Lithium Solvated Electrons Solution Anode
for Rechargeable Lithium batteries

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School of Materials Science and Engineering
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# Table of Contents

Acknowledgements i
Table of Contents ii
Abstract vii
List of Figures ix
List of Tables xvii
List of Abbreviations x
Publications & Patents xxi

1.0 Introduction
1.1 Motivation for the project: Shortcomings of conventional rechargeable batteries for electric vehicles 1
1.2 Redox Flow Batteries (RFB) and Li-Air batteries (LAB) 2
1.3 Liquid based anode and cathode 6
1.4 Objectives of the project 7
1.5 Thesis organization 8

2.0 Literature Review
2.1 Chapter Outline 10
2.2 Lithium Ion Batteries 11
2.3 Lithium Air Batteries 14
2.4 Liquid anode/ Solid-state electrolyte membrane/ Liquid cathode cell configuration 22
2.4.1 The Redox Flow Battery (RFB) 22
2.4.2 Alkali-metals Semi-Flow Batteries 26
2.5 Lithium Solvated Electrons Solution (LiSES) anode 31
2.5.1 Background on Solvated Electrons Solution 31
2.5.2 ESR, NMR Studies and some theoretical computation on PAH-based LiSES 33
2.5.3 Metallic Properties of LiSES 41
2.5.4 PAH-based LiSES 48
2.5.5 Electrochemically generated LiSES 48
3.10 Half-cell OCV Measurements 86
3.11 Concentration Cells 86
3.12 LIPON coating Fabrication & Analysis 88
  3.12.1 Background 88
  3.12.2 Fabrication Process 88
  3.12.3 Impedance Spectroscopy 89
3.13 Experiment on other types of catholytes & Conclusion 90

4.0 Characterisation Studies of Biphenyl-based & Naphthalene-based LiSES 91
  4.1 Introduction and Chapter Outline 91
  4.2 Unveiling the metallic nature of LiSES via conductivity studies 93
    4.2.1 Study on the volume change with PAH concentration in THF 93
    4.2.2 Preparation of LiSES samples 97
    4.2.3 Conductivity measurements at ambient temperature. 98
    4.2.4 Conductivity versus temperature. 101
    4.2.5 Investigating the relationship between viscosity and conductivity. 103
    4.2.6 Conductivity comparison between metallic lithium and LiSES 106
  4.3 Characterization of solvated electrons by FTIR Spectroscopy 108
    4.3.1 Introduction to the use of FTIR spectroscopy to study the formation of LiSES 108
    4.3.2 FTIR Study on biphenyl-based LiSES. 108
    4.3.3 FTIR Study on naphthalene-based LiSES. 116
    4.3.4 Summary of the FTIR results 120
  4.4 Determination of half-cell OCV (vs Li/Li\(^+\)) of LiSES and thermodynamic studies 121
    4.4.1 Half-cell OCV measurements at ambient temperature. 121
    4.4.2 Entropy changes for half-cell reactions. 122
4.5 Concentration Cell Experiments
   4.5.1 Investigation of how half-cell OCV varies with LiSES concentration.
   4.5.2 LiSES concentration cell study.

4.6 Conclusions

5.0 Liquid cathode for LiSES cell: Iodine Catholyte
   5.1 Introduction and Chapter Outline
   5.2 Demonstrating the effectiveness of the iodine/methanol as a catholyte in place of air (oxygen).
      5.2.1 Constant load discharge of LiSES/I\textsubscript{2} full cell
      5.2.2 Constant current discharge of LiSES/I\textsubscript{2} full cell
   5.3 Study of oxygen cathode for the LiSES cell.
   5.4 Conclusion and investigations on other potential catholytes that can yield higher OCVs with LiSES.

6.0 Electrochemical Generation of LiSES and Iodine
   6.1 Introduction and Chapter Outline
   6.2 Investigating the electrochemical generation of LiSES and Iodine.
      6.3 Qualitative verification of LiSES & Iodine formation
         6.3.1 Verification of LiSES formation
         6.3.2 Verification of iodine formation via starch test
         6.3.3 Comparison of half-cell potentials and conclusions of qualitative tests
      6.4 UV-Vis Spectroscopic Study on charged anolyte and catholyte
   6.5 Conclusions

7.0 Effects of LIPON Protective coating on solid membrane electrolyte
   7.1 Introduction and Chapter Outline
   7.2 Investigating LIPON’s effects on the solid membrane electrolyte
      7.2.1 Study on the effect of LIPON on improving the LTAP membrane’s chemical resistance against LiSES
      7.2.2 Impedance Spectroscopy study on how LIPON coating
affect the effective resistance of the LTAP electrolyte.

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>Investigation into the effect of LIPON on the standard potential of LiSES</td>
<td>164</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Observed effect of LIPON coating on OCV of LiSES/I₂ full cells.</td>
<td>164</td>
</tr>
<tr>
<td>7.3.2</td>
<td>OCV study of LIPON coated LTAP using a special LiSES-1//LiSES-2 cell configuration.</td>
<td>166</td>
</tr>
<tr>
<td>7.4</td>
<td>Conclusions about LIPON</td>
<td>169</td>
</tr>
<tr>
<td>8.0</td>
<td>Conclusions and Recommendations for Future Works</td>
<td>170</td>
</tr>
<tr>
<td>8.1</td>
<td>Conclusions</td>
<td>170</td>
</tr>
<tr>
<td>8.2</td>
<td>Recommendations for future work</td>
<td>172</td>
</tr>
<tr>
<td>8.2.1</td>
<td>Future Outlook</td>
<td>172</td>
</tr>
<tr>
<td>8.2.2</td>
<td>Synthesis and characterisation studies on Li-PAH LiSES, for PAH with &gt; 2 benzene rings and for derivatives of PAHs (with substituents)</td>
<td>173</td>
</tr>
<tr>
<td>8.2.3</td>
<td>Investigation of the redox processes underlining LIPON’s effect on LiSES’s standard potentials.</td>
<td>174</td>
</tr>
<tr>
<td>8.2.4</td>
<td>Study of PAH-based M-SES//Air cells where M represents a Group I alkali metal other than Li.</td>
<td>174</td>
</tr>
</tbody>
</table>

References                                                                 | 176  |

Appendix I                                                               | xxii |

Appendix II                                                              | xxv  |
Abstract

At present, most of the research in lithium-air and lithium-ion batteries focused on solid state electrode materials such as metallic lithium, lithium alloys and oxides of lithium (i.e Li$_4$Ti$_5$O$_{12}$). The concept of a room temperature rechargeable Li-Air cell that utilizes liquid-based electrodes, classified as anolyte and catholyte, allows for the cell to be either refuelled or recharged. This project studied the synthesis and characterization of poly-aromatic hydrocarbon (PAH)-based (biphenyl and naphthalene) lithium solvated electrons solution (LiSES) which can be used as a liquid anode defined as anolyte. Complementing this study, iodine/methanol solution has been investigated as an alternative cathode, defined as catholyte, in place of air/oxygen for LiSES//Air cell. Possible reaction mechanisms of different Li concentrations with PAH in THF are formulated. LiSES has been observed to demonstrate a metallic behaviour based on conductivity-temperature studies. The relationship of the half-cell OCV of LiSES versus temperature has been obtained and thermodynamics data ($\Delta G$, $\Delta S$ and $\Delta H$) were determined. In a LiSES//Iodine full cell setup, LiSES & iodine/methanol have both shown promising results as liquid electrodes and their charge/discharge electrochemical reactions have been identified. Successful electro-synthesis of LiSES in the anolyte from the charge process of an uncharged cell with LiI in both liquid electrodes and with initial 0 V open circuit voltage (OCV) has been observed. The oxidative formation of I$_2$ catholyte from Lil in methanol also occurred concomitantly during the same charge process. This demonstrates that the LiSES//Iodine cell can be initially prepared either chemically (charged or partially charged depending on user’s requirements) or electrochemically (uncharged). Lithium Phosphorus Oxynitride’s (LIPON) effectiveness as a protective coating on Lithium Titanium Aluminium Phosphate (LTAP) solid electrolyte membrane against LiSES
corrosion has also been shown. Finally, the unexpected effect of the LIPON layer upon LiSES, causing higher OCVs for LiSES cells, has been observed. The causes of this effect are still under investigation.

There are two main technological implications from the results of this thesis. Firstly, by having both electrodes in the liquid state, the LiSES cell can be refuelled by replenishing the discharged electrodes with fresh ones in several minutes as compared to the minimum 30 min fast-charging time for conventional lithium ion batteries (LIB). Secondly, the option of preparing an initial 0 V OCV uncharged cell for LiSES//I$_2$ configuration that can be charged up to electrochemically synthesise LiSES and I$_2$ allows for safe storage and transportation of both anolyte and the catholyte.
<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Caption</th>
<th>Page(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Specific energy density versus volumetric energy density for different battery systems.</td>
<td>4</td>
</tr>
<tr>
<td>1.2</td>
<td>Energy density comparison between different kinds of battery systems and gasoline.</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic illustration for LIB cell which utilizes graphite anode and LiCoO$_2$ cathode.</td>
<td>13</td>
</tr>
<tr>
<td>2.2a</td>
<td>Aqueous Li-O$_2$ cell (basic medium) operating principle.</td>
<td>15</td>
</tr>
<tr>
<td>2.2b</td>
<td>Organic Li-O$_2$ cell operating principle</td>
<td>17</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic diagram of a full solid-state Li-O$_2$ cell. The solid-state electrolyte laminate is made up of 3 different membrane layers as follows: PC (Li$_2$O) + GC + PC (BN). PC: Polymer ceramic, GC: Glass ceramic, BN: Boron nitride</td>
<td>21</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic diagram of a single redox flow cell.</td>
<td>25</td>
</tr>
<tr>
<td>2.5a</td>
<td>Basic schematic illustration of a Li Redox Flow Battery (Li-RFB) with a thin LISICON separator plate between the two electrodes.</td>
<td>27</td>
</tr>
<tr>
<td>2.5b</td>
<td>Conceptual schematic of the Li-Air RFB with M$^{z+}$/M$^{(z-n)^+}$ catalyst for ORR.</td>
<td>28</td>
</tr>
<tr>
<td>2.6</td>
<td>(a) (TOP LEFT) Schematic diagram of a semi-solid flow cell in which suspensions of lithium-ion cathode and anode materials are used. (b) (TOP RIGHT) Semi-solid</td>
<td>29</td>
</tr>
</tbody>
</table>
suspension of LiCoO₂ powder with Ketjen black conducting additive. (c) (BOTTOM) Test cell with metallic lithium as the reference electrode. Monolithic copper and aluminium are used to construct the current collectors. The slurry is fed by means of tubing through the cell with a peristaltic pump.

2.7a Theoretical ESR spectrum of naphthalene-based lithium solvated electron solution’s lithium-naphthalene ion pair. Experimentally determined hyperfine coupling constants at -70 °C, Aₐ, Aₐ and AₐLi are shown on the top right-hand corner.

2.7b Experimentally obtained ESR spectrum of lithium-naphthalene/diethyl-ether.

2.8a Non-linear relationship between the ⁷Li NMR shift and the radical anion concentration for Li-naphthalenide using THF solvent.

2.8b Linear relationship between the ⁷Li NMR shift and the radical anion concentration for Li-naphthalenide using LiCl/THF solvent.

2.9 Configurations of Li-Naphthalene with their corresponding states and potential energies.

2.10 Graph of intrinsic carrier density, nᵢ, versus temperature, T where nᵢ is shown to increase from 10 cm⁻³ to 10¹⁵ cm⁻³ as temperature increases from 150 K to 500 K.
2.11 Relationship between resistivity and dopant density for the n-type and p-type Ge, GaAs and GaP semiconductors. 44

2.12a Conductivity data of ammonia-based LiSES for various concentrations in mole percent lithium. The added red box shows the temperature range for which ammonia is a liquid (195.42 K ≤ T ≤ 239.81 K). 46

2.12b Conductivity data of ammonia-based LiSES for concentrations exceeding the solubility limit in mole percent lithium. The added red box shows the temperature range for which ammonia is a liquid (195.42 K ≤ T ≤ 239.81 K). 47

2.13 Impedance Spectra showing time dependence of the interfacial resistance (Semi-circular plots’ intersection with real axis) of Li-Al/LTAP/Li-Al cell (Initial: 4510 Ω; after 12 h: 8500 Ω). Insert: Impedance Spectra for just-after-assembly cell: Very small semi-circular plot obtained at high frequencies (10³ kHz) as compared to the large semi-circle obtained at low frequencies (10⁰ kHz). The insert’s small semi-circular plot intersects the real axis at ~ 36 Ω. 54

2.14 Impedance Spectra of Al-Li/LTAP/Li-Al cell conducted at 80 °C for: (ABOVE) Just-after-assembly cell, and (BELOW) After 3 weeks at room temperature. 57

2.15 Discharge profile of a Model 702E Li/I₂ cell under a 100 kΩ load at 37 °C. 59
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.16</td>
<td>Schematic diagram of a Model 802 /35 Li/I$_2$ cell</td>
<td>61</td>
</tr>
<tr>
<td>2.17</td>
<td>Operating concept of the liquid cathode Li-I$_2$ cell for discharge/charge reactions occurring at the cathode and the anode.</td>
<td>63</td>
</tr>
<tr>
<td>3.1</td>
<td>Molecular structures of naphthalene and biphenyl.</td>
<td>66</td>
</tr>
<tr>
<td>3.2</td>
<td>Flow chart for LiSES preparation.</td>
<td>68</td>
</tr>
<tr>
<td>3.3</td>
<td>TetraCon 325 probe’s schematic diagram.</td>
<td>71</td>
</tr>
<tr>
<td>3.4</td>
<td>KBr glass sample cell setups for FT-IR analysis</td>
<td>73</td>
</tr>
<tr>
<td>3.5</td>
<td>Schematic diagram of the Li-SES// air prototype model.</td>
<td>75</td>
</tr>
<tr>
<td>3.6</td>
<td>Schematic diagram of test cell in the following configuration of:</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>(-)Ni / Li-SES, Lil / LTAP Ceramic Membrane/ Catholyte / Ni(-)</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>Test cell consists of two glass side-arms for the liquid electrodes, a PEEK cap as the lid for each side arm, a central portion made of PEEK for securing the LTAP membrane and an external aluminium screw-sleeve for tightening.</td>
<td>79</td>
</tr>
<tr>
<td>3.8</td>
<td>The transparent acrylic chip ((a) <strong>BEFORE</strong>) disintegrated after its immersion in LiSES ((b) <strong>AFTER</strong>) into brown fragments and powder.</td>
<td>81</td>
</tr>
<tr>
<td>3.9</td>
<td>The LiSES//I$_2$ cell is discharged across a 1 kΩ resistor as shown in the circuit setup.</td>
<td>85</td>
</tr>
</tbody>
</table>
3.10 Effect of LiSES on (a) pristine LTAP is shown in (b) and (c). After 120 h, the membrane has completely disintegrated.

4.1 $\Delta V/V_0$ of the $\text{Li}_0\beta(\text{THF})_n$ and $\text{Li}_0\beta(\text{THF})_n$ solutions (No Li present) solution versus the respective PAH/THF molar ratio of $1/n$ at ambient temperature in argon atmosphere.

4.2 Li-SES electrical conductivity at ambient temperature at various PAH/THF compositions, ‘$n$’, Li/Naphthalene mole ratio ‘$y$’ in $\text{Li}_y\beta(\text{THF})_n$ compositional formulae and Li/Biphenyl mole ratio ‘$x$’ in $\text{Li}_x\beta(\text{THF})_n$.

4.3 Conductivity, $\sigma$ (mS/cm), versus temperature, $T$ ($^\circ$C) of LiSES samples, $\text{Li}_x\beta(\text{THF})_{10.4}$ and $\text{Li}_y\beta(\text{THF})_{10.4}$.

4.4 $\text{Li}_y\beta(\text{THF})_n$ viscosity, $\eta$, presented in $\ln[\eta]$ at various PAH/THF compositions, ‘$n$’, and Li/Naphthalene mole ratio ‘$y$’.

4.5 Comparison between the FT-IR spectra of decreasing Li:$\beta$ mole ratios in $\text{Li}_x\beta(\text{THF})_n$ against the spectra of THF and biphenyl in THF.

4.6a FT-IR Spectrum in the 1700 cm$^{-1}$ to 1100 cm$^{-1}$ range, with biphenyl in THF background subtracted.

4.6b FT-IR Spectra in the 1020 cm$^{-1}$ to 980 cm$^{-1}$ range and in the 680 cm$^{-1}$ to 620 cm$^{-1}$ range with biphenyl in THF background subtracted.
List of Figures

4.7 Relationships between IR peaks’ intensity and the lithium composition x. 113
4.8 FT-IR Spectra of Li_xN(THF)_n in the 1600 cm^{-1} to 600 cm^{-1} range. 116
4.9 Standard reduction potentials of Li_{1.0}\beta(THF)_{12.3} and Li_{1.0}N(THF)_{11.1} versus metallic lithium at ambient temperature. The “e_•” denotes solvated electron. 122
4.10 E, versus T profile for Li_x\beta(THF)_{10.4}, (where x = 0.5, 1.0) versus Li metal half-cell. 123
4.11 E, versus T profile for Li_{1.0}N(THF)_{10.4} versus Li metal half-cell. 124
4.12a Relationship between half-cell OCV and log[Li^+] 129
4.12b OCV versus ln\left(\frac{x}{1-x}\right) where x denotes [Li^+] in Figure 4.12a. 130
5.1a Li_{1.0}N(THF)_{10.45}’s full cell discharge profile: (In RED) 135
Open Circuit Voltage, OCV (V) versus Time (h). (In BLUE) Closed Circuit Voltage, CCV (V) versus Time (h).
5.1b Li_{1.0}\beta(THF)_{10.45}’s full cell discharge profile: (In RED) 136
Open Circuit Voltage, OCV (V) versus Time (h). (In BLUE) Closed Circuit Voltage, CCV (V) versus Time (h).
5.2 Standard electrode potentials of $\text{Li}_{1.0}\beta(\text{THF})_{12.3}$, $\text{Li}_{1.0}\text{N}(\text{THF})_{11.1}$, iodine reduction and “tri-iodide to iodide” redox reaction versus Li/Li$^+$ at ambient temperature.

5.3 $\text{Li}_{1.0}\beta(\text{THF})_{10.45}$’s full cell discharge profile: Closed Circuit Voltage, CCV (V) versus Time (h).

The top horizontal axis indicates the % depth of discharge (D.O.D) of the cell.

5.4 Discharge profile for $\text{Li}_{1.0}\beta(\text{THF})_{10.4}$ anolyte, LATP separator membrane and catholyte (0.1 M LiClO$_4$ in DME with 20% vol. PFC, 0.02 ml/min O$_2$ flow rate) for a constant discharge current of 20 μA.

5.5 Standard electrode potentials of the K-salts, LiSES (Biphenyl) and Li.

5.6 Discharge profiles of the Li$\beta(\text{THF})_{10.45}$ full cell using the various K-salt catholytes and iodine.

6.1 Current vs. time profile during CV cycling (voltage sweeping rate $v = 2.5 \times 10^{-4}$ V/s).

Voltage range 0.8 V to 4.4 V.

6.2 Colour change in the catholyte:

(1) Before charging, and

(2) After charging (by 9th cycle).

6.3 UV-VIS spectra of anolyte solutions of S1, S2 and S3

S1: uncharged anolyte
S2: charged anolyte at the 9th cycle

S3: Chemically prepared Li-SES

6.4 UV-VIS spectra of (S4) iodine/methanol, catholyte solutions (S5) before charging and (S6) after charging.

7.1 (a) LIPON coated LTAP membrane after 72h immersion in Li\(_{1.0}\beta\)(THF)\(_{12.3}\)

(b) Pristine LTAP membrane after 72 h immersion in Li\(_{1.0}\beta\)(THF)\(_{12.3}\)

7.2 After 3 days discharge, appearance of (a) LIPON-coated LTAP, and (b) Uncoated LTAP.

The white rim in (b) is the part that is not in contact with the LiSES.

7.3 Impedance measurements of both LIPON coated (RED) and uncoated (BLACK) LTAP membranes.

7.4 (a) Discharge profile for the Li\(_{1.0}N\)(THF)\(_{10.45}/0.1M I_2 full cell using LIPON coated LTAP

7.4 (b) Discharge profile for the Li\(_{1.0}\beta\)(THF)\(_{10.45}/0.1M I_2 full cell using LIPON coated LTAP

7.5(a) Discharge profile of Cell II: Closed Circuit Voltage (V) versus Time (h)

7.5 (b) Discharge profile of Cell III: Closed Circuit Voltage (V) versus Time (h)
## List of Tables

<table>
<thead>
<tr>
<th>Table No.</th>
<th>Caption</th>
<th>Page(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Gravimetric energy densities of Li-O_2 cells and commercial LiCoO_2 LIB</td>
<td>19 - 20</td>
</tr>
<tr>
<td>2.2</td>
<td>Comparison between a fuel cell and a redox flow battery</td>
<td>23-24</td>
</tr>
<tr>
<td>3.1</td>
<td>Characteristics of Li-SES//air battery (with oxygen as the cathode)</td>
<td>76</td>
</tr>
<tr>
<td>3.2</td>
<td>Characteristics of Li-SES//air battery (with water as the solvent)</td>
<td>77</td>
</tr>
<tr>
<td>3.3</td>
<td>Mass of plastic before and after immersion in LiSES</td>
<td>80</td>
</tr>
<tr>
<td>3.4</td>
<td>Deposition parameters for LIPON coating by magnetron sputtering</td>
<td>89</td>
</tr>
<tr>
<td>4.1</td>
<td>Relationships between ln(\eta) and (y) for each (n).</td>
<td>105</td>
</tr>
<tr>
<td>4.2</td>
<td>Prominent peaks associated with Li-SES formation of (\text{Li}_y\text{N(THF)}_n). “0” indicates absence of a peak and each of the Roman numerals I to V denotes the presence of a peak with peak intensity from weakest (I) to strongest (V). Superscript * denotes equal intensities.</td>
<td>118</td>
</tr>
<tr>
<td>4.3</td>
<td>Entropy changes for the LiSES/Li half cells for comparison against Li_xCoO_2/Li (where (0 &lt; x &lt; 1)) half cell</td>
<td>127</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>7.1</td>
<td>Elemental composition of LIPON-coated membrane before and after immersion in LiSES for 72 h.</td>
<td>161</td>
</tr>
<tr>
<td>7.2</td>
<td>Elemental composition of uncoated membrane before and after immersion in LiSES for 72 h.</td>
<td>161</td>
</tr>
</tbody>
</table>
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIB</td>
<td>Lithium Ion Battery</td>
</tr>
<tr>
<td>CCV</td>
<td>Closed Circuit Voltage</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethylyethane</td>
</tr>
<tr>
<td>D.O.D</td>
<td>Depth of Discharge</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron Spin Resonance Spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared (spectroscopy/spectra)</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquids</td>
</tr>
<tr>
<td>Li+</td>
<td>Lithium Ion</td>
</tr>
<tr>
<td>LAB</td>
<td>Lithium Air Battery</td>
</tr>
<tr>
<td>LiSES</td>
<td>Lithium Solvated Electrons Solution</td>
</tr>
<tr>
<td>LIPON</td>
<td>Lithium Phosphorus Oxynitride</td>
</tr>
<tr>
<td>LTAP</td>
<td>Lithium Titanium Aluminium Phosphate</td>
</tr>
<tr>
<td>LPB</td>
<td>Lithium Polymer Battery</td>
</tr>
<tr>
<td>LISICON</td>
<td>An acronym for Lithium Super Ionic Conductor</td>
</tr>
<tr>
<td>LTAPGC</td>
<td>LTAP Glass Ceramic</td>
</tr>
<tr>
<td>MPL</td>
<td>Moles percent lithium</td>
</tr>
<tr>
<td>NaSES</td>
<td>Sodium Solvated Electrons Solution</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal hydrogen electrode</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
</tr>
<tr>
<td>PAH</td>
<td>Poly Aromatic Hydrocarbon</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cell</td>
</tr>
<tr>
<td>P2VP</td>
<td>Poly-2-vinylpyridine</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyether ether ketone</td>
</tr>
<tr>
<td>RFB</td>
<td>Redox Flow Battery</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>Ultraviolet–visible (spectroscopy / spectra)</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Publications and Patents

Some of the results in reported in this thesis have been submitted/published in international journals, a conference paper, a book chapter and two patents.

Publications


Patents


Chapter 1 Introduction

Section 1.1 Motivation for the project: Shortcomings of conventional rechargeable batteries for electric vehicles

It is of utmost importance to develop secondary (rechargeable) batteries as dependable power sources for the development of better electrical vehicles. The Lithium Ion Battery (LIB) has been the most extensively studied and developed among all the different types of commercially available secondary batteries [1-6]. Various parts of the LIB, such as its electrodes and electrolyte, have been extensively researched and improved upon. Currently, the LIB is the most ideal commercial rechargeable battery available due to several reasons. Firstly, the LIB is light and possesses a very high energy density [1, 6-8]. Secondly, it possesses a very high power density by mass [1]. This means that compared to any other type of rechargeable battery that can deliver the same power, the LIB is lighter in weight. Thirdly, an LIB which is left in the charged state has a low self-discharge rate [1, 8]. Fourthly, it does not exhibit any signs of memory effect [1]. Finally, an LIB can be subjected to hundreds of charge/discharge cycles before any noticeable capacity fading occurs [1, 8-10].

Currently, there are several types of electrical vehicles on the market that are powered by such LIBs such as the Mitsubishi iMiEV and the Nissan LEAF. However, the electrodes of the current LIBs are solid-based and their charge-discharge processes consist of the intercalation and de-intercalation of Li\(^+\) across the electrodes [11, 12]. At the end of the day, when the vehicle’s LIB battery pack is depleted, it has to be recharged. Conventional recharging kiosks that are currently available require 6 to 8 hours to fully recharge an electric vehicle’s LIB battery pack. The “fast” charging
kiosks boast of a short charging time of only 30 minutes. In Singapore, the government recently announced its plan to set up 47 normal charging kiosks and 3 fast-charging kiosks (30 min charging) all over Singapore [13]. There are two disadvantages with having these types of charging kiosks. Firstly, for the fast charging kiosks, the damage done to the LIBs when they are charged too quickly is the growth of metallic Li dendrites on the anode side of the LIBs, which is dangerous [14]. Secondly, on the recharging time, it is not difficult when comparing conventional petroleum kiosks and the electric charging kiosks to conclude that even 30 minutes is too long compared to the 5 minutes top-up time needed for petroleum vehicles. In future, if the number of electrical vehicles increases significantly, then these charging kiosks will not be able to cope with the increase in demand. We will soon see long queues outside the charging kiosks which might cause traffic congestion. Thus, for practical electric vehicle applications, a very short charging time is necessary.

Section 1.2 Redox Flow Batteries (RFB) and Li-Air batteries (LAB)

One alternative rechargeable battery to the LIB is the redox flow battery. The redox flow battery utilizes liquid electrodes and has several advantages. Firstly, depending on the needs, the capacity of the battery can be scaled up accordingly by enlarging the sizes of its catholyte and anolyte storage tanks. Secondly, there is no limit to the depth of discharge: a redox flow battery can be completely discharged without sustaining any damage. Thirdly, there is no limit to the cycle life of the battery. Fourthly, there is no restriction on the shapes the tanks have to take, such as being rectangular or cylindrical, and thus they can follow the contours of the vehicle’s body. Finally, in the absence of an external recharging power source, the redox flow battery
can be replenished by simply replacing the spent electrolytes with fresh ones [15, 16]. Hence, redox battery packs can save a large amount of time during re-charging. At the kiosk for instance, the spent electro-active material can be siphoned out of the vehicle’s battery stack and fresh anolyte and catholyte liquids can then be pumped into the vehicle to replenish the stack. In this way, the entire re-fueling process can take roughly the same time as in a conventional petroleum kiosk to re-fuel a vehicle. The discharged liquid products can then be stored at the kiosk for recycling at a latter convenient time, such as during off-peak hours and it can be disposed of or sold later on. That way, the kiosk functions both as a recycling (recharging) station for the liquid electrodes and a re-fuelling station instead of merely doing direct recharging of battery packs of the vehicles at the kiosk.

Unfortunately, current RFBs have very low volumetric energy density and specific energy density as compared to most battery systems such as the LIBs. Figure 1.1 shows the comparison between the different battery systems. This makes them impractical for mobile applications as electric vehicles’ battery stacks.
Finally, the next possible candidate for an electric vehicle’s battery pack is the Li-Air battery (LAB). The Li-air battery currently has the highest gravimetric energy storage density among all other known battery systems as shown in Figure 1.1. When compared against the LIB, the practical energy density of the Li-Air battery is 8 times more than that of the LIB. Figure 1.2 shows the energy density comparison between different battery systems and gasoline.
Figure 1.2

Energy density comparison between different kinds of battery systems and gasoline.
(Reprinted with permission from Ref [7], Copyright 2013, American Chemical Society.)

As shown in Figure 1.2, only the energy density of Li-Air battery is quite close to that of gasoline and it is much higher than all other battery systems. However, despite its high energy density, the Li-Air battery has several disadvantages. For instance, there are still major issues that must be addressed such as safety: specifically the vital need to prevent water and air from coming into contact with the metallic lithium anode [17], before they can be used in electric vehicles. A more in-depth review of different types of RFB and LAB will be covered in Chapter 2.
Hence, we have a situation where, where the existing LIBs offer a very high energy density by mass as compared to other batteries but require a long and impractical charging time for electric vehicles. We also have existing redox batteries which, by having liquid catholytes and anolytes, allow for rapid replenishing of the battery stack by means of siphoning and pumping at the kiosk. Unfortunately, they have extremely low energy densities compared to other battery systems. As for Li-Air batteries, even though they offer a very high energy density close to that of petroleum (gasoline), the metallic lithium anode poses a safety risk to users [17]. Therefore, we need a new kind of rechargeable battery which incorporates the advantages of the Li-Air battery, the LIB and the RFB.

Section 1.3 Liquid based anode and cathode.

To overcome the problems mentioned in the previous section, we should have a liquid based lithium anode and a liquid based cathode, both of which can function at room temperature. This will allow the user to have the dual options of recharging the depleted cell or simply replacing the spent fluids with fresh ones. The anode that is being explored in this project is that of lithium solvated electrons solution (Li-SES) which are prepared by dissolving metallic lithium in a solution of poly-aromatic hydrocarbon (such as biphenyl and naphthalene) in tetrahydrofuran (THF).

An optimized anode using Li-SES must satisfy the following requirements. Firstly, it should have a high energy storage capacity by mass and volume. In other words, as much Li per mole of polycyclic aromatic hydrocarbons (PAH) should be contained in the Li-SES as possible. Secondly, it should have high electronic and ionic conductivity. Thirdly, it should have a low working voltage of < 1 V/ Li. Fourthly, it
should be electrochemically reversible. Finally, it should possess fast electrode kinetics when it is operated over a large temperature range. A suitable liquid cathode must give the highest OCV with LiSES anode and yet remains chemically stable at room temperature.

