojoiu, C., Structure-Relaxation Interplay of a New Nanostructured Membrane Based on Tetraethylammonium...
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries


Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries.


70. Xiang, J.; Wu, F.; Chen, R. J.; Li, L.; Yu, H. G., High voltage and safe electrolytes based on ionic liquid and sulfone for lithium-ion batteries. J Power Sources 2013, 233, 115-120.


Chapter 1

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries


Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium-ion batteries.


111. Bhatt, A. I.; Kao, P.; Best, A. S.; Hollenkamp, A. F., Understanding the Morphological Changes of Lithium Surfaces during Cycling in Electrolyte
Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries


117. Hy, S.; Felix; Chen, Y. H.; Liu, J. Y.; Rick, J.; Hwang, B. J., In situ surface enhanced Raman spectroscopic studies of solid electrolyte interphase formation in lithium ion battery electrodes. *J Power Sources* 2014, 256, 324-328.


Chapter 1


Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Chapter 2  Materials and methods
2.1 Materials and preparation procedures

2.1.1 Electrolytes

2.1.1.1 Room Temperature Ionic Liquids (RTILs)

The following RTILs were provided by Cytec Canada Inc. with > 99.5 % purity:

- trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide: $P_{111i4}FSI$ (i.e. $[P_{111i4}^+][FSI^-]$), where $P_{111i4}^+$ is the cation and $FSI^-\text{ is the anion (FSI} = \text{N(SO}_2\text{F})_2\text{)}$
- a mixture of the FSI anion and the four following cations: $P_{mix}FSI$, tripropyl(methyl)phosphonium ($P_{3331}$), ethyl methyl dipropyl phosphonium ($P_{3321}$), diethyl methyl propyl phosphonium ($P_{3221}$) and triethyl methyl phosphonium ($P_{2221}$). The actual chemical composition is $(P_{3331})_{0.10}(P_{3321})_{0.22}(P_{3221})_{0.35}(P_{2221})_{0.33} + FSI$

The chemical structures of the RTILs are presented below.

![Chemical structure of $P_{111i4}FSI$](image)

![Chemical structure of $P_{mix}FSI$](image)
(i) The description of the preparation of P1114FSI is shown in Figure 17. Isobutylphosphine was reacted with trimethylphosphate (US7,829,744 B2) resulting in the formation of the intermediate. The intermediate was further converted into the desired IL by metathesis with potassium bis(fluorosulfonyl)imide. The final product was isolated and purified.

![Figure 17 Description of preparation of P1114FSI by Cytec Canada Inc.]

(ii) A description of the preparation of PmixFSI is given in Figure 18. A mixture of ethylene and propylene (60:40 ratio) was reacted in an autoclave with phosphine in the presence of toluene and the catalyst Vazo 67 (2,2’azobis-(2-methylbutyronitrile), Dupont) initiating the free radical addition of phosphine to the olefin. The reaction proceeded with the formation of the four specific tertiary alkylphosphines.

![Figure 18 Description of preparation of PmixFSI by Cytec Canada Inc.]

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
The mixture was alkylated with methyl iodide. The resultant mixture of the phosphonium iodides was isolated and converted to the desired IL by aqueous metathesis with potassium bis(fluorosulfonyl)amide.

To better understand the effect of cation contribution to the transport properties of the IL, the initial composition was optimised by Cytec Canada Inc. to synthesise an IL with improved transport properties (e.g. low viscosity, low melting point). Triethyl(methyl)phosphonium FSI (P2221FSI) is a solid at room temperature (melting point: -47 °C) and tripropyl(methyl)phosphonium FSI (P3331FSI) is a liquid with better transport properties (as mentioned by Cytec Canada Inc.). Cytec Canada Inc. found that increasing the content of P2221FSI in mixtures of P2221FSI and P3331FSI improved the viscosity and conductivity of the final mixture. To simplify the synthesis (P2221FSI is a solid at room temperature) and to be cost competitive, Cytec Canada Inc. looked at making blends of four cations and the initial composition with a 60:40 ratio of ethylene:propylene became their preferred IL of this type.

2.1.1.2 Other electrolyte materials

The lithium salt used to formulate the IL electrolytes was lithium bis(fluorosulfonyl)imide (LiFSI) and was provided by Solvionic (France). The salt was used without further purification (purity > 99.5 %, FW = 187.07, M.P = 145 °C).

Sodium hydride (NaH) was provided by Sigma Aldrich (60 % dispersion in mineral oil) and was used for drying the formulated electrolytes.

2.1.1.3 Preparation of IL-based electrolytes

Initially, the binary IL electrolyte mixtures with LiFSI were prepared by adding and dissolving the appropriate amounts (0.5-3.8 mol.kg⁻¹) followed by drying under vacuum for 48 hours at 80 °C in the presence of sodium hydride (NaH, Sigma Aldrich™), as shown in Figure 19, until the water content (determined by Karl Fischer titration analysis) was below 50 ppm. The materials were stored in hermetically sealed glass vials in a controlled environment (argon glovebox with < 5 ppm H₂O; < 10 ppm O₂).
The maximum concentration of LiFSI in this IL was determined by sequential additions of the salt, with stirring at 80 °C for 48 h, until undissolved salt could be observed visually. The saturated solution corresponds to the solution in which the additional lithium salt could not be dissolved at room temperature (25 °C). Table 10 lists the concentrations of each electrolyte and the molar ratio of each ion in solution. The highest Li salt concentration achieved resulting in a saturated solution at 25 °C, is 3.8 mol.kg⁻¹ (55 mol % of Li salt in the IL). In this thesis, the solution of 3.8 mol.kg⁻¹ of LiFSI in P₁₁₁ᵳᵣFSI is referred to as the highly concentrated IL electrolyte whereas the solution of 0.5 mol.kg⁻¹ of LiFSI in P₁₁₁ᵳᵣFSI is referred to as the dilute concentrated IL electrolyte.

<table>
<thead>
<tr>
<th>LiFSI molality (mol.kg⁻¹)</th>
<th>LiFSI molarity (M, mol.L⁻¹)</th>
<th>Mole ratio of each ion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Li⁺</td>
</tr>
<tr>
<td>0 (neat IL)</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>0.6</td>
<td>0.07</td>
</tr>
<tr>
<td>1.0</td>
<td>1.2</td>
<td>0.12</td>
</tr>
<tr>
<td>2.0</td>
<td>2.1</td>
<td>0.19</td>
</tr>
<tr>
<td>3.2</td>
<td>3.0</td>
<td>0.25</td>
</tr>
<tr>
<td>3.8</td>
<td>3.4</td>
<td>0.27</td>
</tr>
</tbody>
</table>
2.1.1.4 Standard organic carbonate electrolyte

An electrolyte that is used in commercially available Li-ion batteries was used as a reference electrolyte. The lithium hexafluorophosphate (LiPF$_6$, 1M) - ethylene carbonate (EC) dimethylcarbonate (DMC) (1:1 v/v) electrolyte was used as a conventional organic electrolyte (Solvionic, 99.9%). This electrolyte is sometimes referred to as LP 30 electrolyte. The chemical structures of the organic carbonates are presented below in Figure 20.

![Figure 20 Chemical structures of ethylene carbonate (left) dimethylcarbonate (right)](#)

2.1.2 Inert atmosphere glovebox (Argon)

Because of the high reactivity of lithium metal with water (H$_2$O), oxygen gas (O$_2$) and nitrogen gas (N$_2$) all samples were stored and handled in a high purity argon atmosphere glovebox (Korea Kiyon), as shown in Figure 21. The water and oxygen levels were maintained below 1 ppm. The purity of the argon (Ar) gas (BOC Australia, 99.9%) was maintained by circulating the atmosphere through molecular sieves and copper catalyst, to remove H$_2$O and O$_2$, respectively.

All relevant chemicals and materials were stored within the glovebox and introduced via an antechamber, which was evacuated to $1.10^3$ mbars and refilled with Ar gas at least three times before any material was introduced into the glovebox. This methodology was standard technique performed to maintain the internal atmosphere. High vacuum was maintained through a diaphragm pump.
2.1.3 Fabrication of high voltage cathodes for Li batteries

The high voltage cathode material that was selected for the fabrication and testing of Li batteries was LiNiMnCoO$_2$, also called NMC (L&F Material). The starting material was a powder. A paste mixture containing the NMC material, conductive carbon black (C65 C-Nergy super, Timcal) and poly(vinylidene fluoride) (PVDF, Solvay) as a binder was prepared with the following weight ratio 80:10:10 to fabricate the cathode film. N-methylpyrrolidinone (NMP, Sigma Aldrich$^\text{TM}$) was used as a dispersant for the formulation.

The paste mixture was spread onto an aluminium (Al) current collector (battery grade, Hohsen) with a drawdown coater. The casted film, shown in Figure 22, was left to dry in a fume cupboard at ambient temperature overnight before being placed inside an oven at 100 °C to ensure the evaporation of the NMP solvent. The content of the active material was ca. 1.5 mg.cm$^{-2}$. Li foil (S.A = 0.785 cm$^2$, 375 μm thickness, 99.9 %, Sigma Aldrich) was used as anode material. For all Li cells the foil was brushed and rinsed in hexane.
2.1.4 Li symmetrical coin cells (CR2032 type)

Li symmetrical cells (CR2032 type, Figure 23) were used to study the cell cycling ability and to investigate the Li metal surface. All Li | Li cells were assembled inside a glove box with Li metal used as the working and counter electrodes, according to the following procedure. CR2032-type lithium symmetrical cells were prepared with 10 mm diameter lithium disks (375 and 100 μm thick) and a 25-μm thick micro-porous polypropylene separator (Celgard Inc.) in an Ar-filled glove box. To standardise the protocol, 80 μL of electrolyte was used in each coin cell. Cells were then stored for 24 hours at 50 °C inside an oven (Precision Compact, Thermo Scientific) and the open circuit potential (OCP) was monitored. The active area of the cells thus fabricated was ca. 1 cm². All Li | Li cells were assembled within a few hours to ensure similar initial SEI properties, then placed inside the oven at 50 ± 0.1 °C. Three replicates were made to assess the reproducibility of the cells and the results reported are representative of the majority.

The production of thin strips of Li metal (100 μm) was performed using a custom-built stainless steel press die, as shown in Figure 24. A 375 μm disk (10 mm diameter) was placed onto the bottom part of the press and covered with the interchangeable die. Firm pressure was applied onto the press die with a roller and a glass plate until the desired thickness was obtained. The thickness was measured with a micrometer caliper.
Figure 23 Coin cell (CR2032 type) and cell components

Figure 24 Interchangeable press die to produce thin strips of metal
Galvanostatic cycling was used to study the cycling behaviour of the electrolytes at the Li electrode. The use of symmetrical cells presents one main advantage: any complex process from another electrode material is removed, ensuring that the only response detected is related to the lithium electrode. Galvanostatic cycling consists of applying a square wave voltage to the cell and observing the cell response over time. With this technique, a Li electrode can be electrochemically tested for cycling, capacity fade, resistance and polarisation effects. It also allows the preparation of representative electrode surfaces for analysis. The cycling data are typically represented as a voltage-time plot, as shown in Figure 25, but also as a cycle number dependence of charge/discharge capacity for calculation of the average coulombic efficiency (CE).

Figure 25 Example of voltage-time profile during subsequent lithium plating/stripping processes on the WE in a Li | Li symmetrical cell containing 3.8 mol.kg\(^{-1}\) LiFSI in P\(_{1114}\)FSI as electrolyte at \(j = 1.5\) mA.cm\(^{-2}\), at 50 °C.

Galvanostatic cycling tests and electrochemical impedance spectroscopy (EIS) measurements were carried out using a Multichannel Potentiostat VMP3 (Bio-Logic) at 50°C in the oven. The current density for the Li metal plating/stripping was typically set to 1.5 (and 12) mA.cm\(^{-2}\) with cut-off voltages of 0.5 and -0.5 V \(v_s\) Li / Li\(^+\). During each cycle, 3 (and 6) mA.h.cm\(^{-2}\) was deposited on the Li substrate at various current densities and then stripped. The cells were thermally equilibrated at 50°C for 24 h before the beginning of each test.
2.2 Electrolyte characterisation

2.2.1 Water content

The water content of the electrolytes and neat IL was measured using a Model 831 Karl Fisher Coulometer (Metrohm) using Hydranal® Coulomat AG as the titrant. The standard error for the water content measurement was about ± 1 %.

2.2.2 Differential Scanning Calorimetry (DSC)

The phase behaviour (glass transition temperatures, melting temperatures, transition entropies and transition enthalpies) of the neat ILs and then the binary IL electrolyte solutions was analysed by using a differential scanning calorimeter (Mettler Toledo DSC1 instrument) with a cooling rate of 5 °C min⁻¹ and a heating rate of 10 °C min⁻¹. Cyclohexane analytical standard (99.5 %, Sigma Aldrich) was used to calibrate the instrument.

The temperature for each phase transition was determined from the onset on the heating scan (with a standard error of ± 0.2 °C) while the enthalpy was derived from integration of the peak area. Entropies were calculated by dividing the enthalpy by the onset temperature. For the glass transitions the midpoint of the peak was used as the glass transition temperature.

2.2.3 Density/Dynamic viscosity

Density measurements was carried out using a density/specific gravity meter (Anton Paar DMA5000) from 20 to 80 °C using 10 °C interval steps. This density meter uses the “oscillating U-tube principle” to determine the density of the liquids. The standard error for the measurements was ± 0.001 g.cm⁻³.

The viscosities of the RTILs were measured using a rolling-ball viscometer (Anton Paar Lovis 2000ME) from 20 to 80 °C using 10 °C interval steps, a 10mm long capillary with a diameter of 2.5 mm and an tilting angle of 60 °. The capillary was sealed thus preventing changes of the samples viscosity during the measurement due to moisture adsorption. The standard error for the viscosity measurement was ± 10 mPa.s.
2.2.4 Ionic conductivity (Electrochemical Impedance Spectroscopy)

Ionic conductivity describes the mobility of ions which can respond to a change of polarisation of an alternating field. From the dependence of this response the conductivity can be determined. Ionic conductivity was measured by AC (Alternating Current) impedance spectroscopy using a SP-200 Impedance/Frequency Response Analyser (Figure 26) over a temperature range of -40 to 120 °C at 10 °C intervals for the frequency range of 0.1 Hz - 1 MHz applying a voltage amplitude of 0.1 V. A custom-built dip-cell containing two platinum wires sheathed in glass (Monash Scientific, Australia), sealed with a rubber O-ring was used to carry out the measurements, as shown in Figure 27. The cell was placed into a cavity of a brass block, which was connected via a thermocouple to a Eurotherm 2240E temperature controller. The temperature was ramped at a steady state of 0.5 °C / min until the desired isothermal temperature was reached (+/- 0.3 °C for 20 min). The cell constant was determined using a standard solution of 0.01 M KCl at 25 °C. The resistances (Ω) were determined from the value of the real axis touchdown of the Nyquist plot, from which the conductivity (S.cm⁻¹) was calculated. The results are presented on a logarithm scale and therefore the errors are contained within the points.

Figure 26 Digital photo of the SP-200 Impedance/Frequency Response Analyser
2.2.5 Nuclear Magnetic Resonance (NMR) – Diffusion measurements

The self-diffusion properties of each ion including the lithium cation can be determined by diffusion NMR, considering each ion has different exclusive atoms. For example, in P1114FSI, hydrogen and carbon atoms are only located in the P1114+ cation while fluorine atoms are only present in the FSI anion, making the determination of diffusivity for each ionic species possible.

As the ionic conductivity is dependent on the temperature, when it does not follow the Arrhenius equation, the temperature dependence of conductivity can follow the Vogel-Tamann-Fulcher (VTF) equation (also called modified Arrhenius equation) as follows:

\[
\sigma(T) = AT^{-\frac{1}{2}}e^{-\frac{B}{T_0 - T}}
\]

(4)

where A is proportional to the ion concentration, B is called the pseudo activation energy. T0 is usually related to a temperature close Tg.
If the ion self-diffusion coefficient and bulk conductivity are combined, the contribution of each ion to the conductivity can be determined and the degree of ion dissociation in the RTIL can be estimated according to the Nernst–Einstein equation as follows:

\[
\Lambda_{NE} = \frac{N_A e^2 (D_+ + D_-)}{kT} = \frac{F^2 (D_+ + D_-)}{RT}
\]  

(5)

where \(\Lambda\) is the molar conductivity, \(N_A\) is the Avogadro’s number, \(e\) is the electric charge on each ion, \(D_+\) is the self-diffusion coefficient of the cation, \(D_-\) is the self-diffusion coefficient of the anion, \(k\) is the Boltzmann’s constant, \(F\) is the Faraday’s constant, \(R\) is the universal gas constant and \(T\) is the absolute temperature.

By calculating the ratio between the molar conductivity obtained by impedance spectroscopy (\(\Lambda_M\), bulk conductivity) and the one calculated with the Nernst-Einstein equation (\(\Lambda_{NE}\)), the degree of ion dissociation in the RTIL (\(\Lambda_M/\Lambda_{NE}\)) can be obtained. This is how Bayley et al.\(^2\) calculated the degree of ion dissociation for \(\text{C}3\text{mpyrTFSI}\) mixed with \(\text{LiTFSI}\); Yoon et al.\(^3\) also used the same method for \(\text{C}3\text{mpyrFSI}\) mixed with \(\text{LiFSI}\).

Pulse-field gradient stimulated echo (PFG-STE) diffusion measurements for \(^1\text{H}\), \(^7\text{Li}\) and \(^19\text{F}\) were performed on a Bruker Avance III 500 MHz Ultrashield wide bore spectrometer equipped with a 5 mm pulse-field gradient probe, following the method described by Bayley et al.\(^4\) The diffusivities of \(^1\text{H}\) and \(^19\text{F}\) nuclei were measured for the phosphonium cation and FSI anion respectively. \(^7\text{Li}\) spectra and diffusivities were also measured. Each sample was filled to a height of 50 mm in a 5 mm Schott E NMR tube in an Argon filled glove box and sealed with Teflon tape and a cap. Each sample was measured at room temperature (25 °C).

One main advantage of the diffusion measurements by NMR technique is that diffusion is chemically specific. Each diffusivity was measured at least twice and the error was relatively small in the range of 0.1 - 1 %.
A little more about the PFGSTE technique\textsuperscript{5-7}

NMR spectroscopy can provide detailed information on the structure and dynamics of a sample down to a molecular level. Specific nuclei can be targeted allowing local characterisation of specific regions of a molecule.

One particular aspect of the NMR technique is that it can follow the Brownian trajectories of spin bearing particles using strong magnetic field gradient pulses.\textsuperscript{8} Such an experiment is described as a pulse field gradient NMR (PFG-NMR) experiment and offers the possibility of measuring diffusion coefficients of specific nuclei in liquid systems. One of the best known PFG-NMR experiment is based on a stimulated spin echo (PFGSTE). In a PFGSTE experiment, the pulse sequence involves three $\Pi/2$ radiofrequency (RF) pulses as illustrated in Figure 28. This sequence is specifically designed for viscous systems and quadrupolar nuclei (e.g. $^7$Li).\textsuperscript{5} By applying a second $\Pi/2$ RF pulse as soon as the first one has finished the magnetisation is flipped back into the longitudinal plane where slower relaxation processes occur and this allows greater signal intensity.

![Figure 28 PFG-NMR diffusion experiment with stimulated spin echo (PGSTE) pulse sequence. Gradient pulses of length $\delta$ are separated by the diffusion time $\Delta$.\textsuperscript{5}](image)

2.2.6 Cyclic voltammetry

Cyclic Voltammetry (CV) was used to investigate the electrochemical stability of the electrolytes and the stability of lithium metal in the electrolytes. During the potential sweep, the potentiostat measured the current resulting from electrochemical reactions (consecutive to the applied potential). The cyclic voltammogram is a current response as a function of the applied potential.
Voltammetric experiments were performed using a BioLogic SP-200 potentiostat. All preparation and electrochemical measurements were performed in an Argon filled glove box. Cyclic voltammograms were obtained using a conventional three electrode arrangement (Figure 29).

A 1.0 mm glassy carbon working electrode (GC, ALS, distributed by BAS Inc., Japan) was used to determine the electrochemical window of the ionic liquid and a 1.5 mm nickel working electrode (Ni, ALS, distributed by BAS Inc., Japan) was used to study lithium cycling in the electrolytes. A platinum wire (APS, 99.95%) was used as the counter electrode. The reference electrode consisted of a silver wire immersed in a solution of the ionic liquid containing 10 mM silver triflate (AgOTf, 99.9 % purity, Aldrich™), separated from the bulk electrolyte by a glass frit, as reported by Snook, et al. It produced stable and reproducible measurements. The potentials were corrected versus ferrocene, which was cycled at the end of each set of measurements. The correction method is further detailed below.

Prior to each experiment, the working electrode was polished with 0.3 μm alumina (Buehler, Lake Bluff, IL) on a clean polishing cloth (Buehler), sequentially rinsed with distilled water, ethanol and then dried with lint-free tissue paper and finally dried in an oven at 70 °C (for one hour). For the reference electrode, the silver (Ag) wire was abraded with silicon carbide paper (P600 grit), then washed with ethanol and dried in the oven. The scan rate was 20 mV.s\(^{-1}\). Measurements were obtained at 25 ± 2 °C.
Table 11 presents the working electrode (WE) specifications from BAS Inc, Japan.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Outer diameter OD (mm)</th>
<th>Inner diameter ID (mm)</th>
<th>Surface area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>3.0</td>
<td>1.0</td>
<td>0.008</td>
</tr>
<tr>
<td>Ni</td>
<td>6.0</td>
<td>1.5</td>
<td>0.018</td>
</tr>
<tr>
<td>Pt</td>
<td>3.0</td>
<td>1.6</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Coulombic efficiencies were a useful and practical method to investigate the stability of lithium deposition and dissolution processes. The efficiency is defined as the ratio of oxidation charge (due to lithium dissolution from the electrode) divided by the reduction charge (due to lithium deposition onto the electrode). The standard error was ~ 5% based on multiple data sets.

Correction method and reference electrode

The method used was similar to the method suggested by Snook, et al. All preparation and electrochemical measurements were performed in an Ar filled glove box. As received P<sub>114</sub>FSI was mixed with 10 mM of silver trifluoromethanesulfonate (AgOTf, Sigma Aldrich™) for 1 hour until complete dissolution of the salt and used as a solution in the reference electrode. Glass compartments with an ultra-fine glass frit salt bridge at one end were filled with these solutions to prepare a reference electrode as shown in Figure 29. A (cyclopentadienyl)iron(II) (ferrocene, Sigma Aldrich™) was dissolved into the IL and stirred until complete dissolution at 50 °C to measure the Fc | Fc⁺ standard potential in the IL media.
Figure 30 Cyclic voltammogram (CV) of Fc | Fc⁺ redox couple in P111i4FSI

Figure 30 shows a Fc | Fc⁺ redox couple cyclic voltammogram at room temperature. Since the Fc | Fc⁺ redox potential is affected by the nature of IL, the measured potential was adjusted by the reported value as per Torriero et al. The Ag | AgOTf redox potential $E_m$ (which is the average of the oxidation ($E_{p^{ox}}$) and reduction ($E_{p^{red}}$) peak potentials [$E_m = \frac{(E_{p^{ox}} + E_{p^{red}})}{2}$]) in 10 mM AgOTf:P111i4FSI is -0.34 V vs. Fc | Fc⁺. The corrected potential was calculated according to the following equations:

$$E_{corrected\ vs.\ Ag\ |\ AgOTf} = E_{Fc\ |\ Fc^+\ vs.\ Ag\ |\ AgOTf} - E_{measured\ vs.\ Fc\ |\ Fc^+}$$

$$E_{corrected\ vs.\ Ag\ |\ AgOTf} = E_m$$

$$E_{Fc\ |\ Fc^+\ vs.\ Ag\ |\ AgOTf} = E_{Fc\ |\ Fc^+\ vs.\ SHE} - E_{Ag\ |\ Ag^+\ vs.\ SHE}$$

$$E_{Fc\ |\ Fc^+\ vs.\ Ag\ |\ AgOTf} = 0.64 - 0.8 = -0.16 \text{ V}$$

2.2.7 Chronoamperometry (CA)

Chronoamperometry (CA) was used to determine a critical parameter for a battery electrolyte, the lithium (Li) transference number. This parameter was determined for each electrolyte at ambient temperature. The experimental method was introduced by Bruce and Vincent. Further details about this parameter and experimental methods are provided in Chapter 6 of this thesis. As a summary, the chronoamperometry (CA) technique consists of the measurement of the current response to an applied potential step. A constant potential $E_0$ is applied for a duration $\Delta t$ and the current is measured.

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
The current-time response reflects the change of the concentration gradient in the vicinity of the surface. In this project the coin cells were polarised at 20 mV for 4 hours (3 times) to confirm consistency of the data acquired.

2.3 Surface characterisation: spectroscopic techniques

The interactions between the RTIL and the Li electrode surface were characterised using different spectroscopic techniques including Electrochemical impedance spectroscopy (EIS), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and Magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR).

2.3.1 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was used to characterise in-situ the Li metal surface impedance after fabrication of the coin cells. The interfacial resistance evolution of the Li metal electrode inside a coin cell was monitored via EIS using a Multi Potentiostat VMP3 (Bio-Logic). The spectra were detected between 50 mHz and 1 MHz with an amplitude of 0.1 V. They were analysed with the EC-Lab software (Z Fit v. 10.44) and the impedance was reported within 2% error. The obtained spectra were then fitted using an equivalent circuit proposed by Zugmann et al.13 (Figure 31). $R_1$ corresponds to the Ohmic resistance of the electrolyte. The sum of $R_2$ and $R_3$ refers to the semicircle shown in the Nyquist plots, which was interpreted as the “Li electrode surface resistance” ($R_{\text{surface}} = R_2 + R_3$) of both electrodes. The constant-phase elements $Q_2$ and $Q_3$ represent the capacitance.

![Figure 31 Equivalent electric circuit for the interpretation of the electrochemical impedance spectra](image-url)
A little bit more about electrochemical impedance spectroscopy (EIS)

The principle of an EIS measurement is the following: a small (typically 1 to 100 mV) AC excitation amplitude is applied to perturb a system from its equilibrium (in the present case, a Li cell) and the response (current through the cell) is measured. The response to this potential is an AC current signal.

The excitation signal has the following form:

\[ E_t = E_0 \sin(\omega t) \]  

(8)

where \( E_t \) is the potential at a time \( t \), \( E_0 \) the amplitude of the signal and \( \omega \) the angular frequency.

For a linear system, the response signal \( I_t \) is shifted by a phase \( \varphi \) and has a different amplitude \( I_0 \):

\[ I_t = I_0 \sin(\omega t + \varphi) \]  

(9)

According to Ohm’s law, the resistance of an element, defined as its ability to resist a flow of electrical current, is expressed as a ratio between a voltage \( E \) and a current \( I \):

\[ R \equiv \frac{E}{I} \]  

(10)

This relationship being limited to one circuit element (the ideal resistor), for more complex circuit elements a new parameter is introduced: the impedance, \( Z \). A similar expression to the Ohm’s law allows us to calculate the impedance of the system as:

\[ Z = \frac{E_t}{I_t} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \varphi)} \text{ where } Z_0 = \frac{E_0}{I_0} \]  

(11)

This relationship is valid only if a small amplitude is applied to ensure a linear relationship between the current and voltage.14

With Euler’s relationship, it is possible to express \( Z \) as a complex function:

\[ Z(\omega) = \frac{E_0 \exp(j\omega t)}{I_0 \exp(j\omega t)} = Z_0(cos\varphi + jsin\varphi) \]  

(12)
The impedance is then composed of a real part \( Z_{\text{real}} \) and an imaginary part \( Z_{\text{imaginary}} \):

\[
Z(\omega) = Z_{\text{real}} - jZ_{\text{imaginary}}
\]  

(13)

where \( j \) is an imaginary number.

The EIS data are usually represented as a Nyquist plot (Figure 32), where the measured impedance is plotted as the real \( Z_{\text{real}} \) vs. the imaginary \( Z_{\text{imaginary}} \) impedance. Each point represents the impedance at one frequency. A Bode plot can also be used to represent the data, where log \( |Z| \) and phase angle \( \phi \), are plotted against the angular frequency \( \omega \).

![Figure 32 An example of Nyquist plot and equivalent electric circuit](image)

Figure 32 shows an example of Nyquist plot for a Li | Li symmetrical cell over a frequency ranging from 50 mHz to 800 KHz. The plot can be used to measure phase angle of cell impedance which may be used to determine processes such as charge transfer and mass transfer processes, ionic conduction and interfacial charging.\(^{14}\)

The EIS data are commonly analysed by fitting them to an equivalent electric circuit (EEC). A Nyquist plot can then be associated to an EEC. An equivalent circuit allows us to describe an electrochemical reaction that takes place at the electrode/electrolyte interface and to interpret the electrical data of a system composed of resistances and capacitances. J. E. B. Randles proposed an equivalent circuit for modelling electrochemical reactions at an electrode interface.\(^{15}\)

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
The equivalent circuit included a resistance related to the reaction happening at the electrode (also called polarisation resistance, $R_2$) in parallel with a capacitance representing the double layer of the electrode surface ($C_2$). These elements were in series with a resistance associated with the electrolyte resistance ($R_1$), shown in Figure 33.

![Figure 33 Equivalent electric circuit of the simplified Randles cell](image)

In this project a number of EEC were applied to fit the EIS data of a typical Li $|$ Li symmetrical cell. Table 12 presents the various circuits, starting from the simplest circuit and then adding more components. The EIS data were fitted using the EC–Lab software (ZFit v.10.44). Before fitting, in order to help the algorithm to find the best values, it was necessary to use initial values as close as possible to the real ones. A randomisation is added before the fitting to select the most suitable set of parameter values. The most suitable set of parameter values are the values that yield the lower $\chi^2$ value. $\chi^2$ gives an estimation of the distance between the real data and the simulated data. The parameter $\chi / \sqrt{N}$ is a normalised expression of $\chi^2$, where $N$ is the number of points.

The impedance spectra (Nyquist and Bode spectra) of a Li $|$ Li symmetrical cell before cycling with the highly concentrated P$\text{[111]}\text{FSI}$-based electrolyte were fitted using these circuits. Figure 34 shows the fitting results obtained for the circuits applied and Table 13 gives an example of parameters obtained from the fitting results in the case of the circuit 2.
Table 12 Equivalent electric circuits and associated equations

<table>
<thead>
<tr>
<th>Circuit</th>
<th>Equivalent model</th>
<th>Equivalent equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>![Diagram 1]</td>
<td>$R_1 + \frac{C_2}{R_2} + \frac{C_3}{R_3}$</td>
</tr>
<tr>
<td>2</td>
<td>![Diagram 2]</td>
<td>$R_1 + \frac{Q_2}{R_2} + \frac{Q_3}{R_3}$</td>
</tr>
<tr>
<td>3</td>
<td>![Diagram 3]</td>
<td>$R_3 + \frac{Q_2}{R_2} + \frac{Q_3}{R_3} + W_4$</td>
</tr>
<tr>
<td>4</td>
<td>![Diagram 4]</td>
<td>$R_3 + \frac{Q_2}{R_2} + \frac{C_3}{R_3 + W_4}$</td>
</tr>
</tbody>
</table>

Figure 34 Various fitting results (and fit parameters) for EIS data acquired from a Li | Li symmetrical cell cycled in the highly concentrated P1114FSI-based electrolyte.
Table 13 An example of fitting results using circuit 2 for EIS data acquired from a Li
| Li symmetrical cell cycled in the highly concentrated P111i4FSI-based electrolyte

<table>
<thead>
<tr>
<th>Element</th>
<th>Freedom</th>
<th>Value</th>
<th>Unit</th>
<th>Error</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>Free(+)</td>
<td>6.328</td>
<td>Ohm</td>
<td>1.055</td>
<td>10.55</td>
</tr>
<tr>
<td>R₂</td>
<td>Free(+)</td>
<td>42.26</td>
<td>Ohm</td>
<td>1.039</td>
<td>10.39</td>
</tr>
<tr>
<td>Q₂ = CPE₂</td>
<td>Free(+)</td>
<td>0.00184</td>
<td>F.s⁻¹</td>
<td>1.321</td>
<td>13.21</td>
</tr>
<tr>
<td>a₂</td>
<td>Free(+)</td>
<td>0.7202</td>
<td></td>
<td>0.5719</td>
<td>5.719</td>
</tr>
<tr>
<td>R₃</td>
<td>Free(+)</td>
<td>56.52</td>
<td>Ohm</td>
<td>1.08</td>
<td>10.8</td>
</tr>
<tr>
<td>Q₃ = CPE₃</td>
<td>Free(+)</td>
<td>9.06E-06</td>
<td>F.s⁻¹</td>
<td>1.776</td>
<td>17.76</td>
</tr>
<tr>
<td>a₃</td>
<td>Free(+)</td>
<td>0.8038</td>
<td></td>
<td>0.591</td>
<td>5.91</td>
</tr>
</tbody>
</table>

Chi-Squared $\chi^2$: 0.018

$\chi^2 / \sqrt{(N)}$: 0.019

Mode: Run Fitting / Freq. Range (0.1 - 200000)

Maximum Iterations: 100

Type of Fitting: Randomize + Simplex

Type of Weighting: Calc-Modulus

The circuit 1 represents the simplest RC model. It only consists of solution resistance
and surface impedance, making it easy to give a physical meaning to each component.
However, Figure 34 shows that this circuit does not fit the EIS data well. This confirms
that the overall resistance of the cell consists of more than one type of resistance (e.g.
diffusion, charge transfer resistance, non-ideal surface).

