LITHIUM-CONDUCTING IONIC MELT ELECTROLYTES FROM OLIGOMERIC ETHYLENE GLYCOLS: SYNTHESIS AND CHARACTERIZATION

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LITHIUM-CONDUCTING IONIC MELT ELECTROLYTES FROM OLIGOMERIC ETHYLENE GLYCOLS: SYNTHESIS AND CHARACTERIZATION

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Boutros B. Hallac
December 2007

Accepted by:
Professor Stephen Creager, Committee Chair
Professor Darryl DesMarteau
Professor George Chumanov
Professor Jason McNeill
ABSTRACT

Commercial lithium ion cells consist of electrolytes that undergo salt concentration polarization which is acute upon high discharge currents. This type of polarization occurs as a result of the mobility of more than one ionic species in the presence of an electric field. One way to overcome it is by employing a material that would allow the mobility of one ionic species. This thesis will describe the synthesis and characterization of several fluorosulfonimide and fluorosulfonate based ionic liquids/melts as electrolytes having lithium as the only mobile ion. These materials were prepared by the nucleophilic addition reaction of a deprotonated polyether onto a perfluorovinyl ether group. Their transport, thermal and rheological properties were studied. Lithium ion cells consisting of LiCO₂ cathode and Li₄Ti₅O₁₂ spinel anode were fabricated and the electrochemical cell performance of the novel electrolytes was investigated under different discharge rates. It was found that the addition of partially fluorinated polyether functionalized with fluorinated lithium imide salt into the cathode composition, and the addition of polyether solvating agent into the electrolyte contributed to improved cell performance in terms of capacity and delivered power.
DEDICATION

This dissertation is dedicated to my family, especially…

  to my parents, Mary and Bishara, for their unconditional love and for
  instilling the importance of higher education;

  to my deceased grandfather, Boutros, who taught me the essence of hard
  work as well as valuable life lessons that will be forever cherished;

  to my uncle Robert, my aunts Rima and Mary and my grandmother
  Emerance for their support and encouragement;

  to my brothers, Bassem and Basseem, and my cousins, Ramzi, Rami and
  Ranya — may you also be motivated to reach your dreams.
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Also, I would like to acknowledge Dr. Christopher White for helping me pursue my higher education. Without his initial support, I would not have the opportunity to come to Clemson for my graduate studies. I am thankful to my undergraduate advisor, Dr. Sherman Parrish, for his encouragement and advice.

Finally, I would like to thank all of my friends for the good times and lasting memories we shared together.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>xv</td>
</tr>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
</tr>
<tr>
<td>I. LITHIUM BATTERY TECHNOLOGY</td>
<td>1</td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Electrodes</td>
<td>3</td>
</tr>
<tr>
<td>High power/high rate cathode materials</td>
<td>5</td>
</tr>
<tr>
<td>Electrolytes</td>
<td>7</td>
</tr>
<tr>
<td>References</td>
<td>14</td>
</tr>
<tr>
<td>II. LITHIUM IONIC LIQUIDS: AN OVERVIEW</td>
<td>20</td>
</tr>
<tr>
<td>Introduction</td>
<td>20</td>
</tr>
<tr>
<td>PEG-based ionic liquids</td>
<td>22</td>
</tr>
<tr>
<td>Lithium Salts</td>
<td>23</td>
</tr>
<tr>
<td>Fluorinated ionic liquids</td>
<td>27</td>
</tr>
<tr>
<td>Transport phenomena studies on ionic melts and single-ion conducting systems</td>
<td>29</td>
</tr>
<tr>
<td>Ionic liquids for high power/high rate secondary lithium batteries</td>
<td>31</td>
</tr>
<tr>
<td>References</td>
<td>33</td>
</tr>
<tr>
<td>III. EXPERIMENTAL ANALYSIS OF THE ELECTROLYTES</td>
<td>41</td>
</tr>
<tr>
<td>Introduction</td>
<td>41</td>
</tr>
<tr>
<td>$^1H$, $^7Li$ and $^{19}F$ NMR spectroscopy</td>
<td>42</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Table of Contents (Continued)</td>
<td></td>
</tr>
<tr>
<td>Differential scanning calorimetry</td>
<td>43</td>
</tr>
<tr>
<td>Electrochemical impedance spectroscopy</td>
<td>43</td>
</tr>
<tr>
<td>DC-galvanostatic polarization</td>
<td>49</td>
</tr>
<tr>
<td>Charge-discharge cell testing</td>
<td>49</td>
</tr>
<tr>
<td>Rheology</td>
<td>51</td>
</tr>
<tr>
<td>References</td>
<td>53</td>
</tr>
<tr>
<td>IV. MONO-FUNCTIONALIZED LITHIUM-CONDUCTING IONIC MELT ELECTROLYTES</td>
<td>54</td>
</tr>
<tr>
<td>Introduction</td>
<td>54</td>
</tr>
<tr>
<td>Experimental</td>
<td>57</td>
</tr>
<tr>
<td>Results and discussion</td>
<td>63</td>
</tr>
<tr>
<td>Conclusions</td>
<td>82</td>
</tr>
<tr>
<td>References</td>
<td>83</td>
</tr>
<tr>
<td>V. IONIC MELT ELECTROLYTES BASED ON DIFUNCTIONALIZED PEG WITH FLUOROSULFONATE OR FLUOROSULFONIMIDE PENDENTS</td>
<td>86</td>
</tr>
<tr>
<td>Introduction</td>
<td>86</td>
</tr>
<tr>
<td>Experimental</td>
<td>87</td>
</tr>
<tr>
<td>Results and discussion</td>
<td>94</td>
</tr>
<tr>
<td>Conclusions</td>
<td>104</td>
</tr>
<tr>
<td>References</td>
<td>105</td>
</tr>
<tr>
<td>VI. THE EFFECT OF LOW MOLECULAR WEIGHT POLYETHERS AS PLASTICIZERS ON THE TRANSPORT PROPERTIES AND RHEOLOGY ON LITHIUM FLUOROSULFONIMIDE IONIC MELTS</td>
<td>107</td>
</tr>
<tr>
<td>Introduction</td>
<td>107</td>
</tr>
<tr>
<td>Experimental</td>
<td>108</td>
</tr>
<tr>
<td>Results and discussion</td>
<td>111</td>
</tr>
<tr>
<td>Conclusions</td>
<td>121</td>
</tr>
<tr>
<td>References</td>
<td>122</td>
</tr>
<tr>
<td>VII. THE EFFECT OF FLUORINATED CHAINS AND BRANCHING ON THE THERMAL AND ELECTROCHEMICAL PROPERTIES POLYETHER- BASED SULFONIMIDE IONIC MELTS</td>
<td>124</td>
</tr>
<tr>
<td>Introduction</td>
<td>124</td>
</tr>
</tbody>
</table>
Table of Contents (Continued) Page

Experimental ........................................................................................125
Results and discussion .......................................................................131
Conclusions .......................................................................................138
References ........................................................................................139

VIII. SWAGE-STYLE ELECTROCHEMICAL CELL TESTING USING VARIOUS ELECTRODE AND ELECTROLYTE FORMULATION ..............................................................................140

Introduction .....................................................................................140
Experimental ....................................................................................142
Results and discussion .....................................................................144
Conclusions .....................................................................................164
References .......................................................................................165
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Classification of the most popular Li salts used in secondary lithium batteries based on their most important properties</td>
</tr>
<tr>
<td>4.1</td>
<td>Abbreviations, chemical formulas and EO:Li ratios for ionic melts synthesized in this work</td>
</tr>
<tr>
<td>4.2</td>
<td>Integrated peak areas $^1$H and $^{19}$F NMR spectral data and calculated EO:Li ratios for ionic melt electrolytes</td>
</tr>
<tr>
<td>4.3</td>
<td>$E_{cell}$ values calculated based on the concentration gradients across the $Li_{left}$/electrolyte/$Li_{right}$ cell after the 50 $\mu$A current step</td>
</tr>
<tr>
<td>5.1</td>
<td>DSC characteristics and VTF parameters for the oligomeric PEG-based ionic melts with lithium fluorosulfonate / fluorosulfonimide functionalities (included is the salt-in-polymer baseline)</td>
</tr>
<tr>
<td>6.1</td>
<td>Materials and their abbreviations</td>
</tr>
<tr>
<td>6.2</td>
<td>Values for the parameters of the VTF Equation obtained from ionic conductivity data fitting</td>
</tr>
<tr>
<td>7.1</td>
<td>Names and chemical formulas of fluorosulfonimide based oligoether ionic melts. The compounds show differences in their fluorocarbon content</td>
</tr>
<tr>
<td>7.2</td>
<td>DSC characteristics and VTF parameters for the ionic melts described in Table 7.1</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>A schematic representation of a lithium-ion cell</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic diagram of siloxyaluminate polymer containing ethylene oxide side chains</td>
<td>11</td>
</tr>
<tr>
<td>1.3</td>
<td>Schematic illustration of a modified silica nanoparticle having a sulfonate anion attached to its surface</td>
<td>11</td>
</tr>
<tr>
<td>2.1</td>
<td>Typical discharge curve of a battery showing the various types of Polarization</td>
<td>22</td>
</tr>
<tr>
<td>2.2</td>
<td>Structure of poly(ethylene oxide) showing the electron donor oxygen atom</td>
<td>23</td>
</tr>
<tr>
<td>3.1</td>
<td>Randles equivalent circuit for an electrochemical cell having a resistor in series with a parallel combination of a capacitor with a resistor</td>
<td>44</td>
</tr>
<tr>
<td>3.2</td>
<td>Impedence plot for an electrochemical system. From the plot, information about $R_s$, $R_{ct}$ and $C_{dl}$ can be obtained</td>
<td>45</td>
</tr>
<tr>
<td>3.3</td>
<td>Equivalent circuit of the blocking electrodes EIS technique</td>
<td>46</td>
</tr>
<tr>
<td>3.4</td>
<td>Experimental setup for impedance measurements: 1 – glass cell, 2 – glove bag, 3 – electrochemical interface, 4 – impedance gain/phase analyzer, 5 – oscilloscope, 6 – computer, 7 – digital thermometer, 8 – temperature controller, 9 – variac</td>
<td>47</td>
</tr>
<tr>
<td>3.5</td>
<td>Equivalent circuit of the symmetric electrochemical cell Li/ electrolyte/Li</td>
<td>49</td>
</tr>
<tr>
<td>3.6</td>
<td>(Left) Stainless steel alloy 20 with a 0.5” diameter used as the current collector for the negative electrode. (Right) Stainless steel alloy 20 current collector for the positive electrode having a diameter of 0.375”</td>
<td>51</td>
</tr>
<tr>
<td>4.1</td>
<td>Structure and synthesis of the target lithium fluorosulfonimide ionic melt electrolyte</td>
<td>56</td>
</tr>
</tbody>
</table>
4.2 (A) $^1$H NMR spectra and (B) $^{19}$F NMR spectra for IM550 ionic melt electrolyte. Peak assignments are as follows:

$$\text{CaH}_3\text{O}-(\text{CbH}_2\text{CbH}_2\text{O})_{10.8}-\text{CbH}_2\text{CcH}_2\text{O}$$

$$\text{CfF}_2\text{C}_6\text{CfH}_4\text{OCfF}_2\text{CF}_2\text{SO}_2\text{N(Li)SO}_2\text{CF}_3.$$  Peaks e and k correspond to the $^1$H and $^{19}$F NMR signals, respectively, of the internal standard $\alpha,\alpha,\alpha,-$ trifluorotoluene, $\text{CfF}_3\text{C}_6\text{CfH}_5$. ……………………..65

4.3 (A) $^7$Li NMR spectrum of IM550 and LiTFSI as an internal standard. (B) $^{19}$F NMR spectrum of IM550 and LiTFSI as an internal standard. ……………………..68

4.4 HPLC chromatograms for (top) ionic melt IM550; and (bottom) starting material PEGME550. The absence in the top chromatogram of a peak near 32 min retention time indicates that the sample is free of PEGME550 reactant as a nonionic impurity. The very small apparent peak at 32 min in the top chromatogram is too narrow to be a peak for unreacted polyether. It is believed to be a noise fluctuation in the detection signal. ……………………..70

4.5 Time-of-flight electrospray-ionization mass spectra of (top) ionic melt sample IM550; and (bottom) starting material PEGME550. Peak at $m/z=970$ in the top spectrum corresponds to

$$[\text{CH}_3\text{O(H)}-(\text{CH}_2\text{CH}_2\text{O})_{12}-\text{CF}_2\text{CFHOCF}_2\text{CF}_2\text{SO}_2\text{N(H)SO}_2\text{CF}_3]^+$$

and that at $m/z=561$ in the bottom spectrum corresponds to $[\text{CH}_3\text{O(H)}-(\text{CH}_2\text{CH}_2\text{O})_{12}-\text{H}]^+$. All other major peaks correspond to differences of $m/z=44$ (CH$_2$CH$_2$O) from these base masses. The absence of peaks in the ionic melt spectrum in the m/z range near 560 Da confirms the finding from HPLC that the sample is free of PEGME550 as a nonionic impurity. …………………………………………..72

4.6 Arrhenius plots of log(ionic conductivity) vs. inverse absolute temperature for three PEGME-derived lithium fluorosulfonimide ionic melts having different PEG chain lengths and thus different EO:Li ratios. A plot for LiTFSI dissolved in PEGDME500 at a EO:Li ratio of 10.3:1 is shown for reference. …………………………………………..75

4.7 Arrhenius plots of log(ionic conductivity) vs. inverse absolute temperature for three PEGME-derived lithium fluorosulfonate ionic melts having different PEG chain lengths and thus different EO:Li ratios. …………………………………………..76
4.8 Voltage-time plots corresponding to DC galvanostatic polarization of electrolytes sandwiched between dual Li electrodes. Top, lithium fluorosulfonimide ionic melt IM550. Bottom, LiTFSI dissolved in PEGDME500 at an EO:Li ratio of 10.3:1.

4.9 Voltage-time plots corresponding to DC galvanostatic polarization of electrolytes sandwiched between dual Li electrodes. Top, lithium fluorosulfonimide ionic melt IM550. Bottom, LiTFSI dissolved in PEGDME500 at an EO:Li ratio of 10.3:1.

5.1A $^1$H NMR spectrum of IM600 - (OC$^{a}$H$_2$C$^{a}$H$_2$)$_{11.2}$-(OC$^{a}$H$_2$C$^{b}$H$_2$-O-CF$_2$CF$^2$HO-CF$_2$CF$_2$SO$_2$N(Li)SO$_2$CF$_3$)$_2$.

5.1B $^{19}$F NMR spectrum of IM600 - (OCH$_2$CH$_2$)$_{11.2}$-(OCH$_2$CH$_2$-O-C$_{12}^{d}$F$_2$CFHOCF$_2$CF$_2$SO$_2$N(Li)SO$_2$CF$_3$)$_2$.

5.2A DSC scans for plots of the new ionic melts prepared from oligomeric PEGs having two lithium fluorosulfonate functionalities ($R_{F,H} =$ CF$_2$CFHOCF$_2$CF$_2$).

5.2B DSC scans for plots of the new ionic melts prepared from oligomeric PEGs having two lithium fluorosulfonimide functionalities ($R_{F,H} =$ CF$_2$CFHOCF$_2$CF$_2$).

5.3A Arrhenius plots of the new ionic melts prepared from oligomeric PEGs having two lithium fluorosulfonate functionalities ($R_{F,H} =$ CF$_2$CFHOCF$_2$CF$_2$). Data for the salt LiTFSI in polymer host PEGME with M = 550 Da are provided for comparison.

5.3B Arrhenius plots of the new ionic melts prepared from oligomeric PEGs having two lithium fluorosulfonimide functionalities ($R_{F,H} =$ CF$_2$CFHOCF$_2$CF$_2$). Data for the salt LiTFSI in polymer host PEGME with M = 550 Da are provided for comparison.

5.4 Arrhenius plots comparing two sulfonimide functionalized ionic melt electrolytes, one is mono-functional (dark circle) and the second is di-functional (dark triangle), but have the same EO : Li ratios.

6.1 Arrhenius plots for the ionic conductivities of IM550 and the gelled ionic melts listed in Table 6.1.

6.2 VTF plots for the ionic conductivities of the pure ionic melt compared to those that are plasticized with unmodified polyether oligomers.
6.3 DSC curves of IM550, IM550_Gel1 and IM550_Gel2 displaying the glass transition temperatures of all the electrolytes..........................115

6.4 Plot of shear stress versus shear rate showing Newtonian behavior for IM550 at ambient conditions.................................................................116

6.5 (a-c) Steady-shear viscosities as function of shear rates taken at ambient temperature for IM550 and the plasticized electrolytes..............................117

6.6 Elastic and viscous moduli as functions of oscillatory frequency $\omega$ for IM550 taken at ambient temperature..................................................118

6.7 (A-B) Potential-time plot as a result of a DC-galvanostatic experiment performed in a symmetric cell Li/Electrolyte/Li. Magnitudes of the currents for the first and the second steps are 10 $\mu$A and 50 $\mu$A respectively for a duration of 1 hour each. (A) DC-galvanostatic polarization data for IM550_Gel2. (B) DC-galvanostatic polarization data for IM550_Gel1........................................................................................................120

7.1 (a) $^1$H NMR spectra (b) $^{19}$F NMR spectra of IM550_Dupont.........................133

7.2 LC chromatogram for IM550_Dupont showing a single peak at a retention of 52 minutes.........................................................................................134

7.3 Arrhenius plots showing the temperature dependent ionic conductivities of the electrolytes listed in Table 7.1...............................................................137

7.4 DSC thermograms of the materials listed in Table 7.1.................................137

8.1 Lithium-ion cell charge profile up to 4.2 V cutoff for 1M LiPF$_6$ in 1:1 EC:DEC using C as the anode and LiCoO$_2$ as the cathode...............................146

8.2 Current profile for the formation experiment done on a lithium-ion cell having 1M LiPF$_6$ in 1:1 EC:DEC using C as the anode and LiCoO$_2$ as the cathode.........................................................................................................................147

8.3 Half cell employing Li metal anode and LiCoO$_2$ cathode with 1M LiPF$_6$ in EC:DEC (1:1) as the electrolyte.................................................................147

8.4 Half cell employing Li metal anode and C cathode with 1M LiPF$_6$ in EC:DEC (1:1) as the electrolyte...........................................................................148

8.5 Cycle performance at a C/5 rate of 1M LiPF$_6$ in 1:1 EC:DEC using LiCoO$_2$ cathode and C anode..............................................................................149
8.6 Specific capacity versus cycle number, obtained at C/5 rate for a lithium ion cell of 1M LiPF<sub>6</sub> in 1:1 EC:DEC using LiCoO<sub>2</sub> cathode and C anode.................................................................150

8.7 Charge profile for a cell consisting of IM550 as the electrolyte, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode and standard LiCoO<sub>2</sub> cathode..............................151

8.8 Charge profile for a cell consisting of IM550 as the electrolyte, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode and LiCoO<sub>2</sub> composite cathode...............................152

8.9 Discharge profile at a C/100 rate for a cell consisting of IM550 as the electrolyte, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode and LiCoO<sub>2</sub> composite cathode........153

8.10 Specific capacity vs. cycle number, obtained at C/5 rate, for two electrolyte formulations of IM550 and carbonate solvents. Black circle is for electrolyte consisting of IM550 with 40 wt% EC:DEC (1:1) and the white circle is for the electrolyte consisting of IM550 with 20 wt% EC:DEC (1:1). Both electrolytes were studied in a cell using C as the anode and LiCoO<sub>2</sub> as the cathode ......................154

8.11 First discharge capacity at a C/100 rate of a cell having IM550 with 50 wt% PEGDME as the electrolyte, Li as the anode and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as the cathode .........................................................155

8.12 Charge-discharge profiles at a C-rate of C/80 showing full capacity utilization for a cell consisting of IM550 + 50 wt% PEGDME as the electrolyte, Li anode and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> cathode..............................................................156

8.13 Performance of the cell consisting of IM550 + 50 wt% PEGDME as the electrolyte, Li anode and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> cathode, at different discharge rates of C/60, C/50 and C/10.........................................................157

8.14 Cycling at RT of a cell having IM550 + 20 wt% PEGDME as the electrolyte, Li anode and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as the cathode..............................................................158

8.15 Cycling at a rate of C/20 for a cell consisting of IM550 + 50 wt% PEGDME as the electrolyte, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as the anode and composite LiCoO<sub>2</sub> as the cathode..............................................................159

8.16 Cell voltage as a function of time for three different discharge C-rates done on a cell consisting of IM550 + 50 wt% PEGDME as the electrolyte, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as the anode and composite LiCoO<sub>2</sub> as the cathode..............................................................160
8.17 Performance at a discharge rate of 1C for a cell consisting of IM550 + 50 wt% PEGDME as the electrolyte, Li$_4$Ti$_5$O$_{12}$ as the anode and composite LiCoO$_2$ as the cathode………………………………………………161

8.18 Cycling at RT of a cell having IM550 + 50 wt% PEGDME as the electrolyte, Li anode and LiCoO$_2$ composite cathode……………………162

8.19 First and second specific discharge capacities at C/100 rate of a cell having IM550 with 50 wt% PEGDME as the electrolyte, Li as the anode and C as the cathode…………………………………………………………163

8.20 Cell voltage as a function of time for two discharge C-rates done on a cell consisting of LiTFSI-in-PEGDME as the electrolyte, Li$_4$Ti$_5$O$_{12}$ as the anode and composite LiCoO$_2$ as the cathode………..164
### LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Chemical structures of the sulfonate and sulfonimide anions</td>
<td>25</td>
</tr>
<tr>
<td>2.2</td>
<td>Chemical structures of imide, acetamide and methanide anions</td>
<td>27</td>
</tr>
<tr>
<td>2.3</td>
<td>Chemical structure of the bis(trifluoromethanesulfonyl)imide anion</td>
<td>28</td>
</tr>
<tr>
<td>4.1</td>
<td>Synthesis of trimethylsilyl-activated trifluoromethanesulfonamide</td>
<td>58</td>
</tr>
<tr>
<td>4.2</td>
<td>Lithium (perfluorovinylether)sulfonimide salt preparation</td>
<td>59</td>
</tr>
<tr>
<td>5.1</td>
<td>Synthetic route for the preparation of lithium perfluorinated vinyl[(ethylene)(methyl)disulfonyl]imide ether</td>
<td>89</td>
</tr>
<tr>
<td>5.2</td>
<td>Synthetic route for the preparation of new PEG-based ionic melts with lithium fluorosulfonimide functionalities (n = 13.2 - 45.0)</td>
<td>91</td>
</tr>
<tr>
<td>7.1</td>
<td>Synthesis of A, R₂SO₂N(Li)Si(CH₃)₃</td>
<td>129</td>
</tr>
<tr>
<td>7.2</td>
<td>Synthesis of B, CF₂(Br)CF(Br)OR₂f-SO₂F</td>
<td>129</td>
</tr>
<tr>
<td>7.3</td>
<td>Synthesis of C, CF₂=CFOR₂fSO₂N(Li)SO₂CF₃</td>
<td>129</td>
</tr>
<tr>
<td>7.4</td>
<td>Synthesis of D, (CF₂=CFOCF₂CF₂SO₂)₂NLi</td>
<td>130</td>
</tr>
<tr>
<td>7.5</td>
<td>Synthesis of E, CF₂=CFOR₂fSO₂N(Li)SO₂(CF₂)₃CF₃</td>
<td>130</td>
</tr>
<tr>
<td>7.6</td>
<td>Synthesis of IM550_Dupont</td>
<td>130</td>
</tr>
<tr>
<td>7.7</td>
<td>Synthesis of (IM550)₂Li and (IM350)₂Li</td>
<td>130</td>
</tr>
<tr>
<td>7.8</td>
<td>Synthesis of the IM550_(CF₂)₃</td>
<td>131</td>
</tr>
</tbody>
</table>
CHAPTER ONE
LITHIUM BATTERY TECHNOLOGY

Introduction

Electricity has been one of the great discoveries that humanity ever witnessed. It is a phenomenon without which our technological advancements would not have been possible. Unfortunately, challenges are inevitable and the increasing demand of the modern society for other means of power sources has made energy storage one of the most critical issues of the twenty-first century. Today’s ecological concerns along with the market’s need for low-cost miniaturized portable devices caused a rapid development in the research of lithium batteries.

