THE DESIGN AND USE OF REDOX ACTIVE IONIC ELECTROLYTES FOR THERMAL ENERGY HARVESTING

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M.Sc

Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

April 2017
DEAKIN UNIVERSITY
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Danah Al-Masri
List of publications


Abstract

The thermoelectrochemical cell (TEC) is a device capable of converting heat directly into electricity. This conversion of energy is based on the Seebeck effect: when a temperature gradient is applied across two identical electrodes in contact with a redox active electrolyte, a potential difference occurs. The magnitude of this potential depends on the Seebeck coefficient, $S_e$. The $S_e$ of a redox couple is related to the entropy change associated with the redox reaction, and is given by $S_e = \frac{\Delta V}{\Delta T}$.

Previous reports in this field primarily describe aqueous electrolytes with the ferri/ferrocyanide redox couple. In more recent reports, ionic liquids have been investigated as electrolytes to overcome the high temperature limitations and volatility problems associated with aqueous systems. A high entropy cobalt bipyridyl redox couple was used in the best performing ionic liquid-based thermoelectrochemical cell to date.

Ionic liquid-based electrolytes are being investigated for this application for their high boiling points, high thermal stability and wide electrochemical windows. Previous work in this group has demonstrated high Seebeck coefficients in ionic liquids using a cobalt bipyridyl (Co$^{2+/3+}$(bpy)$_3$) redox couple.

In this thesis, the factors affecting the TEC power and current outputs were investigated. The Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_{2/3}$ (NTf$_2$: bis(trifluoromethanesulfonylimide) redox complex was studied in a series of ionic liquid-organic solvent mixtures. The TEC performance was analysed with respect to the over-potentials limiting the performance. The diffusion coefficients of the redox species were measured in order to investigate the mass transport over-potential. The charge transfer resistances were measured in order to probe the charge transfer over-potential that relates to the catalytic properties of the TEC electrodes. Finally, the ionic conductivities of the electrolytes were measured to give insight into the role of ohmic over-potential in limiting the TEC performance.

The addition of high boiling point organic solvents to ionic liquids was investigated as a route to improving device performance. Organic solvents with high
boiling points were chosen to withstand the operation of the TEC at high temperatures. This solvent addition was found to reduce the mass transport limitations and increase the diffusion coefficients of the redox species. Further, the presence of the ionic liquid added ionic conductivity to the electrolyte, contributing to the higher performance. The addition of organic solvents was shown to increase the Seebeck coefficient of the Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} in most solvent systems, also contributing to the improved TEC performance. A 3:1 volume ratio of organic solvent to ionic liquid was found to achieve the highest TEC performance with the Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} complex. The good performance was attributed to high Seebeck coefficient and also a balance of favourable electrolyte properties.

The Seebeck coefficient of the Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} was investigated in a range of ionic liquids in order to probe the effect of solvent structure on this parameter. A series of imidazolium ionic liquids was investigated by systematically changing the anion or the alkyl side chain on the cation. The first Seebeck coefficient values of this redox couple in phosphonium ionic liquids were also determined. The size of the Seebeck coefficient was tentatively correlated to the hydrogen bonding capabilities of the solvent system. The Seebeck coefficient was found to be highest in both imidazolium and phosphonium ionic liquids containing sulfonate-based anions. The TEC performance of the phosphonium ionic liquids tested was found to be greatly limited by mass transport over-potential, consistent with the high viscosities and low diffusion coefficients. The addition of propylene carbonate was found to improve the TEC performance of both imidazolium and phosphonium ionic liquid systems at 1:1 volume mixture. However, a 3:1 propylene carbonate to ionic liquid mixture was needed for the phosphonium ionic liquids to reach a performance comparable to the imidazolium systems.

Finally, three cobalt redox complexes, Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3}, Co\textsuperscript{2+/3+}(Bupy-pz)\textsubscript{3} and Co\textsuperscript{2+/3+}(phen)\textsubscript{3}, were reported and compared to Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} in terms of the Seebeck coefficient and TEC performance. Small redox couple size was found to contribute to high Seebeck coefficient. The highest Seebeck coefficient to date in a non-aqueous redox electrolyte system was discovered with the Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} complex. The performance of Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} and Co\textsuperscript{2+/3+}(Bupy-pz)\textsubscript{3} was enhanced by incorporating
carbon-coated electrodes in the TEC, accredited to improved electrochemical reversibility and stability on carbon. This was consistent with the analysis of the couples by cyclic voltammetry in different solvents and with different electrodes, which predominantly showed improved reversibility on glassy carbon and carbon-slurry-coated electrodes. The performance of Co^{2+/3+}(py-pz)₃ and Co^{2+/3+}(Bupy-pz)₃ was also found to be concentration-dependent and the optimum concentration was identified to be 0.2M. On the other hand, the performances of the standard Co^{2+/3+}(bpy)₃ and the newly tested Co^{2+/3+}(phen)₃ were not significantly influenced by the electrode material or redox couple concentration.

To demonstrate longer-term device performance, power and current were continuously drawn from the TEC for 150 minutes. Good stability and no significant drop in performance was observed using either Co^{2+/3+}(bpy)₃ or the three new cobalt complexes. Further, carbon-coated stainless steel electrodes were successfully incorporated in the TEC, eliminating the use of platinum and considerably cutting the device cost.
# Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acknowledgments</td>
<td>III</td>
</tr>
<tr>
<td>List of publications</td>
<td>V</td>
</tr>
<tr>
<td>Abstract</td>
<td>VI</td>
</tr>
<tr>
<td>List of figures</td>
<td>XV</td>
</tr>
<tr>
<td>List of tables</td>
<td>XXIII</td>
</tr>
<tr>
<td>List of abbreviations</td>
<td>XXVII</td>
</tr>
<tr>
<td><strong>Chapter one: Introduction and literature review</strong></td>
<td></td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>2</td>
</tr>
<tr>
<td>1.1.1 Motivation</td>
<td>2</td>
</tr>
<tr>
<td>1.1.2 Waste heat and its recovery</td>
<td>2</td>
</tr>
<tr>
<td>1.1.3 Semiconductor thermoelectrics</td>
<td>3</td>
</tr>
<tr>
<td>1.1.4 Thermoelectrochemical cells</td>
<td>5</td>
</tr>
<tr>
<td>1.1.5 Ionic liquid based thermoelectrochemical cells</td>
<td>8</td>
</tr>
<tr>
<td>1.1.6 Research aims</td>
<td>10</td>
</tr>
<tr>
<td>1.1.7 Thesis structure</td>
<td>11</td>
</tr>
<tr>
<td>1.2 Literature review</td>
<td>12</td>
</tr>
<tr>
<td>2.1 Progress on thermoelectrochemical cells to date</td>
<td>12</td>
</tr>
<tr>
<td>1.2.1.1 The operating principles of thermoelectrochemical cells</td>
<td>12</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------------------</td>
</tr>
<tr>
<td>1.2.1.2</td>
<td>The roles of electrode materials and high surface area</td>
</tr>
<tr>
<td></td>
<td>electrodes</td>
</tr>
<tr>
<td>1.2.1.3</td>
<td>Cell orientation and heat convection</td>
</tr>
<tr>
<td>1.2.1.4</td>
<td>Capacitive systems</td>
</tr>
<tr>
<td>1.2.1.5</td>
<td>Redox couples</td>
</tr>
<tr>
<td>1.2.1.6</td>
<td>Redox couple concentration</td>
</tr>
<tr>
<td>1.2.1.7</td>
<td>Solid and quasi-solid state electrolytes</td>
</tr>
<tr>
<td>1.2.2</td>
<td>The Seebeck coefficient and reaction entropy</td>
</tr>
<tr>
<td>1.2.3</td>
<td>Background on polarity and the Kamlet-Taft parameters.</td>
</tr>
<tr>
<td>1.2.4</td>
<td>Ionic liquid electrolytes</td>
</tr>
<tr>
<td>1.2.5</td>
<td>Ionic liquid-electrolytes for thermoelectrochemical cells</td>
</tr>
<tr>
<td>1.2.6</td>
<td>Conclusions and literature gaps</td>
</tr>
</tbody>
</table>

**Chapter Two: Methodology**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Materials</td>
<td>52</td>
</tr>
<tr>
<td>2.1.1</td>
<td>Redox couples</td>
<td>52</td>
</tr>
<tr>
<td>2.1.2</td>
<td>Ionic liquids and solvents</td>
<td>54</td>
</tr>
<tr>
<td>2.1.3</td>
<td>Drying of ionic liquids</td>
<td>56</td>
</tr>
<tr>
<td>2.2</td>
<td>Experimental techniques</td>
<td>56</td>
</tr>
<tr>
<td>2.2.1</td>
<td>The Seebeck coefficient measurement</td>
<td>56</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Measurements of the Seebeck coefficient under dry conditions or with controlled water content.</td>
<td>57</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>----</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Thermoelectrochemical cell performance</td>
<td>58</td>
</tr>
<tr>
<td>2.2.4</td>
<td>The use of carbon coated electrodes</td>
<td>59</td>
</tr>
<tr>
<td>2.2.5</td>
<td>Cyclic voltammetry</td>
<td>59</td>
</tr>
<tr>
<td>2.2.6</td>
<td>Electrochemical impedance spectroscopy (EIS)</td>
<td>61</td>
</tr>
<tr>
<td>2.2.6.1</td>
<td>Measurement of electrolyte conductivity by EIS</td>
<td>63</td>
</tr>
<tr>
<td>2.2.6.2</td>
<td>Measurements of the charge transfer resistance by EIS</td>
<td>64</td>
</tr>
<tr>
<td>2.2.7</td>
<td>Diffusion coefficient measurements</td>
<td>65</td>
</tr>
<tr>
<td>2.2.8</td>
<td>Measurements of Kamlet-Taft parameters by UV-Visible spectroscopy</td>
<td>66</td>
</tr>
<tr>
<td>2.2.9</td>
<td>Theoretical calculation of redox couple radii.</td>
<td>69</td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td>70</td>
</tr>
</tbody>
</table>

**Chapter Three: The use of ionic liquids, high boiling point organic solvents and mixed electrolytes in thermoelectrochemical cells**

<table>
<thead>
<tr>
<th>3.1</th>
<th>Introduction</th>
<th>72</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>Materials and experimental methods</td>
<td>73</td>
</tr>
<tr>
<td>3.3</td>
<td>Results and discussion</td>
<td>74</td>
</tr>
<tr>
<td>3.3.1</td>
<td>The Seebeck coefficient of $\text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}<em>2)</em>{2/3}$ in $\text{C}_2\text{mim eFAP}$, $\text{C}_2\text{mim B(CN)}_4$ and their mixtures with solvents.</td>
<td>74</td>
</tr>
<tr>
<td>3.3.2</td>
<td>The effect on the Seebeck coefficient of the structure of a series of ionic liquids and their mixtures with DMSO.</td>
<td>77</td>
</tr>
<tr>
<td>3.3.3</td>
<td>The influence of water content on the Seebeck coefficient.</td>
<td>81</td>
</tr>
<tr>
<td>3.3.4</td>
<td>The relationship between Seebeck coefficient and Kamlet-Taft parameters.</td>
<td>83</td>
</tr>
<tr>
<td>3.3.5</td>
<td>The thermoelectrochemical cell performance.</td>
<td>87</td>
</tr>
<tr>
<td>3.3.6</td>
<td>The relationship between thermocell performance and electrolyte properties.</td>
<td>91</td>
</tr>
<tr>
<td>3.4</td>
<td>Conclusions.</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>References.</td>
<td>99</td>
</tr>
</tbody>
</table>

**Chapter Four: The effect of ionic liquid structure on the Seebeck coefficient.**

<p>| 4.1 | Introduction | 102 |
| 4.2 | Materials and experimental methods | 103 |
| 4.3 | Results and discussion | 104 |
| 4.3.1 | The effect of the structure of the imidazolium cation of the ionic liquid on the Seebeck coefficient of Co^{2+/3+}(bpy)<em>3(NTf2)</em>{2/3} | 104 |
| 4.3.2 | The TEC performance of the electrolyte systems. | 110 |
| 4.3.3 | Analyses of the TEC performance with respect to the ionic conductivity and the diffusion coefficient. | 113 |
| 4.3.4 | Application of phosphonium ionic liquids in thermocells | 117 |</p>
<table>
<thead>
<tr>
<th>4.4</th>
<th>Conclusions</th>
<th>123</th>
</tr>
</thead>
<tbody>
<tr>
<td>References</td>
<td>125</td>
<td></td>
</tr>
</tbody>
</table>

**Chapter Five: Investigation of cobalt-based redox couples for TEC applications**

<table>
<thead>
<tr>
<th>5.1</th>
<th>Introduction</th>
<th>128</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>Materials and experimental methods</td>
<td>130</td>
</tr>
<tr>
<td>5.3</td>
<td>Results and discussion</td>
<td>131</td>
</tr>
<tr>
<td>5.3.1</td>
<td>The effect of the structure of redox couple ligand on the Seebeck coefficient.</td>
<td>131</td>
</tr>
<tr>
<td>5.3.2</td>
<td>The TEC performance of the cobalt-based redox complexes</td>
<td>134</td>
</tr>
<tr>
<td>5.3.2.1</td>
<td>The TEC performance of the complexes in 3:1 DMSO:C$_2$H$_4$mim eFAP electrolyte</td>
<td>135</td>
</tr>
<tr>
<td>5.3.2.2</td>
<td>Device testing over an extended time period</td>
<td>136</td>
</tr>
<tr>
<td>5.3.2.3</td>
<td>The influence of solution conductivity and diffusion on TEC performance</td>
<td>138</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Study of the reversibility of the redox couples by cyclic voltammetry</td>
<td>139</td>
</tr>
<tr>
<td>5.3.3.1</td>
<td>An investigation of the reversibility of the redox couples on platinum and glassy carbon electrodes.</td>
<td>140</td>
</tr>
<tr>
<td>5.3.3.2</td>
<td>The reversibility of the redox complexes in different solvents.</td>
<td>142</td>
</tr>
<tr>
<td>5.3.3.3</td>
<td>The reversibility of the redox complexes on carbon slurry-coated electrodes.</td>
<td>144</td>
</tr>
<tr>
<td>5.3.4</td>
<td>TEC performance with carbon electrodes</td>
<td>149</td>
</tr>
<tr>
<td>5.3.5</td>
<td>Further device optimisation.</td>
<td>152</td>
</tr>
<tr>
<td>5.3.5.1</td>
<td>The effect of redox couple concentration on the Seebeck coefficient and TEC performance</td>
<td>152</td>
</tr>
<tr>
<td>5.3.5.2</td>
<td>The use of carbon-coated stainless steel electrodes</td>
<td>156</td>
</tr>
<tr>
<td>5.4</td>
<td>Conclusions.</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>160</td>
</tr>
</tbody>
</table>

**Chapter Six: Conclusions and future work**

| 6.1 | Thesis conclusions | 163 |
| 6.2 | Research aim one: Overcome mass-transport limitations during cell operation in IL electrolytes by investigating mixed solvent systems. | 163 |
| 6.3 | Research aim two: Investigate the effect of IL structure on the Seebeck coefficient and device performance. | 164 |
| 6.4 | Research aim three: Identify high Seebeck coefficient redox couples and investigate the effect of redox couple structure on thermocell performance. | 166 |
| 6.5 | Future work | 168 |
List of figures

Chapter One: Introduction and literature review

<table>
<thead>
<tr>
<th>Figure caption</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1 Schematic of the thermoelectric device, where V is the potential difference across the material. From F. J. DiSalvo, Science, 1999, 285, 703-706. Reprinted with permission from AAAS.</td>
<td>4</td>
</tr>
<tr>
<td>Figure 2 A schematic of a TEC with the ferri/ferrocyanide redox couple.</td>
<td>7</td>
</tr>
<tr>
<td>Figure 3 some of the ionic liquids reported in the literature for TEC application (a) 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (C2mim eFAP) (b) 1-ethyl-3-methylimidazolium tetracyanoborate (C2mim B(CN)4) (c) 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (C4mpyr NTf2) (d) 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C2mim NTf2).</td>
<td>9</td>
</tr>
<tr>
<td>Figure 4 The current-potential curve for an ideal TEC (dashed line) and a typical cell (solid line).</td>
<td>14</td>
</tr>
<tr>
<td>Figure 5 The three investigated cell orientations, a) cold above hot, b) hot above cold and c) Horizontal cell.</td>
<td>18</td>
</tr>
<tr>
<td>Figure 6 The wearable TEC fabricated by Yang et al. reprinted with permission from Yang, P., et al. (2016). Angew Chem Int Ed Engl 128(39): 12229-12232. copyright 2016 Wiley-VCH Verlag GmbH &amp; Co. KGaA, Weinheim</td>
<td>23</td>
</tr>
<tr>
<td>Figure 7 Splitting of the d orbitals of the cobalt complex.</td>
<td>26</td>
</tr>
<tr>
<td>Figure 8 Reaction entropy in water vs $Z_{ox}^2 - Z_{red}^2$. Reprinted with permission from: J. T. Hupp and M. J. Weaver, Inorganic Chemistry, 1984, 23, 3639-3644. Copyright (1984) American Chemical Society. Key to redox couples: (1) Fe(CN)3/4-, (2) Fe(CN)6bpy/2- (3) ferrocenium/ferrocene, (4) Cr(bpy)3/2+, (5) Ru(NH3)5Cl2+/3+, (6) Ru(NH3)5NCS2+/+ (7) Ru(en)33+/2+ (8) Ru(NH3)63+/2+.</td>
<td>28</td>
</tr>
</tbody>
</table>
**Figure 9** Reaction entropies of some redox couples vs solvent acceptor number for some organic solvents reported by Hupp et al." Reprinted with permission from: J. T. Hupp and M. J. Weaver, Inorganic Chemistry, 1984, 23, 3639-3644. Copyright (1984) American Chemical Society. (*) Ru(NH₃)₆³⁺/²⁺, (▾) ferrocenium/ferrocene, (■) Ru(en)₃³⁺/²⁺, (▲) Cr(bpy)₃³⁺/²⁺, (□) ferrocene/ferrocenium in C₄mPyr NTf₂ reported by Migita et al."³⁰.

**Figure 10** The structure of 4-nitroaniline in its ground and excited states. Adapted with permission from Kamlet, M. J. and R. W. Taft (1976), Journal of the American Chemical Society 98(2): 377-383. Copyright (1976) American Chemical Society.

**Figure 11** Solvatochromic comparison of 4-nitroaniline (1) and N,N-diethyl-4-nitroaniline (2) UV spectral data. Reprinted with permission from Kamlet, M. J. and R. W. Taft (1976), Journal of the American Chemical Society 98(2): 377-383. Copyright (1976) American Chemical Society.

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**Chapter Two: Methodology**

**Figure 1** The cations and anions of the ionic liquids used in this thesis. (a) 1-ethyl-3-methylimidazolium (C₃mim), (b) 1-ethyl-2,3-dimethylimidazolium (C₂dmim), (c) 1-butyl-3-methylimidazolium (C₄mim), (d) 1-hexyl-3-methylimidazolium (C₆mim) (e) triethyl(butyl)phosphonium (P₂,₂,₂,₄), (f) 1-(2-Methoxyethyl)-1-methylpyrrolidinium ((MeOEt)mPyr) (g) tris(pentafluoroethyl)trifluorophosphate (eFAP), (h) bis(trifluoromethanesulfonylimide (NTf₂), (i) tetracyanoborate (B(CN)₄), (j) methanesulfonate (MeSO₃) (k) p-toluenesulfonate, (l) trifluoromethanesulfonate (OTf), (m) trihexyl(tetradecyl)phosphonium (P₆,₆,₆,₁₄) and (n) tetrafluoroborate (BF₄).

**Figure 2** The setup used to dry ionic liquids.

**Figure 3** A schematic of the Seebeck coefficient measurement setup.

**Figure 4** The thermoelectrochemical cell setup schematic and photographs.
Figure 5 (a) A schematic of the three electrode experimental set up for cyclic voltammetry (CV) and (b) a CV of Co$_{2+}^{+3+}$(bpy)$_{3}$(NTf$_{2}$)$_{2/3}$ in neat [C$_{2}$mim][NTf$_{2}$]. Reproduced from Abraham, T. J., et al. (2013). Energy & Environmental Science 6(9): 2639. With permission of the Royal Society of Chemistry.

Figure 6 A Nyquist plot obtained from electrical impedance spectroscopy (EIS) for 5mM Co$_{2+}^{+3+}$(bpy)$_{3}$ in C$_{2}$mim eFAP. Parts of the figure were reproduced from A. J. Bard and L. R. Faulkner, Electrochemical methods: fundamentals and applications, Wiley New York, 1980. With permission from John Wiley & Sons, Inc. Copyright 2001 ©.

Figure 7 The dip cell used to measure the electrolyte conductivity by EIS, and the brass block with a cartridge heater used to control the electrolyte temperature.

Figure 8 (a) A typical Chronaomperometry plot obtained for 0.1 M Co$_{2+}^{+3+}$(bpy)$_{3}$ redox couple, when a positive potential was applied and the resulting current can be attributed to the diffusion of the Co$_{2+}^{+3+}$(bpy)$_{3}$. (b) A cyclic voltammetry of the same redox couple showing the depletion regions.

Figure 9 A schematic showing the dimensions of the UV-Vis cuvettes used (Left) and an example of a Uv-Vis spectrum obtained from 4,4-diethyl-4-nitroanaline dissolved in acetonitrile (Right).

Chapter Three: The use of ionic liquids, high boiling point organic solvents and mixed electrolytes in thermoelectrochemical cells

Figure 1 The Seebeck coefficient vs (a) volume ratio and (b) molar ratio of the ionic liquid/solvent electrolyte systems containing 0.1 M Co$_{2+}^{+3+}$(bpy)$_{3}$(NTf$_{2}$)$_{2/3}$.

Figure 2 The structure of tris(pentafluoroethyl)trifluorophosphate (eFAP) (Left) and trifluoromethanesulfonate (OTf) (Right).
**Figure 3** The Seebeck coefficient of the Co\(^{2+/3+}\)(bpy)\(_3\)(NTf\(_2\))\(_{2/3}\) redox couple, at 0.01M, as a function of volume percentage of DMSO in; 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [C\(_2\)mim][eFAP]; 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, [C\(_2\)mim][OTf]; 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate [C\(_4\)mpyr][eFAP]; 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [C\(_6\)mim][eFAP]; and 1-(2-methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate [(MeOEt)mPyr][eFAP].

**Figure 4** The Seebeck coefficient of 0.1M Co\(^{2+/3+}\)(bpy)\(_3\)(NTf\(_2\))\(_{2/3}\) in (a) the C\(_2\)mim eFAP:DMSO electrolyte either measured in air (red) or under dry conditions and (b) in neat DMSO, as a function of water content. The complex was not soluble at this concentration in the dry neat C\(_2\)mim eFAP and so no data is available for this system.

**Figure 5** The Kamlet-Taft parameters of the DMSO:C\(_2\)mim eFAP electrolyte mixtures vs the corresponding Seebeck coefficient measured under dry conditions. Measurements of the Seebeck coefficient under dry conditions are discussed in section 3.3.

**Figure 6** (a) the power density and (b) the current density vs cell potential of all MPN-C\(_2\)mim (B(CN)\(_4\)) electrolyte systems, and (c) the power density and (d) current density vs cell potential of all DMSO-C\(_2\)mim eFAP electrolyte systems.

**Figure 7** (a) The maximum power and current density vs DMSO volume percentage in C\(_2\)mim eFAP and (b) the maximum power and current density vs MPN volume percentage in C\(_2\)mim B(CN)\(_4\).
**Figure 8** The ionic conductivity ($\kappa$) and corresponding solution resistance ($R_{sol}$), in addition to the charge transfer resistance ($R_{CT}$), for (a) MPN-C$_2$mim B(CN)$_4$ electrolyte systems and (b) DMSO- C$_2$mim eFAP electrolyte systems, at 95°C.

**Figure 9** The diffusion coefficients of Co$^{2+}$(bpy)$_3$ and Co$^{3+}$(bpy)$_3$ in DMSO-C$_2$mim eFAP and MPN-C$_2$mim B(CN)$_4$ systems at 95°C, calculated using Cottrell’s equation. Experimental details are shown in chapter two, section 2.7.

### Chapter Four: The effect of ionic liquid structure on the Seebeck coefficient.

**Figure 1** The imidazolium cation where, R and R' are alkyl chains.

**Figure 2** The structure of methanesulfonate MeSO$_3$ (left) and trifluoromethanesulfonate OTf (right) anions.

**Figure 3** The locations of possible hydrogen bond formation in 1,2,3-trimetylimidazolium (C$_3$dmim) (left) and 1-ethyl-3-methylimidazolium (C$_2$mim) (right). Reproduced from K. Fumino et al., Physical Chemistry Chemical Physics, The influence of hydrogen bonding on the physical properties of ionic liquids, 2011, 13, 14064-14075. with permission from the PCCP Owner Societies.

**Figure 4** The structure of 1-butyl-2,3-dimethylimidazolium (left) and 1-butyl-3-methylimidazolium (right).

**Figure 5** (a) The power density and (b) the current density obtained from 0.01M Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_2$/3 in the neat imidazolium ionic liquids. (c) The power density and (d) the current density obtained from 0.01M Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_2$/3 in the 1:1 volume mixtures of the imidazolium ionic liquids with propylene carbonate. The cold and hot electrode temperatures were 30°C and 60°C respectively.

**Figure 6** The Nyquist plots obtained by electrical impedance spectroscopy (EIS) for all electrolyte systems at room temperature.
Figure 7 The structure of (a) trihexyl(tetradecyl)phosphonium \( P_{6,6,6,14} \) (b) triethyl( butyl)phosphonium \( P_{2,2,2,4} \), (c) bis(trifluoromethanesulfonylimide, \( \text{NTf}_2 \), (d) tetrafluoroborate, \( \text{BF}_4 \), (e) \( p \)-toluenesulfonate (Tos) and (f) methanesulfonate (\( \text{MeSO}_3 \)).

Figure 8 (a) the power density and (b) the current density of 0.01M \( \text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_{2/3} \) in the 1:1 volume mixtures of phosphonium ionic liquid and propylene carbonate. (c) The power density and (d) the current density of 0.01M \( \text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_{2/3} \) in the 3:1 volume mixtures of propylene carbonate to phosphonium ionic liquids. The cold and hot electrode temperatures were 30°C and 60°C respectively. 1:3 IL:PC data was obtained by Dr. JiangJing He.

Figure 9 The Nyquist plots obtained from EIS of the three phosphonium ionic liquid systems containing 0.01M \( \text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_{2/3} \) at room temperature.

**Chapter Five: Investigation of cobalt-based redox couples for TEC applications**

Figure 1 The structure of the redox complexes reported in this chapter (a) \( \text{Co}^{2+/3+}(\text{phen})_3(\text{NTf}_2)_2 \), (b) \( \text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_3 \), (c) \( \text{Co}^{2+/3+}(\text{py}-\text{pz})_3(\text{NTf})_{2/3} \), (d) \( \text{Co}^{2+/3+}(\text{Bupy}-\text{pz})_3(\text{NTf}_2)_{2/3} \).

Figure 2 (a) The measured power density (data points) and the fitted power density (dashed line) obtained from the TEC .(b) The current density obtained from the TEC of the four redox couples at 0.1M concentration in 3:1 DMСO:С₂мим eFAP electrolyte. The electrode temperatures were \( T_{\text{cold}}= 30°C \) and \( T_{\text{hot}} = 60°C \).

Figure 3 (a) The maximum power density, (b) maximum current density and (c) cell potential vs time for the four redox complexes at 0.1M concentration in 3:1 DMСO:С₂мим eFAP. The electrode temperatures were \( T_{\text{cold}}= 30°C \) and \( T_{\text{hot}} = 60°C \).
Figure 4 The cyclic voltammograms of the redox complexes at 0.1M concentration in 3:1 DMSO:C₂mim eFAP, (a) Co²⁺/³⁺(bpy)₃, (b) Co²⁺/³⁺(Bupy-pz)₃, (c) Co²⁺/³⁺(phen)₃ and (d) Co²⁺/³⁺(py-pz)₃. PP separation is the difference between the potential values where maximum current was observed for the oxidation and reduction processes. The working electrode was platinum, with geometric surface area of 2.0mm². *Cyclic voltammograms in the 3:1 DMSO:C₂mim eFAP were conducted under atmospheric conditions.

Figure 5 The cyclic voltammograms of the redox complexes at 0.1M concentration in 3:1 DMSO:C₂mim eFAP, (a) Co²⁺/³⁺(bpy)₃, (b) Co²⁺/³⁺(Bupy-pz)₃, (c) Co²⁺/³⁺(phen)₃ and (d) Co²⁺/³⁺(py-pz)₃. The working electrode was glassy carbon with geometric surface area of 2.0mm². *Cyclic voltammograms in the 3:1 DMSO:C₂mim eFAP were conducted under atmospheric conditions.

Figure 6 The cyclic voltammogram of the Co²⁺/³⁺(py-pz)₃ at 5mM concentration in (a) C₂mim eFAP and (b) C₂mim NTf₂, using glassy carbon (GC) working electrode.

Figure 7 The cyclic voltammograms of the Co²⁺/³⁺(py-pz)₃ at 5mM concentration in (a) C₂mim eFAP and (b) C₂mim NTf₂ using a platinum working electrode.

Figure 8 The cyclic voltammograms of 5mM Co²⁺/³⁺(bpy)₃ in neat C₂mim eFAP at 50 mV/s scan rate vs Pt pseudo reference electrode on the following working electrodes: (a) glassy carbon, (b) platinum, (c) carbon-coated glassy carbon and (d) carbon-coated platinum.

Figure 9 The cyclic voltammograms of 5mM Co²⁺/³⁺(py-pz)₃ in neat C₂mim eFAP at 50 mV/s scan rate vs Pt pseudo reference electrode on the following working electrodes: (a) glassy carbon, (b) platinum, (c) carbon-coated glassy carbon and (d) carbon-coated platinum.
**Figure 10** The cyclic voltammograms of 5mM Co$^{2+/3+}$(Bupy-pz)$_3$ in neat C$_2$mim eFAP at 50 mV/s scan rate vs Pt pseudo reference electrode on the following working electrodes: (a) glassy carbon, (b) platinum, (c) carbon-coated glassy carbon and (d) carbon-coated platinum. The Co$^{2+/3+}$(phen)$_3$ redox complex was tested in a 9:1 C$_2$mim eFAP : DMSO solvent system because of poor solubility in neat C$_2$mim eFAP.

**Figure 11** The cyclic voltammograms of 5mM Co$^{2+/3+}$(phen)$_3$ in 9:1 C$_2$mim eFAP : DMSO at 50 mV/s scan rate vs Pt pseudo reference electrode on the following working electrodes: (a) glassy carbon, (b) platinum, (c) carbon-coated glassy carbon and (d) carbon-coated platinum.

**Figure 12** (a) The measured power density (data points) and the fitted power density (dashed line) and (b) the current density obtained from the TEC at 0.1M concentration in 3:1 DMSO:C$_2$mim eFAP using carbon-coated platinum disc electrodes. The electrode temperatures were $T_{cold}=30^\circ$C and $T_{hot}=60^\circ$C. *The electrode temperatures were $T_{cold}=30^\circ$C and $T_{hot}=62^\circ$C when the Co$^{2+/3+}$(bpy)$_2$ was tested, to compensate for the unwanted temperature drop across the electrode that occurred due to the presence of the carbon layer. The internal temperature gradient was evaluated by measuring the open circuit potential, which corresponds to the Seebeck coefficient.

**Figure 13** (a) The maximum power density obtained from each electrolyte system vs redox couple concentration. The electrode temperatures were $T_{cold}=30^\circ$C and $T_{hot}=60^\circ$C. (b) The Seebeck coefficient vs concentration of the four redox complexes.

**Figure 14** (a) The measured power density (data points) and the fitted power density (dashed line) and (b) The current density obtained from the TEC of Co$^{2+/3+}$(py-pz)$_3$ at 0.1M concentration in 3:1 DMSO:C$_2$mim eFAP using carbon-coated platinum disc electrodes, carbon-coated stainless steel (SS) disc electrodes and bare platinum disc electrodes (Pt). The electrode temperatures were $T_{cold}=30^\circ$C and $T_{hot}=60^\circ$C.
List of tables

Chapter one: Introduction and literature review

<table>
<thead>
<tr>
<th>Table caption</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Table 1</strong> some ILs containing the common cation 1-ethyl-3-methylimidazolium, and their electrochemical properties [^87,88] where, C\textsubscript{2}mim OTf is 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, C\textsubscript{2}mim NTf\textsubscript{2} is 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, C\textsubscript{2}mim eFAP is 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate and C\textsubscript{2}mim B(CN)\textsubscript{4} is 1-ethyl-3-methylimidazolium tetracyanoborate.</td>
<td>36</td>
</tr>
<tr>
<td><strong>Table 2</strong> The Seebeck coefficient (S\textsubscript{e}) and entropy change, $\Delta S_{rc}$ of 0.1M Co\textsuperscript{2+/3+}(bpy)\textsubscript{3}(NTf\textsubscript{2})\textsubscript{2/3} redox couple in ILs containing the following cations: 1-ethyl-3-methylimidazolium [C\textsubscript{2}mim], 1-butyl-1-methylpyrroldinium [C\textsubscript{4}mpyr] and 1-butyl-1-methylimidazolium [C\textsubscript{4}mim]; and the following anions: tris(pentafluoroethyl)trifluorophosphate [eFAP], bis(trifluoromethanesulfonate)imide [NTf\textsubscript{2}] also known as [C\textsubscript{2}mim], tetracyanoborate [B(CN)\textsubscript{4}] and tetrafluoroborate [BF\textsubscript{4}] and the organic solvent methoxypropionitrile (MPN).[^18] Reproduced from Abraham, T. J., et al. (2013). Energy &amp; Environmental Science 6(9): 2639. With permission of the Royal Society of Chemistry.</td>
<td>39</td>
</tr>
<tr>
<td><strong>Table 3</strong> The power output of the TEC with 0.1 M Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} redox couple in ILs and MPN. The key to ILs can be found in Table 2.[^10] Reproduced from Abraham, T. J., et al. (2013). Energy &amp; Environmental Science 6(9): 2639. With permission of the Royal Society of Chemistry.</td>
<td>41</td>
</tr>
</tbody>
</table>
Chapter Three: The use of ionic liquids, high boiling point organic solvents and mixed electrolytes in thermoelectrochemical cells

Table 1 The Seebeck coefficient vs volume ratio of the ionic liquid/solvent electrolyte systems containing 0.10M Co\(^{2+/3+}\)(bpy)\(_3\)(NTf\(_2\))\(_{2/3}\).

Table 2 The Seebeck coefficients of Co\(^{2+/3+}\)(bpy)\(_3\)(NTf\(_2\))\(_{2/3}\) at 0.01M concentration in a range of ionic liquids and their mixtures with DMSO.

Table 3 The Seebeck coefficients and Kamlet-Taft parameters of 0.1M Co\(^{2+/3+}\)(bpy)\(_3\) in the DMSO:C\(_2\)mim eFAP electrolyte systems under dry conditions. *measured in water saturated C\(_2\)mim eFAP because of poor solubility in the dry sample. **Reichardts dye (needed for \(\alpha\)) is not soluble in DMSO and so standard procedure is to set \(\alpha\) to 0 when DMSO is used as a reference solvent.

Table 4 The Kamlet-Taft parameters of the four neat ionic liquids and the corresponding Seebeck coefficients. *The Seebeck coefficient was measured under atmospheric conditions. **This value was measured by Prof. Tom Welton’s group in Imperial College London, using the same procedure.

Table 5 The maximum TEC power and current densities for all electrolyte systems.

Table 6 The measured values of the solution resistance (\(R_{sol}\)), charge transfer resistance (\(R_{CT}\)) and ionic conductivity (\(\kappa\)) of all electrolyte systems.