The circuit 2 uses constant phase elements instead of ideal capacitors, this improved
the fitting results.

The circuit 3 adds a Warburg diffusion component to better fit the low frequency
region, however in this case the fitting results were not improved.
The circuit 4 was introduced by Lewandowski\textsuperscript{17} and Lane\textsuperscript{18}. The main purpose of the use of this circuit was to determine the charge transfer resistance ($R_3$) and SEI resistance ($R_2$). However this model is valid only in the case of SEI formation characterised by a homogeneous formation and even distribution on the Li surface. In this project, specific models were chosen for each case but according to the fitting results the circuit 2 was chosen to fit most EIS data.

2.3.2 Scanning electron microscopy (SEM)

The first SEM images of Li metal surfaces were acquired with a Philips XL – 20 microscope and the surfaces were hermetically loaded into the microscope antechamber using an Ar filled glove bag (Sigma Aldrich), as shown in Figure 35, until the JEOL JSM-IT300 microscope was commissioned in Burwood.

In order to investigate the surface of the Li electrodes after the cycling experiments, cycled coin cells were dissembled to recover Li metal disks for further characterisation by SEM. Prior to analysis the electrodes were rinsed with dimethyl carbonate (DMC, 99\% Sigma Aldrich) two times to remove residual IL electrolytes and then dried under vacuum in the chamber of the glove box for 30 min.\textsuperscript{19} SEM images of the Li electrodes for both surface and cross-sections were obtained with a JEOL JSM-IT300 at an accelerated voltage of 2 kV. Cross-sections of Li metal were prepared by vertically cutting the Li electrodes with a surgical blade. To avoid electrode contamination or side reactions of the Li electrodes with atmospheric moisture and oxygen, the samples were transferred from the glove box to the SEM in a sealed stainless steel vessel filled with Argon, as shown in Figure 37. The vessel was introduced into the SEM via a load-lock chamber purposely designed for loading air-sensitive samples into the SEM chamber (Figure 37).
Chapter 2

Investigation of phosphonium bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Figure 35 Digital images of the antechamber of a Philips XL-20 SEM with an Ar filled glove bag setup and sample stage with a Li metal electrode

Figure 36 Digital image of a JEOL JSM-IT300 SEM

Figure 37 Digital images of the transport vessel (left) and the load-lock chamber from the JEOL JSM-IT300 SEM
2.3.3 Attenuated total reflection – Fourier transform infrared spectroscopy (ATR-FTIR)

Fourier transform infrared (FTIR) spectroscopy gives information on functional groups. This technique is mostly applied to organic compounds but can also be important for non-metallic inorganic compounds. Detailed analysis of an infra-red spectrum contains information on molecule structure and symmetry. Covalently bound atoms vibrate with certain frequencies (thermal motion). The energy of the vibration lies in the range of infra-red light (400 – 4000 cm\(^{-1}\)). Certain functional group fragments vibrate with specific frequencies, thus absorbing infra-red light of that energy (vibrational excitation).

Infrared spectra were acquired on a Perkin Elmer IR 101820 series spectrometer using the Spectrum (v.10.4) software. The instrument is shown in Figure 38. Ex situ attenuated total reflectance (ATR) spectra were obtained using a diamond in mid-IR range (4000 - 450 cm\(^{-1}\)). The rinsed and dried electrodes were hermetically sealed between two glass microscope slides inside the glove box prior to being transferred and loaded onto the sample stage with a minimal exposure to air. Firm pressure was applied to press Li disks against the diamond window of the sample stage. All spectra were recorded with a 4 cm\(^{-1}\) resolution and 16 scans.

Figure 38 Digital image of the Perkin Elmer IR 101820 series spectrometer
2.3.4 Synchrotron X-ray photoelectron spectroscopy (SXR XPS)

X-ray absorption spectroscopy (XAS) is a powerful technique that allows identification of chemical species present on a surface. XAS measurements were conducted at the soft x-ray beamline (Australian Synchrotron) primarily for XAS of low atomic number elements (e.g. Li) and XPS. In this project the beamline was used for XPS measurements. Soft x-rays are generally understood to be x-rays in the energy range 100 – 3000 eV to examine core electron levels. An electromagnetic spectrum is provided in Figure 39. Soft x-rays are well suited to characterising surfaces and near-surface interfacial layers.

![Electromagnetic spectrum](http://www.coe.berkeley.edu/AST/sxr2009)

Principle of XPS

The XPS technique is based on the photoelectric effect enunciated by Einstein\(^\text{20}\) in 1905:

\[
E = hv \tag{14}
\]

where \(h\) is the Planck constant (6.62 x 10\(^{-34}\) J.s), \(v\) is the frequency of the radiation (Hz).

“There is a threshold in frequency below which light, regardless of intensity, fails to eject electrons from a metallic surface.”

In photoelectron spectroscopy, the kinetic energy (KE) distribution of the emitted photoelectrons can be measured using an appropriate electron energy analyser and a photoelectron spectrum is recorded.
By using photoionisation and energy-dispersive analysis of the emitted photoelectrons, the composition and electronic state of the surface region of a sample can be investigated. The overall photoelectron process, as shown in Figure 40, can be summarised as follows, for an element of the periodic table A:

\[ A + h\nu = A^+ + e^- \quad (15) \]

(i) The principle of conservation of energy requires that:

\[ E(A) + h\nu = E(A^+) + E(e^-) \quad (16) \]

(ii) As the energy of the electron is only present as kinetic energy (KE), the previous equation can be rearranged to give the following expression of the KE of the photoelectron:

\[ E(e^-) = KE(e^-) = h\nu - [E(A^+) - E(A)] \quad (17) \]

(iii) The last term in brackets represents the difference in energy between the ionised and neutral atoms, it is known as binding energy (BE). The final equation is:

\[ KE = h\nu - BE \quad (18) \]

Figure 40 Ionisation process in an isolated atom (retrieved from D. Attwood’s lecture notes, http://www.coe.berkeley.edu/AST/sxr2009 in April 2016)
Experimental details

For all XPS experiments, careful precautions were taken in order to avoid moisture/air exposure of samples during transfer. Samples were transferred to the spectrometer via a hermetic transfer vacuum suitcase (as shown in Figure 41) encapsulated in the glovebox and opened in the vacuum preparation chamber (at the Synchrotron facility). The binding energy scale was calibrated from the aliphatic hydrocarbon C 1s peak at 285.0 eV. The samples were mounted on a XPS sample stud using conductive carbon adhesive tape and placed in the vacuum suitcase.

Soft X-ray photoelectron spectroscopic measurements were carried out at the Australian synchrotron facility (Figure 42 and Figure 43), where the usable photon energies range from 100 to 2500 eV.21 Photons were monochromatised by a Reixs plane grating monochromator based upon the SX700 monochromator design developed at the Berlin synchrotron BESSY (manufactured by FMB Berlin). The photoelectron kinetic energies (KE) were measured using a Phoibos 100 / 150 analyser. Because of the low photon energies, measurements were conducted so that the same photoelectron K.E was used for all probe elements. Survey spectra were acquired at 20 eV pass energy and 0.5 energy step. High resolution region spectra were acquired at 10 eV pass energy and 0.05 energy step. For high resolution region spectra, the KE was selected at 100 eV above the BE corresponding to the same analysis depth for all spectra. No charge neutraliser was used during the measurements. The pressure in the analysis chamber was about 10^{-10} mbar. Instrument operation was performed using the XPS software (SpecsLab) available at the Australian Synchrotron.

XPS data were analysed using the CASAXPS software (v. 2.3.13). Relative sensitivity factors (RSF) were taken from the Kratos Library and used to determine relative atomic percentages from survey and high-resolution scans of the most intense photoelectron peak for each element. Peak areas were measured after performing a two-point Shirley background subtraction. A pseudo voigt Gaussian:Lorentzian algorithm (70:30 %) was used to fit the peaks to obtain quantitative results. The fit produces an estimated ± 10 % error in the atomic concentration determined for each peak.
Figure 41 Digital images of the vacuum suitcase (sealed position on the left, open position on the right)

Figure 42 Digital image of the Soft X-ray photoelectron spectroscopy beamline at the Australian Synchrotron
2.3.5 Magic angle spinning NMR (MAS NMR)

Liquid state NMR spectra have high spectral resolution because Brownian motion of molecules in their liquid state removes chemical anisotropy while in their solid state there is no such motion which leads to broadening in peaks and spectral resolution becomes poor. MAS (magic angle spinning) in solid state NMR removes an extent of chemical anisotropy which enhances spectral resolution.\textsuperscript{22-23}

MAS NMR is a technique for obtaining high resolution NMR data from solids. For a thorough introduction to this technique the reader is referred to the existing literature.\textsuperscript{23-25} The experiment consists of rotating the sample rapidly around an axis which itself is oriented at the magic angle with respect to the applied magnetic field $B_0$, as illustrated in Figure 44. This sets the time averaged orientation of all the NMR interactions to the magic angle too. So while the interactions are still present at any one instant, over one complete rotation of the sample their net effect is averaged to zero: the interactions are refocused by the sample rotation, just like the chemical shift evolution is refocused by a spin echo pulse sequence (liquid NMR).
All MAS-NMR experiments were carried out at the CNRS-IMN institute (Nantes, France). Li metal electrodes used for the $^7\text{Li}$, $^{31}\text{P}$ and $^{19}\text{F}$ MAS NMR were removed from the coin cell inside the glove box. The deposit on the Li electrode was scraped off the Li substrate with a stainless steel spatula. A 50:50 (wt %) mixture of deposit: alumina powder (Al$_2$O$_3$ AC300) was prepared for the NMR analysis and placed in a cylindrical 2.5 mm diameter zirconia rotor without being washed. $^7\text{Li}$, $^{31}\text{P}$ and $^{19}\text{F}$ MAS NMR experiments were carried out on a Bruker avance-500 spectrometer ($B_0 = 11.8$T, Larmor frequencies $\nu_0(^7\text{Li}) = 194$ MHz, $\nu_0(^{31}\text{P}) = 202$ MHz, $\nu_0(^{19}\text{F}) = 470$ MHz). MAS spectra were obtained by using a Bruker MAS probe. Spinning frequencies up to 25 kHz were used. $^7\text{Li}$ and $^{31}\text{P}$ NMR spectra were acquired with a single pulse sequence and a recycle time of 30s. $^{19}\text{F}$ NMR spectra were acquired using a Hahn echo sequence to discard the significant contribution from the probe signal and a recycle time of 30s. All the spectra were normalised taking into account the number of scans, the receiver gain and the mass of the sample. Integrated intensities were determined by using spectral simulation.
2.4 References


Chapter 2

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries


Chapter 3  Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content
3.1 Introduction

This first research chapter describes the physicochemical and electrochemical properties of ionic liquid (IL) electrolytes based on the IL trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide (P$_{111i4}$FSI) and a range of lithium (Li) salt concentrations. This IL exhibits a higher conductivity and lower viscosity than other phosphonium and ammonium bis(fluorosulfonyl)imide compounds; it is shown that the IL electrolyte containing the highest amount of Li salt exhibits a high Li$^+$ diffusivity and outstanding electrochemical properties at this range of viscosity and conductivity. Only recently in 2013 a highly concentrated IL electrolyte based on the N-propyl-N-methylpyrrolidinium cation and the same anion used in this project (FSI) has been regarded as potential electrolytes for lithium batteries. There are no reports on the use of a highly concentrated IL electrolyte based on a phosphonium cation at a similar Li salt content.

Traditionally a relatively low Li salt concentration dissolved into an IL has been used as an optimal electrolyte composition for lithium cycle ability: commonly used ILs are more viscous and less conductive than the traditional organic carbonate electrolytes. Commercially available Li batteries typically use electrolytes made of a Li salt dissolved into organic carbonate solvents at a concentration ranging from 0.5 to 1.2 M. These typical concentrations give the optimum cell performance, related to optimal transport properties (conductivity and viscosity). However in an IL electrolyte, the determination of the optimal Li salt concentration still remains unclear and this concentration and the Li$^+$ transport mechanism are significantly critical to the overall cell performance. A number of publications have reported on the properties of phosphonium ILs typically using the same range of Li salt concentration.$^{1-6}$

In this chapter, a first section briefly describes the reasons for the selection of the IL trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide (P$_{111i4}$FSI). The second section consists of one publication investigating the effect of Li salt concentration in the P$_{111i4}$FSI ionic liquid on the thermal behaviour, transport properties, ionicity and lithium electrochemistry of the electrolytes using different physical measurements and spectroscopic techniques. The electrochemical performance dependence on the Li salt concentration is also investigated to determine the optimal salt concentration and its relationship to future cell performance.
The aim is to better understand the influence of the Li salt concentration on the Li$^+$ ion transport mechanism in the IL electrolyte. The final section further characterises the electrolyte solutions as a function of Li salt concentration by FTIR analysis.

3.2 Results

3.2.1 Selection of a promising ionic liquid

The chemical structures of four phosphonium ILs sourced from Cytec Solvay Group are shown in Figure 45.

Table 14 presents a summary of the physical properties determined for these ILs.

![Chemical structures of four phosphonium ionic liquids](image)

Figure 45 Chemical structures of four phosphonium ionic liquids: (a) trimethyl isobutyl phosphonium bis(fluorosulfonyl)imide (P_{111i4FSI}); (b) a mixture of the FSI$^-$ anion and 4 phosphonium cations (P_{mixFSI}); (c) triethyl cyanopropyl phosphonium bis(trifluoromethanesulfonyl)imide (P_{222(CH2)3CNTFSI}) and (d) 3,7-dimethyloctane, ethyl, hexyl phosphonium bis(trifluoromethanesulfonyl)imide (P_{cytop17026TFSI})
Table 14 Summary of physical properties of neat phosphonium ionic liquids

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>( T_g / \degree C ) (± 0.2)</th>
<th>( T_c / \degree C ) (± 0.2)</th>
<th>( T_m / \degree C ) (± 0.2)</th>
<th>( \sigma / \text{mS.cm}^{-1} ) (± 0.1)</th>
<th>( d / \text{g.cm}^{-3} )</th>
<th>( \eta / \text{mPa.s} ) (± 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{P}_{111}i4\text{FSI} )</td>
<td>-</td>
<td>-17.3</td>
<td>12.3</td>
<td>6.4</td>
<td>1.303</td>
<td>42</td>
</tr>
<tr>
<td>( \text{P}_{\text{mix}}\text{FSI} )</td>
<td>-49.6</td>
<td>4.2</td>
<td>1.289</td>
<td></td>
<td></td>
<td>49</td>
</tr>
<tr>
<td>( \text{P}_{222(\text{CH}2)3\text{CN}}\text{TFSI} )</td>
<td>-71.9</td>
<td>-</td>
<td>-</td>
<td>0.46</td>
<td>1.392</td>
<td>275</td>
</tr>
<tr>
<td>( \text{P}_{\text{cytop}17026}\text{TFSI} )</td>
<td>-48.7</td>
<td>-</td>
<td>-</td>
<td>0.082</td>
<td>1.327</td>
<td>875</td>
</tr>
</tbody>
</table>

\( T_g \): glass transition. \( T_c \): crystallisation point. \( T_m \): melting point. \( \sigma \): conductivity at 20 °C. \( d \): density at 20 °C. \( \eta \): dynamic viscosity at 20 °C.

\( ^b \)Electrochim Acta 2016, 202, 100-109

Figure 46 presents the temperature dependence of the dynamic viscosity and ionic conductivity of four neat ionic liquids. An important point to note from Figure 46 (b) is the higher conductivity of the FSI-based systems compared to the TFSI-based systems. Two candidate systems were selected for detailed characterisation due to their attractive transport and electrochemical properties (low viscosity/high ionic conductivity and good electrochemical stability). Particular interest in the low temperature conductivity of \( \text{P}_{\text{mix}}\text{FSI} \) (below 0°C) is noted (Figure 46 (b)), suggesting that this IL mixture has a much lower melting point than that of \( \text{P}_{111}i4\text{FSI} \) (later confirmed using DSC analysis), an important feature for application in practical devices.

Of these two ionic liquids, the IL \( \text{P}_{111}i4\text{FSI} \) with low dynamic viscosity and high conductivity was selected for further investigation. The IL \( \text{P}_{\text{mix}}\text{FSI} \) also presented very attractive transport properties, however for intellectual property reasons the work in this thesis focuses on the use of the IL \( \text{P}_{111}i4\text{FSI} \). The maximum solubility of LiFSI in this IL at room temperature was 4.0 mol.kg\(^{-1}\) of LiFSI in \( \text{P}_{\text{mix}}\text{FSI} \). The electrochemical and physicochemical properties of \( \text{P}_{\text{mix}}\text{FSI} \) – LiFSI mixtures (up to 3.3 mol.kg\(^{-1}\)) followed the same trend as those based on the IL \( \text{P}_{111}i4\text{FSI} \). They are presented in the appendix section at the end of this chapter.
Figure 46 (a) Dynamic viscosity of 4 phosphonium-based ionic liquids over a temperature range from 30 to 80 °C; (b) Ionic conductivity of 4 phosphonium-based ionic liquids over a temperature range from -20 to 120 °C.

3.2.2 Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content

This section consists of a publication (including supplementary information) published by the Royal Society of Chemistry (RSC) in the Physical Chemistry Chemical Physics (PCCP) journal. The publication is available online at www.rsc.org/pccp. The reader is invited to go to the next page.

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
# AUTHORSHIP STATEMENT

1. Details of publication and executive author

<table>
<thead>
<tr>
<th>Title of Publication</th>
<th>Publication details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content</td>
<td>Phys. Chem. Chem. Phys., 2015,17, 8706-8713 DOI: 10.1039/C5CP00205B</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name of executive author</th>
<th>School/Institute/Division if based at Deakin; Organisation and address if non-Deakin</th>
<th>Email or phone</th>
</tr>
</thead>
<tbody>
<tr>
<td>G.M.A. GIRARD</td>
<td>Institute for Frontier Materials (IFM), Deakin University, Burwood, Australia</td>
<td><a href="mailto:ggirard@deakin.edu.au">ggirard@deakin.edu.au</a></td>
</tr>
</tbody>
</table>

2. Inclusion of publication in a thesis

<table>
<thead>
<tr>
<th>Is it intended to include this publication in a higher degree by research (HDR) thesis?</th>
<th>Yes / No</th>
<th>If Yes, please complete Section 3 If No, go straight to Section 4.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. HDR thesis author’s declaration

<table>
<thead>
<tr>
<th>Name of HDR thesis author if different from above. (If the same, write “as above”)</th>
<th>School/Institute/Division if based at Deakin</th>
<th>Thesis title</th>
</tr>
</thead>
<tbody>
<tr>
<td>As above</td>
<td>Institute for Frontier Materials (IFM), Deakin University, Burwood, Australia</td>
<td>Investigation of phosphonium bis(fluorosulfonyl)imide based ionic liquid electrolytes for lithium batteries</td>
</tr>
</tbody>
</table>

If there are multiple authors, give a full description of HDR thesis author’s contribution to the publication (for example, how much did you contribute to the conception of the project, the design of methodology or experimental protocol, data collection, analysis, drafting the manuscript, revising it critically for important intellectual content, etc.)

Extent of contribution: 90 %
Solution preparation, water content, DSC, viscosity, density, conductivity (electrochemical impedance spectroscopy), diffusion NMR and cyclic voltammetry.
Data analysis and manuscript writing.

I declare that the above is an accurate description of my contribution to this paper, and the contributions of other authors are as described below.

<table>
<thead>
<tr>
<th>Signature and date</th>
<th>24-Jun-2016</th>
</tr>
</thead>
</table>
4. Description of all author contributions

<table>
<thead>
<tr>
<th>Name and affiliation of author</th>
<th>Contribution(s) (for example, conception of the project, design of methodology or experimental protocol, data collection, analysis, drafting the manuscript, revising it critically for important intellectual content, etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. Hilder</td>
<td>Project initiation, key ideas, editing, experiment planning.</td>
</tr>
<tr>
<td>H. Zhu</td>
<td>Diffusion NMR experiments, experiment planning.</td>
</tr>
<tr>
<td>D. Nucciarone</td>
<td>Project initiation, key ideas, editing, experiment planning.</td>
</tr>
<tr>
<td>K. Whitbread</td>
<td>Project initiation, key ideas, editing, experiment planning.</td>
</tr>
<tr>
<td>S. Zavorine</td>
<td>Synthesis of materials. Project initiation, key ideas, editing, experiment planning.</td>
</tr>
<tr>
<td>M. Moser</td>
<td>Project initiation, key ideas, editing, experiment planning.</td>
</tr>
<tr>
<td>M. Forsyth</td>
<td>Project initiation, key ideas, editing, experiment planning.</td>
</tr>
<tr>
<td>D.R. MacFarlane</td>
<td>Project initiation, key ideas, editing, experiment planning.</td>
</tr>
<tr>
<td>P.C. Howlett</td>
<td>Project initiation, key ideas, editing, experiment planning.</td>
</tr>
</tbody>
</table>
5. Author Declarations
I agree to be named as one of the authors of this work, and confirm:
i. that I have met the authorship criteria set out in the Deakin University Research Conduct Policy,
ii. that there are no other authors according to these criteria,
iii. that the description in Section 4 of my contribution(s) to this publication is accurate,
iv. that the data on which these findings are based are stored as set out in Section 7 below.

If this work is to form part of an HDR thesis as described in Sections 2 and 3, I further
v. consent to the incorporation of the publication into the candidate’s HDR thesis submitted to Deakin
University and, if the higher degree is awarded, the subsequent publication of the thesis by the
university (subject to relevant Copyright provisions).

<table>
<thead>
<tr>
<th>Name of author</th>
<th>Signature*</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. Hilder</td>
<td>Matthias Hilder</td>
<td>24/06/2016</td>
</tr>
<tr>
<td>H. Zhu</td>
<td></td>
<td>24/06/2016</td>
</tr>
<tr>
<td>D. Nucciarone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K. Whitbread</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S. Zavorine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M. Moser</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M. Forsyth</td>
<td></td>
<td>24/06/2016</td>
</tr>
<tr>
<td>D.R. MacFarlane</td>
<td></td>
<td>24/06/2016</td>
</tr>
<tr>
<td>P.C. Howlett</td>
<td></td>
<td>24/06/2016</td>
</tr>
</tbody>
</table>

6. Other contributor declarations
I agree to be named as a non-author contributor to this work.

<table>
<thead>
<tr>
<th>Name and affiliation of contributor</th>
<th>Contribution</th>
<th>Signature* and date</th>
</tr>
</thead>
</table>

* If an author or contributor is unavailable or otherwise unable to sign the statement of authorship, the Head of Academic Unit may sign on their behalf, noting the reason for their unavailability, provided there is no evidence to suggest that the person would object to being named as author.
5. Author Declarations
I agree to be named as one of the authors of this work, and confirm:

I. that I have met the authorship criteria set out in the Deakin University Research Conduct Policy,

II. that there are no other authors according to these criteria,

III. that the description in Section 4 of my contribution(s) to this publication is accurate,

IV. that the data on which these findings are based are stored as set out in Section 7 below.

If this work is to form part of an HDR thesis as described in Sections 2 and 3, I further

V. consent to the incorporation of the publication into the candidate’s HDR thesis submitted to Deakin University and, if the higher degree is awarded, the subsequent publication of the thesis by the university (subject to relevant Copyright provisions).

<table>
<thead>
<tr>
<th>Name of author</th>
<th>Signature*</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. Hilder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H. Zhu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D. Nucelarone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K. Whittbreed</td>
<td>Whittbreed</td>
<td>06/30/2016</td>
</tr>
<tr>
<td>S. Zavorine</td>
<td>Zavorine</td>
<td>06/30/2016</td>
</tr>
<tr>
<td>M. Moser</td>
<td>Moser</td>
<td>06/28/2016</td>
</tr>
<tr>
<td>M. Forsych</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D.R. MacFarlane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P.C. Howlett</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Other contributor declarations
I agree to be named as a non-author contributor to this work.

<table>
<thead>
<tr>
<th>Name and affiliation of contributor</th>
<th>Contribution</th>
<th>Signature* and date</th>
</tr>
</thead>
</table>

* If an author or contributor is unavailable or otherwise unable to sign the statement of authorship, the Head of Academic Unit may sign on their behalf, noting the reason for their unavailability, provided there is no evidence to suggest that the person would object to being named as author.
5. Author Declarations
I agree to be named as one of the authors of this work, and confirm:

i. that I have met the authorship criteria set out in the Deakin University Research Conduct Policy,
ii. that there are no other authors according to these criteria,
iii. that the description in Section 4 of my contribution(s) to this publication is accurate,
iv. that the data on which these findings are based are stored as set out in Section 7 below.

If this work is to form part of an HDR thesis as described in Sections 2 and 3, I further
v. consent to the incorporation of the publication into the candidate’s HDR thesis submitted to Deakin
University and, if the higher degree is awarded, the subsequent publication of the thesis by the
university (subject to relevant Copyright provisions).

<table>
<thead>
<tr>
<th>Name of author</th>
<th>Signature*</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. Hilder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H. Zhu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K. Whitbread</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S. Zavorine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M. Moser</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M. Forsyth</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D.R. MacFarlane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P.C. Howlett</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Other contributor declarations
I agree to be named as a non-author contributor to this work.

<table>
<thead>
<tr>
<th>Name and affiliation of contributor</th>
<th>Contribution</th>
<th>Signature* and date</th>
</tr>
</thead>
</table>

*If an author or contributor is unavailable or otherwise unable to sign the statement of authorship, the Head of Academic Unit may sign on their behalf, noting the reason for their unavailability, provided there is no evidence to suggest that the person would object to being named as author.
7. Data storage

The original data for this project are stored in the following locations. (The locations must be within an appropriate institutional setting. If the executive author is a Deakin staff member and data are stored outside Deakin University, permission for this must be given by the Head of Academic Unit within which the executive author is based.)

<table>
<thead>
<tr>
<th>Data format</th>
<th>Storage Location</th>
<th>Date lodged</th>
<th>Name of custodian if other than the executive author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardcopy (laboratory book)</td>
<td>Building HI, Deakin Burwood Campus</td>
<td>01-Jan-2014</td>
<td></td>
</tr>
<tr>
<td>Digital</td>
<td>IFM-ACES share drive</td>
<td>01-Jan-2014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ifm-aces (\cifs-m.its.deakin.edu.au)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lab-data\Gaetan folder</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This form must be retained by the executive author, within the school or institute in which they are based.

If the publication is to be included as part of an HDR thesis, a copy of this form must be included in the thesis with the publication.
Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content†

G. M. A. Girard, a M. Hilder, a H. Zhu, b D. Nucciarone, b K. Whitbread, b S. Zavorine, b M. Moser, b M. Forsyth, a D. R. MacFarlane c and P. C. Howlett* a

Electrolytes of a room temperature ionic liquid (RTIL), trimethyl(isobutyl)phosphonium (P111i4) bis-(fluorosulfonyl)imide (FSI) with a wide range of lithium bis(fluorosulfonyl)imide (LiFSI) salt concentrations (up to 3.8 mol kg−1 of salt in the RTIL) were characterised using a combination of techniques including viscosity, conductivity, differential scanning calorimetry (DSC), electrochemical impedance spectroscopy (EIS), nuclear magnetic resonance (NMR) and cyclic voltammetry (CV). We show that the FSI-based electrolyte containing a high salt concentration (e.g. 1:1 salt to IL molar ratio, equivalent to 3.2 mol kg−1 of LiFSI) displays unusual transport behavior with respect to lithium ion mobility and promising electrochemical behavior, despite an increase in viscosity. These electrolytes could compete with the more traditionally studied nitrogen-based ionic liquids (ILs) in lithium battery applications.

Introduction

Sustainability of energy supplies has become one of the main challenges of our society. Due to the necessity of moving away from fossil fuels and the growing importance of renewable energies, worldwide developments have identified ionic liquids1,2 as a new potential class of electrolyte materials, able to support a number of sustainable energy related applications, including rechargeable lithium batteries.1–5 Ionic liquid (IL) is the accepted term for low-melting salts, typically melting below 100 °C and ideally below room temperature, resulting from weak electrostatic interactions of the mainly organic ions (in contrast to high melting inorganic salts with strong electrostatic interactions).6–8 Ionic liquid (IL) is the accepted term for low-melting salts, typically melting below 100 °C and ideally below room temperature, resulting from weak electrostatic interactions of the mainly organic ions (in contrast to high melting inorganic salts with strong electrostatic interactions).6–8 If molten at room temperature, they are typically referred to as room temperature ionic liquids (RTILs). RTILs1 are attractive for a wide range of applications including electrochemical devices. An important example of an energy storage alternative is lithium batteries. State of the art electrolytes pose serious safety concerns as they are typically made of the volatile, flammable, and toxic solvents and lithium hexafluorophosphate (LiPF6). Hydrogen fluoride (HF) which is easily generated from LiPF6 has also detrimental effect on battery performance.

For these reasons, there are ongoing efforts to find alternative solvents and salts.

Ionic liquids not only support the chemistry of lithium batteries, but ideally also have the potential to improve their performance, especially with respect to cycle life.1,7–10 Certain ionic liquids also offer a unique suite of properties such as non-flammability, non-volatility, green solvent alternatives, high electrochemical and thermal stability which translates into enhanced safety.

While ILs containing nitrogen-based cations have undergone extensive investigation,1,2,5,7,13–14 only recently there has been interest in phosphonium ionic liquids in this context.15,16 A number of these alternative ILs are available on a large scale17 and show remarkable properties which are essential for electrolyte applications such as superior electrochemical stability,18 thermal stability,18 ionic conductivity18,19 and low vapor pressure.20 Recent studies have shown that many properties of phosphonium bis(fluorosulfonylimide) (FSI) based ILs are superior to the analogous ammonium derivatives, including improved transport properties even at sub-ambient temperature.15,19

Lowering the viscosity of RTILs is one of the major requirements for electrolyte applications. Due to the large cations used, the traditional phosphonium RTILs tended to have high viscosities, so efforts to lower viscosity continue to be undertaken. Only recently the properties of more promising ILs have been reported by Tsunashima et al.15 They designed smaller cations such as trimethyl(propyl)phosphonium bis(fluorosulfonylimide) (P1113FSI) (melting point: 0 °C) and trimethyl(methoxymethyl)phosphonium bis(fluorosulfonylimide) (P111(1O1)FSI),

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cp00205b

a Institute for Frontier Materials (IFM), Deakin University, Burwood, Victoria 3125, Australia. E-mail: patrick.howlett@deakin.edu.au
b Cytec Canada Inc., Niagara Falls, Canada
c School of Chemistry, Monash University, Victoria 3800, Australia

Received 14th January 2015, Accepted 13th February 2015
DOI: 10.1039/c5cp00205b
www.rsc.org/pccp

© the Owner Societies 2015

Published on 17 February 2015. Downloaded by Deakin University on 04/03/2015 23:59:28.
but did not report the effect of lithium concentration on the ion transport mechanism in the electrolytes. The redox process at the anode is believed to dominate the overall performance of lithium batteries. Therefore it is necessary to study the migration of Li$^+$ ions in the electrolyte and better understand the mechanism of lithium transport in a phosphonium IL electrolyte.