The use of lithium in rechargeable batteries technology has two main advantages. First, it is the lightest element that can safely be handled in electrochemical processes. Second, it exhibits the highest oxidation potential (highest negative standard electrode potential) of all elements providing the highest specific capacity (4 A·h/g). The first non-rechargeable (primary) lithium batteries were manufactured in the early 1970s. Attempts to develop rechargeable lithium batteries followed in the 1980s but failed due to safety problems. Secondary lithium batteries, known as lithium-ion or rocking chair, were the first commercial rechargeable lithium batteries manufactured by Sony Corporation in
1991 (based on Carbon anode/ LiCoO$_2$ cathode) and they are one of the great successes of modern materials electrochemistry [1]. Indeed, its success is attributed to the development of insertion compounds (e.g., transition metal chalcogenides, transition metal oxides in spinel phase and others) that could host lithium ions in their crystalline structure and thus reduce the high oxidation states of the transition metal [2]. The basic requirements for a host structure to be a good candidate for an electrode are [3]:

- it is a mixed ionic-electronic conductor;
- the removal of lithium does not change the structure over a large range of solid solutions or compositions;
- the lithiated (reduced) and partially lithiated (partially oxidized) structures exhibit a suitable potential difference versus lithium;
- the host lattice dimension changes on insertion/removal of lithium are not too large;
- it has an operational voltage range that is compatible with the redox range of stability for the accompanying electrolyte.

A lithium ion battery consists of a lithium–ion intercalation negative electrode that is usually made of graphite (anode, theoretical specific capacity of 372 mA·h/g) and a lithium-ion intercalation positive electrode (cathode) that is generally made of a lithium transition metal oxide. The electrodes are coated onto current collectors (often Cu for the anode and Al for the cathode) and separated by a lithium-ion-conducting electrolyte. Figure 1 shows a schematic of a lithium-ion cell. During discharge, the lithium ions de-intercalate from the negative electrode and are shuttled through the electrolyte consisting
of a lithium salt of anions $A^-$ into the positive electrode where they intercalate. A reversible process occurs upon charging.

Figure 1.1: A schematic representation of a typical lithium-ion cell [4].

**Electrodes**

Generally, during discharge, the anode of the secondary lithium battery is the source of lithium ions and the cathode is the sink for the lithium ions. The cell potential is determined by the difference between the chemical potential of lithium in the anode and cathode.
**Anodes:** Of all the different materials that are available, lithiated graphite has proven to be the best candidate as an anode. Although lithium metal would be the best choice as an anode since it would provide the highest energy density, it is very unsafe and gives rise to interfacial instabilities. Alloys of lithium were studied, such as lithium alloys of aluminum, tin and silicon, and found to provide a specific capacity much larger than that of graphite [5, 6]. However, due to the mechanical strain generated during the alloying/de-alloying processes, the electrode cracks and a loss of capacity occurs over a number of cycles [6, 7].

**Cathodes:** Cathode materials are studied quite intensively. Almost all of these materials consist of a transition metal having several oxidation states. The material should react reversibly with lithium without undergoing any change in its structure. Preferably, it should allow one lithium per transition metal to ensure high capacity, and it should be a good electronic conductor with high stability [8].

Early in 1970, it was found that lithium can be intercalated into layered dichalcogenides [9]. Titanium disulfide, TiS$_2$, was the most advantageous because of its ability to undergo no phase change allowing no energy wastage associated with the formation of new phases. TiS$_2$ has a hexagonal close-packed sulfur lattice with titanium ions in octahedral sites between alternating sulfur sheets of sequence ABAB. However, the cathode material that was first used in a commercial battery is the LiCoO$_2$ (spinel form). It has a similar structure to that of TiS$_2$ and can allow lithium to be removed electrochemically [10]. It offers a much higher working voltage than that of TiS$_2$ (3.6 V vs. 2.0 V); also, it exhibits a higher capacity and has an excellent cycle life especially at
low rates, i.e. C/10 and less. A drawback for LiCoO$_2$ cathode is the high cost of cobalt which limits the use of such batteries for only small cells, such as those in computers and cell phones. Another drawback is the reactivity of Co$^{4+}$ with the electrolyte leading to its oxidation and to a slow capacity fade. Another material tested as a cathode was the analogous iron oxide (LiFeO$_2$) but no success was achieved with this material because lithium cannot be reversibly removed from its host structure. In 1997, LiFePO$_4$ was the first cathode material of low cost and with a benign effect toward the environment to be reported [11]. Its discharge potential is about 3.4 V vs. lithium and it has no capacity fading after several hundred cycles. Its theoretical capacity is 170 mA·h/g and provides a long cycle life due to small volume changes upon lithium insertion/extraction [12-14] and low reactivity with the electrolyte. The main disadvantage is its poor electronic conductivity which necessitates its mixing with high amounts of graphite, thus compromising its capacity.

**High Power/High Rate Cathode Materials**

With the increasing need of high power consumer electronics, such as power tools, and the need for developing electric (EV) and hybrid electric cars (HEV), cathode materials play a major contribution in that respect. LiCoO$_2$ and LiFePO$_4$ are some of the materials that have been looked into for such applications, and efforts are being put into improving their performance under high rate currents, i.e. 5C and above. Such materials are important because of their practical commercial applications. High rate capabilities are associated with high electronic conductivities as well as high lithium diffusion.
through the core structure [15, 16]. Decreasing the particle size of the cathode and increasing its specific surface area enhance the activity of the electrode [17-19]. Furthermore, thin films [20] and highly porous electrodes [21] improve the rate capability as well.

The rate capability of LiFePO$_4$ has been improved by admixing it with carbon [14, 22-24], adding 1% Cu or Ag [25, 26], and doping it with heteroatoms [24]. Kinetics studies, using cyclic voltammetry (CV), show that the current peak, $I_p$, increases with increasing the carbon additives from 5-20 wt% [15]. To account for lithium diffusion during intercalation and de-intercalation, electrochemical impedance spectroscopy (EIS) technique was used. It has been shown that the charge transfer resistance, $R_{CT}$, decreases and the lithium diffusion coefficient increases by almost three orders of magnitude [15] with the increasing content of the carbon additive from 5 to 20 wt%.

Improving the rate capability of LiCoO$_2$ can be achieved through similar approaches used with the LiFePO$_4$. One way, that has been recently described, is by coating the active particles with conductive carbon [16]. The surface modification was done by milling the LiCoO$_2$ particles with sucrose and then heating the solids into the air to leave nanolayer-coated LiCoO$_2$ particles. The diffusion coefficient for lithium increased by almost two orders of magnitude upon coating the particles with carbon. This can be explained by the enhancement in electronic conductivity after the carbon coating which translates into a better performance under high rates of current. In addition, the coating improved the charge and discharge capacities by increasing them from 128 to 141 and 110 to 130 mA·h/g, respectively [16].
Besides surface modification of the LiCoO₂ particles, composites of LiCoO₂ with silver improved the high rate discharge capability of the electrodes as well. As reported [27], the composite material was made by ball milling LiCoO₂ (91 wt%) with AgNO₃ (9 wt%) in alcohol until a homogenous mixture is obtained. The solvent was then evaporated and the material was further treated at 50 °C and then allowed to cool down. High rate discharge experiments revealed that the silver additive decreased the overpotential losses and reduced the polarization at the cathode/electrolyte interface. In addition, silver increased the discharge capacity by 20 % at 1C rate and by 15 % at 10C rate. All that translates into an improvement in the reversible capacity and the cycling stability at high charge-discharge rates [27].

Electrolytes

The role of electrolyte in an electrolytic cell is to serve as medium for the transfer of charges. Lithium batteries require electrolytes that contain lithium ions, Li⁺. These electrolytes are divided into two categories. One is lithium-ion conducting liquids and the other one is lithium-ion conducting polymers. This section will focus only on the different forms of electrolytes that have been studied in the literature. A more thorough study of the salts will be discussed in the next chapter.

Liquid electrolytes are obtained by dissolving lithium salts in polar aprotic solvents. The active nature of the strongly reducing anodes and the strongly oxidizing cathodes rules out the use of any solvents that have active protons. Studies have shown that the reduction of the active protons and the oxidation of the corresponding anions
occur between 2.0 – 4.0 V versus Li, which is within the electrochemical window of the potentials of the electrodes (0.0 - 0.2 V for the anode and 3.0 - 4.5 V for the cathode) [28]. Some other criteria have to be met in order for such solvents become applicable. They should have a high dielectric constant and a low viscosity. Also, they should be inert toward the cell components and especially the charged surfaces of the electrodes. Finally, they should have a wide liquid range, i.e. low melting point and high boiling point, and should be safe [29]. Examples of solvents that meet these criteria are ethylene carbonate (EC), propylene carbonate (PC), dimethylcarbonate (DMC), diethylene carbonate (DEC) and mixtures of them. One common feature of these solvents is that they contain a polar carbonyl group (C=O) that dissolves the lithium salt. Despite the fact that liquid electrolytes possess high ionic conductivities, they suffer from major hindrances like mechanical instability and the risk of flammability. Therefore, more of the research interests are directed towards the development of solid-state lithium-ion batteries that use lithium-ion conducting polymer electrolytes.

Polymer electrolytes pave the way for the development of all-solid-state lithium ion batteries. Polymer electrolytes can be solid-like or gel-like. The main advantages of such systems include flexibility, processability of plastics structure and reduced flammability. Avoiding the use of liquids, cheap, low-weight plastic containers can replace heavier and more expensive stainless steel ones. Also, a polymer electrolyte can function as separator between electrodes, which previously was used to avoid short circuits when liquid electrolytes were the choice [30].
Research on solid polymer electrolytes (SPEs) were initiated in 1978 after the discovery of ionic conductivity in alkali metal salt complexes of poly(ethylene oxide) (PEO) in 1973 by P. V. Wright [31]. The transport mechanism of ions in polythere-based SPEs is explained by the presence of the amorphous phase in the polymer as well as the etheric oxygens that coordinate with the positively charged metal cations [32]. In general, SPEs consist of a lithium salt dissolved in a polymer host matrix (most common being PEO, PEG, PPO etc.). Crystallization is a major concern with this kind of SPEs since it hinders polymer chain mobility. It was reported that cross-linking, co-polymerization and comb formation suppress crystallization and enhance ambient ionic conductivity [33]. The most striking advancements in the ionic conductivities of PEO-based SPEs have been attained through the addition of organic carbonates as plasticizers (EC, PC and DEC) to form gelled SPEs. Plasticizers reduce the crystalline content, increase the segmental mobility of the polymer chain, and cause better ion dissociation. Although they have favorable characteristics, gelled SPEs are thermodynamically unstable. They might undergo solvent exudation upon long storage and that increases the electrolyte’s viscosity causing a dramatic decrease in the ionic conductivity [34].

High ionic conductivity is unquestionably the main requirement for any electrolyte to be successful. However, high ionic conductivity is not sufficient if the electrolyte does not also have a high Li⁺ transference number. The transference number is defined as “the net number of Faradays carried by an ion constituent in the direction of the cathode or anode on the passage of a Faraday of charge across the cell” [35]. In the polymer and liquid electrolytes described above, both the cations and the anions
contribute to the ionic conductivity. This is a major drawback for a battery performance especially as the drain rate of the battery is increased. When a battery is subjected to high discharge rates, a gradient in salt concentration is formed due to the accumulation of the lithium ion at the anode and its depletion at the cathode [36, 37]. Such gradients affect negatively the lithium diffusion coefficient and the density of charge carriers across the electrolyte [38]. Therefore, the dc conductivity falls below the initial value leading to a reduction in the capacity of the battery and a decrease in the voltage window. This problem can be overcome if the cationic transference number is closer to unity [39].

Single-ion conductors are examples of polyelectrolytes in which the cation is the only mobile ionic species. Different strategies have been used to synthesize single-ion conductors. Polyanionic salts were blended or alloyed with high molecular weight PEO [40, 41]; anions were attached to linear PEO chain ends [42], tethered to side chains of comb-branched polymers [43], fixed between polymer chains as a crosslinker as in Figure 1.2 [44] or fixed to fumed silica nanoparticles as in Figure 1.3 [45]. Shown below are two schemes for the preparation of single-ion conducting polymer electrolytes.

Figure 1.2 shows an illustration of a siloxialuminate polymer. It was synthesized following hydrosilation chemistry using LiAlH₄ and PtCl₆.6H₂O as the catalyst. FIRST allyl ether of monomethyl ether poly(ethylene glycol) (PEGME) was synthesized and then coupled to dimethoxymethylsilane (HSiMe(OMe)₂) and diethoxysilane (H₂Si(OEt)₂) in the presence of the platinum catalyst. HSiMe(OMe)₂ yielded products with one ether chain, and H₂Si(OEt)₂ gave products with two ether chains attached to the silicon atom.
Figure 1.2: Schematic diagram of siloxyaluminate polymer containing ethylene oxide side chains [44].

\[ \text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3 \]

Figure 1.3: Schematic illustration of a modified silica nanoparticle having a sulfonate anion attached to its surface [45].

The products were then hydrolyzed to form silanediols which were then reacted with LiAlH$_4$ to form the single-ion conductor [44]. However, in Figure 1.3, the anionic moiety is immobilized onto a fumed silica surface. The importance of such materials is not only related to the fact that a single-ion conducting material is achieved, but also to the fact that the incorporation of the fumed silica particles helps to stabilize the interface with the lithium electrode [46].

The interfaces between electrodes and electrolyte in a lithium-ion battery are very critical. The layer that is formed upon the contact of the anode with the electrolyte
consists of insoluble and partially soluble reduction products. Its thickness is determined by the electron-tunneling range and its properties resemble those of a solid electrolyte with high electronic resistivity. Therefore, it is called the solid-electrolyte interphase (SEI) [47]. The SEI determines the safety, power capability, shelf life and cycle life of the battery [48, 49]. To achieve high performance, the SEI must behave as an electronic resistor in order to avoid SEI thickening leading to high internal resistance, self-discharge and low faradaic efficiency. Also, it should be highly-ion conductive to reduce overvoltage. The cathodes (LiCoO₂, LiNiO₂, LiMn₂O₄, etc) are also covered by surface films, and thus their electrochemical processes include the necessary stages of Li ion migration through surface films and charge transfer across the film/electrolyte and the film/active mass interfaces, which contribute a major part to the impedance of these electrodes [50].

Other materials that offer similar features to those of single-ion conductors are ionic liquids or ionic melts that are solvent-free and have the anions immobilized. The second chapter will focus entirely on this type of material along with a thorough discussion on the different types of lithium salts that have been studied and reported in the literature. The third chapter will focus on discussing the various analytical techniques used for the characterization of new electrolytes that were synthesized in this work. The forth chapter will go over the synthesis and characterization of monofunctional sulfonimide and sulfonate ionic liquids. The fifth chapter will discuss the synthesis and characterization of difunctional sulfonate and sulfonimide ionic liquids. The sixth chapter will discuss the effect of polythere plasticizers on the rheology and transport
properties of the ionic melts. The seventh chapter will discuss the properties of extended fluorinated ionic liquids. The eighth chapter will focus solely on the results obtained from different cell testing runs on the different ionic liquid formulations.
References


CHAPTER TWO
LITHIUM IONIC LIQUIDS: AN OVERVIEW

Introduction

The term “ionic liquid” is commonly used for salts whose melting point is relatively low (usually under 100 °C). They are liquids that are composed entirely of ions and in this sense alone resemble the ionic melts which may be produced by heating normal salts such as sodium chloride to high temperature (e.g., NaCl to over 800 °C). In particular the salts that are liquid at ambient temperature are called room-temperature ionic liquids or RTILs. They have been known since 1914 [1] but the field of modern ionic liquid chemistry really took off in the late 1970s [2] and their applications have been envisioned in various technological aspects because of their unique properties which include: non-volatility, high chemical, thermal and electrochemical stability as well as high ionic conductivity. Being non-volatile, they have been used as green solvents for catalysis and chemical synthesis [3-5], and being highly stable and possessing high ionic conductivity have made them potential candidates as electrolytes in electrochemical capacitors, fuel cells and batteries [6-9].

In particular, the use of ionic liquids as electrolytes for secondary lithium batteries, as opposed to the conventional solvent-salt electrolyte mixtures, is highly advantageous for the following reasons. First, as mentioned above, ionic
liquids are primarily salts that are constituted only of ions, which means that ion-pairing is highly reduced. Second, being solvent-free is considered as being both safe and green for the batteries. More than that, being free from solvent can help prevent any density and concentration gradients from building up within the electrochemical cell. Such gradients are major drawbacks for a battery performance because they cause current drop across the cell and thus a decrease in the cell’s potential leading to a premature failure. Figure 2.1 shows the different factors causing polarization losses across the cell upon discharge. Last, having a wide liquid range with low viscosity enhances the ionic mobility and therefore the ionic conductivity which is the product of the charge carrier concentration and the charge carrier mobility [10] as expressed in equation 1:

\[ \sigma = \sum_i n_i \mu_i Z_i e \]  

Where \( \sigma \) – ionic conductivity (S/cm),
\( n_i \) – number of charge carriers (1/cm\(^3\)),
\( \mu_i \) – ionic mobility (cm\(^2\)/V·sec),
\( Z_i \) – charge of ionic species \( i \),
\( e \) – unit charge of electrons (1.609·10\(^{-19}\) C).
Figure 2.1: Typical discharge curve of a battery showing the various types of polarization [11].

**PEG-Based Ionic Liquids**

Research in solid electrolytes has been critical due its promises for the development of solid state batteries [12]. Solid polymer electrolytes (SPE) are prepared by dissolving the salt in a polymer host matrix. Poly(ethylene oxide) (PEO) was heavily studied due to the presence of the ethylene oxide (EO) units that favorably coordinate the lithium ions by the electron donor oxygen atom [13] as shown in Figure 2.2. A disadvantage in chelating the lithium ions by the basic ether groups is that the overall ionic conductivity is dominated by the motion of the anions [14]. Anionic transport should be avoided in order to limit any concentration gradients within the cell. One strategy to overcoming this limitation is to covalently connect (tether) the anions of the lithium salt to a polymer backbone which could be a poly(ethylene glycol) (PEG).
The crystallization issue has been a problem with SPEs made of PEO-salt hybrids and that was because of the crystallization of the salt in the polymer matrix. Tethering the anion of the salt to short chains of PEG overcomes this problem [14]. The only consideration for this approach is that it increases the glass transition temperature and thus provides poor room-temperature ionic conductivities since the mobility of the ions is related to the glass transition temperature of the matrix [15, 16]. To provide higher ambient ionic conductivity, the properties of the molten salts can be tuned by changing the anionic moieties as has been shown by Ohno and co-workers [17-20].

**Lithium Salts**

Ideally, any lithium salt targeted for use in a battery should have the following properties [21]:

- It should have a high dissociation constant in nonaqueous media with high cationic mobility;
- The anion should have a stable oxidative potential;
- The anion and cation should be inert toward cell components (separator and packaging materials);
- It should be thermally stable.
Many lithium salts have been studied over the years and all have advantages and disadvantages. One has to bear in mind that one of the most desirable properties for a lithium salt is its ability to dissociate and to allow high cationic mobility. There are salts of inorganic anions and others of organic anions. LiClO$_4$ for example, has high room-temperature ionic conductivity (9 mS/cm) when mixed with EC/DMC and has a wide electrochemical stability for up to 5.1V [22]. If compared with salts of inorganic superacid anions such as LiPF$_6$ or LiBF$_4$, it has a lower interfacial resistance and is less hygroscopic [23-25]. However, LiClO$_4$ is not as safe as LiBF$_4$ because the perchlorate anion is a strong oxidant which can react with organic solvents under extreme conditions such as high temperature and high current charge [26, 27]. Nonetheless, despite its safety, LiBF$_4$ did not gain much further studies because of its poor Li cycling efficiencies and its moderate ionic conductivity due to its small dissociation constant [28-30].

Much of research interest has been driven toward the lithium salts based on the conjugate bases of the organic superacids where the acid strength is increased because of the stabilization of the anions by the strongly electron-withdrawing groups; most favorable are perfluorinated alkyls (R$_f$) due to their high thermal and electrochemical stabilities. The strong acidity of these anions is derived from the delocalization of the formal negative charge caused by the inductive effect of the electron-withdrawing groups and their conjugated structures [21]. Some of the anionic species that have been investigated in literature are the sulfonate and sulfonimide anions having the chemical structures shown in Scheme 2.1.
Scheme 2.1: Chemical structures of the sulfonate and sulfonimide anions

The sulfonimide based lithium salts proved to have better performance in terms of ionic conductivity than their sulfonate counterparts because of their weaker basicity and thus better ion dissociation. This low basicity is caused by the delocalization of the negative formal charge over the O-S-N skeleton due to the resonance effect [31]. The imide anion was first reported in literature by Dr. DesMarteau at Clemson University in 1984 [32] and its applications in lithium secondary batteries was proposed by Michel Armand in 1989 [33]. Ever since has been adopted as a standard electrolyte of interest in lithium batteries by both academia and R&D. Lithium bis(trifluoromethanesulfonyl) imide, known as LiTFSI, was first commercialized by 3M Corporation in the early 1990s and since then was extensively studied. Despite all the promises that LiTFSI offered in terms of high conductivity in different solvents, good stability and good dissociation in low dielectric media (like ethers), its application in lithium cells was never fully accepted because of its corrosive effect upon the Al or Ni collectors used for the cathode in the Li batteries. One way that proved to overcome the corrosion was to extend the perfluorinated alkyl chain (use of LiBETI salt) or to add a small quantity of LiPF₆ salt as
they both suppressed the corrosion of Al by promoting the formation of passivation layers over the Al [34].