Table 7 The diffusion coefficient of Co\(^{2+}\)(bpy)\(_3\) and Co\(^{3+}\)(bpy)\(_3\) in all electrolytes, measured at 95°C.

Chapter Four: The effect of ionic liquid structure on the Seebeck coefficient.
Table 1 The Seebeck coefficient of 0.01M Co\textsuperscript{2+/3+}(bpy)\textsubscript{3}(NTf\textsubscript{2})\textsubscript{2/3} in a range of ionic liquids containing the imidazolium cation. \textsuperscript{a}Solid at room temperature. \textsuperscript{b}Redox couple partially or completely insoluble at room temperature.

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The Seebeck coefficient of 0.01M Co\textsuperscript{2+/3+}(bpy)\textsubscript{3}(NTf\textsubscript{2})\textsubscript{2/3} in a range of ionic liquids containing the imidazolium cation. \textsuperscript{a}Solid at room temperature. \textsuperscript{b}Redox couple partially or completely insoluble at room temperature.</td>
<td>105</td>
</tr>
<tr>
<td>2</td>
<td>The measured Kamlet-Taft parameters for the ionic liquids C\textsubscript{4}mim NTf\textsubscript{2} and C\textsubscript{4}dmim NTf\textsubscript{2}. \textsuperscript{*}This was measured by a postdoctoral research fellow at Prof. Tom Welton’s group at Imperial College London using the same procedure.</td>
<td>109</td>
</tr>
<tr>
<td>3</td>
<td>The maximum power density from 0.01M Co\textsuperscript{2+/3+}(bpy)\textsubscript{3}(NTf\textsubscript{2})\textsubscript{2/3} in the neat ionic liquids and their 1:1 volume mixtures with propylene carbonate. The cold and hot electrode temperatures were 30°C and 60°C respectively. \textsuperscript{a}Solid at room temperature.</td>
<td>112</td>
</tr>
<tr>
<td>4</td>
<td>The diffusion coefficients of the Co\textsuperscript{2+}(bpy)\textsubscript{3} and Co\textsuperscript{3+}(bpy)\textsubscript{3} redox species in the neat ionic liquids and their 1:1 volume mixtures with propylene carbonate. The measurements were performed at room temperature. \textsuperscript{a}Solid at room temperature.</td>
<td>114</td>
</tr>
<tr>
<td>5</td>
<td>The ionic conductivity of 0.01M Co\textsuperscript{2+/3+}(bpy)\textsubscript{3}(NTf\textsubscript{2})\textsubscript{2/3} in the neat ionic liquids and their 1:1 volume mixtures with propylene carbonate at room temperature. \textsuperscript{*}Solid at room temperature.</td>
<td>116</td>
</tr>
<tr>
<td>6</td>
<td>The Seebeck coefficient of 0.01M Co\textsuperscript{2+/3+}(bpy)\textsubscript{3}(NTf\textsubscript{2})\textsubscript{2/3} in 1:1 mixtures of the phosphonium ILSs with propylene carbonate. \textsuperscript{*}1:3 IL:PC data was obtained by Dr. JiangJing He.</td>
<td>119</td>
</tr>
<tr>
<td>7</td>
<td>The maximum power density of 0.01M Co\textsuperscript{2+/3+}(bpy)\textsubscript{3}(NTf\textsubscript{2})\textsubscript{2/3} in the 1:1 and 3:1 volume mixtures of propylene carbonate to phosphonium ionic liquid. The electrode temperatures were set to 30°C and 60°C. \textsuperscript{*}1:3 IL:PC data was obtained by Dr. JiangJing He.</td>
<td>121</td>
</tr>
<tr>
<td>8</td>
<td>The ionic conductivity of the 1:1 volume mixtures of phosphonium ILSs and propylene carbonate.</td>
<td>122</td>
</tr>
</tbody>
</table>

XXV
Chapter Five: Investigation of cobalt-based redox couples for TEC applications

**Table 1** The complex radii and Seebeck coefficient of 0.1M $\text{Co}^{2+/3+}\text{(bpy)}_3\text{(NTf}_2\text{)}_3$, $\text{Co}^{2+/3+}\text{(phen)}_3\text{(NTf}_2\text{)}_2$, $\text{Co}^{2+/3+}\text{(py-pz)}_3\text{(NTf)}_2\text{/3}$, and $\text{Co}^{2+/3+}\text{(Bupy-pz)}_3\text{(NTf)}_2\text{/3}$ in 3:1 $\text{C}_{2}\text{mim eFAP : DMSO}$ and in neat DMSO. Radius error values were calculated by measuring the radius from three different points corresponding to the three ligands in each complex.

**Table 2** The maximum power density obtained from the different redox couples in 3:1 DMSO:$\text{C}_{2}\text{mim eFAP}$ and the total cell resistance obtained from fitting the power density vs cell potential curves.

**Table 3** The ionic conductivity, diffusion coefficient of $\text{Co}^{3+}$ and charge transfer resistance of the redox complexes in 3:1 DMSO:$\text{C}_{2}\text{mim eFAP}$ at room temperature (22°C).

**Table 4** The maximum power density obtained for the TEC from the four redox couples at 0.1M concentration in 3:1 DMSO:$\text{C}_{2}\text{mim eFAP}$ using carbon-coated platinum disc electrodes, and bare platinum disc electrodes, and the resistance of the cell with the carbon-coated platinum disc electrodes. The electrode temperatures were $T_{\text{cold}}=30°C$ and $T_{\text{hot}}=60°C$. *The electrode temperatures were set to $T_{\text{cold}}=30°C$ and $T_{\text{hot}}=62°C$ when the $\text{Co}^{2+/3+}\text{(bpy)}_2$ was tested on carbon-coated platinum to compensate for a loss of temperature gradient.

**Table 5** The maximum power density, cell resistance and Seebeck coefficient obtained at different concentrations of redox couple for all electrolyte. The electrode temperatures were $T_{\text{cold}}=30°C$ and $T_{\text{hot}}=60°C$.

**Table 6** The maximum power density obtained from the TEC using $\text{Co}^{2+/3+}\text{(py-pz)}_3$ at 0.1M concentration in 3:1 DMSO:$\text{C}_{2}\text{mim eFAP}$. The electrode materials used
carbon-coated platinum disc electrodes or bare platinum disc electrodes. The electrode temperatures were \( T_{\text{cold}} = 30^\circ\text{C} \) and \( T_{\text{hot}} = 60^\circ\text{C} \). The cell resistance \( R_{\text{cell}} \) was calculated from the fitted values of maximum power density and cell potential.

### List of abbreviations

<table>
<thead>
<tr>
<th>Term</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermoelectrochemical cell</td>
<td>TEC</td>
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<tr>
<td>The Seebeck coefficient</td>
<td>( S_e (\text{mV/K}) )</td>
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<tr>
<td>Reaction entropy</td>
<td>( \Delta S_{\text{RC}} (\text{J/K.mol}) )</td>
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<td>IL</td>
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<td>(MeOEt)mPyr</td>
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<td>1-butyl-1-methylpyrrolidinium</td>
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<td>Compound</td>
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</tr>
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<td>ACN</td>
</tr>
</tbody>
</table>
Chapter one

Introduction and literature review
1.1 Introduction

1.1.1 Motivation

In December 2015 the first legally binding agreement was reached to reduce climate change at the climate change conference COP21 held in Paris, France. During the proceedings, 196 countries agreed to limit the global temperature rise to no more than 2°C. The signing countries pledged to reduce their greenhouse gas emissions contributing to climate change. Reaching the goals of the Paris agreement would require significantly decreasing the global reliance on fossil-fuel derived energy. Recent reports predict that up to 80% of the current fossil-fuel reserve should remain unused if temperature rise is not to exceed 2°C. These specific goals may seem ambitious considering the current global energy situation but the move to renewables is certainly possible and underway in several European countries. Sweden has announced that it would become the first fossil-fuel independent country in the world by 2050 in a speech delivered to the 70th UN general assembly by the Swedish Prime Minister Stefan Lofven. In addition to climate change issues, research shows that fossil-fuel reserves are in the early stages of depletion in some of the oil-rich Gulf countries such as Saudi Arabia. Other fossil-fuel producing countries like the U.S. have consumed nearly half of their reserves. The need to seek alternative sustainable energy sources has motivated a lot of research into renewables and other energy technologies.

1.1.2 Waste heat and its recovery

It is estimated by a U.S. Department of Energy report that 20% to 50% of the energy input to industry is lost as heat. Thermal energy may be emitted from hot machine surfaces, exhaust gases or other industrial process. Countless domestic or geothermal sources of thermal energy are also currently unutilised. Waste heat can be considered a largely untapped sustainable energy source. The U.S. Department of Energy report lists several possible technologies to recover waste heat at temperatures categorised into high (over 650°C), medium (230–650°C) and low (below 230°C) grades. The most challenging temperatures to recover would be in the
low temperature range due to the low possible maximum efficiency predicted by the Carnot efficiency relation:

\[ \eta = 1 - \frac{T_L}{T_H} \quad \text{Eqn 1.1} \]

Where \( T_H \) and \( T_L \) are the high and low temperatures or the waste heat and heat sink respectively.

Presently, waste heat recovery in the form of power generation is limited to the medium- and high-temperature ranges used by semiconductor thermoelectric technologies. Semiconductor thermoelectric power generators are commercially available but are not yet widely used in industrial or domestic areas. The current progress and limitations in the field of thermoelectrics are discussed further in the following section.

The focus of this thesis is the development of an alternative technology, of potentially lower cost, using a redox-active electrolyte for power generation from low-temperature waste heat sources. A redox-active electrolyte contains a redox couple which undergoes oxidation and reduction reactions when the device is operated to produce current.

1.1.3 Semiconductor thermoelectrics

In 1822, the thermoelectric effect was discovered by Thomas Seebeck. He found that applying a temperature gradient across a material results in a potential difference. The magnitude of this can be measured by the Seebeck coefficient (\( S_e \)).

\[ S_e = \frac{\Delta V}{\Delta T} \quad \text{Eqn 1.2} \]

Where, \( \Delta T \) is the applied temperature gradient and \( \Delta V \) is the resulting potential difference. Thermoelectrics are solid state devices capable of converting heat to electricity and vice versa based on the thermoelectric effect. A temperature gradient is applied across one or more P-type and N-type semiconductors connected in series, creating a potential difference. A schematic of a thermoelectric device is shown in Figure 1. A P-type semiconductor material is one with a majority of positive
“holes”, while an N-type is one with a majority of negative electrons. The applied temperature gradient drives the movement of electrons and holes from hot to cold, creating the potential difference and current flow.\textsuperscript{11}

Semiconductor thermoelectrics are solid state and highly conductive materials. A well-studied thermoelectric material, Bismuth Telluride (Bi\textsubscript{2}Te\textsubscript{3}), would typically have high electrical conductivity in the order of magnitude 10\textsuperscript{3} S.cm\textsuperscript{-1}.\textsuperscript{12} However, high thermal conductivities limit the efficiency of these materials. The performance of a thermoelectric device can be predicted by the figure of merit, given by:\textsuperscript{10}

\[
ZT = \frac{\sigma S_e^2}{k}\]

\textit{Eqn 1.3}

Where $\sigma$ is the electrical conductivity, $k$ is the thermal conductivity and $S_e$ is the Seebeck coefficient. The performance of thermoelectrics is also limited by low Seebeck coefficient values, in the $\mu$V/K range.

![Schematic of the thermoelectric device](image)

Figure 1 Schematic of the thermoelectric device, where $V$ is the potential difference across the material. From F. J. DiSalvo, Science, 1999, 285, 703-706. Reprinted with permission from AAAS.
It can be deduced from the figure of merit relation that a well-performing thermoelectric material would have a high Seebeck coefficient, high electrical conductivity and low thermal conductivity. However, the electrical and thermal conductivities of a thermoelectric material can be strongly correlated and so the optimisation of these materials can be challenging. Recent technology however, is taking thermoelectrics to the nano-scale, allowing the core figure of merit parameters to be improved by manipulating the thermal and electrical conductivities separately.\textsuperscript{12-14} Commercially-available thermoelectric materials, including the most commonly used Bismuth Telluride (Bi\textsubscript{2}Te\textsubscript{3}), have a figure of merit around one.\textsuperscript{13} Higher figures of merit have been reported since the development of nanostructured materials:\textsuperscript{10, 14, 15} the highest to date is $ZT=3$, at a temperature of 550K, which was reported by Harman et al.\textsuperscript{16} in 2005. The measured Seebeck coefficient of the material was 240 $\mu$V/K.\textsuperscript{16} High figures of merit at relatively low temperatures have also been reported. Zhao et al.\textsuperscript{17} reported a figure of merit of 0.7 at 300K; however, the power produced at this temperature is still in the $\mu$W.cm\textsuperscript{-1} range.

1.1.4 Thermoelectrochemical cells

Thermoelectrochemical cells (TECs) are devices capable of converting heat to electricity. These are also referred to as thermocells or thermogalvanic cells. The general concepts are similar to thermoelectrics, but the inner workings of the liquid device are different. A TEC is a two-electrode system containing a redox-active electrolyte. The Seebeck coefficient is again given by equation 1.2, but is related to a redox couple present in the electrolyte. Thermogalvanic cells have generated interest because of their high Seebeck coefficient values (compared to those of solid state thermoelectrics) – typically in the mV/K range.\textsuperscript{18} The charge in a liquid thermogalvanic cell is carried by mass transport of the redox species rather than electron conduction.\textsuperscript{19} Mass transport processes are considerably slower compared to electron conduction and so the conductivity in a liquid device is significantly lower, in the range of 1 S.cm\textsuperscript{-1} for the well-known ferri/ferrocyanide aqueous electrolyte.\textsuperscript{20}

The TEC is composed of three main components, as illustrated in Figure 2: the electrodes, the electrolyte and the redox couple. Previous studies have investigated
all three components of the cell, as discussed in more detail in the literature review. Here, a brief description of the TEC components and their functionality is given.

The device operation requires a temperature gradient to be applied across the cell, i.e. one of the electrodes is heated while the other is cooled. The electrodes are usually made of an electrocatalytic material, such as platinum, or contain an electrocatalytic layer, preferably with high surface area to increase the current and power density of the device.

The electronic charge in the cell is carried by a redox couple, which undergoes oxidation and reduction reactions at the electrodes. These reactions are driven by the temperature gradient, which shifts the equilibrium position of the redox couple. The movement of the redox couple through the electrolyte is driven by diffusion due to the formation of a concentration gradient in the electrolyte, migration due to the potential difference, and convection of heat when the thermal gradient is formed. The redox reactions of the couple should be fully reversible, so that no material addition is required during the cell operation.

Redox couples for these devices are chosen for their high redox entropies, which lead to high Seebeck coefficient values. The relationship between Seebeck coefficient and entropy change is given by:21

\[ S_e = \frac{\Delta V}{\Delta T} = \frac{\Delta S_{rc}}{nF} \]

Eqn 1. 4

Where \( \Delta S_{rc} \) is the reaction entropy of the redox species, \( n \) is the number of electrons in the reaction and \( F \) is Faraday’s constant.

The redox couple must be dissolved in an electrolyte for the device to operate. The most commonly studied redox couple is potassium ferri/ferrocyanide, which is typically used in an aqueous electrolyte. Figure 2 shows a schematic of the TEC incorporating the ferri/ferrocyanide redox complex. The oxidation reaction of ferrocyanide occurs on the hot electrode yielding ferricyanide species and the reverse occurs on the cold electrode in a cyclic process. The occurrence of the redox reactions and the subsequent reorganisation of the solvation shell around the redox species
produce a change in entropy which, directly relates to the Seebeck coefficient given by equation 1.4. The ferri/ferrocyanide aqueous electrolyte, at 0.4 M concentration, provides a benchmark Seebeck coefficient value of -1.4 mV/K.19 The ferri/ferrocyanide aqueous electrolyte has been at the centre of many studies on thermal-energy harvesting by a liquid device. A vast amount of literature can be found on aqueous electrolytes,22, 23, 19 the most relevant of which will be discussed further in the following literature review sections. A few key points are briefly mentioned here.

The Seebeck coefficient of the aqueous system can be at least an order of magnitude higher than that of a typical thermoelectric. However, as mentioned above, the conductivity is significantly lower because of the slow movement of the charge-carrier species. Recent progress in aqueous devices incorporates separators to limit thermal conductivity across the device and increase performance.24 High surface area carbon-based electrodes have been used to boost performance by providing more reactive sites for the charge-carrying redox species.25 An obvious limitation of an aqueous device is the boiling point of water. The heat harvested would be limited to temperatures less than 100°C. In addition, evaporation of the electrolyte may limit the lifetime of these devices.

Figure 2 A schematic of a TEC with the ferri/ferrocyanide redox couple.

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1.1.5 Ionic liquid based thermoelectrochemical cells

Ionic liquids (ILs) are of interest for this application mainly for their electrochemical and thermal stability. With high boiling points, low volatility and non-flammability, ILs are good candidates for use in a thermoelectrochemical cell. Room-temperature ILs are salts that are liquid at room temperature. They consist entirely of ions, making them conductive without additional supporting electrolyte. ILs (with some exceptions) usually consist of an organic asymmetric cation and a small inorganic anion. By pairing different anions and cations, desired properties can be achieved — including thermal stability, electrochemical stability and negligible vapour pressure. This makes ILs suitable for many applications, particularly as electrolytes.26, 27

The use of IL electrolytes for thermal-energy harvesting has been investigated as an alternative to aqueous and organic solvent systems.28-30 High Seebeck coefficients have been reported in ILs, thereby demonstrating the promise of their use in TECs.18 In addition to the points mentioned above, ILs have wide electrochemical windows, reaching 6 V in some ILs, allowing a variety of redox couples to be investigated. Some of the ILs used in the TEC field are illustrated in Figure 3.

IL TEC devices have progressed significantly in recent years, with research starting with an iodide/triiodide [I-/I3-] redox couple with Seebeck coefficient less than 1.0 mV/K, and progressing to a high-entropy cobalt bipyridine [Co2+/3+(bpy)3] redox couple with Seebeck coefficients of up to 1.88 mV/K.31, 18 However, while the Seebeck coefficient is known to be related to the entropy change of the redox reactions, the source of entropy change and its relation to the structure of the IL is not fully understood.
Figure 3 some of the ionic liquids reported in the literature for TEC application (a) 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (C₂mim eFAP) (b) 1-ethyl-3-methylimidazolium tetracyanoborate (C₂mim B(CN)₄) (c) 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonylimide (C₄mpyr NTf₂) (d) 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonylimide (C₂mim NTf₂).
1.1.6 Research aims

This research project was designed with the following aims:

- Overcome mass-transport limitations during cell operation in IL electrolytes by investigating mixed solvent systems.

The high viscosity of ILs has been the main limitation of these electrolytes in TECs.\textsuperscript{18, 19} Despite high Seebeck coefficients reported for the $\text{Co}^{2+}/\text{Co}^{3+}(\text{bpy})_3$ redox couple in a range of ILs, the mass transport over-potentials meant that the power produced by such cells was lower than that produced by water-based systems. The addition of molecular solvent to the IL was investigated as a route to overcome this.

- Investigate the effect of IL structure on the Seebeck coefficient and device performance.

A range of ILs (chosen for their good stability, high conductivity and low viscosity) have been tested with the $\text{Co}^{2+}/\text{Co}^{3+}(\text{bpy})_3$ redox couple in TECs. The nature of the cation and anion of the IL affected the Seebeck coefficient, but the nature of this influence is not yet well understood.\textsuperscript{18} This was investigated by expanding the range of ILs used and carrying out detailed assessment of the resulting TEC parameters.

- Identify high Seebeck coefficient redox couples and investigate the effect of redox couple structure on TEC performance.

The Seebeck coefficient is arguably the most important parameter in the TEC. The Seebeck coefficient is determined by the structure of the redox couple and its interactions with the surrounding solvent. The most promising redox couples in the literature are: a ferri/ferrocyanide $\text{K}_3/[\text{Fe(CN)}_6]^{3-}/^{4-}$ aqueous system, with a benchmark Seebeck coefficient of $-1.40 \text{ mV/K}$; and a cobalt bipyridyl, $\text{Co}^{2+}/\text{Co}^{3+}(\text{bpy})_3$, redox couple in ILs with Seebeck coefficients up to $1.88 \text{ mV/K.}\textsuperscript{18, 19}$ Reports of other redox couples for TEC applications are limited, with most having Seebeck coefficients lower than $1.0 \text{ mV/K}$. To address this, new cobalt-based redox couples were explored and the relationship between the redox couple structure and the Seebeck coefficient was investigated.
1.1.7 Thesis structure

Chapter One: Introduction. An introduction to the field, a literature review outlining the progress made so far and the knowledge gaps to be addressed in this project.

Chapter Two: Methodology. An outline of the experimental methodology and techniques used in this project.

Chapter Three: The use of ionic liquids, high boiling point organic solvents and mixed electrolytes in thermoelectrochemical cells. Mixing ionic liquids with high boiling point solvents was investigated in terms of Seebeck coefficients and device performance.

Chapter Four: The effect of ionic liquid structure on the Seebeck coefficient. Outlines a study of the influence of ionic liquid structure on the TEC parameters. The effect of small structural changes, such as varying the length of alkyl chains, in addition to new cations and anions, is reported.

Chapter Five: Investigation of cobalt-based redox couples for TEC application. Outlines a study of new redox couples, in terms of the Seebeck coefficient and TEC performance, which aims to identify the criteria of a well performing redox couple.

Chapter Six: Conclusions and future work. An outline of the findings of this project and suggested future work.
1.2 Literature review

1.2.1 Progress on thermoelectrochemical cells to date

Reports on TECs start as early as 1879. Several types of heat recovery devices have been described in review papers in the field. This thesis section will mostly focus on literature dealing with TECs containing a redox couple electrolyte where no stirring or consumption of the redox couple occurs. The device reported in this work requires no external forces (in the form of stirring) to operate and has an electrolyte that allow the device to operate continuously for long periods of time. TEC operating principles and key parameters will also be discussed.

1.2.1.1 The operating principles of thermoelectrochemical cells

While semiconductor thermoelectrics rely on the movement of electrons and positive holes in a solid material, in thermoelectrochemical devices the charge is carried across the cell by the redox species. The temperature gradient applied drives the redox species to undergo oxidation/reduction reactions on the electrodes. The redox species are transported across the cell by mass transport through the electrolyte. The mass transport occurs as a result of the concentration gradient, the potential difference (i.e. migration) and heat convection: the contribution of each of these effects is given by the Nernst-Planck equation:

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \varphi(x)}{\partial x} + C_i v(x) \quad Eqn \ 2.1
\]

Where \( J_i(x) \) is the flux of redox species \( i \) at a distance \( x \) from the electrode. The first term represents the diffusion contribution, where \( D_i \) is the diffusion coefficient and \( \frac{\partial C_i(x)}{\partial x} \) is the concentration gradient. This effect is more dominant in the vicinity of the electrodes, where the redox species are concentrated after reacting. The second term represents the migration contribution, where \( z_i \) is the charge of the redox species, \( C_i \) is its concentration, and \( \frac{\partial \varphi(x)}{\partial x} \) is the potential gradient. The migration is more dominant in the bulk solution, away from the electrodes where the
concentration gradient is weaker. The last term represents convection, where $v(x)$ is the velocity of the solution.

When the TEC cell is operated, the open cell potential is determined by the Seebeck coefficient of the redox couple, given by equation 1.2. The Seebeck coefficient is measured under open-circuit conditions, where no electrical current is drawn (e.g. using the U-tube setup described further in chapter two, section 2.1). When electrical power is drawn from the thermoelectrochemical cell, it is done under closed-circuit conditions and the current produced from the redox reactions is passed through a load resistor. The power output can then be calculated by measuring potential and then using Joule’s law and Ohm’s law: $P = I^2 R = \frac{V^2}{R}$. Maximum power is obtained when the load resistance is equal to the internal resistance of the system. The TEC experiment is explained in more detail in the following experimental chapter.

Figure 4 represents the characteristic potential-current curve of the TEC. An ideal TEC is represented by the dashed line extending from the maximum potential at open-circuit value ($V_{oc}$). In this ideal case the current is increasingly drawn, uninterrupted, until reaching its maximum short-circuit value ($I_{sc}$). In a real cell, however, drawing current results in a series of over-potentials, starting with a current drop between the short-circuit value and point C caused by mass-transport over-potential. A second drop between Points C and B is caused by ohmic over-potential and a final drop following point B is caused by activation over-potential.19
To understand the roles of over-potentials in limiting the IL-based TEC performance, theoretical calculations of the main resistance values within TECs were made by Abraham et al.\textsuperscript{36} using the fundamental electrochemical relationships between current and potential under various conditions in an electrochemical cell.\textsuperscript{35}

The charge-transfer, mass-transfer and ohmic over-potentials can be expressed by a series of resistors. Firstly, the mass-transfer resistance is given by:

\[ R_{mt} = \frac{RT}{nF|ilim|} \]  
\textit{Eqn 2.2}

Where \( R \) is the gas constant, \( T \) is the absolute temperature, \( n \) is the number of electrons, \( F \) is Faraday’s constant and \( ilim \) is the diffusion-limited current. The limiting current is a function of diffusion coefficient \( D_i \) and thickness of diffusion layer \( \delta \):
\[ i_{\text{lim}} = \frac{nFAD_1c}{\delta} \quad \text{Eqn 2.3} \]

The charge-transfer resistance is given by:

\[ R_{ct} = \frac{RT}{F i_o} \quad \text{Eqn 2.4} \]

Where \( i_o \) is the exchange current, which is related to the electrode material and the concentration of redox species. These relationships, along with experimental data, were used to simulate the current-potential curve for the cell using different electrode materials.\(^{36}\) The ratio of the exchange current to the limiting current, \( \frac{i_o}{i_{\text{lim}}} \), gave insight into the limiting factors in the cell. When \( \frac{i_o}{i_{\text{lim}}} \geq 10 \), performance was controlled by mass-transfer, and charge transfer played little role. However for \( \frac{i_o}{i_{\text{lim}}} < 10 \) currents were limited by charge-transfer resistance. To put this into perspective, the TEC performance with non-catalytic stainless steel electrodes was compared to that with catalytic electrodes, using \( \frac{i_o}{i_{\text{lim}}} \). The stainless steel electrode had a \( \frac{i_o}{i_{\text{lim}}} \) ratio of around 0.5, indicating charge-transfer limitation of the cell. In comparison, catalytic electrodes gave \( \frac{i_o}{i_{\text{lim}}} \geq 16 \), indicating that mass-transport over-potentials were dominant in this case. Abraham et al.\(^{36}\) also performed impedance measurements on several electrode materials within a TEC to investigate charge-transfer resistance. The poorest-performing electrode was found to be the stainless steel, while the best performing electrodes were platinum black and PEDOT-coated platinum. This work is also important as it demonstrates viable alternatives to platinum electrodes, which are important for reducing cost and encouraging commercialisation.

1.2.1.2 The roles of electrode materials and high surface area electrodes

In addition to electrocatalytic materials, high surface area electrodes can boost current and power output by providing more reaction sites for the redox species. High surface area electrodes such as carbon-based electrodes are of interest,
particularly for aqueous electrolytes where the charge-transfer resistance (and ohmic resistance) are more of a limitation than mass transport. 24, 25, 37

The efficiency of the ferri/ferrocyanide system was increased threefold by using high surface area carbon-nanotube electrodes in a study performed by Hu et al. 25 This work introduced realistic cell designs, such as coin cells and flexible cells that can be wrapped around pipes. The carbon-based electrodes were proposed to reduce the cost of the cells and also allow different cell designs. In addition, the high surface area and fast electrode kinetics significantly increased the current density of the cells. The cell efficiency in the study by Hu et al. 25 was measured and compared to the efficiency of the Carnot cycle, given by $\frac{\Delta T}{T_h}$ where $\Delta T$ is the temperature gradient and $T_h$ is the hot temperature. The Carnot efficiency indicates the highest efficiency possible when a system absorbs an amount of heat and performs work. In this work, a scroll-like electrode was constructed using carbon multiwalled nanotube (MWNT) buckypaper. A “forest” structure was also made using vertical carbon multiwalled nanotube arrays. The latter electrode performed best, achieving 1.4% of the Carnot efficiency, while conventional cells incorporating platinum electrodes typically give 0.4% due to a smaller number of reaction sites and therefore lower current density. 25 The efficiency of the cell was calculated using the following expression:

$$\eta = \frac{1}{4} \frac{\Delta S_{BA} J_{sc} R_T}{nF}$$

Eqn 2. 5

Where $\Delta S_{BA}$ is the reaction entropy of the redox couple, $J_{sc}$ is the short-circuit current density and $R_T$ is the thermal resistance of the cell. It was also found that the cell discharge improves with electrode thickness and surface area. 25

The effect of electrode spacing was also reported by Kang et al., 24 and two aspects were highlighted. First, smaller electrode spacing led to lower solution resistance and, second, a suitable distance must be kept to maintain the temperature gradient across the cell (which will depend on the thermal conductivity of the solution). Experimentally, for the ferri/ferrocyanide water system, the electrode spacing was reduced from 5 cm to 1 cm and achieved maximum performance at 1 cm. The
authors stated that a further decrease in electrode spacing leads to heat transfer between the electrodes, and therefore a loss of temperature gradient across the cell.\textsuperscript{24} Note, however, that the optimum performance is dependent on the redox couple and solvent system and the temperatures used, and so will likely be different for each TEC system.

1.2.1.3 Cell orientation and heat convection

The role of heat convection in TEC performance can be understood by studying the cell performance under different orientations.\textsuperscript{24, 38} The heat convection transports the redox species from the hot to the cold electrodes, and this can be exploited to mix the electrolyte if the right orientation is chosen. Kang \textit{et al.}\textsuperscript{24} investigated the effect of different parameters on the power outputs of the ferri/ferrocyanide aqueous TEC. The effect of the cell orientation on the discharge behaviour was investigated — the three orientations of the cell are shown in Figure 5.

The open-circuit potential is only dependent on the entropy of the redox species, not on the cell orientation. The short-circuit current and power output, however, were significantly affected by the cell orientation. Powers and currents up to 140\% higher were produced by the vertically-oriented cell with the cold electrode above the hot (Figure 5 a) in comparison to the opposite orientation (Figure 5 b). The effect of orientation is related to heat convection, contributing to the transport of the redox couple and mixing of the solution. The horizontal cell orientation gave the most stable power and current outputs with similar values to the cold-above-hot cell.\textsuperscript{24}
Figure 5 The three investigated cell orientations, a) cold above hot, b) hot above cold and c) Horizontal cell.\textsuperscript{24}
1.2.1.4 Capacitive systems

There are some literature reports on high Seebeck coefficient solutions that do not contain redox couples. Qiao et al. reported a Seebeck coefficient of 3.7 mV/K in an aqueous solution containing sodium chloride, where the potential difference due to temperature was described as general liquid-solid interface potential. Usually in TEC studies this effect is negligible, but here this potential difference was maintained by using high surface area nanoporous-carbon electrodes. The potential eventually collapsed, but was reset by disconnecting and grounding the electrodes. While high Seebeck coefficient was achieved, the potential plot was unstable and therefore this is not a feasible system for actual device applications. Similarly, Bonetti et al. reported “huge Seebeck coefficients” in organic solvent solutions containing tetrabutylammonium nitrate, tetrabutylphosphonium bromide, and tetrabutylammonium nitrate. A Seebeck coefficient of 7.16 mV/K was reported using tetrabutylammonium nitrate in dodecanol. Seebeck values were attributed to structural entropy changes due to salt-solvent interactions. Potential values here were reported to decrease gradually at a given temperature and reach a plateau. Thus, while some high initial potential differences can be obtained in solutions containing only salts and no redox couples, these potentials are unstable and collapse upon reaching steady state. It is also unclear how these systems would perform in a TEC power-output measurement.

1.2.1.5 Redox couples

The thermoelectrochemical cell is similar in some aspects to the dye-sensitised solar cell (DSSC) — in particular, they both use a redox-active electrolyte. The DSSC is a photovoltaic device which produces current when exposed to a light source. Similar to the TEC, the redox couple in the DSSC acts as a charge carrier. The thermoelectrochemical cell development parallels that of DSSC in terms of redox-couple choices.

The iodide/triiodide \((I^-/I_3^-)\) redox couple has been reported in the DSSC literature. \((I^-/I_3^-)\) showed rapid diffusion due to its small size; however, using
\((I^-/I_3^-)\) imposed issues of corrosion and potential limitations in the DSSC. This redox couple was the first to be reported in an IL electrolyte in the thermoelectrochemical cell literature in a study by Abraham et al. A more thorough review of that TEC work is given in section 2.3 on ionic liquid-electrolytes.

A cobalt-based redox couple with bipyridyl ligands \((\text{Co}^{2+/3+}(\text{bpy})_2(\text{PF}_6_2)_2/3)\) was first introduced in DSSCs, and yielded efficiencies exceeding that obtained with \((I^-/I_3^-)\). A range of cobalt-based redox couples in molecular solvents has also been reported to display high redox-entropy values, making them very interesting for thermal-energy harvesting. Abraham et al. later reported high Seebeck coefficients with the cobalt redox couple in ionic-liquid based TECs, discussed further below.

Cobalt complexes with pyridine and pyrazole rings have been more recently reported in the DSSC field. Cobalt pyridine-pyrazole \((\text{Co}^{2+/3+}(\text{py-pz})_3)\) complex was reported to have good electrochemical reversibility and high efficiency performance in the DSSC. The same complex was reported by Burschka et al. with high solubility when countered with a bis(trifluoromethanesulfonate)imide, \((\text{NTf}_2)\) ion. Cobalt pyridine-pyrazole complexes were chosen and tested for TEC application in this thesis. The complexes were also shown to undergo low-to-high spin transitions between the \(\text{Co}^{3+}\) to \(\text{Co}^{2+}\) species, which is know to lead to high entropy changes and high Seebeck coefficients. Similar redox couples have also been reported in IL devices; these will be discussed further in section 2.3 on ionic liquid electrolytes.

Devices with non-continuous power outputs were discussed in the old literature. These usually have an electrode involved in the redox reactions that would typically be consumed during the device discharge. It is important to note the difference to the TEC reported in this work, which incorporates both halves of redox reactions in solution and thus provides continuous power and current output. Nonetheless, two more recent non-continuous systems are discussed briefly below.

The use of a Cu/Cu\(^{2+}\) system was reported by Gunawan et al. CuSO\(_4\) was dissolved in water and a copper electrode was used as the source of neutral Cu species. A maximum Seebeck coefficient of 0.84 mV/K was reported with 0.7 M
CuSO₄. The Cu electrode material is consumed when power is generated from the cell.

Similarly, a non-continuous device incorporating lithium electrodes has been reported by Black et al. using an equimolar lithium salt/tetraglyme electrolyte. Similar equimolar mixtures have been reported for battery applications and referred to as ‘solvate ionic liquids’ in recent literature by Watanabe and colleagues. Black et al. reported a Seebeck coefficient of 1.40 mV/K for a 1:1 mixture of LiNTf₂ and tetraglyme; the high Seebeck coefficient was attributed to a high entropy change associated with the solvation and desolvation of the lithium salt from the glyme molecules. During the operation of the cell, lithium ions are produced from the cold electrode and deposited on the hot electrode, causing changes to the electrode surfaces and eventual consumption of the cold electrode. This mechanism causes the power obtained from the cell to be unstable, with a maximum of 135 mW/m².

1.2.1.6 Redox couple concentration

The effect of redox-couple concentrations on the Seebeck coefficient and TEC performance is known to a certain degree. One of the early detailed reports on the ferri/ferrocyanide system was by Burrows in 1976, who investigated the effect of redox couple concentration to clarify the roles of the three over-potentials in the cell. The ohmic, charge-transfer and mass-transfer over-potentials were measured at different concentrations of redox couple. The cell performance was described as limited by mass-transfer processes. The measured limiting current is directly related to the concentration of the redox couple, as given by equation 2.3. The power density was also found to be proportional to the concentration of redox species and to the temperature gradient. To overcome the mass-transport over-potential, “forced convection” was introduced to the cell, whereby the solution was stirred by rotating the electrodes. While this stirring decreased the over-potentials fourfold, it required constant energy to be provided to the cell.