Section 1.4 Objectives of the project

There are three main objectives in this project. The first objective is to study the feasibility of a new battery chemistry using LiSES and Iodine/Methanol solution as liquid anode & liquid cathode respectively. To realise this objective, the performance of LiSES and Iodine/Methanol during full cell discharge tests has been studied. Also, the effect of LIPON as a protective coating to help solid electrolyte resist the corroding effects of the LiSES is investigated.

The second objective is on understanding the physical chemistry of LiSES. This is achieved by unveiling the metallic nature of LiSES via conductivity studies of LiSES as well as through FTIR Spectroscopy study on LiSES to identify the formation of solvated electrons.

The third objective is to address the electrochemical aspect of the liquid electrodes. This will be accomplished through several steps. The first step is to understand the electrochemical reactions occurring during full cell (LiSES and Iodine/Methanol) discharge. The second step is to determine the LiSES half-cell’s open circuit voltage, OCV (vs Li/Li$^+$) as well as to conduct thermodynamic studies. The third step is to prove the concept of electrochemical generation of LiSES & iodine
This project is divided into several parts. The first part of this project is on the synthesis and characterization of LiSES with a focus on the two-ring PAH biphenyl and naphthalene. Characterization of the LiSES includes the conductivity studies on lithium solvated electrons solutions, half-cell OCV measurements and thermodynamic studies as well as analysis of FTIR spectra. The second part of the project is on synthesizing a protective coating for the ceramic membrane LTAP electrolyte commercially obtained (Ohara, Japan) to increase its chemical stability and lifetime in contact with LiSES. The third part of the project is on investigation of a suitable liquid cathode for the cell to be used with LiSES anode, such as iodine. The fourth part is on electrochemically forming the active liquid cathode (iodine) and the LiSES from an initially uncharged cell with OCV of 0 V, which will allow the liquid electrodes to be safely prepared in uncharged state for transportation.

Section 1.5 Thesis Organizations

Chapter 1 of this thesis covers the motivation and the objectives for this project. Chapter 2 is on literature review of the various RFB and LAB technologies available as well as on the LiSES. Chapter 3 describes the experimental techniques and the cell design used for this project. Chapter 4 covers the synthesis and characterization and of biphenyl-based and naphthalene–based LiSES respectively. Chapter 5 describes the experiments on various liquid catholytes used for the LiSES cell with a focus on iodine. Chapter 6 demonstrates the successful electrochemical formation of active liquid cathode and liquid anode by charging a full cell with initial OCV of 0 V, as well as presenting the techniques to verify their formation. Chapter 7 describes the effects of the LIPON (Lithium Phosphorus Oxynitride) protective coating on the solid electrolyte membrane as well as on the LiSES’s electrode
potential with respect to lithium metal, together with the preliminary analysis and interpretation conducted. Finally, Chapter 8 sums up the conclusion for this thesis with its scientific contributions and technological implications as well as recommendations for possible future work.
Chapter 2  Literature Review

Section 2.1  Chapter Outline

This chapter is a review of the various literature consulted during the course of this project and introduces the concept of a lithium battery using liquid anode and liquid cathode at ambient temperatures.

Section 2.2 will describe the development, principle of operations, advantages and shortcomings of the lithium ion batteries (LIB). This is followed by Section 2.3 which will cover the workings of lithium air batteries (LABs), which in recent years, has become a more viable alternative candidate to other conventional batteries and even LIBs. This is due to the fact that its practical energy density in Wh/kg is comparable to that of gasoline [7].

Section 2.4 covers in greater detail, the concept of a LIB which utilizes liquid electrodes instead of solid electrodes like the conventional LIB. The main advantage of a cell using a liquid cathode and a liquid-based lithium anode separated by a Li-ion conducting solid separator membrane is that the depleted cell has the dual options of refuelling and recharging. Section 2.5 describes a new kind of liquid anode cell operating at ambient temperature in which lithium solvated electrons (LiSES) is used as the liquid anode.

Section 2.6 describes the solid electrolyte membrane that is used for this project and the type of protective coating adopted to increase its lifespan.
Section 2.7 gives a short review of lithium-iodine cells and proposes iodine in methanol or aqueous LiCl [18, 19] as the liquid cathode of a LiSES cell, making it a cell operating with both anode and cathode in the liquid state.

Section 2.2 Lithium Ion Batteries

Lithium Ion Batteries (LIBs) are rechargeable batteries, also known as secondary batteries. Unlike a primary battery which is prepared in the charged state and is good for only one single discharge, a depleted secondary battery can be reused by recharging it. Hence secondary batteries can be reused many times by undergoing many charge/discharge cycles. At present, among all the different commercial rechargeable batteries available, the LIB is the most widely studied and developed [5, 6, 20]. This is because of the LIB’s distinctive advantages over other commercial rechargeable batteries (i.e Lead-Acid, Ni-Cd and Ni-MH), such as its low maintenance properties [1, 21], high energy density [1, 7], high power density by mass, a low rate of self-discharge when left in its charged state, no signs of memory effect and its ability to undergo hundreds of cycles of charging and discharging before any noticeable capacity fading takes place [8-10]. A traditional rechargeable LIB cell uses solid state lithium intercalation and alloying materials for its electrodes as well as a liquid organic electrolyte, with the dry lithium polymer electrolyte battery (LPB) being the exception [21]. The traditional LIB configuration is typically made up of solid state anode/organic electrolyte/solid state cathode. The primary purpose for highlighting the “solid electrodes” feature of both traditional LIB and LPB is for the reader to appreciate the significance of this project’s work on evaluating possible candidate materials for a new lithium-based battery concept using non-traditional chemistry with liquid electrodes.
Figure 2.1 shows the schematic diagram of the traditional LIB which consists of a graphite anode, separator and a LiCoO$_2$ cathode. The separator is a sheet of porous solid polymer material which is wet with liquid electrolyte and is non-electronic conducting. The separator prevents the electrodes from physically touching each other and shorting out within the cell while allowing the passage of Li ions through it.

The charge and discharge of the LIB can be expressed as follows:

**Cathode:** \[ \text{Li}_{1-x} \text{CoO}_2 + \frac{x}{2} \text{Li}^+ + \frac{x}{2} e^- \xrightarrow{\text{charge}} \text{LiCoO}_2 \] where \( 0 \leq x \leq 1 \) \hspace{1cm} (2.1)

**Anode:** \[ \frac{1}{2} \text{Li}_x \text{C}_6 \xrightarrow{\text{charge}} 3\text{C} + \frac{x}{2} \text{Li}^+ + \frac{x}{2} e^- \xrightarrow{\text{discharge}} \] where \( 0 \leq x \leq 1 \) \hspace{1cm} (2.2)

**Overall reaction:** \[ \frac{1}{2} \text{Li}_x \text{C}_6 + \text{Li}_{1-x} \text{CoO}_2 \xrightarrow{\text{charge}} 3\text{C} + \text{LiCoO}_2 \] where \( 0 \leq x \leq 1 \) \hspace{1cm} (2.3)

For Equation (2.1) to be reversible, at most half of the Li in LiCoO$_2$ can be extracted, hence \( \frac{x}{2} \leq 0.5 \) [8]. Any delithiation \( \frac{x}{2} > 0.5 \) Li will result in oxygen evolution with as possible mechanism:

\[ 3\text{CoO}_2 \rightarrow \text{Co}_3\text{O}_4 + \text{O}_2 \] \hspace{1cm} (2.4)

The advantage of the traditional LIB’s construction lies in the condensed matter character of its solid electrodes, which enables the achievement of a high volumetric energy density. However, the disadvantages are: 1) a low lithium mobility in the solid state materials, which limits the power density in ways such as having long charging/discharging durations, and, 2) a relatively short cycle. In order for a LIB powered electric car to be commercially competitive against the regular gasoline cars,
its charging time when its LIB pack is completely depleted, should be reduced to 5-10 minutes from its current 4-6 hours [13] and its driving range should be about 500 km/charge. For comparison, a regular gasoline car with a full tank has a driving range of around 500 km [22] and the typical duration required to fill up its empty fuel tank is usually not more than 10 min.

Figure 2.1: Schematic illustration for LIB cell which utilizes graphite anode and LiCoO\(_2\) cathode. (Reprinted with permission from Ref [5] Copyright 2013 American Chemical Society.)

Unfortunately, the present LIB technology does not permit this level of performance to occur in a sustainable way. For example, the Nissan Leaf 2013 model is one of the top LIB electric vehicles available in the market with a driving range of 135 km/charge. The 135 km range is much shorter than the 500 km range of a gasoline car with a full fuel tank. Furthermore, even with a fast charger, the Nissan Leaf 2013
Chapter 2 - Literature Review

requires 30 min to reach 80% of its full capacity [23], which is way longer than that of the 10 min refuelling time for traditional gasoline cars. As a result of such performance limitations, a huge amount of research activity has been initiated with the goal of increasing both the LIB’s energy density and power density while maintaining its calendar life to achieve over 100,000 km and/or over one decade per battery pack lifespan.

Section 2.3 Lithium Air Batteries (LAB)

The typical lithium-oxygen cell uses oxygen as its cathode material and lithium metal as its anode. Porous carbon is used at its cathode for the diffusion and reduction of oxygen. Often, a catalyst (i.e Pt, Au, Ru) is incorporated into the carbon to improve the energy efficiency of the LAB [24]. Lithium metal is the ideal anode for LAB due to its very low atomic mass of 6.9 g/mol and it has the highest specific capacity among all other existing metal air battery systems. Unlike the conventional lithium cell, which stores all its reactants internally inside itself, the lithium-oxygen cell uses oxygen which is either fed from an external storage tank or taken in directly from the surrounding air. This allows the cell to have potentially a high gravimetric energy density at a low cost. Figure 1.2 of Chapter 1 compares the gasoline’s energy density against the energy densities of other battery systems. From Figure 1.2, it can be quite clearly seen that among all the battery systems, only the LAB has a theoretical energy density that can closely match that of gasoline (around 12,000 Wh/kg). A Li-ion conducting electrolyte separates the cathode and the anode. The LAB can be represented electrochemically by the following:

\[ (+) \text{O}_2 \text{ electrode (with catalyst)/ Electrolyte/ Lithium (-)} \] (2.5)
LABs can be divided into two technologies based on the nature of the electrolyte used, namely aqueous electrolyte Li-O₂ cell and organic electrolyte Li-O₂ cell. The Li-O₂ cell using an aqueous electrolyte (alkaline), has a theoretical OCV of 3.45 V since \( E^0(\text{Li}^+/\text{Li}) = -3.05 \text{ V/NHE} \) & \( E^0(\text{O}_2/\text{H}_2\text{O}) = +0.40 \text{ V/NHE} \). If the aqueous electrolyte is acidic, then \( E^0(\text{O}_2/\text{H}^+) = +1.23 \text{ V/NHE} \) and the theoretical OCV = 4.28 V (Though in practice no one has achieved this OCV yet.).

On the other hand, the Li-O₂ cell using a non-aqueous (organic) electrolyte, has a OCV of 4.17 V since \( E^0(\text{O}_2/\text{O}^2-) = +1.12 \text{ V/NHE} \).

The principle of operation of the lithium air battery using aqueous electrolyte is illustrated in Figure 2.2a. Since metallic lithium is highly reactive towards water, it requires a protective layer to separate it from direct contact with the aqueous electrolyte. The solid protective layer is made of either a polymer or a ceramic such as LATP or \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) which is \( \text{Li}^+ \) conducting [25].

**Figure 2.2a:** Aqueous Li-O₂ cell (basic medium) operating principle. (Reproduced from Ref [26] Copyright 2013 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)
Using basic (i.e LiOH) or neutral aqueous electrolyte, the electrochemical reactions occurring at the electrodes are as follows:

Cathode: \[2\text{H}_2\text{O} + \text{O}_2 + 4e^- \overset{\text{discharge}}{\longrightarrow} 4\text{OH}^- \tag{2.6}\]

Anode: \[4\text{Li} \overset{\text{charge}}{\longrightarrow} 4\text{Li}^+ + 4e^- \tag{2.7}\]

Overall reaction: \[4\text{Li} + 2\text{H}_2\text{O} + \text{O}_2 \overset{\text{discharge}}{\longrightarrow} 4\text{LiOH} \tag{2.8a}\]

\[\Rightarrow 4\text{Li} + 6\text{H}_2\text{O} + \text{O}_2 \overset{\text{charge}}{\longrightarrow} 4\text{LiOH.H}_2\text{O} \tag{2.8b}\]

From Equation (2.8b), one can see that 1 mole of Li will consume 0.25 mole of \text{O}_2 during the discharge reaction to form 1 mole of \text{LiOH.H}_2\text{O} [27].

If an acidic aqueous electrolyte is used, then the electrochemical reactions at the electrodes are:

Cathode: \[4\text{H}^+ + \text{O}_2 + 4e^- \overset{\text{charge}}{\longrightarrow} 2\text{H}_2\text{O} \tag{2.9}\]

Anode: \[4\text{Li} \overset{\text{charge}}{\longrightarrow} 4\text{Li}^+ + 4e^- \tag{2.10}\]

Overall reaction: \[4\text{H}^+ + 4\text{Li} + \text{O}_2 \overset{\text{charge}}{\longrightarrow} 4\text{Li}^+ + 2\text{H}_2\text{O} \tag{2.11a}\]

As an example, if the acid is used in the electrolyte is \text{H}_2\text{SO}_4, Equation (2.11a) will become:
From **Equation (2.11b)**, one can see that in acidic aqueous electrolyte, 1 mole of Li will also consume 0.25 mole of O\textsubscript{2} and form 1 mole of Li\textsubscript{2}SO\textsubscript{4} during the discharge reaction [27], which is the same as in the basic aqueous electrolyte. The only difference is in the amount of electrolyte consumed during the reaction.

For a lithium air battery using an organic electrolyte, the principle of operation is illustrated in **Figure 2.2b**. One should note that even with an organic electrolyte, a Li\textsuperscript{+} conducting membrane that is impermeable to water should be used to separate the metallic lithium anode from the electrolyte. This is because in practical situations, the air which is used as an oxygen source contains moisture and hence water might be introduced into the organic electrolyte which would react violently with lithium [28].

**Figure 2.2b**: Organic Li-O\textsubscript{2} cell operating principle (Reproduced from Ref [26] Copyright 2013 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)
During cell discharge, the oxygen is reduced at the cathode either via two-electron or four-electron process.

**Two-Electron Reduction Process:**

Cathode: \( \text{O}_2 + 2e^- \xrightarrow{\text{discharge}} O_2^{2-} \) \hspace{1cm} (2.12)

Anode: \( 2\text{Li} \xrightarrow{\text{discharge}} 2\text{Li}^+ + 2e^- \) \hspace{1cm} (2.13)

Overall reaction: \( 2\text{Li} + \text{O}_2 \xrightarrow{\text{discharge}} \text{Li}_2\text{O}_2 \) \hspace{1cm} (2.14)

**Four-Electron Reduction Process:**

Cathode: \( \text{Li}_2\text{O}_2 + 2\text{Li}^+ + 2e^- \xrightarrow{\text{discharge}} 2\text{Li}_2\text{O} \) \hspace{1cm} (2.15)

Anode: \( 2\text{Li} \xrightarrow{\text{discharge}} 2\text{Li}^+ + 2e^- \) \hspace{1cm} (2.16)

Overall reaction: \( \text{Li}_2\text{O}_2 + 2\text{Li} \xrightarrow{\text{discharge}} 2\text{Li}_2\text{O} \) \hspace{1cm} (2.17)

Combining Equations (2.14) & (2.17), the following equation can be obtained:

\( 4\text{Li} + \text{O}_2 \xrightarrow{\text{discharge}} 2\text{Li}_2\text{O} \) \hspace{1cm} (2.18)

It is also possible that a superoxide ion can be involved during the discharge process in a competing reaction as follows:
Chapter 2 - Literature Review

Cathode:

\[ \text{O}_2 + e^- \xrightarrow{\text{charge}} \text{O}_2^\text{\text{charge}} \quad (2.19) \]

Anode:

\[ \text{Li} \xleftrightarrow{\text{charge}} \text{Li}^+ + e^- \quad (2.20) \]

Overall reaction:

\[ \text{Li} + \text{O}_2 \xleftrightarrow{\text{charge}} \text{LiO}_2 \quad (2.21) \]

The LiO\textsubscript{2} itself can also undergo a chemical reaction to become Li\textsubscript{2}O\textsubscript{2} with oxygen evolved as follows:

\[ \text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 \quad (2.22) \]

However, it is also possible that the O\textsubscript{2}^\text{\textbullet} can react with one other electron to form O\textsubscript{2}^\text{2\text{-}}, if the lifetime of O\textsubscript{2}^\text{\textbullet} is long enough. In such a case, the two-electron process with Equations (2.12) to (2.14) will occur instead.

The gravimetric energy densities of a Li-O\textsubscript{2} cell with organic electrolyte and aqueous electrolyte are shown in Table 2.1. The third row is that of the commercial LiCoO\textsubscript{2} LIB which is added for comparison.

**Table 2.1** Gravimetric energy densities of Li-O\textsubscript{2} cells and commercial LiCoO\textsubscript{2} LIB

<table>
<thead>
<tr>
<th>Battery</th>
<th>Reaction &amp; theoretical OCV</th>
<th>Gravimetric energy density, ( D_{\text{th}} ) (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{Reaction &amp; theoretical OCV} )</td>
<td>( O_2 ) from storage tank (included in calculation)</td>
</tr>
</tbody>
</table>
| Organic Electrolyte Li-O\textsubscript{2} cell | \( 2\text{Li} + \text{O}_2 \xleftrightarrow{\text{charge}} \text{Li}_2\text{O}_2 \)
\( E^0 = 3.10 \text{ V} \) | 3630 | 12000 |
| Aqueous Electrolyte Li-O\textsubscript{2} cell | \( 4\text{Li} + 2\text{H}_2\text{O} + \text{O}_2 \xleftrightarrow{\text{charge}} 4\text{LiOH} \)
\( \text{(alkaline)} \) | 3870 | 5820 (alkaline) |
Chapter 2 - Literature Review

<table>
<thead>
<tr>
<th>Commercial LiCoO₂ LIB</th>
<th>(alkaline) $E^0 = 3.45$ V</th>
<th>(acidic) $E^0 = 4.28$ V</th>
<th>4800 (acidic)</th>
<th>7650 (acidic)</th>
</tr>
</thead>
</table>

$E^0 = 3.80$ V
(average discharge voltage)

380

The gravimetric energy density values for the Li-O₂ cells in Table 2.1 are calculated based on several steps as shown in Appendix I.

For the two Li-O₂ technologies (aqueous electrolyte and organic electrolyte) described, four categories of electrolyte are developed:

1. Aqueous
2. Non-aqueous (Organic)
3. Hybrid
4. Solid-state

The first two categories, aqueous and non-aqueous, have been described in detail in the previous paragraphs. The hybrid electrolyte consists of an aqueous electrolyte in the cathode and non-aqueous electrolyte in the anode, with a solid LISICON film (Lithium Titanium Aluminium Phosphate - LTAP) separating the two different electrolytes. The LISICON film itself is an ionic conductor which allows $\text{Li}^+$ to travel through it.

The solid-state electrolyte Li-O₂ cell has an ionically conducting solid membrane laminate which is made of purely lithium-based organic polymer gel [29], or inorganic glass ceramic material [30, 31]. In particular, the inorganic solid-state electrolytes have the following advantages over the liquid electrolyte batteries:
(1) Dendritic formation from the use of metallic lithium anode is suppressed, allowing the cell to undergo many cycles of charge/discharge [32].

(2) Cell volume and mass can be saved, thus making the cell compact, unlike liquid electrolyte cells or polymer electrolyte cells [33].

(3) Stable to moisture from the air unlike those cells using non-aqueous electrolyte or organic polymer gel electrolyte [34].

The schematic illustration of a typical solid-state electrolyte cell Li-O₂ cell is shown in Figure 2.3. This project used an inorganic Li-ion glass ceramic electrolyte which will be described in Section 2.6.

**Figure 2.3:** Schematic diagram of a full solid-state Li-O₂ cell. The solid-state electrolyte laminate is made up of 3 different membrane layers as follows: PC (Li₂O) + GC + PC (BN). PC: Polymer ceramic, GC: Glass ceramic, BN: Boron nitride (Adapted from Ref [31]: Figure 1. Copyright 2010 with permission from Electrochemical Society.)
Despite the theoretical high energy densities that the LAB can deliver, the LAB has several limitations. Firstly, the focus of current LAB research is on solid state anode materials, which includes metallic lithium and lithium alloys. As the Li-O2 cell is depleted during discharge, stability of the anode and the solid electrolyte membrane interface becomes a problem, in terms of loss of physical contact to certain parts of the interface. Secondly, a solid-state anode does not permit ion transport as fast as is possible in a liquid anode. Thirdly, like the LIBs for electric vehicles, a secondary solid-state anode LAB for vehicle application operating at ambient temperature requires a charging time longer than 10 min which is not practical. The next section (Section 2.4) will describe a lithium cell utilizing liquid electrodes at ambient temperature which can address these limitations.

Section 2.4 A Liquid anode / Solid state electrolyte membrane /
Liquid cathode cell configuration

2.4.1 The Redox Flow Battery (RFB)

Section 2.2 has described some of the issues faced by LIB-powered electric vehicles. One of these issues is the 30 min charging duration, which is very much longer than the average time required to refuel gasoline vehicles. The long charging time issue for LABs was also mentioned at the end of Section 2.3. One possible solution to this issue is to use liquid state electrodes in association with a solid state electrolyte membrane.
Currently, the only commercial batteries operating with both the anode and cathode materials in the liquid state at ambient temperature are the redox flow batteries (RFB). Examples of RFBs are those that use aqueous vanadium solutions and zinc-bromine solutions [16, 35, 36]. The voltage range of these batteries is from 1 V to 1.8 V.

The redox flow battery (RFB) has several advantages over conventional cells with solid-state electrodes as described in Chapter 1. In some ways, the RFB is similar to fuel cells. Table 2.2 compares several key features of the fuel cell and the RFB.

**Table 2.2** Comparison between a fuel cell and a redox flow battery

<table>
<thead>
<tr>
<th></th>
<th>Fuel Cell</th>
<th>Redox Flow Battery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Reaction between fuel and oxidant generates electricity.</td>
<td>Redox reactions between liquid cathode and liquid anode generate electricity.</td>
</tr>
<tr>
<td>2</td>
<td>External storage of fuel and oxidant</td>
<td>Liquid cathode and liquid anode are stored both internally and externally.</td>
</tr>
<tr>
<td>3</td>
<td>Electrolyte remains at all times inside fuel cell (i.e Nafion membrane for PEMFC)</td>
<td>Solid ion-exchange membrane serves two purposes: Firstly as an ionic conductor and secondly, as a separator between the liquid electrodes to prevent them from mixing. The solid electrolyte remains at all times inside the battery.</td>
</tr>
</tbody>
</table>
Two methods of recharge:
(1) Direct charging from an external power source. (reversible)
(2) Replace spent liquid electro-active materials inside the battery with fresh liquids from external tanks. The spent liquids can be separately recharged outside the battery in another facility.

The fundamental redox flow cell system is shown in Figure 2.4. The cell is divided into two separate compartments by an ion-exchange membrane that does not conduct electrons. The compartments serve as the anode and the cathode of the cell and are each connected to an external storage tank via a pump-operated circuit loop. Fresh electrode solutions are stored in these tanks at the start. The electrode solutions in these tanks are also referred to as “anolyte” and “catholyte” [16]. When the cell is depleted from use, the fresh active liquid electrodes which are stored in these tanks are then circulated using the pumps into the cell to replenish it. The depleted solutions are displaced by the fresh solutions via the circuit loop back into the external tanks for subsequent removal.
Figure 2.4: Schematic diagram of a single redox flow cell. (Reprinted from Ref [16] Copyright 2006, with permission from Elsevier.)

Based on the relevant applications’ needs, the RFB can be scaled up in several ways [16] such as by either increasing the dimensions of the electrodes or by stacking the cells up and connecting them in series or parallel configuration. One important feature of RFB is that unlike other battery systems, the RFB system’s power output and energy storage capacity can be decoupled from each other and separately scaled up or down, thus offering considerable flexibility to adapt the RFB to meet the requirements of different applications [16, 37]. To adjust the power output of the RFB, the following changes can be made: (1) The electrodes’ sizes can be changed; (2) The number of cells in its stack can be changed through the use of bipolar plates and (3) The individual cells in the stack can be connected in series or parallel configurations.
To change the RFB’s energy storage capacity, one can either change the storage tanks’ volumes or the liquid electrodes’ concentrations [16].

Unfortunately, current redox flow batteries, such as the Vanadium Redox Flow Batteries (VRFB), have very low volumetric energy density and specific energy density as compared to most battery systems such as the LIBs as mentioned in Chapter 1. This is because none of these commercial RFBs uses alkali metals. As a result, they do not possess the high energy densities of lithium ion batteries (LIBs) which use oxides of lithium metal as anode materials. The reason why lithium metal is used in the anode for LIB and LAB is because it is the lightest alkali metal and the safest to handle. Thus current commercial RFBs are not practical power sources for electric vehicles.

2.4.2 Alkali-metals Semi-Flow Batteries

The development of alkali-metal (Li or Na) half cells utilizing liquid cathodes and semi-solid rechargeable lithium flow cells [37-44] is the result of attempts to incorporate both the advantages of the LIBs’ high energy density as well as the RFBs’ dual refuelling/recharging options. The redox-flow half cells use a solid anode such as metallic lithium with liquid cathodes containing dissolved reversible redox species to serve as the redox shuttle to the solid cathode reservoir. As an example a Li Redox Flow Battery is shown in Figure 2.5a [37]. This system might be further extended to become a Li Redox Flow Air Battery by the use of oxygen in the air to recharge the discharge liquid cathode product via a chemical oxidation reaction. This would be achieved by means of a properly selected redox couple cathodic ion pair $\text{M}^{2+}/\text{M}^{(2-n)+}$ that can be used to catalyse the oxygen reduction reaction (ORR). Such a concept has
been envisaged but to date no suitable candidate material has been suggested [37].

**Figure 2.5b** extends the schematic Li-RFB to illustrate the Li-Air RFB concept.

---

**Figure 2.5a**: Basic schematic illustration of a Li Redox Flow Battery (Li-RFB) with a thin LISICON separator plate between the two electrodes. (Reproduced from Ref [37] Copyright 2012 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)
Figure 2.5b: Conceptual schematic of the Li-Air RFB with $M^{z+}/M^{(z-n)^+}$ catalyst for ORR. (Reproduced from Ref: [37] Copyright 2012 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)
The semi-solid rechargeable Li-flow cells, however, use viscous slurry-based suspensions comprising of solid electrode materials, electrolyte and conducting carbon additives [30, 32] such as the one shown in Figure 2.6.

**Figure 2.6:** (a) (TOP LEFT) Schematic diagram of a semi-solid flow cell in which suspensions of lithium-ion cathode and anode materials are used. (b) (TOP RIGHT) Semi-solid suspension of LiCoO$_2$ powder with Ketjen black conducting additive. (c) (BOTTOM) Test cell with metallic lithium as the reference electrode. Monolithic copper and aluminium are used to construct the current collectors. The slurry is fed by means of tubing through the cell with a peristaltic pump. (Reproduced from Ref: [38]
Unfortunately, both types of cells have their own disadvantages. Firstly, during the operation of semi-solid flow cells, viscous slurry suspensions from external storage tanks are circulated through the cells. The slurries themselves do not contain metallic lithium and contain non-conducting lithium-based oxide materials (LiFePO$_4$, LiCoO$_2$, Li$_4$Ti$_5$O$_{12}$ etc). Hence, the system requires a large quantity of carbon additives to improve their conductivity, resulting in low energy density. Secondly, there is also the possibility of the circulatory system being clogged by the solid particles present in the slurry during cell operation. Thirdly, the circulatory flow process of the active material into and out of the cell is regulated by an external pump which itself also requires power to operate. Finally, if alkali metal is utilized as the anode in redox-flow half cells, it must be physically replaced once it is depleted. Moreover, the presence of the alkali metal anode inside the cell poses a risk to the users due to its high reactivity with moisture and air [45-47]. In the event that the lithium metal is exposed to air and water due to leakage, there is a risk of fire and/or explosion.

Another recently-developed lithium flow cell is a pump-assisted lithium-ion redox flow cell. This cell operates with its solid anode and cathode materials stored separately in external tanks, with the liquids circulating through the cell consisting of redox-shuttle molecules. In order to save time from recharging, both anode and cathode tanks can be physically replaced once their electrode materials are fully discharged [48]. However, this cell design has two main shortcomings: Firstly, a set of functioning pumps is crucial for the operation of this cell in order to circulate the
liquids. The pumps themselves require an energy source to operate. Secondly, it is a cumbersome process to replace both solid electrode tanks manually instead of simply refuelling.

In the next section, a new kind of liquid anode cell which can operate at ambient temperature is described. A Lithium Solvated Electron Solution (Li-SES) is used as the active material in the liquid anode and the liquid cathode can consist of iodine dissolved in methanol or aqueous LiCl [18, 19]. The liquid anode solution has many advantages as compared to a solid-state anode or a slurry-based anode, one of which is that when used in conjunction with a solid electrolyte, the liquid anode is able to achieve a physically stable anode/ceramic membrane electrolyte interface [18, 19, 49]. The concept of using LiSES as a liquid anode in lithium cells and its advantages will be covered in greater detail in Section 2.5.

**Section 2.5 Lithium Solvated Electrons Solution (LiSES) anode**

**2.5.1 Background on Solvated Electrons Solution**

The first report of solvated electrons solutions dates back to 1808 with Sir Humphry Davy’s observation that alkali metals could be readily dissolved in liquid ammonia to form blue-coloured solutions [50]. The blue colour of the solution was attributed to the presence of solvated electrons which are formed when the alkali metal dissolved in the liquid ammonia [51, 52]. However, the solution’s colour can also be greenish. The colour depends on the type of electron receptor molecule used, or on the concentration of the dissolved alkali metal. It has been observed that highly concentrated alkali metal solvated electrons solutions can be bronze coloured [53].
Thus far, it was known that only the metals from Group I (alkali) and Group II (alkaline-earth) can be readily dissolved in liquid ammonia to form LiSES, with the exceptions of beryllium (insoluble) and magnesium (partially soluble) [54].