Table 2.1 classifies the properties of different lithium salts in terms of ion mobility, ion pair dissociation, solubility in several aprotic solvents, thermal stability, chemical inertness, solid-electrolyte interface (SEI) and Al corrosion. Each has its advantages and disadvantages, and among all LiPF₆ was found to be the best in performance and thus gained potential application in the commercial lithium-ion batteries.

Table 2.1: Classification of the most popular Li salts used in secondary lithium batteries based on their most important properties [35].

<table>
<thead>
<tr>
<th>Property</th>
<th>From Best → to Worst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion mobility</td>
<td>LiBF₄, LiClO₄, LiPF₆, LiAsF₆, LiTf⁴, LiTFSI</td>
</tr>
<tr>
<td>Ion pair dissociation</td>
<td>LiTFSI, LiAsF₆, LiPF₆, LiClO₄, LiBF₄, LiTf</td>
</tr>
<tr>
<td>Solubility</td>
<td>LiTFSI, LiPF₆, LiAsF₆, LiBF₄, LiTf</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>LiTFSI, LiTf, LiAsF₆, LiBF₄, LiPF₆</td>
</tr>
<tr>
<td>Chem. inertness</td>
<td>LiTf, LiTFSI, LiAsF₆, LiBF₄, LiPF₆</td>
</tr>
<tr>
<td>SEI formation</td>
<td>LiPF₆, LiAsF₆, LiTFSI, LiBF₄</td>
</tr>
<tr>
<td>Al corrosion</td>
<td>LiAsF₆, LiPF₆, LiBF₄, LiClO₄, LiTf, LiTFSI</td>
</tr>
</tbody>
</table>

*LiTf = lithium triflate.*
Fluorinated Ionic Liquids

Ionic liquids are usually made of anions that are weakly basic inorganic or organic compounds as mentioned earlier in the previous section. The chemical structures of the anions have a strong influence on the properties of the ionic liquid with respect to viscosity and ionic conductivity. The lowest viscosity ionic liquids are formed from small anions that have a highly delocalized negative charge and do not take part in any hydrogen bonding [36]. Ionic liquids of imide and methanide anions, shown in Scheme 2.2, have low melting points and low viscosities. Fluorination of these anions effectively reduces the hydrogen bonding resulting in a decrease in the melting point as well as an increase in thermal and electrochemical stability [37-39]. In addition, asymmetric groups on the anion, such as 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide ion, reduce the melting point as well [37].

![Chemical structures of imide, acetamide and methanide anions](image)

Scheme 2.2: Chemical structures of imide, acetamide and methanide anions
In the investigation of the effect of the anion fluorination in ionic liquids, it is well known that the TFSI anion, shown in Scheme 2.3, gives ionic liquids with very low melting points and higher fluidity than almost any other anion. The first ionic liquid based on the TFSI anion was reported by Koch et al. in 1995 [39]. As mentioned in the previous section, what gives the TFSA anion advantageous properties, such as the minimal interaction between the anion and the cation, is the diffused charge over the S-N-S core as well as the presence of the electron-withdrawing trifluoromethyl groups.

![Scheme 2.3: Chemical structure of the bis(trifluoromethanesulfonyl)imide anion](image)

Anion fluorination was studied by Pringle et al. who reported the synthesis of a range of novel ionic liquids based on the bis(methanesulfonyl)imide anion [40]. It was shown that the resulting material exhibited an increase in both glass transition temperature and viscosity when compared to the fluorinated analogue. That was due to an increase in hydrogen bonding which in turn, produced a significant drop in ionic conductivity.

Ionic liquids are usually composed of a combination of anions and organic cations, such as imidazolium, pyridinium, pyrrolidinium, ammonium, sulfonium and phosphonium derivatives [41-43]. Overall, the use of different anions has a more
dramatic and wide-ranging effect on the physical and chemical properties of ionic liquids than does a variation in the cation [36].

Transport Phenomena Studies on Ionic Melts and Single-Ion Conducting Systems

In any system consisting of one or more ionic species, mass fluxes are always present as a result of concentration gradients imposed either by diffusion or convection. In the case of a dilute solution, the mass flux of some ionic species \(i\), \(j_i\), is given by

\[
\Phi \nabla - \nabla - = D_i \nabla c_i - z_i F c_i \mu_i \nabla \Phi
\]  

(2)

where \(D_i\) - diffusion coefficient of species \(i\) (cm\(^2\)/sec), \(c_i\) - concentration of charged species \(i\) (mol/cm\(^3\)), \(F\) - Faraday’s constant (96,487 C/equivalent), \(z_i\) - charge of ionic species \(i\), \(\mu_i\) - mobility of ionic species \(i\) (cm\(^2\)/V·sec), \(\nabla \Phi\) - potential gradient (V/cm).

and the current density \(i\) is given by

\[
i = -F \sum z_i \nabla c_i D_i - F^2 \sum z_i^2 c_i \mu_i \nabla \Phi
\]

(3)

As mentioned earlier in the chapter, concentration polarization is often encountered upon the passage of current through an electrochemical cell; one of the mobile species is discharged at the electrodes and a concentration gradient occurs. Let’s consider a system consisting of a binary, unsupported electrolyte between electrodes which are reversible only with respect to the cation. The cell is initially at equilibrium, i.e. no net currents are passing. At very short times, after the imposition of a potential difference, the concentrations of all species in the bulk of the electrolyte are uniform and
the ions move in response to the applied electrical field. The current $i$ is determined by the uniform electrolyte conductivity as:

$$i = -F^2 \sum c_i z_i^2 u_i \frac{d\Phi}{dx}$$  \hspace{1cm} (4)

At long times, on the other hand, the flux of the blocked anion falls to zero and a constant flux of cations passes through the system as shown in Equation 5:

$$j_+ = -c_+ u_+ RT \frac{d\log c}{dx} - c_+ u_+ F \frac{d\Phi}{dx}$$ \hspace{1cm} (5)

Such gradients along with gradients in conductivity, due to variations in salt concentration, contribute to the decrease in the overall potential difference. So, at large potentials, there will be a limiting current density $i_L$, at which point the salt concentration at one of the electrodes has fallen to zero. For example, in a polymer electrolyte, with plane parallel electrodes and a uniform concentration of $c^*$ the limiting current density will be

$$i_L = \frac{4c^* D \gamma F}{l}$$ \hspace{1cm} (6)

where $l$ (cm) is the thickness of the electrolyte.

Therefore, in a system of this kind having more than one mobile ionic species, there is additional impedance, going from high to low frequency, due to salt concentration polarization. In a single-ion conducting system, the passage of electric current does not lead to a concentration gradient and so the steady state current density is [44]:

$$i = -F^2 \sum c_i z_i^2 u_i \nabla \Phi$$ \hspace{1cm} (7)
Ionic Liquids for High Power/High Rate Secondary Lithium Batteries

The use of ionic liquids as electrolytes in lithium ion batteries capable of delivering high power and high currents have attracted the attention of many researchers. Their desirable properties of safety, non-flammability and non-volatility are especially well mattered for hybrid vehicle applications. For this and other applications, these materials have to possess wide electrochemical windows in order to avoid any oxidative or reductive reactions at the anode or the cathode, and they need to have low viscosities. Low viscosity materials allow for better lithium ion transport needed to achieve high charge/discharge rates [10, 45]. For instance, it has been shown that ionic liquids based on aliphatic quaternary ammonium cation such as trimethylpropylammonium or pyrrolidinium cation coupled with the TFSI anion exhibit wide electrochemical windows [46-49]. However, the high viscosity of these materials causes very poor high rate charge/discharge cycles. Tuning the anionic moiety decreases the viscosity. It has been shown that using the bis(fluorosulfonyl)imide (FSI) anion provides low-viscosity ionic liquids [50]. Indeed, the 1-ethyl-3-methylimidazolium (EMI) coupled with the FSI anion provides a room-temperature ionic conductivity of 15.4 mS/cm with a viscosity value of 18 mPa·s. The same cation coupled with the TFSI anion gives an ionic liquid with a viscosity of 33 mPa·s. and a room-temperature ionic conductivity of 8.3 mS/cm [51]. The addition of the lithium salt to the ionic liquids increased the viscosity by 20-25 %; this was unavoidable as the lithium salt was needed in the battery electrolyte. The FSI based ionic liquids proved to retain higher capacities at high discharge rates than the TFSI based ionic liquids. However, the FSI based ionic liquids have slightly reduced
anodic and cathodic stabilities when used with lithium anode and LiCoO₂ cathode [51]. Also, we should mention the high sensitivity of FSI anion in contact with humidity which precludes from start a large-scale applicability for it.

Ionic liquids have also been used as polymer electrolyte systems where the ionic liquids play the role of both a charge carrier and a non-volatile plasticizer [52-54]. In addition, polyelectrolyte-ionic liquid systems were also developed [55]. Both of these classes of materials allow the mobility of the lithium ion alone; a feature that is essential in high rate charge/discharge cycling.
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CHAPTER THREE
EXPERIMENTAL ANALYSIS OF THE ELECTROLYTES

Introduction

All the materials (electrolytes and electrodes) that will be discussed in the following chapters were characterized using the same analytical techniques. $^1$H, $^7$Li and $^{19}$F NMR spectroscopy was used both to monitor the reactions that were performed to obtain the new electrolytes and to determine their structure and assess their purity. Differential scanning calorimetry (DSC) experiments were performed to determine the glass transition temperature ($T_g$) and the melting/crystallization temperatures ($T_m/T_c$) of the new electrolytes. Electrochemical impedance spectroscopy (EIS) was used to measure their impedance from which the ionic conductivity was later calculated. Galvanostatic DC-polarization experiments (constant current mode) were carried out to give an understanding on whether the materials undergo salt concentration polarization under the imposition of a constant current. In addition, rheological experiments were performed to determine the viscosity of the electrolytes since viscosity plays a major role in ionic conduction. Finally, the new electrolytes were tested in a battery testing equipment using a two-electrode cell Swagelok-style configuration. In this chapter, each of the techniques will be introduced along with sample preparation and experimental procedure used with each technique.
1H, 7Li and 19F NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was the technique used for structural determination. Since the ionic melts contain both proton and fluorine elements, 1H and 19F NMR spectra were acquired from each sample. Both spectra give an indication about the progress of the reaction as well as the purity of the product. 1H and 19F NMR spectra were recorded at ambient temperature on a JEOL NMR spectrometer of frequency 300 MHz for 1H NMR and for 282.8 MHz 19F NMR. CD3CN was the deuterated solvent used for all sample analyses. Chemical shifts were reported at δ (ppm); upfield shift was indicated by a negative chemical shift and downfield shift was indicated by a positive chemical shift. Values for H-to-F ratios were calculated using an internal standard, α,α’,α” - trifluorotoluene, which provided distinct fluorine and proton signals at δ of -60.3 and 7.6 ppm, respectively. Calculations to determine the EO:Li ratio using the internal standard, obtained from the H to F ratio, will be discussed in a later chapter. Also, 7Li NMR spectra were acquired for all new electrolytes using an internal standard (LiTFSI in CD3CN) proving quantitatively the Li content of these ionic melts. The internal standard was kept inside a sealed glass tube that was placed inside the NMR tube along with the sample for analysis. From peak integration, the fluorine atoms for the LiTFSI can be assigned and their ratio to those in the ionic melt electrolyte can be calculated.
**Differential Scanning Calorimetry**

The glass transition temperature, $T_g$, is a critical parameter that impacts the ionic conductivity of the electrolytes. DSC measurements were performed using a Mettler-Toledo 820 differential scanning calorimeter. The samples were sealed in aluminum pans and scanned from -100 to 100 °C at a rate of 10 °C/min.

**Electrochemical Impedence Spectroscopy (EIS)**

In one implementation of this technique, a voltage signal $v(t) = V_m \sin(\omega t)$, involving the single frequency $\nu = \omega/2\pi$, is applied to a cell and the resulting steady-state current $i(t) = I_m \sin(\omega t + \theta)$ is measured. The term $\theta$ is the phase difference between the voltage and the current and is zero for purely resistive behavior. The frequency domain voltage/current relations can be rearranged to a form similar to Ohm’s law for dc current as shown in Equation 8,

$$I(\omega) = \frac{V(\omega)}{Z(\omega)}$$  \hspace{1cm} (8)

where for capacitance the complex quantity $Z(\omega)$ is $1/(C \cdot \omega)$ and for inductance $Z(\omega)$ is $L \cdot \omega$. $Z(\omega)$ is defined as the impedance function and its value at a particular frequency is the impedance of the electric circuit [1]. The capacitive element is given as

$$i(t) = \left[\frac{dv(t)}{dt}\right]C$$  \hspace{1cm} (9)

and the inductive element is

$$v(t) = \left[\frac{di(t)}{dt}\right]L$$  \hspace{1cm} (10)
EIS is an ac electrochemical technique where the cell or electrode impedance ($Z$) is measured as a function the frequency ($f$) of the applied voltage. In general, an electrochemical cell can be represented by an equivalent electrical network of resistors and capacitors that pass current with the same amplitude and phase angle that the real cell does under a given current excitation. One such equivalent electrical circuit is called the Randles equivalent circuit and an example is shown in Figure 3.1. The circuit comprises a resistor ($R_s$ which is the electrolyte resistance) in series with a parallel combination of a capacitor ($C_{dl}$ which is the double-layer capacitance), with a resistor ($R_{ct}$ which is the charge-transfer resistance) and an impedance ($Z_w$ which is the Warburg impedance representing the resistance due to mass transfer) [2].

![Randles equivalent circuit](image)

Figure 3.1: Randles equivalent circuit for an electrochemical cell having a resistor in series with a parallel combination of a capacitor with a resistor

In EIS, the impedance of the cell is measured in terms of a resistance value ($Z_{Re}$) which is the real component of the impedance) and a capacitance value ($Z_{Im} = 1/\omega C_B$ which is the imaginary component of the impedance). In other words, the total impedance $Z$ can be expressed as shown in Equation 11. As $Z$ varies with frequency, one
can extract $R_s$, $R_{ct}$ and $C_{dl}$ as shown in Figure 3.2. The figure also shows the regions of mass-transfer and kinetic control. Within the low frequency limit, the electrode process is diffusion controlled and thus the frequency dependence in this regime comes only from $Z_w$. At very high frequencies however, $Z_w$ becomes unimportant; $R_s$, $R_{ct}$ and $C_{dl}$ become the dominant elements.

$$ Z = R_B - j/(\omega \cdot C_B) = Z_{Re} - j \cdot Z_{Im} $$  \hspace{1cm} (11)

where $\omega$ is the angular frequency.

Figure 3.2: Impedence plot for an electrochemical system. From the plot, information about $R_s$, $R_{ct}$ and $C_{dl}$ can be obtained [2].

Ionic conductivity measurements for the ionic melts that will be discussed in the next chapters were made using EIS. It should be noted that the electronic conductivity of the ionic melts is very low and does not contribute to the overall conductivity. Earlier
experiments on SPEs proved this kind of behavior. Rapid current drop was observed during a dc conductivity measurement with ion-blocking electrodes and that was a proof that the conductivity is primarily ionic [3]. The temperature-dependant ionic conductivities were measured using stainless-steel blocking electrodes, i.e. no charge transfer occurs and only the double-layer capacitance plays role. The equivalent circuit for the blocking electrodes EIS technique is shown in Figure 3.3. It represents two capacitors, $C_{dl}$, in series with the electrolyte resistance, $R_s$, all parallel to the geometric cell capacitance $C_{Geometric \ cell}$.

Figure 3.3: Equivalent circuit of the blocking electrodes EIS technique.

The experimental setup for the blocking electrodes EIS is shown in Figure 3.4. The electrochemical cell consists of two cylindrical stainless-steel electrodes, the ionic melt electrolyte and a Kynar O-ring spacer. The ionic melt was sandwiched between the two stainless-steel electrodes and its thickness was maintained constant by using a Kynar O-ring spacer (230 μm in thickness and 5 mm inner diameter). The electrodes were then inserted into an annular PTFE ring to enforce coaxial cell geometry. A heating tape was wrapped around an aluminum frame containing the annular ring along with the
electrodes. To ensure constant compression between the electrodes, the same force was applied on the top electrode by using a compression screw tightened with an adjustable torque wrench. The temperature of the bottom electrode was monitored using a thermocouple that was connected to a temperature controller. The end of the thermocouple wire was fixed in a small hole in the electrode by means of a non-conductive epoxy glue. The entire assembly was placed in an enclosed glass vessel. Each electrode was connected through a low-impedance cable to a Solartron model SI 1287 electrochemical interface coupled to a Solartron model 1260 frequency response analyzer.

Figure 3.4: Experimental setup for impedance measurements: 1 – glass cell, 2 – glove bag, 3 – electrochemical interface, 4 – impedance gain/phase analyzer, 5 – oscilloscope, 6 – computer, 7 – digital thermometer, 8 – temperature controller, 9 – variac.

Impedance spectra were acquired over a frequency range of 1–10^6 Hz. As a general procedure, each sample was first heated to 120 °C and then slowly cooled to
room temperature, and impedance spectra were recorded on the cooling curve in discrete steps every 10 °C until room temperature was reached. The resistance of the ionic melt was obtained from the complex-plane impedance plot [4-6]. Ionic conductivity values (κ, in units of S cm\(^{-1}\)) were obtained by correcting the membrane resistance for geometric effects using the apparent electrode area and the electrolyte’s thickness according to the following equation,

\[
\kappa = \left(\frac{1}{R_s}\right) \times \left(\delta / A\right)
\]

(12)

where \( R_s \) - the electrolyte’s resistance (Ω),
\( \delta \) - the electrolyte’s thickness (cm),
\( A \) – the contact area of the electrode (cm\(^2\)).

Ionic conductivity (κ) is temperature dependent and whenever the conductivity increases approximately exponentially with increasing temperature, an Arrhenius-type conductivity behavior can be expressed as shown in Equation 13. Ionic conductivity data are usually represented as Arrhenius plots in a logarithmic scale of log \( \kappa \) (S cm\(^{-1}\)) versus 1000/[T (K)].

\[
\kappa = \kappa_0 e^{-\frac{E_a}{kT}}
\]

(13)

where \( \kappa_0 \) - the pre-exponential factor (S/cm),
\( E_a \) – the activation energy (kJ/mol),
\( k \) – the Boltzman constant (J/K),
\( T \) – the absolute temperature (K).
DC-Galvanostatic Polarization

DC Galvanostatic polarization experiments infer whether the material allows any salt concentration polarization within the electrochemical cell. DC-galvanostatic polarization is a constant current mode experiment. A small dc current is imposed onto a symmetric electrochemical cell of the following configuration: Li/electrolyte/Li. The equivalent electrical circuit of this cell is shown in Figure 3.5. The figure is similar to that of 3.3 except that in this case the technique is using non-blocking electrodes which means that there are faradaic processes of charge-transfer and mass-transfer. Cell assembly was done using a swage type Teflon body having a Teflon spacer to ensure constant thickness and avoid any short or open circuits. The experiment was performed at room temperature.

Figure 3.5: Equivalent circuit of the symmetric electrochemical cell Li/electrolyte/Li.

Charge-Discharge Cell Testing

Swage-type cells were designed for the purpose of cell testing using an Arbin BT2000 device. The design of the stainless steel Alloy 20 current collectors is shown in
The liquid-type electrolyte was wetted/soaked in a Celgard separator of grade 2320 to avoid any leakage and shorts during the charge-discharge tests. The experiments that were performed on the tester included specific capacity, energy and power tests.

Each cell that was built has to be initially formed in case graphite or Li$_4$Ti$_5$O$_1$$_2$ is used as the anode. Cell formation involved galvanostatically charging the cell at a rate of C/100 until the voltage reaches 4.2 V (constant current or CC charging). Constant voltage (CV) charging was then applied until the current reached C/75 or C/100 to minimize non-faradaic power losses by battery leakage. This CV mode allowed for a complete lithium intercalation into the graphite. Three discharge/charge cycles were then applied to allow the cell to reach to the reversible capacity. It should be noted that the C-rates were calculated based on the theoretical capacity of the cathode material which acts as the limiting factor. For example, the theoretical capacity for LiCoO$_2$ is 150mA·h/g and for LiFePO$_4$ is 170mA·h/g. The weight of the active material used to make the cathode was measured and from this value the C-rate was calculated.

The capacity of the cell was always measured in terms of A·h and it defines the amount of charge that can be shuttled from one electrode to the other over a period of time. There are two types of capacities: charge capacity and discharge capacity. Each can be measured by applying either a charging current or a discharging current. There are always irreversible capacity losses associated with a lithium-ion cell which are caused in part by the irreversible formation of the SEI layer at the anode. From the charge/discharge cycles, the energy of the cell can be calculated at the end of the cycle; the cell energy is the product of the capacity and the cell voltage. The power tests were
performed in a pulse mode under high discharge rates. Each pulse lasted for 10 seconds, an average for the voltage at the depth of discharge could be calculated; the power is the product of that average voltage by the current applied.

Figure 3.6: (Left) Stainless steel alloy 20 with a 0.5” diameter used as the current collector for the negative electrode. (Right) Stainless steel alloy 20 current collector for the positive electrode having a diameter of 0.375”.

Rheology

ARES-LS type rheometer from Rheometric Scientific was used for the rheological studies. A cone-and-plate geometry was used by where a circular plate and a linearly concentric cone are rotated relative to each other. The cone-and-plate geometry produces a flow in which the shear rate is very nearly uniform [7]. The melt electrolyte was placed in the gap between the plate and the cone under nitrogen atmosphere in order to avoid any moisture interference. For determining the viscosity as a function of shear rate or shear stress, steady-shear experiments were performed at room temperature. The
shear viscosity can be calculated by dividing the shear stress by the shear rate [8]. The shear rate applied was in the range of 0.01-100 s\(^{-1}\). It should be noted that the shear rate can be used synonymously with rate of strain or velocity gradient. Also, dynamic rheology measurements were acquired at room temperature. From dynamic rheology, the elastic (storage) modulus \(G'\) (Pa) and the viscous (loss) modulus \(G''\) (Pa) can be obtained as functions of the oscillation frequency \(\omega\) (rad/s). Oscillatory shear experiments are done by imposing a low-amplitude sinusoidal deformation \(\gamma\) at a fixed frequency \(\omega\) and a maximum strain \(\gamma_0\) as indicated in Equation 14:

\[
\gamma = \gamma_0 \sin \omega t
\]  
(14)

The stress resulting from the oscillatory shear is dependent on the elastic and viscous moduli in a sinusoidal fashion according to Equation 15:

\[
\tau = G' \gamma_0 \sin \omega t + G'' \gamma_0 \cos \omega t
\]  
(15)
References


CHAPTER FOUR
MONO-FUNCTIONALIZED LITHIUM-CONDUCTING IONIC MELT ELECTROLYTES

Introduction

One of the limiting factors for high-power performance of lithium ion batteries is salt concentration polarization where, upon discharge, the current decays due to the developing concentration gradients within the cell [1-3]. Upon discharge, the lithium ions are depleted at the cathode and the anions move towards the anode and accumulate there. This might not be a major problem under low rate discharge especially if the electrolyte has high ionic conductivity where relaxation due to diffusion can occur within a reasonable period of time. However, at high discharge rates which are needed for high power, voltage losses are more acute because the salt diffusion is not large enough to prevent concentration polarization [4].