While increasing the redox-couple concentration improves the cell performance, it also reduces the Seebeck coefficient, as observed in several literature reports examining both aqueous and IL electrolytes.
In a recent report by Zhao et al.\textsuperscript{54} cyclodextrin molecules were used to encapsulate the triiodide ($I_3^-$) in the ($I^-/I_3^-$) aqueous electrolyte. The encapsulation was predicted to reduce the concentration of the $I_3^-$ species at the cold electrode and therefore increase the concentration gradient and the Seebeck coefficient.\textsuperscript{54} The Seebeck coefficient of the aqueous ($I^-/I_3^-$) was increased from the reported 0.53 mV/K to 1.45 mV/K when 4 mM of the cyclodextrin encapsulation molecule was added. The power drawn from the cell was reported to be in the µW range, with performance degradation due to precipitation when a supporting electrolyte was added.

1.2.1.7 Solid and quasi-solid state electrolytes

Recent work in the field is taking a direction towards flexible device designs. The use of solid or quasi-solid state electrolytes would allow more flexible cell designs without the concern of leaking or loss of electrolyte through evaporation at high temperatures.\textsuperscript{20, 55-57}

The solidification of the ferri/ferrocyanide aqueous electrolyte was investigated in our group by Jin et al.\textsuperscript{55} Several cross linkers such as poly(vinyl alcohol) and gelatin were tested, but cellulose gave the best physical properties, at 5 wt.% addition. The gel electrolyte had a comparable Seebeck coefficient to that of the liquid aqueous system, although the cell power output was about 30% lower. The gelation of the electrolyte decreased the diffusion coefficient of the redox couple, causing a drop in the overall performance.

Electrically connected TEC arrays have been reported in several studies,\textsuperscript{57-59} and may be a path towards a commercial device. A wearable TEC was developed by Yang et al.,\textsuperscript{57} who used poly (vinyl alcohol) (PVA) to gel the well-known ferri/ferrocyanide electrolyte. In addition, a simple Fe$^{2+}/$Cl$^{2-}/$Cl$^{3-}$ solution was also solidified into a gel to provide a Seebeck coefficient of the opposite sign; this allowed the voltage to add up and the current to flow in the same direction from all the individual cells. The device is illustrated in Figure 6, where PPF and PFC are the ferri/ferrocyanide and ferric/ferrous chloride electrolytes gelled with PVA, respectively, and PI is polyimide, a flexible substrate used to “sandwich” the electrolyte compartments.\textsuperscript{57}
This device design is similar to that of a semiconductor thermoelectric where a positive p-type and a negative n-type semiconductor device are connected (Figure 1). From a device construction perspective, this is much simpler than having to run electrical connections from the top of one cell to the bottom of the other. However, it was found that electrically connecting cells is not trivial, and may result in a drop in current when compared to individual cells. The main issue with the interconnected cells is a mismatch of parameters between the positive and negative cells. The positive Fe$^{2+/3+}$ system has a lower Seebeck coefficient and higher cell resistance than the negative Fe(CN)$_6^{3-/4-}$ system causing a current drop through these cells.

1.2.2 The Seebeck coefficient and reaction entropy.

Research work in the thermoelectrochemical cell field is primarily focussed on high Seebeck coefficient redox couples to produce high open-circuit voltage in the cell. The ferri/ferrocyanide aqueous electrolyte and the Co$^{2+/3+}$(bpy)$_3$ organic electrolytes have been the main focus to give Seebeck coefficients exceeding
1.0 mV/K. However, reports of other high Seebeck coefficient redox couples have been limited. As shown in equation 1.4, there is a direct relationship between the Seebeck coefficient and the entropy change associated with the redox reactions. Thus, in this thesis, the redox couple structure and solvent parameters leading to high reaction-entropy change for the Co^{2+}/^{3+}(bpy)_3 and new cobalt-based complexes were investigated. A review of the literature on reaction entropy of redox complexes to date is given in this section.

In 1959 DeBethune et al.\textsuperscript{21} described measurements of the Seebeck coefficients in a liquid cell containing two electrodes. The change of the electrode potential due to an applied temperature or temperature difference was recorded. The temperature coefficient (Seebeck coefficient) is given by equation 1.4. Older literature has been referenced in this thesis dating back to 1878, but the work of DeBethune et al. in 1959 will be used as the starting point of this literature review of most relevant work in this field leading up to the current date.

The Seebeck coefficient was measured by Debethune et al.\textsuperscript{21} using two methods. The first was described as the “isothermal” temperature coefficient where the electrode potential is measured against a reference electrode in an electrochemical cell at the same temperature. The electrochemical cell is then heated to new temperatures where the potential is measured again, and ultimately a relationship between the potential and the cell temperature is obtained. The isothermal cell method requires only one of the two redox species to be dissolved in the electrolyte to conduct a measurement. However, the potential of the reference electrode may shift with temperature, leading to inaccuracies in the measured potential values. Alternatively, a second method was reported, called the “thermal temperature” coefficient, where the potential of one electrode is measured against another electrode of the same kind while only one is heated and both redox species are present in the electrolyte. The second method is also referred to in the literature as the “non-isothermal” cell method.\textsuperscript{44,61} In this thesis and most related literature, the non-isothermal cell method is used to measure the Seebeck coefficient.
DeBethune et al.\textsuperscript{21} found the Seebeck coefficient to be related to the entropy changes resulting from the redox reactions on the electrode surface. Two sources for the redox entropy change in an aqueous system were proposed: an entropy change related to the process occurring at the electrodes, where the redox species lose and regain their hydration shell upon reacting; and one arising from the migration of ions, surrounded by their hydration shells across the cell. The migration entropy is usually small and can be neglected.\textsuperscript{21}

Studies on the reaction entropy of redox couples were performed by Weaver, Yee and colleagues in the 1980’s.\textsuperscript{44, 61} They examined the effects of different ligands on reaction entropies in aqueous solutions for several transition-metal based redox couples.\textsuperscript{44} The redox couples were chosen based on the strength of hydrogen bonding with the surrounding water molecules, which depends on their structure. It was found that transition-metal redox couples of the form M\textsuperscript{3+/2+} have the highest entropy values when aquo ligands are attached M(OH\textsubscript{2})\textsubscript{n}\textsuperscript{3+/2+}. For example, the Ruthenium aquo redox couple Ru(OH\textsubscript{2})\textsubscript{6}\textsuperscript{3+/2+} has a measured reaction entropy of 150 J. K\textsuperscript{-1}. mol\textsuperscript{-1}, which corresponds to a Seebeck coefficient of around 1.5 mV/K. The high entropy values are credited to the hydrogen bonding between the aquo ligands and the surrounding water molecules. Reaction entropies significantly decrease to 79 J. K\textsuperscript{-1}. mol\textsuperscript{-1}. (S\textsubscript{e} \approx 0.8 mV/K) when the aquo ligands are replaced by amine ligands to form Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+/2+}. This is explained by weaker interactions with surrounding water molecules for the weakly acidic amine compared to the aquo ligands. Yee et al.\textsuperscript{44} also report a decrease in reaction entropy when the aquo and amine ligands are replaced by simple anions such as chloride. The decrease is caused by a decrease in the net charge of the complex and by reduced hydrogen bonding with solvent.

Chelating ligands such as ethylenediamine (en) and bipyridine (bpy) were also investigated by Yee et al.\textsuperscript{44} Chelating ligands were reported to form stable complexes with transition metals. The cobalt complexes containing chelating ligands were found to have noticeably higher entropy than for other metal complexes in aqueous media. For example, Co(en)\textsubscript{3}\textsuperscript{3+/2+} has an entropy of 155 J/K.mol (equivalent to S\textsubscript{e} \approx 1.6 mV/K) while Ru(en)\textsubscript{3}\textsuperscript{3+/2+} has an entropy of 54 J/K.mol (S\textsubscript{e} \approx 0.56 mV/K), demonstrating that
The nature of the transition metal atom affects the entropy changes for complexes containing chelating ligands. The authors note changes in the electron configuration for the cobalt complexes upon reduction: for Co(III) reducing to Co(II) the electron structure is $t_{2g}^6$ changing to $t_{2g}^5e_g^2$, while ruthenium and iron have $t_{2g}^5$ to $t_{2g}^6$ transitions. In more recent literature the high entropy of the cobalt complexes, particularly the cobalt tris(bipyridyl) complex, is again explained by this low-to-high entropy transition upon reduction. The presence of the bipyridyl ligands leads to the splitting of the degenerate $d$ orbitals and a change of spin upon electron transfer. This is illustrated in Figure 7.

![Figure 7 Splitting of the $d$ orbitals of the cobalt complex.](image)

To further investigate the effect of the transition metal atom on the reaction entropy, the authors tested other transition metals — iron, chromium and ytterbium — with aquo ligands, and found that the reaction entropies of their complexes were similar, when tested in water. The authors concluded that, unless there is a significant change in the electronic properties of the redox complex (e.g. the spin transitions in Co$^{2+/3+}$-(bpy)$_3$), the nature of the metal atom has a much smaller influence on the reaction entropy when compared to the effect of changing the ligand.

Yee et al. also reported theoretical values for reaction entropies calculated using the Born equation, a theoretical relation which correlates the reaction entropy of redox species to their charge and the effective radius of the species. This equation was taken from the Born dielectric continuum model derived by Max Born, which can be found in physical chemistry textbooks. The Born equation is:
\[ \Delta S_{rc} = \frac{e^2 N}{2\epsilon rT} \left( \frac{d \ln \epsilon}{dT} \right) (Z_{ox}^2 - Z_{red}^2) \quad \text{Eqn 2.6} \]

Where \( r \) is the radius of the species, \( Z \) is the charge of the oxidised and reduced species and \( \epsilon \) is the static dielectric constant of the solvent. The authors report that the Born equation for reaction entropy is able to predict the reaction entropy for amine ligands but not for aquo ligands. The reason for inaccurate entropy predictions is that the radius used in the equation is that of the “bare cation”, not taking into account the solvent water molecules coordinated to the complex. Complexes having aquo ligands would typically have strong coordination to the surrounding solvent molecules and so would be expected to have a larger “hydrated ion radius”.

Hupp et al. combined the Born equation with experimental data to give a semi-empirical relationship between the reaction entropy and simple physical parameters. They measured reaction entropies of several Ruthenium and Chromium redox couples with amine, bipyridine and other ligands in organic solvents. Some data on redox-couple entropy were also extracted from the literature. The data were then plotted and correlated with several variables related to the redox couple, such as radius and charge. A linear relationship was found between the reaction entropies \( \Delta S_{rc} \) and \( \frac{(Z_{ox}^2 - Z_{red}^2)}{r} \), as shown in Figure 8. This correlation is in agreement with the Born expression in equation 2.6. However, the proportionality constant was found to be larger than predicted by the Born equation. The Born equation also predicts a zero intercept, whereas the experimental data has intercept values that are significantly greater or smaller than zero. These deviations from the Born equation indicate solvent-dependent factors not taken into account by the equation. The semi-empirical relation proposed by Hupp and Weaver for aqueous systems is:

\[ \Delta S_{rc} = 83.5 \frac{Z_{ox}^2 - Z_{red}^2}{r} - 40 \quad \text{Eqn 2.7} \]
Where $Z_{ox}$ and $Z_{red}$ are the absolute charges of the oxidised and reduced species, respectively, and $\Delta S_{rc}$ is in J/K.mol

![Figure 8 Reaction entropy in water vs $\frac{Z_{ox}^2-Z_{red}^2}{r}$. Reprinted with permission from: J. T. Hupp and M. J. Weaver, Inorganic Chemistry, 1984, 23, 3639-3644. Copyright (1984) American Chemical Society. Key to redox couples: (1) Fe(CN)$_3$/$^4$-, (2) Fe(CN)$_6$bpy$^{3^2-}$, (3) ferrocenium/ferrocene, (4) Cr(bpy)$_{3^4}/^{2^+}$, (5) Ru(NH$_3$)$_3$Cl$^{2^+/3^+}$, (6) Ru(NH$_3$)$_3$NCS$^{2^+/+}$ (7) Ru(en)$_3^{3^+/2^+}$ (8) Ru(NH$_3$)$_6^{3^+/2^+}$.]

Hupp and Weaver also attempted to correlate the reaction entropy to solvent-related variables such as donor and acceptor numbers. The donor number, DN, describes the “electron-donating” capabilities of the solvent; no specific trend can be seen in the plot of entropy vs solvent donor number. The acceptor number, however, seems linearly related to the reaction entropy; the correlation is shown in Figure 9. The acceptor number indicates the polarity and electrophilicity of the solvents.

The semi-empirical relation developed by Hupp and Weaver was further investigated by Migita et al. In their work several reaction entropies of iron and chromium complexes were related to the relation $\frac{Z_{ox}^2-Z_{red}^2}{r}$ in the ionic liquid 1-butyl-1-methylpyrroldinium bis(trifluoromethanesulfonyl)imide (C$_4$mPyr NTf$_2$). By fitting their data, the semi-empirical relation was modified for the ionic liquid giving:
\[ \Delta S_{rc} = 74.0 \frac{Z_{ox}^2 - Z_{red}^2}{r} - 6.1 \quad \text{Eqn 2.8} \]

Where, \( \Delta S_{rc} \) is in J/K.mol. The equation was used to estimate the reaction entropy of the ferrocene/ferrocenium redox couple. The authors found the sign of the Seebeck coefficient to be related to the difference between the absolute charge of the oxidants and reductants according to equation 2.8. The authors also successfully related to the acceptor number of the IL under study to the reaction entropy change. This was added to the plot by Hupp et al. in Figure 9.\(^{30} \) However, only one IL was tested. The entropy vs solvent acceptor number relation reported by Hupp et al. as well as the IL reported by Migita et al. are shown in Figure 9.

Figure 9 Reaction entropies of some redox couples vs solvent acceptor number for some organic solvents reported by Hupp et al.\(^{61} \) Reprinted with permission from: J. T. Hupp and M. J. Weaver, Inorganic Chemistry, 1984, 23, 3639-3644. Copyright (1984) American Chemical Society. (•) Ru(NH\(_3\))\(_6\)^{3+/2+}, (▾) ferrocenium/ferrocene, (■)
Ru(en)$_3^{3+/-2+}$, (▲) Cr(bpy)$_3^{3+/-2+}$. (□) ferrocene/ferrocenium in C$_4$MPyr NTf$_2$ reported by Migita et al.$^{30}$

The work of Hupp et al.$^{61}$ and Yee et al.$^{44}$ has shed some light into the parameters affecting the Seebeck coefficient. However, the exact mechanisms determining the Seebeck coefficient and the reaction entropy are not well understood, particularly in IL electrolytes.

The effects of solvent structure as well as redox couple structure will be investigated by testing a range of different redox couples, ILs and organic solvents. The polarity and polarity-related parameters were also investigated by measuring the Kamlet-Taft parameters, which can be used to rank solvents on three scales: the $\alpha$-scale for hydrogen bond donor ability (HBD), $\beta$-scale for hydrogen bond acceptor ability (HBA) and $\pi^*$ for polarity/polarizability. Further introduction to the theory of Kamlet-Taft parameters is given in the following section.

1.2.3 Background on polarity and the Kamlet-Taft parameters.

The work of Hupp et al.$^{61}$ on the entropy of redox couples in aqueous and molecular solvent-based electrolytes drew tentative correlations between the entropy change and solvent’s acceptor number, which is a polarity-related parameter.$^{61}$ However, the trend lines are only approximate, suggesting that the reaction entropy correlates to a sum of different interactions with the surrounding solvent rather than a single parameter. The exact nature of the solvent-redox couple interactions relating to the reaction entropy are still not known; the authors suggest possible correlations between the reaction entropy of the redox couple and other polarity scales such as $\pi$ and $E_T^*$. $^{61}$

Polarity can be defined as the collective effect of all solvent-solute interactions.$^{62}$ This definition indicates that different dyes (i.e. the solute) used to probe polarity of
solvents may give different results due to different solvent-solute interactions. Polarity parameters are more appropriately described as relative to the dye used and should not be taken as absolute. The Kamlet-Taft scales were used in this thesis as they have multiple parameters relating to specific solvent-solute interactions. A brief review of the Kamlet-Taft parameters and other polarity scales is given below.

There are several scales of solvent polarities reported in the literature. The first reported was the $Z$ scale by Kosower et al. in 1957. Kosower observed a change in the absorption band of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide when different solvents were used. This change in absorption band can be used to rank solvents on a polarity scale.

The widely used $E_{T}^{30}$ was reported by Reichardt et al. The absorption spectra of 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate dye, also known as Betaine n30 or simply Reichardt’s dye, was used to place solvents on the polarity scale. The older literature on polarity of solvents mostly deals with organic solvents, but the polarity of a wide range of ionic liquids has also been reported on Reichardt’s $E_{T}^{30}$ scale.

Despite its wide use, $E_{T}^{30}$ is only a single parameter scale capable of describing polarity in broad terms as a collection of different solvent-solute interactions. Three parameter polarity scales were reported by Kamlet and Taft in order to describe the solvents polarity in more specific terms. In their series of publications titled “The Solvatochromic Comparison Method I,2..,6”, Kamlet and Taft described three polarity scales: $\alpha$, $\beta$ and $\pi^*$, which describe solvents in terms of their hydrogen bonding ability. The $\beta$-scale can be used to rank solvents in terms of their hydrogen bond accepting capabilities. The $\alpha$-scale can be used to rank solvents in terms of their hydrogen bond donor abilities. Finally, the $\pi^*$ scale is a more general scale for polarity or polarizability of solvents.

The solvatochromic comparison method is based on the use of two dyes as probes for solvent-dye interactions. UV Visible spectroscopy is used to measure the shifts in
the absorption spectra due to these interactions; more specifically, the maximum wavelength $\lambda_{\text{max}}$ or the corresponding wave number $\nu_{\text{max}} = \frac{1}{\lambda_{\text{max}}}$ is reported.

In the first publication on the solvatochromic method by Kamlet and Taft, the authors described their $\beta$-scale using two dyes. First, 4-nitroanaline, which can act both as a hydrogen bond donor (HBD) through the oxygens on the NO$_2$ site and as a hydrogen bond acceptor (HBA) through the hydrogens on the NH$_2$ site. The transition of the 4-nitroanaline dye from the ground state to the excited state is theorised to lead to strengthening in hydrogen bonding with the solvent which can ultimately be used to rank the solvent on a polarity scale with respect to other solvents. The structure of the 4-nitroanaline dye in the ground and excited state is shown in Figure 10. The second dye used, N,N-diethyl-4-nitroanaline, has ethyl groups on the nitrogen rather than hydrogens and so can only act as a hydrogen bond acceptor (HBA).

Figure 10 The structure of 4-nitroanaline in its ground and excited states. Adapted with permission from Kamlet, M. J. and R. W. Taft (1976), Journal of the American Chemical Society 98(2): 377-383. Copyright (1976) American Chemical Society.

In the Kamlet and Taft study, the dyes were dissolved separately in all solvents under study and UV-Vis absorption spectra were acquired. The authors plotted the wave numbers corresponding to the maximum absorptions obtained for the solvents using both dyes in a $\nu_{\text{max,4-nitroanaline}}$ VS $\nu_{\text{max,N,N-diethyl-4-nitroanaline}}$ plot shown in Figure 11 below. Solvents were categorised into non-hydrogen bonding,
hydrogen bond accepting and amphiprotic solvents, the last being solvents capable of either hydrogen bond accepting or donating. A good linear fit was achieved for non-hydrogen bonding solvents, represented by an open square in Figure 9. All hydrogen bond accepting solvents fall below the line by a significant amount and can be ranked in order of hydrogen bond accepting strengths. The authors used another set of dyes, 4-nitroanisole and 4-nitrophenol, to confirm the validity of their scale. The scales constructed using both dye sets were found to be in good agreement. In addition, fluorine NMR was used to analyse the interactions with a different probe, 4-fluorophenol, dissolved in the solvents, to create another β-scale, which was found to be in good agreement as well. The α and π* scales were later reported using similar methods.

Figure 11 Solvatochromic comparison of 4-nitroaniline (1) and N,N-diethyl-4-nitroaniline (2) UV spectral data. Reprinted with permission from Kamlet, M. J. and
The concept of polarity becomes more complex in ionic liquids as they are composed purely of ions. The Kamlet-Taft polarity scales were constructed based on measurements performed mostly in organic solvents. However, measurements of Kamlet-Taft parameters in ionic liquids have been reported. While the experimental procedure is relatively straightforward, interpretation of the results for ionic liquid electrolytes, compared to molecular solvents, is quite complex as the solvent/dye interactions are very different.

The concept of polarity in ionic liquids has been investigated by Welton and colleagues. To test the feasibility of the Kamlet-Taft polarity scales in ionic liquids, different probes were used to obtain the polarity parameters for the same set of ionic liquids. The authors rule the Kamlet-Taft parameter scales appropriate for use with ionic liquids but with reservations on the interpretation of the data. The authors note that $\pi^*$ is relatively high in ionic liquids compared to solvents due to their ionic nature. $\beta$ was found to be mostly related to the anion of the ionic liquid and its ability to coordinate and accept hydrogen bonds, while $\alpha$ mostly relates to the cation and its ability to coordinate and donate hydrogen bonds. The authors also note that impurities may be present in ionic liquids, particularly in commercial samples, and the presence of impurities may greatly affect the values of the Kamlet-Taft parameters. To address this, high purity ionic liquids and solvents were used for these measurements. Different sets of dyes were used in this study on a wide range of ionic liquids and it was found that despite different dyes giving different absolute values, the trends of polarity across different ILs were almost identical.

### 1.2.4 Ionic liquid electrolytes

IL electrolytes have been investigated for electrochemical devices (including several battery technologies, dye sensitised solar cells, and double layer capacitors) to overcome the drawbacks of conventional solvent-based electrolytes. Their high boiling points, high decomposition temperatures and non-flammability allow their
use over wide temperature ranges. Low volatility prolongs the device lifetime and allows easy handling of the electrolyte. ILs can be chosen for use in TECs based on favourable electrolyte properties — including high conductivity, electrochemical stability and low viscosity — reported for other electrochemical devices. This section will discuss the properties of ILs and review some of the literature on their use in selected electrochemical devices.

ILs have been heavily investigated for several battery technologies including lithium, sodium and metal air batteries. The currently used commercial electrolytes are mostly molecular-solvent based, which introduces issues of flammability, volatility and toxicity. In terms of electrolytes, batteries and TECs have similar requirements and face similar limitations.

ILs with imidazolium, quaternary ammonium or phosphonium cations are mainly of interest in the field of batteries and other electrochemical devices for their low viscosities and high conductivities. A specific example of an imidazolium ionic liquid is the 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide (C<sub>2</sub>mim NTf<sub>2</sub>), which was reported by Garcia et al. for lithium battery applications. This IL has high conductivity (around 10 mS cm<sup>-1</sup> at room temperature), high thermal stability, with degradation at temperatures higher than 400°C, and electrochemical stability over a range of 4.3V. Some electrochemical properties of the widely reported imidazolium ILs are listed in Table 1.

One of the known drawbacks of ILs is high viscosity, which leads to slow diffusion of the charge carriers, lowering the overall device performance. Co-solvents and additives may be used to address this. While the addition of solvents brings back some of the volatility and flammability, the risks can be reduced by having a large volume ratio of ionic liquid. Guerfi et al. found that upon the addition of ≥40% IL to ethylene carbonate, a conventional solvent used in batteries, no flammability was observed. Adding high-boiling-point organic solvents to ILs is investigated in this thesis to enhance the performance of the TEC. This will be discussed in chapter three.
Table 1 some ILs containing the common cation 1-ethyl-3-methylimidazolium, and their electrochemical properties,\textsuperscript{87, 88} where, C\textsubscript{2}mim OTf is 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, C\textsubscript{2}mim NTf\textsubscript{2} is 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, C\textsubscript{2}mim eFAP is 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate and C\textsubscript{2}mim B(CN)\textsubscript{4} is 1-ethyl-3-methylimidazolium tetracyanoborate.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Viscosity (cP at 25\textdegree)</th>
<th>Electrochemical window (V at 20\textdegree)</th>
<th>Conductivity $\kappa$(mS/cm)</th>
<th>Decomposition temp (\textdegree C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{2}mim OTf</td>
<td>70.3</td>
<td>4.3</td>
<td>9.2 (20\textdegree C)</td>
<td>340</td>
</tr>
<tr>
<td>C\textsubscript{2}mim NTf\textsubscript{2}</td>
<td>35.6</td>
<td>4.5</td>
<td>9.0 (20\textdegree C)</td>
<td>455</td>
</tr>
<tr>
<td>C\textsubscript{2}mim eFAP</td>
<td>34.0 at 30C</td>
<td>5.0</td>
<td>6.9 (30\textdegree)</td>
<td>N/A</td>
</tr>
<tr>
<td>C\textsubscript{2}mim B(CN)\textsubscript{4}</td>
<td>15.0 at 30C</td>
<td>&gt;5.0</td>
<td>19.0 (30\textdegree C)</td>
<td>360</td>
</tr>
</tbody>
</table>

The use of ILs in DSSCs has also been reported.\textsuperscript{89-91} The best performing DSSCs reach up to 11% energy conversion efficiency, but those best devices are based on volatile organic solvents.\textsuperscript{41, 76, 92} Longer-lasting alternative electrolytes are being pursued, and therefore ILs were introduced to the DSSC field to deal with electrolyte volatility problems. The higher viscosity of ILs lowers the efficiency of the DSSC, but can also prolong their lifetime – particularly when exposed to higher temperatures. Low-viscosity ILs have been studied for DSSC applications,\textsuperscript{93} and their thermal stability tested over prolonged time periods. The ionic liquid 1-ethyl-3-methylimidazolium tetracyanoborate (C\textsubscript{2}mim B(CN)\textsubscript{4}) was found to be the most stable under these conditions, making it an excellent candidate for DSSCs and other high-temperature applications such as TECs.
1.2.5 Ionic liquid-electrolytes for thermoelectrochemical cells

In 1981 Chum and Osteryoung reviewed thermally-regenerative electrochemical systems. The use of molten salts was reviewed in several publications: the term “molten salt” here refers to liquid salts at high temperatures reaching or exceeding their melting points (over 200°C). Seebeck coefficient values less than 1 mV/K were reported for these systems, at temperatures from 200–800°C. While these systems are composed of ions (similar to ILs), they cannot be used to harvest low-grade heat (<150°C) due to their high melting points.

Abraham et al. have reported their work on harvesting thermal energy using a range of IL electrolytes. The first system they reported was iodide/triiodide ($I^-/I_3^-$) in several ILs. The Seebeck coefficient increased with dilution of the redox couple, similar to the trend previously observed in the aqueous ferri/ferrocyanide electrolyte. This was attributed to a larger change in solvation environment (and hence larger entropy change) when more IL ions are around the redox species. Changing either the cation or the anion of the IL significantly influenced the Seebeck coefficient. For instance, the Seebeck coefficient for C2mim BF4 with $I^-/I_3^-$ is 0.26 mV/K. When the anion was changed to B(CN)4, at the same redox couple concentration, the Seebeck coefficient dropped to 0.094 mV/K. The effects of different cations and anions on reaction entropies in ILs are not yet understood, and form a focus of this thesis.

Mixing the $I^-/I_3^-$ redox couple with ferrocene/ferrocenium in an IL electrolyte was reported by Aldous and colleagues. The mixing was reported to have a synergistic effect which caused an increase in entropy and therefore an increased Seebeck coefficient. The highest value reported was 1.67 mV/K for a dibutanoylferrocene and triiodide system [Fc][I3] in C2mim NTf2. An increase in power density was also observed in the mixed redox couple system going from 0.05 µW/m² for the simple ferrocene/ferrocenium redox couple to about 0.25 µW/m² for the mixed [Fc][I3] system at 30 mM concentration of both redox species. However, the exact charge transport mechanism of the mixed redox couple system is not yet well understood and it is unclear how the system would behave under long-term discharge experiments.
The Seebeck coefficient of IL-based electrolytes was significantly increased using a cobalt redox couple. The Co^{2+/3+}(bpy)₃ redox couple has previously attracted attention in the DSSC field. Abraham et al. changed the anion of the cobalt complex from PF₆ (as used in DSSCs) to NTf₂ to increase the stability and solubility in ILs, up to 0.1 M. Use of the Co^{2+/3+}(bpy)₃ redox couple resulted in unprecedented Seebeck coefficient values of up to 2.19 mV/K in MPN, indicating a high entropy change. As discussed previously, upon reduction, the cobalt complex transitions from low spin Co³⁺:[Ar] ⁴s² ⁴d⁶ to high spin Co²⁺:[Ar] ⁴s² ⁴d⁷, resulting in a high entropy change.

The Seebeck coefficient of Co^{2+/3+}(bpy) was tested in several ILs. Both the anion and cation of the IL were found to influence these values, meaning that both have solvent reorganisation effects following the redox reactions. The Seebeck coefficient curve showed the expected linear behaviour with temperature, indicating stability at temperatures up to 130°C. Entropy and Seebeck coefficient values for the Co^{2+/3+}(bpy)₃ redox couple in different ILs are shown in Table 2. The highest Seebeck coefficient in an IL was for the C₂mim eFAP, at 1.88 mV. eFAP-containing ILs were also reported to have the highest Seebeck coefficients for Co^{2+/3+}(bpy)₃ at the same concentration in a study by Jiao et al.
To understand the role of mass-transport over-potential in the cell, the diffusion coefficient of the Co^{2+/3+}(bpy) was measured\(^\text{18}\). The electrolytes investigated were ionic liquids and also the molecular solvent methoxypropionitrile (MPN). The diffusion coefficient was highest in MPN for both cobalt complexes. At 80°C, Co^{2+}(bpy)\(_3\) has a diffusion coefficient of around 2.5 X 10\(^{-6}\) cm\(^2\)/s in MPN and 6.0 X 10\(^{-7}\) cm\(^2\)/s in C\(_2\)mim B(CN)\(_4\), which gave the highest diffusion of all the ILs tested. This is to be expected, because MPN is significantly less viscous than the ILs. The diffusion

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Redox couple concentration (M)</th>
<th>Seebeck coefficient (mV/K) ± 0.02</th>
<th>(\Delta S_{rc}) (J/K.mol) ±2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPN</td>
<td>0.01</td>
<td>2.19</td>
<td>211</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>1.99</td>
<td>192</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.90</td>
<td>183</td>
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<tr>
<td>C(_2)mim eFAP</td>
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<td>C(_2)mim B(CN)(_4)</td>
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<td>1.55</td>
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</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.59</td>
<td>153</td>
</tr>
</tbody>
</table>

Table 2: The Seebeck coefficient \(S_e\) and entropy change, \(\Delta S_{rc}\) of 0.1M Co\(^{2+/3+}(bpy)\(_3\)(NTf\(_2\))\(_{2/3}\) redox couple in ILs containing the following cations: 1-ethyl-3-methylimidazolium [C\(_2\)mim], 1-butyl-1-methylpyrrolidinium [C\(_4\)mpyr] and 1-butyl-1-methylimidazolium [C\(_4\)mim]; and the following anions: tris(pentafluoroethyl)trifluorophosphate [eFAP], bis(trifluoromethanesulfonate)imide [NTf\(_2\)] also known as [C\(_2\)mim], tetracyanoborate [B(CN)\(_4\)] and tetrafluoroborate [BF\(_4\)] and the organic solvent methoxypropionitrile (MPN).\(^\text{18}\) Reproduced from Abraham, T. J., et al. (2013). Energy & Environmental Science 6(9): 2639. With permission of the Royal Society of Chemistry.
coefficient was also found to increase with temperature and concentration of the redox couple. Thermal conductivity measurements were also carried out or taken from the literature. The thermal conductivities for the ILs and MPN range between 0.12 W/K.m for MPN and 0.12–0.19 W/K.m for ILs, and are either constant or decrease with temperature. This is significantly lower than the thermal conductivity of water at 0.67 W/K.m, which is an additional advantage to the use of ILs over aqueous electrolytes.\textsuperscript{18}

In light of these results, the behaviour of IL systems in the TEC can be better understood. In the TEC measurements the highest-performing system was the Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} redox couple in MPN at T\textsubscript{cold}/T\textsubscript{hot}= 60/130\textdegree C, respectively. This system, however, could not maintain a temperature gradient of T\textsubscript{cold}/T\textsubscript{hot}= 30/130\textdegree C because of the higher thermal conductivity and low viscosity of MPN. The IL electrolytes were tested at T\textsubscript{cold}/T\textsubscript{hot}= 30/130\textdegree C, 60/130\textdegree C and 90/130\textdegree C. It was found that the optimum temperature gradient depended on the IL used. The best-performing IL, C\textsubscript{2}mim B(CN)\textsubscript{4}, had a maximum power of 183 mW/m\textsuperscript{2} at 60/130\textdegree C. A cold electrode temperature of 30\textdegree C was thought to slow down the diffusion in C\textsubscript{2}mim B(CN)\textsubscript{4} due to increased viscosity, resulting in lower performance. The second-best performing IL was C\textsubscript{2}mim NTf\textsubscript{2}, with a maximum power of 133 mW/m\textsuperscript{2} at 30/130\textdegree C. The power outputs reported in this work are shown in Table 3. The main drawback of the IL systems appears to be their high viscosities, which cause slow diffusion of the redox species, especially at lower temperatures.
To compare the performance of the TEC with different electrolytes, a modified figure of merit, $ZT^*$, was developed taking into consideration the concentration and diffusion limitation of the redox species. For solid state thermoelectrics, the figure of merit, $ZT$, is a function of Seebeck coefficient, conductivity and thermal conductivity, as given by equation 1.3. However, in a system where the charge is carried by species in solution, it is the diffusion rate that is the relevant parameter, rather than the electrical conductivity. Thus, the modified figure of merit equation replaces conductivity by the molar conductivity, as given by Nernst-Einstein equation.\[^{31}\]

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$T_{\text{cold}}$/$T_{\text{hot}}$ (°C)</th>
<th>Power density (mW/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPN</td>
<td>60/130</td>
<td>499</td>
</tr>
<tr>
<td></td>
<td>70/130</td>
<td>209</td>
</tr>
<tr>
<td></td>
<td>90/130</td>
<td>143</td>
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<tr>
<td>C$_2$ mim B(CN)$_4$</td>
<td>30/130</td>
<td>165</td>
</tr>
<tr>
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<td>60/130</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>90/130</td>
<td>88</td>
</tr>
<tr>
<td>C$_2$ mim NTf$_2$</td>
<td>30/130</td>
<td>133</td>
</tr>
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<td></td>
<td>60/130</td>
<td>120</td>
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<tr>
<td></td>
<td>90/130</td>
<td>30</td>
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<tr>
<td>C$_2$ mim eFAP</td>
<td>30/130</td>
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</tr>
<tr>
<td></td>
<td>60/130</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>90/130</td>
<td>63</td>
</tr>
</tbody>
</table>

Table 3 The power output of the TEC with 0.1 M Co$^{2+/3+}$(bpy)$_3$ redox couple in ILs and MPN. The key to ILs can be found in Table 2.\[^{10}\] Reproduced from Abraham, T. J., et al. (2013). Energy & Environmental Science 6(9): 2639. With permission of the Royal Society of Chemistry.
\[ \Lambda = \frac{\sigma}{c} = \left( \frac{Z^2 F^2}{RT} \right) [D_{ox} + D_{red}] \quad \text{Eqn 2.9} \]

Where \( z \) is the ion charge, and \( D_{ox} \) and \( D_{red} \) are the diffusion coefficients of the reduced and oxidised species of the redox couple. Substituting this into the figure of merit equation gives:

\[ ZT^* = \left( \frac{Z^2 F^2}{RT} \right) \frac{S_e^2 D_{lim} c}{k} \quad \text{Eqn 2.10} \]

Where \( c \) is the concentration of the redox couple and \( D_{lim} \) is the limiting diffusion coefficient when one of the redox species is diffusion limited.