The term “solvated electrons” refers to free electrons that are solvated in a solution. A solvated electron is not bound to a particular solvent or solute molecule in the solution. Instead, it occupies the spaces or cavities between the solvent/solute molecules and is not strongly bound to any of them. Solvated electron solutions can be pictured in terms of excess electrons existing inside the cavities of clusters of solvent/solute molecules. These solvent cluster anions can be represented by $S_n^-$ where $S$ denotes the type of solvating species (electron receptors) [55] and $n$ denotes the number of $S$ surrounding the solvated electron.

Solvated electrons which are produced by means of ionizing radiation in water are also termed “hydrated electrons” [55-58]. Hydrated electrons, however, are unstable. They have a very short lifetime at most in the order of micro-seconds [55, 59] as compared to those produced by dissolving alkali-metal in ammonia [52] or other non-aqueous organic electron receptors. Hydrated electron solutions are therefore not suitable for anode applications, and thus were not considered in this project.

In recent years, Prof Rachid Yazami has patented poly-aromatic hydrocarbons (PAH) as electron receptors for Li-SES [18]. Other than with liquid ammonia, alkali metals such as lithium and sodium can form solvated electron solutions (Li-SES and Na-SES) with several types of molecules including organic radicals and polycyclic aromatic hydrocarbons (PAH) such as biphenyl and naphthalene. However, the most commonly known solvated electron solutions are the ones which are formed by the dissolution of metallic lithium in liquid ammonia. Solvated electrons solutions have
been used in a number of synthetic methods [60-63] as well as in a range of possible applications and research fields [18, 64-70]. Another term that can be used for “solvated electron” produced in such manners is solvent-stabilized “radical anion” [58]. Like metallic lithium, a Li-SES is also very sensitive to oxygen and moisture from the air and will react exothermically in the presence of water to produce hydrogen gas.

As this project concerns studying the properties of LiSESs to evaluate their potential application in a battery, the work here is confined to using lithium metal to prepare solvated electrons solution (Li-SES).

2.5.2 ESR, NMR Studies and some theoretical computation on PAH-based LiSES

As mentioned earlier, when metallic Li dissolves in a solution of electron acceptors, it forms a solvated electrons solution. The term “solvated” means that when the metallic lithium (solute) has formed a liquid phase after it dissolved into the electron acceptor solution, non-covalent interactions which are weak in nature have taken place between the Li and the electron acceptor molecules [71]. Another term for “solvated electrons” is “radical anions”.

Ways to investigate the solution structures of the LiSES include using Electron Spin Resonance Spectroscopy (ESR) and Nuclear Magnetic Resonance (NMR) spectroscopy [72-76]. The fundamental operation of ESR spectroscopy is as follows: Solutions of molecules containing electrons with unpaired spins are paramagnetic and are thus expected to display electron spin resonances. When they are subjected to an external applied magnetic field, these unpaired electrons (solvated electrons here) will each have a preferred spin either clockwise or anti-clockwise to
Chapter 2 - Literature Review

the field direction. Basically, the ESR spectroscopy then measures the amount of energy needed for an unpaired electron to reverse its direction of spin, with the ESR intensity absorption in the spectrum directly proportional to the solvated electrons’ concentration [77]. ESR has been used to study Li-naphthalenide (the complex formed by electron transfer from Li to naphthalene, a PAH with two fused benzene rings) [73, 78]. Hsieh [73], conducted ESR studies on Li naphthalenide in THF and diethyl ether at room temperature (26 °C) and at temperatures of -30 °C, -70 °C, and -100 °C. He observed that of the two solvents, excess Li dissolved readily in naphthalene/THF to form a dianion, which was consistent with a report by Smid [79]. For diethyl ether, however, solvation of metallic Li only occurs at temperatures of 0 °C and below. Hsieh also reported tuning difficulties with ESR at the low temperatures of -70 °C and -100 °C for the LiSES samples due to the increased conductivity of the samples. The conductivity and metallic behaviour of LiSES is covered in the following section, Section 2.5.3, in this chapter. Figure 2.7a shows the theoretically calculated ESR spectrum for a lithium-naphthalene ion-pair in solution and Figure 2.7b shows the experimentally obtained ESR spectrum of a solution of lithium-naphthalene in diethyl ether at 26 °C and -70 °C. Since the lithium atom’s valence electron is shared between lithium and naphthalene as a solvated electron, the interaction between the unpaired solvated electron with naphthalene molecule produces a spectrum of 25-lines, in which each line is further split into 4 lines through the electron’s interaction with the lithium atom’s nuclear magnetic moment, yielding a total of 100 lines. It has been shown that both the theoretical ESR spectrum and the experimentally obtained spectrum agree with each other [73]. In Figure 2.7b, the sample’s ESR spectrum at 26 °C has more than 25 hyperfine lines. When the spectrum is obtained at a lower temperature of -70 °C, the lines can be subdivided into groups of 4 lines.
Figure 2.7a: Theoretical ESR spectrum of naphthalene-based lithium solvated electron solution’s lithium-naphthalene ion pair. Experimentally determined hyperfine coupling constants at -70 °C, $A_a$, $A_b$ and $A_{Li}$ are shown on the top right-hand corner. (Reprinted from Ref: [73] Copyright 1967, with permission from Elsevier.)
Figure 2.7b: Experimentally obtained ESR spectrum of lithium-naphthalene/diethyl-ether. (Reprinted from Ref: [73] Copyright 1967, with permission from Elsevier.)

NMR studies have also been conducted on LiSES solutions consisting of metallic lithium dissolved in (1) naphthalene, (2) biphenyl, (3) phenanthrene, (4) anthracene, and (5) trans-stilbene [74]. The advantage of using NMR spectroscopy as compared to ESR is that it is capable of measuring the very weak interactions between the solvent and solute molecules [71, 74, 77], by comparing the chemical shifts of their nuclei. NMR studies were conducted by Screttas et al. [74] on the above-mentioned LiSES samples where their paramagnetic NMR shifts were measured as a function of the solvated electrons’ concentration. It was reported that for samples (2) to (5), their $^7$Li NMR shifts ($\delta_{\text{obs}}$) varied linearly with the radical anions’ concentrations. The higher the radical anion concentration, the greater would be the $^7$Li NMR shift. It was
also reported that samples (2) to (4) had very small contact shifts (calculated from $\delta_{\text{obs}}$), indicating that the radical anions in them existed in THF as loose ion-pairs whereas for sample (5), no contact shift was observed, indicating that its radical anion existed as a solvent-separated ion pair. For sample (1), it was observed that the relationship between $\delta_{\text{obs}}$ and the radical anion concentration was nonlinear as in Figure 2.8a. An additional measurement conducted using LiCl/THF as the solvent for Li-naphthalenide showed that the relationship became linear, as shown in Figure 2.8b. The authors believed that the radical anions in Li naphthalenide exist as tight-ion pairs, making exchange of Li$^+$ between identical sites of PAH/solvent less favorable than in the other samples. The reason suggested for the change in relationship to linear was that the Li$^+$ from the Li-naphthalenide were indistinguishable from the Li$^+$ of LiCl. The authors thus concluded that the counter cation (Li$^+$) should not form an integral part of the radical anion which was paramagnetic, indicating that the contact shifts of the Li$^+$ were concentration dependent and should be expressed in terms of ppm mol$^{-1}$. 
Figure 2.8a: Non-linear relationship between the $^7$Li NMR shift and the radical anion concentration for Li-naphthalenide using THF solvent. (Reproduced from Ref: [74] with permission of The Royal Society of Chemistry.)
Figure 2.8b: Linear relationship between the $^7$Li NMR shift and the radical anion concentration for Li-naphthalenide using LiCl/THF solvent. (Reproduced from Ref: [74] with permission of The Royal Society of Chemistry)

Finally, theoretical First Principle Calculations on LiSES are also crucial for understanding the structure of LiSES. As this project is experimental in nature, this paragraph describes the preliminary computational work conducted without going too much into the details. In a study performed prior to this work, the results of which were privately communicated by Prof. Rachid Yazami [80], theoretical analysis of the following PAH-based LiSES were conducted using Maestro, a molecular modeling
software: naphthalene (2 fused benzene rings), anthracene (3 linearly fused benzene rings in a chain), pyrene (4 nonlinearly fused benzene rings) and tetracene (4 linearly fused benzene rings). The purpose was to understand the most thermodynamically stable configuration for Li atoms to pair up with each PAH molecule. The configurations of Li-Naphthalene with their corresponding states and potential energies are shown in Figure 2.9. For a naphthalene-based LiSES, (also known as lithium naphthalenide), its most stable configuration is that of two Li atoms pairing with one naphthalene molecule with one Li above the naphthalene and one below as shown in Figure 2.9(a). The results for the other materials are not relevant to this thesis and so are not shown.

![Figure 2.9](image)

**Figure 2.9**: Configurations of Li-Naphthalene with their corresponding states and potential energies. (Reproduced from [80] with permission from Prof Yazami.)

This is because configuration (a) has a spin of 0 and the lowest potential energy set as 0 eV for comparison to the other 3 systems, indicating it is thermodynamically the
most stable. It has also been found that the Li$_2$(naphthalene) form is thermodynamically more favourable than the Li$_1$(naphthalene) form. No preliminary computational modeling has been conducted for biphenyl-based LiSES.

### 2.5.3 Metallic properties of Li-SES

The electrical conductivity of a material, $\sigma$, is a quantitative measure that indicates how well it is able to conduct electrical current. It is the inverse of resistivity, $\rho$. In order to understand the Li-SES’s unique electrical conduction properties, one has to first look at how the conductivities of other materials, namely metals, semiconductors and solutions, vary with temperature.

Most metals are solids at ambient temperature whose structure consists of a lattice of positive ions in fixed positions surrounded by mobile outer-shell electrons which are contributed by each metal atom. The positive ions can only vibrate in their fixed positions whereas their electrons are free to move throughout the lattice structure and serve as the charge carriers. When a potential difference is applied across a piece of metal, a resultant electric field is set up across the metal with direction from the negative terminal to the positive terminal. Only the mobile electrons will move in the resultant electric field towards the positive terminal. When the temperature of solid metals increases, the increased vibrational motions of their fixed positive ions in the lattice will interfere with the movement of the mobile electrons in the electric field through collisions. This results in the decrease in conductivity of the metals. For mercury, even though it is a liquid at ambient temperature and its electrical conductivity is lower than that of the solid metals at ambient temperature [81], its
behaviour is still metallic in that its conductivity decreases with its temperature increase [82].

For semiconductors, their charge carriers consist of holes and electrons. Unlike metals, semiconductors’ electrical conductivity increases when their temperature increases [83]. The relationship between the intrinsic charge carrier density of silicon (intrinsic semiconductor) versus temperature is shown in Figure 2.10. It can be seen that the carrier density $n_i$ increases with increasing temperature though the increase becomes smaller at higher temperatures. The increase of $n_i$ with temperature is due to a rise in the number of electron-hole pairs generated when the semiconductors absorb more thermal energy. Since conductivity of intrinsic semiconductors increases with temperature, one can deduce from Figure 2.10 that the conductivity of intrinsic semiconductors is proportional to their intrinsic charge carrier density and to their mobility. Even for extrinsic semiconductors, as temperature increases, their conductivity increases, regardless of whether they are N-type (donor impurities doped) or P-type (acceptor impurities doped).

The only exception is that of the degenerate n-type or p-type semiconductors which are so heavily doped with impurity atoms that the dopant density in them exceeds one part in a thousandth host (semiconductor) atoms [83]. Due to their heavy dopant densities, the degenerate semiconductors behave like conductors [83]. This means that just like conductors, their conductivities will decrease with increasing temperature. Figure 2.11 shows the graphical relationships between the density of dopants and the resistivity (inverse of conductivity) for various n-type and p-type semiconductors. For all of them, their resistivities decrease (meaning conductivities increase) with increasing dopant density.
Figure 2.10: Graph of intrinsic carrier density, $n_i$, versus temperature, $T$ where $n_i$ is shown to increase from $10 \text{ cm}^{-3}$ to $10^{15} \text{ cm}^{-3}$ as temperature increases from 150 K to 500 K. (Reproduced from Ref [84] Copyright 2006 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)
For an electrically conducting solution, its conductivity is a quantitative measure of its ability to conduct electricity. In order to conduct electricity, a solution must contain mobile charged species. Aqueous solutions such as salt solutions (i.e NaCl, LiCl, KNO₃), acids (i.e HCl, H₂SO₄) and alkali (i.e NaOH) all contain mobile cations and anions and hence have non-zero conductivity values. These aqueous solutions are thus also known as electrolytes. The conductivity of a solution is a result of the total contribution by all the different ions (cations and anions) present in the solution and is affected by their concentrations in the solution. Pure water has a very small conductivity value, as a result of self-dissociation of some of its H₂O molecules.
Chapter 2 - Literature Review

into \( \text{H}^+ \) and \( \text{OH}^- \). Ionic liquids (IL), which are salts in their liquid state (non-aqueous), also possess mobile ions and thus they also display electric conductivity. For the solutions mentioned in this paragraph, their conductivity increases with temperature. Another significant feature is that semiconductors’ conductivities have exponential conductivity-temperature dependence and are thus non-linear, unlike metals [85].

For a Li-SES, even though it exists as a solution at room temperature, it does not behave like a typical solution containing mobile ionic species. At low Li metal concentration, the LiSES behaves just like an ideal electrolyte with the electron kept in a solvent cavity. However, at increasing Li concentrations, the distances between these solvent cavities became smaller and smaller until it is possible for metallic wave functions to be set up in the LiSES [86]. Electrical current can then propagate through the LiSES in the form of waves of the solvated electrons through the solvent cavities, thus the effective mobility of the solvated electron appears to be many times larger than that of a normal ion [86].

Both Figure 2.12a and Figure 2.12b show the conductivity data of the LiSES for different concentrations of lithium, which illustrates the changes to metallic behaviour as Li concentration increases.
Figure 2.12a Conductivity data of ammonia-based LiSES for various concentrations in mole percent lithium. The added red box shows the temperature range for which ammonia is a liquid (195.42 K ≤ T ≤ 239.81 K).(Adapted from Ref: [85] Figure 1):
Figure 2.12b Conductivity data of ammonia-based LiSES for concentrations exceeding the solubility limit in mole percent lithium. The added red box shows the temperature range for which ammonia is a liquid \((195.42 \text{ K} \leq T \leq 239.81 \text{ K})\). (Adapted from Ref: [85] Figure 2).

Conductivity studies on ammonia-based LiSES showed that the conductivities of all LiSES vary linearly with temperature unlike semiconductors [85]. The “moles percent lithium” \((MPL)\) described in Figures 2.12a and 2.12b are expressions of the lithium metal concentration in the ammonia-based LiSES [50]:

\[
\text{Mole percent lithium: } MPL = \left(\frac{\text{No. of moles of Li}}{\text{No. of moles of Li} + \text{No. of moles of NH}_3}\right) \times 100 \tag{2.23}
\]
Within the red boxes of both figures, Figure 2.12a shows that for dilute concentrations of Li less than 20% $MPL$ the gradients of the linear graphs are positive and for 20% $MPL$ the gradient is zero. Whereas for Figure 2.12b, for >20% $MPL$, the gradients of the linear graphs are negative just like solid metals. This indicates that the conductivity of the LiSES is dependent on the Li concentration for its metallic property.

2.5.4 PAH-based Li-SES

PAH-based alkali metals solvated electrons solution can be prepared using polycyclic aromatic hydrocarbons [87] such as biphenyl and naphthalene as the electron receptors. Since all the PAHs are solids at room temperature, they have to be first dissolved in a suitable organic solvent to become solutions before the alkali metals can be added. LiSES solutions prepared using biphenyl and naphthalene are also known as lithium biphenylide [88] and lithium naphthalenide [74, 78, 89-93]. Preliminary proof-of-concept studies on PAH-based LiSES as anodes have been conducted and the battery concept has been patented [18]. In this project, the PAHs that were selected for the LiSES are the biphenyl and naphthalene, each with two benzene rings but with different structures.

2.5.5 Electrochemically generated Li-SES

In Section 2.5.1, the LiSES was described as being formed chemically by dissolving metallic lithium into liquid ammonia. Solvated electrons can also be obtained in solutions by electrochemical generation [86, 94, 95]. By cathodic generation process, electrons from the electrode can be transferred into the solution.
under high cathode over-potentials to form solvated electrons solution. Subsequently, the concentration of the solvated electrons can be varied through electrolysis of the solution [94]. The advantages of the electrochemical method over the chemical method of preparing SES are as follows [86]:

1. Greater control over the reaction can be exerted by the direct control of the electrode’s potential or its current density,
2. Increased selectivity through control of the products of reaction.
3. Consumption of alkali metals in chemical preparation process can be avoided altogether since alkali metals are both expensive and dangerous to handle.
4. Even for low reactant concentrations, very large current densities can be supported through the exploitation of the solvated electron’s high mobility.

The electron receptor solutions used for dissolving the alkali metals and forming chemically stable solvated electrons are usually the same ones that are used for the cathodic generation process [94, 96] of SES. One can qualitatively determine whether cathodic generation of SES is thermodynamically more effective than the electrolytic deposition of the alkali metal by the following example [94]:

**Example:**

Taking the alkali metal as Li, metallic lithium and its saturated solution exist in electrochemical equilibrium as follows:

**Deposition of Li metal:**  \( \text{Li}^+ + e^- (\text{Li}) \rightleftharpoons \text{Li}^0 \)  

**Generation of solvated electrons:**  \( e^- (\text{Li}) \rightleftharpoons e_s^- \)
where $e^-(\text{Li})$ denotes the electron of the metallic lithium and $e^-_{se}$ denotes the solvated electron. One can use the Nernst equation to obtain the difference in their standard potentials:

$$\Delta E = E_0(\text{Li}/\text{Li}^+) - E_0(e^-_{se}) = -\frac{RT}{F} \ln \left[ a(\text{Li}^+)a(e^-_{se}) \right]$$ (2.26a)

where

“$a$” denotes the activities of the saturated solution’s Li$^+$ and solvated electron.

If “$a$” is taken to be the concentration, then Equation (2.26a) becomes:

$$\Delta E = E_0(\text{Li}/\text{Li}^+) - E_0(e^-_{se}) = -\frac{RT}{F} \ln [\text{Li}^+][e^-_{se}]$$ (2.26b)

Equation (2.26b) is used for qualitative analysis and not quantitative. The higher the solubility of the Li in the solution, the larger will be the magnitude of $\Delta E$ and hence cathodic generation is thermodynamically more effective. This is because it is very hard to determine the individual activities $a(\text{Li}^+)$ and $a(e^-_{se})$ separately due to the complex equilibria in the system [94]. For systems that are thermodynamically more effective for cathodic generation of solvated electrons, Equation (2.24), which is the electrodeposition of lithium metal, will not occur in the bulk of the solution.

Apart from the chemical preparation methods for LiSES, an alternative approach is to prepare the Li-SES cell in its discharged state where the OCV of the cell is zero and the anolyte does not contain solvated electrons. The Li-SES can be
electrochemically generated when the cell is charged. A cell prepared in the discharged state without any solvated electrons initially present in the anode solution allows for safer handling and storage.

2.5.6 Li-SES anodes for Lithium-Air Batteries

The use of Li-SES as an anode material for a liquid lithium cell was first proposed by Sammells where ammonia was used as the electron receptor [69, 70]. Metallic lithium was dissolved in liquid ammonia to form a solution of lithium solvated electrons. This solution could then be used as the liquid anode material of a lithium battery in place of the lithium metal.

The use of LiSES as liquid anode for LABs has several advantages over other existing lithium cells:

(1) The cell uses a true liquid solution as anode which is different from the semi-solid flow energy storage devices of slurry-based suspensions of solids as catholyte and anolyte as described in the previous section, therefore eliminating the issue of particle agglomeration. Hence, the likelihood of the active materials clogging up the pump and circulatory system during recharge/replenishment will be very much lower.

(2) The depleted cell can be recharged in a variety of methods, one of which is replacing the spent liquid anode with fresh ones. Thus allowing electric vehicles using such cells to be replenished in minutes similar to gasoline vehicles at gas stations.

(3) Compared to both solid-state and slurry-based anodes, the LiSES liquid anode possesses faster ion transport capability.
(4) The LiSES anode is able to achieve a physically stable anode/ceramic membrane electrolyte interface, unlike conventional LAB cells which utilise solid anodes [18, 19, 49].

(5) Due to the metal-like property of the LiSES, it does not require a large amount of conducting additives in order to work, unlike for the slurry-flow batteries which use oxides of lithium (i.e. LiCoO$_2$) which are inherently poor conductors.

Unfortunately, liquid ammonia will evaporate to gas during cell discharge which will then lead to a pressure build-up in the Li-SES cell raising safety issues. Hence, the ammonia-based Li-SES cells are not suitable for safe usage at ambient temperature condition. In order to overcome this problem, this project studied the properties of PAH-based LiSES, the results of which will be presented in the later chapters of this thesis.

Section 2.6 Li-ion Conducting Solid Ceramic Electrolyte Membrane

2.6.1 Background on Li-ion solid electrolyte membrane

The electrolyte used for this project has to be in the solid state, so that it can serve as a separator for both the liquid anode and the liquid cathode. Next, it has to be a good Li$^+$ ionic conductor as well as a poor electrical conductor for electrons. There are two types of known Li$^+$ solid electrolyte, one of which is made of polymer and the other made of glass ceramic. Since the LiSES used for this project are PAH-based using the organic solvent tetrahydrofuran, THF (More on the PAH-based LiSES will be covered in details in Chapter 4 and Chapter 5), most polymeric materials will
disintegrate in contact with the solvent. Hence, this project uses Li-ion conducting glass ceramic membranes.

2.6.2 Lithium Aluminium Titanium Phosphate as electrolyte

The electrolyte membranes for this project were purchased from Ohara Inc., Japan. The membranes obtained are Lithium Titanium Aluminium Phosphate (LTAP), a NASICON-type glass ceramic composed of Li$_2$O-Al$_2$O$_3$-SiO$_2$-P$_2$O$_5$-TiO$_2$-GeO$_2$ with an ionic conductivity of $1 \times 10^{-4}$ S cm$^{-1}$ at 25 °C and with a crystalline phase of Li$_{1+x+y}$Al$_3$(Ti,Ge)$_2$Si$_y$P$_{3-y}$O$_{12}$ [97]. The prototype LTAP membrane technology was previously patented by Ohara Inc., Japan, in 1997 [98] and disclosed in a paper in the same year [99]. It is known that the LTAP possesses high ionic conductivity, good impermeability and good stability and is not brittle, which makes it suitable for lithium battery application. The LTAP functions both as an electrolyte and also as a separator for keeping the lithium anode and liquid cathode apart. As mentioned earlier in Section 2.3, this separation is very important because air entering the cathode may carry with it moisture which will undergo violent reaction with lithium. The LTAP has been used by various groups for secondary LAB studies [32, 34, 100-103] and even for Li flow batteries [42-44]. It has been reported that when the LTAP is in physical contact with metallic lithium, it becomes chemically unstable [28, 32, 34, 102-104] because it reacts with lithium to form a highly resistive layer of insulation at the interface [102, 103]. This is verified by impedance measurements conducted at 60 °C in the frequency range of 1 MHz to 0.01 MHz on the Al-Li/LTAP/Li-Al cell configuration for the following situations: (1) just after assembly and (2) after leaving the cell at room temperature for a lapse of time of 12 h, 18 h, 36 h and >120 h (5 days) [102]. The Al shown in the cell configuration is sputtered as a thin layer onto Li to improve contact with the Li and this layer reacted with Li to form a lithium-aluminium
alloy. Figure 2.13 shows the Nyquist plots of the impedance measurements for $t = 12$ h, 18 h and 36 h.

![Figure 2.13](image)

**Figure 2.13**: Impedance Spectra showing time dependence of the interfacial resistance (Semi-circular plots’ intersection with real axis) of Li-Al/LTAP/Li-Al cell (Initial: 4510 Ω; after 12 h: 8500 Ω). *Insert*: Impedance Spectra for just-after-assembly cell: Very small semi-circular plot obtained at high frequencies ($10^3$ kHz) as compared to the large semi-circle obtained at low frequencies ($10^0$ kHz). The insert’s small semi-circular plot intersects the real axis at ~ 36 Ω. (Adapted from Ref [102] Copyright 2008 with permission from Electrochemical Society.)

From Figure 2.13, it can be deduced that the interfacial resistance between Li-Al and LTAP (large semi-circles’ intercept with $Z_{Re}$ axis) increases with time. After 120 h (5 days), it was reported that the impedance spectra obtained show scattered
plots, indicating that an insulating layer has been formed between LTAP and the Li-Al alloy. Hence, right from the start of the contact between Li-Al and LTAP, formation of the insulating material had already started, though not enough to form a complete layer over the whole interface. From 120 h onwards, the layer’s thickness continues to grow. Beyond 1 week, the insulating layer’s thickness had increased so much that its resistance became too high to be measured [102].

It will be shown in a later chapter in this thesis that the effect of LiSES on LTAP is as problematic as metallic lithium, causing corrosion and eventual breakup of the whole membrane over time. As part of this project, solutions will be proposed to reduce if not eliminate the corrosion.

2.6.3 Lithium Phosphorus Oxynitride (LIPON) protective coat

In order to prevent the reaction between the Li anode and LTAP from occurring, a protective layer at the interface of Li/LTAP is required. This protective layer has to be chemically stable in the presence of metallic Li and also be able to conduct Li ions. The Lithium Phosphate Oxynitride (LIPON) film is shown to be efficient in protecting the LTAP electrolyte from metallic lithium corrosion [32, 104, 105]. The elemental composition of LIPON is in the form of \( \text{Li}_a\text{PO}_b\text{N}_c \) where \( a, b \) and \( c \) are varied according to the relevant study such as \( \text{Li}_{3.3}\text{PO}_{3.9}\text{N}_{0.17} \) [33, 106] or \( \text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.24} \) to \( \text{Li}_{3.6}\text{PO}_{3.3}\text{N}_{0.69} \) [105].

In 1992, LIPON was first reported as a suitable \( \text{Li}^+ \) conductor that was stable in contact with metallic lithium [106]. LIPON has an ionic conductivity of \( 10^{-6} \) S cm\(^{-1} \) [32, 33, 104, 106-108], which is of two orders of magnitude lower than that of the LTAP and a very low electronic conductivity of between \( 10^{-13} \) S/cm to \( 10^{-14} \) S/cm [107, 109]. It is also chemically stable with Li. All these properties made it suitable for use
in thin film Li batteries as a solid electrolyte with a thickness of the order of $10^{-6}$ m [33, 106-108].

When LIPON is coated onto LTAP, it is observed that it can suppress the reaction between metallic lithium and LTAP to form an insulating layer at the interface. A cell of the configuration Al-Li/LIPON/LTAP/LIPON/Li-Al is assembled for impedance measurements. Just after assembly, the cell is subjected to impedance measurement at 80 °C and is then kept for 3 weeks at room temperature after which it is again subjected to impedance measurement at 80 °C in the frequency range of 0.1 to 10 MHz [104]. Figure 2.14 shows the the Nyquist plots obtained. Comparison of the two plots in Figure 2.14 showed no significant change in the shape of the plot, indicating that the high resistance insulating layer is not formed.

Since LIPON has such precedent as described above for protecting LTAP against metallic lithium anodes, it is also used in this project to protect the LTAP against LiSES in the LiSES cell, details of which will be covered in a later chapter.
Figure 2.14: Impedance Spectra of Al-Li/LTAP/Li-Al cell conducted at 80 °C for: (ABOVE) Just-after-assembly cell, and (BELOW) After 3 weeks at room temperature. (Reprinted from Ref [104] Copyright 2008, with permission from Elsevier.)
Section 2.7 Iodine as liquid cathode for Lithium-Iodine Cells

2.7.1 Background on Lithium Iodine Cells

Lithium Iodine (Li-I$_2$) cells have been used for a variety of commercial applications such as for powering watches, data loggers and most notably, for implanted pacemakers in patients’ hearts [110]. In this project, iodine was investigated as an alternative cathode to be used in conjunction with LiSES liquid anode for a refuelable LiSES cell. Currently, most Li-I$_2$ primary and secondary batteries utilize solid electrodes. The Li-I$_2$ cell was invented by Moser and Schneider [110-112] and subsequently found its use in powering implanted cardiac pacemakers [113]. Initially, rechargeable Ni-Cd batteries were used for implanted pacemakers. When the Ni-Cd cell was depleted, it was inductively recharged without the need for surgical removal of the pacemaker from inside the patient’s body. However, there were two major problems for using Ni-Cd cells in pacemakers which led to the Ni-Cd cells being discontinued for such use. The first problem was the short life time of Ni-Cd cells which means that the pacemaker requires regular charging. The second was that the patient has to be responsible for recharging his own pacemaker which was not a good practice [114]. Nowadays, Li-I$_2$ primary cells are used for pacemakers owing mainly to the following properties they possess [114]:

1. Long Life (> 10 years before device has to be surgically removed for battery replacement)
2. High energy density
3. Long shelf life (with a loss of 10% capacity in five years compared to one year for alkaline cells)
Figure 2.15 shows the discharge profile of a Li-I\textsubscript{2} cell under a constant resistance load of 100 k\(\Omega\) at a temperature of 37 °C. This temperature is the body temperature of the average healthy adult human. Since the cell is to be inside a pacemaker implanted in the patient’s chest, the temperature of its working environment will also be 37 °C. The lithium metal anode is centered in the cell and surrounded by the cathode material. The long lifetime of the cell is evident from the graph: For instance it took nearly 10 years (10 \(\times\) 12 = 120 months) for the voltage to drop from 2.8 V to around 2.3 V.

![Graph showing discharge profile of Li-I\textsubscript{2} cell](image)

**Figure 2.15**: Discharge profile of a Model 702E Li/I\textsubscript{2} cell under a 100 k\(\Omega\) load at 37 °C. (Reprinted with permission from Ref [111] Copyright 1992 American Chemical Society.)

The Li-I\textsubscript{2} cell has a low rate capability [41, 115], which means that it has a low power density and it is not rechargeable [116]. The Li-I\textsubscript{2} cell is capable of powering
pacemakers and small electronic devices, but it is unsuitable for other applications which require cells with higher rate capability. There is an intrinsic relationship between the Li-I₂ cell’s low rate capability and the high resistance of the LiI discharge product which is between the electrodes. Since LiI is a poor Li⁺ conductor with low conductivity \( \approx 10^{-7} \text{ S cm}^{-1} \) at 25 °C, the internal resistance of the cell increases over time as the cell is discharged [115].

In order to have practical rechargeable Li-I₂ cells, the low rate capability problem has to be resolved. Over the past few decades, a large amount of research has been devoted to decreasing the high internal resistance of the Li-I₂ cells via modification of its electrode designs [117-119]. In recent years, a variety of secondary Li-I₂ cells which can be recharged have been developed. For the secondary Li-I₂ cells using solid-state cathodes, one of them utilizes mainly the ionic conduction of \( I^- \) instead of Li⁺ during cell charge/discharge [115] whereas another one is based on the electrochemical reaction of the \( I_2/I^- \) redox couple which is both fast and highly reversible [41]. However, there are limitations associated with the use of iodine in solid-state cathodes. For example, when iodine is in the solid state instead of the liquid state, its intrinsic low electrical conductivity limits the Li-I₂ cell’s kinetics.