One commonly-used approach to preventing salt concentration polarization in lithium electrolytes is to immobilize the anions, for example by attaching them to a polymer scaffold [5-18]. This approach works insofar as it does prevent salt concentration polarization. Unfortunately the overall ionic conductivity of these lithium-based single-ion-conductor polymer electrolytes tends to be low, due to a combination of anions no longer contributing to the conductivity, cations becoming electrostatically trapped near anions, and the overall matrix having a relatively high viscosity which disfavors rapid ion transport. In addition, it can be difficult to establish good interfacial
contact between polymeric electrolytes and battery electrodes, which are often porous and require liquid-like penetration of the electrolyte into the electrode to function well. These factors are largely responsible for the fact that lithium-conducting polymer electrolytes are not widely used in lithium battery technology.

Another approach to preventing salt concentration polarization is to eliminate the solvent, so that the electrolyte consists of nothing but salt. If the electrolyte remains liquid after all solvent is removed at ambient temperature, then it is referred to as an ambient temperature ionic liquid. There has been much work recently involving study of lithium salts in ionic liquids for possible use in lithium battery technology [19-22]. In most cases the overall electrolyte consists of a lithium salt mixed into an ionic liquid that is comprised principally of other anions and cations. In such a case the ionic liquid behaves as a solvent, and it is still possible to form concentration gradients of the lithium salt within the ionic liquid. All of the problems described above for concentration-polarized electrolytes can still be present, and there is little gain beyond the fact of having eliminated the potentially volatile and/or reactive solvent. For such an approach to work for preventing salt concentration polarization, the ionic liquid electrolyte must contain no potentially mobile cations other than lithium.

This chapter discusses a class ionic melts that consist of lithium (perfluorovinylether)sulfonimide and (perfluorovinylether)sulfonate salts covalently attached to a lithium-solvating polyether chain of variable chain length having an end-capped methyl group. Structures of the target electrolytes are illustrated in Figure 4.1 and also in Table 4.1. Related electrolytes have been previously described in which other
anion groups, mostly carboxylates, sulfonates or sulfonamides, are attached to polyether chain ends, mostly of difunctional oligomers [23-26], but studies combining polyether oligomers and (perfluorovinylether)sulfonimide salts were not reported. The synthesis and characterization of the electrolytes, with special focus on their chemical structure and purity will be discussed along with their ion transport properties and galvanostatic DC polarization data.

Figure 4.1: Structure and synthesis of the target lithium fluorosulfonimide ionic melt electrolyte.
Table 4.1: Abbreviations, chemical formulas and EO:Li ratios for ionic melts synthesized in this work

<table>
<thead>
<tr>
<th>Shorthand</th>
<th>Chemical Formula</th>
<th>EO:Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM350</td>
<td>CH₃O-(CH₂CH₂O)₇.2-CF₂CFHOCF₂CF₂SO₂N(Li)SO₂CF₃</td>
<td>7.2</td>
</tr>
<tr>
<td>IM550</td>
<td>CH₃O-(CH₂CH₂O)₁₁.8-CF₂CFHOCF₂CF₂SO₂N(Li)SO₂CF₃</td>
<td>11.8</td>
</tr>
<tr>
<td>IM750</td>
<td>CH₃O-(CH₂CH₂O)₁₆.₃-CF₂CFHOCF₂CF₂SO₂N(Li)SO₂CF₃</td>
<td>16.3</td>
</tr>
</tbody>
</table>

Experimental

Materials. The starting material, perfluorinated fluorosulfonylethylvinyl ether (CF₂=CFO-CF₂CF₂SO₂F), was donated by the Dow Chemical Company and was kept refrigerated prior to use. Polyethylene glycol monomethylether (PEGME) oligomers of different molecular weights (PEGME, \( M_w = 350, 550, 750 \) Da) and polyethylene glycol dimethylether (PEGDME, \( M_w = 500 \)) were purchased from Aldrich and dried under dynamic vacuum at ambient temperature before use. Lithium bis[(trifluoromethyl)sulfonylimide salt (LiTFSI) was purchased from 3M Company; lithium hydroxide monohydrate (LiOH·H₂O, 98%), sodium hydride (NaH, 95%) and \( \alpha,\alpha,\alpha,- \) trifluorotoluene were all purchased from Aldrich and stored in an argon-filled dry box prior to use except for the trifluorotoluene which was kept outside in a chemical cabinet. All salts used were dried at ambient temperature under dynamic vacuum for at least 12 hours before use. All reagents were handled in a glove bag under a constant flow of purified argon. Acetonitrile (ACN), HPLC grade, was purified by overnight storage.
over calcium hydride followed by distillation over phosphorus pentoxide (P₄O₁₀) prior to use.

*Synthesis of lithium perfluorinated vinyl[(ethylene)(methyl)disulfonyl]imide ether having the structure CF₂=CFO-CF₂CF₂SO₂N(Li)SO₂CF₃.* Scheme 4.2 describes the synthesis of the new lithium perfluorovinylether (PFVE)-derived fluorosulfonimide salt that was subsequently used in reactions with polyether oligomers to prepare the target ionic melts. In brief, the synthesis involved reaction of a perfluorinated fluorosulfonylethylvinyl ether, for which the vinyl group was protected by bromination (structure BrCF₂CFBrO-CF₂CF₂SO₂F), with a trimethylsilyl-activated trifluoromethylsulfonamide (structure CF₃SO₂N(Li)Si(CH₃)₃). CF₃SO₂N(Li)Si(CH₃)₃ was prepared as was reported by Dr. DesMarteau [27] and as shown in Scheme 4.1. CF₂=CFO-CF₂CF₂SO₂F was brominated with elemental bromine to generate BrCF₂CFBrO-CF₂CF₂SO₂F. The yield of BrCF₂CFBrO-CF₂CF₂SO₂F is 98%. ¹⁹F NMR spectra show the following resonances for the product: δ(ppm, center of multiplet): -63.7 (BrCF₂, dd, J=3.2), -72.1 (CFBr, m), -82.3 (OCF₂, dd, J=116.9), -112.7 (CF₂CF₂, s), 45.5 (SO₂F, s).

![Scheme 4.1: Synthesis of trimethylsilyl-activated trifluoromethylsulfonamide.](image)
Scheme 4.2: Lithium (perfluorovinylether)sulfonimide salt preparation

The reaction combining BrCF2CFBrO-CF2CF2SO2F and CF3SO2N(Li)Si(CH3)3 was accomplished by heating in dry ACN. The product was collected by evaporating the solvent and subsequently debrominated with activated Zn metal by heating in dry ACN up to 80°C for 4 hours to form the desired PFVE lithium salt. The resulting white solid was dried at 50°C under dynamic vacuum (0.02 torr) overnight. The yield of recovered material was 92% based on CF3SO2N(Li)Si(CH3)3. $^{19}$F NMR spectra show the following resonances for the product: $\delta$(ppm, center of multiplet): -80 (SO$_2$CF$_3$, s), -83.4 (OCF$_2$, t, J=6Hz), -114 (CF$_2$CF, dd, vinylic, J=64), -117 (CF$_2$SO$_2$, s), -122 (CF$_2$CF, dd, vinylic, J=6), -134 (CF$_2$CF, dd, vinylic, J=6).
Synthesis of ionic melts of general structure \( \text{CH}_3-(\text{OCH}_2\text{CH}_2)_n-\text{O-CF}_2\text{CFH-O-CF}_2\text{CF}_2\text{SO}_2\text{N(Li)SO}_2\text{CF}_3 \). The experimental procedure described below is representative of the method used to synthesize ionic melts corresponding to structures IM350, IM550, and IM750 in Table 4.1, from the lithium (perfluorovinylether)sulfonimide salt and the corresponding poly(ethylene glycol) monomethyl ether. A quantity of NaH (0.0018 mole) was suspended in 15 mL dry ACN in a 50 mL round-bottom flask. A quantity of monomethylated polyether oligomer (0.0018 mole) dissolved in 10 mL of dry ACN was added drop-wise to the suspension. The mixture was stirred with a magnetic stir bar under a dry \( \text{N}_2 \) atmosphere at room temperature for 12 hours. A clear slightly yellowish solution resulted that was injected through a syringe filter (Whatman PVDF, 0.45 \( \mu \text{m} \)) into a solution of lithium (perfluorovinylether)sulfonimide salt (0.0018 mole in 15 mL of dry ACN) under a dry \( \text{N}_2 \) atmosphere. The mixture was stirred at 0 °C and reaction progress was monitored by \( ^{19}\text{F} \) NMR (disappearance of vinylic fluorine signals at -134, -122 and -114 ppm). After the \( ^{19}\text{F} \) NMR showed that all vinylic fluorines had been transformed (which typically took ~5 hours), the mixture was quenched with 1 mL of deionized (DI) water. Solvent (including water) was removed by rotary evaporation at 40 °C under reduced pressure, and the resulting yellowish viscous liquid was dried for 4 hours at 60 °C under dynamic vacuum (0.02 torr) for 4 hours. The resulting material was re-dissolved in dry ACN and the solution was filtered through a syringe filter (Whatman PVDF, 0.45 \( \mu \text{m} \)) to remove the solid NaOH. The product was acidified by stirring it at ambient temperature with concentrated \( \text{H}_2\text{SO}_4 \) (80 %) overnight, followed by extraction of the product by \( \text{CH}_2\text{Cl}_2 \). The solvent was then evaporated and the resulting material
was lithiated with excess LiOH·H₂O in DI water. Water was evaporated to give a yellow viscous liquid, which was further dried overnight at 60°C under dynamic vacuum (0.02 torr). Isolated amounts and yields, calculated assuming that the lithium (perfluorovinylether)sulfonimide salt was the limiting reagent, were as follows: IM₃₅₀, 1.41 g (92%); IM₅₅₀, 1.83 g (95%); IM₇₅₀, 2.20 g (95%). Figure 4.2A shows the \(^1\)H NMR spectrum of IM₅₅₀ \(\text{CH}_3-(\text{OC}_2\text{H}_2\text{C}_6\text{H}_2)_{10.8}-\text{OC}_2\text{H}_2\text{C}_6\text{H}_2-\text{O}-\text{CF}_2\text{CF}_2\text{HO}-\text{CF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3\) with the following resonances, \(\delta\) (ppm, center of multiplet):

- 6.29, 6.11 (d, d-t, \(J=54\text{Hz}, 3.1\text{Hz}\) CHF), 4.10 (c, br triplet, CH₂OCF₂), 3.60 (b, br m, (CH₂CH₂O)ₙ), 3.29 (a, s, OCH₃).

Figure 4.2B shows the \(^1\)F NMR spectrum of IM₅₅₀ \(\text{CH}_3-(\text{OCH}_2\text{CH}_2)_{10.8}-\text{OCH}_2\text{CH}_2-\text{O}-\text{CF}_2\text{CF}_2\text{OF}_2\text{C}^\text{F}_2\text{C}^\text{F}_2\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{C}^\text{F}_3\) shows the following resonances, \(\delta\) (ppm, center of multiplet):

- -83.0 (h, dd, \(J=146.5\)), -89.4 (f, m), -116.9 (i, s), -143.8 (g, m), -80.1 (j, s).

*Synthesis of lithium perfluorinated vinyl[(ethylene)]sulfonate ether having the structure CF₂=CFO-CF₂CF₂SO₃Li.* In an Ar purged glove bag, a quantity of CF₂=CFO-CF₂CF₂SO₂F (0.01 mol) was added drop-wise to a suspension of LiOH.H₂O (0.02mol) in 20 mL of dry ACN in a 50 mL round-bottom flask. The reaction mixture was stirred with a magnetic stir bar at room temperature overnight. Reaction completion was confirmed by the complete disappearance of the \(^1\)F NMR peak at 46 ppm for –SO₂F. The cloudy colorless solution was filtered to remove LiF, and the solvent was evaporated under reduced pressure at 40 °C. The resulting white solid was dried at 50 °C under dynamic vacuum at 0.02 torr. The solid was redissolved in dry ACN to precipitate the last traces of LiF. The solution was filtered through a syringe filter (Whatman PVDF, 0.45μm) and the
solvent again evaporated at 40 °C under reduced pressure. The resulting white solid was
dried at 50 °C under dynamic vacuum (0.02 torr) overnight. Yield was quantitative. $^{19}$F
NMR spectrum for the final product shows: δ(ppm, center of multiplet) -83.4 (t, OCF$_2$CF$_2$SO$_3$Li), -114 (dd, vinylic, J=64Hz), -117 (s,CF$_2$SO$_3$Li), -122 (ddt, vinylic, J=6Hz), -134 (ddt, vinylic, J=6).

*Synthesis of ionic melts of general structure CH$_3$-(OCH$_2$CH$_2$)$_n$-O-CF$_2$CFH-O-CF$_2$CF$_2$SO$_3$Li.* The synthesis of the sulfonate ionic melt electrolytes was done similarly to that of the imide melts but using CF$_2$=CFO-CF$_2$CF$_2$SO$_3$Li as the starting material.

*Preparation of LiTFSI-in-PEGDME electrolyte.* A quantity of PEGDME (0.002 mole) was weighed into a tared round-bottom flask. A quantity of solid LiTFSI (0.002 mole) was weighed and added to the flask. 20 mL of dry ACN was added to the mixture and was stirred at room temperature for 24 hours. The ACN was evaporated and the resulting viscous liquid dried under dynamic vacuum. A $^1$H NMR spectrum was acquired to confirm the absence of residual solvent.

*Liquid chromatographic (LC) and mass spectrometric (MS) analyses:* The purity of ionic melt electrolytes was established by LC and MS analyses. The LC analyses were performed using a Waters model 1525 HPLC fitted with a 4.5 mm diameter 150 mm long Symmetry® C18 column with 5μm particle size, and a Waters model 2487 dual wavelength UV absorption detector operated at 280 nm. Mobile phase was 90 % acetonitrile (HPLC grade) / 10% methanol (analytical-reagent grade) containing 0.1 % ammonium acetate/acetic acid, pH = 4.0. Elution was isocratic at 1 mL/min flow rate. Mass spectrometric analyses were accomplished by direct injection of samples into a
flowing stream of mobile phase, same as above, which entered an electrospray ionization source, from which time-of-flight mass spectra were acquired using a Micromass model Q-TOF Micro™ mass spectrometer.

*Electrochemical Impedance Spectroscopy.* Ionic conductivity measurements were made as described in chapter 3 using a Solartron model SI 1287 electrochemical interface coupled to a Solartron model 1260 frequency response analyzer [28]. The resistance of the electrolyte layer, that is sandwiched between two blocking stainless-steel electrodes held apart at a fixed distance by an annular ring spacer made of kynar, was obtained from the Nyquist complex-plane impedance plot [29-31].

*DC polarization.* The symmetric cell included a Swage-type Teflon body with two stainless-steel cylindrical current collectors of 0.5” in diameter. Lithium foil was used as the electrode on both current collectors and the space in between them was held constant using a Teflon O-ring. In a typical experiment, a square-wave current function was applied for 6.5 hours and the cell potential was monitored with respect to time. The description of one cycle is as follows. Zero current was initially applied for 0.5 hour, then the current was increased to 10 μA for 1 hour, then again zero current was applied for 0.5 hour, after which -10 μA was applied for 1 hour. A cycle of 50 μA current magnitude was applied.

**Results and Discussion**

*Synthesis and characterization.* Ionic melt syntheses were accomplished by the following sequence of reaction steps: (i) deprotonation of terminal hydroxyl group of a
PEGME oligomer to yield the corresponding sodium alkoxide salt; (ii) nucleophilic attack of the alkoxide anion on the terminal olefinic carbon of the lithium (perfluorovinylether)sulfonimide salt to yield the coupled product as a carbanion; and (iii) protonation of the carbanion with water to generate the target ionic melt electrolyte mixed with NaOH. Subsequent purification steps removed the NaOH to produce pure ionic melt electrolyte in lithium form.

The data in Figures 4.2 – 4.5 confirm that the ionic melt electrolytes synthesized as described above have the indicated structures and are highly pure. Figure 4.2 presents $^1$H and $^{19}$F NMR spectra of IM550 as a representative ionic melt electrolyte. Peak assignments given in the figure caption are fully consistent with the structure in Figure 4.1. The absence of resonances in the $^{19}$F NMR spectrum near -134, -122 and -114 ppm indicates that all trifluorovinylether reactant has been consumed, and the absence of any unassigned resonances in either spectrum strongly suggests that the indicated compound is the only product present. Of particular note is doublet d at resonances of 5.9 and 6.2 ppm in the $^1$H NMR spectrum, which appears only in the final product. The doublet character of this resonance is due to the $^2$J$_{HF}$ coupling. The chirality of the carbon attached to that proton is seen in the $^{19}$F NMR spectra in peak h that displays an ABA’B’ pattern typical of a diastereomeric system.
Figure 4.2: (A) $^1$H NMR spectra and (B) $^{19}$F NMR spectra for IM550 ionic melt electrolyte. Peak assignments are as follows: $^{a}$H$_2$O-$(^{b}$H$_2$C$^{b}$H$^{b}$O)$_{10.8}$-$^{b}$H$_2$C$^{c}$H$^{c}$O-$^{c}$F$_2$C$^{d}$F$_2$HO$^{e}$F$_2$C$^{f}$F$_2$SO$_2$N(Li)SO$_2$C$^{g}$F$_3$. Peaks e and k correspond to the $^1$H and $^{19}$F NMR signals, respectively, of the internal standard $\alpha,\alpha,\alpha-$trifluorotoluene, $^{k}$F$_3$C$_6$H$_5$. 
A detailed analysis of the relative magnitudes of the $^1$H and $^{19}$F resonances can provide a value for the ethylene oxide oxygen-to-lithium (EO:Li) ratio of the target material. Such an analysis is simplified when a small amount of an internal standard containing both H and F is added to the sample, to provide an internal calibration of the relative sensitivities of $^1$H and $^{19}$F in the NMR measurement. We used $\alpha,\alpha,\alpha$-trifluorotoluene for this purpose, and resonances e and k in Figure 4.2 correspond to the proton and fluorine resonances, respectively, of this internal standard. With this knowledge in hand we may readily calculate EO:Li ratios using the following equation:

$$\frac{\text{EO}}{\text{Li}} = \frac{(A_b + A_c)}{4} \cdot \frac{10}{(A_f + A_g + A_h + A_l + A_j)} \cdot \left(\frac{A_k}{3} \cdot \frac{5}{A_e}\right) \quad (16)$$

This equation may be understood as follows: the quantity $(A_b + A_c)/4$ corresponds to the total proton signal per EO in the main polyether chain; the quantity $(A_f + A_g + A_h + A_l + A_j)/10$ corresponds to the total fluorine signal per fluorosulfonimide end group; and the quantity $(A_c/5)/(A_e/3)$ corresponds to the sensitivity ratio for one proton per one fluorine. Table 4.2 presents values for the EO:Li ratio calculated from $^1$H and $^{19}$F NMR spectra for the compounds IM350, IM550, and IM750 using this equation. They are in excellent agreement with expectations from the known molecular weights of the PEGME reactants, assuming that the resulting ionic melt products have the indicated structures.
Table 4.2: Integrated peak areas $^1$H and $^{19}$F NMR spectral data and calculated EO:Li ratios for ionic melt electrolytes

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>A_a</th>
<th>A_b</th>
<th>A_c</th>
<th>A_d</th>
<th>A_e</th>
<th>A_f</th>
<th>A_g</th>
<th>A_h</th>
<th>A_i</th>
<th>A_j</th>
<th>A_k</th>
<th>EO:Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM350</td>
<td>3.02</td>
<td>30.</td>
<td>2.2</td>
<td>1.1</td>
<td>18.</td>
<td>1.9</td>
<td>1.0</td>
<td>1.9</td>
<td>2.0</td>
<td>3.0</td>
<td>10.</td>
<td>7.55</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>876</td>
<td>84</td>
<td>0</td>
<td>985</td>
<td>02</td>
<td>00</td>
<td>18</td>
<td>18</td>
<td>65</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>IM550</td>
<td>3.00</td>
<td>46.</td>
<td>2.0</td>
<td>0.9</td>
<td>6.3</td>
<td>1.9</td>
<td>1.0</td>
<td>1.9</td>
<td>2.1</td>
<td>3.1</td>
<td>3.8</td>
<td>11.89</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>089</td>
<td>82</td>
<td>99</td>
<td>81</td>
<td>06</td>
<td>00</td>
<td>89</td>
<td>8</td>
<td>84</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>IM750</td>
<td>3.08</td>
<td>66.</td>
<td>2.0</td>
<td>1.0</td>
<td>30.</td>
<td>1.9</td>
<td>1.0</td>
<td>1.9</td>
<td>1.9</td>
<td>3.1</td>
<td>17.</td>
<td>16.47</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>05</td>
<td>56</td>
<td>03</td>
<td>074</td>
<td>09</td>
<td>00</td>
<td>62</td>
<td>27</td>
<td>63</td>
<td>534</td>
<td></td>
</tr>
</tbody>
</table>

In addition to the $^1$H and $^{19}$F NMR spectra, $^7$Li NMR spectra were acquired to ensure that Li is the only cationic species present in the electrolyte. It is undesirable to have other cationic species in the electrolyte, such as Na, since that will affect the polarization experiments that will be explained later and also will affect the overall cell capacity when this electrolyte is tested in a lithium-ion cell. The $^7$Li NMR spectrum of IM550 is shown in Figure 4.3 along with the $^{19}$F NMR spectrum of that same sample. Here, LiTFSI is used as the internal standard with a $^7$Li NMR signal at -2.5ppm and a $^{19}$F NMR signal at -80ppm. The signal at -80ppm from the $^{19}$FNMR spectrum shows an integration value of 15.7 corresponding to six F atoms from LiTFSI and three F atoms from IM550. The $^7$Li NMR spectrum shows an integration value of 2.4 for LiTFSI at a chemical shift of -2.5 ppm and 1 for IM550 at a chemical shift of -1.3 ppm. The integration ratio between F atoms and Li atom in the LiTFSI is calculated to be close to 6. This means that the purity of the ionic melt with respect to Li is 100%.
Figure 4.3: (A) $^7$Li NMR spectrum of IM550 and LiTFSI as an internal standard. (B) $^{19}$F NMR spectrum of IM550 and LiTFSI as an internal standard.
The purity of these ionic melt electrolytes is of great concern because even small amounts of non-ionic impurities, especially unreacted PEGME, could compromise the all-ionic character of the ionic melts, causing them to be more properly viewed as concentrated salt solutions than pure ionic melts. The NMR analysis above suggests that the materials are highly pure however a more definitive assessment of purity was required to ensure the absence of unreacted PEGME. The chromatographic data presented in Figure 4.4 provide such an assessment. Two chromatograms are presented, one for ionic melt IM550 (top) and another for the corresponding PEGME reactant (bottom). The PEGME exhibits a retention time between 31 and 32 minutes, whereas the IM550 exhibits a much longer retention time, between 51 and 52 minutes. The complete absence of any peak near 31-32 minutes in the top chromatogram confirms that unreacted PEGME is absent in this sample.
Figure 4.4: HPLC chromatograms for (top) ionic melt IM550; and (bottom) starting material PEGME550. The absence in the top chromatogram of a peak near 32 min retention time indicates that the sample is free of PEGME550 reactant as a nonionic impurity. The very small apparent peak at 32 min in the top chromatogram is too narrow to be a peak for unreacted polyether. It is believed to be a noise fluctuation in the detection signal.