Seebeck coefficient and diffusion coefficient measurements were performed by Abraham et al.\(^{31}\) to calculate the modified figure of merit for all the systems tested. The figure of merit showed similar trends to that of the power density and current outputs, with a maximum of 1.3E-4 for the best performing IL, C\(_2\)mim B\(_F\)\(_4\). The authors concluded that, while the modified figure of merit helps to predict and compare the performances of different electrolytes, a more detailed electrochemical model is required to fully understand the TEC mechanism.\(^{31}\)

1.2.6 Conclusions and literature gaps

The conversion of waste heat to electricity using thermoelectrochemical cells is a promising contribution to overcoming future energy challenges. However, this field is relatively new and fundamental studies are required to fully understand the variables affecting cell operation. This can be approached in three ways:

1. Undertaking of fundamental studies to understand the thermodynamics of the systems and the factors affecting the Seebeck coefficient; and
2. Understanding of the factors affecting the TEC power and current output, which are mostly dependent on electrolyte properties (i.e. conductivity, viscosity and charge transfer kinetics).
3. Device optimisation in the form of electrode materials, electrode spacing and the use of separator.

The main conclusions from the literature review are as follows.

The redox reaction entropy was previously studied, and correlated with several variables related to the structure of the redox species, such as ligands, radius and ionic charge. The entropy was also related to solvent properties such as polarity-related parameters. In ILs, the entropy of the redox species was affected by both the cation and the anion of the ionic liquid used. However, the influence of different ILs, organic solvents and mixed IL-organic solvent systems on the reaction entropy is not yet fully understood.

The limited understanding of the mechanisms leading to high Seebeck coefficients may be the reason why only a few redox couples with Seebeck coefficients exceeding 1.0 mV/K have been reported in this field. Investigation of a wider range of redox species is needed to understand the effects of redox-couple structure on the entropy changes related to the redox reactions.

In terms of thermoelectrochemical cell measurements, aqueous systems incorporating the potassium ferri/ferrocyanide redox couple have been the main focus in the field. These aqueous systems are mainly limited by the volatility, plus ohmic and charge-transfer over-potentials. High surface area electrodes have been investigated to increase the performance of water-based devices. IL systems were introduced to this field for their ionic conductivity, low volatility and high boiling points. The Co$^{2+/3+}$(bpy)$_3$ redox couple was also introduced, with entropy values exceeding that of the ferri/ferrocyanide aqueous system. The IL electrolytes are, however, limited by their higher viscosities which cause high mass-transport over-potentials.
The gaps in the knowledge can be summarised as:

- Limited understanding of the parameters affecting the Seebeck coefficient in terms of the structure of redox couple, the structure of the surrounding solvent and the interactions between the two.
- Limited understanding of the effects of IL cation and anion on the Seebeck coefficient of a given redox couple.

Thus, this thesis will present a fundamental study on the effect of the structure of redox couple and surrounding solvent system (ionic liquid, organic solvent and their mixtures) on the Seebeck coefficient and TEC device performance. The electrolytes under investigation will be further characterised by electrochemical methods to shed light on the over-potentials limiting the performance of the TEC.
References

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59. M. S. Romano, Intelligent Polymer Research Institute, PhD, University of Wollongong, Carbon nanomaterials as electrodes in thermogalvanic cells for waste heat recovery, 2014.


trifluorophosphate and 1-Ethyl-3-methylimidazolium Tetracyanoborate, 2012, 159, A967-A971.


Chapter Two Methodology
2.1 Materials

2.1.1 Redox couples

Synthesis of [tris(bipyridyl)cobalt(II) bis(trifluoromethanesulfonyl) amide] 
\[ \text{Co}^{2+}(\text{bpy})_3(\text{NTf}_2)_2 \]
The cobalt redox couple was synthesised according to literature procedures.\(^1\) Cobalt chloride hexahydrate (2.9 g, 12.1 mmol,) and 2,2-bipyridine (6.4 g, 40.9 mmol) were refluxed together in methanol (40 mL) for 2 hours before adding an excess (8.3 g, 28.9 mmol) of lithium bis(trifluoromethanesulfonyl)amide (LiNTf\(_2\)). After 1 hour of further stirring at room temperature and the addition of water (15 mL) the precipitated \([\text{Co}^{2+}(\text{bpy})_3(\text{NTf}_2)_2]\) complex was isolated by filtration, washed several times with deionised water and dried under vacuum for 8 hours.

Synthesis of [tris(bipyridyl)cobalt(III) bis(trifluoromethanesulfonyl) amide] 
\[ \text{Co}^{3+}(\text{bpy})_3(\text{NTf}_2)_3 \]
To make the \([\text{Co}^{3+}(\text{bpy})_3(\text{NTf}_2)_3]\) an aliquot (3 g, 2.75 mmol) of the cobalt(II) complex was oxidised using nitrosyl tetrafluoroborate (0.4 g, 3.4 mmol) at room temperature, in acetonitrile (30mL), followed by the addition of excess LiNTf\(_2\) (4 g, 13.9 mmol). Deionised water (15 mL) was then added to precipitate the \([\text{Co}^{3+}(\text{bpy})_3(\text{NTf}_2)_3]\), which was separated by filtration, washed thoroughly with deionised water and dried under vacuum for 8 hours. The purity of the cobalt complexes was confirmed by NMR and cyclic voltammetry, consistent with previous reports.\(^1\)

Synthesis of [tris-(1,10-phenanthroline)-cobalt(II) bis(trifluoromethanesulfonyl)imidide] \[ \text{Co}^{2+}\text{(phen)}_3(\text{NTf}_2)_2 \]
\(\text{CoCl}_2.6\text{H}_2\text{O} (2g, 8.4 \text{ mmol})\) and 1,10-phenanthroline (9.2g, 28 mmol) were separately dissolved in 30 mL of methanol, which gave a purple and colourless solution respectively. The above solutions were mixed and instantly formed a mustard colour solution, which was refluxed for 2 hours. Lithium bis(trifluorosulfonyl)imidide (10.5g, 37 mmol) was added to the above solution and the solution was stirred for another 30 minutes. Methanol was removed under vacuum followed by washing the yellow
solid product with water (3*30mL). The yellow product was dissolved in acetonitrile
and filtered using a syringe filter (teflon 0.22 µm) to remove any solid impurity. The
acetonitrile was removed under vacuum. The yellow product was dried under high
vacuum at 50 ºC for 24 hours which then gave a yellow solid of \([\text{Co}^{2+}\text{(phen)}_3](\text{NTf}_2)_2\)
(7.2g, 81% yield). \(^1\)H NMR (400 MHz, d$_6$-DMSO): 7.75 ppm (dd, \(J_{HH} = 4\) Hz, \(^1\)H), 7.98 (s, \(^1\)H), 8.48 (d, \(J_{HH} = 7.2\) Hz, \(^1\)H), 9.03 (d, \(J_{HH} = 2.8\) Hz, \(^1\)H).
Anal. Calcd for 
C$_{40}$H$_{24}$N$_8$F$_{12}$O$_8$S$_4$Co: C, 41.42; H, 2.08; N, 9.66. Found: C, 41.72; H, 1.78; N, 9.20.

Synthesis of \([\text{tris-(1,10-phenanthroline)-cobalt(III)}\text{bis(trifluoromethanesulfonylimide)] Co}^{3+}\text{(phen)}_3\] (NTf$_2$)$_3$

The \([\text{Co}^{2+}\text{(phen)}_3](\text{NTf}_2)_2\) (2.7g, 23 mmol) was dissolved in CH$_3$CN (20 mL) and nitrosyl
tetrafluoroborate (0.34g, 28.7 mmol) was added slowly, with stirring, to the solution.
The reaction mixture was stirred for 30 minutes at room temperature. Lithium
bis(trifluoromethanesulfonylimide) (3.3g, 114.6 mmol) was added and the solution
was again stirred for 1 hour. The product was filtered and washed with water (3*30
mL). The product was dried under high vacuum at 50 ºC for 24 hours to give
\([\text{Co}^{3+}\text{(phen)}_3]\] (NTf$_2$)$_3$ (3.2g, 96% yield) as a yellow solid. \(^1\)H NMR (400 MHz, DMSO):
7.68 ppm (dd, \(J_{HH} = 5.6\) Hz, \(J_{HH} = 1.04\) Hz, \(^1\)H), 8.00 (dd, \(J_{HH} = 5.6\) Hz, \(J_{HH} = 8.3\) Hz, \(^1\)H),
8.6 (s, \(^1\)H), 9.2 (dd, \(J_{HH} = 8.4\) Hz, \(J_{HH} = 1.15\) Hz \(^1\)H). \(^{13}\)C NMR (100 MHz, DMSO): 119.94
(q, \(J_{CF} = 312\) Hz, CF3), 129.20 (phen), 129.68 (phen), 132.44 (phen), 142.44 (phen),
146.11 (phen), 154.08 (phen). Anal. Calcd for 
C$_{42}$H$_{24}$N$_9$F$_{18}$O$_{12}$S$_6$Co: C, 35.03; H, 1.68; N, 8.76. Found: C, 35.11; H, 1.65; N, 8.71.

Tris[2-(1H-pyrazol-1-yl)pyrimidine]cobalt(III)
tris[tris(trifluoromethanesulfonylimide) and the analogous cobalt(II) complex,
Co$^{2+/3+}$(py-pz)$_3$(NTf)$_{2/3}$, were purchased from Dyesol and used as received (purity
$\geq$98%)

Tris[2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(II)
bis[tris(trifluoromethanesulfonylimide) and the analogous cobalt (II) complex,
Co$^{2+/3+}$(Bupy-pz)$_3$(NTf)$_{2/3}$, were also purchased from Dyesol and used as received
(purity$\geq$98%). All Dyesol complexes were stored in an argon glove box.
2.1.2 Ionic liquids and solvents

The structure of the ionic liquid cations and anions used are shown in Figure 1. The ionic liquids were used as received unless otherwise stated. The ionic liquids 1-ethyl-3-methylimidazolium tetracyanoborate, \([\text{C}_2\text{mim}][\text{B(CN)}_4]\), 1-(2-Methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate \([\text{MeOEt}][\text{mPyr}][\text{eFAP}]\), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, \([\text{C}_4\text{mim}][\text{eFAP}]\), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate \([\text{C}_6\text{mim}][\text{eFAP}]\), 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, \([\text{C}_2\text{mim}][\text{eFAP}]\) and 1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate \([\text{C}_{\text{ampyr}}][\text{eFAP}]\) were purchased from Merck (purity 99%).

1-butyl-2-methylimidazolium trifluoromethanesulfonate, \([\text{C}_4\text{mim}][\text{MeSO}_3]\) was purchased from io-li-tec (purity 99%).

The ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide, \([\text{C}_4\text{mim}][\text{NTf}_2]\), 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonylimide, \([\text{C}_3\text{dmin}][\text{NTf}_2]\), 1-butyl-2,3-dimethylimidazolium trifluoromethanesulfonate, \([\text{C}_3\text{dmin}][\text{OTf}]\), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, \([\text{C}_2\text{mim}][\text{OTf}]\), 1-butyl-3-methylimidazolium tetrafluoroborate, \([\text{C}_4\text{mim}][\text{BF}_4]\), 1-butyl-3-methylimidazolium methanesulfonate, \([\text{C}_4\text{mim}][\text{MeSO}_3]\), 1-ethyl-3-methylimidazolium methanesulfonate, \([\text{C}_2\text{mim}][\text{MeSO}_3]\) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonylimide, \([\text{C}_2\text{mim}][\text{NTf}_2]\), were purchased from Sigma Aldrich with purity >98%.

The ionic liquids trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonylimide, \([\text{P}_{6,6,6,14}][\text{NTf}_2]\), triethyl(butyl)phosphonium p-toluenesulfonate, \([\text{P}_{2,2,2,4}][\text{Tos}]\) and trihexyl(tetradecyl)phosphonium tetrafluoroborate, \([\text{P}_{6,6,6,14}][\text{BF}_4]\) were obtained from Cytec or Sigma Aldrich, with a purity of at least 97%.

The propylene carbonate, (PC), dimethyl sulfoxide, (DMSO), dimethyl sulfoxide anhydrous (<0.005% water), 3-methoxypropionitrile, (MPN), dichloromethane,
(DCM), cyclohexane, and acetonitrile, (ACN), were purchased from Sigma Aldrich (>99.7% purity).

Figure 1 The cations and anions of the ionic liquids used in this thesis. (a) 1-ethyl-3-methylimidazolium (C₅mim), (b) 1-ethyl-2,3-dimethylimidazolium (C₆dmim), (c) is 1-butyl-3-methylimidazolium (C₄mim), (d) 1-hexyl-3-methylimidazolium (C₆mim) (e) triethyl(butyl)phosphonium (P₂₂₂₄), (f) 1-(2-Methoxyethyl)-1-methylpyrrolidinium ((MeOEt)mPyr) (g) tris(pentafluoroethyl) trifluorophosphate (eFAP), (h) bis(trifluoromethanesulfonyl)imide (NTf₂), (i) tetracyanoborate (B(CN)₄), (j) methanesulfonate (MeSO₃) (k) p-toluenesulfonate, (l) trifluoromethanesulfonate (OTf), (m) trihexyl(tetradecyl)phosphonium (P₆₆₆₁₄) and (n) tetrafluoroborate (BF₄).
2.1.3 Drying of ionic liquids

Ionic liquids were dried under vacuum at 50°C for 48 hours in the presence of a drying agent, sodium hydride, (NaH, 60% dispersion in mineral oil), purchased from Sigma Aldrich and held in a separate container. A drying vessel connected to a vacuum line was used: the setup is shown in Figure 2. The dried samples were stored in an Argon glove box. The water content of the samples was < 100 ppm (0.01%), measured by Karl Fischer titration analysis.

![Figure 2 The setup used to dry ionic liquids.](image)

2.2 Experimental techniques

2.2.1 The Seebeck coefficient measurement

The Seebeck coefficient measurement was performed using a non-isothermal cell setup described in the literature and shown in Figure 3. Two platinum wire electrodes were immersed in the electrolyte in two sample vials containing approximately 1ml of solution. The sample vials were connected by a salt bridge containing the same solution. One sample vial was kept at room temperature by a water bath and the temperature was measured by a digital thermometer. The other was heated using a brass block with a cartridge heater connected to a Shimaden FP21
programmable controller. The potential difference across the Pt wire electrodes was measured using a UNI-T UT803 TRMS bench voltmeter. The Seebeck coefficient measurement setup is illustrated in Figure 3. The setup was tested by reproducing the benchmark Seebeck coefficient of the 0.4M potassium ferri/ferrocyanide redox couple in water, giving the expected value of -1.4 mV/K. The Seebeck coefficient measurements showed good reproducibility, with an uncertainty margin of ± 0.02 mV/K.

Figure 3 A schematic of the Seebeck coefficient measurement setup.

2.2.2 Measurements of the Seebeck coefficient under dry conditions or with controlled water content.

The Seebeck coefficient was measured under dry or water controlled conditions using a nitrogen-filled glove bag purchased from Sigma Aldrich. The Seebeck coefficient setup was moved to the glove bag which was then sealed and purged with nitrogen three times. The glove bag was then filled with nitrogen and a small flow of
nitrogen gas was maintained throughout the experiment to ensure isolation from the atmosphere. The water content of the samples was controlled by adding known amounts of water to the dry ionic liquid samples containing the redox couple in a nitrogen filled glove bag.

2.2.3 Thermoelectrochemical cell performance
The thermoelectrochemical cell, or thermocell, was composed of two platinum disc electrodes in a cylindrical cell with an active electrode diameter of ca. 9mm and electrode spacing of ca. 1cm (Figure 4). The cell was cooled in an ice box and the electrode temperatures were controlled by adhesive heaters (Minco Products Asia
Pacific Pt Ltd) attached to the back of the electrodes connected to a Manson NP-9613 DC regulated power supply. The temperature of the electrode surface was measured by temperature sensors (Onetemp Pty Ltd) connected to Novus NI020 temperature controllers (uncertainty ±0.2°C). A Keithley 2700 voltmeter was used to record the cell potential upon application of a series of eight known resistances, applied using external resistors with known values. The current and power outputs of the thermocell were then calculated using Ohms law $I = \frac{V}{R}$ and Joule’s law $P = I^2 R$. The cell was allowed ten to fifteen minutes to equilibrate at each applied resistance. The maximum power is achieved when the external load resistance is equal to the internal resistance of the cell.

2.2.4 The use of carbon coated electrodes

A carbon slurry was prepared by mixing conductive carbon black (C65 C-Nergy super, Timcal) with poly(vinylidene fluoride) (Solef PVDF, Solvay) at 75% to 25% weight ratio respectively. The mixture was then dissolved in N-methyl-2-pyrrolidone (NMP) (Sigma Aldrich) and mixed until a smooth slurry was obtained. The TEC disc electrodes were coated with a thin layer or slurry and left to dry over night. The electrodes were further dried in a 70°C oven for several hours before use. The carbon layer weight around 20mg±5mg after drying.

2.2.5 Cyclic voltammetry

Cyclic voltammetry is the electrochemical technique used to investigate the electrochemical behavior of the redox couples. Figure 5 (a) shows a schematic of the experimental set up used for the cyclic voltammetry. The setup is composed of three electrodes; a working electrode, a counter electrode and a reference electrode. A Biologic VMP3/Z potentiostat was used to apply a potential sweep and measure the current response. The working electrodes were purchased from eDAQ Australia or ALS Japan, typically with surface area of 2.0 mm² unless otherwise specified. The reference electrode used was a refillable miniature Ag/AgCl, also purchased from eDAQ Australia, or a platinum wire. The counter electrode used was a platinum mesh.
The working electrode was polished with 0.3 µm alumina powder paste then rinsed thoroughly with deionized water and dried before each measurement.

Figure 5 (b) shows the typical shape of the cyclic voltammetry (CV) of Co^{2+/3+}(bpy)_3 in an ionic liquid. The peak on the right hand side of the figure (with positive current) is due to the oxidation of Co^{2+}(bpy)_3. As the applied potential is increased, the current starts to drop when the concentration of the Co^{2+}(bpy)_3 species begins to be depleted in the vicinity of the working electrode, i.e. the process becomes limited by mass transport through the electrolyte. The opposite process (reduction) occurs when the potential is reversed and becomes less than the equilibrium redox potential, giving rise to the negative peak on the left hand side of the figure.

The size of separation between the two peaks is the first indication of the electrochemical reversibility of the redox reaction. A redox reaction can be described as fully electrochemically reversible when the peak-to-peak separation is no more than 59 mV. A second feature indicating reversibility is the ratio of oxidation to reduction peak currents, which should be close to unity. Thirdly, the peak positions should remain unchanged with varying scan rate. A redox reaction may be described as quasi-reversible if all three reversibility conditions are not met.
Figure 5 (a) A schematic of the three electrode experimental set up for cyclic voltammetry (CV) and (b) a CV of Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_{2/3}$ in neat [C$_2$ mim][NTf$_2$]. Reproduced from Abraham, T. J., et al. (2013). Energy & Environmental Science 6(9): 2639. With permission of the Royal Society of Chemistry.

2.2.6 Electrochemical impedance spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is an electrochemical technique where frequency dependent potential is applied in the form of a sine wave and the current response is measured. The data can be analysed and represented in several forms, most commonly a Nyquist plot. The Nyquist plot can be used to obtain information about the different sources of resistance which occur when current is drawn from an electrochemical system. EIS was used to measure the ionic conductivity of the redox active electrolytes used, and the charge transfer resistance of the electrodes when in contact with different redox active electrolytes.

The applied alternating potential signal can be described by a sine function wave given by: \(^3\)
\[
E_t = E_0 \sin(\omega t)
\]  
Eqn 1. 1

Where \( E_t \) is the applied potential as a function of time \( t \), \( E_0 \) is the amplitude of the potential wave and \( \omega \) is the angular frequency. The response current wave \( (I_t) \) occurs with a phase shift and can be given by:

\[
I_t = I_o \sin(\omega t + \varphi)
\]  
Eqn 1. 2

Where, \( \varphi \) is the phase shift and \( I_o \) is the amplitude of the current wave.

The impedance can then be given by the ratio of the applied voltage to the response current according to Ohm’s law:

\[
Z = \frac{E_t}{I_t} = Z_o \frac{\sin(\omega t)}{\sin(\omega t + \varphi)}
\]  
Eqn 1. 3

Where, \( Z_o = \frac{E_0}{I_o} \). This equation can be used when the relationship between the applied voltage and response current is linear, which requires the application of small wave amplitudes. The impedance can be expressed as a complex function according to Euler’s relation:

\[
Z(\omega) = \frac{E_o \exp(j\omega t)}{I_o \exp(j\omega t - \varphi)} = Z_o (\cos \varphi + jsin \varphi)
\]  
Eqn 1. 4

The impedance can be described in terms of a real and an imaginary term. The Nyquist plot is a plot between the imaginary term of the system’s impedance \( Z_{Im} \) versus the real term \( Z_{Re} \). For the redox active species analysed in this project, this yields a semi-circle and a linear region referred to as the Warburg impedance.

The range of frequencies applied were 0.1 Hz to 1.0MHz. The potential wave amplitude was 10 mV unless otherwise specified. A schematic of a typical Nyquist plot for an electrolyte is shown in Figure 6. The first touchdown corresponds to the solution resistance \( (R_{sol}) \). The electrolyte ionic conductivity can be calculated from this value. The second touchdown corresponds to the sum of the solution resistance and the charge transfer resistance at the electrode surface \( (R_{sol+R_{CT}}) \). The charge transfer resistance can be calculated from the second touchdown.
Figure 6 A Nyquist plot obtained from electrical impedance spectroscopy (EIS) for 5mM Co^{2+/3+}(bpy)_3 in C_{2}mim eFAP. Parts of the figure were reproduced from A. J. Bard and L. R. Faulkner, Electrochemical methods: fundamentals and applications, Wiley New York, 1980. With permission from John Wiley & Sons, Inc. Copyright 2001 ©.

2.2.6.1 Measurement of electrolyte conductivity by EIS

The electrolyte conductivity was measured using a biologic MTZ 35 potentiostat. Electrical Impedance Spectroscopy (EIS) was applied to obtain the Nyquist plots. A custom built dip cell with two identical platinum wire electrodes was used. A schematic of the dip cell is shown in Figure 7. The dip cell was immersed in the sample contained in a sample vial. The sample vial was placed in a custom made brass block with a cartridge heater connected to a Eurotherm 2240E temperature controller. The temperatures were held at 25°C unless otherwise specified. A potassium chloride (KCl) solution with known conductivity was used to determine the cell constant $G = \frac{l}{A'}$, where, $A'$ is surface area of the electrodes and $l$ is the inter-electrode spacing. The electrolyte conductivity was calculated using:
\[ \kappa (S/cm) = \frac{R_{exp}(KCl) \kappa_{Known}(KCl)}{R_{sample}} \]  

Eqn 1. 5

Where, \( \kappa \) is the ionic conductivity in S.cm\(^{-1} \), \( R_{exp}(KCl) \) is the solution resistance of the \( KCl \) solution with known conductivity (\( \kappa_{Known} \)) obtained from the first touchdown of the Nyquist plot (Figure 6) and \( R_{sample} \) is the resistance of the sample under study, also obtained from the first touchdown of the Nyquist plot.

Figure 7 The dip cell used to measure the electrolyte conductivity by EIS, and the brass block with a cartridge heater used to control the electrolyte temperature.

2.2.6.2 Measurements of the charge transfer resistance by EIS

The charge transfer resistance of the redox active electrolytes was measured using the three electrode setup described in section 2.5. The working electrode was polished with 0.3 µm Alumina powder, rinsed thoroughly with deionized water then dried before each measurement. A Bio-Logic multichannel potentiostat VMP3 was used to perform the electrical impedance spectroscopy (EIS) and obtain the Nyquist plots. The second touchdown in the Nyquist plots corresponds to the combination of
solution resistance ($R_{solution}$) and charge transfer resistance ($R_{CT}$). The charge transfer resistance was calculated by subtracting the resistance of the first touch down from the second, $R_{\text{second touchdown}} - R_{\text{first touchdown}}$, and normalised using the geometric surface area of the working electrode which was 2.0mm$^2$ unless otherwise specified. $R_{CT}$ error values were given in the corresponding result sections unless found to be insignificant.

2.2.7 Diffusion coefficient measurements

The diffusion coefficient of each redox active species, in the presence of both halves of the redox couple, was measured using the three electrode system described in section 2.5. A Bio-Logic multichannel potentiostat VMP3 was used to perform chronoamperometry, where a known potential is held and the resulting current is measured as a function of time. Cottrell’s equation can then be used to extract the diffusion coefficient. Cottrell’s equation is given by:

$$i(t) = \frac{nFAD_0^{1/2}C_o^*}{\pi^{1/2}t^{1/2}}$$  \hspace{1cm} \text{Eqn 1.6}

Where, $i(t)$ is the current as a function of time, $n$ is the number of electrons involved in the reaction, $F$ is Faraday’s constant, $A$ is the surface area of the working electrode, $D_0$ is the diffusion coefficient and $C_o^*$ is the concentration of the reactant.

The boundary conditions of Cottrell’s equation state that the concentration of the reactants is homogenous at the start of the experiment ($t=0$) and during the experiment at a distance far from the electrode surface ($X=\infty$), meaning that only the reactant species in the vicinity of the electrode are affected by the applied potential. The boundary conditions also state that the reactant species are depleted at the vicinity of the electrode during the experiment ($t>0$) and the current measured is diffusion controlled. To meet the last boundary condition, the potential applied needs to be of sufficient value appropriate to the experiment to achieve depletion of the redox species in the vicinity of the electrode. The appropriate potential can be determined by performing a cyclic voltammetry and choosing a potential value in the depletion region following the oxidation or reduction peaks, as shown in Figure 8.
When measuring the diffusion coefficient by the Cottrell method, experimental limitations may apply. A contribution to the initial current value may occur due to non-Faradic current arising from the charging of the double layer capacitance at the electrode surface (see Figure 8). To account for this, when analysing the data, the initial current value should be neglected up to a time period five times greater than the time constant \( \tau = R_u C_d \), where \( R_u \) is an uncompensated resistance and \( C_d \) is the double layer capacitance. At longer time periods, convective currents may start to occur, resulting in current values larger than predicted by Cottrell’s equation. In this work the chronoamperometry was performed for 10 s unless otherwise specified, and the first two seconds of data were neglected. The data was analysed by plotting the current density \( J (\text{mA/cm}^2) \) versus the inverse of the square root of time, \( 1/t^{1/2} \). A linear plot was obtained and the diffusion coefficient was extracted from the slope of the line.

![Figure 8](image.png)

**Figure 8** (a) A typical Chronoamperometry plot obtained for 0.1 M \( \text{Co}^{2+/3+} \)(bpy)\text{3} redox couple, when a positive potential was applied and the resulting current can be attributed to the diffusion of the \( \text{Co}^{2+} \)(bpy)\text{3}. (b) A cyclic voltammetry of the same redox couple showing the depletion regions.
2.2.8 Measurements of Kamlet-Taft parameters by UV-Visible spectroscopy

The Kamlet-Taft parameters were measured using three solvatochromic dyes; 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate, also known as Reichardt’s dye, was purchased from Sigma Aldrich (90% dye content). The 4-nitroanaline was also purchased from Sigma Aldrich (purity ≥99%). The 4,4-diethyl-4-nitroanaline was purchased from Oakwood Chemicals. A stock solution was prepared for each dye dissolved in dichloromethane (DCM) at about 0.9 mM concentration. The stock solution was then added to the sample under study at ca. 1:10 volume ratio of dye solution to sample. The DCM was then removed under high vacuum. A UV-vis absorbance of ≤ 1.0 was obtained for all samples. The samples were diluted if the absorbance was larger than 1.0. All samples studied had water content under 100ppm, measured by Karl Fischer titration analysis. The samples were sealed from the atmosphere after preparation, in a Quartz UV-Vis cuvette purchased from Starna with path length of 5mm and internal width of 2mm. A schematic of the cuvette is shown in Figure 9. A Shimadzu Uv-Vis spectrophotometer (UV-2600) was used to obtain the absorbance spectra. Samples were scanned between 250 nm and 800 nm.

Figure 9 A schematic showing the dimensions of the UV-Vis cuvettes used (Left) and an example of a Uv-Vis spectrum obtained from 4,4-diethyl-4-nitroanaline dissolved in acetonitrile (Right).
To calculate the Kamlet-Taft parameters for a given solvent, three different samples were prepared using each of the three dyes dissolved in the solvent under study. The Uv-Vis spectrum was obtained from each sample five times giving a total of 15 spectra obtained from each dye. The wavelength associated with maximum absorbance and the corresponding wavenumber were determined for each spectrum. Figure 9 shows an example spectrum obtained from 4,4-diethyl-4-nitroaniline dissolved in acetonitrile.

Two reference solvents, cyclohexane and dimethyl sulfoxide (DMSO), were used to represent the two ends of each polarity scale. The average wave number associated with maximum absorbance was obtained for each dye in both solvents, i.e. \( \bar{\nu}_{\text{cyclohexane}} \) and \( \bar{\nu}_{\text{DMSO}} \). \( \pi^* \) was calculated using the spectra obtained from 4,4-diethyl-4-nitroaniline using:

\[
\pi^* = \frac{\bar{\nu}_{\text{solvent}} - \bar{\nu}_{\text{cyclohexane}}}{\bar{\nu}_{\text{DMSO}} - \bar{\nu}_{\text{cyclohexane}}}
\]

Where, \( \bar{\nu}(cm^{-1}) = \frac{10^7}{\lambda_{\text{max}}(nm)} \). \( \beta \) was calculated from the spectra obtained using both 4,4-diethyl-4-nitroaniline and 4-nitroaniline using the relation:

\[
\beta = \frac{0.76(\Delta\bar{\nu}_{\text{solvent}} - \Delta\bar{\nu}_{\text{cyclohexane}})}{\Delta\bar{\nu}_{\text{DMSO}} - \Delta\bar{\nu}_{\text{cyclohexane}}}
\]

Where, \( \Delta\bar{\nu} = \bar{\nu}_{N,N-diethyl-4-nitroaniline} - \bar{\nu}_{4-nitroaniline} \). \( \alpha \) was calculated using the spectra obtained from Reichardt’s dye and \( \pi^* \) values obtained for the same solvent under study. \( \alpha \) is given by:

\[
\alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^*
\]

Where, \( E_T(30) = \frac{28591}{\lambda_{\text{max}}} \).
2.2.9 Theoretical calculation of redox couple radii.

The radii of the redox complexes was measured by Avogadro molecular modelling software version 1.1.1. The redox couple structure was optimised using universal force filed. The reported error values were calculated by calculating the complex radius from the central cobalt atom to three different end points corresponding to each ligand.
References


Chapter Three

The use of ionic liquids, high boiling point organic solvents and mixed electrolytes in thermoelectrochemical cells
3.1 Introduction

This chapter reports the use of mixed ionic liquid/organic solvent electrolytes for thermal energy harvesting application using the thermoelectrochemical cell (TEC). In this study, the mixed electrolytes were studied from two perspectives. First, a fundamental one, where the Seebeck coefficient in different volume ratio mixtures of ionic liquid/organic solvent was investigated. The effect of solvent environment on the Seebeck coefficient was assessed. In addition, the electrolytes were studied in terms of the Kamlet-Taft parameters in an attempt to correlate the Seebeck coefficient to measurable solvent parameters.

The Kamlet-Taft parameters are used in this chapter to rank ionic liquid electrolytes and their mixtures with solvents in terms of polarity and the ability to hydrogen bond. In accordance with the discussion above, the parameters are used to compare different systems rather than to give absolute values. One set of dyes was used for these measurements: N,N-diethyl-4-nitroaniline, 4-nitroanaline and Reichardt’s dye.

The second perspective is a study of the mixed electrolytes in terms of device performance. The TEC performance can be assessed in terms of three over-potentials present in the cell when current is drawn, as discussed in detail in the literature review (section 2.1.1). Briefly, these are the (i) charge transfer over-potential which relates to the catalytic properties of the electrode material, (ii) the ohmic over-potential that primarily relates to the ionic conductivity of the electrolyte, and (iii) mass transport over-potential that relates to the diffusion of the redox species and the viscosity of the electrolyte material.

The nature and size of the limiting over-potential will vary with each electrolyte and temperatures used, and determining the limiting over-potential for a given electrolyte is key when it comes to device optimisation. For instance, in TECs with ionic liquids, the high viscosity leads to high mass transport over-potential, which is evident in low diffusion coefficients measured for these electrolytes when compared
In contrast, generally when the more fluid aqueous ferri/ferrocyanide electrolyte is used with conventional flat electrodes, the number of reaction sites on the electrode limits TEC performance. This has led to recent studies focused on high surface area carbon-based electrodes, which provide an increased number of reaction sites and enhance the cell performance. The over-potentials in the TEC were investigated, in particular, the mass transport over-potential which is expected to be limiting when viscous electrolytes are used. To overcome the mass transport over-potential, the use of high boiling point co-solvents was investigated.

3.2 Materials and experimental methods

The materials in this study were chosen based on a previous related study, as introduced in Chapter one. The Co^{2+/3+}(bpy)_3(NTf_2)_2/3 was reported to have high Seebeck coefficient in ionic liquids, exceeding that of the benchmark value ($S_e = -1.40$ mV/K) reported for the ferri/ferrocyanide aqueous electrolyte. In addition, the use of the NTf_2$^-$ counter ion, rather than PF_6$, increased the solubility and electrochemical stability of this redox couple in the ionic liquids studied. Increasing the concentration of the redox couple can reduce the mass transport over-potential due to increased number of the redox active species.

The ionic liquid C_2mim eFAP was chosen for study as it has the highest Seebeck coefficient in the ionic liquids previously tested with the Co^{2+/3+}(bpy)_3(NTf_2)_2/3 redox couple (1.88 mV/K at 0.10M Co^{2+/3+}(bpy)_3). The investigations into this IL will be compared to the results of parallel investigations into the ionic liquid C_2mim B(CN)_4, chosen for having the highest power density obtained from the TEC, which is attributed to high diffusion coefficient for Co^{2+/3+}(bpy)_3 in this IL.

All measurements on the MPN-C_2mim B(CN)_4 electrolyte were performed by a postdoctoral fellow on the project, Dr. Manoj Lazar. However, the author also made significant intellectual input into the measurement and interpretation of this data and so it will be included in this chapter.
Thus, the following electrolytes were investigated in this chapter:

- Neat C2mim eFAP, neat dimethylsulfoxide (DMSO) and their volume mixtures at 1:3, 1:1 and 3:1 DMSO to C2mim eFAP.
- Neat C2mim B(CN)4, neat 3-methoxypropionitrile (MPN) and their volume mixtures at 1:3, 1:1 and 3:1 MPN to C2mim B(CN)4.

The ionic liquids, organic solvents and their mixtures were characterised for the following properties: measurement of the Seebeck coefficient, the thermoelectrochemical cell performance and diffusion coefficient measurements. The ionic conductivity and charge transfer resistance were measured by EIS. A dip cell with two platinum wire electrodes was used in this thesis for both conductivity and charge transfer resistance measurements (see chapter two, section 2.6). Typically, an electrode with known surface area is used for charge transfer resistance measurements. The results are normalized by the surface area of the electrode and reported in Ω.cm². However, the surface area of the platinum wires of the dip cell could not be measured with sufficient accuracy and so the charge transfer resistance values in this chapter are reported in ohms, Ω. This still provides valuable insights as the significance of this data is in the trends across different solvent systems, rather than the absolute values. This chapter also reports the Seebeck coefficient and the Kamlet-Taft parameters in the ionic liquids C4mim NTf2 and C4dmim NTf2.