Another type of Li-I₂ redox flow cell using liquid iodine cathode is also based on the \( I_3^-/I^- \) redox couple’s reactions. It utilizes an aqueous iodine/iodide cathode [43, 44, 120]. When the iodine cathode is used in a liquid state, the formation of the resistive LiI product between the electrodes during cell discharge is circumvented. This allows the Li-I₂ cell to be recharged for > 100 cycles [44].
2.7.2 Primary Lithium Iodine Cell

The schematic diagram of a typical solid-state Li-I$_2$ primary cell is shown in Figure 2.16. The cathode consists of an iodine/P2VP (poly-2-vinylpyridine composite and the anode is a sheet of lithium metal envelope.

![Figure 2.16: Schematic diagram of a Model 802 /35 Li/I$_2$ cell (Reproduced with permission from McGraw-Hill Education from Ref: [121].)](image)

The electrolyte of the cell is lithium iodide (LiI) and it can be made in two ways. The first is by in-situ formation through the physical contact of the cathode and the anode, during which metallic lithium will react chemically with the iodine in the cathode. The formation of LiI by lithium metal contact is aided by the iodophore P2VP present inside the cathode composition [119]. The second way is via coating of
a layer on the lithium anode with LiI or other halides by exposing the lithium to iodine or other halogens [112].

During discharge, iodine is reduced to iodide. The reactions occurring at the cell’s electrodes are as follows:

Cathode: \[ I_2 + 2e^- \rightarrow 2I^- \] (2.27a)

Iodine will form tri-iodide with only one electron as follows:

\[ \frac{3}{2} I_2 + e^- \rightarrow I_3^- \] (2.27b)

Anode: \[ 2Li \rightarrow 2Li^+ + 2e^- \] (2.28)

Overall reaction: \[ 2Li + I_2 \rightarrow 2LiI \] (2.29)

When P2VP is used in the cathode composition, Equation (2.27), the reaction at the cathode during cell discharge, becomes [121]:

Cathode: \[ 2Li^+ + 2e^- + P2VP.nI_2 \rightarrow P2VP.(n-1)I_2 + 2LiI \] (2.30)

Thus the overall cell reaction is:

Overall reaction: \[ 2Li + P2VP.nI_2 \rightarrow P2VP.(n-1)I_2 + 2LiI \] (2.31)

From Equations (2.27) to (2.31), it can be seen that as Li and I_2 are both consumed during discharge, LiI is precipitated as a discharge product between the electrodes. Despite being a discharge product, the LiI precipitate can still serve as both an electrolyte (on top of the existing LiI electrolyte) for the cell and as a separator between the electrodes.
2.7.3 Secondary Lithium Iodine Cell using iodine as a liquid cathode

This section describes the operation of the Li-I₂ cell which uses liquid cathode [31, 33, 34]. Figure 2.17 illustrates the operating concept of such a cell.

![Diagram of Li-I₂ cell](image)

**Figure 2.17**: Operating concept of the liquid cathode Li-I₂ cell for discharge/charge reactions occurring at the cathode and the anode. (Reproduced with permission from Nature Publishing Group from Ref [44])

During cell discharge, the I₃⁻ is reduced at the cathode to I⁻ via two-electrons reaction.

Cathode: \[ 	ext{I}_3^- + 2e^- \overset{\text{discharge}}{\underset{\text{charge}}{\rightleftharpoons}} 3\text{I}^- \] (2.32)

Anode: \[ \text{Li} \overset{\text{discharge}}{\underset{\text{charge}}{\rightleftharpoons}} \text{Li}^+ + e^- \] (2.33)

Overall reaction: \[ 2\text{Li} + \text{I}_3^- \overset{\text{discharge}}{\underset{\text{charge}}{\rightleftharpoons}} 2\text{Li}^+ + 3\text{I}^- \] (2.34)
The $\text{I}_3^-/\text{I}^-$ redox reaction in Equation (2.43) occurs at $E^0 = +3.57$ V versus Li/Li$^+$. 

In this project, the liquid cathode consisting of iodine dissolving in a solution of methanol is also studied so as to achieve a lithium cell with both liquid anode and liquid cathode that can operate at ambient temperature condition. The work on the liquid cathode will be covered in Chapter 6.

**Section 2.8 Conclusions**

In conclusion, this chapter covers the fundamental parts which are relevant to the PAH-based LiSES cell’s research namely the solvated electron solution anode, the solid separator membrane electrolyte and its protective LIPON coating and finally the liquid iodine cathode. The focus of this project is on the LiSES-based anode, with the studies on the liquid iodine cathode and the LIPON coating being complementary studies to better understand the anode. The next chapter, Chapter 3, will cover the experimental techniques for this project.
Chapter 3  Experimental Techniques

Section 3.1  Chapter Outline

There are four main parts of this project. The first is the synthesis and characterization of the PAH-based LiSES. The second part is on the electrochemical studies involving the fabrication of a working half-cell and subsequently a full-cell. The third part is on the synthesis and characterization of an iodine catholyte for the full-cell. Finally, the last part of the project involves miscellaneous experiments such as fabrication and characterization of a protective coating for the solid electrolyte to increase its lifespan and formulation of new types of anolytes and catholytes. This chapter will describe the experimental techniques and analysis methodologies used for all these experiments.

Section 3.2 will describe the preparation process of LiSES. Sections 3.3 to 3.4 are the characterisation experiments for the LiSES with Section 3.3 covering the conductivity experiments for studying the LiSES’s conductivity and Section 3.4 describing the FTIR Spectroscopy experiment. The test cell design and set-ups are detailed in Section 3.5. Section 3.6 covers the preparation process for the Iodine catholyte and Section 3.7 describes the electrochemical generation of both LiSES and Iodine in a full-cell configuration. Section 3.8 describes the UV-VIS Spectroscopy experiments for characterising both the LiSES and the Iodine catholyte. Section 3.9 describes the constant load full cell discharge experiments. Section 3.10 describes the OCV measurement experiments for the half and full cell configurations. The rationale, fabrication and impedance study of protective coating on the solid electrolyte membrane will be depicted in Section 3.11. Finally, Section 3.12 wraps up this
chapter by covering the various miscellaneous experiments such as new catholytes and new PAHs for the liquid lithium battery, all of which will lay the foundations for future works.

Section 3.2 Preparation of the Li-SES

The entire process of preparing the Li-SES was carried out in an argon atmosphere inside a Model EQ-VGB-4, MTI Glovebox. The lithium foils, anhydrous tetrahydrofuran (THF) and poly-aromatic hydrocarbons (PAH) were purchased from Sigma Aldrich.

Only the following PAHs have been used as electron acceptors in this study: biphenyl and naphthalene. Figure 3.1 shows the molecular structures of these PAH. Both of these PAHs are solids at room temperature and require a solvent (in this case THF) to form a solution.

![Molecular structures of naphthalene and biphenyl](image)

**Figure 3.1:** Molecular structures of naphthalene and biphenyl.
There are two parts to the preparation process. Firstly, stoichiometric amounts of THF, PAH and Li were measured out separately. Next, the PAH was dissolved in THF in a transparent glass bottle to give a clear solution. For both naphthalene and biphenyl, the resulting solution is colourless. Stirring was done with a Teflon coated magnetic stirrer bar after which the stirrer bar was removed from the solution when all the PAH had dissolved. Next, the Li foil (cut into small slices) were added to the PAH/THF solution and the mixture was subjected to overnight stirring using borosilicate glass-coated stirrer. No Teflon-coated stirrer bar was used for the dissolving of Lithium in the PAH/THF solution because contact between either the metallic lithium or the resulting Li-SES with the stirrer bar’s Teflon coating can result in a chemical reaction in which the F from the Teflon is extracted to form LiF. What is left of the Teflon on the stirrer bar’s coating becomes C. The flowchart for preparation of LiSES is shown in Figure 3.2.

The LiSES will be represented in the later chapters in the form of $\text{Li}_x(\text{PAH})(\text{THF})_n$ where the subscripts $x$ and $n$ denote the number of moles of Li and THF present in the solution for one mole of PAH. The italicised symbols $\beta$ and $N$ will be used to represent the biphenyl and naphthalene respectively.
The goals of preparing LiSES samples of different stoichiometric amounts of Li and PAH and then to measure their conductivities are: (1) To obtain an optimal ratio of Li:PAH:THF which will yield the Li-SES with the highest conductivity, and (2) To obtain an Li-SES that can yield the highest energy density per litre, depending on the amount of metallic lithium dissolved in one litre of the LiSES solution. The following section will cover the conductivity measurement technique used.
Section 3.3 Conductivity Measurements

3.3.1 Conductivity Concept and Equipment

The conductivity of a solution refers to its ability to sustain an electrical current and is measured in S/cm. The conductivity, \( \sigma \), is a characteristic of the solution and does not depend on geometrical factors. It is a property of the solution at a particular temperature that will remain constant unless its composition is changed. For a simple two-electrode cell of uniform cross-section, \( A \), with electrodes separated at both ends by a distance, \( l \), the conductivity of the solution is given by the following equation [122]:

\[
\sigma = G \left( \frac{l}{A} \right) \tag{3.1}
\]

where \( G \) is the conductance of the solution

From Ohm’s Law,

\[
\Delta V = IR \tag{3.2}
\]

where \( I \) (measured) is the current through the solution across the electrodes,

\( \Delta V \) is the a.c potential difference (applied) across the electrodes and

\( R \) is the resistance of the solution \( \left( R = \frac{1}{G} \right) \)

The conductance, the reciprocal of \( R \), can then be obtained as follows:
\[ G = \frac{I}{\Delta V} \]  

However, the two-electrode cell method is unable to account for possible damage or contamination to the electrodes’ surfaces, such as from deposits formation on the surfaces of the electrodes which will increase the contact resistance [123]. A more reliable technique is to use the four-electrode cell principle. The four-electrode cell uses a reference voltage to compensate for any damage to the electrode plates or electrodes’ contamination [124]. The reference voltage ensures that measurements indicate the actual conductivity of the solution independent of the condition of the electrodes.

For this project, a TetraCon 325 Standard conductivity cell probe with a measurement range of 1 \( \mu \text{S/m} \) to 2 \( \text{S/cm} \) is used to measure the conductivity of the Li-SES. The probe is attached to a Cond3310 meter. The TetraCon 325 cell utilizes the four-electrode measuring principle.

**Figure 3.3** shows the schematic diagram of the TetraCon 325 conductivity probe cell [125]. For measurements, the conductivity cell is held vertically and immersed in the Li-SES up to the dotted line in **Figure 3.3**.
Part    Name
1    1 pair of voltage electrodes
2    1 pair of current electrodes
3    Temperature sensor
4    Shaft
5    Connection Head

Figure 3.3: TetraCon 325 probe’s schematic diagram. (Adapted from Ref [125] with permission from Xylem Analytics, Inc.).

Measurements of the conductivity of LiSES samples at room temperature are carried out in the glovebox in argon atmosphere to avoid contamination with moisture and air. The meter is pre-calibrated using a standard KCl solution before use.

3.3.2 Conductivity versus Temperature

The Li-SES was sealed inside the glovebox by wrapping parafilm around the whole bottle before it was taken out and immersed in a container of dry ice. The LISES was cooled down to ~ 8 °C (which takes approximately 15 min), before it was transferred back into the glovebox. After that, the bottle was unsealed and the
Chapter 3 – Experimental Techniques

contents transferred into an insulated container. The conductivity of LiSES was then measured as its temperature slowly rose to that of ambient temperature (~ 26 °C). The whole process took about one to two hours. A graph of conductivity versus temperature was then plotted to determine the relationship between the LiSES’s conductivity and temperature.

Section 3.4 FT-IR Spectroscopy

FT-IR Spectroscopy uses IR radiation which is not energetic enough (low frequency) to cause electronic transitions in the sample’s molecules, but can cause the sample’s molecules to undergo vibrational and rotational changes [126].

The FT-IR spectra of the LiSES anolytes and the iodine catholyte are obtained using a Shimadzu IRPrestige-21 and a Perkin Elmer Frontier. The spectra are obtained using the absorbance mode of the spectrometers instead of the transmittance mode. This is because in absorbance mode, the absorbance of the spectra, $A$, is directly proportional to $c$, the concentration of the sample whereas in transmittance mode, the transmittance of the spectra, $T$, is not directly proportional to the concentration of the sample. This is because of the Lambert Beer-Lambert Law [127], which has a first equation:

$$A = \log \left( \frac{I_0}{I} \right) = \log \left( \frac{1}{T} \right)$$

(3.4)

where $A$ is the absorbance

$T$ is the transmittance.

$I_0$ is the incident light’s intensity.

72
I is the light intensity after it has passed through the sample.

And a second equation:

$$A = \varepsilon bc$$  \hspace{1cm} (3.5)

where

\(\varepsilon\) is the molar absorptivity (absorption coefficient) with units of \(\text{L mol}^{-1}\text{cm}^{-1}\)

\(b\) is the path length of the potassium bromide (KBr) glass cell in which the Li-SES sample is contained in cm (sample thickness).

\(c\) is the concentration of the sample in \(\text{mol L}^{-1}\).

Since samples of different Li concentrations were studied (different Li:PAH mole ratios), it was worthwhile to look at the absorbance of the samples so that any changes in peak intensities could be related directly to the Li concentration of the samples.

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\(b\) is the path length of the potassium bromide (KBr) glass cell in which the Li-SES sample is contained in cm (sample thickness).

\(c\) is the concentration of the sample in \(\text{mol L}^{-1}\).

Since samples of different Li concentrations were studied (different Li:PAH mole ratios), it was worthwhile to look at the absorbance of the samples so that any changes in peak intensities could be related directly to the Li concentration of the samples.

\(\varepsilon\) is the molar absorptivity (absorption coefficient) with units of \(\text{L mol}^{-1}\text{cm}^{-1}\)

\(b\) is the path length of the potassium bromide (KBr) glass cell in which the Li-SES sample is contained in cm (sample thickness).

\(c\) is the concentration of the sample in \(\text{mol L}^{-1}\).

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\(c\) is the concentration of the sample in \(\text{mol L}^{-1}\).

Since samples of different Li concentrations were studied (different Li:PAH mole ratios), it was worthwhile to look at the absorbance of the samples so that any changes in peak intensities could be related directly to the Li concentration of the samples.
Figures 3.4a and 3.4b shows the KBr glass cell setup used for storing the Li-SES samples. In Figure 3.4a, the KBr glass cell is shown in a horizontal position. Loading of a sample into the cell was accomplished inside a glove box (argon atmosphere). The sample was injected using a glass syringe via either of the holes covered by the Teflon stoppers indicated by the red arrows. Both stoppers had to be uncovered to allow the sample liquid to go into the cell. Only a very small quantity (< 1ml) of the sample was needed. The sample formed a thin layer between the twin pieces of thick KBr glass plates at the location indicated by the red dotted line. After the Teflon stoppers were put back firmly in place, the cell was quickly transferred into the FTIR spectrometer to minimize the air from outside the cell from reaching the LiSES sample. Figure 3.4b shows the cell mounted into the spectrometer in a vertical position. After the spectrum collection for each sample was completed, the cell was cleaned by flushing it first with liquid chloroform and then with dry argon gas through the cell holes.
Section 3.5 Test Cell Design and setup

3.5.1 Basic Test Cell Concept & Materials Testing

In 2010, a simple prototype Li-SES (Solvated-Electrons-Solution)//air model was patented by Prof Rachid Yazami as proof-of-concept for the PAH-based LiSES cell. The schematic diagram of the cell is shown in Figure 3.5.

**Figure 3.5**: Schematic diagram of the Li-SES// air prototype model. (Adapted from Ref: [18] with permission from Prof Rachid Yazami.)
The test cell shown in Figure 3.5 is H-shaped with the solid electrolyte ceramic membrane located in the middle of the cell. Epoxy glue (Torr Seal) is used to prevent leakage of liquids from either side of the membrane across the membrane or out of the cell. The solid electrolyte used is Li$^+$ conducting LTAP by Ohara, Inc. as described in Chapter 2. As shown in Figure 3.5, the Torr Seal is applied onto three locations on the cell at the centre of the H cell to secure the membrane and at the top of each of the two hermetic caps to prevent air from entering the cell from the grooves between the stainless steel wires and the caps. The metal grids and stainless steel wires serve as the current collectors. The liquid anode (anolyte) and liquid cathode (cathode) are to be loaded into the glass tubes (cell arms) and sealed shut with hermetic tops to make them air-tight. In the event that air is used as the cathode material, the top of the cell arm containing the liquid cathode will be unscrewed to allow air from outside to reach the liquid cathode. The characteristics of this new Li-SES//air cell are as shown in Tables 3.1 and 3.2.

### Table 3.1 Characteristics of Li-SES//air battery (with oxygen as the cathode)

<table>
<thead>
<tr>
<th>Cell Structure:</th>
<th>Li-SES (Anode)// Li-conducting ceramic membrane //Oxygen (Cathode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge reactions</td>
<td>Anode: Li$_n$(PAH) $\rightarrow$ $n$Li$^+$+$n$e$^-+PAH</td>
</tr>
<tr>
<td></td>
<td>Cathode: $n$Li$^+$+$n$e$^-+\frac{n}{2}$O$_2$ $\rightarrow$ \frac{n}{2}$Li_2$O$_2$</td>
</tr>
<tr>
<td></td>
<td>Overall cell discharge reaction: Li$_n$(PAH)+\frac{n}{2}$O$_2$ $\rightarrow$ \frac{n}{2}$Li_2$O$_2$+PAH</td>
</tr>
</tbody>
</table>
Table 3.2  Characteristics of Li-SES//air battery (with water as the solvent)

<table>
<thead>
<tr>
<th>Cell Structure:</th>
<th>Li-SES (Anode)// Li-conducting ceramic membrane //Water (Cathode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge reactions</td>
<td>Anode: Liₙ(PAH) → nLi⁺e⁻ + PAH</td>
</tr>
<tr>
<td></td>
<td>Cathode: nLi⁺ + ne⁻ + nH₂O → nLiOH + \frac{n}{2}H₂</td>
</tr>
<tr>
<td></td>
<td>Overall cell discharge reaction: Liₙ(PAH) + nH₂O → nLiOH + \frac{n}{2}H₂ + PAH</td>
</tr>
</tbody>
</table>

Using a conservative assumption, the two systems shown in Tables 1.2 and 1.3 can deliver energy densities of 695 Wh/kg and 1470 Wh/kg, respectively [18].

However, the prototype shown in Figure 3.5 cannot be used for this project due to the following limitations of the cell:

1. Torr Seal can partially be dissolve in LiSES, hence it is likely to contaminate the LiSES liquid anode.

2. Torr Seals are extremely difficult to remove once hardened, making it very difficult to retrieve the fragile solid electrolyte membrane without breakage after each experiment, as well as to remove the current collector wires from the hermetic caps for replacement or maintenance (cleaning).

3. Teflon (from the Hermetic Caps) can react with LiSES to form LiF and C.
4. Teflon acts like a sponge for air, i.e the plastic is porous and allows air to enter into the cell over time. Teflon by itself is extremely hydrophobic. However, manufactured Teflon sheets and rods are often found to be porous [128-130]. Also, it is very difficult to clean contaminated Teflon by washing.

5. Longer term tests such as charge/discharge over a few days require the cell to be leak proof. The cell cannot just rely on the Torr Seal to hold the cell arms containing the liquid electrodes together. Instead, the cell has to be easy to dismantle and made from a material that is not porous to air.

3.5.2 Cell Design

The test cell design for this project is shown in Figure 3.6.

![Figure 3.6: Schematic diagram of test cell in the following configuration of: (-)Ni / Li-SES, LiI / LTAP Ceramic Membrane/ Catholyte / Ni(-)](image)
Both current collectors in Figure 3.6 are each made of a Ni mesh spot-welded onto Ni wire. No platinum meshes or wires are used because (1) LiSES reacts with Pt chemically to form an Li-Pt alloy, thus permanently damaging the current collector and (2) Pt is too expensive to be used as a single-use consumable. Photographs of the final prototype cell for this project are shown in Figure 3.7.

**Figure 3.7**: Test cell consists of two glass side-arms for the liquid electrodes, a PEEK cap as the lid for each side arm, a central portion made of PEEK for securing the LTAP membrane and an external aluminium screw-sleeve for tightening.
3.5.3 Test Cell Plastic Materials Selection Process

Due to the corrosive effect of LiSES and its solvent THF upon many plastics, an appropriate polymer material had to be selected for the test cell. Five different forms of plastics were tested for their chemical resistance against LiSES, namely: Acrylic, Pomalux, Durlin, PEEK (Poly-Ethyl-Ether-Ketone) and Nylon. (Separately, Teflon had already been tested against LiSES and its surface was found to turn black (carbon) permanently, even though it did not break apart.) These materials were selected for testing because they were easily accessible in local plastic machining workshops.

Sample pieces of the above mentioned plastics are soaked in a sealed bottle filled with 2 ml of Li1.0N(THF)11.1 inside the Ar-filled glovebox for about 3 days. After that, they are rinsed inside the glovebox with anhydrous THF and dried. Their masses are compared (weighed) before and after their immersion in LiSES. Table 3.3 shows the results of the LiSES treatment.

Table 3.3 Mass of plastic before and after immersion in LiSES

<table>
<thead>
<tr>
<th>Bottle</th>
<th>Plastic</th>
<th>Mass before</th>
<th>Mass after</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acrylic</td>
<td>168.7</td>
<td>Degraded</td>
</tr>
<tr>
<td>2</td>
<td>Pomalux (change in colour)</td>
<td>554.2</td>
<td>594.9 ↑</td>
</tr>
<tr>
<td>3</td>
<td>Derlin</td>
<td>320</td>
<td>342.4 ↑</td>
</tr>
<tr>
<td>4</td>
<td>PEEK (Poly-Ethyl-Ether-Ketone)</td>
<td>436.7</td>
<td>438.2</td>
</tr>
<tr>
<td>5</td>
<td>Nylon (slight change in colour)</td>
<td>370.7</td>
<td>370.97</td>
</tr>
</tbody>
</table>
The acrylic was degraded after its immersion in the LiSES as shown in Figure 3.8.

![Figure 3.8: The transparent acrylic chip ((a) BEFORE) disintegrated after its immersion in LiSES ((b) AFTER) into brown fragments and powder.](image)

All the other plastic samples, with the exception of PEEK, showed either a change in mass or colour. Hence the plastic material selected for test cell construction is PEEK. Preliminary trial tests for prototype cells using PEEK parts and Teflon parts showed that PEEK is more effective in keeping the air from entering the cell as compared to Teflon.

### 3.5.4 Half Cell Configuration Setup

In the event that the test cell shown in Figure 3.6 is to be used for half-cell configuration set-up, one of the Ni-mesh will be wrapped with a fresh metallic Li foil. The half-cell is schematically described as follows:

\[
(+) \text{Ni} / \text{LiSES} / \text{LTAP Ceramics membrane} / \text{Li, 1 M LiPF}_6 \text{ in EC:DEC} / \text{Ni} (–)
\]
Note: Metallic Li, with an electrode potential lower than that of LiSES, becomes the anode of this cell configuration.

The metallic Li foil is immersed in an electrolyte solution of 1 M LiPF₆ in EC:DEC (1:1 vol.%) This configuration allows the measurement of standard electrode potentials of different LiSES samples versus metallic lithium.

Section 3.6 Iodine Liquid Cathode Preparation

Anhydrous iodine beads and anhydrous methanol are both purchased from Sigma Aldrich whereas anhydrous lithium iodide is obtained from Alfa Aesar. The liquid cathode is made up of iodine dissolved in methanol. The preparation process is carried out in the glovebox in argon atmosphere. First, 0.9 M lithium iodide is dissolved into the anhydrous methanol to form a solution of LiI/methanol prior to the addition of iodine. Next, anhydrous elemental iodine beads are dissolved into the LiI/methanol solution to the required concentration, $c$, which is in the range of $0 \text{ M} \leq c \leq 1.0 \text{ M}$. 
Section 3.7 Electrochemical Generation of LiSES & Iodine

3.7.1 Full Cell Configuration setup

For this experiment, the anolyte used is 0.9 M of lithium iodide in a solution of 0.5 M Biphenyl (β) in THF. The catholyte used is 0.9 M of lithium iodide dissolved in methanol. 25 ml of each solution is used for the cell. Initially, both anolyte and catholyte are colourless. The uncharged full-cell, with an OCV = 0 V, similar to the setup shown in Figure 3.6 is schematically described as follows:

(+){Ni/ 0.5M β(THF), 0.9M LiI / LTAP Ceramics membrane/ 0.9M LiI, Methanol /Ni(-)}

*Note*: Metallic Li, with an electrode potential lower than that of LiSES, becomes the **anode** of this cell configuration.

Cyclic voltammetry is conducted on the cell in argon atmosphere. Glass coated magnetic stirrers are placed in both anolyte and catholyte chambers to aid the mass transport of the ions in the solutions. The uncharged cell is first charged to 4.4V and then cycled between 0.8 V and 4.4 V over 8 cycles.

The custom-made magnetic stirrers used in the cell are glass-coated instead of Teflon-coated. This is to prevent the chemical reaction between Teflon and LiSES from taking place.

3.7.2 Qualitative Analysis of the charged anolyte and catholyte

A direct proof of Li-SES formation is given by the following test: Cell at its charged state up to 4.4 V is removed from the glovebox and a few drops of the anolyte are added to a dilute aqueous HCl solution. Any observed evolution of gas bubbles
Chapter 3 – Experimental Techniques

will most likely be H₂ gas, which will indicate that Li-SES is formed in the anolyte solution:

$$\text{Li-SES} + \text{HCl} \rightarrow \text{LiCl} + \frac{1}{2}\text{H}_2$$ (3.6)

Separately, a Li-SES solution of the composition Li₂₀β(THF)₂₂₂ is also prepared chemically and a few drops of this Li-SES is also added to a beaker of dilute HCl for comparison.

For the electrochemical formation of I₂ from I⁻, there are two indicators: (1) The solution shows a colour change from colourless to dark orange, and (2) a colour change of the charged catholyte from dark orange to blue black by adding a few drops of the charged catholyte solution to starch and distilled water. This is due to the fact that I₂ molecules will form I₃⁻ with I⁻, which can then slip into the amylose coils of the starch solution to form a deep blue colour [131].

Section 3.8 UV-Vis Spectroscopy

UV-Vis radiation falls in the wavelength ranges [132, 133] of ~160 nm to 400 nm for UV and 400 nm to 780 nm for visible light. Unlike the higher wavelengths IR radiation of FTIR spectrometer which causes vibrational transitions in molecules, the UV-Vis radiation causes electronic transitions in molecules, exciting their electrons from the ground state to higher energy states [133].

UV-Vis spectroscopy measurements were carried out with a Shimadzu UV2450 spectrometer using a scan speed of 400 nm/min. The baseline correction procedure was executed prior to each measurement session. UV-Vis spectroscopy is used for this project to detect the formation of I₂/I₃⁻ from the electrochemical oxidation
of $\Gamma$ [134] as well as for the detection of the electrochemical formation of LiSES, as described in Section 3.7.

Section 3.9 Constant load (resistance) Discharge Test

A ceramic 1 kΩ resistor is used for the constant load cell discharge experiments.

An APPA 505 True RMS Multimeter cum data-logger was used to register the data points for the constant load discharge. The circuit diagram for the experiment is shown in Figure 3.9.

![Circuit Diagram](image)

**Figure 3.9:** The LiSES//I$_2$ cell is discharged across a 1 kΩ resistor as shown in the circuit setup.
Section 3.10 Half-cell OCV Measurements

For OCV measurements, the Li-SES is placed in a half-cell configuration with Li-metal as the reference electrode in contact with 1 M LiPF₆ in EC: DEC (volume ratio 1:1), a Li-ion conducting ceramic membrane serving as the separator and electrolyte between the Li-SES and Li-metal in the setup described in Section 3.5.4.

The OCV of the freshly prepared half-cell is measured at ambient temperature and atmospheric conditions. Subsequently, the half cell is placed in an ESPEC PR-1FP Temperature & Humidity Chamber for thermodynamic study, where its OCV is measured in the temperature range of 10 °C ≤ T ≤ 25 °C with the aid of an APPA 505 True RMS digital multi-meter cum data-logger.

Section 3.11 Concentration Cells

The concentration cell experiments use the same test cell as shown in Figure 3.6. Both current collectors are made of Ni but are each immersed in the same type of LiSES, but with different Li concentrations, separated by the Li⁺ conducting LTAP.

When the concentrations of the LiSES are the same, then the OCV of the cell is 0 V as it is in equilibrium. The concentration cell can be used for comparing the concentrations of LiSES samples. The LiSES sample with a higher Li concentration becomes the anode of the cell. The cell configuration of Figure 3.6 becomes:

(+) Ni / LiSES Sample 1 / LTAP Ceramics membrane / LiSES Sample 2 / Ni (-)

Using the Nernst Equation as shown in Equations (3.7a) & (3.7b), the unknown concentration of the LiSES sample can be determined.
Chapter 3 – Experimental Techniques

\[ E_1 = E^0 + \frac{RT}{F} \ln a_1 \] (3.7a)

\[ E_2 = E^0 + \frac{RT}{F} \ln a_2 \] (3.7b)

where \( a_1 \) and \( a_2 \) denote the activities of Li in the LiSES samples. Taking the activities to be the concentrations, \( c \), Equations (3.7a) & (3.7b) become:

\[
(3.7a) - (3.7b): \quad \Delta E = E_1 - E_2 = \frac{RT}{F} \ln \frac{c_1}{c_2}
\]

\[
\Rightarrow \quad \Delta E = E_1 - E_2 = 0.059 \log_{10} \frac{c_1}{c_2}
\] (3.8)

The measured OCV of the concentration cell is \( \Delta E \).
Section 3.12 LIPON coating Fabrication & Analysis

3.12.1 Background

As described in Chapter 2, pristine LTAP is chemically unstable when it is in contact with either metallic Li or LiSES, hence the need for a protective coating. Figure 3.10 shows the effect of immersion of the pristine LTAP into LiSES over time.

![Figure 3.10: Effect of LiSES on (a) pristine LTAP is shown in (b) and (c). After 120 h, the membrane has completely disintegrated. (Figure 3.10(a) is adapted from Ref: [97] with permission from Ohara, Inc., Japan.)](image)

3.12.2 Fabrication Process

LIPON is coated onto LTAP by the magnetron sputtering technique using a target of Li$_3$PO$_4$ at Ar/N$_2$ ambient temperature condition. The deposition parameters for the process are listed in Table 3.4.