Figure 4.5 presents a pair of electrospray time-of-flight mass spectra (TOF-MS), one corresponding to ionic melt electrolyte IM550 (top) and the other to PEGME reactant, that provide further confirmation of structure and purity of the ionic melt electrolytes. The top spectrum shows two principal peaks at m/z = 926 and 970, which almost certainly correspond to structures [\(\text{CH}_3\text{O(H)-(CH}_2\text{CH}_2\text{O)}_n\text{-CF}_2\text{CFHOCF}_2\text{CF}_2\text{SO}_2\text{N(H)SO}_2\text{CF}_3\)]\(^+\) where \(n = 11\) and 12 respectively. All of the other
principal peaks in this mass spectrum represent differences from the main peaks of m/z = 44 which corresponds to the repeating monomeric unit, ethylene oxide CH₂CH₂O. The peak intensity distribution reflects the polydispersity of the IM550 sample, which in turn reflects the polydispersity of the parent PEGME that was used to make it. The mass spectrum at the bottom of Figure 4 confirms that the polydisperse distribution of PEGME reactant closely matches with that of IM550. Significantly, the mass spectrum for IM550 is completely devoid of any peak at m/z = 561 which is the principal peak for PEGME. This fact provides further assurance of the high purity of this ionic melt electrolyte.
Figure 4.5: Time-of-flight electrospray-ionization mass spectra of (top) ionic melt sample IM550; and (bottom) starting material PEGME550. Peak at m/z=970 in the top spectrum corresponds to \([\text{CH}_3\text{O(H)-(CH}_2\text{CH}_2\text{O)}_{12-}\text{CF}_2\text{CFHOCF}_2\text{CF}_2\text{SO}_2\text{N(H)SO}_2\text{CF}_3]^+\) and that at m/z=561 in the bottom spectrum corresponds to \([\text{CH}_3\text{O(H)-(CH}_2\text{CH}_2\text{O)}_{12-}\text{H}]^+\). All other major peaks correspond to differences of m/z=44 (CH\(_2\)CH\(_2\)O) from these base masses. The absence of peaks in the ionic melt spectrum in the m/z range near 560 Da confirms the finding from HPLC that the sample is free of PEGME550 as a nonionic impurity.
**Elemental Analysis:** Elemental microanalysis of the sample IM550 was performed by Galbraith Laboratories. Calculated for C$_{30}$H$_{52}$F$_{10}$NO$_{18}$S$_{2}$Li: C, 36.40 %; H, 5.25 %; N, 1.14 %; F, 19.40 %. Found: C, 36.04 %; H, 5.31 %; N, 1.16 %; F, 19.30 %.

**Ion Transport.** Figure 4.6 presents Arrhenius plots of log(conductivity) vs. reciprocal absolute temperature for the three lithium-conducting ionic melt electrolytes studied in this work. For reference a plot is also shown for an electrolyte consisting of the binary salt LiTFSI dissolved in PEGDME of molecular weight 550 Da. We refer to this electrolyte as LiTFSI-in-PEGDME. All of the ionic melts exhibit lower conductivity than the reference LiTFSI-in-PEGDME electrolyte which is not surprising given the lower viscosity and the expectation of a greater contribution from anion transport in the LiTFSI-in-PEGDME electrolyte. The viscosity of the LiTFSI-in-PEGDME electrolyte is less than 0.5 Pa s compared to 117 Pa s to that of IM550 at room-temperature. The unexpected thing about these ionic melts conductivities is that they are much higher than those reported for the conventional single ion conductors. At the highest temperature tested (120 °C) the IM550 sample exhibits a conductivity of 1 mS/cm which is within a factor of eight of that for the reference electrolyte, LiTFSI-in-PEGDME. This value is much higher than any value which has been reported for a polymeric single-ion conductor, and it is higher than the conductivities reported for the few known examples of polyethers functionalized with ionic end groups [32-34]. The high conductivity of the ionic melt electrolytes probably derives from a combination of the low lattice energy of the lithium fluorosulfonimide salt relative to other lithium salts, the lower viscosity of these melts relative to higher molecular weight polymer electrolytes, and the higher ion
content of these electrolytes relative to longer-chain-length functionalized polyethers. We note that the conductivity of IM550 at 60 °C is close to 0.1 mS/cm which has been cited, from USABC goals and modeling studies as a critical conductivity value above which a single-ion-conductor electrolyte could be used in a practical large-format secondary lithium ion battery [35].

The trend in conductivity with EO:Li ratio, or equivalently in these materials, polyether chain length, among the ionic melts is such that the material with the intermediate PEG chain length corresponding to an intermediate EO:Li ratio of approximately 12:1, has the highest conductivity at all temperatures. This finding is consistent with the behavior of salt-in-polymer polyether-based electrolytes [37], for which an EO:Li ratio in the 8:1 to 12:1 range has also been shown to be optimal for achieving high conductivity, and also for several oligomeric PEO/lithium salt hybrids [25, 37, 38] which showed maximum ionic conductivity values at a cation concentration of ca. 10 mol% per EO unit (EO/Li = 10:1). Within the range of EO:Li values studied here the conductivity variations are small, however as more extreme EO:Li values are accessed it is easy to imagine that conductivity would diminish more strongly, and as EO:Li becomes small, conductivity should diminish because of the loss of sufficient polyether to solvate the lithium cations. As EO:Li becomes large conductivity should diminish because the number of charge carriers per unit mass or volume diminishes. Previous experiments on electrolytes prepared using very short and long PEGME chains confirm these expectations [25].
Conductivity diminishes with decreasing temperature for all the electrolytes studied, as is expected because ion transport is a thermally activated process. The diminution is greater for the ionic melts than for the LiTFSI-in-PEGDME electrolyte, which indicates that the apparent activation energy associated with ion transport is higher in the ionic melts than in the reference electrolyte. Further study will be required to assign a mechanistic cause to this higher apparent activation energy. One possibility is that ion transport rates will scale with macroscopic viscosity.

Figure 4.6: Arrhenius plots of log(ionic conductivity) vs. inverse absolute temperature for three PEGME-derived lithium fluorosulfonimide ionic melts having different PEG chain lengths and thus different EO:Li ratios. A plot for LiTFSI dissolved in PEGDME500 at a EO:Li ratio of 10.3:1 is shown for reference.
The ionic conductivities for the sulfonate ionic melts having the same polyether chains as those of the imide ionic melts were also studied. Slightly lower ionic conductivity values over the range of temperatures were observed for the sulfonate ionic melts. Better ion dissociation in the imide ionic melts contributes to that slight improvement.

Figure 4.7: Arrhenius plots of log(ionic conductivity) vs. inverse absolute temperature for three PEGME-derived lithium fluorosulfonate ionic melts having different PEG chain lengths and thus different EO:Li ratios.
DC-galvanostatic polarization experiments were performed to study the salt concentration polarization effect on the electrolyte systems that we have developed. Here, a DC current is applied and the voltage response is monitored as a function of time. Figure 4.8 presents data from galvanostatic DC polarization experiments, using ionic melt IM550 and LiTFSI-in-PEGDME electrolytes. Salt concentration polarization is manifest in galvanostatic DC polarization experiments in two ways. First, as a slow increase in the applied cell potential following application of a constant DC current, and second, as a non-zero cell potential following interruption of the current. The increase in applied potential is necessary to compensate for potential losses associated with formation of the salt concentration gradient. This behavior is exactly what was observed following application of current steps to the cell containing the salt-in-solvent electrolyte. In contrast, voltage changes following application of current steps were minimal for the IM550 ionic melt electrolyte, reflecting the fact that salt concentration gradients do not form in this electrolyte as DC current is passed through it. The modest increase in cell voltage following application of the first current step probably reflects changes in interfacial impedance that occur as the cell is broken in. One can also observe the difference in the cell voltage upon current interruption, i.e. upon passing 0 A, for the IM550 and salt-in-solvent electrolyte as shown in Figure 4.9. The former shows immediate relaxation to almost 0 V. On the contrary, the latter displays slow relaxation down to hundreds of millivolts, 190 mV, upon applying 0 A after the 50 μA polarization. This voltage relaxation caused by salt diffusion and is exhibited by the salt-in-solvent electrolyte is caused by the concentration gradients induced after passing the DC current.
Figure 4.8: Voltage-time plots corresponding to DC galvanostatic polarization of electrolytes sandwiched between dual Li electrodes. Top, lithium fluorosulfonimide ionic melt IM550. Bottom, LiTFSI dissolved in PEGDME500 at an EO:Li ratio of 10.3:1.
Figure 4.9: Voltage-time plots corresponding to DC galvanostatic polarization of electrolytes sandwiched between dual Li electrodes. Top, lithium fluorosulfonimide ionic melt IM550. Bottom, LiTFSI dissolved in PEGDME500 at an EO:Li ratio of 10.3:1.
The degree of salt concentration that gives rise to the $E_{\text{cell}}$ values upon current interruption after the 50 $\mu$A current step can be calculated from the Nernst equation. As shown in Table 4.3, the different $E_{\text{cell}}$ values reflect different values for salt concentration gradients across the cell. For the LiTFSI-in-PEGDME electrolyte, the initial salt concentration is approximately 1.5 M. After passing the DC current, concentration gradients are induced within the cell such that the salt concentration at one end of the cell (left side) is larger than that of the other end (right side). From the table below, the concentration gradient that gives rise to the $E_{\text{cell}}$ value observed for LiTFSI-in-PEGDME upon current interruption is 2.998 M.
Table 4.3: $E_{\text{cell}}$ values calculated based on the concentration gradients across the Li$_{\text{left/electrolyte/Li}_{\text{right}}}$ cell after the 50 μA current step

<table>
<thead>
<tr>
<th>$E_{\text{cell}}$ (V)</th>
<th>Salt Concentration M/M (left/right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.5 / 1.5</td>
</tr>
<tr>
<td>0.0034</td>
<td>1.6 / 1.4</td>
</tr>
<tr>
<td>0.0069</td>
<td>1.7 / 1.3</td>
</tr>
<tr>
<td>0.0104</td>
<td>1.8 / 1.2</td>
</tr>
<tr>
<td>0.0141</td>
<td>1.9 / 1.1</td>
</tr>
<tr>
<td>0.0178</td>
<td>2 / 1</td>
</tr>
<tr>
<td>0.0218</td>
<td>2.1 / 0.9</td>
</tr>
<tr>
<td>0.0260</td>
<td>2.2 / 0.8</td>
</tr>
<tr>
<td>0.0306</td>
<td>2.3 / 0.7</td>
</tr>
<tr>
<td>0.0356</td>
<td>2.4 / 0.6</td>
</tr>
<tr>
<td>0.0414</td>
<td>2.5 / 0.5</td>
</tr>
<tr>
<td>0.0481</td>
<td>2.6 / 0.4</td>
</tr>
<tr>
<td>0.0565</td>
<td>2.7 / 0.3</td>
</tr>
<tr>
<td>0.0679</td>
<td>2.8 / 0.2</td>
</tr>
<tr>
<td>0.0866</td>
<td>2.9 / 0.1</td>
</tr>
<tr>
<td>0.147</td>
<td>2.99 / 0.01</td>
</tr>
<tr>
<td><strong>0.206</strong></td>
<td><strong>2.999 / 0.001</strong></td>
</tr>
<tr>
<td>0.265</td>
<td>2.9999 / 0.0001</td>
</tr>
<tr>
<td>0.324</td>
<td>2.999999 / 0.000001</td>
</tr>
</tbody>
</table>
Conclusions

Synthesis of the target ionic melt electrolytes, lithium (perfluorovinylether)sulfonimide salts attached covalently to a lithium-solvating oligomeric polyether chain, in pure form and free of any nonionic impurities, was demonstrated. Ionic conductivities are high over a range of temperatures between ambient and 120 °C. Galvanostatic DC polarization studies indicate that salt concentration polarization does not occur in these electrolytes as current is passed through them using electrodes that are non-blocking for lithium. All these observations are promising for potential applications of the electrolytes in secondary lithium ion battery technology.
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CHAPTER FIVE
IONIC MELT ELECTROLYTES BASED ON DIFUNCTIONLIZED OLIGOMERIC PEG WITH LITHIUM FLUOROSULFONATE OR FLUOROSULFONIMIDE PENDENTS

Introduction

The previous chapter focused on mono-functionalized ionic melt electrolytes prepared from monomethyl ether polyethylene glycols. This chapter will focus on di-functionalized ionic melt electrolytes from polyethylene glycols. These electrolytes possess higher ambient temperature ionic conductivities than conventional polymer electrolytes based on poly(ethylene oxide) (PEO) as has been reported [1-2]. They also undergo no concentration polarization. Liquid electrolytes based on LiPF$_6$ and LiTFSI, and polymer electrolytes undergo concentration polarization because of low lithium transference [3]. The use of ionic liquids or room-temperature molten salts avoid any safety issues since they behave as both charge carriers and non-volatile, non-flammable plasticizers [4-9]. The use of imidazolium or pyrrolidinium based ionic liquids as solvents for inorganic salts provides wide electrochemical windows [10] and high lithium transference when compared to polymer electrolytes [11]. Still, those ionic liquids undergo concentration polarization because of the presence of more than one mobile ionic species. The ionic melt electrolytes that will be discussed in this chapter use low molecular weight oligomers of poly(ethylene glycol) (PEG) $M_w = 600-2000$ Da both as a
scaffold and a plasticizing agent in the preparation of lithium fluorosulfonate or fluorosulfonimide based ionic liquids.

**Experimental**

*Materials.* Poly(ethylene glycol) oligomers of different molecular weights (M<sub>w</sub> = 600, 1000, 2000 Da) and poly(ethylene glycol) monomethylether (PEGME) with M<sub>w</sub> = 550 Da were purchased from Aldrich and dried at 50 °C overnight under dynamic vacuum before use. Lithium bis[(trifluoromethyl)sulfonyl]imide salt (LiTFSI) was purchased from 3M Company and dried as stated previously [12]. The starting material, perfluorinated fluorosulfonylethylvinyl ether (CF<sub>2</sub>=CFO-CF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F), was donated by Dow Chemical and was kept refrigerated prior to use. Lithium hydroxide monohydrate (LiOH·H<sub>2</sub>O, 98%) and sodium hydride (NaH, 95%) were purchased also from Aldrich and stored in an argon-filled dry box prior to use. All reagents were handled either in a dry box or a glove bag under a constant flow of purified argon. Acetonitrile (ACN), HPLC grade, was purified by overnight storage over calcium hydride followed by distillation over phosphorous pentoxide (P<sub>4</sub>O<sub>10</sub>) prior to use while CH<sub>2</sub>Cl<sub>2</sub> provided by VWR was used as received.

*Synthesis of lithium perfluorinated vinyl[(ethylene)(methyl)disulfonyl]imide ether having the structure CF<sub>2</sub>=CFO-CF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>N(Li)SO<sub>2</sub>CF<sub>3</sub>.* Scheme 5.1 describes the synthetic route for the preparation of the new lithium perfluorovinylether (PFVE)-derived sulfonimide salt that was subsequently used in the reaction with polyether oligomers to prepare the target ionic melts. Shortly, the synthesis involved the reaction of a
perfluorinated fluorosulfonylethylvinyl ether, for which the vinyl group was protected by bromination (structure BrCF$_2$CFBrO-CF$_2$CF$_2$SO$_2$F), with a trimethylsilyl-activated trifluoromethylsulfonamide (structure CF$_3$SO$_2$N(Li)Si(CH$_3$)$_3$) which was prepared as described in chapter four and elsewhere [13]. CF$_2$=CFO-CF$_2$CF$_2$SO$_2$F was brominated with elemental bromine to generate BrCF$_2$CFBrO-CF$_2$CF$_2$SO$_2$F. A white powder was obtained with a yield of 98%. $^{19}$F NMR spectrum shows the following resonances: 

\[ \delta \text{(ppm, center of multiplet, 282.8 MHz, CDCl$_3$)}: -63.7 \text{ (BrCF$_2$, dd, } J=3.2), -72.1 \text{ (CFBr, m), -82.3 \text{ (OCF$_2$, dd, } J=116.9), -112.7 \text{ (CF$_2$CF, s), 45.5 \text{ (SO$_2$F, s).}} \]

The reaction combining BrCF$_2$CFBrO-CF$_2$CF$_2$SO$_2$F and CF$_3$SO$_2$N(Li)Si(CH$_3$)$_3$ was accomplished by refluxing the mixture in dry ACN for several days [13]. The product was collected by evaporating the solvent and subsequent debromination with activated Zn metal by heating in dry ACN up to 80 °C for several hours to form the desired PFVE lithium salt. The resulting white solid was dried at 50 °C under dynamic vacuum (0.002 torr) overnight. The yield of recovered material was 92% based on CF$_3$SO$_2$N(Li)Si(CH$_3$)$_3$. $^{19}$F NMR spectrum shows the following resonances: \( \delta \text{(ppm, center of multiplet): -80 \text{ (SO$_2$CF$_3$, s), -83.4 \text{ (OCF$_2$, t, } J=6\text{Hz), -114 \text{ (CF$_2$CF, dd, vinylic, } J=64), -117 \text{ (CF$_2$SO$_2$, s), -122 \text{ (CF$_2$CF, dd, vinylic, } J=6), -134 \text{ (CF$_2$CF, dd, vinylic, } J=6).} \)
Scheme 5.1: Synthetic route for the preparation of lithium perfluorinated vinyl[(ethylene)(methyl)disulfonyl]imide ether

Scheme 5.2 shows the preparation of one class of an ionic liquid prepared through the nucleophilic addition reaction of the deprotonated PEG onto the vinyl group of the lithium perfluorinated vinyl[(ethylene)(methyl)disulfonyl]imide ether prepared previously. Those particular molecular weights of PEG were chosen because it had been shown in the literature that, for lithium salts dissolved in PEO hosts, EO/Li ratios of 7-16 provide optimum ionic
conductivity [14]. A quantity of polyether oligomer dissolved in dry ACN was added drop-wise to a suspension of NaH (slight excess) in dry ACN and stirred continuously with a magnetic stir bar under a dry N₂ atmosphere at room temperature for 12 hours. A clear slightly yellowish solution resulted that was injected through a syringe filter (Whatman PVDF, 0.45 μm) into a dry ACN solution of lithium (perfluorovinylether)sulfonimide salt (stoichiometrically added) under a dry N₂ atmosphere. The mixture was stirred at 0 °C and the reaction progress was monitored by ¹⁹F NMR (disappearance of vinylic fluorine signals at -134, -122 and -114 ppm). After the ¹⁹F NMR spectrum showed that all vinylic fluorines had been transformed (which typically took ~5 hours), the mixture was quenched with several drops of deionized (DI) water. Solvent (including water) was removed by rotary evaporation at 40 °C under reduced pressure, and the resulting yellowish viscous liquid was dried for 4 hours at 60 °C under dynamic vacuum (0.02 torr) for 4 hours. The resulting material was re-dissolved in dry ACN and the solution was filtered through a syringe filter (Whatman PVDF, 0.45 μm) to remove the solid NaOH. The solvent was again removed to regenerate the yellow viscous liquid, which was further dried overnight at 60°C under dynamic vacuum (0.02 torr). Generally, the yield, calculated assuming that the lithium (perfluorovinylether) sulfonimide salt was the limiting reagent was over 95 wt%.
Next, $^7$Li NMR spectrum showed that no Li was present in the ionic melt due to its replacement by Na. Therefore, it was necessary to acidify ionic melt by stirring it at ambient temperature with concentrated H$_2$SO$_4$ (80 %) overnight, followed by extraction of the product by CH$_2$Cl$_2$. The solvent was then evaporated and the resulting material was lithiated with excess LiOH/H$_2$O in DI water. Subsequent $^1$H, $^7$Li and $^{19}$F NMR spectra showed the desired product in very high purity with lithium as the only cation present.
The water was then removed by rotary evaporator and the sample was dried at 50 °C overnight under dynamic vacuum. The ionic melt was extracted from the mixture using CH₂Cl₂ and the resulting mixture was filtered through celite to retain all the inorganic salts. The solvent from the resulting solution was evaporated by rotary evaporator and the ionic melt was further dried at 50 °C overnight under dynamic vacuum.

**Synthesis of lithium perfluorinated vinyl[(ethylene)sulfonate having the structure CF₂=CFO-CF₂CF₂SO₃Li.** This synthesis was much straightforward and started by dissolving the Dow monomer (CF₂=CFO-CF₂CF₂SO₂F) in DI water together with excess LiOH·H₂O and stirring for several hours. The ¹H, ⁷Li and ¹⁹F NMR spectra showed that the reaction proceeded completely. The resulting white solid was dried at 50 °C under dynamic vacuum (0.002 torr) overnight and the ionic melt was extracted from the mixture using CH₂Cl₂. The resulting mixture was filtered through celite to retain all the inorganic salts. The solvent from the resulting solution was evaporated by rotary evaporator and the ionic melt was further dried at 50 °C overnight under dynamic vacuum.

**Synthesis of ionic melts of general structure (OCH₂CH₂)ₙ-(O-CF₂CFH-OCF₂CF₂SO₃Li)₂.** The preparation of this class of ionic liquids follows exactly the same steps as in the case of the lithium fluorosulfonimide PEG-derivatives but using the fluorosulfonate functionality.

**Preparation of LiTFSI-in-PEGME electrolyte.** A quantity of PEGME (Mₘ = 550 Da) was weighed into a tarred round-bottom flask and the corresponding quantity of LiTFSI was added to the flask to reach the desired EO/Li ratio of 11.8:1. Next, dry ACN
solvent was added to the mixture and was stirred at room temperature for 24 hours. The ACN was evaporated and the resulting viscous liquid dried at 50 °C overnight under dynamic vacuum. A $^1$H NMR spectrum was acquired to confirm the absence of residual solvent.

**Nuclear magnetic resonance (NMR).** Proton ($^1$H), lithium ($^7$Li) and fluorine ($^{19}$F) NMR spectra were acquired for each of the ionic melts while monitoring the reactions and also to test for the purity of the final products. Spectra were acquired using a JEOL model AC 300 MHz NMR spectrometer with the solution in a 5-mm diameter tube containing CD$_3$CN as a lock solvent.

**Differential scanning calorimetry (DSC).** Differential scanning calorimetry thermograms were obtained using a TA Instruments DSC Q1000 system with a sample loading robot. The general procedure was to first cool down the sample to – 100 °C using a rate of – 10 °C/min, then was heated at a rate of 10 °C/min up to 100 °C to acquire the first scan. The procedure was repeated immediately to acquire the second scan. The glass transition temperature, $T_g$, was taken as the midpoint temperature of the baseline shift measured during the transition. The melting temperature of the crystalline region, $T_m$, was taken as the peak of the melting endotherm.