3.3 Results and discussion

3.3.1 The Seebeck coefficient of Co²⁺/³⁺(bpy)₃(NTf₂)₂/₃ in C₂mim eFAP, C₂mim B(CN)₄ and their mixtures with solvents.

The performance of Co²⁺/³⁺(bpy)₃(NTf₂)₂/₃ in the ionic liquids C₂mim eFAP, C₂mim B(CN)₄ and in the organic solvent MPN (i.e. without any ionic liquid), has been reported by Abraham et al.¹ This was discussed in detail in the literature review in chapter one, but a summary of the outcomes of the study that led to the investigations in this chapter are summarised here.
In the previous study, the authors report the ionic liquid electrolytes to be mass transport limited when compared to the more fluid MPN, which can be seen in the lower diffusion coefficient for Co$^{2+/3+}$ (bpy)$_3$ redox couple in the ionic liquid systems. The authors also reported an increase in power and current density obtained from the TEC when the temperature of the cold electrode was increased from 30°C to 60°C, indicating mass transport limitations at the colder temperatures for these systems.\(^1\)

In this chapter, the high boiling point organic solvents DMSO or MPN were added to the two ionic liquids under investigation in order to reduce the viscosity of the electrolytes and overcome the mass transport limitations of ionic liquids. In addition, the effect of solvent environment on the Seebeck coefficient of Co$^{2+/3+}$ (bpy)$_3$(NTf$_2$)$_{2/3}$ was examined.

The Seebeck coefficient of Co$^{2+/3+}$ (bpy)$_3$(NTf$_2$)$_{2/3}$ at 0.1 M was measured in the neat ionic liquid, the neat solvents and the DMSO:C$_2$ mim eFAP and mixed MPN:C$_2$ mim B(CN)$_4$ 1:3, 1:1 and 3:1 volume mixtures. The Seebeck coefficients vs solvent volume ratio are shown in Figure 1 (a) and Table 1.

Figure 1 The Seebeck coefficient vs (a) volume ratio and (b) molar ratio of the ionic liquid/solvent electrolytes containing 0.1 M Co$^{2+/3+}$ (bpy)$_3$(NTf$_2$)$_{2/3}$. 

75
The Seebeck coefficient of $\text{Co}^{2+/3+}(\text{bpy})_3$ was found to be slightly higher in neat $\text{C}_2\text{mim eFAP}$ than neat $\text{C}_2\text{mim B(CN)}_4$, which is consistent with the previously report.$^1$ A 5% increase in Seebeck coefficient can be seen in both electrolytes when solvents are introduced to the system at 25% volume ratio. The Seebeck coefficient continues to increase in a non-linear trend and reaches a maximum in the neat solvent systems. A notable increase in the Seebeck coefficient occurs at 50 vol% solvent addition, and is more obvious in the $\text{C}_2\text{mim eFAP:DMSO}$ system. In terms of mol%, this correlates to a noticeable increase between 60 and 80 mol% solvent addition in both systems, shown in Figure 1 (b).

The non-linearity of the trend suggests complex interactions between the redox couple and surrounding solvent. It is known that the Seebeck coefficient is related to entropy changes that occur when the redox reactions take place.$^4$ These entropy changes have been the subject of significant prior investigation, as discussed in detail in the literature review. Literature reports suggest that the entropy changes are mostly related to reorganisation of the solvation shell around the redox couple following the reaction. This indicates that changes in the strong coordination between the redox couple and surrounding solvent leads to a high reaction entropy change.$^5,^6$ In light of these prior observations, it can be hypothesised that in the organic solvents the higher Seebeck coefficients indicate that the solvation shell reorganises more significantly.

A recent report by Kim et al.$^7$ on the ferri/ferrocyanide redox couple in a water/methanol mixture suggests preferential solubility for different halves of the redox couple in the different solvent, leading to high entropy changes in this system. A maximum Seebeck coefficient of 2.90 mV/K was reported when 20 weight percent of methanol was added (24% volume).$^7$ However, these results should be interpreted with caution as this solvent system also produces significant precipitation of the redox couple, which will affect the Seebeck coefficient ($S_e$) measurements.
3.3.2 The effect on the Seebeck coefficient of the structure of a series of ionic liquids and their mixtures with DMSO.

The Seebeck coefficient of Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_{2/3}$ was also measured in a series of ionic liquids as a function of composition and IL chemistry. Specifically, the effect of variation of the cation (eg. nature of alkyl chains), the anion, and the mixture composition with DMSO were explored. This set of measurements was designed to investigate the effect of the structure of the ionic liquid on the Seebeck coefficient of Co$^{2+/3+}$(bpy)$_3$ and also confirm the trend of increasing Seebeck coefficient with solvent addition for other ionic liquids.

Previous reports show high Seebeck coefficients for the Co$^{2+/3+}$(bpy)$_3$ in the ionic liquid C$_2$ mim eFAP when compared to a range of other ionic liquids.$^{1,8}$ The high Seebeck coefficient was attributed to strong interactions of the ionic liquid with the positively charged Co$^{2+/3+}$(bpy)$_3$ redox complex. In this section, the Seebeck coefficient of Co$^{2+/3+}$(bpy)$_3$ in the ionic liquid C$_2$ mim eFAP was measured as a function of composition and IL chemistry. The effect of the cation (eg. nature of alkyl chains), the anion, and the mixture composition with DMSO were explored. This set of measurements was designed to investigate the effect of the structure of the ionic liquid on the Seebeck coefficient of Co$^{2+/3+}$(bpy)$_3$ and also confirm the trend of increasing Seebeck coefficient with solvent addition for other ionic liquids.
coefficient of the Co$^{2+/3+}$(bpy)$_3$ was measured in C$_2$mim eFAP and compared to other ionic liquids with systematic changes in the structure of the anions and cations. The Seebeck coefficient in C$_2$mim eFAP reported here is slightly lower than the previously reported value.$^1$ This is attributed to differences in the setup and equipment used, plus any differences in the ionic liquid and redox couple purity/water content.

The concentration of Co$^{2+/3+}$(bpy)$_3$ was reduced to 0.01 M in this investigation to ensure good solubility in all the ionic liquids tested. The following ionic liquid electrolytes were used in their neat form and in combination with DMSO at 1:3, 1:1 and 3:1 volume mixtures:

- 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, (C$_2$mim eFAP).
- 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, (C$_2$mim OTf).
- 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate (C$_4$mpyr eFAP).
- 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (C$_6$mim eFAP).
- 1-(2-methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ((MeOEt)mPyr eFAP).

Figure 3 and Table 2 show the Seebeck coefficients of Co$^{2+/3+}$(bpy)$_3$ in all ionic liquids and their mixtures with DMSO. The Seebeck coefficient was found to be significantly affected by changing either the cation or anion of the ionic liquid. The highest Seebeck coefficient measured in a neat IL in this data set was for C$_2$mim eFAP at 1.69 mV/K. The Seebeck coefficient drops to 1.43 mV/K when eFAP is replaced by OTf, in C$_2$mim OTf. The structure of eFAP and OTf are shown in Figure 2. The high Seebeck coefficient in C$_2$mim eFAP points to high entropy changes accompanying the reaction of the redox species, as predicted by equation 1.4 in chapter one. Large entropy changes occur as a result of reorganisation of the solvation shell surrounding
the redox species when the redox species strongly coordinates with the surrounding solvent.

![Chemical structures](image)

Figure 2 The structure of tris(pentafluoroethyl)trifluorophosphate (eFAP) (Left) and trifluoromethanesulfonate (OTf) (Right).

A change of the cation of the ionic liquid from \(\text{C}_2\text{mim eFAP}\) to \(\text{C}_4\text{mpyr eFAP}\) results in a drop in the Seebeck coefficient to 1.46 mV/K. This shows the significant role of the cation of the ionic liquid in determining the Seebeck coefficient, despite being positively charged and therefore less likely to interact directly with the \(\text{Co}^{2+/3+}(\text{bpy})_3\) species. However, both the cation and anion will have a role in any long-range ordering of the ionic liquid.\(^9\) Similarly, studies on the electrode-electrolyte interface show significant differences in the ionic liquid layer structuring on the electrode surface when the cation is varied.\(^{10, 11}\)

The role of alkyl chains attached to the imidazolium cation on the Seebeck coefficient was also investigated. The alkyl chain was varied from ethyl in \(\text{C}_2\text{mim eFAP}\) to hexyl in \(\text{C}_6\text{mim eFAP}\). This change has resulted in a slight decrease in the Seebeck coefficient in \(\text{C}_6\text{mim eFAP}\). Studies show an increase in the nano-scale structuring of ionic liquids with longer alkyl chains.\(^{12, 13}\) Thus, this result might suggest that an increase in long-range ordering and structuring of the solvent leads to a decrease in total entropy change associated with the redox reaction and therefore a decrease in the Seebeck coefficient. This may indicate that the longer range structure in such ILs can act to constrain the reorganisation of the coordination shell during the redox reaction. However, the observation of high Seebeck coefficients in phosphonium ionic liquid/solvent systems, which are believed to possess significant long-range order (discussed in Chapter four), is not consistent with this hypothesis. This illustrates the complexity of factors influencing Se, particularly in mixed IL/solvent systems.
systems. It is also likely that increasing the length of the alkyl chain on the imidazolium cation would reduce the strength of interaction with the redox couple, through a decrease in the charge density on the cation, which could also contribute to a decrease the Seebeck coefficient. These results highlight the need for further study, using a wider range of solvent systems. To this end, the effect of the chemical structure of the neat ionic liquid on the Seebeck coefficient is discussed further in chapter four.

An increase in the Seebeck coefficient of $\text{Co}^{2+/3+}(\text{bpy})_3$ occurred when DMSO was introduced as co-solvent to all the ionic liquids tested. Figure 3 shows the effect of DMSO addition on the Seebeck coefficients in all ionic liquids tested. A non-linear trend of increase in the Seebeck coefficient with DMSO addition can be seen here, consistent with the results presented ion section 3.1.

![Figure 3](image_url)

Figure 3 The Seebeck coefficient of the $\text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_{2/3}$ redox couple, at 0.01M, as a function of volume percentage of DMSO in; 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, $[\text{C}_2\text{mim}][\text{eFAP}]$; 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, $[\text{C}_2\text{mim}][\text{OTf}]$; 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate $[\text{C}_4\text{mpyr}][\text{eFAP}]$; 1-
hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [C₆mim][eFAP]; and 1-(2-methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate [(MeOEt)mPyr][eFAP].

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Table 2 The Seebeck coefficients of Co²⁺/³⁺(bpy)₃(NTf₂)₂/₃ at 0.01M concentration in a range of ionic liquids and their mixtures with DMSO. Key to abbreviations given in Figure 3.

3.3.3 The influence of water content on the Seebeck coefficient.

Discussions on the Seebeck coefficient of Co²⁺/³⁺(bpy)₃(NTf₂)₂/₃ in ionic liquids and organic solvent electrolytes in this thesis so far, and in previous reports,¹ ¹⁴ have related to those measured under atmospheric conditions. Measurements of the Seebeck coefficient under atmospheric conditions are most relevant to understanding the TEC performance, as the device is usually filled and operated under atmospheric conditions – as they would be in commercial applications. However, the influence of water content in the solvent on the reaction entropy of the redox reaction, and thus the Seebeck coefficient, for this redox couple is not well known. On the other hand, the Seebeck coefficient measured under dry conditions allows better correlation with the Kamlet-Taft parameter, which is also measured
under dry conditions. Therefore, in this section the Seebeck coefficient of $\text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_2/3$ in DMSO under dry conditions and with controlled additions of water was investigated.

The Seebeck coefficient of $\text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_2/3$ was measured in $\text{C}_2\text{mim eFAP}$, DMSO and their mixtures under dry conditions in a nitrogen filled glove bag (see chapter 2 for the experimental details). Figure 4 (a) shows the Seebeck coefficients of all electrolytes under dry and atmospheric conditions. The complex was not soluble at 0.01M in the dry neat $\text{C}_2\text{mim eFAP}$.

The Seebeck coefficient shows a slight increase in the dry samples for all the volume mixtures and neat DMSO sample. The highest value measured was in neat and dry DMSO (water content <0.01%) at 2.10 mV/K, which is about 4.7% increase from the water saturated sample (water content 13-15%) with Seebeck coefficient of 2.01 mV/K. The trend of Seebeck coefficient vs DMSO volume percentage remains unchanged. However, the values for the dry samples are slightly above those of the water-saturated ones, shown in Figure 4(a).

To further investigate the role of water on the reaction entropy of the redox couple, water was systematically introduced in incremental amounts to a sample of 0.1M $\text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_2/3$ in neat DMSO. The Seebeck coefficients of the samples vs water content are shown in Figure 4 (b). The Seebeck coefficient showed a significant decrease as more water was introduced into the sample, with the lowest value of 1.75 mV/K at 10wt% water content; the redox couple started to precipitate with further water addition and therefore the maximum water content investigated here was 10 wt%. Both of these sets of results indicate that a lower entropy change is associated with the redox reactions when water is present in the sample. This suggests that $\text{Co}^{2+/3+}(\text{bpy})_3$ coordinates with some water molecules and that the presence of these in the coordination shell lowers the extent of reorganisation during the redox process.
Figure 4 The Seebeck coefficient of 0.1M Co^{2+/3+}[(bpy)_3(NTf_2)]_{2/3} in (a) the C_2mim eFAP:DMSO electrolyte either measured in air (red) or under dry conditions and (b) in neat DMSO, as a function of water content. The complex was not soluble at this concentration in the dry neat C_2mim eFAP and so no data is available for this system.

3.3.4 The relationship between Seebeck coefficient and Kamlet-Taft parameters.

The Kamlet-Taft parameters α, β and π* were measured for the neat DMSO, neat C_2mim eFAP and their volume mixtures (1:3, 1:1 and 3:1 DMSO:C_2mim eFAP) under dry conditions. The DMSO-C_2mim eFAP system was chosen for study as this has the biggest change in Seebeck coefficient upon solvent addition; the lowest for neat C_2mim eFAP, at 1.64 mV/K, and the highest for neat DMSO, at 2.01 mV/K. The trend of Seebeck coefficient vs volume % of DMSO is again nonlinear (Figure 1) and shows a sharp increase at the 1:1 volume mixture.

To reiterate, the Seebeck coefficient is directly related to the entropy change associated with the redox reaction, as discussed in the literature review, thus:

\[ S_e = \frac{\Delta V}{\Delta T} = \frac{\Delta S_{rc}}{nF} \]
This entropy change is known to be heavily influenced by the nature of the solvent used. Thus, the aim of this part of the investigation was to determine any correlation between the solvent properties represented by the Kamlet-Taft parameters and the Seebeck coefficient.

The Kamlet-Taft parameters for all electrolytes and corresponding Seebeck coefficients are shown in Figure 5 and Table 3. An increase in β value occurred when the percentage of DMSO in the electrolyte system was increased. DMSO was described by Kamlet and Taft as a hydrogen bond acceptor (HBA), which is consistent with the highest β values measured here for the 3:1 DMSO:IL and neat DMSO systems.\textsuperscript{15} The increase in β comes in parallel with an increase in the Seebeck coefficient of Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} redox couple. The Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} redox couple is positively charged and so can be expected to have interactions with hydrogen bond donor-type solvents. The Seebeck coefficient is highest in neat DMSO, which indicates stronger interactions that lead to a higher entropy change when solvent reorganisations occur, associated with the redox reactions. The indicator of hydrogen bond donor ability, α, drops with DMSO addition, and correlates with an increased Seebeck coefficient. Finally, the polarity/polarizability, \(\pi^*\), fluctuates between 0.9 and 1.0 for all solvent systems. The preliminary investigations do not show any linear correlation between the Seebeck coefficient and any of the Kamlet-Taft parameters measured. This indicates more complex interactions between the redox couple and surrounding solvent system than can be represented by any one of the Kamlet-Taft parameters.
Figure 5 The Kamlet-Taft parameters of the DMSO:C$_2$ mim eFAP electrolyte mixtures vs the corresponding Seebeck coefficient measured under dry conditions. Measurements of the Seebeck coefficient under dry conditions are discussed in section 3.3. The experimental details of the Kamlet-Taft parameter measurements is given in Chapter two, section 2.8.

<table>
<thead>
<tr>
<th>DMSO volume%</th>
<th>$S_e$(mV/K) (dry conditions)</th>
<th>$\alpha$±0.03</th>
<th>$\beta$±0.03</th>
<th>$\pi^*$±0.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.64*</td>
<td>0.69</td>
<td>0</td>
<td>0.93</td>
</tr>
<tr>
<td>25</td>
<td>1.76</td>
<td>0.63</td>
<td>0.57</td>
<td>0.9</td>
</tr>
<tr>
<td>50</td>
<td>2.04</td>
<td>0.53</td>
<td>0.72</td>
<td>0.93</td>
</tr>
<tr>
<td>75</td>
<td>2.07</td>
<td>0.47</td>
<td>0.78</td>
<td>0.96</td>
</tr>
<tr>
<td>100</td>
<td>2.10</td>
<td>0.0**</td>
<td>0.76</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3 The Seebeck coefficients and Kamlet-Taft parameters of 0.1M Co$^{2+/3+}$(bpy)$_3$ in the DMSO:C$_2$ mim eFAP electrolytes under dry conditions. *measured in water saturated C$_2$ mim eFAP because of poor solubility in the dry sample. **
Reichardts dye (needed for $\alpha$) is not soluble in DMSO and so standard procedure is to set $\alpha$ to 0 when DMSO is used as a reference solvent.

To further investigate any correlation between the Kamlet-Taft parameters and the Seebeck coefficient, the Kamlet-Taft parameters were measured for four neat ionic liquids, following literature procedures.\textsuperscript{16-19} The ionic liquids were chosen to provide the widest range in Seebeck coefficients and thus the biggest possible change in Kamlet-Taft parameters; C$_2$ mim eFAP, chosen for having the highest Seebeck coefficient, and C$_2$ mim B(CN)$_4$, chosen for having the lowest. In addition, C$_2$ mim NTf$_2$ and C$_2$ dmim NTf$_2$ were chosen to investigate the effect of replacing the relatively acidic proton on the imidazolium cation with a methyl group. The Kamlet-Taft parameters of the four ionic liquids, and their corresponding Seebeck coefficients, are shown in Table 4.

The ionic liquid C$_2$ mim eFAP has the lowest $\beta$ value, at nearly zero. In ionic liquids, $\beta$ mostly relates to the anion’s ability to coordinate with the probe used and accept a hydrogen bond. This ionic liquid has the highest Seebeck coefficient in this set of data. This is in contrast with the previous set of data where DMSO had the highest $\beta$ value and the highest Seebeck coefficient.

In the two NTf$_2$ ionic liquids, replacing the methyl group on the cation with a proton results in a slight increase in the $\alpha$ value, which corresponds to the cation’s ability to coordinate and donate a hydrogen bond. A slight increase in the Seebeck coefficient in C$_4$ mim NTf$_2$ compared to C$_4$ dmim NTf$_2$ is also evident. The presence of the C2 proton on the imidazolium ring may result in stronger interactions with the Co$^{2+/3+}$(bpy)$_3$ and therefore higher Seebeck coefficients. It has also been shown that this proton, which is relatively acidic, increases the extent of hydrogen bonding in the ionic liquid.\textsuperscript{20}

The measurement of Kamlet-Taft parameters in ILs has been a topic of many discussions in the literature and the interpretations of these parameters is not
trivial.\textsuperscript{16,18} A wider set of data may be needed to fully understand each of the Kamlet-Taft parameters in different solvents, ionic liquids and their mixtures.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>$S_e$(mV/K)$\pm0.02$</th>
<th>$\alpha\pm0.03$</th>
<th>$\beta\pm0.03$</th>
<th>$\pi^*\pm0.03$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{2}mim eFAP</td>
<td>1.64$^*$</td>
<td>0.68</td>
<td>0.01</td>
<td>0.93</td>
</tr>
<tr>
<td>C\textsubscript{2}mim B(CN)\textsubscript{4}</td>
<td>1.59$^*$</td>
<td>0.57</td>
<td>0.44</td>
<td>1.04</td>
</tr>
<tr>
<td>C\textsubscript{4}mim NTf\textsubscript{2}</td>
<td>1.54$^*$</td>
<td>0.62</td>
<td>0.22</td>
<td>0.97</td>
</tr>
<tr>
<td>C\textsubscript{4}dim mim NTf\textsubscript{2}</td>
<td>1.49$^*$</td>
<td>0.38**</td>
<td>0.24</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Table 4 The Kamlet-Taft parameters of the four neat ionic liquids and the corresponding Seebeck coefficients. *The Seebeck coefficient was measured under atmospheric conditions. **This value was measured by Prof. Tom Welton’s group in Imperial College London, using the same procedure.

3.3.5 The thermoelectrochemical cell performance.

The thermoelectrochemical cell (TEC) performance was investigated in relation to several variables in order to identify the conditions that lead to optimum cell performance with respect to power and current density. The TEC performance was investigated in terms of electrolyte composition (by mixing ionic liquids and organic solvents) and electrolyte properties relating to over-potentials in effect during the cell’s operation. In the following sections, the findings with respect to each variable are reported and the conclusions on the best electrolyte system and conditions for TEC application are given.

The redox couple concentration was chosen to be 0.1 M based on an earlier study on the effect of redox couple concentration in the MPN-C\textsubscript{2}mim B(CN)\textsubscript{4} electrolyte (detailed in full in the paper from this work, ref \textsuperscript{21}). In that study, the concentration of the Co\textsuperscript{2+/3+}(bpy)\textsubscript{3}(NTf\textsubscript{2})\textsubscript{2/3} was varied between 0.025M and 0.4M, and 0.1M was
found to be the optimum concentration in terms of the Seebeck coefficient and also
the TEC performance. It was concluded that the TEC performance initially increased
with concentration due to increased number of charge carriers and enhanced mass
transport. However, further increases in concentration leads to higher viscosity,
which is detrimental to the TEC performance.21

The TEC power and current densities produced by all the electrolyte systems
under study (neat IL, neat solvent and 1:3, 1:1, 3:1 solvent:IL volume ratios) was
measured with 60°C and 130°C cold and hot electrode temperatures, respectively.
Figure 8 (a) and (b) show the power density and current densities, respectively, of all
mixtures of MPN and C2mim B(CN)4. Figure 8 (c) and (d) show the power density and
current densities, respectively, of all mixtures of DMSO and C2mim eFAP.

The most notable feature in these results is that the 3:1 organic solvent to ionic
liquid electrolyte is the best performing in both ionic liquid/solvent systems. The
maximum power density obtained from the TEC was for 3:1 MPN:C2mim B(CN)4. This
trend slightly differs from that of the Seebeck coefficient trend shown in Figure 1,
where the neat solvent systems achieve the highest Seebeck coefficient. This higher
Seebeck coefficient (Se) gives the highest open circuit cell potential. However, when
current is drawn from the cell, the over-potentials at work in the cell come into play.
Measurements of parameters such as the conductivity, viscosity and charge transfer
resistance can help shed light on the role of ohmic over-potential, mass transport
over-potential and activation over-potential, respectively, on determining cell
performance. This is discussed in more details in section 3.6.

In a previous study, the neat MPN electrolyte was shown to have a maximum
power density about triple that of the neat C2mim B(CN)4, giving 499 mW/m².1 The
maximum power density was further increased to a maximum of 776±77 mW/m²
when MPN was mixed with the ionic liquid C2mim B(CN)4 at a 3:1 volume ratio. The
maximum power and current densities obtained from each electrolyte vs the volume
composition of the electrolyte are shown in Figure 7. The addition of ionic liquid adds
charge carriers to the molecular solvent, which increases the conductivity and the cell performance. This was explored further in the following section.

The same effect of solvent addition can be seen for the DMSO-C$_2$ mim eFAP, where the power density was increased by a factor of five going from high volume of ionic liquid in a 1:10 DMSO to IL system, with maximum power density of 158 mW/m$^2$, to a 3:1 DMSO to ionic liquid system with a maximum power density of 776 mW/m$^2$. The performance in neat C$_2$ mim eFAP could not be tested due to precipitation of the redox couple.

Figure 6 (a) the power density and (b) the current density vs cell potential of all MPN-C$_2$ mim (B(CN)$_4$) systems, and (c) the power density and (d) current density vs cell potential of all DMSO-C$_2$ mim eFAP systems. The electrodes were held at $T_{\text{Cold}}/T_{\text{Hot}}=60/130^\circ$C.
Figure 7 (a) The maximum power and current density vs DMSO volume percentage in C$_2$ mim eFAP and (b) the maximum power and current density vs MPN volume percentage in C$_2$ mim B(CN)$_4$.

Another notable feature in the electrolytes’ performance can be seen in Table 5, where the maximum power and current densities obtained from each electrolyte system are given. The MPN:C$_2$ mim B(CN)$_4$ system outperforms the DMSO:C$_2$ mim eFAP system at all volume ratios tested. This is attributed primarily to the higher viscosity of the C$_2$ mim eFAP (43 mPa.s at 30°C) compared to C$_2$ mim B(CN)$_4$ (15 mP.s at 30°C), which causes more mass transport limitations.22
<table>
<thead>
<tr>
<th>MPN volume % in C$_2$ mim B(CN)$_4$</th>
<th>Power density (mW/m$^2$)</th>
<th>Error(±mW/m$^2$)</th>
<th>Current density (A/m$^2$)</th>
<th>Error (±A/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>221</td>
<td>10</td>
<td>6.0</td>
<td>0.25</td>
</tr>
<tr>
<td>25</td>
<td>409</td>
<td>12</td>
<td>11.2</td>
<td>0.2</td>
</tr>
<tr>
<td>50</td>
<td>612</td>
<td>37</td>
<td>14.2</td>
<td>1.05</td>
</tr>
<tr>
<td>75</td>
<td>784</td>
<td>30</td>
<td>17.9</td>
<td>1.6</td>
</tr>
<tr>
<td>100</td>
<td>452</td>
<td>22</td>
<td>11.3</td>
<td>0.3</td>
</tr>
<tr>
<td>DMSO volume % in C$_2$ mim eFAP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>158</td>
<td>16</td>
<td>3.3</td>
<td>0.0</td>
</tr>
<tr>
<td>25</td>
<td>282</td>
<td>28</td>
<td>5.9</td>
<td>0.3</td>
</tr>
<tr>
<td>50</td>
<td>594</td>
<td>59</td>
<td>9.9</td>
<td>0.5</td>
</tr>
<tr>
<td>75</td>
<td>776</td>
<td>77</td>
<td>12.5</td>
<td>0.6</td>
</tr>
<tr>
<td>100</td>
<td>554</td>
<td>55</td>
<td>10.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 5 The maximum TEC power and current densities of 0.1M Co$^{2+/3+}$(bpy)$_3$ in all electrolyte systems measured at $T_{\text{Cold}}/T_{\text{Hot}}$ = 60/130°C.

3.3.6 The relationship between thermocell performance and electrolyte properties.

The performance of the electrolyte systems under study was further analysed by investigating the over-potentials in the TEC when current is drawn. This was done by measuring the electrolyte conductivity ($\kappa$), charge transfer resistance ($R_{CT}$) and diffusion coefficients ($D$) to probe the ohmic over-potential, activation over-potential and mass transport over-potential, respectively. Figure 8 and Table 6 show the ionic conductivity and corresponding solution resistance $R_{sol}$, plus the charge
transfer resistance of the electrolyte, $R_{CT}$, obtained by electrical impedance spectroscopy (EIS) at 95°C. This is the average operating temperature of the TEC when 60-130°C cold and hot electrode temperatures are used.

The trend in ionic conductivity can be understood in terms of the total number of charged species present in each electrolyte system, and in terms of the viscosity of the sample.\textsuperscript{23, 24} The positively charged cobalt complexes ($\text{Co}^{2+/3+}(\text{bpy})_3$) and their negatively charged counter ions ($\text{NTf}_2$) are present in all the samples. The addition of ionic liquid to the systems adds more charged species, according to the volume ratio used. In contrast, in neat solvents, the only charged species present are $\text{Co}^{2+/3+}(\text{bpy})_3$ and the $\text{NTf}_2$ anions.

The highest conductivity was measured for the 1:1 and 3:1 solvent:IL system in both cases, consistent with the good TEC device performance for these systems. The ionic conductivity is lower for the neat solvent systems, reaching the lowest values for neat MPN and neat DMSO. This can be attributed to the absence of ionic liquid in these samples (i.e. a lower number of charged species). The neat ionic liquid samples contain the highest number of charged species but also the highest viscosity of all samples tested and, as a result, the neat ionic liquid samples show lower ionic conductivity than those mixed with organic solvent. At high ion concentration the formation of neutral aggregates can also occur (e.g. ion pairs or larger), which do not contribute to conductivity and decrease the total number of charge carriers, thereby decreasing the total ionic conductivity.

The charge transfer resistance (also shown in Figure 8 and Table 6) can be used to look at the activation over-potential associated with the electron transfer reaction (the redox reaction) at the electrode. This relates to the catalytic properties of the electrode material and the kinetics of the reaction on the surface. The charge transfer resistance is highest in the neat ionic liquids, reaching its maximum value in neat $\text{C}_2\text{mim eFAP}$ at 98Ω. It is predicted by Marcus theory that charge transfer resistance will increase with solvent viscosity.\textsuperscript{25} The combination of high charge transfer resistance and low ionic conductivity explain the lower power and current densities.
obtained from the TEC with this ionic liquid compared to the neat C$_2$ mim B(CN)$_4$ system. The charge transfer resistance decreases when organic solvent is added, reaching its lowest values in the neat solvents. This is attributed primarily to the effect of viscosity.

Figure 8 The ionic conductivity ($\kappa$) and corresponding solution resistance ($R_{sol}$), in addition to the charge transfer resistance ($R_{CT}$), for (a) MPN-C$_2$ mim B(CN)$_4$ systems and (b) DMSO- C$_2$ mim eFAP systems, at 95°C.
<table>
<thead>
<tr>
<th>MPN volume % in C\textsubscript{2}mim B(CN)\textsubscript{4}</th>
<th>Solution resistance $R_{sol}$</th>
<th>Charge transfer resistance $R_{CT}$ (Ω)</th>
<th>Ionic conductivity $\kappa$(S/cm)±0.001</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>37</td>
<td>26</td>
<td>0.037</td>
</tr>
<tr>
<td>25</td>
<td>30</td>
<td>15</td>
<td>0.045</td>
</tr>
<tr>
<td>50</td>
<td>29</td>
<td>7</td>
<td>0.046</td>
</tr>
<tr>
<td>75</td>
<td>36</td>
<td>17</td>
<td>0.037</td>
</tr>
<tr>
<td>100</td>
<td>88</td>
<td>6</td>
<td>0.015</td>
</tr>
<tr>
<td>DMSO volume % in C\textsubscript{2}mim eFAP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>87</td>
<td>98</td>
<td>0.015</td>
</tr>
<tr>
<td>25</td>
<td>60</td>
<td>20</td>
<td>0.030</td>
</tr>
<tr>
<td>50</td>
<td>51</td>
<td>10</td>
<td>0.031</td>
</tr>
<tr>
<td>75</td>
<td>52</td>
<td>8</td>
<td>0.026</td>
</tr>
<tr>
<td>100</td>
<td>104</td>
<td>4</td>
<td>0.018</td>
</tr>
</tbody>
</table>

Table 6 The measured values of the solution resistance ($R_{sol}$), charge transfer resistance ($R_{CT}$) and ionic conductivity ($\kappa$) of 0.1M Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} in all electrolytes measured at 95°C.

The diffusion coefficient of the redox couple gives insight into the mass transport over-potential in the TEC during its operation. The mass transport over-potential is perhaps the most significant limiting factor in the TEC when ionic liquids are used, due to their high viscosity compared to aqueous or organic solvent electrolytes.\textsuperscript{1} The addition of organic solvent was introduced in this chapter mainly to overcome this
issue. Figure 9 and Table 7 show the diffusion coefficients of the Co^{2+}(bpy)_3 and Co^{3+}(bpy)_3 species in DMSO-C_2mim eFAP and MPN-C_2mim B(CN)_4 systems at 95°C.

The diffusion coefficients of both Co^{2+}(bpy)_3 and Co^{3+}(bpy)_3 show an increase when organic solvent is added to the ionic liquids, reaching the maximum values in neat DMSO and neat MPN. This can be explained in terms of the viscosity, which is significantly lowered as more solvent is added. The diffusion coefficients of both Co^{2+}(bpy)_3 and Co^{3+}(bpy)_3 are higher in the MPN-C_2mim B(CN)_4 systems. This also helps to explain the higher TEC performance in these electrolytes when compared to the DMSO:C_2mim eFAP systems.

Another notable feature in Figure 9 is the higher diffusion of the Co^{2+}(bpy)_3 redox species compared to Co^{3+}(bpy)_3 in most cases. This reflects weaker Coulombic interactions between the Co^{2+}(bpy)_3 and surrounding ions present in the solvent, due to its lower absolute charge.

![Figure 9](image_url)

**Figure 9** The diffusion coefficients of Co^{2+}(bpy)_3 and Co^{3+}(bpy)_3 in DMSO-C_2mim eFAP and MPN-C_2mim B(CN)_4 systems at 95°C, calculated using Cottrell’s equation. Experimental details are shown in chapter two, section 2.7.
<table>
<thead>
<tr>
<th>MPN volume % in C$_2$mim B(CN)$_4$</th>
<th>Diffusion coefficient ±0.02 (×10$^{-5}$ cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co$^{2+}$(bpy)$_3$</td>
</tr>
<tr>
<td>0</td>
<td>1.51</td>
</tr>
<tr>
<td>25</td>
<td>1.19</td>
</tr>
<tr>
<td>50</td>
<td>0.76</td>
</tr>
<tr>
<td>75</td>
<td>0.49</td>
</tr>
<tr>
<td>100</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td><strong>DMSO volume % in C$_2$mim eFAP</strong></td>
</tr>
<tr>
<td>10</td>
<td>0.10</td>
</tr>
<tr>
<td>25</td>
<td>0.22</td>
</tr>
<tr>
<td>50</td>
<td>0.47</td>
</tr>
<tr>
<td>75</td>
<td>0.62</td>
</tr>
<tr>
<td>100</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Table 7 The diffusion coefficient of Co$^{2+}$(bpy)$_3$ and Co$^{3+}$(bpy)$_3$ in all electrolytes, measured at 95°C.

In conclusion, the mixed ionic liquid/organic solvent electrolytes achieve the best TEC performance in comparison to pure ionic liquid and pure solvent. The combination of increased ionic conductivity and high diffusion coefficients in these systems has proven effective in overcoming the over-potentials in the TEC, particularly the mass transport over-potential.
The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was tested in MPN at 1.1M concentration — this concentration was chosen to match the ionic concentration of C$_2$ mim B(CN)$_4$ in the 3:1 MPN to C$_2$ mim B(CN)$_4$ electrolyte system in order to draw a direct comparison between the addition of an ionic liquid and a conventional (solid state) supporting electrolyte. The addition of 1.1M TBAPF$_6$ increased the conductivity of the electrolyte by 30%. However, the power density was not significantly changed compared to pure MPN. In contrast, the addition of the same molar amount of C$_2$ mim B(CN)$_4$ results in a 140% increase in conductivity and a 70% increase in the power density drawn from the cell compared to neat MPN. 21

3.4 Conclusions.

The ionic liquids C$_2$ mim eFAP and C$_2$ mim B(CN)$_4$ were mixed with high boiling point organic solvents DMSO or MPN, respectively, in order to reduce the viscosity and overcome mass transport limitations in the TEC. The addition of organic solvents increased the Seebeck coefficient of Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_{2/3}$, and a maximum value of 2.0 mV/K was measured in neat DMSO. High Seebeck coefficients lead to high open circuit potentials in the TEC. The trend of increasing Seebeck coefficient with solvent addition is not a linear one, indicating complex interactions between the redox couple and the surrounding solvent system.