LIPON is coated on the side of the LTAP membrane that is facing the LiSES in the test cell. The pristine LTAP membranes used have an average thickness of 150 \( \mu \text{m} \)
each. After the LIPON coating, the total thickness of each membrane will be around 150.5 μm.

Table 3.4  Deposition parameters for LIPON coating by magnetron sputtering

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure (Torr)</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>Working pressure (mTorr)</td>
<td>4</td>
</tr>
<tr>
<td>Ar:N$_2$ gas pressure ratio</td>
<td>10 sccm : 20 sccm</td>
</tr>
<tr>
<td>Plasma etching duration</td>
<td>15 min</td>
</tr>
<tr>
<td>Substrate temperature ($^\circ$C)</td>
<td>-</td>
</tr>
<tr>
<td>RF Power density of Li$_3$PO$_4$ (W/cm$^2$)</td>
<td>1.1</td>
</tr>
</tbody>
</table>

### 3.12.3  Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a technique used in this project to compare the resistance of LTAP in its LIPON-coated form and uncoated form as well as the resistance of the LIPON film [33, 108]. The sample (uncoated LTAP or LIPON coated) was placed between two pieces of stainless steel. The scanning frequency range was from 1 MHz to 10 mHz. The signal amplitude was set at 10 mV. The measurement is carried out at ambient temperature.
Section 3.13  

**Experiment on other types of catholytes &**

**Conclusion**

Other possible candidates for cathode solutions are explored. Three types of potassium salts, namely potassium manganate (VII) (KMnO$_4$), potassium dichromate (VI) (K$_2$Cr$_2$O$_7$) and potassium persulphate (K$_2$S$_2$O$_8$) were tested as aqueous cathodes versus the LiSES anode. These crystalline salts are all obtained from Alfa Aesar.

0.15 M aqueous cathode solutions of KMnO$_4$, K$_2$Cr$_2$O$_7$ and K$_2$S$_2$O$_8$ are separately prepared in charged full-cell configurations versus 1.0 M LiSES anode, Li/β(THF)$_{10.5}$. 0.04 M H$_2$SO$_4$ is used for acidification of KMnO$_4$ and K$_2$Cr$_2$O$_7$. H$_2$SO$_4$ is not necessary for aqueous K$_2$S$_2$O$_8$ because its redox reaction as shown in Equation (3.9) does not involve H$^+$.  

\[
[S_2O_8^{2-}] + 2e^- \rightleftharpoons 2[SO_4^{2-}] \quad \text{(3.9)}
\]

The cell is schematically described as follows:

(+) Ni/ 1 M LiSES/ Ceramics membrane/ 0.15 M K-salt(aq)/Ni (-)

The cell is cathode limited. Similar to the LiSES//I$_2$ charged cell, each one of the full cells is then discharged over a 1 kΩ constant resistance load. The OCV of each cell was recorded every 2 to 3 hours for each cell until the end of discharge.
Chapter 4  Characterisation Studies of Biphenyl-based & Naphthalene-based LiSES\textsuperscript{i,ii}

Section 4.1  Introduction and Chapter outline

This chapter is on the characterisation studies carried out on the poly-aromatic hydrocarbon (PAH)-based LiSES for this project, which forms the bulk of the scientific investigations for the PAH-based LiSES in this thesis. It is important to note that there is surprisingly very little specific literature available on the physical and electrochemical characterisation of PAH-based LiSES, hence the need for this fundamental study.

There are two kinds of PAH-based LiSES described in this chapter [135-137], prepared using biphenyl [137] and naphthalene as the electron receptors respectively. The biphenyl molecule consists of two weakly coupled benzene rings that are linked to each other by a C-C bond. When biphenyl is in its solid crystalline state at ambient temperature, it has a planar structure [138-140] whereas in solution [140-143], or in its crystalline state below 40 K [144] biphenyl adopts a twisted structure. One of the

\textsuperscript{i} Part of this chapter is adapted from my own publication adapted with permission from: K. S. Tan, A. C. Grimsdale, and R. Yazami, "Synthesis and Characterisation of Biphenyl-Based Lithium Solvated Electrons Solutions," \textit{The Journal of Physical Chemistry B}, vol. 116, pp. 9056-9060, Copyright 2012. American Chemical Society.

\textsuperscript{ii} Part of this chapter has also been used for a book chapter submission of which I am a co-author: A. Rinaldi, K. S. Tan, O. Wijaya, Y. Wang, and R. Yazami, "Chapter 11: Lithium-air batteries, for medium- and large-scale energy storage." in \textit{Advances in batteries for medium- and large-scale energy storage applications in power systems and electric vehicles}, C. Menictas, M. Skyllas-Kazacos, T. M. Lim, and S. Hughes, Eds., ed UK: Woodhead Publishing, 2014.
important differences between these two structures is the degree of $\pi$-electron conjugation, which is much greater when the rings are coplanar. The amount of $\pi$-electron conjugation can be changed drastically by the addition of electrons to the biphenyl molecule such as in a SES or by the excitation of an electron in the biphenyl molecule [145]. Like biphenyl, naphthalene is a PAH which possesses a pair of benzene rings. However, the pair of benzene rings in naphthalene is fused together with each ring sharing two carbon atoms [146, 147]. In solution, the naphthalene molecules cannot take on a twisted structure like biphenyl. However, the benzene rings may bend along the fused C-C bond, so that the molecule is no longer planar, although the deviation from planarity is much less than in biphenyl.

This chapter describes a systematic study of the LiSES using FTIR spectroscopy and conductivity measurements in a broad range of $x$ and $n$ compositions, as well as half-cell OCV measurements and thermodynamic studies. Section 4.2 covers the electrical conductivity studies carried out on LiSES which verifies its metallic nature. Section 4.3 describes the FTIR results for identification of solvated electrons as well as proposals for possible mechanisms for the formation of LiSES. Section 4.4 covers the OCV (vs Li/Li$^+$) measurements of the LiSES half-cells as well as thermodynamics studies. Section 4.5 describes the concentration cell experiments carried out on the LiSES. Section 4.6 is the conclusion of this chapter which summarizes the results and their scientific implications for LiSES full cell design.
Section 4.2 Unveiling the metallic nature of LiSES via conductivity studies

4.2.1 Study on the volume change with PAH concentration in THF

Section 4.2 covers the conductivity studies on LiSES to unveil its metallic nature. The experimental procedure for the preparation of LiSES samples has been detailed earlier in Chapter 3. The biphenyl-based Li-SES samples consist of lithium, biphenyl ($\beta$) (a simple PAH) and anhydrous tetrahydrofuran (THF) in the molar composition range of $\text{Li}_x\beta(\text{THF})_n$ where $0.50 \leq x \leq 2.56$ and $4.11 \leq n \leq 24.7$. 

Equation (4.1) illustrates the formation of solvated electrons for $\text{Li}_x\beta(\text{THF})_n$ as follows:

$$x\text{Li} + \beta + n\text{THF} \rightarrow x\text{Li}^+ + [xe^-(1-\alpha)\beta, (n-m)\text{THF}]^{\alpha^-} + \alpha\beta + m\text{THF}$$ (4.1)

where $[xe^-(1-\alpha)\beta, (n-m)\text{THF}]$ represents $x$ moles of the solvated electrons, and $n\text{THF}$ and $m\text{THF}$ represent initial $n$ and final $m$ moles of free THF in the solution, respectively. $(n - m)$ thus represents the number of moles of THF bound to the solvated electrons and $\alpha$ the fraction of $\beta$ not bound to electrons. As for the naphthalene-based Li-SES, it is made up of lithium, naphthalene ($N$) as PAH and anhydrous tetrahydrofuran (THF) in the molar composition of $\text{Li}_yN(\text{THF})_n$ where $0.50 \leq y \leq 2.00$ and $3.08 \leq n \leq 23.4$. Equation (4.2) is a schematic of the Li-SES formation with naphthalene.

$$y\text{Li} + N + n\text{THF} \rightarrow y\text{Li}^+ + [y(e^-(1-\omega)N, (n-p)\text{THF})]^{\omega^-} + \omega N + p\text{THF}$$ (4.2)
Chapter 4 - Characterisation Studies of Biphenyl-based & Naphthalene-based LiSES

where \([ye^-(N),(n-p)THF]\) represents \(y\) moles of the solvated electrons, \(n\)THF and \(p\)THF represent the initial \(n\) moles and final \(p\) moles of free THF in the solution, respectively. \((n-p)\) thus represents the number of moles of THF bound to the solvated electrons and \(\omega\) the fraction of \(N\) not bound to electrons as in above.

Before preparation of the LiSES had begun, the total volume, \(V\), of PAH in THF solutions \(\text{Li}_nN(\text{THF})_n\) as a function of the PAH/THF molar ratio was first measured for both biphenyl and naphthalene. This is to allow for the computation of the actual concentration of PAH based on the final total volume of PAH in THF, where 100 ml of anhydrous THF is used to dissolve each of the two PAHs under an argon atmosphere in the glovebox since the entire LiSES preparation process was subsequently conducted under an argon atmosphere. One must note that in Singapore’s humid environment, when this volume expansion experiment was carried out in air, the results obtained were very different due to the rapid absorption of moisture by anhydrous THF from the air.

For biphenyl, its total volume, \(V\), of \(\text{Li}_n\beta(\text{THF})_n\) solution is measured as a function of the biphenyl/THF molar ratio from \(0 \leq \frac{1}{n} \leq 0.244\). For naphthalene, its total volume, \(V\), of \(\text{Li}_nN(\text{THF})_n\) solutions is measured as a function of the naphthalene/THF molar ratio from \(0 \leq \frac{1}{n} \leq 0.487\).

The relative volume expansions \(\frac{\Delta V}{V_0}\), where \(\Delta V = V - V_0\), \(V_0 =\) initial volume of THF = 100 ml, are depicted in Figure 4.1 for both PAHs which show linear dependence within the error bars following Equation (4.3) (for biphenyl) and Equation (4.4) (for naphthalene).
\[
\frac{\Delta V}{V_0} = 1.77 \left( \frac{1}{n} \right)
\]

(4.3)

\[
\frac{\Delta V}{V_0} = 1.38 \left( \frac{1}{n} \right)
\]

(4.4)

For the biphenyl, Equation (4.3) is valid up to the saturation of biphenyl in THF at ambient temperature in argon, which is around \( \frac{1}{n} = 0.24 \) ([\(\beta\]) = 2.10 M). For the naphthalene, Equation (4.4) is valid up to the saturation of naphthalene in THF at ambient temperature in argon, which is around \( \frac{1}{n} = 0.49 \) ([\(\beta\]) = 3.64 M).
Figure 4.1: $\frac{\Delta V}{V_0}$ of the Li$_0$$\beta$(THF)$_n$ and Li$_0$N(THF)$_n$ solutions (No Li present) solution versus the respective PAH/THF molar ratio of $1/n$ at ambient temperature in argon atmosphere.

The linear trend as shown by Equation (4.4) is similar to that of biphenyl dissolved in THF except that for biphenyl, the expansion of volume is larger than that of naphthalene when biphenyl is dissolved in THF (Since $\frac{\Delta V}{V_0} = 1.77\left(\frac{1}{n}\right)$). An increase in the viscosity of PAH/THF solutions is also observed for both PAHs when their concentrations increased. For instance, the viscosity of Li$_0$N(THF)$_n$ solution
Chapter 4 - Characterisation Studies of Biphenyl-based & Naphthalene-based LiSES

increases with naphthalene concentration when measured using a portable Viscolite 700-T15 Small Sample Viscometer from 0.3 cP \( (n = 23.4) \) to 0.8 cP \( (n = 3.08) \).

4.2.2 Preparation of LiSES samples

For LiSES prepared using biphenyl as the electron receptors, the colour of the \( \text{Li}_x\beta(\text{THF})_n \) solutions for \( 0.50 \leq x \leq 2.56 \) ranged from dark blue for low concentrations of Li to dark green for higher concentrations of Li. This is consistent with the observation reported by Melero et. al. [148] that when an excess of metallic lithium was dissolved into biphenyl in the mole ratio of 12:1 in THF, the suspension obtained was a deeply greenish-blue colour. They had attributed this colour to the formation of biphenyl dianions by lithium metal’s reduction of biphenyl in THF solution. As for the LiSES samples that used naphthalene as the electron receptors, the colour of the \( \text{Li}_y\beta(\text{THF})_n \) solutions for \( 0.50 \leq y \leq 2.00 \) ranged from dark bluish green (low Li concentration) to very dark bluish green (high Li concentration). The observation of the dark green colour formation from the dissolution of metallic lithium in the naphthalene/THF solution is quite consistent with the observations reported in other works [89, 149, 150], which attributed the colour to the presence of naphthalene anions generated by reduction of naphthalene in THF by lithium. These LiSES samples were then subjected to conductivity measurements and the results are presented in 4.2.3 and 4.2.4.
4.2.3 Conductivity measurements at ambient temperature.

All conductivity measurements on the LiSES at ambient temperature had been conducted in an argon atmosphere inside the glovebox to avoid contamination with moisture and oxygen. The results of the conductivity measurements are shown in Figure 4.2.

Figure 4.2: Li-SES electrical conductivity at ambient temperature at various PAH/THF compositions, ‘n’, Li/Naphthalene mole ratio ‘y’ in Li_yN(THF)_n compositional formulae and Li/Biphenyl mole ratio ‘x’ in Li_xβ(THF)_n.
From Figure 4.2, the highest absolute conductivity measurements for \( \text{Li}_x\beta(\text{THF})_n \) and \( \text{Li}_y\text{N}(\text{THF})_n \) at ambient temperature were 12.0 mS/cm for \( \text{Li}_{1.2}\beta(\text{THF})_{8.2} \) and 12.4 mS/cm for \( \text{Li}_{0.5}\text{N}(\text{THF})_{6.2} \) respectively. One difference observed between these two types of Li-SES was that although the \( \text{Li}_y\text{N}(\text{THF})_n \) had less THF solvent molecules in the solution composition of \( \text{Li}_{0.5}\text{N}(\text{THF})_{6.2} \), it required only a mole ratio of \( \text{Li} : \text{N} = 0.5:1 \) to achieve the highest conductivity of 12.4 mS/cm, whereas the \( \text{Li}_x\beta(\text{THF})_n \) required a mole ratio of \( \text{Li} : \beta = \sim 1:1 \) and hence more lithium per biphenyl to achieve 12 mS/cm.

Both types of Li-SES also shared the following common results:

1. When no lithium was present in the solutions, for instance \( \text{Li}_0\beta(\text{THF})_n \) and \( \text{Li}_0\text{N}(\text{THF})_n \), the solutions’ conductivities were below the measuring range of the conductivity probe. This indicates that when only biphenyl or naphthalene is dissolved in THF, the amount of charge carriers formed in the solution, if any, is too small to be detectable. Hence, conductivity readings were close to 0.

2. Conductivity could only be measured when metallic Li was added to the PAH/THF solutions. This indicates that sufficient charge carriers were formed in the process of Li dissolution.

3. Contribution to the conductivity readings comes from both the solvated electrons and the \( \text{Li}^+ \) in LiSES.
(4) LiSES with the highest Li content did not have the highest conductivity. This indicates that there is a trade-off between having the highest Li content in the LiSES’s solution composition and the highest conductivity.
4.2.4 Conductivity versus temperature.

The temperature dependence of conductivity $\sigma$ was studied for LiSES samples of the following solution compositions: $\text{Li}_x\beta(\text{THF})_{1.0.4}$ for $x = 0.5, 1, 1.5 \& 2$, and $\text{Li}_y\text{N}(\text{THF})_{1.0.4}$ for $y = 0.5, 1, 1.5 \& 2$, in the temperature range of $8 \degree C < T < 24 \degree C$.

Note that $\text{Li}_x\beta(\text{THF})_{1.0.4}$ or $\text{Li}_y\text{N}(\text{THF})_{1.0.4}$ corresponds to 1 M solution of $\beta (x = 1)$ or $\text{N} (y = 1)$ in THF.

**Figure 4.3:** Conductivity, $\sigma$ (mS/cm), versus temperature, $T$ ($\degree C$) of LiSES samples, $\text{Li}_x\beta(\text{THF})_{1.0.4}$ and $\text{Li}_y\text{N}(\text{THF})_{1.0.4}$. 

101
As shown in Figure 4.3, a metallic behaviour was observed for all the solutions in the temperature range of $8 ^\circ C < T < 24 ^\circ C$, i.e. decrease in conductivity with increase in temperature with a quasi-linear behaviour. At ambient temperature, for biphenyl-based Li-SES of the composition $\text{Li}_{1.0}\beta(\text{THF})_{10.4}$, $\sigma(T)$ follows the relationship: $\sigma = -0.0941T + 13.5$ ($\sigma$ in mS/cm and $T$ in $^\circ C$) with overall conductivity higher than all the $\text{Li}_y\text{N}(\text{THF})_{10.4}$ ($y = 0.5, 1, 1.5$ and 2) samples. The $\text{Li}_{0.1}\beta(\text{THF})_{10.4}$ sample had a very low Li concentration of 0.1 M, but it still exhibited a metallic behaviour. However, its slope of $-0.0177$ mS cm$^{-1}$K$^{-1}$ was very much lower than that of $\text{Li}_{1.0}\beta(\text{THF})_{10.4}$ and was much closer to a horizontal line’s slope of 0 mS cm$^{-1}$K$^{-1}$. This indicates that the Li concentration in LiSES is responsible for both its conductivity and metallic behaviour (i.e the magnitude of its negative slope) similar to that of the ammonia-based LiSES described in Chapter 2, Section 2.5.3. For the $\text{Li}_y\text{N}(\text{THF})_{10.4}$ ($y = 0.5, 1, 1.5$ and 2) samples, the solution composition of $\text{Li}_{0.5}\text{N}(\text{THF})_{10.4}$ yielded the highest slope among all of the four naphthalene-based samples even though its conductivity was overall below that of $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$ in the temperature range of $8 ^\circ C < T < 24 ^\circ C$. This indicates that the naphthalene-based LiSES was already metal-like at mole ratio of $\text{Li}:	ext{N} = 0.5:1$, but its optimal composition of $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$ yielded the highest conductivity.
4.2.5 Investigating the relationship between viscosity and conductivity.

Viscosity of the naphthalene-based LiSES samples, Li$_y$N(THF)$_n$ ($y = 0.5, 1, 1.5$ and 2), were also measured using a portable Viscolite 700-T15 Small Sample Viscometer inside the glovebox in argon atmosphere at ambient temperature condition. The results of the viscosity measurements are shown in Figure 4.4.

![Viscosity Measurement](image)

**Figure 4.4:** Li$_y$N(THF)$_n$ viscosity, $\eta$, presented in ln[$\eta$] at various PAH/THF compositions, ‘$n$’, and Li/Naphthalene mole ratio ‘$y$’.

Figure 4.4 shows that as both the Li concentration and naphthalene concentration in THF increases, the viscosity of the solution also increases. Looking at...
the relationship between the natural logarithm of viscosity, $\ln \eta$ versus $y$ for each $n$, with the exception of $[N] = 0.5$ M, $\ln \eta$ versus $y$ follows a linear trend for other $[N]$s. The fitted trends for the data in Figure 4.4 for $\ln \eta$ versus $y$ are shown in Table 4.1. The linear $\ln \eta$ versus $y$ relationships in the table indicates that for these LiSES solutions, there is complete dissolution of the metallic lithium. Also, each of the slopes in the linear relationships in Table 4.1 indicate $\frac{1}{\eta_{inh}}$, where $\eta_{inh}$ is a quantity known in polymer sciences as the inherent viscosity. However, for $[N] = 0.5$ M, the trend of $\eta$ versus $y$ plot is already linear and $\eta$ is directly proportional to $y$ according to the relationship: $\eta = 0.171y$ (Though for $[N] = 0.5$ M, $\ln \eta$ can also be expressed in terms of $y$ by $\ln \eta = 0.142y - 0.29$). This is not surprising given that the solutions are quite dilute for $n = 24.10$ and that dilute solutions with viscosity up to twice that of water have linear relationships between viscosity and concentration [151] (viscosity of water $= 0.894$ cP). Incidentally, the relationship of $\ln \eta$ versus $n$ for each $y$ was non-linear other than the feature that for each $y$, $\ln \eta$ increases with increasing concentration of $N$ (as $n$ becomes smaller), even though the naphthalene has completely dissolved into THF for each solution.
Table 4.1  Relationships between $\ln \eta$ and $y$ for each $n$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$[N]/\text{M}$</th>
<th>Fitted trend of $\ln \eta$ versus $y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.23</td>
<td>1.9</td>
<td>$\ln \eta = 4.05y - 0.19$</td>
</tr>
<tr>
<td>6.18</td>
<td>1.6</td>
<td>$\ln \eta = 3.35y - 0.49$</td>
</tr>
<tr>
<td>6.99</td>
<td>1.5</td>
<td>$\ln \eta = 3.20y - 0.69$</td>
</tr>
<tr>
<td>9.27</td>
<td>1.2</td>
<td>$\ln \eta = 1.33y - 0.34$</td>
</tr>
<tr>
<td>12.90</td>
<td>0.9</td>
<td>$\ln \eta = 1.17y - 0.84$</td>
</tr>
<tr>
<td>24.10</td>
<td>0.5</td>
<td>$\eta = 0.171y$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(\ln \eta = 0.142y - 0.29)$</td>
</tr>
</tbody>
</table>

As the lithium concentration in the LiSES increases initially from 0 M, the LiSES’s conductivity increases as well. Subsequently, as the lithium concentration is further increased, the LiSES’s conductivity reaches a maximum value before it decreases or levels off. Hence one can deduce that the conductivity of the LiSES at low Li and PAH concentrations should be controlled by the concentration of charge carriers, whereas the viscosity of the LiSES should be the controlling factor for conductivity at higher concentrations as indicated by the results shown in Figure 4.3 and Figure 4.4. The charge carriers in LiSES consist of both $\text{Li}^+$ and solvated electrons. Both the “cationic” and “anionic” contributions account for the conductivity measurements that have been carried out [137]. Therefore, it can be concluded here
that there is a trade-off between having a very high Li content in the LiSES and a high conductivity.

4.2.6 Conductivity comparison between metallic lithium and LiSES

The conductivity of metallic lithium at 300 K is $\sigma_{Li} = 1.047 \times 10^8$ mS/cm [152].

The conductivities for $Li_{1.2} \beta(THF)_{8.2}$ and for $Li_{0.5}N(THF)_{6.2}$ are $\sigma_{\beta \text{LiSES}} = 12$ mS/cm and $\sigma_{N \text{LiSES}} = 12.4$ mS/cm respectively. For one $Li_{1.2} \beta(THF)_{8.2}$ (visualize it as a single LiSES cluster of molecules), the mass is:

$$m_{\beta \text{LiSES}} = \frac{1.2(6.941)+154.21+8.2(72.11)}{6.022 \times 10^{23}} = 1.252 \times 10^{-21} \text{g.}$$

Similarly, for one $Li_{0.5}N(THF)_{6.2}$, $m_{N \text{LiSES}} = 9.61 \times 10^{-22} \text{g}$. The mass of a free electron is, $m_e = 9.109 \times 10^{-28} \text{g}$.

By taking the ratios of the conductivity of metallic lithium against conductivities of both $Li_{1.2} \beta(THF)_{8.2}$ and $Li_{0.5}N(THF)_{6.2}$, and the free electron mass against masses of both of $Li_{1.2} \beta(THF)_{8.2}$ and $Li_{0.5}N(THF)_{6.2}$, the following results are obtained:

Conductivity ratios: $$\frac{\sigma_{Li}}{\sigma_{\beta \text{LiSES}}} = 8.7 \times 10^6 \text{ and } \frac{\sigma_{Li}}{\sigma_{N \text{LiSES}}} = 8.4 \times 10^6$$

Mass ratios: $$\frac{m_{\beta \text{LiSES}}}{m_e} = 1.4 \times 10^6 \text{ and } \frac{m_{N \text{LiSES}}}{m_e} = 1.1 \times 10^6$$
These results imply a $10^6$ times difference in conductivity and in mass between the LiSES and metallic lithium.

From the Drude’s expression for electrical conductivity of metals [153], one can obtain the inverse relationship between electrical conductivity and electron mass as $\sigma \propto \frac{1}{m_e}$. From the ratio comparisons of the conductivity and mass between LiSES and Li, the conclusion is that the conductivity of LiSES is also inversely related to the effective mass of one solvated electron cluster, in the form of $\sigma_{\text{LiSES}} \propto \frac{1}{m_{\text{LiSES Cluster}}}$. 
Section 4.3 Characterization of solvated electrons by FTIR Spectroscopy

4.3.1 Introduction to the use of FTIR spectroscopy to study the formation of LiSES

Section 4.3 covers the identification of solvated electrons formed during metallic lithium dissolution in PAH/THF by FTIR spectroscopy. The procedure for conducting FTIR spectroscopy on the LiSES has been detailed in Chapter 3. This section will also propose the different mechanisms for the formation of the \( \text{Li}_x \beta(\text{THF})_n \) and the \( \text{Li}_x N(\text{THF})_n \). Even though both biphenyl and naphthalene are two-ring PAHs, the difference between them is that the naphthalene molecule consists of a pair of fused benzene rings which share a common carbon-carbon bond, whereas the pair of benzene rings of the biphenyl molecule are joined to each other by a single –C-C- bond between one carbon atom on each benzene ring.

4.3.2 FTIR Study on biphenyl-based LiSES.

For the biphenyl-based LiSES, FT-IR analysis was conducted on the following six samples: THF only \((x = 0, n = \infty)\); \(\beta\) in THF \((x = 0, n = 24.7)\) and for the \(\text{Li}_x \beta(\text{THF})_{24.7}\) samples with \(x = 0.56, x = 1.11, x = 1.67\), and finally \(x = 2.22\). The spectra are shown in Figure 4.5.

Spectra (1) to (4) in Figure 4.5 are from the \(\text{Li}_x \beta(\text{THF})_n\) samples where \(n = 24.7\) and \(x > 0\). Comparing with spectrum (5) where \(x = 0, n = 24.7\) (biphenyl/THF solution), additional modes are found which can be attributed to the formation of the
Chapter 4 - Characterisation Studies of Biphenyl-based & Naphthalene-based LiSES

Li-SES: 1604.77 cm\(^{-1}\), 1568.13 cm\(^{-1}\), 1323.17 cm\(^{-1}\), 1157.29 cm\(^{-1}\), 1107.14 cm\(^{-1}\), 1004.91 cm\(^{-1}\) and 987.55 cm\(^{-1}\). Besides the appearance of these new modes, spectrum (5) also has two existing modes that undergo changes in their intensity as the amount of Li increases in the Li-SES: They are (i) a peak shift from 1483.26 cm\(^{-1}\) to 1490.77 cm\(^{-1}\), including changes in intensity to the peak and (ii) changes in peak intensity at 659.66 cm\(^{-1}\).

Figure 4.5: Comparison between the FT-IR spectra of decreasing Li:β mole ratios in Li,\(\beta\)(THF)\(_n\) against the spectra of THF and biphenyl in THF.
Chapter 4 - Characterisation Studies of Biphenyl-based & Napthalene-based LiSES

Figures 4.6a, and 4.6b show the Li-SES spectra from Figure 4.5 after the background spectrum, $x = 0$, $n = 24.7$ is subtracted from spectra (1) to (4). In order to account for the additional modes appearing in the spectra of Li-SES, the following two possible models for LiSES formation were proposed.

Model 1 - $\text{Li}_1\beta\text{(THF)}_{n1}$ is formed first following Equation (4.5):

For $0 \leq m \leq 1$,

$$m\text{Li} + \beta\text{(THF)}_n \rightarrow m\left[\text{Li}_1\beta\text{(THF)}_{n1}\right] + (1-m)\beta\text{(THF)}_n; \quad (4.5)$$

which is followed by the formation of $\text{Li}_2\beta$ for $m > 1$:

$$\text{Li}_1\beta\text{(THF)}_{n1} + (m-1)\text{Li} \rightarrow (2-m)\left[\text{Li}_1\beta\text{(THF)}_{n1}\right] + (m-1)\left[\text{Li}_2\beta\text{(THF)}_{n1}\right] \quad (4.6)$$

Since biphenyl has two benzene rings connected to each other by a C-C bond, the postulate here is that one biphenyl molecule should be able to coordinate with at least 2 Li atoms. Hence from Equations (4.5) and (4.6), when $m = 2$, there is only $\text{Li}_2\beta\text{(THF)}_{n1}$. Model 1 is based on the assumption that 1 Li atom will react with 1 biphenyl molecule first in an excess of biphenyl in THF as shown in Equation (4.5). When each one of the biphenyl molecules in THF have reacted with an Li atom to form $\text{Li}_1\beta\text{(THF)}_{n1}$, subsequent Li atoms will then react with $\text{Li}_1\beta\text{(THF)}_{n1}$ to form $\text{Li}_2\beta\text{(THF)}_{n1}$.
Chapter 4 - Characterisation Studies of Biphenyl-based & Naphthalene-based LiSES

**Model 2**: Li$_2$β(THF)$_n$ is formed first following **Equation (4.7)**:

For $0 < m < 2$,

$$m\text{Li} + \beta(\text{THF})_n \rightarrow \frac{m}{2}\left[\text{Li}_2\beta(\text{THF})_n\right] + \left(1 - \frac{m}{2}\right)\beta(\text{THF})_n.$$  \hspace{1cm} (4.7)

For **Model 2**, **Equation (4.7)** is based on the assumption that 2 Li atoms will readily react with 1 biphenyl molecule first in an excess of biphenyl in THF to yield Li$_2$β(THF)$_n$ instead of Li$_1$β(THF)$_n$ as suggested in **Model 1**.

**Figure 4.6a**: FT-IR Spectrum in the 1700 cm$^{-1}$ to 1100 cm$^{-1}$ range, with biphenyl in THF background subtracted.
Figure 4.6b: FT-IR Spectra in the 1020 cm\(^{-1}\) to 980 cm\(^{-1}\) range and in the 680 cm\(^{-1}\) to 620 cm\(^{-1}\) range with biphenyl in THF background subtracted.

The relationship between the peak intensity of Li\(_x\)β(THF)\(_{24-x}\), and \(x\) for the seven new peaks from Figures 4.6a and 4.6b are presented in Figure 4.7.
Figure 4.7: Relationships between IR peaks’ intensity and the lithium composition $x$. 