**Electrochemical impedance spectroscopy (EIS).** This method was used to measure the electrolyte resistance. Measurements were done similarly to what has been previously described [3, 12, 15] and as described in chapter three.
Results and Discussion

Nuclear magnetic resonance. $^1$H, $^7$Li and $^{19}$F NMR spectra acquired for each of the ionic melts testified for the high purity of each of the final products. Figure 5.1A shows the $^1$H NMR spectrum of PEG600-based lithium fluorosulfonimide ionic melt $(OC^aH^bC^cH^d_2)_{11.2}-(OC^aH^bC^bH^c_2-O-CF^dC^eF^fHO-CF^gCF^hSO^iN(Li)SO^jCF^k_3)_2$ with the following resonances, $\delta$(ppm, center of multiplet): 6.29, 6.11 (c, d-t, J= 54Hz, 3.1Hz CHF), 4.10 (b, br triplet, CH$_2$OCF$_2$), 3.60 (a, br m, (CH$_2$CH$_2$O)$_n$). Figure 5.1B shows the $^{19}$F NMR spectrum of the same PEG600-based lithium fluorosulfonimide ionic melt $(OCH^aCH^b_2)_{11.2}-(OCH^aCH^b_2-O-C^dF^eC^fF^gHO-C^fF^gC^hF^iSO^iN(Li)SO^jCF^k_3)_2$ shows the following resonances, $\delta$(ppm, center of multiplet): -83.0 (f, dd, J=146.5), -89.4 (d, m), -116.9 (g, s), -143.8 (e, m), -80.1 (h, s). The $^7$Li NMR spectrum was acquired using also an internal standard (LiTFSI in CD$_3$CN) proving quantitatively the Li content of these ionic melts.
Figure 5.1A: $^1$H NMR spectrum of **IM600** - (OCH$_2$CH$_2$)$_{11.2}$-(OCH$_2$H$_2$-O-CF$_2$CF$^\circ$HO-CF$_2$CF$_2$SO$_2$N(Li)SO$_2$CF$_3$)$_2$

Figure 5.1B: $^{19}$F NMR spectrum of **IM600** - (OCH$_2$CH$_2$)$_{11.2}$-(OCH$_2$H$_2$-O-CdF$_2$CeFHO-CfF$_2$CgF$_2$SO$_2$N(Li)SO$_2$ChF$_3$)$_2$
**Differential scanning calorimetry.** Thermal properties such as glass transition temperature ($T_g$) and melting/crystallization temperatures ($T_m$, $T_c$), were determined from scanning DSC thermograms for all ionic melts samples. A representative thermogram is shown in Fig. 5.2A for PEG-based (M=600-2000 Da) ionic melts with two lithium fluorosulfonates functionalities, while Fig. 5.2B shows the same thing for PEG-based ionic melts with two lithium fluorosulfonimide functionalities. The feature between –5 to –40 °C reflects the change in heat capacity at the glass transition. Also, for PEG2000-based ionic melt with lithium fluorosulfonate functionalities, the endothermic peak near +30 °C reflects heat absorption associated with melting the crystalline region of the host polymer, while the exothermic peak at around +10 °C reflects the heat released with the formation of a crystalline region for the same ionic melt (Figure 5.2A). Consistently, in both series, $T_g$ is decreasing monotonically with increasing the molecular weight of the host polymer but are lower than the $T_g$ of -58.7 °C for a salt-in-polymer electrolyte (LiTFSI dissolved in PEGME with M=550 Da, EO/Li=11.8:1) which serves as a baseline for comparison.
Figure 5.2A: DSC scans for plots of the new ionic melts prepared from oligomeric PEGs having two lithium fluorosulfonate functionalities ($R_{F,H} = CF_2CFHOCF_2CF_2$).

Figure 5.2B: DSC scans for plots of the new ionic melts prepared from oligomeric PEGs having two lithium fluorosulfonimide functionalities ($R_{F,H} = CF_2CFHOCF_2CF_2$).
Electrochemical impedance spectroscopy. The ionic conductivity is the most critical property of these ionic melts relating to their use in rechargeable lithium batteries. Figures 5.3A and 5.3B present Arrhenius plots of log [ionic conductivity, $\kappa$ (S/cm)] vs. 1000/[temperature, $T$ (K)] for electrolytes made from PEG (M=600-2000 Da) to which were attached two identical lithium fluorosulfonate or fluorosulfonimide pendants, respectively. Their preparation has already been described earlier. In each case, the data are presented in comparison to the salt-in-polymer electrolyte baseline (LiTFSI in PEGME550).

Some general trends are immediately apparent in the data. First, all the members of both series have an ionic conductivity lower than the salt-in-polymer electrolyte baseline over the entire temperature range. This fact is a consequence of the fact that the conductivity in most lithium salt-based polymer electrolytes is dominated by anion transport [16, 23-24] while in the new PEG-based ionic melts anion mobility is expected to be almost completely suppressed. Second, in both series, ionic conductivity is increasing with the molecular weight of the PEG. Third, the ionic conductivities of the lithium fluorosulfonate series are higher than that of the lithium fluorosulfonimide series over the entire temperature range. Fourth, the Arrhenius curve for the PEG2000-based lithium fluorosulfonate ionic melt (Figure 5.5) exhibits an abrupt change in conductivity near $\pm 30 \, ^\circ$C. This change is commonly seen in dilute PEO-based electrolytes [16-17] and is attributed to a crystalline transition of the polymeric host, as seen in the thermogram in Figure 5.2. The transition is suppressed in all of the other PEG-based ionic melts as has previously been observed for LiTFSI-based SPEs in an EO/Li range.
near 10:1 [18-19]. This fact is also undoubtedly related to the lack of crystallinity of the low molecular weight PEGs.

Figure 5.3A: Arrhenius plots of the new ionic melts prepared from oligomeric PEGs having two lithium fluorosulfonate functionalities (R_{F,H} = CF_{2}CFHOCF_{2}CF_{2}). Data for the salt LiTFSI in polymer host PEGME with M = 550 Da are provided for comparison.
Figure 5.3B: Arrhenius plots of the new ionic melts prepared from oligomeric PEGs having two lithium fluorosulfonimide functionalities (R_F,H = CF_2CFHOCF_2CF_2). Data for the salt LiTFSI in polymer host PEGME with M = 550 Da are provided for comparison.

Close inspection of the Arrhenius curves over the entire temperature region reveals a slight but significant curvature which is commonly observed in SPEs and other glassy ionic conductors. It is indicative of mechanical coupling between the motions of the charge carriers and the motions of the matrix. Curved Arrhenius plots may be fit using the semi-empirical relation of Vogel, Tammann and Fulcher, also known as the VTF relation, given in Eq. (1):

$$\kappa = A \cdot T^{-1/2} \exp \left[ - \frac{B}{(T - T_0)} \right]$$  \hspace{1cm} (17)
The terms A and B in this expression are phenomenological fitting parameters; A is related in a general way to the number of charge carriers while B, in the configurational entropy model, is related to the apparent activation energy opposing the rearrangement of the polymer segmental units [20-21]. The term T₀ is called the equilibrium glass transition temperature and it corresponds to the temperature at which the configurational entropy approaches zero. The values of A and B were determined by nonlinear least-squares fits of the data to the VTF equation using a value of T₀ equal to 25 K lower than the T₉ values, which has been utilized previously for LiTFSI- or CF₃SO₃Li-based solid polymer electrolytes [18-19, 22]. The values for T₉, Tₘ / Tₐ, A, B and EO/Li ratio for each of the ionic melts and the salt-in-polymer electrolyte are listed in Table 5.1.

Table 5.1: DSC characteristics and VTF parameters for the oligomeric PEG-based ionic melts with lithium fluorosulfonate / fluorosulfonimide functionalities (included is the salt-in-polymer baseline)

<table>
<thead>
<tr>
<th>Polymer Mₘ (Da)</th>
<th>Func.</th>
<th>T₉ (°C)</th>
<th>Tₘ / Tₐ (°C)</th>
<th>A (Kⁱ/₂ S/cm)</th>
<th>B (K)</th>
<th>EO/Li (at/at)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550 LiTFSI</td>
<td>-58.7</td>
<td>-</td>
<td>1.198</td>
<td>642</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>600 Sulfonate</td>
<td>-15.0</td>
<td>-</td>
<td>2.032</td>
<td>969</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>1000 Sulfonate</td>
<td>-25.5</td>
<td>-</td>
<td>1.218</td>
<td>832</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>2000 Sulfonate</td>
<td>-37.1</td>
<td>30 /10</td>
<td>1.076</td>
<td>793</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>600 Sulfonimide</td>
<td>-4.4</td>
<td>-</td>
<td>0.443</td>
<td>737</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>1000 Sulfonimide</td>
<td>-20.9</td>
<td>-</td>
<td>0.808</td>
<td>865</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>2000 Sulfonimide</td>
<td>-26.6</td>
<td>-</td>
<td>0.895</td>
<td>773</td>
<td>22.5</td>
<td></td>
</tr>
</tbody>
</table>
Comparison of the $T_g$, $A$ and $B$ values from the VTF fits in Table 1 also lends some insight. Except for the salt-in-polymer electrolyte which has the lowest $T_g$ and $B$ values and one of the highest $A$ values, the main difference among the various ionic melts lies in the $T_g$ and $A$ values. All the ionic melts of the lithium fluorosulfonate series have a lower $T_g$ and a higher charge carrier concentration ($A$ values) than their counterparts in the lithium fluorosulfonimide series which explains the higher ionic conductivity of the first series over the entire temperature range (exception PEG2000-based lithium sulfonate at ambient temperature for reasons already presented). Inside each series, ionic conductivity is rising monotonically with the increase in the molecular weight of the polymer host, but for different reasons. In the lithium fluorosulfonate series conductivity is increasing with decreasing $T_g$, apparent activation energy value of the segmental motion ($B$ values) and charge carrier concentration ($A$ values) while in the lithium fluorosulfonimide series conductivity is increasing with decreasing $T_g$, and increasing charge carrier concentration ($A$ values). These findings suggest that the major reason for the diminished conductivity in the latter series is that there are fewer free charge carriers present in these electrolytes, which is an unexpected finding taking into account that generally the fluorosulfonimide anions exhibit less basicity (which means less ion-pairing) than their fluorosulfonate counterparts.

For both series, the diminishing of the apparent activation energy ($B$ values) is obvious with the increase in the number of repeating ethylene oxide units, which may indicate a plasticizing effect. The increase in PEG molecular weight has affected the
local microstructure and chain dynamics of the polymer in the vicinity of ions, so as to diminish the apparent activation energy for ion transport.

For the ionic melt electrolytes having the same EO:Li ratios but with different end-capped groups, i.e. monofunctional versus difunctional sulfonimide ionic melts, it was observed that the ionic conductivities for the monofunctional are larger than those of the difunctional. The $T_g$ and the charge carrier concentration contribute to the better performance of the monofunctional which possesses lower value of $T_g$ and higher value for $A$.

Figure 5.4: Arrhenius plots comparing two sulfonimide functionalized ionic melt electrolytes, one is mono-functional (dark circle) and the second is difunctional (dark triangle), but have the same EO : Li ratios
Conclusions

Two series of new oligomeric PEG-based ionic melts having either lithium fluorosulfonate or lithium fluorosulfonimide functionalities have been prepared and characterized by $^1$H, $^7$Li, $^{19}$F NMR, DSC and EIS. All the members of the lithium fluorosulfonate series exhibited higher ionic conductivity over the entire temperature range than the corresponding members of the lithium fluorosulfonimide series. In both series ionic conductivity increased with the molecular weight of the polymer host indicating a possible plasticizing effect of the repeating ethylene oxide units.
References

CHAPTER SIX
THE EFFECT OF LOW MOLECULAR WEIGHT POLYETHERS AS PLASTICIZERS ON THE TRANSPORT PROPERTIES AND RHEOLOGY OF LITHIUM FLUOROSULFONIMIDE IONIC MELTS

Introduction

Ion transport in a lithium-ion battery highly influences its performance. It is very important for the electrolyte in the battery to have both high ionic conductivity as well as high lithium transference number. Such desirable properties allow for high power density which is critical in EV and HEV applications [1, 2]. Moreover, lithium ion batteries offer three to four times higher energy densities than the Ni-Cd and Ni-MH batteries and that is necessary for hybrid technologies if lithium batteries are envisioned to be used along with capacitors that provide high power densities [3, 4].

In the fourth chapter, we reported novel ionic liquids that do not allow any salt concentration polarization. Salt concentration polarization in the electrochemical cell causes voltage losses that leads to limiting currents [5, 6]. These new oligomeric ionic melts exhibit ambient ionic conductivities of around 5 *10^{-6} S/cm. It is desirable to increase the ambient ionic conductivity while maintaining a relatively high lithium-transference number in order for such materials to have practical applicability. The most common approaches to improve ionic conductivities, especially at the room-temperature ones, is by plasticization [7, 8]. Plasticizers enhance ion dissociation, because of their
high dielectric constant, and they improve ion mobility as well as segmental motion in polymer based electrolytes [9].

In this chapter, the plasticizing effect on the transport properties as well as the mechanical properties of the ionic liquids reported in chapter four and [10] will be explained. Low-molecular-weight polyethers, which have proven to enhance the ionic conductivity [11, 12], were used as plasticizers. Low molecular weight polyethers have relatively high boiling points and low vapor pressure. Their ethylene oxide EO units have high donor number for Li$^+$ and they have high chain flexibility which are both important for high ionic conductivity [13].

**Experimental**

*Chemicals.* The ionic melt having the chemical formula CH$_3$O-(CH$_2$CH$_2$O$_{11.8}$)CF$_2$CFHOCF$_2$CF$_2$SO$_2$N(Li)SO$_2$CF$_3$, denoted as IM550, was prepared as described in chapter 4. The melt electrolyte was kept under dry conditions in an argon-filled glove bag prior to use. Polyethylene glycol monomethyl ether PEGME of $M_w = 550$ Da was purchased from Aldrich and was dried under dynamic vacuum before use. HPLC grade acetonitrile (ACN) was kept over CaH$_2$ overnight and was dried by refluxing it over P$_2$O$_5$ for more than 24 hrs. Lithium ribbon of thickness 0.75 mm was purchased from Aldrich and was stored in an argon filled dry box.

*Electrolyte Preparation.* Plasticized electrolytes consisting of IM550 with 20 wt% and 50 wt% PEGME550 were prepared by mixing the appropriate quantities of IM550 and PEGME550 in a round-bottom flask. The mixture was dissolved in dry ACN and was
homogenized by stirring at room temperature for 5 hrs. ACN was then evaporated and the electrolyte was dried at 80 °C under dynamic vacuum for 12 hrs. \(^1\)H NMR spectra confirmed the absence of residual solvent. Table 6.1 summarizes these plasticized electrolytes.

Table 6.1: Materials and their abbreviations

<table>
<thead>
<tr>
<th>Material</th>
<th>IM550_Gel1</th>
<th>IM550_Gel2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>IM550 + 50 wt%</td>
<td>IM550 + 20 wt%</td>
</tr>
<tr>
<td></td>
<td>PEGME550</td>
<td>PEGME550</td>
</tr>
</tbody>
</table>

**Ionic Conductivities.** The plasticized oligomeric electrolytes were tested by EIS to determine the ionic conductivities as a function of temperature using the procedure described in chapter 3.

**Calorimetric Measurements.** DSC measurements were performed for all samples using a Mettler-Toledo 820 differential scanning calorimeter to determine glass transition temperature (Tg). The samples were sealed in aluminum pans and scanned from -150 to 150 °C at a rate of 10 °C/min. The Tg was taken as the midpoint temperature of the baseline shift measured during the transition.

**Rheological Experiments.** ARES-LS type rheometer from Rheometric Scientific was used for the rheological studies and the procedure is explained in chapter 3.
Galvanostatic Polarization Experiments. To account for voltage losses within the electrochemical cell, galvanostatic experiments were performed at RT. The symmetric cell consisted of the electrolyte sandwiched between two lithium electrodes that were separated by a Teflon spacer of thickness 3 mm. Two square-wave current steps of magnitudes 10 μA and 50 μA were applied for 1 hour each. A current of 0 A was applied at the beginning of the experiment and after each step for 0.5 hours.
Results and Discussions

Ionic Conductivity. Figure 6.1 presents the Arrhenius plots of the ionic conductivities of the previously reported IM550 along with those of the plasticized IM550 with 20 and 50 wt% of PEGME550. All of the Arrhenius plots show convex curvatures indicating that the ion conduction mechanism of the ionic melt and those that are plasticized with unmodified polyether is partly associated with the segmental motion of the EO chains. It is clearly observed that there is a drastic increase in the ionic conductivities in the low-temperature range by increasing the fraction of the unmodified polyether oligomer in the sample. For example, the ambient-temperature conductivity of the IM550_Gel1 is more than one order of magnitude higher than that of the IM550. The ionic conductivity value increases from 2.48*10^{-6} S/cm for the pure ionic melt to 5.3*10^{-5} S/cm upon adding 50 wt% PEGME550. Such a considerable increase is attributed to the decrease in viscosity as a result of the plasticizing effect which will be later revealed in the rheological studies. The unmodified polyether is considered to be a plasticizer that increases the chain flexibility and the dynamic free volume of the ionic melt. In other words, the addition of the unmodified polyether causes an increase in the hole free-volume that is available for ion transport leading to a higher ionic conductivity [14]. Moreover, as the concentration of the EO unit increases, there will be more etheric coordination sites available for the transport of lithium ions. Worth mentioning also is the good dissociation of the sulfonimide anion with lithium cation in the dielectric medium of the polyether oligomer.
Figure 6.1: Arrhenius plots for the ionic conductivities of IM550 and the gelled ionic melts listed in Table 6.1.

**Data Fitting and VTF Parameters.** Since the Arrhenius plots exhibit positively curved profiles, it is necessary to interpret the ionic conductivity data by the Vogel-Tamman-Fulcher (VTF) equation [15, 16]

\[
\sigma = AT^{-1/2} \exp\left[ -\frac{E_a}{R(T - T_0)} \right]
\]

where $A$ is a preexponential constant proportional to the number of ionic carriers, $E_a$ is the effective activation energy for ion conduction, and $T_0$ is the ideal glass transition temperature at which the ionic conduction is completely frozen. The data fitting was done over the temperature range where the ionic conductivities between the three materials start to display significant changes. That temperature range was chosen between ambient
temperature and 90 °C. The plot for the VTF model, displayed in Figure 6.2 as a plot of 
log(σT^{1/2}) vs. 1000*(T-T_0)^{-1} is linear for all three electrolytes. The values for the 
parameters of the VTF equation obtained from linear curve fitting are summarized in 
Table 6.2 along with the standard deviation for Ea with 95% confidence interval. These 
values offer a better understanding of the ionic conductivity trends shown in Figure 6.1. 
Only parameters A and Ea were modeled. T_0 was calculated from the experimental T_g 
according to Equation 2. It is observed that A, Ea and T_0 values for IM550_Gel1 are both 
lower than those values for IM550_Gel 2. The trend could be explained by the fact that 
the former consists of a higher concentration of polyether oligomers that contributes to a 
lower charge carrier concentration (A). Also, the segmental motion of the more 
concentrated polyether oligomers provides lower activation energy for lithium ion 
transport. Finally, the lower T_g value for IM550_Gel1 than the other electrolytes explains its higher ionic conductivity.

\[ T_0 = T_g - 25 \]  

Table 6.2: Values for the parameters of the VTF Equation obtained from ionic conductivity data fitting

<table>
<thead>
<tr>
<th>Material</th>
<th>A/S cm^{-1} (K)^{1/2}</th>
<th>Ea±σa/kJ mol^{-1}</th>
<th>T_0/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM550</td>
<td>7.78</td>
<td>8.91±0.10</td>
<td>210.7</td>
</tr>
<tr>
<td>IM550_Gel1</td>
<td>0.77</td>
<td>6.20±0.33</td>
<td>188.0</td>
</tr>
<tr>
<td>IM550_Gel2</td>
<td>1.08</td>
<td>6.38±0.50</td>
<td>199.0</td>
</tr>
</tbody>
</table>

σa Errors corresponding to the standard deviation from the slope of linear regression
Figure 6.2: VTF plots for the ionic conductivities of the pure ionic melt compared to those that are plasticized with unmodified polyether oligomers.

**Thermal Analysis.** The DSC results shown in Figure 6.3 provide further insight regarding the increase in ionic conductivity upon the addition of PEGME550. The glass transition temperature $T_g$ for IM550 is -37.3 °C as compared to -49.0 °C and -60.0 °C to those of the IM550_Gel2 and the IM550_Gel1 respectively. For polymer electrolytes, $T_g$ is correlated to the transport mechanism of the ionic species through the segmental motion of the EO chains in the polyether oligomers. A decrease in the $T_g$ due to the increase in the polymer chain mobility always gives rise to a higher ionic conductivity. Interestingly, both DSC plots do not reveal any crystalline phases. This trend explains the
ionic conductivity profiles that do not show any steep drop at a particular temperature and especially the ambient one.

![DSC curves of IM550, IM550_Gel1 and IM550_Gel2 displaying the glass transition temperatures of all the electrolytes.](image)

**Figure 6.3**: DSC curves of IM550, IM550_Gel1 and IM550_Gel2 displaying the glass transition temperatures of all the electrolytes.

**Rheological Studies.** Such studies involve the understanding of the flow and deformation of the material. Particularly for lithium battery applications, it is necessary to investigate the electrolytic materials with respect to shear stress and flow since this aspect is critical during fabrication and packaging. Moreover, rheology gives an insight onto the mechanical properties of the material with respect to viscosity and elasticity.

Figure 6.4 presents the plot of shear stress (Pa) versus shear rate (s\(^{-1}\)) which is linear. This linearity indicates that IM550 is a Newtonian fluid and the liquid behavior is
simple [17]. Figures 6.5a-c exhibit the steady-shear response at room temperature. No significant change in the viscosity as a function of the rate is observed for any of the electrolytes. This means that the materials do not experience any shear thinning or shear thickening. As can be anticipated, the increase in wt% of PEGME550 gives rise to a lower viscosity which is the primary cause for the increase in ionic conductivity. The room-temperature viscosity decreases from 117 Pa.s at a shear rate of 1.0 s\(^{-1}\) to 4.8 Pa.s at the same shear rate upon the addition of 20 wt% PEGME550. It decreases further to 0.97 Pa.s when 50 wt% of PEGME550 is added.

![Figure 6.4](image.png)

Figure 6.4: Plot of shear stress versus shear rate showing Newtonian behavior for IM550 at ambient conditions.
Figure 6.5: (a-c) Steady-shear viscosities as function of shear rates taken at ambient temperature for IM550 and the plasticized electrolytes.
The results from the dynamic, or oscillatory, measurements are illustrated in Figure 6.6. The elastic modulus $G'$ is very low independent upon the frequency while the viscous modulus $G''$ increases linearly with frequency, and it clearly exceeds the elastic modulus. Such an observation is consistent with a viscous liquid. Visual investigation indicates such an observation as well.