In this present study, we investigate a further, novel member of this family of phosphonium ionic liquids, trimethyl-(isobutyl)phosphonium bis[(fluorosulfonyl)imide (P$_{1114}$FSI), prepared via a halide-free synthesis route (see ESI†). This has been mixed with various amounts of lithium bis[(fluorosulfonyl)imide (LiFSI) as a potential electrolyte for lithium secondary batteries. The LiFSI has high solubility in this IL and mixtures containing 1:1 mol ratio of cations are easily obtained. The properties of the formulated electrolytes (including density, viscosity, thermal behavior, ionic conductivity and electrochemical stability) are presented.

## Experimental

### Materials and electrolyte preparation

The ionic liquid trimethyl-(isobutyl)phosphonium bis[(fluorosulfonyl)imide (P$_{1114}$FSI, Fig. 1) was provided by Cytec Canada Inc. with >99.5% purity. The structure and purity were confirmed by $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR. LiFSI (Solvionic, France) was used without further purification.

Initially, the binary IL electrolyte mixtures with LiFSI were prepared by adding and dissolving the appropriate amounts (0.5–3.8 mol kg$^{-1}$) followed by drying under vacuum for 48 hours at 80 °C in the presence of sodium hydride (NaH) until the water content was below 50 ppm (determined by Karl Fischer titration analysis).

The maximum concentration of LiFSI in this IL was determined by sequential additions of the salt, with stirring at 80 °C for 48 h, until undissolved salt could be observed visually. The saturated solution corresponds to the solution in which the additional lithium salt could not be dissolved at room temperature (25 °C). Table 1 lists the concentrations of each electrolyte and the molar ratio of each ion in solution. The highest Li salt concentration achieved resulting in a saturated solution at 25 °C, is 3.8 mol kg$^{-1}$ (55 mol% of Li salt in the IL).

### Water content

The water content of the electrolytes and neat IL was measured using a Model 831 Karl Fisher Coulometer (Metrohm) using Hydranal® Coulomat AG as the titrant.

### Differential Scanning Calorimetry (DSC)

The phase behavior (glass transition temperatures, melting temperatures, transition entropies and transition enthalpies) of the neat ILs and then the binary IL electrolyte solutions was analysed by using a differential scanning calorimeter (Mettler Toledo DSC1 instrument) with a cooling rate of 5 °C min$^{-1}$ and a heating rate of 10 °C min$^{-1}$. Cyclohexane analytic standard (Sigma Aldrich) was used to calibrate the instrument.

The temperature for each system was determined from the onset of the heating scan while the enthalpy was derived from integration of the peak area. Entropies were calculated by dividing the enthalpy by the onset temperature. For the glass transitions the midpoint was used as the glass transition temperature.

### Density

The density measurement was carried out using a density/ specific gravity meter (Anton Paar DMA5000) from 20 to 80 °C using 10 °C interval steps. This density meter uses the “oscillating U-tube principle” to determine the density of the liquid.

### Dynamic viscosity

The viscosities of the RTILs were measured using a rolling-ball viscometer (Anton Paar Lovis 2000ME) from 20 to 80 °C using 10 °C interval steps, a 10 mm long capillary with a diameter of 2.5 mm and a tilting angle of 60°.

### Ionic conductivity

Ionic conductivity was measured by AC (Alternating Current) impedance spectroscopy using a BioLogic SP-200 Impedance/ Frequency Response Analyser over a temperature range of 40 to 120 °C at 10 °C intervals for the frequency range between 0.1 Hz and 1 MHz applying a voltage amplitude of 0.1 V.

A custom-built dip-cell containing two platinum wires sheathed in glass (Monash Scientific, Australia), sealed with a rubber O-ring was used to carry out the measurements. The cell was placed into a cavity of a brass block, which was connected via a thermocouple to a Eurotherm 2240E temperature controller. The temperature was ramped at a steady state of 0.5 °C min$^{-1}$ until the desired isothermal temperature was reached (±0.3 °C for 20 min). The cell constant was determined using a standard solution of 0.01 M KCl at 25 °C. The resistance (Ω) was determined from the value of the real axis touchdown of the Nyquist plot, from which the conductivity (S cm$^{-1}$) was calculated.

### Table 1 Composition of electrolytes investigated (P$_{1114}$FSI)

<table>
<thead>
<tr>
<th>LiFSI concentration (mol kg$^{-1}$)</th>
<th>Mole ratio of each ion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$^+$</td>
</tr>
<tr>
<td>0 (neat IL)</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>0.07</td>
</tr>
<tr>
<td>1.0</td>
<td>0.12</td>
</tr>
<tr>
<td>2.0</td>
<td>0.19</td>
</tr>
<tr>
<td>3.2</td>
<td>0.25</td>
</tr>
<tr>
<td>3.8</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Published on 17 February 2015. Downloaded by Deakin University on 04/03/2015 23:59:28.

and 19F nuclei were measured for the phosphonium cation and LiFSI based electrolytes as discussed further below.

Prior to each experiment, the working electrode was milled alumina (Buehler, Lake Bluff, IL) on a m: melting point (°C). T<sub>c</sub>: crystallization point (°C). T<sub>m</sub>: melting point (°C). d: density at 25 °C. η: dynamic viscosity at 25 °C. σ: ionic conductivity at 25 °C.

Nuclear magnetic resonance (NMR) spectroscopy

Pulse-field gradient stimulated echo (PFG-STE) diffusion measurements for <sup>1</sup>H, <sup>7</sup>Li and <sup>19</sup>F were performed on a Bruker Avance III 500 MHz Ultrashield wide bore spectrometer equipped with a 5 mm pulse-field gradient probe, following the method described by Bayley et al. The diffusivities of <sup>1</sup>H and <sup>19</sup>F nuclei were measured for the phosphonium cation and FSI anion respectively. <sup>7</sup>Li spectra and diffusivities were also measured. Each sample was filled to a height of 50 mm in a 5 mm Schott E NMR tube in an Argon filled glove box and sealed with Teflon tape and a cap. Each sample was measured at room temperature (22 °C).

Cyclic voltammetry (CV)

Voltammetric experiments were performed using a BioLogic SP-200 potentiostat. Cyclic voltammograms were obtained using a conventional three electrode arrangement. A 1.0 mm glassy carbon working electrode (GC, ALS, distributed by BAS Inc., Japan) was used to determine the electrochemical window of the ionic liquid and a 1.5 mm nickel wire working electrode (Ni, ALS, distributed by BAS Inc., Japan) was used to study lithium cycling in the electrolytes. A platinum wire (APS, 99.95%) was used as the counter electrode. The reference electrode consisted of a silver wire immersed in a solution of the ionic liquid containing 10 mM silver triflate (AgOTf, 99.95%) was used as the counter electrode. The reference electrode consisted of a silver wire immersed in a solution of the ionic liquid containing 10 mM silver triflate (AgOTf, 99.95% purity, Aldrich), separated from the bulk electrolyte by a glass frit, as reported by Snook et al. It produced stable and reproducible measurements. The potentials were corrected versus ferrocene, which was cycled at the end of each set of measurements.

Prior to each experiment, the working electrode was polished with 0.3 μm alumina (Buehler, Lake Bluff, IL) on a clean polishing cloth (Buehler), sequentially rinsed with distilled water, ethanol and then dried with lint-free tissue paper and finally dried in an oven at 70 °C (for one hour). For the reference electrode, the silver (Ag) wire was abraded with silicon carbide paper (P600 grit), then washed with ethanol and dried in the oven. The scan rate was 20 mV s<sup>-1</sup>. Measurements were obtained at 25 ± 2 °C.

Results and discussion

Table 2 summarizes the physicochemical properties of P<sub>1114</sub>FSI-LiFSI based electrolytes as discussed further below.

**Table 2** Physicochemical properties of P<sub>1114</sub>FSI–LiFSI mixtures at 25 °C<sup>a</sup>

<table>
<thead>
<tr>
<th>[LiFSI] mol kg&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>T&lt;sub&gt;d&lt;/sub&gt; °C (±0.2)</th>
<th>T&lt;sub&gt;c&lt;/sub&gt; °C (±0.2)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; °C (±0.2)</th>
<th>d/g cm&lt;sup&gt;-3&lt;/sup&gt; (±0.001)</th>
<th>η/mPa s (±10)</th>
<th>σ/mS cm&lt;sup&gt;-1&lt;/sup&gt; (±0.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>—</td>
<td>−17.3</td>
<td>12.3</td>
<td>1.300</td>
<td>41</td>
<td>7.3</td>
</tr>
<tr>
<td>0.5</td>
<td>96.1</td>
<td>−51.8</td>
<td>5</td>
<td>1.345</td>
<td>55</td>
<td>4.4</td>
</tr>
<tr>
<td>1.0</td>
<td>92.2</td>
<td>−34.9</td>
<td>−18</td>
<td>1.382</td>
<td>79</td>
<td>3.3</td>
</tr>
<tr>
<td>2.0</td>
<td>81.7</td>
<td>—</td>
<td>—</td>
<td>1.446</td>
<td>163</td>
<td>1.9</td>
</tr>
<tr>
<td>3.2</td>
<td>72.9</td>
<td>—</td>
<td>—</td>
<td>1.508</td>
<td>323</td>
<td>0.9</td>
</tr>
<tr>
<td>3.8</td>
<td>70.7</td>
<td>—</td>
<td>—</td>
<td>1.531</td>
<td>571</td>
<td>0.8</td>
</tr>
</tbody>
</table>

<sup>a</sup> T<sub>d</sub>: glass transition (°C). T<sub>c</sub>: crystallization point (°C). T<sub>m</sub>: melting point (°C). d: density at 25 °C. η: dynamic viscosity at 25 °C. σ: ionic conductivity at 25 °C.

Thermal behavior

Differential Scanning Calorimetry (DSC) was used to determine the phase transition behavior of the systems. Since the performance of an ionic liquid strongly depends on the matter of state (e.g. transport properties are in general better in the liquid state) low transition temperatures are desirable.

An endothermic transition in neat P<sub>1114</sub>FSI is detected at 12.3 ± 0.2 °C. With addition of 0.5 mol kg<sup>-1</sup> of LiFSI, the freezing of the IL is suppressed and the solution behaves as a supercooled liquid upon cooling. An extremely low glass transition (T<sub>g</sub>) was detected (−96 ± 1 °C) followed by an exothermic crystallization peak and a melting point (T<sub>m</sub>). The melting point decreases, as does the enthalpy of the melting transition when compared to the neat IL. The exothermic crystallization peak (T<sub>c</sub>) also shifts to lower temperature with increasing lithium salt concentration. The same behavior is observed for the solution of 1.0 mol kg<sup>-1</sup> LiFSI, but the glass transition is slightly higher and the crystallization and melting transitions are much less pronounced. When the lithium salt concentration is increased to 2.0 mol kg<sup>-1</sup>, the crystallization and melting peaks completely disappear and the electrolytes behave as pure glass-forming liquids with low glass transition temperatures, even though the glass transition increases with increased lithium salt content. This suggests that interactions between the lithium ions and the ionic liquid (most likely with the FSI anion) have disrupted the crystallization and the system becomes less mobile due to the increase in T<sub>g</sub>. Thus for electrolyte applications, the solutions with a salt concentration...
above 2.0 mol kg\textsuperscript{-1} of LiFSI in P\textsubscript{111i4FSI} characterised by a low glass transition could potentially be used over a wider temperature range than those with lower concentration (0.5 and 1.0 mol kg\textsuperscript{-1} of LiFSI in P\textsubscript{111i4FSI}) (Fig. 2).

**Transport properties of electrolytes: dynamic viscosity, ionic conductivity and ion diffusion**

Fig. 3 shows the temperature dependence of ionic conductivity and dynamic viscosity. As expected, as the temperature increases the ionic conductivity increases and the viscosity decreases. The ionic conductivity values of the neat P\textsubscript{111i4FSI} are 6.4 ± 0.1 mS cm\textsuperscript{-1}, 7.3 ± 0.1 mS cm\textsuperscript{-1}, and 8.5 ± 0.1 mS cm\textsuperscript{-1} at 20, 25 and 30 °C respectively, which is higher than, or close to, the values recently reported for other phosphonium FSI-based ILs\textsuperscript{15,19,25,26} but slightly lower than the conductivity of the traditional carbonate electrolytes, such as the standard LiPF\textsubscript{6}-EC-EMC previously reported\textsuperscript{19}. The remarkable point here is that the conductivity of P\textsubscript{111i4FSI} at 25 °C (7.3 mS cm\textsuperscript{-1}) is similar to that of P\textsubscript{1113FSI} (7.1 mS cm\textsuperscript{-1}) recently reported by Tsunashima et al.\textsuperscript{15} even though P\textsubscript{111i4FSI} appears to be more viscous (respectively 41 mPa s for P\textsubscript{111i4FSI} and 31 mPa s for P\textsubscript{1113FSI}). This may suggest a higher ionicity for P\textsubscript{111i4FSI}.

A high lithium ion mobility is important for device performance. The most commonly used equation to correlate the conductivity (1) and viscosity (2) with temperature is the Arrhenius law, however for many glass forming materials the Vogel-Tammann-Fulcher (VTF) equation is more appropriate:\textsuperscript{27}

\[ \sigma = \sigma_0 \exp \left( -\frac{B}{T - T_0} \right) \]  
\[ \eta = \eta_0 \exp \left( \frac{B}{T - T_0} \right) \]

The parameters \(\sigma_0\) and \(\eta_0\) are assumed to have a weak temperature dependence. The \(B\) parameter is related to the activation energy (generally called the pseudo-activation energy). The \(T_0\) parameter is related to the ideal glass transition (often \(T_g - T_0 \approx 30\) K for polymers).\textsuperscript{27} The parameters obtained by fitting the data to the VTF equation are given in the ESI.\textsuperscript{†} The fits for low concentrations (<2 mol kg\textsuperscript{-1} LiFSI in the IL) were unreliable due to the narrow temperature range available. In general, the fits are more reliable over a wide temperature range close to \(T_g\). Therefore the fitting results are more reliable for the ionic conductivity (data fitted from −40 to 120 °C) than the viscosity (data fitted from 20 to 80 °C). The pseudo activation energy (parameter \(B\)) is related to the energy needed for ion motion in the ionic liquid and seems to increase with increasing Li salt content. This implies that more energy is required for a diffusive motion that leads to conductivity in the highly concentrated electrolytes. \(T_0\) is correlated to \(T_g\) as expected.

Several studies have reported that the conductivity of lithium-based ionic liquid electrolytes decreases with increasing lithium salt concentration and that this is related to the possible formation of ion-aggregates.\textsuperscript{14,28} The concentration dependence of both ionic conductivity and dynamic viscosity are shown in Fig. 4; the higher the salt concentration, the higher the viscosity and these observations are also consistent with the VTF parameters determined for the selected electrolytes. The conductivity increases with increasing temperature, but decreases continuously.
with increasing salt concentration. One particular effect to notice here is that, above 3 mol kg$^{-1}$ of LiFSI, the rate of conductivity decrease with increasing concentration appears to be tending towards a plateau.

**Diffusion NMR**

To understand the environment surrounding Li$^+$ and its effects on ionic mobility and conductivity, NMR spectra and PFG-STE NMR diffusion coefficients for $^7$Li, $^1$H, and $^{19}$F were measured. The diffusivities of each ion in both the neat IL and the LiFSI solutions are presented in Fig. 5.

The diffusivity of all ions decreases as the Li$^+$ concentration in the IL electrolyte increases, consistent with a decrease in fluidity, however, the Li$^+$ ion mobility exhibits unusual behavior. At Li concentrations above 2 mol kg$^{-1}$, the $^7$Li diffusivity exceeds the $^1$H diffusivity, suggesting that Li$^+$ ions become more mobile than the phosphonium cation. This implies a higher transport number of Li$^+$ above 2 mol kg$^{-1}$, suggesting promising properties of the concentrated electrolytes for battery applications.

The Li$^+$ ions, being much smaller than the phosphonium cation, could be expected to be much more mobile, however, in many electrolyte systems they display a significantly lower diffusion coefficient which is attributed to strong ion association with the anions in the IL.\(^{29}\)

For the highly concentrated solutions the Li$^+$ mobility decreases at a slower rate than either the anion or cation. Thus the Li$^+$ ion transport seems to become more decoupled from the ionic liquid matrix dynamics at higher salt concentrations, suggesting that a fraction of the Li ions are less hindered by ion-association. This is explored further in the following sections.

**Walden and ionicity analysis**

A Walden plot based on the Walden Rule, as described by Angell and co-workers\(^ {30}\) is an effective qualitative method to characterize the ion interactions in an IL.

The Walden Rule (3) is:

$$\frac{\text{A} \eta}{\text{C}} = C$$

Fig. 5 Diffusivities of Li$^+$, P$_{1114}$\(^{+}\), and FSI$^{-}$ ions measured using PFG-STE NMR as a function of salt concentration at 22 °C. (Error bars are contained within the data point markers).

where \(\Lambda\) is the molar conductivity, \(\eta\) is the viscosity, \(z\) is an adjustable parameter and \(C\) is a temperature dependent constant.\(^ {16,31}\) Dilute aqueous solutions of KCl are often used as a point of reference. They represent a close to ideal solution in which the ions are of similar size and thought to be well dissociated from one another and any ion interactions can be neglected. In contrast to dilute KCl solution, ILs are characterized by many ion–ion interactions that impede independent conductive motions. In particular ionic associations that produce neutral species (e.g., ion-pairs) do not contribute to the conductive flux. Thus deviations from the Walden rule are taken as a measure of these interactions.

A Walden plot (log \(\Lambda_{\text{M}}\) vs. log \(1/\eta\)) of each concentrated electrolyte based on P$_{1114}$FSI is shown in Fig. 6. A dashed line on Fig. 6 drawn one log unit below the KCl (aq) line indicates the situation where the liquid is exhibiting only 10% of the molar conductivity that it should possess according to the Walden Rule for a given viscosity. The data sets as a function of temperature lie fairly close together, thus, there is little sign of strong ion-association and the addition of lithium does not seem to have a large effect on the degree of ion association. Even the 1 : 1 Li/P$_{1114}$FSI mixture indicates good ion dissociation; thus one hypothesis for the structure of this electrolyte that envisages the substantial formation of the Li(FSI)$_2$\(^{-}\) anion (which creates one charge carrier from three ions) does not seem to be supported by this data.

With a similar purpose to a Walden plot, as described previously,\(^ {31}\) Fig. 7 shows the ionicity plot of the P$_{1114}$FSI data at 22 °C with various lithium salt concentrations; the data set is limited to a single temperature as the diffusivity data is only available at that temperature.

The ‘ionicity’ is defined as the ratio of the measured conductivity by impedance spectroscopy \(\Lambda_{\text{M}}\), and the conductivity from diffusion NMR measurements calculated from the Nernst–Einstein (NE) eqn (4), \(\Lambda_{\text{NE}}\):

$$\Lambda_{\text{NE}} = \frac{N_A e^2}{k_B T} (D^+ + D^-)$$

Fig. 6 Walden plot showing relationships between inverse viscosity and molar conductivity for P$_{1114}$FSI with different LiFSI concentrations.

Here, \(N_A\) is Avogadro’s number, \(e\) the electronic charge, \(k_B\) the Boltzmann constant and \(D^+\) and \(D^-\) are the diffusion coefficients.
of the cation and anion, respectively. The self-diffusion coefficients required were obtained from PFG-STE NMR measurements. From the Nernst–Einstein equation, the molar conductivity can be calculated if the individual diffusion coefficients are known. The ionicity formulated in this also describes the degree of ion dissociation in the ionic liquid since the value obtained by impedance spectroscopy, $\Lambda_M$, only contains contributions from mobile, charged species in the solution, while the conductivity calculated from the Nernst–Einstein equation includes contributions from all species.\(^{31}\) The data in Fig. 7 show a similar trend to the Walden Plot. The calculated ionicity values for each solution at room temperature are presented in Table 3. Overall the ionicity decreases with increased salt concentration and this is consistent with the previous interpretation of the diffusivity data. The ionicity of the neat IL is the highest and all solutions of lithium salt in the IL show lower ionicity. Interestingly the solutions of lithium salt in the IL have ionicity only 40% lower than the neat IL even at the highest concentrations; by comparison analogous ammonium ILs (with the TFSI anion) already show a range of decrease of 27 and 24% at concentrations less than 1.0 mol kg\(^{-1}\).\(^{32,33}\) Hence this FSI system allows more than four times higher lithium content but with a similar degree of ion association.

### Electrochemical measurements in LiFSI containing ILs

Fig. 8 illustrates a typical linear sweep voltammogram measured in neat $\text{P}_{1114}\text{FSI}$. It was found that the electrochemical window of $\text{P}_{1114}\text{FSI}$, in which no decomposition currents were observed, lies between $-3.5$ and $2.5$ V vs. Ag/AgOTf using a glassy carbon working electrode. The small reduction processes starting at $-1$ V might be related to reduction of the anion contributing to the ionic liquid film formation.\(^{34}\)

<table>
<thead>
<tr>
<th>[LiFSI] (mol kg(^{-1}))</th>
<th>$\Lambda_M/\Lambda_{NE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.71</td>
</tr>
<tr>
<td>0.5</td>
<td>0.59</td>
</tr>
<tr>
<td>1.0</td>
<td>0.63</td>
</tr>
<tr>
<td>2.0</td>
<td>0.56</td>
</tr>
<tr>
<td>3.2</td>
<td>0.51</td>
</tr>
<tr>
<td>3.8</td>
<td>0.43</td>
</tr>
</tbody>
</table>

The electrochemical stability of $\text{P}_{1114}\text{FSI}$ as a function of temperature is presented in the ESL.\(^{\dagger}\) When increasing the temperature from 25 to 100 °C, the electrochemical window becomes narrower as the redox processes within the system are facilitated and therefore occur at slightly lower potentials. Cyclic voltammograms of selected concentrations of LiFSI dissolved in $\text{P}_{1114}\text{FSI}$ (0.5, 3.2 and 3.8 mol kg\(^{-1}\)) at room temperature using a Ni working electrode are presented in Fig. 9. These indicate a quasi-reversible Li deposition–dissolution process. A small shift of the onset potential towards less negative values is observed with increasing lithium ion concentration as expected from the Nernst equation. The oxidation current densities for the reversible peak decrease significantly with increasing lithium salt concentration as expected from the transport property trends. On the other hand, very significant current densities are reached (Fig. 10) with increasing temperature, with the high concentration 3.8 mol kg\(^{-1}\) electrolyte exhibiting the highest current density (up to 40 mA cm\(^{-2}\) at 100 °C) and the highest deposition–dissolution charge efficiency.

---

**Fig. 7** Ionicity plot of $\text{P}_{1114}\text{FSI}$ and various LiFSI concentrations at 22 °C.

**Fig. 8** Linear sweep voltammograms for neat $\text{P}_{1114}\text{FSI}$ at a glassy carbon working electrode with a potential sweep rate of 20 mV s\(^{-1}\) at 25 °C.

**Fig. 9** Linear sweep voltammograms (1st cycle) for neat $\text{P}_{1114}\text{FSI}$ and solutions of 0.5, 3.2 and 3.8 mol kg\(^{-1}\) LiFSI in $\text{P}_{1114}\text{FSI}$ at a Ni working electrode with a potential sweep rate of 20 mV s\(^{-1}\) at 25 °C.
Fig. 11(a) shows the CV response for P111i4FSI with 0.5 mol kg\(^{-1}\) LiFSI at 25°C as a function of the negative limit switching potentials on a nickel electrode. Switching the potential at less negative values (from \(-3.8\) V vs. Ag/AgOTf to \(-3.8\) V) causes an increase in the cathodic and anodic currents at high temperature. However, while holding the potential at \(-4.0\) V vs. Ag/AgOTf, the anodic currents are still retained. This is interpreted as a result of a competition between IL (cation) decomposition and lithium reduction, indicating that Li deposition is no longer the dominant electrochemical process at these more negative potentials and that, most likely, reduction of the phosphonium cation begins to dominate in the potential region below \(-3.8\) V vs. Ag/AgOTf.

Fig. 11(b) shows the CV response for P111i4FSI + 3.2 mol kg\(^{-1}\) LiFSI at 25°C as a function of switching potential. The electrochemical stability of Li is improved with increased concentration suggesting promising behavior of the highly concentrated electrolyte in a lithium battery; furthermore, the anodic current is significantly increased when switching the potential at \(-4.3\) V vs. Ag/AgOTf, with no indication of IL breakdown even under these extreme conditions. This represents an overpotential with respect to Li of around 1.1 V, which offers an impressive range of electrolyte stability from the point of view of overpotentials during battery charging.

Conclusions

The electrochemical and physicochemical properties of lithium ion containing P111i4FSI electrolytes were investigated. As the concentration of lithium salt was increased, the \(T_g\) of the electrolytes increased and the freezing/melting behaviour was completely suppressed. The dynamic viscosities and ionic conductivities can be well described by the VTF model. With increasing lithium ion concentration the viscosity increases while the conductivity decreases. P111i4FSI has a large electrochemical window (6 V vs. Ag/AgOTf at a glassy carbon electrode) and supports lithium reversible cycling at various concentrations and temperatures. At more negative switching potentials however, reduction of the phosphonium cation competes with lithium deposition in the lower Li concentration electrolytes. However, in the 1:1 mol ratio mixture, significantly more reversible and efficient Li deposition/dissolution was observed, even at switching overpotentials as high as 1.1 V, indicating high electrolyte stability at these compositions. Solutions of
LiFSI in the ionic liquid PrFSI exhibit reasonable transport properties. NMR diffusion measurements reveal unusual behaviour of mobility of Li ions at high Li concentration with the lithium diffusion coefficient being higher than the phosphonium cation diffusion for the more highly concentrated electrolytes. These solutions could thus be promising electrolytes for lithium batteries.

Acknowledgements

The authors would like to thank the ARC (Australian Research Council) and Cytec Canada Inc. for funding this research as part of a Linkage Project LP120200181. Prof. Maria Forsyth and Prof. Douglas R. MacFarlane are also grateful to the ARC for their Australian Laureate Fellowships. The authors would also like to acknowledge the NMR LIEF grant for the NMR diffusion measurements.

Notes and references

Supplementary Information

to accompany

Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content

G. M. A. Girard\textsuperscript{a}, M. Hilder\textsuperscript{a}, H. Zhu\textsuperscript{a}, D. Nucciarone\textsuperscript{c}, K. Whitbread\textsuperscript{c}, S. Zavorine\textsuperscript{c}, M. Moser\textsuperscript{c}, M. Forsyth\textsuperscript{a}, D. R. MacFarlane\textsuperscript{b} and P. C. Howlett\textsuperscript{a}.

\textsuperscript{a} Institute for Frontier Materials (IFM), Deakin University, Burwood, Victoria 3125, Australia.

\textsuperscript{b} School of Chemistry, Monash University, Victoria 3800, Australia.

\textsuperscript{c} Cytec Canada Inc., Niagara Falls, Canada.

Content

1 Preparation of trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide (P\textsubscript{111}i4\textsubscript{4}FSI) ................................................................................................................................................1
2 Nuclear Magnetic Resonance spectra of P\textsubscript{111}i4\textsubscript{4}FSI ..................................................................................2
3 Electrospray mass spectra of P\textsubscript{111}i4\textsubscript{4}FSI .............................................................................5
4 Transport properties – VTF parameters ...........................................................................5
5 Electrochemical measurements of tri(methyl)isobutylphosphonium bis(fluorosulfonyl)imide (P\textsubscript{111}i4\textsubscript{4}FSI) .........................................................................................7
Preparation of trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide (P$_{111i4}$FSI)

Isobutylphosphine (CYTOP®141, Cytec Industries) was reacted with trimethyl phosphate (>3 mol) at a temperature 110-130 °C using the process described in US patent 7,829,744 B2. The trimethyl(isobutyl)phosphonium dimethylphosphate intermediate was further reacted with 1.05 equivalents of potassium bis(fluorosulfonyl)imide (KFSI) in the presence of dichloromethane. The organic phase was treated with saturated NaHCO$_3$ in water followed by additional washes with H$_2$O, hexanes, and a number of washes with deionized H$_2$O and checked for the presence of any residual halide with the use of AgNO$_3$ in water. After removal of the volatiles on the Rotovap, the resulting product was additionally purified using short-path evaporator. Its structure was confirmed by $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR analyses (deuterated acetone ((CD$_3$)$_2$CO)).