The Kamlet-Taft parameters do not seem to correlate directly with the measured Seebeck coefficients in the mixed electrolyte systems. Further investigation of the relationship between the Seebeck coefficient and the solvent properties, with respect to their structure and properties such as polarity and hydrogen bonding ability, is needed.

The presence of water slightly lowers the Seebeck coefficient of Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_{2/3}$, which indicates smaller overall entropy changes when the redox reactions occur in the presence of water.
Optimisation of the TEC performance was found to be dependent on a balance of multiple parameters, some of which relate to the redox couple, such as the concentration and the Seebeck coefficient, and others that relate to the solvents, including the ionic conductivity and the viscosity.

The 3:1 organic solvent : ionic liquid ratio performed best for both electrolyte systems tested, due to a combination of ionic conductivity (primarily from the IL) plus high diffusion coefficients and an increase in Seebeck coefficient by the addition of solvent.
References.


Chapter Four

The effect of ionic liquid structure on the Seebeck coefficient.
4.1 Introduction

In this chapter, the reaction entropy changes related to the reactions of the Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_{2/3}$ redox couple in a new range of ionic liquids was investigated. It was previously concluded that the structure of both the cation and anion of ionic liquids affect the reaction entropy change and, therefore, the Seebeck coefficient. Previous studies and the data presented in chapter three investigated the reaction entropy in a range of ionic liquids mainly chosen for having favourable electrolyte properties such as high ionic conductivity and relatively low viscosity.

This chapter is focused on further understanding the role of specific structural changes to the anion and cation of the ionic liquids on the reaction entropy change of the Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_{2/3}$ complex. For instance, the length of the alkyl chain on the imidazolium cation on the third position (Figure 1) was varied to investigate the influence of alkyl chains on the reaction entropy change.

![Figure 1 The imidazolium cation where, R and R’ are alkyl chains.](image)

Ionic liquids containing a quaternary phosphonium cation are generally good candidates for application in electrochemical devices as they can have good ionic conductivity, fluidity and, of particular relevance for TECs, good thermal stability and high decomposition temperatures.$^{1, 2}$ The use of phosphonium based ionic liquid electrolytes in lithium ion batteries and other battery technologies has been reported.$^{3-5}$ The phosphonium ionic liquids used in this thesis were chosen with two variations to the alkyl groups attached to the cation and with three different counter ions, to investigate the effect of ionic liquid structure on the Seebeck coefficient and TEC performance.
4.2 Materials and experimental methods

The imidazolium cations were chosen as these ionic liquids have previously shown high Seebeck coefficients and favourable electrolyte properties with anions such as B(CN)$_4$, eFAP and NTf$_2$, as discussed in previous reports and also in chapter three in this thesis. The length of the alkyl chain on the C3 position was varied between ethyl and butyl, with the C2 position either protonated or methylated. The anions paired with the imidazolium cations were chosen in order to investigate the role of specific structural changes on the Seebeck coefficient and TEC performance.

The organic solvent propylene carbonate was chosen as co-solvent as it has a high boiling point of 242°C. The Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_2/3$ redox couple was used at 0.01M of both species in the following ionic liquids and their 1:1 volume mixtures with propylene carbonate:

- 1-butyl-2-methylimidazolium trifluoromethanesulfonate, C$_4$mim MeSO$_3$.
- 1-ethyl-3-methylimidazolium methanesulfonate, C$_2$mim MeSO$_3$.
- 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, C$_4$mim eFAP.
- 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, C$_4$mim NTf$_2$.
- 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide, C$_4$dmim NTf$_2$.
- 1-butyl-3-methylimidazolium tetrafluoroborate, C$_4$mim BF$_4$.
- 1-butyl-2,3-dimethylimidazolium trifluoromethanesulfonate, C$_4$dmim OTf.
- 1-butyl-3-methylimidazolium trifluoromethanesulfonate, C$_4$mim OTf.
- 1-butyl-2,3-dimethylimidazolium tetrafluoroborate C$_4$dmim BF$_4$.
- trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)imide, P$_{6,6,6,14}$ NTf$_2$.
- triethyl(butyl)phosphonium $p$-toluenesulfonate, P$_{2,2,2,4}$ Tos.
- trihexyl(tetradecyl)phosphonium tetrafluoroborate, P$_{6,6,6,14}$ BF$_4$. 
The electrolyte systems were analysed using the following experimental techniques: measurement of the Kamelett-Taft parameters, the Seebeck coefficient, the thermoelectrochemical cell performance, diffusion coefficient measurements, and measurement of ionic conductivity by EIS. Details on the experimental techniques were given in chapter two.

The majority of TEC and Seebeck coefficient measurements were performed by Dr. JiangJing He, a postdoctoral research fellow on the project at the time. However, the author of this thesis had significant intellectual input into the experimental design, experimental procedure, data analysis and interpretation.

4.3 Results and discussion

4.3.1 The effect of the structure of the imidazolium cation of the ionic liquid on the Seebeck coefficient of $\text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_{2/3}$

Table 1 shows the Seebeck coefficients of 0.01M $\text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_{2/3}$ in ionic liquids containing an imidazolium cation, and also their 1:1 volume mixtures with propylene carbonate. Propylene carbonate was used as co-solvent to further investigate the effect of organic solvents on the Seebeck coefficient and, ultimately, TEC performance. Propylene carbonate has been reported to give high reaction entropy change with $\text{Co}^{2+/3+}(\text{bpy})_3(\text{ClO}_4)_{2/3}$ (46 cal/K.mol equivalent to 1.99 mV/K).\textsuperscript{7} The use of propylene carbonate also improves the solubility of the $\text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_{2/3}$ redox couple and allows the testing of ionic liquids that are otherwise solid or highly viscous at room temperature. Table 1 shows the Seebeck coefficients in all ionic liquids tested and their 1:1 volume mixtures with propylene carbonate.
<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Neat IL</th>
<th>1:1 IL:PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄mim MeSO₃</td>
<td>N/Aᵃ</td>
<td>2.16</td>
</tr>
<tr>
<td>C₂mim MeSO₃</td>
<td>2.13</td>
<td>2.14</td>
</tr>
<tr>
<td>C₄mim eFAP</td>
<td>1.69</td>
<td>1.88</td>
</tr>
<tr>
<td>C₂mim eFAP</td>
<td>1.69*</td>
<td>N/A</td>
</tr>
<tr>
<td>C₄mim NTf₂</td>
<td>1.54</td>
<td>1.76</td>
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<tr>
<td>C₄dmim NTf₂</td>
<td>1.49</td>
<td>1.71</td>
</tr>
<tr>
<td>C₄mim BF₄</td>
<td>1.32</td>
<td>1.57</td>
</tr>
<tr>
<td>C₄dmim BF₄</td>
<td>N/Aᵃ</td>
<td>1.55</td>
</tr>
<tr>
<td>C₄mim OTf</td>
<td>N/Aᵇ</td>
<td>1.64</td>
</tr>
<tr>
<td>C₄mim OTf</td>
<td>1.34</td>
<td>1.64</td>
</tr>
<tr>
<td>C₂mim OTf</td>
<td>1.43*</td>
<td>N/A</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>1.86</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 The Seebeck coefficient of 0.01M Co^{2+/3+}(bpy)₃(NTf)₂ in a range of ionic liquids containing the imidazolium cation. ᵃSolid at room temperature. ᵇRedox couple partially or completely insoluble at room temperature. ᵇFrom Chapter 3, Table 2.

The Seebeck coefficient in pure propylene carbonate is higher than the Seebeck coefficient in any of the neat imidazolium ionic liquids tested, except in C₂mim MeSO₃. This is consistent with the results discussed in chapter three for the DMSO and MPN as these molecular solvents also give higher Seebeck coefficients than neat ionic liquids. The mixing of propylene carbonate with ionic liquids has the effect of
increasing the Seebeck coefficient in all the imidazolium ionic liquids tested, although for C$_2$ mim MeSO$_3$ the change is not statistically significant.

The Seebeck coefficients measured in neat ionic liquids range between 1.32 mV/K and 2.13 mV/K. The range of values clearly indicates the significant influence of ionic liquid structure on the Seebeck coefficient. The highest Seebeck coefficients, exceeding 2.0 mV/K for the Co$^{2+/3+}$(bpy)$_3$, were measured in the ionic liquid C$_2$ mim MeSO$_3$ and its 1:1 volume mixture with propylene carbonate. To the best of our knowledge, this is the highest Seebeck coefficient reported to-date in a neat ionic liquid at this concentration of redox couple.

Prior discussion in the literature has linked the Seebeck coefficient to strong coordination between the redox couple and surrounding solvent, particularly in the form of hydrogen bonding. For example, it was shown by Weaver and colleagues that redox complexes with ligands more prone to hydrogen bond with water produced the highest Seebeck coefficients in aqueous media.$^8$,$^9$

In this chapter, we probe the effect of hydrogen bonding on the Seebeck coefficient by choosing ionic liquids likely to form stronger hydrogen bonds with the Co$^{2+/3+}$(bpy)$_3$ redox species. The ionic liquids C$_2$ mim OTf and C$_2$ mim MeSO$_3$ have a similar structure, but with the methyl group on the sulfonate anion replaced by a trifluoromethane in C$_2$ mim OTf. The structure of the anions under study here, OTf and MeSO$_3$, are shown in Figure 2. Fluorination of the anion is believed to lead to weaker hydrogen bonding in the ionic liquid. For example, it was shown by Pringle et al.$^{10}$ that fluorination of the methyl group in bis(trifluoromethanesulfonate)imide (NTf$_2$) anion of an ionic liquid can lead to weaker hydrogen bonding compared to the analogous bis(methanesulfonate)imide. It is interesting to note here that C$_2$ mim MeSO$_3$ is the first ionic liquid to have a Seebeck coefficient exceeding that of an organic solvent. The Seebeck coefficient of C$_2$ mim MeSO$_3$ is also significantly higher than that of the C$_2$ mim OTf ionic liquid at 1.43 mV/K at the same concentration of redox couple. The MeSO$_3$ cation was shown in the literature to be a strong hydrogen bond acceptor when compared to OTf, BF$_4$, NTf$_2$ and other anions, when paired with C$_4$ mim cation.$^{11}$ This is in line with high Seebeck coefficient measured for ILs
containing MeSO₃ in light of the relationship, drawn by Weaver and colleagues, between the reaction entropy of redox complexes and solvents acceptor number.⁸

![Figure 2](image1)

Figure 2 The structure of methanesulfonate MeSO₃ (left) and trifluoromethanesulfonate OTf (right) anions.

The analogous C₄mim MeSO₃ is solid at room temperature, but its mixture with propylene carbonate was also found to give a high Seebeck coefficient, of 2.16 mV/K.

The effect of hydrogen bonding was also investigated by methylating the imidazolium ring at the 2-position in the ionic liquids, by comparison of C₄mim NTf₂ and C₄dmim NTf₂. The role of this proton in increasing the extent of hydrogen bonding within ionic liquids has been discussed extensively in the literature.¹²-¹⁴ It was shown by Fumino et al.¹³ That C₂mim NTf₂ forms stronger hydrogen bonds through the C2 site compared to the analogues C₁dmim NTf₂. The sites of possible hydrogen bond formation in both cations are shown in Figure 3.

![Figure 3](image2)

Figure 3 The locations of possible hydrogen bond formation in 1,2,3-trimetylimidazolium (C₁dmim) (left) and 1-ethyl-3-methylimidazolium (C₂mim) (right). Reproduced from K. Fumino et al., Physical Chemistry Chemical Physics, The
influence of hydrogen bonding on the physical properties of ionic liquids, 2011, 13, 14064-14075. with permission from the PCCP Owner Societies.

The structure of the C₄mim and C₄dmim cations is shown in Figure 4. The Seebeck coefficient was indeed found to be 0.05 mV/K higher in the C₂mim NTf₂ consistent with the idea that there exists stronger coordination between the redox couple and this ionic liquid through stronger hydrogen bonding with the cation. To further investigate the interactions of these two ionic liquids with the redox couple, the Kamlet-Taft parameters were measured for the two ionic liquids. A brief literature review and a discussion on the Kamlet-Taft parameters were given in chapter one, section 2.3 and chapter three section 3.4 respectively.
Figure 4 The structure of 1-butyl-2,3-dimethylimidazolium (left) and 1-butyl-3-methylimidazolium (right).

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>$\alpha \pm 0.03$</th>
<th>$\beta \pm 0.03$</th>
<th>$\pi^* \pm 0.03$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_4\text{mim NTf}_2$</td>
<td>0.62</td>
<td>0.22</td>
<td>0.97</td>
</tr>
<tr>
<td>$\text{C}_4\text{dmim NTf}_2$</td>
<td>0.38*</td>
<td>0.24</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Table 2 The measured Kamlet-Taft parameters for the ionic liquids $\text{C}_4\text{mim NTf}_2$ and $\text{C}_4\text{dmim NTf}_2$. *This was measured by a postdoctoral research fellow at Prof. Tom Welton’s group at Imperial College London using the same procedure.

The ionic liquid $\text{C}_4\text{mim NTf}_2$ has a higher $\alpha$ value, at 0.62, which is consistent with a stronger ability to donate a hydrogen bond compared to the methylated cation in $\text{C}_4\text{dmim NTf}_2$. The $\beta$ value, which mostly relates to the anion NTf$_2$ and its ability to accept a hydrogen bond, remains unchanged for the two ionic liquids. $\pi^*$, which relates to the general polarity of the ionic liquid, is also not significantly changed. It can be tentatively concluded that $\text{C}_4\text{mim NTf}_2$ may coordinate with the Co$^{2+/3+}$(bpy)$_3$ more strongly than the analogous $\text{C}_4\text{dmim NTf}_2$, which leads to a higher Seebeck coefficient value. However, more ionic liquids could be tested in order to confirm this effect of imidazolium methylation.

The role of the alkyl chain at the three-position on the imidazolium ring (Figure 1) was also investigated in two sets of ionic liquids; the $\text{C}_8\text{mim eFAP}$ and $\text{C}_8\text{mim OTf}$,
where R was either an ethyl or a butyl group. The Seebeck coefficients are shown in Table 1. The Seebeck coefficient in the eFAP ILs do not show any change between the two cations. The OTf salts, however, give a lower Seebeck coefficient by 0.10 mV/K when a butyl group is present rather than an ethyl on the three position of the imidazolium cation. The difference in the Seebeck coefficients is significant considering the error margins in these measurements are typically 0.02 mV/K.

4.3.2 The TEC performance of the electrolyte systems.

The imidazolium ionic liquids and their 1:1 volume mixtures with propylene carbonate were tested in the TEC with 0.01M Co^{2+/3+}(bpy)_3(NTf_2)_{2/3}. The hot and cold electrode temperatures were 30°C and 60°C, respectively. The resultant current and power densities obtained are shown in Figure 5 a and b. Table 3 shows the maximum power density obtained from each system. The C_4mim OTf systems gave unstable potentials in the TEC, and a colour change in the sample was observed following the TEC experiments. This indicates decomposition of the sample during the measurement.
Figure 5 (a) The power density and (b) the current density obtained from 0.01M Co\(^{2+/3+}\)(bpy)_3(NTf_2)_2/3 in the neat imidazolium ionic liquids. (c) The power density and (d) the current density obtained from 0.01M Co\(^{2+/3+}\)(bpy)_3(NTf_2)_2/3 in the 1:1 volume mixtures of the imidazolium ionic liquids with propylene carbonate. The cold and hot electrode temperatures were 30°C and 60°C respectively.

Propylene carbonate gives the highest power and current density in the TEC. This is likely because propylene carbonate is significantly less viscous (2.5cP)\(^{16}\) than the ionic liquid-containing systems and gives a high Seebeck coefficient, of 1.86mV/K. The poorest performance was obtained from the neat C\(_2\)mim BF\(_4\) ionic liquid system in both the neat form and its mixture with propylene carbonate. This is consistent with the fact that this ionic liquid gives the lowest Seebeck coefficient, of 1.32mV/K, and thus the lowest open circuit potential at 0.04V. The C\(_2\)mim MeSO\(_3\) ionic liquid system gives the second lowest power and current density in the TEC. This is despite having the highest Seebeck coefficient, as evident in its high open circuit potential value of 0.07 V. C\(_2\)mim MeSO\(_3\) has relatively high viscosity, at 113 cP at 30°C,\(^{17}\) which limits the mass transport of the redox couple and thus results in lower performance.
Mixing $\text{C}_2\text{mim MeSO}_3$ with propylene carbonate improves the TEC performance, but the maximum power is still lower than that of the $\text{C}_4\text{mim FAP}$ and $\text{C}_4\text{mim NTf}_2$ systems despite having a higher open circuit potential. The performance limitations caused by a high viscosity can also be seen in the performance of $\text{C}_4\text{dmim NTf}_2$ compared to $\text{C}_4\text{mim NTf}_2$. The two ionic liquids give a similar Seebeck coefficient but the TEC power and current output with $\text{C}_4\text{dmim NTf}_2$ is significantly below that of $\text{C}_4\text{mim NTf}_2$. To further investigate the limiting effect of viscosity in TEC performance, the diffusion coefficient of the redox species in the different solvents was measured and is presented in the following section.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Neat IL</th>
<th>Neat IL:PC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Power density ± 0.05 (mW/m²)</td>
<td>Power density ± 0.05 (mW/m²)</td>
</tr>
<tr>
<td>$\text{C}_2\text{mim MeSO}_3$</td>
<td>0.67</td>
<td>6.02</td>
</tr>
<tr>
<td>$\text{C}_4\text{mim eFAP}$</td>
<td>0.94</td>
<td>7.98</td>
</tr>
<tr>
<td>$\text{C}_4\text{mim NTf}_2$</td>
<td>2.04</td>
<td>7.78</td>
</tr>
<tr>
<td>$\text{C}_4\text{dmim NTf}_2$</td>
<td>1.15</td>
<td>6.44</td>
</tr>
<tr>
<td>$\text{C}_4\text{mim BF}_4$</td>
<td>0.34</td>
<td>3.91</td>
</tr>
<tr>
<td>$\text{C}_4\text{dmim TfO}$</td>
<td>N/A$^\text{a}$</td>
<td>4.88</td>
</tr>
<tr>
<td>$\text{C}_4\text{mim MeSO}_3$</td>
<td>N/A$^\text{a}$</td>
<td>3.33</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>9.59</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 The maximum power density from 0.01M $\text{Co}^{2+/3+}$$\text{(bpy)}_3(\text{NTf}_2)_2/3$ in the neat ionic liquids and their 1:1 volume mixtures with propylene carbonate. The cold and hot electrode temperatures were 30°C and 60°C respectively. $^\text{a}$Solid at room temperature.
4.3.3 Analyses of the TEC performance with respect to the ionic conductivity and the diffusion coefficient.

The TEC performance can be further understood in light of the modified figure of merit relationship for liquid devices \( ZT^* = \left( \frac{T^2 F^2}{RT} \right) \left( \frac{S D_{limc}}{k} \right) \), which shows that the TEC performance is not only related to the Seebeck coefficient but also to key electrolyte parameters that give insight into the over-potentials limiting the TEC output current and power density. The ionic conductivity was measured by EIS to investigate the role of solution resistance in limiting the TEC performance. The diffusion coefficients of \( \text{Co}^{2+}(\text{bpy})_3 \) and \( \text{Co}^{3+}(\text{bpy})_3 \) species were also measured, to evaluate the role of mass transport over-potential in limiting the performance. Charge transfer resistance data is not presented in this chapter because of poor reproducibility of this parameter in the ionic liquids under study.

The diffusion coefficients of the \( \text{Co}^{2+}(\text{bpy})_3 \) and \( \text{Co}^{3+}(\text{bpy})_3 \) redox species were calculated using Cottrell’s equation, which relates the electrical current produced to the time under a constant potential. The currents were measured under constant potential by chronoamperometry in a three electrode setup. More details on the experimental procedure are given in chapter two.

The diffusion coefficients of the redox species is mostly related to the viscosity of the solvent, and is of most relevance with respect to its effect on the mass transport of the redox couple species when current is drawn from the TEC. The measured diffusion coefficients of the \( \text{Co}^{2+} \) and \( \text{Co}^{3+} \) species are shown in Table 4.

The highest diffusion rates for both redox species were measured in propylene carbonate. Propylene carbonate is significantly more fluid (viscosity ~ 2.5cP) than the ionic liquids and the mixed systems. The 1:1 volume mixture with \( \text{C}_4\text{mim NTf}_2 \) gives the highest diffusion coefficient of all ionic liquid/propylene carbonate mixtures tested, for both redox species. This system also has one of the highest TEC performances, which shows the importance of high diffusion rate in determining TEC performances.
performance. The 1:1 mixtures of C$_2$mim MeSO$_3$ or C$_4$mim MeSO$_3$ with propylene carbonate have the highest Seebeck coefficients, but are still outperformed in terms of TEC performance by the 1:1 C$_4$mim NTf$_2$: propylene carbonate system that allows faster redox couple diffusion.

The neat ionic liquid systems exhibit TEC performance trends that are consistent with the trends in measured diffusion rates, with the exception of C$_4$mim BF$_4$ that has similar diffusion rates to C$_2$mim MeSO$_3$ but the lowest Seebeck coefficient, thus resulting in C$_4$mim BF$_4$ having the lowest TEC performance.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Diffusion coefficient, D, $10^{-7}$ cm$^2$/s ± 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Neat IL</td>
</tr>
<tr>
<td></td>
<td>C$_2$mim NTf$_2$</td>
</tr>
<tr>
<td></td>
<td>1.2 1.2</td>
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<tr>
<td></td>
<td>C$_4$dmm NTf$_2$</td>
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<td></td>
<td>0.65 0.58</td>
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<td>C$_4$mim eFAP</td>
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<td>0.45 0.40</td>
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<td>C$_4$dmm OTf</td>
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<td></td>
<td>N/A$^a$ 5.8</td>
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<td></td>
<td>C$_4$mim BF$_4$</td>
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<td></td>
<td>0.32 0.29</td>
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<td>C$_2$mim MeSO$_3$</td>
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<td>0.22 0.27</td>
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<td>N/A$^a$ 1.8</td>
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<tr>
<td></td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td></td>
<td>16 18</td>
</tr>
</tbody>
</table>

Table 4 The diffusion coefficients of the Co$^{2+}$(bpy)$_3$ and Co$^{3+}$(bpy)$_3$ redox species in the neat ionic liquids, their 1:1 volume mixtures with propylene carbonate and neat propylene carbonate. The measurements were performed at room temperature.$^a$Solid at room temperature.
The ionic conductivity was also measured for all electrolyte systems and is presented in Table 5. The conductivity values were calculated from the solution resistance obtained from the first touchdown in the Nyquist plots. The Nyquist plots were obtained by EIS measurements for all electrolyte systems at room temperature. The Nyquist plots used to obtain the solution resistance and ionic conductivity are shown in Figure 6. More details on the measurement methods were given in chapter two.

The initial increase in ionic conductivity with added salt to the PC can be attributed to the addition of more charged species to the electrolyte sample. This, however, does not lead to higher TEC performance, which again demonstrates the significant limitations caused by mass transport over-potential in these systems. This is evident in lower diffusion coefficients in the ionic liquid-containing systems compared to the pure propylene carbonate.

This data also shows the increase in ionic conductivity values when propylene carbonate is present as co-solvent in the 1:1 samples, due to reduced viscosity compared to the neat ionic liquids. The lowest ionic conductivity in the 1:1 systems was measured for the C₄mim MeSO₃ system, which contributes to the lowest TEC performance. The rest of the ionic conductivity data does not correlate clearly with the trend in TEC performance, which again points to mass transport of the redox couple as the most limiting factor in these systems, e.g. compared to the ohmic over-potential. The theoretical role of charge transfer resistance can be discussed here in terms of Marcus theory, but no data is presented here due to poor experimental reproducibility of the measurements of this parameter in the electrolytes tested. Marcus theory suggests that the charge transfer resistance is proportional to the viscosity of the solvent. Thus, all else being equal, we may expect highest charge transfer resistance to be present in systems with lowest diffusion coefficient, namely, C₄mim MeSO₃, C₂mim MeSO₃ and their 1:1 mixtures with propylene carbonate. This would further contribute to a reduced TEC performance by these electrolytes. However, factors such as structuring of the ionic liquid on the electrode surface may contribute to charge transfer resistance and decrease the applicability of Marcus theory to ionic liquid-based systems.
<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Ionic conductivity $\kappa$(mS/cm) ± 5%</th>
<th>Ionic conductivity $\kappa$(mS/cm) ± 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_4\text{mim} \text{ BF}_4$</td>
<td>3.9</td>
<td>10.4</td>
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<tr>
<td>$\text{C}_2\text{mim} \text{ MeSO}_3$</td>
<td>3.7</td>
<td>11.0</td>
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<td>$\text{C}_4\text{mim} \text{ NTf}_2$</td>
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<td>11.1</td>
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<td>$\text{C}_4\text{mim} \text{ eFAP}$</td>
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<td>$\text{C}_4\text{dmim} \text{ OTf}$</td>
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<td>propylene carbonate</td>
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Table 5 The ionic conductivity of 0.01M $\text{Co}^{2+/3+}$($\text{bpy}$)$_3$(NTf$_2$)$_{2/3}$ in the neat ionic liquids, their 1:1 volume mixtures with propylene carbonate and neat propylene carbonate at room temperature. *Solid at room temperature.
Figure 6 The Nyquist plots obtained by electrical impedance spectroscopy (EIS) for all electrolyte systems at room temperature.

4.3.4 Application of phosphonium ionic liquids in thermocells

This section discusses the use of quaternary phosphonium ionic liquids in the TEC. Phosphonium ionic liquids have been shown to have good thermal stability, electrochemical stability and wide electrochemical windows.\(^1\), \(^19\) The ionic liquids were chosen with two variations of alkyl chain on the cation, namely, trihexyl(tetradecyl)phosphonium (P\(_{6,6,6,14}\)) and triethyl(butyl)phosphonium (P\(_{2,2,2,4}\)). Studies on phosphonium ionic liquids have suggested a large degree of ordering and strong ion pairing in these ILs, especially when long alkyl chains are present.\(^20\), \(^21\) Studies on tetraalkyl phosphonium ionic liquids (P\(_{n,n,n,n}\)), where \(n\) is an alkyl chain, show the formation of polar and non-polar nano-domains within the ionic liquid that are proportional in size to the length of alkyl chains.\(^19\)

In this thesis, the BF\(_4\) and NTf\(_2\) anions were chosen to allow comparison of the phosphonium salts with the analogous imidazolium ILs. The p-toluenesulfonate (Tos) anion was chosen for having an aromatic ring that may interact strongly with the bipyridyl rings on the Co\(^{2+/3+}\)(bpy)\(_3\) species. The structure of the anions and cations of the ionic liquids under study in this section is shown in Figure 7 (a) to (e).

The Co\(^{2+/3+}\)(bpy)\(_3\)(NTf\(_2\))\(_{2/3}\) couple was tested in three phosphonium ionic liquids at 0.01M concentration. However, poor solubility of the redox couple prevented
measurements in the neat ionic liquids. The data presented here are for 1:1 volume mixtures with propylene carbonate.

All of the phosphonium ILs give high Seebeck coefficients, exceeding 2.0 mV/K, the highest of which was measured in the 1:1 P_{2,2,2,4} Tos : PC system at 2.09 mV/K. This supports the hypothesis of increased Seebeck coefficient when strong interactions between the redox couple and surrounding solvent are present. The Co^{2+/3+}(bpy)_3 is predicted to form \textit{pi-pi} interactions with the tosylate anion. \textit{Pi-pi} interactions are expected to form between aromatic species. Ionic liquids with higher Seebeck coefficient than organic solvent are not common and thus-far have only been measured in imidazolium ionic liquids containing MeSO_3 with Seebeck coefficients up to 2.16 mV/K in 1:1 C_4mim MeSO_3:PC electrolyte (Table 1). The structures of the tosylate and MeSO_3 anions are shown in Figure 7 (e) and (f). Future work in the field should look into more sulfonate-containing ionic liquids to further investigate the source of high Seebeck coefficients in this IL.

![Figure 7](image)

Figure 7 The structure of (a) trihexyl(tetradecyl)phosphonium P_{6,6,6,14} (b) triethyl(butyl)phosphonium P_{2,2,2,4}, (c) bis(trifluoromethanesulfonyle)imide, NTF_2, (d) tetrafluoroborate, BF_4, (e) p-toluenesulfonate (Tos) and (f) methanesulfonate (MeSO_3).

The effect of using ionic liquids with a phosphonium cation was also investigated by pairing the P_{6,6,6,14} cation with the BF_4 and NTF_2 anions and comparing this to the performance of ionic liquids when these anions were paired with imidazolium cations, discussed in section 3.1. The P_{6,6,6,14} cation had the effect of significantly
increasing the Seebeck coefficient, from 1.57 mV/K for the C₄mim BF₄ to 1.92 mV/K for the P₆,₆,₆,₁₄ BF₄. This substantial change in the Seebeck coefficient points to the important role of the cation in determining the Seebeck coefficient, even though it is positively charged and thus unlikely to coordinate significantly with the positively charged Co²⁺/³⁺ species. The additional entropy change of the redox reaction in phosphonium ionic liquids compared to most other imidazolium systems is postulated to occur as a result of disturbance to the large scale ordering present in these ionic liquids when the redox reactions occur.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Se (mV.K⁻¹) ± 0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1 IL:PC</td>
<td>1:3 IL:PC*</td>
</tr>
<tr>
<td>P₂,₂,₂,₄ Tos</td>
<td>2.09</td>
</tr>
<tr>
<td>P₆,₆,₆,₁₄ NTf₂</td>
<td>2.04</td>
</tr>
<tr>
<td>P₆,₆,₆,₁₄ BF₄</td>
<td>1.92</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td></td>
</tr>
</tbody>
</table>

Table 6 The Seebeck coefficient of 0.01M Co²⁺/³⁺(bpy)₃(NTf₂)₂/₃ in 1:1 mixtures of the phosphonium ILs with propylene carbonate. *1:3 IL:PC data was obtained by Dr. JiangJing He.

The phosphonium ionic liquids were also tested in 3:1 mixtures of propylene carbonate to IL, and the Seebeck coefficients of these systems are shown in Table 6. It is interesting to note a further decrease in Seebeck coefficient when additional propylene carbonate was added to the systems. However, the high viscosity of these ILs is detrimental to the TEC performance, and the addition of solvent has a significant role in improving the diffusion of the redox couple and, therefore, the overall current and power outputs. The current and power densities obtained from the TEC are shown in Figure 8.
Figure 8 (a) the power density and (b) the current density of 0.01M Co$^{2+/3+}$ (bpy)$_3$(NTf$_2$)$_2$ in the 1:1 volume mixtures of phosphonium ionic liquid and propylene carbonate. (c) The power density and (d) the current density of 0.01M Co$^{2+/3+}$ (bpy)$_3$(NTf$_2$)$_2$ in the 3:1 volume mixtures of propylene carbonate to phosphonium ionic liquids. The cold and hot electrode temperatures were 30°C and 60°C respectively. 1:3 IL:PC data was obtained by Dr. JiangJing He.

The TEC performance of the phosphonium ionic liquids was tested in propylene carbonate to IL mixtures of 1:1 and 3:1 volume ratios. The ionic liquids were not tested in the neat state due to poor solubility of the redox couple.

Despite the presence of 50% volume ratio of propylene carbonate in the phosphonium ionic liquids, the 1:1 mixture systems are still outperformed by the best analogous imidazolium electrolytes, the 1:1 C$_4$mim NTf$_2$:PC and 1:1 C$_4$mim eFAP:PC. This is most likely a result of high viscosity of the phosphonium ionic liquids. For instance, P$_{6,6,6,14}$ BF$_4$ has a viscosity of 787 cP at room temperature, while C$_4$mim BF$_4$ has a significantly lower viscosity of 280 cP.
The further addition of propylene carbonate, to give the 3:1 propylene carbonate:phosphonium ionic liquid electrolytes, further increased the power density obtained. The highest powers were measured with $P_{6,6,6,14}$ NTf$_2$, with a maximum power density of 6.7 mW/m$^2$. It's interesting to note that the 3:1 PC : $P_{6,6,6,14}$ NTf$_2$ has a maximum power density comparable to the best 1:1 imidazolium:PC systems. The maximum power densities obtained from the phosphonium ionic liquid systems are shown in Table 7.

<table>
<thead>
<tr>
<th></th>
<th>Power density ± 0.1 / mW m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:1 IL:PC</td>
</tr>
<tr>
<td>$P_{6,6,6,14}$ NTf$_2$</td>
<td>4.5</td>
</tr>
<tr>
<td>$P_{6,6,6,14}$ BF$_4$</td>
<td>3.2</td>
</tr>
<tr>
<td>$P_{2,2,2,4}$ Tos</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 7 The maximum power density of 0.01M Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_{2/3}$ in the 1:1 and 3:1 volume mixtures of propylene carbonate to phosphonium ionic liquid. The electrode temperatures were set to 30°C and 60°C. *1:3 IL:PC data was obtained by Dr. JiangJing He.

To further understand the TEC performance obtained from the phosphonium ionic liquid systems, the ionic conductivity of the 1:1 phosphonium:PC systems was measured. The conductivity data is shown in Table 8, and the Nyquist plots obtained from EIS are shown in Figure 9. The first touchdown in the Nyquist plot indicates the solution resistance in the sample. The ionic conductivity of the phosphonium ionic liquids is lower than the ionic conductivity of the imidazolium ionic liquids in all cases. The phosphonium ionic liquids have long alkyl chains and are highly viscous (787 mPa.S at 25°C for $P_{6,6,6,14}$ BF$_4$) which is detrimental to the mass transport processes. For this reason, it was not possible to measure the diffusion coefficient in these systems due to poor reproducibility resulting from very low values.
Table 8 The ionic conductivity of the 1:1 volume mixtures of phosphonium ILs and propylene carbonate.

<table>
<thead>
<tr>
<th></th>
<th>1:1 IL:PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic conductivity $\kappa$ (mS/cm) ± 5%</td>
<td></td>
</tr>
<tr>
<td>$[P_{6,6,6,14}NTf_2]$</td>
<td>2.6</td>
</tr>
<tr>
<td>$[P_{6,6,6,14}BF_4]$</td>
<td>3.0</td>
</tr>
<tr>
<td>$[P_{2,2,2,4}Tos]$</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Figure 9 The Nyquist plots obtained from EIS of the three phosphonium ionic liquid systems containing 0.01M Co$^{2+}$/3+(bpy)$_3$(NTf$_2$)$_{2/3}$ at room temperature.

The lowest ionic conductivity was measured for the 1:1 $[P_{2,2,2,4}Tos]$:PC system, consistent with the lowest power densities obtained from the TEC. Beyond this
observation, no conclusive trend can be seen as the ionic conductivity with the 1:1 P_{6,6,6,14} NTf₂:PC and 1:1 P_{6,6,6,14} BF₄:PC systems have comparable values. It was not possible to obtain charge transfer resistance values for these systems because of poor reproducibility in the measurements. The Nyquist plot obtained from the 1:1 P_{2,2,2,4} Tos: PC system shows a much larger semi-circle than the other two electrolytes, this indicates a large charge transfer resistance value which can be obtained from the diameter of the semi-circle ($R_{CT}=$second touchdown-first touchdown). The exact value, however, is not reported here due to poor reproducibility.

In terms of the three over-potentials present in the cell when current is drawn, it can be tentatively concluded that the mass transport over-potential is the dominant limiting factor in the phosphonium ionic liquid systems. This is consistent with the high viscosity of these systems reported when compared to equivalent imidazolium ionic liquids. The imidazolium ionic liquid systems and their mixtures with propylene carbonate however, are also predominantly mass transport limited compared to pure propylene carbonate. The role of the activation over-potential is still inconclusive at this point and more measurements with different electrode materials is part of the future work suggested. From the conductivity data, the role of ohmic over-potential can be concluded to be less significant than mass transport for these electrolytes.