(a) Peak intensity of 1604.77 cm$^{-1}$
(b) Peak intensity of 1568.13 cm$^{-1}$
(c) Peak intensity of 1323.17 cm$^{-1}$
(d) Peak intensity of 1157.29 cm$^{-1}$
(e) Peak intensity of 1107.14 cm$^{-1}$
(f) Peak intensity of 1004.91 cm$^{-1}$
(g) Peak intensity of 987.55 cm$^{-1}$
With the exception of the 1604.77 cm\(^{-1}\) peak in Figure 4.7a which shows the intensity of the peak increasing with the Li concentration in Li-SES, the other six peaks show an increase then a maximum about \(x = 2.46\) and a subsequent decrease in intensity. The origin of the 1604.77 cm\(^{-1}\) peak appearing after Li is added to the biphenyl in THF is likely due to the localization effect of the \(\pi\) electrons in the biphenyl aromatic rings. When a Li atom donates one electron to one of the two benzene rings of biphenyl, the biphenyl becomes an anion and the localized \(-\text{C=C-}\) in the anion ring shows up as the 1604.77 cm\(^{-1}\) peak. Also, the existing peak from the biphenyl in THF (spectrum (5) in Figure 3) is shifted from 1483.26 cm\(^{-1}\) to 1490.77 cm\(^{-1}\). The original peak at 1483.26 cm\(^{-1}\) is due to the aromatic \(-\text{C=C-}\) stretching vibration [154]. The peak shift from 1483.26 cm\(^{-1}\) to a higher wave number position of 1490.77 cm\(^{-1}\) indicates that the \(\pi\) electrons in the aromatic ring have become more localized [155].

For the other peaks in Figures 4.7b-g including the peak at 659.66 cm\(^{-1}\) from the biphenyl in THF spectrum in Figure 4.5, it can be seen that the peaks have a maximum intensity at the Li: \(\beta\) mole ratio of \(\sim 1:1\) before decreasing for higher mole ratios. These peaks are characteristic fingerprint peaks for Li-SES using biphenyl in THF. Accordingly, Model 1 seems more likely than Model 2 that is, the intermediate species formed when Li metal is dissolved in biphenyl in THF is initially \(\text{Li}_1\beta(\text{THF})_{n_1}\) followed by \(\text{Li}_2\beta(\text{THF})_{n_1}\). After every free biphenyl molecule has bonded with one Li, there will only be \(\text{Li}_1\beta(\text{THF})_{n_1}\) in THF. The subsequent product when Li is added to \(\text{Li}_1\beta(\text{THF})_{n_1}\) is \(\text{Li}_2\beta(\text{THF})_{n_1}\). From Figure 4.5, there are two additional peaks formed at 1604.77 cm\(^{-1}\) and 680.87 cm\(^{-1}\) when the Li / \(\beta\) ratio is greater than 1 (Spectra (1) and (2)). The appearance of these two additional peaks can
be attributed to the formation of $\text{Li}_2\beta(\text{THF})_{n1}$. Also, the intensity of these two peaks increases with increasing Li: $\beta$ mole ratio indicating an increase in the population of $\text{Li}_2\beta(\text{THF})_{n1}$.

Since $\text{Li}_2\beta(\text{THF})_{n1}$ is an asymmetric molecule, as more of $\text{Li}_2\beta(\text{THF})_{n1}$ are formed, the intensity of its characteristic peaks becomes higher. A symmetric molecule has IR-inactive symmetric stretches and bends and hence we expect fewer IR peaks for symmetric than unsymmetric molecules. When only $\text{Li}_2\beta(\text{THF})_{n1}$ molecules are left in the solution after all the $\text{Li}_2\beta(\text{THF})_{n1}$ have become $\text{Li}_2\beta(\text{THF})_{n1}$, the peaks intensities decrease. The peaks do not disappear totally because $\text{Li}_2\beta(\text{THF})_{n1}$ is not necessarily symmetrical and planar. While it might be possible for some molecules of $\text{Li}_2\beta(\text{THF})_{n1}$ to exist in a symmetric form in the SES, there might be other instances where the two benzene rings of the $\text{Li}_2\beta(\text{THF})_{n1}$ may not be planar. This is because of the structure of the biphenyl molecule, where the two benzene rings can rotate around their internal C-C bond which links both rings together.
4.3.3 FTIR Study on naphthalene-based LiSES.

For the naphthalene-based LiSES, the FTIR spectra of Li$_y$N(THF)$_n$ solutions are shown in Figure 4.8 for THF only ($y = 0$, $n = \infty$); $y = 0$ and $n = 23.4$ (naphthalene in THF only), and for $y = 0.5$, 1.0, 1.5 and 2.0, with the THF background spectrum subtracted.

![Figure 4.8](image)

**Figure 4.8:** FT-IR Spectra of Li$_y$N(THF)$_n$ in the 1600 cm$^{-1}$ to 600 cm$^{-1}$ range.

Spectra (1) to (4) in Figure 4.8 were obtained from the Li$_y$N(THF)$_n$ samples where $n = 23.4$ and $y > 0$. Comparing with spectrum (5) where $n = 23.4$ and $y = 0$, additional peaks were found which could be attributed to the formation of the Li-SES.
Additional peaks were for $0.5 \leq y \leq 1.5$: 710 cm$^{-1}$, 996 cm$^{-1}$ and 1184 peak which indicated the formation of LiSES. In addition, four more peaks appeared at 694 cm$^{-1}$, 970 cm$^{-1}$, 1411 cm$^{-1}$ and 1451 cm$^{-1}$ exclusively for spectrum (1), where $y = 2.0$.

In order to account for the appearance of these peaks for Li-SES, the following two possible models for Li-SES formation were proposed.

Model 1 – Two step formation of Li$_2$N(THF)$_n$

Step 1: Li$_i$N(THF)$_n$ is formed first following Equation 4.8:

$$mLi + N(THF)_n \rightarrow m\left[Li_iN(THF)_n\right] + (1-m)N(THF)_n', \quad (4.8)$$

where $n = mn_1 + (1-m)n'$

Step 2: Formation of Li$_2$N(THF)$_n$ according to Equation (4.9):

$$1 < m \leq 2$$

$$Li_iN(THF)_n + (m-1)Li^{+}pTHF \rightarrow (2-m)\left[Li_iN(THF)_n\right] + (m-1)\left[Li_2N(THF)_{n_2}\right] \quad (4.9)$$

where $n_2 = n_1 + \frac{p}{1-m}$

Table 4.2 shows the IR absorption bands for different Li$_i$N(THF)$_n$ solutions, which compares the presence/absence of the peaks 711 cm$^{-1}$, 788 cm$^{-1}$, 996 cm$^{-1}$, 1184 cm$^{-1}$ and 1488 cm$^{-1}$ in THF solvent and Li$_i$N for $y = 0, 0.5, 1.0, 1.5$ and 2.0. Of these
peaks, 711 cm\(^{-1}\), 788 cm\(^{-1}\), 1184 cm\(^{-1}\) and 1488 cm\(^{-1}\) can be attributed exclusively to the formation of solvated electrons in Li\(_y\)N(THF)\(_n\) with reference to the work of Abdullah et. al [156].

**Table 4.2** Prominent peaks associated with LiSES formation of Li\(_y\)N(THF)\(_n\). “0” indicates absence of a peak and each of the Roman numerals I to V denotes the presence of a peak with peak intensity from weakest (I) to strongest (V). Superscript * denotes equal intensities.

<table>
<thead>
<tr>
<th>(\nu) (cm(^{-1}))</th>
<th>THF only</th>
<th>Spectrum for Li(_y)N (y)</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>711</td>
<td>0</td>
<td>II</td>
<td>0</td>
<td>0</td>
<td>II</td>
<td>III</td>
<td>IV</td>
</tr>
<tr>
<td>788</td>
<td>0</td>
<td>III*</td>
<td>0</td>
<td>III*</td>
<td>III*</td>
<td>II</td>
<td>I</td>
</tr>
<tr>
<td>996</td>
<td>0</td>
<td>III</td>
<td>0</td>
<td>III</td>
<td>II</td>
<td>IV</td>
<td>I</td>
</tr>
<tr>
<td>1184</td>
<td>0</td>
<td>III</td>
<td>0</td>
<td>III</td>
<td>I</td>
<td>II</td>
<td>IV</td>
</tr>
<tr>
<td>1488</td>
<td>0</td>
<td>III</td>
<td>0</td>
<td>III</td>
<td>I</td>
<td>IV</td>
<td>I</td>
</tr>
</tbody>
</table>

The 711 cm\(^{-1}\) band appears only after Li is added to the naphthalene/THF solution and can be attributed to the formation of Li-SES and subsequent aromatic –C-H out-of-plane vibration.

The 788 cm\(^{-1}\) peak is present in the naphthalene/THF solution even without the addition of Li. It is attributed to an in-plane aromatic –CCC- vibration of the naphthalene molecule. It can be observed that the 788 cm\(^{-1}\) peak intensity decreases with increasing \(y\) and almost vanished for \(y = 2.0\). This can be due to the decrease in aromacity with the localization of \(\pi\) electrons after addition of the Li’s electron.
Chapter 4 - Characterisation Studies of Biphenyl-based & Napthalene-based LiSES

The 1184 cm\(^{-1}\) peak is associated with in-plane \(-C-H\) vibration of napthalene anion. This peak appears only after Li is added to the napthalene/THF solution. The strong intensity of this peak with \(y = 0.5\) can be due to the asymmetry of the Li\(_y\)N(THF)\(_{23.4}\) structure formed. Also, by \(y = 2.0\), there will be two Li pairing up with one napthalene molecule forming di-anion. The in-plane \(-C-H\) vibration contribution from both aromatic rings can also give rise to a high intensity for \(y = 2.0\).

The 1488 cm\(^{-1}\) peak is attributed to the in-plane aromatic ring’s \(-CCC-\) stretching of the napthalene anions. The peak intensity decreases with increase in \(y\) probably due to the symmetry of the Li\(_2\)N(THF)\(_{23.4}\).

Finally, the 996 cm\(^{-1}\) peak is also caused by the formation of napthalene anions. This mode comes about from a combination of both in-plane \(-C-H\) vibration and aromatic ring \(-CCC-\) vibration.

For the peaks 694 cm\(^{-1}\), 970 cm\(^{-1}\), 1411 cm\(^{-1}\) and 1451 cm\(^{-1}\) attributed solely to spectrum (1): Li\(_2\)N(THF)\(_{23.4}\), the 694 cm\(^{-1}\) is due to a combination of out-of-plane \(-C-H\) and aromatic ring \(-C-C-\) vibration of the napthalene anion. The 1411 cm\(^{-1}\) is attributed to a combination of in-plane \(-CCC-\) aromatic ring stretching and \(-C-H\) vibration. The 1451 cm\(^{-1}\) peak comes about from solely in-plane \(-C-C-\) aromatic ring stretching. At present, we can only say that the un-assigned peak 970 cm\(^{-1}\) is solely a characteristic peak for Li\(_2\)N(THF)\(_{23.4}\).

Due to the fact that peaks that appear only for spectrum (1), it is highly probable that Model 1 is valid (i.e. \(y = 2.0\) is not formed first). Furthermore, from the analysis of the FTIR spectra, no significant difference between the spectra of Li\(_{0.5}\)N(THF)\(_n\) and Li\(_1\)N(THF)\(_n\) could be seen. This suggests Li\(_{0.5}\)N(THF)\(_n\) and
Chapter 4 - Characterisation Studies of Biphenyl-based & Naphthalene-based LiSES

Li$_i$N(THF)$_n$ may be involved in an equilibrium between “stage 2” and “stage 1” formulations, respectively according to Equation (4.10):

$$\text{Li}_{0.5}N(\text{THF})_n \rightleftharpoons \frac{1}{2}\text{Li}_{1.0}N(\text{THF})_n + \frac{1}{2}N(\text{THF})_n$$

(4.10)

The results of a preliminary density functional theory (DFT) study indicated that in the Li-Naphthalene-THF system, Li$_2$(naphthalene) (-0.127 eV) is thermodynamically more stable than Li$_1$(naphthalene) (0.168 eV) at 0 K [80]. However, Li$_{1.0}$N(THF)$_n$ may be stabilized by entropy at ambient temperature ($T\Delta S \simeq -0.9$ eV) as discussed in Section 4.4.

4.3.4 Summary of the FTIR results

For Li$_i$β(THF)$_n$, it is possible to distinguish between the two forms, Li$_1$β(THF)$_n$ and Li$_2$β(THF)$_n$, from the intensity variations of the spectra’s prominent peaks in Figure 4.7.

For Li$_i$N(THF)$_n$, distinguishing between Li$_1$N(THF)$_n$ and Li$_2$N(THF)$_n$ is a more straightforward task from the appearance of the four additional peaks of 694 cm$^{-1}$, 970 cm$^{-1}$, 1411 cm$^{-1}$ and 1451 cm$^{-1}$ for $y = 2$.

Since wave numbers of characteristic peaks are in the fingerprint region of less than 1500 cm$^{-1}$ [132, 154], the spectra obtained for both Li$_i$β(THF)$_n$ and Li$_y$N(THF)$_n$ can also be used as reference spectra for future identification of LiSES formed using biphenyl/THF and naphthalene/THF.
Section 4.4 Determination of half-cell OCV (vs Li/Li\(^+\)) of LiSES and thermodynamic studies

4.4.1 Half-cell OCV measurements at ambient temperature.

For biphenyl-based LiSES, the OCV measurement at ambient temperature in a Li half-cell of the following configuration:

\[ (-) \text{Ni/ Li, 1 M LiPF}_6 \text{ in EC:DEC } / \text{Ceramics membrane/ Li}_{1.0}\beta(\text{THF})_{12.3}/\text{Ni (+) } \]

yielded an OCV of ~ 0.68 V.

For naphthalene-based LiSES, the OCV measurement at ambient temperature in a Li half-cell of the following configuration:

\[ (-) \text{Ni/ Li, 1 M LiPF}_6 \text{ in EC:DEC/ Ceramics membrane/ Li}_{1.0}\alpha(\text{THF})_{11.1}/\text{Ni (+) } \]

yielded an OCV of ~ 0.65 V.

Therefore, the standard reduction potentials of these two LiSES samples can be arranged with respective to metallic lithium as shown in Figure 4.9 (Taking the standard reduction potential of metallic lithium to be 0 V). Against the more electronegative metallic lithium, the two LiSES became cathodes in their respective half cells.
Table 4.9  Standard Electrode Potential versus Lithium

<table>
<thead>
<tr>
<th></th>
<th>Standard Electrode Potential versus Lithium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl-based LiSES</td>
<td>Li$^+$ + $e^-$ + $\beta$(THF)$<em>{12.3}$ ⇌ Li$\beta$(THF)$</em>{12.3}$ +0.68 V</td>
</tr>
<tr>
<td>Naphthalene-based LiSES</td>
<td>Li$^+$ + $e^-$ + $N$(THF)$<em>{11.1}$ ⇌ Li$N$(THF)$</em>{11.1}$ +0.65 V</td>
</tr>
<tr>
<td>Metallic Li:</td>
<td>Li$^+$ + $e^-$ ⇌ Li 0 V</td>
</tr>
</tbody>
</table>

**Figure 4.9** Standard reduction potentials of $Li_{1.0}\beta$(THF)$_{12.3}$ and $Li_{1.0}N$(THF)$_{11.1}$ versus metallic lithium at ambient temperature. The “$e_s$” denotes solvated electron.

### 4.4.2 Entropy changes for half-cell reactions.

The experimental procedure for measurement of half-cell open circuit voltage (OCV), $E$, of $Li_x\beta$(THF)$_n$ and $Li_yN$(THF)$_n$ in the controlled temperature range of $283.15 \, K \leq T \leq 298.15 \, K$ has been described earlier in Chapter 3, Section 3.10.

For $Li_0\beta$(THF)$_{10.4}$, the half cell configuration is described as follows:

$$ (+) \, Ni/ \, Li_x\beta$(THF)$_{10.4}/ \text{Ceramics membrane}/ \, Li, \, 1 \, M \, LiPF_6 \, \text{in EC:DEC/Ni (−)} $$

for $x = 0.5$ and 1.0.

For $Li_{1.0}N$(THF)$_{10.4}$, the half cell configuration is described as follows:

$$ (+) \, Ni/ \, Li_{1.0}N$(THF)$_{10.4}/ \text{Ceramics membrane}/ \, Li, \, 1 \, M \, LiPF_6 \, \text{in EC:DEC/Ni (−)} $$
The temperature profiles of $E$ for these three half-cells in the range of $285.15 \, \text{K} \leq T \leq 298.15 \, \text{K}$ are presented in Figures 4.10 and 4.11.

**Figure 4.10:** $E$, versus $T$ profile for $\text{Li}_x\beta(\text{THF})_{10.4}$, (where $x = 0.5, 1.0$) versus Li metal half-cell.
Figure 4.1: $E$, versus $T$ profile for Li$_{1.0}$N(THF)$_{10.4}$ versus Li metal half-cell.

From Figure 4.10, the temperature profiles of $E$ for both Li$_{0.5}$β(THF)$_{10.4}$ and Li$_{1.0}$β(THF)$_{10.4}$ are linear in the stated temperature range under study, with negative slopes. The linear relationships are:

For Li$_{0.5}$β(THF)$_{10.4}$: \[ E = -4.35T + 2037 \text{ (in mV)} \] (4.11)

For Li$_{1.0}$β(THF)$_{10.4}$: \[ E = -4.84T + 2157 \text{ (in mV)} \] (4.12)

From Equations (4.11) and (4.12), the entropy change, $\Delta S$, for each of these half-cells can be determined. According to the classical thermodynamics equation:

\[ -\nu FE(n, x) = \Delta G(n, x) = \Delta H(n, x) - T\Delta S(n, x) \] (4.13)

where $E$ is the OCV of the cell.
From the $E$ versus $T$ slope of the graphs in Figure 4.10, $\Delta S = \nu F \frac{\partial E}{\partial T}$, (4.14)

Equation (4.13) takes the form of:

$$\Delta H = -\nu F \left( E - T \frac{\partial E_0}{\partial T} \right)$$

(4.15)

Hence, $\Delta S(n,x) = F \left( \frac{\partial E(n,x,T)}{\partial T} \right)_{n,x}$

(4.16)

The calculated entropy changes are as follows:

For the half-cell reaction of $\text{Li}_{0.5} \beta(\text{THF})_{10.4}$, in which

$$0.5\text{Li}^+ + 0.5e^- + \beta(\text{THF})_{10.4} \rightleftharpoons \text{Li}_{0.5} \beta(\text{THF})_{10.4}$$

(4.17)

the entropy change, $\Delta S(10.4,0.5) = (0.5) F \left( \frac{\partial E(10.4,0.5,T)}{\partial T} \right)_{10.4,0.5} = -210 \text{ J/(K mol)}$

with its corresponding $\Delta H$ calculated to be $-98 \text{ kJ/mol}$ for all temperatures $T$.

For the half-cell reaction of $\text{Li}_{1.0} \beta(\text{THF})_{10.4}$, in which

$$\text{Li}^+ + e^- + \beta(\text{THF})_{10.4} \rightleftharpoons \text{Li}_{1.0} \beta(\text{THF})_{10.4}$$

(4.18)

the entropy change, $\Delta S(10.4,1.0) = (1.0) F \left( \frac{\partial E(x,T)}{\partial T} \right)_{10.4,1.0} = -467 \text{ J/(K mol)}$

with its corresponding $\Delta H$ calculated to be $-208 \text{ kJ/ mol}$ for all temperatures $T$.

The calculated $\Delta S$ for both $\text{Li}_{0.5} \beta(\text{THF})_{10.4}$ and $\text{Li}_{1.0} \beta(\text{THF})_{10.4}$ should be mostly configurational (mixing) entropy for each of their respective solution system. Incidentally, the OCV of the $\text{Li}_{1.0} \beta(\text{THF})_{10.4}$ half-cell at an initial temperature of 29.5
Chapter 4 - Characterisation Studies of Biphenyl-based & Napthalene-based LiSES

°C (302.7 K) before the experiment is \( E = 0.687 \) V, which is quite close to that of \( \text{Li}_{1.0}\beta(\text{THF})_{12.3} \) at ambient temperature of 25 °C in Section 4.4.1 and follows the linear relationship of Equation (4.12) as well as also yielding a calculated \( \Delta H \) of -208 kJ/mol.

For the \( \text{Li}_{1.0}\gamma(\text{THF})_{10.4} \) half–cell, Figure 4.11 presents a linear temperature profile of \( E \) of the following form:

\[
E = -3.01T + 1644 \quad \text{(in mV)}
\] (4.19)

in which \( E \) decreases with increasing \( T \).

Its half-cell reaction is:

\[
\text{Li}^+ + e^- + \gamma(\text{THF})_{10.4} \rightleftharpoons \text{Li}_{1.0}\gamma(\text{THF})_{10.4}
\] (4.20)

The entropy change of the \( \text{Li}_{1.0}\gamma(\text{THF})_{10.4} \) half–cell is:

\[
\Delta S(10.4,1.0) = (0.05) F \left( \frac{\partial E(x,T)}{\partial T} \right)_{10.4,1.0} = -290 \text{ J/(K mol)} \quad \text{and its corresponding \( \Delta H \)}
\]

= -159 kJ/mol. However, it has also been observed that beyond \( T = 298 \) K, there is a sharp drop in \( E \). At 27 °C (300.15 K), the OCV of the half-cell is measured to be ~0.65 V before and after the experiment.

The calculated entropy changes for the LiSES half cells are very high as shown in Table 4.3 as compared to the conventional \( \text{Li}_{x}\text{CoO}_2/\text{Li} \) (\( 0 < x \leq 1 \)) half cell which has an entropy change magnitude of < 10 \( k_B \)/atom [157]. This could be because the LiSES is in the liquid phase which gives the molecules more degrees of freedom than in solid electrode materials.
Table 4.3  Entropy changes for the LiSES/Li half cells for comparison against Li$_x$CoO$_2$/Li (where $0 < x \leq 1$) half cell

<table>
<thead>
<tr>
<th>Type of half cell</th>
<th>$\Delta S$ (J/(K mol))</th>
<th>$\Delta S$ ($k_B$/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{0.5}$ (THF)$</em>{10.4}$/Li</td>
<td>-210</td>
<td>-25.3</td>
</tr>
<tr>
<td>Li$<em>{1.0}$ (THF)$</em>{10.4}$/Li</td>
<td>-467</td>
<td>-56.2</td>
</tr>
<tr>
<td>Li$<em>{1.0}$ N(THF)$</em>{10.4}$/Li</td>
<td>-290</td>
<td>-34.9</td>
</tr>
<tr>
<td>Li$_x$CoO$_2$/Li (Ref: [157])</td>
<td>$-70 &lt; \Delta S &lt; 20$</td>
<td>$-8.42 &lt; \Delta S &lt; 2.41$</td>
</tr>
</tbody>
</table>
Section 4.5 Concentration Cell Experiments

4.5.1 Investigation of how half-cell OCV varies with LiSES concentration.

A stock solution of Li$_{1.0}$(THF)$_{1.1}$ was prepared from which the other LiSES concentrations were prepared by diluting the stock solution down with anhydrous THF. No Li salt was added to the LiSES as supporting electrolyte. The half cell was set up as described in Chapter 3, Section 3.5.4:

(+) Ni / LiSES / LTAP Ceramics membrane / Li, 1 M LiPF$_6$ in EC:DEC / Ni (-)

The LiSES becomes the cathode in this half-cell configuration because metallic Li is more electronegative than LiSES.

Figure 4.12a shows how the half cell’s OCV varies with the log of the LiSES concentration. The results do not show a linear trend and do not follow Nernst’s Equation. This could be due to the fact that LiSES is not ionic in behaviour but metallic as it is a mixed conductor (both ionic and electronic), hence the concentration of the solvated electrons in the LiSES solution also contributed to the OCV of the half cell.
Figure 4.12a resembled the profile of an OCV versus state-of-charge (SOC) for a lithium ion battery insertion electrode such as Li$_x$TiS$_2$ which is a solid solution mixed conductor. To verify that the profiles of these two different types of cells are similar, the data from Figure 4.12a was re-presented in the form of OCV versus $\ln\left(\frac{x}{1-x}\right)$, where $x$ denotes [Li$^+$]/1M (maximum concentration of LiSES used is 1 M) from Figure 4.12b. From Figure 4.12b, one could observe that the trend was linear:
\[ OCV = -0.15 \ln \left( \frac{x}{1-x} \right) + 1.69 \] (4.21)

This verifies that the two types of cells are similar and that LiSES is a mixed conductor liquid solution.

**Figure 4.12b**: OCV versus \( \ln \left( \frac{x}{1-x} \right) \) where \( x \) denotes \([\text{Li}^+]\) in Figure 4.12a.

### 4.5.2 LiSES concentration cell study.

The concentration cell was set up as described in Chapter 3, Section 3.11 in which the LiSES with lower Li concentration served as the catholyte:
Chapter 4 - Characterisation Studies of Biphenyl-based & Naphthalene-based LiSES

(+)(-) Ni/ LiSES, \( \text{Li}^+ \) (0.001 M) / LTAP Ceramics membrane / LiSES, \( \text{Li}^+ \) (1.0 M) /Ni (-)

For this study, the lower concentration LiSES sample of 0.001M was also obtained by diluting down the \( \text{Li}_{1.0}\beta(\text{THF})_{11.1} \) with anhydrous THF. The OCV of the cell was measured with and without the use of supporting electrolyte (0.05 M LiCl) added to both samples. The results are as follows:

Without 0.05 M LiCl, OCV = +1.75 V

With 0.05M LiCl, OCV = +0.37 V

The use of the supporting electrolyte significantly decreases the OCV of the concentration cell.

From the half cell reaction of LiSES:

\[
\text{Li}^+ + e^- + \beta(\text{THF})_n \rightleftharpoons \text{Li}\beta(\text{THF})_n \text{ where } e^-: \text{solvated electron} \quad (4.22)
\]

If Nernst’s Equation is to be applied to this half cell in the form as shown in Equation (4.23):

\[
E_{1.0M} - E_{0.001M} = -0.0592 \log \left( \frac{[\text{Li}^+]_{1.0M}}{[\text{Li}^+]_{0.001M}} \right) \quad (4.23)
\]

the calculated OCV is 0.178 V which is half the magnitude of the experimental OCV.

Since LiSES is not an ionic solution, Equation (4.23) is not valid. However, if the solvated electron’s concentration is to be taken into account as in Equation (4.24):

\[
E_{1.0M} - E_{0.001M} = -0.0592 \log \left( \frac{[\text{Li}^+]_{1.0M} [e^-]_{1.0M}}{[\text{Li}^+]_{0.001M} [e^-]_{0.001M}} \right) \quad (4.24)
\]
then the calculated OCV is 0.356 V which is quite close to the experimental OCV of 0.37 V. This indicates that the solvated electrons’ concentration plays a contributing role in the OCV of the half cell and further reinforces the result that the LiSES is metallic and not ionic.

Section 4.6 Conclusions

This chapter seeks to investigate the characteristics of the naphthalene-based and biphenyl-based LiSES. Several key results had been obtained. The first is that the metallic behaviour of LiSES was demonstrated via the conductivity studies and concentration cell experiments. The second is that the temperature profiles of the LiSES half cells’ OCV were obtained for both the naphthalene-based and biphenyl-based LiSES, which allows for the entropy change ($\Delta S$) and enthalpy change ($\Delta H$) of the half cells to be calculated. The third is the identification of LiSES formation using FTIR spectroscopy. The fourth is the formulation of possible mechanisms of how metallic Li reacts with the PAH (naphthalene or biphenyl) in THF at different Li concentrations. The technological implication of these results is that an LiSES full cell with high OCV and hence high energy density can be developed with a suitable catholyte. The investigation of iodine as a suitable liquid cathode will be covered in Chapter 5.
Chapter 5  Liquid cathode for LiSES cell: Iodine Catholyte

Section 5.1 Introduction and Chapter Outline

This chapter explores the study of possible candidate materials for a liquid cathode which can be used in conjunction with the LiSES liquid anode for a refuelable liquid lithium cell. The focus of the study will be on solutions of iodine in methanol. The application of iodine as active cathode material in Li cells is not new as was discussed in Chapter 2, Section 2.7. The main advantages of using iodine as a liquid cathode are its high theoretical energy density [42, 43, 120], its low cost, its abundance and its low toxicity. Also, the end of the discharge when all the iodine has been reduced to iodide can be easily observed by the colour of the iodine solution changing from brown to colourless. Another advantage is that iodine might aid the homogeneous catalysis of oxygen reduction to prevent Li$_2$O$_2$ passivation of the cathode current collector during cell discharge. Therefore, when the Li-SES cell is used with an iodine/oxygen cathode, the current collector’s lifespan might be prolonged during discharge.

However, this is the first time that iodine solution in methanol has been used as a cathode in conjunction with Li-SES anode in a rechargeable Lithium cell operating at ambient temperature in which both electrodes are in the liquid state.

Section 5.2 describes the experimental results proving the effectiveness of the iodine/methanol as an alternative catholyte in place of air. Section 5.3 covers the study of oxygen cathode for the LiSES full cell. Section 5.4 concludes this chapter by covering the preliminary results on other potential candidates for catholytes as well as on copper (II) sulphate as a catalyst for iodine recovery from iodide in air.
Section 5.2 Demonstrating the effectiveness of the iodine/methanol as a catholyte in place of air (oxygen).

5.2.1 Constant load discharge of LiSES//I\textsubscript{2} full cell

Iodine was dissolved in methanol as a liquid cathode to be used with the Li-SES. Lithium iodide was used as supporting electrolyte for both liquid anode and liquid cathode. Detailed preparation process for the full cell and iodine/methanol catholyte are described in Chapter 3, Sections 3.5.2 and 3.6.1 respectively. The full cell configuration (See Figure 3.6 for schematic diagram) is as follows:

(-)Ni / 1 M Li-SES, 0.5 M LiI, THF / LTAPGC/ 0.1 M I\textsubscript{2}, 0.5 M LiI, methanol/ Ni(+)

The cell is cathode-limited. In all these full cells set up, the anode capacity is about 536 mAh whereas the cathode’s capacity is about 20 \% that of the anode. The Li-SES anolyte and the Iodine catholyte are separated by a Li-ion conducting solid electrolyte membrane, LTAPGC (Ohara, Japan). The full cell is discharged across a constant load of 1 kΩ as shown in the circuit diagram of Chapter 3, Figure 3.9.

Figure 5.1a shows the discharge profile of the naphthalene-based Li-SES cell discharge profile of a cell consisting of 1.0 M Li\textsubscript{1.0}N(THF)_{10.4}, 0.1 M of I\textsubscript{2} in methanol and 0.1 M of LiI in both liquid anode and liquid cathode, together with OCV in the red plot. The blue plot (CCV across 1 kΩ load) takes into account the internal resistances of the cell and polarization. The discharge profile of the biphenyl-based Li-SES cell is also similar to that of the naphthalene-based Li-SES and is shown in Figure 5.1b.
Figure 5.1a  \( \text{Li}_{1.0}\text{M(THF)}_{10.45} \)'s full cell discharge profile: (\textbf{In RED}) Open Circuit Voltage, OCV (V) versus Time (h). (\textbf{In BLUE}) Closed Circuit Voltage, CCV (V) versus Time (h).
Figure 5.1b  Li_{1.00}(THF)_{10.45}’s full cell discharge profile: (In RED) Open Circuit Voltage, OCV (V) versus Time (h). (In BLUE) Closed Circuit Voltage, CCV (V) versus Time (h).