Nuclear Magnetic Resonance spectra of P$_{111i4}$FSI

Figure S3 $^{31}$P NMR spectrum of P$_{111i4}$FSI
Figure S4 $^{19}$F NMR spectrum of $P_{1114}$FSI

Figure S5 $^1$H NMR spectrum of $P_{1114}$FSI
Figure S6 $^{13}$C NMR spectrum of P$_{1114}$FSI
3 Electrospray mass spectra of $\text{P}_{1114}\text{FSI}$

![Mass spectra of $\text{P}_{1114}\text{FSI}$](image)

Figure S7 Mass spectra of $\text{P}_{1114}\text{FSI}$

4 Transport properties – VTF parameters

![VTF plots of ionic conductivity (a) and dynamic viscosity (b) for $\text{P}_{1114}\text{FSI}$ electrolytes and various concentrations of LiFSI](image)

Figure S1 VTF plots of ionic conductivity (a) and dynamic viscosity (b) for $\text{P}_{1114}\text{FSI}$ electrolytes and various concentrations of LiFSI
Table S1 VTF equation parameters of ionic conductivity from -40 to 120°C (\( \sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right) \))

<table>
<thead>
<tr>
<th>LiFSI concentration</th>
<th>Molar ratio Li⁺: P⁺</th>
<th>Ln ( \sigma_0 ) / mS.cm⁻¹</th>
<th>B (K)</th>
<th>( T_0 ) (K)</th>
<th>R (correlation coefficient)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.19:0.31</td>
<td>6.36±0.09</td>
<td>791±24</td>
<td>160±2</td>
<td>0.9999</td>
</tr>
<tr>
<td>3.2</td>
<td>0.25:0.25</td>
<td>6.07±0.002</td>
<td>768±5</td>
<td>173±0.3</td>
<td>0.9999</td>
</tr>
<tr>
<td>3.8</td>
<td>0.27:0.23</td>
<td>6.35±0.004</td>
<td>844±8</td>
<td>171±0.5</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

Table S2 VTF equation parameters of dynamic viscosity from 20 to 80°C (\( \eta = \eta_0 \exp\left(\frac{-B}{T - T_0}\right) \))

<table>
<thead>
<tr>
<th>LiFSI concentration</th>
<th>Molar ratio Li⁺: P⁺</th>
<th>Ln ( \eta_0 / P )</th>
<th>B (K)</th>
<th>( T_0 ) (K)</th>
<th>R (correlation coefficient)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.19:0.31</td>
<td>-4.84±0.38</td>
<td>589±100</td>
<td>188±11</td>
<td>0.9998</td>
</tr>
<tr>
<td>3.2</td>
<td>0.25:0.25</td>
<td>-5.69±0.39</td>
<td>863±117</td>
<td>173±10</td>
<td>0.9999</td>
</tr>
<tr>
<td>3.8</td>
<td>0.27:0.23</td>
<td>-5.16±0.64</td>
<td>742±170</td>
<td>186±15</td>
<td>0.9996</td>
</tr>
</tbody>
</table>
Electrochemical measurements of tri(methyl)isobutylphosphonium bis(fluorosulfonyl)imide (P$_{111i4}$FSI)

Figure S2 Linear sweep voltammograms for neat P$_{111i4}$FSI at a glassy carbon working electrode with a potential sweep rate of 20mV.s$^{-1}$ at different temperatures 25-50-75-100°C.
3.2.3 FTIR studies of P111i4FSI electrolytes

Further characterisation of the electrolytes was conducted using Fourier transform infrared (FTIR) spectroscopy in order to investigate the interactions between the three ions present in the IL electrolytes: the Li⁺ cation, the IL cation (P111i4⁺) and the IL anion (FSI⁻). FTIR spectra for the IL electrolytes and pure LiFSI salt are presented in Figure 47. The majority of peaks were assigned based on the assignments for a solution of LiFSI in C₃mpyrFSI reported by Yoon et al.⁷ Peak assignments for the FTIR spectra of neat P111i4FSI and P111i4FSI electrolytes are presented in Table 15. Figure 47 (a) presents the IR spectra for the different salt concentrations. The results showed S-N-S stretching vibration peaks (asymmetric and symmetric stretching vibrations at 828 and 731 cm⁻¹ respectively) shifting to a higher wavenumber with increasing Li salt concentration. The S-F asymmetrical stretching, previously assigned by Yoon et al. at 830 cm⁻¹,⁷ shifts closer to the peak position found for the pure LiFSI salt. Figure 47 (b) shows the FTIR spectra for the asymmetric SO₂ bending vibrations located at 566 cm⁻¹. The spectra reveal the appearance of a shoulder at ~ 595 cm⁻¹ with increasing intensity as the LiFSI concentration increases. These observations could suggest changes in speciation between Li⁺ and FSI⁻ ions and were confirmed by diffusion NMR analysis in Chapter 3. Similar results were previously reported for solutions based on C₃mpyrFSI.⁷ Based on Raman spectroscopy and simulations, their results indicated a change in coordination from Li(FSI)₃ to Li(FSI)₂ species and from trans to cis conformation of the FSI anion.
Figure 47 FTIR transmittance spectra: (a) from 900 to 680 cm\(^{-1}\); (b) from 700 to 500 cm\(^{-1}\)
Table 15 Assignment for the FTIR spectrum data of neat P$_{111i4}$FSI and P$_{111i4}$FSI electrolytes

(v: stretching, δ: bending, s: strong, m: medium, w: weak)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Neat P$_{111i4}$FSI</th>
<th>0.5 mol.kg$^{-1}$ LiFSI in P$_{111i4}$FSI</th>
<th>3.8 mol.kg$^{-1}$ LiFSI in P$_{111i4}$FSI</th>
<th>Pure LiFSI salt</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ$_a$(SO$_2$)</td>
<td>566 (s)</td>
<td>566</td>
<td>566</td>
<td>567</td>
<td>8</td>
</tr>
<tr>
<td>ν$_a$(SNS)</td>
<td>731 (m)</td>
<td>737</td>
<td>746</td>
<td>757</td>
<td>7-10</td>
</tr>
<tr>
<td>ν$_a$(SNS) and ν(SF)</td>
<td>828 (m)</td>
<td>830</td>
<td>843</td>
<td>856</td>
<td>7, 10-11</td>
</tr>
<tr>
<td>ν$_a$(SO$_2$-N-SO$_2$)</td>
<td>1100</td>
<td>1103</td>
<td></td>
<td></td>
<td>8, 11-12</td>
</tr>
<tr>
<td>ν(SO$_2$-N-SO$_2$)</td>
<td>1172 (s)</td>
<td>1171</td>
<td>1114</td>
<td>1178</td>
<td>8, 11-12</td>
</tr>
<tr>
<td></td>
<td>1216 (w)</td>
<td>1217</td>
<td>1168</td>
<td>1234</td>
<td></td>
</tr>
<tr>
<td>τ(CH$_2$)</td>
<td>1307</td>
<td>1307</td>
<td>1307</td>
<td></td>
<td>8, 10</td>
</tr>
<tr>
<td>ν$_a$(SO$_2$)</td>
<td>1359 (s)</td>
<td>1359</td>
<td>1358</td>
<td>1365</td>
<td>8, 10-11</td>
</tr>
<tr>
<td>ν$_d$(SO$_2$)</td>
<td>1376 (s)</td>
<td>1376</td>
<td>1374</td>
<td></td>
<td>8, 11</td>
</tr>
<tr>
<td>δ(CH$_2$) from P-CH$_2$</td>
<td>1423 (w)</td>
<td>1425</td>
<td>1421</td>
<td></td>
<td>8, 10</td>
</tr>
<tr>
<td>ν(CH$_2$)ν(CH$_3$)</td>
<td>1470 (m)</td>
<td>1471</td>
<td>1471</td>
<td></td>
<td>8, 13-14</td>
</tr>
<tr>
<td>ν(CH$_2$)</td>
<td>2878 (w)</td>
<td>2878</td>
<td>2882</td>
<td></td>
<td>8, 10, 12, 14</td>
</tr>
<tr>
<td>ν(CH$_2$)</td>
<td>2928 (w)</td>
<td>2929</td>
<td>2931</td>
<td></td>
<td>8, 10, 12, 14</td>
</tr>
<tr>
<td>ν(CH$_2$)</td>
<td>2970 (w)</td>
<td>2971</td>
<td>2973</td>
<td></td>
<td>8, 10, 12, 14</td>
</tr>
<tr>
<td>ν(CH$_2$)</td>
<td>3006 (w)</td>
<td>3006</td>
<td>3006</td>
<td></td>
<td>8, 10, 14</td>
</tr>
</tbody>
</table>
3.3 Conclusions

In this chapter we described the physicochemical and electrochemical properties of solutions based on a phosphonium bis(fluorosulfonyl)imide (FSI⁻) ionic liquid with the LiFSI salt. This ionic liquid can dissolve this lithium salt up to 1:1.2 IL:Li salt concentration ratio.

The addition of lithium salt into the IL had a significant positive impact on the thermal behaviour of the solutions. Highly concentrated IL electrolytes were characterised by low glass transitions, making them very practical for electrolyte applications over a wide temperature range.

In spite of higher viscosity and lower conductivity the electrolyte containing 3.2 mol.kg⁻¹ of lithium salt (i.e., a 1:1 molar ratio of salt and IL) showed distinctive lithium deposition / dissolution enhanced by high lithium salt content. NMR diffusivity measurements showed that, at high lithium salt content, the mobility of the Li⁺ cation relative to that of the other ionic species is greater than in solutions with lower lithium salt content. On the other hand FTIR analysis combined with NMR diffusivity measurements confirmed a change in Li speciation in the IL electrolytes with high Li salt content. The results imply that the lithium transport mechanism in these highly concentrated IL electrolytes may differ to that in IL electrolytes with low lithium salt content. Finally the IL electrolyte with the highest lithium salt content is expected to show remarkable plating and stripping capability with a lithium metal electrode.

Similar results were obtained using another phosphonium ionic liquid consisting of the same anion (FSI⁻) and a mixture of four phosphonium cations (Pmix). This IL can dissolve similar quantities of LiFSI; the solutions of PmixFSI with highest lithium salt content maintained reasonable ionic conductivities at temperatures below 0 °C.
3.4 References


Chapter 3 Appendices

Figure S 1 $^7$Li NMR chemical shifts at 25 °C for $P_{1114}$FSI – LiFSI mixtures (2 M LiCl reference). The arrow indicates the direction of increasing LiFSI concentration and a shift to higher fields, consistent with a more electron-shielded environment as the Li$^+$ concentration increases.

Figure S 2 Chemical structures of the ionic liquid consisting of a mixture of the bis(fluorosulfonyl)imide FSI$^-$ anion and four phosphonium cations ($P_{mix}$FSI)
Chapter 3

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Table S 1 Physicochemical properties of P_{mix}FSI – LiFSI mixtures at 25°C^a

<table>
<thead>
<tr>
<th>[LiFSI] (mol.kg^{-1})</th>
<th>FW</th>
<th>T_g ± 0.2(°C)</th>
<th>T_m ± 0.2(°C)</th>
<th>d ± 0.001 (g.cm^{-3})</th>
<th>η ± 10 (mPa.s)</th>
<th>σ ± 0.1 (mS.cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>304</td>
<td>-</td>
<td>-49.6</td>
<td>1.285</td>
<td>35</td>
<td>5.4</td>
</tr>
<tr>
<td>0.5</td>
<td>294</td>
<td>-104.3</td>
<td>-</td>
<td>1.331</td>
<td>69</td>
<td>4.5</td>
</tr>
<tr>
<td>1.0</td>
<td>285</td>
<td>-98.9</td>
<td>-</td>
<td>1.367</td>
<td>99</td>
<td>3.8</td>
</tr>
<tr>
<td>3.3</td>
<td>260</td>
<td>-81.1</td>
<td>-</td>
<td>1.487</td>
<td>414</td>
<td>0.8</td>
</tr>
</tbody>
</table>


Figure S 3 DSC traces for neat P_{mix}FSI and solutions of LiFSI in P_{mix}FSI as a function of LiFSI concentration at a scan rate of 10 °C min^{-1}
Figure S 4 Dependence of ionic conductivity (a) and dynamic viscosity (b) on temperature for neat P_{mixFSI} and solutions of LiFSI in P_{mixFSI}. (Error bars were smaller than the data point markers)

Figure S 5 Walden plot showing relationships between inverse viscosity and molar conductivity for P_{mixFSI} with different LiFSI concentrations
Figure S 6 Linear sweep voltammograms for neat P_{mix}FSI at a glassy carbon working electrode with a potential sweep rate of 20 mV.s^{-1} at 25 °C.

Figure S 7 Linear sweep voltammograms (1st cycle) for a solution of (a) 0.5 mol.kg^{-1}; (b) 1.0 mol.kg^{-1} at a nickel electrode with a 20 mV.s^{-1} potential sweep rate as function of temperature. Switching potential was -3.8 V vs. Ag/AgOTf.
Chapter 4  Rate and cycling performance of lithium metal electrodes in trimethyl(isobutyl)phosphonium bis(fluorosulfonylelimide)imide ionic liquid
Chapter 4

4.1 Introduction

In the previous chapter the electrochemical and physicochemical properties of lithium containing \( \text{P11}_{34}\text{FSI} \) electrolytes were investigated. It was shown that these electrolyte solutions were promising electrolytes for lithium batteries with attractive properties including a wide electrochemical window and sufficient lithium ion diffusivity. Improved reversibility and efficiency of lithium deposition / dissolution were also reported in highly concentrated IL electrolytes (55 mol % \( \text{Li}^+ \)). This chapter describes the rate and cycling performance of lithium metal electrodes in these lithium containing \( \text{P11}_{34}\text{FSI} \) electrolytes, highlighting the importance of salt concentration on the solid electrolyte interphase (SEI) and lithium deposition morphology. The advantages and problems of the use of Li metal electrodes and the importance of the SEI have already been discussed in Chapter 1 (sections 2.3, 4.6 and 4.7).

In this Chapter we demonstrate that the use of a highly concentrated IL electrolyte based on the IL \( \text{P11}_{34}\text{FSI} \) and LiFSI salts supports dendrite-free plating of Li metal at high rates and capacities. We also show that this exceptional performance is made possible by the formation of a stable, compact and low resistance SEI layer at the Li metal anode. In this chapter, the cycling performance of Li | Li symmetrical cells is investigated:

- as a function of Li salt concentration, with increasing amounts of charge of Li reduced and oxidised (from \( 6.4 \times 10^{-3} \) to \( 0.13 \text{ mg.cm}^{-2} \), \( i.e. 25 \times 10^{-3} \) to \( 0.5 \text{ mAh.cm}^{-2} \) respectively)
- as a function of Li salt concentration and temperature (25 and 50 °C), with high amount of charge applied comparable to that of a practical rate of a commercial Li battery with a 1 C loading of \( 3 \text{ mAh.cm}^{-2} \) (up to \( 6 \text{ mAh.cm}^{-2} \))
- providing an example of a Li metal electrode rate capability study in the phosphonium IL electrolyte with the highest Li salt concentration (amount of charge applied of \( 4.0 \times 10^{-2} \text{ mg.cm}^{-2} \), \( e.g. 0.16 \text{ mAh.cm}^{-2} \))
- a study of the Li surface morphology of cycled Li metal electrodes, developing suitable ex-situ surface preparation methods and applying SEM characterisation.
4.2 Experimental methods

Electrolytes were prepared as described in Chapter 2. A lithium hexafluorophosphate (LiPF$_6$, 1M) - ethylene carbonate (EC) - dimethylcarbonate (DMC) (1:1 v/v) electrolyte was the conventional organic electrolyte (Solvionic) used for comparison. As already mentioned in Chapter 2, the experimental methods relevant to the studies presented in this Chapter were:

- Li | Li cell assembly and testing (galvanostatic cycling and EIS)
- SEM

4.3 Results

4.3.1 Li metal plating / stripping cycling stability and rate capability of P$_{1114}$FSI IL electrolytes

4.3.1.1 Lithium salt concentration dependence of the cycling performance

Cycling measurements were conducted to determine any significant correlation between salt concentration and Li | Li symmetrical cell cycling performance and the cycling stability of Li metal. The IL electrolytes studied in this section were solutions of 0.5, 1.0, 2.0 and 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI. These were compared to an organic carbonate reference electrolyte commonly used in Li batteries: 1 M LiPF$_6$ in EC:DMC (1/1 vol/vol). Cells were cycled at different current densities ranging from 0.05 mA.cm$^{-2}$ to 1.0 mA.cm$^{-2}$ (0.05, 0.1, 1.0 and 0.05 mA.cm$^{-2}$ corresponding to the amounts of charge of Li reduced / oxidised of 6.4 x 10$^{-3}$, 1.3 x 10$^{-2}$ and 0.13 mg.cm$^{-2}$, i.e. 25 x 10$^{-3}$, 0.05 and 0.5 mAh.cm$^{-2}$ respectively) for 30 min (one plating process for 30 min and one stripping process for 30 min each) at room temperature (25 °C). The Li metal electrode impedance was recorded each time the current density was varied. The potential of the Li metal working electrode (WE) during constant Li plating / stripping in a Li | Li cell and EIS spectra of the Li WE are shown in the following graphs for the different electrolytes (Figure 48 to Figure 52).
In lithium plating / stripping processes, polarisations are generated by kinetic barriers in the electrolyte (e.g. Li$^+$ ion transport, SEI formation, reduction / oxidation processes and charge transfer resistances at the Li electrode). The contributions of these processes to the overall cell resistance (R) can be identified by EIS.

Figure 48 (a) Voltage time profiles for a Li | Li symmetrical cell with 1 M LiPF$_6$ in EC:DMC (1/1 vol/vol) over 10 plating / stripping processes at 0.05, 0.1, 1.0 mA.cm$^{-2}$. All cells cycled at 25 °C. (b) EIS spectra of the cell before and after cycling.

Figure 49 (a) Voltage time profiles for a Li | Li symmetrical cell with 0.5 mol.kg$^{-1}$ of LiFSI in P$_{111}$aFSI over 10 plating / stripping processes at 0.05, 0.1, 1.0 mA.cm$^{-2}$. All cells cycled at 25 °C. (b) EIS spectra of the cell before and after cycling.
Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Figure 50 (a) Voltage time profiles for a Li | Li symmetrical cell with 1.0 mol.kg\(^{-1}\) of LiFSI in P_{111i4}FSI over 10 plating / stripping processes at 0.05, 0.1, 1.0 mA.cm\(^{-2}\). All cells cycled at 25 °C. (b) EIS spectra of the cell before and after cycling.

Figure 51 (a) Voltage time profiles for a Li | Li symmetrical cell with 2.0 mol.kg\(^{-1}\) of LiFSI in P_{111i4}FSI over 10 plating / stripping processes at 0.05, 0.1, 1.0 mA.cm\(^{-2}\). All cells cycled at 25 °C. (b) EIS spectra of the cell before and after cycling.

Figure 52 (a) Voltage time profiles for a Li | Li symmetrical cell with 3.8 mol.kg\(^{-1}\) of LiFSI in P_{111i4}FSI over 10 plating / stripping processes at 0.05, 0.1, 1.0 mA.cm\(^{-2}\). All cells cycled at 25 °C. (b) EIS spectra of the cell before and after cycling.
Smaller Li surface impedances were recorded in the case of $\text{P}_{11114}\text{FSI}$ electrolytes with high Li salt content in comparison to the organic carbonate electrolyte. These first results suggest a better compatibility of the phosphonium IL electrolytes with the Li metal electrode. Yoon et al.\textsuperscript{3} already reported that the salt concentration dependence on the cell cycling performance was not significant in the case of pyrrolidinium FSI IL electrolytes. In the case of a phosphonium IL electrolyte herein each cell shows that, for any given applied current density, the polarisation remains relatively stable over 10 plating / stripping processes for each current density. The most significant changes occur when the salt concentration changes: significant instantaneous polarisation was observed for every cell (e.g., polarisation values increased from 0.025 to 0.05 V when the current density applied was increased to 1.0 mA.cm\textsuperscript{-2} in the case of the IL electrolyte with highest Li salt content), however an important decrease of impedance was monitored as the current density was increased.

The cell resistance obtained from EIS measurements decreases with increased salt concentration of Li salt up to 3.8 mol.kg\textsuperscript{-1}. For the cells containing 0.5 mol.kg\textsuperscript{-1} of LiFSI in $\text{P}_{11114}\text{FSI}$ as the electrolyte, an unusual behaviour of cell resistance was observed at that specific concentration: the cell resistance decreases with increasing current density applied (i.e., with increasing charge applied as the time is kept constant) as shown in Figure 49.

When the salt concentration increases, the cell resistivity starts to increase when small current densities are applied (0.05 and 0.1 mA.cm\textsuperscript{-2}) whereas the cell resistance drops when the current density applied is 10 times higher. This behaviour was attributed to the beneficial presence of the FSI\textsuperscript{-} anion in the electrolyte, as reported by Yoon et al. and Passerini et al.\textsuperscript{3-4} When reapplying a small current density (0.05 mA.cm\textsuperscript{-2}) the cell resistance remains almost constant regardless of the salt concentration but does not go back to its initial value over 10 plating / stripping processes. These observations suggest a good compatibility between the phosphonium IL electrolytes and Li metal under these specific cycling conditions.
4.3.1.2 Conventional amount of charge applied (4.0 x 10^{-2} mg.cm^{-2}, e.g. 0.16 mAh.cm^{-2}) – rate capability study

In this thesis, Chapter 6 reports on the cycling performance of lithium cells incorporating a high voltage cathode material, LiNiMnCoO_{2}, also called NMC. The current rates (C-rates and current densities applied in Chapter 6 are calculated based on a cathode loading of 1.5 mg.cm^{-2} and theoretical capacity of 160 mAh.g^{-1}. The present chapter focuses on the lithium metal itself, however the current densities applied to the Li | Li symmetrical cells with 3.8 mol.kg^{-1} of LiFSI in P_{111}4FSI electrolyte are equivalent to the C-rates based on the same cathode loading presented in Chapter 6; as shown in Table 16. This allowed to study the cycling behaviour of the highly concentrated electrolyte against Li metal when the same amount of charge is applied. Since there is no cathode material used in a Li | Li symmetrical cell setup we only refer to the current densities. We know that the quantity of charge contained in a current running for a specified time can be calculated with the following equation:5-6

\[ Q = I \times \Delta t \]  

(19)

where \( Q \) is the quantity of electricity or charge in amp hours (A.h), \( I \) is the current in amps (A), \( \Delta t \) is the time in hours (h). By assuming \( Q = 160 \) mA.h for 1 mg of active material, the corresponding current densities were calculated and reported below in Table 16.

<table>
<thead>
<tr>
<th>Equivalent C-rate</th>
<th>Time ( \Delta t ) (h)</th>
<th>Current density ( j ) (mA.cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 C</td>
<td>10 h</td>
<td>0.016</td>
</tr>
<tr>
<td>0.2 C</td>
<td>5 h</td>
<td>0.08</td>
</tr>
<tr>
<td>1 C</td>
<td>1 h</td>
<td>0.16</td>
</tr>
<tr>
<td>2 C</td>
<td>0.5 h (30 min)</td>
<td>0.32</td>
</tr>
<tr>
<td>4 C</td>
<td>0.25 h (15 min)</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 16 Summary of current rates (C-rate) and corresponding current densities based on a cathode loading of 1.5 mg.cm^{-2} and theoretical capacity of 160 mAh.g^{-1}
Li | Li symmetrical cells were cycled at different current densities from 0.016 mA.cm\(^{-2}\) to 0.64 mA.cm\(^{-2}\) over 10 plating / stripping processes for each current density at 25 °C. The Li surface impedance was monitored before each increase in current density. A current density of 0.08 mA.cm\(^{-2}\) was reapplied at the end of the experiment to assess any reversibility in the variation of the Li surface impedance. The polarisation profiles are shown in Figure 53 and expanded views of the cell polarisation at different times are provided in Figure 54.

The shape of the polarisation profiles in the plating / stripping experiments is very similar during cycling (increased rate) as illustrated by the expanded views in Figure 54. An increase C rate led to an instantaneous increase of polarisation, followed by a slight decrease over 10 cycles. Apart from this general initial increase, the profile shape rapidly stabilises within a few cycles. The impedance data in Figure 8(b) also indicated a general decrease of the Li surface impedance as the current density was increased, suggesting the formation of a film on the Li surface that becomes less resistive, or increased Li surface area as higher rates are applied.

![Figure 53](image-url)  
Figure 53 (a) Voltage time profiles for a Li | Li symmetrical cell with 3.8 mol.kg\(^{-1}\) of LiFSI in P\(_{1114}\)FSI over 10 plating / stripping processes at 0.016, 0.08, 0.16, 0.32, 0.64 and 0.08 mA.cm\(^{-2}\) at 25 °C. (b) EIS spectra of the cell before and after cycling.
Figure 54 Expanded views of voltage time profiles for a Li | Li symmetrical cell with 3.8 mol.kg\(^{-1}\) of LiFSI in P\(_{1114}\)FSI at 0.08, 0.16, 0.64, 0.64 and 0.08 mA.cm\(^{-2}\) at 25 °C

For each applied current density the following observations were made according to the rate capability study and acquired impedance spectra illustrated in Figure 53 (b):

- cycling at 0.016 mA.cm\(^{-2}\): a slight increase in impedance was monitored after 10 cycles. The same behaviour was observed by Yoon et al.\(^7\) with a pyrrolidinium FSI IL electrolyte at such low current densities and was attributed to the presence of the FSI anion in contact with Li metal.
- cycling at higher rates (from 0.08 to 0.64 mA.cm\(^{-2}\)): a gradual decrease in impedance was monitored after cycling. The Nyquist plot still reveals 2 semi-circles after cycling, suggesting the presence of at least 2 separate conduction paths/layers on the surface.
4.3.2 Cycling performance of Li symmetric cells at 25 °C: ‘0.5C’ 3 mAh.cm⁻²

Symmetric Li | Li cells can also be used to investigate the reversibility of Li deposition and stripping. The advantage of symmetric Li | Li cells is that the only active material present is the Li metal, which is the target electrode material in this study and therefore it is possible to study the Li | Li⁺ couple without the interference of an insertion cathode material. In the previous sections of this chapter, the deposition and dissolution of substantial quantities of Li metal was reported, however the values rarely exceeded 0.1 mAh.cm⁻², which is in the range typically reported in most studies.²⁻³ However, for practical batteries the transfer of much larger amounts of charge is required (i.e., commercial Li-ion cells for laptop, smartphone applications typically incorporate cathode loadings which cycle between 3 and 6 mAh.cm⁻²).⁸⁻⁹

In the rest of this chapter, unless otherwise stated, the battery loading was chosen on the basis of a practical rate used in a commercial Li battery characterised by a 0.5 C current and a loading of 3 mAh.cm⁻².⁶,¹⁰ This is equivalent to the loading of a Li | LiCoO₂ battery having a specific capacity of 150 mAh.g⁻¹ from 3.0 V to 4.2 V vs. Li | Li⁺ (i.e. a loading of 20 mg.cm⁻² of active material). The three different electrolytes studied are: an organic carbonate electrolyte (1M LiPF₆ in EC: DMC (1:1)), a dilute (0.5 mol.kg⁻¹ salt in IL) and a highly concentrated (3.8 mol.kg⁻¹ salt in IL) P₁₁₁i₄FSI IL electrolyte. Figure 55 shows the mid-term cycling stability of a coin-type Li | Li cell with each electrolyte after 50 cycles (each electrode was plated/stripped for 2 hours at 1.5 mA.cm⁻²).
Figure 55 Voltage profile during subsequent lithium plating / stripping processes on the WE in \( \text{Li} \mid \text{Li} \) symmetrical cells containing different electrolytes at \( j = 1.5 \) mA.cm\(^{-2} \) (3 mAh.cm\(^{-2} \)), at 25 °C: (a) 1M LiPF\(_6\) in EC:DMC (1/1 vol/vol) electrolyte; (b) 0.5 mol.kg\(^{-1}\) LiFSI in \( P_{1114}\)FSI electrolyte and (c) 3.8 mol.kg\(^{-1}\) LiFSI in \( P_{1114}\)FSI electrolyte.

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Figure 56 Nyquist plots of the impedance spectra of Li | Li cell with different electrolytes (a) after 1 day under OCP conditions, (b) after 1, (c) 10 and (d) 50 lithium plating / stripping processes at \( j = 1.5 \text{ mA.cm}^{-2} \) at 25 °C.

Besides a slight decrease of polarisation for the IL electrolytes under repeated cycling (Figure 55 (b) and (c)) the shape of the polarisation profile differs between the organic carbonate electrolyte and the IL electrolytes. The different shapes of the impedance spectra under repeated cycling, illustrated in Figure 56, are coherent with the polarisation profiles. For the organic carbonate electrolyte, an increase in polarisation during cycling (Figure 55 (a)) is related to a more resistive film formed on the Li surface between 10 and 50 cycles (Figure 56 (c) and (d)).
As illustrated in the polarisation profiles in Figure 55, the first lithium plating process starts with an immediate drop in potential (to –1 V at \( j = 1.5\) mA.cm\(^{-2}\), Figure 55 (c)). This large drop, which follows the maximum polarisation in the experiment, can be explained by a high kinetic barrier for lithium deposition underneath the Li electrode prepared film. This film consists of the film formed during electrode preparation in the glovebox (brushed and rinsed in hexane). The related surface resistance is observed in the EIS measurements.

The previous measurements were conducted at 25 °C. For electric vehicle applications it is of particular interest to study the cycling performance of a Li battery at elevated temperature. Li symmetrical cells were assembled with a solution 3.8 mol.kg\(^{-1}\) of LiFSI in P\(_{111}\)FSI. The same cycling conditions as those mentioned in the previous section were applied, only the cycling temperature was increased to 50 °C.

### 4.3.3 In-situ EIS characterisation of Li metal electrodes

Electrochemical impedance spectroscopy was used to record the evolution of the interfacial properties of symmetrical cells employing three different electrolytes: an organic carbonate electrolyte (1M LiPF\(_6\) in EC: DMC (1:1)), a dilute (0.5 mol.kg\(^{-1}\) salt in IL) and a highly concentrated (3.8 mol.kg\(^{-1}\) salt in IL) P\(_{111}\)FSI IL electrolyte.

First, the LiFSI temperature dependence of the Li surface resistance after the 24h rest step prior to cycling was investigated by monitoring Li | Li symmetrical cells after 1 day under open-circuit potential (OCP) conditions at both 25 and 50 °C. The Nyquist plots of the impedance spectra are presented in Figure 57.

![Figure 57 Nyquist plots of the impedance spectra of Li | Li cell after 1 day under OCP conditions at 25°C (left) and 50°C (right).](image-url)
The spectra start from the bulk electrolyte resistance at higher frequencies and then show a semicircle at lower frequencies. Whereas the Ohmic part of the cell resistance is determined by the ionic conductivity of the electrolyte ($R_{\text{electrolyte}}$ or $R_1$), the low frequency semicircle corresponds to the processes at the two electrodes: capacitive properties of the SEI and charge-transfer resistances at the Li electrodes (including the SEI). These are interpreted as “Li electrode surface resistance” ($R_{\text{surface}} = R_2 + R_3$) and the determined resistance values recorded for a range of conditions are given in Table 17 and Table 18. These values are representative of a series of cells prepared in a single experiment, which compared well with the results obtained from two other replicate sets of experiments ($R_2$ and $R_3$ values within +/- 5 %). It is interesting to note that, at 50 °C, the ohmic resistance of the 0.5 mol.kg$^{-1}$ cell is higher than the 3.8 mol.kg$^{-1}$ cell, even though the 0.5 mol.kg$^{-1}$ electrolyte has higher conductivity (9.6 mS.cm$^{-1}$ for the 0.5 mol.kg$^{-1}$ electrolyte against 2.2 mS.cm$^{-1}$ for the 3.8 mol.kg$^{-1}$ electrolyte). This must be due to differences in the lithium ion conductivity and the interactions and wetting that occurs between the bulk electrolyte and the Celgard separator employed, which presents another important avenue of investigation not studied here.

Figure 57 demonstrates that the Li salt content has a significant effect on the Li surface resistance and stability. The initial surface film (i.e., formed after 24h exposure of the Li native film to the electrolyte) formed in the highly concentrated IL electrolyte (3.8 mol.kg$^{-1}$ salt in IL) is the least resistive when compared to the other electrolytes. Furthermore, the surface film resistance measured at 50 °C is also lower than that measured at 25 °C, regardless of the Li salt content in the IL.

The evolution of the overall cell resistance $R$ ($R = R_1 + R_2 + R_3$) as a function of conditioning time was also of particular interest to characterise the electrode stability in each electrolyte. Figure 58 presents the time dependence of the cell resistance of Li | Li symmetrical cells after 0, 1, 3, 6 and 12 days under open-circuit potential (OCP) conditions at either 25 °C or 50 °C. The results show that the SEI resistance exhibits a significant temperature dependence as previously reported in other IL electrolytes and this suggests that the SEI character will be critical in determining cell performance at ambient and sub-ambient temperature. However, this also demonstrates that the conductive nature of the SEI formed at 25 °C becomes more practical at 50 °C.

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
The cell resistance (dominated by the impedance of the SEI layer formed on the plated Li metal) remains low when Li metal is stored in 3.8 mol.kg\(^{-1}\) LiFSI in P\(_{1114}\)FSI in spite of the increased viscosity of the electrolyte at this concentration.\(^{12}\)

The increase in cell resistance as a function of conditioning time indicates continued formation of the surface film on the untreated (i.e. uncycled) Li foil and a thickening of this film. Under OCP conditions, the rate of increase in resistance decreases after several days. The results suggest that these resistances converge to a maximal value within 2 weeks.

The graphs also reveal that the 3.8 mol.kg\(^{-1}\) LiFSI IL electrolyte promotes the formation a stable film of low resistance on the Li surface (at 25 and 50 °C) whereas the organic carbonate electrolyte promotes the formation of a significantly more resistive film on the Li surface. As expected, after 12 days under OCP conditions the cell resistance after conditioning at 25 °C (669 \(\Omega\) measured at 25 °C) is much higher than that at 50 °C (107 \(\Omega\) measured at 50 °C). This is related to the improved transport properties of the electrolyte and SEI layers at elevated temperature. Surprisingly, the cell resistance of the 0.5 mol.kg\(^{-1}\) sample remains comparatively low and stable over the term of the experiment. This may be due to relatively inhomogeneous SEI coverage of the electrode, which contributes to poor cycling of the electrode discussed later.