4.4 Conclusions.

In this chapter, the highest Seebeck coefficients of the Co²⁺/³⁺,(bpy)₃ redox couple in neat ionic liquid systems was discovered in phosphonium and imidazolium ionic liquids that contain a sulfonate group. The Seebeck coefficient, which is directly proportional to the reaction entropy change associated with the redox reactions, is dependent on the structure of both the cation and anion of the ionic liquid. This indicates that the entropy changes accompanying the redox reaction may be related to the restructuring of the solvent beyond the first solvation shell.

Mixing with propylene carbonate increases the Seebeck coefficient in imidazolium ionic liquids, apart from C₂mim MeSO₃. The performance of the ionic
liquids investigated in this chapter in the TEC was concluded to be primarily limited by mass transport over-potential due to the high electrolyte viscosity. The addition of propylene carbonate increased the power and current outputs in all of the imidazolium ionic liquid systems tested.

Phosphonium ionic liquids were found to give Seebeck coefficients exceeding that of propylene carbonate, which is hypothesised to be the result of additional entropy changes resulting from changes to larger scale structuring present in these ILs. However, the phosphonium ionic liquids are highly viscous, which was found to greatly limit the TEC performance. The addition of propylene carbonate improves the TEC power output, increases the solubility of Co²⁺/³⁺(bpy)₃(NTf₂)₂/₃ and also allowed measurements to be performed on ionic liquids that are solid at room temperature. Future work following this thesis should look into ionic liquids with smaller quaternary phosphonium cations, to reduce viscosity while possibly still retaining the high Seebeck coefficients.
References


Understanding the polarity of ionic liquids, 2011, 13, 16831-16840.


Chapter Five

Investigation of cobalt-based redox couples for TEC applications
5.1 Introduction

This chapter describes an investigation of four different redox couples for TEC applications. The fundamental aspects of the effect of redox couple structure are investigated through measurement of the Seebeck coefficient. Furthermore, an investigation of the electrochemical behaviour of the redox couples with different solvent and electrode materials is presented. This chapter also reports a study of the four different redox complexes for device application in terms of power and current outputs. The requirements for a redox couple that performs well in the TEC, and the limitations in terms of the three over-potentials, are explored.

The field of liquid TEC devices is presently mainly focused on two high entropy redox couples: (i) the ferri/ferrocyanide redox couple reported in aqueous electrolytes, with a Seebeck coefficient of -1.4 mV/K at 0.4M concentration.\(^1\)\(^-\)\(^2\) Prior work on this system has focused on optimisation of the TEC in terms of cell design by investigating separator materials, to limit thermal conductivity and maintain the temperature gradient, and high surface area electrodes.\(^3\)\(^-\)\(^4\) (ii) the Co\(^{2+/3+}\)(bpy)\(_3\) redox couple, which was first reported for TEC applications by Abraham et al.\(^5\) with Seebeck coefficients reaching 2.19 mV/K in 3-methoxypropionitrile (MPN) at 0.01M. Research in the ionic liquid TEC field, generally speaking, has primarily been concerned with overcoming mass transport limitations caused by the viscosity of ionic liquids compared to aqueous electrolytes.\(^6\)\(^-\)\(^7\) However, when it comes to TEC performance, the Seebeck coefficient is arguably the most significant factor according to the figure of merit relation which shows that performance is proportional to the Seebeck coefficient squared (chapter one equations 1.3 and equation 2.10).

The cobalt-based redox couples studied in this chapter were chosen to allow investigation into the effect of variations of the chelating ligands. Chelating ligands have been shown to produce high entropy changes when combined with transition metal complexes such as Co\(^{2+/3+}\)(bpy)\(_3\) and Co\(^{2+/3+}\)(en)\(_2\) in aqueous media, where (en) is ethylene diamine.\(^8\) Three different ligands were chosen for study, and the performance of the complexes compared to that of the Co\(^{2+/3+}\)(bpy)\(_3\) redox couple, reported in chapter three and previous studies.\(^5\)\(^-\)\(^9\) The structures of the complexes
studied: Co$^{2+/3+}$(phen)$_3$, Co$^{2+/3+}$(py-pz)$_3$, Co$^{2+/3+}$(Bupy-pz)$_3$ and Co$^{2+/3+}$(bpy)$_3$ are shown in Figure 1. The NTf$_2$ counter ion was chosen as it was predicted to allow improved solubility of the redox couples in ionic liquids and organic solvents. Further, the Co$^{2+/3+}$(py-pz)$_3$ and Co$^{2+/3+}$(Bupy-pz)$_3$ redox complexes have been reported to undergo low to high spin transitions upon reaction from Co$^{3+}$ to Co$^{2+}$; this is similar to Co$^{2+/3+}$(bpy)$_3$, an effect that leads to additional entropy change and higher Seebeck coefficients, as discussed in chapter one.

This chapter also reports investigations into the use of carbon-based electrode materials in the TEC, as an alternative to the platinum that was otherwise used in this thesis and in previous studies from this research group. The carbon-based electrodes were investigated as they have higher surface area and increased number of reaction sites, which is expected to increase the power and current density obtained from the device. In addition, the use of carbon-based electrodes and, ultimately, elimination of platinum, would greatly reduce the cost of the device. Carbon-based electrodes have reported to have improved catalytic properties compared to platinum in acetonitrile for Co$^{2+/3+}$(bpy)$_3$, Co$^{2+/3+}$(phen)$_3$ and Co$^{2+/3+}$(bpy-pz)$_3$ (bpy-pz: bipyridine-pyrazole) complexes in dye sensitised solar cells. It was also reported that the catalytic properties of films of carbon nanotubes, used as the counter electrode material, improved with increased thickness of the carbon layer. This was evidenced by lower charge transfer resistances for thicker electrode materials.

Initial investigations into the use of high surface area electrodes for TEC application with ionic liquids has been reported: the use of platinum black coated platinum increased the power density obtained from the TEC by about 25% for a neat ionic liquid electrolyte incorporating Co$^{2+/3+}$(bpy)$_3$. The same effect was reported with the 3:1 MPN:C$_2$mim B(CN)$_4$ mixed electrolyte (as discussed in chapter 3), with an increase of 11% in power density from the TEC. The use of stainless steel electrodes with a deposited thin platinum layer was also reported, to potentially reduce the cell costs, and produced equivalent TEC power densities to that with platinum disc electrodes.
Studies on the aqueous ferri/ferrocyanide electrolyte have previously incorporated carbon based electrodes with high surface area to enhance the power density of the TEC, discussed in more detail in chapter one, section 2.1.2. Briefly, porous carbon materials such as carbon paper, multi walled carbon nanotube (MWNT) foam and carbon cloth were incorporated. The use of high surface area electrodes, in combination with other enhancements such as increasing the redox couple concentration and use of separators to inhibit thermal conductivity across the cell, led to the highest power density reported to date: 12.0 mW/m$^2$ in an aqueous TEC. The highest power density was obtained using activated carbon cloth electrode, with a 70% increase in power output compared to that with traditional platinum electrodes.

5.2 Materials and experimental methods

The redox couples used in this chapter are:

- tris(1,10-phenanthroline)cobalt(II/III) bis(trifluoromethanesulfonylimide), $\text{Co}^{2+/3+}(\text{phen})_3(\text{NTf}_2)_2$.
- tris[2-(1H-pyrazol-1-yl)pyrimidine]cobalt(II/III) bis(trifluoromethanesulfonylimide), $\text{Co}^{2+/3+}(\text{py-pz})_3(\text{NTf})_{2/3}$.
- tris(bipyridyl)cobalt(II/III) bis(trifluoromethanesulfonyl)amide, $\text{Co}^{2+/3+}(\text{bpy})_3(\text{NTf}_2)_3$.
- tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(II/III) bis(trifluoromethanesulfonylimide), $\text{Co}^{2+/3+}(\text{Bupy-pz})_3(\text{NTf}_2)_{2/3}$.
Figure 1 The structure of the redox complexes reported in this chapter (a) Co$^{2+/3+}$(phen)$_3$(NTf$_2$)$_2$, (b) Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_3$, (c) Co$^{2+/3+}$(py-pz)$_3$(NTf)$_2/3$, (d) Co$^{2+/3+}$(Bupy-pz)$_3$(NTf)$_2/3$.

The solvent system used in this chapter was 3:1 DMSO:C$_2$mim eFAP. This was chosen as it was previously found to be the best in terms of TEC performance with the Co(bpy)$_3$, as discussed in chapter three, section 3.5.

The electrolytes in this chapter were tested using the following experimental techniques: Seebeck coefficient measurement, thermoelectrochemical cell (TEC) measurement, ionic conductivity by EIS, diffusion coefficient measurements and cyclic voltammetry. Details on the experimental methods were presented in chapter two.

5.3 Results and discussion

5.3.1 The effect of the structure of redox couple ligand on the Seebeck coefficient.

The Seebeck coefficient was measured for the redox couples under study at 0.1M concentration in two solvent systems: the 3:1 DMSO:C$_2$mim eFAP, and the neat DMSO. The counter ion was NTf$_2$ in all of the cobalt-based redox couples, again chosen for optimum stability. The presence of the NTf$_2$ anion may have an effect on the Seebeck coefficient; however, eFAP, the anion of the ionic liquid is present at a significantly higher concentration (1.5M), which is likely to have a larger effect on the Seebeck coefficient of the redox complex. Furthermore, this electrolyte is composed
of 93.2 mol% DMSO which is likely to have the largest effect on the Seebeck coefficient, as demonstrated in chapter three, section 3.1. The redox couple radius was estimated using Avogadro molecular modelling software. The calculated radii and Seebeck coefficients of the redox couples are shown in Table 1.

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Complex radius (Å) ± 0.03*</th>
<th>3:1 DMSO:C$_2$mmim eFAP</th>
<th>neat DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$^{2+/3+}$(bpy)$_3$</td>
<td>5.75</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Co$^{2+/3+}$(phen)$_3$</td>
<td>6.10</td>
<td>1.70</td>
<td>1.90</td>
</tr>
<tr>
<td>Co$^{2+/3+}$(py-pz)$_3$</td>
<td>5.76</td>
<td>2.36</td>
<td>2.43</td>
</tr>
<tr>
<td>Co$^{2+/3+}$(Bupy-pz)$_3$</td>
<td>6.73</td>
<td>2.23</td>
<td>2.34</td>
</tr>
</tbody>
</table>

Table 1 The complex radii and Seebeck coefficient of 0.1M Co$^{2+/3+}$(bpy)$_3$(NTf$_2$)$_3$, Co$^{2+/3+}$(phen)$_3$(NTf)$_2$, Co$^{2+/3+}$(py-pz)$_3$(NTf)$_2$, and Co$^{2+/3+}$(Bupy-pz)$_3$(NTf)$_2$ in 3:1 C$_2$mmim eFAP : DMSO and in neat DMSO. Radius error values were calculated by measuring the radius from three different points corresponding to the three ligands in each complex.

The Seebeck coefficients measured in neat DMSO are consistently higher than those measured in the 3:1 DMSO:C$_2$mmim eFAP, with the exception of Co$^{2+/3+}$(bpy)$_3$ which has the same Seebeck coefficient (2.0 mV/K) in both solvent systems. The decrease in Seebeck coefficient when ionic liquid was introduced as co-solvent is consistent with the results presented in chapter three, section 3.1, where the highest Seebeck coefficients were measured for the Co$^{2+/3+}$(bpy)$_3$ in neat organic solvents, namely DMSO and MPN, compared to electrolytes containing ionic liquids.

The Seebeck coefficient measured for the four redox couples shows notable variations with different solvent and ligand structure. The lowest was measured for Co$^{2+/3+}$(phen)$_3$, at 1.7 mV/K in the 3:1 DMSO:C$_2$mmim eFAP electrolyte, and the highest was measured for Co$^{2+/3+}$(py-pz)$_3$, at 2.43 mV/K in neat DMSO. The Seebeck
Coefficient of the redox complexes can be tentatively correlated with the effective radius of the redox species. It was shown by Hupp et al.\textsuperscript{20} and Migita et al.\textsuperscript{21} that the experimentally determined entropy change associated with the redox reactions ($\Delta S_{rc}$) can be related to the effective radius and absolute charge of the redox couple based on the Born equation (chapter one, section 2.2, equation 2.6). The empirical relation reported by Migita et al.\textsuperscript{21} was derived for the ionic liquid C\textsubscript{4}mpyr NTf\textsubscript{2} and is given by:

\[
\Delta S_{rc} = 74.0 \frac{Z_{ox}^2 - Z_{red}^2}{r} - 6.1 \quad \text{Eqn 1.1}
\]

Where $Z_{ox}$ and $Z_{red}$ are the absolute charge of the oxidised and reduced species respectively, and $\Delta S_{rc}$ is in J. K\textsuperscript{-1}. mol\textsuperscript{-1}. All the redox complexes investigated in this chapter have the same absolute charge of the oxidised and reduced species (Co\textsuperscript{2+/3+}) which leaves the effective radius as the only variable in the above equation. The radii of the redox complexes were calculated using Avogadro molecular modelling software. In instances where two different radii were calculated for a single redox complex due to asymmetry in the structure, the larger radius is reported. The radii of the different complexes are shown in Table 1. Two comparisons can be made based on redox couple size: first, the Co\textsuperscript{2+/3+}(phen)\textsubscript{3} has a larger calculated radius, at 6.10 Å, compared to the Co\textsuperscript{2+/3+}(bpy)\textsubscript{3}, with a radius of 5.75 Å, which is consistent with the lower Seebeck coefficients measured in both solvent systems for the Co\textsuperscript{2+/3+}(phen)\textsubscript{3}.

The second comparison based on redox couple size can be made between the Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} and Co\textsuperscript{2+/3+}(Bupy-pz)\textsubscript{3}, with radii of 5.76 Å and 6.73 Å respectively. In the latter case, the butyl groups are sufficiently far apart that it is possible that some solvent molecules could come in between them, thereby approaching closer to the central cobalt atom (i.e. making the effective radii nearer to the 5.76 Å imparted by the py-pz groups). However, in terms of estimating charge density and the radii that most influences mass transport, the larger 6.73 Å is considered more relevant. This
larger radii correlates to lower Seebeck coefficients of Co$^{2+3+}$(Bupy-pz)$_3$ in both solvents compared to the equivalent Co$^{2+/3+}$(py-pz)$_3$.

The calculated radii of the redox couples, however, do not show a complete correlation with the trend in the Seebeck coefficient. For instance, the Co$^{2+/3+}$(Bupy-pz)$_3$ complex has the largest calculated radius of the four complexes, which according to equation 1.1, should lead to the lowest Seebeck coefficient. However, the Co$^{2+/3+}$(Bupy-pz)$_3$ complex has the second highest Seebeck coefficient. Thus, while the Born equation and subsequent empirical relations attempt to correlate the reaction entropy change to the radius of the redox complex, the results reported here show that this relationship does not always hold. This is consistent with other studies that suggest that the Born equation fails to provide completely accurate entropy predictions by not taking into account the interactions between the redox complex and surrounding solvent, which are affected by redox couple structure.$^8, 20$ Thus, while some correlation with redox couple radii is observed, and provides useful insight into one of the parameters that determines the Seebeck coefficient, more sophisticated methods of prediction are required to fully account for all of the different effects of solvent and redox couple structure.

5.3.2 The TEC performance of the cobalt-based redox complexes.

The cobalt-based complexes were tested in the TEC at 0.1M in 3:1 DMSO:C$_2$mim eFAP solvent. The mixed IL/solvent system was used in order to mitigate the mass transport limitations in the cell (as discussed in chapter three, section 3.5). The mass transport over-potential was found to be the most limiting factor in TEC operation in previous chapters and in literature dealing with ionic liquid-based TECs.$^5-7$

The three over-potentials present within the cell under operation can be thought of as three resistors in series, the total summation of which gives the total cell resistance, i.e. $R_{cell} = R_{diff} + R_{sol} + R_{CT}$. An approximate value of the total cell resistance ($R_{cell}$) can be obtained by fitting the power density vs cell potential curve and using the relation:
\[ P_{\text{Max}} = \frac{V^2}{(R_{\text{cell}} \cdot A)} \quad \text{Eqn 1.2} \]

Where, \( P \) is power density in W/m\(^2\), \( A \) is the surface area of the electrode. This \( R_{\text{cell}} \) value is used in this chapter to help to understand the effect of different solvents and redox couples on the TEC performance.

5.3.2.1 The TEC performance of the complexes in 3:1 DMSO:C\(_2\)mim eFAP electrolyte

The TEC power and current density vs cell potential plots are presented in Figure 2. The total cell resistance obtained from fitting the power vs cell potential curves (\( R_{\text{cell}} \)), as well as the maximum power density obtained from each electrolyte, are shown in Table 2.

Figure 2 (a) The measured power density (data points) and the fitted power density (dashed line) obtained from the TEC. (b) The current density obtained from the TEC of the four redox couples at 0.1M concentration in 3:1 DMSO:C\(_2\)mim eFAP electrolyte. The electrode temperatures were \( T_{\text{cold}} = 30^\circ\text{C} \) and \( T_{\text{hot}} = 60^\circ\text{C} \).

The power and current density are highest for the Co\(^{2+/3+}\)(bpy)\(_3\) electrolyte, at 34 mW/m\(^2\) and 2.0 A/m\(^2\) respectively. The Co\(^{2+/3+}\)(bpy)\(_3\) exceeded both the Co\(^{2+/3+}\)(py-pz)\(_3\) and Co\(^{2+/3+}\)(Bupy-pz)\(_3\) in TEC performance, in spite of having lower Seebeck coefficient (Table 1). The total cell resistance, \( R_{\text{cell}} \), shows a consistent trend with the TEC performance, with the highest resistance giving the lowest performance. The
highest $R_{\text{cell}}$ value was measured for Co$^{2+/3+}(\text{Bupy-pz})_3$, at 2230 Ω, and second highest for the Co$^{2+/3+}(\text{py-pz})_3$, at 945 Ω. Despite having the highest Seebeck coefficients, the Co$^{2+/3+}(\text{py-pz})_3$ and Co$^{2+/3+}(\text{Bupy-pz})_3$ complexes seem to be greatly limited by the over-potentials in the cell, particularly the Co$^{2+/3+}(\text{Bupy-pz})_3$ which gives the lowest power density of all complexes.

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Power density (mW/m$^2$) ± 2.0</th>
<th>$R_{\text{Cell}}$ (Ω) ± 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$^{2+/3+}(\text{bpy})_3$</td>
<td>34</td>
<td>537</td>
</tr>
<tr>
<td>Co$^{2+/3+}(\text{phen})_3$</td>
<td>23</td>
<td>441</td>
</tr>
<tr>
<td>Co$^{2+/3+}(\text{py-pz})_3$</td>
<td>24</td>
<td>945</td>
</tr>
<tr>
<td>Co$^{2+/3+}(\text{Bupy-pz})_3$</td>
<td>10</td>
<td>2230</td>
</tr>
</tbody>
</table>

Table 2 The maximum power density obtained from the different redox couples in 3:1 DMSO:C$_2$mim eFAP and the total cell resistance obtained from fitting the power density vs cell potential curves.

5.3.2.2 Device testing over an extended time period

The performance of the TEC with the four redox complexes was tested over a prolonged time in order to investigate the stability of the power and current density. Figure 3 (a) shows the maximum power density obtained from the TEC vs time from the four different redox electrolytes. The power density drawn from the cell was very stable over the 150 minutes, showing only a slight decrease of about 1.0 mW/m$^2$ over this time period. The power output with the Co$^{2+/3+}(\text{bpy})_3$ shows a slight increase at 108 minutes, which was caused by a fluctuation in the temperature of the hot electrode. However, the device operation was not interrupted. The current drawn from the TEC, also shown in Figure 3 (b), shows good stability over the time period tested, with the biggest decrease, of 0.01 A/m$^2$, observed for the Co$^{2+/3+}(\text{Bupy-pz})_3$
complex. Finally, the cell potential, shown in Figure 3 (c), shows good stability, with negligible decrease - less than 2 mV after 150 minutes of testing.

These preliminary results on long-term device operation show high stability in the performance of the TEC over a time of 150 minutes using all four redox complexes. The results presented in this section are of great significance with respect to prior literature, considering that up till now TEC device testing typically collects data for only a short period of time.

Figure 3 (a) The maximum power density, (b) maximum current density and (c) cell potential vs time for the four redox complexes at 0.1M concentration in 3:1 DMSO: C2mim eFAP. The electrode temperatures were T_{cold} = 30°C and T_{hot} = 60°C.

5.3.2.3 The influence of solution conductivity and diffusion on TEC performance

The limitations on TEC performance was further examined by measuring the ionic conductivity, diffusion coefficient and charge transfer resistance of the different redox electrolytes (Table 3). The diffusion coefficient and charge transfer resistance measurements were not reproducible for the Co^{2+}(py-pz)_3 and Co^{2+}(Bupy-pz)_3 species and therefore only the diffusion coefficients of the Co^{3+} species are presented here.
This poor reproducibility is attributed to poor electrochemical reversibility in these solvents, which is discussed further in section 3.3.

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Ionic conductivity $\kappa$(mS.cm$^{-1}$)±0.3</th>
<th>Diffusion coefficient of Co$^{3+}$ D(cm$^2$.S$^{-1}$)$^{*}10^{-7}$±0.3</th>
<th>Charge transfer resistance, $R_{CT}$ (Ω.cm$^2$) ±0.08</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$^{2+/3+}$(bpy)$_3$</td>
<td>5.6</td>
<td>10.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Co$^{2+/3+}$(phen)$_3$</td>
<td>5.5</td>
<td>9.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Co$^{2+/3+}$(py-pz)$_3$</td>
<td>6.0</td>
<td>9.8</td>
<td>*</td>
</tr>
<tr>
<td>Co$^{2+/3+}$(Bupy-pz)$_3$</td>
<td>4.6</td>
<td>8.6</td>
<td>*</td>
</tr>
</tbody>
</table>

Table 3 The ionic conductivity, diffusion coefficient of Co$^{3+}$ and charge transfer resistance of the redox complexes in 3:1 DMSO:C$_2$mim eFAP at room temperature (22°C). *Was not measured due to poor reproducibility.

The ionic conductivity and diffusion coefficient are lowest for the Co$^{2+/3+}$(Bupy-pz)$_3$ complex, which is consistent with the lowest TEC performance from this complex. The three butyl groups attached to this complex increase its size compared to the other redox couples, which is believed to cause lower values of ionic conductivity and diffusion coefficient and, subsequently, poor TEC performance.

No significant change can be seen in ionic conductivity and diffusion coefficient of the other redox complexes. The Co$^{2+/3+}$(phen)$_3$ has a diffusion coefficient slightly lower than the Co$^{2+/3+}$(bpy)$_3$ and Co$^{2+/3+}$(py-pz)$_2$, which can also be attributed to the larger size of this complex. The Co$^{2+/3+}$(phen)$_3$ complex also has the lowest Seebeck coefficient, at 1.7 mV/K, which is arguably the most limiting factor for the TEC performance of this complex.
The ionic conductivity and diffusion coefficient data does not, however, appear to explain the poor performance of the Co\(^{2+}/3+\)(py-pz)\(_3\) complex compared to the Co\(^{2+}/3+\)(bpy)\(_3\). The Co\(^{2+}/3+\)(py-pz)\(_3\) complex has equivalent ionic conductivity, equivalent diffusion coefficient and higher Seebeck coefficient than the Co\(^{2+}/3+\)(bpy)\(_3\) and should, by these standards, give higher power density. These observations point to the charge transfer resistance as a limiting factor for the Co\(^{2+}/3+\)(py-pz)\(_3\). However, we were unable to obtain the charge transfer resistance for this complex due to poor reproducibility/electrochemical reversibility: the measured Nyquist plots showed an unrealistically large second touch-down (associated with R\(_{CT}\)) and changed significant with each fresh preparation of the electrode surface.

5.3.3 Study of the reversibility of the redox couples by cyclic voltammetry

Cyclic voltammetry was performed on all of the redox complexes in order to investigate the electrochemical reversibility and stability. Details on the experimental procedure and electrode preparation, and the criteria of a reversible redox reaction, was given in chapter two, section 2.5.

Three scan rates were used in all experiments: 20 mV/s, 50 mV/s and 100 mV/s, but only the results obtained at 50 mV/s scan rate are shown here, to improve the clarity of the plots. Varying the scan rate did not change the behaviour of the redox species. Each sample was analysed over 10 cycles at each scan rate.

5.3.3.1 An investigation of the reversibility of the redox couples on platinum and glassy carbon electrodes.

The four redox couples were tested by cyclic voltammetry at 0.1M concentration in 3:1 DMSO:C\(_2\)mim eFAP using a platinum working electrode, shown in Figure 4. These parameters were chosen to simulate conditions under which the redox couples were tested in the TEC.
Figure 4 The cyclic voltammograms of the redox complexes at 0.1M concentration in 3:1 DMSO:C$_2$mim eFAP, (a) Co$^{2+/3+}$(bpy)$_3$, (b) Co$^{2+/3+}$(Bupy-pz)$_3$, (c) Co$^{2+/3+}$(phen)$_3$ and (d) Co$^{2+/3+}$(py-pz)$_3$. PP separation is the difference between the potential values where maximum current was observed for the oxidation and reduction processes. The working electrode was platinum, with geometric surface area of 2.0mm$^2$. *Cyclic voltammograms in the 3:1 DMSO:C$_2$mim eFAP were conducted under atmospheric conditions.

The cyclic voltammograms of Co$^{2+/3+}$(bpy)$_3$ and Co$^{2+/3+}$(phen)$_3$, shown in Figure 4 a and c, show quasi-reversible behaviour with peak-peak separations at 170 mV and 180 mV respectively. The oxidation and reduction currents were stable over 10 cycles. In contrast, the Co$^{2+/3+}$(py-pz)$_3$ and Co$^{2+/3+}$(Bupy-pz)$_3$ show poor reversibility in this electrolyte. The oxidation currents were unstable and dropped with increasing cycles. The poor reversibility of the Co$^{2+/3+}$(py-pz)$_3$ and Co$^{2+/3+}$(Bupy-pz)$_3$ may contribute to the poor TEC performance when compared to the Co$^{2+/3+}$(bpy)$_3$ redox couple.

The complexes were also tested in the 3:1 DMSO:C$_2$mim eFAP electrolyte system on a glassy carbon working electrode, shown in Figure 5. The Co$^{2+/3+}$(bpy)$_3$ and
Co^{2+/3+}(phen)_3 complexes show quasi-reversible behaviour with peak-peak separation of 180 mV in both systems (Figure 5 a and c). The behaviour of Co^{2+/3+}(bpy)_3 and Co^{2+/3+}(phen)_3 does not show a significant change on the glassy carbon working electrode compared to platinum. The Co^{2+/3+}(py-pz)_3 and Co^{2+/3+}(Bupy-pz)_3 complexes show poor reversibility and sluggish oxidation processes on glassy carbon (Figure 5 b and d).

![Cyclic voltammograms](image)

**Figure 5** The cyclic voltammograms of the redox complexes at 0.1M concentration in 3:1 DMSO:C2mim eFAP, (a) Co^{2+/3+}(bpy)_3, (b) Co^{2+/3+}(Bupy-pz)_3, (c) Co^{2+/3+}(phen)_3 and (d) Co^{2+/3+}(py-pz)_3. The working electrode was glassy carbon with geometric surface area of 2.0mm^2. *Cyclic voltammograms in the 3:1 DMSO:C2mim eFAP were conducted under atmospheric conditions.

5.3.3.2 The reversibility of the redox complexes in different solvents.

To further investigate the behaviour of Co^{2+/3+}(py-pz)_3 and Co^{2+/3+}(Bupy-pz)_3, the effect of solvent was investigated. The Co^{2+/3+}(py-pz)_3 was chosen for additional tests in two neat ionic liquids, C2mim eFAP and C2mim NTf2, to probe the effect of solvent
on the reversibility of this complex. The concentration of the $\text{Co}^{2+/3+}\text{(py-pz)}_3$ redox couple was reduced to 5mM to ensure good solubility in the ionic liquids chosen. Figure 6 shows the cyclic voltammetry of $\text{Co}^{2+/3+}\text{(py-pz)}_3$ in both ionic liquids using a glassy carbon working electrode.

Figure 6 The cyclic voltammogram of the $\text{Co}^{2+/3+}\text{(py-pz)}_3$ at 5mM concentration in (a) $\text{C}_2\text{mim eFAP}$ and (b) $\text{C}_2\text{mim NTf}_2$, using glassy carbon (GC) working electrode.

The $\text{Co}^{2+/3+}(\text{py-pz})_3$ complex shows quasi-reversible behaviour on the glassy carbon working electrode in both ionic liquids. The currents were stable over 10 cycles in neat ionic liquids, unlike in the 3:1 DMSO:$\text{C}_2\text{mim eFAP}$ solvent system (Figure 5) where the oxidation currents were unstable and decreased with cycling. The peak-peak separation is slightly lower in $\text{C}_2\text{mim eFAP}$, indicating better reversibility in this IL compared to $\text{C}_2\text{mim NTf}_2$.

The $\text{Co}^{2+/3+}(\text{py-pz})_3$ redox complex was also tested in the two ionic liquids using a platinum working electrode, shown in Figure 7. The redox reaction on the platinum working electrode was sluggish, with peak-peak separation reaching 875 mV in $\text{C}_2\text{mim eFAP}$, compared to on glassy carbon where the peak-peak separation was only 180 mV. This is consistent with the poor reversibility of cobalt-redox complexes in acetonitrile on platinum compared to glassy carbon previously reported in the DSSC literature.\textsuperscript{22} Similarly, poor catalytic performance of platinum during oxygen reduction reactions and the redox reactions of $\text{Co}^{2+/3+}\text{(phen)}_3$ and $\text{Co}^{2+/3+}\text{(bpy)}_3$ were attributed to adsorption of the anions of the complexes, present in the electrolyte, to the electrode surface.\textsuperscript{23, 24} However, fundamental research on the redox reaction
kinetics on different electrode materials is required to further understand the behaviour of these complexes.

Figure 7 The cyclic voltammograms of the Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} at 5mM concentration in (a) C\textsubscript{2}mim eFAP and (b) C\textsubscript{2}mim NTf\textsubscript{2} using a platinum working electrode.

It can be concluded that the of Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} complex shows poor reversibility in the 3:1 DMSO:C\textsubscript{2}mim eFAP solvent system, with a decaying oxidation current. The behaviour improves in neat ionic liquids, particularly in C\textsubscript{2}mim eFAP, with stable currents and quasi-reversible behaviour. The Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} shows improved reversibility on glassy carbon compared to platinum working electrode. In a prior study on the Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} in acetonitrile, sluggish oxidation behaviour was observed and attributed to passivation of the electrode material when the reaction occurs in atmospheric conditions.\textsuperscript{25} Passivation of the electrode material is the formation of a non-catalytic layer on the electrode surface. This is consistent with our observation of decaying oxidation current of the Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} and Co\textsuperscript{2+/3+}(Bupy-pz)\textsubscript{3} in the 3:1 DMSO : C\textsubscript{2}mim eFAP under atmospheric conditions (Figure 5). In the prior study, the authors found the oxidation of Co\textsuperscript{2+/3+}(bpy)\textsubscript{3} to be stable in dry acetonitrile under a nitrogen atmosphere, indicating that formation of the passivation layer was not a result of the direct reaction of the complex but most likely due to the presence of water.\textsuperscript{25} This is also consistent with our observation of stable oxidation/reduction currents of Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} and Co\textsuperscript{2+/3+}(Bupy-pz)\textsubscript{3} in dry ionic liquids under argon atmosphere (Figure 7).
5.3.3.3 The reversibility of the redox complexes on carbon slurry-coated electrodes.

Glassy carbon was shown to be a good electrocatalyst for the Co$^{2+/3+}$,(py-pz)$_3$ compared to platinum in section 3.3.2. To build further on these promising results using electrode materials more amenable to use in the full TEC device, the electrochemical behaviour of the four redox couples on carbon-slurry coated electrodes was investigated by cyclic voltammetry. The carbon slurry (synthesis details in chapter two, section 2.4) was coated onto the surface of either platinum or glassy carbon electrodes then dried overnight before use.

Here, the current density values (given in mA/m$^2$) was calculated using the geometric surface area of the platinum and glassy carbon working electrodes without carbon coating, which was 2.0 mm$^2$. The electrochemical surface area of the electrodes is expected to have significantly increased with the addition of the high surface area carbon coating. However, this could not be measured because of the fragility of the carbon coating. In addition, each carbon coating was freshly applied in order to prevent cross contamination of other samples. Thus, small variations in the current density measured for the different complexes on carbon-coated working electrodes may be a result of changes to the surface area of the electrodes. However, this did not affect the reproducibility of the peak-peak separation, used to assess reversibility. All the cyclic voltammograms were performed at 20 mV/s, 50 mV/s and 100 mV/s scan rates, but for clarity only the 50 mV/s is shown here. No change in peak positions was observed with different scan rates and the oxidation and reduction currents were stable over 10 cycles. The ratio of the peak currents was close to unity in all the cyclic voltammograms in this section.

Figure 8 shows the cyclic voltammograms of Co$^{2+/3+}$,(bpy)$_3$ in neat C$_2$ mim eFAP on platinum, glassy carbon and carbon-coated platinum and glassy carbon.
Figure 8 The cyclic voltammograms of 5mM Co\(^{2+/3+}\)(bpy)\(_3\) in neat C\(_2\)mim eFAP at 50 mV/s scan rate vs Pt pseudo reference electrode on the following working electrodes: (a) glassy carbon, (b) platinum, (c) carbon-coated glassy carbon and (d) carbon-coated platinum.

The Co\(^{2+/3+}\)(bpy)\(_3\) redox complex shows improved reversibility on carbon-coated platinum and glassy carbon electrodes, with reduced peak-peak separation that indicates improved catalytic properties as a result of the carbon coating. The improved catalytic properties of the carbon slurry coating are attributed to the non-uniformity of the surface compared to glassy carbon. A report by Banks and colleagues found the catalytic properties of graphite to improve in the presence of defects and “edge-plane” surfaces compared to single layer basal surfaces.\(^{26}\) The study found the cyclic voltammogram of ferri/ferrocyanide to have lower peak-peak separation when a graphite electrode containing “edges” was used compared to a flat surface graphene electrode.\(^{26}\) Thus, the use of a rough carbon-slurry coating, which will have a rougher and less uniform surface and higher surface area, is likely
to have more reaction sites and better electrocatalytic activity than the very smooth glass carbon electrode.

Figure 9 shows the cyclic voltammograms of the $\text{Co}^{2+}/3+(\text{py-pz})_3$ complex on the different electrode materials. The smallest peak-peak separation was achieved with the carbon slurry-coated glassy carbon working electrode (Figure 9 c). The reversibility improved greatly compared to bare platinum.

![Cyclic Voltammograms](image)

Figure 9 The cyclic voltammograms of 5mM $\text{Co}^{2+}/3+(\text{py-pz})_3$ in neat $\text{C}_2\text{mim eFAP}$ at 50 mV/s scan rate vs Pt pseudo reference electrode on the following working electrodes: (a) glassy carbon, (b) platinum, (c) carbon-coated glassy carbon and (d) carbon-coated platinum.

The reversibility of $\text{Co}^{2+}/3+(\text{Bupy-pz})_3$ on these different working electrodes was also investigated, as shown in Figure 10. The $\text{Co}^{2+}/3+(\text{Bupy-pz})_3$ shows the largest peak-peak separation on platinum, at 1.28V, which is consistent with the lowest performance in the TEC with platinum electrodes (Figure 2). The reversibility
improves on glassy carbon and is best on the carbon slurry-coated glassy carbon.

Figure 10 The cyclic voltammograms of 5mM Co^{2+}/3+(Bupy-pz)₃ in neat C₂mim eFAP at 50 mV/s scan rate vs Pt pseudo reference electrode on the following working electrodes: (a) glassy carbon, (b) platinum, (c) carbon-coated glassy carbon and (d) carbon-coated platinum.
The Co$^{2+}/3+(\text{phen})_3$ redox complex was tested in a 9:1 C$_{2}$mim eFAP : DMSO solvent system because of poor solubility in neat C$_{2}$mim eFAP.