Figure 6.6: Elastic and viscous moduli as functions of oscillatory frequency $\omega$ for IM550 taken at ambient temperature.

DC-galvanostatic polarization. To account for voltage losses that a material could induce in an electrochemical cell, a constant current is applied and the potential is monitored. Under controlled-current conditions, we can observe the changes, if any, on the cell’s potential. The experiment was run on the two gelled ionic melts and the difference in polarization due to the effect of the percent plasticizer added to the IM550...
was studied. As shown in Figure 6.7, an increase in the cell potential after applying a current step clearly occurred for the IM550_Gel1 which is due to the accumulation of the salt within the active material of the cathode [18]. The cell polarized less for the IM550_Gel2; this is due to the lower concentration of the dielectric in the melt electrolyte. The polarization in the IM550_Gel2 is more apparent at the 50 \( \mu \text{A} \) current step and less obvious at the 10 \( \mu \text{A} \) which is probably due to the higher salt diffusion at the larger current step. For the IM550_Gel1, both applied current steps caused the potential to reach increasing values. Such potential losses are due to the anionic diffusion within the dielectric polyether matrix that causes salt concentration gradient to occur within the cell. When the current was interrupted after the 50 \( \mu \text{A} \) step, the cell voltage drops to 27 mV in the case of IM550_Gel2, and down to 30 mV in the case of IM550_Gel1. Voltage relaxation is due to the salt concentration gradient.
Figure 6.7: (A-B) Potential-time plot as a result of a DC-galvanostatic experiment performed in a symmetric cell Li/Electrolyte/Li. Magnitudes of the currents for the first and the second steps are 10 μA and 50 μA respectively for a duration of 1 hour each. (A) DC-galvanostatic polarization data for IM550_Gel2. (B) DC-galvanostatic polarization data for IM550_Gel1
Conclusions

The transport and rheological properties of the novel plasticized ionic melts were studied. Upon the addition of polyether plasticizers, the ionic conductivities and especially the room temperature values show dramatic improvement by more than an order of magnitude when 50 wt% unmodified polyether was used. The effect of the plasticizer additive can be explained by its lower $T_g$ as shown in the DSC data, and by its lower viscosity as shown in the rheology data. This improvement in ionic conductivities was compromised by voltage losses as proven by the dc-galvanostatic experiments.
References


CHAPTER SEVEN

THE EFFECT OF FLUORINATED CHAINS AND BRANCHING ON THE THERMAL AND ELECTROCHEMICAL PROPERTIES OF POLYETHER-BASED SULFONIMIDE IONIC MELTS

Introduction

The imide anion is well known to be the most effective ion in producing low melting point materials [1]. This is very useful in a lithium salt since it is advantageous for the ionic conductivity. It has been shown by Pringle et al. [2], that fluorination enhances the ionic conductivity of certain imidazolium based ionic liquids. It was shown that the fluorinated analogue of a hydrocarbon ionic liquid has a much higher ionic conductivity that the non-fluorinated analogue. In addition, fluorocarbons are better electron withdrawing groups that further increase the acidity of the imide anion. This provides better ion dissociation and results in lower negative charge density per unit area on anions [3]. In the context of an oligoether-based sulfonimide ionic melt, we tried that approach of fluorination by increasing the fluorocarbon content in the molecule either by adding three more –CF₂- groups to the previously discussed IM550, or by using a different starting material made by DuPont that consists of a branched fluorocarbon chain, or by delocalizing the negative charge of the imide anion over two PFVE groups. This chapter will discuss the synthesis of these new materials that were partly made by Dr. Rajagopal along with the results from EIS and DSC.
Experimental

Chemicals. The perfluorinated fluorosulfonylethylvinyl ether (CF₂=CF-O-CF₂CF(CF₃)-O-CF₂CF₂SO₂F) reactant was purchased from China and kept refrigerated prior to use. Trifluoromethane sulfonylethylvinyl ether (CF₃SO₂)₂O was purchased from SynQuest and kept in a glove bag under very dry conditions. Hexamethyldisilazane HMDS was purchased from Alfa Aesar and used as it is. Polyethylene glycol monomethyl ether oligomers of molecular weights $M_w = 550, 350$ were purchased from Aldrich and dried under dynamic vacuum at ambient temperature before use. LiOH monohydrate (LiOH·H₂O) of 98% purity was purchased from Aldrich; and NaH of 95% purity was purchased from Aldrich and stored in a dry box prior to use. Acetonitrile (ACN) was purified by distillation from calcium hydride and phosphorous oxide (P₄O₁₀) prior to use.

Synthesis. The compounds that were synthesized are listed in Table 7.1 which presents their molecular formula along with their names. The synthesis of IM550 was explained in Chapter 4. The rest of the compounds followed similar procedures of preparation as of IM550.
Table 7.1: Names and chemical formulas of fluorosulfonimide based oligoether ionic melts. The compounds show differences in their fluorocarbon content.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM550</td>
<td>CH₃O-(CH₂CH₂O-)₁₁.₈CF₂CFHOCF₂CF₂SO₂N(Li)SO₂CF₃</td>
</tr>
<tr>
<td>(IM550)₂Li</td>
<td>CH₃O-(CH₂CH₂O-)₁₁.₈CF₂CFHOCF₂CF₂SO₂⁻N(Li)-SO₂⁻CF₂CF₂OCFHCF₂-(CH₂CH₂O-)₁₁.₈OCH₃</td>
</tr>
<tr>
<td>IM550_(CF₂)₃</td>
<td>CH₃O-(CH₂CH₂O-)₁₁.₈CF₂CFHOCF₂CF₂SO₂N(Li)SO₂⁻(CF₂)₃CF₃</td>
</tr>
<tr>
<td>IM550_Dupont</td>
<td>CH₃O-(CH₂CH₂O-)₁₁.₈CF₂CFHOCF₂CF₂SO₂⁻N(Li)SO₂⁻CF₂CF₂OCFHCF₂-(CH₂CH₂O-)₁₁.₈OCH₃</td>
</tr>
<tr>
<td>(IM350)₂Li</td>
<td>CH₃O-(CH₂CH₂O-)₇.₂CF₂CFHOCF₂CF₂SO₂N(Li)-SO₂⁻CF₂CF₂OCFHCF₂-(CH₂CH₂O-)₇.₂OCH₃</td>
</tr>
</tbody>
</table>

Synthesis of $R_f$-SO₂N(Li)Si(CH₃)₃, $R_f = CF₃$ (A). The method used to synthesize compound (A) is illustrated in Scheme 7.1. In an Ar purged glove bag, a quantity of (R₆SO₂)₂O (0.035 mol) was added drop-wise using an addition funnel to 30mL of liquid NH₃ that was cooled in a r.b. flask immersed in liquid N₂ dewar. A stir bar was previously placed in the flak and the mixture was allowed to react overnight with warming up to room-temperature conditions. After reaction completion, excess NH₃ was removed by vacuum and the white solid residue of R₆SO₂NH₂ was purified by means of sublimation. Sublimation gets rid of NH₄SO₄ as the reaction by-product.

R₆SO₂NH₂ was then neutralized with LiOH.H₂O in DI H₂O up to pH of 8.4. H₂O was then evaporated and R₆SO₂NHLi was dried overnight at 110 °C under vacuum. R₆SO₂NHLi was later reacted with 30.0 mL HMDS under reflux in ACN at 90 °C for
14hrs. After reaction completion, solvent was evaporated and A was dried under vacuum at 90 °C.

**Synthesis of CF₂(Br)CF(Br)-O-R₂f-SO₂F, R₂f = CF₂CF₂, CF₂CF(CF₃)-O-CF₂CF₂** (B). The method used to synthesize B is illustrated in Scheme 7.2. Liquid Br₂ was added into an addition funnel. CF₂=CF-O-R₂f-SO₂F was cooled to cryogenic temperature in a r.b. flask and stirred for sometime. Br₂ was slowly added into it until reaction mixture’s color changed from colorless to permanent light red. After the color change was achieved, the reaction was allowed to continue for two more hours.

Reaction work-up was done as follows. Sodium thiosulfate, Na₂S₂O₃, solution was added to the reaction mixture and stirred until solution is colorless. Two layers were formed and the bottom one was separated using a separatory funnel. That extracted layer was dried on P₂O₅ and then distilled over vacuum at RT to collect the excess CF₂=CF-O-R₂f-SO₂F.

**Synthesis of CF₂=CF-O-R₂f-SO₂N(Li)SO₂R₂f (C).** The method used to synthesize C is illustrated in Scheme 7.3. A was mixed with B in ACN and refluxed for 48hrs. After reaction completion, solvent was evaporated and the resulting product was debrominated using 2.0g of metal Zn in ACN at 70 °C for 12hrs. C was collected as a white solid after solvent evaporation and drying under vacuum for 12hrs.

**Synthesis of (CF₂=CF-O-CF₂CF₂SO₂)₂NLi (D).** The method used to synthesize compound (D) is illustrated in Scheme 7.4 and is similar to that of A. Liquid NH₃ was cooled in a r.b. flask immersed in liquid N₂ dewar. A stir bar was placed in the flask and B was added. The mixture was allowed to react overnight up to room-temperature
conditions. After reaction completion, excess NH$_3$ was removed by vacuum and the white solid residue of BrCF$_2$CFBr-O-CF$_2$CF$_2$SO$_2$NH$_2$ was purified by means of sublimation. Sublimation gets rid of NH$_4$SO$_4$ as the reaction by-product.

BrCF$_2$CFBr-O-CF$_2$CF$_2$SO$_2$NH$_2$ was then neutralized with LiOH.H$_2$O in DI H$_2$O up to pH of 8.4. H$_2$O was then evaporated and BrCF$_2$CFBr-O-CF$_2$CF$_2$SO$_2$NHLi was dried overnight at 110 ºC under vacuum. BrCF$_2$CFBr-O-CF$_2$CF$_2$SO$_2$NHLi was later reacted with 30.0 mL HMDS under reflux in ACN at 90 ºC for 14hrs. After reaction completion, solvent was evaporated and the product was dried under vacuum at 90 ºC. The brominated product was then refluxed with Zn in ACN for 12 hrs. Solvent was then evaporated and D was dried.

_Synthesis of CF$_2$=CF-O-CF$_2$CF$_2$SO$_2$N(Li)SO$_2$(CF$_2$)$_3$CF$_3$ (E)._ The method used to synthesize E is illustrated in Scheme 7.5. C$_4$F$_9$SO$_2$F was reacted with liquid NH$_3$ to form the amide. The lithium salt of the amide was made from LiOH and was reacted with HMDS. That product was then reacted with B in ACN and refluxed for 48hrs. After reaction completion, solvent was evaporated and the resulting product was debrominated using 2.0g of metal Zn in ACN at 70 ºC for 12hrs. E was collected as a white solid after solvent evaporation and drying under vacuum for 12hrs.

_Synthesis of IM550_Dupont._ The method used to synthesize IM550_Dupont is illustrated in Scheme 7.6. The trifluorovinyl coupling was achieved through the nucleophillic addition onto the vinyl group. The strong nucleophile was prepared by reacting the polyether oligomer with NaH for 5hrs in ACN after which the reaction vessel was cooled down to 0 ºC using ice bath. C was added drop-wise and the reaction was
allowed to continue until the $^{19}$F NMR reveals the disappearance of the vinylic fluorines at resonances

*Synthesis of $(\text{IM550})_2\text{Li}/(\text{IM350})_2\text{Li}$.* $(\text{IM550})_2\text{Li}$ was prepared by using PEGME of $M=550$ and $(\text{IM350})_2\text{Li}$ was prepared by using PEGME of $M=350$. Both are prepared similarly by reacting a mole of $D$ with two moles of deprotonated PEGME in ACN at 0 °C. The synthesis is illustrated in Scheme 7.7.

*Synthesis of $(\text{IM550})_{(\text{CF}_2)_3}$.* Scheme 7.8 illustrates the synthesis of $(\text{IM550})_{(\text{CF}_2)_3}$. $E$ was reacted in a 1:1 mole ratio with the deprotonated PEGME of $M=550$ in ACN at 0 °C.

\[
\begin{align*}
(R_i\text{SO}_2)_2\text{O} & \quad \text{liq. NH}_3 & \quad R_i\text{SO}_2\text{NH}_2 & \quad \text{Li(OH)}_2 & \quad R_i\text{SO}_2\text{NHLi} & \quad \text{HMDS} & \quad \text{ACN, reflux} \\
& \quad & \quad & \quad & \quad & \quad & \\
& \quad & \quad & \quad & \quad & \quad & \\
R_i\text{SO}_2\text{N}(\text{Li})\text{Si(CH}_3)_3 & \quad A \\
\end{align*}
\]

Scheme 7.1: Synthesis of $A$, $R_i\text{SO}_2\text{N}(\text{Li})\text{Si(CH}_3)_3$

\[
\begin{align*}
\text{CF}_2=\text{CF}-\text{O}-R_2\text{f}-\text{SO}_2\text{F} & \quad \text{liq. Br}_2 & \quad \text{CF}_2(\text{Br})\text{CF}(\text{Br})-\text{O}-R_2\text{f}-\text{SO}_2\text{F} & \quad B \\
\end{align*}
\]

Scheme 7.2: Synthesis of $B$, $\text{CF}_2(\text{Br})\text{CF}(\text{Br})\text{OR}_2\text{f}-\text{SO}_2\text{F}$

\[
\begin{align*}
\text{A} + \text{B} & \quad \text{ACN, reflux} & \quad \text{CF}_2(\text{Br})\text{CF}(\text{Br})-\text{O}-R_2\text{f}-\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{R}_f & \quad \text{Zn} & \quad \text{ACN, reflux} \\
& \quad & \quad & \quad & \quad & \\
\text{CF}_2=\text{CF}-\text{O}-R_2\text{f}-\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3 & \quad C \\
\end{align*}
\]

Scheme 7.3: Synthesis of $C$, $\text{CF}_2=\text{CFOR}_2\text{f}-\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$
Scheme 7.4: Synthesis of D, \((\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2)_2\text{Li}\)

\[
\begin{align*}
\text{B} + \text{NH}_3 & \rightarrow \text{BrCF}_2\text{CFBrOCF}_2\text{CF}_2\text{SO}_2\text{NH}_2 & \text{LiOH} & \rightarrow \text{BrCF}_2\text{CFBrOCF}_2\text{CF}_2\text{SO}_2\text{NHLi} \\
\text{HMDS} & \rightarrow \text{BrCF}_2\text{CFBrOCF}_2\text{CF}_2\text{SO}_2\text{NLiSi(\text{CH}_3)_3} & \text{B} & \rightarrow (\text{CFBrCFBr-O-CF}_2\text{CF}_2\text{SO}_2)_2\text{NLi} \\
\text{Zn} & \rightarrow (\text{CF}_2=\text{CF-O-CF}_2\text{CF}_2\text{SO}_2)_2\text{NLi} \\
& \text{D}
\end{align*}
\]

Scheme 7.5: Synthesis of E, \((\text{CF}_2=\text{CFOR}_2\text{SO}_2\text{N}((\text{CF}_2)_3\text{CF}_3)

\[
\begin{align*}
\text{C}_4\text{F}_9\text{SO}_2\text{F} & \xrightarrow{\text{liq. NH}_3} \text{C}_4\text{F}_9\text{SO}_2\text{NH}_2 & \text{Li(OH)}_2 & \rightarrow \text{C}_4\text{F}_9\text{SO}_2\text{NHLi} & \xrightarrow{\text{HMDS}} \text{C}_4\text{F}_9\text{SO}_2\text{N((Li)SO}_2\text{C}_4\text{F}_9 \\
& \text{ACN, reflux}
\end{align*}
\]

\[
\begin{align*}
\text{C}_4\text{F}_9\text{SO}_2\text{N(Li)Si(\text{CH}_3)_3} + \text{B} & \xrightarrow{\text{ACN, reflux}} \text{CF}_2(\text{Br})\text{CF(}\text{Br-}\text{O-R}_2\text{SO}_2\text{N(Li)SO}_2\text{C}_4\text{F}_9 \\
& \text{E}
\end{align*}
\]

Scheme 7.6: Synthesis of \((\text{IM550})_2\text{Li}\) and \((\text{IM350})_2\text{Li}\)

\[
\begin{align*}
\text{CH}_3(\text{OCH}_2\text{CH}_2^-)_{11.8}\text{OH} & \xrightarrow{\text{NaH}} \text{CH}_3(\text{OCH}_2\text{CH}_2^-)_{11.8}\text{O}^-\text{Na}^+ + \text{C} & \xrightarrow{\text{i)ACN, 0 }^\circ\text{C ii) } \text{H}_2\text{O}} \text{CH}_3(\text{OCH}_2\text{CH}_2^-)_{11.8}\text{O}^-\text{CFFH-O-CF}_2\text{CF(CF}_3^-\text{O-CF}_2\text{CF}_2\text{SO}_2\text{N(Li)SO}_2\text{CF}_3 \\
& \text{IM550}_\text{Dupont}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3(\text{OCH}_2\text{CH}_2^-)_{n}\text{OH} & \xrightarrow{\text{NaH}} \text{CH}_3(\text{OCH}_2\text{CH}_2^-)_{n}\text{O}^-\text{Na}^+ + 0.5 \text{D} & \xrightarrow{\text{i)ACN, 0 }^\circ\text{C ii) } \text{H}_2\text{O}} \text{CH}_3(\text{OCH}_2\text{CH}_2^-)_{n}\text{O}^-\text{CFHF-O-CF}_2\text{CF}_2\text{SO}_2\text{N(Li)SO}_2\text{CF}_2\text{CF}-\text{O-CH}_2\text{CH}_2\text{O})_n\text{CH}_3 \\
& \text{(IM550)}_2\text{Li, n = 11.8} \\
& \text{(IM350)}_2\text{Li, n = 7.2}
\end{align*}
\]

Scheme 7.7: Synthesis of \((\text{IM550})_2\text{Li}\) and \((\text{IM350})_2\text{Li}\)
Results and Discussion

$^1H$ and $^{19}F$ NMR spectra: The final compounds that were prepared and are listed in Table 7.1 were analyzed by NMR spectroscopy. Like IM550, the final product should show the absence of the vinylic fluorines from the $^{19}F$ NMR spectra and the appearance of the doublet of triplets, in the $^1H$ NMR spectra, for the H attached to the chiral C. Here, the $^1H$ and $^{19}F$ NMR spectra of IM550_Dupont are illustrated in Figure 7.1a and b respectively. The doublet of triplets at 6.1 and 6.3 ppm $^1H$ NMR spectra, and the singlets at -117 and -143 ppm in the $^{19}F$ NMR spectra confirm the reaction of the starting Dupont material with the deprotonated polyether oligomer. The $^1H$ NMR spectra is exactly the same as the one described for IM550. The only difference in the $^{19}F$ NMR spectra is the presence of the peaks designated to the –CF2-CF(CF3)- chain. Figure 7.1a shows the $^1H$ NMR spectrum of IM550_Dupont $\text{CaH}_3-(\text{OCbH}_2\text{CbH}_2)_{10.8}-\text{OCbH}_2\text{CcH}_2-O-\text{CF2CF(CF3)-O-}$

\[ \text{CH}_3-(\text{OCH}_2\text{CH}_2-)_{11.8}\text{OH} \xrightarrow{\text{NaH, ACN, RT}} \text{CH}_3-(\text{OCH}_2\text{CH}_2-)_{11.8}\text{O}^-\text{Na}^+ + \text{E} \]

\[ \xrightarrow{i) \text{ACN, 0} \text{oC} \]

\[ \xrightarrow{\text{ii) H}_2\text{O}} \text{CH}_3-(\text{OCH}_2\text{CH}_2-)_{11.8}\text{O-CF2CFH-O-CF2CF2SO}_2\text{N(Li)SO}_2\text{(CF}_2)_3\text{CF}_3 \]

Scheme 7.8: Synthesis of the IM550_(CF2)3
$^{h}\text{C}_2\text{F}_2\text{C}_i\text{F}_2\text{SO}_2\text{N(Li)}\text{SO}_2\text{C}_i\text{F}_3$ shows the following resonances, $\delta$(ppm, center of multiplet):

-83.0 (h, dd, $J=146.5$), -89.4 (f, m), -116.9 (i, s), -145.6 (g, m), -80.1 (j, s), -80.3 (m, s),

-79 (k, m), -145.4 (l, m).
Figure 7.1: (a) $^1$H NMR spectra (b) $^{19}$F NMR spectra of IM550_Dupont.
**LC analysis.** The purity of the materials was assessed by LC. Figure 7.2 shows a chromatogram of the IM550_Dupont with a retention peak of 51-52 minutes. No other peaks related to unmodified polyether were observed. The peak for the unmodified polyether comes at a retention of 32 minutes as it has been illustrated in chapter four. Therefore from the LC chromatogram, the purity of the material was confirmed.

![Figure 7.2: LC chromatogram for IM550_Dupont showing a single peak at a retention of 52 minutes](image)

**Ionic conductivities.** Figure 7.3 presents Arrhenius plots of log [ionic conductivity, κ (S/cm)] vs. 1000/[temperature, T (K)] for the ionic melts listed in Table 7.1. It can be clearly seen that the ionic conductivity did not improve by adding more fluorocarbon chains into the ionic melt electrolyte IM550. Still IM550 possesses relatively higher ionic conductivity values over the temperature range of RT-120 °C except for the room-temperature value of (IM350)$_2$Li. From the data, we assume that our materials follow the Walden rule [4] which if interpreted in the same manner as the Stokes-Einstein equation, the ionic conductivity of an ionic liquid is then directly
proportional to its density and inversely proportional to its formula weight and viscosity [5]. Equation 1 describes the Stokes-Einstein equation which states that the diffusion coefficient of a particle, $D_i$, in a free volume depends on the Boltzmann constant $k_B$, the absolute temperature $T$, the viscosity of the solution $\eta$, and the hydrodynamic radius $r_i$ of the particle.

$$D_i = \frac{k_B T}{6\pi \eta r_i}$$

Therefore, although the electron withdrawing fluorocarbon group increases the acidity of the imide anion and allows for better ion dissociation, it does not necessarily improve the ionic conductivity simply because of the increase in the viscosity of the material due to the increase in its molecular weight. Slight improvement was observed however for the room-temperature ionic conductivity of (IM350)$_2$Li if compared to the IM550.

Further explanation to the trend observed in the ionic conductivities can be obtained from DSC and the VTF model. Figure 7.4 shows the DSC thermograms from which the $T_g$ can be extracted. The thermogram for the IM550 has been reported in chapter 6. The $T_g$ values were then used to model the VTF parameters over the temperature range of RT-120 °C as has been described in chapters 5 and 6. The values of these parameters are summarized in Table 7.2 along with the standard deviation of $E_a$ for 95% confidence interval.