![Figure 58 Time dependence of the overall cell resistance (R = R\(_1\) + R\(_2\) + R\(_3\)) of Li \(\mid\) Li cells with all electrolytes after 0, 1, 3, 6 and 12 days under OCP conditions at (a) 25 °C and (b) 50 °C.](image)
4.3.4 Cycling performance of Li symmetric cells at 50 °C: ‘0.5C’ - 3 mAh.cm⁻²

In order to benefit from the increased fluidity and conductivity of the electrolyte, cells were cycled at elevated temperatures (50 °C), in the range of many common operating environments.¹⁴ Galvanostatic cycling was used to further investigate the stability of the Li metal anode in the concentrated and dilute IL electrolytes.

The amount of charge applied was set to 3 mA.h.cm⁻², a value comparable to those in commercial Li-ion cells, as previously shown for the 25 °C experiments in section 3.2 of this chapter. Figure 59 shows the mid-term cycling stability of a coin-type Li | Li cell with each electrolyte after 50 cycles (each electrode was plated/stripped for 2 hours at 1.5 mA.cm⁻²). A voltage profile presents the potential of the Li metal working electrode (WE) during constant current Li deposition and dissolution. The positive potentials of the Li WE represent the polarisation potentials appearing during Li dissolution whereas the negative potentials represent the polarisation potentials during Li deposition on the WE. The interpretation of these potentials allows an in situ observation of different stages of these processes.

The Li | Li cells cycled in the organic carbonate electrolyte are characterised by increasing polarisation due the build-up of mossy and ‘dead-lithium’ deposits, with subsequent increased SEI resistance, along with the possibility of dendrite formation under the same cycling conditions⁸ (Figure 59 (a)) whereas the voltage profiles of Li | Li cells cycled in the highly concentrated IL electrolyte (Figure 59 (c)) suggest an improved cycling stability in comparison to the cells cycled in the dilute IL electrolyte which exhibited considerable variations of voltage after around 40 cycles (Figure 59 (b)). The voltage profile of a Li | Li cell with the highly concentrated 3.8 mol.kg⁻¹ LiFSI in P₁₁₁₄FSI electrolyte is very stable over 50 cycles (Figure 59 (c)) during both plating and stripping processes, indicating that the electrolyte and SEI on the Li anode are both stable.
To confirm this, the stability of the Li surface resistance with cycling in these electrolytes was also studied. Figure 60 shows the Nyquist plot of the impedance spectra of Li | Li cells (for each electrolyte) after 1, 10 and 50 cycles and extracted cell resistance ($R_{\text{cell}}$) values plotted versus cycle number.

The impedance of the Li | Li cell with high LiFSI concentration electrolyte decreases with increasing cycle number, as previously observed for pyrrolidinium FSI IL electrolytes and ascribed to Li ‘surface reorganisation’ and ‘consolidation of the SEI’. These results indicate that the SEI layer formed on the former surface is highly conductive, thus the cell polarisation does not increase, even after 50 cycles.

These results could indicate that the SEI layer formed on the former surface is highly conductive, thus the cell polarisation remains constant even after 50 cycles as shown in Figure 59 (c). However the same observations would be made if the SEI is soluble or porous (these conditions would lead to Li consumption from electrolyte reactions during cycling) or if the Li surface area were increasing during cycling.
Figure 59 Voltage profile during subsequent lithium plating / stripping processes on the WE in Li | Li symmetrical cells containing different electrolytes at $j = 1.5$ mA.cm$^{-2}$ (3 mAh.cm$^{-2}$), at 50 °C: (a) 1M LiPF$_6$ in EC:DMC (1/1 vol/vol) electrolyte; (b) 0.5 mol.kg$^{-1}$ LiFSI in P$_{1114}$FSI electrolyte and (c) 3.8 mol.kg$^{-1}$ LiFSI in P$_{1114}$FSI electrolyte.
Figure 60 Nyquist plots of the impedance spectra of Li | Li cell with different electrolytes (a) after 1 day under OCP conditions, (b) after 1, (c) 10, (d) 50 lithium plating/stripping cycles at $j = 1.5 \text{ mA.cm}^{-2}$ at 50 °C and (e) extracted cell resistance ($R_{\text{cell}}$) values.
In sharp contrast, the impedance of the cell with the organic solvent electrolyte increased markedly with cycling, which has been attributed to factors including electrolyte breakdown and consumption, the formation of ‘dead-lithium’ and subsequent SEI buildup.\textsuperscript{1,16-17} The contrasting dramatic decrease in cell impedance for the IL containing cells indicates an absence of these processes and has been suggested to result from a combination of improved electrolyte fluidity and Li\textsuperscript{+} diffusivity through the modified SEI, but also from surface area increase and SEI modification.\textsuperscript{4,15}

With the highly concentrated IL electrolyte, it can be seen that the surface resistance (\(R_{\text{surface}}\)) after 50 cycles is very close to that measured directly after assembly (0 days, Figure 4 (b)) and nearly one order of magnitude lower than that measured after 6 days under OCP conditions. This effect correlates with the polarisation behaviour (relatively low and stable) in the plating/stripping experiments presented earlier (Figure 59 (c)) and can, in part, be explained by an increase in the surface area of active lithium at the electrode during cycling. Interestingly, \(R_{\text{surface}}\) after 50 cycles has the same order of magnitude in the case of both IL electrolytes, independent of the Li salt concentration.

In the case of the highly concentrated IL electrolyte, the shape of the voltage profile also changes during cycling (Figure 61). The first Li dissolution process starts with an immediate increase of the potential (\(\sim 0.09\) V at \(j = 1.5\) mA.cm\(^{-2}\)). This increase, which is the maximum polarisation potential recorded during the whole experiment, can be explained by a specific kinetic hindrance for Li dissolution/deposition through the initial native surface film formed after immersion of Li into the IL electrolyte.\textsuperscript{18} By the 50\textsuperscript{th} cycle, the cell voltage profile has stabilised completely and there is no indication of any mass transport limitations in the response.
Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Chapter 4

Figure 61 Selected voltage profiles of subsequent Li stripping / plating process on the Li WE, denotes as cycles in Li | Li symmetrical cells containing 3.8 mol.kg⁻¹ LiFSI in P₁₁₁₁₁₄FSI electrolyte at \( j = 1.5 \text{ mA.cm}^{-2} \), at 50 °C (1ˢᵗ, 2ⁿᵈ, 10ᵗʰ and 50ᵗʰ cycles from the left to the right).

4.3.5 Post cycling impedance spectroscopic characterisation of Li metal electrodes in contact with the highly concentrated IL electrolyte

The post-cycling stability of the cell resistance as a function of resting time was studied for the high concentration IL electrolyte. The impedance of the cell after completing 50 cycles at 50 °C was monitored after 1 and 8 weeks storage at 50 °C and then again after storage at 25 °C for a further 8 weeks after which the cell was returned to the oven for 24 h at 50 °C, the data is presented in Figure 62. The cell resistance decreased slightly when the cell was at rest at 50 °C and remained stable for over 8 weeks, indicating that the interphase exhibits a low and stable resistance under these conditions.
Placing the cell outside the oven at 25 °C for a further 2 months resulted in a slight increase in cell resistance, indicating that the SEI layer is also stable for prolonged periods at room temperature. The Nyquist plot in Figure 62(a) shows a decrease of the electrolyte resistance (from 20 Ω at 25 °C to 7 Ω at 50 °C, related to an improved fluidity and decrease of viscosity at higher temperature). The Li surface resistance also decreases again (from 32 Ω at 25 °C to 9 Ω at 50 °C). These spectra strongly illustrate a highly stable SEI layer formed at the Li surface over this specific temperature range.

Figure 62 (a) Nyquist plot of the impedance spectra of Li | Li cell with 3.8 mol.kg⁻¹ LiFSI in P₁₁₃₁₄FSI electrolyte after 1, 8 and 16 weeks rest after 50 lithium plating / stripping cycles at \( j = 1.5 \text{ mA.cm}^{-2} \) at 50 °C (the cell was stored at 25 °C between 8 and 16 weeks); (b) Time dependence of the overall cell resistance of the Li | Li cell.

4.3.6 Summary of the impedance spectroscopic characterisation of Li metal electrodes in each electrolyte

A comparison of the resistances (\( R_{\text{electrolyte}} \) and \( R_{\text{surface}} \)) of the cells under OCP condition with the resistances of the cycled cells is given in Table 17 and Table 18. These results reveal that the ohmic resistance of the electrolyte \( R_{\text{electrolyte}} \) is far lower than the resistances at the electrode surface, \( R_{\text{surface}} \), and is very stable (Table 17). This could be observed for all electrolytes. Notably, \( R_{\text{electrolyte}} \) was observed to increase substantially for the carbonate electrolyte, particularly at 50 °C, highlighting the instability of this system with Li metal and reflecting the likely decomposition of the electrolyte plus the build-up of ‘mossy’ Li deposits which result in increased tortuosity for ion transport in the electrolyte.⁸, ¹⁹-²¹
Interestingly, the 3.8 mol.kg\(^{-1}\) LiFSI system shows a decrease in \(R_{\text{electrolyte}}\), which may be due to measurement artefacts but could also reflect an improvement and alteration in the separator dimensions and wetting that occurred during cycling.

Table 17 Electrolyte resistance \(R_{\text{electrolyte}}\) (±1 Ω) and surface resistance \(R_{\text{surface}}\) (± 1 Ω) of Li | Li cells with three electrolytes before and after 6 days under OCP conditions and after 1, 10 and 50 lithium plating / stripping cycles at \(j = 1.5\) mA cm\(^{-2}\) at 25°C.

<table>
<thead>
<tr>
<th>Cycling conditions</th>
<th>1 M LiPF(<em>6) in EC:DMC (1:1) (R</em>{\text{electrolyte}})</th>
<th>0.5 mol.kg(^{-1}) of LiFSI in P(<em>{1114})FSI (R</em>{\text{electrolyte}})</th>
<th>3.8 mol.kg(^{-1}) of LiFSI in P(<em>{1114})FSI (R</em>{\text{electrolyte}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unycled, 0d</td>
<td>6</td>
<td>4</td>
<td>24</td>
</tr>
<tr>
<td>6d</td>
<td>507</td>
<td>276</td>
<td>101</td>
</tr>
<tr>
<td>1 cycle</td>
<td>7</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>10 cycles</td>
<td>7</td>
<td>67</td>
<td>15</td>
</tr>
<tr>
<td>50 cycles</td>
<td>16</td>
<td>4</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 18 Electrolyte resistance \(R_{\text{electrolyte}}\) (±1 Ω) and surface resistance \(R_{\text{surface}}\) (± 1 Ω) of Li | Li cells with three electrolytes before and after 6 days under OCP conditions and after 1, 10 and 50 lithium plating / stripping cycles at \(j = 1.5\) mA cm\(^{-2}\) at 50°C.

<table>
<thead>
<tr>
<th>Cycling conditions</th>
<th>1 M LiPF(<em>6) in EC:DMC (1:1) (R</em>{\text{electrolyte}})</th>
<th>0.5 mol.kg(^{-1}) of LiFSI in P(<em>{1114})FSI (R</em>{\text{electrolyte}})</th>
<th>3.8 mol.kg(^{-1}) of LiFSI in P(<em>{1114})FSI (R</em>{\text{electrolyte}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unycled, 0d</td>
<td>3</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>6d</td>
<td>54</td>
<td>55</td>
<td>9</td>
</tr>
<tr>
<td>1 cycle</td>
<td>5</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>10 cycles</td>
<td>5</td>
<td>48</td>
<td>8</td>
</tr>
<tr>
<td>50 cycles</td>
<td>100</td>
<td>32657</td>
<td>8</td>
</tr>
</tbody>
</table>
4.3.7 Li metal cycling stability under aggressive cycling conditions

Of particular interest with respect to the possible application of these electrolytes in real devices, was the study of the cycling behaviour of the highly concentrated IL electrolyte when the amount of charge applied is increased (e.g., from 3 to 6 mA.h.cm\(^{-2}\)) at the same temperature and under more aggressive cycling conditions (i.e., \(j = 12.0\) mA.cm\(^{-2}\), 50 °C, equivalent to 2 C rate for a cell with a high cathode active material loading). Figure 63 shows the long-term cycling stability of a Li | Li cell with 3.8 mol.kg\(^{-1}\) LiFSI in P\(_{11,14}\)FSI as electrolyte. Figure 64 and Figure 65 show an expanded view of several cycles (including the first cycle). A very high current density of 12 mA.cm\(^{-2}\) was used and the cell was cycled for over 20 days.

The voltage time profile suggests that the cell can sustain stable polarisations for an extended period; up to 20 days continuous cycling is demonstrated (450 cycles and 6 mA.h.cm\(^{-2}\) of Li transferred per plating/stripping process) i.e., this stimulates 20 days of continuous 2C charge/discharge cycling in a “commercial” device. Larger polarisations are also recorded (e.g., after 15 days as shown in the inset) and these are interpreted as a signature of active lithium surface modification. These events do not seem to be related to lithium dendrite short-circuits, based on microscopic examinations of electrode surfaces presented in the next section and on previous observations using optical cells, nor do they seem related to electrolyte decomposition which typically results in steadily increasing cell resistance.

The increase in polarisation could be an indication of the pore clogging mechanism suggested by Grande et al.\(^4\) who proposed that ion diffusion channels in the native SEI (e.g. at grain boundaries within the mostly inorganic SEI components close to the Li surface) become clogged by electrolyte decomposition products during cycling. High efficiencies were reported and it was suggested that cycle life was limited due to the pore clogging mechanism. The presence of an outer “organic/polymer” SEI layer composed of electrolyte decomposition products slowed the clogging process, but ultimately it was this process, not consumption of all available lithium due to poor efficiency, that led to cell polarisation and failure.
Hence these authors suggested that the efficiency values estimated by symmetrical cell cycling were lower than the true efficiency. In the case of the high concentration phosphonium system shown here, this failure mechanism could be suppressed, or perhaps overcome by the larger polarisations visible in the voltage profile and subsequent to these events the cell continues to cycle with a low and stable overpotential. This is interpreted as being the result of the formation of a highly conductive and uniform SEI on an “active” high surface area nanostructured Li deposit, which does not incorporate the original native SEI components.

Figure 63 Voltage profile during subsequent lithium plating / stripping processes on the WE in Li/Li symmetrical cells containing 3.8 mol.kg⁻¹ LiFSI in P₁₁₁₄FSI electrolyte at \( j = 12.0 \text{ mA.cm}^{-2} \), at 50 °C.
Figure 64 Voltage profile of several cycles (1, 2, 3, 10) during subsequent lithium plating / stripping processes on the WE in Li | Li symmetrical cells containing 3.8 mol.kg\(^{-1}\) LiFSI in P\(_{1114}\)FSI electrolyte at \(j = 12.0\) mA.cm\(^{-2}\), at 50 °C.

Figure 65 Voltage profile of several cycles (50, 100, 200 and 400) during subsequent lithium plating / stripping processes on the WE in Li | Li symmetrical cells containing 3.8 mol.kg\(^{-1}\) LiFSI in P\(_{1114}\)FSI electrolyte at \(j = 12.0\) mA.cm\(^{-2}\), at 50 °C.
As shown by Grande et al. this experiment allows for determination of the minimum Coulombic Efficiency (CE) occurring in the cell, which indicates a CE > 99.3% after 450 cycles at the very high rates and charge transfer applied in these experiments. It should be noted that the cell was still cycling after the experiment was stopped and so the true efficiency is underestimated by this calculation. In contrast, the cycling of Li | Li cells with 0.5 mol.kg\(^{-1}\) LiFSI in \(\text{P}_{1114}\text{FSI}\) electrolyte at this current density often results in random voltage oscillations and increased polarisation events, as shown in Figure 66, suggesting intermittent cell shunting.

The SEM images presented in the following section highlight the formation and uniformity of a compact active Li deposit formed during cycling of these cells and further confirm the demonstration of exceptionally high coulombic efficiencies in these cells.

![Figure 66 Voltage profile during subsequent lithium plating / stripping processes on the WE in Li | Li symmetrical cells containing 0.5 mol.kg\(^{-1}\) LiFSI in \(\text{P}_{1114}\text{FSI}\) electrolyte at \(j = 12.0\) mA.cm\(^{-2}\), at 50°C.](image)

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
As supplementary information the following graphs (Figure 67 to Figure 69) present the polarisation profiles of the cell (E vs. capacity) with the highly concentrated IL electrolyte as well as the cycling dependence of the amount of charge plated and stripped.

Figure 67 (a) Plating and (b) stripping capacity profile during selected subsequent lithium plating/stripping processes (cycles 1, 2, 10 and 50) on the WE in Li | Li symmetrical cells containing 3.8 mol.kg\(^{-1}\) LiFSI in P\(_{1114}\)FSI electrolyte at \(j = 12.0\) mA.cm\(^{-2}\), at 50°C.

Figure 68 (a) Plating and (b) stripping capacity profile during selected subsequent lithium plating/stripping processes (cycles 100, 200 and 400) on the WE in Li | Li symmetrical cells containing 3.8 mol.kg\(^{-1}\) LiFSI in P\(_{1114}\)FSI electrolyte at \(j = 12.0\) mA.cm\(^{-2}\), at 50°C.
Figure 69 Cycle dependence of the stripping capacity and coulombic efficiency (CE) of a Li | Li symmetrical cell containing 3.8 mol.kg\(^{-1}\) LiFSI in P\(_{111i4}\)FSI electrolyte at \(j = 12.0\) mA.cm\(^{-2}\), at 50°C.

4.3.8 Li metal deposition morphology

4.3.8.1 Solubility test results and choice of rinsing solvent

Table 19 presents solubility results of the phosphonium IL P\(_{111i4}\)FSI in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Acetonitrile</th>
<th>DMC</th>
<th>Hexane</th>
<th>Diethyl ether</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>S / I</td>
<td>S</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
</tbody>
</table>

Hexane is the solvent used to rinse the pristine Li metal surface so it would be ideal to be able to use it to remove any residue of IL on the Li surface, however, the IL is not soluble in this solvent. Therefore the use of hexane to wash the IL residue does not allow us to access any information on the Li surface morphology as illustrated in the SEM images compared with dimethyl carbonate (DMC) as shown in Figure 70. Since acetone is not a suitable solvent to store in an argon filled glove box, and the solubility results suggest that DMC could be suitable as a washing agent, this was the solvent of choice for these experiments. The low reactivity of DMC with Li metal was also confirmed by FTIR spectroscopy and explained in Chapter 5.
Figure 70 SEM images (EHT = 5.00 kV) of the plated Li WE after 50 cycles at $j = 1.5 \text{ mA.cm}^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI at 50 °C rinsed with hexane (left) and DMC (right)

4.3.8.2 SEM images of the prepared film and cycled Li surfaces

To identify the mechanism supporting the cycling stability of the Li metal electrode in the highly concentrated IL electrolyte, cycled cells were stopped at different plating/stripping stages (after 1 and 50 cycles in the case of 3 mAh.cm$^{-2}$; after 450 cycles in the case of 6 mAh.cm$^{-2}$) and SEM images of their electrodes were acquired to observe morphological changes. Selected images are presented in this section and the reader is provided with more images in the appendix section at the end of this chapter.

Figure 71 presents SEM images of a pristine Li metal surface brushed and rinsed in hexane. This surface will be referred to as the prepared film. Winter et al. recently demonstrated that direction and control of the Li deposition process were promoted by introducing surface patterns favourable for Li deposition.\textsuperscript{22}
In the literature, several groups have reported the corrosion of Li metal as well as dendrite growth as a failure mechanism.\textsuperscript{13, 15, 23-24} In contrast, a different surface morphology of a plated Li metal electrode cycled in the highly concentrated IL electrolyte was observed after 1 and 50 cycles.

Lv et al.\textsuperscript{8} recently demonstrated in cross sectional images, that the Li metal anode’s porous interphase grows inward towards the bulk (fresh) Li metal and the accumulation of this highly resistive layer is accelerated at high current densities (> 0.3 mA.cm\textsuperscript{-2}) which would explain any increase in cell impedance and battery failure.

Figure 72 (a) gives an overview of the general appearance of the plated electrode after 1 cycle, which is very different to that of the plated electrode after 50 cycles, depicted in Figure 72 (b). The deposit on the electrode after 1 cycle is characterised by nodule-like features. The mossy dense features packed into bundles observed on the surface after 1 cycle remained unchanged after 50 cycles. This observation confirms the good compatibility between Li metal and the IL electrolyte with continuous plating, as well as the formation of a stable SEI. This SEI layer appears to hinder dendrite formation through inhomogeneities as well as the breakdown/clogging during long-term cycling.
Figure 72 SEM images (EHT = 2.00 kV) of the plated Li electrode after (a) 1 cycle; (b) 50 cycles at $j = 1.5$ mA.cm$^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI at 50°C after rinsing with DMC.

The comparison of the morphology of the pristine Li surface (Figure 71) with that of the plated surface suggests that ‘plateau’ features, as indicated in the figure, only appear after lithium plating / stripping cycles. In the case of the novel phosphonium electrolytes employed here, a dense and compact metal deposit is formed on the surface of the original Li metal electrode, as shown in Figure 72 (b).

An estimation of the thickness of this deposit (≈12 μm after 50 cycles) suggests a high cycling efficiency (when comparing the volume of metal deposit with the theoretical volume calculated from the charge applied, 3 mAh.cm$^{-2}$, i.e., 12 μm thickness for a 0.5 g.cm$^{-3}$ Li deposit) and this is consistent with a CE $> 95\%$, indicating that a small amount of charge has been consumed by side reactions (which would form a very thin, and low resistivity SEI layer as discussed above). Further micrographs of the plated surface are provided in Figure 73 and in the appendix section at the end of this chapter.
Figure 73 SEM images (EHT = 2.00 and 5.00 kV) of the plated Li electrode after 50 cycles at $j = 1.5 \text{ mA.cm}^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in $\text{P}_{11144}$FSI at 50°C after rinsing with DMC; surface area close to the cross section (top left and bottom graphs) and further away from the cross section (top right only).

Under the more aggressive cycling conditions (i.e., 12 mA.cm$^{-2}$ corresponding to 6 mAh.cm$^{-2}$) a metal deposit with similar features was formed on the surface of the Li metal, as shown in Figure 74. The compactness and uniformity of the electrode once again denotes the very high stability of Li metal in the highly concentrated IL electrolyte under these conditions. In this case of the thickness of the deposit, approaching 100 $\mu$m, indicates a different distribution of Li metal filling/covering the nanostructured deposit, given that the estimated thickness for the 6 mAh.cm$^{-2}$ should be in the vicinity of 24 $\mu$m. This suggests a more voluminous stripped deposit, which may reflect the increased number of cycles or the higher applied current used in this experiment.
Figure 74 SEM images (EHT = 2.00 kV) of the plated Li electrode after 450 cycles at $j = 12 \text{ mA.cm}^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{11144}$FSI at 50°C after rinsing with DMC.

SEM micrographs of the stripped Li surface cycled in the highly concentrated IL electrolyte are presented in Figure 75 and show a sparse deposit in comparison to the images of the plated surface. The appearance of the stripped surface closely resembles that of the plated surface, but the remnant deposit appears to be of much higher surface area, with porosity and structure approaching the meso- nano-scale. The features of this deposit are believed to be critical in supporting the excellent cycling performance obtained and the following postulate is made: the deposit is composed mainly of SEI coated, nanoscale Li metal which supports a “breathing” mode of Li cycling, with the charged surface having the appearance of an “inflated version” of the remnant deposit.

Figure 75 SEM images (EHT = 2.00 kV) of the stripped Li electrode after (a) 1 cycle; (b) 50 cycles at $j = 1.5 \text{ mA.cm}^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{11144}$FSI at 50°C after rinsing with DMC.
Perhaps even more striking is the appearance of the underlying bulk Li metal “substrate”, which appears almost featureless and smooth. The nodule-like features observed on the plated Li surface after 1 cycle are also present on the stripped Li surface (Figure 75 (a)).

Micrographs of a Li WE surface (plated and stripped) cycled in the dilute IL electrolyte (0.5 mol.kg⁻¹ LiFSI in P₁₁₁₄FSI) are presented respectively in Figure 76 and Figure 77: by comparison these images demonstrate a relatively uneven coverage of the plated Li surface; the distinct layer obtained for the highly concentrated IL electrolyte is less obvious and the underlying Li surface is more roughened. This indicates distinct differences in the progression of the plating/stripping processes for the two electrolyte systems and may be the basis for the improved performance exhibited by the high concentration electrolyte.

The evidence presented thus far indicates that the compact deposit layer formed on the Li electrode surface in the high concentration phosphonium FSI system does not undergo significant corrosion or side reactions and the underlying Li electrode appears almost pristine, all of which is critical for high CE and long-term cycling stability. The stable lithium electrode morphology observed here after cycling is in good agreement with the consistency of the recorded impedance spectra previously discussed.

Figure 76 SEM images (EHT = 2.00 kV) of the plated Li electrode after 50 cycles at \( j = 1.5 \text{ mA.cm}^{-2} \) in 0.5 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI at 50°C after rinsing with DMC.
Figure 77 SEM images (EHT = 2.00 kV) of the stripped Li electrode after 50 cycles at $j = 1.5$ mA.cm$^{-2}$ in 0.5 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI at 50°C after rinsing with DMC.

From the previous microscopic analysis the following observations were made:

- the dimethyl carbonate (DMC) solvent used to cleanse the Li surface allowed access to more detailed information on the lithium surface morphology
- significant differences arise in morphology between the pristine Li surface and those plated in the phosphonium IL electrolyte
- a nanostructured electrode was created after 50 plating / stripping processes at $j = 1.5$ mA.cm$^{-2}$ at 50°C in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI
- the formation of a stable porous interphase growing towards the Li substrate is enhanced by high Li salt content
4.4 Conclusions

The interpretation of the polarisation profiles of lithium dissolution and deposition on lithium metal allowed an in situ observation of different stages of these processes. Comparative studies through galvanostatic cycling experiments combined with EIS and SEM analysis an insights into SEI formation and evolution in a phosphonium FSI IL electrolyte with high Li salt content.

An outstanding rate and cycling stability of Li metal electrodes in a phosphonium FSI IL, enhanced by high Li salt content, was demonstrated. Compact and non-dendritic Li metal can be deposited / stripped at rates and areal capacities equivalent or superior to those found for commercial graphite Li-ion electrodes when using a highly concentrated IL electrolyte based on P1114FSI and LiFSI salt. These electrolytes are characterised by a low reactivity on Li metal and lead to the formation of a stable SEI layer. This results in a uniform Li deposition process which is improved with the addition of high concentration of LiFSI salt and the large amount of Li$^+$ cations available enables high current densities to be used for Li metal plating.

The resistance of the SEI layer significantly decreases after the first cycle and the film is characterised by a low and stable resistance, indicating that a highly conductive SEI layer is formed. SEM images highlight the compact features of the metal deposition layer and the retained pristine condition of the underlying Li metal electrode. The electrochemical and surface characterisation data indicate that minimal corrosion or reaction of the Li electrode occurs in these systems and this contributes to the excellent stability of the Li metal electrode demonstrated here. The surface features on Li metal in these electrolytes indicate that these materials are apt for safe use in Li metal batteries. This study provides an insight into understanding the role of these highly concentrated electrolytes in achieving stable cycling and this will be further explored in the next chapter.
4.5 References


Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Chapter 4 Appendices

Figure S 8 SEM images of the plated Li electrode after 50 cycles at $j = 1.5$ mA.cm$^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{111}$FSI at 50°C after rinsing with DMC.

Figure S 9 SEM images of the plated Li electrode after 1 cycle at $j = 1.5$ mA.cm$^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{111}$FSI at 50°C after rinsing with DMC.
Figure S 10 SEM images of the stripped Li electrode after 50 cycles at $j = 1.5$ mA.cm$^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI at 50°C after rinsing with DMC.

Figure S 11 SEM images of the stripped Li electrode after 1 cycle at $j = 1.5$ mA.cm$^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI at 50°C after rinsing with DMC.

Figure S 12 SEM images (EHT = 2.00 kV) of the plated Li electrode after 450 cycles at $j = 12$ mA.cm$^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI at 50°C after rinsing with DMC.
Figure S 13 SEM images of the plated Li electrode after 50 cycles at $j = 1.5$ mA.cm$^{-2}$ in 0.5 mol.kg$^{-1}$ of LiFSI in P$_{111}$SiFSI at 50°C after rinsing with DMC.
Chapter 5  Spectroscopic characterisation of the SEI layer at the lithium metal electrode in contact with P_{11i4}FSI - based electrolytes
5.1 Introduction

It is well known that the SEI layer formed on lithium (Li) metal is critical to the overall battery performance.\textsuperscript{1-2} Therefore the cycling efficiency of a Li battery depends on the formation mechanism and stability of the SEI. While most studies have focused on the SEI formation at the graphite electrode in the context of Li-ion batteries, the SEI formation at the Li metal electrode is still being investigated.\textsuperscript{1} Researchers are looking at the mechanisms of SEI formation prior to and during cycling. The standard electrolytes used in Li-ion batteries are based on organic carbonate solvents and their incompatibility with the Li metal electrode has been demonstrated in many studies due to dendrite formation, ‘mossy’ Li deposition and the formation of ‘dead-lithium’.\textsuperscript{3-4} Most approaches published in the literature have investigated new electrolyte components: new solvents,\textsuperscript{5-7} solvent mixtures,\textsuperscript{8-11} alternate Li salts.\textsuperscript{12-18} However, reports detailing SEI formation at the Li metal electrode in IL electrolytes remain limited.\textsuperscript{2, 19-24}

The research in this field has recently increased due to the design of novel ILs with more beneficial properties for SEI formation to prevent short circuit and thermal runaway (e.g. low vapor pressure, wide electrochemical window, thermal stability).\textsuperscript{2} Initial studies reported on the use of ILs based on the TFSI and FSI anions due to their superior ionic conductivity and their wide electrochemical window to facilitate reversible $Li^+/Li^0$ deposition without any decomposition.\textsuperscript{18, 25} Basile et al.\textsuperscript{22} monitored the Li surface morphology as a function of immersion time in a pyrrolidinium FSI IL and demonstrated that the SEI formed initially was compatible with the Li metal electrode by smoothing its surface. After 12 days of immersion a roughening of the Li surface was observed with formation of coral crystal structures growing into grain boundaries. After 18 days of immersion these coral-like structures were not visible anymore and the surface had again become smooth.

The commonly studied ILs for Li metal battery electrolytes include the following: pyrrolidinium and imidazolium TFSI ILs,\textsuperscript{23, 26-27} pyrrolidinium FSI ILs,\textsuperscript{22, 28-30} morpholinium FSI ILs,\textsuperscript{31} piperidinium TFSI and FSI ILs.\textsuperscript{31-32}
Most studies have used ILs with a nitrogen-based cation whereas there have only been limited studies of the SEI formed at the Li metal electrode in an IL with a phosphonium-based cation; for example a detailed XPS analysis of phosphonium ILs with relevant peak assignments to our study. An understanding of the mechanism of interaction between a phosphonium IL and the Li metal electrode is therefore important as novel phosphonium-based ILs with superior electrolyte properties are described.

The previous chapter revealed that a solution of 3.8 mol.kg\(^{-1}\) of LiFSI in P_{114}FSI allowed repetitive plating / stripping of Li suggesting the formation of a stable SEI at the Li metal electrode. The previous chapter also revealed the formation of a compact deposit on the Li substrate during cycling in this electrolyte leading to high cycling efficiency. In this chapter, the composition of the SEI formed in this highly concentrated IL electrolyte will be characterised to provide a better understanding of the SEI formation in this type electrolyte. A comparison of the nature of the SEI formation in the dilute IL electrolyte will be provided.