The Co$^{2+}/3+(\text{phen})_3$ shows the best reversibility on bare glassy carbon, with a peak-peak separation of 90 mV (Figure 11, a). The electrochemical behaviour was not significantly changed with the additional carbon layer. The appearance of an additional redox process at ca. 0.4 V is tentatively attributed to residual solvent/electroactive impurity introduced within the carbon slurry, but further investigation is required to confirm this. Additional peaks were also present for Co$^{2+}/3+$ (Bupy-pz)$_3$ at 0.2 V on carbon-coated glassy carbon electrode (Figure 10 c).

It can be concluded from this section that the four redox complexes tested show improved reversibility on a glassy carbon working electrode compared to platinum.
The reversibility improved further when the glassy carbon electrode was coated with a high surface area carbon layer. Coating with a carbon layer has the greatest impact on the reversibility of the Co^{2+/3+}(py-pz)_3 and Co^{2+/3+}(Bupy-pz)_3 complexes, which show irreversible behaviour and unstable oxidation processes on platinum electrodes. Following these conclusions, the carbon slurry coating was used to cover the platinum disc electrodes used in the TEC - these results are discussed in the following section.

5.3.4 TEC performance with carbon electrodes

The TEC performance of the four redox complexes was tested using high surface area carbon slurry-coated platinum disc electrodes. The preparation of the carbon-coating was detailed in chapter two, section 2.4. Use of the carbon layer was shown to greatly improve the reversibility of the redox complexes in section 3.3, particularly for the Co^{2+/3+}(py-pz)_3 and Co^{2+/3+}(Bupy-pz)_3 complexes which show a significant decrease in the oxidation/reduction peak-peak separation, indicating improved reversibility of the redox reactions.

Figure 12 shows the TEC power density and current density vs cell potential curves obtained using carbon-coated platinum disc electrodes. Table 4 shows the maximum power density values obtained from the TEC using carbon-coated platinum and also bare platinum (from section 3.2) to allow comparison of the results. Table 4 also shows the cell resistance values calculated from fitting the power density vs cell potential.

The most significant observation in this set of data is the great increase in power and current density obtained using Co^{2+/3+}(py-pz)_3 and Co^{2+/3+}(Bupy-pz)_3 electrolytes with carbon-coated platinum electrodes. The power density obtained using the Co^{2+/3+}(py-pz)_3 electrolyte shows an increase of 27% when the carbon layer is present on the electrode. The improved performance is accredited to two factors: first, the higher surface area of the electrode surface, which provides larger number of reaction sites for the redox complex when the TEC is operated, and second the improved reversibility of the Co^{2+/3+}(py-pz)_3 on carbon-based electrodes (discussed in section 3.3). The calculated cell resistance drops from 945Ω to 535Ω when platinum
is coated with the carbon layer, which is arguably a result of a drop in the charge transfer resistance, $R_{CT}$, as this relates to the electrode material. The solution resistance, $R_{sol}$, and diffusion resistance, $R_{diff}$, are expected to remain unchanged given that the electrolyte composition is the same in this instance.

Figure 12 (a) The measured power density (data points) and the fitted power density (dashed line) and (b) the current density obtained from the TEC at 0.1M concentration in 3:1 DMSO:C2mim eFAP using carbon-coated platinum disc electrodes. The electrode temperatures were $T_{cold}$=30°C and $T_{hot}$= 60°C. *The electrode temperatures were $T_{cold}$= 30°C and $T_{hot}$= 62°C when the Co^{2+/3+}(bpy)$_2$ was tested, to compensate for the unwanted temperature drop across the electrode that occurred due to the presence of the carbon layer. The internal temperature gradient was evaluated by measuring the open circuit potential, which corresponds to the Seebeck coefficient.

The TEC performance with Co^{2+/3+}(py-pz)$_3$ in the same solvent shows a significant increase in power and current density when carbon-coated electrodes are used. The power density was 60% higher, at 25 mW/m$^2$, compared to the power density obtained using bare platinum, at 10 mW/m$^2$. The corresponding cell resistance shows a similar decrease of 65%, from 2230Ω to 765Ω, expected to be a result of a drop in charge transfer resistance. The improved TEC performance is therefore concluded to be the result of reduced charge transfer resistance due to improved catalytic properties of the carbon-based electrode material, improved reversibility of the redox reactions and the use of high surface area electrodes.
### Redox couple

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Power density (mW/m²)±2.0 on carbon</th>
<th>Power density (mW/m²)±2.0 on Pt</th>
<th>$R_{\text{Cell}}$-carbon (Ω)±5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_{2+}/3+$ (bpy)$_3$</td>
<td>32</td>
<td>34</td>
<td>503</td>
</tr>
<tr>
<td>Co$_{2+}/3+$ (Phen)$_3$</td>
<td>23</td>
<td>23</td>
<td>550</td>
</tr>
<tr>
<td>Co$_{2+}/3+$ (py-pz)$_3$</td>
<td>33</td>
<td>24</td>
<td>535</td>
</tr>
<tr>
<td>Co$_{2+}/3+$ (Bupy-pz)$_3$</td>
<td>25</td>
<td>10</td>
<td>765</td>
</tr>
</tbody>
</table>

Table 4 The maximum power density obtained for the TEC from the four redox couples at 0.1M concentration in 3:1 DMSO: C$_2$mim eFAP using carbon-coated platinum disc electrodes, and bare platinum disc electrodes, and the resistance of the cell with the carbon-coated platinum disc electrodes. The electrode temperatures were $T_{\text{cold}}$=30°C and $T_{\text{hot}}$= 60°C. *The electrode temperatures were set to $T_{\text{cold}}$ = 30°C and $T_{\text{hot}}$ = 62°C when the Co$_{2+}/3+$ (bpy)$_2$ was tested on carbon-coated platinum to compensate for a loss of temperature gradient.

The TEC performance of the Co$_{2+}/3+$ (bpy)$_3$ and Co$_{2+}/3+$ (phen)$_3$ electrolytes is not greatly affected by the presence of the carbon layer on the electrodes. The power density obtained from the Co$_{2+}/3+$ (phen)$_3$ remained unchanged. The cyclic voltammograms presented in section 3.3.2 for the Co$_{2+}/3+$ (phen)$_3$ complex on platinum and carbon-coated platinum did not show significant improvement in the reversibility of this complex when the carbon layer was present. Similarly, the reversibility of Co$_{2+}/3+$ (phen)$_3$ did not show significant change when carbon-coated...
platinum was used compared to bare platinum (see Figure 11). Thus, as the 
Co\(^{2+/3+}\)(bpy)\(_3\) and Co\(^{2+/3+}\)(phen)\(_3\) redox complexes showed relatively good quasi-reversible behaviour in the 3:1 DMSO:C\(_2\)mim eFAP electrolyte on the platinum electrode (Figure 4), with stable oxidation/reduction currents, the presence of a carbon layer has a less significant effect on reversibility and performance than it does for other redox couples that are poorly reversible on bare platinum.

A drop of temperature gradient across the carbon layer may have limited the TEC performance of these complexes. Furthermore, these results point to good reversibility of the redox reactions as a key factor for the improved TEC performance of Co\(^{2+/3+}\)(py-pz)\(_3\) and Co\(^{2+/3+}\)(Bupy-pz)\(_3\), in addition to the benefits of the high surface area of the carbon electrodes. The poor reversibility observed on platinum for Co\(^{2+/3+}\)(py-pz)\(_3\) and Co\(^{2+/3+}\)(Bupy-pz)\(_3\) is an indication of redox couple decomposition or formation of a passivating layer on the electrode surface. This would ultimately lead to a decrease in the number of available redox species and therefore decreased TEC power and current density (Figure 2) compared to the TEC with carbon electrodes where improved reversibility was observed (Figure 12).

5.3.5 Further device optimisation.

This chapter was designed to investigate the fundamental parameters affecting the TEC performance. In this section, a further route towards optimisation of the TEC power and current outputs is investigated by increasing the redox couple concentration in the electrolytes. Additionally, the use of stainless steel electrodes is presented as an effective way to reduce the device cost.

5.3.5.1 The effect of redox couple concentration on the Seebeck coefficient and TEC performance

In the results discussed in this chapter up to this point, the redox complexes were used at 0.1M concentration. This concentration was chosen as it previously gave the best TEC performance in a study on the Co\(^{2+/3+}\)(bpy)\(_3\) in the 3:1 DMSO:C\(_2\)mim eFAP
electrolyte. In this section, the concentration of the redox complexes was increased from 0.1M to 0.25M for the Co$^{2+/3+}$(py-pz)$_3$ and Co$^{2+/3+}$(Bupy-pz)$_3$ redox couples and to 0.2M for the Co$^{2+/3+}$(bpy)$_3$ and Co$^{2+/3+}$(phen)$_3$ complexes. The 3:1 DMSO:C$_2$mim eFAP solvent system was used. Figure 13 shows the maximum TEC power density output from each electrolyte vs redox couple concentration.

Prior work found the TEC performance to drop at concentrations higher than 0.1M, when the cell was operated at cold and hot electrode temperatures of 60°C and 130°C respectively. This was hypothesised to be an effect of higher viscosity of the sample, which is limiting to mass transport processes. In this thesis section, the TEC was operated at lower temperatures (cold electrode and hot electrode of 30°C and 60°C respectively) where the mass transport limitation will be more dominant and therefore an increase in the concentration of the redox complex is more effective.

The Seebeck coefficient of the electrolytes at different redox couple concentrations is shown in Figure 13 and Table 5. The Seebeck coefficient decreases with increased concentration of redox species, which is consistent with prior studies on the aqueous ferri/ferrocyanide redox complex and the Co$^{2+/3+}$(bpy)$_3$ in 3:1 MPN to C$_2$mim B(CN)$_4$ electrolyte. However, it is also interesting to note that the Seebeck coefficient of the Co$^{2+/3+}$(bpy)$_3$ was not greatly affected by the concentration in neat ionic liquids in a prior study.
Figure 13 (a) The maximum power density obtained from each electrolyte system vs redox couple concentration. The electrode temperatures were $T_{\text{cold}} = 30^\circ\text{C}$ and $T_{\text{hot}} = 60^\circ\text{C}$. (b) The Seebeck coefficient vs concentration of the four redox complexes.

A significant increase in the power density obtained from the TEC with increased redox couple concentration was observed for the $\text{Co}^{2+/3+}(\text{py-pz})_3$ and the $\text{Co}^{2+/3+}(\text{Bupy-pz})_3$ redox couples. The power density shows an increase of about 30% for the $\text{Co}^{2+/3+}(\text{py-pz})_3$ complex, going from 24 mW/m$^2$ at 0.1M to 35 mW/m$^2$ at 0.2M. Table 5 shows the maximum power density obtained from each electrolyte at all concentrations of redox couples, as well as the cell resistance obtained from fitting the power density vs cell potential curves. The cell resistance dropped from 945$\Omega$ to 580$\Omega$ when the concentration was increased from 0.1M to 0.2M, which can be attributed to an increase in mass transport processes and a decrease in the diffusion resistance ($R_{\text{diff}}$). The increased number of redox active charged species in the electrolytes appears to more than compensate for any increase in viscosity, leading to an increase in the ionic conductivity and therefore a reduction in $R_{\text{sol}}$. However, the power density remained relatively unchanged when the concentration was further increased to 0.25M. This suggests that at this higher concentration the detrimental effect of increased viscosity and/or ion pairing balances the benefits of increased redox species concentration and thus no overall increase in power is observed.

The $\text{Co}^{2+/3+}(\text{Bupy-pz})_3$ redox complex shows an increase in power density of about 50% when the concentration was increased from 0.1M to 0.2M going from 10 mW/m$^2$ to 22 mW/m$^2$ respectively. The increase in power density was accompanied
by a large decrease in cell resistance, from 2230Ω to 703Ω. The drop in cell resistance is most likely a collective effect of reduced $R_{\text{diff}}$ and $R_{\text{sol}}$. The increase in power is also attributed to enhanced mass transport processes, as a result of an increased number of charge carriers and redox species. However, the power obtained from the system decreased to 17 mW/m² when the concentration of redox couples was further increased to 0.25M. This is also credited to an increased viscosity of the electrolyte, which is evident in the increase in total cell resistance, to 826Ω at 0.25M.

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>concentration (M)</th>
<th>Se (mV/K)±0.02</th>
<th>Power density (mW/m²)±2</th>
<th>$R_{\text{Cell}}$ (Ω)±5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$^{2+/3+}$(bpy)$_3$</td>
<td>0.10</td>
<td>2.00</td>
<td>34</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>1.96</td>
<td>37</td>
<td>414</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>1.86</td>
<td>37</td>
<td>434</td>
</tr>
<tr>
<td>Co$^{2+/3+}$(phen)$_3$</td>
<td>0.10</td>
<td>1.70</td>
<td>23</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>1.62</td>
<td>25</td>
<td>445</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>1.60</td>
<td>22</td>
<td>493</td>
</tr>
<tr>
<td>Co$^{2+/3+}$(py-pz)$_3$</td>
<td>0.10</td>
<td>2.36</td>
<td>24</td>
<td>945</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>2.25</td>
<td>32</td>
<td>714</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>2.12</td>
<td>35</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2.07</td>
<td>33</td>
<td>589</td>
</tr>
<tr>
<td>Co$^{2+/3+}$(Bu py-pz)$_3$</td>
<td>0.10</td>
<td>2.23</td>
<td>10</td>
<td>2230</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>2.11</td>
<td>16.9</td>
<td>1204</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>2.04</td>
<td>22.0</td>
<td>703</td>
</tr>
</tbody>
</table>
The TEC performance of the Co$^{2+/3+}$(bpy)$_3$ and Co$^{2+/3+}$(phen)$_3$ complexes, on the other hand, was not greatly affected by increased concentration of redox species. The power density obtained from the Co$^{2+/3+}$(bpy)$_3$ complex shows a slight increase, with a maximum at 37 mW/m$^2$. In this case, the concentration was not increased further because of this small effect the redox couple concentration has on the TEC performance.

It is interesting to note that the four redox couples had good solubility in the 3:1 DMSO:C$_2$ mim eFAP electrolyte at the concentrations tested and therefore this could be increased if required. The optimum balance between redox couple concentration and viscosity is likely to depend on both the nature of the couple (i.e. the diffusion rate) and the operating temperature of the cell. Thus, for example if the TEC were to be used with higher operating temperature, then a further increase in redox couple concentration could result in a further increases in the power and current density as the electrolyte would be more fluid.

5.3.5.2 The use of carbon-coated stainless steel electrodes

The performance of the Co(py-pz)$_3$ couple in a TEC operated using stainless steel disc electrodes coated with a carbon layer was then investigated, shown in Figure 14. This complex was chosen for achieving the highest power and current density on carbon-coated platinum electrodes. The objective of this test was to eliminate the use of platinum in the TEC and significantly reduce the costs of its operation, while maintaining equivalent power and current outputs to those achieved using platinum. Stainless steel was chosen as a low cost metal. Stainless steel is also expected to be resistive to corrosion by the redox complexes.
The power density drawn from the TEC drops slightly upon use of carbon-coated stainless with a maximum power density of 28 mW/m² compared to 33 mW/m². The maximum power density obtained from the TEC with the different electrode materials, and the corresponding cell resistances, are shown in Table 6. The drop in power density upon use of carbon-coated stainless steel is hypothesised to be the result of poor catalytic properties of stainless steel compared to platinum.

Figure 14 (a) The measured power density (data points) and the fitted power density (dashed line) and (b) The current density obtained from the TEC of Co²⁺/³⁺(py-pz)₃ at 0.1M concentration in 3:1 DMSO:C₂mim eFAP using carbon-coated platinum disc electrodes, carbon-coated stainless steel (SS) disc electrodes and bare platinum disc electrodes (Pt). The electrode temperatures were Tcold = 30°C and Thot = 60°C.

The TEC with carbon-coated stainless steel electrodes outperforms that with bare platinum in terms of power and current density, which can be credited to the high surface area of the carbon layer. The use of carbon-coated stainless steel represents a significant reduction to the cost of the TEC and therefore the power production. Despite a drop in performance compared to carbon-coated platinum, the use of stainless steel and carbon materials is an important step towards real device application.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Power density (mW/m²)±2</th>
<th>RCell (Ω)±5</th>
</tr>
</thead>
</table>

157
Table 6 The maximum power density obtained from the TEC using Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} at 0.1M concentration in 3:1 DMSO:C\textsubscript{2}mim eFAP. The electrode materials used were: carbon-coated platinum disc electrodes, carbon-coated stainless steel disc electrodes or bare platinum disc electrodes. The electrode temperatures were T\textsubscript{cold}= 30°C and T\textsubscript{hot} = 60°C. The cell resistance $R_{cell}$ was calculated from the fitted values of maximum power density and cell potential.

<table>
<thead>
<tr>
<th></th>
<th>24</th>
<th>945</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon-coated</td>
<td>33</td>
<td>535</td>
</tr>
<tr>
<td>Platinum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon-coated</td>
<td>28</td>
<td>842</td>
</tr>
<tr>
<td>stainless steel</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.4 Conclusions.

The criteria for a redox couple that performs well in the TEC was investigated. It was found that a good redox couple for TEC applications ideally has reversible (or quasi-reversible) redox reactions and stable oxidation/reduction currents. An optimal redox couple is also small in size, which is hypothesised to contribute to high Seebeck coefficients and high diffusion coefficients during cell operation. An additional contribution to Seebeck coefficient is acquired when spin transitions occur as a result of the redox reactions.

The Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} and Co\textsuperscript{2+/3+}(Bupy-pz)\textsubscript{3} redox complexes show poor reversibility on platinum electrodes, which reduces their performance in the TECs with platinum disc electrodes. The Co\textsuperscript{2+/3+}(py-pz)\textsubscript{3} and Co\textsuperscript{2+/3+}(Bupy-pz)\textsubscript{3} show the best reversibility in neat ionic liquids and on carbon-based electrodes. However, the viscosity of neat ionic liquids is detrimental to mass transport processes in the TEC. Future work should therefore investigate lower viscosity ionic liquids or ionic liquid-based electrolytes with less molecular solvent, to optimise reversibility and transport of these complexes in a device incorporating carbon electrodes.
Coating the platinum disc electrodes with a carbon layer greatly improves the performance of the $\text{Co}^{2+/3+}(\text{py-pz})_3$ and $\text{Co}^{2+/3+}(\text{Bupy-pz})_3$ complexes in the TEC due to improved reversibility and the high surface area carbon providing an increased number of reaction sites. Future work focusing on high TEC performance should test the higher concentration electrolytes of these complexes in the TEC incorporating a carbon layer.

The $\text{Co}^{2+/3+}(\text{phen})_3$ redox complex is mainly limited by a low Seebeck coefficient compared to the other redox couples, which causes low cell potential during TEC operation. Increasing the concentration of $\text{Co}^{2+/3+}(\text{phen})_3$ and the use of carbon electrodes does not have a great effect of the TEC performance of this complex. The TEC performance of the $\text{Co}^{2+/3+}(\text{bpy})_3$ did not show a significant change when the concentration was increased or when the carbon layer on the electrode was used.

The TEC performance of the $\text{Co}^{2+/3+}(\text{py-pz})_3$ and $\text{Co}^{2+/3+}(\text{Bupy-pz})_3$ redox complexes improves when the concentration is increased, because of improved mass transport processes. The highest TEC performance was obtained at 0.2M concentration in the 3:1 DMSO:Clmim eFAP solvent system for these redox couples.

The use of carbon-coated stainless steel greatly reduces the potential cost of the TEC, and therefore of the power produced. This represents a promising step towards future commercial device application.
References


26. C. E. Banks, T. J. Davies, G. G. Wildgoose and R. G. Compton, *Chemical Communications*, Electrocatalysis at graphite and carbon nanotube modified electrodes: edge-plane sites and tube ends are the reactive sites, 2005, 829-841.

Chapter Six

Conclusions and future work
6.1 Thesis conclusions

The conclusions of this thesis can be summarised based on the three main research questions. The research questions and subsequent conclusions are presented below.

6.2 Research aim one: Overcome mass-transport limitations during cell operation in IL electrolytes by investigating mixed solvent systems.

The Seebeck coefficient was found to be influenced by the cation and anion of the ionic liquids tested. The anion tris(pentafluoroethyl)trifluorophosphate (eFAP) produced high Seebeck coefficient for the Co$^{2+/3+}$(bpy)$_3$ when combined with different cations. The cation of the ionic liquid was found to have significant influence on the Seebeck coefficient. This is hypothesised to be a result of the effect of the cation (of the ionic liquids) on the structuring of these solvents. This is believed to affect the reorganisation of the solvation shell following the redox reaction, which directly relates to the Seebeck coefficient. For imidazolium ionic liquids, the Seebeck coefficient of Co$^{2+/3+}$(bpy)$_3$ was found to decrease when longer alkyl chain were present on the cation of the ionic liquid.

The addition of high boiling point solvents, namely DMSO and MPN, to ionic liquids had the effect of reducing the viscosity of the electrolyte and increasing the TEC power and current output. However, the addition of high boiling point solvents had another effect - increasing the Seebeck coefficient of the Co$^{2+/3+}$(bpy)$_3$ redox couple in the mixed electrolytes compared to neat ionic liquids. The Seebeck coefficient of the Co$^{2+/3+}$(bpy)$_3$ has a maximum value in neat DMSO and neat MPN. These high Seebeck coefficients suggest strong coordination between the redox couple and the organic solvents tested, which leads to a high entropy change associated with the reorganisation of the solvation shell around the redox complex following electron transfer.

The presence of water in the electrolytes containing the Co$^{2+/3+}$(bpy)$_3$ has the effect of lowering the Seebeck coefficient compared to dry solvent samples. This
suggests that the Co\(^{2+/3+}\)(bpy)\(_3\) is likely to associate more strongly with the organic solvents and ionic liquid samples tested compared to water.

No direct correlation was established between the Kamlet-Taft parameters, which indicate the polarity and hydrogen bonding capabilities of the solvent system, and the Seebeck coefficient of the Co\(^{2+/3+}\)(bpy)\(_3\). However, further investigation into the relationship between Seebeck coefficient and other solvent parameters is encouraged.

Understanding the TEC performance requires the study of multiple parameters, summarised in the figure of merit relationship modified for a liquid device. Briefly, the device performance can be assessed based on the Seebeck coefficient of the redox couple, the concentration and diffusion coefficient of the redox couple, and the thermal conductivity of the electrolyte system. The 3:1 organic solvent : ionic liquid electrolyte system containing 0.1M Co\(^{2+/3+}\)(bpy)\(_3\) was found to achieve the best performance in the TEC, by achieving the optimum balance of the above parameters.

6.3 Research aim two: Investigate the effect of IL structure on the Seebeck coefficient and device performance.

The Seebeck coefficient of Co\(^{2+/3+}\)(bpy)\(_3\) was measured in a range of imidazolium ionic liquids with the aim of correlating this with the nature of the cation and anion tested. The effect of specific structural properties of the ionic liquids tested on the Seebeck coefficient were concluded to be as follows:

- The Seebeck coefficient was found to be highest in ionic liquids containing a sulfonate group, namely C\(_2\)mim MeSO\(_3\) and P\(_{2,2,2,4}\) Tos. This is believed to reflect an increased interaction between the ionic liquid and the redox couple, as a result of increased hydrogen bonding and/or the increased charge-localisation of the negative charge on the sulfonate group compared with more charge diffusion anions such as eFAP.
• The Seebeck coefficient of the Co^{2+/3+}(bpy)_3 in P_{2,2,2,4} Tos is believed to be influenced by pi-pi interactions between the aromatic rings on the Tos anion and the pyridine rings of the redox complex, leading to an additional contribution to the Seebeck coefficient.

• The Seebeck coefficient of Co^{2+/3+}(bpy)_3 was found to be higher in C_{2}mim MeSO_3 than C_{2}mim OTf, this is believed to be the result of weaker hydrogen bonding between the complex and the latter IL, as a result of fluorination of the anion.

• A direct comparison was drawn between the Seebeck coefficient of Co^{2+/3+}(bpy)_3 in C_{4}mim NTf_2 and C_{4}dmim NTf_2. It was found that the Seebeck coefficient was lower in C_{4}dmim NTf_2, the result of weaker hydrogen bonding with the redox complex when the imidazolium cation is methylated at the C-2 position, rather than having an acidic proton at this position.

• The Seebeck coefficient of the Co^{2+/3+}(bpy)_3 complex was found to be lower when long alkyl chains replace shorter ones in C_{n}mim OTf, where R is an alkyl chain.

The Seebeck coefficient of the Co^{2+/3+}(bpy)_3 was also measured in three phosphonium ionic liquids, and was found to exceed the Seebeck coefficient of the same complex in propylene carbonate. This higher Seebeck coefficient in an IL rather than an organic solvent was only observed in phosphonium ionic liquids and in one imidazolium ionic liquid, C_{2}mim MeSO_3. It is postulated that additional entropy changes occurring due to the disturbance to long range structuring present in these phosphonium ILs contributes to the high Seebeck coefficients. However, further investigation of the impact of long-range ordering in the IL is required as a similar trend is not observed in the comparison of different imidazolium ILs with increasing chain lengths. The high viscosity of phosphonium ionic liquids is detrimental to mass transport processes and, therefore, TEC performance. The addition of propylene carbonate, in a 1:1 volume ratio, was necessary to test these ILs, which are highly viscous (and in some cases solid) at room temperature. Propylene carbonate was chosen for its high boiling point and dielectric constant. The addition of propylene
carbonate in a 3:1 ratio with the IL increases the TEC performance, sufficient to match the performance of the imidazolium systems at 1:1 volume addition of propylene carbonate.

6.4 Research aim three: Identify high Seebeck coefficient redox couples and investigate the effect of redox couple structure on thermocell performance.

The new complexes were tested from a fundamental perspective, in terms of the structure/Seebeck coefficient relation, and also in terms of device performance. It was concluded that redox couples for TEC application should have:

- Reversible or quasi-reversible redox reactions, with stable oxidised/reduced species.
- High entropy changes associated with the redox reactions, which leads to high Seebeck coefficients. Large entropy changes are expected to be linked to a small radius of the redox couple and electronic spin transitions upon conversion between the oxidised and reduced species.

The difference in Seebeck coefficients between the four complexes redox couples tested, \( \text{Co}^{2+/3+}(\text{bpy})_3 \), \( \text{Co}^{2+/3+}(\text{Bupy-pz})_3 \), \( \text{Co}^{2+/3+}(\text{phen})_3 \) and \( \text{Co}^{2+/3+}(\text{py-pz})_3 \), were attributed to redox couple size. This is inversely proportional to the Seebeck coefficient according to Born’s theoretical model and subsequent empirical relations. The lowest Seebeck coefficient was measured for the \( \text{Co}^{2+/3+}(\text{phen})_3 \) complex, at 1.7mV/K in 3:1 DMSO:Clmim eFAP. The highest Seebeck coefficient was measured for \( \text{Co}^{2+/3+}(\text{py-pz})_3 \), at 2.36mV/K in the same electrolyte system. This exceeds the previously reported highest Seebeck coefficient in a non-aqueous electrolyte for the \( \text{Co}^{2+/3+}(\text{bpy})_3 \) complex, achieved in ionic liquids and mixed IL/solvent systems.

The \( \text{Co}^{2+/3+}(\text{py-pz})_3 \) and \( \text{Co}^{2+/3+}(\text{Bupy-pz})_3 \) redox complexes were shown to have poor reversibility on platinum working electrodes, with unstable oxidation processes. The poor catalytic properties of platinum is believed to be the result of adsorption of the redox couple anion onto the platinum surface or the formation of a passivation
layer in the presence of water under atmospheric conditions. The reversibility and stability was greatly improved when carbon-based electrodes were used, particularly carbon slurry-based electrode, which are believed to have superior catalytic properties to flat electrodes due to their non-uniformity, high surface area and the presence of defects on the electrode surface. The use of carbon-coated platinum electrodes in the TEC improved the power density obtained from these two complexes by 27% and 59% respectively.

The TEC performance of the Co$^{2+/3+}$(py-pz)$_3$ and Co$^{2+/3+}$(Bupy-pz)$_3$ complexes showed great improvement when the concentration was doubled from 0.1M to 0.2M, with power density increases of 30% and 50% respectively.

The TEC performance of Co$^{2+/3+}$(bpy)$_3$ and Co$^{2+/3+}$(phen)$_3$ showed no significant improvement with use of carbon-coated platinum electrodes in the TEC compared to bare platinum electrodes. This was attributed to the fact that these two complexes show good reversibility on platinum, in the 3:1 DMSO : C$_2$mim eFAP electrolyte, and therefore the TEC performance was not limited by the electrode material. The TEC performance of Co$^{2+/3+}$(bpy)$_3$ and Co$^{2+/3+}$(phen)$_3$ also shows no great improvement when the concentration of the redox couple was increased. This indicates that either the TEC performance of these complexes are not limited by mass transport processes, or that the benefit of increasing the redox couple concentration is balanced by the disadvantage of the likely increase in viscosity.

The reversibility and electrochemical stability of the redox complexe was found to be a key factor in determining the TEC performance. The Co$^{2+/3+}$(py-pz)$_3$ and Co$^{2+/3+}$(Bupy-pz)$_3$ complexes have shown significant improvement in the reversibility carbon electrodes which was reflected in higher power and current obtained from the device. On the other hand, the reversibility and electrochemical stability of Co$^{2+/3+}$(bpy)$_3$ and Co$^{2+/3+}$(phen)$_3$ was found to be good on both platinum and carbon-electrodes, therefore, the TEC performance was not effected by the electrode material.
To demonstrate longer-term performance, the TEC was operated continuously for 150 minutes. There was no significant drop in performance using any of the four redox couples, in the 3:1 DMSO:C2mim eFAP electrolyte system.

The use of carbon-coated stainless steel electrodes in the TEC resulted in a slight drop in power compared to the TEC with carbon-coated platinum electrodes. However, the use of stainless steel eliminates the use of platinum in the TEC and therefore greatly reduces the device cost. This is a promising step towards a commercial device.

6.5 Future work

Future work towards developing a fundamental understanding of the Seebeck coefficient:

Further fundamental investigation into the parameters affecting the Seebeck coefficient of redox complexes. Fundamental understanding of the reaction entropy changes associated with the redox reactions are vital for future development and choice of redox couples for this application. In particular, studies into the role of solvent polarity and polarity-related parameters in determining the Seebeck coefficient are encouraged. Despite the lack of a clear trend between the Kamlet-Taft parameters and the Seebeck coefficient for the systems investigated here, literature reports point to a strong role of solvent polarity and hydrogen bonding in determining the redox reaction entropy and, therefore, the Seebeck coefficient. Future studies should look into additional specific parameters such as solvent acceptor number, which has previously been directly correlated to the reaction entropy in prior literature on some molecular solvent systems. However, the measurement and interpretation of polarity and related parameters such as acceptor or donor numbers in ionic liquids is complex and their relationship to TEC properties not yet well established.
Computational modelling of the redox reactions of $\text{Co}^{2+/3+}(\text{bpy})_3$ in organic solvents, ionic liquids and mixtures; Such computational modelling of the factors believed to influence the Seebeck coefficient should include spin changes, reorganisation of the first solvation shell, redox couple radii and interactions with the surrounding solvent system, including hydrogen bonding. However, techniques for computational modelling of the reaction entropy that take into account all of these variables is complex, it would require large computer power and long computational time. A simplistic model, which allows investigation of a single effect, such as spin transitions in the redox couple or interactions in the first solvation shell, is suggested as a starting point.

Further investigation of the structure of the ionic liquid, on the electrode surface and in the bulk, and its effects on the Seebeck coefficient; Studies have shown the formation of layers in ionic liquids when an electric field is present. This is likely to have an effect on the reaction entropy changes and, ultimately, the Seebeck coefficient. Computational modelling of the redox reactions on the electrode surface in the presence of an electric field is suggested as an interesting area of future work.

Choice of redox couple

Redox complexes chosen for TEC applications have to meet key requirements in terms of electrochemical stability, reversibility and high Seebeck coefficients. Further, future choice of redox couples should be made with three additional considerations: First, choices that increase fundamental understanding of the redox couple structure/Seebeck coefficient relation. It is suggested that Seebeck coefficient measurements are performed under water controlled conditions (e.g. in an argon or nitrogen filled glove box) as many complexes of interest are water or air sensitive, such as $\text{Co}^{2+/3+}(\text{en})_3$ (en: ethylene diamine) and $\text{Fe}^{2+/3+}(\text{bpy})_3$. Second, redox complexes that are smaller in size are suggested for investigation, as they are expected to have favourable properties in the electrolyte, such as high conductivity and diffusion coefficient. Thirdly: redox couples with low-cost and low toxicity, contributing towards a more commercially viable device.
Future choice of ionic liquids for TEC electrolyte application:

Investigation of low viscosity ionic liquids for TEC application to eliminate or reduce the need for solvent addition; In this thesis, ionic liquids were found to produce relatively high Seebeck coefficients - higher than that of the benchmark aqueous ferri/ferrocyanide electrolyte system. High Seebeck coefficients produce a high cell potential. However, ionic liquids are limited by high viscosity compared to aqueous or organic solvent electrolytes, which leads to slow diffusion of the redox species across the device and lowers the TEC performance.

Investigation of phosphonium ionic liquids with short alkyl chains on the cation, and lower viscosity; The phosphonium ionic liquids investigated in this thesis produced some of the highest Seebeck coefficients measured to date. However, their high viscosity greatly limited the current and power output during TEC operation. Ionic liquids using quaternary phosphonium cations with shorter alkyl chains are suggested for future work, to reduce the viscosity and maintain the high Seebeck coefficient measured for the Co$^{2+/3+}$(bpy)$_3$.

Further investigation of ionic liquids containing a sulfonate group; The highest Seebeck coefficients measured in this thesis were for an imidazolium ionic liquid and a phosphonium ionic liquid both containing a sulfonate group. The specific role of the sulfonate group in increasing the Seebeck coefficient should be further investigated through exploration of more ionic liquids with this functional group. Ionic liquids containing a sulfonate group should also be tested with other redox complexes such as Co$^{2+/3+}$(py-pz)$_3$ and Co$^{2+/3+}$(phen)$_3$ to confirm the effect of the sulfonate group in increasing the Seebeck coefficient of redox species.

Improving TEC device design:

Improvement of cell design and engineering towards future application; The most practical path towards future application of TECs is perhaps the combining several cells in a P-N design, which has been demonstrated in recent literature with aqueous devices. In addition, high surface area carbon-based electrodes, and separator materials that prevent heat convection, can greatly improve TEC performance. Future
devices modelled towards application should also be focussed on low device cost in order to compete with the commercially available semiconductor-based thermoelectrics. These are generally limited to niche applications due to their high cost and low power conversion efficiency at moderate temperatures.

*Investigation of robust and reusable carbon electrode-materials for the TEC;* In this thesis the carbon layer used to coat the electrodes showed degradation over multiple uses in the TEC. A more permanent and robust carbon electrode-material should be investigated for future device development. The performance of carbon materials as electrodes can be limited by their low thermal conductivity, which can cause a drop in the temperature gradient at the TEC electrode and therefore a drop in performance. Future choices could include carbon materials incorporating metal nano-particles, to increase thermal and electrical conductivity and, if possible, electrocatalytic activity. Further investigation into current collector materials is also encouraged. Stainless steel was chosen for its low cost and resistivity to corrosion, however, other metals with increased catalytic activity can be beneficial to the TEC performance. The current collector material should be cheap, thermally and electrically conductive. It should also be electrochemically stable during the device operation.

*Long-term operation of the TEC should be tested, e.g. over several days or until the powers show a significant drop;* Preliminary tests in this thesis showed stability of the TEC performance over several hours, with negligible drop in power or current density. Long term testing is vital for future commercialisation of the TEC device.