The lowest $T_g$ is exhibited by IM550_Dupont and that is caused by the branched fluorocarbon group in its structure. However, it has the highest activation energy causing
the drop in its ionic conductivity over the entire range of temperatures. IM550\(_{(\text{CF}_2)_3}\) shows similar \(T_g\) to that of IM550 but lower charge carrier concentrations and higher activation energy. The increase in activation energy was observed for both IM550_Dupont and IM50\(_{(\text{CF}_2)_3}\) which means that the added hydrophobic fluorocarbon groups to the IM550 structure diminished the segmental motion of the polymer and increased the viscosity of the material. All that contributed to lower ionic conductivities.

Regarding the (IM350)\(_2\)Li and (IM550)\(_2\)Li electrolytes, a totally different trend in the VTF parameters was observed. \(T_g\) is lower for (IM350)\(_2\)Li than that of (IM550)\(_2\)Li which explains the good ambient ionic conductivity for the former. The charge carrier concentration and the activation energy for the latter are lower due to its higher EO:Li ratio. The increase in the EO:Li ratio proved once again, as it has been shown for the mono-functional ionic melts, that the optimum ionic conductivity is achievable within a value close to 12. Over the entire temperature range, (IM350)\(_2\)Li displays poorer performance than IM550.
Figure 7.3: Arrhenius plots showing the temperature dependent ionic conductivities of the electrolytes listed in Table 7.1

Figure 7.4: DSC thermograms of the materials listed in Table 7.1
Table 7.2. DSC characteristics and VTF parameters for the ionic melts described in Table 7.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>A (S cm&lt;sup&gt;-1&lt;/sup&gt; (T/K)&lt;sup&gt;1/2&lt;/sup&gt;)</th>
<th>E&lt;sub&gt;a±σ&lt;/sub&gt; (kJ mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>EO/Li (at/at)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM550</td>
<td>-38</td>
<td>4.57</td>
<td>8.22±0.10</td>
<td>11.8</td>
</tr>
<tr>
<td>IM550_Dupont</td>
<td>-45</td>
<td>4.45</td>
<td>9.42±0.12</td>
<td>11.8</td>
</tr>
<tr>
<td>IM550_(CF&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-38</td>
<td>3.22</td>
<td>8.36±0.21</td>
<td>11.8</td>
</tr>
<tr>
<td>(IM550)&lt;sub&gt;2&lt;/sub&gt;Li</td>
<td>-35</td>
<td>0.87</td>
<td>7.14±0.23</td>
<td>23.6</td>
</tr>
<tr>
<td>(IM350)&lt;sub&gt;2&lt;/sub&gt;Li</td>
<td>-42</td>
<td>1.46</td>
<td>7.72±0.23</td>
<td>14.4</td>
</tr>
</tbody>
</table>

σ Errors corresponding to the standard deviation from the slope of linear regression

**Conclusions**

Several ionic melt electrolytes based on the sulfonimide lithium salt were prepared and characterized with respect to chemical structure, purity, ionic conductivities and thermal properties. It can be concluded that extending the fluoro-carbon chain does not enhance the ionic conductivities because it is hydrophobic and it increases the activation energy for ion conduction, and also the iso-fluoropropyl group in the DuPont material might have some hindrance effect with lithium coordination and lithium hopping. Delocalizing the negative charge of the imide anion over two oligo-ether chains decreases the activation energy but also decreases the charge carrier concentrations and thus causing a drop in the overall range of ionic conductivities.
References


CHAPTER EIGHT
SWAGE-STYLE ELECTROCHEMICAL CELL TESTING USING VARIOUS ELECTRODE AND ELECTROLYTE FORMULATIONS

Introduction

To fully characterize a lithium ion battery material, it is necessary to characterize it in a full or half cell configuration by employing an anode, a cathode and an electrolyte sandwiched in between. Several parameters define the performance of a lithium ion cell. Among the more important parameters are the following: cell capacity, cell energy, cycling efficiency, safety and cell power. All of these parameters depend upon the choice of electrode material, the separator and the electrolyte. The studies in this chapter will focus on the electrolyte part of the cell. The electrolytes that were studied are different formulations of those discussed in the previous chapters and specifically IM550. The electrode materials used are lithium, carbon, Li$_4$Ti$_5$O$_{12}$, and LiCoO$_2$.

Spinel Li$_4$Ti$_5$O$_{12}$ was introduced in the early 1990’s as a host material for lithium without creating any strain. Therefore it provides good reversibility without any structural changes during lithium intercalation and de-intercalation [1-3]. It accommodates lithium with a theoretical capacity of 175mAh/g as follows:

\[
\text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{e}^- + 3\text{Li}^+ \xleftrightarrow{\text{charge}} \text{Li}_7\text{Ti}_5\text{O}_{12}
\]
Its formal potential of lithium insertion is 1.55 V vs. Li/Li\(^+\) and thus the formation of the SEI layer is avoided since the reduction of most organic solvents in the electrolyte is between 0.8-0.9 V at the anode [4, 5]. This is an important feature for studying our ionic melt electrolytes as it avoids any concerns of lithium reactions and slow ion diffusion through the SEI under discharge circumstances. The only disadvantage of using this material as an anode is that it lowers the equilibrium potential difference of the lithium-ion cell. In case of a LiCoO\(_2\) cathode, that potential difference is around 2.4 - 2.5 V instead of 4.1 -4.2 V if carbon is used.

Carbon provides higher theoretical capacity than Li\(_4\)Ti\(_5\)O\(_12\) of around 380 mAh/g corresponding to the first stage of LiC\(_6\) graphite intercalation compound. The charge/discharge total reactions and the anode reaction based on Li\(^+\) intercalation and de-intercalation are as follows:

\[
\text{LiCoO}_2 + y\text{C} \underset{\text{discharge}}{\overset{\text{charge}}{\leftrightarrow}} \text{Li}_{1.5}\text{CoO}_2 + \text{Li}_y\text{C}_y
\]

\[
y\text{C} + x\text{Li}^+ + xe^- \underset{\text{discharge}}{\overset{\text{charge}}{\leftrightarrow}} \text{Li}_x\text{C}_y
\]

In this chapter, cell test data will be provided based on standard commercial electrolytes and the electrolytes that have been described in the previous chapters and especially the IM550 electrolyte.
Experimental

**Chemicals.** LiPF$_6$ (+99% purity) was purchased from Alfa Aesar and was handled inside an argon-filled dry box. Ethylene carbonate (EC), diethyl carbonate (DEC) and propylene carbonate (PC) were purchased from Ferro and stored inside an argon-filled dry box. PEGDME $M=500$g/mol was purchased from Sigma Aldrich and dried under vacuum prior to use. N-methylpyrrolidone (NMP) over molecular sieves was purchased from Sigma Aldrich. The PTFE-PFA type straight unions were purchased from Cole Parmer to be used for cell testing. LiCoO$_2$ powder (106 grade), graphite powder (LPG 320) and LHB-108P aqueous binder were purchased from Pred Materials. Carbon Black (Acetylene Black, 99.9%) was purchased from VWR. Stainless-steel (Alloy 20) current collectors in the form of metal rods were purchased from McMaster Carr. Li$_4$Ti$_5$O$_{12}$ electrode sheets coated on aluminum foil were provided by Hydro Quebec and were dried at 120 °C under vacuum prior to use. They consisted of a mixture of Li$_4$Ti$_5$O$_{12}$, carbon black, graphite and polyvinylidene fluoride (PVDF) as binder (the entire ensemble was 7 mils thick). Polypropylene/Polyethylene type separator (3400 grade) was purchased from Celgard. Fluorolink E of $M_w=1000$ was purchased from Solvay Solexis.

**Electrolyte Preparation.** 1M LiPF$_6$ in ethylene carbonate EC and diethyl carbonate DEC solvents was prepared inside an argon-filled dry box to avoid any salt hydrolysis and decomposition. 1.52 g of LiPF$_6$ (10 mmol) was dissolved in 1:1 (by volume) of EC and DEC (6.6 g of EC and 5mL of DEC). The importance of using carbonate solvents in binary electrolytes is attributed to the fact that EC forms stable films on the surface of Li or C, and DEC is good because of its low viscosity and its
contribution to good ionic conductivities and good performance at low temperatures \([6, 7]\). IM550 electrolyte with 20 wt\% and 50 wt\% of PEGDME plasticizer was prepared by mixing in dichloromethane solvent. The solvent was later evaporated and the mixture was dried under dynamic vacuum.

**Cathode Preparation.** First, in a beaker, 7 wt\% of binder was dissolved in NMP using a stir bar for 15 minutes. 88 wt\% LiCoO\(_2\) was then added to the solvent and was stirred for 15 minutes. Finally, 5 wt\% carbon black was added to the mixture and was again stirred for 15 minutes. The amount of solvent used was 10 times the weight of solid content. The composite cathode material was prepared in a similar manner except that the wt\% of binder was reduced to 4 \%, the wt\% of the LiCoO\(_2\) was reduced to 86 % and 5 % of partially fluorinated diol Fluorolink E, functionalized with the imide salt, was added along with binder in the very first step. The structure of the partially fluorinated polyether that is functionalized with a lithium sulfonimide salt is shown below and was prepared in DMF solvent by the same nucleophilic addition reaction described in previous chapters. The composite formulation offers better capacity utilization.

\[
XO-(\text{CH}_2\text{CH}_2\text{O})_n-\text{CH}_2\text{CF}_2\text{O}-(\text{CF}_2\text{CF}_2\text{O})_p-\text{(CF}_2\text{O})_q-\text{CF}_2\text{CH}_2-(\text{OCH}_2\text{CH}_2)_n-\text{OX}
\]

where X is \(-\text{CF}_2\text{CFH-O-CF}_2\text{CF}_2-\text{SO}_2\text{N(Li)SO}_2\text{CF}_3\), \(n=0.467\), \(p=5.897\), and \(q=1.474\)

**Anode Preparation.** In a beaker, 10 wt\% of binder was dissolved in NMP and was kept mixing using a stir bar for 15 minutes. 90 wt\% of graphite was then added and the mixture was stirred for another 15 minutes.
Electrochemical Cell Testing. Prior to any cell build, the stainless steel current collectors, used as both negative and positive collectors, were washed with water and acetone and dried at 120 °C for 20 minutes. The electrode slurries were mixed well prior to coating and then applied over the current collectors. The weight of the coating was calculated by subtracting the weight of the current collector before and after coating. The final weight should be taken after drying the coating in the vacuum oven at 150 °C under vacuum. The theoretical capacity was calculated based on the weight of active material of the cathode (LiCoO₂).

Cell assembly was done inside an argon-filled dry box. The separator was soaked in the electrolyte for couple of hours and was placed on top of the anode electrode previously coated on the ½” diameter stainless steel current collector. The cathode was coated on the 3/8” diameter stainless steel current collector. Both assemblies were then put inside a Teflon union and sealed. Cell formation is done after assembling. This involves charging the cell at a very low charge rate (e.g. C/100) until it reaches the target voltage.

Results and Discussion

Cell testing and experimental validation using standard electrolyte: Initially, some standard experiments were done with commercially used electrolytes to standardize the cell build and cell configuration. Those benchmark experiments are necessary to validate the results with our electrolytes.
A typical formation experiment for a lithium ion cell is shown in Figure 8.1 which is for a full cell employing a carbon anode, LiCoO₂ cathode and 1M LiPF₆ in EC: DEC (1:1 by volume). Figure 8.2 shows the current profile for that formation experiment which includes a C/100 charge followed by C/10 and then a potentiostatic charge down to C/20. Typical charge profile is shown in Figure 8.1 when LiCoO₂ cathode material is used. Preferably, the cut-off charge voltage is around 4.2 V. Beyond that voltage, the electrolyte will be more readily oxidized leading to thermal runaway.

Before building a full cell however, material balance is very important when designing a lithium ion cell. To determine that, one has to know the voltage profile for the cathodic half-cell reaction and the irreversible capacity related to the anode material which is mainly due to the SEI formation (only when graphite is used). The relationship between the cathode and anode capacities is as follows:

\[
\text{Cathode capacity} = \text{anode capacity} + \text{SEI layer capacity}
\]

The profiles for each half cell are shown in Figures 8.3 and 8.4. Figure 8.3 reveals the charge capacity of the LiCoO₂ cathode up to 4.2 V as the cutoff voltage. The cathode capacity is the limiting capacity that is considered when designing a lithium-ion cell. From Figure 8.3, the cathode capacity is calculated to be 138 mAh/g. From the half cell that uses C, Figure 8.4, the irreversible capacity can be calculated. In this case, the irreversible capacity is 20%. Preferably, very low irreversible capacity and very high reversible capacity should be obtained. For this type of graphite, the irreversible capacity matches the one reported from the supplier. Going back to the relationship between the
anode capacity and the cathode capacity, the anode capacity has to be 20% more than the cathode capacity in order for the cell to be balanced.

Figure 8.1: Lithium-ion cell charge profile up to 4.2 V cutoff for 1M LiPF₆ in 1:1 EC:DEC using C as the anode and LiCoO₂ as the cathode
Figure 8.2: Current profile for the formation experiment done on a lithium-ion cell having 1M LiPF$_6$ in 1:1 EC:DEC using C as the anode and LiCoO$_2$ as the cathode.

Figure 8.3: Half cell employing Li metal anode and LiCoO$_2$ cathode with 1M LiPF$_6$ in EC:DEC (1:1) as the electrolyte.
Figure 8.4: Half cell employing Li metal anode and C cathode with 1M LiPF$_6$ in EC:DEC (1:1) as the electrolyte.

Cycle performance of the cell is an important factor that needs to be looked at. Usually, the cell performance is plotted as the specific capacity (mAh/g) versus the cycle number. For the LiPF$_6$ system using LiCoO$_2$ cathode and carbon anode, the specific capacity is around 140 mAh/g at a C/5 discharge rate. Of course, the capacity for a fixed set of limiting cell voltages is dependant upon the discharge rate. Higher discharge rates usually cause a decrease in the cell capacity because of diffusion limitations and salt concentration polarization. Figure 8.5 shows the cycle performance of a lithium ion cell between 4.2 V and 2.5 V at a discharge rate of C/5 up to 10 cycles. From that plot, the specific discharge capacity can be calculated based on the weight of the active material in
the cathode. Figure 8.6 shows the specific discharge capacity of the cell versus the cycle number.

Figure 8.5: Cycle performance at a C/5 rate of 1M LiPF₆ in 1:1 EC:DEC using LiCoO₂ cathode and C anode
Figure 8.6: Specific capacity versus cycle number, obtained at C/5 rate for a lithium ion cell of 1M LiPF$_6$ in 1:1 EC:DEC using LiCoO$_2$ cathode and C anode

Cell test results on the IM550 electrolyte using standard LiCoO$_2$ cathode: The ionic melt electrolyte IM550 was studied extensively in different formulations to evaluate its performance in a lithium ion cell. Initially cells were built with only IM550 as the electrolyte, LiCoO$_2$ cathode and Li$_4$Ti$_5$O$_{12}$ anode. At a rate of C/100, the full theoretical cell capacity of 0.3mAh was not achieved. As shown in Figure 8.7, only 50% of the cell capacity was obtained. The electrolyte’s poor wetting properties with the separator and the poor lithium transport within the pores of the electrodes contributed to the capacity loss.
Cell test results on the IM550 electrolyte using LiCoO\textsubscript{2} composite cathode: Figure 8.8 shows the charge profile of IM550 in a cell consisting of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} anode and LiCoO\textsubscript{2} composite cathode. By incorporating a partially fluorinated polyether binder functionalized with a lithium sulfonimide salt, full capacity was achieved upon charging the cell at an initial rate of C/200 and then increasing it up to C/100 when half of the capacity was reached. After the cell was formed, it was then discharged at a rate of C/100 to obtain only 7% of the full cell capacity as shown in Figure 8.9. Low viscosity and large ohmic polarization contribute to capacity losses.
Figure 8.8: Charge profile for a cell consisting of IM550 as the electrolyte, Li$_4$Ti$_5$O$_{12}$ anode and LiCoO$_2$ composite cathode
Figure 8.9: Discharge profile at a C/100 rate for a cell consisting of IM550 as the electrolyte, Li$_4$Ti$_5$O$_{12}$ anode and LiCoO$_2$ composite cathode

**Cell test results on the IM550 electrolyte with solvating agents using standard LiCoO$_2$ cathode:** To improve the transport properties and decrease the ohmic losses, solvating agents were used. Figure 8.10 shows the cell performance upon 10 cycles at C/5 rate using the IM550 with different wt% of carbonate solvents (EC and DEC). The capacity is higher for the formulation with the higher wt% of carbonate mixtures. A combination of both higher ionic conductivity and lower viscosity would cause the improvement in the capacity. The discharge capacity is highly reversible at the C/5 rate for the electrolyte with 40 wt% carbonate solvents, but it is only 42 % of the theoretical capacity.
Figure 8.10: Specific capacity vs. cycle number, obtained at C/5 rate, for two electrolyte formulations of IM550 and carbonate solvents. Black circle is for electrolyte consisting of IM550 with 40 wt% EC:DEC (1:1) and the white circle is for the electrolyte consisting of IM550 with 20 wt% EC:DEC (1:1). Both electrolytes were studied in a cell using C as the anode and LiCoO₂ as the cathode.

*Cell test results on the IM550 electrolyte with PEGDME solvating agent:* Figure 8.11 shows the first lithium intercalation process into a Li₄Ti₅O₁₂ electrode using IM550 with 50 wt% PEGDME. The discharge was done at a C/100 rate for most of the experiment except at the very beginning where it was C/200 and C/150. 100 % capacity was achieved on the first discharge process. The theoretical capacity of the Li₄Ti₅O₁₂, as
has been reported by Hydro Quebec, is 0.842 mAh cm$^{-2}$. From Figure 8.11, the normalized capacity per active surface area was calculated to be 0.8 mAh cm$^{-2}$.

The same cell configuration was also studied at a higher rate of C/80, and again 100% discharge capacity was achieved. Figure 8.12 illustrates Li intercalation into and its de-intercalation from Li$_4$Ti$_5$O$_{12}$. Full capacity utilization was achieved in both processes.
Figure 8.12: Charge-discharge profiles at a C-rate of C/80 showing full capacity utilization for a cell consisting of IM550 + 50 wt% PEGDME as the electrolyte, Li anode and Li$_4$Ti$_5$O$_{12}$ cathode.

Figure 8.13 shows the performance of the above cell at higher discharge rates of C/60, C/50 and C/10. At C/60 discharge rate, the cell delivered 91% of its capacity, and delivered 33% and 1.4% of its capacity at C/50 and C/10 respectively.
Poor cycling performance at a C-rate of C/80 was also observed for the cell that consists of IM550 + 20 wt% PEGDME as the electrolyte, Li anode and Li$_4$Ti$_5$O$_{12}$ as the cathode as shown in Figure 8.14. Loss of activity of the active material of the Li$_4$Ti$_5$O$_{12}$ cathode due to slow Li diffusion or intercalation upon charging could possibly cause the observed loss in capacity [8]. This behavior was not observed with the similar cell where 50 wt% of PEGDME was used.
Figure 8.14: Cycling at RT of a cell having IM550 + 20 wt% PEGDME as the electrolyte, Li anode and Li₄Ti₅O₁₂ as the cathode

Cell test results on the IM550 electrolyte with PEGDME solvating agent and LiCoO₂ composite cathode: The plasticized ionic melt electrolyte with 50 wt% PEGDME was also studied in a cell that consists of a Li₄Ti₅O₁₂ anode and LiCoO₂ composite cathode. As has been shown with the pure IM550, capacity utilization was improved upon adding the functionalized binder into the cathode formulation. After the cell formation at a C/100 rate, the cell was cycled at a rate of C/20. The discharge capacity retained is 100% of the theoretical capacity and also 100% reversible capacity was achieved upon the three cycles as shown in Figure 8.15.
Figure 8.15: Cycling at a rate of C/20 for a cell consisting of IM550 + 50 wt% PEGDME as the electrolyte, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as the anode and composite $\text{LiCoO}_2$ as the cathode.

The performance of the above cell was studied at variant discharge C-rates of C/14, C/10, C/5 and 1C. The results obtained are shown in Figure 8.16 for the discharge rates of C/14, C/10 and C/5 and in Figure 8.17 for the discharge rate of 1C. 100 % capacity utilization was achieved for the C/14 and C/10 discharge rates, 82 % of the capacity was achieved at the C/5 rate and only 4 % of the capacity was achieved at 1C rate. The decrease in the capacity utilization at the higher discharge C-rates is due to larger initial ohmic drops and slow Li$^+$ transfer.
Figure 8.16: Cell voltage as a function of time for three different discharge C-rates done on a cell consisting of IM550 + 50 wt% PEGDME as the electrolyte, Li$_4$Ti$_5$O$_{12}$ as the anode and composite LiCoO$_2$ as the cathode.
Figure 8.17: Performance at a discharge rate of 1C for a cell consisting of IM550 + 50 wt% PEGDME as the electrolyte, Li$_4$Ti$_5$O$_{12}$ as the anode and composite LiCoO$_2$ as the cathode

Poor cycling performance at a C/80 rate was observed for the cell that consists of IM550 with 50 wt% PEGDME as the electrolyte, Li as the anode and LiCoO$_2$ composite cathode. Fading in capacity was observed immediately after the first discharge process as shown in Figure 8.18. If compared to the same cell that employed Li$_4$Ti$_5$O$_{12}$ anode, highly reversible capacity was achieved. The SEI formation on the Li anode surface could play a major contribution to such capacity losses.
Cell test results on the IM550 electrolyte with PEGDME solvating agent and C anode: The electrolyte formulation of IM550 with 50 wt% PEGDME was studied in a graphite and lithium cell. Usually, an OCV of more than 3.1 V is obtained upon fabricating the cell with lithium as the anode and C as the cathode. Figure 8.19 shows the fade in capacity upon the second lithium intercalation at a C-rate of C/100. On the first intercalation, only 42% of the specific theoretical capacity (380 mAh/g) was achieved. Upon the second intercalation, only 16% of the specific theoretical capacity was achieved. The decrease in capacity is likely caused by the formation of an SEI layer that contributes to a large irreversible capacity.
Figure 8.19: First and second specific discharge capacities at C/100 rate of a cell having IM550 with 50 wt% PEGDME as the electrolyte, Li as the anode and C as the cathode

Cell test results on the LiTFSI-in-PEGDME electrolyte: Figure 8.20 shows the effect of discharge rate on capacity utilization for a salt-in-solvent. 85% and 76% of the capacity was achieved at C/20 and C/10 respectively. Lower capacity utilization was achieved for the salt-in-solvent electrolyte than the IM550 with 50 wt% PEGDME electrolyte tested in the same cell configuration. Possible reasons for the improved performance of the solvated IM550 are lower concentration overpotentials as has been shown in Chapter six.
Conclusions

Cell test data using various electrolyte formulations and cell configurations were presented in this chapter. The use of Li₄Ti₅O₁₂ electrodes prove to be useful as they provide zero-strain lithium intercalation/de-intercalation and do not form SEI on their surfaces. Adding 50 wt% PEGDME into the IM550 electrolyte and using a binder functionalized with lithium sulfonimide salt are beneficial as they enhance the transport properties in the electrolyte and within the bulk of the electrodes.
References