5.2 Experimental methods

Electrolytes and Li metal surfaces were prepared as described in Chapter 2. As already mentioned in Chapter 2, the experimental methods relevant to the studies presented in this Chapter are:

- Magic Angle Spinning Nuclear Magnetic Resonance spectroscopy (MAS NMR)
- Attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR)
- Soft x-ray photoelectron spectroscopy (XPS)
- Electrochemical impedance spectroscopy (EIS)
5.3 Results

5.3.1 MAS NMR characterisation of the IL - Li substrate

Ex-situ Magic Angle Spinning Nuclear Magnetic Resonance spectroscopy (MAS NMR) was used to get a better understanding of the nature of the interaction of the IL and the Li substrate, as well as the chemical nature of the resultant film. This technique was recently reported in the context of characterisation of the SEI layer in Li batteries. The previous chapter revealed the outstanding cycling performance of the highly concentrated IL electrolyte on Li metal when 3 mAh.cm\(^{-2}\) \((\dot{\jmath} = 1.5 \text{ mA.cm}^{-2}\) \) was applied over 50 plating / stripping processes at 50 °C. In this work we have investigated the Li metal substrate following the same cycling conditions in the highly concentrated \(\text{P}_{1114}\text{FSI} - \text{based electrolyte using solid} - \text{state NMR spectroscopy.}\)

The deposit on the plated Li electrode (unrinsed) was scraped off the Li substrate. A 50:50 (wt %) mixture of deposit: alumina powder (Al\(_2\)O\(_3\) AC300) was prepared and used for the \(^7\text{Li}, ^{31}\text{P} \) and \(^{19}\text{F}\) MAS NMR analysis. To confirm the reproducibility of the preparation of cycled Li electrodes, Li surfaces extracted from two different coin cells were analysed by \(^7\text{Li} \) and \(^{19}\text{F}\) MAS NMR. The spectra obtained were considered as identical as exemplified by the comparative \(^7\text{Li} \) and \(^{19}\text{F}\) spectra shown in Figure 78 and Figure 80.

Figure 78 (a) presents the \(^7\text{Li}\) NMR spectra for the SEI deposit of sample 1. The small signal at 260 ppm is assigned to Li metal. All the other resonances are around 0 ppm and correspond to diamagnetic species. These broad overlapping resonances were fitted and the fitted results are presented in Figure 79. There is a sharp resonance at -1.3 ppm that corresponds to LiF. The broadest resonance rises at approximately 2.8 ppm and may correspond to Li\(_2\)O. The intermediate signal (0.5 ppm) could correspond to other diamagnetic species (such as Li\(_2\)CO\(_3\) or organic lithiated species such as LiF, Li\(_2\)S). For the \(^7\text{Li}\) NMR of sample 2 (Figure 78 (b)), the resonance was a little narrower compared to the first sample. It corresponds to the -1.3 ppm already observed in the sample 1 (LiF). The \(^7\text{Li}\) NMR spectra show that LiF is the main lithiated SEI component.
Figure 78 $^7$Li NMR spectra (500 MHz, 25 kHz spinning speed) for the 50:50 (wt %) mixture of SEI deposit: alumina powder (Al$_2$O$_3$ AC300) for (a) sample 1 and (b) sample 2. The SEI deposit was scraped off the plated Li electrode.

Figure 79 $^7$Li NMR spectra with fitted peaks (500 MHz, 25 kHz spinning speed) for the 50:50 (wt %) mixture of deposit: alumina powder (Al$_2$O$_3$ AC300) for sample 1. The deposit was scraped off the plated Li electrode.
The $^{19}$F NMR spectrum of sample 1 is shown in Figure 80 (a). The signal at -205 ppm corresponds to LiF, which is in agreement with the signal detected at -1.3 ppm on the $^7$Li spectrum (Figure 79).\textsuperscript{41-42} Several broad resonances can be observed between -140 and –170 ppm. In this region, the resonances are typically assigned to the following groups: CHF = CR$_2$, CF = CF$_2$, RCH$_2$F where R can be attributed from ethyl- to butyl-groups.\textsuperscript{41, 43} These species could be lithiated compounds.\textsuperscript{45} For $^{19}$F NMR of sample 2 (Figure 80 (b)), the same resonances as those in sample 1 can be observed, although the relative intensities are slightly different. The same fluorinated species are found in the SEI.

![Figure 80 $^{19}$F NMR spectra with fitted peaks (500 MHz, 23 kHz spinning speed) for the 50:50 (wt %) mixture of deposit: alumina powder (Al$_2$O$_3$ AC300) for (a) sample 1 and (b) sample 2. The deposit was scraped off the plated Li electrode.](image)

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
The $^{31}$P NMR spectra of sample 1 only are illustrated in Figure 81 and show one sharp resonance at 24 ppm and indicate that the cation is unaffected by the presence of the inorganic surface. The resonance could also be attributed to the phosphonium cation itself.$^{46-47}$

![Figure 81](image-url)

**Figure 81** $^{31}$P NMR spectra (500 MHz, 25 kHz spinning speed) for the 50:50 (wt %) mixture of SEI deposit: alumina powder (Al$_2$O$_3$ AC300) for sample 1. The SEI deposit was scraped off the plated Li electrode.

From this analysis the following mechanisms of SEI formation can be considered:

1. An adsorption mechanism: the anion is adsorbed onto the metal (or metal oxide layer) where an electrostatic interaction with the cation occurs to maintain charge neutrality, this mechanism implies the formation of a layered structure (two layers)
2. The anion interacts with the metal cation itself (e.g. Li$^+$)
3. The IL ions (anion and/or cation) break down into several chemical species which can then interact with the Li surface via chemical adsorption or remain on top of the surface film if insoluble.
The NMR study has given more insight into the chemical composition of the deposit formed on Li metal under specific cycling conditions (highly concentrated IL electrolyte, after 50 plating / stripping processes). The cycling dependence of the chemical composition of the deposit formed on the Li metal and its stability during cycling became of particular interest and was studied using FTIR, XPS and EIS spectroscopy in the aim of supporting the results obtained by NMR.

5.3.2 FTIR studies of cycled Li electrodes

The lithium disks removed from cycled Li | Li symmetrical cells containing the highly concentrated P111i4FSI-based electrolyte are expected to reflect interactions with only three species: the IL cation (P111i4⁺), the IL anion (FSI⁻) or the rinsing agent (DMC). No significant conclusion on the SEI properties can be drawn from the non-rinsed surfaces (the same observations were made from the SEM analysis). The rinsing agent is necessary to be able to establish differences in the SEI properties according to the composition of the IL electrolyte. The use of DMC as rinsing agent has become an established method to remove residual IL electrolyte from the Li surface.21, 27, 31, 48

Peak assignments for the FTIR spectrum data of the prepared film and uncycled Li surfaces can be found in Table 20. The Li surface used in the coin cells (i.e. pristine Li surface brushed and rinsed with hexane) is referred to as the prepared film. The IR spectra of the prepared film, pure lithium hydroxide (LiOH) and lithium carbonate (Li₂CO₃) are provided in Figure 82.
Figure 82 FTIR spectra of the prepared film, pure lithium hydroxide (LiOH) and pure lithium carbonate (Li$_2$CO$_3$).

Figure 83 FTIR spectra of control samples: pure LiFSI salt, neat P$_{1114}$FSI ionic liquid, unused Li surface immersed into DMC, prepared film. The prepared film is a pristine Li surface brushed and rinsed with hexane.
Table 20 Assignment for the FTIR spectrum data of prepared film and other unycled Li surfaces. The prepared film corresponds a pristine Li surface brushed and rinsed in hexane; the unycled Li surface was subsequently immersed in P11i4FSI and DMC (ν: stretching, δ: bending, s: strong, m: medium, w: weak)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Prepared film</th>
<th>Uncycled Li</th>
<th>Li rinsed in DMC</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₈(SNS)</td>
<td>731</td>
<td></td>
<td></td>
<td>23, 49-51</td>
</tr>
<tr>
<td>ν₆(SNS) and ν(SF)</td>
<td>832</td>
<td></td>
<td></td>
<td>50, 52</td>
</tr>
<tr>
<td>ν₆(SO₂-N-SO₂)</td>
<td>1105</td>
<td></td>
<td></td>
<td>23, 52-53</td>
</tr>
<tr>
<td>ν(SO₂-N-SO₂)</td>
<td>1188</td>
<td></td>
<td></td>
<td>23, 52-53</td>
</tr>
<tr>
<td>ν₆(SO₂)</td>
<td>1386</td>
<td></td>
<td></td>
<td>23, 50</td>
</tr>
<tr>
<td>ν(Li₂CO₃)</td>
<td>1435 (w)</td>
<td>1426 (w)</td>
<td></td>
<td>23, 50, 52</td>
</tr>
<tr>
<td>ν(CH₂) ν(CH₃)</td>
<td>1470 (w)</td>
<td>1470 (w)</td>
<td></td>
<td>23, 54</td>
</tr>
<tr>
<td>ν(CH₂)</td>
<td>2852</td>
<td>2880</td>
<td>2854</td>
<td>23, 50, 53, 55</td>
</tr>
<tr>
<td>ν(CH₂)</td>
<td>2926</td>
<td>2928</td>
<td>2925</td>
<td>23, 50, 53, 55</td>
</tr>
<tr>
<td>ν(CH₂)</td>
<td>2963</td>
<td>2967</td>
<td>2960</td>
<td>23, 50, 53, 55</td>
</tr>
<tr>
<td>ν(CH₂)</td>
<td>3004</td>
<td></td>
<td></td>
<td>23, 50, 55</td>
</tr>
<tr>
<td>ν(LiOH)</td>
<td>3677</td>
<td>3677</td>
<td>3678</td>
<td>23, 31, 50, 52</td>
</tr>
</tbody>
</table>

Figure 84 (a) shows the IR spectra of the Li metal surfaces for electrodes removed from the cycled P11i4FSI type cells. Peak assignments are indicated on the figure and will be discussed below. Figure 84 (b) shows the low-frequency end of the Li metal spectra and illustrates significant differences in SEI properties between non-cycled and cycled Li surfaces. Peak assignments for the FTIR spectrum data of cycled Li surfaces can be found in Table 21.
Figure 84 (a) FTIR spectra and (b) low-frequency portion FTIR spectra of SEI films of plated and stripped Li surface from P_{111i4}FSI-based cells after 50 cycles at $j = 1.5 \text{ mA cm}^{-2}$ in 3.8 mol kg$^{-1}$ of LiFSI in P$_{111i4}$FSI at 50°C after rinsing with DMC. The prepared film is a pristine Li surface brushed and rinsed with hexane.
Peaks derived from the FSI anion: strong peaks in Figure 85 at 1175 and 1380 cm\(^{-1}\) (with no significant shift) denote SO\(_2\) asymmetrical and symmetrical stretching, respectively, and indicate that the SO\(_2\) portion of the anion has remained intact and is part of the SEI. Some peak splitting is visible, as observed for the pure LiFSI salt IR spectrum. The SO\(_2\) group may belong to multiple species in the SEI but from FTIR spectra we cannot make any conclusion regarding the exact structure. There does not seem to be a peak that can be assigned to the S-F stretch in the lithium electrode spectrum. The strong peaks corresponding to SN stretch are clearly present in the lithium electrode spectrum at ~ 744 and 832 cm\(^{-1}\) (in the LiFSI spectrum at ~ 757 and 853 cm\(^{-1}\)) whereas a broader peak corresponding to the native oxide layer formed on the uncycled Li surface in contact with the IL is observed in the IR spectrum.

Peaks derived from the P\(_{111i4}^+\) cation: all C-H based vibrations that do not arise from DMC reaction residue must be due to interactions with the P\(_{111i4}\) cation. There are clearly peaks associated with the CH\(_3\) stretch at 2880, 2928 and 2968 cm\(^{-1}\) which precisely match the positions of those in the IL spectrum (see IR spectrum of control sample in Figure 83). This indicates that, at least in most cases, the alkyl chains are preserved during SEI formation and suggest the presence of the intact phosphonium cation in the SEI.

Figure 85 shows the dependence of cycle number on the low-frequency end of the plated Li metal spectra. The low-frequency end of the spectra of the stripped Li metal surface are shown in Figure 86. The IR spectra of the plated Li metal surface (after ½, 1 and 50 plating processes) are similar and mostly dominated by functional groups that belong to the IL; whereas the IR spectrum of the plated Li metal surface after 250 plating processes shows much less vibrations.
The IL seems to be a major component on the plated Li surface (after extraction from the cell and rinsing / drying process) but after reaching several hundreds of plating processes, the observations suggest the formation of a more robust SEI where the IL and other chemical species could be trapped, as shown in the IR spectrum in Figure 85. Absorptions at ca. 1425 cm\(^{-1}\) attributed to Li\(_2\)CO\(_3\) were observed only in the IR spectra of plated Li surfaces after 50 and 250 cycles, as shown in Table 21. The \(\nu\)(OH) absorption typically present at 3675 cm\(^{-1}\) in the IR spectra cannot be an evidence of formation of LiOH during cycling as the Li surfaces were exposed to air for a short period of time before being pressed onto the diamond on the ATR stage.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Peak (cm(^{-1})) for plated Li surfaces (x number of plating / stripping processes)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_s)(SNS)</td>
<td>751</td>
<td>780</td>
</tr>
<tr>
<td>(\nu_a)(SNS) and (\nu)(SF)</td>
<td>833</td>
<td>852</td>
</tr>
<tr>
<td>(\nu_a)(SO(_2)-N-SO(_2))</td>
<td>1103</td>
<td>1104</td>
</tr>
<tr>
<td>(\nu)(SO(_2)-N-SO(_2))</td>
<td>1177</td>
<td>1118</td>
</tr>
<tr>
<td></td>
<td>1173</td>
<td>1218</td>
</tr>
<tr>
<td></td>
<td>1221</td>
<td>1220</td>
</tr>
<tr>
<td>(\tau)(CH(_2))</td>
<td>1311</td>
<td>1307</td>
</tr>
<tr>
<td>(\nu_d)(SO(_2))</td>
<td>1356</td>
<td>1360</td>
</tr>
<tr>
<td>(\nu_d)(SO(_2))</td>
<td>1378</td>
<td>1377</td>
</tr>
<tr>
<td>(\nu)(Li(_2)CO(_3))</td>
<td>1424</td>
<td>1425</td>
</tr>
<tr>
<td>(\nu)(CH(_2))(\nu)(CH(_3))</td>
<td>1461 (w)</td>
<td>1469 (w)</td>
</tr>
<tr>
<td>(\nu)(CH(_2))</td>
<td>2883</td>
<td>2879</td>
</tr>
<tr>
<td>(\nu)(CH(_2))</td>
<td>2928</td>
<td>2928</td>
</tr>
<tr>
<td>(\nu)(CH(_2))</td>
<td>2965</td>
<td>2967</td>
</tr>
<tr>
<td>(\nu)(CH(_2))</td>
<td>3003</td>
<td>3006</td>
</tr>
<tr>
<td>(\nu)(LiOH)</td>
<td>3676</td>
<td>3676</td>
</tr>
</tbody>
</table>

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Figure 85 Dependence of cycle number on low-frequency portion of FTIR spectra of SEI films of plated Li surface from P$_{111i4}$FSI-based cycled cells with 3.8 mol.kg$^{-1}$ of LiFSI in P$_{111i4}$FSI electrolyte (after ½, 1, 50 and 250 cycles). The prepared film is a pristine Li surface brushed and rinsed with hexane.

Figure 86 Dependence of cycle number on low-frequency portion of FTIR spectra of SEI films of stripped Li surface from P$_{111i4}$FSI-based cycled cells with 3.8 mol.kg$^{-1}$ of LiFSI in P$_{111i4}$FSI electrolyte (after ½, 1, 50 and 250 cycles). The prepared film is a pristine Li surface brushed and rinsed with hexane.

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
By comparing the IR spectra of plated and stripped Li surfaces, the percentage of transmittance is higher in the IR spectrum of the plated surface than that of the stripped surface (stretching vibrations corresponding to the anion and cation are more intense in the case of the plated surface) and secondly, the IR spectra are very similar at different stages of cycling (after \( \frac{1}{2}, 1, 50 \) and 250 plating processes). Due to the thin nature of the SEI film signal intensities are generally weak and thus carry a large error which may be the reason for small discrepancies in the 1200 and 700 cm\(^{-1}\) regions. Therefore no significant compositional changes were identified, as exemplified in the IR spectra with normalised intensity in Figure 87.

Figure 87(a) FTIR spectra and (b) low-frequency portion FTIR spectra with normalised intensity of SEI films of plated and stripped Li surface from P\(_{1114}\)FSI-based cells after 50 cycles at \( j = 1.5 \text{ mA.cm}^{-2} \) in 3.8 mol.kg\(^{-1}\) of LiFSI in P\(_{1114}\)FSI at 50°C after rinsing with DMC.

According to the previous observations, the following conclusions can be made. The FTIR spectroscopic analysis showed evidence that the CH\(_3\) group from the cation, the SO\(_2\) and SN groups from the anion are present in the SEI on the lithium metal electrode. It also appears that the SO\(_2\) group of the FSI anion is a major component in the SEI layer. The main outcome from the comparison of the Li surfaces at different plating / stripping stages is that the IR spectra of the plated and stripped Li surface acquired at the same stage are very similar. These results suggest highly effective and stable formation of the SEI on the plated / stripped surfaces early after cycling.
5.3.3 XPS analysis of the SEI products

XPS high-resolution spectra peak identities were assigned from the Handbook of X-ray Photoelectron Spectroscopy,\textsuperscript{57} the NIST XPS online database,\textsuperscript{58} published values and from previously reported XPS studies of Li metal surfaces in contact with ILs.\textsuperscript{22-23, 33} It is important to note that XPS only shows the outer layer (~ 10 nm) – therefore any species present underneath this outer layer (which can be detected by FTIR and NMR analysis) are not detected.

5.3.3.1 A comparison between native and prepared film on Li surfaces

Figure 88 presents the chemical composition (atomic percent) from the survey spectra for the native film (oxide film present on the Li metal stored inside the glove box) and the prepared film (after brushing and rinsing the surface in hexane) on a Li metal surface. Survey scans were conducted on two different spots on each surface and herein the average values are reported. Both films are mainly composed of oxygen, carbon and lithium. A slight difference can be observed in terms of chemical composition of the films: a larger amount of oxygen was detected on the prepared film in comparison to the native film; very small amounts of fluorine and sulphur (< 0.5 %) were detected on the prepared film.

![Figure 88 Chemical composition (atomic %) summary determined from the survey spectra for the untreated Li surface (native film) and the Li surface brushed and rinsed in hexane (prepared film)](image)

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
XPS analysis of the high resolution scans of the prepared Li surface revealed the presence of several chemical elements coming from impurities as can be seen in Figure 89 and listed in Table 22. The Li 1s peak was located at 54.5 eV, this value being close to peaks previously assigned as LiOH / Li₂CO₃. The O 1s and C 1s spectra confirm the evidence of the chemical specie Li₂CO₃, with peaks detected at 531.2 eV and 287.1 on the O 1s and C 1s spectra respectively. These impurities are most likely a result of surface handling, preparation and transportation (in a sealed vessel) outside the glove box. The F 1s spectrum can confirm the presence of LiF with a peak detected at 683.8 eV. On the same spectrum another peak at 686.1 eV can be identified and can be attributed to a fluorocarbon specie. When combining all these information the prepared film on the Li surface can be characterised as a surface layer composed of LiOH, Li₂CO₃ and possible LiF, with pure Li⁰ metal underneath.

Figure 89 Li 1s, F 1s, C 1s and O 1s XPS spectra of the pristine lithium surface after washing with hexane
Table 22 Summary of XPS data and assignments for the prepared lithium surface (brushed and rinsed in hexane)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak position (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>F (1s)</td>
<td>686.1</td>
<td>Fluorocarbon</td>
</tr>
<tr>
<td></td>
<td>683.8</td>
<td>LiF</td>
</tr>
<tr>
<td>O (1s)</td>
<td>531.2</td>
<td>LiOH</td>
</tr>
<tr>
<td></td>
<td>530.7</td>
<td></td>
</tr>
<tr>
<td>C (1s)</td>
<td>289.7</td>
<td>C\text{hetero}</td>
</tr>
<tr>
<td></td>
<td>287.1</td>
<td>Li\text{2CO}_3</td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>C\text{aliphatic}</td>
</tr>
<tr>
<td>Li (1s)</td>
<td>54.5</td>
<td>Li\text{2CO}_3 / LiOH, LiF and Li$^{0}$</td>
</tr>
</tbody>
</table>

5.3.3.2 XPS analysis of cycled Li surfaces

5.3.3.2.1 Reproducibility of XPS measurements and homogeneity of the SEI formed on Li surfaces

Survey scans were conducted on two different spots on each surface to assess any significant differences in the chemical elements detected and the calculated atomic percent. Figure 90 provides an example of atomic concentrations for each element for a Li surface after 50 plating / stripping processes in the IL electrolytes. The similarities in atomic concentration of each element on both spot areas reflects the homogeneity of the film formed on the Li surface in the highly concentrated IL electrolyte. In the case of the dilute IL electrolyte the atomic percent of carbon and lithium vary more significantly from one spot area to another (6 – 9 at. % difference). Very small amounts of nitrogen and phosphonium were detected (at. % (P) < 0.5 %, at. % (N) < 2 %) while smaller amounts of sulphur and larger amounts of lithium were detected. These observations suggest that the film formed on the Li surface in the dilute IL electrolyte could be thinner (supposedly composed of less species) and is not as homogeneous. This was also supported by EIS analysis (Chapter 4) where the overall film resistance was lower in the case of the dilute IL electrolyte.
The surface composition is affected by the electrode surface preparation and nature of electrolyte: the surface cycled in the dilute electrolyte is more dominated by Li and C elements whereas the surface cycled in the highly concentrated electrolyte has relatively less of these elements and more of the other elements (S, O and F).

Figure 90 Chemical composition (atomic %) summary determined from the survey spectra for two spot areas (1 and 2) of a Li surface after 50 plating / stripping processes in (a) the highly concentrated IL electrolyte and (b) dilute IL electrolyte

5.3.3.2.2 Cycling dependence of SEI composition in the highly concentrated IL electrolyte

Initial measurements clearly revealed that chemical species from the IL chemical elements were present on the surface of the sample in significant quantities, as expected after sample preparation. This shows the ultralow volatility of the electrolyte materials under ultrahigh vacuum ($10^{-10}$ mbar).

Figure 91 presents a summary of the results obtained from typical survey spectra comparing the atomic concentration of the chemical elements (F, O, N, C, S, P, Li) for plated Li surfaces (after 1, 50 and 250 plating / stripping processes). The results provide further details on the homogeneity of the film formed on the Li surface related to cycling performance. Survey scans were conducted on two different spots on each surface and herein the average values are reported.
While the survey spectra are dominated by carbon, oxygen and lithium, other chemical elements such as fluorine, nitrogen and sulphur are present in significant amounts on cycled Li surfaces. As indicated by the NMR and FTIR measurements, these elements are also derived from the IL FSI⁻ anion and the presence of some of their chemical species is a signature of the SEI composition. These spectra indicate that the SEI composition remains broadly similar throughout extensive cycling, comprised of similar overall proportions of each element.

Figure 91 Chemical composition (atomic %) summary determined from the survey spectra for the Li surfaces after 1, 50 and 250 plating / stripping processes in 3.8 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI

In order to gain further understanding of the chemical species that compose the SEI layer during cycling, XPS measurements were conducted at different numbers of plating / stripping processes (after 1, 50 and 250) and high-resolution scans were acquired. Table 23 provides a summary of XPS data and peak assignments for the different Li surfaces.
Table 23 Summary of XPS data and assignments for the lithium surfaces (plated state) after 1, 50 and 250 plating / stripping process at $j = 1.5 \text{mA.cm}^{-2}$ in 3.8 mol.kg$^{-1}$ of LiFSI in $\text{P}_{1114}\text{FSI}$

<table>
<thead>
<tr>
<th>Element</th>
<th>Assignment</th>
<th>Peak position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$x = 1$</td>
</tr>
<tr>
<td>F (1s)</td>
<td>-SO$_2$F</td>
<td>686.9</td>
</tr>
<tr>
<td></td>
<td>LiF</td>
<td>684.2</td>
</tr>
<tr>
<td>O (1s)</td>
<td>Li$_2$CO$_3$, LiOH, Li$_2$O</td>
<td>531.6</td>
</tr>
<tr>
<td>N (1s)</td>
<td>$\text{N}^-$</td>
<td>399.9, 399.0</td>
</tr>
<tr>
<td>C (1s)</td>
<td>$C_{\text{hetero}}$</td>
<td>287.6</td>
</tr>
<tr>
<td></td>
<td>Li$_2$CO$_3$</td>
<td>285.9</td>
</tr>
<tr>
<td></td>
<td>$C_{\text{aliphatic}}$</td>
<td>285</td>
</tr>
<tr>
<td>S (2p$_{3/2}$)</td>
<td>-SO$_2$F</td>
<td>168.7, 166.4</td>
</tr>
<tr>
<td></td>
<td>Li$_2$S</td>
<td>163.8</td>
</tr>
<tr>
<td></td>
<td>S$^0$</td>
<td>-</td>
</tr>
<tr>
<td>P (2p$_{3/2}$)</td>
<td>$\text{P}^+$</td>
<td>133.6</td>
</tr>
<tr>
<td>Li (1s)</td>
<td>Li$_2$CO$_3$, LiOH, Li$_2$O</td>
<td>55.8</td>
</tr>
<tr>
<td></td>
<td>LiF</td>
<td>55.3</td>
</tr>
<tr>
<td></td>
<td>Li$^0$</td>
<td>-</td>
</tr>
</tbody>
</table>

**Li 1s and F 1s spectra**

Figure 92 presents the high resolution spectra of Li 1s and F 1s. The intensity of the Li 1s peaks is smaller than that of the prepared Li surface (Figure 89), which agrees with the observations from the SEM images presented earlier, that showed a more compact and robust SEI layer forming on the bulk Li surface during cycling. After the 250 cycles the Li 1s spectra became broader and their amplitude slightly decreased. Given that the sampling depth of a photoelectron line is typically 5 to 10 nm,$^{59}$ the SEI likely prevents ejection of photoelectrons from the underlying Li metal surface. The Li 1s peak envelops a broad domain where LiF and LiOH - Li$_2$CO$_3$ are known to reside at ca. 55 and 56 eV respectively.$^{57}$
The F 1s spectra also show a peak at ca. 685 eV in all cases and this peak validates the presence of LiF on the surface. The results suggest that a layer of LiF was present on all surfaces. When looking at the amount of LiF on the surfaces (65 % at 1 cycle, 81 % at 50 cycles and 75 % at 250 cycles) the Li surfaces seem to quickly become dominated by LiF. A significant peak at ca. 688 eV was also detected on all surfaces corresponding to -SO_{2}F.\textsuperscript{58} However, a quantitative comparison of the surfaces of 50 and 250 cycles reveals a decrease in the abundance of the -SO_{2}F group while the intensity of the LiF peak increased from 1 cycle onwards (nearly doubled from 1 to 250 cycles). The same observations as a function of etching time were reported for Li surfaces cycled in ammonium-based ILs for smaller amounts of charge passed (0.25 mA.cm\textsuperscript{-2} over 10 cycles).\textsuperscript{23}

Figure 92 High-resolution Li 1s and F 1s photoelectron spectra for the plated Li surfaces in 3.8 mol.kg\textsuperscript{-1} of LiFSI in P_{1114}FSI
C 1s and O 1s spectra

Figure 93 presents the high resolution C 1s and O 1s spectra. The spectra indicated the presence of species associated with C-C / C-H at ca. 285 eV. On the C 1s spectra, the appearance of a ‘shoulder’ at ca. 286 eV at 50 and 250 cycles can be attributed to lithium carbonate (CO$_3^{2-}$)\(^{57-58}\) and C$_{\text{hetero}}$ at ca. 288-289 eV (e.g. C-P bond).\(^{33}\) The C 1s peak area is also becoming larger at 250 cycles. The overall C 1s peak shapes do not change for all samples, only the ratios vary.

The O 1s spectra show a broad peak at ca. 532.0 eV and this peak corresponds to Li$_2$O / Li$_2$CO$_3$.\(^{14, 22-23, 57}\) This peak suggests the presence of Li$_2$O and Li$_2$CO$_3$ species in the outermost layers of the SEI, these species were reported to be present in other SEI formed in IL electrolytes\(^{22-23}\) and carbonate electrolytes.\(^{8, 13}\) Minor peaks of unknown origin are also present at ca. 528 eV (less than 2 at. con. %).

![Figure 93 High-resolution C 1s and O 1s photoelectron spectra for the plated Li surfaces in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI](image-url)
N 1s, S 2p and P 2p spectra

Figure 94 presents the N 1s, S 2p and P 2p high resolution spectra. These elements were not present in the prepared film (or were in very small quantities, < 0.5 at. %). From their high-resolution spectra their presence is most likely a result of the interaction between the IL and the Li surface. The chemical species including the N and S elements that can be detected from these spectra are mainly attributed to the reaction of the FSI anion with the Li surface.

The N 1s spectra show one broad peak that could overlap two distinct peaks attributed to the chemical environment of the element N if there is a cleavage of the anion with a main component at ca. 399.9 eV.22-23

The S 2p spectra become very complex after 50 and 250 cycles with broad signals that contain at least two components corresponding to spin-orbit doublets 2p$_{1/2}$ and 2p$_{3/2}$). Two to three signals are observed at 1 cycle, with a broad signal at ca. 166.4 eV that could contain two distinct peaks, whereas at least 5 components are observed at 50 and 250 cycles. The most intense peak (broad shouldered peak) observed at ca. 168.7 eV after 1 cycle is attributed to –SO$_2$F species and is most likely overlapping a doublet.22, 23, 58 After 50 and 250 cycles this peak becomes broader and slightly shifts to a new position at 169.4 eV after 50 cycles and 168.6 eV after 250 cycles. This peak is enveloping several components that could be oxidised sulphur species such as sulfone or sulphite and breakdown products from the FSI anion.22-23, 58 The FTIR spectra discussed in the previous section confirmed the presence of O$_2$S-N-SO$_2$ species on the surface. A number of smaller peaks from 167 to 160 eV are observed at 50 and 250 cycles: a small component (at ca. 161.8 eV at 50 cycles and 161.1 eV at 250 cycles) appears in comparison to the S 2p spectrum at 1 cycle and this peak was assigned to lithium sulphide (Li$_2$S) by Howlett et al.23 However this component is present in small amounts (ca. 7 at. %).
The P 2p spectra present one broad peak (two components 2p$_{1/2}$ and 2p$_{3/2}$) at 133.6 eV at 1 cycle, 133.8 eV at 50 cycles and 133.2 eV at 250 cycles. This peak is attributed to the phosphonium cation$^{33, 58}$ and does not shift after 1, 50 and 250 cycles. This is in agreement with the data obtained with FTIR spectroscopy. The FTIR spectra revealed the presence of –CH$_3$ group (coming from the cation) on the surface after 1, 50 and 250 cycles. This validates the hypothesis that the cation could be trapped within the SEI after several hundreds of cycles.

The absence of a phosphate group (typically with a peak at ca. 132 – 133 eV)$^{57-58}$ a phosphonate group (peak at 133.6 eV)$^{57-58}$ or a phosphonic acid group (peak at 134.3 eV)$^{57-58}$ on the surface, indicates that the formation of these types of species from the phosphonium cation does not occur during cycling. These results confirm that the chemical nature of the Li surfaces is very similar after 1, 50 and 250 cycles.