Two plateaus can be clearly seen from the discharge profiles of both Li_{1.00}(THF)_{10.45} and Li_{1.00}N(THF)_{10.45}. However, at the end of the first plateau, the dark brown liquid cathode had become yellow, indicating that there was still some I\textsubscript{2} present. The regions where the liquid cathode changed colour completely can be divided into two phases: Phase I and Phase II. By the end of Phase I (Time ~ 60h), the dark brown liquid cathode had become totally colourless, indicating most the I\textsubscript{2} dissolved in methanol had been converted to I\textsuperscript{-}. Further discharge of the cell into Phase II would lead to the irreversible formation of hydrogen gas from the methanol in the
catholyte. This would not be desirable as (1) hydrogen is highly flammable when mixed with oxygen at a concentration of as low as 4% hydrogen by volume in air [158] and (2) hydrogen gas formation leads to a pressure build-up in the cathode chamber if the chamber is sealed, although it can be used in a fuel cell (hydrogen fuel).

For Phase I, the electrochemical reactions taking place in a charged Li-SES//I$_2$ cell is illustrated as follows:

Anode: $\text{Li-SES} \rightarrow \text{Li}^+ + e^- + \Theta$ \hspace{1cm} (5.1)

Cathode: $2\text{Li}^+ + 2e^- + \text{I}_2 \rightarrow 2\text{LiI}$ \hspace{1cm} (5.2)

Overall cell reaction: $2\text{Li-SES} + \text{I}_2 \rightleftharpoons 2\text{LiI} + 2\Theta$ \hspace{1cm} (5.3)

where $\Theta$ denotes the PAH/solvent solution.

**Equations (5.1) to (5.3)** are electrochemical reactions taking place during charging/ discharging of the cell in Phase I. Since iodine can be in the form of I$_3^-$ ($\text{I}_2 + \text{I}^-$), the cathode’s half-cell reaction may also be written as:

$$3\text{Li}^+ + 2e^- + \text{I}_3^- \xrightleftharpoons{\text{charge}}^{\text{discharge}} 3\text{LiI}$$ \hspace{1cm} (5.4)

In this case, from Equations (5.1) and (5.4), the overall cell reaction for Phase I becomes:

$$2\text{Li-SES} + \text{I}_3^- \xrightleftharpoons{\text{charge}}^{\text{discharge}} 2\text{LiI} + \text{I}^- + 2\Theta$$ \hspace{1cm} (5.5)

The rationale for using 0.1 M iodine is that this is the maximum solubility of iodine in methanol and that any excess iodine added will remain as solid inside the solution [159]. Solid iodine can be used as the reserve to increase the energy density of the cell as it dissolves during discharge to the solubility limit.
Chapter 5 – Liquid cathode for LiSES cell: Iodine Catholyte

The reaction occurring in Phase II in the absence of iodine is as follows:

\[
\text{Overall cell reaction: } \text{CH}_3\text{OH} + 2\text{Li-SES} \rightarrow \text{CH}_3\text{-O-Li} + \frac{1}{2}\text{H}_2 + 2\Theta
\] (5.6)

where \( \Theta \) denotes the PAH/solvent solution.

As a matter of fact, hydrogen will most likely be evolved similar to the case when metallic lithium is added physically into alcohol. However, the evolution of the hydrogen gas in \textbf{Equation (5.6)} will be slow. Hence no bubbling or violent effervescence will be observed unlike for the case of the chemical reaction between metallic lithium and alcohol.

After connection to the battery tester, the initial measured OCVs of the \( \text{Li}_{1.0}N(\text{THF})_{10.4}/I_2 \) cell and the \( \text{Li}_{1.0}\beta(\text{THF})_{10.4}/I_2 \) cell prior to cell discharge were 2.65 V and 2.77 V respectively. Repeated OCV measurements on separately prepared fresh \( \text{Li}_{1.0}N(\text{THF})_{10.4}/I_2 \) and \( \text{Li}_{1.0}\beta(\text{THF})_{10.4}/I_2 \) cells yield 2.75 V and 2.83 V respectively. When the \( \text{Li}_{1.0}\beta(\text{THF})_{10.4}/I_2 \) cell was taken out of the glovebox after preparation and the catholyte was exposed to air as follows:

\((-)\text{Ni} / 1.0 \text{ M Li}_{1.0}\beta(\text{THF})_{10.45}, 0.5 \text{ M LiI} / \text{LTAPGC}/ 0.1 \text{ M I}_2, 0.5 \text{ M LiI, Air/ Ni}(+)\)

subsequent OCV measurement on the cell showed that the cell’s OCV had shot up from 2.83 V to 2.98 V. This could be due to the moisture (H\(_2\)O) and air absorption from the surroundings by the iodine/methanol. From the redox potential for aqueous iodine in Figure 5.2, the expected OCV = 3.670 – 0.68 = 2.99 V, which is quite close to the measured OCV.
According to the standard reduction potential values in Figure 5.2, the expected OCVs of the following cell reactions are:

For $\text{Li}_{1.0} N(\text{THF})_{10.4} / 0.1 \text{ M I}_2$ cell:

$$2\text{LiN(THF)}_{10.4} + \text{I}_2 \iff 2\text{LiI} + 2N(\text{THF})_{10.4}, \text{OCV} = 2.935 \text{ V} \quad (5.7)$$

$$2\text{LiN(THF)}_{10.4} + \text{I}_3^- \iff 2\text{LiI} + \Gamma^- + 2N(\text{THF})_{10.4}, \text{OCV} = 2.936 \text{ V} \quad (5.8)$$

**Standard Electrode Potential versus Lithium**

<table>
<thead>
<tr>
<th>Standard Electrode Potential</th>
<th>Reaction</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Iodine</td>
<td>$\text{I}_2 (aq) + e^- \iff 2\Gamma$</td>
<td>$+3.670 \text{ V}$</td>
</tr>
<tr>
<td>Tri-iodide to iodide</td>
<td>$\text{I}_3^- + 2e^- \iff 3\Gamma$</td>
<td>$+3.586 \text{ V}$[^44]</td>
</tr>
<tr>
<td>Iodine reduction</td>
<td>$\text{I}_2 + e^- \iff 2\Gamma$</td>
<td>$+3.585 \text{ V}$</td>
</tr>
<tr>
<td>Biphenyl-based LiSES</td>
<td>$\text{Li}^+ + e^- + \beta(\text{THF})<em>{12.3} \iff \text{Li}\beta(\text{THF})</em>{12.3}$</td>
<td>$+0.68 \text{ V}$</td>
</tr>
<tr>
<td>Naphthalene-based LiSES</td>
<td>$\text{Li}^+ + e^- + N(\text{THF})<em>{11.1} \iff \text{LiN(THF)}</em>{11.1}$</td>
<td>$+0.65 \text{ V}$</td>
</tr>
</tbody>
</table>

**Figure 5.2** Standard electrode potentials of $\text{Li}_{1.0}\beta(\text{THF})_{12.3}$, $\text{Li}_{1.0}N(\text{THF})_{11.1}$, iodine reduction and “tri-iodide to iodide” redox reaction versus Li/Li$^+$ at ambient temperature.

For $\text{Li}_{1.0}\beta(\text{THF})_{10.4} / 0.1 \text{ M I}_2$ cell:
Chapter 5 – Liquid cathode for LiSES cell: Iodine Catholyte

\[ 2\text{Li}^{\beta}(\text{THF})_{10.4} + I_2 \rightleftharpoons 2\text{LiI} + 2\beta(\text{THF})_{10.4}, \text{OCV} = 2.905 \text{ V} \quad (5.9) \]

\[ 2\text{Li}^{\beta}(\text{THF})_{10.4} + I_3^- \rightleftharpoons 2\text{LiI} + \Gamma^- + 2\beta(\text{THF})_{10.4}, \text{OCV} = 2.906 \text{ V} \quad (5.10) \]

If the OCVs were adjusted for the concentration of the 0.1 M Iodine using Nernst’s Equation, then the OCVs of Equations (5.7) to (5.10) become 2.91 V (for \( \text{Li}_{1.0}N(\text{THF})_{10.4} / 0.1 \text{ M I}_2 \text{ cell} \)) and 2.88 V (for \( \text{Li}_{1.0}^{\beta}(\text{THF})_{12.3} / 0.1 \text{ M I}_2 \text{ cell} \)). Therefore, the measured OCVs were close to the expected OCVs within experimental error.

Hence, the successful Li-SES/I\(_2\) full cell discharge tests using both biphenyl and naphthalene based Li-SES demonstrated the feasibilities of these LiSES as liquid anodes in lithium batteries, as well as iodine/methanol as liquid cathode in place of air.

5.2.2 Constant current discharge of LiSES/I\(_2\) full cell

The objective of this experiment is to study the constant current discharge profile of the LiSES/I\(_2\) full cell. For this test, the full cell configuration was as follows:

\((-)\text{Ni} / 1.0 \text{ M Li}_{1.0}^{\beta}(\text{THF})_{10.45}, 0.5 \text{ M LiI} / \text{LTAPGC/ 0.1 M I}_2, 0.5 \text{ M LiI/ Ni(+)})\)

Throughout the test, the cell was kept inside the glovebox in argon atmosphere. Leads installed inside the glovebox connected the cell to an external Basytec Battery Test System. The cell was subjected to galvanostatic discharge at a constant discharge current of 0.5 mA. In this condition, the cell lasted 198 h (~ 8 days) before the unprotected LTAP electrolyte membrane broke down. The discharge profile of the cell is shown Figure 5.3, where CCV denotes the closed circuit voltage (potential difference across the cell.) and D.O.D indicates the % depth of discharge of the cell.
Figure 5.3 \( \text{Li}_{1.0} / (\text{THF})_{10.45} \)'s full cell discharge profile: Closed Circuit Voltage, CCV (V) versus Time (h). The top horizontal axis indicates the % depth of discharge (D.O.D) of the cell.

The constant current discharge profile in Figure 5.3 shows a single plateau which indicates that the Phase I reaction has not completed yet. At 198 h, the D.O.D of the cell was 73.9 % and the colour of the catholyte had changed from an initial opaque dark brown to transparent light reddish orange. Since the amount of iodine in the cell was such that the cathode’s capacity was 134 mAh, the cell would have lasted 268 h at a constant discharge current of 0.5 mA if the LATP had not broken down. The anode’s
capacity was 670 mAh, therefore the cell here was also cathode limited. Chapter 7 will cover the study of the effectiveness of LIPON coating on LATP membrane as a protection to minimise the membrane’s corrosion by the LiSES and increase its lifespan.

\textbf{Section 5.3 Study of oxygen cathode for the LiSES cell.}

The LiSES was assembled in the following configuration in the glovebox in argon atmosphere:

\((-\text{Ni} / \text{Li}_{1.0}\beta(\text{THF})_{0.4}, 0.1 \text{ M LiI} / \text{LTAPGC} / 0.1 \text{ M LiClO}_4 \text{ in DME with } 20\% \text{ vol. PFC } / \text{C} (+))\)

which was similar to the setup shown in Chapter 3, Figure 3.6. DME denotes dimethoxyethane and PFC denotes the perfluorocarbon additive, 1-methoxyheptafluoropropane, which functions as the O\(_2\) carriers in the catholyte. 1-methoxyheptafluoropropane was used as the catholyte’s additive because it could be dissolved in DME. The anolyte LiSES chamber was kept air-tight. The supporting electrolytes for the anode and the cathode solutions were 0.1 M LiI and 0.1 M LiClO\(_4\) respectively. For the catholyte, anhydrous DME and anhydrous LiClO\(_4\) were both purchased from Sigma Aldrich and the 1-methoxyheptafluoropropane (HFE 7000 99.5 %) additive was purchased from 3M.

The assembled cell was taken out of the glovebox and oxygen was bubbled into the catholyte solution at a rate of 0.02 ml/min to serve as the cathode. The OCV of the fresh cell was measured to be 2.44 V prior to galvanostatic discharge (Basytec Battery Tester) at a constant discharge current of 20 \(\mu\)A. In Chapter 4, the half-cell
OCV of Li$_{1.0}β$(THF)$_{12.3}$ was reported to be $\sim 0.68$ V versus Li/Li$^+$. Since the possible standard reduction potentials for oxygen in a metallic Li-Oxygen cell are 3.0 V or 3.1 V according to the following half-cell reactions [160]:

\[
\text{O}_2 + \text{Li}^+ + e^- \underset{\text{discharge}}{\rightarrow} \text{LiO}_2 \quad \quad E = 3.0 \text{ V}, \tag{5.11}
\]

\[
\text{LiO}_2 + \text{Li}^+ + e^- \underset{\text{discharge}}{\rightarrow} \text{Li}_2\text{O}_2 \quad \quad E = 3.1 \text{ V}, \tag{5.12}
\]

Hence, this means that the LiSES//O$_2$ cell’s measured OCV of 2.44 V was within expectation as the expected OCV = 3.1 – 0.68 = $2.42 \text{ V}$, if Equation (5.12) is taken as the half cell reaction occurring in the LiSES//O$_2$ cell. This result was also quite close to that of an initial test conducted using the following cell configuration:

\((-\) Pt / Li$_{1.0}β$(THF)$_{10.6}$, 0.5 M LiI / LTAPGC / 0.5 M LiCl in H$_2$O, (Air) / Pt (+)\)

in which the catholyte chamber of the set up was simply exposed to air (No oxygen supplied via bubbling) measured OCV = 2.48 V. Incidentally, the use of platinum metal as current collectors was discontinued as (1) platinum will undergo an irreversible alloying reaction with lithium in the LiSES, and (2) platinum is too expensive a metal (more than that of gold) to be utilized only as a one-time-use consumable (for each cell test).

**Figure 5.4** shows a single horizontal plateau in the plot of closed-circuit voltage, $CCV$ (V) versus discharge time, $t$ (h). The cell was discharged for $\sim 16$ hours before the LTAP electrolyte membrane broke down. The cause of the membrane breakdown could be due to the physical agitations of the catholyte solution by the oxygen bubbles on the LTAP membrane already weakened by the LiSES (the side of the LTAP that is in contact LiSES will turn black immediately upon contact. More
details on the LTAP separator membrane and LIPON coating will be discussed in Chapter 7.

![Figure 5.4](image)

**Figure 5.4** Discharge profile for $\text{Li}_{1.0}\beta(\text{THF})_{10.4}$ anolyte, LATP separator membrane and catholyte (0.1 M LiClO$_4$ in DME with 20% vol. PFC, 0.02 ml/min O$_2$ flow rate) for a constant discharge current of 20 μA.
Section 5.4 Conclusion and investigations on other potential catholytes that can yield higher OCVs with LiSES.

The results presented in this chapter demonstrated the feasibility of the iodine/methanol catholyte as new battery chemistry for the LiSES full cell. In the absence of air, an Li\(_{1.0}\)(THF)\(_{10.45}\)//0.1 M I\(_2\) cell could be subjected to a constant 0.5 mA current discharge for approximately 8 days. Also, the OCV of the Li\(_{1.0}\)(THF)\(_{10.6}\)//Air cell was found to be lower than that of the Li\(_{1.0}\)(THF)\(_{10.45}\)//0.1 M I\(_2\) cell. The technological implications of these results are that (1) iodine/methanol catholyte can provide the cell with a higher energy density (due to the higher OCV), (2) the iodine/methanol catholyte can function as a cathode in the absence of air/oxygen, allowing for applications in environments where oxygen is not readily available (i.e. underwater submersible power sources and space shuttles & satellites application), and (3) given that both electrodes are in liquid forms, the cell can be refuelled for large cell stacks (fresh liquid electrodes replacement) instead of recharging, which saves precious charging time. In the scientific aspect, each identified feature (plateau) in the LiSES full cells’ discharge profiles was attributed to a particular electrochemical reaction based on the redox potentials of the anolyte and the catholyte used.

Besides iodine, other possible candidates for cathode solutions were also explored. Three types of potassium salts, namely potassium manganate (VII) (KMnO\(_4\)), potassium dichromate (VI) (K\(_2\)Cr\(_2\)O\(_7\)) and potassium persulphate (K\(_2\)S\(_2\)O\(_8\)) were tested as aqueous cathodes versus the LiSES anode in full cell configuration in the hope of achieving even higher OCVs than the LiSES//I\(_2\), and hence higher energy densities.

0.15 M cathode solutions of KMnO\(_4\), K\(_2\)Cr\(_2\)O\(_7\) and K\(_2\)S\(_2\)O\(_8\) were separately prepared in charged full-cell configurations versus Li/\(\beta\)(THF)\(_{10.45}\) anode as described in
Chapter 3, Section 3.13.2. The initial OCVs of the three full cells were: 3.76 V (KMnO₄), 3.10 V (K₂Cr₂O₇) and 3.24 V (K₂S₂O₈). These OCVs are the highest values ever achieved for any reported room temperature liquid lithium cells.

The possible reactions occurring at the electrodes could be as follows:

\[
\begin{align*}
\text{Li} \quad &\beta(\text{THF})_{10.5} \rightarrow \text{Li}^{+} + e^- + \beta(\text{THF})_{10.5} \quad (5.13) \\
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- &\rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (5.14) \\
\text{MnO}_4^- + 8\text{H}^+ + 5e^- &\rightarrow 4\text{H}_2\text{O} + \text{Mn}^{2+} \quad (5.15) \\
\text{S}_2\text{O}_8^{2-} + 2e^- &\rightarrow 2\text{SO}_4^{2-} \quad (5.16)
\end{align*}
\]

The respective standard reduction potentials of Equations (5.13) to (5.16) are shown in the form of a scale in Figure 5.5.

**Figure 5.5:** Standard electrode potentials of the K-salts, LiSES (Biphenyl) and Li.
From **Figure 5.5**, the expected OCVs of the three full cells were: 3.88 V (KMnO₄), 3.70 V (K₂Cr₂O₇) and 4.42 V (K₂S₂O₈). Hence the closest match between the expected and measured OCVs is cell the KMnO₄ catholyte, whereas the other two K-salts’ OCVs were far from the expected values.

Similar to the LiSES/I₂ charged cell, each one of the full cells was then discharged over a constant 1 kΩ resistance. The OCV of each cell was recorded every 2 to 3 hours for each cell and preliminary results for the OCV profiles (% Depth of Discharge, DOD (%) versus OCV (V)) are shown in **Figure 5.6** together with that of the \( \text{Liβ(THF)_{10.45}}// 0.1 \text{ M I₂} \) cell for comparison. Even though all the cells were cathode limited, the end of discharge for KMnO₄ and K₂Cr₂O₇ was marked by the breakage of the membranes and not by the colour change of the catholytes. There was no noticeable drop in OCV at the time of membrane failure for KMnO₄ and K₂Cr₂O₇. For K₂Cr₂O₇, there was a slight change in colour from orange to greenish yellow. For KMnO₄, the membrane had blackened on both sides: on the side in contact with the KMnO₄ catholyte and also on the side facing the LiSES. For K₂S₂O₈, even though it was initially colourless, there was a drop in OCV at around 80 % DOD which could signal the end of discharge.
Figure 5.6: Discharge profiles of the Liβ(THF)$_{10.45}$ full cell using the various K-salt catholytes and iodine.

In conclusion, more tests are required to understand the mechanism behind the cathode reactions for the aqueous K-salts and to improve the lifespan of the membranes.
Chapter 6 Electrochemical Generation of LiSES and Iodine

Section 6.1 Introduction and Chapter Outline

This chapter shows for the first time, Li-SES/I₂ cells that operate at room temperature, can be prepared in fully discharged state (~0 V OCV) for safe handling, transportation and storage. Li-SES and iodine are then electrochemically generated during charging, which is confirmed by UV-VIS and a qualitative test. Section 6.2 describes the OCV measurement of an uncharged full cell without the initial presence of either Li-SES in the anolyte or I₂ in the catholyte, and the subsequent generation of the Li-SES and I₂ from the LiI present in both the anolyte and the catholyte via cyclic voltammetry. Section 6.3 covers the qualitative tests to check for the presence of Li-SES by dropping a small quantity of the charged anolyte solution into dilute HCl (to generate hydrogen gas) and starch test on the charged catholyte to test for the presence of iodine. Section 6.4 covers the UV/Vis spectroscopic test results before and after CV charging to verify the formation of Li-SES and I₂ in the anolyte and catholyte respectively. Section 6.5 concludes this chapter by summarizing the results and highlighting their technological implication on the development of refuelable LiSES cells.
Section 6.2 Investigating the electrochemical generation of LiSES and Iodine.

The electrochemical reactions taking place during discharge and charge of a Li-SES//I\textsubscript{2} cell can be schematized as follows:

Anode: \[ \text{Li-SES} \xrightarrow{\text{discharge}} \text{Li}^+ + e^- + \Theta \]  \hspace{1cm} (6.1)

Cathode: \[ 2\text{Li}^+ + 2e^- + \text{I}_2 \xrightarrow{\text{discharge}} 2\text{LiI} \]  \hspace{1cm} (6.2)

Overall cell reaction: \[ 2\text{Li-SES} + \text{I}_2 \xrightarrow{\text{discharge}} 2\text{LiI} + 2\Theta \]  \hspace{1cm} (6.3)

where \( \Theta \) denotes the PAH/solvent solution.

In the charged state, as described in Chapter 5, both the Li-SES and I\textsubscript{2} are prepared chemically and loaded into the cell, whereas in this Chapter, the uncharged cell is loaded with LiI in both the catholyte and the anolyte which give a \( \sim 0 \) V initial OCV, then charged to form iodine and Li-SES. The cell schematic is similar to the one shown in Chapter 3, Figure 3.6 with the following configuration:

\[ (+)\text{Ni} / \beta(\text{THF})_{22.4}, 0.9 \text{ M LiI} / \text{LTAPGC} / 0.9 \text{ M LiI}, \text{Methanol} / \text{Ni(-)} \]

Details of the cell configuration and charging set up can be found in Chapter 3, Section 3.7.1.

The initial OCV of the cell was \( \sim 0 \)V. When the cell was subjected to cyclic voltammetry, the colourless catholyte gradually turned dark orange with each cycle, indicating the formation of I\textsubscript{2} (or I\textsubscript{3}\textsuperscript{-}) from I\textsuperscript{-} in methanol according to Equation (6.2).
The colourless anolyte became a very pale amber colour indicating a low concentration of Li-SES was formed. With each charge/discharge cycle, the colours of the solutions became more intense, suggesting the possibility of some irreversible processes having occurred during each cycle. This went on until the 9th cycle when cycling was stopped at 4.4 V. The OCV of the cell was 2.97 V at the end of the 9th charging cycle. The CV profiles are shown in Figure 6.1. Earlier studies on electrochemical generation of solvated electrons have shown that solvated electrons that are thus formed are stable at ambient temperature in several types of solvents [86, 95, 161, 162].

From Figure 6.1, it can be seen that the cell becomes more stable by the 4th cycle. Figure 6.1 shows the current versus time profile from the CV data. From the areas under each cycle curve, we can determine the amount of charge transferred during each charge/discharge cycle. The Coulombic efficiency during the first cycles is quite low, but increases after the third cycle to above 50%. Hence the first three cycles can be considered as the formation cycles. Integration of the CV data show, at the end of the 9th cycle charge, the Li-SES formed in the anolyte is \(7.43 \times 10^{-3}\) M and the \(I_2\) formed in the catholyte is \(3.72 \times 10^{-3}\) M, which is about half of the concentration of the Li-SES formed, as predicted by Equation (6.3).
Section 6.3 Qualitative verification of LiSES & Iodine formation

6.3.1 Verification of LiSES formation

When charging of the cell was stopped at 4.4 V, the OCV of the charged cell was 2.97 V. A small quantity of anolyte was extracted from the cell at its charged state at 4.4 V and added to dilute HCl as described in Chapter 3, Section 3.7.2. Effervescence of a colourless, odourless gas (hydrogen) was observed, indicating the formation of LiSES via electrochemical charging from Chapter 3, Equation (3.6). The same test was performed on a chemically prepared Li$_{2.0}$$\beta$(THF)$_{22.4}$ sample for comparison which yielded identical result. Prior to the charging of the cell, a few drops from the anolyte solution of $\beta$(THF)$_{22.4}$ + 0.9 M LiI did not yield any effervescence in dilute HCl.
6.3.2 Verification of iodine formation via starch test

For the electrochemical formation of I\(_2\) from I\(^-\), there were two indicators. The first indicator was that the catholyte showed a colour change from colourless to dark orange (See Figure 6.2).

![Figure 6.2: Colour change in the catholyte: (1) Before charging, and (2) After charging (by 9\(^{th}\) cycle).](image)

The second indicator was a colour change of the charged catholyte from dark orange to blue black when a few drops of the dark orange solution from Figure 6.2 (2) were added to a mixture of starch and distilled water. This is due to the fact that I\(_2\) molecules will form I\(_3^-\) with I\(^-\), which can then slip into the amylose coils of the starch solution to form a deep blue colour [131, 163, 164].
6.3.3 Comparison of half-cell potentials and conclusions of qualitative tests

From the results of Section 6.3.2, it was very conclusive that iodine had been electrochemically generated. From Section 6.3.1, the initial conclusion from the acid test was that the anolyte solution behaved like LiSES in dilute HCl after charging, indicating that solvated electrons had been electrochemically generated and that it was now in the form of Li,β(THF)_{22.4} where \( x > 0 \). Also, since the OCV of the charged cell was 2.97 V, from the half-cell potentials of LiSES and iodine in Chapter 5, Figure 5.2, the standard reduction potentials of the charged anolyte versus Li/Li^{+} was 3.67 - 2.97 = 0.7 V which was very close to that of the Liβ(THF)_{12.3} \( (\text{The standard reduction potential of I}_2(\text{aq}), 3.67 \text{ V vs Li/Li}^+ \), was used.\)

Section 6.4 UV-Vis Spectroscopic Study on charged anolyte and catholyte

As discussed in Chapter 4, the LiSES, Li,β(THF)_{n}, can be formed in a two-step process according to \( x \) value of Li.

To provide additional evidence of the electrochemical generation of solvated electrons, UV-VIS spectroscopy measurements were carried out on the anolyte solutions before 1\textsuperscript{st} charging (S1) and after 9\textsuperscript{th} charging to 4.4 V (S2) and are presented in Figure 6.3. S3, the spectrum of the chemically prepared Li-SES matched the one of S2. Therefore, the emerging of the single absorbance peak centred at 305.5 nm in S2 could be caused by the presence of the solvated electrons in the sample.
Figure 6.3:  UV-VIS spectra of anolyte solutions of S1, S2 and S3

S1: uncharged anolyte
S2: charged anolyte at the 9th cycle
S3: Chemically prepared Li-SES

For verifying the formation of iodine in the catholyte, FT-IR was not able to conclusively distinguish between iodide and iodine unlike UV-VIS, which was able to do so. As presented in Figure 6.4, the UV-Vis spectrum of the charged catholyte solution (S6) at the 6th cycle CV was different from the spectrum of lithium iodide dissolved in methanol (uncharged catholyte, S5). In the range 250 nm to 600 nm, S5 did not have any peaks as compared to S6. However, S5 matched the spectrum of iodine crystals dissolved in methanol (S4) in the range of 200 nm to 400 nm, which indicated the presence of iodine in the charged catholyte.
Figure 6.4: UV-VIS spectra of (S4) iodine/methanol, catholyte solutions (S5) before charging and (S6) after charging.

In the range of 200 nm to 600 nm in Figure 6.4, the spectrum of I$_2$/CH$_3$OH, S4, had the following peaks: 226 nm, 291 nm, 361 nm and 450 nm with the 226 nm (I) peak being the strongest and 450 nm peak being the weakest. The spectrum of the colourless LiI/CH$_3$OH, S5, had only one peak at 221 nm. Finally, the charged catholyte’s spectrum S6 had three peaks at 224 nm, 291 nm, and 359 nm, with the 224 nm peak being the weakest.
For S4, the 450 nm peak was attributed solely to I$_2$ according [165, 166]. The 226 nm peak was attributed to I$^-$ [134] in the sample and also because it was close to the only peak (221 nm) of the LiI/CH$_3$OH spectrum. The two peaks, 291 nm, 361 nm, were attributed to I$_3^-$. The presence of all three species I$^-$, I$_2$, and I$_3^-$ in the I$_2$/CH$_3$OH sample was not surprising given that they could exist in the following [44, 165]:

$$I_2 + I^- \rightleftharpoons I_3^- \quad \text{(6.4)}$$

Based on the intensities of the absorbance peaks, iodine existed in the sample solution predominantly in I$^-$ form then followed by the I$_3^-$ form, with the least amount in the sample in I$_2$ form. The presence of I$^-$ in the sample was also due to the fact that iodine reacts with methanol to produce HI [167].

For S6, the appearance of the tri-iodide peaks at 291 nm and 359 nm in the charged catholyte’s spectrum, as compared to the uncharged catholyte’s (LiI/CH$_3$OH) spectrum, S5, indicated that iodine had been successfully generated electrochemically by charging. However, most of the species in the charged catholyte were predominantly I$_3^-$ with a very small amount of I$^-$ left which accounted for the weak 224 nm peak. The trace amount of I$_2$ in the charged catholyte, according to **Equation (6.4)**, was too small to produce an absorbance peak.

FTIR analysis had been conducted on the anolyte of the uncharged cell before and after charging. However, the amount of solvated electrons formed from the electrochemical process was too small to be detected by FTIR.
Section 6.5 Conclusions

The results of this chapter demonstrated the successful electrochemical formation of Li-SES anolyte and I$_2$ catholyte from a discharged cell of 0 V OCV in a full cell configuration. UV-Vis spectroscopy was able to conclusively verify the electrochemical formation of iodine in the catholyte. Also, a combination of qualitative tests and comparison of standard half-cell potentials enabled the verification of LiSES and I$_2$ formation. Separately, UV-Vis spectroscopic study on the charged anolyte and is also another alternative means of identification of LiSES formation, though the results obtained were not as conclusive as the qualitative tests and standard potentials comparison.

This discovery allows us to build a Li-SES//I$_2$ cell that has purely liquid based anode and cathode and a solid state electrolyte membrane in either charged or discharged states for refuelable lithium battery applications. The rationale for preparing cells in discharge state is the convenience and safety of the system. The cell can also be prepared in a partial charged state depending on the user’s needs.
Chapter 7  Effects of LIPON Protective coating on solid membrane electrolyte

Section 7.1  Introduction and Chapter Outline

This chapter describes the efforts made to introduce a protective coating, LIPON, on the Ohara LTAP solid electrolyte membrane to minimise its corrosion by the LiSES anolyte as shown in Chapter 3, Section 3.12, Figure 3.10 and the studies made on the effects of this coating. Section 7.2 will cover the effects of LIPON on LTAP in two parts. The first part will be on how it affects the LTAP’s chemical resistance against LiSES whereas the second part will be on how it affects the effective resistance of the solid electrolyte. Section 7.3 will cover the effects of LIPON on the standard potential of the LiSES anolyte. Finally, Section 7.4 describes the conclusions obtained concerning the suitability of LIPON for use in future LiSES cells.