Figure 94 High-resolution N 1s, S 2p and P 2p photoelectron spectra for the plated Li surfaces in 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
5.3.4 EIS analysis of cycled Li surfaces: fitting

EIS is another technique that has been used to understand the SEI composition and structure.\textsuperscript{23, 28, 60-61} The Li surface impedance was monitored after 1, 10 and 50 plating / stripping processes. The acquired impedance data were fitted with the equivalent electric circuits (EECs) presented in Chapter 2 (Table 12). The fitting results are presented in Table 25. Since constant phase elements (CPEs) gave better fitting results than ideal capacitances (C) as discussed below, the results using the EEC 1 are not reported. We attempted to fit acquired impedance data with two other models: the polymer electrolyte interphase (PEI) model developed by Thevenin and Muller\textsuperscript{62}, the layer model originally proposed by Aurbach et al.\textsuperscript{63-65}

Table 24 Equivalent electric circuits and associated equations

<table>
<thead>
<tr>
<th>EEC</th>
<th>Equivalent model</th>
<th>Equivalent equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td><img src="image" alt="Diagram" /></td>
<td>$R_1 + \frac{Q_2}{R_2} + \frac{Q_3}{R_3}$</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Diagram" /></td>
<td>$R_1 + \frac{Q_2}{R_2} + \frac{Q_3}{R_3} + W_4$</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Diagram" /></td>
<td>$R_1 + \frac{Q_2}{R_2} + \frac{C_3}{(R_3 + W_4)}$</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="Diagram" /></td>
<td>$R_1 + \frac{Q_2}{R_2} + \frac{Q_3}{R_3} + W_4$</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Diagram" /></td>
<td>$R_1 + \frac{Q_2}{R_2} + \frac{Q_3}{R_3} + \frac{Q_4}{R_4} + \frac{Q_5}{R_5} + W_6$</td>
</tr>
</tbody>
</table>

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Table 25 Fitting models and results for a cycled Li | Li with 3.8 mol.kg\(^{-1}\) of LiFSI in \(\text{P}_{1114}\text{FSI}\) electrolyte

<table>
<thead>
<tr>
<th>EEC</th>
<th>Before cycling</th>
<th>1 cycle</th>
<th>10 cycles</th>
<th>50 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\chi^2)</td>
<td>(\chi / \sqrt{N})</td>
<td>(\chi^2)</td>
<td>(\chi / \sqrt{N})</td>
</tr>
<tr>
<td>2</td>
<td>1.8 x 10(^2)</td>
<td>1.9 x 10(^{-2})</td>
<td>7.196 x 10(^{-3})</td>
<td>1.06 x 10(^{-2})</td>
</tr>
<tr>
<td>3</td>
<td>6.918 x 10(^{-2})</td>
<td>3.569 x 10(^{-2})</td>
<td>1.294 x 10(^{-2})</td>
<td>1.591 x 10(^{-3})</td>
</tr>
<tr>
<td>4</td>
<td>1.029 x 10(^{-2})</td>
<td>1.226 x 10(^{-2})</td>
<td>1.361 x 10(^{-2})</td>
<td>1.428 x 10(^{-3})</td>
</tr>
<tr>
<td>5</td>
<td>1.304 x 10(^{-1})</td>
<td>7.364 x 10(^{-1})</td>
<td>9.923 x 10(^{-3})</td>
<td>1.784 x 10(^{-3})</td>
</tr>
</tbody>
</table>

Along with the supporting information already provided by the MAS NMR, FTIR and XPS analysis, the EIS data can be incorporated to validate a model for the structure of the SEI. The best fits were obtained when using layer models with CPEs: the EEC 2 (two-component layer model) gave the best fit of the impedance spectra before and after cycling. The addition of a Warburg diffusion component to the equivalent circuit (EEC 3) did not show any improvement as shown in Table 25. Figure 95 and Figure 96 give an example of a fitted impedance spectrum obtained from a Li | Li symmetrical cell cycled in the highly concentrated \(\text{P}_{1114}\text{FSI}\) based electrolyte after 1 plating / stripping process.

The fitted spectra show that the error in the fits usually comes from the contribution of the high-frequency EIS data. This confirms that it is difficult to say that one model fits the data better than another. Therefore, precaution must be taken when interpreting the nature of the SEI structure from EIS alone. The ability to fit EIS data with a resistance / capacitance (RC) type equivalent circuit suggests a multilayer structure, in other words several layers parallel to the electrode surface.\(^{66-67}\)

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Constant phase elements (CPEs) are used to represent a “non-ideal” capacitance (Q) behaviour of the interface in opposition to an ideal capacitance (C). Their use can also suggest a complex interfacial composition with several conduction pathways. This explains why the use of R / Q elements is relevant to the modelisation of the SEI interface, suggesting the formation of films on an electrode (inner compact layers and outer diffuse layers).

The EIS spectra from a Li | Li symmetrical cell cycled in the highly concentrated P111i4FSI-based electrolyte at 1, 10 and 50 cycles (presented in Chapter 4) are very similar in shape so it is difficult to make any significant conclusion in terms of formation / dissolution of layers on the Li electrode between 1 and 50 cycles by analysing the EIS data alone.

In summary the EIS analysis provides evidence suggesting the formation of at least two layers in SEI on the Li surface after the 1st cycle according to the EEC used to get the best fit (EEC 2, two-component layer model).

Figure 95 Fitting results of EEC 2 (two-component model) for EIS data obtained from a Li | Li symmetrical cell cycled in the highly concentrated P111i4FSI-based electrolyte (after 1 plating / stripping process).
5.4 Discussion

5.4.1 Effect of Li salt content on the interfacial properties at Li metal electrodes

It was of particular interest to investigate the effect of the Li salt concentration in the IL electrolyte on the structure and chemical composition of the film formed on the Li surface. This section provides a comparison of the nature of the films formed in the highly concentrated (3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI) and dilute (0.5 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI) IL electrolyte. FTIR, XPS and EIS were the techniques used to characterise the film formed in the dilute IL electrolyte on a Li surface for which 3 mAh.cm$^{-2}$ ($j = 1.5$ mA.cm$^{-2}$) were applied over 50 plating / stripping cycles at 50 °C. FTIR analysis of the plated surface revealed the presence of $-SO_2$ and $-SN$ functional groups from the FSI$^-$ anion, as shown in Figure 97. The IR spectra of the stripped and plated Li surfaces were very similar with absorptions from the same functional groups detected.
Similar to the results obtained with the highly concentrated IL electrolyte, the IR spectra show evidence that the CH$_3$ group from the cation, the SO$_2$ and SN groups from the anion are major functional groups present in the SEI.

Figure 97 FTIR spectra and (b) low-frequency portion FTIR spectra of SEI films of plated and stripped Li surface from P$_{111i4}$FSI-based cells after 50 cycles at $j = 1.5$ mA.cm$^{-2}$ in 0.5 mol.kg$^{-1}$ of LiFSI in P$_{111i4}$FSI at 50°C after rinsing with DMC. Peaks marked with X are due to DMC (rinsing agent) reaction residue and are not due to the SEI formed during cycling.

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
XPS analysis of the plated Li surface is reported below. Figure 98 and Figure 99 present the high-resolution photoelectron spectra for F 1s, O 1s, C 1s, Li 1s and N 1s, S 2p and P 2p. XPS data and the peak assignments are presented in Table 26. Again the S 2p spectra were complex and contained at least six components (with two broad signals). Combining information from the different photoelectron lines, peaks attributed to the following species were detected: LiF (684.4, 685.9 eV on the F 1s spectra and 55.8, 56.9 eV on the Li 1s spectra), -SO₂F (687.6 eV on the F 1s spectra, 169.8 and 168.6 eV on the S 2p spectra), Li₂CO₃ (287.2 eV on the C 1s spectra, 531.5 eV on the O 1s spectra, 55.1 eV on the Li 1s spectra), Li₂O (531.5 eV on the O 1s spectra, 55.8 eV on the Li 1s spectra) and Li₂S (163.9 and 161.2 eV on the S 2p spectra). In general, the chemical species detected on the Li surface cycled in the dilute IL electrolyte were very consistent with those detected in the case of the highly concentrated IL electrolyte.

Figure 98 High-resolution F 1s, O 1s, C 1s and Li 1s photoelectron spectra for the plated Li surface in 0.5 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI
Figure 99 High-resolution N 1s, S 2p and P 2p photoelectron spectra for the plated Li surface in 0.5 mol.kg\(^{-1}\) of LiFSI in P\(_{1114}\)FSI
Table 26 Summary of XPS data and assignments for the lithium surface (plated state) after 50 plating / stripping processes at $j = 1.5 \text{ mA.cm}^{-2}$ in 0.5 mol.kg$^{-1}$ of LiFSI in $\text{P}_{1114}\text{FSI}$

<table>
<thead>
<tr>
<th>Element</th>
<th>Assignment</th>
<th>Peak position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Li surface after 50 cycles</td>
</tr>
<tr>
<td>F (1s)</td>
<td>-SO$_2$F</td>
<td>687.6</td>
</tr>
<tr>
<td></td>
<td>LiF</td>
<td>685.9, 684.4</td>
</tr>
<tr>
<td>O (1s)</td>
<td>Li$_2$CO$_3$, LiOH, Li$_2$O</td>
<td>533.5, 531.5</td>
</tr>
<tr>
<td>N (1s)</td>
<td>N$^+$</td>
<td>400.9, 399.2</td>
</tr>
<tr>
<td>C (1s)</td>
<td>C$_{\text{hetero}}$</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td>Li$_2$CO$_3$</td>
<td>287.2, 285.7</td>
</tr>
<tr>
<td></td>
<td>C$_{\text{aliphatic}}$</td>
<td>285</td>
</tr>
<tr>
<td>S (2p$_{3/2}$)</td>
<td>-SO$_2$F</td>
<td>169.8, 168.6, 166.1</td>
</tr>
<tr>
<td></td>
<td>Li$_2$S</td>
<td>163.8, 161.2</td>
</tr>
<tr>
<td></td>
<td>S$^0$</td>
<td>159.5</td>
</tr>
<tr>
<td>P (2p$_{3/2}$)</td>
<td>P$^+$</td>
<td>133.9</td>
</tr>
<tr>
<td>Li (1s)</td>
<td>Li$_2$O, LiF</td>
<td>56.9, 55.8</td>
</tr>
<tr>
<td></td>
<td>Li$_2$CO$_3$, LiOH</td>
<td>55.1</td>
</tr>
<tr>
<td></td>
<td>Li$^0$</td>
<td>53.7</td>
</tr>
</tbody>
</table>

When looking at a quantitative analysis of the high-resolution XPS spectra, the amount of the LiF component on the F 1s spectra is smaller in the case of the dilute vs. highly concentrated IL electrolyte (ca. 45 % vs. > 69 %). The same trend was observed for the Li$_2$O component on the O 1s spectra (64 % vs. 79 %), for the Li$_2$CO$_3$ component on the C 1s spectra (48 % vs. 60 %), for the Li$_2$S component on the S 2p spectra (ca. 18 % vs. 22 %) and for the Li$_2$CO$_3$ components on the Li 1s spectra (ca. 38 % vs. 56 %). These observations suggest that the mechanism of SEI formation in the highly concentrated IL electrolyte leads to larger amounts of more reduced chemical species coming from reduction of the FSI$^-$ anion.
The Li surface impedance was also monitored after 1, 10 and 50 plating / stripping processes in the dilute IL electrolyte. The acquired impedance data were fitted with the equivalent electric circuits (EECs) used earlier and the fitting results are presented in Table 27. The EEC 2 (two-element layer model) gave the best fit and the same EEC best fitted the impedance spectra in the case of the highly concentrated IL electrolyte. This again validates the formation of a layered structure on the Li surface in both electrolytes. As mentioned in Chapter 4 the overall cell resistance over cycling was lower in the case of the low Li salt concentration (consecutively 55 $\Omega$.cm$^{-2}$ before cycling, 38 and 11 $\Omega$.cm$^{-2}$ after 1 and 50 plating / stripping processes) in comparison with the high Li salt concentration (consecutively 50 $\Omega$.cm$^{-2}$ before cycling, 40 and 23 $\Omega$.cm$^{-2}$ after 1 and 50 plating / stripping processes). In general EIS fitting analysis showed that in both cases (low and high Li salt concentration) a layered structure most likely represents the SEI formation at the Li metal electrode. These observations validate the formation of a thinner SEI with the dilute IL electrolyte in comparison to the highly concentrated IL electrolyte.

### Table 27 Fitting models and results for a cycled Li | Li with 0.5 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI electrolyte

<table>
<thead>
<tr>
<th>Circuit</th>
<th>1 cycle</th>
<th>10 cycles</th>
<th>50 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>$\chi / \sqrt{N}$</td>
<td>$\chi^2$</td>
</tr>
<tr>
<td>2</td>
<td>4.121 x 10$^{-2}$</td>
<td>2.182 x 10$^{-1}$</td>
<td>5.097 x 10$^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>1.755 x 10$^{-2}$</td>
<td>1.838 x 10$^{-1}$</td>
<td>8.47 x 10$^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>8.087 x 10$^{-2}$</td>
<td>2.883 x 10$^{-1}$</td>
<td>2.787 x 10$^{-2}$</td>
</tr>
<tr>
<td>5</td>
<td>7.635 x 10$^{-2}$</td>
<td>2.786 x 10$^{-1}$</td>
<td>8.537 x 10$^{-3}$</td>
</tr>
<tr>
<td>6</td>
<td>8.563 x 10$^{-2}$</td>
<td>3.074 x 10$^{-1}$</td>
<td>1.674 x 10$^{-2}$</td>
</tr>
</tbody>
</table>
5.4.2 A proposed mechanism of SEI formation at the lithium metal electrode

The combination of SEM, MAS NMR, FTIR, XPS and EIS techniques has given a better understanding of SEI formation via chemical reactions of the P11114FSI IL-based electrolytes at the Li metal interface. A generalised mechanism can be postulated for the structure of the SEI formed at the Li surface. The complimentary techniques used to obtain a detailed picture of the SEI were highly consistent in general. Based on MAS NMR, FTIR and XPS evidence the chemical nature of SEI components was revealed. Combined with EIS analysis, the model herein proposed indicates a layered structure formed after the first plating / stripping process. This model suggests the presence of:

- an inner layer dominated by LiF and Li2O, chemical species related to the FSI- anion (e.g. Li2S) and anion related functional groups (-SO2F and -N-SO2)
- species related to the P+ cation most likely present in an outer layer close to the electrolyte interface.

A mechanism of SEI formation in the highly concentrated IL electrolyte is proposed in Figure 100. This is the model we have chosen based on our conclusions and it is important to note that it is not an established mechanism.

This thorough spectroscopic characterisation provided a better understanding of SEI formation and chemical composition as a function of Li salt concentration and cycle number dependence. In the case of the dilute IL electrolyte the spectroscopic study revealed evidence of a similar mechanism of SEI formation to that of the highly concentrated IL electrolyte. The main differences confirmed by SEM, XPS and EIS revealed the formation of a thinner SEI with nearly identical SEI components (same chemical nature) after the first plating / stripping process. Similarities in chemical composition of the plated and stripped Li electrodes in both low and high Li salt concentration cases were also found, suggesting a static behaviour of SEI formation. In the case of the highly concentrated IL electrolyte, by looking at differences in Li surfaces after 1, 50 and 250 plating / stripping processes, the study revealed the formation of a chemically stable SEI after the first cycle. SEI composition and thickness were found to be stable with increasing number of cycles.
A structure of the SEI and mechanism of formation during cycling can be developed by combining the information extracted from the previous analysis (NMR, FTIR and XPS). The SEI seemed to be composed of an outer layer of the FSI⁻ anion reduction products e.g., Li₂S, Li₂NSO₂F as well as Li₂O, LiOH, Li₂CO₃ and LiF. Products of this type (reduction products of TFSI/FSI – based electrolytes) have previously been proposed by Aurbach et al., Howlett et al. and Basile et al.

In the literature several mechanisms of SEI formation by the FSI⁻ anion reduction have been proposed. Basile et al. proposed a single electron reduction pathway leading to the formation of four anion species via the intermediate radical specie:

\[
N(SO₂F)₂^- + e^- \rightarrow N(SO₂F)_2^- \rightarrow SO₂NSO₂F^- + F^-
\]  

(20)

In this mechanism the FSI⁻ anion is dissociated and forms a radical.
A few years earlier Howlett et al. proposed a mechanism with cleavage of the S-N bond in the TFSI⁻ anion:

\[ N(SO_2CF_3)_2 + e^- \rightarrow N(SO_2CF_3)_2^{2-} \rightarrow NSO_2CF_3^{--} + SO_2CF_3^- \] (21)

The authors also reported with XPS etching experiments the formation of an inner layer dominated by LiF on the Li surface.

Basile et al. reported that this pathway was more favourable in the FSI⁻ system: one S-N bond becomes broken due to reduction of the sulphur atom and leads to the formation of two species, \( NSO_2F^- \) and \( SO_2F^- \). These two species can then be reduced to form \( SO_2^- \) and \( F^- \) via the following equations:

\[ NSO_2F^- + e^- \rightarrow NSO_2^- + F^- \] (22)
\[ SO_2F^- + e^- \rightarrow SO_2^- + F^- \] (23)

By combining the proposed mechanisms available in the literature and our analysis a mechanism of anion reduction can be proposed. The MAS NMR, FTIR and XPS analysis showed that these two species, \( SO_2^- \) and \( F^- \), are bound to the Li surface. The FTIR analysis also revealed the presence of Li-SNS bending vibrations, this implies the existence of fluoride free FSI⁻ anions that can be formed via the following equation:

\[ SO_2NSO_2F^- + e^- \rightarrow O_2NSO_2^- + F^- \] (24)

Any of these pathways lead to the formation of species detected to be part of the SEI according to the spectroscopic characterisation. Analogous to the SEI components in the ammonium C₃mpyrFSI system, the SEI layer formed at the Li metal in the P₁₁₁₄FSI electrolytes is made of the FSI⁻ anion breakdown products, including Li₂S, LiSO₂, Li₂NSO₂F as well as Li₂O, Li₂CO₃, LiF and possibly LiOH.

From the analysis and observations mentioned in this chapter the following conclusions can be postulated:

(i) The SEI formed by chemical reaction of Li metal with P₁₁₁₄FSI is composed of chemical compounds containing fluorine, oxygen and sulfur and are the products of the FSI⁻ anion decomposition. The following compounds were identified: lithium fluoride (LiF), lithium oxide (Li₂O), lithium sulfide (Li₂S) and lithium carbonate (Li₂CO₃).
(ii) These compounds form structural layers on the Li metal surface or are trapped within the Li surface.

(iii) We did not find clear evidence showing chemical reductions from the cation (in particular over the temperature range studied). If any reaction occurs, breakdown products from the cation could result from a pyrolysis reaction (via Hofmann elimination) and stay trapped within the SEI formed structure. Dissolution of these products into the electrolyte could also be considered.

(iv) The reduction reaction of the FSI- anion is the critical step for SEI formation. The cleavage of the FSI anion at its nitrogen center seems to happen almost instantly upon interaction with the lithium metal. This cleavage releases the –SO₂F functional group that itself undergoes another reaction that releases fluoride anions F⁻. The F⁻ ions react instantly with the Li surface to form a stable compound during cycling, LiF. After 1 cycle the compounds LiF and LiSO₂F are already present on the Li surface. The formation of LiOH is possible via reaction between the Li metal with oxygen and hydrogen. The oxygen is available from the reduced specie $\text{NSO}_2^-$ and hydrogen can be available from the IL cation. The compounds LiF, LiOH and Li₂S and anionic species become more abundant on the Li surface over cycling.
5.3 Conclusions

The SEI formed in P1114FSI-based electrolytes was characterised using MAS NMR, FTIR, XPS and EIS techniques. This study provides a first understanding of the composition and structure of the SEI formed in these electrolytes. The chemical nature of the SEI formed on the Li metal surface was found to be similar in both electrolytes (low and high Li salt concentration). Similarities in chemical composition were observed between the SEI formed in the dilute IL electrolyte and the highly concentrated IL electrolyte during cycling. However the main differences were found to be the formation of a thicker SEI with larger amounts of reduced species from the anion in the case of the high Li salt concentration. This was consistent with the differences observed in the cycling properties and deposit morphologies exhibited in the previous chapter.

Herein we proposed one reduction pathway possible to describe the mechanism of LiFSI / IL mixture breakdown leading to SEI formation on Li metal in the highly concentrated IL electrolyte. With an increased Li salt concentration the reduction pathway leading to SEI formation seems to be altered in favour of a more strongly reduced layer. Equivalent circuit modeling using the EIS technique suggested a layered structure.

Native species present on the prepared Li surface appeared to persist in the SEI and to even dominate its composition during cycling. However, significant quantities of chemical species associated with the FSI⁻ anion were formed on the surface film whereas the cation appeared to be inactive. Some evidence for trapping of the cation within the surface film structure along with anion reduction species was provided by FTIR and XPS measurements. The major components of the SEI composition after several hundreds of cycles were LiF and L₂O (LiOH) and breakdown products from the FSI⁻ anion including Li₂S. As such, the SEI formed using P1114FSI-based electrolyte exhibits a complex chemical composition which is however stable over several hundreds of cycles.

This chapter represents the first report on the characterisation of the SEI formed on a lithium metal surface in a small phosphonium FSI IL electrolyte with high lithium salt content.
Chapter 5

5.4 References


Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Investigation of Phosphonium Bis(ﬂuorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries


40. Dupré, N.; Martin, J.-F.; Guyomard, D.; Yamada, A.; Kanno, R., Characterization of interphases appearing on LiNi0.5Mn0.5O2 using 7Li MAS NMR. *J Power Sources* 2009, 189 (1), 557-560.


Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Chapter 5


Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries


Chapter 6  Lithium cell studies using high voltage NMC cathodes
6.1 Introduction

The previous chapters described the cycling stability and rate capability of lithium metal electrodes in a phosphonium ionic liquid based electrolytes in Li | Li symmetrical cells, as well as the characterisation of the chemical nature of the film formed on the lithium metal electrode during cycling. Finally, this chapter focuses on the charge and discharge capability of a fast-charging cathode material in the highly concentrated IL electrolyte shown to perform exceptionally for efficient lithium metal cycling.

Room Temperature Ionic Liquids (RTILs) based on the bis(fluorosulfonyl)imide (FSI) anion have recently been of particular interest as alternative electrolytes for lithium rechargeable batteries due to their superior transport properties and safety assets in opposition to commonly used organic carbonate electrolytes. However high cost and poor cycling performance related to poor transport properties (high viscosity, low ionic conductivity) has mainly prevented them from being used as electrolytes in commercial devices.

Novel FSI ionic liquids (ILs) based on a phosphonium cation have been reported with promising properties that make them candidates for alternative electrolytes. These features include improved transport properties and wide electrochemical window in comparison to more commonly studied ammonium-based ILs.

One of the critical factors dictating the cycling performance of a lithium battery is the lithium salt concentration present in the electrolyte. As detailed in Chapter 3, an increase in salt concentration generally leads to an increase in viscosity and decrease in conductivity, but it also greatly increases the amount of lithium cation available in the electrolyte. Indeed highly concentrated electrolytes (> 1 M salt concentration in solvent) have only been studied in the last few years. In 2013, Yoon et al. reported for the first time the cycling performance at room temperature of a Li | LiCoO₂ lithium cell with a solution of up to 3.2 mol.kg⁻¹ of lithium salt into an IL electrolyte. The IL used was an ammonium-based IL, N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (C₃mpyrFSI). The cells with the highest salt content IL electrolyte showed better rate capability even at high C rate (3 C and 5 C) than that of a cell with an organic electrolyte.
In Chapters 3 and 4 it was shown that the trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide (P111i4FSI) IL was as an excellent candidate for a lithium battery electrolyte: this IL, available on a large scale production, could dissolve up to 3.8 mol.kg⁻¹ of lithium bis(fluorosulfonyl)imide (LiFSI) salt. This investigation also demonstrated an excellent compatibility with the lithium metal electrode; this highly concentrated IL electrolyte was able to cycle a significantly high amount of charge (up to 6 mAh.cm⁻²) and a stable nanostructured uniform layer was formed on the lithium electrode surface, without any lithium dendrite formation. Therefore it seems relevant to evaluate the cycling performance of this highly concentrated IL electrolyte for a lithium battery incorporating a high voltage and fast charging cathode material, LiNiMnCoO₂ (NMC).

Early work focused on the use of ammonium-based RTILs with conventional cathode materials such as LiCoO₂ (LCO) and LiFePO₄ (LFP) cathode materials. For example, Matsumoto et al. reported good performance of a piperidinium-based (C₃mpipFSI) and pyrrolidinium-based (C₃mpyrFSI) RTILs in a Li | LiCoO₂ cell. They demonstrated that a cell using a C₃mpyrFSI-based electrolyte had a capacity retention close to 100 % after 100 cycles at 0.1C rate. Only in 2008 Tsunashima et al. showed the cycling performance of a phosphonium IL (P2225TFSI) with LCO and LiNi₀.₈ Co₀.₁ Mn₀.₁O₂ electrodes. An initial discharge capacity of 147 mAh.g⁻¹ and 96% capacity retention ratio after 30 cycles was reached with LiNi₀.₈ Co₀.₁Mn₀.₁O₂ (against 140 mAh.g⁻¹ and 90 % capacity retention with LCO). Lower capacities and retention ratio were reported in the P2225TFSI IL.

Only a few studies reported the use of RTIL-based electrolytes in a Li | NMC cell, but none with a phosphonium-based IL. In 2012 Matsui et al. reported a reversible capacity of 163 mAh.g⁻¹ with a mixture of EMIMFSI and LiTFSI as electrolyte. More recently a study conducted by Evans et al. showed that the addition of organic solvents (e.g. EC, EMC) to a pyrrolidinium FSI IL led to an oxidation and dissolution of aluminium at the NMC cathode. Chaudoy et al. also evaluated the use of NMC as a cathode in the same IL and the effect of Li salt concentration on the cell performance. The authors showed a discharge capacity of the NMC cathode of 161 mAh.g⁻¹ at 25 °C under the 0.1 C discharge rate. Interestingly, this study revealed that an increase of Li salt concentration (from 0.6 to 1 mol.L⁻¹) improved the discharge capacity at high discharge rate (1 C rate) while a slight decrease is observed at lower rate (0.1 C rate).
The cycling performance of NMC in a phosphonium FSI IL has recently been reported by Hilder et al.\textsuperscript{15} The IL triethyl cyanopropyl phosphonium bis(fluorosulfonyl)imide (PCNFSI) was revealed to be a promising candidate to prepare battery prototypes based on NMC as a cathode material and lithium metal as the anode. The paper showed that the performance of a Li | NMC cell with 1 M LiFSI in PCNFSI matches that of a commercial standard electrolyte, producing high discharge capacities (140 mAh.g\textsuperscript{-1}) and efficiencies of > 98 % at 0.1 C and 0.2 C rates.

In this chapter, we describe the effect of lithium salt concentration on the lithium transference number in \textit{P}\subscript{111}i\subscript{4}FSI electrolytes. We also report the effect of a highly concentrated \textit{P}\subscript{111}i\subscript{4}FSI electrolyte (3.8 mol.kg\textsuperscript{-1} of LiFSI in \textit{P}\subscript{111}i\subscript{4}FSI) on the charge-discharge property of the lithium metal battery cells using lithium metal and LiNiMnCoO\textsubscript{2} (NMC) electrodes. The rate capability (from 0.2 C to 4 C rates) and cell performance at 1C at room temperature and elevated temperature (50°C) is also discussed. The results are compared to those obtained for cells with a standard organic commercial electrolyte (1M LiPF\textsubscript{6} in EC:DMC 1/1 vol/vol).

6.2 Experimental methods

Electrolytes were prepared as described in Chapter 2. A lithium hexafluorophosphate (LiPF\textsubscript{6}, 1M) - ethylene carbonate (EC) - dimethylcarbonate (DMC) (1:1 v/v) electrolyte was the conventional organic electrolyte (Solvionic, 99.9 %) used for comparison.

6.2.1 Lithium transference numbers

Chronoamperometry was used to determine the Li\textsuperscript{+} transference number for each electrolyte using a lithium symmetrical cell setup (CR2032 type) and a Multi Potentiostat VMP3 (Bio-Logic Science Instruments) according to the method developed by Evans, Bruce, and Vincent.\textsuperscript{16, 17} The cells were polarised at 25 °C with a constant voltage of 20 mV for 4 hours and the currents were measured during the polarisation.
EIS spectra were measured before and after the polarisation using a perturbation amplitude of 1mV (0.1 MHz to 50 mHz). A 24-hour resting period was allowed between each measurement. The EIS spectra were fitted with the option Z-Fit from the EC-Lab software (v. 10.44).

6.2.2 Lithium battery tests

The lithium secondary batteries used for the charge-discharge tests were fabricated using coin cells (type CR2032). The fabrication was carried out in an argon-atmosphere glove box ([H₂O] < 1ppm and [O₂] < 1ppm). A paste mixture containing LiNiMnCoO₂, also called NMC (L&F Material), conductive carbon black (C65 C-Nergy super, Timcal) and poly(vinylidene fluoride) (PVDF, M.W = 3 x 10⁵, Targray) as a binder was prepared with the following weight ratio 80:10:10 to fabricate the cathode film. N-methylpyrrolidinone (NMP, Sigma Aldrich, 97%) was used as a dispersant for the formulation. The paste mixture was spread onto an Al current collector (battery use, Hohsen). The casted film was left to dry in a fume cupboard at ambient temperature overnight before being placed inside an oven at 100 °C to ensure the evaporation of the NMP solvent. The content of the active material was ca. 1.5 mg.cm⁻². Li foil (10mm diameter, 375 μm thickness, Sigma Aldrich, 99.9 %) was used as anode material. The polypropylene sheets (PP, 25 μm thick, Celgard Inc., 3501) were employed as separators. The charge-discharge tests of the Li cells were conducted using a charge-discharge system (Neware battery testing system V5.3) at 4.2 - 2.75 V of cut-off voltages with 0.5 C, 1 C, 2 C and 4 C current rates at 25 °C. The cells were respectively charged and discharged by constant current (CC) modes.

6.2.3 Immersion tests

PVDF membranes were prepared using the same PVDF material mentioned in the previous paragraph (3000 psi, 1 hour). The samples were pressed into pellets (1.8 mm thick and 13 mm in diameter) using a KBr die (13 mm diameter) in a hydraulic press at 3000 psi for one hour).
6.2.4 SEM

Prior to analysis the NMC electrodes were rinsed with N-methylpyrrolidinone (NMP, Sigma Aldrich) two times and then dried under vacuum in the chamber of the glove box for 30 min. The electrodes were rinsed to remove residual NMC material and to be able to image the Al foil underneath it. SEM images of the electrode surfaces were obtained with a Desktop JEOL JCM 5000 microscope at an accelerated voltage of 5 kV. To avoid electrode contamination or side reactions of the Li electrodes with atmospheric moisture and oxygen, the samples were transferred from the glove box to the SEM in sealed vessels which were filled with Ar gas.

6.2.5 ATR-FTIR

Surfaces were analysed by FTIR spectroscopy as previously described in Chapter 2.
6.3 Results and Discussion

6.3.1 Lithium transference numbers

The Li\(^+\) transference number is defined by the fraction of current transported by the Li\(^+\) cation within the electrolyte in a Li cell, making it a critical parameter for lithium batteries.\(^{18, 19}\) The Hittorf method is the traditional method used to determine a transference number.\(^{20}\) This method consists of applying a constant current, and the resulting voltage is monitored with time. This allows a comparison between the effective charge carried and the applied charge. However this method is limited to electrolytes that are composed of single ionic species. In the case of electrolytes containing multiple ionic species or in the case of the formation of a growing passivating film on the electrode, this method cannot be used. When a symmetric cell is polarized, all positive ions (in our case the Li\(^+\) and P\(_{1114}\)\(^+\) cations) move in the direction of the negatively polarised electrode, while negative ions (FSI\(^-\)) move towards the positively polarised electrode. A steady state is then reached after a certain time when only the Li\(^+\) cation moves towards the negatively polarised electrode. By measuring the current initially and at the steady state regime, the fraction of charge carried by the Li\(^+\) cation can be determined. This is how, by taking into consideration the growing passivation layer at the electrode and the concentration gradient, Evans, Bruce and Vincent demonstrated that the Li\(^+\) transference number in a polymer electrolyte using a symmetric cell setup can be calculated as:\(^{17, 20}\)

\[
t_{Li}^{+} = \frac{I_s(\Delta V - I_s R_0)}{I_0(\Delta V - I_s R_s)}
\]  

(25)

where \(t(\text{Li}^+)\) is the lithium transference number, \(\Delta V\) is the potential applied across the cell, \(I_0\) and \(I_s\) are the initial and steady state currents during polarisation, and \(R_0\) and \(R_s\) are the initial and steady state resistances of the passivation layers. Other groups\(^{21, 22}\) have shown that this equation could be used for ionic liquid electrolytes by applying a constant voltage, measuring the initial and steady state currents and the resistance of the electrode surface before and after polarisation. This approach is also justified by the stability of the IL electrolyte towards the Li metal electrode, the change in impedance of the bulk electrolyte before and after polarisation being negligible.

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
However in the case of the solution of 0.5 mol.kg\(^{-1}\) of LiFSI in P111i4FSI, this method could not be applied due to an increase of impedance after polarisation, in this case the equation is not valid anymore, further highlighting the relative instability of the lithium electrode in the lower concentration system, as shown in Chapter 4. The resistances of the Li metal electrode surface before and after polarisation was determined with the following equivalent circuit proposed by Zugmann et al. (as shown in Figure 101).\(^{18}\)

![Figure 101 Equivalent circuit used to determine electrode resistances](image)

To experimentally determine the initial and steady state currents (I\(_0\) and I\(_s\) respectively), any cell which showed an increase in current after 4h and did not reach a steady state or showed a short circuit was eliminated. For the remaining cells and for each electrolyte concentration the average values were reported. The cells were polarised at 20 mV for 4 hours (3 times) to confirm consistency of the data acquired. It should also be noted that the changes in Li surface impedance were not significant after polarisation.

Figure 102 gives an example of the polarisation profile of a symmetrical cell containing 3.8 mol.kg\(^{-1}\) LiFSI in P111i4FSI for 4 hours. Even though the cells seem to reach a steady state current within several minutes, the polarisation was maintained for 4 hours to obtain consistent results as previously reported with polymer (e.g. PEO) or plastic crystal electrolytes, which required several hours to reach a steady state current.\(^{20}\) After 30 min of polarisation, an increase in current was observed after the cell had reached an apparent steady state (Figure 102a). This is interpreted as a fingerprint of a reaction of the IL electrolyte on the lithium surface during polarisation (this should cause decomposition products to form and reduce the current) or an increasing Li surface area. However this effect became less pronounced as more lithium salt was present in the electrolyte.
Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Figure 102 Polarisation profile of a Li | Li symmetrical cell containing 3.8 mol.kg\(^{-1}\) LiFSI in P_{1114}FSI as electrolyte and reaching a steady state current \((\Delta V = 20 \, \text{mV}, \Delta t = 4 \, \text{h})\) at 25 °C. The insert is an expanded view of the polarisation profile over the first 20 minutes.

Figure 103 (a) is an example of a Nyquist plot of a Li symmetric cell containing 3.8 mol.kg\(^{-1}\) Li salt in the IL electrolyte, while Figure 104 shows the EIS of a cell containing (a) 1.0 mol.kg\(^{-1}\) Li salt in the IL and (b) the organic carbonate solvent (1M LiPF\(_6\)-EC-DMC). With increasing salt concentration, the electrolyte resistance \((R_e)\) increases from 10 – 11 Ω (before and after steady state respectively) in 1.0 mol.kg\(^{-1}\) compared with 48 – 59 Ω in 3.8 mol.kg\(^{-1}\), while the Li surface resistance \((R_1 + R_2)\) decreases from approximately 160 to 150 Ω in 1.0 mol.kg\(^{-1}\) and from 178 to 159 Ω in 3.8 mol.kg\(^{-1}\). This implies that the resistance of the IL native film formed on the lithium electrodes depends on the Li salt concentration. Interestingly in spite of an increase in Li\(^+\) concentration (increase in viscosity) the surface impedance is still reduced after polarising the Li electrode in the highly concentrated IL electrolyte (as has already been discussed in detail in chapter 4). This suggests the formation of a stable IL native film characterised by a low resistance. In opposition to the IL electrolyte, the Li surface in contact with the organic carbonate electrolyte is characterised by a higher resistance (before and after polarisation), as shown in Figure 104 (b), suggesting a more resistive passivating layer formed on the Li surface.
Chapter 6

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Figure 103 (a) Nyquist plot of the cell before and after polarisation (0.1 MHz to 50 mHz); (b) Nyquist plot of the cell taken before polarisation, fitted to equivalent circuit shown in Figure 101.

Figure 104 Nyquist plots of a Li | Li symmetrical cell containing (a) 1.0 mol.kg\(^{-1}\) LiFSI in P1114FSI; (b) 1 M LiPF\(_6\)-EC-DMC as electrolyte before and after polarisation.
The calculated transference numbers for different salt concentrations (including error bars) are shown in Figure 105 and are reported in Table 28, along with conductivities and viscosities, of the electrolytes at 25 °C. The transference numbers vary from 0.28 to 0.46 as the LiFSI concentration changes. These values show that an increase in salt concentration increases transference number. The same trend was previously reported by Yoon et al. in their N-methyl-N-propylpyrrolidinium FSI and LiFSI systems. However for an equivalent electrolyte molar composition, the transference numbers reported here are much higher (0.40 for 3.2 mol.kg\(^{-1}\) LiFSI in P\(_{1114}\)FSI vs. 0.18 for 3.2 mol.kg\(^{-1}\) LiFSI in C\(_{3}\)mpyrFSI) but are still lower than the 0.65 value reported by Han et al. for an ammonium FSI IL (equimolar mixture of LiFSI and N\(_{23(102)}\)FSI).\(^{23}\)

Fernicola et al. also reported a value of 0.4 for a TFSI-based system.\(^{22}\) It should be noted that only Yoon et al. reported transference numbers in the case of highest Li salt concentration whereas Martins et al.\(^{5}\) recently reported a high transference number (0.54) in a phosphonium IL electrolyte (P\(_{222(201)}\)TFSI + 1 M LiTFSI) at a lower Li salt content; most electrolyte research has been conducted in the range of 0.5 to 1.0 mol.kg\(^{-1}\) of added Li salt concentrations. However the authors used a recently adopted method and there are likely still some inconsistencies in how the method is applied and in the results obtained.

![Figure 105 Li⁺ transference number for different LiFSI concentrations in P\(_{1114}\)FSI, including average values and standard deviations.](image)

---

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Table 28 Ionic conductivity, viscosity and lithium transference number of various electrolytes at 25 °C\(^a\)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(\sigma) / mS.cm(^{-1}) (± 0.1)</th>
<th>(\eta) / mPa.s (± 10)</th>
<th>(t(\text{Li}^+))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M LiPF(_6)-EC-DMC</td>
<td>10.7(^{24})</td>
<td>5.1 (&lt; 10)(^{24})</td>
<td>0.26 ± 0.07</td>
</tr>
<tr>
<td>Neat P(_{1114})FSI</td>
<td>7.3</td>
<td>41</td>
<td>-</td>
</tr>
<tr>
<td>0.5 mol.kg(^{-1}) LiFSI in P(_{1114})FSI</td>
<td>4.4</td>
<td>55</td>
<td>-</td>
</tr>
<tr>
<td>1.0 mol.kg(^{-1}) LiFSI in P(_{1114})FSI</td>
<td>3.3</td>
<td>79</td>
<td>0.28 ± 0.05</td>
</tr>
<tr>
<td>2.0 mol.kg(^{-1}) LiFSI in P(_{1114})FSI</td>
<td>1.9</td>
<td>163</td>
<td>0.30 ± 0.06</td>
</tr>
<tr>
<td>3.2 mol.kg(^{-1}) LiFSI in P(_{1114})FSI</td>
<td>0.9</td>
<td>323</td>
<td>0.40 ± 0.01</td>
</tr>
<tr>
<td>3.8 mol.kg(^{-1}) LiFSI in P(_{1114})FSI(^b)</td>
<td>0.8(^4)</td>
<td>571(^4)</td>
<td>0.46 ± 0.04</td>
</tr>
</tbody>
</table>

\(^a\)\(\sigma\): conductivity at 25 °C. \(\eta\): dynamic viscosity at 25 °C. \(t(\text{Li}^+)\): lithium transference number at 25 °C.

\(^b\)LiFSI: P\(_{1114}\)FSI = 1.2: 1.0 (mol/mol)

6.3.2 Rate capability of Li battery cells

A promising, known, high voltage cathode material was used in this study: the NMC material (LiNiMnCoO\(_2\)) with a particularly high Ni content (47 %).\(^{25}\) Herein the rate capability for lithium cells containing the 1M LiPF\(_6\)-EC-DMC electrolyte (Figure 106 (a)) and the highly concentrated P\(_{1114}\)FSI electrolyte (Figure 106 (b)) is compared. The cells were subsequently charged and discharged ten times at 4 increasing C-rates: 0.2 C, 1 C, 2 C, 4 C then 0.2 C. The evolution of the charge and discharge capacity as a function of cycle number at different discharge rates at 25 °C is shown in Figure 106.

The performance of the highly concentrated IL electrolyte was superior to that of the organic carbonate electrolyte at moderate discharge rates (i.e. 0.2 C), maintaining a higher charge/discharge capacity. It should be noted that these capacity values were reversibly maintained after increasing the discharge rate up to 4C and decreasing it again down to 0.2 C, as shown in Figure 106 (b). Both the standard carbonate electrolyte and the concentrated ionic liquid electrolyte exhibited a comparable discharge capacity at faster rates from 1 C to 2 C. Indeed, even though the 1M LiPF\(_6\)-EC-DMC standard electrolyte has more appropriate transport properties (i.e. higher ionic conductivity and lower viscosity) for rapid charge/discharge, the concentrated phosphonium IL system exhibited comparable discharge capacities.
However, by increasing the discharge rate up to 4 C, a more significant decrease in specific capacity was observed with the highly concentrated IL electrolyte compared with the more fluid organic electrolyte. Notably, the subsequent 0.2 C charge/discharge experiment showed that the high capacities are maintained with both electrolytes. This highlights the stability of the ionic liquid electrolyte of interest in this work.

Figure 106 Dependence of cycle number on the charge-discharge capacity at 25 °C at different C-rates (0.2 C, 1 C, 2 C and 4 C) for Li | NMC cells containing (a) 1M LiPF6-EC-DMC (LP30) and (b) solution of 3.8 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI electrolytes.

Investigation of Phosphonium Bis(fluorosulfonylelimide)-based ionic liquid electrolytes for lithium222 batteries
6.3.3 Longer term cycling behaviour of Li battery cells at 25 °C

In this set of experiments, the cycling performance of Li | NMC cells containing the two electrolytes (1M LiPF$_6$-EC-DMC and solution of 3.8 mol.kg$^{-1}$ of LiFSI in P$_{111i4}$FSI) were investigated at 25 °C. Figure 107 presents the charge-discharge curves of lithium battery cells containing the highly concentrated P$_{111i4}$FSI IL electrolyte which can be compared with cells containing the LiPF$_6$-EC-DMC electrolyte in Figure 108. The charge-discharge capacity and coulombic efficiency as a function of cycle number are also presented. The cells exhibit typical charge-discharge behaviour, however, the capacities obtained with the phosphonium electrolyte over long-term (200 cycles) are significantly more stable than those for the LiPF$_6$-EC-DMC electrolyte. As shown in Figure 107 (a), the cell containing the phosphonium P$_{111i4}$FSI electrolyte with high Li salt content indicated sufficiently high discharge capacities (e.g. 176 mAh.g$^{-1}$ at the first cycle) with an average capacity retention of 90 % after 100 cycles. The coulombic efficiencies also approached 100 % (ca. 98-99 %) after the third cycle and are maintained above 95 % after 200 cycles. This is significantly superior to the overall cycling performance of the cell containing the highly fluid LiPF$_6$-EC-DMC electrolyte (Figure 108), showing that the highly concentrated P$_{111i4}$FSI leads to an improvement of cycling efficiency and capacity retention for this NMC cathode at the rate of 1C used here.

Indeed, in the case of a cell containing the organic carbonate electrolyte, the discharge capacity obtained over 200 cycles is lower (e.g. 135 mAh.g$^{-1}$ at the first cycle), even though the coulombic efficiencies are close to 99-100 %; the capacity retention also drops more significantly after 100 cycles (70 % after 200 cycles) whereas the cell with the phosphonium electrolyte still retains a capacity retention > 76 % after 200 cycles. Therefore favourable charge-discharge performance was observed despite the fact that the transport property of the P$_{111i4}$FSI electrolyte (containing 3.8 m LiFSI) is lower than that of the LiPF$_6$-EC-DMC electrolyte (Table 14). Thus it is clear that, even with its higher viscosity and lower conductivity, the cells with P$_{111i4}$FSI + 3.8 m LiFSI electrolyte exhibit a superior discharge capacity at 1C rate compared with the standard electrolyte solution.
Figure 107 (a) Dependence of cycle number on the charge-discharge capacity for Li | NMC cells at 25 °C at 1 C (CC mode, 1 h, 0.25 mA.cm⁻²) of charge and discharge current rate containing 3.8 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI electrolyte; (b) Charge-discharge curves of the cells.
Figure 108 (a) Dependence of cycle number on the charge-discharge capacity for Li | NMC cells at 25 °C at 1 C (CC mode, 1h, 0.25 mA.cm$^{-2}$) of charge and discharge current rate containing LiPF$_6$ (1M)-EC-DMC electrolyte; (b) Charge-discharge curves of the cells.
The results given in Figure 107 and Figure 108 strongly suggest that the high Li salt concentration in the phosphonium IL electrolyte might help form a stable and uniform conductive passivating film (SEI-like film) on the NMC cathode surface to prevent further decomposition of the electrolyte. The specific effect of this phosphonium salt with high Li salt content on the cell performance requires further investigation. Further investigation of both anode and cathode surfaces should be required to obtain clear information on the effect of the electrolyte on the NMC cathode.

Here the results show an improving effect of phosphonium RTILs with high Li salt content on the charge-discharge performance. Stable and effective cycling was demonstrated at practical C-rates (1 C) with large capacities (> 130 mAh.g\(^{-1}\)) being transferred with each cycle.

6.3.4 Li battery cells performance at elevated temperature (50 °C)

This set of experiments describes the cycling performance of Li | NMC cells containing the two electrolytes (1M LiPF\(_6\)-EC-DMC and solution of 3.8 mol.kg\(^{-1}\) of LiFSI in P\(_{1114}\)FSI) at 50 °C. At 25 °C the phosphonium IL electrolyte showed remarkable cycling stability and did not show any decomposition. At 50 °C, the organic electrolyte (1M LiPF\(_6\)-EC-DMC) demonstrated different initial discharge capacity as the 3.8 mol.kg\(^{-1}\) of LiFSI in P\(_{1114}\)FSI (142 vs. 128 mAh.g\(^{-1}\) at 1 C). Unexpectedly, for both electrolytes the capacity continuously faded at 1 C and 4 C, as illustrated in Figure 109. During the first 10 cycles the capacity loss was ~ 1 mAh.g\(^{-1}\) per cycle in the case of 1M LiPF\(_6\)-EC-DMC and ~ 1.5 mAh.g\(^{-1}\) per cycle in the case of 3.8 mol.kg\(^{-1}\) of LiFSI in P\(_{1114}\)FSI. The capacity of cells containing P\(_{1114}\)FSI initially showed a sharp drop in capacity in the first 10 cycles at 1 C followed by a slower decrease in capacity of ~ 1 mAh.g\(^{-1}\) per cycle up to 30 cycles and ~ 0.6-0.3 mAh.g\(^{-1}\) per cycle up to 100 cycles, as shown in Figure 110 and Figure 109. Similar trends were recently reported in the case of LTO | NMC cells with ammonium-based ILs (C\(_4\)mimTFSI and C\(_4\)mpyrTFSI with 1 M LiTFSI).\(^{26}\)
Chapter 6

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries

Figure 109 Dependence of cycle number on the discharge capacity for Li | NMC cells at 50 °C at 1 C and 4 C (CC mode, 1 h, 0.25 mA.cm⁻² and 15 min, 0.98 mA.cm⁻²) of discharge current rates containing 1M LiPF₆-EC-DMC and 3.8 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI electrolytes

Figure 110 (a) Dependence of cycle number on the charge-discharge capacity and coulombic efficiency for Li | NMC cells at 50 °C at 1 C (CC mode, 1h, 0.25 mA.cm⁻²) of charge and discharge current rate containing 3.8 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI electrolyte; (b) Charge-discharge curves of the cells

The following graphs in Figure 111 are expanded views of voltage - time profiles of Li | NMC cells at 50 °C at (a) 1 C (CC mode, 1 h, 0.25 mA.cm⁻²) and (b) 4 C (CC mode, 15 min, 0.98 mA.cm⁻²) of charge - discharge current rates containing 3.8 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI electrolyte.

Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Figure 111 Voltage – time profiles of Li | NMC cells at 50 °C at (a) 0.2 C (CC mode, 5 h, 0.025 mA.cm\(^{-2}\)); (b) 1 C (CC mode, 1 h, 0.25 mA.cm\(^{-2}\)) and (c) 4 C (CC mode, 15 min, 0.98 mA.cm\(^{-2}\)) of charge - discharge current rates containing 3.8 mol.kg\(^{-1}\) of LiFSI in P\(_{1114}\)FSI electrolyte.
Further characterisation was carried out to understand the failure mechanism of Li | NMC cells containing 3.8 mol.kg$^{-1}$ of LiFSI in P$_{1114}$FSI electrolyte at 50 °C using immersion tests, SEM and ATR-FTIR spectroscopy as discussed below.

A pristine NMC composite electrode was completely immersed in the highly concentrated IL electrolyte (3.8 mol.kg$^{-1}$ LiFSI in P$_{1114}$FSI) at 25 °C for 24 hours and then placed inside an oven at 50 °C for one week. No dissolution of the NMC material into the IL electrolyte could be observed at any point. Further immersion tests were completed to assess any dissolution of the binder PVDF into the IL electrolyte at 50 °C. PVDF membranes were immersed into the highly concentrated IL electrolyte and the organic carbonate electrolyte at 50 °C for one week. Whenever it was possible the diameter, thickness and mass of the PVDF membranes were measured before and after immersion. In the case of the organic carbonate electrolyte a fast dissolution of PVDF membranes was observed along with the formation of a gel. This PVDF-based gel swollen with the organic electrolyte would form an effective coating on the NMC electrode allowing conduction and repeated charge and discharge at 50 °C. In the case of the highly concentrated IL electrolyte an increase in diameter and thickness of PVDF membranes were measured before and after immersion (from 12.75 to 13 ± 0.025 mm for the diameter and from 0.67 to 0.96 ± 0.04 mm for the thickness). However, the results do not suggest any obvious dissolution of the PVDF in the IL electrolyte. At this stage the role of the PVDF binder in the failure mechanism remains unclear.

The FTIR spectra of a PVDF membrane is presented in Figure 112; the FTIR spectra (including the low frequency region) of the highly concentrated IL electrolyte and a mixture of PVDF and IL electrolyte are presented in Figure 113. Peak assignments are given in Table 29. The FTIR spectroscopic analysis does not suggest any chemical reaction between PVDF and the IL electrolyte.
Figure 112 FTIR spectrum of PVDF

Figure 113 (a) FTIR spectra and (b) low-frequency portion FTIR spectra of a solution of 3.8 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI and mixture of PVDF and 3.8 mol.kg⁻¹ of LiFSI in P₁₁₁₄FSI. The mixed solution was stored for one week at 50°C.
Table 29 Assignment for the FTIR spectrum data of PVDF, mixture of PVDF and solution of 3.8 mol.kg\(^{-1}\) LiFSI P\(_{111\text{i}4}\)FSI (\(\nu\): stretching, \(\delta\): bending, \(\omega\): wagging, \(\tau\): twisting, \(\rho\): rocking, \(s\): strong, \(m\): medium, \(w\): weak)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>PVDF Peak position (cm(^{-1}))</th>
<th>PVDF + 3.8 mol.kg(^{-1}) LiFSI P(_{111\text{i}4})FSI Peak position (cm(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_\text{a}(\text{CH}_2))</td>
<td>3025 (w)</td>
<td></td>
<td>27, 28</td>
</tr>
<tr>
<td>(\nu_\text{a}(\text{CH}_2))</td>
<td>2984 (w)</td>
<td></td>
<td>27, 28</td>
</tr>
<tr>
<td>(\nu(\text{CH}_2))</td>
<td>-</td>
<td>3009</td>
<td>27-29</td>
</tr>
<tr>
<td>(\nu(\text{CH}_2))</td>
<td></td>
<td>2973</td>
<td>27-30</td>
</tr>
<tr>
<td>(\nu(\text{CH}_2))</td>
<td></td>
<td>2931</td>
<td>27-29</td>
</tr>
<tr>
<td>(\nu_\text{a}(\text{SO}_2))</td>
<td>-</td>
<td>1358</td>
<td>27, 29, 31</td>
</tr>
<tr>
<td>(\omega(\text{CH}_2))</td>
<td>1404 (w)</td>
<td></td>
<td>27, 28</td>
</tr>
<tr>
<td>(\nu_\text{a}(\text{CF}_2))</td>
<td>1213 (s)</td>
<td></td>
<td>27, 28, 32</td>
</tr>
<tr>
<td>(\nu_\text{a}(\text{CF}_2))</td>
<td>1185 (s)</td>
<td></td>
<td>27, 28, 32</td>
</tr>
<tr>
<td>(\nu_\text{a}(\text{C-C}))</td>
<td>1069 (s)</td>
<td></td>
<td>27, 28</td>
</tr>
<tr>
<td>(\nu(\text{SO}_2-N-\text{SO}_2))</td>
<td>-</td>
<td>1169</td>
<td>29-31</td>
</tr>
<tr>
<td>(\nu_\text{a}(\text{SNS})) and (\nu(\text{SF}))</td>
<td>-</td>
<td>844</td>
<td>6, 27, 31</td>
</tr>
<tr>
<td>(\tau(\text{CH}_2))</td>
<td>976 (w)</td>
<td>1308</td>
<td>27, 28</td>
</tr>
<tr>
<td>(\nu_\text{a}(\text{C-C}))</td>
<td>875 (s)</td>
<td></td>
<td>27, 28</td>
</tr>
<tr>
<td>(\rho(\text{CH}_2))</td>
<td>842 (w)</td>
<td></td>
<td>27, 28</td>
</tr>
<tr>
<td>(\omega(\text{CF}_2))</td>
<td>765 (m)</td>
<td></td>
<td>27, 32</td>
</tr>
</tbody>
</table>

SEM images of the aluminium foil underneath the NMC coating were acquired and are shown in Figure 114. The images do not shown any sign of pits related to corrosion of the aluminium. Figure 115 shows SEM images of the NMC coating and once again no major differences in surface features could be observed between cycling at 25°C and 50°C.
Figure 114 SEM images (EHT = 5.00 kV) of (a) pristine Al foil; (b) Al foil under NMC coating after cycling at 1C at 25°C and (c) Al foil under NMC coating after cycling at 1C at 50°C
From the previous analysis the following conclusions can be made: a plasticisation and swelling of PVDF in the highly concentrated IL electrolyte (e.g. modification of mechanical properties of PVDF) could explain the low capacity obtained and failure of the Li | NMC cells cycled at 1 C at 50 °C. No apparent chemical reaction seems to explain battery failure at this temperature compared with 25°C cycling. Further investigation of the failure mechanism associated with either NMC or Li metal electrodes at 50 °C is required to understand the capacity fade mechanism.
6.4 Conclusions

In this chapter the battery performance of lithium cells containing the phosphonium RTIL (P$_{1114}$FSI) electrolytes has been presented as a demonstration of potential of this phosphonium RTILs with high lithium salt content as a suitable electrolyte for high voltage NMC cathodes, as shown by the charge-discharge cycling performance, especially at room temperature.

One of the characteristic features of the phosphonium IL electrolyte with high lithium salt content is the higher lithium transference number, higher than the 1 M LiPF$_6$-EC-DMC electrolyte, in spite of a lower conductivity and higher viscosity. The latter properties are usually desired for high performance Li cells, however, here we show that even though the high concentration ionic liquid electrolyte is more viscous and has lower ionic conductivity compared to the traditional organic electrolytes, it still leads to better performance in many cases. For example it was shown that the charge-discharge cyclability of the cells containing the highly concentrated IL electrolyte was superior to that of the 1 M LiPF$_6$-EC-DMC electrolyte at 1 C rate at 25 °C (initial discharge capacity of 176 mAh.g$^{-1}$ vs. 135 mAh.g$^{-1}$ respectively). In this context, it is possible that these concentrated phosphonium IL electrolytes can be regarded as effective candidates for lithium rechargeable batteries to improve their charge-discharge cycling performance. However, the unexpected poorer performance and failure of the cells at 50 °C is still unclear. The possibility of alternative, more IL compatible binders and optimisation of the cathode formulation is required to further the application of these electrolytes in advanced Li-metal based batteries.
6.5 References


30. Bednarska-Bolek, B.; Jakubas, R.; Bator, G.; Baran, J., Vibrational study of the structural phase transition in bis(pyrrolidinium)-chloride-


Chapter 7  Summary and Future Work
This chapter summarises the work presented in this thesis and comments on the issues related to the use of ionic liquid based electrolytes for lithium battery applications as well as suggestions for any future research relevant to this project.

7.1 Summary

This thesis examined a room temperature ionic liquid (RTIL) based on a phosphonium cation (P_{111i4}^+) and the FSI⁻ anion. This IL was chosen for its attractive physicochemical and electrochemical properties: high ionic conductivity, low dynamic viscosity, high lithium salt solubility and wide electrochemical stability.

Solutions of LiFSI in P_{111i4}FSI were investigated as a function of LiFSI salt concentration. In spite of higher viscosity and lower ionic conductivity, the solutions with highest Li salt concentration (3.8 mol.kg⁻¹ LiFSI in P_{111i4}FSI, or 1:1.2 molar ratio IL:Li) exhibited unusual transport behaviour suggesting changes in Li⁺ solvation at these concentrations and enhancing the lithium deposition / dissolution efficiency: they showed a more ideal behaviour in a Walden plot, greater ionic dissociation and superior Li⁺ diffusivities compared to those of the other ionic species present. These observations confirm that the mechanism of Li⁺ transport in a phosphonium RTIL is strongly influenced by the Li salt concentration. Similar results were obtained in the case of a different phosphonium IL based on a mixture of four phosphonium cations and the same anion (FSI⁻) with similar physical properties.

Outstanding rate and cycling stability of lithium metal electrodes were achieved in the highly concentrated IL electrolytes. Significant amounts of charge, up to 6 mAh.cm⁻² were plated / stripped at 25 and 50°C. Remarkable current densities (up to 12 mA.cm⁻²) were successfully applied to Li | Li symmetrical cells with 3.8 m LiFSI / P_{111i4}FSI. “Rate capability” achieved exceeded that of cells with lower LiFSI content (0.5 m LiFSI / P_{111i4}FSI) and a conventional electrolyte (1 M LiPF₆ / EC + DMC) probably owing to the low resistance at the electrode / electrolyte interface revealed by EIS measurements. SEM imaging revealed the formation of a stable and compact deposit on the lithium surface enhanced by the presence of high Li⁺ content.
The nature of the film formed on the lithium surface was characterised using several spectroscopic techniques. Spectroscopic measurements including MAS NMR, FTIR and XPS showed a chemical stability of the film deposited on the lithium surface over several hundreds of cycles (up to 250 cycles). A study of the chemical composition of the film revealed the major presence of the following species including LiF, LiOH, Li₂O, Li₂CO₃, Li₂S and possibly other anionic species. An increase of Li⁺ content in the IL electrolyte also improved the film homogeneity.

We evaluated the charge-discharge performance of a LiNiMnCoO₂ (NMC) high voltage cathode material in the highly concentrated IL electrolyte at 25 °C. At 130 mAh g⁻¹ after 200 cycles, the discharge capacity of the NMC cathode in 3.8 m LiFSI / P₁₁₁₄FSI at 1 C in the voltage range 2.8 – 4.2 V (vs. Li/Li⁺) exceeds that in the conventional electrolyte, 1 M LiPF₆ / EC + DMC (< 100 mAh g⁻¹ after 200 cycles), probably owing to a low resistance at the electrode / electrolyte interface. Moreover, the rate capability of the cell with 3.8 m LiFSI / P₁₁₁₄FSI is comparable to that with 1 M LiPF₆ / EC + DMC, especially at low rates. These results suggest that 3.8 m LiFSI / P₁₁₁₄FSI is a suitable electrolyte for lithium batteries utilising the NMC cathode. The improved transport properties of the phosphonium systems in comparison with their competitive ammonium counterparts (e.g. C₃mpyrFSI) seem to generate a better performance.

7.2 What are the main challenges for the use of ionic liquid electrolytes in lithium batteries

Although highly concentrated FSI-based IL electrolytes using the LiFSI salt have shown superior rate capability in comparison to standard organic electrolytes, some challenges have been reported.

For example Wang et al. investigated the reactions between the pyrroldinium IL C₃mpyrFSI and charged electrodes (Li₁Si, Li₇Ti₄O₁₂ and Li₀.₄₅CoO₂) using accelerating rate calorimetry (ARC) and reported that the IL was not safer than organic electrolytes.¹

Investigation of Phosphonium Bis(flurosulfonyl)imide-based ionic liquid electrolytes for lithium batteries
Vijayaraghavan et al. reported exothermic and self-heating behaviours of FSI-based ILs above 200°C. Another significant issue when using the FSI anion is the corrosion of aluminium current collector at 3.3 V vs. Li / Li+. Some other challenges have previously been reported when increasing the LiFSI salt concentration. In a study from Paillard et al. the presence of high amounts of impurities in the commercial grade of the LiFSI salt used was reported to be the cause of a reduction of the electrochemical cathodic stability in the IL C4mpyrFSI. Unlike studies which reported an increase in cathodic stability enhanced by an increase in Li salt content, Yoon et al. did not find any benefit from increasing the LiFSI concentration up to 3.2 mol.kg⁻¹ in C3mpyrFSI towards the cathodic stability. The authors only showed the cycling performance of Li | LiCoO₂ cells over 20 cycles. Further research is still needed on the cathodic instability and choice of optimal materials in FSI-based electrolytes.

In this research it was shown that the interaction between the NMC cathode film and the IL electrolyte has a critical impact on the overall Li cell performance and is strongly dependent on operating temperature. It is very interesting that the highly concentrated phosphonium IL electrolyte (3.8 m LiFSI in P111i4FSI) does not show any remarkable cycling ability at 1 C at 50 °C, but shows better cycling performance than an organic electrolyte at 25 °C. The search for alternate formulation components in cathode film formulations such as carboxymethyl cellulose (CMC) as a binder in combination with the NMC cathode may improve the performance of the cells at elevated temperature.

7.3 Suggestions for future work

One of the main areas of focus for the next generation lithium batteries is their possible applications in the automotive industry (e.g. electric vehicles). Governments and car companies are pushing towards increased power range and reduced cost. Different research approaches are already based on the improvement of battery components in existing technologies whereas others consist of developing novel battery technologies.
Today one of the main trends is the development of high voltage cathode materials, while there is still a need for novel electrolytes for high voltage applications. Several ionic liquids have been considered as potential promising electrolyte candidates, mostly based on the TFSI$^-$ anion and asymmetric FSI$^-$ analogues.

Another important application that industrial partners are interested in is fast charging technologies (sometimes called pulse charging). Electrode performance rather than electrolyte performance has been reported as the main critical factor for fast charging capability.

In this thesis the insights provided into the mechanism of lithium ion transport in highly concentrated IL electrolytes, the outstanding rate capability and cycling stability of lithium metal electrodes, the chemical nature of the film formed on lithium metal electrodes during cycling and the charge-discharge cycling performance of fast-charging NMC cathodes will provide a better understanding in the importance of lithium transport in phosphonium ionic liquid based electrolytes and their potential contribution to further improvements as effective electrolytes for safe and durable lithium rechargeable batteries. Additional and continuing investigations for lithium battery applications using these quaternary phosphonium salts are in progress (e.g. silicon composite anodes). In particular a forthcoming publication on the cycling performance of silicon composite anodes in these phosphonium salts with high lithium content is not included in this thesis.
7.4 References


Investigation of Phosphonium Bis(fluorosulfonyl)imide-based ionic liquid electrolytes for lithium batteries