Section 7.2  Investigating LIPON’s effects on the solid membrane electrolyte

7.2.1  Study on the effect of LIPON on improving the LTAP membrane’s chemical resistance against LiSES

Based on the literature review in Chapter 2, Section 2.6, lithium phosphorus oxynitride (LIPON), which was a material used solely as the solid electrolyte or as a protective layer on other ceramic electrolytes against lithium for metallic Li-Air cells,
Chapter 7 – Effects of LIPON protective coating on solid membrane electrolyte

was selected for this project as the LTAP’s protective coating. All the LTAP membranes used in this project were manufactured by Ohara [97-99].

Figure 3.10 had already shown the consequence of using the bare LTAP without coating. The white portions in Figure 3.10 (b), after 72 hrs immersion in LiSES were actually the layers beneath the original surface which had blackened and exfoliated in parts.

To test the effectiveness of LIPON against LiSES, a single pristine Ohara LTAP membrane was divided equally into two semi-disks and a 1 µm thick layer of LIPON was coated onto both sides of one semi-disk by means of magnetron sputtering as described in Chapter 3, Section 3.12.1. Both semi-disks (coated and uncoated) were then immersed in separate sealed bottles containing Li$_{1.0}$β(THF)$_{12.3}$ for 72 h in argon atmosphere in the glovebox. Figure 7.1 shows the results of the immersion test.

Figure 7.1: (a) LIPON coated LTAP membrane after 72h immersion in Li$_{1.0}$β(THF)$_{12.3}$
(b) Pristine LTAP membrane after 72 h immersion in Li$_{1.0}$β(THF)$_{12.3}$

*Note: All Ohara LTAP membranes used for this project were 150 µm thick.
Chapter 7 – Effects of LIPON protective coating on solid membrane electrolyte

It was evident from Figure 7.1 (a) that the LIPON layer was able to offer protection against the LiSES. The thin black edge and the few tiny black dots were probably due to incomplete coverage of the LIPON on the LTAP, thus allowing for the LiSES to come into contact with the LTAP at these locations.

The elemental surface compositions of both the LIPON-coated LTAP and the uncoated LTAP were compared before and after their immersion in LiSES. Their % elemental compositions were determined by XPS and shown in Tables 7.1 and 7.2.

Table 7.1 Elemental composition of LIPON-coated membrane before and after immersion in LiSES for 72 h.

<table>
<thead>
<tr>
<th>Element</th>
<th>Before (at.%)</th>
<th>After (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>66.4±2.4</td>
<td>60.7±3.7</td>
</tr>
<tr>
<td>Ti</td>
<td>2.5±0.6</td>
<td>nil</td>
</tr>
<tr>
<td>P</td>
<td>11.5±0.3</td>
<td>nil</td>
</tr>
<tr>
<td>Si</td>
<td>1.1±0.3</td>
<td>1.1±0.5</td>
</tr>
<tr>
<td>Al</td>
<td>3.5±0.2</td>
<td>nil</td>
</tr>
<tr>
<td>Li</td>
<td>10.0±0.7</td>
<td>32.8±2.1</td>
</tr>
<tr>
<td>Ge</td>
<td>3.4±0.4</td>
<td>nil</td>
</tr>
</tbody>
</table>

Table 7.2 Elemental composition of uncoated membrane before and after immersion in LiSES for 72 h.

<table>
<thead>
<tr>
<th>Element</th>
<th>Before (at.%)</th>
<th>After (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>54.7±2.2</td>
<td>56.1±3.5</td>
</tr>
<tr>
<td>Li</td>
<td>31.0±1.5</td>
<td>38.2±3.9</td>
</tr>
<tr>
<td>N</td>
<td>3.9±0.5</td>
<td>3.0±0.3</td>
</tr>
<tr>
<td>P</td>
<td>10.4±0.6</td>
<td>8.1±0.7</td>
</tr>
</tbody>
</table>
Chapter 7 – Effects of LIPON protective coating on solid membrane electrolyte

With this promising result, the next step was then to coat one side of an LTAP membrane prior to full cell assembly. Subsequent LIPON coatings were only 0.5 μm thick in order not to increase the effective ionic resistance of the whole electrolyte membrane. Only the side facing the LiSES required protection as (1) the iodine catholyte (including the 1 M LiPF$_6$ in EC:DEC electrolyte) would not damage the LTAP, and (2) an additional coating would have increased the effective ionic resistance of the LTAP and hence an increased internal resistance for the full cell.

A full cell configuration of the following was assembled:

(-)Ni / Li$_{1.0}$(THF)$_{10.45}$, 0.5M LiI / 0.5μm LIPON/ LTAPGC/ 0.1M I$_2$, 0.5M LiI/ Ni(+) and discharged across a 1 kΩ resistor over three days. The discharge profile of this cell will be presented later in Section 7.3. When the membrane was removed, it was found to be still white in colour as in Figure 7.2(a) as compared to the blackened condition when used in a similar configuration without the LIPON coating.

Figure 7.2: After 3 days discharge, appearance of (a) LIPON-coated LTAP, and (b) Uncoated LTAP. The white rim in (b) is the part that is not in contact with the LiSES.
7.2.2 Impedance Spectroscopy study on how LIPON coating affect the effective resistance of the LTAP electrolyte.

The detailed experimental procedure on the impedance study on LIPON coated LTAP membranes is provided in Chapter 3, Section 3.12.2, where the test sample was sandwiched between a pair of stainless steel discs. The impedance measurements of both coated and uncoated membranes are presented in Figure 7.3. Comparison of the two measurements indicates that the additional 0.5 μm layer of LIPON coating leads to a decrease in its ionic conductivity and hence leading to an increase in the coated membrane’s resistance.

![Figure 7.3: Impedance measurements of both LIPON coated (RED) and uncoated (BLACK) LTAP membranes.](image)
Section 7.3 Investigation into the effect of LIPON on the standard potential of LiSES

7.3.1 Observed effect of LIPON coating on OCV of LiSES/I₂ full cells.

Similar to the cell configurations described in Chapter 5, 0.5 µm LIPON-coated membranes were used as follows:

(-)Ni / Li₁₀β(THF)₁₀.₄₅, 0.5M LiI / 0.5µm LIPON/ LTAPGC/ 0.1M I₂, 0.5M LiI/ Ni(+) with an initial OCV of 3.21 V, and

(-)Ni / Li₁₀β(THF)₁₀.₄₅, 0.5M LiI / 0.5µm LIPON/ LTAPGC/ 0.1M I₂, 0.5M LiI/ Ni(+) with an initial OCV of 3.25 V.

Each of these cells was then discharged across a 1 kΩ constant resistor. Their discharge profiles are shown in Figures 7.4(a) and 7.4(b). The shapes of the discharge profiles for both cells in Figure 7.4 are similar to those shown in Chapter 5, Figure 5.1 for the same cells using uncoated LTAPs. The two plateaus in each discharge profile for Figure 7.4 also indicate the two phases where Phase II (second plateau) represents the phase where all the iodine in the catholyte had been reduced.

The theoretical OCV of the Li₁₀β(THF)₁₀.₄₅ vs 0.1 M iodine cell is about 2.95 V. Based on the measured OCV of about 3.21 V for a coated electrolyte membrane, about 9 % enhancement over the theoretical OCV can be achieved by providing a protective coating on the electrolyte membrane.
Figure 7.4 (a): Discharge profile for the $\text{Li}_{1,0}(\text{THF})_{10.45}/\text{0.1 M I}_2$ full cell using LIPON coated LTAP.

Figure 7.4 (b): Discharge profile for the $\text{Li}_{1.0}(\text{THF})_{10.45}/\text{0.1 M I}_2$ full cell using LIPON coated LTAP.
Similarly, the theoretical OCV of the Li\(_{1.0}\beta\) (THF)\(_{10.45}\) vs 0.1 M iodine cell is about 2.91 V. Based on the measured OCV of about 3.25 V for a coated electrolyte membrane, about 12 % enhancement over the theoretical OCV can be achieved by providing a protective coating to the electrolyte membrane.

### 7.3.2 OCV study of LIPON coated LTAP using a special LiSES-1//LiSES-2 cell configuration.

The following cells were setup as a means of further investigation into the LIPON’s special effect on LiSES’s reference based cell’s standard potential. Pristine LTAP was used for Cell I. The LIPON coatings on the LTAPs used for cells II and III were single-sided 0.5 \(\mu\)m coat.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Configuration</th>
<th>Electrolyte details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell I</td>
<td>Symmetric</td>
<td>(-)Ni / Li(<em>{1.0}\beta) (THF)(</em>{10.45}) / LTAP/ Li(<em>{1.0}\beta) (THF)(</em>{10.45})/ Ni(+)</td>
</tr>
<tr>
<td>Cell II</td>
<td>Asymmetric</td>
<td>(-)Ni / Li(<em>{1.0}\beta) (THF)(</em>{10.45}) / LIPON/ LTAP/ Li(<em>{1.0}\beta) (THF)(</em>{10.45})/ Ni(+)</td>
</tr>
<tr>
<td>Cell III</td>
<td>Asymmetric</td>
<td>(-)Ni / Li(<em>{1.0}\beta) (THF)(</em>{10.45}) / LIPON/ LTAP/ Li(<em>{1.0}\beta) (THF)(</em>{10.45})/ Ni(+)</td>
</tr>
</tbody>
</table>

“Symmetric” cell configuration refers to the setup where both sides of the LTAP are uncoated and in direct contact with both LiSES samples. “Asymmetric” cell configuration refers to the setup where one side of the LTAP membrane is coated with LIPON.

Cell II and III were each discharged across a constant 1 k\(\Omega\) resistor. Their discharge profiles are presented in Figures 7.5(a) and 7.5(b).
The OCVs of these cells from I to III were 0.002 V, 0.378 V and 0.410 V respectively. From Figure 7.5(a), there is only a single plateau in the discharge profile of closed circuit voltage (V) versus time (h). This indicates that there is only one phase of electrochemical reaction occurring during the discharge. From Figure 7.5(b), the discharge profile of Cell III is highly unusual in that it showed multiple plateaus, indicating that unlike the case for Cell II, there is more than one phase of electrochemical reaction occurring during the discharge. However, it could also be likely that the uncoated side of the LTAP in Cell III which was in contact with Li_{1.0}N(THF)_{10.45} was attacked more aggressively by Li_{1.0}N(THF)_{10.45} than in the case of Cell II between the uncoated side of LTAP and Li_{1.0}\beta(THF)_{10.45}, hence resulting in more than one phase as shown in Figure 7.5 (b).

Figure 7.5(a): Discharge profile of Cell II: Closed Circuit Voltage (V) versus Time (h)
The OCV of Cell I (0.002 V) indicated that both LiSES had about the same electrode potential with the $\text{Li}_{1.0}\beta(\text{THF})_{10.45}$ being only slightly more electropositive than $\text{Li}_{1.0}\text{N}(\text{THF})_{10.45}$. However, the LiSES in contact with the LIPON coating became more electronegative as seen by the increased OCV reading. The increased OCV readings occur due to an unknown redox couple reaction between the LiSES and the LIPON coating. This does not mean that the LiSES anolyte had reacted with LIPON to form another liquid with a potential more electronegative than LiSES. Rather, it is
believed at this point in time that something had occurred at the interface between the LIPON and the LTAP, i.e a higher Fermi level in the LTAP in contact with the LiSES than the Fermi level in the LIPON in contact with the other LiSES which caused a potential drop in the latter.

Section 7.4 Conclusions about LIPON

In liquid-based Li batteries, Li$^+$-conducting ceramic membranes typically play the dual-role of electrolyte and separator, allowing ions or charge carriers transfer through them while separating the anodic and cathodic components. Therefore, it is of utmost importance for these membranes to be both structurally and chemically stable so that they will not break easily. However, the chemical stability of the LTAP electrolyte membranes in LiSES is very poor. In order to overcome this problem, LIPON had been selected as the protective coating for the LTAP. The experimental results demonstrated LIPON’s effectiveness in enhancing the LTAP’s chemical stability against LiSES. However, at the same time LIPON also caused the standard potential of the LiSES anolyte to increase, leading to an overall higher OCV for the whole cell. This positive effect was totally unexpected and new and hence opened up another area for further in-depth study and understanding of the LIPON-LiSES chemistry.
Chapter 8  Conclusions and Recommendations for Future Work

Section 8.1  Conclusions

The ambient temperature refuelable lithium battery of this project uses both anodes and cathodes that are liquid and is new and innovative. The results of this work have been filed for patent [19, 49]. It must be emphasized that the LiSES anolyte is a liquid at room temperature and not the same as that of a slurry or suspension mixture as reported in others’ works that were passed off in news as “liquid” lithium batteries [37, 40, 168].

The main results of this project are as follows. The metallic behaviour of LiSES has been demonstrated via temperature studies in which the conductivity of the LiSES is seen to decrease with increasing temperature. Also, LiSES behaves like a mixed conductor liquid solution from concentration cell experiments as shown in Section 4.5.1. Possible mechanisms for how metallic Li reacts with PAH in THF at different concentrations of Li have been formulated based on FTIR studies of the LiSES. The relationship of half-cell OCV of LiSES versus temperature has been obtained from the temperature studies of LiSES half cells, and thermodynamics data ($\Delta G$, $\Delta S$ and $\Delta H$) have been determined. LiSES & Iodine/methanol have both shown promising results as liquid electrodes in full cell configuration. The charge/discharge electrochemical reactions for LiSES/Iodine full cell have been identified. The LIPON protective coating is shown to be effective in preventing corrosion due to LiSES on the solid electrolyte membrane. LIPON-covered surfaces did not turn black and disintegrate in contact with LiSES as compared to an unprotected membrane. Liquid
electrodes can be prepared either chemically or electrochemically, from the successful
electrochemical formation of LiSES and iodine by charging a cell with initial 0 V
OCV. Thus, cells can be prepared in either charged or uncharged state depending on
the need of the user. Finally, an unexpected effect of the LIPON layer upon LiSES has
been observed, which can cause higher OCVs for the LiSES cells. The redox processes
underlining this unexpected effect are still under investigation.

The scientific contributions of this thesis are in the following. The mechanism
of LiSES formation has been revealed. The thermodynamics of LiSES, including
entropy have been determined. The successful electro-synthesis of LiSES in the
anolyte during the charge process of a cell with LiI in both liquid electrodes with an
initial 0 V OCV. The same charging process is also concomitant to the oxidative
formation of I\textsubscript{2} from LiI in the catholyte. Understanding of these first three items
allows the PAH-based LiSES to be effectively utilized in full-cell designs. Next, the
effectiveness of Iodine/methanol as a liquid cathode has been demonstrated in full cell
discharge tests indicates that iodine can be an alternative cathode in place of
air/oxygen. Finally, the last contribution is in proving the effectiveness of LIPON as a
protective coating to prevent LiSES from corroding the solid electrolyte membrane,
which means that the solid electrolyte membrane of the cell need not be constantly
replaced.
Section 8.2 Recommendations for future work

8.2.1 Future Outlook

The characterization studies conducted on the two-ring PAHs, biphenyl and naphthalene, yielded some fundamental results and understanding about the PAH-based LiSES. This allows for further investigation into other PAHs with more than two benzene rings as well as their derivatives.

The cause of the high entropy changes for the LiSES half cells in Chapter 4, Section 4.4.2 as well as the origins of the entropy of mixing of the LiSES merit further study.

As discussed in Chapter 7, further investigation into the cause of LIPON’s unexpected effect on LiSES’s standard potentials is another new area that can be explored.

Proof-of-concept results on other catholytes such as the aqueous acidified KMnO$_4$ described in Chapter 5 yielded high OCVs in a full configuration with LiSES. Further work can be carried out to discover other catholytes that can deliver higher OCVs and hence higher energy densities.

Three possible ideas for future work are provided in the following sub-sections: 8.2.2, 8.2.3 and 8.2.4.
8.2.2 Synthesis and characterisation studies on Li-PAH LiSES, for PAH with > 2 benzene rings and for derivatives of PAHs (with substituents)

By using PAHs with more benzene rings, it is hoped that the Li/PAH ratio can be increased in the LiSES thus increasing its energy density. Attempts to extend the study into using other PAHs as electron receptors have to done in a progressive and systematic manner starting with similar synthesis and characterization processes like the LiSES for this thesis. One noticeable difference is that PAHs with 4 benzene rings and above, such as pyrene (4 fused benzene rings) and corannulene (1 cyclopentane ring fused with 5 benzene rings) have a yellowish tint as compared to the white biphenyl and naphthalene. When pyrene was dissolved in THF, a clear orange-yellow solution was obtained and dissolving of metallic lithium into pyrene yielded a magenta coloured solution. This might require a break from the traditional mindset that all LiSES have to be blue in colour. Other factors to consider in the study of these other PAHs include the chemical stability of their LiSES over a range of temperatures and their cost.

Another possible extension of this study is to explore different kinds of derivatives of PAHs such as the substituted tetraphenylcyclopenta-2,4-dienones. (Brief results presented in Appendix II). Different groups of substituents can be explored to enhance the PAHs' ability to form solvated electrons solution with metallic lithium.
8.2.3 Investigation of the redox processes underlining LIPON’s effect on LiSES’s standard potentials.

For most people working on LIB research, it is well known that the standard reduction potential of metallic lithium, $E^0$, relative to standard hydrogen electrode (SHE) is -3.04 V at 25 °C:

$$\text{Li} \rightleftharpoons \text{Li}^+ + e^- \quad (8.1)$$

Just slightly more electronegative than metallic lithium is the hydrozoic acid at -3.09 V versus SHE:

$$\text{N}_3\text{H} \rightleftharpoons \frac{3}{2} \text{N}_2 + \text{H}^+ + e^- \quad (8.2)$$

At the present moment, since LIPON coating is made by sputter coating from a Li$_3$PO$_4$ target in N$_2$ atmosphere onto a substrate (the LTAP) and hence contains the element N, it is postulated that one or more redox reaction(s) could have taken place between LIPON and LiSES similar to that of Equation (8.2) to give an $E^0$ which is more electronegative than LiSES. This is subject to further experimental work for verification.

8.2.4 Study of PAH-based $M$-SES//Air cells where $M$ represents a Group I alkali metal other than Li.

It is possible to replace lithium with other Group I metals such as sodium (or even potassium), which are more abundant in nature than lithium, to prepare PAH-based LiSES. For starters, sodium (Na) can be used to prepare LiSES with biphenyl and naphthalene as PAHs for FTIR characterisation studies. However for half cell and
full cell tests, a solid electrolyte membrane that is Na\(^+\) conducting is a necessity. Synthesis and characterisation of a Na\(^+\) conducting ceramic membrane will become another subset of this study. The membrane has to have high ionic conductivity and be mechanically stable (non-brittle) and chemically stable in the presence of solvents and even the NaSES. In the event that the membrane is chemically unstable in the presence of NaSES, a suitable protective coating has to be found and used as a combination similar to the LIPON/LTAP configuration.

Since metallic sodium is more reactive than lithium in the presence of moisture and oxygen, it is much more dangerous and is often supplied in a form immersed in oil. Test cells storing the NaSES must be designed to remain hermetic at all times to prevent the occurrence of fires. Likewise, the Na-conducting membranes have to be more mechanically stable than the LTAPs to prevent breakage and direct contact between the NaSES and oxygen.
References


References


References


References


References


References


References


References

190


http://www.wtw.de/no_cache/en/downloads-support/operating-manuals.html

http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy


Available:

http://chemwiki.ucdavis.edu/Biological_Chemistry/Carbohydrates/Case_Studies/Starch_and_Iodine


Available:

http://chemwiki.ucdavis.edu/Organic_Chemistry/Organic_Chemistry_With_a_Biological_Emphasis/Chapter__4%3A_Structure_Determination_I/Section_4.3_Ultraviolet_and_visible_spectroscopy


Y. Sasaki and H. o. Hamaguchi, "Raman spectra and structure of biphenyl isoatomers (the S_0, S_1, T_1 states and the cation and anion radicals),"


APPENDIX I

Calculations of gravimetric energy density values for Table 2.1 (Chapter 2).

Firstly, the amount of electrical energy required to convert one mole of active material into product is computed using Faraday’s law [27]:

\[
m = R_F \left( \frac{M_r Q}{nF} \right)
\]

(A1)

where

- \( m \) (calculated in g) denotes the product’s mass at the electrode.
- \( R_F \) denotes the faradaic efficiency.
- \( M_r \) denotes the molar mass of the products (in g/mol).
- \( Q \) denotes the amount of electricity measured in C (1 electron carries \( 1.602 \times 10^{-19} \) C)
- \( n \) denotes the number of electrons exchanged per mole of product.
- \( F \) denotes the Faraday’s Constant \( (F = 96485 \text{ C/mol}) \)

The faradaic efficiency, \( R_F \), also known as the coulombic efficiency, refers to the ratio between the number of electrons delivered from the secondary battery and the number of electrons injected into the secondary battery computed over one charge/discharge cycle. In the idealized scenario, it is taken that \( R_F = 1 \).
The theoretical gravimetric capacity, $C_{th}$, is deduced from Faraday’s Law from

**Equation (A1):**

$$C_{th} = \frac{nF}{M_r} \left( \frac{1000}{3600} \right)$$  \hspace{1cm} (A2)

The term $\frac{1000}{3600}$ is included in **Equation (A2)** to convert the units of $C_{th}$ from C/g into mAh/kg.

Next, the theoretical energy density, $D_{th}$, is calculated as follows:

$$D_{th} = E^0 \times C_{th} = E^0 \times \left( \frac{n \times 96485}{M_r} \right) \left( \frac{1000}{3600} \right)$$

$$\Rightarrow D_{th} = E^0 \times \left( \frac{n}{M_r} \right) \times 26801$$  \hspace{1cm} (A3)

With reference to the equation from the first row of **Table 2.1**, for Li-O$_2$ battery using organic electrolyte, if O$_2$ is stored as part of the battery, then using **Equation (A2):**

$$\text{Organic } E_{th, \text{stored } O_2} = 3.1 \times \left( \frac{2}{2(6.9) + 2(16)} \right) \times 26801 = 3630 \text{ Wh/kg}$$  \hspace{1cm} (A4)

If the O$_2$ is taken from the air, then the $M_r$ of O$_2$ is not included in the calculation as part of the $M_r$ of the reactants. In this case, the theoretical energy density becomes:

$$\text{Organic } E_{th, \text{O}_2 \text{ from air}} = 3.1 \times \left( \frac{2}{2(6.9)} \times 26801 \right) = 12000 \text{ Wh/kg}$$  \hspace{1cm} (A5)
Similarly, for Li-O₂ battery using aqueous alkaline electrolyte (using the equation from 2nd row of Table 2.1):

Aqueous \( E_{\text{th}, \text{stored } O_2} = 3.45 \times \left( \frac{2}{4(6.9) + 2(2+16) + 2(16)} \right) \times 26801 = 3870 \text{ Wh/kg} \) \hspace{1cm} (A6)

Aqueous \( E_{\text{th}, \text{O}_2 \text{ from air}} = 3.45 \times \left( \frac{2}{4(6.9) + 2(2+16)} \right) \times 26801 = 5820 \text{ Wh/kg} \) \hspace{1cm} (A7)

For Li-O₂ battery using aqueous acidic electrolyte, the left-hand side of the balanced equation will still remain the same with the difference being \( 4\text{Li}^+ \) and \( 2\text{H}_2\text{O} \) as the products. The \( E_{\text{th}} \) for such a cell with stored \( O_2 \) and \( O_2 \) taken from the air are 4800 Wh/kg and 7650 Wh/kg respectively.

It can be seen quite clearly from these calculations that even though the Li-O₂ battery using organic electrolyte has a lower OCV, its theoretical energy density is quite high \( (E_{\text{th}} = 12041 \text{ Wh/kg}) \) if the cell configuration is such that the oxygen needed is taken from the air. Compared to the commercial LiCoO₂ LIB shown in Row 3 of Table 2.1, the LIB’s \( D_{\text{th}} = 380 \text{ Wh/kg} \) shows that the gravimetric energy densities of the LABs are much higher than that of LIB by at least 9 to 10 times.
Appendix II Miscellaneous Experimental Results: Other Types of PAH as electron receptor

Section II.1 Introduction and Outline

Appendix II covers the LiSES OCV measurement results using substituted tetraphenylcyclopenta-2,4-dienones as possible candidates for LiSES and comparing them against lithium-saturated biphenyl-based LiSES. Section II.2 describes the experimental procedure and results. Finally, Section II.3 covers the conclusion. These are preliminary experiments conducted on > 2-ring PAHs as possible electron receptors.

Section II.2 OCV Measurements of Solvated Electrons Solutions

II.2.1: Experimental Procedure

As mentioned in the earlier sections in Chapter 3, expanded aromatic systems such as polycyclic aromatic hydrocarbons (PAHs) that can delocalize electrons over large areas due to their extended π-systems, can be used to prepare LiSES. Considerable attention has already been given to them as possible materials for a variety of applications, including LIB electrodes, because of their special electronic properties and that they have a tendency to form self-assembled graphitic nanostructures or columnar assemblies [169]. Another possibility is to use hetero-

3 The results presented here forms a part of the following paper submitted for publication of which I am a co-author: Z. B. Lim, K. S. Tan, H. Li, S. Cho, R. Yazami, and A. C. Grimsdale, "Synthesis and assessment of new cyclopenta-2,4-dienone derivatives for energy storage applications " Synthetic Metals 200 (2015), 85-90.
atoms to help stabilize the anions due to their high electronegativity. One such system is the cyclopenta-2,4-dienone system as this can accept 2 electrons to form a dianion in which one negative charge will be delocalized round the aromatic cyclopentadienyl ring, while the other will be localized on the oxygen as shown in Figure II.1.

![Figure II.1: Reduction of a cyclopentadienone ring to form a dianion. (Reproduced from Ref: [170].)](image)

A series of tetraphenylcyclopenta-2,4-dienes with various substituents has been prepared (Samples 3 to 5 as shown in Figure II.2). The aim of this experiment is to compare their suitability as materials for forming alkali metal-based (Li or Na) solvated electron solutions (SESs) for potential use as anode materials for liquid lithium flow-batteries under ambient temperature condition [170]. This work was done in collaboration with another group in the School of Material Science & Engineering, NTU.

The molecular structures of the samples tested are shown in Figure II.2. Sample 3 is unsubstituted cyclopentadienone. Samples 4 and 5 are the substituted cyclopentadienone after synthesised process as described in Ref [170].

The sample preparation and testing are all carried out in argon atmosphere in a glovebox. To determine whether samples 3-5 can form solvated electron solutions
with metallic lithium, each sample will be dissolved in a glass bottle of 0.50 M LiI in THF. The mixtures, will be stirred for about an hour until the samples are dissolved to give dark brown solutions after which lithium foils are added to each mixture. Then the glass bottles are resealed and subjected to overnight stirring using glass-coated magnetic stirrers.

![Molecular structures of (3) unsubstituted cyclopentadienone, (4) MeO-substituted cyclopentadienone and (5) dithienyladduct substituted cyclopentadienone.](image)

**Figure II.2:** Molecular structures of (3) unsubstituted cyclopentadienone, (4) MeO-substituted cyclopentadienone and (5) dithienyladduct substituted cyclopentadienone. (Reproduced from Ref: [170].)

After overnight stirring, any undissolved lithium fragments are separated from each solution. For each sample solution, OCV is measured between a metallic lithium sheet electrode and a nickel mesh electrode, both of which are immersed in the solution. A schematic drawing of the OCV measurement cell is shown in **Figure II.3**. OCV measurements are also taken from a blank solution of 0.50 M LiI in THF and a Li-saturated Li-SES formed from dissolving an excess of metallic Li in a solution consisting of 0.40 M Biphenyl and 0.50 M LiI in THF. The biphenyl-based LiSES will show an OCV closest to 0 V because of its metallic property (shorting of the circuit between that of metallic Li and the Ni mesh. Among the 3 samples, the ones showing the closest OCV measurement to 0 V are the ones likely to have solvated electrons.
II.2.2: Results

There was no immediate colour change to the mixtures from compounds 3-5 upon adding the metallic lithium foils. Undissolved lithium metal fragments were observed in all three samples after overnight stirring indicating that the so-formed solvated electron solutions, if any were saturated with lithium. Only samples 3 and 4 showed a colour change from dark brown to bright reddish brown. The solution based on compound 5 did not change in colour and metallic lithium became covered with a dark brown coloured layer indicating the molecule reacted with the alkali metal.

The measured OCV values are tabulated in Table II.1. If solvated electrons solutions are formed, then the OCV measured should be lower than 2.18V achieved with the blank solution of 0.50 M LiI in THF as shown in Table II.1. This is because
lithium solvated electrons solutions should be more chemically reductive than the blank solution. From Table II.1, it can be seen that the OCV measurements for samples 3 and 4 showed 1.59 V which was lower than the one measured for the blank LiI in THF solution. This indicates the possibility that some solvated electrons may be formed in samples 3 and 4, even though not in as great a quantity as the Li-SES formed from biphenyl dissolved in LiI/THF. However, for sample 5, the OCV measured was 2.33 V which was actually higher than 2.18 V. This indicates that no solvated electrons were generated when metallic Li was dissolved in sample 5’s solution. A higher OCV in solution 5 could be due to the presence of the element S in sample 5 which could react with Li to form lithium polysulphides Li$_2$S$_n$ instead. In fact when the lithium foil electrode was removed from the cell for cleaning, it was completely covered with a dark layer of sticky gel. Hence, out of the three samples tested, samples 3 and 4 are the more promising candidates for Li-SES formation.

Table II.1 OCV data for: Li dissolved in samples 3-5, LiI in THF and Biphenyl-based LiSES.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Concentration in THF (M)</th>
<th>LiI concentration in THF (M)</th>
<th>OCV (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.50</td>
<td>1.59</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>0.50</td>
<td>1.59</td>
</tr>
<tr>
<td>5</td>
<td>0.07</td>
<td>0.50</td>
<td>2.33</td>
</tr>
<tr>
<td>Blank sample of LiI in THF</td>
<td>0</td>
<td>0.50</td>
<td>2.18</td>
</tr>
<tr>
<td>Li-SES (Li in 0.40 M Biphenyl &amp; 0.50 M LiI in THF)</td>
<td>0.40</td>
<td>saturated</td>
<td>0.030</td>
</tr>
</tbody>
</table>
Section II.3 Conclusion

OCV measurements conducted on three of the samples (3-5) showed that samples 3 (unsubstituted) and 4 (MeO-substituted) can form Li-SES. Thus the type of substituents can influence the ability of the macrocyclic trimers to form SES with alkali metals. Such SES can be used as anolytes for $M$-SES/Air batteries ($M$ = Alkali Metals such as Li, Na) at ambient temperature condition.